THE EFFECT OF FATTY ACID UNSATURATION ON PROPERTIES AND PERFORMANCE OF MONOMERS AND LATEX POLYMERS FROM PLANT OILS

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ABSTRACT

The interest in renewable natural resources, including plant oils, has become increasingly appealing due to the oil abundance, availability, and wide range of applications for polymers and polymeric materials thereof.

In this dissertation, a library of plant oil-based acrylic monomers (POBMs) with a broad range of unsaturation was synthesized using a one-step transesterification. It is demonstrated that the unsaturation degree of plant oil remains preserved during the synthesis and determines the structure and properties of POBMs. The life cycle assessment (LCA) was conducted in this study to evaluate the environmental impact of soybean oil-based acrylic monomer (SBM) production. LCA was applied to provide guidance for SBM synthesis optimization, including the type of catalyst, the ratio between reactants, renewable sources (soybean oil/biodiesel), and solvent recycling. The performed LCA shows the positive effect of the inclusion of the solvent recycling step in the SBM synthesis.

This study shows that POBMs behave as conventional vinyl monomers in free radical polymerization and copolymerization. The monomer unsaturation impacts polymerization rate and molecular weight of resulted polymers decreasing as follows: poly(OVM) > poly(SFM) > poly(SBM) > poly(LSM), due allylic termination presented during polymerization.

A series of stable POBM-based latexes with high solid content (40-45 %) and monomer conversion (95-97 %) were synthesized using miniemulsion process. The incorporation of POBMs fragments provides the plasticizing effect on the resulting latex polymers, as seen by a noticeable decrease in their glass transition temperature (Tg). The crosslink density of POBM-based latex films follows the linear dependence vs. monomer feed unsaturation, providing a tool for controlling latex mechanical properties, including hardness, toughness, Young's modulus, etc.

Besides, the presence of highly hydrophobic POBM fragments enhances water resistivity of latex coatings and films.

Following the "greener" vector of research, a variety of stable latexes from high oleic soybean oil-based monomer (HOSBM) and cardanol, eugenol, and guaiacol derivatives were synthesized in miniemulsion. Resulting polymer materials advantageously combine flexibility provided by HOSBM fragments with strength facilitated by aromatic biobased units.

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DEDICATION

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TABLE OF CONTENTS

ABSTRACT iii

ACKNOWLEDGMENTS v

DEDICATION vii

LIST OF TABLES xv

LIST OF FIGURES xvii

LIST OF SCHEMES xxi

LIST OF APPENDIX TABLES xxii

LIST OF APPENDIX FIGURES xxiii

LIST OF APPENDIX SCHEMES xxv

CHAPTER 1. THE EFFECT OF PLANT OIL FATTY ACID COMPOSITION ON SYNTHESIS AND PROPERTIES OF LATEX POLYMERS 1

- 1.1. Vegetable Oils as Renewable Source for Sustainable Polymers 1
- 1.2. The Impact of Fatty Acids Structure on the Properties of Polymers Derived from Plant Oils 5
- 1.3. Utilization of Plant Oils for Polymer Synthesis 7
  - 1.3.1. Synthesis of Fatty Acid-Based Building Blocks 7
  - 1.3.2. Synthesis of Vinyl Monomers from Fatty Acid Derivatives 10
- 1.4. The Fundamentals of Emulsion and Miniemulsion Polymerization for the Latex Synthesis 14
- 1.5. The Feasibility of Synthesis of Biobased Latexes from Vegetable Oil-Based Monomers 19
- 1.6. Summary and Outlook 22
- 1.7. Research Objectives 24
- 1.8. Organization of the Dissertation 25
- 1.9. References 27

CHAPTER 2. ACRYLIC MONOMERS FROM PLANT OILS: SYNTHESIS AND CHARACTERIZATION 35

2.1. Introduction 35

2.2. Experimental 37

2.2.1. Materials 37

2.2.2. Characterization of Plant Oils Composition 38

2.2.3. Synthesis of POBMs 39

2.2.4. Characterization of POBMs Chemical Structure 40

2.3. Results and Discussions 43

2.4. Conclusions 52

2.5. References 53

CHAPTER 3. LIFE CYCLE ENVIRONMENTAL IMPACT CONSIDERATION IN THE DESIGN OF SOYBEAN OIL-BASED ACRYLIC MONOMERS 56

3.1. Abstract 56

3.2. Introduction 57

3.3. Materials and Methods 59

3.3.1. Materials 60

3.3.2. Synthesis of Soybean Oil-Based Biodiesel 60

3.3.3. Synthesis of Soybean Oil-Based Monomers (SBM_O/SBM_D) 60

3.3.4. Modeling Section: Building the LCA Model 62

3.3.4.1. The Goal and Scope of the LCA Study 62

3.3.4.2. System Boundary 62

3.3.4.3. Functional Unit 63

3.3.4.4. Life Cycle Inventory Data Collection 63

3.4. Results and Discussion 64

3.4.1 Testing the Effect of Soybean Oil and Soybean Biodiesel to HEAA Ratio on Monomers' Yields 64

3.4.2. Impact of Catalyst Selection 65

3.4.3. Evaluating the Environmental Performance of SBM_O and SBM_D 66

3.4.3.1. Solvent Recycling 69

3.4.3.2. Catalyst Selection 70

3.4.3.3. Comparing SBMs with Commercially Available Petroleum-Based Stearyl Acrylate 71

3.5. Conclusions 72

3.6. References 73

CHAPTER 4. FREE RADICAL POLYMERIZATION BEHAVIOR OF THE VINYL MONOMERS FROM PLANT OIL TRIGLYCERIDES 76

4.1. Abstract 76

4.2. Introduction 77

4.3. Materials and Methods 79

4.3.1. Materials 79

4.3.2. Plant Oil-Based Acrylic Monomer Synthesis and Characterization 79

4.3.3. Plant Oil-Based Acrylic Monomers Characterization 80

4.3.3.1. Iodine Value 80

4.3.3.2. Aqueous Solubility 81

4.3.3.3. Refractive Index 81

4.3.4. Free Radical Polymerization of Plant Oil-Based Monomers 82

4.4. Results and Discussion 82

4.4.1. Plant Oil-Based Monomer Synthesis and Characterization 82

4.4.2. Free Radical Polymerization of Plant Oil-Based Monomers 85

4.5. Conclusions 93

4.6. References 94

CHAPTER 5. FREE-RADICAL COPOLYMERIZATION BEHAVIOR OF PLANT OIL-BASED VINYL MONOMERS AND THEIR FEASIBILITY IN LATEX SYNTHESIS 97

5.1. Abstract 97

5.2. Introduction 98

5.3. Experimental Section 101

5.3.1. Materials 101

5.3.2. Plant Oil-Based Acrylic Monomer Synthesis and Characterization 102

5.3.3. Free-Radical Copolymerization of Plant Oil-Based Monomers with St/Vac 102

5.3.4. Plant Oil-Based Copolymer Characterization 103

5.3.5. Synthesis of Plant Oil-Based Latexes in Miniemulsion 103

5.3.6. Synthesis of Plant Oil-Based Latexes Using Emulsion Polymerization with Vac 104

5.3.7. Characterization of Plant Oil-Based Latexes 105

5.4. Results and Discussion 106

5.4.1. Radical Copolymerization of Plant Oil-Based Monomers 106

5.4.2. Synthesis and Properties of Biobased Latexes 111

5.5. Conclusions 117

5.6. References 117

CHAPTER 6. PLASTICIZING AND HYDROPHOBIZING EFFECT OF PLANT OIL-BASED ACRYLIC MONOMERS WITH STYRENE AND METHYL METHACRYLATE 121

6.1. Abstract 121

6.2. Introduction 121

6.3. Materials 124

6.4. Experimental Section 124

6.4.1. Plant Oil-Based Monomer (POBM) Synthesis 124

6.4.2. Biobased Latex Synthesis 125

6.4.3. Plant Oil-Based Latex Characterization 125

6.5. Results and Discussions 127

6.6. Conclusion 136

6.7. References 137

CHAPTER 7. VERSATILE PLATFORM FOR CONTROLING PROPERTIES OF PLANT OIL-BASED LATEX POLYMER NETWORK 139

7.1. Abstract 139

7.2. Introduction 140

7.3. Materials and Methods 142

7.3.1. Materials 142

7.3.2. Synthesis of POBM 142

7.3.3. Synthesis of POBM-Based Latexes Using Miniemulsion Copolymerization 144

7.3.4. Characterization of POBM-Based Latexes 145

7.3.5. POBM-Based Latex Crosslinked Films 146

7.4. Results and Discussion 148

7.5. Conclusion 155

7.6. References 156

CHAPTER 8. SYNERGISTIC EFFECTS OF CARDANOL- AND HIGH OLEIC SOYBEAN VINYL MONOMERS IN MINIEMULSION POLYMERS 161

8.1. Abstract 161

8.2. Introduction 162

8.3. Materials and Methods 165

8.3.1. Materials 165

8.3.2. Synthesis of HOSBM 165

8.3.3. Synthesis of CBM 165

8.3.4. Iodine Value 166
8.3.5. Free Radical (Co)Polymerization of CBM and HOSBM in Solution 167
8.3.6. Biobased Latex Synthesis 167
8.3.7. Characterization of Biobased Latexes and Latex Films 168
8.4. Results and Discussion 171
8.5. Conclusions 182
8.6. References 184
CHAPTER 9. BIOBASED LATEXES FROM NATURAL OIL DERIVATIVES 187
9.1. Abstract 187
9.2. Introduction 188
9.3. Materials and Methods 191
9.3.1. Materials 191
9.3.2. High Oleic Soybean Oil-Based Monomer (HOSBM) Synthesis 192
9.3.3. Synthesis of Eugenol-Based Monomer (EBM) 192
9.3.3.1. Step 1. Synthesis of 2-(2-methoxy-4-propylphenoxy) ethan-1-ol 192
9.3.3.2. Step 2. Synthesis of 2-(2-methoxy-4-propylphenoxy) ethyl Methacrylate 192
9.3.4. Synthesis of Guaiacol-Based Monomer (GBM) - triethyl(2-methoxy-4-vinylphenoxy) Silane 193
9.3.5. Characterization of HOSBM, EBM, and GBM 194
9.3.6. Free Radical Polymerization of EBM and GBM in Solution 194
9.3.7. Free-Radical Copolymerization of EBM and GBM with Styrene 194
9.3.8. Biobased Latex Synthesis 196
9.3.9. Characterization of Biobased Latexes and Latex Films 196
9.4. Results and Discussion 199
9.5. Conclusions 209
9.6. References 211

CHAPTER 10. CONCLUSIONS AND FUTURE DIRECTIONS 215

10.1. Conclusions 215

10.2. Future Studies 220

APPENDIX A. SUPPLEMENTAL MATERIAL FOR CHAPTER 3 223

APPENDIX B. SUPPLEMENTAL MATERIAL FOR CHAPTER 4 225

B.1. Reasoning of Reaction Order with Respect to Initiator Determination........................... 226

B.2. Initiation... 227

B.3. Chain Propagation 228

B.4. Chain Transfer 228

APPENDIX C. SUPPLEMENTAL MATERIAL FOR CHAPTER 5 232

APPENDIX D. SUPPLEMENTAL MATERIAL FOR CHAPTER 7 236

APPENDIX E. SUPPLEMENTAL MATERIAL FOR CHAPTER 8.. 238

APPENDIX F. SUPPLEMENTAL MATERIAL FOR CHAPTER 9.. 239

LIST OF TABLES

Table Page

2.1. The list of chemicals used in the study 38

2.2. Correlation of peak intensity of fatty acid fragments 46

2.3. Calculated fatty acid composition in plant oils using ^{1}H NMR spectroscopy 47

2.4. Unsaturation profile of POBMs 51

2.5. The physicochemical properties of plant oil-based monomers 52

3.1. SBM_O/SBM_D synthetic yield for two soy feedstocks and catalysts 68

4.1. Physico-chemical properties of plant oil-based acrylic monomers 85

4.2. Rate of polymerization and selected number-average molecular weight and polydispersity index of the resulting homopolymers synthesized from plant oil-based monomers at different temperatures 87

5.1. Monomer reactivity ratios for copolymerization of plant oil-based monomers and styrene 109

5.2. Q-e parameters of plant oil-based monomers. 109

5.3. Experimental and calculated monomer reactivity ratios in copolymerization of plant oil-based monomers with vinyl acetate 111

5.4. Characteristics of latexes from plant oil-based monomers and methyl methacrylate synthesized in miniemulsion process 113

5.5. Characteristics of latexes from plant oil-based monomers and vinyl acetate 113

5.6. Tensile properties (at room temperature) of latex films from OVM and SBM copolymerized with MMA 115

5.7. Surface energy of latex films from PVA and copolymers of vinyl acetate and plant oil-based monomers synthesized in emulsion polymerization process 116

6.1. Characteristics of latexes from POBM and MMA 129

6.2. Characteristics of latexes from POBM and St 129

6.3. Molecular weight between crosslinks (Mc) in polymer networks from POBM and St 131

6.4. Tensile properties of latex films from OVM and SBM copolymerized with MMA 133

6.5. Tensile properties of latex films from OVM and SBM copolymerized with St 133
6.6. Surface energy of latex films from copolymers of MMA and OVM or SBM 136
7.1. POBM-based latex polymer properties 151
7.2. Cured POBM-latex films properties 155
8.1. Characteristics of CBM and HOSBM latexes synthesized in miniemulsion 175
8.2. Cured biobased latex films properties 179
8.3. Cured biobased latex films tensile properties 180
8.4. Properties of CBM-HOSBM biobased latex coatings 181
9.1. Monomer reactivity ratios for copolymerization of GBM and EBM with St 203
9.2. Biobased latex polymer properties 204
9.3. Cured biobased latex films properties made from plant-based derivatives 206

LIST OF FIGURES

Figure Page

1.1. General structure of common vegetable oils and their typical fatty acid fragments composition (Reproduced from [12]). 3

1.2. Drying of vegetable oil through autooxidation mechanism.................. 4

1.3. The stress-strain plot of polyurethanes derived from different plant oils. (Reproduced from [24]). 6

1.4. Scheme of vegetable oil maleinization process. (Reproduced from [38]).................. 9

1.5. Acrylated epoxidized soybean oil structure. (Reproduced from [41]). 10

1.6. Scheme of methods of fatty acid conversion to reactive monomers. (Reproduced from [44]).................. 11

1.7. Chemical structure of (a) vinyl acetate (VAc), (b) vinyl oleate, and (c) vinyl linoleate. (Reproduced from [45]) 12

1.8. Synthesis of fatty acid-based methacrylates via Steglich esterification. (Reproduced from [47]) 12

1.9. Synthesis of soybean methacrylate (SBMA) from high oleic soybean oil via a two-step process. (Reproduced from [51]) 13

1.10. Scheme of emulsion polymerization mechanism. (Reproduced from [67]) 16

1.11. Schematic illustration of droplet nucleation mechanism in miniemulsion polymerization: a - at the start of the process; b - during the miniemulsion polymerization. (Reproduced from [68]). 18

1.12. Chemical structure of fatty acid-based monomers used in eco-paint latex synthesis. (Reproduced from [58]). 21

2.1. The chemical structure of plant oil triglyceride 35

2.2. The general scheme of the synthesis of plant oil-based monomer via transesterification reaction 40

2.3. Chemical structure of plant oil unsaturated fatty acids 44

2.4. The ^{1}H NMR spectrum and chemical structure of olive oil.................. 46

2.5. The ^{1}H NMR spectrum (left) and FT-IR spectrum (right) of high oleic soybean oil-based monomer (HOSBM).................. 49

2.6. The ^{1}H NMR spectrum (left) and FT-IR spectrum(right) of high oleic sunflower oil-based monomer (HOSBM)........ 49

2.7. ESI mass spectra of high oleic soybean monomer (HOSBM)........ 50

2.8. Solution transparency vs. concentration for olive oil-based monomer (left) and linseed oil-based monomer (right)........ 52

3.1. The chemical reactions of soybean oil-based acrylic monomers synthesis from soybean oil (A) and soybean biodiesel (B)........ 61

3.2. The flow chart of soybean oil-based acrylic monomers synthesis........ 63

3.3. Variation of diglycerides (A) and monoglycerides (B) formed during transesterification reaction of soybean oil (R-fatty acid chain)........ 65

3.4. The SBMs yield obtained through varying reaction components........ 66

3.5. Contribution of components used in SBMO synthesis to evaluate targeted environmental impact categories........ 67

3.6. Environmental performance of lab-scale and scaled-up SBMO production in targeted impact categories........ 70

3.7. Comparative contribution of tested SBMO and SBMD scenarios of various optimization pathways to TRACI 2 impact categories........ 71

3.8. Comparative environmental performance of SBMO with stearyl acrylate for targeted impact categories........ 72

4.1. ^{1}H NMR spectra of linseed (LSM) and olive (OVM) oil-based monomers........ 84

4.2. FT-IR spectra of LSM and OVM........ 84

4.3. Free radical polymerization kinetics of different [LSM] initiated by 0.038 mol/L of AIBN at 75 °C (A) and polymerization rate vs monomer concentration for the plant oil-based monomers (B)........ 86

4.4. Free radical polymerization kinetics of LSM (1 mol/L) at different concentrations of AIBN at 75 ^{o}C (A) and polymerization rate vs. initiator concentration for the plant oil-based monomers (B)........ 88

4.5. Chain transfer constant on monomer (C_M) in homopolymerization of plant oil-based monomers determined using the Mayo method (A) and dependence of C_M on temperature for SBM (B)........ 90

4.6. ^{1}H NMR spectrum of poly(LSM), and poly(OVM) polymers........ 92

5.1. Experimental content of plant oil-based monomer in the copolymers with styrene vs. content of plant oil-based monomer in the initial feed mixture 108

5.2. Calculated and experimental plant oil-based monomer content in LSM-based (A) and SBM-based (B) copolymer with VAc vs. plant oil-based monomer content in the initial feed mixture 110

6.1. Crosslink density vs. unsaturation amount (U_{MF}) and vs. plant oil-based content in monomer feed 132

6.2. The effect of monomer structure on properties of latex coatings 135

7.1. POBM molecular structure, typical chemical compositions of the plant oils used in this study in percentages and experimental iodine value for each monomer. R (x:y) is the structure of the fatty acids (x is the number of carbon atoms in the fatty acid chain, and y is the number of double bonds in the fatty acid). 144

7.2. DSC plot of the HSBM homopolymer (A), the crosslinking density $\boldsymbol{\upsilon}$ of POBM latex films with different unsaturations in the monomer feed (B), the influence of the POBM nature and HSBM content on the pendulum hardness, (C) the number above each bar corresponds to the value of $\boldsymbol{\upsilon}\cdot 105$) 154

8.1. Chemical structure of CBM (A) and HOSBM (B) 171

8.2. Rate of polymerization vs. initiator concentration (A) and monomer concentration (B) for HOSBM and CBM 172

8.3. Monomer chain transfer constant (C_M) in the polymerization of HOSBM and CBM determined using the Mayo method 174

8.4. ^{1}H NMR spectrum of poly (CBM-co-HOSBM) latex copolymer 176

8.5. DSC thermograms of latex polymers from 100% CBM (A), 75% CBM and 25% HOSBM (B) 50% - 50% (C) 100% HOSBM (D) in the feed 178

8.6. Storage modulus (E') (A) vs. temperature and DMA tan δ plots (B) of biobased crosslinked latex free films from 100% CBM – 1, 75% CBM and 25% HOSBM – 2, 50% CBM and 50 % HOSBM - 3, 25% CBM and 75% HOSBM – 4, 10 % CBM and 90 % HOSBM – 5 179

8.7. Stress-strain plots of biobased latex films from 100% CBM – 1, 50% CBM and 50 % HOSBM - 2, 25% CBM and 75% HOSBM – 3, 10 % CBM and 90 % HOSBM– 4 (A). Effect of HOSBM-CBM copolymer composition on pendulum hardness of biobased latex coatings (B) 180

9.1. Chemical structure of eugenol and guaiacol 190

9.2. Chemical structure of CBM (A), EBM (B), and GBM (C) 199

9.3. FTIR (A) and ^{1}H NMR (B) spectra of GBM ... 200

9.4. Monomer chain transfer constant (C_M) in the polymerization of EBM and GBM (inset) determined using the Mayo method ... 201

9.5. Experimental biobased content in the GBM-St and EBM-St copolymers vs. biobased content in the initial feed mixture ... 202

9.6. Stress – strain plots for biobased latex films from (A) EBM and HOSBM (A, 10 (1), 15 (2), 17 (3), 25 (4) wt.% of HOSBM), (B) GBM and HOSBM (10 (1), 15 (2), 17 (3), 20 (4), 25 (5) wt.% of HOSBM, respectively) ... 207

9.7. Effect of renewable monomers feed composition on pendulum hardness (A) and impact resistance (B) of biobased latex coatings ... 208

9.8. Effect of renewable monomers feed composition adhesion of biobased latex coatings to the metal substrate ... 209

LIST OF SCHEMES

Scheme Page

4.1. Allylic transfer mechanism in free radical polymerization... 89

5.1. Chemical structure of plant oil-based monomers and typical chemical compositions of plant oils used in this study for monomer synthesis.............................. 99

5.2. Selected monomer structure of (acryloylamino)ethyl linoleate..................................... 102

9.1. Two-step synthesis of 2-(2-methoxy-4-propylphenoxy) ethyl methacrylate (EBM) 193

9.2. The synthesis of triethyl(2-methoxy-4-vinyl-phenoxy) silane (GBM)........................... 193

LIST OF APPENDIX TABLES

Table Page

A1. Inventory of all chemicals used in LCA modelling 224

B1. Typical chemical compositions of plant oils used in this study in percentages 225

C1. Surface energy of latex films from copolymers of methyl methacrylate and OVM or SBM 233

LIST OF APPENDIX FIGURES

Figure Page

A1. Contributional distribution for targeted impact categories of catalyst optimization pathways used in SBM_O synthesis from soybean oil ... 223

A2. Contributional distribution for targeted impact categories of catalyst optimization pathways used in SBM_D synthesis from soybean biodiesel ... 223

B1. ^1H NMR spectra of soybean oil-based (SBM) and sunflower oil-based (SFM) monomers. ... 225

B2. Characteristic mass spectra of linseed oil-based and olive oil-based monomers. ... 226

B3. Free radical polymerization kinetics of different monomers [SFM] (A) and [SBM] (B) initiated by 0.038 mol/l of AIBN at 75 ^oC. ... 226

B4. GPC measurements of poly[(acryloylamino)ethyl oleate] synthesized in homopolymerization of [OVM] = 1 mol/L initiated by 0.038 mol/L of AIBN at 80^oC. ... 231

B5. FTIR spectra of poly(SBM) (A) and poly(LSM) (B). ... 231

C1. ^1H NMR spectra of copolymers from olive oil-based monomer (OVM) and methyl methacrylate (A) or vinyl acetate (B). ... 232

C2. TEM micrographs of latex particles OVM-MMA5 (A), OVM-MMA15 (B), SFM-MMA20 (C). ... 233

C3. ^1H NMR spectra of plant oil-based monomers. ... 234

C4. Mass spectra of plant oil-based monomers (A – from linseed oil, B – from olive oil, C- from soybean oil, D – from sunflower oil). ... 235

D1. Oxidatively cured POBM-based latex copolymer films with 60 wt.% of biobased content. ... 236

D2. Stress-strain diagrams (A) and the change of tan d with temperature (B) for OVM-based latex films at increasing HSBM content in copolymerization feed (wt.%). ... 236

D3. Stress-strain diagrams (A) and the change of tan δ with temperature (B) for SBM-based latex films at increasing HSBM content in copolymerization feed (wt.%). ... 237

D4. Stress-strain diagrams (A) and the change of tan δ with temperature (B) for LSM-based latex films at increasing HSBM content in copolymerization feed (wt.%). ... 237

E1. Selected water contact angle measurement on latex copolymer film with 50 wt.% of CBM and HOSBM content 238

F1. FT-IR (spectra A) and ^{1}H NMR (B) of EBM. 239

F2. Characteristic mass spectrum of GBM. 239

F3. Conversion–time changes in the copolymerization of St with GBM and EBM in various ratios. 240

LIST OF APPENDIX SCHEMES

Scheme Page

B1. Molecular structure of (acryloylamino)ethyl linoleate in SBM. 227

B2. Formation of allylic radicals in SBM and OVM. 230

CHAPTER 1. THE EFFECT OF PLANT OIL FATTY ACID COMPOSITION ON SYNTHESIS AND PROPERTIES OF LATEX POLYMERS

1.1. Vegetable Oils as Renewable Source for Sustainable Polymers

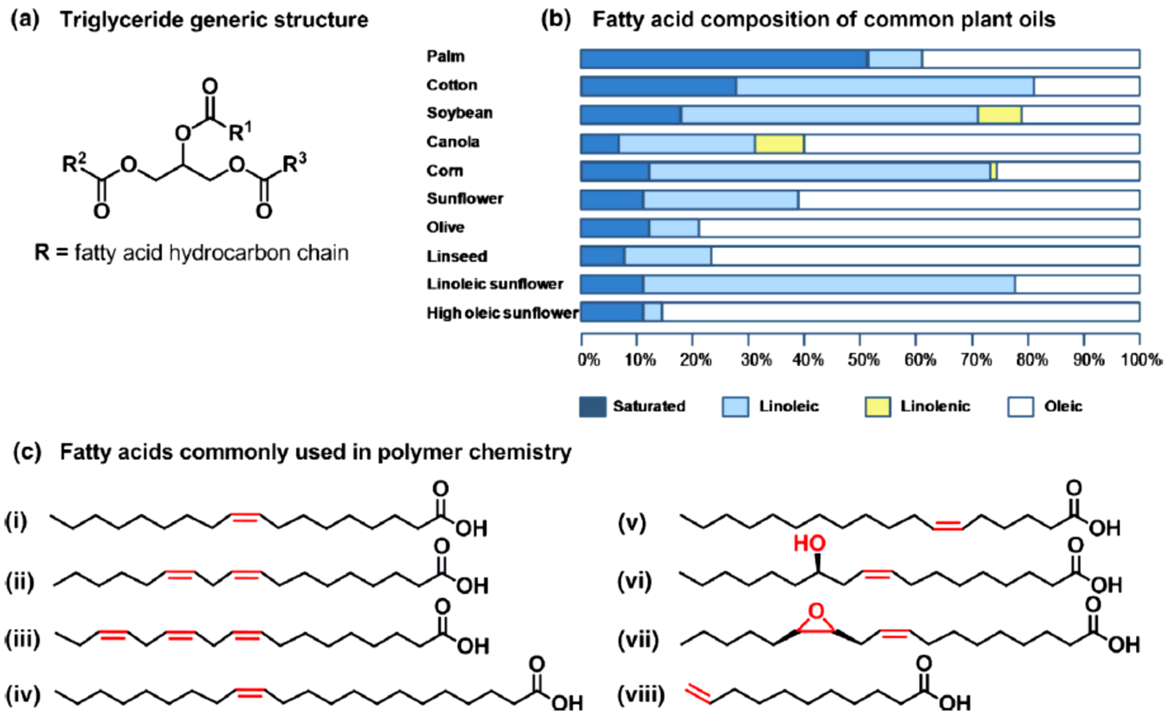
Nowadays, the industry becomes more concerned about sustainability and renewability issues associated with sources for material synthesis. Based on the forecast of fossil fuel feedstocks reserves, due to planet population growth and increase of energy demands, in 50 years, there will be no available sources (oil, gas, coal) for the material production. Finding a potential alternative resource is crucial for the industry in these years.[1-3] Moreover, the fast depletion of available petroleum feedstocks over the past years pushes the industry to focus on using renewables for material synthesis, which has a positive environmental impact, potential biodegradability, and can be renewed in a short period of time.

The scientific community is increasingly interested in utilizing renewable raw materials for polymer synthesis.[2] The definition of "polymers from renewables" means macromolecular materials that are natural or can be converted to polymers using synthetic procedures from biomass or formed by polymerization of monomers derived from renewable resources.[2-5] Therefore, researchers are currently developing strategies to synthesize polymers from renewable resources for the application in different areas, including composites, coatings, adhesives, etc.

For centuries, a variety of vegetable oils has been found as non-pollutive renewable resources, providing a broad range of fatty acid compositions with diverse applications. In recent years, worldwide availability, abundance, inheritable biodegradability are increasingly making oils a unique, promising resource in developing various polymeric materials.[6] One of the most prominent applications of vegetable oils is making binders and additives for paints and coatings applications[7-8]. Due to their drying behavior being exposed in the air and crosslinking via the autooxidation mechanism, plant oils can be incorporated in numerous coatings formulations.[9] In addition to plant oils used as essential edible components in food processing, they are also used in making soaps, lubricants, lacquers, biofuels. The utilization of non-edible oils in material formation has also brought interest due to lowering the extent of interfering with food supply and the opportunity to utilize unproductive lands to grow non-edible crops.[10] The utilization of renewable raw materials, like vegetable oils, in material synthesis meets one of the principles of Green Chemistry, contributing to the process sustainability overall. Following the sustainable pathway in material synthesis makes one step closer to be qualified in the future as an alternative source for producing polymers in the commercial framework. As the interest of these abundant renewable resources is rising enormously, the global production of vegetable oils has doubled in the last decade, counting 195 Mt in 2016/2017 with a forecast of 205 Mt by 2021.[11]

The main components of plant oils are triglycerides - the esterification products of glycerol and fatty acid chains. The unsaturation of fatty acid fragments and their chain length make each vegetable oil unique and diverse even between the same crop type. Due to the presence of ester linkages, double bonds in the fatty acid chain and functional groups (like OH group in castor oil) provide a broad opportunity for either tailoring new chemical structures or introducing reactive sites to form crosslink networks for thermoset systems. The presence of long fatty acid chains in triglycerides features perceptible hydrophobic properties of plant oils. The apparent hydrophobicity of these renewable materials makes them applicable for various applications, including hydrophobizing agents, chemicals for material protection and preservation, etc. The general structure of common vegetable oils and their composition is shown in Figure 1.1.[12]

Plant oil-based polymeric materials can be synthesized by various pathways via functionalization of the triglycerides to be utilized in polymerization processes or in post-polymerization reactions via crosslinking chemistry. The most common approach is modifying double bonds in triglycerides via epoxidation to deliver epoxidized vegetable oils that can be used directly in thermoset synthesis or can be further transformed into acrylates, carbonates, or other reactive blocks for polymer production.[13]


(a) Triglyceride generic structure

(b) Fatty acid composition of common plant oils

(c) Fatty acids commonly used in polymer chemistry

Figure 1.1. General structure of common vegetable oils and their typical fatty acid fragments composition (Reproduced from [12]).

The other appealing approach of vegetable oil modification is breaking down the triglyceride molecules and formation of plant oil-based monomers for various polymerization mechanisms, including free radical, cationic, or polycondensation, etc.[14-16] Such methods of vegetable oil modification result in the formation of vegetable oil-based building blocks for the synthesis of linear or crosslinked polymers.[17] The plant oil composition has an important aspect in material functionalization and determines the final properties of resulted products. The level of plant oil unsaturation is a factor that distinguishes these renewable resources into a broad range of materials with varying physical properties and performance.[12] The unsaturated sites in fatty acid structure allow material functionalization or undergo direct crosslinking reactions via autooxidation mechanism. The direct oxidation of double bonds in fatty acid fragments proceeds through the abstraction of hydrogen atom H from a bis-allylic group located between double bonds in a polyunsaturated fatty acid chain leading to crosslinking due to radical recombination in the presence of oxygen molecules. The detailed mechanism of the drying process of vegetable oils is shown in Fig. 1.2.[31].

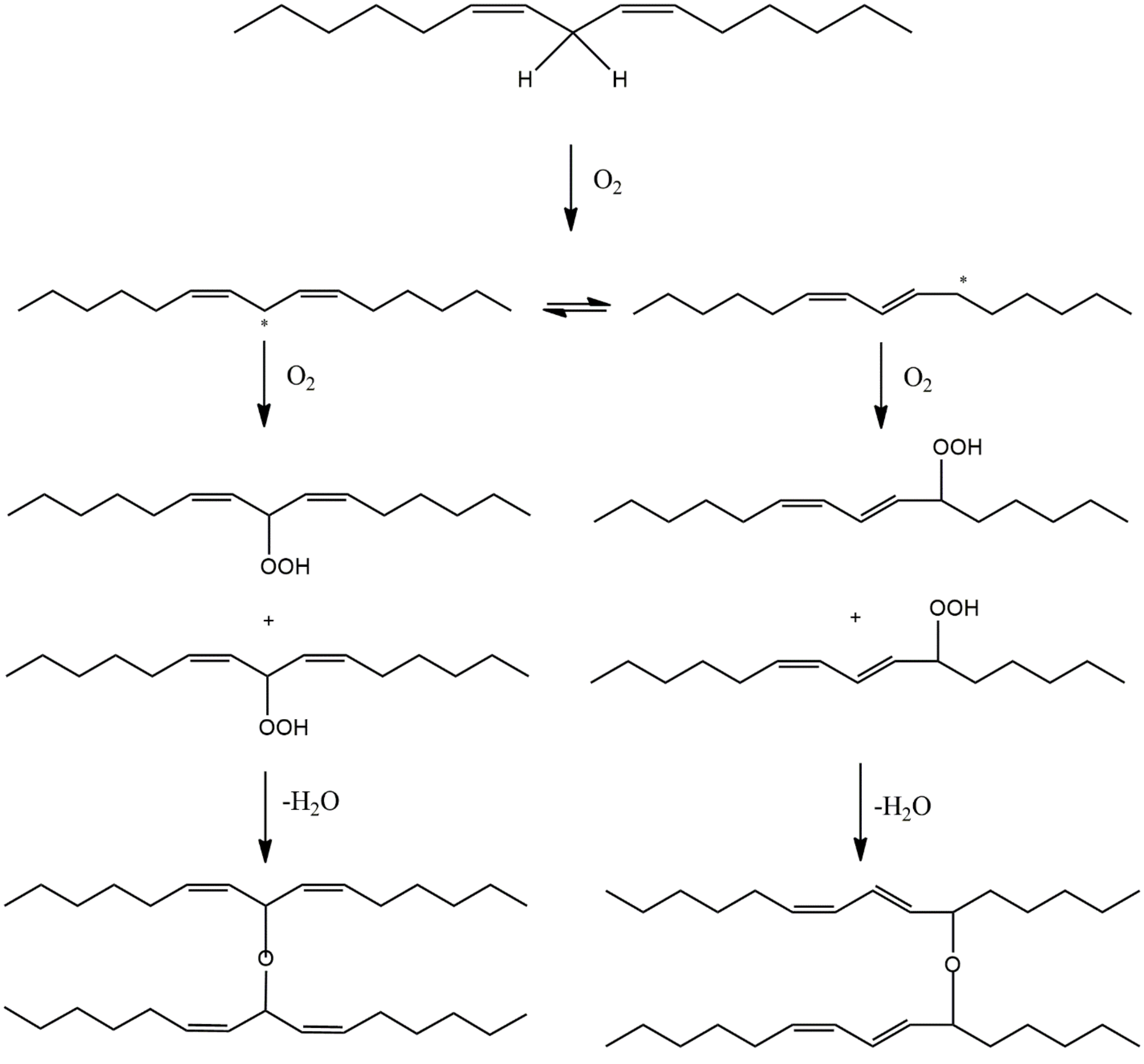


Figure 1.2. Drying of vegetable oil through autooxidation mechanism

1.2. The Impact of Fatty Acids Structure on the Properties of Polymers Derived from Plant Oils

The composition of vegetable oil can control the properties of biobased polymers derived thereof. It is desirable to form polymeric materials with pre-determined properties based on the plant oil chosen for the synthesis[6]: the chain length and degree of unsaturation impact the physical and chemical properties of vegetable oils. The latter is evaluated by measuring the iodine value (IV) - the main characteristic of the unsaturation degree of fatty acid determining how much iodine (g) reacts with double bonds presented in fatty acid chains. Plant oils are classified as low-unsaturated non-drying (IV<100), semi-drying with medium unsaturation (100<IV<130), and high-unsaturated drying oils (IV>130).[18] Such a wide variety of vegetable oil and current advanced methods of modification provide an opportunity to synthesize a broad range of materials for a wide range of applications from highly crosslinked thermosets to linear thermoplastics.[19]

The chain length of fatty acid fragments and its degree of unsaturation determine the physicochemical and mechanical properties of resulted polymeric materials.[18] It was found that increasing the fatty acid chain length leads to a change of the thermo-mechanical behavior of formed polymeric materials from the amorphous state to semi-crystalline in specific cases.[20,21] The main reason for this transformation is a phenomenon of non-polar interactions on long alkyl dangling chains, which restricts mobility and results in the crystallinity of formed polymers.[22] The difference in fatty acid composition with a diverse degree of unsaturation demonstrated an even higher impact on the properties of polymeric materials rather than the chain length. This effect is more pronounced due to the versatility of C=C double bond presented in the fatty acid chain. These double bonds can be modified to epoxy, hydroxyl, acrylic functionalities or directly used in crosslinking reaction via autooxidation mechanism.[23] Therefore, the level of unsaturation is directly related to the functionality of plant oil-based derivatives and contributes to the effect on thermomechanical properties of resulted materials.

Larock et al. has reported a noticeable effect of the unsaturation amount of vegetable oils on the thermal and mechanical properties of waterborne polyurethanes, where the higher degree of unsaturation leads to improvement of toughness, Young's modulus, and break strength.[24] The double bonds presented in vegetable oils that were not involved in forming polyols for polyurethane synthesis provide the platform for crosslinking network formation via autooxidation mechanism. The enhanced thermomechanical properties of formed polyurethane materials were achieved in the cases where high unsaturated oils (linseed, corn) were used for the synthesis of polyols with residual unsaturation (Fig 1.3).

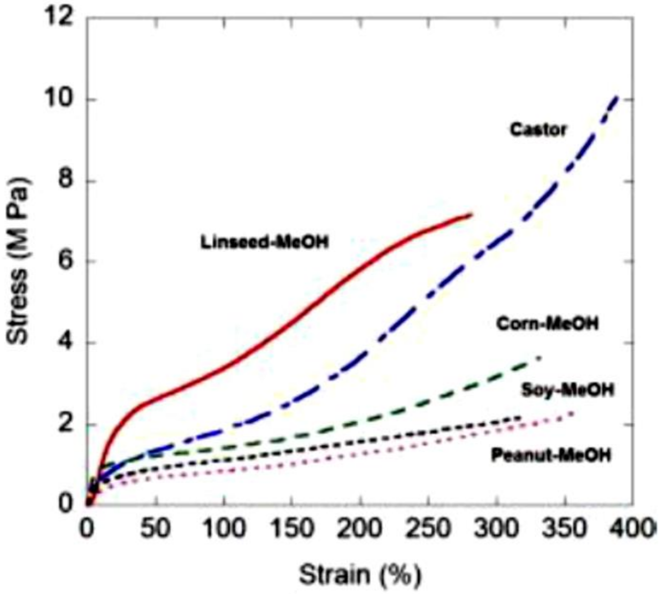


Figure 1.3. The stress-strain plot of polyurethanes derived from different plant oils. (Reproduced from [24]).

Another study performed by Petrovic and coworkers has shown similar behavior in the characterization of polyurethanes derived from vegetable oils with different unsaturation degree.

The glass transition temperature, tensile stress at break, and flexural modulus in linseed oil derivatives have shown the highest values than others due to the high density crosslinked network formed in the synthesis of polyurethanes.[25] The resulted crosslink network in linseed-based polyurethanes restricts the mobility of polymer chains leading to the limited elongation and impacts resistance value. The difference in fatty acid composition and degree of unsaturation affect the viscosity of resulted materials. The higher unsaturation of fatty acid chains leads to the lowering of viscosity due to the formation of kinks along fatty acid chains that enhance intermolecular spacing and decrease the effect of intramolecular interactions.[26]

The unsaturation effect could be used as a parameter that can tune the material performance by varying the amount of double bonds, functionality, or process conditions. However, the deep understanding of how the degree of unsaturation relates to the thermomechanical properties and how it can be used to tune the performance of resulted polymers still remains unclear. Therefore, finding a rational approach to address these relations between unsaturation and material performance would be desirable.

1.3. Utilization of Plant Oils for Polymer Synthesis

1.3.1. Synthesis of Fatty Acid-Based Building Blocks

For the last few decades, vegetable oils have become a unique renewable source to produce polymeric materials through various polymerization mechanisms.27 The reason why plant oil chemical structure has brought great attention for the researchers is the availability of many sites (double bonds in fatty acid fragments) for its direct modification via free radical polymerization mechanism28, inherent hydrophobicity and biodegradability, and providing flexibility due to the presence of long fatty acid chains.29 Double bonds presented in plant oils can undergo direct modification using oxidation mechanism or can be converted into more reactive species like epoxides, acrylates, carbonates to further its utilization in the formation of thermoset polymers.30

Although the autooxidation process is applicable for the vegetable oil modification and formation of crosslinked networks, the reactivity of non-conjugated double bonds in fatty acid fragments is lower compared to other pathways of double bonds modification in vegetable oils.32 Therefore, the conversion of vegetable oils through conjugation enhances the reactivity of double bonds. Few studies reported the utilization of conjugated linseed and soybean oils in free-radical copolymerization with acrylonitrile and dicyclopentadiene yielding thermosets with outstanding mechanical properties and thermal stability.33,34 Liu and coworkers have explored the successful formation of thermosets using thermal copolymerization of tung oil with styrene and divinylbenzene at elevated temperatures up to 160 °C with a broad range of Tg from -2 °C to 116 °C.[87] This polymerization process requires high energy input and mostly applicable for highly unsaturated vegetable oils.

More advanced approaches are desired to improve the reactivity and effectiveness of vegetable oils in the free radical polymerization process. Apart from the conjugation of double bonds in fatty acid fragments, incorporating a more reactive C=C double bond into vegetable oil structure can improve the polymerizability of plant oil-based derivatives and add more value to the oil-based products.[35] This approach was explored by several researchers where the vegetable oil was converted to monoglyceride following by maleinization reaction yielding high reactive vegetable oil-based derivatives (Fig.1.4).[36,37] Such route of vegetable oil modification has resulted in a reactive vegetable oil monomer utilized for the formation of rigid biobased thermosets by copolymerization with styrene using conventional free radical polymerization initiated by AIBN.[38]

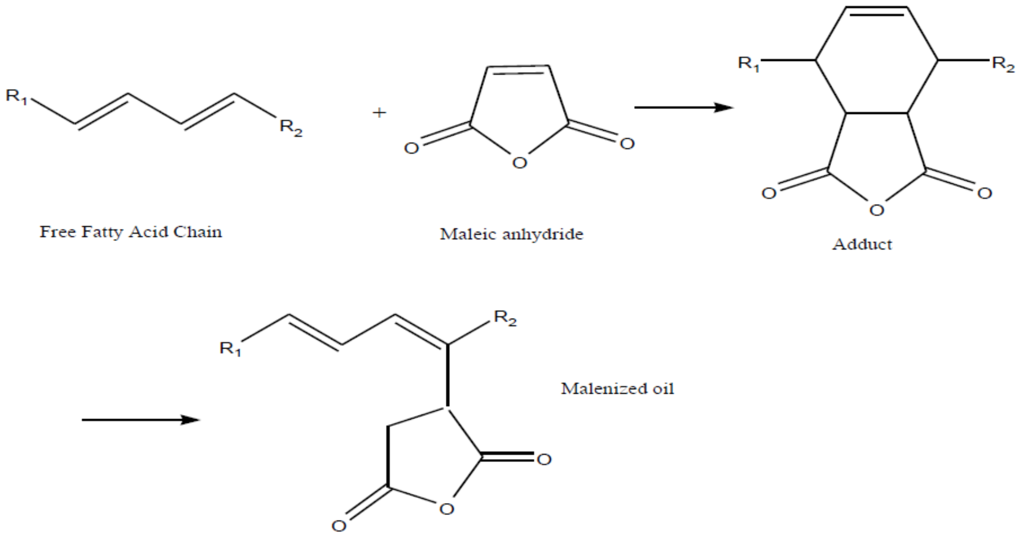


Figure 1.4. Scheme of vegetable oil maleinization process. (Reproduced from [38])

Other alternative approaches have been established by introducing acrylic moieties to vegetable oil structure through the acrylation of triglyceride to various extent.[39] The resulted material, commonly used in UV-curable resins, is known as acrylated epoxidized vegetable oil, where the double bonds undergo functionalization by acrylic fragments.[40] The modification of double bonds in triglyceride structure leads to the formation of highly functionalized molecules with molecular weight over 1000 g/mol that are used as building blocks for the formation of crosslinked networks (Fig. 1.5).

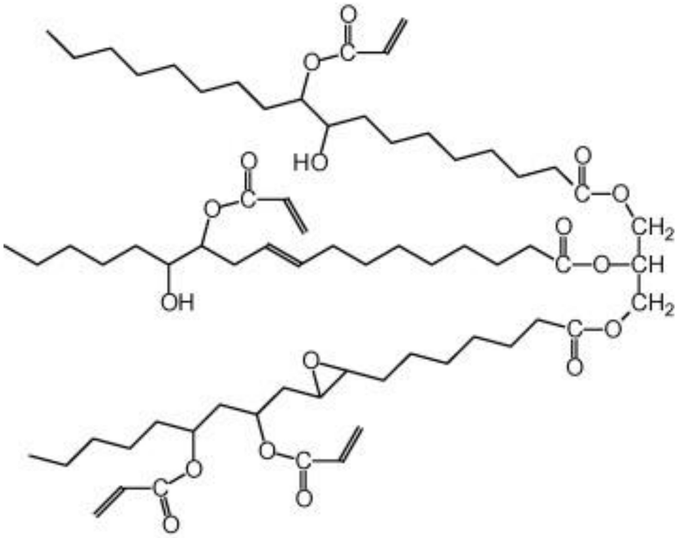


Figure 1.5. Acrylated epoxidized soybean oil structure. (Reproduced from [41]).

There are alternative approaches to synthesize linear polymers that appeared as the chemical modification of triglycerides via hydrolysis, alcoholysis, or transesterification to produce polymeric materials by using directly fatty acids or for the synthesis of building blocks with more sophisticated monomer structures.[28] These methods can be considered as industrially feasible and have advantages in terms of sustainability, allowing functionalization of fatty acid fragments without extensive chemical modification to produce monomers for free radical polymerization processes.[42]

1.3.2. Synthesis of Vinyl Monomers from Fatty Acid Derivatives

The importance of the synthesis of vinyl monomers from plant oils has brought a lot of interest among researchers to form linear polymer/copolymers with advanced properties and for special applications.[43] Few methods have been established to synthesize reactive vegetable oil-based monomers for free radical polymerization, including transvinylation, acrylamidation, transesterification, modification through epoxidation followed by ring-opening, esterification, and two-step process via (meth)acrylation and fatty acid amide derivatives (Fig. 1.6).[44]

Vilela et al. reported the utilization of transition metal-catalyzed transvinylation of oleic and linoleic acid with vinyl acetate (Fig. 1.7). The resulted fatty acid monomers have been copolymerized with vinyl acetate yielding flexible copolymers with potential applications in coatings. However, the yield (~50%) and low molecular weight of these copolymers (~2500 g/mol) have a negative effect on the mechanical properties of resulted polymers designed for specific applications.[45]

Recently, the transesterification of fatty acid derivatives has been established as a promising pathway for synthesizing fatty acid-based monomers for free radical polymerization. The concept is underlaying in the modification of fatty acids/vegetable oils by breaking down the ester bonds (in triglycerides) or conducting the esterification reaction of the carboxyl group presented fatty acid by introducing the vinyl bond to the resulted molecular structure.

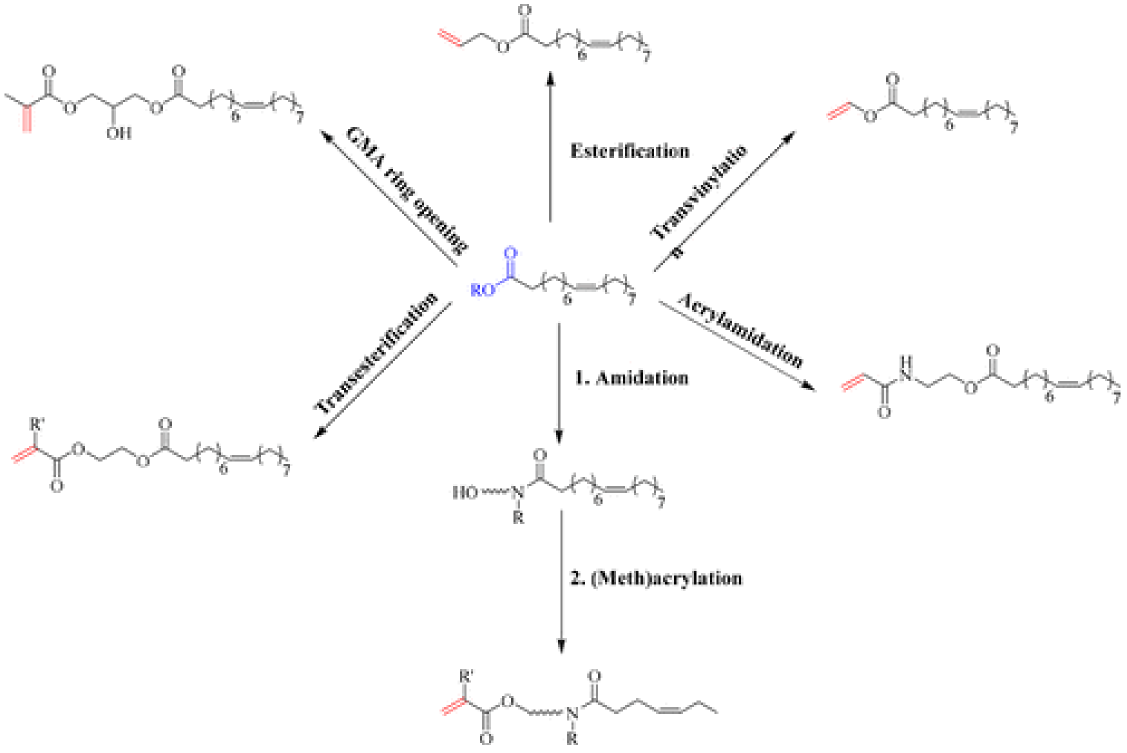


Figure 1.6. Scheme of methods of fatty acid conversion to reactive monomers. (Reproduced from [44])

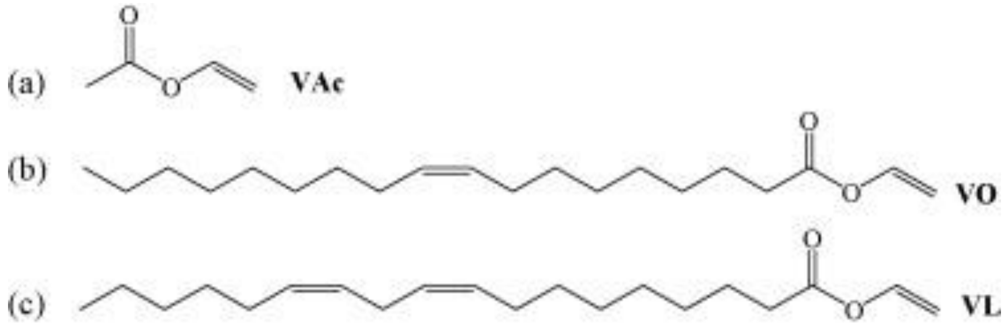


Figure 1.7. Chemical structure of (a) vinyl acetate (VAc), (b) vinyl oleate, and (c) vinyl linoleate. (Reproduced from [45])

Maiti and co-workers have synthesized a series of methacrylated fatty acid derivatives using Steglich esterification of N-hydroxyethyl methacrylate with a range of fatty acids in the presence of a coupling agent dicyclohexyl carbodiimide and 4-dimethyl aminopyridine as a catalyst at room temperature conditions (Fig.1.8).[46] The resulted monomers have shown good polymerizability in reversible addition-fragmentation chain transfer (RAFT) polymerization yielding polymeric materials with a broad range of physical properties, including the difference in crystallinity and solubility.[46,47]

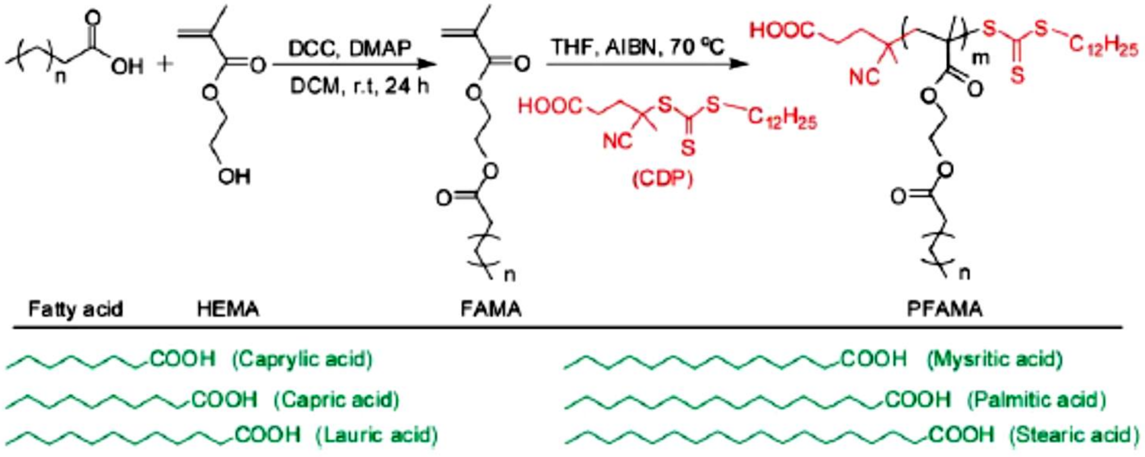


Figure 1.8. Synthesis of fatty acid-based methacrylates via Steglich esterification. (Reproduced from [47])

Another transesterification approaches were reported in literature utilizing fatty acids to form the reactive fatty acid-based monomers. However, these methods require harsh process conditions, including temperature, excess of the reactant, or using hazardous compounds like phosphorous chloride to enhance the reactivity of fatty acids in transesterification reaction with acrylic alcohols.[48-50] More recently, Tang et al. has established the two-step method for the synthesis of the reactive monomer from high oleic soybean oil by formation a soybean fatty hydroxyl amide intermediate following the methacrylation step via Steglich esterification mechanism.[51] The performed research approaches found in the literature require a two-step synthesis pathway and harsh process conditions to produce fatty acid-based monomers with high yield (Fig.1.9).

Decostanzi et al. developed a similar approach utilizing Steglich esterification to obtain oleic acid methacrylates that later were incorporated into thermosets by crosslinking with succinic anhydride for potential coatings applications.[52]

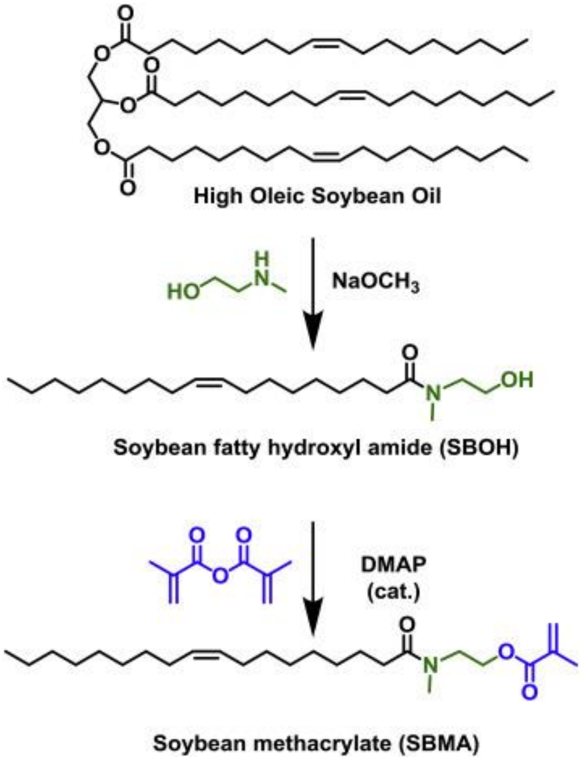


Figure 1.9. Synthesis of soybean methacrylate (SBMA) from high oleic soybean oil via a two-step process. (Reproduced from [51])

Finding an alternative method to synthesize reactive monomers by direct transesterification reaction at mild conditions will provide a safe and easier way for the synthesis of acrylic monomers from plant oils.

Reactive fatty acid-based acrylic monomers can be polymerized in free radical polymerization reactions, including solution, emulsion, suspension processes, and form biobased polymers with enhanced hydrophobicity, flexibility, and inherent biodegradability.[50,53-55]

Acrylic monomers have been widely used in binder synthesis for paint and coatings applications due to good exterior stability, UV-resistance, excellent performance, and alkali resistance.[56,57,29] The incorporation of acrylic monomers in latexes to produce waterborne polymers has many advantages over solvent-borne paints, including low volatility, environmental friendliness, faster drying time, and easier clean-up.[58] Therefore, the formation of latexes from plant oil-based acrylic monomers would even improve the importance and value of acrylic latexes by providing the hydrophobicity, film-forming, and renewable aspects to waterborne paints.

1.4. The Fundamentals of Emulsion and Miniemulsion Polymerization for the Latex Synthesis

The development of waterborne polymers has been even adding value to the coatings systems by providing the “greener” alternative to the conventional solvent-borne coatings by lowering VOC content and flammability.[59] The increased environment and health legislation linked with the use of solvents for coatings applications make waterborne polymer systems a prominent replacement in the coatings area. The formation of latex coating requires coalescence to happen, where latex particles are softening and merging, forming a uniform surface coverage.[60] Therefore, the inclusion of vegetable oil-based derivatives in waterborne polymer systems will benefit in lowering the glass transition temperature of latex, allowing coalescence of a film without using additional coalescent aids.[61] Additionally, the presence of double bonds in the fatty acid fragment can be used for crosslinking reactions resulting in a durable coating surface.[12] However, the highly hydrophobic nature of vegetable oil-based derivatives used in waterborne coatings systems is challenging in the emulsification and stabilization of waterborne systems. Finding the rational way to synthesize stable vegetable oil-based waterborne polymers has brought an enormous interest of study among researchers.[62]

Emulsion polymerization is a unique polymerization process known among various chemical industries to produce latex products.[63,64] The emulsion polymerization process attracts more attention among researchers and scientists since the development of styrene-butadiene copolymers and poly(vinyl acetate) latexes for paint production in the post-World War II period.[65] The process involves using water as a media and monomers with limited aqueous solubility. This is a heterogeneous process of latex formation that can be directly used for application after synthesis. The outstanding heat transfer, the controlled molecular weight of resulted polymers, and low viscosity make this process more feasible for industrial uses. The formation of waterborne latexes as environmentally friendly materials has been appealing among researchers. There is continuously growing interest in establishing the fundamentals of the mechanism and kinetics of emulsion polymerization.[66] The method represents a water-insoluble monomer dispersion in aqueous media stabilized using surfactant and polymerized via free radical polymerization mechanism in the presence of a water-soluble initiator. The emulsion polymerization process consists of three stages, including nucleation of monomer-swollen micelles, latex particle growth, and consumption of residual monomer (Fig. 1.10).[67]

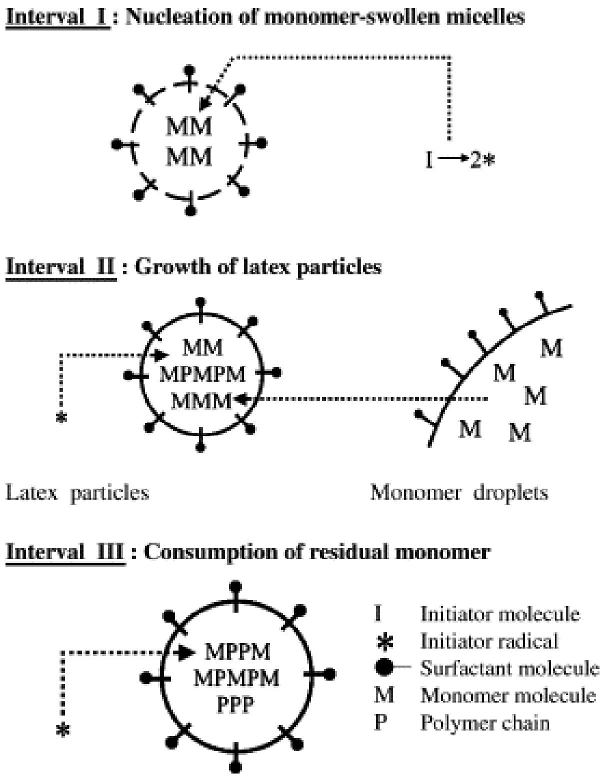


Figure 1.10. Scheme of emulsion polymerization mechanism. (Reproduced from [67])

The hydrophobicity of the monomer mixture impacts the particle nucleation mechanism ranging from homogeneous to micellar nucleation.[68] The essential stage in emulsion polymerization is monomer diffusion from the monomer droplets through the aqueous phase meaning that monomer should have limited solubility in water sufficient for its transfer from monomer droplets to micelles. Monomers with insufficient for diffusion aqueous solubility have difficulties polymerizing in conventional emulsion polymerization; thus, miniemulsion polymerization can be applied.

The privilege of miniemulsion polymerization is to provide an opportunity to polymerize highly hydrophobic monomers in latex synthesis. Miniemulsion polymerization was discovered in 1973 by Ugelstad et al. by introducing monomer emulsion droplets as a locus for polymerization that was not much considered before.[69] The method involves the use of co-stabilizer and oil-soluble initiators, making the polymerization running feasible in monomer droplets as “nanoreactors” for the miniemulsion process (Fig. 1.11).

The miniemulsion process requires the monomer droplet size below 500 nm, where mostly all monomer droplets serve as reservoirs for the polymerization process. The absence of monomer diffusion and micelles in the media turn the miniemulsion polymerization process to have only a droplet nucleation mechanism where monomer and oil-soluble initiators are located in small monomer droplets formed by sonication of high homogenization techniques.[70]

In most cases, the amount of initiator does not affect the number of polymer particles obtained after the completion of the miniemulsion polymerization process. It can be used as clear evidence of the droplet nucleation mechanism.[71]

The synthesis starts with the formation of pre-emulsion containing hydrophobic monomers, co-stabilizer (usually, hexadecane), oil-soluble initiator, surfactant, and water. The resulted pre-emulsion undergoes the homogenization or sonication processes forming monomer particles with finite particle numbers in the range of 5-300 nm.

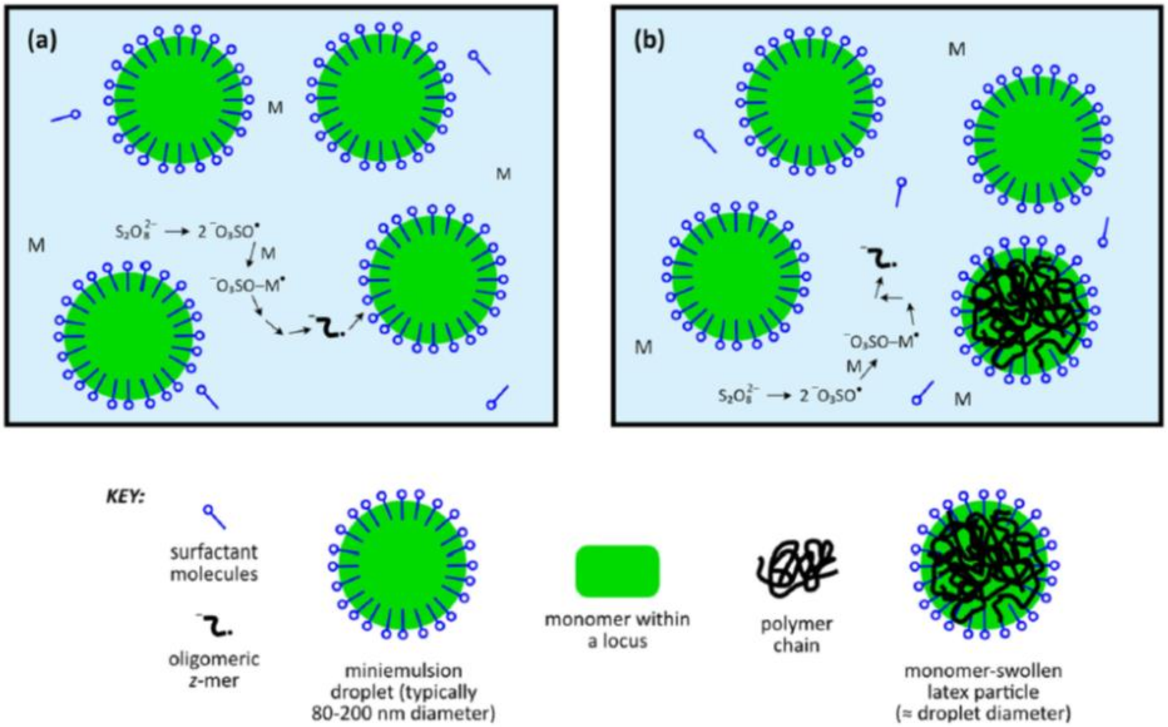


Figure 1.11. Schematic illustration of droplet nucleation mechanism in miniemulsion polymerization: a - at the start of the process; b - during the miniemulsion polymerization. (Reproduced from [68]).

The effective ratio between surfactant and co-stabilizer provides an opportunity to stabilize of the prepared miniemulsion and eliminate the Ostwald ripening happening during the polymerization.[70] The Ostwald ripening evolves the shrinkage of smaller droplets to larger sizes due to the diffusion mechanism to reduce the interfacial free energy of the system.[72] The inclusion of hydrophobic co-stabilizer minimizes the miniemulsion instability leading to the uniform distribution of monomer droplets in the aqueous phase. Due to the high surface area of monomer droplets in the miniemulsion, all surfactant molecules are used for monomer stabilization leading to the depletion of surfactant molecules used to form micelles. Hence, in the ideal miniemulsion process, all monomer droplets are nucleated and converted to polymer particles after completing the polymerization.

Miniemulsion polymerization has shown several advantages over emulsion polymerization, including high shear stability, lower viscosity compared to latex produced by emulsion polymerization, and good reproducibility of particle nucleation under the constant conditions.[73] The lower viscosity of latexes synthesized using miniemulsion polymerization is attributed to the polydispersity of latex (broader particle size distribution), considering that small particles fit in the voids of an array of big particles.[70] The better shear stability of latexes formed by the miniemulsion is attributed to the intensive Brownian motion latex polymer particles with a size less than one half of micron keeping the miniemulsion from creaming.[74] Additionally, since the miniemulsion polymerization is carrying out in monomer droplets containing oil-soluble initiator stabilized by surfactant, the monomer transport through the aqueous phase is not required allowing the possibility to prepare latexes from highly hydrophobic monomers. Few studies are reporting the use of the miniemulsion process for encapsulation of drugs, pigments, and other specific materials; designing hybrid and grafted materials from existing polymers; and finally, the study of controlled radical polymerization processes to synthesize high molecular weight polymers.[68, 70]

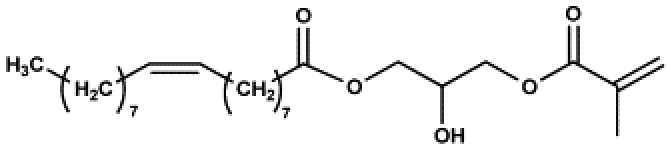
Miniemulsion polymerization is a unique process and well-suitable for synthesizing latexes from highly hydrophobic vegetable oil-based monomers that overcome limitations linked with emulsion polymerization and provide an opportunity to synthesize high-solid stable latexes.

1.5. The Feasibility of Synthesis of Biobased Latexes from Vegetable Oil-Based Monomers

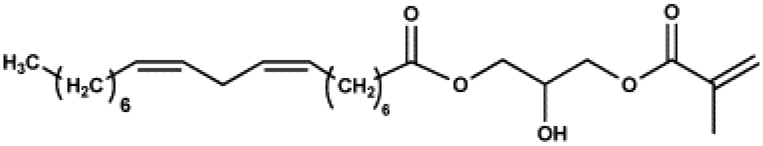
The evolution of latexes from renewable resources has brought a lot of interest in the past ten years.[75] Researchers are trying to incorporate vegetable oil-based reactive monomers into emulsion polymerization to form latexes, which can be directly used for application after synthesis. The reports show that incorporating vegetable oil-based monomers into emulsion polymerization has limitations due to low monomer aqueous solubility and limited monomer diffusion through the aqueous phase, which is required in the emulsion process. Machado et al. have incorporated up to 10% acrylate soybean oil-based monomer into terpolymer with MMA and BA to form terpolymers with tailored properties.[76] A similar method was established by Barbosa et al., synthesizing tert-polymers with 10 % of the acrylic fatty acid derivative using emulsion polymerization to provide the opportunity for tert-polymer to undergo crosslinking via autoxidative curing process.[77] Another approach utilized the excessive amount of acrylic acid to polymerize the acrylated methyl oleate in emulsion polymerization.[78] The reported attempts adding a small amount of acrylic acid to induce the monomer mix aqueous solubility delivered low molecular weight and low conversion latex polymers. Kingsley et al. provided valuable insights about emulsion polymerization kinetics of vegetable oil-based monomers with styrene, incorporating hydrophobic monomer into latex copolymers. The emulsion polymerization kinetics has seemed to have no changes while adding plant oil-based hydrophobic monomers into copolymers with styrene following Smith-Ewart theory. The molecular weight and conversion have dropped due to several reasons, including the difficulty of monomer diffusion at higher biobased content (20 % and above) and degradative chain transfer processes.[79]

For better feasibility of the synthesis of stable latex from highly hydrophobic monomers, it is more likely to follow the miniemulsion polymerization utilizing the droplet nucleation mechanism.

M. Moreno and co-workers have claimed the formation of sustainable latexes via miniemulsion polymerization using oleic- and linoleic acid-based monomers synthesized by methacrylation of the carboxylic acid with glycidyl methacrylate using two-step processes. It was also determined that the unsaturation amount of these monomers has a noticeable effect on molecular weight and glass transition temperature of resulted polymers (Fig. 1.12).[58, 80-82]



Methacrylated Oleic Acid (MOA)



Methacrylated Linoleic Acid (MLA)

Figure 1.12. Chemical structure of fatty acid-based monomers used in eco-paint latex synthesis. (Reproduced from [58]).

Earlier, another research has reported the incorporation of 35% vegetable oil-based macromonomers using miniemulsion to produce highly branched or crosslinked network upon film application.[83] Flexible low Tg polymers were synthesized using acrylated methyl oleates via miniemulsion copolymerization with methyl methacrylate and 1,4-butanediol diacrylate for pressure-sensitive adhesive applications; however, it requires an excessive amount of surfactant (15%) to stabilize latex that could affect lowering the adhesion performance.[84] In further research, Medeiros and co-workers copolymerized acrylated fatty acid methyl esters with styrene using miniemulsion to use the resulted latexes in several fields, including paints, coatings, adhesives since their range of Tg was varying from -55 to 50 ^{o}C.[85]

The synthesis of fully renewable latexes using miniemulsion polymerization is even more attractive nowadays to lower the toxicity and low biodegradability related to using petroleum-based materials in latex formation.[86] Thus, using highly biobased monomers and environmentally friendly miniemulsion could noticeably enhance the sustainability of resulted latex materials. This approach has not been widely established yet and can bring some challenges while polymerizing monomers from renewable resources. Moreno et al. has been developed a range of latexes via miniemulsion polymerization from renewable oleic acid-based methacrylate and α-methylene-γ-butyrolactone. The incorporation of lactone moieties provides the opportunity to obtain copolymers with a broad Tg range while improving the mechanical properties and thermal stability of latex materials.[55] Another renewable feedstock, eugenol, was used by Molina-Gutiérrez and co-workers to deliver low solids fully renewable latexes using emulsion polymerization with different initiation systems. The resulted eugenol-based copolymers with Tg ranging from 20 to 70 ^{o}C were claimed to be used for coatings and adhesive applications in the future.[86]

Therefore, the synthesis of biobased latex polymers for coatings and adhesive applications is a fascinating strategy since they significantly induce the environmental friendliness and renewability of resulted materials. However, obtaining the established approach to form high-performance renewable polymers from plant oils remains as future challenges.

1.6. Summary and Outlook

The present chapter summarizes the current focus of the dissertation research study to introduce renewable monomers and polymers thereof with the potential to be used in various industrial applications such as coatings, adhesives, personal care, etc. The renewability aspect is playing a significant role in the design of reactive monomers from plant oils since it allows to produce materials with inherent biodegradability and positive environmental impact. Choosing plant oils as a renewable feedstock for the polymer industry has brought promising opportunities due to its low cost, hydrophobicity, worldwide availability, and rich application possibilities. The presence of long fatty acid chains with various unsaturation amount provides features properties to polymeric materials while being incorporated in their structure. Except for enhanced adhesion, flexibility, and water-resistant properties, the unsaturated bonds in fatty acid structures act as sites for material functionalization or/and crosslinking reactions via autooxidation mechanism. This feature of fatty acid chains allows tailoring of the thermomechanical properties of resulted polymeric materials to a different extent by varying the degree of plant oil unsaturation.

Synthesis of monomers from plant oils has been appealing among researchers since transforming plant oils or its derivatives into renewable building blocks for polymer synthesis provides a sustainable platform for forming renewable thermoplastic and thermosets. The advanced developments of polymeric materials are focused on linear chain-growth polymers that are encouraged due to their ability to provide a range of properties and applications. The reported in the literature results show the positive impact of plant oil-based reactive monomers being incorporated into polymers to produce high-performed sustainable polymers with advanced mechanical properties (toughness, modulus, elongation, etc.) and broad Tg range [44,50].

Following the “greener” approach toward sustainability of polymeric materials, the synthesis of a library of plant oil-based vinyl monomers with a broad unsaturation range has been showing twice as much value and higher market needs. Producing biobased polymers offers robustness of feedstock, environmental friendliness, and safety aspects while handling [50,55]. Turning the focus to real industrial applications like coatings and adhesives, the incorporation of renewable plant oil-based monomers into the latexes has been encouraged due to prominent latex features such as direct application after synthesis, low odor, easier handling, low volatility, and environmentally safe media (water). There is a strong need to develop proper polymerization conditions for highly hydrophobic plant oil-based vinyl monomers to form stable latexes with high yield and solid content.

Plant oil-based monomers with various unsaturation have revealed the incredible potential to be polymerized in miniemulsion polymerization resulting in high-performance latex materials. After the polymerization, unaffected unsaturation of fatty acid fragments can be used for post-polymerization crosslinking reactions allowing the formation of low- to high dense crosslink networks. This innovative approach could provide an opportunity to utilize plant oils in the design of renewable acrylic monomers with variable unsaturation forming latex materials with tailored properties and performance.

1.7. Research Objectives

This research study has five main objectives:

I. Convert plant oils with broad unsaturation profile through transesterification in a range of plant oil-based vinyl monomers

II. Evaluate the potential of soybean oil-based monomer to be produced industrially by process optimization and evaluation of its environmental impact

III. Access the effect of plant oil-based monomer unsaturation on polymerization kinetics and its reactivity profile (reactivity ratios, Q,e values) in free-radical copolymerization

IV. Establish the impact of plant oil-based monomer unsaturation on the formation of plant oil-based latexes in miniemulsion and thermomechanical properties of latex materials

V. Synthesize highly biobased latexes from plant-based monomers with improved mechanical properties and renewable content

1.8. Organization of the Dissertation

The dissertation explores the synthesis of plant oil-based vinyl monomers and polymers thereof using miniemulsion polymerization and the impact of plant oil unsaturation on the polymerization behavior and thermomechanical properties of resulted latex materials.

The dissertation contains ten distinguished chapters. **Chapter 1** introduces an overview of the advantages of utilization of renewable resources, plant oils, in the synthesis of polymeric materials for industrial applications, sustainability concerns, and existed problems linked with polymers produced from fossil fuels. The ongoing trends of exploitation of vegetable oils in polymer synthesis and the impact of its unsaturation profile of material properties are described through the chapter. The core part of the introduction chapter focuses on the synthesis of renewable monomers from plant oils and the challenges and successes towards developing waterborne polymeric materials (latexes) from plant oil-based derivatives ending by summarizing the objectives of this research.

The majority of the chapters are presented in journal format and have been published in peer-reviewed journals. **Chapter 2** explores the detailed synthesis and characterization of the chemical structure and physicochemical properties of a library of vinyl monomers synthesized via transesterification reaction from plant oils with various unsaturation.

Chapter 3 investigates the environmental impact of soybean oil-based monomer production and examines the possibility of process optimization by variation reaction conditions, including reactants ratio, type of catalyst, and soybean source (soybean oil vs. soybean biodiesel). The research investigates the inclusion of solvent recycling at the industrial scale of soybean oil-based monomer synthesis using modeling technique and evaluates its environmental performance along with comparing it with the commercial prototype profile.

Chapter 4 evaluates the effect of vinyl monomer unsaturation derived from olive, sunflower, soybean, and linseed oils on polymerization kinetics, the polymerization rate, and molecular weight of resulted polymers. The impact of monomer unsaturation is established on the extent of the degradative chain transfer. Using ^{1}H NMR spectroscopy, the amount of unaffected unsaturation sites (double bonds) in fatty acid fragments of obtained homopolymers is examined after completion of free radical polymerization.

Chapter 5 studies the free radical copolymerization of vinyl monomers from olive, sunflower, soybean, and linseed oils with commercial comonomers (styrene, methyl methacrylate, and vinyl acetate) and determines its copolymerization parameters (Q-e values, reactivity ratios). The prospect of latex formation from plant oil-based monomers in miniemulsion free radical polymerization and the effect of plant oil-based monomers' unsaturation in copolymers with MMA is established, including contact angles measuring, toughness, modulus, and elongation at break for resulted latex films.

Chapter 6 explores the feasibility of olive- and soybean oil-based monomer incorporation in latexes with high biobased content. The effect of the monomers' degree of unsaturation on latex characteristics and thermomechanical properties of latex-free films is evaluated. The plasticization and hydrophobization effect of incorporated unsaturated fatty acid fragments into copolymers with "rigid" comonomers like styrene and methyl methacrylate is examined.

Chapter 7 describes the formation of an unsaturation profile platform for controlling the thermomechanical properties of latex materials by varying the unsaturation degree in the comonomer feed. The effect of olive, soybean, and linseed oil-based monomers' versatility in the formation of different degree crosslink density of the resulted networks is confirmed and achieved by variation of plant oil-based monomer unsaturation by the inclusion of saturated fatty acid fragments derived from hydrogenated soybean oil-based monomer in comonomer mixture.

Chapter 8 reports the feasibility of synthesizing highly biobased latex library from cardanol methacrylate and high oleic soybean oil-based monomers. The combination of "soft" fatty acid derivative and "rigid" cardanol-based moiety results in the synthesis of latex materials with tunable properties by variation of the comonomer ratio in the feed. The inclusion of even small amounts of each monomer in copolymer composition provides a synergistic behavior to the performance of the resulted latex films. The chapter also contains the results on copolymer biorenewability estimated by the calculation of the biorenewable carbon index.

Chapter 9 focuses on developing highly renewable latexes and latex materials from high oleic soybean oil-based monomer and aromatic eugenol- and guaiacol-based monomers. Chemical structure of renewable aromatic monomers provides a possibility to synthesize high-molecular-weight plant-based latex copolymers and suppress retardation during polymerization. The obtained results confirm the versatility of chosen plant-based monomers in the formation of broad Tg range latex copolymers with tunable properties upon post-polymerization crosslinking reactions using the autooxidation mechanism.

Chapter 10 reviews the conclusions and future pathways of the current research study.

1.9. References

[1] M.J.L. Tschan, E. Brule, P. Haquette, C. M. Thomas Synthesis of biodegradable polymers from renewable resources *Polym. Chem.*, **2012**, 3, 836-851.

[2] E. Chiellini, F. Chiellini, P. Cinelli Polymers from Renewable Resources. In: Scott G. (eds) Degradable Polymers. Springer, Dordrecht, **2002**.

[3] E. Stephens, I. L. Ross, J. H. Mussgnug, L. D. Wagner, M. A. Borowitzka, C. Posten, O. Kruse, B. Hankamer Future prospects of microalgal biofuel production systems *Trends in Plant Science*, **2010**, 15(10), 554-564.

[4] M. N. Belgacem, A. Gandini Monomers, Polymers and Composites from Renewable Resources *Elsevier*, **2011**, p. 560.

[5] G. Z. Papageorgiou Thinking Green: Sustainable Polymers from Renewable Resources *Polymers,* **2018**,10, 952-987.

[6] K.F. Adekunle A Review of Vegetable Oil-Based Polymers: Synthesis and Applications. *Open Journal of Polymer Chemistry,* **2015**, 5, 34-40.

[7] Y. Zhu, C. Romain, C. K. Williams Sustainable polymers from renewable resources. *Nature*, **2016**, 540(7633):354-362.

[8] M. Alama, D. Akrambc, E. Sharmincd, F. Zafarce, S. Ahmad Vegetable oil-based eco-friendly coating materials: A review article *Arabian Journal of Chemistry,* **2014**, 7(4), 469-479.

[9] H. Hintze-Brüning Utilization of vegetable oils in coatings *Industrial Crops and Products*, **1992**, 1(2-4), 89-99.

[10] A. K. M. Aminul Islam, S. R. P. Primandari, Z. Yaakob Non-Edible Vegetable Oils as Renewable Resources for Biodiesel Production: South-East Asia Perspective Advances in Biofuels and Bioenergy, **2018**.

[11] C.A. Colombo, L.H. C. Berton, B. G. Diaz, R. A. Ferrari Macauba: a promising tropical palm for the production of vegetable oil *OCL,* **2018**, 25(1), D108.

[12] G. Lligasdas, J.C. Ronda, M. Galia, V. Gadiz Renewable polymeric materials from vegetable oils: a perspective *Materials Today,* **2013**, 16(9), 337-343.

[13] A.H. Noor Armylisas, M.F. Siti Hazirah, S.K. Yeong, A.H. Hazimah Modification of olefinic double bonds of unsaturated fatty acids and other vegetable oil derivatives via epoxidation: A review *Grasas Aceites,* **2017**, 68 (1), e174.

[14] V. Sharma, P.P. Kundu Addition polymers from natural oils—A review *Progress in Polymer Science,* **2006**, 31(11), 983-1008.

[15] H. Kalita, S. Selvakumar, A. Jayasooriyamu, S. Fernando, S. Samanta, J. Bahr, S.Alam, M. Sibi, J. Vold, C. Ulven Bio-based poly (vinyl ether) s and their application as alkyd-type surface coatings *Green Chemistry,* **2014**, 16 (4), 1974-1986.

[16] L.Yuan, Z. K. Wang, N. M. Trenor, C. B. Tang Robust Amidation Transformation of Plant Oils into Fatty Derivatives for Sustainable Monomers and Polymers *Macromolecules,* **2015,** 48 (5), 1320-1328.

[17] M. A. R.Meier, J. O. Metzger, U. S. Schubert Plant oil renewable resources as green alternatives in polymer science *Chem. Soc. Rev.,* **2007,** 36 (11), 1788-1802.

[18] Y. Lu, R.C. Larock Novel Polymeric Materials from Vegetable Oils and Vinyl Monomers: Preparation, Properties, and Applications *Chem. Sus. Chem.,* **2009**, 2, 136 – 147.

[19] A. Abbasi, M.M. Nasef, W.Z.N. Yahya Copolymerization of vegetable oils and bio-based monomers with elemental sulfur: A new promising route for bio-based polymers *Sustainable Chemistry and Pharmacy,* **2019** (13), 100158.

[20] P. Willberg-Keyriläinen, J. Vartiainen, A. Harlin, J. Ropponen The effect of side-chain length of cellulose fatty acid esters on their thermal, barrier and mechanical properties *Cellulose,* **2017**, 24, 505–517.

[21] L. Maisonneuve, T. Lebarbé, E. Grau, H. Cramail Structure-properties relationship of fatty acid-based thermoplastics as synthetic polymer mimics. *Polymer Chemistry, Royal Society of Chemistry - RSC*, **2013**, 4 (22), 5472-5517.

[22] L. Maisonneuve, T. Lebarb´e, E. Grauaband, H. Cramail Structure–properties relationship of fatty acid-based thermoplastics as synthetic polymer mimics *Polym. Chem.,* **2013**, 4, 5472-5517.

[23] U. Biermann, J.O. Metzger Functionalization of Unsaturated Fatty Compounds Across the C=C Double Bond *AOCS Lipid Library,* **2017**.

[24] T.F. Garrison, M.R. Kessler, R.C. Larock Effects of unsaturation and different ring-opening methods on the properties of vegetable oil-based polyurethane coatings *Polymer,* **2014**, 55, 1004-1011.

[25] Z. C. Petrovic Polyurethanes from Vegetable Oils *Polymer Reviews,* **2008**, 48(1), 109-155.

[26] J.J. La Scala, J.M. Sands, J.A. Orlicki, G.R. Palmese, E.J. Robinette Fatty Acid-Based Monomers as Styrene Replacements for Liquid Molding Resins *Polymer,* **2004**, 45, 7729–7737.

[27] Y. Gan, X.Jiang Photo-cured Materials from Vegetable Oils *Green Materials from Plant Oils,* **2014**, 1-27.

[28] L. Montero de Espinosa, M.A.R. Meier Plant oils: The perfect renewable resource for polymer science?! *European Polymer Journal,* **2011**, 47(5), 837-852.

[29] P. Jia, H. Xia, K. Tang, Y. Zhou Plasticizers Derived from Biomass Resources: A Short Review *Polymers (Basel),* **2018**, 10(12): 1303.

[30] N. Karak Vegetable Oil-Based Polymers 1st Edition Properties, Processing and Applications *Woodhead Publishing,* **2012**, 336.

[31] N. A. Porter, S.E. Caldwell, K.A. Mills Mechanisms of free radical oxidation of unsaturated lipids *Lipids,* **1995**, 30, 277-290.

[32] Z. O. Oyman, W. Ming, R. van der Linde Oxidation of drying oils containing non-conjugated and conjugated double bonds catalyzed by a cobalt catalyst *Progress in Organic Coatings*, **2005**, 54(3):198-204.

[33] L. Yang, C. Dai, L. Ma, S. Lin Conjugation of Soybean Oil and It's Free-Radical Copolymerization with Acrylonitrile *J. Polym. Environ*., **2011**, 19:189–195

[34] M. Valverde, D. Andjelkovic, P.P. Kundu, R.C. Larock Conjugated Low-Saturation Soybean Oil Thermosets: Free-Radical Copolymerization with Dicyclopentadiene and Divinylbenzene *Journal of Applied Polymer Science,* **2006**, 423-430.

[35] A. H. N. Armylisas, M.F.S. Hazirah, S.K. Yeong, A.H. Hazimah Modification of olefinic double bonds of unsaturated fatty acids and other vegetable oil derivatives via epoxidation: A review *Grasas Aceites*, **2017**, 68, e174.

[36] A. Zlatanic, C. Lava, W. Zhang, Z.S. Petrovic Effect of Structure on Properties of Polyols and Polyurethanes Based on Different Vegetable Oils *Journal of Polymer Science: Part B: Polymer Physics,* **2004**, 42, 809–819.

[37] R. C. Chikhalonde, M. Bhalerao, V. Y. Karadbhajane Study on modification processes of vegetable oils and detrimental effects of petroleum products *International Research Journal of Engineering and Technology,* **2019**, 6(5), 707-709.

[38] P. A. Dhakite, B. C. Burande, B. B. Gogte Ecofriendly maleinized oils for liquid detergent *International Journal of Researchers in Bioscience, Agriculture and Technology,* **2014**, 2(1), 306-316.

[39] Y. Su, H. Lin, S. Zhang, Zh. Yang, T. Yuan One-Step Synthesis of Novel Renewable Vegetable Oil-Based Acrylate Prepolymers and Their Application in UV-Curable Coatings *Polymers*, **2020**, 12(5), 1165.

[40] F. Habib, M. BajPai Synthesis and Characterization of Acrylated Epoxidized Soybean Oil for UV Cured Coatings *Chemistry&Chemical Technology*, **2011**, 5(3), 317-326.

[41] J. K. Fink Chapter 1 - Unsaturated Polyester Resins Reactive *Polymers Fundamentals and Applications (Second Edition)* A Concise Guide to Industrial Polymers Plastics Design Library, **2013**, 1-48.

[42] K.Adekunle A Review of Vegetable Oil-Based Polymers: Synthesis and Applications *Open Journal of Polymer Chemistry*, **2015**, 5, 34-40.

[43] G. Capiel, N.E. Marcovich, M.A. Mosiewicki From the synthesis and characterization of methacrylated fatty acids based precursors to shape memory polymers *Polymer International,* **2019**, 68(3), 546-554.

[44] J. Lomège, V. Lapinte, C. Negrell, J.J. Robin, S.Caillol Fatty Acid-Based Radically Polymerizable Monomers: From Novel Poly(meth)acrylates to Cutting-Edge Properties *Biomacromolecules ACS*, **2019**, 20 (1), 4-26.

[45] C. Vilela, R. Rua, A.J.D. Silvestre, A. Gandini Polymers and copolymers from fatty acid-based monomers *Industrial Crops and Products*, **2010**, 32, 97–104.

[46] B. Maiti, S. Kumar, P. De Controlled RAFT Synthesis of Side-Chain Oleic Acid Containing Polymers and Their Post-Polymerization Functionalization. *RSC Adv.,* **2014**, 4 (99), 56415– 56423, DOI: 10.1039/C4RA08872G.

[47] B. Maiti, P. De RAFT Polymerization of Fatty Acid Containing Monomers: Controlled Synthesis of Polymers from Renewable Resources *RSC Adv.*, **2013**, 3 (47), 24983-24990.

[48] S.P. Chang, T. K. Miwa, Allyl Esters of Crambe-Derived Long-Chain Fatty Acids and Their Polymers *J. Appl. Polym. Sci.*, **1979**, 24 (2), 441– 454, DOI: 10.1002/app.1979.070240212.

[49] R. C. L. Chow, C. S. Marvel Copolymerization of Allyl Esters of Some Fatty Acids *J. Polym. Sci., Part A-1: Polym. Chem*. **1968**, 6 (6), 1515– 1521, DOI: 10.1002/pol.1968.150060610.

[50] J. Lomège, V. Lapinte, C. Negrell, J.J. Robin, S.Caillol Fatty Acid-Based Radically Polymerizable Monomers: From Novel Poly(meth)acrylates to Cutting-Edge Properties *Biomacromolecules ACS*, **2019**, 20 (1), 4-26.

[51] M.E. Lamm, P. Li, Hankinson, S.; Zhu, T.; Tang, C. Plant oil-derived copolymers with remarkable post-polymerization induced mechanical enhancement for high-performance coating applications *Polymer,* **2019,** 174 (12), 170-177.

[52] M. Decostanzi, J. Lomège, Y. Ecochard, A.S. Mora, C. Negrell, S. Caillol Fatty acid-based cross-linkable polymethacrylate coatings *Progress in Organic Coatings,* **2018**, 124, 147-157.

[53] G. R. Ferreira, J.R. Braquehais, W. N. Silva, F. Machado Synthesis of soybean oil-based polymer lattices via emulsion polymerization process *Industrial Crops and Products*, **2015**, 65, 14-20.

[54] J.S. Neves, L. F. Valadares, F. Machado Tailoring Acrylated Soybean Oil-Containing Terpolymers through Emulsion Polymerization *Colloids Interfaces,* **2018**, 2(4), 46.

[55] M. Moreno, M. Goikoetxea, J. C. de la Cal, M. J. Barandiaran From fatty acid and lactone biobased monomers toward fully renewable polymer latexes *Polymer Chemistry*, **2014**, 52(24), 3543-3549.

[56] G. Boivin, A. M. Ritcey, V. Landry UV-Vis-Resistant Acrylic Latexes for Wood Coating Applications by Encapsulation of Inorganic NPs Using Mini-Emulsion Polymerization *Paints&Coatings Industry Magazine*, **2019**.

[57] M. L. Picchio, M.C.G. Passeggi, M.J. Barandiaran, L. M. Gugliotta, R. J. Minari Waterborne acrylic–casein latexes as eco-friendly binders for coatings *Progress in Organic Coatings,* **2015**, 88, 8-16.

[58] M. Moreno, C. Lampard, N. Williams, E. Lago, S. Emmett, M. Goikoetxea, M.J. Barandiaran Eco-paints from bio-based fatty acid derivative latexes *Progress in Organic Coatings*, **2015**, 81, 101-106.

[59] J. Ho, B. Mudraboyina, C. Spence-Elder, R. Resendes, M.F. Cunningham, P. G. Jessop Water-borne coatings that share the mechanism of action of oil-based coatings *Green Chem.,* **2018**, 20, 1899-1905.

[60] W. Yi, C. Zhonghua, Y. Fei Coalescing Aid Influences on Acrylic Latexes Property and Film Formation Process *Indian Journal of Materials Science*, **2016**, 2016, 8.

[61] G. Lligadas, J.C. Ronda, M. Galia, V. Cadiz Renewable polymeric materials from vegetable oils: a perspective *Mat. Today,* **2013**, 16(9), 337 - 343.

[62] Z. Liu, G. Kraus Green materials from plant oils *RSC Green Chemistry*, **2015**, 29, 305.

[63] D. Distler Emulsion Polymerization *Encyclopedia of Materials: Science and Technology,* **2001**, 2769-2774.

[64] A. Rudin, P. Choi Dispersion and Emulsion Polymerizations *The Elements of Polymer Science & Engineering (Third Edition)*, **2013**.

[65] Ch.Chern Principles and application of emulsion polymerization *John Wiley & Sons,* **2008**. - 272 p.

[66] J.M. Asua, Emulsion Polymerization: From Fundamental Mechanisms to Process Developments *J. Polym. Sci. Part A: Polym. Chem.*, **2004**, 43, 1026-1041.

[67] C. Chern, Emulsion polymerization mechanisms and kinetics *Progress in Polymer Science,* **2006**, 31 (5), 443-486.

[68] P.A. Lovell, F.J. Schork Fundamentals of Emulsion Polymerization *Biomacromolecules,* **2020**.

[69] J. Ugelstad, M. S. El-Aasser, J. W. Vanderhoff Emulsion Polymerization - Initiation of Polymerization in Monomer Droplets. *J. Polym. Sci., Polym. Lett. Ed.,* **1973**, 11, 503−513.

[70] J. M. Asua Miniemulsion Polymerization *Prog. Polym. Sci.* **2002**, 27, 1283-1346.

[71] C. Autran, J.C. de la Cal, J. M. Asua (Mini)emulsion Polymerization Kinetics Using Oil-Soluble Initiators *Macromolecules,* **2007**, 40(17), 6233–6238.

[72] S. Tcholakova, Z. Mitrinova, K. Golemanov, N.D. Denkov, M. Vethamuthu, K. P. Ananthapadmanabhan Control of Ostwald Ripening by Using Surfactants with High Surface Modulus *Langmuir*, **2011**, 27(24), 14807–14819.

[73] A.E.R. Polloni, A.Valério, D. de Oliveira, P. H. H. de Araújo, C. Sayer Ultrasound assisted miniemulsion polymerization to prepare poly(urea-urethane) nanoparticles *Polímeros,* **2018**, 28(2), 155-160.

[74] F. J. Schork, Y. Lup, W. Smulders, J. P. Russum, A. Butté, K. Fontenot Miniemulsion Polymerization *Polymer Particles,* **2005**, 129-255.

[75] Zh. Bao, W. Li, Zh. Fu, L. Chen A Review of the Application of Renewable Resources in Preparing Acrylic Polymer Latex *Polymers from Renewable Resources,* **2016**, 7(1), 13-19.

[76] J.S. Silva Neves, L.F. Valadares, F. Machado Tailoring Acrylated Soybean Oil-Containing Terpolymers through Emulsion Polymerization *Colloids Interfaces,* **2018**, 2, 46-60, DOI:10.3390/colloids2040046.

[77] J.V. Barbosa, J. Moniz, A. Mendes, F. D. Magalhães, M. M. S. M. Bastos Incorporation of an acrylic fatty acid derivative as comonomer for oxidative cure in acrylic latex *J. Coat. Technol. Res.,* **2014**, 11 (5), 765–773.

[78] S.P. Bunker, R.P. Wool Synthesis and characterization of monomers and polymers for adhesives from methyl oleate *Polymer Chemistry,* **2002**, 40(4), 451-458.

[79] K. Kingsley, O. Shevchuk, Z. Demchuk, S. Voronov, A. Voronov The features of emulsion copolymerization for plant oil-based vinyl monomers and styrene *Industrial Crops and Products,* **2017**, 109(15), 274-280.

[80] M. Moreno, M. Goikoetxea, M.J. Barandiaran Biobased-waterborne homopolymers from oleic acid derivatives *J. Polym. Sci. A: Polym. Chem.,* **2012**, 50(22), 4628-4637.

[81] M. Moreno, M. Goikoetxea, M.J. Barandiaran Surfactant-Free Miniemulsion Polymerization of a Bio-Based Oleic Acid Derivative Monomer *Macromolecular Reaction Engineering,* **2014**, 8(5), 434-441.

[82] M. Moreno, J.I. Miranda, M. Goikoetxea, M.J. Barandiaran Sustainable polymer latexes based on linoleic acid for coatings applications *Progress in Organic Coatings,* **2014**, 77(11), 1709-1714.

[83] C. Quintero, S. K. Mendon, O. W. Smith, S. F. Thames Miniemulsion Polymerization of Vegetable Oil Macromonomers *Progress In Organic Coatings,* **2002**, 57(3), 195-201.

[84] S. Bunker, C.Staller, N. Willenbacher, R. Wool Miniemulsion polymerization of acrylated methyl oleate for pressure-sensitive adhesives *International Journal of Adhesion & Adhesives,* **2003**, 23, 29–38.

[85] A. M. M. S. Medeiros, F. Machado, J.C. Rubim, T. F. L. McKenna Bio-based copolymers obtained through miniemulsion copolymerization of methyl esters of acrylated fatty acids and styrene *Polymer Chemistry,* **2017**, 55(8), 1422-1432.

[86] S.Molina-Gutiérrez, V. Ladmiral, R. Bongiovanni, S. Caillol, P. Lacroix-Desmazes Emulsion Polymerization of Dihydroeugenol-, Eugenol-, and Isoeugenol-Derived Methacrylates *Ind. Eng. Chem. Res.*, **2019**, 58(46), 21155–21164.

[87] C. Liu, X. Yang, J. Cui, Y. Zhou, L. Hu, M. Zhang, and H. Liu Tung oil based monomer for thermosetting polymers: synthesis, characterization and copolymerization with styrene *Bioresources,* **2012**, 7(1), 447-463.

CHAPTER 2. ACRYLIC MONOMERS FROM PLANT OILS: SYNTHESIS AND CHARACTERIZATION

2.1. Introduction

For centuries, plant oils are a promising feedstock in various applications, including the food industry, lubricants, adhesives, and coatings.[1] The abundance and chemical composition of these materials have brought the attractiveness of their utilization in making biobased polymeric materials. The worldwide availability and high functionality of vegetable oils make them a valuable feedstock for chemical modifications in high-performance polymers production. The triglyceride structure of vegetable oils provides various sites for modification, including ester bonds and double bonds in fatty acid chains (Fig.2.1).[2]

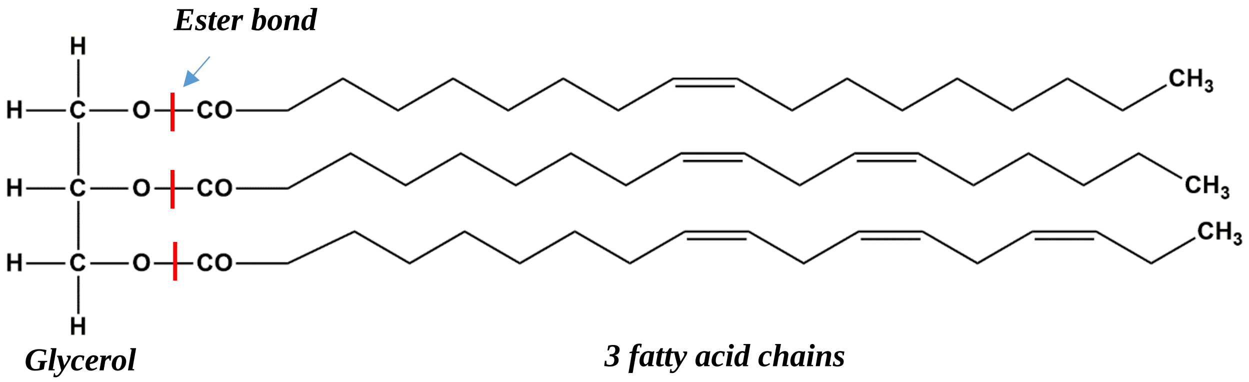


Figure 2.1. The chemical structure of plant oil triglyceride

The unsaturation degree of vegetable oils is considered a valuable characteristic of this feedstock when it undergoes chemical modification since it could predetermine the end product's functionality.[3] This characteristic has been used to classify plant oils according to its drying behavior. The degree of unsaturation for vegetable oils is commonly determined by evaluating the iodine value of oil. The iodine value (IV) is the amount of iodine added to saturate the double bonds of 100 g vegetable oil.[4] Therefore, the determined iodine value is used to categorize the vegetable oil as non-drying (IV<90), semi-drying (90<IV<130), or drying (IV>130).

Commonly, vegetable oils can be chemically modified via functionalization of double bonds by epoxidation, acrylation, carbonization, thiol-ene reactions, etc..[5] These methods introduce functional groups to the vegetable oil structure to produce hyperbranched building blocks for further crosslinking reactions in the formation of thermosets systems.[6-8]

The advanced methods of vegetable oil modification were recently reported by breaking down the triglyceride molecule towards the functionalization of fatty acid fragments to produce linear polymers.[9] Several studies were conducted using free fatty acids, alcohols, or its esters as vegetable oil modification products to synthesize monomers for free radical polymerization.[9,10] Barbosa et al. have conducted a study on the synthesis of acrylic fatty acid derivative via the two-step process to produce reactive monomers for free-radical polymerization.[11] Bunker and coworkers performed strategies to utilize epoxidized fatty acid methyl esters via a multi-step process to produce waterborne polymeric materials for adhesive applications.[12] The obtained results indicate a branching effect during polymerization of methyl oleate derivative, which is commonly undesired and brings some challenges in forming linear polymers, including low molecular weight, chain termination reactions, etc..[12] Similar research conducted by Wather et al. demonstrates a modification pathway of methyl oleate to form hydroxyl- and bromo-derivatives to synthesize photocured fatty acid ester-based polymers.[13] It showed challenges in the reactivity of resulted fatty acid ester derivatives in the presence of a low concentration of photoinitiator. Maiti et al. have discovered a method of esterification condensation of a range of fatty acids with hydroxyethyl methacrylate into fatty acid acrylic monomers to synthesize polymers with predetermined molecular weight and properties (solubility, crystallinity) using RAFT polymerization.[14] Other works involved the synthesis of various fatty acid-based radically active monomers utilizing common synthetic pathways including (meth)acrylation, trans vinylation, esterification, etc. of fatty acids.[15] All previously mentioned synthetic approaches are based on converting fatty acid derivatives (pristine fatty acids, alcohols, and esters) into reactive monomers radically polymerized in free radical polymerization processes (solution, emulsion, RAFT, etc.). In most cases, these methods require multi-step processes, long reaction times, special reaction conditions, including catalysts, and expensive chemicals. Finding a rational way to convert vegetable oils directly into monomers for free radical polymerization remains a promising and perspective alternative toward existing synthetic pathways for the design of vegetable oil-based polymers.

In the earlier study, Tarnavchyk et al. developed a method of acrylic monomer synthesis from soybean oil using a one-step transesterification reaction.[16] The synthesized soybean oil-based monomer (SBM) can be used in free radical polymerization and copolymerization.

Following the developed approach, a synthesis of plant oil-based acrylic monomers (POBMs) library with a broad range of unsaturation was targeted in this study by the transesterification reaction of crude plant oils and N-hydroxyethyl acrylamide. The resulted library of vinyl monomers from high oleic sunflower, olive, high oleic soybean, canola, corn, sunflower, soybean, camelina, linseed oils has been synthesized and characterized in terms of physicochemical properties. POBMs unsaturation in chemical structure is similar to the chemical structure and composition of oil chosen for monomer synthesis.

2.2. Experimental

2.2.1. Materials

Chemicals primarily used in the synthesis and purification process of POBMs are listed in Table 2.1.

Table 2.1. The list of chemicals used in the study

#	Name	Abbreviation	Source
1.	N-hydroxyethyl acrylamide	HEAA	TCI America
	Plant Oils		
2.	High Oleic Sunflower Oil	HOSFO	Cargill, Fargo, ND
3.	Olive Oil	OVO	Bertolli, Houston, TX
4.	High Oleic Soybean Oil	HOSBO	Perdue Agribusiness LLC, Salisbury, MD
5.	Canola Oil	CNO	SuperValu Inc., Eden Prairie, MN
6.	Corn Oil	CRO	ACH Food Companies, Oakbrook Terrace, IL
7.	Soybean oil	SBO	Crisco, The J.M. Smucker Company, Orville, OH
8.	Sunflower oil	SFO	Kirlangic, Turkey
9.	Camelina Oil	CMO	Health&Beauty Oil Center, Westchester, IL
10.	Linseed oil	LSO	Sunnyside corp., Wheeling, IL
11.	Sodium hydroxide	NaOH	Alfa Aesar, Ward Hill, MA
12.	Sodium chloride	NaCl	VWR International, USA
13.	Tetrahydrofuran	THF	VWR International, USA
14.	Dichloromethane	CH_2Cl_2	Sigma-Aldrich, USA
15.	Deionized water	DI H_2O	Local supplier
16.	Chloroform-d_1	CH_2Cl_2-d_1	EMD Millipore Corporation, USA
17.	Acetone	CH_3COCH_3	Sigma-Aldrich, USA
18.	Magnesium sulfate	$MgSO_4$	VWR International, USA

2.2.2. Characterization of Plant Oils Composition

The characterization of plant oils composition was conducted to determine the percentage of each fatty acid fragment (saturated and unsaturated) presented in the triglyceride structure of each specific oil. The determination of fatty acid composition was studied using ^{1}H NMR spectroscopy performed on a Bruker AVANCE 400 NMR spectrometer and JEOL ECA 400 MHz NMR spectrometer. To conduct ^{1}H NMR study, 12 mg of each plant oil was dissolved in 0.6 ml of chloroform-d_1 and transferred to 5-mm NMR tubes. ^{1}H NMR spectra were recorded by accumulating 32 scans at room temperature (around 22 ^{o}C). The resulted spectra were characterized to determine the amount of oleic, linoleic, linolenic, and saturated fatty acids according to [17].

2.2.3. Synthesis of POBMs

A library of plant oil-based monomers was synthesized via direct transesterification reaction of plant oil and N-hydroxyethyl acrylamide (Fig 2.2). For this purpose, 150 g of each plant oil was placed in a 500-ml VWR round bottom flack along with the excess of N-hydroxyethyl acrylamide (115 g) in the molar ratio of 1:5.9. The reactants mixture was diluted by tetrahydrofuran in the amount of 150 ml. To prevent the polymerization of HEAA during monomer synthesis, 0.035% (based on reactant amount) of n-butyl-p-cresol was placed in the flask. The reaction mixture was put into a water bath, continuously mixed using a magnetic stir bar at 650 r.p.m. and heated up to 40 ^{o}C. 1.5 g of catalyst (NaOH pellets) were milled and added quickly to the reaction mixture, continuously stirred at 675 r.p.m. The reaction was conducted for 4 hours at 40 ^{o}C till utterly homogenized.

The purification of resulted monomer mixture starts with the preparation of 2000 ml of 5% brine solution by dissolving 100 g of NaCl in DI water. The monomer mixture is then transferred from the flask to the separation funnel, followed by adding 100 ml of CH_2Cl_2. The purification of the reaction mixture is conducted to remove the by-product-glycerol along with unreacted catalyst. The brine solution is divided into five portions and added to the oil phase, then intensively stirred, and the water phase is removed after the washing step. The monomer mixture drying process includes adding anhydrous $MgSO_4$ by scoops to mixed monomer mixture continuously until it stops dissolving. The monomer mixture is centrifuged and filtered to remove $MgSO_4$ solid particles from the monomer mixture. Finally, to remove solvents, the monomer mixture was evaporated at 40 ^{o}C using a rotary evaporator.

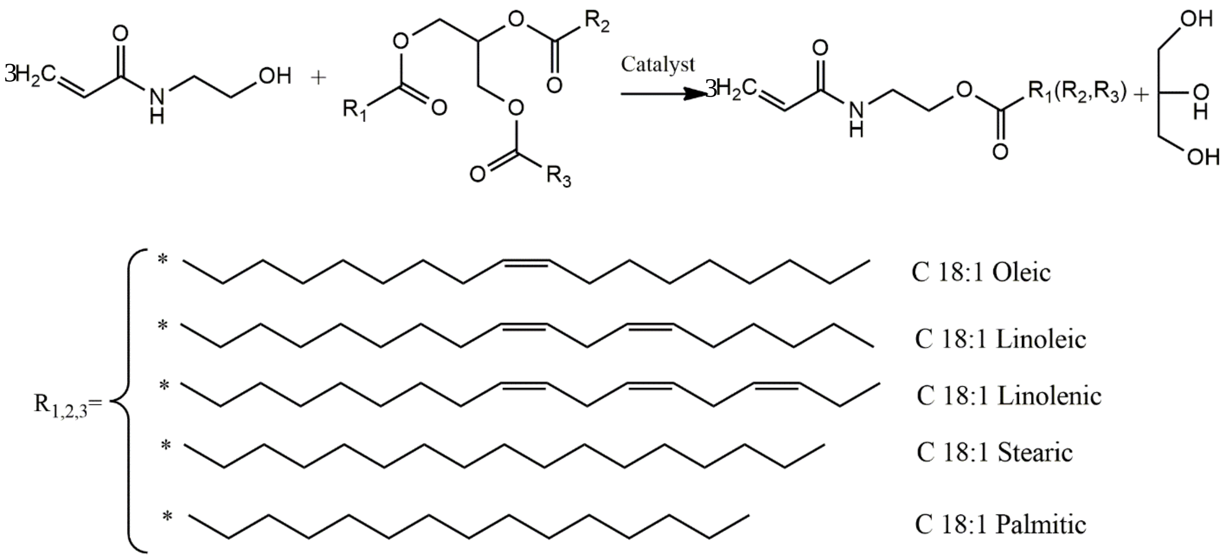


Figure 2.2. The general scheme of the synthesis of plant oil-based monomer via transesterification reaction

The resulting POBM mixture is a composition of vinyl monomers where the mixture's composition is similar to the plant oil composition chosen for the synthesis. It has been observed that the composition of fatty acid unsaturated fragments remains preserved during POBMs synthesis via explored one-step transesterification method. POBMs were characterized using ^{1}H NMR, FT-IR spectroscopy, and its solubility, iodine value, molecular weight, refractive index, and density were determined.

2.2.4. Characterization of POBMs Chemical Structure

NMR Spectroscopy: To characterize POBMs chemical structure, ^{1}H NMR spectra were recorded using AVANCE III HDTM 400 high-performance digital NMR spectrometer (Bruker, Billerica, MA) using chloroform-d$_1$ as a solvent. The monomer solution in 2% wt. concentration was placed into the NMR tube to accumulate 32 scans at room temperature. The recorded proton NMR spectra analysis was conducted using standard tables of chemical shifts of specific atom groups and evaluation of peak intensity via integration.

FT-IR Spectroscopy: The chemical structure of POBMs was characterized using Fourier transmission infrared spectroscopy (FTIR) by applying the monomer solution in acetone (0.1 g/ml) on KBr and using Thermo Scientific Nicolet spectrometer S8700 in the range of 400–4000 cm^{-1}. The analysis of the obtained FTIR spectra was conducted by identifying the chemical bonds in the molecule's chemical structure according to standardized absorption peaks of functional groups.

Electrospray Ionization (ESI) High-Resolution Mass Spectrometry: The ESI mass spectra of POBMs were determined using a Waters Synapt G2–Si high-resolution Mass Spectrometer. To conduct the mass-spectra measurement, diluted methanol solutions of POBMs were injected into the electrospray ion source (ESI) via a syringe pump using a flow rate of 10 µL/min. The Q/TOF MS parameters were adjusted as capillary voltage 2.9 kV, cone voltage 35.0 V, desolvation temperature 100 °C, cone gas flow 6.0 L/h, desolvation gas flow 198 L/h, nebulizer pressure 6.5 Bar, positive ion mode of electrospray ionization. The scanning of mass spectra of POBMs was recorded in the range m/z 100–3000.

Iodine Value(IV): To evaluate the unsaturation degree of plant oils and POBMs, the iodine value of those materials was determined.[18] The plant oil/plant oil-based monomer in the amount of 0.1 g was placed in Erlenmeyer flask, followed by adding 20 ml of tetrachloromethane CCl_4 as a solvent and 25 ml of Wijs solution. The Wijs solution is an iodine monochloride dissolved in acetic acid commonly used to determine the iodine value of a tested substance. The resulted mixture was placed in a dark place and incubated for 1-1.5 h. The resulted substance was mixed with 30 ml of 10% potassium iodide (KI) solution and 100 ml of cooled previously boiled water. The magnetic stir bar was placed inside the flask, and the mixture was titrated with 0.1 N sodium thiosulfate solution $Na_2S_2O_8$. The starch indicator was used in the amount of 1-2 ml to precisely detect the endpoint of the titration when the yellow color disappeared. The blank test was conducted along with plant oil tests simultaneously. The iodine value of tested plant oil/plant oil-based monomers was evaluated using the following equation:

$$IV = \frac{(V_S - V_B) \cdot N \cdot 12.49}{m_{sample}} \tag{2.1}$$

where V_s- the amount of $Na_2S_2O_8$ used for titration of the sample, ml; V_s- the amount of $Na_2S_2O_8$ used for titration of the blank, ml; N- normality of $Na_2S_2O_8$ solution; m_{sample}- the mass of tested plant oil/plant oil-based monomer sample.

Aqueous Solubility: To determine the solubility of POBMs in water, UV−Vis spectrometry method was used. A small amount of POBM (5-10 mg) was placed in a vial and dispersed by adding 100 mL of distilled water. The resulted aqueous dispersion was vortexed for 20 min to obtain a stable well-dispersed mixture. The resulting dispersion of known concentration was gradually diluted with distilled water to obtain solutions of various concentrations ranging from $1 \cdot 10^{-4}$ % wt. to 0.5 % wt. The aqueous solubility of highly hydrophobic POBMs was determined by measuring the solution's cloud point, meaning the point where it loses transparency. The cloud point of the resulting dispersions was measured using a UV−vis spectrophotometer at transmittance mode (Varian Cary 5000 UV−vis-NIR spectrophotometer) at a wavelength of $\lambda = 350$ nm. The threshold when the transparency of the solution is getting lower and starts to deviate from 100% was taken as POBMs aqueous solubility.

Refractive Index: The refractive index of POBMs was measured by placing two drops of each monomer onto the prism's surface using a Bausch & Lomb Refractometer. The borderline's adjustment between the bright and the dark region at the center of the crosshair provides the value of the refractive index of the tested material.[19]

Density: The determination of density of plant oils and POBMs was conducted using pycnometer measurement according to ASTM D 369 (5).[20] Each 10 ml pycnometer was filled with tested material and inserted in a water bath equilibrated at 25 ^{o}C. The incubation of the pycnometer was carried out for 2 hours at a specific temperature. The pycnometer was calibrated to 10 ml level, and the mass of the pycnometer was measured. The density of plant oil/plant oil-based monomer was calculated using the following equation:

$$\rho = \frac{m_{p+s} - m_p}{V_p}, \text{ g/ml} \tag{2.2}$$

where ρ-density of the tested compound, g/ml; m_{p+s}-mass of the pycnometer with the sample; m_p-mass of the empty pycnometer; V_p-volume of pycnometer, ml.

2.3. Results and Discussions

Plant oils are constituted from triglyceride molecules mainly formed from fatty acid fragments esterified to glycerol units. Unsaturated fatty acids presented primarily on plant oils are shown in Fig.2.3.[2] The composition of plant oil from each natural resource varies from plant to plant depending on the type of source, cultivation method, temperature conditions, etc..[21] In this study, ^{1}H NMR spectroscopy was used to evaluate the composition of saturated and unsaturated fatty acid fragments presented in plant oil used for monomer synthesis and compared with POBMs chemical structure.

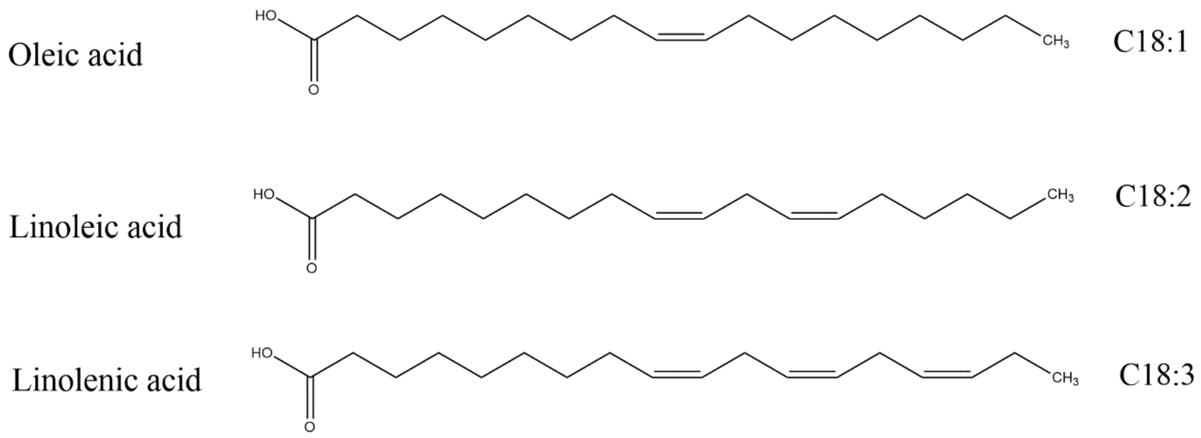


Figure 2.3. Chemical structure of plant oil unsaturated fatty acids

^{1}H NMR spectroscopy is an excellent alternative method to measure vegetable oil composition compared to the already known gas chromatography method, which appeared to be time- and chemical-consuming to quantify fatty acid composition in oil.[13] Utilization of proton NMR spectroscopy was conducted to evaluate the percentage of oleic, linoleic, linolenic, and saturated fatty acid fragments in plant oils used for POBM synthesis.

The amount of each fatty acid fragment in the plant oil sample was determined by evaluating the intensity of peak corresponded to each fatty acid fragment in relation with a peak intensity of glycerol unit in ^{1}H NMR spectrum of plant oil.[17]

The amount of linolenic acid in plant oil was measured by determining the peak intensity in the range of 1.03-0.95 ppm corresponded to methyl hydrogens of the linolenic acid fragment (peak E), in relation to the area of one of two signals from α hydrogens in glycerol backbone. The α hydrogens of the glycerol molecule at a signal of 4.27 ppm (peak α) (Fig. 2.4) were considered in determining the area ratio of two α glycerol hydrogens to three methylic linolenic acid hydrogens. Considering glycerol molecule esterified by three linolenic units, the corrected area ratio is two α glycerol hydrogens to nine methylic linolenic acid hydrogens. The ratio of 22.2 α glycerol to 100 linolenic acid hydrogens can be achieved by converting the peak intensity into percentages. By conducting the calibration of peak related to one of α glycerol hydrogens and considering it as 22.2, the amount of linoleic acid (in percentages) was determined by evaluating the peak intensity in the range of 1.03-0.95 ppm.

The same pathway was considered to determine the number of linoleic acid fragments in plant oil samples. In this case, the peak, which relates to hydrogen atoms of α glycerol units, was calibrated as 33.3, where the amount of linoleic acid fragments was calculated by evaluating the peak intensity in the range of 2.80-2.60 ppm (peak A). The peak of α glycerol units was calibrated to 33.3, considering the ratio of 2 hydrogens in α glycerol unit to 6 hydrogens in glyceryl linoleate. This peak was related to the amount of hydrogens between two double bonds. The percentage of linoleic acid fragments was determined by subtracting twice the amount of linolenic acid from the peak intensity in the range of 2.80-2.60 ppm. The reason why the amount of linolenic acid was abstracted twice is due to the presence of 4 hydrogens between linolenic acid fragments, whereas the linoleic has only two.

The content of oleic acid fragments was calculated by measuring the peak intensity in the range of 2.08-1.90 ppm in correlation with the α glycerol unit's peak intensity in glycerol fragment. The peak of 2.08-1.90 ppm (peak C) refers to all hydrogens presented in an unsaturated fatty acid fragment area that is 12. Considering this number and calibration of α glycerol peak to 16.7, the percentage of oleic acid fragments can be measured by subtracting the amount of linoleic and linolenic acid fragments from the intensity of the peak at the range of 2.08-1.90 ppm.

The amount of saturated acid fragment was calculated by subtracting the amount of oleic, linoleic, and linolenic acid fragments from the peak intensity in the range of 2.35-2.25 ppm (peak

B) corresponding to 6 carbonyl hydrogens of all fatty acids esterified to the glycerol molecule. In this case, the intensity of α glycerol unit was calibrated as 33.3.

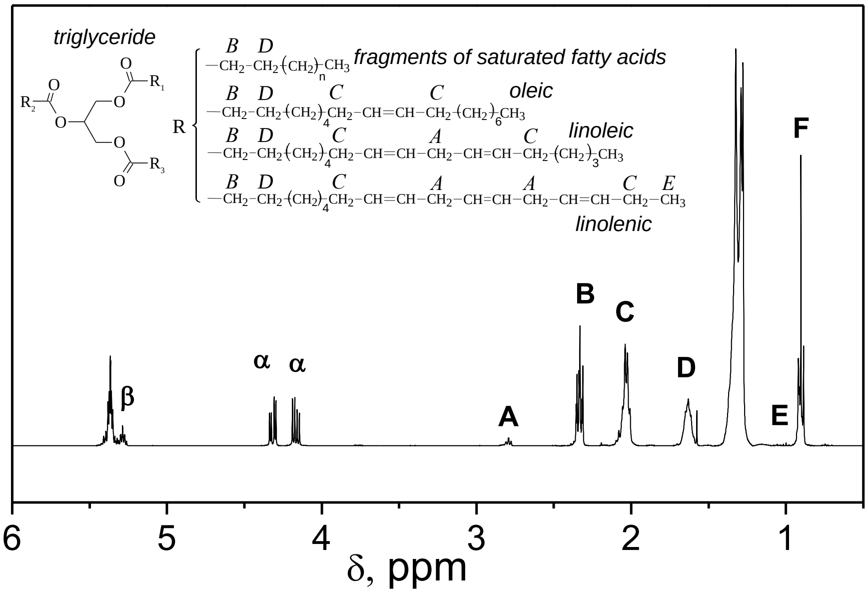


Figure 2.4. The ^{1}H NMR spectrum and chemical structure of olive oil

The evaluation of fatty acid compositions in a range of selected plant oils further used for plant oil-based monomers synthesis was conducted according to the procedure[17] (Table 2.2). The determined plant oil composition is presented in Table 2.3:

Table 2.2. Correlation of peak intensity of fatty acid fragments

		Peak calibration	
Fatty acid fragments	Peak	Ratio	%
Linolenic C 18:3 (E)	0.95-1.03 ppm (-C**H**$_3$)	2H/9H	22.2
Linoleic C 18:2 (A)	2.60-2.80 ppm (-CH=CH-C**H**$_2$-CH=CH-)	2H/6H	33.3
Oleic C 18:1 (C)	1.90-2.08 ppm (-C**H**$_2$-CH=CH-C**H**$_2$-)	2H/12H	16.7
Saturated C 16:0, 18:0 (B)	2.25-2.35 ppm -C**H**$_2$-CH$_2$-	2H/6H	33.3

Table 2.3. Calculated fatty acid composition in plant oils using ^{1}H NMR spectroscopy

Plant Oil		Composition of fatty acid fragments, %			
		Oleic C18:1	Linoleic C18:2	Linolenic C18:3	Saturated C16:0, C18:0
High Oleic Sunflower	Exp.	88.1	2.3	2.5	7.1
	Theor.	86-89	3-6	0.5-1	3-7
Olive	Exp.	80.2	6.6	0.7	12.5
	Theor.	55-83	3.5-21	0.2-1	1-20
High Oleic Soybean	Exp.	70.2	15.3	1.2	13.3
	Theor.	70-73	13-16	0-1.5	11-17
Canola	Exp.	67.9	12.8	12.5	6.9
	Theor.	62-68	12-15	8-13	5-9
Corn	Exp.	33.9	47.4	5.0	13.7
	Theor.	23-33	46-62	0-4	10-15
Sunflower	Exp.	35.6	50.4	1.2	12.8
	Theor.	14-36	44-75	0-1.5	7-14
Soybean	Exp.	23.9	41.7	10.1	24.3
	Theor.	22-34	41-55	7-10	15-29
Camelina	Exp.	25.1	25.2	36.5	18.2
	Theor.	12-23	15-24	32-40	15-24
Linseed	Exp.	32.0	1.5	50.6	15.9
	Theor.	12-34	15-24	35-60	10-18

The composition of plant oils used for POBM synthesis correlates with theoretical data found in literature, where the slight variation is based on source, area of harvesting, etc..[22] The characterized plant oils are different in terms of the fatty acid composition, which is an important experimental parameter in this study to synthesize a library of acrylic monomers with a broad unsaturation range and study POBMs polymerizability.

The synthesis of plant oil-based monomers was conducted according to the procedure where crude plant oil is directly transesterified with N-hydroxyethyl acrylamide in the molar ratio of 1 to 5.9 in the presence of a catalyst. The resulted monomer mixture was purified, evaporated from the solvent with the final yield of about 92-96 %. The obtained ^{1}H NMR and FT-IR spectra (Fig. 2.5, 2.6) confirm the presence of an N-acryloyl fragment in the chemical structure of POBMs, providing monomer reactivity in free radical radical polymerization.

Specific peaks of the acrylic double bond protons at 6.05-6.65 ppm along with the characteristic signals of the protons of the ethylene linkage between the amide fragment and ester groups in the range of 3.55-4.18 ppm, as well as of the fatty acid fragments between 0.85 to 2.8 ppm characterize the structure of synthesized vinyl monomers from plant oils. The spectra were obtained using the NMR spectrometer at 400 MHz and with the presence of chloroform-d_1 as a solvent. The characterization of peaks is following: peak at 0.87 ppm - (3H, CH_3); peak at 1.26 ppm (16-18H, $(CH_2)_{3\text{-}9}$); peak at 1.61ppm (2H, C(O)-CH_2-CH_2); peak at 2.10 ppm (3-4H, CH_2-CH_2-CH=); peak at 2.33 ppm (2H, C(O)-CH_2-CH_2); peak at 2.77 ppm (2H, =CH-CH_2-CH=); peak at 3.6 ppm (2H, NH-CH_2); peak at 4.2 ppm (2H, CH_2-O-); peak at 5.35 ppm (2-3H, CH=CH); peak at 5.66 ppm (^{1}H, CH_2=CH-C(O)); peak at 6.12 ppm (^{1}H, HCH=CH-C(O)); peak at 6.3 ppm (^{1}H, HCH=CH-C(O)).

The FT-IR spectra of plant oil-based monomers were obtained using Thermo Scientific Nicolet spectrometer S8700 in the range of 400– 4000 cm^{-1}. The structure of monomers was determined by the presence of a strong NH adsorption band at 3200-3400 cm^{-1}, he carbonyl (amide I) band at 1670 cm$^{-1,}$ and finally, the NH adsorption band (amide II) at 1540 cm^{-1}. The obtained results confirm the presence of the acrylamide species attachment to the fatty acid fragments. The successful esterification of plant oil by N-hydroxyethyl acrylamide was confirmed by the presence of strong ester bonds at 1740, 1245, and 1180 cm^{-1}.

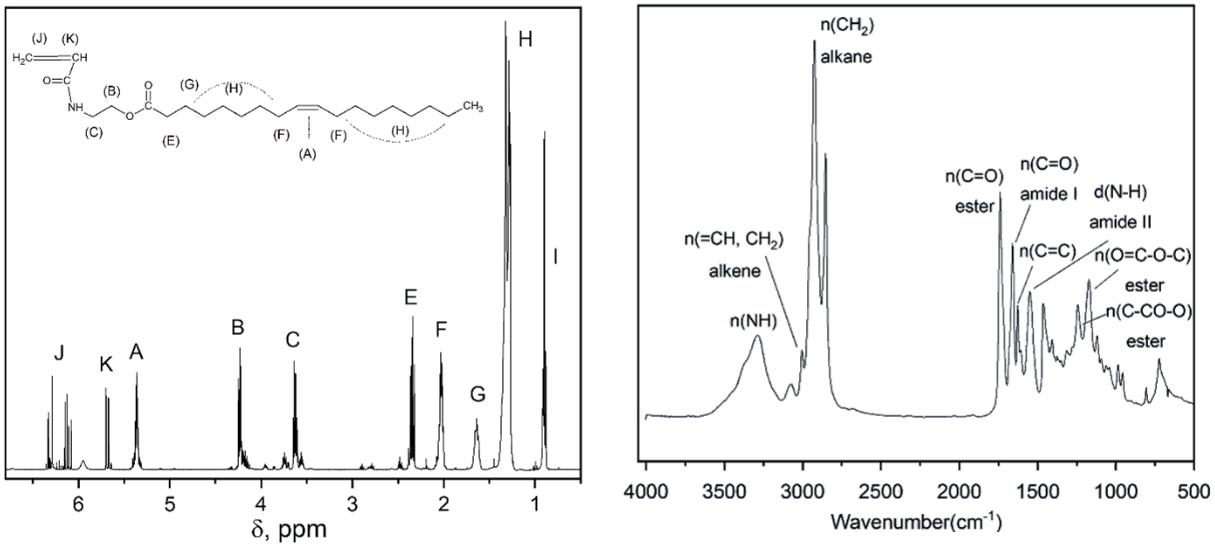


Figure 2.5. The ^1H NMR spectrum (left) and FT-IR spectrum (right) of high oleic soybean oil-based monomer (HOSBM)

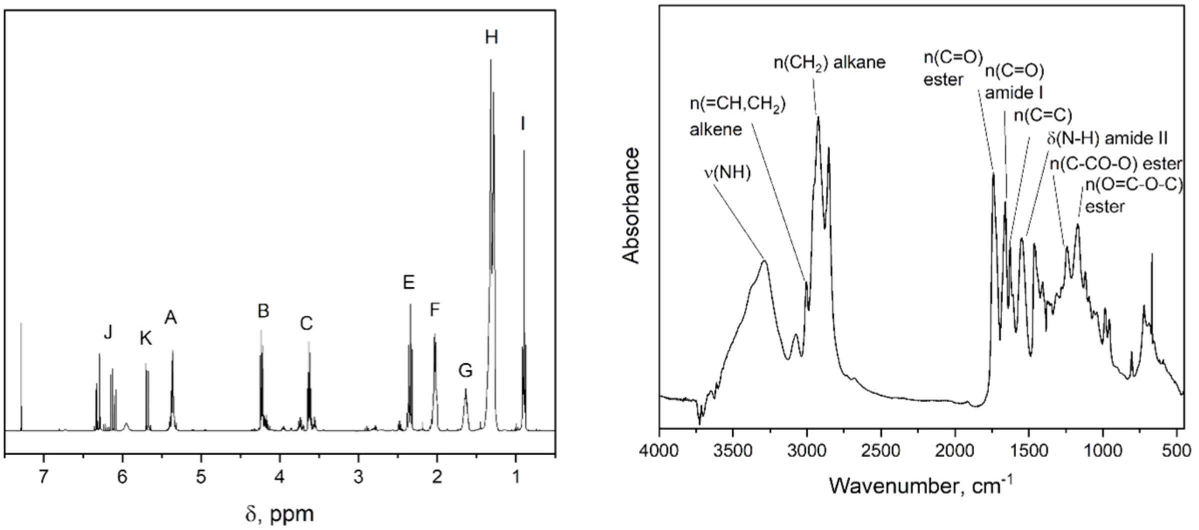


Figure 2.6. The ^1H NMR spectrum (left) and FT-IR spectrum(right) of high oleic sunflower oil-based monomer (HOSBM)

The characterization of the molecular weight of POBMs was conducted using ESI-mass spectrometry. The ESI mass spectrum of HOSBM shows the highest peak at m/z 402.3 (Fig. 2.7) corresponding to [oleate HOSBM + Na]$^+$ fraction, which correlates with the fatty acid composition of high oleic soybean oil where the amount of oleic acid fragments is around 70 % wt. This demonstrates that the majority of HOSBM is (acryloylamino)ethyl oleate. To determine the molecular weight of POBM, the subtraction of the mass of the sodium ion was applied. After calculations, the molecular weight of HOSBM was determined as 379.3. Additionally, HOSBM molecules consist of small fractions of other fatty acid chains confirmed by mass peaks at 376.3, 404.3, and 400.3m/z.

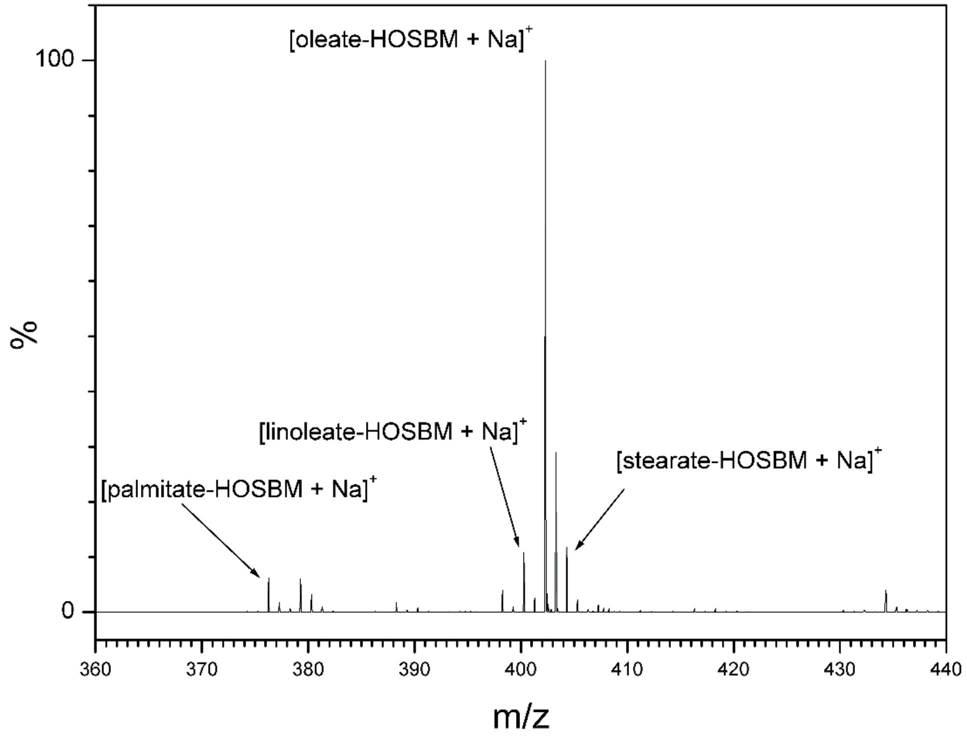


Figure 2.7. ESI mass spectra of high oleic soybean monomer (HOSBM)

Thus, electrospray ionization–mass spectrometry was applied to determine the POBMs' molecular weight in the synthesized library (Table 2.4.).

To determine the degree of unsaturation of each POBM synthesized via transesterification reaction, the iodine value was measured both for monomers and plant oils chosen for POBM synthesis. The iodine value (IV) indicates the amount of iodine (g) reacting with 100 g of oil. As expected, the iodine value of POBMs shows higher value if compared to IV of plant oils that due to the presence of acryloyl amide fragment in each POBM molecule (Table 2.4).

Table 2.4. Unsaturation profile of POBMs

Monomer from Oil	Iodine value, g/g		Molar mass, g/mol
	Oil	Monomer	
High Oleic Sunflower Oil (HOSFM)	82	105	379.0#
Olive Oil (OVM)	90	110	379.3*
High Oleic Soybean Oil (HOSBM)	105	124	379.3*
Canola Oil (CLM)	96	137	379.0*
Corn Oil (COBM)	120	139	377.0#
Sunflower Oil (SFM)	128	146	377.5*
Soybean Oil (SBM)	139	149	377.3*
Camelina Oil (CMM)	144	155	375.0#
Linseed Oil-based (LSM)	177	194	375.6#

*-experimental data from ESI mass spectrum; #-calculated value based on monomer structure.

Aqueous solubility of POBMs was determined using UV-Vis spectroscopy by evaluating the transparency of diluted monomer solutions in distilled water (Fig. 2.8). The point where the transparency of the diluted solution deviates from 100 % was considered as the solubility threshold. Since all synthesized POBMs are highly hydrophobic, its aqueous solubility was limited and ranges of $0.7\text{-}1.05 \cdot 10^{-3}$ %.

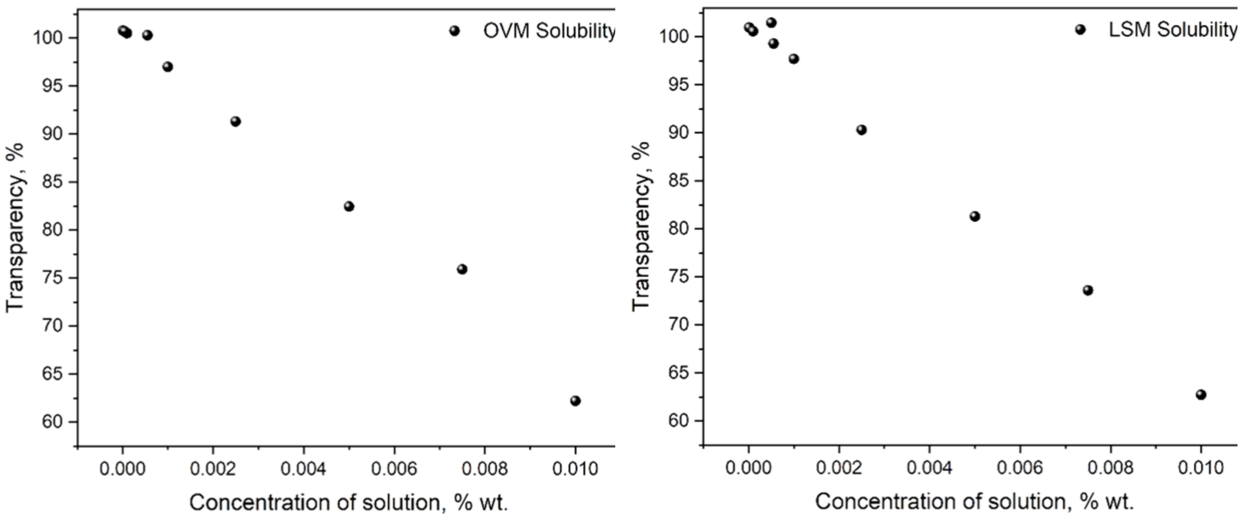


Figure 2.8. Solution transparency vs. concentration for olive oil-based monomer (left) and linseed oil-based monomer (right)

The density and refractive index were measured for plant oil and POBMs using standard procedures[20].

Table 2.5. The physicochemical properties of plant oil-based monomers

Monomer from oil	Density (for oil), g/ml	n_D^{20} (for oil)
High Oleic Sunflower	0.941 (0.907)	1.472 (1.467)
Olive	0.953 (0.912)	1.473 (1.469)
High Oleic Soybean	0.945 (0.910)	1.475 (1.469)
Sunflower	0.965 (0.915)	1.478 (1.469)
Soybean	0.963 (0.921)	1.478 (1.474)
Linseed	0.967 (0.930)	1.483 (1.480)

The values of plant oil-based monomers density were slightly higher compared to density of plant oils, which can be explained by small differences in the chemical composition of monomer vs. oil considering the incorporation of acryloyl amide moiety into the monomer structure.

2.4. Conclusions

A new method based on direct transesterification of crude plant oils with N-hydroxyethyl acrylamide has been used to synthesize the library of plant oil-based monomers with various degree of unsaturation (IV values from 105 to 194). The resulting POBMs contain the incorporated vinyl group (confirmed by ^{1}H NMR and FT-IR spectroscopies), making them reactive in free radical polymerization processes. Plant oil fatty acids chemical structure remains preserved during monomer synthesis and determines the resulting chemical composition of synthesized POBMs mixture. Physico-chemical properties of resulted plant oil-based monomers were evaluated. POBMs are considered to be reactive renewable building blocks for free radical polymerization to form polymers and materials with unique properties for various industrial applications.

2.5. References

[1] G. Lligasdas, J.C. Ronda, M. Galia, V. Gadiz Renewable polymeric materials from vegetable oils: a perspective *Materials Today,* **2013**, 16(9), 337-343.

[2] L. E. Oi, M-Y. Choo, H. V. Lee, N. A. Rahman, J. C.Juan Chapter 9 - Mesoporous and other types of catalysts for conversion of non-edible oil to biogasoline via deoxygenation *Sustainable Bioenergy Advances and Impacts,* **2019**, 257-281.

[3] X. Liu, T. Jain, Q. Liua, A. Joy Structural insight into the viscoelastic behavior of elastomeric polyesters: effect of the nature of fatty acid side chains and the degree of unsaturation *Polym. Chem.*, **2020**,11, 5216-5224.

[4] R. Przybylski, N.A. M. Eskin 7 - Oil Composition and Properties *Canola Chemistry, Production, Processing, and Utilization,* **2011**, 189-227.

[5] Ionescua, M.; Radojčića, D.; Wana, X.; Petrovića, Z.S.; Upshaw, T. A. Functionalized vegetable oils as precursors for polymers by thiol-ene reaction *European Polymer Journal,* **2015**, 67, 439-448.

[6] Sun, J.; Aly, K.I.; Kuckling, D. Synthesis of hyperbranched polymers from vegetable oil-based monomers via ozonolysis *pathway J. of Pol. Sci., PART A: Pol. Chem.,* **2017**, 55, 2104–2114.

[7] Pelletier, H.; Belgacem, N.; Gandini, A. Acrylated vegetable oils as photo-crosslinkable materials *Journal of Applied Polymer Science,* **2006**, 99(6):3218 – 3221.

[8] Kim, J.R.; Sharma, S. The development and comparison of bio-thermoset plastics from epoxidized plant oils *Industrial Crops and Products,* **2012**, 36(1), 485-499.

[9] J. Lomège, V. Lapinte, C. Negrell, J.J. Robin, S. Caillol Fatty Acid-Based Radically Polymerizable Monomers: From Novel Poly(meth)acrylates to Cutting-Edge Properties *Biomacromolecules ACS*, **2019**, 20 (1), pp.4-26.

[10] G. Capiel, N.E. Marcovich, M.A. Mosiewicki From the synthesis and characterization of methacrylated fatty acids based precursors to shape memory polymers *Polymer International*, **2019**, 68(3), 546-554.

[11] Barbosa, J. V.; Moniz, J.; Mendes, A.; Magalhães, F. D.; Bastos, M. M. S. M. Incorporation of an Acrylic Fatty Acid Derivative as Comonomer for Oxidative Cure in Acrylic Latex *J. Coat. Technol. Res.*, **2014**, 11 (5), 765– 773.

[12] Bunker, S. P.; Wool, R. P. Synthesis and Characterization of Monomers and Polymers for Adhesives from Methyl Oleate *J. Polym. Sci., Part A: Polym. Chem.*, **2002**, 40 (4), 451–458.

[13] Walther, S.; Strehmel, N.; Schlorholz, M.; Strehmel, B.; Strehmel, V. Photopolymerization of functionalized monomers derived from methyl oleate *Journal of Photopolymer Science and Technology*, **2016**, 29(1), 123-132.

[14] Maiti, B.; De, P. RAFT polymerization of fatty acid-containing monomers: controlled synthesis of polymers from renewable resources *RSC Adv.*, **2013**, 3, 24983-24990.

[15] Pryde, E.H.; Gast, L.E.; Frankel, E. N.; Carlson, K.D. Vegetable Oils and Animal Fats as Renewable Resources for Plastics and Coatings Applications *Polymer-Plastics Technology and Engineering*, **1976**, 7(1), 1-26.

[16] Tarnavchyk, I.; Popadyuk, A.; Popadyuk, N.; Voronov, A. Synthesis and Free Radical Copolymerization of a Vinyl Monomer from Soybean Oil *ACS Sustainable Chem. Eng.*, **2015**, 3, 7, 1618–1622.

[17] Barison, A.; Pereira da Silva, C.W.; Campos, F.R.; Simonelli, F.; Lenz, C.A.; Ferreira, A.G. A simple methodology for the determination of fatty acid composition in edible oils through ^{1}H NMR spectroscopy *Magn. Reson. Chem.*, **2010**, 48, 642–650.

[18] Firestone, D. Determination of the Iodine Value of Oils and Fats: Summary of Collaborative Study *J. of AOAC Int.*, **1994**, 77(3), 674-676.

[19] http://www2.ups.edu/faculty/hanson/labtechniques/refractometry/SOP

[20] H. Noureddini, B.C. Teoh, L. Davis Clements Densities of Vegetable Oils and Fatty Acids *JAOCS*, **1992**, 69(12), 1184-1188.

[21] F.D. Gunstone Vegetable oils in food technology: composition, properties and uses CRC Press, **2002**.

[22] A. N. Annisa, W. Widayat A Review of Bio-lubricant Production from Vegetable Oils Using Esterification Transesterification Process *MATEC Web of Conferences*, **2018**, 156 (15).

CHAPTER 3. LIFE CYCLE ENVIRONMENTAL IMPACT CONSIDERATION IN THE DESIGN OF SOYBEAN OIL-BASED ACRYLIC MONOMERS[1]

3.1. Abstract

Improving the sustainability of polymeric materials through integrating biobased components while maintaining their functionality can be challenging. Using plant oils for the synthesis of biobased acrylic monomers can potentially provide an opportunity for improving the environmental performance of the polymeric materials. In this study, we use life cycle assessment (LCA) methods as a guide, early in the design of the vinyl monomers from soybean oil, to evaluate and improve their environmental performance. We use LCA to pinpoint hotspots along with the process steps and identify greener choices in the process design. The process modifications performed in this study, including reactant/soy-based material loading ratio, alternative catalyst and feedstock, and solvent recycling, resulted in enhanced yield and better environmental performance of the monomers compared to the original synthesis design. Among the modifications tested, adding a solvent recycling step in the synthetic process demonstrated the most significant improvement in the environmental performance in all tested impact categories. Compared to the conventional fossil-based acrylic counterpart (stearyl acrylate), the monomers from soybean oil show better environmental performance in 8 out of 10 of tested categories within the TRACI II method. Given the ability of new monomers in being employed

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[1] The material in this chapter was co-authored by Zoriana Demchuk, Na Wu, Ghasideh Pourhashem and Andriy Voronov. Zoriana Demchuk had the primary responsibilities of synthesizing soybean oil-based monomer, collecting data for LCA modeling and performing the process optimization including varying the reactivity ratios, type of catalyst and soybean source. Zoriana Demchuk was responsible for evaluating the environmental impact of soybean oil-based monomer synthesis and performing LCA modeling. Na Wu was in charge to model the monomer synthesis a industrial scale and involved solvent recycling step in monomer production process. Zoriana Demchuk performed all experimental studies, made the initial draft and was involved in all versions of this chapter. Ghasideh Pourhashem and Andriy Voronov helped evaluate the environmental impact and discuss the relationship between monomer synthesis parameters and Life Cycle Assesment modeling. Published article can be found at https://doi.org/10.1021/acssuschemeng.0c03266.

in a wide range of applications, this study demonstrates their capacity for improving the sustainability of the polymeric materials at large scale and, therefore, the polymer industry.

3.2. Introduction

Increasing environmental problems caused by using petrochemicals has brought growing awareness to the scientific community creating the urge for seeking alternative resources for materials production. Biomass sources, such as starch, cellulose, lignin, and plant oils have become increasingly appealing in making polymeric materials due to their renewability, low cost, abundance, and ability to offer a range of functionalities[1]. For example, similarities in chemical structure between major components of plant oils, triglycerides (fatty acid esters), and some petroleum-based hydrocarbon analogs can make the plant oil-based alternatives feasible in the production of new biobased monomers, polymers, and polymeric materials[2,3]. Various ways for converting triglycerides of plant oils into chemicals suitable for making biobased polymers and polymeric materials have been reported[4], along with a developed in our group one-step method that converts a range of plant (olive, soybean, high oleic soybean, canola, linseed, corn, sunflower) oils into acrylic monomers for free-radical polymerization, including emulsion processes to yield latex polymers[5-8].

A number of challenges, however, are present when monomers are synthesized from renewable resources, including reproducibility, consistency of feedstock, reactivity of the products, complications during synthesis, cost, and environmental performance of alternative production pathways[9,10]. Ensuring an optimized environmental performance of monomers from biomass is a necessary step in demonstrating their commercial feasibility[11].

Life cycle assessment (LCA) is a powerful and standardized tool that is used to quantify the environmental impact of a product, process, or service over their entire life cycle. The implementation of LCA for chemical processes can provide valuable feedback on the extent of the environmental impacts such reactions generate as well as it can be used to improve parts of the process with the highest environmental burden. LCA can help guide scientists on reactions and pathways that should be optimized or chemicals that could be replaced in this regard[12,13]. Performing LCA before claiming a process or product's sustainability is important for the chemical industry[14].

In this study, we first build an initial LCA model of new soybean oil-based monomers synthesis based on experimental data from our laboratory tests. We then use the data from the preliminary LCA results to give directions to improve the synthesis and refine the overall LCA results. Strategies considered to enhance the synthesis of the monomers include changing the type of catalyst, the ratio between reactants, different soy-based sources, and potential solvent recycling. Moreover, the environmental impact of monomers production is estimated and compared to a commercial petroleum-based analog. The prospective LCA of monomers synthesis provides an overview and direction for process improvement and move it closer to the scaling-up step for industrial applications. Employing LCA early in the design will help make the process of designing a product environmentally and potentially economically more efficient.

The main objectives of this study are to 1) evaluate and optimize the production of monomers from soybean oil (SBM_O) and soybean biodiesel (SBM_D), and 2) compare the environmental impacts of two resulted soybean oil-based monomers (SBMs) with a functionally similar commercial counterpart (stearyl acrylate). We use LCA method to evaluate the sustainability of SBMs production, find routes for potential improvement of SBM_O and SBM_D synthesis by process optimization, and compare the environmental impact of resulted monomers with petroleum-based monomer with similar chemical structure and properties.

3.3. Materials and Methods

Several studies have demonstrated the potential of using acrylic monomers from soybean oil in the synthesis of waterborne polymeric materials for various industrial applications[6,7]. The pathway of synthesizing SBM_O established by our group involves using the transesterification reaction of crude soybean oil and N-(hydroxyethyl) acrylamide in the presence of the catalytic amount of sodium hydroxide[5-8]. This process comprises several steps, including monomers synthesis, purification, and solvent evaporation.

The growth in biodiesel production as a renewable energy alternative has made this material to be a feasible potential source in the production of chemicals. The development and testing of a new alternative pathway of soy monomer production from biodiesel can be beneficial by improving the process conditions, yield, and environmental impact. In this study, soybean biodiesel was selected as an additional source for the synthesis of soy-based monomer (SBM_D). We hypothesize that using biodiesel will simplify the synthetic pathway as the byproduct (methanol) can be separated during the process and recycled, thus, improving the resulted monomer product purity.

The methodology of this study is comprised of experimental and modeling sections. First, we test the synthesis of SBM_O and SBM_D. Then we build LCA models based on the obtained laboratory results. We will use the results of the initial LCA models to make and test changes to monomers synthesis needed to improve their environmental performance. Finally, we refine and finalize the LCA models based on the improved synthesis. The initial and the final LCA models are referred to as lab-scale and scaled-up LCA models in the study, respectively.

3.3.1. Materials

Soybean oil (Crisco; The J.M Smucker Company, Orville, OH), and N-hydroxyethyl acrylamide (HEAA; TCI America) are used as reacting agents in the synthesis of SBMO. Soybean biodiesel was synthesized from soybean oil, as will be described below. 2,6-Di-tertbutyl-p-cresol (99 %, TCI America); methanol, tetrahydrofuran, and dichloromethane (ACS grade, VWR International LLC, Radnor, PA) are solvents used in the synthesis. Potassium hydroxide (pellets, EMD Millipore Corporation, Darmstadt, Germany), sodium hydroxide (98 %, Alfa Aesar, Ward Hill, MA), magnesium sulfate (99.5 %, Alfa Aesar, Ward Hill, MA) were used as received. Deionized water (DI water) was used for monomers' purification.

3.3.2. Synthesis of Soybean Oil-Based Biodiesel

To synthesize soybean biodiesel (SBB), a transesterification reaction was carried out between 150 g of soybean oil and 45 g of methanol (1:3 molar ratio, respectively) in the presence of the catalytic amount of potassium hydroxide at 60 ^{o}C for 90 min. After the reaction, the mixture was purified to remove catalyst and glycerol (byproduct) using a brine solution (reaction yield is 92%). The synthesized SBB was dried under vacuum to remove traces of unreacted methanol. The purified product was characterized using ^{1}H NMR spectroscopy to confirm its chemical structure.

3.3.3. Synthesis of Soybean Oil-Based Monomers (SBM_O/SBM_D)

The soybean oil-based acrylic monomers (SBMs) were synthesized using a one-step transesterification reaction of crude soybean oil or soybean biodiesel and N-(hydroxyethyl) acrylamide in the presence of 1.5 % of catalyst (NaOH or KOH) in tetrahydrofuran for 4 hours at 40 ^{o} C. The monomer mixture was purified using a brine solution at a concentration of 5 % of NaCl and adding dichloromethane (CH_2Cl_2) as a co-solvent. The resulted oil phase containing

SBMs was dried under the magnesium sulfate layer. The dried oil phase was filtered using a vacuum pump, and rotary evaporated to remove the solvent residues. The resulted monomers were characterized using ^{1}H NMR spectroscopy, showing a 98% purity. The process of SBMs synthesis was accomplished by various ratios of reagents in the presence of two different catalysts. The assay of changing the parameters in the synthesis was aimed for further LCA optimization processes. The ratio between soybean oil-based source and HEAA was varied from 1:1 to 1:2 (1:3 – 1:6 in the molar ratios, respectively) to improve the monomers yield during synthesis. Since NaOH and KOH show different catalytic activity, both reagents were used in SBMs synthesis at the same concentration to evaluate the impact of their variation on reaction yield. The proposed pathways of the SBM$_O$/SBM$_D$ synthesis, as well as the synthesis of SBB are illustrated in Figure 3.1.

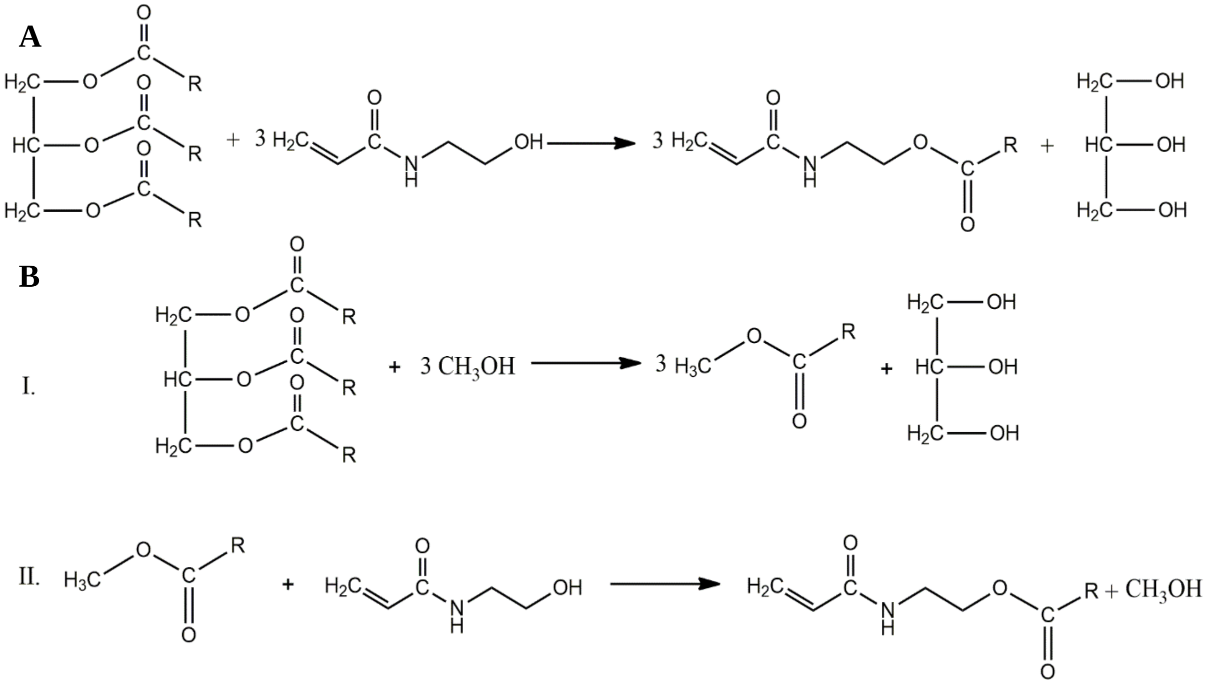

Figure 3.1. The chemical reactions of soybean oil-based acrylic monomers synthesis from soybean oil (**A**) and soybean biodiesel (**B**)

3.3.4. Modeling Section: Building the LCA Model

We used the LCA method as a tool to environmentally improve the synthesis of the soybean oil-based monomers. We built the LCA model according to the international standards ISO 14040 and ISO 14044 (ISO, 2006b, c). To conduct the LCA, the SimaPro V 8.3 software and TRACI II (U.S., 2008) method were used[15]. The lab-scale LCA model was created based on the initial experimental results to identify significant environmental contributors. The results of the lab-scale LCA were then used to improve the monomers synthesis. Finally, we used the laboratory data from the modified synthesis assay as well as a scaled-up process simulation[16] to refine the initial lab-scale LCA model.

3.3.4.1. The Goal and Scope of the LCA Study

This research was conducted to compare the environmental performance of two synthetic pathways of the renewable monomers made from two different soy-based sources. We use these LCA models to compare the environmental impacts of soybean oil-based monomers production at a laboratory scale by varying the process conditions, including solvent recycling, reactants ratio and source, and catalyst (NaOH vs. KOH). The environmental performance of the SBMs was investigated within ten main impact categories, including global warming, oxygen depletion, energy demand, eutrophication, and toxicity.

3.3.4.2. System Boundary

This LCA study is a “cradle-to-gate” model, where the “gate” means the ready-to-be-packaged soybean oil-based monomer would be considered the final product of the chemical facility (Fig.3.2). The main LCA steps within the system boundary include the synthesis of SBMs and its purification step. The waste treatment was not included in the LCA study.

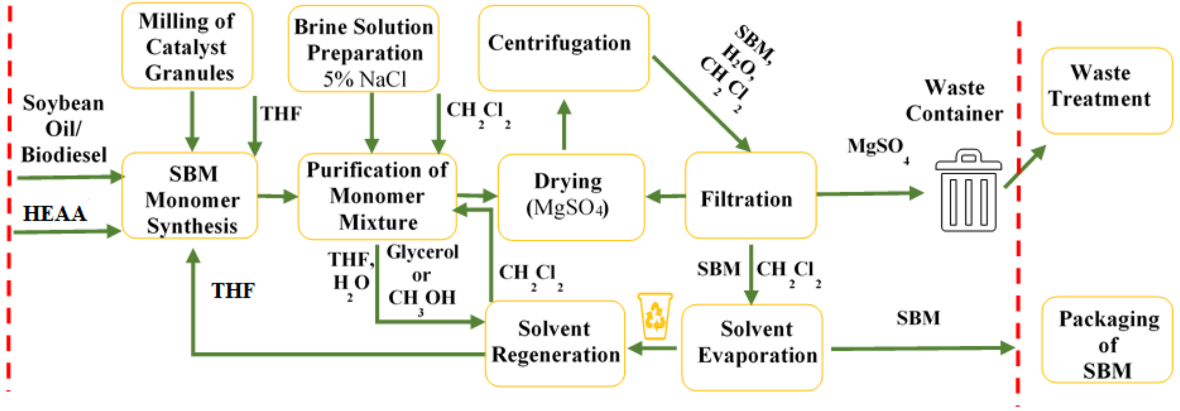

Figure 3.2. The flow chart of soybean oil-based acrylic monomers synthesis

3.3.4.3. Functional Unit

The LCA analysis was conducted using the functional unit (FU) of 1 kg of the SBMs synthesized through the two different studied pathways.

3.3.4.4. Life Cycle Inventory Data Collection

Data collected for this study was based on a combination of primary data derived from the laboratory experiments for material balance and literature when information on chemicals used in the synthesis was missing from various LCA databases. Synthesis of SBMs includes using a high-grade chemical, N-(hydroxyethyl) acrylamide, which was supplied by chemical companies, and its lifecycle production information could not be found in most LCA databases. The overall LCA input data of this study has been divided into the following parts:

- Primary data was obtained using experimental results of laboratory-scale monomer synthesis from soybean oil and soybean biodiesel at the various ratios of soybean oil derivatives with HEAA while using NaOH and KOH as a catalyst.
- Secondary data was collected based on the literature review for the specific chemical used in the synthesis of soybean oil-based monomer – HEAA. All the data regarding

the synthesis of this chemical was generated based on the experimental results found in the literature[17-19].

- All other data on the production of commonly used solvents, catalysts, and chemicals utilized in this study were obtained from USLCI when possible; otherwise, they were taken from Ecoinvent V3[20].

3.4. Results and Discussion

This LCA study is designed to evaluate the environmental impacts of laboratory pathways of SBMs synthesis using a transesterification reaction with HEAA. Since initially reactants' ratio was selected as 1:2, the variations of process parameters and gradual reduction of HEAA in reactants mixture was targeted to improve the environmental impact of monomers synthesis while ensuring that process changes do not diminish the monomers yield.

3.4.1 Testing the Effect of Soybean Oil and Soybean Biodiesel to HEAA Ratio on Monomers' Yields

The synthesis of SBMs was carried out using transesterification of soybean oil or soybean biodiesel with HEAA at various ratios in tetrahydrofuran to determine the effect of reactants ratio on monomers' yields. We observed that at the soybean oil to HEAA ratio of 1:1.25 transesterification reaction can successfully be carried out, while this reaction does not fully proceed at the ratios 1:1 to 1:1.2 leading to the formation of byproducts, mono- and diglycerides (Fig. 3.3). The formation of mono and diglycerides is even more pronounced during the synthesis of SBM_D where homogenization can only be achieved at 1:1.5 ratio. This can be explained by the higher thermodynamic stability of soybean biodiesel, resulting in a larger HEAA amount needed to yield the monomer product. The obtained results indicate that overall higher monomer yield is achieved when crude soybean oil is used for monomers synthesis.

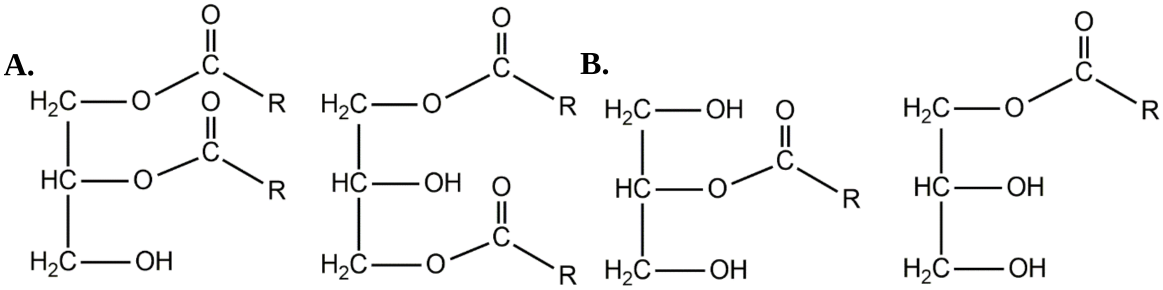

Figure 3.3. Variation of diglycerides (**A**) and monoglycerides **(B**) formed during transesterification reaction of soybean oil (R-fatty acid chain)

3.4.2. Impact of Catalyst Selection

To improve monomers' synthesis, changing the type of catalyst was considered next. It was assumed that while being located in the heterogeneous reactive mixture and having high catalytic activity, NaOH can undergo partial deactivation. Since its catalytic activity is determined by the lower electronegativity of Na atom, readily releasing the OH^- group, the KOH can be expected to be catalytically active for longer reaction times. In fact, higher SBM yield at different reagents ratio was observed in the presence of KOH as a catalyst if compared to NaOH (Fig. 3.4).

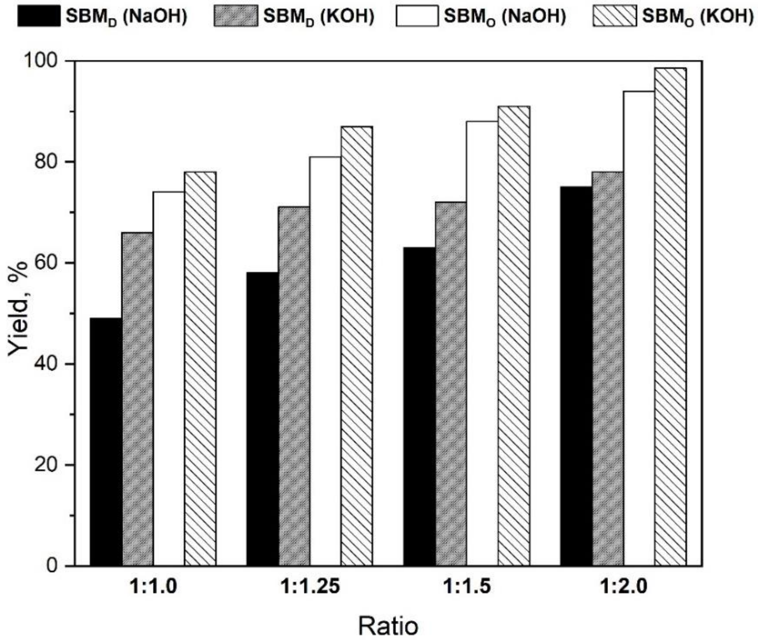

Figure 3.4. The SBMs yield obtained through varying reaction components

When using KOH as the catalyst, soybean oil to HEAA ratio of 1:2.0 facilitates the highest yield for both SBM$_O$ and SBM$_D$. However, already at a ratio of 1:1.25, the yield of SBM$_O$ in the presence of both catalysts can be considered as tolerable (> 80%) for further scaling-up stages of the process.

3.4.3. Evaluating the Environmental Performance of SBM$_O$ and SBM$_D$

We ran the LCA model we built for original SBMs laboratory scale syntheses as well as for the scale optimized for yield and environmental impacts. The relative environmental impacts of the original lab-scale SBM$_O$ synthesis and contribution of each component used in the process were evaluated (Fig. 3.5). The obtained results indicate that solvents are the main contributors to the environmental impacts of SBM$_O$ synthesis by mainly affecting ozone depletion, global warming, acidification, and human toxicity categories. This information was used to further modify the synthetic process for finding potential routes to improve the environmental performance of monomers synthesis. Moreover, it was demonstrated that one of the reagents in

SBMs synthesis – N-hydroxyethyl acrylamide – plays a major role in the overall environmental impact of monomers production process.

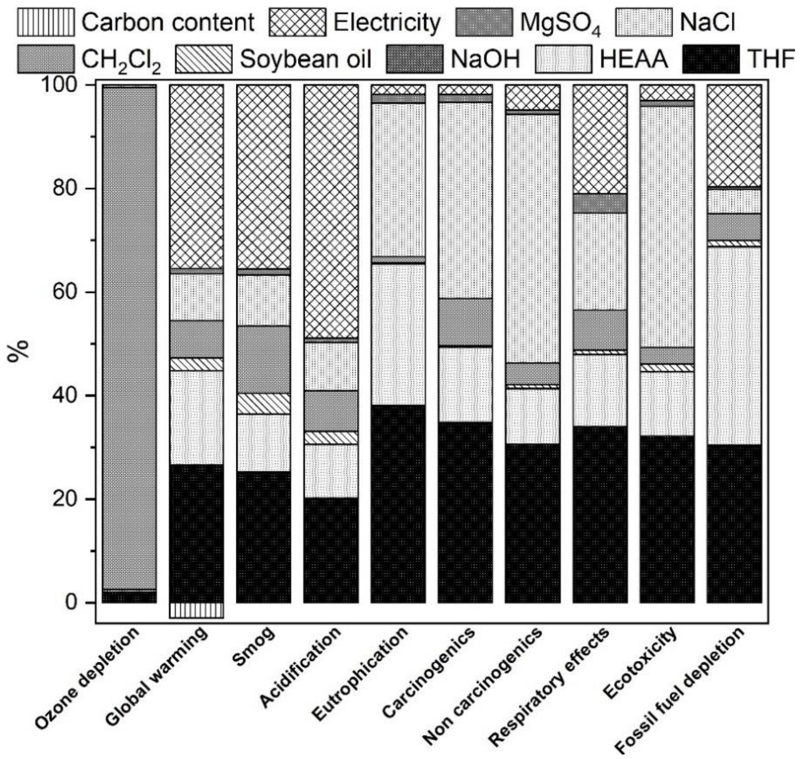

Figure 3.5. Contribution of components used in SBM_O synthesis to evaluate targeted environmental impact categories

In addition to solvent and HEAA, electricity and NaCl are next in contributing to the overall environmental impacts in most categories. Here, electricity is the representative of the energy consumed in all stages of SBMs monomer synthesis at a laboratory scale, including heating, mixing, filtration, and solvent evaporation. The major impacted categories are global warming, smog, and acidification, where the impact on environmental performance from electricity usage amounts in the range of 35-50% within the tested category. However, energy use in the laboratory scale setups is often inefficient or non-optimized as often energy efficiency (depending in the synthesis) is not the focus of the experiment, while reaction conversion and yields are. When scaled-up, process energy consumption is optimized, and therefore its overall impact is diminished.

Table 3.1. SBM_O/SBM_D synthetic yield for two soy feedstocks and catalysts

Catalyst	Ratio (Feedstock to HEAA)	SBMs Yield (%)	
		SBM_O	SBM_D
Sodium Hydroxide	1 : 1	73.9	49
	1 : 1.1	75	-
	1 : 1.25	81	58
	1 : 1.4	86.3	-
	1 : 1.5	90	63
	1 : 2	94	75
	1 : 2.5	-	75.8
Potassium Hydroxide	1 : 1	78	66
	1 : 1.25	87	70.8
	1 : 1.5	91	72
	1 : 2	98.5	78
	1 : 2.5	-	78.1

Furthermore, this study was focused on testing the environmental impacts of the SBMs production while considering various synthetic reaction modifications, including catalyst type, and soybean oil-based source, and solvent recycling considerations. Among the feedstock/HEAA ratios tested (Table 3.1), it was shown that ratio 1:1.25 offers the optimum SBMs yield that keeps the unwanted byproduct at lower level while maintaining a favorable yield of monomers. Therefore, the 1:1.25 was used as the base case scenario for our further scaling-up model[15]. Considering that the current process is at the early stages of product development, the scaling-up process simulation of SBMs production, which is based on experimental data, can help with assessing plant performance and judging the full commercial potential. In the preliminary process simulation model[15], we estimated the mass and energy balance of monomers production at an industrial scale. The scaled-up process considered downstream processes such as solvent recycling (not applied at the current laboratory scale) and showed a high potential for up to 90% recycling of solvents. The process simulation results (more representative of commercial-scale production) were used to refine the LCA model.

3.4.3.1. Solvent Recycling

Solvent recycling is a process step performed at industrial scales and is considered here in the scaled-up process scenario, where both THF and dichloromethane can be recycled. The LCA results showed that the solvent recycling step in the production of monomers noticeably improves the environmental impact in all categories, including ozone depletion, smog, acidification, eutrophication, and non-carcinogenic effects. We assume another petroleum-based solvent is used for solvent recovery, along with associated equipment and energy required for solvent recycling. Although some environmental impact categories such as fossil fuel depletion did not depict significant change following the recycling process, this step is necessary for every industrial-scale production for both sustainability and cost-saving purposes. In fact, most of the remaining impact categories demonstrate better performance when the solvents are recycled (Fig. 3.6).

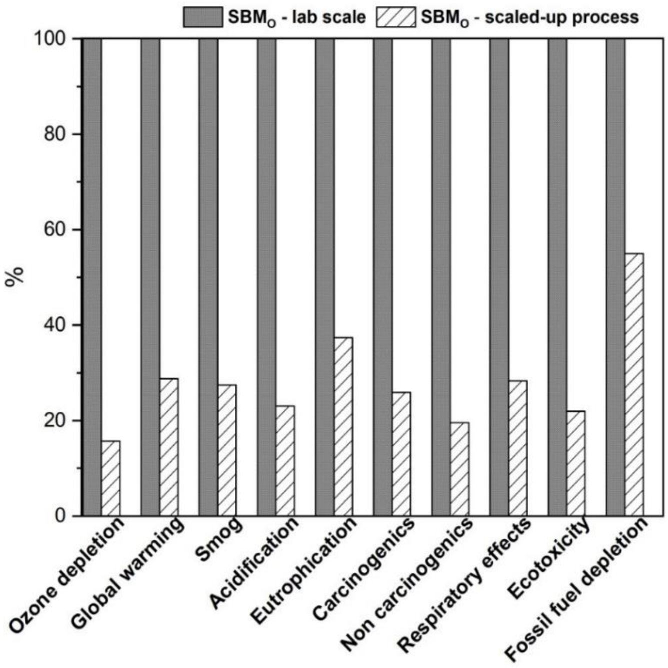

Figure 3.6. Environmental performance of lab-scale and scaled-up SBM$_O$ production in targeted impact categories

3.4.3.2. Catalyst Selection

We tested multiple formulations for each monomer made from soybean oil and soybean biodiesel, with two different catalysts, NaOH and KOH, while changing molar ratios of the two main inputs (Table 3.1). As discussed before, it was observed that using KOH results in higher yield in both SBM$_O$ and SBM$_D$ synthesis. Among all formulations tested, the higher monomer yield achieved by using soybean oil and KOH as a catalyst in transesterification reaction with HEAA leads to lowering the environmental impact by around 30%, compared to using NaOH, suggesting this pathway as a promising alternative for future SBMs production at the industrial scale (Fig. 3.7).

The positive improvement of the environmental impact of the production of monomer from soybean oil and soybean biodiesel using KOH as the catalyst is presented on Figures A1 and A2 in Appendix A, respectively.

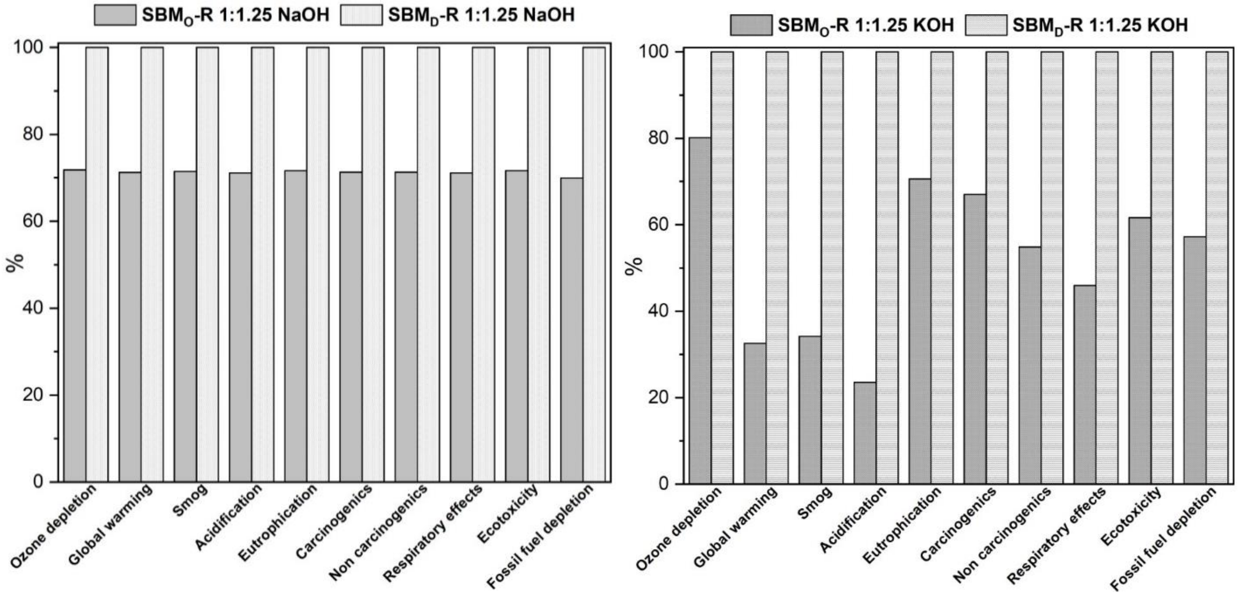

Figure 3.7. Comparative contribution of tested SBM_O and SBM_D scenarios of various optimization pathways to TRACI 2 impact categories

3.4.3.3. Comparing SBMs with Commercially Available Petroleum-Based Stearyl Acrylate

Finally, we compare the environmental impacts of the SBM_O (scaled-up process, 1:1.25) with a commercially available stearyl acrylate, reactive in free radical polymerization having a functionally similar chemical structure. The comparative LCA provides information on where the SBMs may need further improvement (Fig. 3.8).

The comparative LCA results show that SBM_O production offers a better environmental impact in eight categories except for ozone depletion and eutrophication. Using dichloromethane as one of the solvents imposes the highest pressure in the ozone depletion category for monomers production. SBM_O performance in this category can be improved by replacing the chlorinated solvent used in synthesis with a solvent with a lower environmental impact and similar functionality.

Eutrophication in SBMs production, on the other hand, when looked closer at the inventory and process contributions of all SBM_O components and their supply chains in their respective database in our model, can be mainly attributed to 3 components. Eutrophication in

SBM_O mainly originates from ammonia used within the supply chain of acetonitrile, which is one of the main components of HEAA, energy used along the supply chain of Butane-1,4 diol, which is a main component of THF, and energy used for NaCl production. For future research or scaled-up production, considering methyl-THF instead of THF can potentially help to reduce the environmental effect of this component.

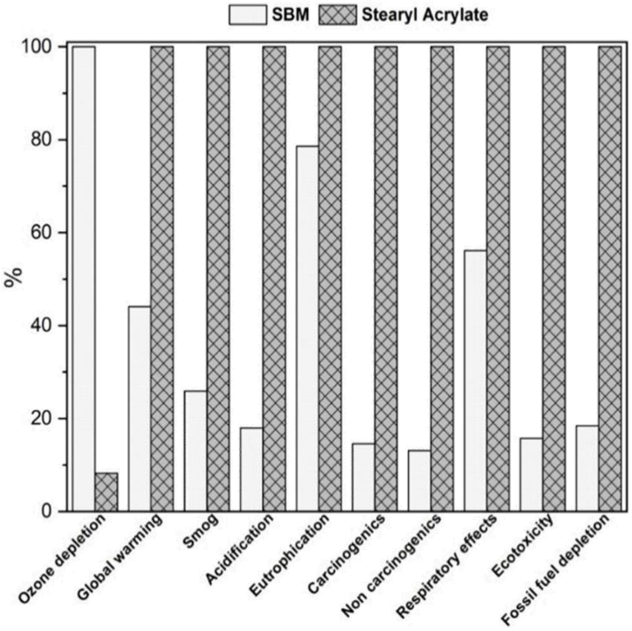

Figure 3.8. Comparative environmental performance of SBMO with stearyl acrylate for targeted impact categories

These obtained LCA results open an opportunity for soybean oil-based monomers to become commercialized and produced in industrial scales for a wide range of applications.

3.5. Conclusions

We demonstrated that using LCA early in the synthesis of a material can help direct the design of the product for sustainability. We improved our initial synthesis path for better conversion yield and environmental performance. The modifications applied to soybean oil-based monomers synthesis demonstrated improvement in the monomers environmental performance in several impact categories, while the extent of this improvement varies depending on the reaction condition. Our LCA study demonstrated that solvent recycling is a crucial step in the SBMs production optimization process and can noticeably improve its environmental performance. Changing the catalyst considerably enhances the reaction yield, which is more noticeable when crude soybean oil is used for monomer synthesis. Through performing a comparative LCA study, we demonstrated that producing SBMs generates lower negative environmental impacts than commercially available stearyl acrylate, a functionally similar petroleum-based counterpart. Given the ability of SBM to be used in a wide range of applications, including coatings, adhesives, and plasticizers, this study shows the capacity for using it for improving the sustainability of polymeric materials. However, considering the scale and maturity of the new processes included, future research is needed to address the coherent scaling-up of experimental data as well as the end of life scenarios – the entire life cycle.

3.6. References

[1] Harding, K.G.; Dennis, J.S.; Blottnitz, H.; Harrison, S.T.L. Environmental analysis of plastic production processes: Comparing petroleum-based polypropylene and polyethylene with biologically-based poly--hydroxybutyric acid using life cycle analysis *J.Biotechnol.* **2007**, *130*, 57–66, DOI 10.1016/j.jbiotec.2007.02.012.

[2] Williams, C. K.; Hillmyer, M. A. Polymers from renewable resources: A perspective for a special issue of polymer reviews. *Polym. Rev.* **2008**, *48,*1−10,DOI 10.1080/15583720701834133.

[3] Demchuk, Z., Shevchuk, O.; Tarnavchyk, I.; Kirianchuk, V.; Lorenson, M.; Kohut, A.; Voronov, S.; Voronov, A. Free-Radical Copolymerization Behavior of Plant-Oil-Based Vinyl Monomers and Their Feasibility in Latex Synthesis *ACS Omega* **2016**, *1*, 1374−1382, DOI 10.1021/acsomega.6b00308.

[4] Gü ner, F. S.; Yagci, Y.; Erciyes, A. T. Polymers from triglyceride oils. *Prog. Polym. Sci.* **2006**, *31,* 633−670, DOI 10.1016/j.progpolymsci.2006.07.001.

[5] Tarnavchyk, I.; Popadyuk, A.; Popadyuk, N.; Voronov, A. Synthesis and Free Radical Copolymerization of a Vinyl Monomer from Soybean Oil. *ACS Sustainable Chem. Eng.* **2015**, *3,* 1618−1622, DOI 10.1021/acssuschemeng.5b00312.

[6] Demchuk, Z.; Shevchuk, O.; Tarnavchyk, I.; Kirianchuk, V.; Kohut, A.; Voronov, S.; Voronov, A. Free Radical Polymerization Behavior of the Vinyl Monomers from Plant

Oil Triglycerides. *ACS Sustainable Chem. Eng.* **2016**, *4*, 6974-6980, DOI 10.1021/acsomega.6b00308.

[7] Demchuk, Z.; Kohut, A.; Voronov, S.; Voronov, A. Versatile Platform for Controlling Properties of Plant Oil-Based Latex Polymer Networks *ACS Sustainable Chem. Eng.* **2018**, *6*, 2780−2786, DOI 10.1021/acssuschemeng.7b04462.

[8] Kohut, A.; Demchuk, Z.; Kingsley, K.; Voronov, S.; Voronov, A. Dual role of methyl-β-cyclodextrin in the emulsion polymerization of highly hydrophobic plant oil-based monomers with various unsaturations *European Polymer Journal*, **2018**, *108,* 322-328, DOI 10.1016/j.eurpolymj.2018.09.010.

[9] Molina-Gutiérrez, S.; Ladmiral, V.; Bongiovanni, R.; Caillol, S.; Lacroix-Desmazes, P. Radical polymerization of biobased monomers in aqueous dispersed media *Green Chem.,* **2019**, *21,* 36–53, DOI 10.1039/C8GC02277A.

[10] Nakajima, H.; Dijkstra, P.; Loos, K. The Recent Developments in Biobased Polymers toward General and Engineering Applications: Polymers that Are Upgraded from Biodegradable Polymers, Analogous to Petroleum-Derived Polymers, and Newly Developed *Polymers* **2017**, *9,* 523, DOI 10.3390/polym9100523.

[11] Dube, M. A.; Salehpou, S. Applying the Principles of Green Chemistry to Polymer Production Technology *Macromol. React. Eng.* **2014**, *8*, 7–28, DOI 10.1002/mren.201300103.

[12] Ögmundarson, Ó.; Herrgård, M.J.; Forster, J.; Hauschild, M.Z.; Fantke, P. Addressing the environmental sustainability of biochemicals. *Nat. Sustain.* **2020,** *3*, 167–174, DOI 10.1038/s41893-019-0442-8.

[13] Groot, W.J.; Boren, T. Life cycle assessment of the manufacture of lactide and PLA biopolymers from sugarcane in Thailand *Int J Life Cycle Assess,* **2010**, *15(9)*, 970-984, DOI 10.1007/s11367-010-0225-y.

[14] Delgove, M.A.F.; Laurent, A.L.; Woodley, J.M.; De Wildeman, S.M.A.; Bernaerts, K.V.; Van der Meer, Y. A Prospective Life Cycle Assessment (LCA) of Monomer Synthesis: Comparison of Biocatalytic and Oxidative Chemistry *Chem. Sus. Chem,* **2019**, *12*, 1349 –1360, DOI 10.1002/cssc.201900007.

[15] PRé Consultants 2019 SimaPro 9 (Amersfoort, Netherlands: PRé Consultants).

[16] Wu, N.; Demchuk, Z.; Voronov, A.; Pourhashem, G. Sustainable manufacturing of polymeric materials: life cycle and techno-economic assessment of soybean oil-based acrylic monomers production *ISSST* **2019**.

[17] Zhang, T.; Kusukawa, N.; Garner, M. Method for producing hydrophilic monomers and uses thereof *U.S. Patent* # US6464850B1, **1999**.

[18] Yu, Y.; Fan, Y.; Chen, S. Technique for preparing octadecyl acrylate with fusion esterification method *CN Patent #* 101270046A, **2008**.

[19] Manyar, H.G.; Paun, C.; Pilus, R.; Rooney, D.W.; Thompson, J.M.; Hardacre, C. Highly Selective and Efficient Hydrogenation of Fatty acids to Alcohols using Pt supported over TiO_2 catalysts *Chem.Comm.*, **2010**, ***46***, 6279-6281, DOI 10.1039/C0CC01365J.

[20] Nemecek, T. Barley Production, Swiss Integrated Production, Extensive, CH (Switzerland), Allocation, cut-off by classification, ecoinvent database version 3.3.

CHAPTER 4. FREE RADICAL POLYMERIZATION BEHAVIOR OF THE VINYL MONOMERS FROM PLANT OIL TRIGLYCERIDES[1]

4.1. Abstract

A one-step method of plant oil direct transesterification was used to synthesize new vinyl monomers from sunflower (SFM), linseed (LSM), soybean (SBM), and olive (OVM) oils. The degree of unsaturation in plant oil fatty acids was used as a criterion to compare the free radical polymerization behavior of new monomers. The number-average molecular weight of plant oil-based homopolymers synthesized in toluene in the presence of AIBN at 75 °C varies at 11 000−25 000 and decreases as follows: poly(OVM) > poly(SFM) > poly(SBM) > poly(LSM), corresponding to increasing degree of unsaturation in the monomers. Rate of polymerization depends noticeably on the degree of unsaturation in monomers. Due to the allylic termination, chain propagation coexists with effective chain transfer during polymerization. The obtained values of CM (ratio of chain transfer and propagation rate constants) depends on monomer structure as follows: C_M(LSM) > C_M(SBM) > C_M(SFM) > C_M(OVM). ^{1}H NMR spectroscopy shows that the fraction of the reacting allylic atoms does not vary significantly for the synthesized monomers (7−12%) and is determined entirely by plant oil degree of unsaturation. The glass transition temperature of homopolymers [Tg = 4.2 °C for poly(SFM), Tg = −6 °C for poly(SBM)] from new monomers indicates that varying biobased fragments in copolymers might

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[1] The material in this chapter was co-authored by Zoriana Demchuk, Oleh Shevchuk, Ihor Tarnavchyk, Vasylyna Kirianchuk, Ananiy Kohut, Stanislav Voronov, and Andriy Voronov. Zoriana Demchuk had the primary responsibilities of synthesizing and characterizing plant oil-based monomers, evaluation their polymerizability and determination the polymerization kinetics. Oleh Shevchuk and Vasylyna Kirianchuk were helping to determine reaction orders with respect to monomer and initiator. Zoriana Demchuk was also responsible for evaluating chain transfer processes during polymerization and quantifying chain transfer constants using Mayo method. Oleh Shevchuk and Ananiy Kohut were helping to quanify the extent of remaining usaturation in fatty acid fragments after completion of polymerization process. Ananiy Kohut, Ihor Tarnavchyk and Andriy Voronov were helping to explain the experimental data of polymer kinetics and trends in reaction order and chain transfer constants. Published article can be found at https://doi.org/10.1021/acssuschemeng.6b01890.

considerably change the intermolecular interactions of macromolecules and their physicochemical properties.

4.2. Introduction

Development of renewable polymers is a promising platform to provide new materials with industrially viable properties and a positive environmental impact,[1,2] with some of the biobased polymeric materials surpassing their petroleum-based counterparts. [3,4] However, only a small share (less than 5%) of renewable polymers is used in the commercial market, largely due to their high cost and mediocre performance.[5–7] To improve the cost-performance of renewable polymers, several areas are being considered for exploration, including new monomer synthesis and achieving polymerization control at a level similar to that of petroleum-based monomers and their polymers.[5]

Plant oils consist predominantly of esters of glycerol with three fatty long chain acids (triglycerides) with varying compositions of fatty acids, which depend on the plant and the growing conditions (season, crop, etc.).[8] Due to their abundance, biodegradability, low cost, nontoxicity, and ability to undergo versatile organic reactions, plant oils have become the most important renewable feedstock in the replacement of petroleum-based sources in the chemical industry, particularly in the production of biobased polymers.[9–13] Different organic reactions of transformation of triglycerides into a variety of fatty derivatives are considered in the synthesis of sustainable biobased monomers, as well as in further development of polymers and polymeric materials. These reactions include hydrolysis, transesterification, amidation of ester groups, epoxidation, hydrogenation, and metathesis for double bonds,[5] with the most commercially successful reaction being triglyceride transesterification into fatty esters in the presence of methanol.[14] Most currently available syntheses of polymers from plant oils are limited to polycondensation and oxypolymerization. Both mechanisms result in the formation of exclusively crosslinked polymers, which are widely applicable in industrial coatings.[15–21] Tang et al. reported on a new strategy of triglyceride amidation by amino alcohols for the preparation of fatty monomers from high oleic soybean oil (HOSO) and their further polymerization by free radical mechanism to develop thermoplastic polymers.[22] Synthesized in a two-stage process, HOSO-based (meth)acrylate monomers of a broad library yield macromolecules, which demonstrate wide glass transition temperatures and properties, depending on the backbone and amide structures in the side chain.[23] As a result, polymers exhibiting Tg in a range of more than 100 °C difference and demonstrating physical properties of materials with viscoelastic and thermoplastics behavior were obtained. Because of the highly hydrophobic nature of triglyceride molecules, the development of waterborne polymeric materials (latexes in particular) from plant oils has been challenging.

Recently, we reported a one-step synthesis of a new vinyl monomer, acryloylamino)ethyl soyate, via direct transesterification reaction of commodity soybean oil triglycerides with N-(hydroxyethyl)acrylamide.[24] Although the vinyl bond of this monomer is reactive in conventional addition chain polymerization and facilitates macromolecular chain growth, the double bonds of the fatty acid chains are unaffected during the free radical polymerization process that yields linear macromolecules. [24] The reactivity ratios of the new soybean oil-based acrylic monomer (SBM) in free radical copolymerization with styrene, methyl methacrylate, and vinyl acetate indicate that SBM behaves in copolymerization as a conventional vinyl monomer. The resulting macromolecules are capable of post-polymerization oxidative reactions to form cross-linked polymer structures or of modification of unsaturated fatty acid chains. Such biobased vinyl monomers can function as a polymer modifier (specialty monomer) to design polymers and polymeric materials with unique properties and performance for various industrial applications.[25,26] Being used in small quantities (5−10% wt), they can improve paints, coatings, etc., by customizing their properties (water resistance, hydrophobicity, mechanical performance, intermolecular plasticization, etc.) Inspired by the work on soybean oil-based acrylic monomers, herein we report employment of the synthetic approach for the preparation of new monomers from linseed, sunflower, and olive oil, which possess remarkably different compositions of fatty acids in triglycerides. Features of free radical homopolymerization of the developed monomers were studied in detail. The degree of unsaturation in fatty acids was utilized in this study as a criterion for comparing the behavior of new monomers and demonstrating their feasibility for use in addition chain polymerization.

4.3. Materials and Methods

4.3.1. Materials

Soybean oil (Crisco, The J.M. Smucker Company, Orville, OH), sunflower oil (Kirlangic, Turkey), olive oil (Bertolli, Houston, TX), linseed oil (Sunnyside corp., Wheeling, IL), and N-(hydroxyethyl)acrylamide (HEAAm; TCI America) were used as received. Azobis(isobutyro-nitrile) (AIBN; Sigma−Aldrich, St. Louis, MO) was purified with recrystallization from methanol. Toluene (Sigma−Aldrich, St. Louis, MO) was distilled prior to use. Other solvents and chemicals, all analytical grade or better, were used as received. Deionized water was used for purification purposes (Milli-Q, 18 MΩ).

4.3.2. Plant Oil-Based Acrylic Monomer Synthesis and Characterization

About 115 g of N-(hydroxyethyl)acrylamide was added to 150 g of each plant oil (with acrylamide alcohol to triglyceride molar ratio of 5.9 to 1), 150 mL of tetrahydrofuran, and 0.1 g of 2,6- di-tert-butyl-p-cresol in a two-neck 500 mL round-bottomed flask equipped with a mechanical stirrer. Each reaction mixture was heated up to 40 °C in the presence of a catalytic amount of ground sodium hydroxide (1.5 g) and slowly added to the reaction mixture with continuous stirring. The reaction mixture was stirred at 40 °C until complete homogenization (approximately 3 h) and was allowed to remain overnight at room temperature. The reaction mixture was diluted with CH_2Cl_2, purified by washing with brine, treated with magnesium sulfate, and dried under a vacuum, yielding about 170 g of acrylic monomer (94−96% of the theoretical yield). The resulting monomer products contain one acrylic double bond linked to one fatty chain, which varies between fully saturated, mono-, and polyunsaturated, depending on plant oil composition.

4.3.3. Plant Oil-Based Acrylic Monomers Characterization

To confirm the chemical structure of the four synthesized monomers, ^1H NMR spectra were recorded on an AVANCE III HDTM 400 high performance digital NMR spectrometer (Bruker, Billerica, MA) using $CDCl_3$ as a solvent. The ESI high-resolution mass spectrum of the monomers was obtained using a Bruker Daltonics BioTOF mass spectrometer. For each monomer, iodine value (to determine the degree of unsaturation of monomers and hence their potential to undergo oxidation, including autoxidation), aqueous solubility, and refractive index were determined as follows:

4.3.3.1. Iodine Value

A 0.1 g portion of each monomer sample was placed in a 500 mL glass flask, to which 20 mL of CCl_4 has been added. Wijs solution, 25 mL, was added with swirling to the flask, which was then stored in the dark for 1 h at 20 °C. After incubation, 30 mL 0.1 N KI solution followed by 100 mL of recently boiled and cooled water was added. The solution was titrated with 0.1 N sodium thiosulfate solution, gradually and with constant stirring. The titration was continued until the yellow color had almost disappeared; 1−2 mL starch indicator solution was then added, and the titration continued until the blue color had just disappeared. A blank test was carried out simultaneously. Iodine value was expressed as grams of iodine absorbed per 100 g sample utilizing the following formula:

$$\text{Iodine value (IV)} = [(\mathrm{B} - \mathrm{S}) \times \mathrm{N} \times 12.69]/m_{\text{sample}} \tag{4.1}$$

where B is the titration of the blank in milliliters, S is the titration of the sample in milliliters, and N is the normality of the sodium thiosulfate solution.

4.3.3.2. Aqueous Solubility

The aqueous solubility of the plant oil-based monomers was determined using UV−vis spectrometry. A quantity equivalent to 10 mg of substance was dispersed in 100 mL of distilled water, and the dispersion was vortexed for 20 min. Various aliquots were pipetted from this dispersion and diluted to obtain concentrations ranging from 0.1 to 50 μg/mL. The transparency of the resulting solutions was measured using a UV−vis spectrophotometer (Varian Cary 5000 UV−vis-NIR spectrophotometer) at $\lambda = 350$ nm. The point when the transparency of the solution drops and begins to deviate from 100% was taken as the aqueous solubility of the monomer.

4.3.3.3. Refractive Index

The refractive index of plant oil-based monomers was determined using a Bausch & Lomb Refractometer. The surface of the prism was covered by placing 2 drops of each monomer sample. Refractive index was determined by adjusting the borderline between the bright and the dark region at the center of the crosshair. The measurements were performed at 20 °C. For each sample, three measurements were carried out.

4.3.4. Free Radical Polymerization of Plant Oil-Based Monomers

Each plant oil-based monomer (0.5 M) and AIBN (0.038 M) was dissolved in toluene and stirred. The reaction mixture was purged with argon at room temperature for 30 min and heated at 70 °C−80 °C (different temperatures were used) under an argon blanket for 8 h. The resulting homopolymers were precipitated using a large excess of methanol and purified by multiple precipitations from toluene in methanol. The purified polymer was dried under reduced pressure at room temperature until a constant weight was obtained. The average molecular weight of the homopolymer was determined by gel permeation chromatography (GPC) using a Waters Corporation modular chromatograph consisting of a Waters 515 HPLC pump, a Waters 2410 Refractive Index Detector, and a set of two 10 μm PL-gel mixed-B columns; the column temperature was set at 40 °C. Tetrahydrofuran (THF) was used as the carrier solvent. The glass transition temperature of the plant oil-based homopolymers was determined via modulated differential scanning calorimetry (MDSC) using a TA Instruments Q1000 calorimeter. Dry nitrogen with a flow rate of 50 mL/min was purged through the sample. The samples were subjected to an underlying heating rate of 10 °C/min.

4.4. Results and Discussion

4.4.1. Plant Oil-Based Monomer Synthesis and Characterization

The goal of this work is to employ the procedure of crude plant oil direct transesterification with N-(hydroxyethyl)- acrylamide[24] in the synthesis of new plant oil-based acrylic monomers and validate monomers polymerizability in chain addition polymerization. The synthesized acrylic monomers will be further employed in chain copolymerization with their petroleum-based counterparts and in the formation of biobased latexes. Soybean, sunflower, linseed, and olive oils, which all contain remarkably different compositions of fatty acids in triglycerides, were used in this study. The most important parameter that might affect plant oil-based monomer polymerization, as well as the physical and chemical properties of the resulting plant oil-based polymers and materials, is the fatty acid chains' degree of unsaturation and their length.[27] Table B1 in Appendix B summarizes the chemical composition of plant oils used in this work. Although the lengths of fatty acid carbon chains in the chosen oils are similar to oleic, linoleic, and linolenic acids being the most common, the average number of double bonds per triglyceride varies significantly. Rich in oleic acid (R = 18:1), olive oil is the least unsaturated of the chosen oils, whereas linseed oil contains the most linolenic acid (R = 18:3) and is, therefore, the most unsaturated of the chosen oils. The chemical composition of sunflower and soybean oil is similar, although the latter contains more linolenic acid, thus making soybean oil more polydisperse in terms of the unsaturated double bonds. To yield the plant oil-based monomer molecules, each crude plant oil was reacted in one step with N-(hydroxyethyl)- acrylamide in the presence of a catalytic amount of sodium hydroxide using the synthetic procedure described in our earlier work.[24] The choice of an appropriate catalyst and solvent is important to obtain a high yield for the transesterification reaction. As a result, about 93−96% yield-synthesis of soybean oil-based (SBM), linseed oil-based (LSM), olive oil-based (OVM), and sunflower oil-based (SFM) monomers was achieved in tetrahydrofuran. The yield depends on the initial concentration of the reactants and the ratio of base catalyst to reactants.[24] The chemical structure of the synthesized monomers was confirmed using ^{1}H NMR spectroscopy (Fig. 4.1) and FT-IR spectroscopy (Fig 4.2). The spectra show that the (acryloylamino)ethyl oleate and (acryloylamino)ethyl linoleate molecules contain an N-acryloyl fragment that provides monomer reactivity in chain radical polymerization (see both insets).

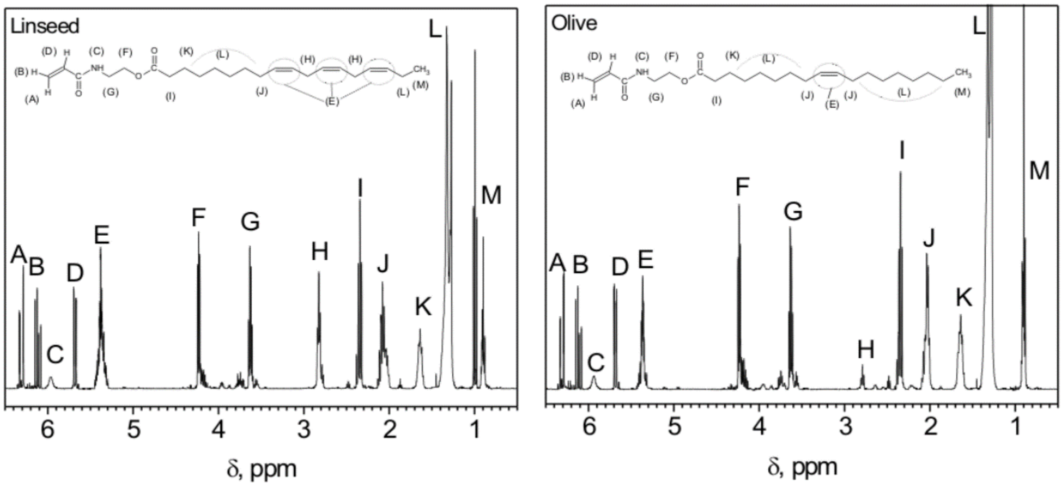


Figure 4.1. ^{1}H NMR spectra of linseed (LSM) and olive (OVM) oil-based monomers

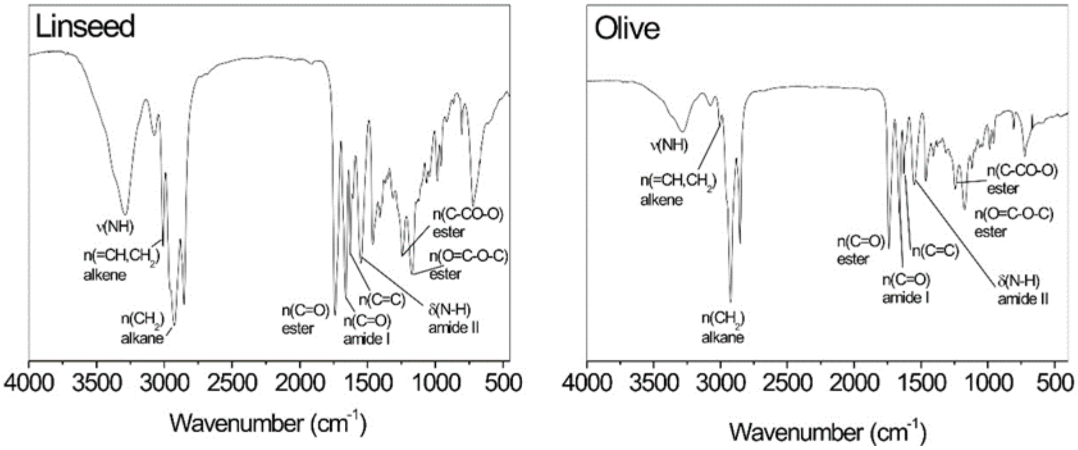


Figure 4.2. FT-IR spectra of LSM and OVM

^{1}H NMR spectra of the SFM and SBM are provided in Figure B1 in Appendix B. The molecular weight of the monomers determined using mass-spectrometry (Table 4.1), after deducing the molecular weight of a sodium atom, is in good agreement with the theoretical average molecular weight. Characteristic mass spectra of LSM and OVM are provided in Figure B2 in Appendix B. To characterize monomers in terms of degree of unsaturation, the iodine value was determined (amount of iodine in g that reacts with fatty acid chain double bonds at specified conditions) and compared to the iodine value of each oil chosen for monomer synthesis. Table 4.1 displays the obtained results, showing that iodine value for all monomers is larger than for oils, providing the presence of the additional unsaturation of the N-acryloyl fragment.

Table 4.1 also shows the density and refractive index values for plant oil-based monomers, which are slightly larger when compared to each crude plant oil. Finally, the low aqueous solubility determined by cloud point confirms the highly hydrophobic nature of the new monomers.

Table 4.1. Physico-chemical properties of plant oil-based acrylic monomers

Monomer	Iodine value (for oil), g/g	Aqueous solubility, %	Density, (for oil) g/cm^3	Molecular weight, g/mol	n_{20} (for oil)
OVM	110 (90)	$0.92\cdot10^{-3}$	0.953 (0.912)	379.3*	1.473 (1.469)
SFM	146 (128)	$1.15\cdot10^{-3}$	0.965 (0.915)	375.5$^{\#}$	1.478 (1.469)
SBM	149 (139)	$1.08\cdot10^{-3}$	0.963 (0.921)	375.3[39]	1.478 (1.474)
LSM	194 (177)	$1.10\cdot10^{-3}$	0.967 (0.93)	375.3*	1.483 (1.480)

*- determined using mass-spectrometry (spectra provided in Appendix B), # -calculated average molecular weight

4.4.2. Free Radical Polymerization of Plant Oil-Based Monomers

To establish the plant oil-based monomers' capability for free radical reactions and investigate the effect of monomer structure (unsaturation degree of fatty acid fragments) on reaction rate, homopolymerization of OVM, SBM, LSM, and SFM was carried out in solution. It is well known that the free radical polymerization rate is described by eq 4.2, showing a first order dependence of Rp on the monomer concentration and square root dependence on the initiator concentration.

$$R_{\mathrm{p}} = -\frac{d[\mathrm{M}]}{dt} = k_p\left(\frac{k_d f[\mathrm{I}]}{k_t}\right)^{1/2}[\mathrm{M}] \qquad (4.1)$$

where [M] and [I] are the monomer and initiator concentrations, respectively, f is the initiator efficiency, k_d is the rate constant of initiator decomposition, k_p is the propagation rate constant, and kt is the rate constant for termination. The dependence of R_p on $[I]^{1/2}$ is a consequence of a bimolecular termination reaction (coupling or disproportionation) between growing radicals (macroradicals). At the same time, so-called premature termination (chain transfer reactions) of a growing macroradical by transfer of hydrogen (or another atom) to it from other compound-monomer, initiator, inhibitor, etc.-might lead to a higher than 0.5 (up to 1) order of R_p on [I].[28] The first goal was to examine the kinetic features of chain radical polymerization of plant oil-based monomers in solution and to determine the R_p dependence order on [I] and [M] to validate (4.2) for new monomers. For this purpose, a polymerization reaction was carried out for four different monomer concentrations and low conversion of monomers into polymers (less than 10% in order to have [M] constant throughout this period), and the reaction rate was calculated in each experiment. Figure 4.3 shows the typical experimental kinetics data recorded for the monomer from linseed oil by changing [M] (A), as well as the dependence of calculated polymerization rate on [M] for each plant oil-based monomer in this study (B).

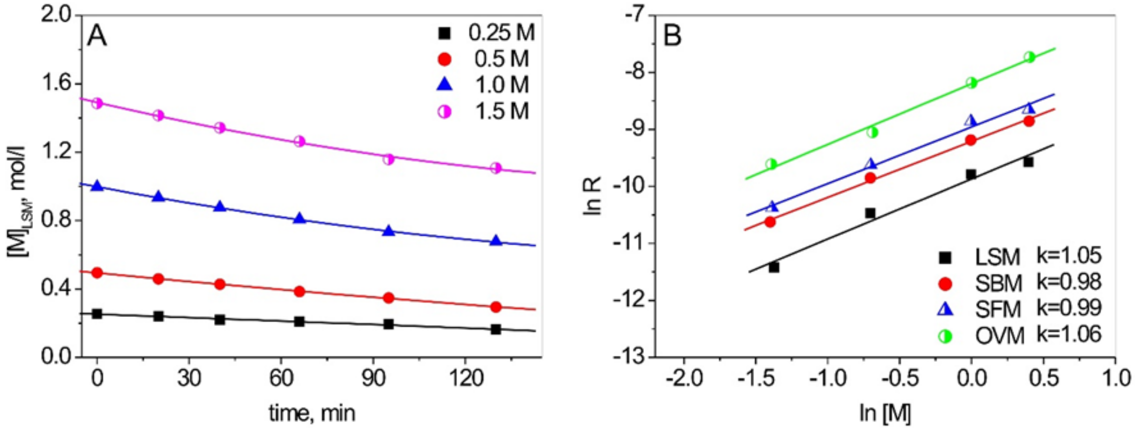


Figure 4.3. Free radical polymerization kinetics of different [LSM] initiated by 0.038 mol/L of AIBN at 75 °C (A) and polymerization rate vs monomer concentration for the plant oil-based monomers (B)

Based on the correlation coefficient (R_2) = 0.99 for all four linear regressions in Fig. 4.3B, the obtained data clearly indicate that polymerization rate is proportional to the first power of concentration for each plant oil-based monomer (the order of reaction with respect to monomer is 1). Similar kinetic data for polymerization of SBM and SFM at different concentrations can be found in Appendix B (Figure B3).

Table 4.2 summarizes the obtained results on polymerization rate and the resulting number-average molecular weight of homopolymers from plant oil-based monomers synthesized at four different temperatures ([M] = 1 mol/L, [I] = 0.038 mol/L). The data show that the rate of polymerization depends noticeably on the chemical structure of monomers and decreases as follows: OVM > SFM > SBM > LSM. For the less unsaturated OVM, the reaction proceeds faster, whereas the most unsaturated LSM polymerizes much more slowly than its counterparts. Similar trends were observed for the number-average molecular weight values of the resulting homopolymers. Hence, the number-average molecular weight of homopolymers synthesized at 75 °C decreases as follows: poly[(acryloylamino)ethyl oleate], poly(OVM) > poly(SFM) > poly[(acryloylamino)ethyl soyate], poly(SBM) > poly- [(acryloylamino)ethyl linoleate], poly(LSM), corresponding to increasing degree of unsaturation in the plant oil-based monomers (Table B1 in Appendix B).

Table 4.2. Rate of polymerization and selected number-average molecular weight and polydispersity index of the resulting homopolymers synthesized from plant oil-based monomers at different temperatures

	$R \cdot 10^5$, mol L^{-1} s^{-1} (M_n, PDI)			
T, °C	LSM	SBM	SFM	OVM
70	2.08	4.3 (14,300, 1.32)	4.0	12.2 (23,200, 1.49)
75	5.2 (11,700, 1.26)	7.9 (14,200, 1.3)	11.6 (15,100, 1.36)	26.1 (21,200, 1.37)
80	7.4	11.3 (13,600, 1.36)	15.0	45.3 (16,800, 1.43)
85	11.0	-	21.0	62.3 (17,600. 1.44)

[a] Data in the parentheses correspond to Mn (g/mol) and PDI of the obtained homopolymers.

The reason for decreasing molecular weight and lowering rate of polymerization within monomer range may be allylic inhibition, chain transfer reaction to the fatty acid double bonds. To experimentally confirm this assumption, more studies on polymerization kinetics, including determining monomer chain transfer constants, were carried out. To further elaborate the kinetic features of homopolymerization in relation to plant oil-based monomer structure, the reaction rate and order with respect to the initiator were determined in the polymerization of 1 mol/L of monomer initiated by different concentrations of the initiator AIBN at 75 °C. Fig. 4.4 shows the typical experimental kinetics data recorded for the 1 mol/L of LSM with varying concentrations of AIBN (Fig. 4.4A) at 75 °C, as well as the dependence of the reaction rate on initiator concentration for each plant oil-based monomer (Fig. 4.4B).

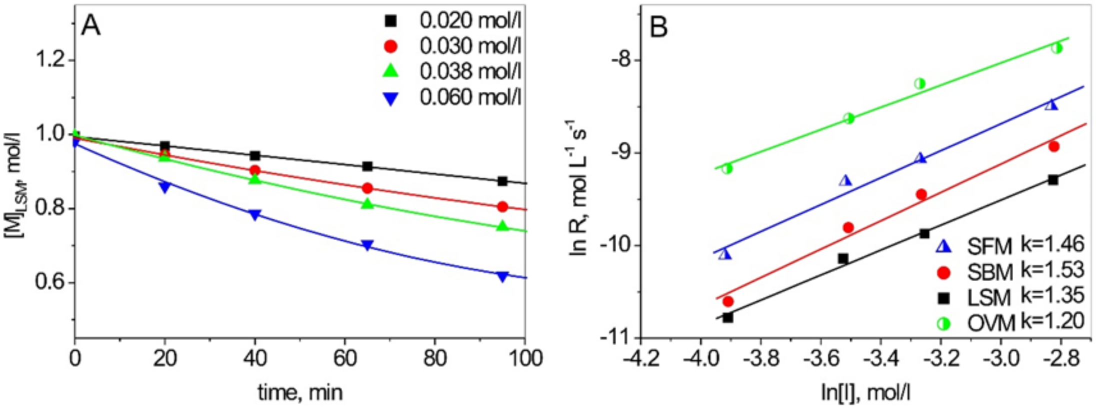
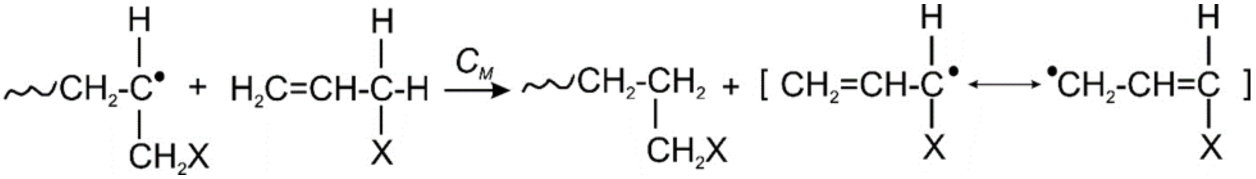


Figure 4.4. Free radical polymerization kinetics of LSM (1 mol/L) at different concentrations of AIBN at 75 ^{o}C (A) and polymerization rate vs. initiator concentration for the plant oil-based monomers (B)

It is evident that for each polymerization of a plant oil-based monomer showing a first-order rate dependence on [M] (Fig. 4.3B), we observed a reaction order of 1.2−1.5 with respect to the initiator, indicating some deviations from the normal kinetics of polymerization of vinyl monomers (Fig. 4.4B). It can be seen that the initiator reaction order increases with an increasing degree of monomer unsaturation. In fact, the effects of unsaturation in fatty monomers on the susceptibility to undergoing chain transfer reactions during their polymerization has been discussed in the literature.[27,29–32] However, there are no detailed reports on the quantitative determination of the retardation effect of isolated fatty double bonds in monomers or on how this effect impacts polymer structure and properties.

To evaluate the extent of the effect of chain transfer on polymerization in this work, the established Mayo method was employed[28,33] to determine the values of C_M (ratio of the chain transfer and propagation rate constants) in the polymerization of plant-oil based monomers at 75 °C. In this method, the inverse value of the number-average degree of polymerization is plotted against the polymerization rate, and C_M is determined by the intercept or by extrapolating to zero rate.[34] The obtained values of C_M clearly depend on monomer structure (Fig. 4.5A) as follows: 0.033 (most unsaturated LSM) > 0.026 (SBM) > 0.023 (SFM) > 0.015 (least unsaturated OVM) with respect to decreasing number of C−H groups in the α-position of the fatty acid double bonds (Scheme 4.1).

In the literature, such a C−H group is described as an “allylic C−H”[35] in which hydrogen easily abstracts and can take part in chain transfer reactions, thus terminating the kinetic chain (premature termination). Although the propagating radical might be very reactive, once the chain is transferred to this allylic C−H, the newly formed radical becomes more stable due to resonance stabilization and does not readily initiate new chains.[28,35] The allylic transfer is often also referred to as degradative chain transfer of free radical polymerization.



Scheme 4.1. Allylic transfer mechanism in free radical polymerization

The C_M values of plant oil-based monomers experimentally obtained in our study are well-supported by the data on C_M reported for one of the most typical allylic monomers, allyl acetate (0.07).[36] The obtained results indicate that allylic termination occurs by interaction between rowing macroradicals and unsaturated fatty fragments of plant oil-based monomers during polymerization.

Scheme B2 in Appendix B shows a schematic of allylic radical formation for SBM and OVM. It is obvious that larger C_M and more unsaturated monomers result in lower molecular weight of the resulting macromolecules. No effect of reaction temperature on a C_M of plant oil-based vinyl monomers was observed in this work, indicated by SBM polymerization at three different temperatures (70−80 °C) (Fig. 4.5B). The observed deviations from polymerization kinetics can be explained by two simultaneous reactions (chain propagation and transfer) occurring with reactive sites within the same vinyl monomer molecules, as reported in the literature.[37]

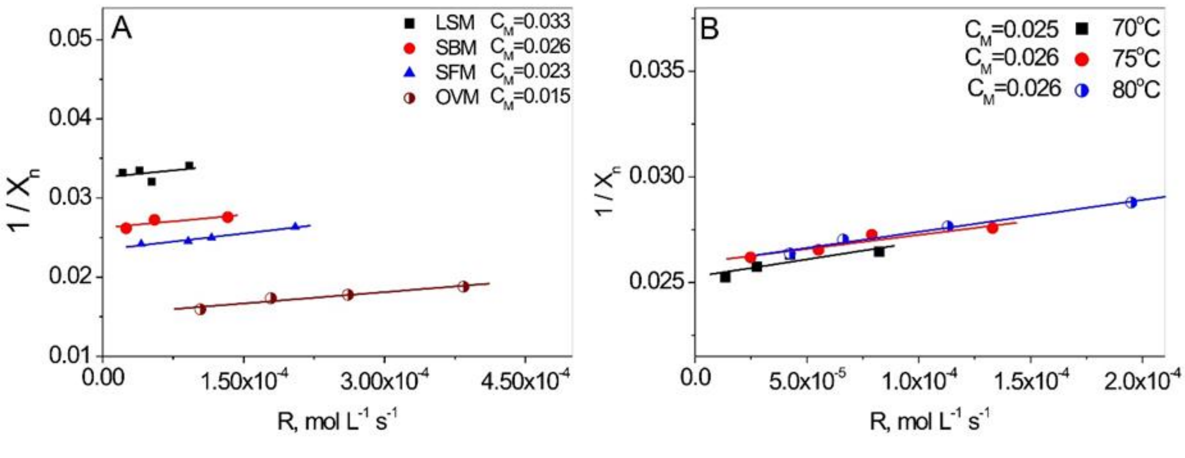


Figure 4.5. Chain transfer constant on monomer (C_M) in homopolymerization of plant oil-based monomers determined using the Mayo method (**A**) and dependence of C_M on temperature for SBM (**B**)

Chain propagation is a monomer addition to the growing macroradical, followed by bimolecular termination of macroradicals and formation of the resulting polymer. On the other hand, Chen and Bufkin demonstrated that isolated double bonds in fatty (linolenyl, linoleyl, and oleyl) acrylates retard propagation by chain transfer reaction,[29,30] whereas Moreno et al. observed similar retardation due to the formation of stable macroradicals in the polymerization of methacrylated linoleic acid.[31] It is seen from the obtained results in this study that chain propagation and effective chain transfer to monomers coexist during the polymerization of plant oil-based SBM, LSM, OVM, and SFM. The transfer occurs due to the abstraction of allylic hydrogen, and it yields macroradicals by not readily initiating new chains (allylic chain termination).[36] In this regard, reaction order values with respect to the initiator are determined by the concentrations of macroradicals involved in the chain propagation and transfer reactions (the kinetic reasoning for the higher initiator order values in this work is provided in Appendix B).[38]

To quantify the extent of monomer chain transfer in plant oil-based monomer polymerization and estimate how this reaction contributes to the resulting macromolecular composition (i.e., the fraction of unsaturated fatty acid fragments involved in chain transfer), ^{1}H NMR spectra of the poly(LSM) and poly(OVM) (Fig. 4.6) were compared to the respective monomer spectra (Fig. 4.1).

Both polymers' spectra show the absence of the vinyl double bond of the acrylic functional group that confirms the formation of macro chains from the LSM and OVM monomer links. The unsaturated fatty acid fragments have two reactive sites: (i) the alkyl carbon−carbon double bonds and (ii) the allylic hydrogen atoms, both of which can react during the free radical polymerization of the plant oil-based monomers. In order to determine whether the fatty acid double bonds undergo addition to growing radicals and whether there is the abstraction of the allylic hydrogen atoms by growing radicals (i.e., chain transfer), the peak of the methyl group protons of the fatty acid chain (protons M in the monomers in Fig. 4.1 and protons I in the homopolymers in Fig. 4.6) was used as a reference.

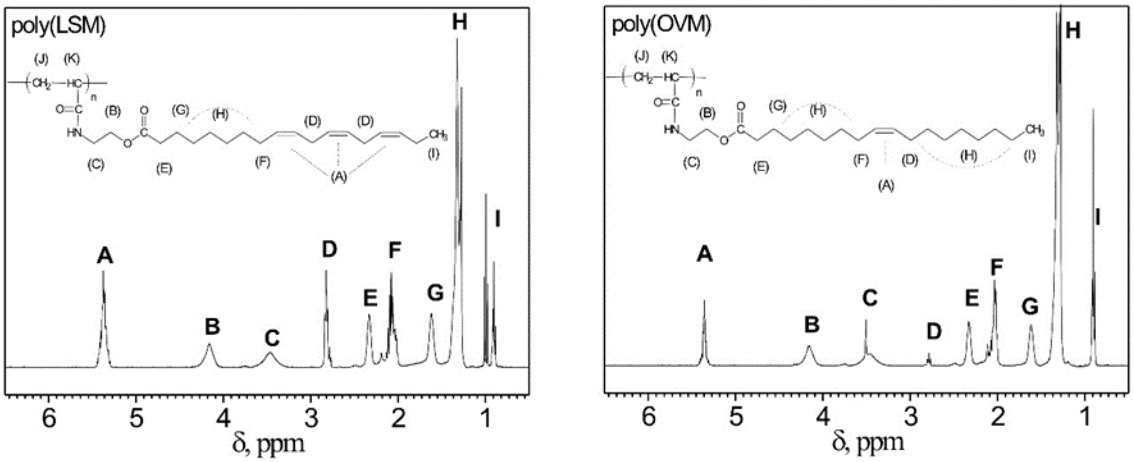


Figure 4.6. ^{1}H NMR spectrum of poly(LSM), and poly(OVM) polymers

In comparison with the monomers, the number of protons E (5.37−5.38 ppm, Fig. 4.1) of the alkyl carbon−carbon double bonds changed little after the polymerization (3.65 H in poly(LSM) vs. 3.67 H in LSM and 1.97 H in poly(OVM) vs. 1.98 H in OVM). These data clearly show that most fatty acid double bonds of the plant oil-based monomers remain intact during polymerization. On the contrary, the number of the allylic hydrogen atoms (protons H at 2.8 ppm, Fig. 4.1) decreased by 7.3% for LSM and by 6.7% for OVM (2.25 H in poly(LSM) vs. 2.44 H in LSM and 0.28 H in poly(OVM) vs. 0.30 H in OVM). For SBM and SFM, these figures are 12.6% and 8.8%, respectively. FT-IR spectra of poly(SBM) and poly(LSM) are shown in Appendix B (Figure B5). Hence, it could be concluded that hydrogen atoms of allylic C−H bonds in the fatty acid fragments are indeed involved in the chain transfer process during polymerization.

The ^{1}H NMR study shows that the fraction of the reacting allylic atoms does not vary significantly in the chosen monomer range; thus, the effect of chain transfer on monomers is rather determined by the initial degree of unsaturation (plant oil chemical composition). Glass transition temperature was measured for selected homopolymers from sunflower and soybean oil using dynamic scanning calorimetry (DSC). The obtained values of Tg = 4.2 °C for poly(SFM) (number-average molecular weight 18 850) and Tg = −6 °C for poly(SBM), (15 100) show that the presence of biobased fragments in copolymers from new plant oil-based monomers and conventional vinyl counterparts might considerably change the intermolecular interactions of macromolecules. The latter fact will obviously lead to changing segmental mobility, thus providing a broader range of physicochemical properties, determined in particular by varying macromolecular flexibility.

4.5. Conclusions

A recently developed method was used for one-step synthesis of vinyl monomers by direct transesterification of sunflower, linseed, soybean, and olive oil triglycerides with N-(hydroxyethyl)acrylamide. ^{1}H NMR spectroscopy, FT-IR spectroscopy, and mass spectrometry were used to confirm the chemical structure of the monomers in terms of the degree of unsaturation, aqueous solubility, density, refractive index, and other physicochemical properties. The feasibility of plant oil-based monomers undergoing chain addition polymerization was confirmed by studying polymerization kinetics. As a criterion to compare the kinetics data, the degree of unsaturation in plant oil fatty acids was used. The number-average molecular weight of plant oil-based homopolymers synthesized in toluene in the presence of AIBN at 75 °C varies at 11 000−25 000 and decreases as follows: poly(OVM) > poly(SFM) > poly(SBM) > poly(LSM), corresponding to the increasing degree of unsaturation in the monomers. Due to the abstraction of allylic hydrogen in fatty acids fragments and yielding macroradicals not readily initiating new chains (allylic termination), chain propagation coexists with effective chain transfer during polymerization. The obtained values of C_M (ratio of chain transfer and propagation rate constants) clearly depend on monomer structure as follows: C_M(LSM) > C_M(SBM) > C_M(SFM) > C_M(OVM) ^{1}H NMR spectroscopy shows that the fraction of the reacting allylic atoms does not vary significantly among the synthesized monomers (7−12%); thus, the susceptibility of new monomers to chain transfer reactions is determined entirely by plant oil composition (degree of unsaturation). Glass transition temperature measurements for selected plant oil-based homopolymers [Tg = 4.2 °C for poly(SFM), Tg = −6 °C for poly(SBM)] indicate that varying biobased content in copolymers synthesized from new plant oil-based monomers and their vinyl counterparts might considerably change the intermolecular interactions of macromolecules and physicochemical properties, determined in particular by varying macromolecular flexibility.

4.6. References

[1] Belgacem, M.N.; Gandini, A. Monomers, Polymers and Composites from Renewable Resources, **2008,** Elsevier, Amsterdam, 560 p.

[2] Lu, Y.; Larock, R.C. Novel Polymeric Materials from Vegetable Oils and Vinyl Monomers: Preparation, Properties and Applications *Chem.Sus.Chem.,* **2009,** *2*, 136-147.

[3] Gallezot, P. Conversion of biomass to selected chemical products *Chem.Soc.Rev*., **2012**, *41*, 1538-1558.

[4] Lligadas, G.; Ronda, J.C.; Galia, M.; Cadiz, V. Renewable polymeric materials from vegetable oils: a perspective *Mat. Today*, **2013**, *16(9).*337 - 343.

[5] Yao, K.; Tang, C. Controlled polymerization of next-generation renewable monomers and beyond *Macromolecules,* **2013**, *46*, 1689-1712.

[6] US Biobased Products: Market Potential and Projections Through 2025: Office of the Chief Economist, Office of Energy Policy and New Uses, USDA, **2008**, 294 p.

[7] Anastas, P.; Eghbali, N. Green chemistry: principles and practice *Chem Soc Rev*, **2010,** *39*, 301-312.

[8] Gunstone, F.D. The Lipid Handbook, **2004**, Taylor & Francis LTF, UK. 1472 p.

[9] Verhe, R.G. Industrial products from lipids and proteins, in *Renewable Bioresources: Scope and Modification for Non-Food Applications* **2004**, Stevens C.V.; Verhe R.G., John Wiley & Sons, Ltd , Chichester, 328 p.

[10] Guner, F.S.; Yagci, Y.; Erciyes, A.T. Polymers from triglyceride oils *Prog.Polym.Sci.,* **2006**, *31*, 633-670.

[11] Sharma, V.; Kundu, P.P. Addition Polymers from Natural Oils-A Review *Prog. Polym. Sci.,* **2006**, *31,* 983-1008.

[12] Wool, R.P.; Sun, X.S. Bio-Based Polymers and Composites, **2005**, Elsevier, Amsterdam, 620 p.

[13] Gunstone, F. Fatty acid and lipid chemistry, **1996**, Blackie Academic & Professional, New York, 252 p.

[14] Borges, M.E.; Diaz I. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review *Renewable Sustainable Energy Rev.,* **2012**, *16,* 2839-2849.

[15] Bailey, A.E. Bailey's Industrial Oil and Fat Products, **1996**, Wiley, New York, 560 p.

[16] Johnson, R.W.; Fritz, E.E. Fatty Acids in Industry, **1989**, Marcel Dekker, New York, 667 p.

[17] Pan, X.; Sengupta, P.; Webster, D.C. High Biobased Content Epoxy–Anhydride Thermosets from Epoxidized Sucrose Esters of Fatty Acids *Biomacromolecules,* **2011**, *12*, 2416–2428.

[18] Lligadas, G.; Ronda, J.C.; Galia, M.; Cádiz, V. Plant Oils as Platform Chemicals for Polyurethane Synthesis: Current State-of-the-Art *Biomacromolecules,* **2010**, *11*, 2825–2835.

[19] Wang, Z.; Zhang, X.; Wang, R.; Kang, H.; Qiao, B.; Ma, J.; Zhang L.; Wang, H. Synthesis and Characterization of Novel Soybean-Oil-Based Elastomers with Favorable Processability and Tunable Properties *Macromolecules,* **2012**, *45*, 9010–9019.

[20] Türünç, O.; Meier, M.A. The thiol-ene (click) reaction for the synthesis of plant oil derived polymers *Eur. J. Lipid Sci. Technol.,* **2013**, *115*, 41–54.

[21] Raquez, J.M.; Deléglise, M.; Lacrampe, M.F.; Krawczak, P. Thermosetting (bio)materials derived from renewable resources: A critical review *Prog. Polym. Sci.,* **2010**, *35*, 487–509.

[22] Yuan, L.; Wang, Z.; Trenor N.M.; Tang, C. Robust Amidation Transformation of Plant Oils into Fatty Derivatives for Sustainable Monomers and Polymers *Macromolecules,* **2015**, *48,* 1320-1328.

[23] Yuan, L.; Wang, Z.; Ternor, N.M., Tang, C. Amidation of triglycerides by amino alcohols and their impact on plant oil-derived polymers *Polym.Chem.,* **2016,** *7,* 2790-2798.

[24] Tarnavchyk, I.; Popadyuk, A.; Popadyuk, N.; Voronov, A. Synthesis and Free Radical Copolymerization of a Vinyl Monomer from Soybean Oil *ACS Sustainable Chem. Eng.*, **2015**, *3*, 1618–1622.

[25] Alfrey T. Copolymerization, **1964**, Interscience Publisher, University of Michigan. 939 p.

[26] Havelka, K.O., McCormick C.L. Specialty Monomers and Polymers: Synthesis, Properties, and Applications, **2000,** ACS Symposium Series (Book 755) 1st Edition, 246 p.

[27] Harrison, S.A.; Wheeler, D.H. The Polymerization of Vinyl and Allyl Esters of Fatty Acids *J.Am.Chem.Soc.*, **1951**, *73*, 839-842.

[28] Odian, G. Principles of Polymerization, 4th Edition, **2004**, Wiley, New York, 812 p.

[29] Chen, F.B.; Bufkin, G. Crosslinkable emulsion polymers by autoxidation. II *J.Appl.Pol. Sci.*, **1985**, *30*, 4551-4570.

[30] Chen, F.B.; Bufkin, G. Crosslinkable Emulsion Polymers by Autoxidation. I. Reactivity Ratios *J.Appl.Pol.Sci.*, **1985**, *30*, 4571-4582.

[31] Moreno, M.; Miranda, J.I.; Goikoetxea, M.; Barandiran, M. Sustainable polymer latexes based on linoleic acid for coatings applications *Prog.Org.Coat.*, **2014**, *77*, 1709-1714.

[32] Mayo, F.R.; Gould, C.W. Copolymerization of Methyl Esters of Unsaturated C_{18} Fatty Acids *J.Am.Oil.Chem.Soc.*, **1964**, *41*, 25 - 29.

[33] Brandrup, J.; Immergut, E.H. Eds. Polymer Handbook; 3rd ed., **1989** Wiley-Interscience: New York, 1217 p.

[34] Kukuli, D.; Davis, T.P.; Gilbert, R.G. Chain Transfer to Monomer in the Free-Radical Polymerizations of Methyl Methacrylate, Styrene, and α-Methylstyrene *Macromolecules*, **1998,** *31*, 994-999.

[35] Chanda, M. Introduction to Polymer Science and Chemistry. A Problem Solving Approach, **2006**, Taylor & Francis, CRC Press, Boca Raton, FL, 640 p.

[36] Bagdasar'yan, Kh.S. Theory of Free Radical Polymerization, London, Humphrey LTD, **1968**, 317 p.

[37] Bresler, S.Ye.; Yerusalimsky, *B*.L. Macromolecule Chemistry and Physics, **1965**, Nauka, Moscow, 508 p.

[38] Emanuel, N.M., Knorre, D.G. Chemical Kinetics: Homogeneous Reactions, IPCT, 2nd Edition, **1974**, 460 p.

CHAPTER 5. FREE-RADICAL COPOLYMERIZATION BEHAVIOR OF PLANT OIL-BASED VINYL MONOMERS AND THEIR FEASIBILITY IN LATEX SYNTHESIS[1]

5.1. Abstract

Vinyl monomers from soybean, sunflower, linseed, and olive oils were copolymerized with styrene (St), methyl methacrylate (MMA), and vinyl acetate (VAc) to determine the reactivity of biobased monomers in radical copolymerization, as well as their feasibility in emulsion processes for the synthesis of biobased latexes. Radical copolymerization of plant-oil-based monomers is described with the classical Mayo−Lewis equation. Using emulsion (or miniemulsion) polymerization with MMA or VAc, stable aqueous polymer dispersions with latex particles measuring 80−160 nm and containing 3−35 wt. % of biobased monomer units were successfully synthesized. The number-average molecular weight of the latex copolymers (20 000−150 000) decreases by increasing the degree of unsaturation in monomers and their content in the reaction feed. The presence of plant-oil-based fragments changes the Tg of resulting copolymers from 105 to 79 °C in copolymerization with MMA and from 30 to 11 °C in copolymerization with Vac. As a result, biobased units provide considerable flexibility (elongation at break of about 250 %) and improve the toughness of the normally rigid and brittle poly(MMA). Even a small amount (2−5%) of biobased fragments incorporated into the structure

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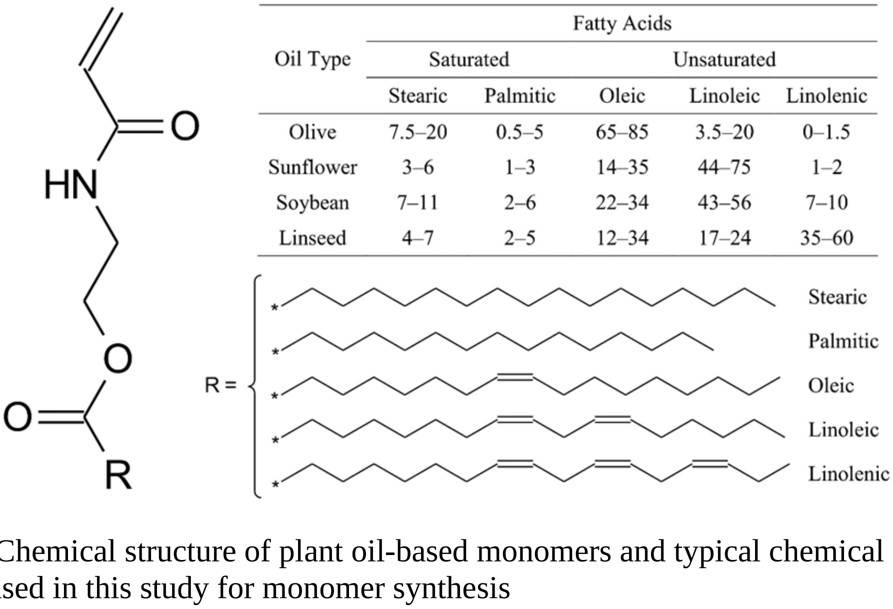
[1] The material in this chapter was co-authored by Zoriana Demchuk, Oleh Shevchuk, Ihor Tarnavchyk, Vasylyna Kirianchuk, Maria Lorenson, Ananiy Kohut, Stanislav Voronov, and Andriy Voronov. Zoriana Demchuk had the primary responsibilities of evaluation the copolymerization behavior of plant oil-based monomers in free radical polymerization. The copolymerization parameters including Q, e values and reactivity ratios were evaluated by Zoriana Demchuk with help of Oleh Shevchuk and Vasylyna Kirianchuk. Zoriana Demchuk with help of SURE 2016 student Maria Lorenson were performing initial studies in evaluation of feasibility of plant oil-based mnomers in the sunthesis of biobased latexes with methyl methacrylate and vinyl aceate. Additionally, Zoriana Demchuk was characterizing the performance of latex films in terms of mechanical properties and evalution of the effect of plant oil-based monomer incorporation of toughness, flexibility and modulus of latex materals. Andriy Voronov and Ananiy Kohut were helping to characterize the copolymerizability of biobased monomers and the relation of monomer incorporation on mechanical properties of latex films. Zorian Demchuk was involved in drafting and revision of all versions of manuscript. Published article can be found at https://doi.org/10.1021/acsomega.6b00308.

of poly(VAc) significantly improves water resistance and provides hydrophobicity to the resulting polymer latex films. The obtained results clearly indicate that the vinyl monomers from plant oils can be considered as good candidates for the internal plasticization of polymeric materials through reducing intermolecular interactions in copolymers.

5.2. Introduction

The compositions of most plant oils, including oils from annual crops, consist of a wide range of triglycerides (esters of glycerol and three long-chain fatty acids), varying across different plant species and growth conditions.[1] Plant oils represent good renewable sources for oleochemical industrial products, particularly biobased polymers, because their structures are similar to those of petroleum-based long-chained hydrocarbons, with the main difference being that plant oils are much more unsaturated.[1−6] These structural differences provide additional opportunities for chemical modifications of plant-oil-based macromolecules and the possibility of developing new types of biobased polymers. To obtain cross-linked polymers from plant oils, an oxidative mechanism is typically used as the polymerization method for triglycerides with different types of unsaturated fatty acid chains having one or several double bonds.[7−10] Cross-linked macromolecules have also been developed by modification of triglycerides with vinyl monomers (e.g., styrenation of unsaturated fatty acid chains) in the presence of radical initiators (benzoyl peroxide, di-tert-butyl peroxide).[11,12] To prepare thermosetting polyesters, polyurethanes, polyamides, acrylic resins, and epoxy resins from triglyceride oils, various polycondensation strategies can be used, including polycondensation of diacids, diols, diisocyanates, and epoxy resins via epoxidation of unsaturated fatty acid chains of triglyceride oils.[13] Coatings based on water-soluble alkyd resins prepared from maleinized triglyceride oils have been described by Solomon[14] and reported in several papers.[15−17] Free-radical chain copolymerization is an efficient method for the synthesis of an almost unlimited number of different macromolecules by variation in the nature or/and amount of two or more monomers, as well as for tailoring the resulting macromolecules with specifically desired properties.[18] In particular, copolymerization of the second monomer into the polymer structure can plasticize the resulting material by lowering the intermolecular interactions between the chains, thus softening the polymers and decreasing the glass-transition temperature, or the modulus (internal plasticization).[19,20] Long nonpolar fragments of bulky comonomers (C_{16}–C_{18}) included in the macromolecules can be considered good candidates for the internal plasticization of polymeric materials. It should be noted that the latter approach is more efficient than external plasticization (a method that provides plasticity through physical mixing of polymers with compounds of low vapor pressure) or mixtures of two or more polymers.[21] Recently, we reported on the synthesis and free-radical polymerization behavior of a vinyl monomer from soybean oil triglycerides,[22] as well as homopolymerization of new monomers based on sunflower, linseed, and olive oils[23] (Scheme 5.1).



Oil Type	Fatty Acids				
	Saturated		Unsaturated		
	Stearic	Palmitic	Oleic	Linoleic	Linolenic
Olive	7.5–20	0.5–5	65–85	3.5–20	0–1.5
Sunflower	3–6	1–3	14–35	44–75	1–2
Soybean	7–11	2–6	22–34	43–56	7–10
Linseed	4–7	2–5	12–34	17–24	35–60

Scheme 5.1. Chemical structure of plant oil-based monomers and typical chemical compositions of plant oils used in this study for monomer synthesis

Conventional radical chain polymerization of these monomers yields linear macromolecules, whereas the double bonds of the fatty acid chains remain unaffected and thus capable of post-polymerization oxidative reactions to modify the polymer if needed.

In radical copolymerization, newly developed monomers with long, nonpolar C_{18} fragments of differing unsaturation can act as a specialty monomer (polymer modifier), even at their low content (2−5 wt. %), to provide unique properties and performance (flexibility, toughness, water resistance, adhesion, etc.) of resulting polymeric materials in various industrial applications. Particularly, water resistance of coatings and their mechanical properties can be improved by internal plasticization provided by copolymerizing the plant-oil-based monomers. Emulsion polymerization is a predominant process widely employed in industry for commercial radical copolymerization and for producing waterborne polymeric materials (latexes in particular). Because of the highly hydrophobic nature of triglyceride molecules, using plant oils in this process has been challenging. In the synthesis of most available copolymers from plant oils for making industrial coatings, radical copolymerization, including the emulsion copolymerization technique, is not currently employed due to the absence of the respective monomers.[24−30]

Recently, Tang et al. developed a new strategy for synthesizing fatty monomers from high oleic soybean oil (HOSO) and demonstrated their ability to yield thermoplastic polymers in free-radical polymerization.[31] As a result, macromolecules with a wide range of glass-transition temperatures and properties were synthesized from a library of HOSO-based (meth)acrylate monomers.[32] Polymers exhibiting T_g in a range of more than 100 °C difference and demonstrating physical properties of materials with viscoelastic and thermoplastic behaviors were obtained. Vilela et al. employed transition-metal-catalyzed transvinylation to obtain vinyl monomers from oleic and linoleic acids and vinyl acetate (VAc).[33] Variation of resulting fatty acid vinyl ester monomers yielded copolymers with VAc in a range of Mn = 1000−3000 and glass-transition temperatures between −5 and 16 °C. Inspired by the feasibility of recently synthesized new vinyl monomers from sunflower (SFM), linseed (LSM), soybean (SBM), and olive (OVM) oils in chain radical polymerization, we report about their copolymerization behavior in reactions with conventional vinyl comonomers. The ability to control the content of plant-oil-based monomer units in the resulting macromolecules using the classical Mayo−Lewis equation was investigated. Another objective of this study was to synthesize latexes from new monomers and evaluate how the fraction of the plant-oil-based monomer units in the resulting macromolecules affects the latex properties, glass-transition temperature (T_g), and mechanical performance of films and coatings made from the obtained biobased latexes, as well as polymer latex film hydrophobicity.

5.3. Experimental Section

5.3.1. Materials

Soybean oil (Crisco; The J.M. Smucker Company, Orville, OH), sunflower oil (Kirlangic; Turkey), olive oil (Bertolli; Houston, TX), linseed oil (Sunnyside Corp., Wheeling, IL), and N-(hydroxyethyl)acrylamide (HEAAm; TCI America) were used as received. 2,2′-Azobis(2-methyl propionitrile) (AIBN; Sigma-Aldrich, St. Louis, MO) was purified with recrystallization from methanol. St (Sigma-Aldrich, St. Louis, MO), MMA (TCI America), and Vac (TCI America) monomers were distilled under a vacuum to remove the inhibitor and stored in a refrigerator. Toluene (Sigma-Aldrich, St. Louis, MO) was distilled before use. Other solvents and chemicals, analytical grade or better, were used as received. Deionized water was used for purification purposes (Milli Q, 18 MΩ).

5.3.2. Plant Oil-Based Acrylic Monomer Synthesis and Characterization

Plant-oil-based acrylic monomers were synthesized from soybean, linseed, sunflower, olive oils, and N-(hydroxyethyl)acrylamide using previously reported methods. [22,23] The resulting monomers contain one acrylic double bond linked to one fatty chain, which varied between fully saturated, mono-, and polyunsaturated, depending on plant-oil composition (Scheme 5.2). To confirm the chemical structure of the synthesized monomers, ^{1}H NMR spectra were recorded on an AVANCE III HDTM 400 high-performance digital NMR spectrometer (Bruker, Billerica, MA) using $CDCl_3$ as a solvent (Figure C3 in Appendix C). The electrospray ionization high-resolution mass spectrum of the monomers was obtained using a Bruker Daltonics BioTOF mass spectrometer (Figure C4 in Appendix C).

$CH_2{=}CH{-}C(O){-}NH{-}CH_2CH_2{-}O{-}C(O){-}(CH_2)_6{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}(CH_2)_3CH_3$

Scheme 5.2. Selected monomer structure of (acryloylamino)ethyl linoleate.

5.3.3. Free-Radical Copolymerization of Plant Oil-Based Monomers with St/Vac

Each plant-oil-based monomer (0.4−2 g; 0.1−0.9 mole part), vinyl monomer (0.1−0.5 g; St or VAc; 0.9−0.1 mole part, total monomer concentration 1−2 M), and AIBN (0.04 g 0.038 M) were dissolved in 5 mL of toluene, and the mixture was stirred. The reaction mixture was purged with argon at room temperature for 30 min. Copolymerization was carried out under an argon blanket at 60 °C for 2 h until a total monomer conversion of 10−15% was reached. Samples (0.6−0.7 g) of the reaction mixture were taken to monitor the progress of the copolymerization reaction using a gravimetric method after precipitation of the copolymer using a large excess of methanol or a methanol/water mixture. The resulting copolymers were purified by multiple precipitations from methanol. The purified polymer was dried under a nitrogen blanket at room temperature until it reached a constant weight. The resulting copolymers containing various amounts of plant-oil-based fragments are highly soluble in dichloromethane, chloroform, ethyl acetate, heptane, toluene, dioxane, and tetrahydrofuran (THF) and less soluble in acetone, dimethylformamide, methanol, and water.

5.3.4. Plant Oil-Based Copolymer Characterization

To determine the composition of copolymers from each plant-oil based monomer and St or VAc, ^{1}H NMR spectra were recorded as described above. The average molecular weight of the copolymers was determined by gel permeation chromatography (GPC) using a Waters Corporation modular chromatograph consisting of a Waters 515 HPLC pump, a Waters 2410 Refractive Index Detector, and a set of two 10 μm PL-gel mixed-B columns; the column temperature was set at 40 °C. THF was used as the carrier solvent.

5.3.5. Synthesis of Plant Oil-Based Latexes in Miniemulsion

To synthesize latexes from each plant-oil-based monomer and MMA or VAc in miniemulsion, two oil phases were prepared. Two separate miniemulsions of MMA (or Vac) and plant oil-based monomers were used instead of emulsifying the monomer mixture to minimize possible chain transfer reactions on the biobased monomer during copolymerization[23] to increase total monomer conversion and, thus, copolymer molecular weight. For Oil Phase 1, a different amount of each plant-oil-based monomer (0.75−6 g) was dissolved in 1-octanol (weight ratio 2:1). Oil Phase 2 was prepared by mixing a different amount of VAc (or MMA) (9−14 g), 1.5 wt. % of hexadecane (0.13−0.21 g) (based on VAc/MMA weight) to prevent Ostwald ripening, and 1.5 wt. % of initiator AIBN (0.2−0.3 g) (based on monomer weight). For the aqueous phase, 5 wt. % sodium dodecyl sulfate (SDS, 0.75 g) (emulsifier) was dissolved in water. For pre-emulsification, Oil Phase 1 and Oil Phase 2 were added dropwise to the aqueous phase, divided into two parts, and homogenized using a magnetic stirrer for 45 min at 1200 r.p.m. Two miniemulsions were prepared by ultrasonication of the pre-emulsified mixtures for 180 s at 90%

amplitude (digital sonicator 500 Watt, 1/2″ tip, 20 kHz; Q-Sonica, Newtown, CN) at room temperature. VAc- (or MMA)-containing miniemulsion was purged with nitrogen and heated to 60 °C at 350 r.p.m. The miniemulsion containing plant-oil monomer was slowly added to the other miniemulsion and polymerized for 20 h under stirring. The plant-oil-monomer content varied between 10 and 40 wt. % in copolymerization with MMA and between 5 and 10 wt. % in copolymerization with VAc.

By varying the weight ratio between the oil and aqueous phase (25:75, 30:70, and 40:60), a series of biobased latexes with varying biobased contents were successfully prepared. As an example, for the synthesis of latex from a soybean-oil based monomer and MMA (40:60 wt. % ratio, solid content 30%), two oil phases were prepared. For Oil Phase 1, 6 g (0.016 mol) of soybean-oil-based monomer was dissolved in 3 g of 1-octanol (weight ratio 2:1). Oil Phase 2 was prepared by mixing 9 g (0.09 mol) of MMA, 0.13 g of hexadecane (1.5 wt. % based on MMA weight) to prevent Ostwald ripening, and 1.5 wt % of initiator AIBN (0.225 g, 0.035 M) (based on monomer weight). For the aqueous phase, 5 wt % SDS (0.75 g) (emulsifier) was dissolved in 35 mL of water.

5.3.6. Synthesis of Plant Oil-Based Latexes Using Emulsion Polymerization with Vac

A 250 mL reactor equipped with a mechanical stirrer, reflux condenser, nitrogen purge, and feed tubes was filled with 83 g of deionized water, 4.83 g of a 65% aqueous solution of the commercial nonionic surfactant Triton 405 (highly ethoxylated fatty alcohol), 3.25 g of a 20 wt. % aqueous solution of SDS, 1.66 g of a 30 wt. % aqueous solution of sodium vinyl sulfonate, and 0.19 g of sodium acetate. The aqueous phase was heated up to 65 °C while slowly adding 5 g of VAc. When the temperature reached 65 °C, 1.58 g of a 6.2 wt. % aqueous solution of ammonium persulfate (initiator) was added, and the temperature was raised to 70 °C. At this point, either 15, 45, or 75 g of VAc and 4.58 g of a 3.3 wt. % ammonium persulfate aqueous solution were added to the reaction mixture over 240 min, and the temperature was raised to 75 °C. When VAc conversion reached 15, 50, or 75%, a mixture comprising 5 g of plant-oil-based monomer and 75, 45, or 15 g of VAc, respectively, was added. Subsequently, 1 g of a 9% ammonium persulfate aqueous solution was added, and the temperature was raised to 80 °C and maintained for 60 min.

5.3.7. Characterization of Plant Oil-Based Latexes

The solid content of the synthesized plant-oil-based latexes was determined gravimetrically after drying the samples at 110 °C. The size distribution of latex particles was measured using a Zetasizer Nano-ZS90 (Malvern, Worcestershire, U.K.) at a single scattering angle of 90° and a temperature of 25 °C (for measurement, 50 μL drop of each latex was placed in 5 mL of water). For each latex sample, copolymer composition and average molecular weight were determined using ^{1}H NMR spectroscopy and GPC, as described above.

The morphology of latex particles was observed on a tungsten filament 100 kV transmission electron microscope (TEM) JEOL JEM-100CX II, (JEOL, Peabody, MA). For the TEM measurements, a drop of latex dispersion diluted with deionized water was placed onto a copper mesh covered with a thin carbon film. The samples were characterized after drying.

The glass-transition temperature of the resulting latexes was determined via modulated DSC using a TA Instruments Q1000 calorimeter. Dry nitrogen was purged through the sample at a flow rate of 50 mL/min. The samples were subjected to an underlying heating rate of 5−10 °C/min.

Latex films were prepared using a drawdown bar of 6 mm in thickness, which was cleaned by acetone before the application of steel substrate QD36 and after drying the films at

105 °C for 2 h. The dynamic mechanical behavior of the latex films was determined using a dynamic mechanical analyzer (TA Instruments Q800) with tensile mode and a heating rate of 5 °C/min. Samples of films with a typical size of 13 mm × 5 mm (length × width) were used. The mechanical properties of the latex films were determined using an Instron testing machine 2710-004 with a crosshead speed of 5 mm/min, a maximal load of 500 N, and a temperature range of 0−100 °C. Rectangle samples with a size of about 25 mm × 5 mm (length × width) were used. At least five replicates of each latex sample were used to obtain an average value.

To determine the surface energy of latex films with varying biobased contents, water and diiodomethane contact angle measurements were carried out using a contact angle/surface tension analyzer (FTA 125) and the static sessile drop (50 μL) method. An average value of at least five measurements on each film was taken. Surface energy, λS, and its components, λS_d, λS_h, were estimated using Owens and Wendt expression for modified Young's equation.[42] For selected latex films from copolymers of VAc and plant oil-based monomers, water resistance (using ASTM D5402-15) was determined.

5.4. Results and Discussion

5.4.1. Radical Copolymerization of Plant Oil-Based Monomers

Two reactive sites are present in a plant-oil-based monomer's structure: a vinyl double bond, $CH_2{=}CH{-}C(O)$, which determines chain propagation, and isolated double bonds in fatty fragments, $CH_2{-}CH{=}CH{-}CH_2$, containing allylic hydrogen atoms prone to degradative chain transfer by the formation of less active $-CH{=}CH{-}CH\bullet-$ radicals.[23] Recently, we reported on the synthesis and free-radical copolymerization behavior of a vinyl monomer from soybean oil triglycerides with methyl methacrylate (MMA).[22] Nevertheless, growing PMMA radicals are known to undergo chain transfer reactions to a lesser extent.[23] At the same time, homopolymerization of new monomers based on sunflower, linseed, and olive oils revealed that (1) the number-average molecular weight of plant-oil-based homopolymers decreases in the range of poly(OVM) > poly(SFM) > poly(SBM) > poly(LSM), corresponding to the increasing degree of unsaturation in the monomers; (2) the obtained values of the chain transfer constant on monomer C_M clearly depend on the monomer structure as follows: C_M(LSM) > C_M(SBM) > C_M(SFM) > C_M(OVM). Such behavior is explained by the presence of differing numbers of allylic hydrogen atoms in the monomer molecules and the corresponding reaction of chain termination through degradative chain transfer on monomers (allylic termination).[27]

Taking into account that VAc is widely used for the development of industrial aqueous polymer dispersions (latexes), radical copolymerization of LSM, SBM, SFM, and OVM with VAc was explored in this study to evaluate plant-oil based monomers' feasibility in the use of copolymerization and ability to vary the biobased content in the resulting macromolecules. Unlike PMMA radicals, growing PVAc radicals show higher reactivity in chain transfer reactions. Hence, one of the experimental goals was to determine whether the chain transfer reactions observed during the homopolymerization of plant-oil based monomers[27] impact the radical copolymerization behavior of LSM, SBM, OVM, and/or SFM. First, the Q−e parameters, which provide a semiquantitative prediction of monomer reactivity ratios of monomers, allowing for the description of the behavior of monomers in radical copolymerization, were targeted. For this purpose, in copolymerization of the SBM, LSM, SFM, and OVM with styrene (St), monomer reactivity ratios r_1 and r_2 were experimentally determined for each monomer pair by measuring an instantaneous copolymer composition (at low monomer conversions of 5−10%, using ^{1}H NMR spectroscopy) (Figure C1 in Appendix C) and employing the Fineman−Ross method to a solution of the Mayo−Lewis copolymerization equation (Fig. 5.1).[18,33] Employing a Fineman−Ross equation[34] yields a straight line plot with slope r_1 and intercept r_2.

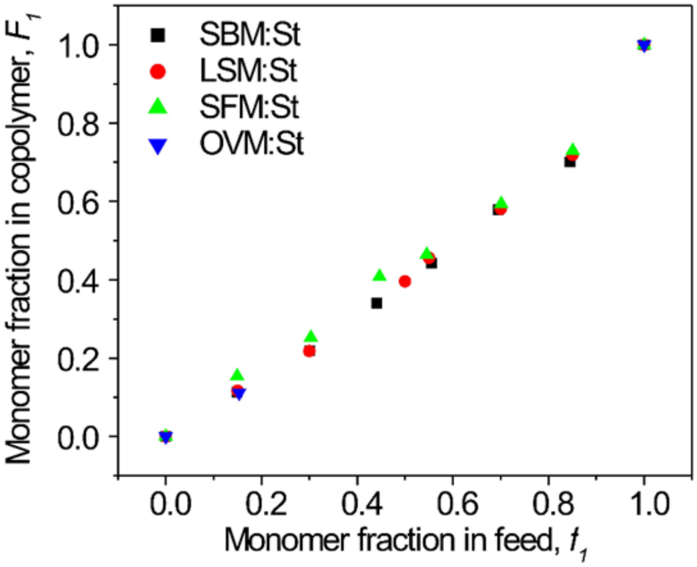


Figure 5.1. Experimental content of plant oil-based monomer in the copolymers with styrene vs. content of plant oil-based monomer in the initial feed mixture

For each monomer pair, the experimental data of the feed composition $F_i = [M_1]_i/[M_2]_i$ and copolymer composition $f_i = [m1]_i/[m2]_i$ were calculated, where $[M_1]$ and $[M_2]$ are each monomer's concentration in a feed and $[m_1]$ and $[m_2]$ are each monomer's content in a copolymer.

$$r_2 = Q_2/Q_1 \exp\{-e_2(e_2-e_1)\}, \quad r_1 = Q_1/Q_2 \exp\{-e_1(e_1-e_2)\} \qquad (5.1)$$

Experimental data on r_1 and r_2 for monomer pairs are shown in Table 5.1. It could be concluded that all of the growing plant oil-based monomer radicals are mainly added to the St monomer ($r_1 < 1$). Given the experimental r_1 and r_2 values for each monomer pair, as well as literature data on St Q−e parameters ($Q = 1$ and $e = -0.8$),[35] the Alfrey−Price scheme (eq 5.1) was applied to calculate the Q−e of the SBM, LSM, SFM, and OVM (Table 5.2). The obtained results show that both Q and e values are similar for all four plant-oil-based monomers. Because in an empirical Q−e scheme, the Q value describes the effects of the resonance factor and (to a smaller extent) the steric factor, it appears that both these factors affect plant-oil-based monomer reactivity in copolymerization in a similar way.

In the Q–e approach, the e value describes the polar factor by defining the role of monomer polarity in copolymerization. The data indicate that among the four monomers, the less unsaturated, thus, less polar, olive oil-based monomer possesses the smallest e value. Otherwise, polar effects do not seem to have a significant impact on plant-oil-based monomer reactivity in copolymerization. In general, differences between the Q–e values of the biobased vinyl monomers are small, as might be expected, assuming similarities in the structure of the monomer molecules.

Table 5.1. Monomer reactivity ratios for copolymerization of plant oil-based monomers and styrene

Comonomer pair	r_1	r_2
SBM – St	0.35 ± 0.03	1.11 ± 0.10
LSM – St	0.37 ± 0.06	1.10 ± 0.05
OVM – St	0.39 ± 0.05	1.19 ± 0.28
SFM – St	0.37 ± 0.02	0.83 ± 0.09

Table 5.2. *Q-e* parameters of plant oil-based monomers.

Plant oil-based monomer	Q	e
SBM	0.41 ± 0.01	0.18 ± 0.06
LSM	0.43 ± 0.06	0.15 ± 0.12
OVM	0.42 ± 0.05	0.09 ± 0.08
SFM	0.51 ± 0.02	0.28 ± 0.05

To further demonstrate that experimentally determined Q–e parameters can be applied to control the composition of copolymers from plant-oil-based monomers, a series of studies on radical copolymerization of LSM, OVM, SFM, and SBM with VAc were carried out. The chemical composition of each resulting copolymer (10 for each monomer pair) was determined using ^{1}H NMR spectroscopy and compared with the theoretical copolymer compositions. The theoretical compositions were assessed using the Alfrey−Price scheme (eq 5.1) and Q−e values for Vac (Q = 0.026, e = −0.88),[35] as well as for plant-oil-based monomers, as shown in Table 5.3, to determine r_1 and r_2 for each monomer pair. In the next step, these r_1 and r_2 were applied to calculate each theoretical copolymer composition using the Mayo−Lewis copolymerization equation (eq 5.2).

$$\frac{[m_1]}{[m_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{(r_1 \cdot [M_1] + [M_2])}{(r_2 \cdot [M_2] + [M_1])} \tag{5.2}$$

It can be seen (Fig. 5.2) that the experimental and calculated plots are in good agreement, indicating that radical copolymerization of both LSM (Fig. 5.2A) and SBM (Fig. 5.2B) with VAc is described by the Mayo−Lewis copolymerization equation. The determined Q−e values can be employed in estimating plant-oil-based monomer reactivity in copolymerization with other monomers to control biobased content in the resulting copolymers. In terms of polymerizability in radical copolymerization, the plant-oil-based monomers LSM, OVM, SFM, and SBM can be classified as vinyl monomers.

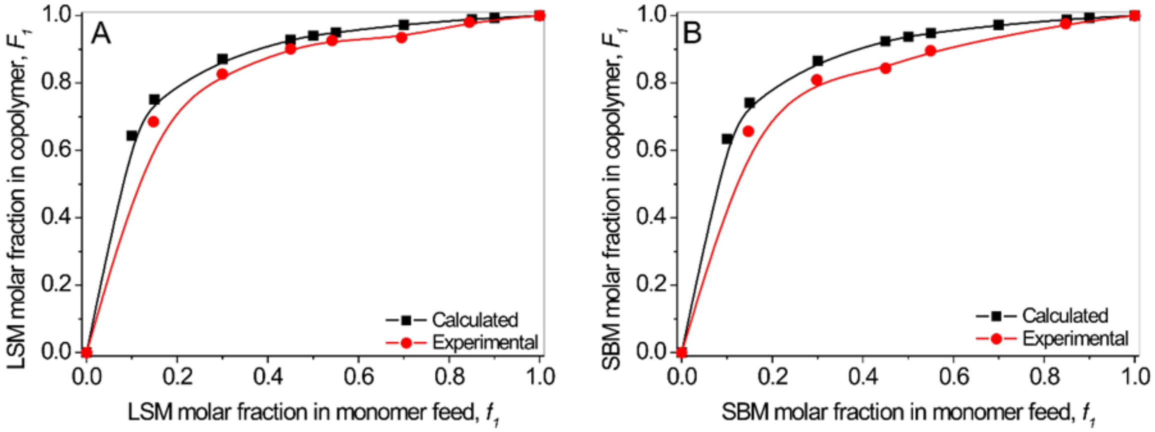


Figure 5.2. Calculated and experimental plant oil-based monomer content in LSM-based (**A**) and SBM-based (**B**) copolymer with VAc vs. plant oil-based monomer content in the initial feed mixture

Table 5.3. Experimental and calculated monomer reactivity ratios in copolymerization of plant oil-based monomers with vinyl acetate

Pair	SBM: VAc		LSM: VAc		OVM : VAc		SFM : VAc	
	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp
r_1	13.0	7.1±0.3	14.0	10.8±0.7	14.8	3.4±0.2	14.2	6.0±0.7
r_2	0.03	0.08±0.04	0.02	0.08±0.03	0.06	0.08±0.03	0.02	0.09±0.01

5.4.2. Synthesis and Properties of Biobased Latexes

Latexes based on VAc and acrylic monomers are widely applied as adhesives and binders in various coatings, as well as in the impregnation of different materials (paper, nonwoven, etc.). Incorporation of small amounts of hydrophobic monomers (e.g., 2-ethylhexyl acrylate) into latex polymers is known to improve their properties and performance (flexibility, toughness, water resistance, and adhesion).[36] VAc and acrylic monomers (particularly MMA) are known to be moderately soluble in water (2.5 and 1.6 g/100 mL, respectively),[37] whereas plant-oil-based monomers are hydrophobic and almost insoluble in water.[23] The synthesis of latex polymers from highly hydrophobic monomers has been conducted through conventional emulsion polymerization under certain conditions (e.g., higher surfactant concentration).[38]

The miniemulsion (when the reaction starts in the monomer droplet) polymerization technique was developed and studied by Ugelstad and Schork.[39–41] Hydrophilic monomers have been shown to be successfully copolymerized with hydrophobic octadecyl methacrylate using miniemulsion polymerization.[39,40] Even fluorinated monomers can be easily polymerized and copolymerized using miniemulsions.[41] Special approaches have been used, such as higher shear rate, adding osmotic agents, and using initiators soluble in oleo phase (AIBN).[41] Miniemulsion polymerization occurs in nanosized droplets, which can be considered as nanoreactors. The large interfacial area between the aqueous and oil phases facilitates radical reactions at the interface and increases copolymerization feasibility for monomers with a very different aqueous solubility.

In this study, latexes from LSM, SBM, OVM, SFM, and MMA or VAc were synthesized using emulsion and miniemulsion polymerization. Two oil phases, from the plant oil-based monomer (Oil Phase 1) and from the comonomer (MMA or VAc) and radical initiator (AIBN) (Oil Phase 2), were applied in the miniemulsion process. Each oil phase was miniemulsified in a surfactant-containing aqueous phase to obtain two separate miniemulsions. Polymerization started by slowly adding a miniemulsion, containing a plant-oil-based monomer, into a comonomer-containing one at 60 °C under stirring. The characteristics of the resulting stable biobased latexes are shown in Tables 5.4 and 5.5. Miniemulsion copolymerization of plant-oil-based monomers and MMA was completed within 3 h, during which essentially all monomers were polymerized; the conversion of monomers was about 87−99% (Table 5.4). The resulting latexes with an average particle size of 80−160 nm and biobased content of 5− 35 wt. % exhibit high stability at room temperature within several months. The molecular weight of the resulting copolymers decreases as follows: poly(MMA-co-OVM) > poly(MMA-co-SBM) > poly(MMA-co-SFM) > poly(MMA-co-LSM), corresponding to increasing degree of unsaturation in the monomers. A similar effect was observed by increasing the fraction of the plant-oil-monomer in the initial mixture.

Table 5.4. Characteristics of latexes from plant oil-based monomers and methyl methacrylate synthesized in miniemulsion process

Biobased content (feed), wt.%	Biobased content (polymer), wt.%	Conversion, %	Latex solid content, %	Latex particles size, nm	M_n, g/mol	T_g, °C
10OVM	6.5	97	38.8	73 ± 18	152,200	97
10SBM	6.9	92	36.8	39 ± 16	81,230	97
10SFM	6.4	99	40.3	99 ± 14	98,040	97
10LSM	3.5	98	39.3	113 ± 15	66,250	96
35OVM	21.2	94	28.0	116 ± 38	60,000	85
40OVM	28.0	87	22.0	131 ± 37	95,600	79
35SBM	21.7	92	27.6	156 ± 39	22,700	88
40SBM	33.8	88	22.3	76 ± 21	34,400	87

Decreasing molecular weight can be explained by the effect of degradative chain transfer on the monomer (allylic termination) provided by differing numbers of allylic hydrogen atoms in the monomer molecules.[23] Analysis of Tg data measured by differential scanning calorimetry (DSC) shows that the presence of biobased fragments in the resulting copolymers decreases the glass-transition temperature in comparison to that of poly(MMA) (Tg = 105 °C).

Table 5.5. Characteristics of latexes from plant oil-based monomers and vinyl acetate

Biobased content (feed), wt. %	Biobased content (polymer), wt. %	Conversion, %	Latex solid content, %	Latex particle size, nm	M_n, g/mol	T_g, °C
Miniemulsion						
5OVM	13.4	69.0	21.0	163 ± 65	77,500	20
5SBM	7.7	67.5	27.0	139 ± 65	27,270	29
5SFM	6.4	65.6	26.2	168 ± 41	20,875	25
5LSM	9.8	38.3	7.5	97 ± 49	25,550	24
Emulsion						
5OVM (50)	8.2	79.0	42.6	148 ± 16	18,330	15
5SBM (15)	5.1	70.0	35.9	140 ± 52	20,950	11
5SFM (15)	4.8	69.5	36.1	384 ± 94	34,950	19
5LSM (75)	2.8	87.8	45.6	112 ± 42	56,250	26

*in brackets, conversion of VAc (wt.%) before the plant oil-based counterpart was added

The obtained data indicate that variation of biobased content in macromolecules changes the thermal properties of the resulting copolymers from MMA and plant-oil-based monomers to a large extent. After 6 h of miniemulsion copolymerization of plant oil-based monomers and VAc, the total monomer conversion was about 70%. This can be explained by allylic termination, as well as high reactivity of the VAc radical.[18]

The increasing unsaturation of plant-oil-based monomers leads to an increase in the number of allylic hydrogen atoms and effective chain transfer reactions and lowers the molecular weight of the resulting polymers. This is confirmed by the fact that the highest molecular weight was detected for VAc copolymers with the least unsaturated OVM. Using the emulsion technique when the plant-oil-based monomer is fed into the reaction mixture after VAc is partially converted, both conversion and latex solid content can be increased (Table 5.5). DSC data show that the impact of oil-based fragments (3−13 wt. %) on the Tg of copolymers with Vac is more significant than that of copolymers with MMA. For both copolymers from MMA and VAc, biobased fragments make the resulting macromolecules more flexible, as indicated by decreasing glass-transition temperature. Softening the polymer usually increases the elongation of break at room temperature and toughness and lowers Young’s modulus. These effects are targeted by plasticization of coating or film to facilitate easier processing. To provide more insights into the plasticizing effect of plant oil-based fragments, tensile properties of the resulting latex copolymer films with MMA were evaluated at room temperature as a function of the biobased content. The results were obtained for the MMA copolymers with SBM and with less unsaturated OVM (Table 5.6). Although poly(MMA) does not form a film at 18−25 °C, 40−45 μm latex films were successfully created for testing from copolymers with various biobased contents.

Table 5.6 shows that although Young's modulus and tensile strength decrease by increasing the biobased content in the copolymers with MMA, elongation at break increases significantly for both comonomer pairs.

Table 5.6. Tensile properties (at room temperature) of latex films from OVM and SBM copolymerized with MMA

	$G'(\omega)$, MPa	E, MPa	σ, MPa	ε_b, %	Toughness, x 10^{-4}, J/m^3
15 OVM	1634	1429 ± 166	10.3	0.95	3.8
35 OVM	697	542 ± 48	9.5	17.5	23
40 OVM	342	131 ± 30	3.3	243	180
20 SBM	1615	1159 ± 6	11.3	1.3	5.2
35 SBM	916	407 ± 26	6.6	3.2	5.8
40 SBM	263	171 ± 38	3.1	68.1	6.7

Where $G'(\omega)$ – storage modulus, E – Young's modulus, σ – tensile strength at break, ε_b – elongation at break

The obtained data indicate that although poly(MMA) is a rigid and brittle material with limited ability for elongation, the presence of the biobased fragments makes the latex films much softer and increases material toughness. The latter behavior is much more pronounced for MMA copolymerized with the less unsaturated OVM than for MMA copolymerized with SBM. The results clearly indicate that the vinyl monomers from plant oils can be considered as good candidates for internal plasticization of polymeric materials through chain copolymerization into the macromolecular structure and reducing intermolecular interactions in copolymers.

Table 5.7. Surface energy of latex films from PVA and copolymers of vinyl acetate and plant oil-based monomers synthesized in emulsion polymerization process

					Surface energy, N/m		
Sample	Film thickness, μm	Water resistance (double rubs)	Water contact angle, θ, °	CH_2I_2 contact angle, θ, °	λ_S^d, N/m	λ_S^h, N/m	λ_S, N/m
5OVM	42 ± 8	>400	66 ± 2	45 ± 2	29.2	13.5	42.7
5SBM	41 ± 5	340	59 ± 3	47 ± 2	26.7	18.9	45.6
5SFM	42 ± 6	390	69 ± 2	40 ± 1	33.0	10.1	43.1
5LSM	44 ± 6	>400	69 ± 2	40 ± 2	32.9	10.3	43.2
PVA	42 ± 8	0	0	51 ± 3	18.8	54.2	73.0

In addition to improving mechanical properties, plant-oil based fragments can provide water resistance and hydrophobicity to latex films (coatings). In particular, poly(VAc) aqueous emulsions often need to be modified because of inherently poor properties with respect to water resistance. Water molecules act as plasticizers in such latex films and worsen their mechanical properties; thus, hydrophobic additives are often needed to reduce water sensitivity of the polymer. Table 5.7 displays the data on the surface energy and water resistance of the latex films from VAc copolymerized with a relatively small amount of plant-oil-based monomers in a reactive mixture. Both water resistance and hydrophobicity of the films increase dramatically in the presence of biobased fragments in the resulting structure of macromolecules. Table C1 in Appendix C shows a similar change in the surface energy of latex films based on MMA copolymerized with plant-oil-based monomers. Transmission electron microscopy (TEM) analysis of the synthesized latexes indicates that predominantly spherical particles from plant-oil-based monomers and MMA or Vac are formed, possessing unimodal size distributions (Figure C2 in Appendix C). In general, TEM results are in agreement with the DLS data recorded for copolymers with various biobased contents (Tables 5.4 and 5.5).

5.5. Conclusions

Vinyl monomers from soybean, sunflower, linseed, and olive oils were copolymerized with St, MMA, and VAc to determine the reactivity of biobased monomers in radical copolymerization, as well as their feasibility in emulsion processes for the synthesis of biobased latexes. Radical copolymerization of plant oil-based monomers is described with the classical Mayo−Lewis equation. Both Q (0.41−0.51) and e (0.09−0.28) values do not essentially depend on the structure of the biobased monomers. Emulsion (or miniemulsion) polymerization of plant oil-based monomers with MMA or VAc yields stable aqueous polymer dispersions with latex particle sizes of 80−160 nm, biobased monomer units containing latex polymer macromolecules of 3−35 wt. %, and a number-average molecular weight of the resulting copolymers of 20 000−150 000. The molecular weight of the synthesized macromolecules decreases by increasing the degree of unsaturation in the biobased monomers and monomer content in the reaction feed.

Thermal analysis shows that the presence of oil-based fragments in the copolymers decreases the glass-transition temperature of both copolymers with MMA and VAc. The tensile properties of latex films indicate that the presence of the biobased fragments increases PMMA toughness (elongation at break up to about 250%). Small amount of plant-oil-based fragments copolymerized with VAc significantly increases the water resistance and hydrophobicity of the resulting latex films. The results clearly show the potential of vinyl monomers from plant oils as candidates for internal plasticization of polymeric materials through radical copolymerization into a macromolecular structure and reducing intermolecular interactions in copolymers.

5.6. References

[1] Gandini, A., Lacerda, T. *Polymers from Plant Oils*, **2015**, Smithers Rapra, 180 p.

[2] Verhe, R.G. Industrial products from lipids and proteins, in *Renewable Bioresources: Scope and Modification for Non-Food Applications* **2004**, Stevens C.V.; Verhe R.G., John Wiley & Sons, Ltd, Chichester, 328 p.

[3] Guner, F.S.; Yagci, Y.; Erciyes, A.T. Polymers from triglyceride oils *Prog.Polym.Sci.,* **2006**, *31* ,633-670.

[4] Sharma, V.; Kundu, P.P. Addition Polymers from Natural Oils-A Review. *Prog. Polym. Sci.,* **2006**, *31,* 983-1008.

[5] Wool, R.P.; Sun, X.S. *Bio-Based Polymers and Composites*, **2005**, Elsevier, Amsterdam, 620 p.

[6] Gunstone, F. *Fatty acid and lipid chemistry,* **1996**, Blackie Academic & Professional, New York, 252 p.

[7] Mallegol, J.; Lemaire, J.; Gardette, J. L. Drier influence on the curing of linseed oil *Prog. Org. Coat.* **2000**, *39,* 107–113.

[8] Hess, P.S.; O'Hare, G.A. Oxidation of Linseed Oil—Temperature Effects *Ind. Eng. Chem.,* **1950**,*42(7)*,1424–1431.

[9] Yıldız, G.; Wehling, R. L.; Cuppet, S. L. Method for determining oxidation of vegetable oils by near-infrared spectroscopy *J Am. Oil Chem. Soc.,* **2001,** *78(5),* 495–502.

[10] Asadauskas, S.; Erhan, S. Z. Thin-Film Test to Investigate Liquid Oxypolymerization of Nonvolatile Analytes: Assessment of Vegetable Oils and Biodegradable Lubricants *J Am. Oil Chem. Soc.*, **200**1, *78(10),* 1029–1035.

[11] Erkal, F.S.; Erciyes, A.T.; Yagci, Y. Styrenation of triglyceride oils by macromonomer technique *J Coat. Technol.* **1993**, *65*, 37–43.

[12] Kabasakal, O.S.; Guner, F.S.; Erciyes, A.T.; Yagci, Y. Styrenation of Oils Based on Secondary Esters of Castor Oil. *J Coat. Technol*., **1995**, *67*, 47–51.

[13] Guner, F.S.; Yagci, Y.; Erciyes, A.T. Polymers from triglyceride oils *Prog.Polym.Sci.,* **2006**, *31* ,633-670.

[14] Solomon, D.H. The Chemistry of Organic Film Formers, **1971**, Wiley, New York. 369 p.

[15] Hofland, A. Waterborne coatings for decorative and protective coatings-A comparative survey *Surf Coat Int* **1994**, *7,* 270-281.

[16] Rodstrud, G.; Sutcliffe, J.F. Alkyd emulsions-properties and application. Results from comparative investigations of penetration and aging of alkyds, alkyd emulsions and acrylic dispersions *Surf Coat Int.,* **1994**, *1,* 7-16.

[17] Aigbodion, A.I.; Okieimen, F.E.; Obazee, E.O., Bakare, I.O. Utilization of maleinized rubber seed oil and its alkyd resin as binders in water-borne coatings *Prog Org Coat*., **2003**, *46 (1)*, 28-31.

[18] Odian, G. Principles of Polymerization, **1981**, Wiley, New York, 812 p.

[19] Havelka, K.O., McCormick C.L. Specialty Monomers and Polymers: Synthesis, Properties, and Applications, **2000,** ACS Symposium Series (Book 755) 1st Edition, 246 p.

[20] Alfrey T. Copolymerization, **1964**, Interscience Publisher, University of Michigan. 939 p.

[21] Immergut, E.H., Mark, H.F. Principles of Plasticization, Advances in Chemistry Series, *Plasticization and Plasticizers Properties,* Ed. N.J.A. Platzer **1965**, 48, Ch.1, pp.1-26.

[22] Tarnavchyk, I.; Popadyuk, A.; Popadyuk, N.; Voronov, A. Synthesis and Free Radical Copolymerization of a Vinyl Monomer from Soybean Oil *ACS Sustainable Chem. Eng.,* **2015**, *3*, 1618–1622.

[23] Demchuk, Z., Shevchuk, O., Tarnavchyk, I., Kirianchuk, V., Kohut, A., Voronov, S., Voronov, A. Free Radical Polymerization Behavior of the Vinyl Monomers from Plant Oil Triglycerides *ACS Sustainable Chem. Eng.*, **2016**, DOI: 10.1021/acssuschemeng.6b01890

[24] Bailey, A.E. Bailey's Industrial Oil and Fat Products, **1996**, Wiley, New York, 560 p.

[25] Johnson, R.W.; Fritz, E.E. Fatty Acids in Industry, **1989**, Marcel Dekker, New York, 667 p.

[26] Pan, X.; Sengupta, P.; Webster, D.C. High Biobased Content Epoxy–Anhydride Thermosets from Epoxidized Sucrose Esters of Fatty Acids *Biomacromolecules,* **2011**, *12*, 2416–2428.

[27] Lligadas, G.; Ronda, J.C.; Galia, M.; Cádiz, V. Plant Oils as Platform Chemicals for Polyurethane Synthesis: Current State-of-the-Art *Biomacromolecules,* **2010**, *11*, 2825–2835.

[28] Wang, Z.; Zhang, X.; Wang, R.; Kang, H.; Qiao, B.; Ma, J.; Zhang L.; Wang, H. Synthesis and Characterization of Novel Soybean-Oil-Based Elastomers with Favorable Processability and Tunable Properties *Macromolecules,* **2012**, *45*, 9010–9019.

[29] Türünç, O.; Meier, M.A. The thiol-ene (click) reaction for the synthesis of plant oil derived polymers *Eur. J. Lipid Sci. Technol.,* **2013**, *115*, 41–54.

[30] Raquez, J.M.; Deléglise, M.; Lacrampe, M.F.; Krawczak, P. Thermosetting (bio)materials derived from renewable resources: A critical review *Prog. Polym. Sci.,* **2010**, *35*, 487–509.

[31] Yuan, L.; Wang, Z.; Trenor N.M.; Tang, C. Robust Amidation Transformation of Plant Oils into Fatty Derivatives for Sustainable Monomers and Polymers *Macromolecules,* **2015**, *48*, 1320-1328.

[32] Yuan, L.; Wang, Z.; Ternor, N.M., Tang, C. Amidation of triglycerides by amino alcohols and their impact on plant oil-derived polymers *Polym.Chem.,* **2016,** *7,* 2790-2798.

[33] Vilela, C., Rua, R., Silvestre, A.J.D., Gandini, A. Polymers and copolymers from fatty acid-based monomers, *Industrial Crops and Products*, **2010**, *32,* 97-104.

[34] Chanda, M. Introduction to Polymer Science and Chemistry. A Problem Solving Approach, **2006**, Taylor & Francis, CRC Press, Boca Raton, FL, 640 p.

[35] C.E. Carraher, Introduction to Polymer Chemistry, 2nd edition, **2010**, Taylor & Francis, CRC Press, Boca Raton, FLm 554 p.

[36] Greenley, R.Z. *Q* and *e* values for Free Radical Copolymerizations of Vinyl Monomers and Telogens, in Polymer Handbook; 3rd ed., **1989** Wiley-Interscience: New York, 2336 p.

[37] Haloi, D.J. Poly(2-Ethylhexyl Acrylate) and Its Copolymers Prepared by ATRP: Poly(2-ethylhexyl acrylate) and its copolymer via Atom Transfer Radical Polymerization, **2014** Scholars’ Press, 184 p.

[38] Gardon, J.L. Emulsion Polymerization, in Polymerization Processes, Ed: Schildknecht C.E., Skeist, I., **1977**, Wiley-Interscience, New York, 768 p.

[39] Jenkins, A.D., Ledwith, A. Reactivity, Mechanism and Structure in Polymer Chemistry, **1974** Wiley, London, 613 p.

[40] Ugelstad, J.; El-Aasser, M.S. Vanderhoff, J.W. Emulsion polymerization: initiation of polymerization in monomer droplets *J.Polym.Sci.Pol.Lett*, **1973**, *11*, 503.

[41] Schork, F.J.; Luo Yingwu ; Smulders, W.; Russum, J.; Butte, A.; Fontenot, K. Miniemulsion Polymerization *Adv.Polym.Sci.,* **2005**, *175*, 129-255.

[42] Van Krevelen, D.W. Njenhuis, K. Properties of Polymers, **2009**, Elsevier, Amsterdam, 1031 p.

CHAPTER 6. PLASTICIZING AND HYDROPHOBIZING EFFECT OF PLANT OIL-BASED ACRYLIC MONOMERS WITH STYRENE AND METHYL METHACRYLATE[1]

6.1. Abstract

Latex nanoparticles from acrylic monomers (made from olive and soybean oil, which are significantly different in terms of fatty acid unsaturation amount) were synthesized using miniemulsion copolymerization with styrene and methyl methacrylate. Presence of plant oil-based fragments impacts thermomechanical properties of latex films by decreasing glass transition temperature and creating a plasticizing effect. The thermomechanical properties of resulting latex nanoparticles depend considerably on the amount of incorporated oil-derived fragments. As a result, biobased ingredients make latex copolymers more flexible, improve material film-forming properties, and provide flexibility and toughness when compared to the normally rigid polystyrene and poly(methyl methacrylate). In addition, plant oil-based fragments enhance the hydrophobicity of the crosslinked latex films and can be considered as additives to reduce water sensitivity of the polymer network.

6.2. Introduction

Commodity plasticizers are low molecular non-volatile compounds that are widely used as additives in polymer production.[1] The function of a plasticizer is to reduce the forces between

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[1] The material in this chapter was co-authored by Zoriana Demchuk, Vasylyna Kirianchuk, Kyle Kingsley, Stanislav Voronov, and Andriy Voronov. Zoriana Demchuk had the primary responsibilities of synthesizing and characterizing of polymer latexes from plant oil-based monomers in free radical copolymerization with styrene and nethyl methacrylate. The plasticizing and hydrophobizing behavior of plant oil-based monomers in resulted latex copolymers were evaluated by Zoriana Demchuk using DMA, DSC, tensile testing and water contact angle measuring.Vasylyna Kirianchuk was helping in latex copolymer characterization including evaluation of copolymer composition and molecular weight. Zoriana Demchuk had estimated the relationship between monomer content in copolymer and the thermo-mechanical properties of latex films. Andriy Voronov and Stanislav Voronov were proving their support and assistance in helping to evaluate the effect of monomer unsaturation on film-forming abilities and properties of latex films.Zoriana Demchuk was primarily drafting the manuscript and was involved in all its revisions. Published article can be found at https://doi.org/ 10.11159/ijtan.2018.005.

the macromolecules, thereby increasing chain mobility and leading to polymer softening, which may facilitate better material processing. In the past decade, the world production of plasticizers has grown up to 5 million tons a year. Plasticizers are used in the manufacturing of many polymers and polymeric materials for different types of applications.[2] Incorporation of a plasticizer in a polymer matrix decreases the material glass transition temperature (T_g), tensile stress, hardness, density, viscosity, etc. The presence of plasticizer molecules leads to increased polymer and polymer network flexibility, as well as dielectric constant and resistance to damage, all of which can impact polymer crystallinity, transparency, electric conductivity, fire resistivity, and biodegradability.[2-4].

According to the International Union of Pure and Applied Chemistry (IUPAC), the definition of a plasticizer is “a substance or material, which is incorporated in material (usually a plastic or an elastomer) to increase its flexibility and workability”. The most widely used low molecular commodity plasticizer is di-(2-ethylhexyl) phthalate, also known as dioctyl phthalate. However, due to toxicity based on migration of small phthalate molecules from the polymer matrix (e.g., polyvinyl chloride [PVC]), utility of dioctyl phthalate in some applications is limited.[5,6] Fatty acid esters, benzoates, tartrates, and chlorinated hydrocarbons, esters of adipic, azelaic, and sebacic acid are other commonly used types of plasticizers.[7]

For the last few decades, the chemical industry has been looking for new plasticizers based on natural materials. Derived from biobased renewable resources, such plasticizers would be non-toxic and safe. Moreover, polymer-based plasticizers from natural resources (e.g., vegetable oils) may be less able to migrate from the material due to the higher level of intermolecular interactions between (macro)molecules of the plasticizer and polymer matrix. Already developed examples of biobased plasticizers include materials from epoxidized vegetable oils (soybean, linseed, castor, sunflower) and esters of fatty acids.[8,9] Fabra et al. demonstrated that the addition of oleic acid in hydrophilic caseinate films plasticizes the resulting material, improving the mechanical properties of the films and increasing their water permeability.[10]

Fragments of plant oil-based acrylic monomers (POBMs) recently synthesized in our group while being incorporated in macromolecules impacted thermomechanical properties of the resulting copolymers by decreasing their *Tg*.[11,12] This indicates that the presence of such constituents in the copolymer structure can provide internal plasticization effects, making the resulting materials more environmentally friendly compared to conventional products where low molecular phthalates are used.

The internal plasticization effect can be achieved by copolymerization of various commercial vinyl monomers with a library of POBMs developed in our group.[11–13] When long unsaturated fatty acid fragments (C18) of POBMs are incorporated into the macromolecules, they can reduce the intermolecular interactions and increase intermolecular distance, thus increasing chain mobility and facilitating polymer softening (plasticizing).

Suitability of POBMs in free radical copolymerization reaction with other vinyl monomers was demonstrated in our previous study.[11–13] Considering the highly hydrophobic nature of POBMs and limited aqueous solubility, the miniemulsion process was employed for polymerization in this study. Miniemulsion polymerization occurs in nanosized droplets (nanoreactors) and results in the formation of latex nanoparticles (latexes), one of the most advanced polymeric materials, which is widely used for making coatings and paints. In the miniemulsion process, copolymerization feasibility for hydrophobic monomers is provided by the large interfacial area between aqueous and oil phases where radical reactions can occur.

In this study, we report in more detail the internal plasticizing effect of incorporating plant oil-based fragments into latex copolymers. For this purpose, a range of biobased latexes (latex nanoparticles) from two POBMs (acryloyl aminoethyl oleate [OVM] and acryloyl aminoethyl soyate [SBM]) and two petroleum-based vinyl monomers (styrene [St] and methyl methacrylate [MMA]) were synthesized in miniemulsion polymerization. SBM and OVM are significantly different in terms of fatty acid fragment unsaturation because SBM is more unsaturated. To this end, the effect of POBM unsaturation amount on the thermal and mechanical properties of latex films was studied. In addition, the impact of incorporated biobased copolymer fragments on hydrophobicity of crosslinked latex films was evaluated in this work.

6.3. Materials

Olive oil (Pompeian Inc., Baltimore, MD), Soybean Oil (Crisco; The J.M. Smucker Company, Orville, OH), N-hydroxyethyl acrylamide (HEAAm; TCI America), sodium dodecyl sulfate (SDS; VWR, Solon, OH) and 2,2’-Azobis(2-methyl-propionitrile) were used as received and stored at low temperature in the fridge. St and MMA (99%, stab., Alfa Aesar, Heysham, England) were distilled under vacuum before use. The deionized water for the latex synthesis was produced by Mili-Q Integral Water Purification System (18MQ).

6.4. Experimental Section

6.4.1. Plant Oil-Based Monomer (POBM) Synthesis

Acrylic monomers from olive and soybean oil were synthesized using one-step transesterification reaction of N-hydroxyethyl acrylamide with plant oil triglycerides in the presence of catalytic amounts of sodium hydroxide. The detailed synthesis procedure of POBM synthesis and its characterization are described in [11].

6.4.2. Biobased Latex Synthesis

The olive oil-based and soybean oil-based latexes were synthesized in miniemulsion copolymerization of respective acrylic monomers from plant oils with St and MMA. For this purpose, oil phase (15g) was prepared by mixing of POBM (10–60 wt.%, 1.5-9g) with MMA or St at different ratios (6-13.5g) in the presence of 1.5 wt% (0.225g) oil-soluble initiator.

The aqueous phase was formed by dissolving the emulsifier (SDS, 2–4 wt.%) (0.3-0.6g) in Millipore water with added small amounts of NaCl (0.02 mol/l) (0.04g). The oil phase was added dropwise to the aqueous phase and mixed for 45 min to form pre-emulsion. The pre-emulsions were sonicated with three pulses for 60 sec each using Q-Sonica (500 W digital sonicator, ½ in. tip, 20kHz, Newtown, CN) and placed in an ice bath to maintain the temperature at 25°C. Resulting miniemulsions were purged with nitrogen for 10 min and polymerized at 60°C for 5 hr. The latex solid content was kept at 30 wt.%.

6.4.3. Plant Oil-Based Latex Characterization

Total monomer conversion was determined by multiple precipitations of latex in methanol in order to remove residual unreacted monomers. The purified copolymers were dried in an oven until a constant weight was achieved.

The latex solid content was measured gravimetrically by drying the latex samples in an oven at elevated temperature for 45 min.

The latex copolymer composition was analyzed using ^{1}H NMR spectroscopy (AVANCE III HDTM 400 high-performance digital NMR spectrometer, Bruker, Billerica, MA) using $CDCl_3$ as a solvent.

Molecular weight of the copolymers was determined in gel permeation chromatography (GPC) (Waters Corporation Modular Chromatograph, consists of a Waters 1515 HPLC pump, a

Waters 2410 refractive index detector, and two 10µm PL-gel mixed-B columns) at 40°C using tetrahydrofuran as a carrier solvent.

Particle size of the plant oil-based latex particles was measured using dynamic light scattering (Particle Sizing Systems Nicomp 380, Santa Barbara, CA) at a scattering angle of 90° at room temperature.

The glass transition temperature of latexes was determined by differential scanning calorimetry (DSC) (TA Instruments Q1000 calorimeter) at heat/cool/heat mode (-40°C/150°C) with dry nitrogen purging through the sample at 50mL/min flow rate. The heating/cooling rate of latex samples was 10–20°C/min.

Latex free films were formed by applying latex to the clean glass substrate using a drawdown bar of 8 mils of thickness and curing at elevated temperature for 3–5 hours using autooxidation process. The resulting films were peeled off from the substrate after curing.

The unsaturation amount of latexes in monomer feed (U_{MF}) was calculated using the approach described in [11].

The latex films were subjected to dynamic mechanical analysis (DMA; TA Instruments Q800) with a heating rate of 5°C/min to investigate the dynamic mechanical behavior of plant oil-based latex films. The crosslink density of the latex films (v) was calculated using rubber elasticity theory where the storage modulus (G') is expressed by the equation below [14]:

$$G' = \nu \cdot R \cdot T = (\rho / Mc) \cdot R \cdot T \tag{6.1}$$

where v is crosslink density in mol/cm3, R is gas constant, and T is absolute temperature.

Molecular weight in g/mol between crosslinks was determined using the equation:

$$Mc = \rho/\nu \tag{6.2}$$

where ρ is density of latex film.

Mechanical properties of latex films were tested using Instron tensile testing machine 2710-004 (maximum load 500 N). The film samples had a rectangular shape (length: 25 mm, width: 5mm). The thickness of the films was measured before each testing.

Performance of coatings based on synthesized latexes was tested by measuring the flexibility, hardness, and adhesion of the coating to the substrate. Flexibility of the latex coatings was evaluated using the conical mandrel bend method according to American Society for Testing and Materials (ASTM) D 522. It measures the ability of coating to resist cracking when elongated. The hardness was tested using the pendulum hardness method (ASTM D 4366-16), where hardness of the organic coating is defined as the resistance of the coating to the deformation by calculating the damping time of a pendulum which touches the coating surface. The plant oil-based latex coatings adhesion was identified by the cross-hatch adhesion method (ASTM 3359) using a tape test.

The surface free energy of the latex coatings from olive oil-based and soybean oil-based monomers copolymerized with St or MMA was characterized by measuring the contact angle (five measurements for each sample) of water and diiodomethane on the coating surface using FTA 125 contact angle/surface energy analyzer. Surface free energy of each coating was calculated using Owens and Wendt's modification of Young's equation [15].

6.5. Results and Discussions

Plant oils have recently become one of the most important renewable feedstocks for replacement of petroleum-based sources in the chemical industry. In the synthesis of biobased polymers, plant oils are widely used due to their broad availability, biodegradability, low cost, non-toxicity, and ability to undergo diverse organic reactions [16–20]. Organic reactions of transformation of triglycerides into different fatty derivatives have been considered, particularly in the synthesis of renewable biobased monomers and further polymerization to develop polymers and polymeric materials [21].

Recently, we developed a one-step method of plant oil direct transesterification into vinyl monomers for free radical polymerization and copolymerization [11–13,22]. It was demonstrated that the rate of POBM homopolymerization, where chain propagation coexists with chain transfer reaction on monomers, is determined primarily by the amount of unsaturation in each plant oil triglycerides. In the next step, stable latexes containing up to 50 wt. % of plant oil-based content were synthesized using miniemulsion copolymerization of POBM with their petroleum-based counterparts [13].

For this study, monomers from olive (OVM) and soybean (SBM) oils were chosen to investigate plasticization effect and the impact of monomer unsaturation on latex film properties. The choice of POBM was based on a considerable difference in unsaturation of fatty acid fragments in OVM and SBM. It was demonstrated in our previous work that *CM* (ratio of chain transfer and propagation rate constants) depends on monomer unsaturation. This value is larger for more unsaturated SBM (C_M, $OVM = 0.15$, C_M, $SBM = 0.26$) [13]. It has also been demonstrated that monomer unsaturation amount (U_{MF}) impacts resulting copolymer molecular weight and can be used as a parameter for comparing physicochemical and thermomechanical properties of latex films. For this purpose, a series of latexes were synthesized from OVM and SBM in miniemulsion copolymerization with St and MMA.

Miniemulsion copolymerization of POBM with petroleum-based comonomers yields latexes with an average particle size of 50–100 nm and 7–55 wt. % of biobased content, exhibiting stability at room temperature within several months. Characteristics of resulting materials (Tables 6.1 and 6.2) show that latexes with a polymer content of 22–40 % and monomer conversion of 65–95% were obtained. Conversion varies with a POBM unsaturation amount in feed (higher conversion was obtained in copolymerization of less unsaturated OVM for both St and MMA).

As Tables 6.1 and 6.2 indicate, biobased content (determined using ^{1}H NMR spectroscopy) in resulting latexes only slightly deviated from the POBM content in monomer feed, confirming that waste majority of plant oil-based ingredients is incorporated into the copolymer macromolecules during miniemulsion polymerization.

Table 6.1. Characteristics of latexes from POBM and MMA

Biobased content, %wt.					
feed	polymer	S^*, %	Latex solid content, %	M_n, g/mol/ PDI	T_g, °C
10 OVM	6.5	97	39	152,200/4.3	98
20 OVM	14.3	94	29	82,100/3.1	93
40 OVM	33.4	87	23	95,600/5.2	63
10 SBM	6.9	92	37	81,230/6.7	97
20 SBM	14.2	91	28	39,200/4.0	88
40 SBM	32.2	81	22	34,400.3.5	57

* S- total monomer conversion

Table 6.2. Characteristics of latexes from POBM and St

Biobased content, %wt.					
feed	polymer	S^*, %	Latex solid content, %	M_n, g/mol/PDI	T_g, °C
25 OVM	20.3	89	34	180,000/4.9	84
40 OVM	30.1	83	30	168,000/3.1	57
50 OVM	46.0	82	40	117,000/4.6	39
60 OVM	56.5	80	34	108,500/3.2	18
25 SBM	15.5	79	29	119,500/4.8	75
40 SBM	28.0	73	29	65,100/3.8	50
50 SBM	43.2	74	29	58,000/2.7	27
60 SBM	56.1	64	26	39,100/3.0	5

*S- total monomer conversion

As expected, molecular weight of the resulting latex copolymers decreased with an increasing POBM concentration in monomer feed. Molecular weight follows poly(MMA-*co*-

OVM) > poly(MMA-*co*-SBM), as well as poly(St-*co*-OVM) > poly(MMA-*co*-SBM), corresponding to increasing unsaturation amounts of POBM. A similar effect was observed by increasing the fraction of plant oil-monomer in the initial mixture in our previous study [11–13,22]. Decreasing molecular weight is explained by the effect of degradative chain transfer on the monomer (allylic termination) provided by differing numbers of allylic hydrogen atoms in the monomer molecules. The latter effect is more pronounced for reactions of SBM compared to OVM.

Analysis of Tg data measured by DSC (Tables 6.1 and 6.2) showed that the presence of plant oil-based fragments in latex copolymers decreases glass transition temperature, and thus, plasticizes the polymers. As a result of the internal plasticizing effect (due to the presence of unsaturated POBM fragments), the synthesized latex copolymers are considerably more flexible compared to poly(methyl methacrylate) (PMMA; $Tg = 105^oC$) and polystyrene (PSt; $Tg = 100^oC$) homopolymers.

The extent of the transforming rigid PSt and PMMA into film-forming flexible polymers depends on POBM chemical structure. To this end, a more pronounced change of T_g for more unsaturated SBM-based latexes was observed compared to OVM-based copolymers. In this regard, Tables 6.1 and 6.2 indicate that incorporation of 7–55 wt.% of SBM/OVM fragments in copolymer decreased the T_g of latex films at about 95^{o}C for SBM and 80^{o}C for OVM in copolymerization with St, as well as at about 48^{o}C for SBM, and 43^{o}C for OVM in copolymerization with MMA.

Overall decrease in T_g corresponds to the bio-based content in the resulting macromolecules and is more pronounced for latexes with higher plant oil-based amounts.

To explain the difference in plasticizing effect of SBM and OVM-based fragments, unsaturation amount and chemical structure of both monomers should be considered. SBM consists predominantly of more unsaturated linoleic fatty acid fragments (with two double bonds), while OVM contains mostly oleic acid fragments (with one double bond). To this end, being incorporated in the copolymers with MMA and St, more unsaturated fragments of SBM present a spatial arrangement that diminishes the packing ability of macromolecules due to the macromolecular configuration and, thus, the plasticizing effect is more expressed in SBM-based latexes.

Crosslinking is often applied to improve polymer properties and design materials for specific purposes and applications. In this regard, mechanical properties of polymeric materials, such as hardness, elongation at break (ε_B), and Young's modulus (E), essentially depend on crosslink density ($\boldsymbol{\upsilon}$), which particularly depends on the structure of a polymer network [23]. In fact, the mobility of polymer chains in a crosslinked network is a function of $\boldsymbol{\upsilon}$ and determines the mechanical and thermal properties of polymeric materials. To characterize homogeneous polymer networks, linear viscoelastic behavior (polymer response to a periodic force and polymer deformation at this force) can be determined using DMA to calculate crosslink density. To provide further insights into the plasticizing effect of oil-based fragments, the tensile properties of films from the latexes synthesized in this study were evaluated at room temperature. As an additional parameter, effective molecular weight between crosslinking nodes (M_c) in polymer network was calculated using density of latex copolymers from POBM and St: ρ(poly[OVM-St]) = 0.955 g/mol, ρ(poly[SBM-St]) = 0.970 g/mol (Table 6.3).

Table 6.3. Molecular weight between crosslinks (M_c) in polymer networks from POBM and St

Biobased latex	50 OVM	60 OVM	50 SBM	60 SBM
M_c, g/mol	8,300	5,600	4,800	3,700

From the DMA data, the value of storage modulus *G'* in rubber elasticity region (at $T >$ [Tg + 50°C]) was determined from a tan δ plot to calculate crosslink density ($\boldsymbol{\upsilon}$). In addition, Young's modulus (E), tensile strength (σ), and elongation at break (ε_B) were measured to characterize mechanical properties of the crosslinked latex films and demonstrate plasticizing effect of POBM fragments. The obtained results showed that the crosslink density of latex polymernetwork noticeably depends on POBM content in monomer feed and latex copolymers. Increasing the unsaturation amount in monomer feed led to increasing $\boldsymbol{\upsilon}$ (Figure 6.1) and, respectively, decreasing M_c (Table 6.3). The obtained data indicated that the crosslink density of POBM-based latex films can be controlled by monomer feed unsaturation amount, as well as by nature (chemical structure) of POBM.

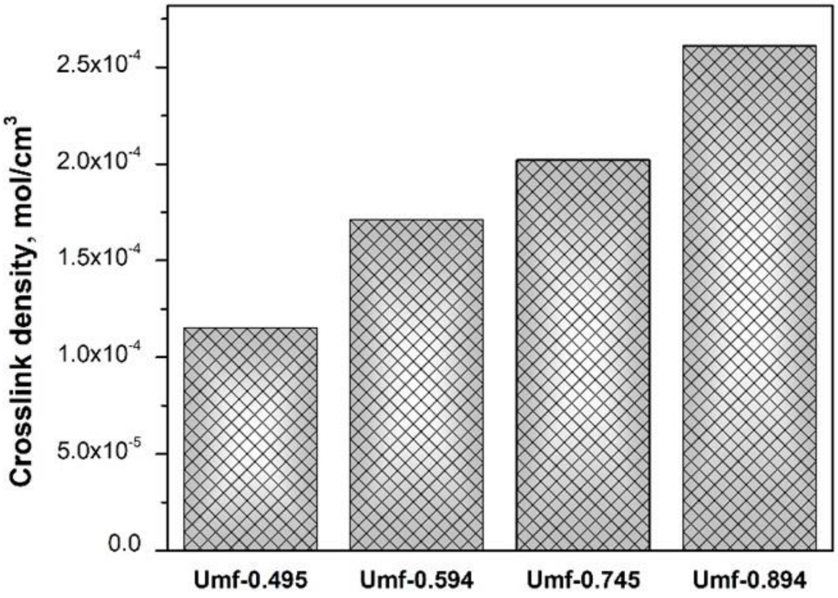

Figure 6.1. Crosslink density vs. unsaturation amount (U_{MF}) and vs. plant oil-based content in monomer feed

Table 6.4. Tensile properties of latex films from OVM and SBM copolymerized with MMA

Biobased latex	E, MPa	σ, MPa	ε_{br}, %	U_T, $\times 10^{-4}$, J/m^3
20 OVM	420 ± 45	1.4	0.7	1.8
40 OVM	131 ± 30	3.3	243	180
20 SBM	1159 ± 6	11.3	1.3	5.2
40 SBM	171 ± 38	3.1	68.1	6.7

Table 6.5. Tensile properties of latex films from OVM and SBM copolymerized with St

Biobased latex	E, MPa	σ, MPa	ε_{br}, %	U_T, $\times 10^{-4}$, J/m^3
25 OVM	710	8.8	4	15
40 OVM	290	4.4	24	25
50 OVM	92	3.3	245	130
60 OVM	2.1	2.3	275	170
25 SBM	890	6.9	1	2
40 SBM	550	5.9	9	28
50 SBM	220	5.7	130	31
60 SBM	6.3	3.5	128	105

Tables 6.4 and 6.5 show that although Young’s modulus and tensile strength both decrease by increasing the biobased content, elongation at break increases significantly for all co-monomer pairs. The obtained data indicated that the presence of plant oil-based fragments makes latex films much softer and increases toughness (U_T) of the material. The latter is much more pronounced when petroleum-based monomers are copolymerized with less unsaturated OVM compared to MMA and St reacted with SBM. The data confirmed that being incorporated into the copolymer, acrylic monomers from plant oils perform as internal plasticizers of crosslinked latex films and reduce intermolecular interactions between macromolecules.

As a result, $\mathcal{E}_B$ of latex films increases from a few % (for PSt and PMMA) up to 275% (for films from St and 60 wt. % OVM). Overall, higher $\mathcal{E}_B$ was recorded for OVM-based latexes compared to SBM-containing polymer films due to the formation of shorter crosslinks between nodes in the polymer network that correlate with higher crosslink degree (Table 6.3).

At the same biobased content in copolymers, higher Young's modulus and tensile strength were observed for latex films from both PSt and PMMA and more unsaturated SBM compared to films from OVM-containing latexes. This can be explained by higher crosslink density (due to higher amount of unsaturation) of SBM-based latex films and corresponding higher elastic deformation.

For a more comprehensive understanding of the effect of POBM structure on material performance, model coatings were prepared from latexes synthesized in copolymerization of MMA and 50 wt. % each of OVM and SBM. Resulting coatings were characterized in terms of flexibility, hardness, and adhesion to the metal surface, according to ASTM methods.

In the crosshatch adhesion test (ASTM 3359), coating adhesion to the substrate was identified on a scale of 0 to 5, where 0 indicates no adhesion and 5 indicates high adhesion. Figure 6.2 shows that POBM structure (monomer unsaturation amount) impacts adhesion of the latex coating to the metal. Better adhesion was observed for coatings made from more unsaturated SBM-containing latexes. As can also be seen from Figure 6.2, the pendulum hardness of the crosslinked latex films changes with the POBM's unsaturation amount and crosslink density. Resulting hardness was higher for the polymer network formed from more unsaturated POBM SBM copolymerized with MMA.

In addition to improving mechanical properties of latex films, plant oil-based fragments can enhance water resistance by increasing hydrophobicity of the film (coatings) made from latex. In fact, aqueous emulsions often need to be modified because of inherently poor properties with respect to water resistance. Water molecules act as plasticizers in such latex films and worsen their mechanical properties; thus, hydrophobic additives are often needed to reduce water sensitivity of the polymer.

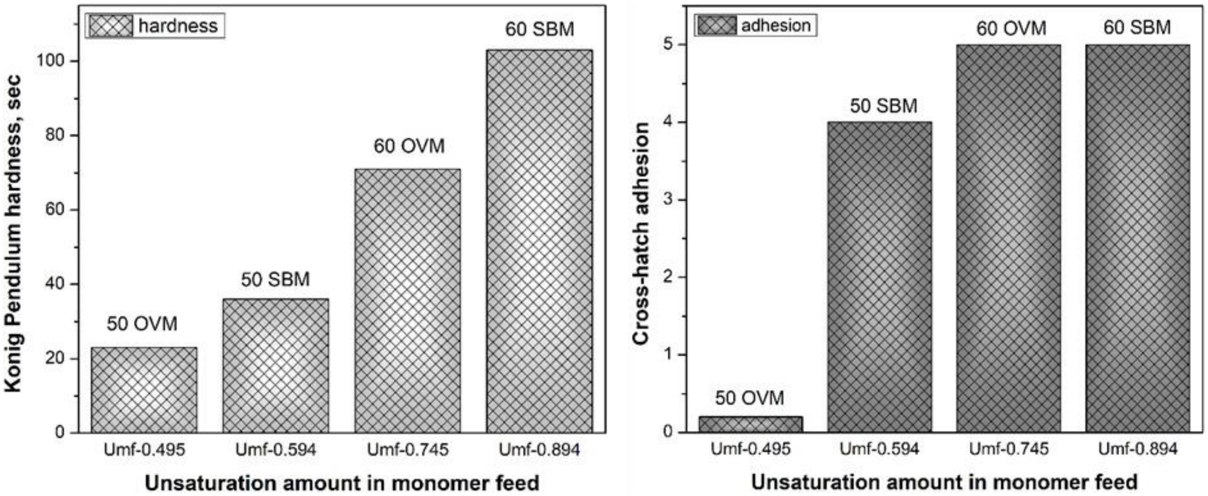

Figure 6.2. The effect of monomer structure on properties of latex coatings

To determine the extent of hydrophobicity provided by the presence of POBM fragments to latex films, water and diiodomethane contact angles (CA; Table 6.6) were measured, and surface energy was calculated for coatings formulated from latexes synthesized in copolymerization of MMA with 40 wt% each of OVM and SBM.

Coatings made from plant oil-based latexes are indeed more hydrophobic compared to PMMA homopolymer (Table 6.6). Water contact angle raised from 68° for PMMA up to 95° for 40wt% SBM copolymer. Differences in water contact angle and surface energy were observed for coatings made from latexes based on SBM in comparison to OVM. SBM-containing coatings (biobased fragments with higher unsaturation amounts) were more hydrophobic compared to material with same weight fraction of less unsaturated OVM.

This finding can be explained by formation of a polymer network with higher density, which enhances the effect of incorporated hydrophobic fatty acid fragments into the latex coatings. The calculated surface energy for POBM-based copolymers decreases in comparison to PMMA homopolymer (Table 6.6), indicating that presence of POBM fragments can be beneficial for formation of low surface energy latex materials when water repellent properties are needed.

Table 6.6. Surface energy of latex films from copolymers of MMA and OVM or SBM

Bio-based coating	Film thickness, μm	Water CA, θ, °	CH_2I_2 CA, θ, °	Surface energy, N/m		
				λ_S^d	λ_S^h	λ_S
40 OVM	35 ± 7	80	46	32	5	37
40 SBM	31 ± 5	95	55	30	1	31

* Surface energy of PMMA- 41.0 N/m

6.6. Conclusion

Latex nanoparticles from acrylic monomers (synthesized from olive and soybean oil and different in terms of triglyceride fatty acids unsaturation) were prepared by miniemulsion copolymerization with St and MMA. Decreasing glass transition temperature of latex copolymers indicated that the presence of plant oil-based fragments impacts the thermomechanical properties of resulting copolymers by providing strong plasticizing effects. Plant oil-based ingredients make the copolymers more flexible, improve film-forming properties, and provide toughness compared to the normally rigid PS and PMMA.

It has been demonstrated that the unsaturation amount of the POBM (corresponding to the chemical structure of the oil) can be utilized as a reliable experimental parameter in controlling resulting latex properties, including the influence of variation in monomer feed unsaturation on the crosslink density of latex films and, consequently, polymer thermal and mechanical properties.

In addition, it has been shown that plant oil-based fragments enhance hydrophobicity of the latex film coatings; thus, these can be considered as additives to reduce water sensitivity of the polymer materials (coatings).

Assuming ability of POBMs to act as internal plasticizers by making the polymer material more flexible and to enhance hydrophobicity of the polymer films, as well as the broad availability of plant/vegetable oils for synthesis of new monomers, this study can be considered a promising platform for improving properties of latex polymers and latex polymer networks in various applications, including coatings and paints.

6.7. References

[1] F. T. Sejidov, Y. Mansoori, N. Goodarzi Esterification reaction using solid heterogeneous acid catalysts under solvent-less condition *Journal of Molecular Catalysis A: Chemical,* **2005,** 240 (1-2), 186–190.

[2] E. Białecka-Florjanczyk, Z. Florjanczyk Solubility of plasticizers, polymers and environmental pollution *Thermodynamics, Solubility and Environmental Issues*, Letcher T, Eds. *New York: Elsevier*; **2007**, 397–408.

[3] S. L. Rosen, *Fundamental principles of polymeric materials.* New York: John Wiley & Sons, Inc., **1993**, pp. 82-101.

[4] L. Savenkova, Z. Gercberga, V. Nikolaeva, A. Dzene, I. Bibers, M. Kalnin Mechanical properties and biodegradation characteristics of PHB-based films *Process Biochemistry,* **2000**, 35(6), 573-579.

[5] K. Pielichowski, B. Swierz-Motysia Influence of polyesterurethane plasticizer on the kinetics of poly(vinyl chloride) decomposition process *Journal of Thermal Analysis and Calorimetry,* **2006**, 83(1), 207–212.

[6] O. Fenollar, L. Sánchez-Nacher, D. García-Sanoguera, J. López, R. Balart The effect of the curing time and temperature on final properties of flexible PVC with an epoxidized fatty acid ester as natural-based plasticizer *Journal of Materials Science,* **2009**, 44(14), 3702–3711.

[7] M. Vieira, M. Silva, L. Santos, M. Beppu “Natural- based plasticizers and biopolymer films: A review” *European Polymer Journal,* **2011**, 47(3), 254–263.

[8] H. Baltacioglu, D. Balköse Effect of zinc stearate and/or epoxidized soybean oil on gelation and thermal stability of PVC-DOP plastigels *Journal of Applied Polymer Science,* **1999**, 74(10), 2488–98.

[9] J. S. Choi, W. H. Park Effect of biodegradable plasticizers on thermal and mechanical properties of poly(3-hydroxybutyrate) *Polymer Testing,* **2004**, 23(4), 455–460.

[10] M. José Fabra, P. Talens, A. Chiralt Tensile properties and water vapor permeability of sodium caseinate films containing oleic acid–bees wax mixtures *Journal of Food Engineering*, **2008**, 85(3), 393-400.

[11] Z. Demchuk, O. Shevchuk, I. Tarnavchyk, V. Kirianchuk, M. Lorenson, A. Kohut, S. Voronov, A. Voronov Free Radical Copolymerization Behavior of Plant Oil-Based Vinyl Monomers and Their Feasibility in Latex Synthesis *ACS Omega,* **2016,** 1, 1374-1382.

[12] Z. Demchuk, A. Kohut, S. Voronov, A. Voronov Versatile platform for controlling properties of plant oil-based polymer networks *ACS Sustainable Chemistry & Engineering*, **2018,** 6(2), 2780-2786.

[13] Z. Demchuk, O. Shevchuk, I. Tarnavchyk, V. Kirianchuk, A. Kohut, S. Voronov, A. Voronov Free radical polymerization behavior of the vinyl monomers from plant oil triglycerides *ACS Sustainable Chemistry & Engineering*, **2016,** 4(12), 6974–6980.

[14] H. Ishida, D. J. Allen Mechanical characterization of copolymers based on benzoxazine and epoxy *Polymer,* **1996**, 37(20), 4487-4495.

[15] M. Żenkiewicz Methods for the calculation of surface free energy of solids *Journal of Achievements in Materials and Manufacturing Engineering*, **2007** 24(1), 137-145.

[16] R. G. Verhe Industrial products from lipids and proteins *Renewable Bioresources: Scope and Modification for Non-Food Applications*, C. V. Stevens, R. G. Verhe, Eds. John Wiley & Sons, Ltd., Chichester, **2004**, p. 328.

[17] F. S. Guner, Y. Yagci, A. T. Erciyes Polymers from triglyceride oils *Progress in Polymer Science,* **2006**, 31(7), 633-670.

[18] V. Sharma, P. P. Kundu Addition Polymers from Natural Oils—A Review *Progress in Polymer Science,* **2006,** 31(11), 983-1008.

[19] R. P. Wool, X. S. Sun *Bio-Based Polymers and Composites.* Elsevier, Amsterdam, **2005**, p. 620.

[20] F. Gunstone, *Fatty acid and lipid chemistry*. Blackie Academic & Professional, New York, **1996**, p. 252.

[21] Borges, M.E.; Diaz, I. Recent Developments of Heterogeneous Catalysts for Biodiesel Production by Oil Esterification and Transesterification Reactions: A Review. *Renew. Sustainable Energy Rev.,* **2012,** *16,* 2839-2849.

[22] Kingsley, K., Shevchuk, O., Voronov, S., Voronov, A. Features of Emulsion Copolymerization for Plant Oil-Based Vinyl Monomers and Styrene *Industrial Crops and Products*, **2017**, *109*, 274-280.

[23] A. Zosel, G. Ley Influence of Cross-Linking on Structure, Mechanical Properties, and Strength of Latex Films" *Macromolecules*, **1993**,26, 2222-2227.

CHAPTER 7. VERSATILE PLATFORM FOR CONTROLING PROPERTIES OF PLANT OIL-BASED LATEX POLYMER NETWORK[1]

7.1. Abstract

A series of latexes from acrylic monomers (made from olive, soybean, linseed, and hydrogenated soybean oils), significantly different in terms of fatty acid unsaturation, were synthesized using miniemulsion copolymerization with styrene. The number-average molecular weight and the glass transition temperature of the resulting copolymers with high levels of biobased content (up to approximately 60 wt %) depend essentially on the amount of unsaturation (the number of double bonds in triglyceride fatty acid fragments of plant oil-based monomers) in the reaction feed. When plant oil-based latex films are oxidatively cured, the linear dependence of the cross-link density on reaction feed unsaturation is observed. Dynamic mechanical and pendulum hardness measurements indicate that the properties of the resulting plant oil-based polymer network are mainly determined by cross-link density. On the basis of the linear dependence of the cross-link density on monomer feed unsaturation, it can be concluded that the latex network formation and thermomechanical properties can be adjusted by simply combining various plant oil-based monomers at certain ratios ("given" unsaturations) in the reaction feed. Assuming a broad variety of plant/vegetable oils available for new monomers synthesis, this can be considered as a promising platform for controlling properties of plant oil-based latex polymer networks.

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[1] The material in this chapter was co-authored by Zoriana Demchuk, Ananiy Kohut, Stanislav Voronov, and Andriy Voronov. Zoriana Demchuk had the primary responsibilities of synthesizing and characterizing a range of polymer latexes from olive, soybean, and linseed monomers and styrene. Zoriana Demchuk was involved in characterization of mechanical properties of latex films including DMA, DSC, and tensile testing. Ananiy Kohut helped with the synthesis of monomer from hydrogenated soybean oil that was used to create a matrix of different unsaturations in monomer mix. Zoriana Demchuk was involved in drafting and revising all versions of this chapter. Ananiy Kohut and Andriy Voronov provided a support in expressing the relationships between monomer unsaturation and thermo-mechanical properties of latex films. Published article can be found at https://doi.org/10.1021/acssuschemeng.7b04462.

7.2. Introduction

There is a constantly growing demand worldwide for using renewable bio-based raw materials to replace their petroleum-originated counterparts in the production of polymeric materials, including paints and coatings.[1,2] For the last two decades, abundant and easily replenishable plant oils have been considered as a low-cost chemical feedstock for making polymers.[3–5] Since the structure of plant oils is similar to long-chained petroleum-based hydrocarbons (with the difference being that plant oil triglycerides are much more unsaturated), the molecules of plant oils represent a potentially good alternative for synthesizing bio-based polymers.[6–10] The development of waterborne polymeric materials from plant oils, however, remains the challenging task because of the highly hydrophobic nature of triglycerides.[5] Widely employed for making such materials (latexes, in particular), free radical polymerization in emulsion requires finite levels of aqueous solubility for monomers to be diffused through the aqueous phase into growing polymer particles.[11] The extremely low aqueous solubility of plant oils limits the transport of oil-originated monomers in water and incorporation into the resulting (co)polymers during emulsion polymerization.[12,13] As a result, in the synthesis of most commercially available copolymers from plant oils for industrial coatings, free radical polymerization—including the emulsion process—is not employed due to the lack of the respective monomers.[14–20]

In prior work,[21] soybean oil has primarily been chosen as the chemical feedstock for synthesizing latexes in emulsion polymerization. The grafting of the acrylate monomers onto the soybean oil-based polyurethane network resulted in significant improvement of the thermal and mechanical properties of the synthesized hybrid latexes. The same group reported on the synthesis of high-performance waterborne polyurethane from soybean-oil-based polyols obtained in the ring-opening reaction of epoxidized soybean oil with methanol.[22] In another example, a waterborne polyurethane coating based on castor oil, cured with a crosslinker from aziridine has been reported,[23] as well as polyurethane wood coating based on rapeseed fatty acid methyl esters[24] and coating from waterborne epoxidized linseed oil.[25]

Recently, our group developed a one-step method of plant oil direct transesterification for the synthesis of new vinyl monomers from sunflower, linseed, soybean, and olive oil.[26–29] The rate of plant oil-based monomer (POBM) homopolymerization, where chain propagation coexists with the chain transfer on monomers, depends on the POBM chemical structure and is determined primarily by the amount of unsaturation in plant oil triglycerides. In the next step, stable latexes containing up to 50 wt% of bio-based content were synthesized using the emulsion or miniemulsion copolymerization of POBMs with methyl methacrylate and styrene.[27,29]

It is common for a renewable additive or ingredient to be designed using raw materials of both petroleum- and bio-based origins. A significant part of the prior work done with plant oils was focused on using the oils as the minor component of the resulting polymers.

This study shows the feasibility of latex synthesis with renewable POBMs, significantly different in terms of fatty acid unsaturation, as basic constituents of the latex polymers, with controlled thermal and mechanical properties. Inspired by previous findings, latexes based on vinyl monomers (POBMs) from olive oil (OVM), soybean oil (SBM), and linseed oil (LSM) were synthesized in a miniemulsion process using styrene as the comonomer. The unsaturation amount in the triglyceride fatty acids was utilized as a criterion in studying the resulting latex properties, including the influence of variation in monomer feed unsaturation on the crosslink density of latex films and, consequently, on polymer thermal and mechanical properties.

To provide a broader experimental range of feed unsaturation, an additional new acrylic monomer was synthesized from hydrogenated soybean oil with no unsaturation in the fatty acid moiety. Structural (configurational) similarity of hydrogenated soybean oil (HSO) and petroleum-based monomers that induce macromolecular side chain crystallinity (side chain > C_{12}) motivated us to synthesize a new acrylic monomer from HSO (hydrogenated soybean oil-based monomer, HSBM), and further elaborate on its feasibility for latex formation in combination with OVM, SBM, or LSM. Various amounts of HSBM (0–20 wt. %) were added into the monomer feed to investigate whether changes in the feed unsaturation amount results in crosslink density (network structure) variation, leading to a corresponding alteration in the properties of crosslinked latex films.

7.3. Materials and Methods

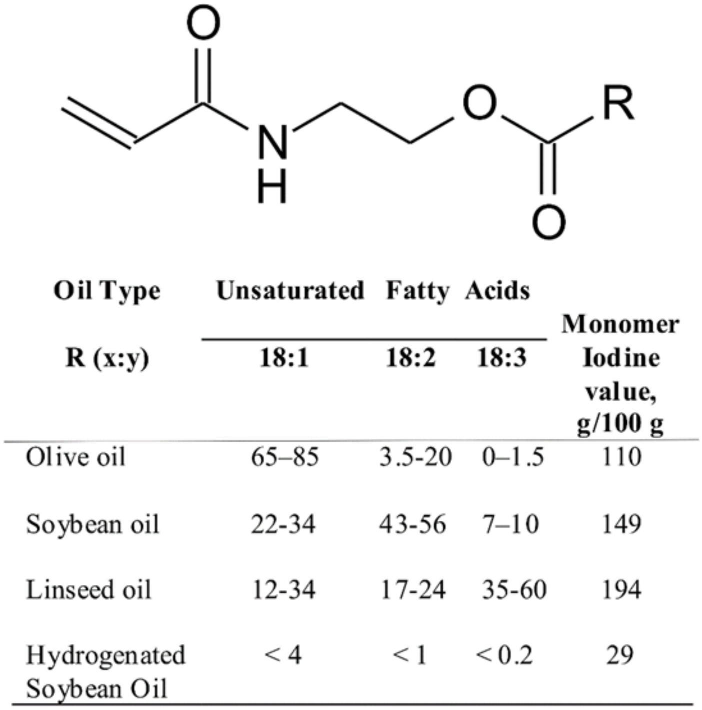
7.3.1. Materials

Soybean oil (Crisco; The J.M. Smucker Company, Orville, OH), olive oil (Bertolli; Houston, TX), linseed oil (Sunnyside Corp., Wheeling, IL), hydrogenated soybean oil (Koster Keunen, Watertown, CT), N-(hydroxyethyl)acrylamide (HEAAm; TCI America), and sodium dodecyl sulfate (SDS, VWR; Solon, OH), were used as received. 2,2’-azo-bis(2-methyl-propionitrile) (AIBN; Sigma–Aldrich, St. Louis, MO) was purified with recrystallization from methanol. Styrene (Sigma-Aldrich; St. Louis, MO) was distilled under a vacuum to remove the inhibitor and was then stored in a refrigerator. All solvents that we used were reagent grade or better and were used as received. Deionized water was used for all reactions (MilliQ, 18 MΩ).

7.3.2. Synthesis of POBM

The synthesis of POBMs from olive, soybean, and linseed oil with N-(hydroxyethyl) acrylamide (OVM, SBM, and LSM, respectively) was previously reported by the current research group.[27–29] In brief, about 115 g of N-(hydroxyethyl)acrylamide was added to 150 g of each plant oil (with acrylamide alcohol to triglyceride molar ratio of 5.9 to 1), 150 mL of tetrahydrofuran, and 0.1 g of 2,6-di-tert-butyl-p-cresol in a two-neck 500 mL round-bottomed flask equipped with a mechanical stirrer. Each reaction mixture was heated up to 40 °C in the presence of a catalytic amount of ground sodium hydroxide (1.5 g) and slowly added to the reaction mixture with continuous stirring. The reaction mixture was stirred at 40 °C until complete homogenization (approximately 3 h) and was allowed to remain overnight at room temperature. The reaction mixture was diluted with CH_2Cl_2, purified by washing with brine, treated with magnesium sulfate, and dried under a vacuum, yielding about 170 g of acrylic monomer (94–96% of the theoretical yield). The resulting monomers contain one acrylic double bond linked to one fatty chain, which varied between fully saturated, mono-, and poly-unsaturated, depending on the plant oil composition (Fig. 7.1).

Using the same reaction pathway, new acrylic monomer from hydrogenated soybean oil (HSBM) was synthesized. For this purpose, HSO with a significantly reduced to virtually no unsaturation in the HSO triglycerides (down to 0.5% wt.) was used in the transesterification reaction with N-(hydroxyethyl) acrylamide at temperature 50°C to synthesize HSBM.



Oil Type	Unsaturated Fatty Acids			Monomer Iodine value, g/100 g
R (x:y)	18:1	18:2	18:3	
Olive oil	65–85	3.5-20	0–1.5	110
Soybean oil	22-34	43-56	7–10	149
Linseed oil	12-34	17-24	35-60	194
Hydrogenated Soybean Oil	< 4	< 1	< 0.2	29

Figure 7.1. POBM molecular structure, typical chemical compositions of the plant oils used in this study in percentages and experimental iodine value for each monomer. R (x:y) is the structure of the fatty acids (x is the number of carbon atoms in the fatty acid chain, and y is the number of double bonds in the fatty acid).

7.3.3. Synthesis of POBM-Based Latexes Using Miniemulsion Copolymerization

To synthesize POBM-based latexes in copolymerization with styrene in miniemulsion, oil and aqueous phases were prepared. For the *oil phase,* a certain amount of each plant oil-based monomer—OVM, or SBM, or LSM (or combinations of OVM, or SBM, or LSM with HSBM) was mixed with styrene and 1.5 wt. % of initiator AIBN (based on monomers weight). For the *aqueous phase*, 4 wt. % sodium dodecyl sulfate (SDS) (emulsifier) and 0.02 mol/l NaCl were dissolved in water. For pre-emulsification, the *oil phase* was added dropwise to the *aqueous phase* and homogenized using a magnetic stirrer for 45 minutes at 1,200 r.p.m. The miniemulsion was prepared by ultra-sonicating the pre-emulsified mixtures for 180 seconds at a 90% amplitude (digital sonicator 500 Watt, 1/2” tip, 20 kHz, Q-Sonica, Newtown, CN) at room temperature. The resulting miniemulsion was purged with nitrogen, heated to 60^{o}C at 350 rpm, and polymerized for 5 hours under stirring. The total POBM content in feed was kept at 60 wt.% (the HSBM content was varied between 0 and 20 wt.% of the total POBM feed content). Miniemulsion copolymerization yielded latexes with a solid content of about 30-35%; the monomer conversion was 75-95%. Conversion varies with a reaction feed unsaturation amount (thus, the highest conversion was obtained in copolymerization of less unsaturated OVM).

7.3.4. Characterization of POBM-Based Latexes

For each copolymerization in miniemulsion, the characteristic unsaturation amount of the monomer feed and a resulting copolymer was calculated from the numbers of the C=C double bonds in the fatty acid fragments of the OVM, SBM, and LSM molecules. The numbers of the C=C double bonds (DB) were experimentally calculated from ^{1}H NMR spectroscopy data. The unsaturation amount of a monomer feed (U_{MF}) and a resulting copolymer (U_P) was calculated as

$$U_{MF} = DB_{UnsMon} \cdot C_{UnsMon} \tag{7.1}$$

$$U_P = DB_{UnsMon} \cdot C_{UnsMon} \tag{7.2}$$

where DB_{UnsMon} – numbers of the C=C double bonds in the fatty acid fragments of OVM, SBM, and LSM (“unsaturated” monomers); C_{UnsMon} – content of OVM, SBM, or LSM (“unsaturated” monomers) in the monomer feed or in a resulting copolymer.

Since each C=C double bond in the fatty acid fragments contains two hydrogen atoms, the number of these C=C double bonds was determined as

$$DB_{UnsMon} = H_{UnsMon}/2 \tag{7.3}$$

where H_{UnsMon} – number of the protons of the carbon−carbon double bonds in the fatty acid fragments at 5.37−5.38 ppm (1.98H for OVM,[26] 2.98H for SBM,[28] and 3.67H for LSM[26]).

For each latex sample, the copolymer composition and the average molecular weight were determined using ^{1}H NMR spectroscopy (AVANCE III HDTM 400 high-performance digital NMR spectrometer (Bruker, Billerica, MA), $CDCl_3$ as a solvent) and GPC (Waters Corporation modular chromatograph consisting of a Waters 515 HPLC pump, a Waters 2410 Refractive Index Detector, and a set of two 10 µm PL-gel mixed-B columns (temperature 40°C, tetrahydrofuran (THF) as the carrier solvent). The solid content of the synthesized POBM-based latexes was determined gravimetrically after drying the samples at 110 ^{o}C. The glass transition temperature of the resulting latexes was determined via modulated differential scanning calorimetry (MDSC) using a TA Instruments Q1000 calorimeter. Dry nitrogen was purged through the sample at a flow rate of 50 mL/minute. The samples were subjected to an underlying heating rate of 10^{o}C/min.

7.3.5. POBM-Based Latex Crosslinked Films

POBM-based latex films were prepared using a drawdown bar of 8 mil in thickness on cleaned glass panels. Coatings were dried at elevated temperature for a certain period of time. The curing of the polymer films was performed in two ways. The first one involved films from less unsaturated OVM- and SBM-based latexes (U_P = 0.4–0.7). In this case, films were drowned onto the steel substrate and placed in an oven for 5 hours. The second way involved films from more unsaturated LSM-based latexes with $U_P > 0.7$, where a one hour shorter curing cycle was employed. The crosslinking was justified by gel-content measurements of films performed with a good solvent for the resulting copolymers. For each POBM-latex film, the gel content (fraction of crosslinked polymer) was determined using the Soxhlet method after exhaustive extraction with toluene for 24 hours. The weight of the film at the end of each extraction cycle was considered to be a crosslinked fraction.

The dynamic mechanical behavior (storage and loss modulus) of the crosslinked latex films was determined using a dynamic mechanical analyzer (TA Instruments Q800 with tensile mode and a heating rate of 5°C/minutes. Samples of films with a typical size of 13 mm x 5 mm (length x width) and 0.05 mm of thickness were used for testing. The glass transition temperature of the resulting films was measured as a peak at $tan\ \delta$ curve, which corresponds to the "leather-like" midpoint between glassy and rubbery states of a polymer film.

The crosslink density, $\boldsymbol{\upsilon}$ and the effective molecular weight between crosslinks M_c was calculated using rubber elasticity theory.[4] According to this theory, for the elastomer with a network structure, Young's modulus E is proportional to the crosslink density and the average number of crosslinks per unit volume as $E = 3\boldsymbol{\upsilon}RT = 3dRT/M_c$ at small deformations,[30] where R is the gas constant, d is the polymer density, M_c is the effective molecular weight between crosslinks. To determine the density of polymer samples, specimens of a certain dimension of 10x15x0.05 mm^3 were prepared from the samples for DMA. Using a digital balance (0.0001 g accuracy), the mass of the samples was determined. The exact dimensions of the samples were determined using a caliper (accuracy 0.01 mm) to calculate the volume. From the volume and mass data, the density for each polymer sample was calculated.

The tensile strength and the elongation at break $\mathcal{E}_b$ of the latex films were determined using stress/strain measurements in an Instron testing machine 2710–004 with a crosshead speed of 5 mm/minute and a maximal load of 500 N at ambient temperature. Rectangle samples with a size of approximately 25 mm x 5 mm (length x width) were used. At least five replicates of each latex sample were used to obtain an average value.

The evaluation of sample hardness was performed using a Pendulum Hardness tester, according to ASTM D 4366. The principle is based on measuring the damping of a pendulum oscillating on the latex film. The damping time (in sec) of a pendulum was taken as a hardness of the film.

7.4. Results and Discussion

It was shown in our earlier work[27] that the POBMs' reactivity in copolymerization is close (the $Q-e$ parameters vary between Q = 0.41–0.43 and e = 0.09–0.18). This can be explained by similarities in the structure of the POBM molecules, namely the presence of the same acrylamide moiety $CH_2=CH–C(O)NH–$ that participates in chain growth. Besides, the POBM molecules all contain long fatty acid fragments with a different number of isolated double bonds (18:1, 18:2, 18:3), which form side chains of the macromolecules. It should be expected that varying the ratio of different POBMs with different unsaturation amounts in a monomer feed would allow for the formation of copolymers with a controlled unsaturation. Following this concept, to provide a broader experimental feed unsaturation amount, we synthesized the new acrylic monomer with no unsaturation in the fatty acid moiety (HSBM) and used the HSBM in miniemulsion copolymerization with styrene and POBMs.

Having a side-saturated aliphatic group C_{18}, HSBM belongs to monomers forming comb-like macromolecules being able to organize into crystalline domains.[34-36] Typically, long-chain hydrocarbons with no functional groups form finely ordered microcrystalline structures with the type of crystal determined by the chain length. At the same time, it is well-established that long-side chained vinyl homopolymers having linear side fragments in excess of 10–12 carbon atoms and over can form controlled ordered crystalline structures[37–39] with better chemical resistance, low flammability, a high modulus, and a range of practical applications.[40–43]

In this study, there were two purposes of adding HSBM into the initial monomer mixture for polymer synthesis. The first was to vary the monomer feed unsaturation to determine whether it results in variation in the physicomechanical properties of the crosslinked latex network. The second was to investigate whether the similarity of HSBM to long-side chain petroleum-based monomers can have an additional effect on the properties of plant oil-based latex polymers.

For the synthesis of latexes, emulsion and miniemulsion polymerization processes are conventionally employed. Miniemulsion polymerization is widely used for the (co)polymerization of poorly water-soluble monomers. Even extremely hydrophobic fluorinated monomers can be easily polymerized and copolymerized using miniemulsions.[33] Considering the hydrophobicity of POBMs and HSBM and their limited aqueous solubility, the miniemulsion process was employed in this study.

Latexes from an initial monomer mixture containing high OVM, SBM, or LSM levels (40–60 wt%), also in combination with HSBM (0–20 wt.%), and styrene (40 wt.%) were synthesized using miniemulsion polymerization at 60°C under stirring (Table 7.1).

Synthesized latexes with an average particle size of 60–80 nm exhibit high stability at room temperature within several months. The characteristics of the resulting POBM-based latex polymers are shown in Table 7.1. As it was determined using ^{1}H NMR spectroscopy, the plant content in the latex copolymers ranges from 50–55 wt.% regardless of an initial unsaturation in monomer feed (U_{MF}); the waste majority (80–95%) of double bonds in POBM fatty fragments are retained during the miniemulsion polymerization (shown by values of unsaturation in polymer U_P in Table 7.1). This indicates that fatty acid double bonds are readily available for post-polymerization reactions, particularly the cross-linking of latex films. These findings are in good agreement with our previous results on the POBM homopolymerization in toluene solution. It was shown by ^{1}H NMR spectroscopy that in comparison with the monomers, the number of protons of the fatty acid carbon−carbon double bonds almost does not change after the polymerization (3.65 H in poly(LSM) vs. 3.67 H in LSM and 1.97 H in poly(OVM) vs. 1.98 H in OVM).[26]

The molecular weight of the latex copolymers decreases in a range corresponding to the increasing unsaturation of POBM (Table 7.1). A similar effect was observed during copolymerization in solution by increasing the fraction of plant oil-monomers in the initial mixture, as our group reported elsewhere.[27–29] The decrease of M_n can be explained by the effect of degradative chain transfer on the POBM monomer provided by differing numbers of allylic hydrogen atoms in the molecules.[27] The values of chain transfer constant on monomers determined earlier[26] clearly depend on the monomer structure (number of C−H groups in the α-position of the fatty acid double bonds) and increases with an increasing monomer unsaturation. The extent of the chain transfer reaction is obviously more pronounced for the most unsaturated LSM. As shown in Table 7.1, the presence of the saturated HSBM in the initial feed does not impact the molecular weight of latex polymers. This monomer does not contain allylic hydrogen atoms in fatty fragments and does not undergo a chain transfer reaction.

The obtained in DSC measurements T_g values indicate that variation in the bio-based content in resulting macromolecules changes, to a large extent, the thermal properties of latex copolymers.

Table 7.1. POBM-based latex polymer properties

Plant content (feed), wt.%*		Plant content (polymer), wt.%	U_P/U_{MF}, polymer/feed	T_g, °C	M_n, g/mol
OVM	HSBM				
60	0	56.5	0.56/0.59	18	108,500
55	5	55.8	0.51/0.54	27	95,500
50	10	53.8	0.44/0.50	32	105,800
45	15	57.1	0.42/0.45	33	94.000
40	20	56.1	0.37/0.40	33	119,100
SBM	HSBM				
60	0	56.1	0.84/0.89	5	39,100
55	5	54.2	0.74/0.82	6	45,300
50	10	49.6	0.62/0.75	12	48,800
45	15	54.6	0.61/0.67	14	50,000
40	20	48.7	0.48/0.60	19	30,700
LSM	HSBM				
60	0	49.5	0.91/1.10	-5	27,100
55	5	54.1	0.91/1.01	6	30,000
50	10	51.7	0.79/0.92	5	30,100
45	15	48.7	0.67/0.83	19	33,500
40	20	46.2	0.57/0.74	19	39,000

*Styrene content (feed) is 40 wt. %.

Overall, the presence of POBM fragments decreases the glass transition temperature in comparison to polystyrene (T_g = 110 °C) due to the internal plasticization effect of the copolymers (Table 7.1). It can be concluded that a controlled number of the non-polar long fatty acid side chains decreases intermacromolecular interactions and allows for the tuning of T_g of the POBM copolymers**.** At the same time, an increasing HSBM content in the monomer feed results in higher T_g values if compared to latexes with no saturated monomer (Table 7.1). It might be reasonable to explain the latter effect by the formation of crystalline regions in copolymers containing different amounts of saturated fatty fragments. Fig. 7.2A presents the DSC thermogram of HSBM homopolymer (synthesized using 0.5 M monomer, 0.04 M AIBN in toluene solution at 75 °C for 2 h). A typical thermogram shows an endothermic peak at approximately 71°C, which can be attributed to the melting of crystals formed by the long alkyl chain fragments of the HSBM. Although the influence of crystallinity on the T_g of polymers is not readily predictable,[37,44] for many homopolymers crystallites are considered as tying certain chains together, restricting chain segmental mobility, and thus, the glass transition temperature raises.[37,44,45–48] The latter effect of HSBM fragments is interesting because it provides an easy experimental tool for controlling the T_g of the plant oil-based latex polymers in this work (Table 7.1).

Mechanical properties, such as hardness, elongation at break $\mathcal{E}_{\mathrm{b}}$, and Young's modulus E, are considered when polymeric materials for specific purposes are designed by crosslinking. Those properties essentially depend on the structure of a polymer network, particularly crosslink density, $\boldsymbol{\nu}$. The mobility of polymer chains in a crosslinked network is a function of $\boldsymbol{\nu}$ and determines the mechanical and thermal properties of polymeric materials.

Based on the U_P value (Table 7.1), the drawn down latex films with characteristic U_P = 0.7–0.9 were crosslinked at elevated temperatures for 4 hours, while a one hour longer crosslinking cycle was employed for latexes with U_P = 0.4–0.7. After curing, the resulting films exhibited crosslinking of 75–82% determined by measuring the gel content for each latex sample (selected POBM-based latex films are shown on Figure D1 in Appendix D).

The effect of the U_{MF} on the experimentally determined $\boldsymbol{\nu}$ and the effective molecular weight between crosslinking nodes (M_c) of cured films is shown in Table 7. 2. Increasing the U_{MF} led to an almost linear increase in the $\boldsymbol{\nu}$ (Fig. 7.2B) and, respectively, to a decrease in M_c (Table 7.2). The presence of the HSBM in the feed decreases the unsaturation of both the monomer feed and polymer and, as it can be expected, results in a decrease in the crosslink density for each comonomer pair, as it increases the length of the linear segments between the crosslinking nodes. The obtained result shows that the given value of unsaturation amount of a monomer feed U_{MF} provides a particularly nice compromise in the control and optimization of the crosslink density for POBM-based latex films.

As can be seen from Fig. 7.2C, the pendulum hardness of the crosslinked latex films in general changes proportionally with the $\boldsymbol{\upsilon}$, and increases if the polymer network is made from more unsaturated plant oil-based monomers (especially, LSM). It is worth pointing out that while elastic modulus E for less unsaturated OVM-based films increases with an increasing HSBM content (Table 7.2), both SBM- and LSM-based materials show the opposite trend. Table 7.2 data indicate that OVM-based films are more flexible, as the elongation at break ($\mathcal{E}_b$) data demonstrate. Increasing the HSBM content increases the copolymer crystallinity and reinforces the material. In turn, more unsaturated fragments of SBM and LSM in the copolymers present a spatial arrangement that diminishes the packing ability of macromolecules due to the macromolecular configuration. As a result, the configurations of SBM- and LSM-based macromolecules can interfere with the crystal packing efficiency of HSBM fragments more than is found in macromolecules made from OVM. This could explain the decreasing elastic modulus E with an increase in the HSBM content for latexes based on more unsaturated SBM and LSM monomers.

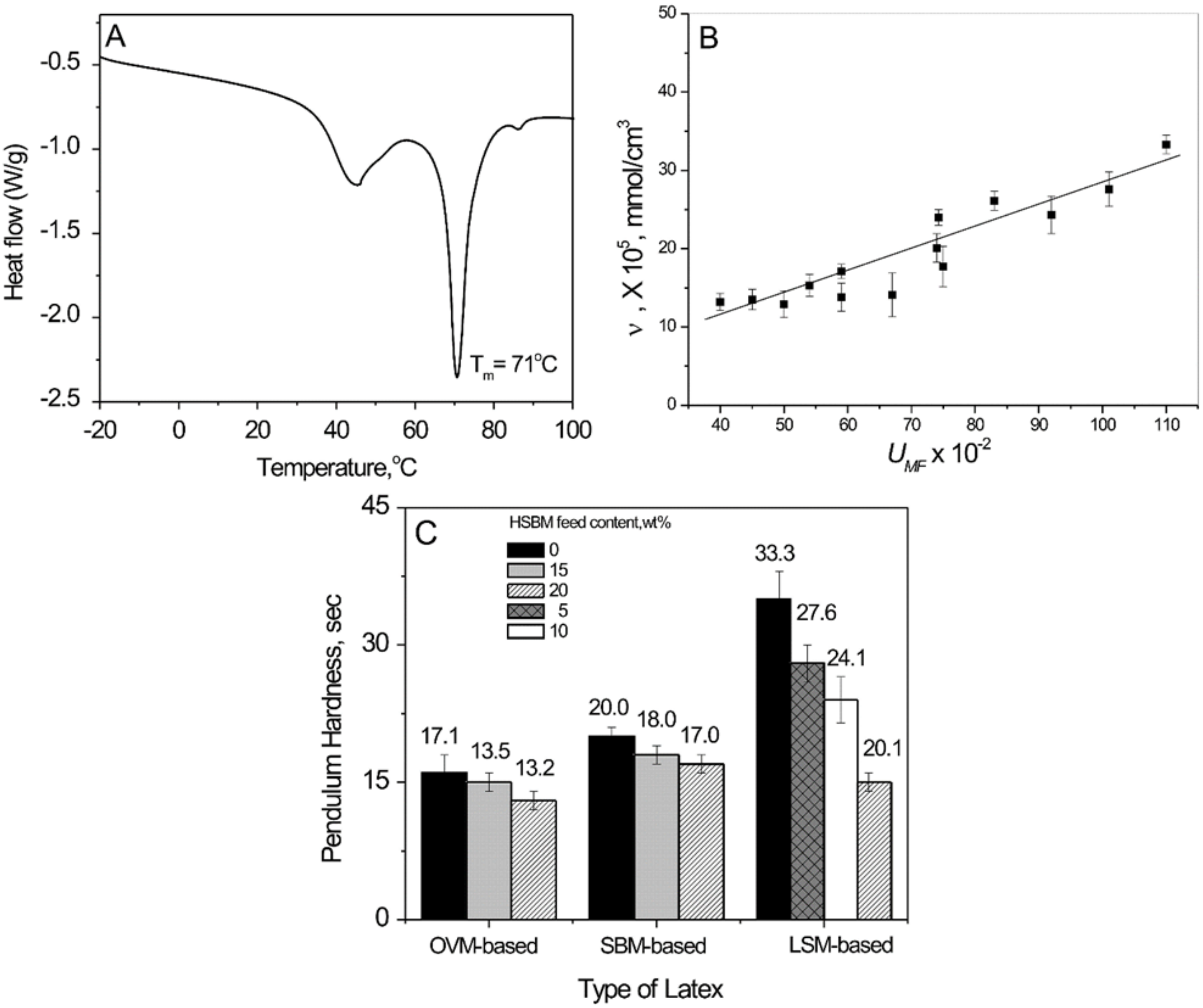


Figure 7.2. DSC plot of the HSBM homopolymer (A), the crosslinking density ***υ*** of POBM latex films with different unsaturations in the monomer feed (B), the influence of the POBM nature and HSBM content on the pendulum hardness, (C) the number above each bar corresponds to the value of ***υ***·105)

Table 7.2. Cured POBM-latex films properties

Plant content (feed), wt. %*		Plant content (polymer), wt.%	Tg, °C	$\upsilon \cdot 10^5$ mol/cm^3	M_c, *g/mol*	*E*, MPa	ε_b, %
OVM	HSBM						
60	0	56.5	53	17.1	5,580	2.1	275
55	5	55.8	51	15.3	6,250	1.3	245
50	10	53.8	54	12.9	7,400	3.7	205
45	15	57.1	53	13.5	7,070	7.3	228
40	20	56.1	51	13.2	7,240	11.3	203
SBM	HSBM						
60	0	56.1	44	26.1	3,720	6.3	128
55	5	54.2	51	18.6	5,220	4.7	115
50	10	49.6	49	17.7	5,500	3.4	101
45	15	54.6	48	14.1	6,880	3.5	120
40	20	48.7	50	13.8	7,040	2.9	103
LSM	HSBM						
60	0	49.5	46	33.3	2,990	4.6	133
55	5	54.1	34	27.6	3,610	3.3	146
50	10	51.7	47	24.3	4,100	3.8	108
45	15	48.7	39	24.0	4,170	2.4	134
40	20	46.2	41	20.1	4,950	1.8	160

*Styrene content (feed) is 40 wt. %.

Stress-strain diagrams and the change of tan δ with temperature for plant oil-based latex films are shown in Figure D2–D4 in Appendix D.

Hence, the thermomechanical properties of POBM-based latex films depend considerably on the crosslinking density of the polymer network that can be controlled by the nature of incorporated plant oil-based fragments, including saturated fragments of the newly synthesized HSBM.

7.5. Conclusion

Series of latexes from acrylic monomers (made from olive, soybean, linseed, and hydrogenated soybean oils), significantly different in terms of fatty acid unsaturation were synthesized using miniemulsion copolymerization with styrene. Newly synthesized monomer from hydrogenated soybean oil (HSBM) was used to provide a broader range of triglycerides' fatty acids unsaturation in the copolymerization, and determine its' impact on the mechanical and thermal properties of crosslinked latex films, as well as to investigate the effect of HSBM structure (ability of long alkyl fragments to form crystalline domains) on latex polymer properties.

The number-average molecular weight and the T_g of the resulting copolymers with high levels of bio-based content (up to approximately 60 wt. %) depend essentially on the amount of unsaturation (the number of double bonds in triglyceride fatty acid fragments of plant oil-based monomers) in the reaction feed. When plant oil-based latex films are oxidatively cured, the linear dependence of the crosslink density on reaction feed unsaturation is observed. Dynamic mechanical and pendulum hardness measurements indicate that the properties of the resulting plant oil-based polymer network are mainly determined by crosslink density.

Based on the linear dependence of the crosslink density on monomer feed unsaturation, it can be concluded that the latex network formation and thermomechanical properties can be adjusted by simply combining various plant oil-based monomers at certain ratios ("given" unsaturations) in the reaction feed. Assuming a wide variety of plant/vegetable oils available for the synthesis of new monomers synthesis, this can be considered as a promising platform for controlling properties of plant oil-based latex polymer networks.

7.6. References

[1] Bozell, J.J. Feedstocks for the future – biorefinery production of chemicals from renewable carbon *Clean: Soil, Air, Water*, **2008**, *36*, 641–647. DOI: 10.1002/clen.200800100

[2] Williams, C.K.; Hillmyer, M.A. Polymers from renewable resources: A perspective for a special issue of polymer reviews *Polym. Re*v., **2008**, *48*, 1–10. DOI: 10.1080/15583720701834133

[3] Ying Xia; Larock, R.C. Vegetable oil-based polymeric materials: Synthesis, properties, and applications *Green Chem*, **2010**, 12, 1893–1909. DOI:10.1039/C0GC00264J

[4] Can, E.; Wool, R.P.; Kusefoglu, S. Soybean- and Castor-oil-based thermosetting polymers: Mechanical properties *J.Appl.Polym.Sci.*, **2006**, *102*, 1497–1504. DOI: 10.1002/app.24423

[5] Van De Mark, M.R.; Sandefur, K. Vegetable oils in paint and coatings, in: S.Z. Erhan (Ed.), Industrial Uses of Vegetable Oils, AOCS Press, Illinois, **2005**, pp. 149–168.

[6] Verhe, R.G. Industrial products from lipids and proteins, in Renewable Bioresources: Scope and Modification for Non-Food Applications **2004**, Stevens C.V.; Verhe R.G., John Wiley & Sons, Ltd, Chichester, 328 p.

[7] Guner, F.S.; Yagci,Y.; Erciyes, A.T. Polymers from triglyceride oils *Prog.Polym.Sci.*, **2006**, *31* ,633-670. DOI: 10.1016/j.progpolymsci.2006.07.001

[8] Sharma, V.; Kundu, P.P. Addition polymers from natural oils—A review. *Prog.Polym. Sci.*, **2006**, *31*, 983–1008. DOI: 10.1016/j.progpolymsci.2006.09.003.

[9] Wool, R.P.; Sun, X.S. Bio-Based Polymers and Composites, **2005**, Elsevier, Amsterdam, 620 p.

[10] Gunstone, F. Fatty Acid and Lipid Chemistry, **1996**, Blackie Academic & Professional, New York, 252 p.

[11] Ugelstad, J.; Hansen, F.K. Kinetics and mechanism of emulsion polymerization *Rubber Chem. and Technology*, **1976**, *49 (3)*, 536–609. DOI: 10.5254/1.3534976

[12] Chern, C.S. Emulsion polymerization mechanisms and kinetics *Prog.Polym.Sci.*, **2006,** *31*, 443–486. DOI: 10.1016/j.progpolymsci.2006.02.001

[13] Booth, G.; Delatte, D.E., Thames, S.F. Incorporation of drying oils into emulsion polymers for use in low-VOC architectural coatings *Ind. Crops and Products*, **2007**, *25*, 257–265. DOI: 10.1016/j.indcrop.2006.12.004

[14] Bailey, A.E. Bailey's Industrial Oil and Fat Products, **1996**, Wiley, New York, 560 p.

[15] Johnson, R.W.; Fritz, E.E. Fatty Acids in Industry, **1989**, Marcel Dekker, New York, 667 p.

[16] Pan, X.; Sengupta, P.; Webster, D.C. High biobased content epoxy–anhydride thermosets from epoxidized sucrose esters of fatty acids *Biomacromolecules*, **2011**, *12*, 2416–2428. **DOI:** 10.1021/bm200549c

[17] Lligadas, G.; Ronda, J.C.; Galia, M.; Cádiz, V. Plant Oils as Platform Chemicals for Polyurethane Synthesis: Current State-of-the-Art *Biomacromolecules*, **2010**, *11*, 2825–2835. **DOI:** 10.1021/bm100839x

[18] Wang, Z.; Zhang, X.; Wang, R.; Kang, H.; Qiao, B.; Ma, J.; Zhang L.; Wang, H. Synthesis and characterization of novel soybean-oil-based elastomers with favorable processability and tunable properties *Macromolecules*, **2012**, *45*, 9010–9019. **DOI:** 10.1021/ma301938a

[19] Türünç, O.; Meier, M.A. The thiol-ene (click) reaction for the synthesis of plant oil derived polymers *Eur. J. Lipid Sci. Technol*, **2013**, *115*, 41–54. DOI: 10.1002/ejlt.201200148

[20] Raquez, J.M.; Deléglise, M.; Lacrampe, M.F.; Krawczak, P. Thermosetting (bio)materials derived from renewable resources: A critical review *Prog. Polym. Sci.*, **2010**, *35*, 487–509. DOI: 10.1016/j.progpolymsci.2010.01.001

[21] Lu, Y; Larock, R.C. New Hybrid Latexes from a Soybean Oil-Based Waterborne Polyurethane and Acrylics via Emulsion Polymerization *Biomacromolecules*, **2007**, *8*, 3108–3114. DOI: 10.1021/bm700522z.

[22] Lu,Y.; Larock, R.C. Soybean-Oil-Based Waterborne Polyurethane Dispersions: Effects of Polyol Functionality and Hard Segment Content on Properties *Biomacromolecules*, **2008**, *9*, 3332–3340. DOI: 10.1021/bm801030g/

[23] Philipp, C.; Eschig, S. Waterborne polyurethane wood coatings based on rapeseed fatty acid methyl esters *Prog. Org. Coat.*, **2012**, *74*, 705–711. DOI: 10.1016/j.porgcoat.2011.09.028

[24] M.Y. Shah, S. Ahmad, Waterborne vegetable oil epoxy coatings: Preparation and characterization *Prog. Org. Coat.*, **2012**, *75*, 248–252. DOI: 10.1016/j.porgcoat.2012.05.001

[25] Y. Xia, R.C. Larock, Castor-Oil-Based Waterborne Polyurethane Dispersions Cured with an Aziridine-Based Crosslinker *Macromol. Mater. Eng.*, **2011**, *296*, 703–709. DOI: 10.1002/mame.201000431.

[26] Demchuk, Z., Shevchuk, O., Tarnavchyk, I., Kirianchuk, V., Kohut, A., Voronov, S., Voronov, A. Free radical polymerization behavior of the vinyl monomers from plant oil triglycerides, *ACS Sustainable Chemistry & Engineering*, **2016**, *4 (12)*, 6974–6980. DOI: 10.1021/acssuschemeng.6b01890

[27] Demchuk, Z., Shevchuk, O., Tarnavchyk, I., Kirianchuk, V., Lorenson, M., Kohut, A., Voronov, S., Voronov, A. Free-radical copolymerization behavior of plant-oil-based vinyl monomers and their feasibility in latex synthesis *ACS Omega*, **2016**, *1(6)*, 1374–1382. DOI: 10.1021/acsomega.6b00308

[28] Tarnavchyk, I., Popadyuk, A., Popadyuk, N. Voronov, A. Synthesis and free radical copolymerization of vinyl monomer from soybean oil *ACS Sustainable Chemistry & Engineering*, **2015,** *3(7)*, 1618–1622. DOI: 10.1021/acssuschemeng.5b00312

[29] Kingsley, K., Shevchuk, O., Voronov, S., Voronov, A. Features of Emulsion Copolymerization for Plant Oil-Based Vinyl Monomers and Styrene *Industrial Crops and Products*, **2017**, *109*, 274-280. DOI: 10.1016/j.indcrop.2017.08.043

[30] Van Krevelen, D.W.; Hoftyzer, P. Properties of Polymers: Their Estimation and Correlation with Chemical Structure, Elsevier, Amsterdam, **1976**.

[31] Tsavalas, J.G., Gooch, J.W., Schork, F.J. Water-based crosslinked coatings via miniemulsion polymerization of acrylic monomers in the presence of unsaturated polyester resin *J.App.Polym.Sci*. **2000**, *75*, 916–927.

[32] Ugelstad, J.; El-Aasser, M.S. Vanderhoff, J.W. Emulsion polymerization: initiation of polymerization in monomer droplets *J.Polym.Sci.Pol.Lett*, **1973**, *11*, 503-513. DOI: 10.1002/pol.1973.130110803

[33] Schork, F.J.; Luo, Y.; Smulders, W.; Russum, J.; Butte, A.; Fontenot, K. Miniemulsion Polymerization *Adv.Polym.Sci.* **2005**, *175*, 129–255. DOI: 10.1007/b100115

[34] Holger, G.A.; Winkler, J. Crystal-Growth Poisoning of *n*-Paraffin Wax By Polymeric Additives and its Relevance to Polymer Crystallization Mechanisms *Nature* **1965**, *207*,719-721. DOI:10.1038/207719a0.

[35] Subramanyam B.; Baruah, S.D.; Rahman, M.; Baruah, J.N.; Dass, N.N. Kinetic studies on the n-alkyl acrylate polymerization *J.Polym.Sci.Part A: Pol.Chem.* **1992**, *30*, 2531–2549. DOI: 10.1002/pola.1992.080301207

[36] Plate, N.A.; Shibaev, V.P. Comb-like polymers. Structure and properties *J.Pol.Sci: Macromolecular Reviews,* **1974**. *8(1),* 117-253.

[37] Nielsen, L.E. Mechanical Properties of Polymers, Reinhold, New York, **1962**.

[38] Wiley, R.H., Brauer, G.M. Refractometric determination of second-order transition temperatures in polymers. III. Acrylates and methacrylates *J.Polym.Sci.,* **1948**, *3*, 647-651. DOI: 10.1002/pol.1948.120030506

[39] Greenberg, S.A.; Alfrey, T. Side chain crystallization of n-alkyl polymethacrylates and polyacrylates *J.Am.Chem.Soc.,* **1954**, *76*, 6280-6285. **DOI:** 10.1021/ja01653a015

[40] Neher, H.T.; Bauer, L.V.N. Van Horne, V.L. US Pat., 2,600,422, **1952**.

[41] Popkin, A.H. US Pat., 2,604,453, **1952**.

[42] Miller, K.D.; Parker, L.C. US Pat., 3,675,671, **1972**.

[43] Exxon Research and Engineering Co., Ger.Pat., 2,613,315, **1976**.

[44] Shen, M., Eisenberg, A. Recent advances in glass transitions in polymers *Rubber Chem and Technol.*, **1970**, *43*, 95-155. DOI: 10.5254/1.3547241

[45] Newman, S.; Cox, W.P. The glass transition temperature of semicrystalline polymers *J.Pol.Sci.*, **1960**, *46*, 29-49. DOI: 10.1002/pol.1960.1204614704

[46] Read, B.E. Mechanical relaxation in some oxide polymers *Polymer*, **1962**, *3*, 529-542.

[47] Woods, D.W. Effects of Crystallization on the Glass–Rubber Transition in Polyethylene Terephthalate Filaments *Nature*, **1954**, *174*, 753-754. DOI:10.1038/174753b0

[48] Nielsen, L.E.; Landel, R.F. Mechanical Properties of Polymers and Composites; Marcel Dekker, New York, **1994**.

CHAPTER 8. SYNERGISTIC EFFECTS OF CARDANOL- AND HIGH OLEIC SOYBEAN VINYL MONOMERS IN MINIEMULSION POLYMERS[1]

8.1. Abstract

Along with characterization of vinyl monomers from high oleic soybean oil (HOSBM) and cardanol (CBM) in free radical (co)polymerization, a series of stable latexes based on various ratios of these fully renewable plant-based monomer mixtures have been synthesized using a miniemulsion process. The combination of aliphatic fatty acid fragments of HOSBM with aromatic CBM structure led to the formation of durable latexes from fully renewable feeds as well as the ability of the resulting cross-linked latex films to balance thermomechanical properties. Biobased latexes were synthesized from 10 to 75 wt. % of CBM and 25−90 wt. % of HOSBM in the feed, characterized and tested in films and coatings performances. The synergistic 16 effects of both the constituents in the films and coatings were observed. The incorporation of cardanol-based fragments enhances Young's modulus of the films, whereas the plant oil-based units contribute to softer and more flexible films. Even small (10 wt. %) fractions of CBM can provide noticeable strength to the soft latex polymer material based entirely on HOSBM. All cross-linked latex films in this study exhibit decent properties and performance in terms of pendulum and pencil hardness, water and solvent resistance, as well as adhesion to the steel substrate. To the best of our knowledge, latexes from fully renewable plant-based monomer mixtures have not been reported before in literature.

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[1] The material in this chapter was co-authored by Zoriana Demchuk, W.S. Jenifer Li, Hermella Eshete, Sylvain Caillol and Andriy Voronov. Zoriana Demchuk had performed the synthesis and characterization of range of plant-based latexes from high oleic soybean oil-based monomer and cardanol methacrylate. W.S. Jenifer Li and Sylvain Caillol had supported this research study by providing cardanol methacrylate synthesized by two-step process from cardanol. Zoriana Demchuk and Hermella Eshete were responsible for characterizing the mechanical properties of plant-based latex films and coatings.Zoriana Demchuk had primary responsibilities in drafting and revising all versions of this chapter. Sylvain Caillol and Andriy Voronov supported the research study by evaluation structure-property relationship of monomer structure on thermo-mechanical properties of latex matrials based on data collected by Zoriana Demchuk. Published article can be found at https://doi.org/10.1021/acssuschemeng.9b01137.

8.2. Introduction

For the past few decades, the industry has been looking for new methods of synthesizing polymers and polymeric materials from renewable resources. Using renewable ingredients in the production of biobased polymers can address concerns regarding the global lowering of oil feedstock reserves of fossil fuels while creating a positive environmental impact.[1] Additionally, polymeric materials synthesized from renewables offer a great range of application possibilities, with properties and performance which can compete and sometimes even outperform conventional petroleum-based polymers. In this regard, extensive research studies have been performed on the synthesis and polymerization of various biobased monomers, thus providing a broad platform for the utilization of the resulting polymers in coatings, plastics, adhesives, composites, etc.[2–5] Due to their worldwide availability, low cost, abundance, rich application potential, and renewable nature, plant oils and their derivatives are widely used in the synthesis of polymers for paints, coatings, thermosetting resins, polymer composites, etc. Biobased polymers from plant oil derivatives exhibit a wide range of thermo-physical and mechanical properties, from soft and flexible to hard and brittle, thus presenting a promising way to replace petroleum-based polymers with biobased polymeric counterparts.[6,7] The major components in plant oils are triglycerides, esters of glycerol, and three different fatty acids possessing various amounts of unsaturations (double bond fragments), which can be modified to yield new compounds, in particular, plant oil-based monomers.[8]

In recent years, the incorporation of acrylate groups and OH groups into plant oil molecular structures and the epoxidizing of plant oil fatty acid double bonds have been successfully demonstrated.[9,10] Furthermore, various newly synthesized plant oil-based monomers have been investigated in the formation of polymer latex materials through emulsion and miniemulsion processes.[11,12,16] The incorporation of plant oil-based monomers in copolymerization with conventional petroleum-based counterparts provides several benefits to the final copolymers such as plasticizing properties, the elimination of coalescence aids in latex applications, the reduction of minimum film formation temperature, and film-forming properties. The ability of fatty acid fragments to undergo autoxidation (due to the presence of allylic double bonds in resulting macromolecules) after latex application and yield the cross-linked polymer networks can balance the mechanical properties of final latex products, which can be beneficial as well.[13,17,20]

Another interesting plant-based renewable resource that has attracted a lot of attention in the past few years is cardanol. This is a byproduct of the cashew nut industry and refers to an aromatic class of organic compounds. Cardanol is extracted from the cashew nut shell liquid after its thermal treatment. The combination of a benzene ring and the long hydrophobic alkenyl fragments in its structure provides a lot of opportunities in terms of tuning material performance.[14] Due to its fascinating chemical structure, cardanol has multiple reaction sites, which can be used for further functionalization. Both cardanol and cardanol derivatives have been applied in the synthesis of materials for different applications, such as surfactants, plastics, thermosets, plasticizers, antioxidants, etc.[18–21] Cardanol was reported to be used in the synthesis of cardanol-based benzoxazine resin for biocomposite formation. [22] Also, cardanol methacrylates were applied in polymer synthesis for dental applications and provided a noticeable reduction of dentin permeability and resistance to acid exposure in the resulting materials.[23] We hypothesized that the synthesis of the emulsion polymers from cardanol- and plant oil-based monomers might provide opportunities to replace petroleum-based constituents in latex synthesis and reduce VOC content in the resulting polymeric materials. However, due to the highly hydrophobic nature of both the natural components, the synthesis of latexes using conventional emulsion polymerization can be challenging.

Recently, we reported on emulsion polymers, with a biobased content of up to 60 wt. %, synthesized in miniemulsion from new vinyl monomers derived from a variety of plant oils using a transesterification reaction.[15–17] The incorporation of plant oil-based fragments into the latex copolymers provided plasticization and hydrophobization, as well as improved the toughness of the final cross-linked latex polymer films. Nevertheless, with an increase in the plant oil-based content in the latex copolymers above 60 wt. %, an excessive softening of the polymeric material has been experienced to the point where it becomes "too soft" and thus is not applicable for latex film preparation. To be able to further increase the biobased content in the emulsion polymers without deteriorating the material properties and performance, cardanol methacrylate (CBM) was considered as a comonomer in the miniemulsion process with high oleic soybean oil-based (HOSBM) monomer. CBM was synthesized in a two-step reaction by cardanol hydroxyethylation and further methacrylation[24] and was copolymerized with methyl methacrylate to form latexes in miniemulsion.[25]

To benefit from the HOSBM and CBM chemical structures and their ability to undergo radical polymerization, this study combines both the newly synthesized biobased monomers in miniemulsion to yield latex copolymers with various ratios of CBM/HOSBM. It is expected that this fully renewable plant-based monomer feed will yield a range of new emulsion polymers with properties and performance enhanced with plasticizing HOSBM residues and strength-improving CBM fragments, acting synergistically. Additionally, the presence of unsaturated fragments in both the monomers provides an opportunity to cross-link latex films to different degrees and thus control the mechanical properties of the resulting polymer network. These aspects distinguish our work from previous studies. To the best of our knowledge, latexes from fully renewable plant-based monomer mixtures have not been reported in the literature.

8.3. Materials and Methods

8.3.1. Materials

High oleic soybean oil (Perdue Agribusiness LLC, Salisbury, MD), N-(hydroxyethyl) acrylamide (TCI America, Portland, OR), cardanol NX2026 (Cardolite), ethylene carbonate (99%, Aldrich), 1,5- diazabicyclo[4.3.0]non-5-ene (DBN, 98%, Aldrich), triethylamine (99.5%, Aldrich), methacrylic anhydride (94%, Aldrich), sodium hydroxide (98%, Alfa Aesar, Ward Hill, MA), sodium sulfate (99%, Aldrich) sodium dodecyl sulfate (VWR, Radnor, PA), and sodium chloride (ACS grade, VWR, Radnor, PA) were used as received. 2,2′-Azobis(2-methylpropionitrile) (AIBN; Sigma-Aldrich, St. Louis, MO) was purified with recrystallization from methanol. All solvents (tetrahydrofuran, dichloromethane, methanol) were reagent grade or better and were used as received. Deionized water was used for all reactions (Milli-Q, 18 MΩ).

8.3.2. Synthesis of HOSBM

High oleic soybean oil-based monomer (HOSBM) was synthesized via a one-step transesterification reaction of crude high oleic soybean oil with N-hydroxyethyl acrylamide (HEAA) in the presence of 1.5 wt. % of sodium hydroxide (NaOH) as a catalyst. The resulting monomer mixture was purified using 5 wt. % brine solution, dried under a magnesium sulfate layer with continuous stirring, and rotary evaporated to remove the solvent. The detailed procedure of the plant oil-based monomer synthesis can be found in reference [26].

8.3.3. Synthesis of CBM

Cardanol methacrylate (CBM) was synthesized using the facile one-pot, two-step reaction through the hydroxyethylation of the phenolic hydroxyl group of pure cardanol, followed by a methacrylation step of the cardanol derivative. A detailed description of CBM synthesis and characterization can be found in reference. [24] Characterization of HOSBM and CBM. The synthesized HOSBM and CBM were characterized using ^{1}H NMR spectroscopy (AVANCE III HDTM 400 high performance digital NMR spectrometer, BRUKER, Billerica, MA) using d-dichloromethane as a solvent to confirm the chemical structures of the monomers.

8.3.4. Iodine Value

Using a standard procedure, iodine value (IV) was determined in order to characterize biobased monomers in terms of the amount of unsaturation. A 0.1 g portion of each monomer sample was placed in a 500 mL glass flask and dissolved in 20 mL of CCl_4. A 25 ml portion of Wijs solution was added to the mixture, and the mixture was kept in the dark place for 1 h at 20 °C. After the incubation period, 30 mL of 0.1 N KI solution was mixed with 100 mL of cold boiled water, and the mixture was added to the flask. The resulting solution was titrated with 0.1 N sodium thiosulfate solution with constant mixing. The addition of $Na_2S_2O_3$ was continued until the yellow color almost disappeared; 3 mL of a starch indicator solution was added to the flask, and the titration continued until the solution became white. A blank test was conducted at the same time. Iodine value was calculated as grams of iodine absorbed per 100 g of sample using the following formula:

$$IV = \frac{(V_B - V_S) \cdot N \cdot 12.69}{m_s} \tag{8.1}$$

where V_B and V_S are volumes of $Na_2S_2O_3$ solution used for the titration of the blank and monomer samples, respectively; N- normality of $Na_2S_2O_3$ solution; m_s – mass of the monomer sample used for titration.

8.3.5. Free Radical (Co)Polymerization of CBM and HOSBM in Solution

For homopolymerization, HOSBM and/or CBM and AIBN were dissolved in toluene. The reaction mixture was purged with nitrogen at room temperature and heated at 75 °C for 5 h under continuous stirring.

To determine the reactivity of CBM and HOSBM in copolymerization, biobased monomers were copolymerized with styrene (St) at various ratios ([CBM or HOSBM]: St - 15:85, 30:70, 45:55, 55:45, 70:30 and 85:15, wt. %) in toluene at 75°C under a nitrogen blanket for 3 h until total monomer conversion of 10−15% was reached. Copolymer samples (0.5 g) were taken out from the flask to check the extent of the copolymerization using gravimetry after precipitation of the copolymers in methanol and drying under nitrogen flow.

Polymers synthesized in solution were precipitated in a large excess of methanol and purified three times by reprecipitation. The final (co)polymer samples were dried under nitrogen flow until constant mass. The average number and weight molecular weight of the (co)polymers were determined by gel permeation chromatography (GPC), and their chemical structure and composition were characterized by ^{1}H NMR spectroscopy.

8.3.6. Biobased Latex Synthesis

A series of biobased latexes were synthesized using miniemulsion polymerization of CBM and HOSBM at various ratios. To synthesize latexes with 30 % solids content, the oil phase was prepared by mixing certain amounts of HOSBM (3.75-13.5 g) and CBM (1.5-11.25 g) and 0.23 g of AIBN (1.5 wt.% of oil phase) as initiator.

The aqueous phase was prepared by dissolving 0.6 g of surfactant (SDS, 4 wt.%) and 0.04 g of sodium chloride (0.02M) in distilled water under constant stirring. The pre-emulsion formation started by the drop-wise addition of the oil phase to the aqueous phase at a high stirring rate (800 r.p.m) and mixing for 40 min. In order to form the miniemulsion, the pre-emulsion was placed in an ice bath and sonicated using a Q-Sonica digital sonicator (500 W, 1-inch tip, 20kHz, Newtown, CT) for 4 minutes with high energy pulses of 1 min each.

The resulting stable miniemulsions were placed in a round-bottom flask, purged with argon for 5 minutes and polymerized at 75 ºC for 6 hours under continuous stirring at 350 r.p.m.

8.3.7. Characterization of Biobased Latexes and Latex Films

The latex polymer yield was measured by gravimetry. For this purpose, latex aliquots were reprecipitated in methanol three times to remove all unreacted monomer residuals. The precipitated polymer samples were dried under nitrogen flow to constant mass. The latex solids content was determined by drying the latex sample on an aluminum dish in the oven at 120 ºC for 45 min.

The latex copolymers composition was examined using ^{1}H NMR spectroscopy after dissolving the biobased copolymers in $CDCl_3$.

Number and weight average molecular weight of latex copolymers was determined in gel permeation chromatography (GPC) using a Waters Corporation modular chromatograph which consists of a Waters 515 HPLC pump, a Waters 2410 Refractive Index Detector, and a set of two 10 μm PL-gel mixed-B columns; the column temperature was set at 40 °C and THF was applied as a carrier with 0.35ml/min of flow rate.

Latex particles sizes and size distributions were determined by dynamic light scattering (DLS) (Particle Sizing Systems Nicomp 380, Santa Barbara, CA). For DLS measurements, latex solutions were prepared by adding 1 drop of latex to 5 ml of Millipore water. The prepared samples were analyzed at a 90 º scattering angle, and the average of five measurements was calculated.

The glass transition temperature (T_g) of latex copolymers was determined using differential scanning calorimetry (DSC) (TA instruments Q 1000 calorimeter) with a heating/cooling/heating regime in the temperature range of -50 to 150 ºC with a dry nitrogen purge of the sample at 50ml/min. The latex polymer samples (10-20 mg) were heated/cooled at a rate of 10 ºC/min.

Biobased latex coatings and free films were prepared by applying 5ml of latex sample, using a drawdown bar with a thickness of 8μm, on steel panels (for coatings) or glass substrates (for preparing free films) and cured at 135 ºC for 4-5 hours in the oven using autoxidation mechanism without the addition of catalyst. The resulting biobased films were peeled off from the glass substrate. The thickness of the latex coatings and free films was measured using a Byko-test 8500 coatings thickness gauge.

Crosslinked latex films were characterized using dynamical mechanical analysis (DMA) (TA Instruments Q 800) in the temperature range of -50 to 150 ºC with a heating rate of 5 ºC/min and soaking time of 3 min at -50 ºC. Rectangular-shaped latex films were analysed in order to evaluate its dynamical mechanical behavior. Then, the crosslink density of the latex free films (ν) was determined using rubber elasticity theory:

$$\nu = \frac{G\prime \cdot 1000}{R \cdot T}, mmol/cm^3 \qquad (8.2)$$

where *G'* – storage modulus within the rubbery plateau; *R*-gas constant; *T*-absolute temperature.

T_g of crosslinked latex films was taken as the temperature of tan δ =*f*(T) peak maximum[27].

Mechanical behavior of biobased latex free films was evaluated using an Instron tensile testing machine (Model 2710-004) with maximum load of 500 N. The tested films had a rectangular shape with a constant width of 5mm. The dimensions of latex free films were evaluated before each measurement.

Contact angle of water on biobased latex films was measured (five measurements for each sample) using FTA 125 contact angle/surface energy analyzer.

Biobased latex coatings performance was characterized by measuring the hardness, flexibility, water/solvent resistivity, and adhesion of each selected coating to the metal substrate. The hardness of the latex coatings was measured using pencil and pendulum hardness tests according to ASTM D3363-05 and ASTM D4366-16 standards, respectively. Latex coating flexibility was evaluated using an impact test (ASTM D2794), which demonstrates the ability of tested coating to “absorb” an attack from external impact without forming cracks on the surface, and a conical mandrel bend test (ASTM D522), which shows bending behavior. The solvent and water resistivity were estimated using the water/solvent double rubs test according to ASTM D4752, which counts the number of rubs applied to dissolve the surface of the coating. The adhesion of the latex coating to the metal substrate was characterized using ASTM method 3359 by applying and peeling pressure-sensitive tape over the cross-cut made on the coating surface.

To evaluate the extent of biorenewability of the synthesized latexes, the biorenewable carbon index (BCI) was calculated for all copolymers in this study using the established method[32]. BCI expresses the ratio of carbon atoms which comes from renewable resources to the total amount of carbon atoms present in the molecule and can be calculated using the following equation:

$$BCI = \frac{N^C_{biorenew.}}{N^C_{total}} \cdot 100\ \% \tag{8.3}$$

where $N^C_{biorenew.}$- is the number of carbon atoms from renewable resources in the molecule; N^C_{total}- is the total number of carbon atoms in the molecule.

8.4. Results and Discussion

Successful syntheses of CBM and HOSBM (Fig. 8.1) have been reported in our recent publications along with the feasibility of free radical (co)polymerization in both monomers, including emulsion and miniemulsion processes.[15–20]

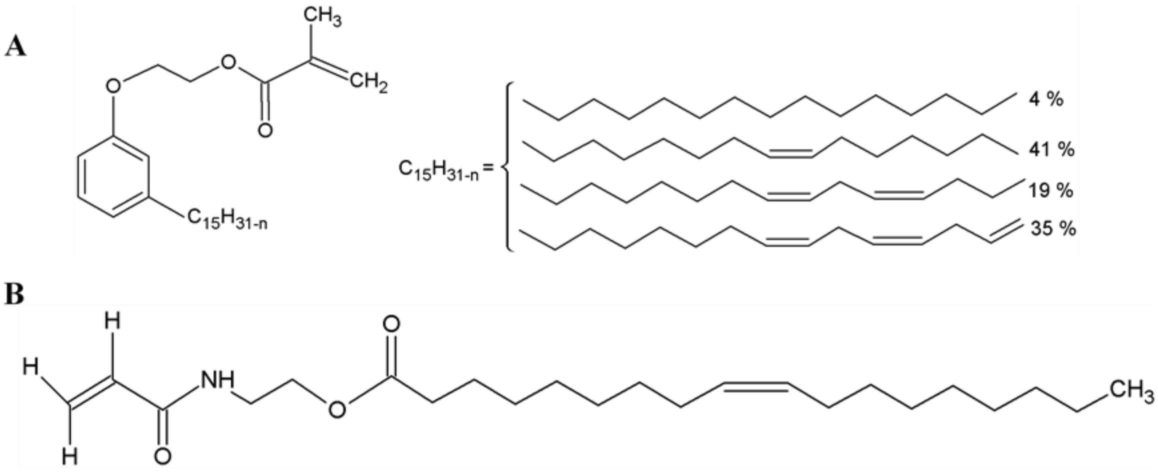

Figure 8.1. Chemical structure of CBM (A) and HOSBM (B)

For the previously reported plant oil-based monomers, the rate of polymerization depends noticeably on their chemical structures and is higher for the monomers derived from lower quantities of unsaturated plant oil. This retardation effect (causing lower final molecular weight of polymers) is due to allylic inhibition, which is a chain transfer reaction to the fatty acid double bonds resulting in chain growth coexisting with the transfer reactions during polymerization. With this finding in mind, to evaluate the extent of unsaturation in HOSBM and CBM, the iodine value was determined for both monomers. The iodine value was noticeably higher for CBM (IV = 202) compared to HOSBM (IV = 123) due to natural differences in unsaturations in parent cardanol and high oleic soybean oil.

To establish the effects of CBM and HOSBM unsaturation amounts on the reaction rate, homopolymerization of both monomers was carried out in solution. It is well-known that radical polymerization rate is described by equation (4), showing a first order dependence of Rp on the monomer concentration ([M]) and square root dependence on the initiator concentration ([I])[15]

$$R_p = -\frac{d[M]}{dt} = k_p \cdot \left(\frac{k_d f[I]}{k_t}\right)^{\frac{1}{2}} \cdot [M] \quad (8.4)$$

where f is the initiator efficiency and k_d, k_p, and k_t are the rate constants of initiator decomposition, propagation, and termination, respectively.

HOSBM and CBM were homopolymerized in toluene at four different concentrations of [M] (0.25−1.5 M) and [I] (0.02−0.06 M) to examine kinetic features and determine monomer and initiator reaction orders. The polymerization of HOSBM and CBM was carried out to monomer conversions lower than 15% to keep [M] constant throughout the kinetic period in the calculation of the polymerization rate. Fig. 8.2B shows the dependence of the calculated polymerization rate Rp on [M] for HOSBM and CBM and clearly indicates that R_p is proportional to the first power of concentration for each monomer (order of reaction with respect to monomer is 1).

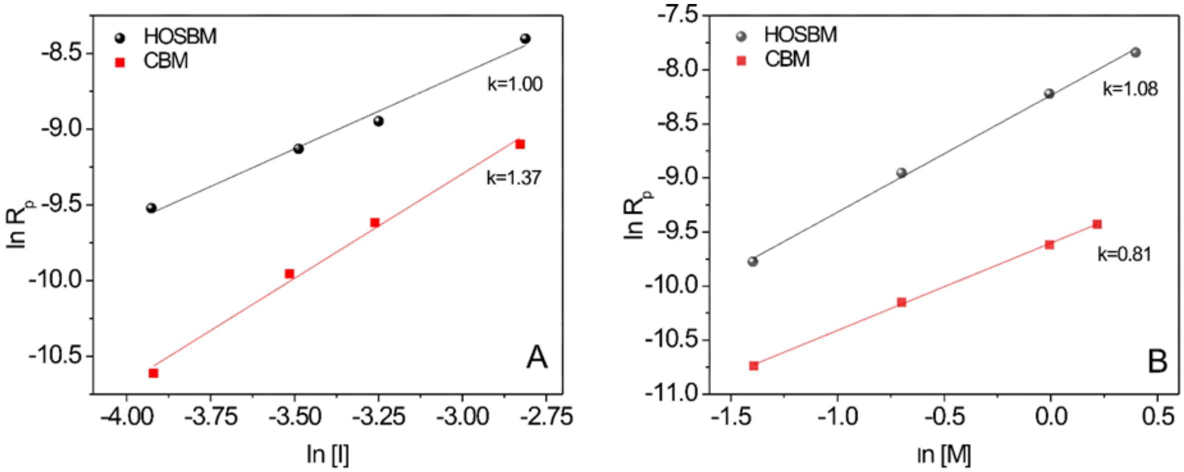

Figure 8.2. Rate of polymerization vs. initiator concentration **(A)** and monomer concentration **(B)** for HOSBM and CBM

To further investigate the kinetics of HOSBM and CBM homopolymerization, the reaction rate and order with respect to the initiator were determined. Fig. 8.2A shows the dependence of R_p on [I] and indicates a reaction order of 1−1.37, deviating from the normal kinetics of the polymerization of vinyl monomers. The initiator order is higher for the polymerization of more unsaturated CBM, which can be expected based on degradative chain transfer reactions (due to the more expressed abstraction of the hydrogen atoms in the alkenyl groups of CBM molecules) established for plant oil-based monomers in our previous publications.[28–31] The latter observation is in good agreement with number-average molecular weight (M_n) values for both homopolymers, which is 26,000 g/mol for poly-(HOSBM) and 14,000 g/mol for poly(CBM). To further evaluate the extent of the effect of chain transfer on the polymerization of HOSBM and CBM, the Mayo method was employed[20] to determine the values of C_M (ratio of the chain transfer and propagation rate constants) in the polymerization of biobased monomers at 75 °C. In this method, the inverse value of the number-average degree of polymerization is plotted against the polymerization rate, and C_M is determined by the intercept or by extrapolation to a rate.

As expected, the obtained C_M depends on the monomer structure (Fig. 8.3). This value is significantly higher in the case of more unsaturated CBM. It is seen from the obtained results that during CBM and HOSBM polymerization, chain propagation coexists with effective chain transfer to monomer fragments of HOSBM and alkenyl fragments of CBM and the fact that new macroradicals do not readily propagate the chains), and this effect is more pronounced for more unsaturated CBM.

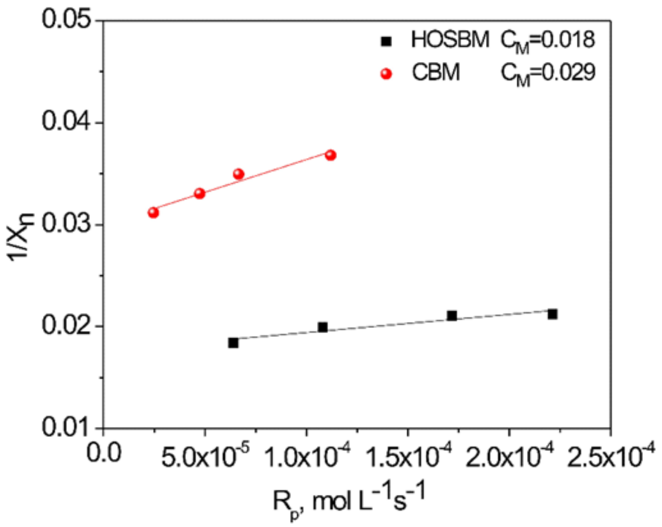

Figure 8.3. Monomer chain transfer constant (C_M) in the polymerization of HOSBM and CBM determined using the Mayo method

Our previous study has shown that the fraction of chains taking part in chain transfer of allylic atoms, in fact, is not very high (8−12%) and that it does not vary significantly among the synthesized plant oil-based monomers.[15] Both CBM and HOSBM are expected to behave likewise. The number-average molecular weights of poly(HOSBM) and poly(CBM) were determined to be 18500−21000 g/mol and 11000−13000 g/mol, respectively, confirming the effects of the higher amount of unsaturation in the cardanol-based monomer. To describe HOSBM and CBM behaviors in chain copolymerization, Q-e parameters, which provide a semiquantitative prediction for monomer reactivity ratios, were experimentally determined. For this purpose, instantaneous copolymer compositions in the copolymerization of HOSBM and CBM with styrene (at total monomer conversions below 10%, determined by ^{1}H NMR spectroscopy) were measured.

Furthermore, by employing the Fineman−Ross method (to determine monomer reactivity ratios r_1 and r_2) and the Alfrey−Price scheme, quantitative descriptors Q-e were calculated for HOSBM and CBM. The obtained results (Q = 0.44 (HOSBM), 0.54 (CBM); e =0.14 (HOSBM), 0.51(CBM)) showed similarity as was expected, assuming the similarities in the chemical structures of the monomer molecules. The determined Q-e values can be used to estimate the reactivities of the plant-based monomers in copolymerization with other monomers in order to control the content of HOSBM and CBM in the final copolymer compositions.

With the confirmed feasibility of both plant-based vinyl monomers in radical polymerization, latexes from HOSBM, CBM, and their mixtures were synthesized using a miniemulsion process. For this purpose, the oil phase from various mixtures and a radical initiator (AIBN) were miniemulsified in a surfactant-containing aqueous phase. Polymerizations were started by heating the miniemulsions at 75 °C under stirring, and they were completed within 3 h, during which most of the monomers were polymerized; the conversions of the monomers were 75−85%. The resulting latexes with an average particle size of 50−130 nm containing 30 wt. % solids (biobased polymer) were stable at room temperature for several months (Table 8.1).

The molecular weights of the resulting copolymers decreased with increasing content of unsaturated CBM in the feed, corresponding to more chain transfer reactions, as discussed above. Nevertheless, the more pronounced chain breaking reactions did not impact the total monomer conversion to the extent observed for HOSBM-based reactions. Table 8.1 shows that the mixtures with higher CBM concentrations polymerized to overall higher monomer conversions.

Table 8.1. Characteristics of CBM and HOSBM latexes synthesized in miniemulsion

Composition in feed, %wt.		Composition in polymer, %wt.		S, %	Solid content, %	M_n, g/mol
CBM	HOSBM	CBM	HOSBM			
100	0	100	0	84	29	14,500
75	25	85.8	14.2	81	31	18,400
50	50	44.5	55.5	72	29	19,000
25	75	25.5	76.5	70	29	19,300
10	90	12.9	87.1	78	29	24,920
0	100	0	100	71	20	26,000

One plausible explanation for this observation can be the differences in the reactivities of CBM ("methacrylate") and HOSBM ("acrylate") radicals in chain copolymerization. One additional benefit of using CBM in latex copolymerization of highly hydrophobic plant-based monomers is that this liquid substance at room temperature can be used as a (reactive) diluent for significantly more waxy HOSBM counterparts. This facilitates a much more consistent preparation of the monomer feed and thus the miniemulsion. As determined by ^{1}H NMR spectroscopy (Fig. 8.4), the chemical compositions of the resulting copolymers mainly followed the composition of the initial monomer feed (Table 8.1).

The polymerization yielded latexes with 100 wt. % plant-based polymer content. As the NMR spectrum shows, a vast majority of double bonds in the HOSBM and CBM fatty fragments were retained after polymerization. This indicates that fatty acid double bonds are available for post-polymerization reactions, particularly for the cross-linking of latex films and polymer network formation. These findings are in good agreement with our previous results.[15–17]

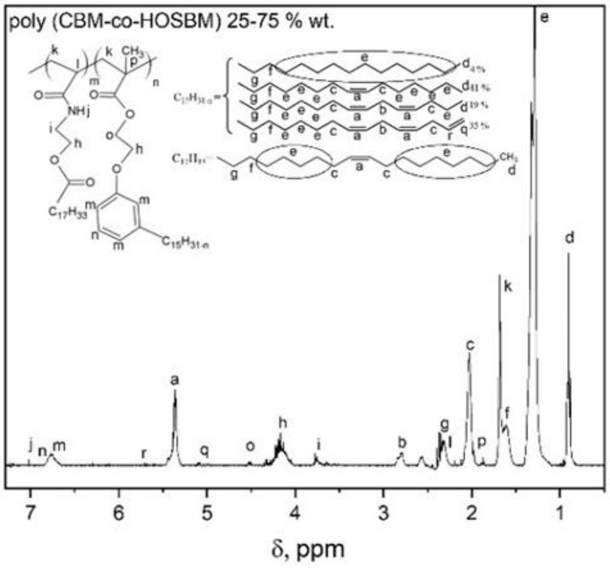

Figure 8.4. ^{1}H NMR spectrum of poly (CBM-co-HOSBM) latex copolymer

Glass transition temperature (Tg) is one of the most important thermophysical properties of amorphous polymers, which gives an indication of their suitability for specific applications. The determination of Tg by DSC of the latex polymers from CBM and HOSBM showed that the synthesized biobased copolymers all possess a Tg in the lower temperature region (−35-10 °C) and that this value increases when the HOSBM content in the copolymer increases (Fig. 8.5).

The obtained values indicate that the variation in the biobased content in the macromolecules changes the thermal properties of the latex copolymers to a large extent. The presence of unsaturations in the HOSBM and CBM fragments makes the resulting latex polymers suitable for post-polymerization cross-linking, which can improve the thermomechanical properties of the materials due to polymer network formation.

Hardness, tensile strength, and Young's modulus depend on the crosslinked polymer network structure, particularly cross-link density, ν. The mobility of the polymer chains in cross-linked networks is a function of ν and thus determines the mechanical and thermal properties of a material. In this work, biobased latex free films and coatings were formed by applying latexes onto steel substrates and their curing at an elevated temperature for 4 h to cross-link via autoxidation mechanism, without catalyst (dryer). The resulting films were characterized using dynamic mechanical analysis (DMA) in order to determine the cross-link density, glass transition temperature, and storage modulus, E′. After curing, the films showed a cross-linking extent of 75−82%, as determined by gel content measurements for each latex sample.

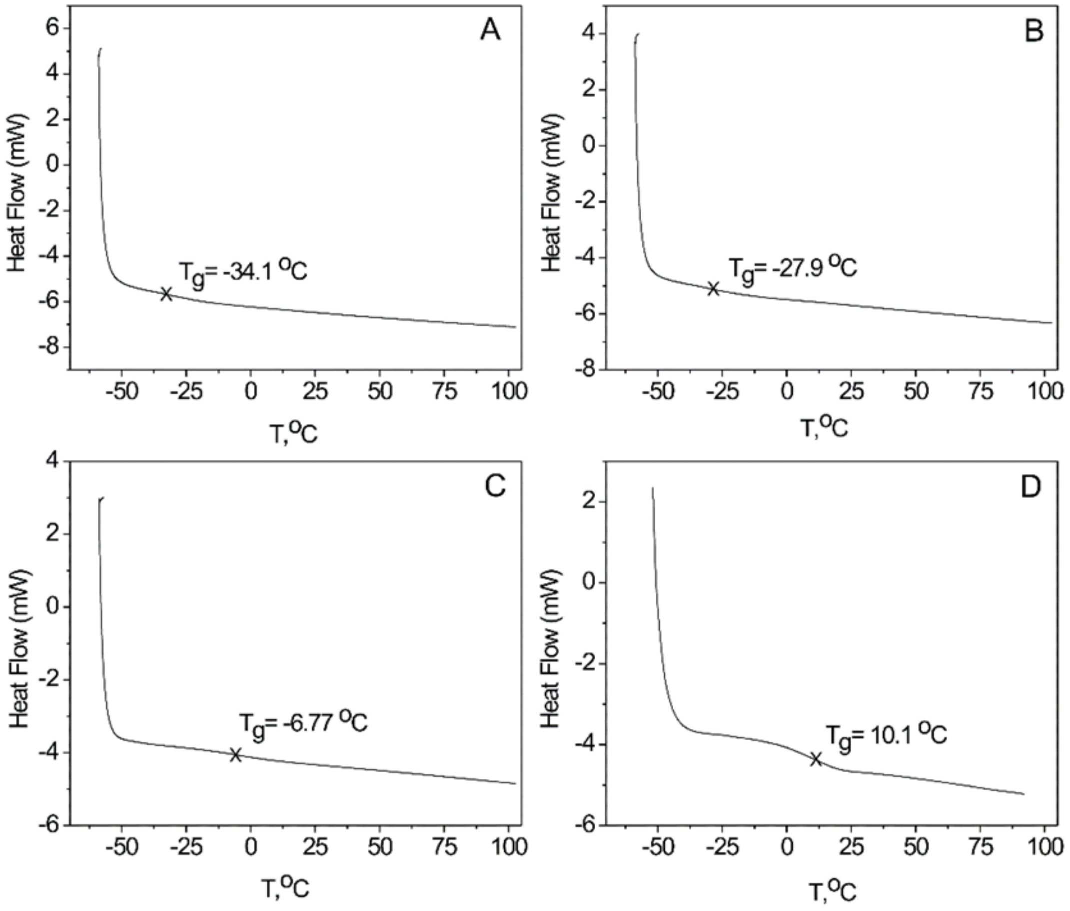

Figure 8.5. DSC thermograms of latex polymers from 100% CBM **(A)**, 75% CBM and 25% HOSBM **(B)** 50% - 50% **(C)** 100% HOSBM **(D)** in the feed

Cross-link density, ν, of the polymer networks was calculated using eq 8.2, where the value of the storage modulus was determined from the E′ vs. T dependence in the rubber elasticity region (50 °C above Tg) (Fig. 8.6A). The increasing CBM content in the monomer feed increases its unsaturation content, which results in the increased cross-link density of the polymer network, as the obtained results indicate (Table 8.2).

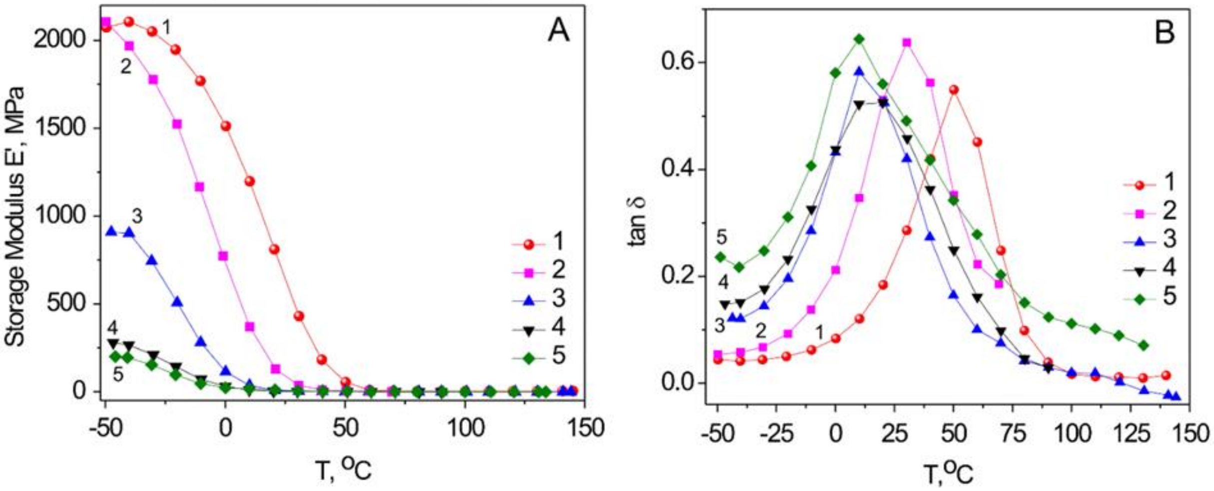

Figure 8.6. Storage modulus (*E'*) **(A)** *vs.* temperature and DMA tan δ plots **(B)** of biobased crosslinked latex free films from 100% CBM – 1, 75% CBM and 25% HOSBM – 2, 50% CBM and 50 % HOSBM - 3, 25% CBM and 75% HOSBM – 4, 10 % CBM and 90 % HOSBM – 5

The latter observation is in good agreement with the increasing glass transition temperature values obtained for the cross-linked latex free films (Table 8.2) when the unsaturation content of the feed increases. The mobility of the polymer chains decreases in higher CBM-based networks, thus impacting Tg.

Table 8.2. Cured biobased latex films properties

Composition in feed, %wt.			
CBM	HOSBM	Crosslink density$\cdot 10^5$, mol/cm^3	T_g, °C
10	90	26.1	5.2
25	75	31.4	13.7
50	50	54.6	15.5
75	25	115.4	31.2
100	0	137.3	53.0

It is worth pointing out that the absolute values of the storage modulus E′, determined using DMA (Fig. 8.6A), justify the trend observed for Tg, which can be explained by the higher cross-link density of the films from the mixtures with higher CBM content. Similarly, more flexible films were developed from copolymers with higher contents of less unsaturated HOSBM.

To provide more insight on the effect of different plant-based fragments on the thermomechanical properties of latex films, tensile properties were evaluated at room temperature as a function of biobased content. Toughness, Young's modulus, and elongation at break were determined for each film (Fig.8.7A and Table 8.3).

Table 8.3. Cured biobased latex films tensile properties

Composition in feed, %wt.			
CBM	HOSBM	Young's modulus, MPa	Toughness·10 $^{-4}$, J/m^3
10	90	0.9	7.0
25	75	1.1	5.5
50	50	1.9	13.6
100	0	2.3	15.0

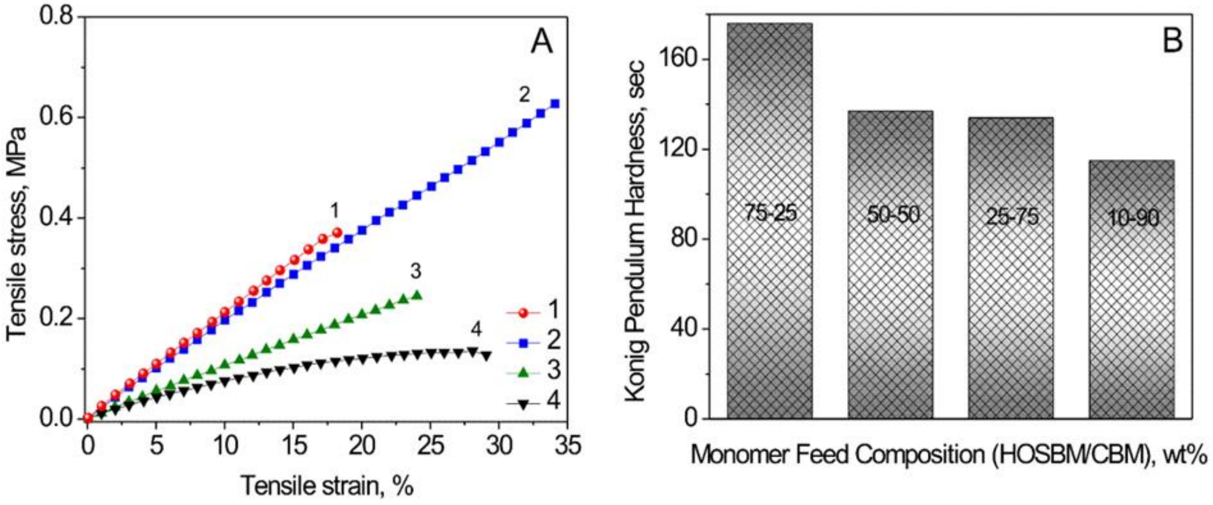

Figure 8.7. Stress-strain plots of biobased latex films from 100% CBM – 1, 50% CBM and 50 % HOSBM - 2, 25% CBM and 75% HOSBM – 3, 10 % CBM and 90 % HOSBM– 4 **(A)**. Effect of HOSBM-CBM copolymer composition on pendulum hardness of biobased latex coatings **(B)**

While Young's modulus and toughness increase with an increasing CBM content, both plant-based constituents contribute to the tensile properties of the latex films. The presence of HOSBM fragments makes the films more flexible, as the data demonstrate. Therefore, the mechanical properties of the biobased latex films depend considerably on the cross-linking density of the polymer network, which can be controlled by the presence and ratio of HOSBM and CBM. The incorporation of cardanol-based fragments enhanced Young's modulus of the films, whereas the high oleic soybean oil-based constituents made them softer and more flexible. To this end, even 10% of CBM provided noticeable strength to the entirely weak poly-(HOSBM) latex polymer material.

In addition to tensile properties, plant-based fragments can impact water and solvent resistance, hardness, and adhesion of biobased latex coatings. Using ASTM methods, Konig pendulum and pencil hardness values of biobased latex coatings were evaluated (Fig. 8.7B and Table 8.4). As expected, the hardness was higher for coatings formulated with more unsaturated latexes containing higher CBM content, thus giving greater cross-link density networks (Fig. 8.7B).

Table 8.4. Properties of CBM-HOSBM biobased latex coatings

Composition in feed, %wt.		Thickness, μm	Pencil hardness[1]	X-Cut adhesion[2]	Water DR[3]	MEK DR[3]
CBM	HOSBM					
75	25	97.8 ±14	8H	2B	256	52
50	50	62.2 ±13	5H	3B	294	32
25	75	84.0 ±23	3H	5B	285	31
10	90	92.7 ±24	2H	5B	274	29

[1] ASTM D3363-05; [2] ASTM 3359; [3]ASTM D4752.

Next, flexibility and bending behavior of latex copolymer coatings were characterized. The impact and conical mandrel bend tests showed the highest values, which indicate excellent flexibility and bending behavior of the tested materials (Table 8.4). This superior behavior can be compared with selected, commercially available latex polymers (in particular, in terms of elongation of a break, to the films from poly(vinyl acetate) latexes), indicating their potential in adhesive applications.[33] The cross-cut method was employed to test the effect of biobased copolymer composition on the adhesion of formulated coatings to the metal substrate. The data indicated that higher HOSBM content in latexes promotes polymer adhesion, making the synthesized biobased latexes relevant in terms of commercial applications.[34] Beyond the improvement of mechanical properties, the incorporation of both highly hydrophobic fragments of HOSBM and CBM into latex copolymers improved the water-resistance of the coatings, as demonstrated by water double rubs (water DR) testing (Table 8.4). As was determined, the water contact angle on the latex copolymer film was 90° ± 5 (selected measurement is shown in Figure E1 in Appendix E). Using the double rubs technique, the solvent (methyl ethyl ketone, MEK) resistance of the biobased latex coatings was also examined. Data showed that MEK resistance increased with increasing cross-link density of the polymer networks.

For latex polymers synthesized from CBM and HOSBM, the biorenewable carbon index (BCI) was calculated. BCI shows the percentage of carbon atoms which originate from animal or vegetable origins in each macromolecule. It is considered to be a robust parameter in the evaluation of material biorenewability.

On the basis of the final polymer composition, the calculated BCIs of the latexes showed similar values for poly(CBM), poly(HOSBM), and poly(CBM-co-HOSBM), varying in the range of 77.5−78.5. This can be expected based on the similarity between the chemical structures of CBM and HOSBM. Thus, a vast majority of the carbon atoms in the synthesized latexes is from natural origin.

8.5. Conclusions

Vinyl monomers derived from cardanol (CBM) and high oleic soybean oil (HOSBM) were successfully (co)polymerized in order to determine their reactivity in radical (co)-polymerization and the feasibility of the synthesis of biobased latexes using miniemulsion. The rate of (co)polymerization depends noticeably on the monomer's unsaturation. Due to the allylic termination (pronounced for more unsaturated CBM), chain propagation coexists with effective chain transfer. Nevertheless, most (>90%) of the fatty acid double bonds of HOSBM and double bonds in the alkenyl groups of CBM remain intact and can be used for postpolymerization reactions (cross-linking). Q and e values were similar for CBM and HOSBM, as was expected due to similarities in their chemical structures. The obtained results indicated that both monomers are well suited for chain copolymerization. The miniemulsion (co)polymerization of fully renewable plant-based monomer mixtures of CBM and HOSBM yielded stable aqueous polymer dispersions with latex particle diameters of 50−130 nm. Thermal analysis showed that the synthesized biobased copolymers possessed lower Tg (−35 to 10 °C) values, which increased with increasing HOSBM content. Tensile testing showed that the mechanical properties of cross-linked latex films depend considerably on the polymer network cross-linking density, which can be controlled by varying the ratio of CBM and HOSBM. Both biobased fragments contributed to the mechanical properties of the resulting polymeric materials. The incorporation of CBM fragments enhanced Young's modulus of the films, whereas the HOSBM constituents made them softer and more flexible. Even small (10 wt %) fractions of CBM can provide noticeable strength to the soft latex polymer material that is based entirely on HOSBM. All cross-linked latex films from HOSBM and CBM demonstrated decent properties and performance in terms of pendulum and pencil hardness, water and solvent resistance, as well as adhesion to the steel substrate. The obtained results clearly demonstrate the potential of vinyl monomers derived from cardanol and high oleic soybean oil as candidates for the synthesis of polymeric materials with higher biorenewable carbon index values (BCI) through radical copolymerization. To the best of our knowledge, latexes from fully renewable plant-based monomer mixtures have not been reported in the literature.

8.6. References

[1] Gandini, Al. Polymers from Renewable Resources: A Challenge for the Future of Macromolecular Materials *Macromolecules*, **2008**, 41 (24), 9491–9504, **DOI:**10.1021/ma801735u.

[2] Moreno, M.; Goikoetxea, M.; de la Cal, J. C.; Barandiaran, M. J. From Fatty Acid and Lactone Biobased Monomers Toward Fully Renewable Polymer Latexes *J. Polym. Sci., Part A: Polym. Chem.*, **2014**, 52, 3543-3549, DOI: 10.1002/pola.27422.

[3] Kalita, D.J.; Tarnavchyk, I.; Sibi, M.; Moser, B. R.; Webster, D.C.; Chisholm, B.J. Biobased poly(vinyl ethers) derived from soybean oil, linseed oil, and camelina oil: Synthesis, characterization, and properties of crosslinked networks and surface coatings *Progress in Organic Coatings*, **2018**, 125, 453–462, DOI: 10.1016/j.porgcoat.2018.09.033.

[4] Wool, R. P.; Sun, X. S. *Bio-Based Polymers and Composites*; Elsevier: Amsterdam, **2005**.

[5] Zhu, Y.; Romain, Ch.; Williams, Ch. K. Sustainable polymers from renewable resources *Nature*, **2016**, 540, 354–362, DOI: 10.1038/nature21001.

[6] Sharma, V.; Kundu, P. P. Addition Polymers from Natural Oils A Review *Prog. Polym. Sci.*, **2006**, 31, 983−1008, DOI: 10.1016/j.progpolymsci.2006.09.003.

[7] Babu, R.P.; Connor, K.O.; Seeram, R. Current progress on bio-based polymers and their future trends *Progress in Biomaterials*, **2013**, 2-8, DOI: 10.1186/2194-0517-2-8.

[8] Lligadas, G.; Ronda, J.C.; Galià, M.; Cádiz, V. Renewable polymeric materials from vegetable oils *Materials Today*, **2013**, 16(9), 337-343, DOI: 10.1016/j.mattod.2013.08.016.

[9] Lu, Y.; Larock, R. C. Novel Polymeric Materials from Vegetable Oils and Vinyl Monomers: Preparation, Properties, and Applications *Chem. Sus. Chem*., **2009**, 2, 136 – 147, DOI: 10.1002/cssc.200800241.

[10] Lomège, J.; Lapinte, V.; Negrell, C.; Robin, JJ.; Caillol, S. Fatty Acid-Based Radically Polymerizable Monomers: From Novel Poly(meth)acrylates to Cutting-Edge Properties *Biomacromolecules*, **2019**, *20* (1), 4–26, DOI: 10.1021/acs.biomac.8b01156.

[11] Molina-Gutiérrez, S.; Ladmiral, V.; Bongiovanni, R.; Caillol, S.; Lacroix-Desmazes, P. Radical polymerization of biobased monomers in aqueous dispersed media *Green Chemistry*, **2019**, 21, 36-53, DOI:10.1039/c8gc02277a.

[12] Kingsley, K.; Shevchuk, O.; Demchuk, Z.; Voronov, S.; Voronov, A. The features of emulsion copolymerization for plant oil-based vinyl monomers and styrene *Industrial Crops & Products*, 109, **2017**, 274–280, DOI: 10.11159/ijtan.2018.005.

[13] Kaya, E.; Mendon, Sh. K.; Delatte, D.; Rawlins, J. W.; Thames, S. F. Emulsion copolymerization of vegetable oil macromonomers possessing both acrylic and allylic functionalities *Macromol. Symp.*, **2013**, 324, 95–106, DOI: 10.1002/masy.201200072.

[14] Voirin, C.; Caillol, S.; Sadavarte, N. V.; Tawade, B. V.; Boutevin, B.; Wadgaonkar P. P. Functionalization of cardanol: towards biobased polymers and additives *Polymer Chemistry*, **2014**, 5, 3142-3162, DOI: 10.1039/c3py01194a.

[15] Demchuk, Z.; Shevchuk, O.; Tarnavchyk, I.; Kirianchuk, V.; Kohut, A.; Voronov, S.; Voronov, A. Free Radical Polymerization Behavior of the Vinyl Monomers from Plant Oil Triglycerides *ACS Sustainable Chem. Eng.*, **2016,** 4, 6974−6980, DOI: 10.1021/acssuschemeng.6b01890.

[16] Demchuk, Z.; Kohut, A.; Voronov, S.; Voronov, A. Versatile Platform for Controlling Properties of Plant Oil-Based Latex Polymer Networks *ACS Sustainable Chem. Eng.*, **2018**, 6, 2780−2786, DOI: 10.1021/acssuschemeng.7b04462.

[17] Demchuk, Z.; Kirianchuk, V.; Kingsley, K.; Voronov, S.; Voronov, A. Plasticizing and Hydrophobizing Effect of Plant Oil-Based Acrylic Monomers in Latex Copolymers with Styrene and Methyl Methacrylate *J. of Theor. and Appl. Nanotech*., **2018**, 6, 29-37, DOI: 10.11159/ijtan.2018.005.

[18] Greco, A.; Maffezzoli, Alf. Cardanol derivatives as innovative bio-plasticizers for poly-(lactic acid) *Polym. Degradation and Stability*, 132, **2016**, 213-219, DOI: 10.1016/j.polymdegradstab.2016.02.020.

[19] Saladino, R.; Neri, V.; Mincione, En.; Marini, S.; Coletta, M.; Fiorucci, C.; Filippone, P. A new and efficient synthesis of *ortho*- and *para*-benzoquinones of cardanol derivatives by the catalytic system $MeReO_3$–H_2O_2. *J. Chem. Soc., Perkin Trans*. 1, **2000**, 581–586, DOI: 10.1039/a908073b.

[20] da Silva, A. L. ; Rocha da Silva, L. R.; de Andrade Camargo, I.; da Silva Agostini, D. L.; dos Santos Rosa, D.; Vasconcelos de Oliveira1 D. L., Almeida Fechine, P. B.; Mazzetto, S. E. Cardanol-based thermoset plastic reinforced by sponge gourd fibers (Luffa cylindrica) *Polímeros*, **2016**, 26(1), 21-29, DOI : 10.1590/0104-1428.2276.

[21] Briou, B.; Caillol, S.; Robin, J.J.; Lapinte, V. Non-endocrine disruptor effect for cardanol based plasticizer *Industrial Crops and Products*, **2019**, 130, 1-8, *DOI:* 10.1016/j.indcrop.2018.12.060.

[22] Calo, E.; Maffezzoli, A.; Mele, G.; Martina, F.; Mazzetto, S. E.; Tarziac, A.; Stifanic, C. Synthesis of a novel cardanol-based benzoxazine monomer and environmentally sustainable production of polymers and bio-composites *Green Chem*., **2007**, 9, 754–759, DOI: 10.1039/b617180j.

[23] Moreira, M.M.; Rocha da Silva, L.R.; Mendes, T.A.D.; Santiago, S.L.; Mazzetto, S.E.; Lomonaco, D.; Feitosa, V.P. Synthesis and characterization of a new methacrylate monomer derived from the cashew nut shell liquid (CNSL) and its effect on dentinal

tubular occlusion *Dental Materials,* **2018**, 34 (8), 1144-1153, DOI: 10.1016/j.dental.2018.04.011.

[24] Li, W.S.J.; Negrell, C.; Ladmiral, V.; Lai-Kee-Him, J.; Bron, P.; Lacroix-Desmazes, P.; Joly-Duhamel, C.; Caillol, S. Cardanol-based polymer latex by radical aqueous miniemulsion polymerization *Polym. Chem,* **2018**, 9, 2468-2477, DOI: 10.1039/c8py00167g.

[25] Ladmiral, V.; Jeannina, R.; Lizarazua, K.F.; Lai-Kee-Himb, J.; Bronb, P.; Lacroix-Desmazesa, P.; Caillol, S. Aromatic biobased polymer latex from cardanol *European Polym. J.*, **2017**, 93,785-794, *DOI:* 10.1016/j.eurpolymj.2017.04.003.

[26] Kohut, A.; Demchuk, Z.; Kingsley, K.; Voronov, S.; Voronov, A. Dual Role of Methyl-β-Cyclodextrin in the Emulsion Polymerization of Highly Hydrophobic Plant Oil-Based Monomers with Various Unsaturations *European Polym. J.*, **2018**, 108, 322-328, *DOI: 10.1016/j.eurpolymj.2018.09.010.*

[27] Barszczewska-Rybarek, Iz. M.; Korytkowska-Walach, A.; Kurcok, M.; Chladek, G.; Kasperski, J. DMA analysis of the structure of crosslinked poly(methyl methacrylate)s *Acta of Bioengineering and Biomechanics*, **2017**, 19(1), 47-53, DOI: 10.5277/abb-00590-2016-01.

[28] Demchuk, Z.; Shevchuk, O.; Tarnavchyk, I.; Kirianchuk, V.; Lorenson, M.; Kohut, A.; Voronov, S.; Voronov, A. Free-Radical Copolymerization Behavior of Plant-Oil-Based Vinyl Monomers and Their Feasibility in Latex Synthesis *ACS Omega*, **2016**, *1* (6), 1374–1382, DOI: 10.1021/acsomega.6b00308.

[29] G. Odian: *Principles of Polymerization* Ch. 6, **2004**, 464-543.

[30] Morrison, R. T., Boyd, R. N. *Organic Chemistry*, 4th Edition, Allyn and Bacon, Inc., **1983**.

[31] Wen, M.; Ng, Li V.; Payne, J. A.; Francis, L. F.; Scriven, L. E.; McCormick, A. V. Kinetic Study of Free-Radical Polymerization of Multifunctional Acrylates and Methacrylates *IS&T's 50th Annual Conference*, **1997**, 564-569.

[32] Pytel, J. Biorenewable carbon index for green formulations *HAPPI*, **2009**, 58–60.

[33] Erbil, Y. H. Vinyl Acetate Emulsion Polymerization and copolymerization with Acrylic Monomers *CRC Press LLC*, **2000**, 135.

[34] Shaffei, K.A.; Moustafa, A.B.; Hamed, A.I. The Emulsion Polymerization of Each of Vinyl Acetate and Butyl Acrylate Monomers Using bis (2-ethylhexyl) Maleate for Improving the Physicomechanical Properties of Paints and Adhesive Films *International Journal of Polymer Science*, **2009**, 1-6, DOI: 10.1155/2009/731971.

CHAPTER 9. BIOBASED LATEXES FROM NATURAL OIL DERIVATIVES[1]

9.1. Abstract

Vinyl monomers from eugenol (EBM) and guaiacol (GBM) were copolymerized in miniemulsion process with high oleic soybean oil-based (HOSBM) counterpart to yield latexes with higher biobased content. Fully renewable monomer feed yields a broad range of new emulsion polymers with the number-average molecular weight varying at 25,000 – 650,000 g/mol. Increasing GBM/EBM content in the reactive feed leads to improving latex molecular weight due to the decreasing unsaturation degree (lower content of HOSBM). The monomer feed unsaturation effect was found to be more pronounced for latexes from EBM and HOSBM since GBM shows higher reactivity in free radical polymerization if compared to GBM. The presence of oil-derived unsaturated fragments in emulsion polymers provides an opportunity to crosslink latexes in a controlled way and adjust the resulting polymer networks' mechanical properties. Biobased latexes from 25 - 90 wt.% of GBM/EBM and 10 – 75 wt.% of HOSBM were synthesized, characterized and tested in terms of thermomechanical properties of latex crosslinked films and coatings. It is demonstrated that the characteristics of latex films and coatings are determined by the nature and ratio of aliphatic oil residues of HOSBM and aromatic fragments of EBM/GBM in the macromolecular backbone. Incorporation of rigid fragments of GBM/EBM enhances Young's modulus of the films, whereas the soft plant oil-based units

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[1] [1]The material in this chapter was co-authored by Zoriana Demchuk, Anna-Sophie Mora, Sanjana Choudhary, Sylvain Caillol and Andriy Voronov. Zoriana Demchuk had performed the synthesis and characterization of series of plant-based latexes from high oleic soybean oil-based monomer and eugenol-/guaiacol-based monomers. Anna-Sophie Mora and Sylvain Caillol had supported this research study by providing aromatic renewable monomers (EBM and GBM) synthesized from dihydroeugenol and vinyl guaiacol, respectively. Zoriana Demchuk and her summer student-Sanjana Choudhary were responsible for characterizing the mechanical properties of plant-based latex films and coatings.Zoriana Demchuk had primary responsibilities in drafting and revising all versions of this chapter. Sylvain Caillol and Andriy Voronov supported the fundamentals of research study by evaluating the relationship of latex material properties vs. monomer structure based on the results collected by Zoriana Demchuk. The article is submitted to Industrial Crops and Product Journal and is under review process.

contribute to the flexibility of films and coatings. All crosslinked latex films exhibited decent properties and performance in terms of hardness, impact resistance, as well as adhesion to the steel substrate. By combining aliphatic fatty acid fragments of HOSBM with aromatic GBM/EBM structure, durable latexes can be synthesized with the ability to balance the thermomechanical properties of the latex polymer networks a broad range.

9.2. Introduction

Biobased polymers and polymeric materials can provide a broad range of application possibilities, including coatings, plastics, adhesives, composites, etc., with properties and performance which can compete with and sometimes outperform the commodity petroleum-based counterparts.[1-3] Using polymers from renewables addresses concerns of global lowering of the oil feedstock, as well as have a positive environmental impact, due to the inherent safety and potential biodegradability of the biobased polymeric materials.[4] Extensive research studies are being performed on the synthesis of renewable monomers for free radical polymerization, including from vegetable oils, cardanol, vanillin, eugenol, terpenes, etc.[5-7]

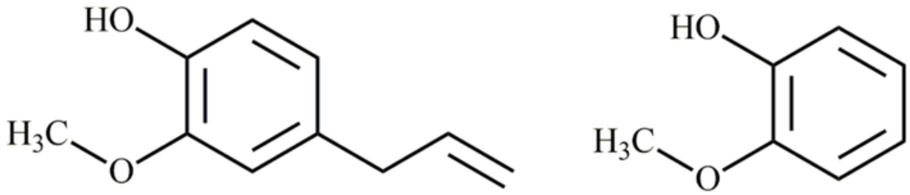
Free radical polymerization in emulsion is the process for producing emulsion polymers (latexes), one of the most advanced polymeric materials, widely used for making coatings, paints, adhesives etc.[8]. Because of the high hydrophobicity of the majority of currently considered in the synthesis of renewable monomers plant-based chemicals, their incorporation in commercial latex polymerization at high levels remains a challenge.[9,10] Nevertheless, synthesizing latexes with high biobased content becomes an attractive alternative approach for replacing petroleum-based counterparts in commercial polymeric materials.[11-14]

In this regard, Kaya et al. reported the synthesis of latexes with varying amounts of soybean oil-based macromonomers in copolymerization with methyl methacrylate.[15] Moreno et al. used miniemulsion polymerization to polymerize monomer synthesized by incorporating methacrylic functionality into linoleic acid.[16] Fully renewable polymer latexes based on naturally occurring α-methylene-γ-butyrolactone were synthesized in miniemulsion by Moreno and coworkers[1]. Both miniemulsion[17,18] and emulsion[19-22] polymerization processes were successfully attempted for the synthesis of latex adhesives based on various renewable biomass sources.

Despite the reported advances, high biobased content latexes are not widely employed for making industrial coatings based on polymers and copolymers from plant derivatives, predominantly due to the limited availability of the respective monomers that can be applied in free radical polymerization.[23-25]

In our recent study, vinyl monomers derived from cardanol (CBM) and high oleic soybean oil (HOSBM) were successfully (co)polymerized in miniemulsion to yield biobased stable latexes with varying CBM and HOSBM content.[14] Both biobased fragments contribute to the mechanical properties of the resulting crosslinked latex films, when the incorporation of aromatic CBM fragments enhances Young's modulus, whereas the aliphatic fatty acid HOSBM constituents make films softer and more flexible. Resulted biobased latex polymer networks demonstrated promising performance in terms of mechanical properties, water and solvent resistance, and adhesion.

Although the obtained results clearly indicate the potential of both CBM and HOSBM in latexes with high biobased content, synthesis of emulsion polymers in a wide range of properties and performance, from this monomeric pair is challenging due to the fatty acid unsaturated fragments presented in the chemical structure of both monomers and limiting final polymers molecular weight. Those functional groups trigger the allylic termination when chain propagation coexists with effective degradative chain transfer, extensively occurring during copolymerization of HOSBM and CBM and diminishing degree of polymerization. To overcome this challenge, renewable aromatic monomers with a minimized chain transfer impact on latex polymers properties need to be considered.



Eugenol

Guaiacol

Figure 9.1. Chemical structure of eugenol and guaiacol

Eugenol is a naturally occurring phenol derived from clove oil, also a lignin breakdown product, found to be a promising aromatic building block for the synthesis of novel molecular structures (Fig. 9.1). Due to the high functionality, eugenol can be converted into a range of biobased reactive monomers used to form renewable thermoplastics and thermosets.[26] Guaiacol is another aromatic derivative, found in all types of lignin (Fig. 9.1). The utilization of guaiacol as a renewable building block was reported for the synthesis of benzoxazines for the development of thermoset systems.[27] Due to the presence of the hydroxyl group, guaiacol molecules can be functionalized by attaching the vinyl group and converted into the monomer for free radical polymerization.

We hypothesized that synthesis of emulsion polymers from a combination of eugenol/guaiacol - and plant oil-based monomers might provide an opportunity to increase the molecular weight of biobased latex polymers with properties and performance, still affected by softer plant oil residues and rigid aromatic fragments of either eugenol or guaiacol derivatives in the resulted copolymers. With this in mind, this study combines eugenol-based (EBM), as well as newly synthesized from guaiacol (GBM) vinyl monomers with HOSBM in miniemulsion to yield latex copolymers with various ratios of GBM/EBM and HOSBM. It is expected that this fully renewable monomer feed yields a broad range of new emulsion polymers with higher molecular weight. Additionally, the presence of HOSBM unsaturated fragments provides an opportunity to crosslink latex films in a controlled manner to adjust the mechanical properties of the biobased polymer network. A range of new latex polymers with properties and performance determined by soft HOSBM residues and rigid EBM/GBM fragments is expected as a result of benefits from renewable monomers chemical structure and their ability to undergo radical polymerization and yield emulsion polymers.

9.3. Materials and Methods

9.3.1. Materials

Dihydroeugenol (2-methoxy-4-propylphenol, 98%, Aldrich), ethylene carbonate (98%, Aldrich), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 98%, Aldrich), triethylamine (99.5%, Aldrich), methacrylic anhydride (94%, Aldrich), 2-methoxy-4-vinylphenol (4VG, ≥98%, Aldrich), chlorotriethylsilane (TESCl, ≥98%, Alfa Aesar), imidazole (≥99%, Aldrich), sodium hydroxide (NaOH, 98%, Aldrich), dichloromethane (DCM, >99%, VWR), ethyl acetate (>99%, VWR), *n*-heptane (>99%, VWR), tetrahydrofuran (THF, >99%, VWR), high oleic soybean oil (Perdue Agribusiness LLC, Salisbury, MD), N-(hydroxyethyl) acrylamide (TCI America, Portland, OR), triethylamine (99.5 %, Aldrich), potassium hydroxide (98 %, Alfa Aesar, Ward Hill, MA), magnesium sulfate (99%, Aldrich), sodium dodecyl sulfate (VWR, Radnor, PA), sodium chloride (ACS grade, VWR, Radnor, PA) were used as received. 2,2′-Azobis(2-methyl propionitrile) (AIBN; Sigma-Aldrich, St. Louis, MO) was purified with recrystallization from methanol. All solvents (tetrahydrofuran, dichloromethane, methanol) were reagent grade or better and were used as received. Deionized water was used for all reactions (Milli-Q, 18 MΩ).

9.3.2. High Oleic Soybean Oil-Based Monomer (HOSBM) Synthesis

Monomer from high oleic soybean oil was synthesized using direct transesterification reaction of crude high oleic soybean oil with N-hydroxyethyl acrylamide (HEAA) in the presence of the catalytic amount of potassium hydroxide (NaOH) (1 % wt.). A detailed procedure of the HOSBM synthesis and purification can be found in [14,28].

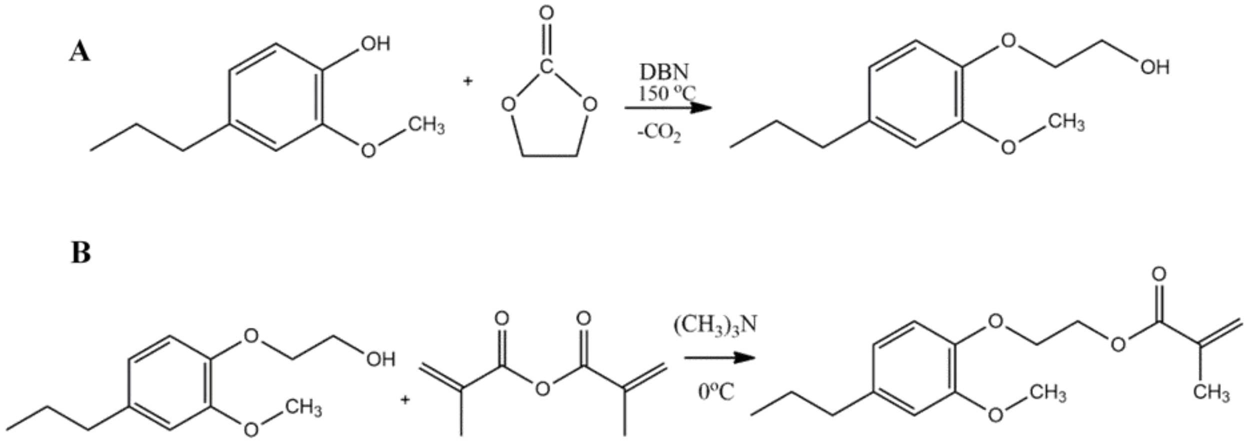
9.3.3. Synthesis of Eugenol-Based Monomer (EBM)

9.3.3.1. Step 1. Synthesis of 2-(2-methoxy-4-propylphenoxy) ethan-1-ol

A 2-neck round-bottom flask was charged with dihydroeugenol (79 g, 480 mmol, 1 equiv.) and ethylene carbonate (47 g, 528 mmol, 1.1 equiv.) with a reflux condenser. The mixture was stirred for 30 min at 150°C under inert gas. Then, DBN (0.18 g, 1.47 mmol, 0.003 equiv.) was added drop-wise into the reaction mixture. After 30 min of reaction at 150°C, the bath temperature was increased to 180°C for 4 hours (Scheme 9.1A). Then, the reaction crude was dissolved in 500 mL of DCM and extracted with DI water. The organic phase was dried, filtered, and then the solvent was removed on a rotary evaporator. A slightly green solid was obtained (98%).

9.3.3.2. Step 2. Synthesis of 2-(2-methoxy-4-propylphenoxy) ethyl Methacrylate

2-(2-methoxy-4-propylphenoxy) ethan-1-ol (1 equiv.) was placed in a sealed round-bottom flask in dichloromethane under inert gas. Triethylamine (2.4 equiv.) was then added. Methacrylic anhydride (1.1 equiv.) was added drop-wise at 0°C (Scheme 9.1B).

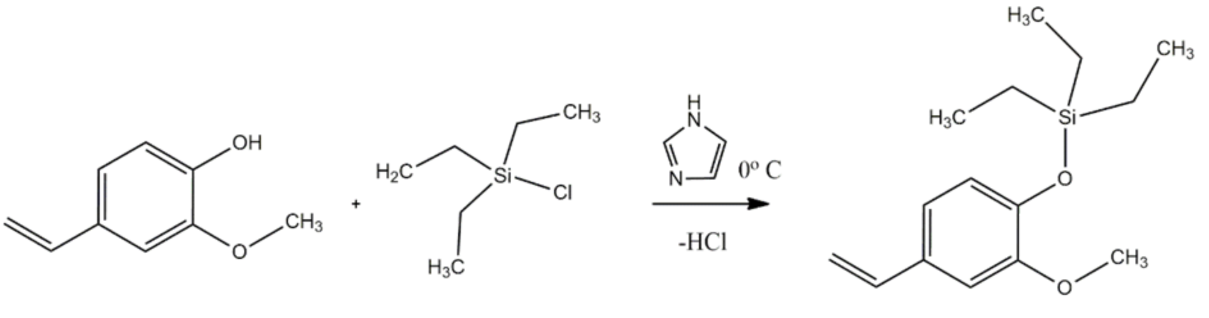


Scheme 9.1. Two-step synthesis of 2-(2-methoxy-4-propylphenoxy) ethyl methacrylate (EBM)

The reaction crude was stirred for 18 hours at room temperature, washed with 1 M NaOH solution and with DI. Finally, ethyl acetate was used to extract the final product. The organic phase was dried, filtered, and the solvent was removed at 30°C on a rotary evaporator. A slightly yellow liquid was obtained (95%).

9.3.4. Synthesis of Guaiacol-Based Monomer (GBM) - triethyl(2-methoxy-4-vinyl-phenoxy) Silane

4-vinyl guaiacol (45.0 mL, 0.333 mol) and imidazole (56.5 g, 0.830 mol) were dissolved in THF (175 mL). Then, TESCl (67.0 mL, 0.400 mol) was added drop-wise at 0°C under stirring (Scheme 2). Afterward, the reaction crude was stirring at room temperature for 18 h, and then diluted with *n*-hexane and washed with DI. The organic phase was dried and the solvent was removed on a rotary evaporator. A colorless liquid was obtained (95%).



Scheme 9.2. The synthesis of triethyl(2-methoxy-4-vinyl-phenoxy) silane (GBM)

9.3.5. Characterization of HOSBM, EBM, and GBM

Synthesized HOSBM, EBM, and GBM were characterized using ^{1}H NMR and ^{13}C NMR spectroscopy (AVANCE III HDTM 400 high-performance digital NMR spectrometer, BRUKER, Billerica, MA), as well as FTIR spectroscopy to confirm the chemical structure of the monomers. Additionally, GBM and EBM were characterized using High-Resolution Mass Spectrometry to determine the molecular mass of the resulted monomers.

9.3.6. Free Radical Polymerization of EBM and GBM in Solution

For homopolymerization, 1 M of EBM/GBM and AIBN (0.02 - 0.06 M) were dissolved in toluene; the solution was stirred and purged under a nitrogen blanket at room temperature for 5 min following by heating to 60°C for 5 h (total monomer conversion of 87 ÷ 95%). Small samples (0.5 g) of the reaction mixture were taken over polymerization time to determine the monomer conversion. The EBM and GBM homopolymerization rate was determined by plotting the monomer conversion vs. time at a linear region at the lower conversion values (up to 25%). The resulting homopolymer was precipitated in a large excess of methanol and purified 3-4 times by reprecipitation. The purified homopolymer samples were dried at room temperature until constant mass. The average number and weight molecular weight of the homopolymers synthesized in the presence of various AIBN concentrations were determined by gel permeation chromatography (GPC). Then, utilizing Mayo method, chain transfer constants on EBM/GBM were determined by plotting the reciprocal value of the degree of polymerization vs. polymerization rate for both monomers and extrapolating to zero rate.

9.3.7. Free-Radical Copolymerization of EBM and GBM with Styrene

To determine reactivity of EBM/GBM in chain copolymerization, various ratios of each monomer (0.2 − 1.2 g; 0.15 - 0.85 mole part), and styrene (0.05 − 0.4 g; 0.85 - 0.15 mole part, total monomer concentration 1 M), and AIBN (0.037 - 0.04 g, 0.038 M) were dissolved in toluene. The reaction mixture was purged with nitrogen at room temperature for 5 min and heated under an argon blanket at 75°C for 1.5 - 2 h until a total monomer conversion of 10 - 25% was reached. The aliquots of 0.5 g of the reaction mixture were taken from the reactor every 15 - 25 min to monitor monomer conversion progress during the copolymerization using a gravimetric method after precipitation of the copolymer in a large excess of methanol (1:10). The resulting copolymers were purified three times by reprecipitation, dried under a nitrogen blanket at room temperature (for NMR study), and at 100°C (to determine total monomer conversion) until constant mass. The chemical structure and composition of the copolymers were determined by ^{1}H NMR spectroscopy. For this, 12 mg of the copolymer sample was dissolved in chloroform-d_1 and tested using JEOL ECA 400 MHz NMR Spectrometer.

The data on resulted copolymers composition was applied for the determination of EBM/GBM reactivity ratios in copolymerization with styrene (r_1, r_2). For this purpose, Finemann-Ross method and equation (1) yielding a straight line plot with slope r_1 and intercept r_2 were employed:

$$\frac{f(1-F)}{F} = r_2 - \frac{f^2}{F} r_1 \tag{9.1}$$

where f- a molar fraction of monomer in feed; F-molar fraction of monomer fragments in copolymer; r_1, r_2 -reactivity ratios of EBM/GBM and styrene, respectively.

For each comonomer pair, feed composition $F_i = [M_1]_i/[M_2]_i$ and copolymer composition $f_i = [m_1]_i/[m_2]_i$ where [M_1] and [M_2] are each monomer’s concentration in a feed and [m_1] and [m_2] are each monomer’s content in resulted copolymers, were calculated.

Utilizing the determined reactivity ratios and the *Q*-*e* parameters for styrene, the *Q*-*e* values of GBM/EBM were calculated using the Alfrey-Price scheme (Eq.9.2 - 9.3).

$$r_1 = \frac{Q_1}{Q_2} \cdot \exp\left(-e_1(e_1 - e_2\right) \tag{9.2}$$

$$r_2 = \frac{Q_2}{Q_1} \cdot \exp\left(-e_2(e_2 - e_1\right) \tag{9.3}$$

9.3.8. Biobased Latex Synthesis

A range of biobased latexes was synthesized using miniemulsion polymerization of HOSBM with GBM or EBM at various monomeric ratios. The miniemulsion process was carried out at 30% solids content, where the oil phase comprised of the mixture of HOSBM and EBM/GBM at certain amounts (15 g total) and AIBN (0.23 g, 1.5 wt.% of oil phase). First, the aqueous phase was prepared by dissolving 0.6 g of surfactant (SDS, 4 wt.%) and 0.04 g of sodium chloride (0.02M) in distilled water under constant stirring at 700 r.p.m. Next, pre-emulsion was formed by slow drop-wise adding the oil phase to the aqueous phase at a high stirring rate (1000 r.p.m) and mixing for 45 min. The resulting pre-emulsion was placed in an ice bath and sonicated using a Q-Sonica digital sonicator (500 W, 1-inch tip, 20kHz, Newtown, CT) with high energy three pulses of 1 min each.

The formed stable miniemulsions were transferred in a round-bottom flask with an egg-shaped magnetic stirrer, purged with nitrogen for 5 minutes, and polymerized at 75ºC for 8 hours under continuous stirring at 300 r.p.m.

9.3.9. Characterization of Biobased Latexes and Latex Films

Conversion and solid content of biobased latex polymers were characterized by gravimetric analysis. To quantify the latex polymer yield, the latex sample (0.5 g) was reprecipitated in methanol (5 g) three times, dried in the oven at 120ºC until a constant mass. The latex solids content was measured by placing the latex sample (1 g) on an aluminum dish and drying in the oven at 120ºC for 45 min.

The latex copolymers composition was examined using ^{1}H NMR spectroscopy after dissolving the biobased copolymers in $CDCl_3$.

Number- and weight-average molecular weight of latex copolymers was determined by gel permeation chromatography (GPC) using a Waters Corporation modular chromatograph which consists of a Waters 515 HPLC pump, a Waters 2410 Refractive Index Detector, and a set of two 10 μm PL-gel mixed-B columns; the column temperature was set at 40 °C and THF was applied as a carrier with 0.35ml/min of flow rate.

Latex particle size distributions were determined by DLS (Particle Sizing Systems Nicomp 380, Santa Barbara, CA). For DLS measurements, one drop of each latex was diluted by 5 ml of distilled water. The prepared samples were analyzed at a 90º scattering angle for a 5 min running time.

To determine the glass transition temperature (T_g) of latex copolymers, Differential Scanning Calorimetry (DSC) (TA instruments Q 2000 calorimeter) with a heating/cooling/heating regime in the temperature range of -150 to 120ºC with a dry nitrogen purge of the sample at 50 ml/min was used. The latex polymer samples (20 mg) were heated/cooled at a rate of 10ºC/min.

Biobased latex coatings and free films were prepared by applying 5ml of latex sample, using a drawdown bar with a thickness of 8μm, on steel panels (for coatings) or glass substrates (for preparing free films) and cured at 135ºC for 4 - 5 hours in the oven using autoxidation mechanism without the addition of the catalyst. The resulting biobased films were peeled off from the glass substrate. The thickness of the latex coatings and free films was measured using a Byko-test 8500 coatings thickness gauge.

Crosslinked latex films were characterized using dynamical mechanical analysis (DMA) (TA Instruments Q 800) in the temperature range of -50 to 150ºC with a heating rate of 5ºC/min and soaking time of 3 min at -50ºC. Rectangular-shaped latex films were analyzed in order to evaluate its dynamical mechanical behavior. Then, the crosslink density of latex-free films (ν) was determined using the rubber elasticity theory:

$$\nu = \frac{G'}{R \cdot T}, mol/cm^3$$

where G' – storage modulus within the rubbery plateau; R - gas constant; T - absolute temperature, K.

Mechanical behavior of biobased latex free films was evaluated using an Instron tensile testing machine (Model 2710-004) with a maximum load of 500 N. The tested films had a rectangular shape with a constant width of 5mm. The dimensions of latex free films were evaluated before each measurement.[29-31]

Biobased latex coatings performance was characterized by measuring the hardness, flexibility, and adhesion to the metal substrate of each selected coating. The hardness of the latex coatings was evaluated using pencil and pendulum hardness tests according to ASTM D3363-05 and ASTM D4366-16 standards, respectively. Latex coating flexibility was determined using an impact test (ASTM D2794), which demonstrates the ability of a tested coating to "absorb" an attack from external impact without forming cracks on the surface. The adhesion of the biobased latex coatings to the metal substrate was characterized using ASTM method 3359 by applying and peeling pressure-sensitive tape over the cross-cut made on the coating surface and comparing with ASTM standards.

9.4. Results and Discussion

In a recent publication, we reported about durable latexes from fully renewable monomer feeds containing aliphatic high oleic soybean oil-based monomer (HOSBM) (Fig. 9.2A) and aromatic cardanol-based monomer (CBM).[14] For the biobased emulsion polymers from HOSBM and CBM, the rate of polymerization depends noticeably on fatty acids' unsaturation presented in both monomers, causing the retardation effect and diminishing final molecular weight of emulsion polymers. This effect is determined by allylic inhibition, a chain transfer reaction to the fatty acid double bonds leading to the chain propagation coexisting during the polymerization with the chain transfer on both monomers. As a result, the latex polymers with a lower degree of polymerization are synthesized.

To increase the molecular weight of biobased emulsion polymers without deteriorating the material properties and performance, two newly synthesized biobased monomers – derivatives of eugenol and guaiacol - with no fatty acid unsaturation in the chemical structure were considered in this study as counterparts in miniemulsion process with HOSBM.

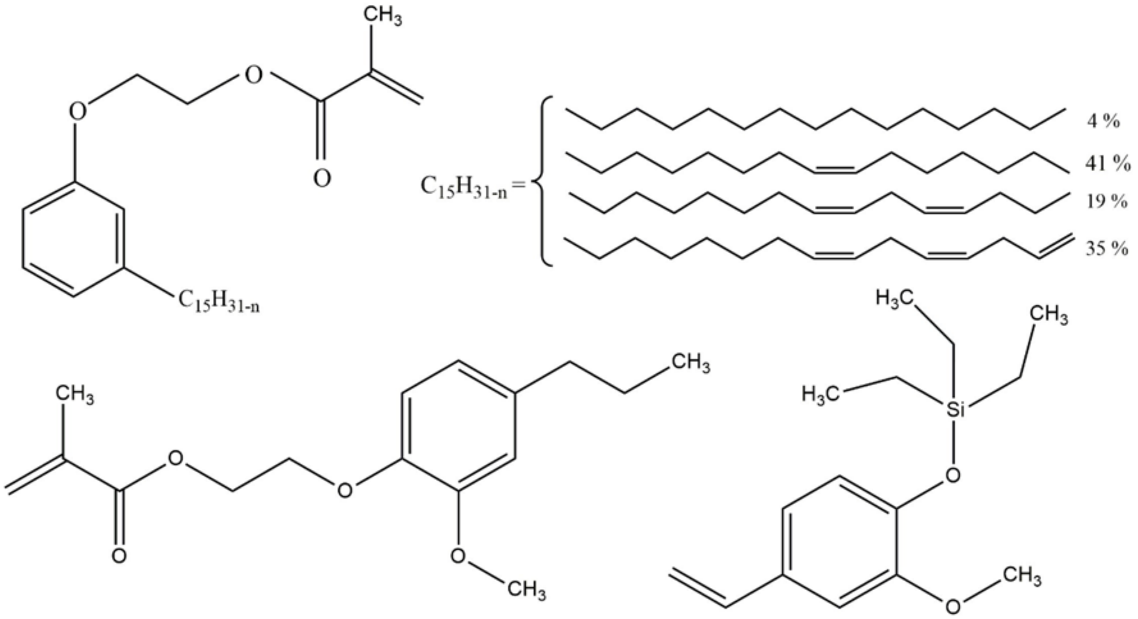


Figure 9.2. Chemical structure of CBM (**A**), EBM (**B**), and GBM (**C**)

Synthesis of eugenol-based monomer (EBM) (Fig. 9.2B) and its feasibility in free radical copolymerization, including miniemulsion processes, have been reported by our group recently[26,32-34]. Synthesis of the renewable aromatic monomer from guaiacol (GBM) (Fig. 9.2C) was successfully developed in this study. Guaiacol is a naturally occurring lignin derivative biosynthesized by microorganisms while found in various essential oils; eugenol is an allyl chain-substituted guaiacol.

In fact, both these compounds can be considered as natural aromatic oils. The chemical structure of the newly synthesized GBM was confirmed using ^{1}H NMR spectroscopy (Fig. 9.3A) and FT-IR spectroscopy (Fig. 9.2B**).** The spectra show that the triethyl (2-methoxy-4-vinylphenoxy) silane 4-vinyl guaiacol, the GBM molecules contain a fragment that can provide monomer reactivity in chain radical polymerization. ^{1}H NMR and FTIR spectra of the EBM are provided in Figure F1 in Appendix F. The molecular weight of the monomers was determined using mass-spectrometry, and is in good agreement with the theoretical average molecular weight. Characteristic mass spectra of GBM is provided in Figure F2 in Appendix F.

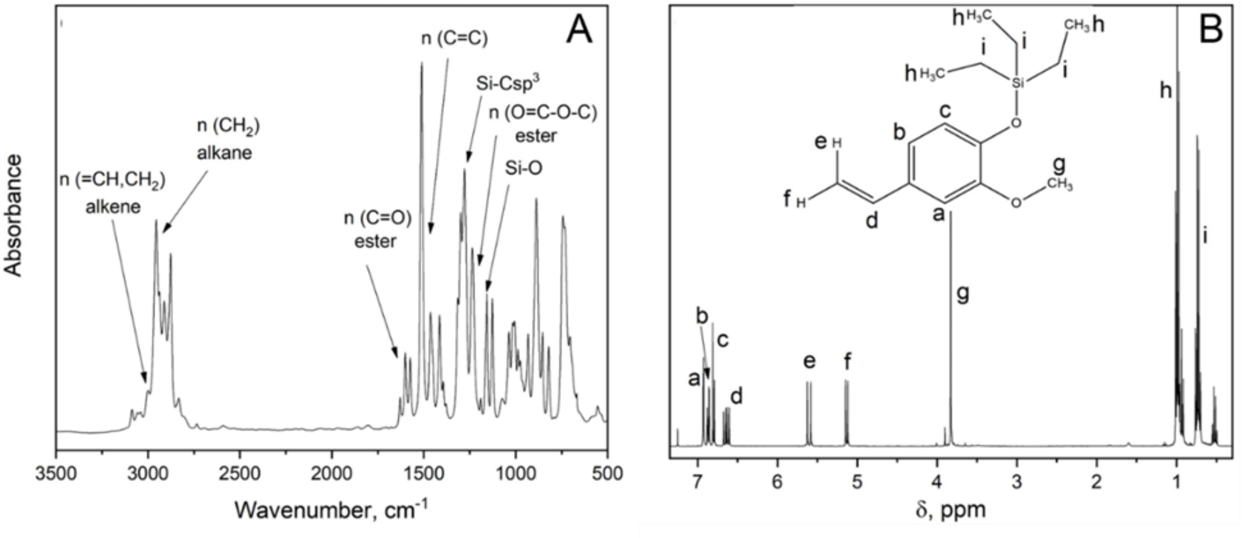


Figure 9.3. FTIR (**A**) and ^{1}H NMR **(B**) spectra of GBM

To establish potential effects of GBM and EBM chemical structure on their capability in their free radical reactions, their both homopolymerization was carried out in solution. Using the established Mayo method, we determined the extent of the effect of chain transfer on each monomer on reaction rate by determining the values of C_M (ratio of the chain transfer and propagation rate constants) in polymerization of GBM and EBM at 75°C. For this purpose, the inverse value of the number-average degree of polymerization was plotted against the polymerization rate, and C_M was determined by the intercept or by extrapolating to zero rate.[29] For both monomers, the obtained values of C_M are low (9.5 x 10-4 for GBM, 2.8 x 10-4 for EBM) (Fig. 9.4), thus indicating that chain propagation during polymerization of GBM and EBM is not significantly impacted by effective chain transfer to monomer.

To this end, both biobased monomers can be considered as counterparts in copolymerization with HOSBM, yielding latex copolymers with higher molecular weight, if compared to unsaturated CBM previously investigated in our group.

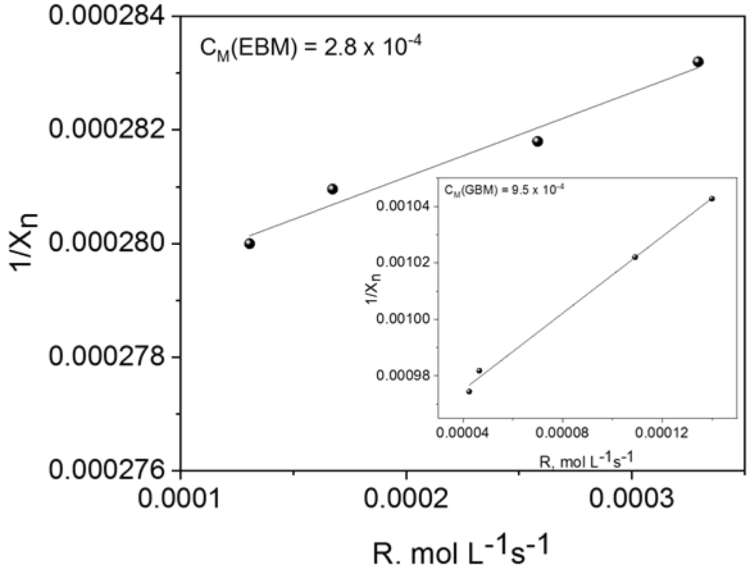


Figure 9.4. Monomer chain transfer constant (C_M) in the polymerization of EBM and GBM (inset) determined using the Mayo method

The further step of this study was to evaluate the reactivity of the GBM and EBM in free radical copolymerization by determining their Q-e values. First, two biobased monomers were copolymerized with styrene (St). Monomer reactivity ratios r_1 and r_2 for two monomer pairs (GBM-St and EBM-St) were calculated using (measured with ^{1}H NMR spectroscopy at low monomer conversions of 5–10%) instantaneous copolymer composition (Fig. 9.5) and the Kelen–Tudos approach to a solution of the Mayo–Lewis copolymerization equation.[14,35]

Experimental data of feed composition $F_i = [M_1]_i/[M_2]_i$ and copolymer composition $f_i = [m_1]_i/[m_2]_i$, y_i values were calculated and plotted vs. x_i values.[35] $[M_1]$, $[M_2]$ are each monomer concentration in a feed, and $[m_1]$, $[m_2]$ are each monomer content in a copolymer.

Experimental data on r_1 and r_2 for GBM-St and EBM-St monomer pairs are shown in Table 9.1.

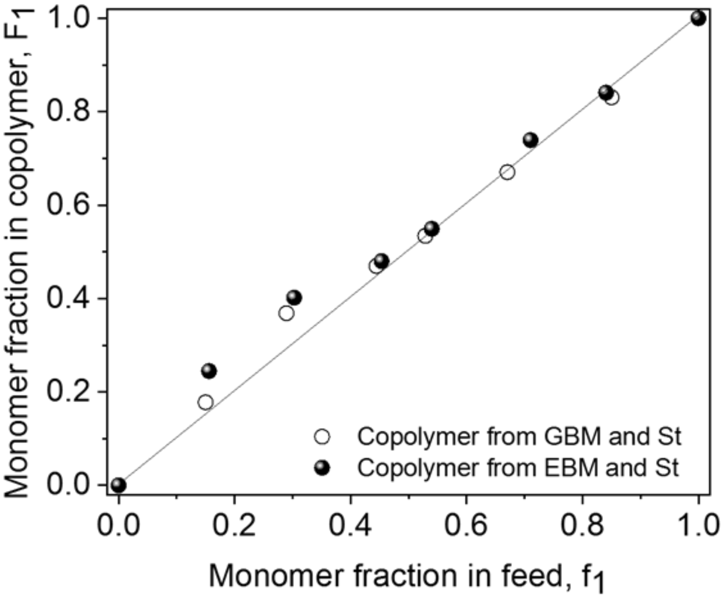


Figure 9.5. Experimental biobased content in the GBM-St and EBM-St copolymers vs. biobased content in the initial feed mixture

Table 9.1. Monomer reactivity ratios for copolymerization of GBM and EBM with St

Comonomer pair	r_1	r_2
GBM - St	0.79 ± 0.05	0.65 ± 0.03
EBM – St	0.87 ± 0.04*	0.32 ± 0.04

Figure F3 in Appendix F shows the effect of biobased comonomer chemical structure on copolymerization rate for various ratios of EBM and GBM in monomer feed with St. One can see that copolymerization rate is overall higher for the monomer mixtures which contain EBM and St. This can be explained by the effect of the higher chain transfer on the GBM, as indicated by chain transfer constant values determined using Mayo method.

Based on the r_1 and r_2 shown in Table 9.1, their product equals 0.51 for GBM and St, 0.27 for EBM and St. The obtained data indicate that copolymerization of both comonomer pairs results in random copolymers. Having the experimental r_1 and r_2 for GBM and St, EBM and St as well as literature data on styrene Q-e values (Q = 1 and e = -0.8),[35] the Alfrey–Price scheme was applied to calculate the Q-e of the GBM and EBM monomer. This calculation yields Q = 1.26±0.05 and e = 0.33±0.03 for the EBM, Q = 0.80±0.06 and e = 0.02±0.01 for the GBM.

For a wide variety of polymeric materials applications, replacing petroleum-based ingredients with a natural renewable component in emulsion polymers and synthesizing fully biobased latexes can be beneficial. The latter aspect is the primary long-term target of this research study. Latexes from fully biobased monomer mixture containing different levels of GBM and EBM (25-90 wt.%.) in combination with HOSBM (10–50 wt.%) were synthesized using miniemulsion polymerization at 75^{o}C under stirring. Synthesized latexes with an average particle size of 50–120 nm exhibit high stability at room temperature within several months. The characteristics of the resulted biobased emulsion polymers are shown in Table 9.2.

Table 9.2. Biobased latex polymer properties

Feed content, wt%*		Copolymer content, wt%	Conversion, %	T_g, ºC	M_n, g/mol
EBM	HOSBM				
50	50	56:44	84	-19	139,100
75	25	84:16	93.5	-12	203,700
85	15	89:11	97	5	108,900
90	10	96:4	97.5	13.4	125,900
GBM	HOSBM				
25	75	30:70	71.5	-85	24,300
50	50	54:46	81.3	6	81,300
75	25	79:21	96	9	93,300
90	10	90:10	98	28	66,400

The obtained results indicate that the molecular weight of the latex copolymers decreases in a range corresponding to increasing unsaturation in monomer feed (increasing HOSBM content), as we previously reported and explained by the effect of degradative chain transfer on the HOSBM provided by allylic hydrogen atoms in the molecules.[14,28] It is also evident that copolymerization of EBM and HOSBM yields latex polymers with the overall higher molecular weight if compared to latexes based on GBM and HOSBM and explained by the more expressed chain transfer reaction in the case of GBM if compared to EBM.

The obtained in DSC measurements T_g values (Table 9.2) indicate that variation in the biobased monomer feed composition changes, to a large extent, the thermal properties of latex copolymers. As expected, the presence of HOSBM fragments decreases the glass transition temperature due to the internal plasticization effect of plant oil-based copolymers reported in our previous study.[14,31] It can be concluded that a combination of the non-polar long fatty acid side chains of HOSBM with aromatic fragments of GBM and EBM impacts intermacromolecular interactions and provides the way for adjusting the T_g of the resulting materials**.** This effect is clearly more pronounced for latex copolymers based on GBM and HOSBM because of differences in emulsion polymers molecular weight.

As it was determined in our previous study, the vast majority of double bonds in HOSBM fatty fragments are retained during the polymerization.[29] The presence of those double bonds makes the resulted latex copolymers suitable for post-polymerization crosslinking reactions.

Crosslinking impacts such mechanical properties, as hardness, elongation at break, Young's modulus making them all essentially dependent on the resulting polymer network, particularly crosslink density, ν. This is because the mobility of polymer chains in a crosslinked network determines the thermomechanical behavior of polymer materials and is a function of ν.

In this study, biobased latex free films and latex coatings were formed by applying latexes to a steel substrate and curing at elevated temperature for a certain period of time. Curing protocols were chosen based on data for the films exhibited an extent of autooxidative crosslinking determined by measuring the gel content in our previous studies.[14,30]

Crosslinked latex films were investigated using dynamic mechanical analysis (DMA) to determine the glass transition temperature and crosslink density. The ν of the biobased polymer networks was calculated as described elsewhere [30] using the storage modulus *E'* *vs.* T dependence in the rubber elasticity region (50°C above T_g). It is evident that for both monomeric pairs, increasing HOSBM content in the feed increases its unsaturation content, which results in an increased crosslink density of the biobased polymer network (Table 9.3).

The obtained data show that incorporating soft plant oil-based fragments in copolymer decreases the T_g of latex films. As it can be expected, the effective molecular weight between crosslinking nodes (M_c) of cured films (shown in Table 9.3) decreases with an increasing

HOSBM content in latex copolymers corresponding to the higher crosslink density of the films. This effect is more pronounced for the films made of latexes based on GBM and HOSBM.

To provide more insights on the effect of different biobased fragments on the mechanical properties of biobased latex films, tensile properties were evaluated at room temperature as a function of latex copolymer composition. Toughness, Young's modulus, and elongation at break were determined for each crosslinked latex film (Table 9.3 and Fig.9.6).

The obtained results confirm that the incorporation of different amounts of either eugenol- or guaiacol-based fragments in combination with HOSBM enhances Young's modulus of the films, whereas the plant oil-based constituents made the crosslinked material softer and more flexible.

Table 9.3. Cured biobased latex films properties made from plant-based derivatives

Feed content, wt.%		Copolymer content, wt.%	*Tg*, °C	$\nu \cdot 10^5$ mol/cm^3	*M$_c$*, *g/mol*	*E*, MPa	$K \cdot 10^{-4}$ J/m^3	ε_b, %
EBM	HOSBM							
90	10	96:4	33	3.5	30,400	66.5	87.3	427.7
85	15	89:11	32	6.7	15,900	0.34	78.8	462.5
83	17	86:16	29	6.8	15,600	0.21	62.6	487.9
80	20	81:19	27	7.1	15,500	0.14	53.8	322.2
75	25	84:16	26	9.5	11,200	0.11	48.7	442.1
GBM	HOSBM							
90	10	90:10	51	5.2	20,500	170.6	73.4	67.3
85	15	86:14	44	6.6	16,100	77.2	76.4	377.1
83	17	83:17	42	9.9	10,800	45.9	86.8	438.2
80	20	82:18	40	11.7	9,100	42.8	136.3	542.5
75	25	79:21	32	12,8	8,300	0.26	152.6	712.4

While Young's modulus increases with an increasing of either EBM or GBM content in both series of experiments, the presence of aromatic constituents contributed in a different manner to the changes in the toughness of the crosslinked films. Although overall, the presence of HOSBM fragments makes the films more flexible, as the data demonstrates, the toughness of the GBM-based materials increases with increasing HOSBM content. In contrast, the effect of plant oil-based fragments was almost not noticeable for the films based on EBM (Fig. 9.6A and 9.6B). In fact, as Table 9.3 shows, as crosslinking density increases in the latter films, the elongation at break almost does not change, thus even causing a slight decrease of the toughness resulting from a fact that Young's modulus of the films decreases. Therefore, the mechanical properties of the biobased latex films in this study depend considerably on the crosslinking density and composition of the polymer network, which can be controlled by the ratio of HOSBM and aromatic fragments in latex copolymers.

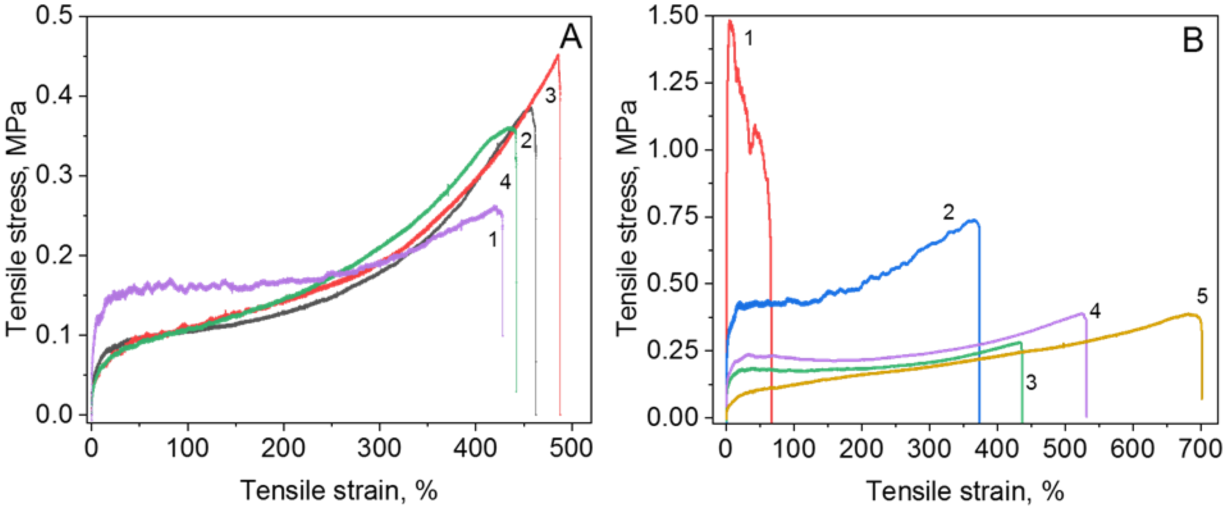


Figure 9.6. Stress – strain plots for biobased latex films from (A) EBM and HOSBM (A, 10 (1), 15 (2), 17 (3), 25 (4) wt.% of HOSBM), (B) GBM and HOSBM (10 (1), 15 (2), 17 (3), 20 (4), 25 (5) wt.% of HOSBM, respectively)

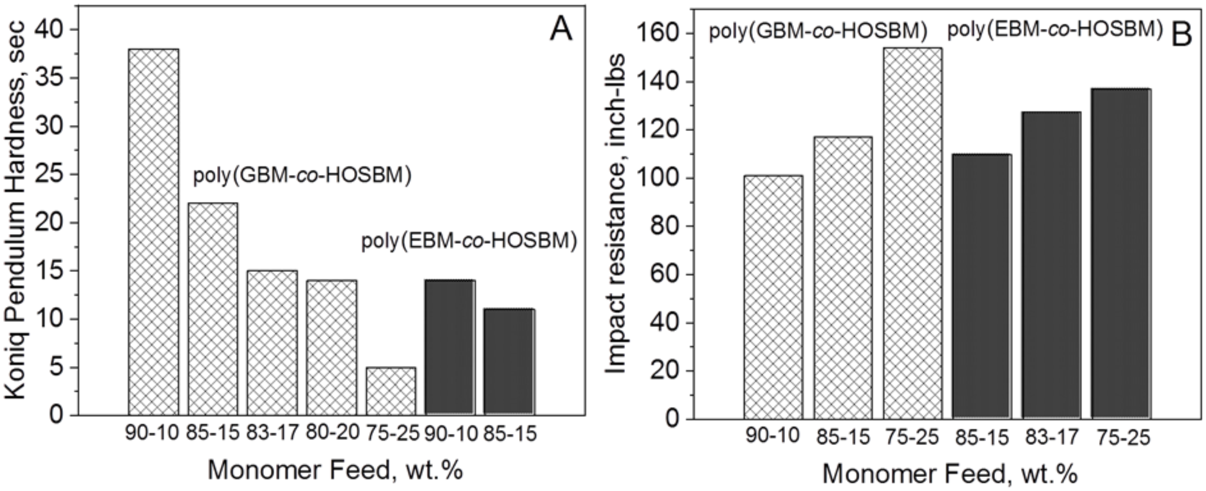


Figure 9.7. Effect of renewable monomers feed composition on pendulum hardness (**A**) and impact resistance (**B**) of biobased latex coatings

In addition to tensile properties, latex characteristics can impact hardness, flexibility, and adhesion of biobased latex coatings. Using ASTM methods, Konig pendulum hardness and impact resistance of coatings were evaluated (Fig. 9.7). As it can be expected, the obtained hardness is higher for latex coatings made from a higher amount of aromatic renewable fragments in the crosslinked polymer network (Fig. 9.7A) while increasing the plant oil-based fragments content in resulted latexes leads to increasing impact resistance, proportionally to the changes of material crosslinking density (Fig. 9.7B).

The biobased latex coatings' adhesion to the metal substrate was measured by a cross-cut adhesion test and found to be impacted by the latex copolymer composition. The data indicated that higher plant oil-based content in latexes enhances polymer coatings adhesion (Fig. 9.8).

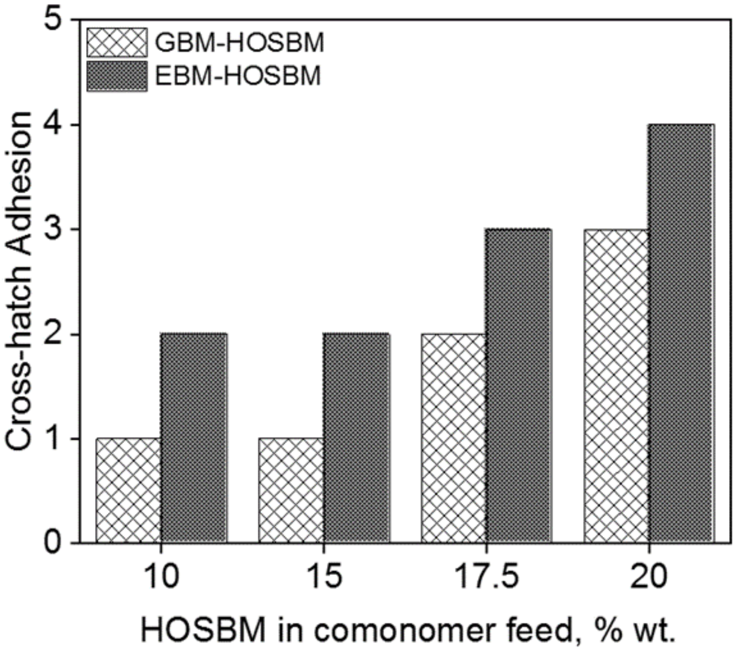


Figure 9.8. Effect of renewable monomers feed composition adhesion of biobased latex coatings to the metal substrate

Overall, the obtained biobased latex coatings show superior behavior in terms of flexibility for all tested copolymer compositions. The provided data indicate that mechanical properties of coatings can be tuned by combination of incorporated fatty acid fragments and aromatic fragments of latex copolymers.

9.5. Conclusions

Vinyl monomers derived from eugenol (EBM) guaiacol (GBM) were successfully (co)polymerized with high oleic soybean oil-based monomer (HOSBM) in miniemulsion in order to demonstrate EBM/GBM feasibility in the synthesis of biobased latexes. To characterize reactivity of GBM and EBM in chain copolymerization, *Q*-*e* values for each renewable aromatic monomer were determined. The obtained results indicate that both monomers are well suited for chain copolymerization.

Miniemulsion (co)polymerization of 25 - 90 wt.% of GBM/EBM and 10 – 75 wt.% of HOSBM yields stable aqueous polymer dispersions with latex particle diameters of 50 - 120 nm.

The fully renewable monomer feeds yield a broad range of new emulsion polymers with the number-average molecular weight varying at 25,000 – 650,000, overall higher for the copolymerization of EBM and HOSBM. As expected, the rate of GBM/EBM copolymerization with HOSBM depends noticeably on the plant oil-based monomer unsaturation due to allylic termination of HOSBM. Increasing GBM/EBM content in the monomer feed corresponds to a decreasing degree of unsaturation and leads to increasing molecular weight of latex polymers. The effect of monomer feed unsaturation is more pronounced for latexes from EBM due to higher reactivity in free radical polymerization.

Synthesized biobased copolymers are characterized by T_g in a range of -19 – 35^{o}C, which increases with each aromatic monomer content. Both biobased fragments contribute to the mechanical properties of the resulting polymeric materials. It is demonstrated that latex films and coatings characteristics are determined by nature and ratio of soft oil residues of HOSBM and rigid aromatic fragments of EBM/GBM in the macromolecular backbone. The presence of unsaturated HOSBM fragments in emulsion polymers provides an opportunity to crosslink latex films to different degrees and control the polymer network mechanical properties. Incorporation of aromatic fragments of GBM/EBM enhances Young's modulus of the films, whereas the plant oil-based units contribute to softer and more flexible films. Tensile testing shows that the mechanical properties of crosslinked latex films depend considerably on the polymer network crosslinking density, which can be controlled by varying the ratio of GBM/EBM and HOSBM. All crosslinked latex films from HOSBM and GBM/EBM show decent hardness, impact resistance, and adhesion to the steel substrate.

The obtained results demonstrate the potential of vinyl monomers derived from eugenol and guaiacol in copolymerization with high oleic soybean oil-based monomer as candidates for the synthesis of renewable waterborne polymeric materials. By the combination of aliphatic fatty acid fragments of HOSBM with aromatic GBM/EBM structure, durable latexes can be synthesized with the ability to balance thermomechanical properties of resulting crosslinked latex films in a broad range.

9.6. References

[1] Moreno, M. Goikoetxea, J. C. de la Cal, M. J. Barandiaran From Fatty Acid and Lactone Biobased Monomers Toward Fully Renewable Polymer Latexes *J. Polym. Sci., Part A: Polym. Chem.,* **2014**, 52, 3543-3549. DOI: 10.1002/pola.27422.

[2] Wool, R. P.; Sun, X. S. Bio-Based Polymers and Composites; Elsevier: Amsterdam, **2005**.

[3] Y. Zhu, Ch. Romain, Ch. K. Williams Sustainable polymers from renewable resources *Nature,* **2016**, 540, 354–362. DOI: 10.1038/nature21001.

[4] Al. Gandini Polymers from Renewable Resources: A Challenge for the Future of Macromolecular Materials *Macromolecules,* **2008**, *41* (24), 9491–9504. DOI: 10.1021/ma801735u.

[5] C. Voirin, S. Caillol, N.V. Sadavart, B.V. Tawade, B. Boutevin, P.P. Wadgaonkar Functionalization of cardanol: towards biobased polymers and additives *Polym. Chem.,* **2014**, 5, 3142-3162. DOI: 10.1039/C3PY01194A.

[6] M. Fache, E. Darroman, V. Besse, R. Auvergne, S. Caillol, B. Boutevina Vanillin, a promising biobased building-block for monomer synthesis *Green Chem.,* **2014**,16, 1987-1998. DOI: 10.1039/C3GC42613K.

[7] I. Tarnavchyk, A. Popadyuk, N. Popadyuk, A. Voronov Synthesis and Free Radical Copolymerization of a Vinyl Monomer from Soybean Oil *ACS Sustainable Chem. Eng.,* **2015**, 3, 7, 1618–1622. DOI: 10.1021/acssuschemeng.5b00312.

[8] C.S. Chern Emulsion polymerization mechanisms and kinetics *Prog. Polym. Sci.,* **2006**, 31, 443-486. DOI: 10.1016/j.progpolymsci.2006.02.001.

[9] C. Quintero, D. Delatte, K. Diamond, S.K. Mendon, J.W. Rawlins, S.F. Thames Reaction calorimetry as a tool to determine diffusion of vegetable oil macromonomers in emulsion polymerization *Prog .Org. Coatings,* **2006**, 57, 202-209. DOI: 10.1016/j.porgcoat.2006.08.009.

[10] G. Booth, D.E. Delatte, S.F. Thames Incorporation of drying oils into emulsion polymers for use in low-VOC architectural coatings *Ind. Crops and Products,* **2007**, 25, 257-265. DOI: 10.1016/j.indcrop.2006.12.004.

[11] A. Tiwari, A. Galanis, M. D. Soucek Biobased and Environmental Benign Coatings, Scrivener Publishing, Beverly, MA, **2016**.

[12] L.I. Atanase, C. Larraya, J.F. Tranchant, M. Save Rational design of tetrahydrogeraniol-based hydrophobically modified poly(acrylic acid) as emulsifier of terpene-in-water transparent nanoemulsions *Eur. Polym. J.,* **2017**, 94, 248–258. DOI: 10.1016/j.eurpolymj.2017.07.011.

[13] M. Droesbeke, A. Simula, J.M. Asua, F.E. Du Prez Biosourced terpenoids for the development of sustainable acrylic pressure-sensitive adhesives via emulsion polymerization *Green Chem.*, **2020**, 22, 4561. DOI: 10.1039/D0GC01350A.

[14] Z. Demchuk, W. S. J. Li, H. Eshete, S. Caillol, A. Voronov Synergistic Effects of Cardanol- and High Oleic Soybean Oil Vinyl Monomers in Miniemulsion Polymers *ACS Sustainable Chem. Eng.* **2019**, 7, 10, 9613–9621. DOI: 10.1021/acssuschemeng.9b01137.

[15] E. Kaya, S.K. Mendon, D. Delatte, J.W. Rawlins, S.F. Thames Emulsion copolymerization of vegetable oil macromonomers possessing both acrylic and allylic functionalities *Macrom. Symp.*, **2013**, 324, 95-106. DOI: 10.1002/masy.201200072.

[16] M. Moreno, J.I. Miranda, M. Goikoetxea, M. Barandiran Sustainable polymer latexes based on linoleic acid for coatings applications *Prog. Org. Coat.*, **2014**, 77, 1709-1714. DOI: 10.1016/j.porgcoat.2014.05.016.

[17] S. Bunker, C. Staller, N. Willenbacher, R. Wool Miniemulsion Polymerization of Acrylated Methyl Oleate for Pressure Sensitive Adhesives *Int. J. Adhes. Adhes.* **2003**, 23 (1), 29−38. DOI: 10.1016/S0143-7496(02)00079-9.

[18] G. Pu, M. R. Dubay, J. Zhang, S. J. Severtson, C. J. Houtman Polyacrylates with High Biomass Contents for Pressure-Sensitive Adhesives Prepared via Miniemulsion Polymerization *Ind. Eng. Chem. Res.* **2012**, 51 (37), 12145−12149. DOI: 10.1021/ie301492v.

[19] S. Roberge, M. A. Dubé Emulsion-Based Pressure Sensitive Adhesives from Conjugated Linoleic Acid/Styrene/Butyl Acrylate Terpolymers *Int. J. Adhes. Adhes.,* **2016**, 70, 17−25. DOI: 10.1016/j.ijadhadh.2016.05.003.

[20] N. Pokeržnik, M. Krajnc Synthesis of a Glucose-Based Surfmer and Its Copolymerization with n-Butyl Acrylate for Emulsion Pressure Sensitive Adhesives *Eur. Polym. J.,* **2015**, 68, 558−572. DOI: 10.1016/j.eurpolymj.2015.03.038.

[21] S. Ren, M. A. Dubé Modification of Latex Microstructure and Adhesive Performance Using D-Limonene as a Chain Transfer Agent *Int. J. Adhes. Adhes.,* **2017**, 75, 132−138. DOI: 10.1016/j.ijadhadh.2017.03.003.

[22] A. Badía, J. Movellan, M.J. Barandiaran, J. R. Leiza High Biobased Content Latexes for Development of Sustainable Pressure Sensitive Adhesives *Ind. Eng. Chem. Res.,* **2018**, 57, 14509−14516. DOI: 10.1021/acs.iecr.8b03354.

[23] J.M. Raquez, M. Deléglise, M.F. Lacrampe, P. Krawczak Thermosetting (bio)materials derived from renewable resources: A critical review *Prog. Polym. Sci.*, **2010**, 35, 487–509. DOI: 10.1016/j.progpolymsci.2010.01.001.

[24] G. Lligadas, J.C. Ronda, M. Galia, V. Cádiz Plant Oils as Platform Chemicals for Polyurethane Synthesis: Current State-of-the-Art *Biomacromolecules*, **2010**, 11, 2825–2835. DOI: 10.1021/bm100839x.

[25] O. Türünç, M.A. Meier The thiol-ene (click) reaction for the synthesis of plant oil derived polymers *Eur. J. Lipid Sci. Technol.*, **2013**, 115, 41–54. DOI: 10.1002/ejlt.201200148.

[26] S. Molina-Gutiérrez, A. Manseri, V. Ladmiral, R. Bongiovanni, S. Caillol, P. Lacroix-Desmazes Eugenol: A Promising Building Block for Synthesis of Radically Polymerizable Monomers *Macromolecular Chemistry and Physics,* **2019**, 220 (14). DOI: 10.1002/macp.201900179.

[27] J. R. Oliveira, L.R. V. Kotzebue, F. W. M. Ribeiro, B. C. Mota, D. Zampieri, S. E. Mazzetto, H. Ishida, D. Lomonaco Microwave-assisted solvent-free synthesis of novel benzoxazines: A faster and environmentally friendly route to the development of bio-based thermosetting resins *Journal of Polymer Science Part A: Polymer Chemistry,* **2017**, 55, 3534–3544. DOI: 10.1002/pola.28755.

[28] A. Kohut, Z. Demchuk, K. Kingsley, S. Voronov, A. Voronov The Effects of Methyl-β-Cyclodextrin on Emulsion Polymerization of Highly Hydrophobic Plant Oil-Based Vinyl Monomers *European Polymer Journal***,** **2018**, 108, pp.322-328. DOI: 10.1016/j.eurpolymj.2018.09.010.

[29] Z. Demchuk, O. Shevchuk, I. Tarnavchyk, V. Kirianchuk, A. Kohut, S. Voronov, A. Voronov Free Radical Polymerization Behavior of the Vinyl Monomers from Plant Oil Triglycerides *ACS Sustainable Chem. Eng.,* **2016**, 4, 6974−6980. DOI: 10.1021/acssuschemeng.6b01890.

[30] Z. Demchuk, A. Kohut, S. Voronov, A. Voronov Versatile Platform for Controlling Properties of Plant Oil-Based Latex Polymer Networks *ACS Sustainable Chem. Eng.,* **2018**, 6, 2780−2786. DOI: 10.1021/acssuschemeng.7b04462.

[31] Z. Demchuk, V. Kirianchuk, K. Kingsley, S. Voronov, A. Voronov Plasticizing and Hydrophobizing Effect of Plant Oil- Based Acrylic Monomers in Latex Copolymers with Styrene and Methyl Methacrylate *J. of Theor. and Appl. Nanotechnol.*, **2018**, 6, 29−37. DOI: 10.11159/ijtan.2018.005.

[32] S. Molina-Gutierrez, V. Ladmiral, R. Bongiovanni, S. Caillol, P. Lacroix-Desmazes Emulsion Polymerization of Dihydroeugenol-, Eugenol-, and Isoeugenol-Derived Methacrylates *Ind. Eng. Chem. Res.,* **2019**, 58, 21155−21164. DOI: 10.1021/acs.iecr.9b02338.

[33] S. Molina-Gutierrez, S. D. Vacche, A. Vitale, V. Ladmiral, S. Caillol, P. Lacroix-Desmazes Photoinduced Polymerization of Eugenol-Derived Methacrylates *Molecule*s, **2020**, 25, 3444; DOI:10.3390/molecules25153444.

[34] S. Molina-Gutierrez, W.S.J. Li, R. Perrin, V. Ladmiral, R. Bongiovanni, S. Caillol, P. Lacroix-Desmazes Radical Aqueous Emulsion Copolymerization of Eugenol-Derived Monomers for Adhesive Applications *Biomacromolecules,* **2020**, Just published. DOI: 10.1021/acs.biomac.0c00461.

[35] Z. Demchuk, O. Shevchuk, I. Tarnavchyk, V. Kirianchuk, M. Lorenson, A. Kohut, S. Voronov, A. Voronov Free-Radical Copolymerization Behavior of Plant-Oil-Based Vinyl Monomers and Their Feasibility in Latex Synthesis *ACS Omega*, **2016**, 1 (6), 1374–1382, DOI: 10.1021/acsomega.6b00308.

CHAPTER 10. CONCLUSIONS AND FUTURE DIRECTIONS

10.1. Conclusions

The main goal of this research study is to synthesize a library of novel vinyl monomers from plant oils with different level of unsaturation, explore their polymerizability and potential to be applied in the latex synthesis. The main objective is to investigate the impact of plant oil unsaturation on POBMs polymerization behavior and thermo-mechanical properties and performance of POBM-based latex materials. In *Chapter 2*, the synthesis of POBMs library from high oleic sunflower, olive, high oleic soybean, canola, corn, sunflower, soybean, camelina, and linseed oil via direct one-step transesterification of plant oils with N-hydroxyethyl acrylamide is discussed. Prior to the synthesis, each plant oil composition was determined in order to evaluate the expected unsaturation extent in the chemical structure of POBMs. The latter was determined using proton NMR and FT-IR spectroscopy to demonstrate the successful incorporation of the vinyl group into the fatty acid-derived POBM molecules. The physicochemical properties of POBMs are evaluated to determine the extent of unsaturation (iodine value), aqueous solubility, density, refractive index, etc. In the following chapters, POBMs are considered to be renewable building blocks in free radical polymerization to form polymers and polymeric materials with unique properties for various industrial applications.

Having in mind the synthesized library of POBMs, *Chapter 3* discusses the sustainability aspect of soybean oil-based monomer (SBM) synthesis by evaluating environmental performance and undertaking process optimization to improve the potential industrial scale's production profile. The Life Cycle Assessment (LCA) was applied to estimate the environmental performance of SBM production in ten categories, including ozone depletion, climate change, eutrophication, etc. The LCA modeling showed a positive effect while incorporating the solvent recycling step in the industrial-scale process. Furthermore, LCA study was conducted to compare the environmental impact of SBM production and synthesis of commercial prototype-stearyl acrylate. LCA modeling has established the environmental friendliness of soybean oil-based monomer in 9 out of 10 categories.

Chapter 4 explores the feasibility of POBMs in free radical polymerization and examines the effect of POBMs unsaturation on the solution reaction kinetics. It was demonstrated that POBMs perform as conventional vinyl monomers in free radical polymerization. However, a noticeable impact of fatty acid unsaturation of POBMs on polymerization kinetics and properties of the obtained copolymers was observed. The number-average molecular weight of POBMs homopolymers diminishes (from 24,000 g/mol for OVM(IV=110) to 12,000 g/mol for LSM(IV=195) with increasing the unsaturation degree of POBM, acting as retardants in polymerization. The polymerization chain transfer established during the reaction is caused by the abstraction of allylic hydrogens leading to retardation. The experimentally determined chain transfer constant (C_M) for each POBM depends on monomer structure and unsaturation profile (C_M(OVM)=0.018<C_M(SFM)=0.023<C_M(SBM)=0.026<C_M(LSM)=0.031). ^{1}H NMR spectroscopy shows that the fraction of atoms undergoing allylic termination does not vary significantly among the synthesized from different plant oil sources monomers (7–12%). Thus, the vast majority of unsaturated fatty acid bonds remain in macromolecular structure and can be utilized for post-polymerization crosslinking.

With the established polymerizability of POBMs, *Chapter 5* is focused on their reactivity in chain copolymerization. Radical copolymerization of POBMs from olive, sunflower, soybean, and linseed oil follows a classical Mayo-Lewis copolymerization equation. Their Q and e values, determined in copolymerization with styrene by applying the Alprey-Price scheme, do not depend on POBMs structure and can be used to control the POBM-based copolymer composition. Furthermore, the feasibility of latex synthesis from POBMs and petroleum-based counterparts in miniemulsion polymerization was demonstrated. The copolymerization of POBMs with MMA in miniemulsion yields high solid stable latexes with the particle size range of 50-185 nm and molecular weight of 20,000-150,000 g/mol. The unsaturation of POBMs and monomer feed composition impact the molecular weight and thermomechanical properties of resulted latexes.

Following the research focus described in the previous chapter, *Chapter 6* assesses the formation of latexes from olive- and soybean oil-based monomers with St and MMA using miniemulsion copolymerization. The presence of plant oil-based fatty acid fragments provides plasticization and hydrophobization effects to normally rigid poly(styrene) and poly(methyl methacrylate). It has been shown that the incorporation of flexible fatty acid fragments increases the mobility of the polymer chain while enhancing the toughness of the resulted latex films. The unsaturation amount of the POBMs can be exploited as a robust experimental parameter to tailor the resulting latex properties, including the degree of the crosslink density of latex films and, subsequently, thermomechanical properties of latex films and coatings. Moreover, the presence of plant oil-based fragments enhances the hydrophobicity of the latex film coatings by lowering the surface energy of latex materials. Overall, the explored features of POBMs have shown a promise to utilize these acrylic monomers as additives to reduce water sensitivity and provide film-forming properties of the polymer materials, including latex coatings/films.

Continuing to explore the effect of POBMs unsaturation on the properties and performance of polymers thereof, *Chapter 7* describes the formation of series of latexes with various monomer unsaturation profiles from olive-, soybean- and linseed-oil based monomers copolymerized with styrene. To form a broader range of fatty acid unsaturation in monomer feed composition, the acrylic monomer from hydrogenated soybean oil (H-SBM) has been synthesized using the direct transesterification reaction as described above. It was shown that the copolymer's molecular weight, Tg, and crosslink density of the resulted cured films are affected by the unsaturation degree of comonomer feed. When plant oil-based latex films are oxidatively cured, the linear dependence of the crosslink density vs. monomer feed unsaturation is observed. Taking into account that the crosslink density of resulted polymer networks controls the mechanical properties and hardness of latex materials, the thermomechanical properties of latex networks can be tuned by combining various ratios of plant oil-based monomers in the monomer feed. Assuming a broad library of POBMs, this finding can be considered as a platform for controlling the mechanical properties of polymer networks in POBM-based latex materials.

Chapter 8-9 explore the advancement in the development of POBM-based latex materials with high biobased content renewable latex by copolymerizing high oleic soybean oil-based monomer with cardanol methacrylate (CBM) (Chapter 8) and eugenol (EBM)/guaiacol-based (GBM) monomers (Chapter 9). The incorporation of renewable aromatic monomers into POBM-based copolymers provides the additional stiffness to resulted latex materials, whereas the film-forming effect is facilitated by the presence of fatty acid fragment in copolymer composition. The synergistic behavior of HOSBM and CBM has been observed where the latex material properties essentially depend on the ratio of monomers in the feed. Additionally, CBM has served as a reactive diluent in latex synthesis. The incorporation of CBM fragments increases Young's modulus of the films, whereas the HOSBM constituents made them softer and more flexible. Even small (10 wt %) fractions of CBM can noticeably improve strength of the soft latex polymer material that is based entirely on HOSBM. Poly(HOSBM-co-CBM) cross-linked latex films have shown decent properties and performance in terms of pendulum and pencil hardness, water, and solvent resistance, as well as cross-hatch adhesion. The obtained results clearly demonstrate the potential of vinyl monomers derived from cardanol and high oleic soybean oil as candidates for the synthesis of polymeric materials with higher biorenewable carbon index values (BCI) through radical copolymerization. However, due to the chain transfer presented in the copolymerization of CBM and HOSBM and impacted molecular weight of latex copolymer, looking for other aromatic renewable monomers with low or no retardation effect was continued to employ them in latex synthesis. As a result, the copolymerization of vinyl monomers derived from eugenol (EBM) guaiacol (GBM) with HOSBM in miniemulsion was successfully established in order to demonstrate EBM/GBM feasibility in the synthesis of biobased latexes. Q-e values for each renewable aromatic monomer were determined to characterize the reactivity of GBM and EBM in chain copolymerization. The obtained data indicate the suitability of EBM and GBM for chain copolymerization.

Using miniemulsion (co)polymerization of 25 - 90 wt.% of GBM/EBM and 10 – 75 wt.% of HOSBM, stable aqueous polymer dispersions were formed with latex particle diameters of 50 - 120 nm. The fully renewable monomer feeds yield a broad range of new latex polymers with the number-average molecular weight (M_n) varying at 25,000 – 650,000, overall higher for the copolymerization of EBM and HOSBM. As expected, the GBM/EBM copolymerization rate with HOSBM depends noticeably on the plant oil-based monomer unsaturation due to allylic termination of HOSBM. Increasing GBM/EBM content in the monomer feed leads to a decreasing degree of unsaturation and increasing latex polymers' molecular weight. The effect of monomer feed unsaturation is more pronounced for latexes from EBM due to higher reactivity in free radical polymerization.

Synthesized biobased latex copolymers are characterized by DSC, where Tg (range of -19 – 35ºC) increases with each aromatic monomer content. Both soft oil residues of HOSBM and rigid aromatic fragments of EBM/GBM in the macromolecular backbone contribute to the mechanical properties of the resulting polymeric materials. The presence of unsaturated HOSBM fragments in emulsion polymers allows them to crosslink latex films to various degrees, as well as control the polymer network mechanical properties. Incorporation of aromatic renewable fragments enhances Young's modulus of the films, whereas the plant oil-based units contribute to softer and more flexible films. The crosslinking density, controlled by varying the ratio of GBM/EBM and HOSBM affects the mechanical properties of crosslinked latex films.

The combination of aliphatic fatty acid fragments of HOSBM with aromatic GBM/EBM structure allows the formation of durable latexes with decent latex film properties, including hardness, impact resistance, and adhesion to the steel substrate, as well as the ability to balance thermomechanical properties of resulting crosslinked latex films in a broad range.

10.2. Future Studies

In this study**,** a library of POBMs was successfully synthesized using the transesterification reaction of crude plant oils with N-hydroxyethyl acrylamide at the presence of a catalytic amount of sodium hydroxide. The unsaturation degree of the synthesized POBMs has been varied in a range of iodine value of 90 to 195 g/g. In the future, it would be interesting to evaluate the performance and mechanical properties of polymers and polymeric materials synthesized from biobased monomers with iodine value lower than 90 g/g, which are essentially less unsaturated. Such monomers can be synthesized from coconut or palm oil, animal-derived fats as by-products of the meat industry such as tallow and lard. Resulted renewable monomers with low unsaturation could yield polymers with higher molecular weight by eliminating the retardation process during free radical polymerization. Besides, there is a potential for interesting physical properties caused by intramolecular interactions of saturated hydrophobic fragments in resulted macromolecules.

In this study, the LCA modeling provided a precise estimation of environmental impacts linked to the production of soybean oil-based monomer. Future studies can explore the effect of plant oil-based monomer synthesis from camelina oil and investigate the effect of plant oil source, plant cultivation conditions on POBMs' environmental performance. Camelina oil is considered to be a highly unsaturated non-edible oil, extracted from the plant, commonly grown on non-productive lands; therefore, examining its environmental impact is interesting to compare with the production of the monomer from commodity soybean oil. Additionally, it is important to conduct uncertainty analysis for SBM production. This would estimate possible errors by identifying, quantifying, and combining the obtained results to evaluate the total uncertainty of measurement, including a variation of soybean source, its composition, etc.

In this study, the feasibility of latex synthesis has been investigated using miniemulsion copolymerization of POBMs with different petroleum- and bio-based counterparts. Aiming the potential commercialization of the resulted latexes to be applied in coatings and adhesives, high total monomer conversion in latex synthesis should be achieved above 98%. Optimization of the process can be performed by changing the monomer feeding mode. Therefore, the dropwise addition of monomers during semi-batch polymerization process can be used for latex formation. After the latex synthesis, total monomer conversion can additionally be boosted by adding a RedOx initiator. The proposed RedOx pair can be ammonium peroxydisulfate $(NH_4)_2S_2O_8$ and sodium metabisulfite $Na_2S_2O_5$ generating radicals at 35-40°C. Another challenge that sometimes interferes with properties of the POBM-based latexes is an excess of surfactant in the product, commonly, sodium lauryl sulfate, which deteriorates material properties. To overcome this issue, partial replacement of sodium lauryl sulfate with biobased alternatives like high oleic lecithin or POBMs copolymers with maleic anhydride can be employed. In perspective, surfactant-free miniemulsion polymerization for the synthesis of latexes from POBMs can be explored as well. For this purpose, fatty acids could be used to stabilize the monomers' droplets in miniemulsion.

The effect of monomer unsaturation determines the curing profile of latex films and resulted latex material properties. Finding a sustainable approach to crosslink latexes and form polymer networks at room temperature can be beneficial to reduce energy consumption and diminish the yellowness of latex coatings and films eventually occurring during curing. Using autooxidation catalysts, like iron-based, may accelerate the autooxidation cross-linking at room temperature.

Application of POBMs with various unsaturation degree can also be a good fit for synthesis of rheology modifiers. Degree of unsaturation of fatty acid fragments in polymers can impact viscosity by changing intermolecular interactions of POBM-based polymers. Moving this direction, the incorporation of POBMs with low unsaturation profile into copolymers with hydroxyethyl acrylate may enable the synthesis of rheology modifiers for aqueous dispersions.

Lastly, following the “greener” vector of this research, the evaluation of biodegradability of POBMs and polymers thereof is a valuable aspect to investigate the relation between monomer chemical structure and biodegradation profile. This could be achieved via the determination of biochemical oxygen demand to evaluate the materials’ biodegradability and compostability.

APPENDIX A. SUPPLEMENTAL MATERIAL FOR CHAPTER 3

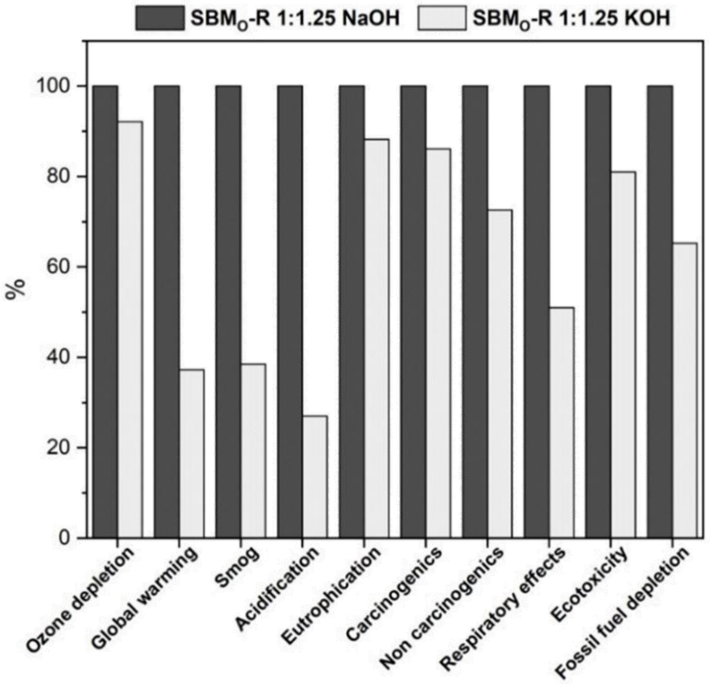


Figure A1. Contributional distribution for targeted impact categories of catalyst optimization pathways used in SBM_O synthesis from soybean oil

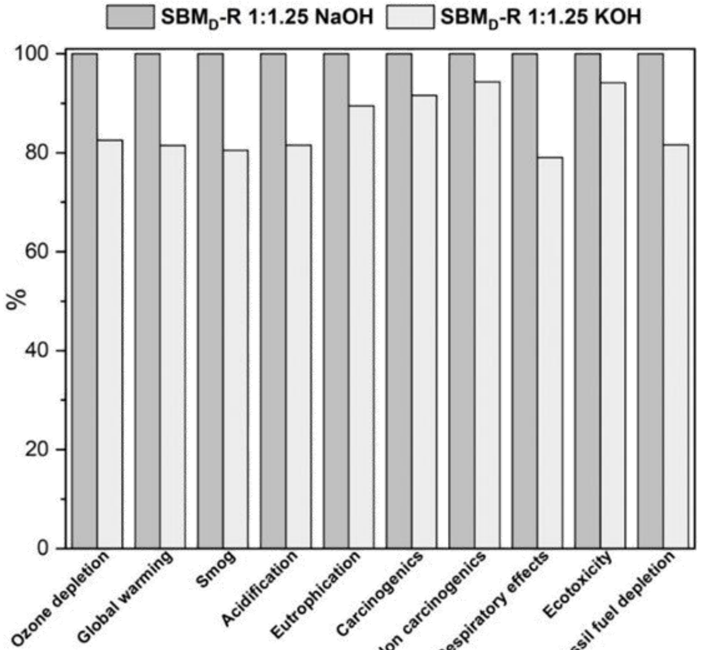


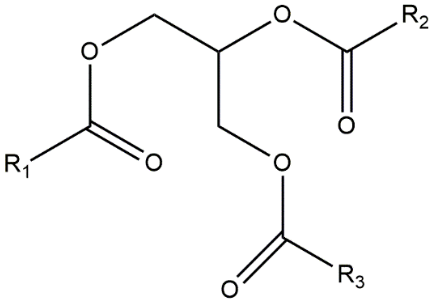
Figure A2. Contributional distribution for targeted impact categories of catalyst optimization pathways used in SBM_D synthesis from soybean biodiesel

Table A1. Inventory of all chemicals used in LCA modelling

#	Name of the component	Database	Year	Location
1.	Soybean Oil	US LCI	2015	US
2.	Soybean Biodiesel	US LCI	2015	US
3.	Electricity	US LCI	2015	North America
4.	Tetrahydrofuran	US LCI	2018	Rest of World (ROW)
5.	Sodium hydroxide	US LCI	2015	North America (US & Canada)
6.	Sodium chloride	US LCI	2015	North America
7.	Magnesium sulfate	Eco invent 3	2018	Rest of World (ROW)
8.	Dichloromethane	Eco invent 3	2018	Rest of World (ROW)
9.	Toluene	US LCI	2015	North America
10.	Diethanolamine	Eco invent 3	2018	Rest of World (ROW)
11.	Acetonitrile	Eco invent 3	2018	Rest of World (ROW)
12.	Acrylic acid	Eco invent 3	2018	Rest of World (ROW)
13.	Deionized water	Eco invent 3	2018	Rest of World (ROW)

APPENDIX B. SUPPLEMENTAL MATERIAL FOR CHAPTER 4

Table B1. Typical chemical compositions of plant oils used in this study in percentages



R (x:y)	**16:0**	**18:0**	**18:1**	**18:2**	**18:3**
Olive oil	7.5–20	0.5–5	65–85	3.5–20	0–1.5
Sunflower oil	3–6	1–3	14–35	44–75	1–2
Soybean oil	7–11	2–6	22–34	43–56	7–10
Linseed oil	4–7	2–5	12–34	17–24	35–60

R (x:y) is the structure of the fatty acids (x is the number of carbon atoms in fatty acid chain and y is the number of double bonds in the fatty acid).[1]

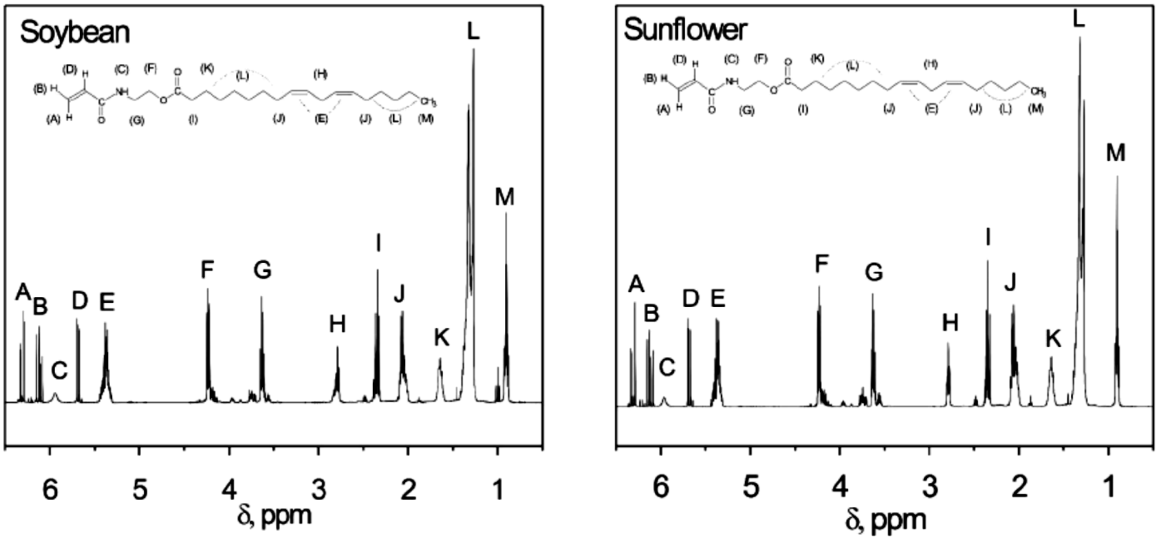


Figure B1. ^{1}H NMR spectra of soybean oil-based (SBM) and sunflower oil-based (SFM) monomers

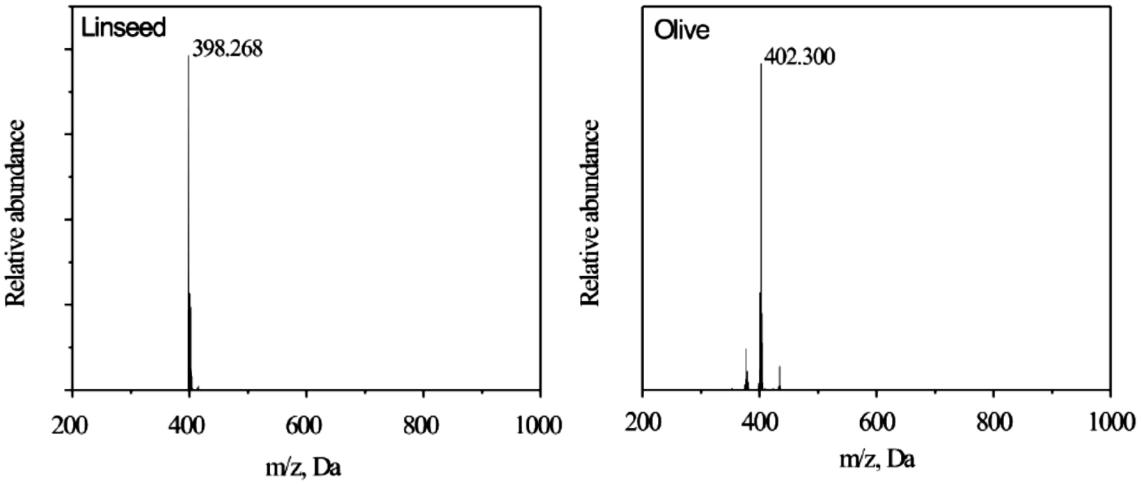


Figure B2. Characteristic mass spectra of linseed oil-based and olive oil-based monomers

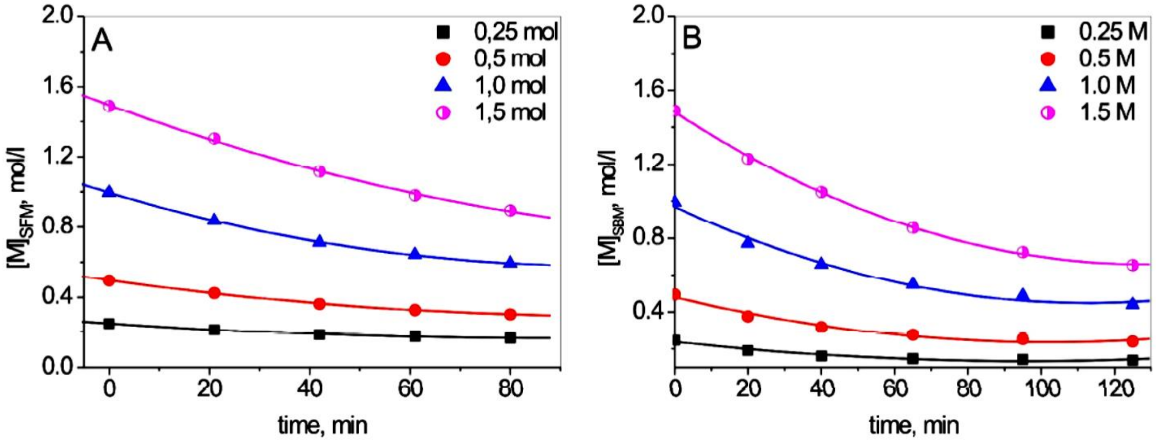


Figure B3. Free radical polymerization kinetics of different monomers [SFM] (**A**) and [SBM] (**B**) initiated by 0.038 mol/l of AIBN at 75 °C

B.1. Reasoning of Reaction Order with Respect to Initiator Determination

All kinetic experiments were carried out in a purged with nitrogen reactor; thus, presence of no oxygen traces in a reaction mixture is expected, as well as oxygen impact on polymerization kinetics.

It is experimentally determined that initiator reaction order in homopolymerization of plant oil-based monomers varies between 1.2 and 1.53 and depends on unsaturation in monomer fatty acid fragments. These values indicate deviations from the normal kinetics of polymerization of vinyl monomers, as well as the presence of specific reactions, not typical for conventional chain radical polymerization.

It is obvious that polymerization kinetics of vinyl monomers from plant oil triglycerides is determined by monomer molecular structure (Scheme B1).

$\mathbf{CH_2{=}CH}\text{–C(O)–NH–}CH_2CH_2\text{–O–C(O)–}(CH_2)_6\text{–C}\mathbf{H_2}\text{–CH=CH–C}\mathbf{H_2}\text{–CH=CH–C}\mathbf{H_2}\text{–}(CH_2)_3CH_3$

Scheme B1. Molecular structure of (acryloylamino)ethyl linoleate in SBM

To this end, the presence of two reactive sites (both shown in bold in Scheme B1) in monomer molecules has to be considered, i. vinyl double bond (determining chain propagation) and ii. isolated double bonds in fatty fragments (with allylic hydrogen atoms prone to chain transfer). Both reactive sites may contribute to polymerization kinetics, as overall schematics of plant oil-based monomers chain radical polymerization shows below:

B.2. Initiation

$$I \rightarrow 2R\bullet \qquad \text{(B 1.1)}$$

$$R\bullet + M \rightarrow M\bullet \qquad \text{(B 1.2)}$$

where I – initiator, M – plant oil-based monomer, M● – monomer primary radical.

The M● can either *i*. add another molecule of M and repeat addition in quick succession, resulting in many M molecules joining the chain (*chain growth*, E_a = 20–25 kJ/mol) or *ii*. abstract an “allylic” hydrogen atom from C-H groups in the α−position to the fatty acid double bonds in monomer molecules (**Scheme B1**) (*chain transfer*, E_a = 25–30 kJ/mol) to form radicals that do *not readily initiate new growing chains* (allylic [premature] termination).

We assume that part of primary radicals M● undergoes chain propagation, and other part of M● participates in chain transfer:

$$[M\bullet] = [M_1\bullet] + [M_2\bullet] \qquad \text{(B 1.3)}$$

where $[M_1\bullet]$ – fraction of primary radicals undergoing chain propagation, $[M_2\bullet]$ – fraction of primary radicals participating in chain transfer.

Schematics of chain propagation and chain transfer during homopolymerization of plant oil-based monomers can be considered as follows:

B.3. Chain Propagation

$$M_1\bullet + nM\!= \rightarrow M\bullet n \tag{B 1.4}$$

$$R_p = k_p\,[M\!=]\,[M_1\bullet]$$

where $[M\!=]$ – monomer fraction undergoing chain propagation,

*Reaction (*A 1.4*) is followed by bimolecular termination of growing macroradicals* M•n *and polymer formation (*A 1.5*) (reaction order with respect to initiator 0.5).*

$$2\ M\bullet n \rightarrow M_n\text{–}M_n \tag{B 1.5}$$

B.4. Chain Transfer

$$M_2\bullet + M_{C\text{-}H} \rightarrow M_2\text{-}H + MC\bullet \tag{B 1.6}$$

$$R_{tr} = k_{tr}\,[M_{C\text{-}H}]\,[M_2\bullet]$$

$[M_{C\text{-}H}]$ – monomer fraction undergoing chain transfer, thus, $[M] = [M\!=] + [M_{C\text{-}H}]$

*Reaction (A 1.6) is followed by chain termination through degenerative chain transfer (*A 1.7*) between the growing macroradicals* M•n and low-active MC● *(reaction order with respect to initiator approaches 1).*

$$M\bullet n + MC\bullet \rightarrow Mn\text{–}MC \tag{B 1.7}$$

In chemical kinetics, rate of reaction is proportional to the product of reactant concentrations, in which the power of the concentration in a rate expression is called *reaction order with respect to the certain reactant*. (A 1.8). Experimental value of reaction order shows how reaction rate depends on reactants concentration. The overall order of the chemical reaction can be found by adding orders with respect to each reactant. (A 1.9).

$$R= k[A_1\ ]^{n1}\ [A_2\ ]^{\ n2}\ [A_i\ ]^{ni}= \cdot \cdot \cdot \text{ (A 1.8)}$$

where $[Ai]$ - i^{th} reactant concentration, n_i – reaction order with respect to certain reactant.

$$n = n_1 + n_2 + n_3 + \ldots + n_i \qquad \text{(B 1.9)}$$

where n – overall reaction order.

Based on the assumptions above, total homopolymerization rate of plant oil-based monomers (POBM), R_{POBM} can be expressed as:

$$R_{POBM} = k\ ([M=]\ [M_1\bullet])^{0.5} \text{ x } ([M_{C\text{-}H}]\ [M_2\bullet])^1 \qquad \text{(B 1.10)}$$

According to schemes (A 1.4) and (A 1.6), interactions between $M_1\bullet$ and M= result in the formation of $M\bullet n$ (A 1.4), whereas interaction of $M_2\bullet$ and MC-H leads to the formation of $MC\bullet$(A 1.6) Both macroradicals, $M\bullet n$ and $MC\bullet$, can be, thus, considered as reagents in homopolymerization of biobased monomers with a rate written as:

$$R_{POBM} = k\ [M\bullet n]^{0.5}\ [MC\bullet]^{\ \sim 1,0} = k\ [M\bullet]^{\sim 1.5} \qquad \text{(B 1.11)}$$

or

$$\lg R_{POM} = \lg k + 1.5 \lg [M\bullet] \qquad \text{(B 1.12)}$$

Eq. (A 1.12) indicates linear dependence of lg R_{POM} on lg $[M\bullet]$ which is in agreement with experimental data obtained in this work (**Fig. 4.4B**).

$CH_2{=}CH{-}C(O){-}NH{-}CH_2CH_2{-}O{-}C(O){-}(CH_2)_6{-}C\mathbf{H_2}{-}CH{=}CH{-}C\mathbf{H_2}{-}CH{=}CH{-}C\mathbf{H_2}{-}(CH_2)_3CH_3$

SBM $\Downarrow$

$CH_2{=}CH{-}C(O){-}NH{-}CH_2CH_2{-}O{-}C(O){-}(CH_2)_7{-}CH{=}CH{-}\mathbf{CH\bullet}{-}CH{=}CH{-}CH2{-}(CH_2)_3CH_3$

$CH_2{=}CH{-}C(O){-}NH{-}CH_2CH_2{-}O{-}C(O){-}(CH_2)_7{-}CH{=}CH{-}CH2{-}CH{=}CH{-}\mathbf{CH\bullet}{-}(CH_2)_3CH_3$

$CH_2{=}CH{-}C(O){-}NH{-}CH_2CH_2{-}O{-}C(O){-}(CH_2)_6{-}\mathbf{CH\bullet}{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}(CH_2)_3CH_3$

$CH_2{=}CH{-}C(O){-}NH{-}CH_2CH_2{-}O{-}C(O){-}(CH_2)_6{-}C\mathbf{H_2}{-}CH{=}CH{-}C\mathbf{H_2}{-}(CH_2)_6CH_3$

OVM $\Downarrow$

$CH_2{=}CH{-}C(O){-}NH{-}CH_2CH_2{-}O{-}C(O){-}(CH_2)_6{-}\mathbf{CH\bullet}{-}CH{=}CH{-}CH_2{-}(CH_2)_6CH_3$

$CH_2{=}CH{-}C(O){-}NH{-}CH_2CH_2{-}O{-}C(O){-}(CH_2)_6{-}CH_2{-}CH{=}CH{-}\mathbf{CH\bullet}{-}(CH_2)_6CH_3$

Scheme B2. Formation of allylic radicals in SBM and OVM

The provided schematic explains experimentally determined values of reaction order with respect to initiator ranging between 1.2 and 1.53. It is also obvious that [MC●] depends on the degree of unsaturation of the plant oil-based monomer (which relates to the degree of unsaturation of initial plant oil). The latter explains different initiator reaction order for four monomers from plant oil with different degree of unsaturation. Contribution of chain transfer reaction to polymerization kinetics grows with an increasing degree of unsaturation in the molecules of plant oil-based monomers. In this regard, six allylic hydrogen atoms of SBM, as well as four allylic hydrogens of the OVM molecule, can undergo chain transfer and become allylic radicals, which do not readily initiate new chains (Scheme B2).

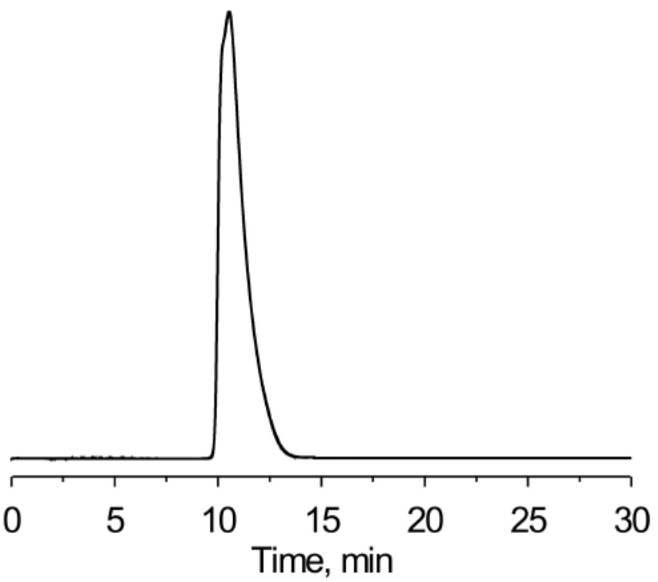


Figure B4. GPC measurements of poly[(acryloylamino)ethyl oleate] synthesized in homopolymerization of [OVM] = 1 mol/L initiated by 0.038 mol/L of AIBN at 80^{o}C

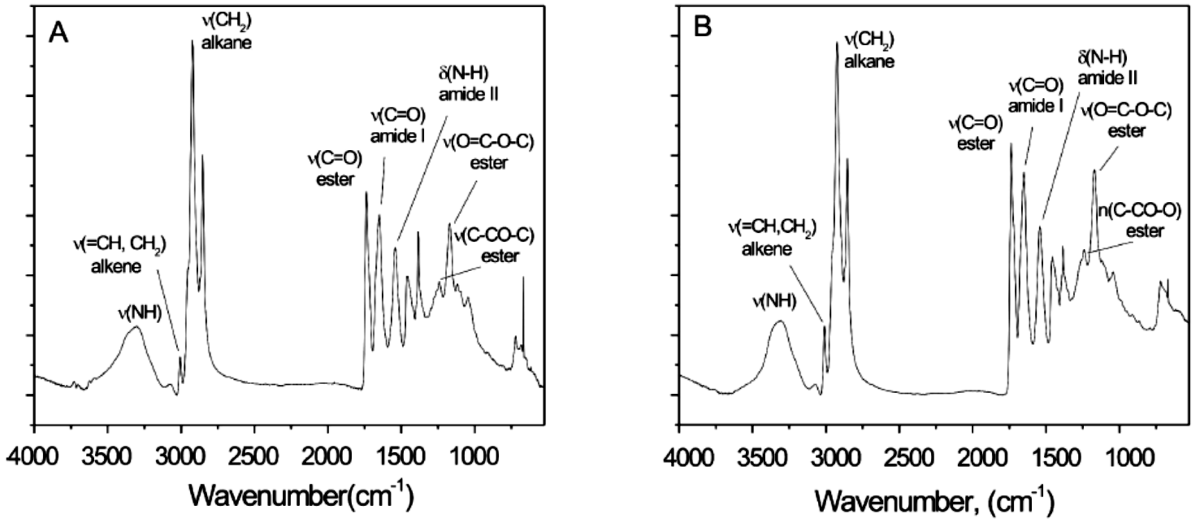


Figure B5. FTIR spectra of poly(SBM) (**A**) and poly(LSM) (**B**)

APPENDIX C. SUPPLEMENTAL MATERIAL FOR CHAPTER 5

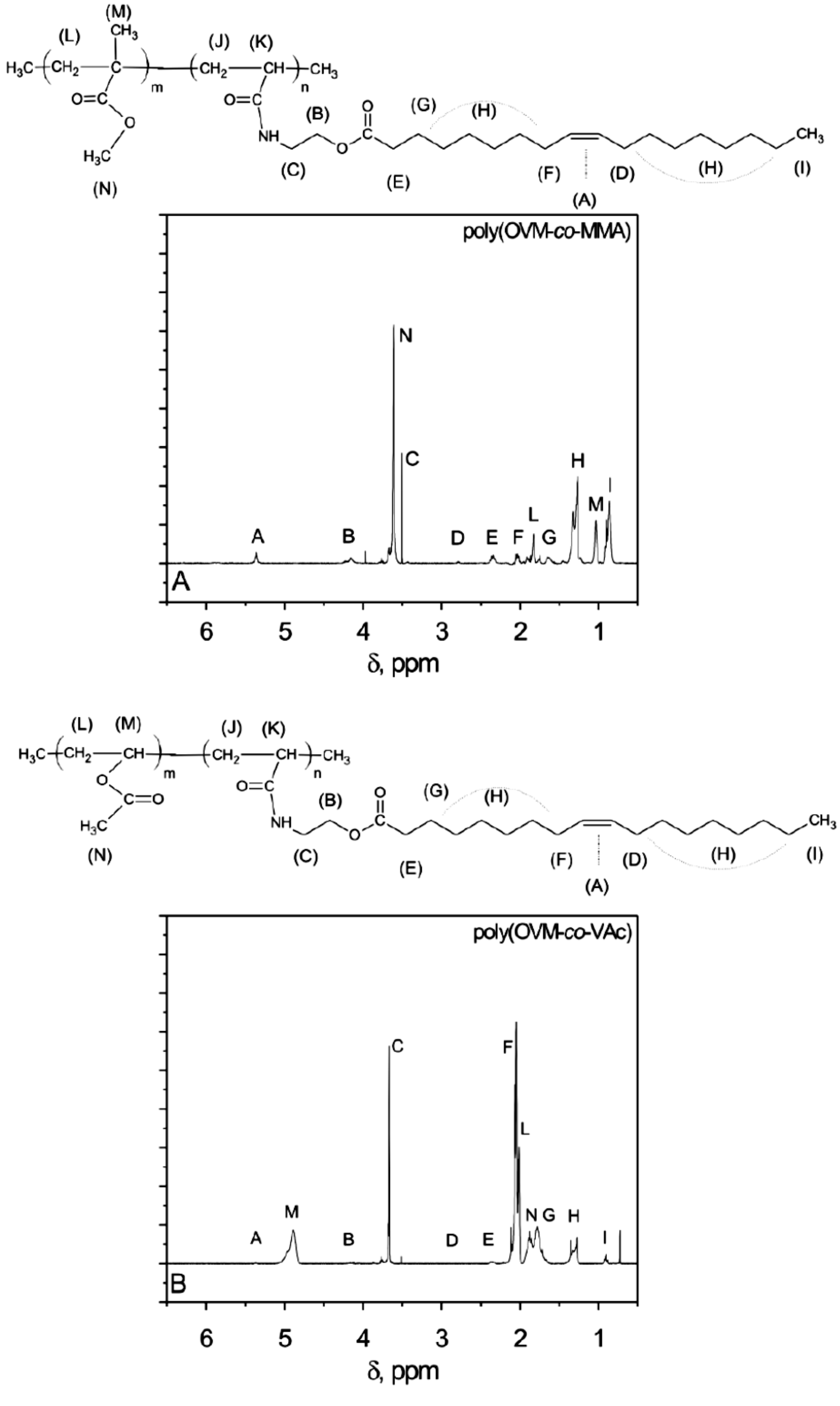


Figure C1. ^{1}H NMR spectra of copolymers from olive oil-based monomer (OVM) and methyl methacrylate (**A**) or vinyl acetate (**B**)

Table C1. Surface energy of latex films from copolymers of methyl methacrylate and OVM or SBM

Sample	Film thickness, μm	Water contact angle, θ, °	CH_2I_2 contact angle, θ, °	Surface energy, N/m		
				λ_{Sd}, *N/m*	λ_{Sh}, *N/m*	λ_S, *N/m*
35SBM	22 ± 4	77 ± 2	51 ± 2	28.6	7.6	36.2
40SBM	31 ± 5	95 ± 1	55 ± 3	30.0	1.1	31.2
35OVM	26 ± 7	87 ± 4	51 ± 2	31.4	2.8	34.2
40OVM	35 ± 7	80 ± 4	46 ± 2	32.3	5.0	37.4

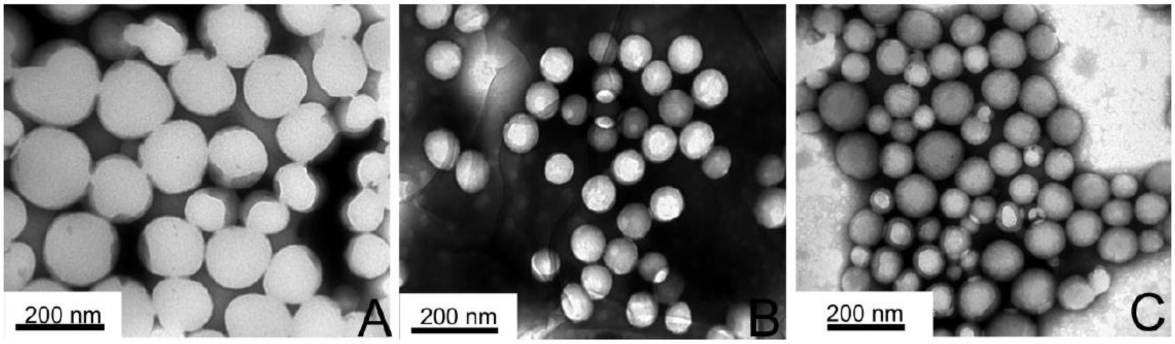


Figure C2. TEM micrographs of latex particles OVM-MMA5 (**A**), OVM-MMA15 (**B**), SFM-MMA20 (**C**)

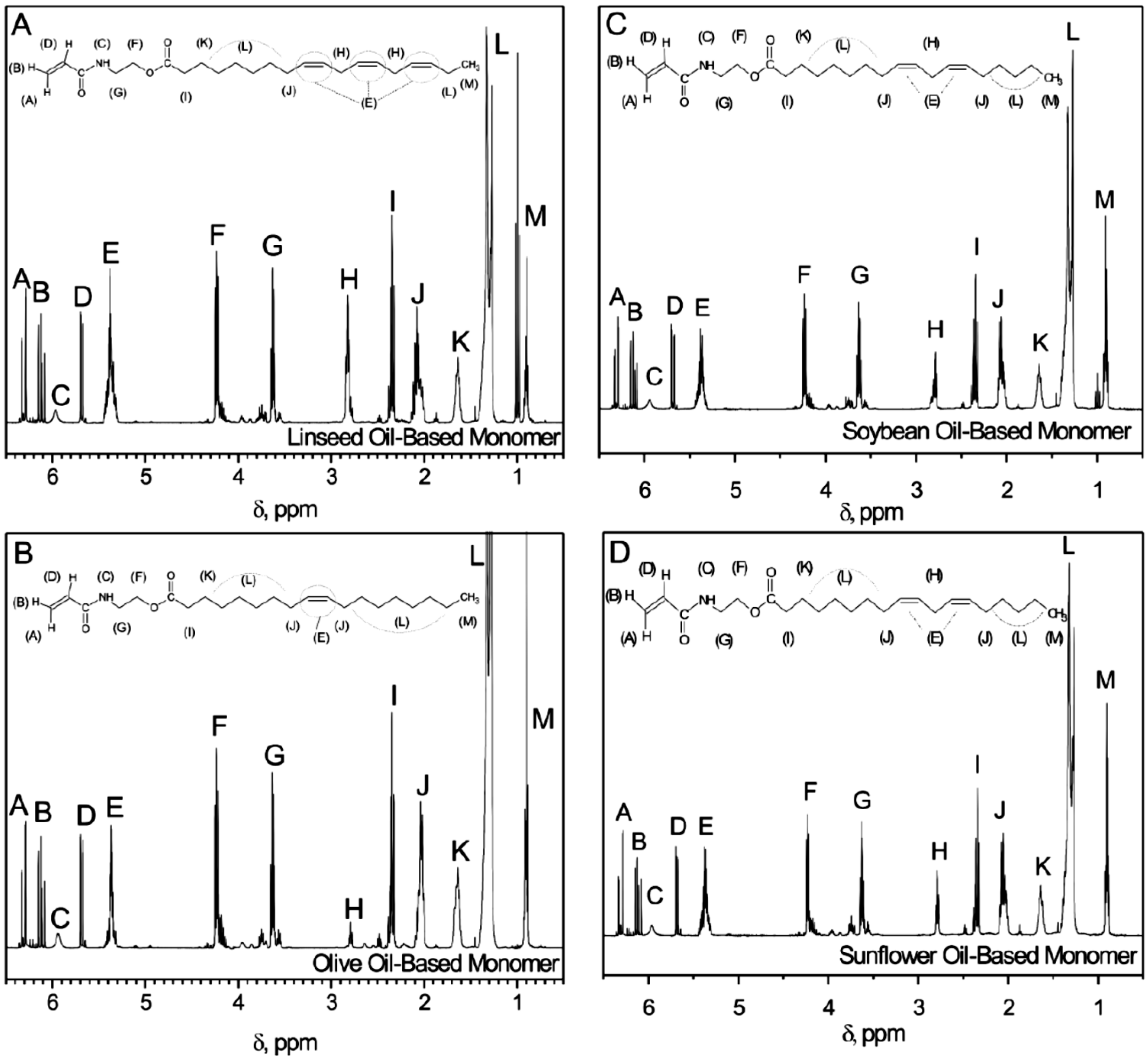


Figure C3. ^{1}H NMR spectra of plant oil-based monomers

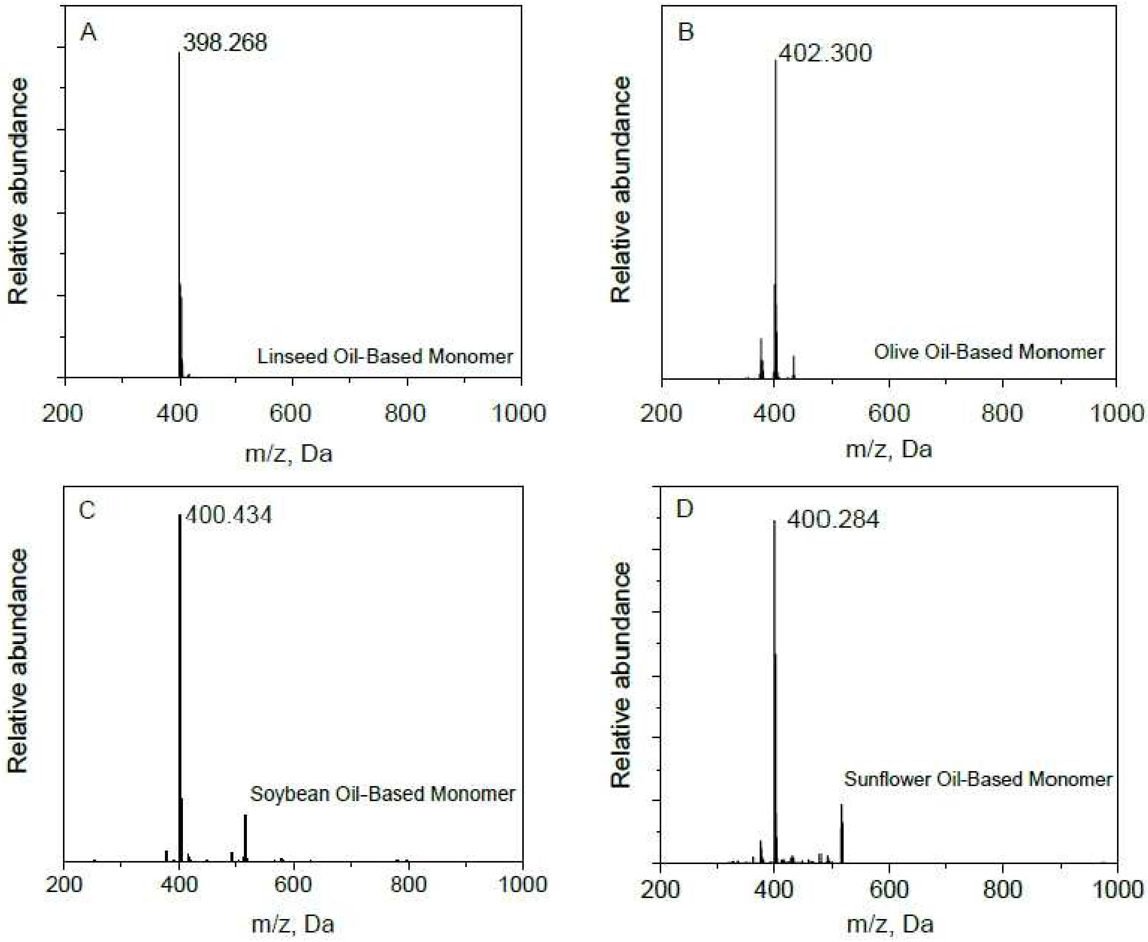


Figure C4. Mass spectra of plant oil-based monomers (A – from linseed oil, B – from olive oil, C- from soybean oil, D – from sunflower oil)

APPENDIX D. SUPPLEMENTAL MATERIAL FOR CHAPTER 7

Figure D1. Oxidatively cured POBM-based latex copolymer films with 60 wt.% of biobased content

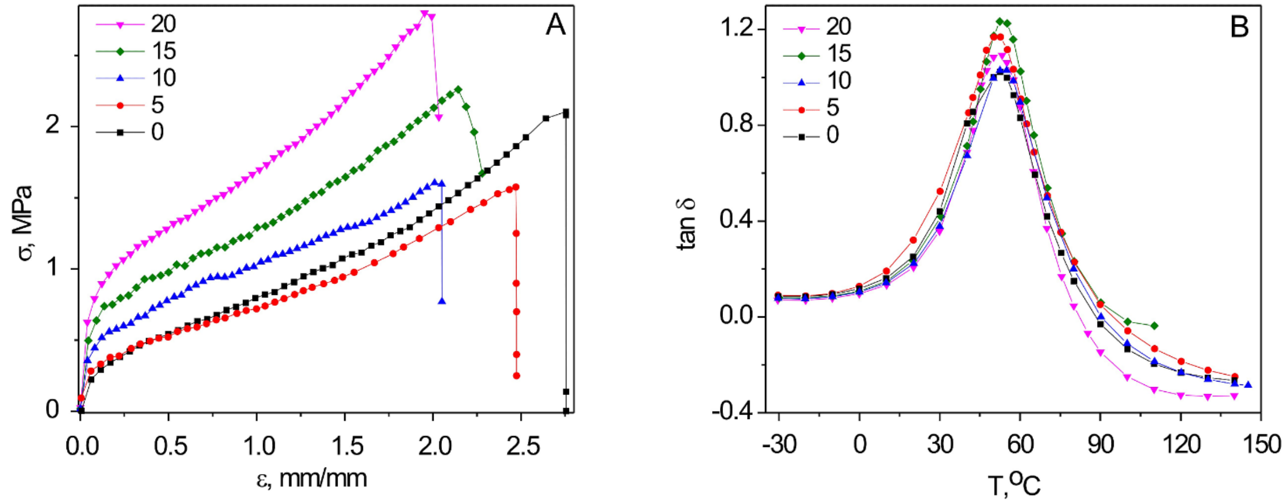


Figure D2. Stress-strain diagrams (**A**) and the change of tan δ with temperature (**B**) for OVM-based latex films at increasing HSBM content in copolymerization feed (wt.%)

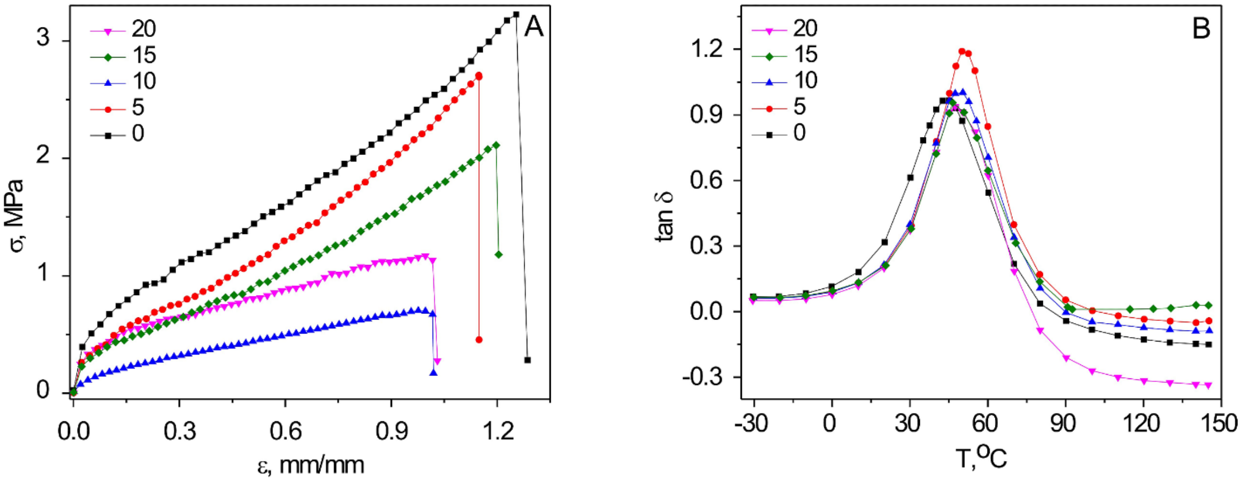


Figure D3. Stress-strain diagrams (**A**) and the change of tan δ with temperature (**B**) for SBM-based latex films at increasing HSBM content in copolymerization feed (wt.%)

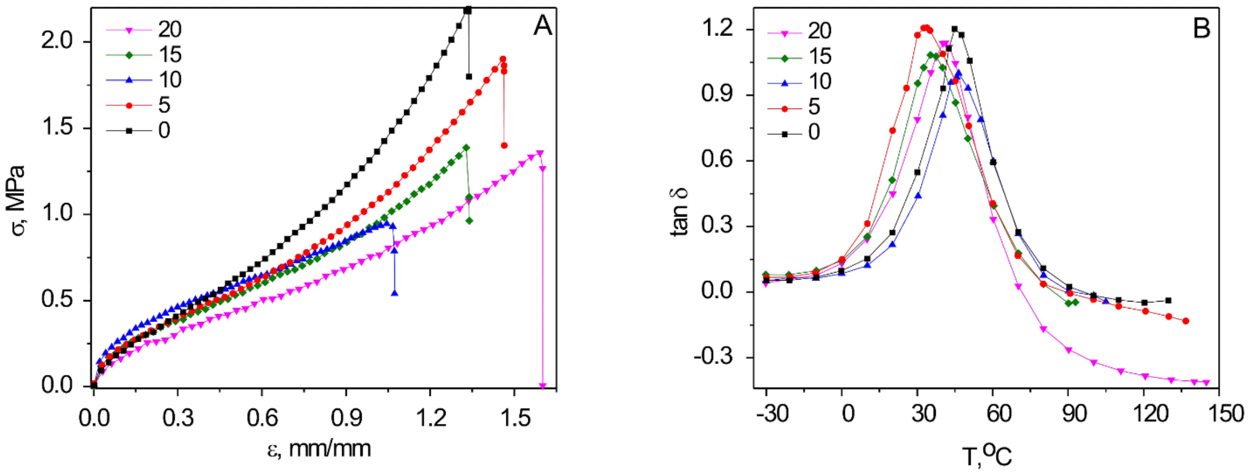


Figure D4. Stress-strain diagrams (**A**) and the change of tan δ with temperature (**B**) for LSM-based latex films at increasing HSBM content in copolymerization feed (wt.%)

APPENDIX E. SUPPLEMENTAL MATERIAL FOR CHAPTER 8

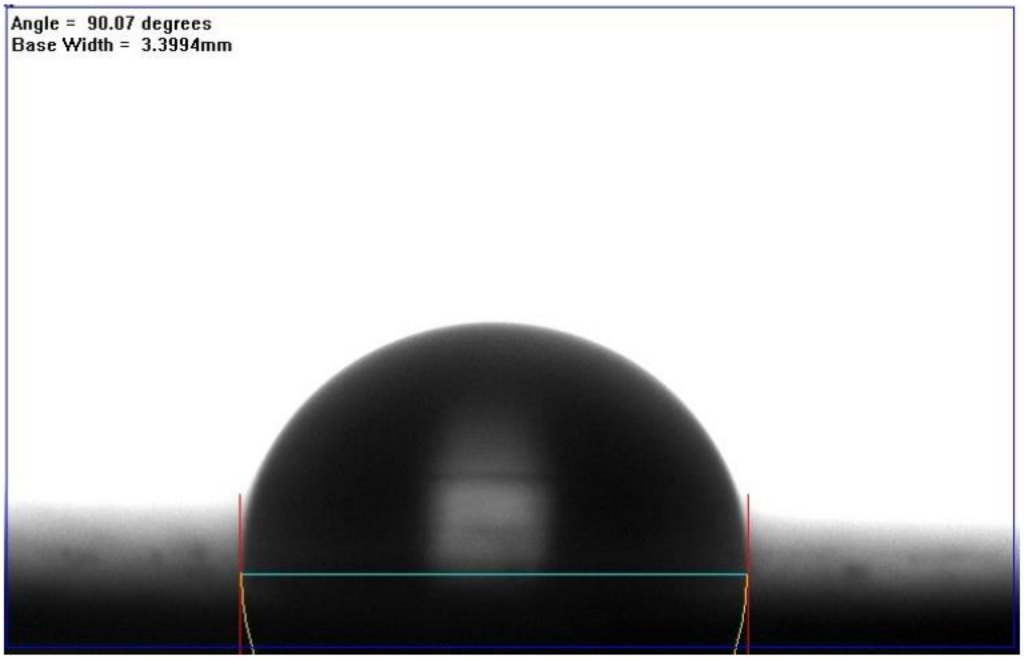


Figure E1. Selected water contact angle measurement on latex copolymer film with 50 wt.% of CBM and HOSBM content

APPENDIX F. SUPPLEMENTAL MATERIAL FOR CHAPTER 9

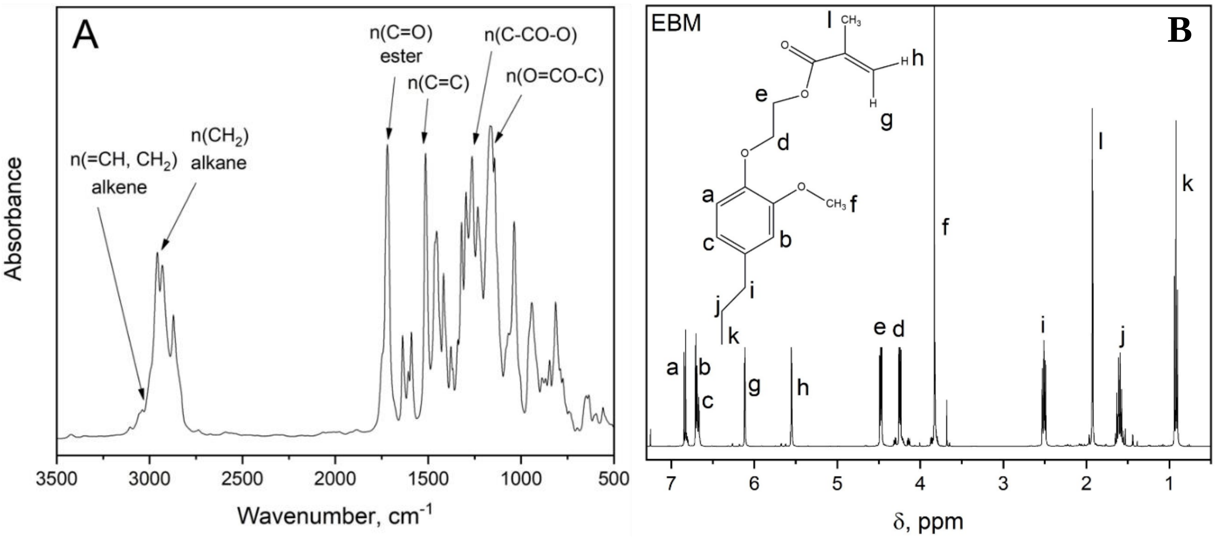


Figure F1. FT-IR (spectra **A**) and ^{1}H NMR **(B**) of EBM

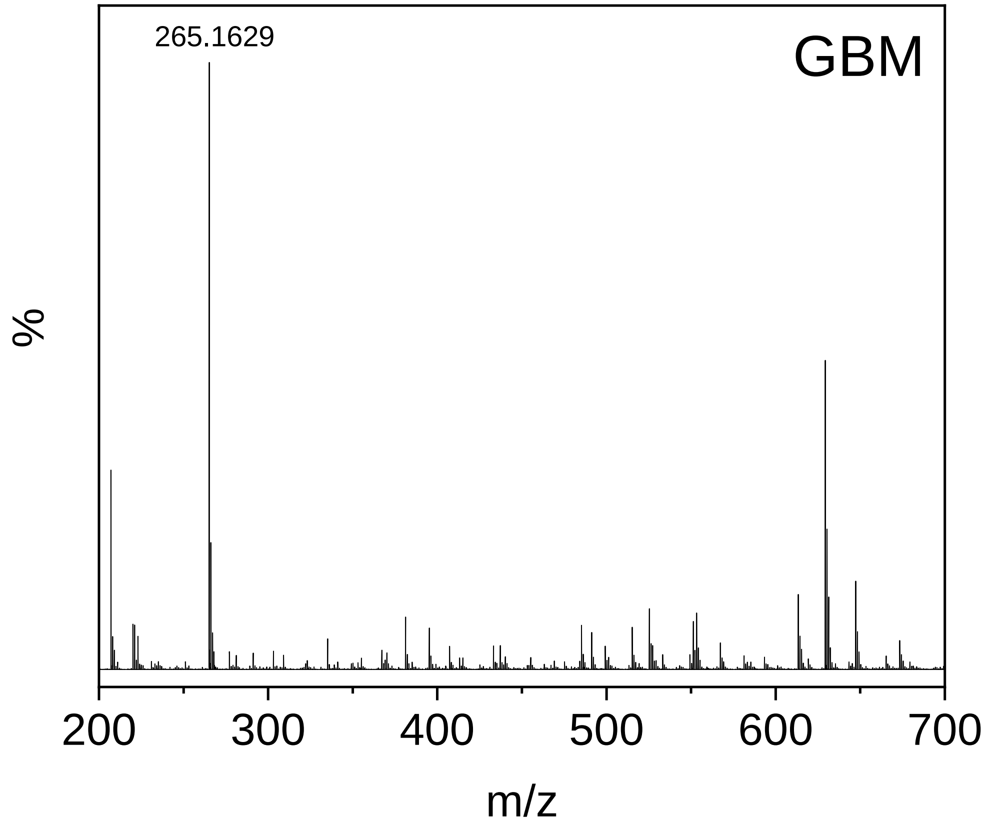


Figure F2. Characteristic mass spectrum of GBM

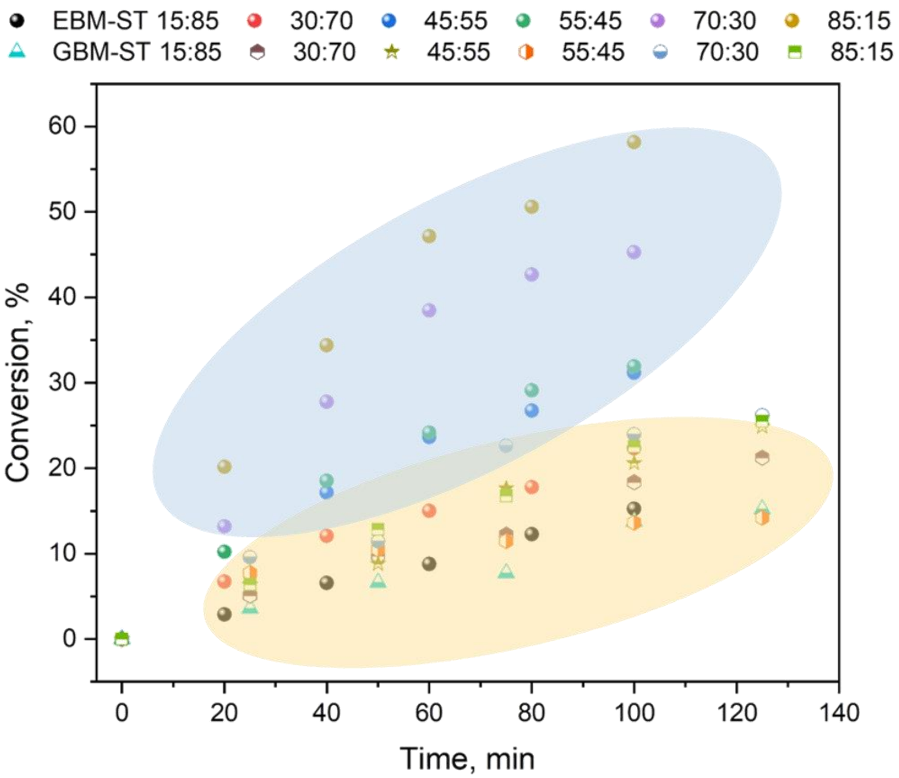


Figure F3. Conversion–time changes in the copolymerization of St with GBM and EBM in various ratios