CHARACTERIZATION OF ACTIVITIES OF CRUMB RUBBER IN INTERACTION WITH ASPHALT AND ITS EFFECT ON FINAL PROPERTIES

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

DOCTOR OF PHILOSOPHY

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ABSTRACT

Recycling of millions of scrap tires produced everyday is crucial challenge encountered by waste management systems. Recycling tire rubbers in form of ground tire rubber, known as crumb rubber modifier (CRM), in asphalt industry was introduced in early 1960's and is proved as an effective recycling method. Interaction between CRM and asphalt is physical in nature which happens mainly due to exchange of components between CRM and asphalt and enhances the time temperature dependant properties of asphalt.

In this work, the interaction between CRM and asphalt was evaluated through monitoring the evolutions of CRM in asphalt in macro and micro-level. The mechanism and extent of CRM dissolution were monitored under several interaction conditions. The composition of materials released from CRM was investigated using thermo-gravimetric analysis (TGA). The molecular status of the released components were studied using gel permeation chromatography (GPC) analysis. The composition analysis indicated that the CRM start releasing its polymeric components into the asphalt matrix at dissolutions higher than 20%. The released polymeric component of CRM alters the microstructure of the asphalt and creates an internal network at certain interaction temperatures according to viscoelastic analysis. At these temperatures, the released polymeric components are at their highest molecular weight based on GPC results.

The effect of released components of CRM on the time temperature dependent properties of asphalt and its glass transition kinetic was monitored using dynamic shear rheometer (DSR) and differential scanning calorimetry (DSC), respectively. The DSC results showed that the intensity of glass transition of the asphalt binder which is mainly defined by the aromatic components in asphalt reduced by absorption of these components by CRM.

The evolution of CRM was investigated during short-term aging of the modified asphalt binder. In addition, the effect of presence of CRM and release of its component on oxidization of asphalt binder was evaluated using Fourier transform infrared spectroscopy (FTIR). The results revealed that CRM continue absorbing the aromatic components of asphalt during aging which stiffen the asphalt binder. Also, it was observed that release of oily components of the CRM, which contain antioxidant, reduces oxidization rate of asphalt significantly.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AC	Asphalt cement
BBR	Bending beam rheometer
CRM	Crumb rubber modifier
CRMA	Crumb rubber modified asphalt
CRMA-RTFO-AC	Extracted liquid phase of short-term aged crumb rubber modified asphalt
CRMA-AC	Extracted liquid phase of crumb rubber modified asphalt
CRMA-AC-RTFO	Short-term aged liquid phase of crumb rubber modified asphalt
DSR	Dynamic shear rheometer
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
PAV	Pressure aging vessel
RTFO	Rolling thing film oven
TGA	Thermo-gravimetric analysis

LIST OF SYMBOLS

A……………....Area

G*……………..Complex modulus

δ........................Phase angle

S(60)…………..Creep stiffness

m-Value……….Rate of the change in creep stiffness by time

T_g…………......Glass transition temperature

a……………....Radius of the dispersed particle

$\Delta\rho$…………….The difference of density between the particle and the Newtonian liquid medium

g…………….. Gravitational acceleration

η…………….. Viscosity of the liquid medium

v_t……………. Terminal Velocity

LIST OF APPENDIX FIGURES

CHAPTER 1. INTRODUCTION

Introduction

In 2005, approximately 300 Million scrap tires were generated in US, 14% of which have been disposed in landfills [3]. Disposing scrap tires in landfills poses two major problems: waste of valuable materials and environmental pollution. To eliminate these problems several approaches have been followed in waste management system to create market for scrap tires [4]. Major portion of scrap tires have been used in markets like: tire derived fuel, civil engineering material and ground rubbers. Each of these markets roughly consumed 52%, 16% and 12% of generated scrap tires, respectively, in 2005 [5]. Among all these approaches, tire derived fuel market shows a very significant capacity to use scrap tires, but it is still a very low value recovery process of waste rubbers and suffering from air pollution problem. Therefore, using tires in other two markets seems more economical and environmental friendly and shows significant potential for growth [6].

Tire rubber is basically a complex engineered vulcanized compound which is mainly comprised of natural rubber (NR), Polyisoperene, and synthetic rubber (SR), Styrene-Butadiene Rubber and/or Butadiene Rubber, which are cross-linked with sulfur and reinforced with Carbon Black (CB). Also, other additives like aromatic hydrocarbons and antioxidants have been added to improve its workability and softness and prevent it from aging and oxidization, respectively [7]. The concept of using ground tire, known as Crumb Rubber Modifier (CRM), in asphalt for surface treatment was initially introduced in the mid 1960s and the application of CRM expanded to hot mix asphalt industry as an asphalt modifier in 1970s [6].

Modifying asphalt using CRM can be done mainly in two different ways: the dry process and wet process. The dry process corresponds to those methods that add CRM to preheated aggregate before introducing the asphalt into it, whereas the wet process are those processes in which the rubber interacted with asphalt before adding asphalt to aggregate [8]. However, among these two processes, wet process got the attention of researchers and industries due to its relatively lower production cost along with better performance of final product [6, 9].

The performance related properties of asphalt and modified asphalt were defined by Strategic Highway Research Program (SHRP) in 1990s [10]. Asphalt binder properties are categorized based on three major binder related distresses and the mechanism of their development on pavement. Rutting and fatigue cracking are being developed through dissipation of energy on pavement via permanent deformation and micro-cracks, respectively. The more energy being dispersed, the more distresses are being created on the pavement. Rutting, which happens at high service temperatures, is due to dispersion of the applied energy through viscose deformation of material which lead to the permanent deformation of the pavement. The amount of the work is being dispersed in this distress mode in conversely relates to $\frac{G^*}{Sin(\delta)}$. Therefore, to improve the physical properties of the asphalt, to prevent rutting, it is necessary to increase its stiffness, higher G* and/or increase its elasticity, lower phase angle (δ). Fatigue cracking, which happens at intermediate service temperatures of the pavement is due to dispersion of applied energy through creation of micro-cracks in pavement which eventually lead to creation of cracks on pavement. The energy which is being dispersed in this distress mode is defined by $G^*.Sin(\delta)$. Therefore, to prevent fatigue and thermal cracking o, it is necessary to decrease asphalt stiffness, lower G*, and/or increase elasticity, lower phase angle (δ). Thermal cracking occurs when the temperature drops rapidly and leads to fast contraction of the pavement layers. If the contraction happens fast enough, resulting stresses exceed the stress relaxation ability of the binder and lead to the creation of cracks on pavement. To prevent thermal cracking, the stiffness of the asphalt binder needs to be decreased and the rate of the relaxation, denoted as m-value, needs to be increased. It is also important to note that these properties of asphalt change during the service life of the pavement because of the aging and hardening phenomena. Each of the main distresses happens at different lifetime of the pavement. Rutting happens at early ages of the pavement (2 to 3 years after construction) when the asphalt's stiffness and elasticity is at its minimum level. On the other hand, thermal and fatigue cracking happens at the end of the life of pavement (after 7 to 10 years), when the stiffness and elasticity of the pavement have been increased significantly due to aging of the asphalt binder. To be able to predict the asphalt behavior at different ages, asphalt binders are being aged at two levels, short-term aging through Rolling Thin Film Oven (RTFO) and long term aging through Pressure Aging Vessel (PAV), before being tested based on SHRP grading system.

Developing properties of asphalt, like stiffness and elasticity, highly depends on asphalts microstructure and composition. The elasticity of asphalt is related to the type and amount of internal networking in the asphalt matrix, while the stiffness of the asphalt is highly related to its average molecular weight and polarity [11]. Therefore, in any type of modification it is important to characterize the effect of the modifier on the microstructure and composition of the asphalt and how the modifier affects asphalt's properties.

CRM modifies asphalt's properties in different aspects. It improves the rutting [12-14] and fatigue resistance [15-16] of the binder. However, its effect on low service temperature properties is controversial. It decreases the stiffness of asphalt at low service temperatures, which improvers low service temperature performance of asphalt [13, 17-19], but decreases the rate of relaxation which adversely affects low service temperature performance of asphalt [9, 20]. Also, CRM drastically affect the storage stability of asphalt, which leads to separation of CRM particles from liquid phase of asphalt during storage and handling of CRM Asphalt (CRMA) at high temperatures [21-22].

CRM is a complex modifier and its composition and structure transform throughout the interaction with asphalt. The changes in CRM result in changes in composition and microstructure of asphalt matrix and consequently develop its physical properties. Basically, changes in CRM during interaction with asphalt depends on many different parameters and can be categorized into two general levels; swelling [23] and dissolution [17, 24]. At low interaction conditions, CRM particles absorb light molecular weight components of asphalt and increase in their size up to 5 times of their original size [23, 25-26]. At more intensive interaction conditions or longer interaction time, CRM particles dissolve into the asphalt matrix and release their components into the asphalt matrix [26-27].

CRM behavior during interaction depends on different parameters [26, 28]. In general, these parameters can be divided into two main groups; interaction parameters and material parameters [28]. Interaction parameters include temperature, mixing rate, and time. Material parameters can be divided into two subgroups including; CRM parameters and asphalt parameters. CRM parameters include CRM source, processing method, size, and concentration. Asphalt parameters include its grade, chemical composition or molecular weight distribution.

Behavior of CRM particles under different interaction parameters modifies asphalts properties differently. Swollen CRM particles modify physical properties of asphalt by means of absorption of its low molecular weight components and also acting as elastic filler in asphalt which increase its viscosity and complex modulus [23, 29]. Dissolution of CRM particles results in partial release of CRM components in the asphalt matrix, which changes its composition, and in combination with remaining swollen particles improves asphalt viscoelastic properties [13, 17].

Dissolution of CRM results in release of its different components into the asphalt matrix. Each of the components in CRM particles can individually interact with asphalt components and consequently change asphalt properties. The effect of each of these individual components on asphalt modification is shown in different research works [18, 30-32]. It is shown that carbon black attracts the asphaltene portion of asphalt because of its high polarity [30]. Also, it is shown that Natural Rubber (NR) has more compatibility with asphalt in comparison with Synthetic Rubbers (SR) (i.e. Styrene-Butadiene Rubber (SBS)) and poly butadiene block of the SBS has higher compatibility with asphalt components than its styrene block which mostly role as cross-linking agent [33-34]. Moreover, antioxidants can prevent asphalt from oxidation [35]. Therefore, it is necessary to investigate the possibility of release of each of these components from CRM during interaction with asphalt and their possible contribution in asphalt modification. Also, to have full control on the interaction and reach to the optimum properties, it is necessary to investigate the effect of different parameters (interaction and material) on CRM behavior during the interaction with asphalt.

Problem Statement

One of the main issues in CRM modification of asphalt is to control its properties during the interaction process as well as through the lifetime of the pavement. In this respect, it is necessary to indicate the effective factors on developing CRM modified binder with superior physical properties. CRM particles evolve during the interaction with asphalt. They swell and expand in their size and then start dissolving into the asphalt matrix. During these evolutions, CRM particles exchange materials with asphalt and enhance its physical properties accordingly. To be able to develop modified asphalt with improved performance, it is necessary to fundamentally characterize the CRM activities at molecular level during interaction with asphalt and define the effective factors that control these activities.

Understanding the activities of CRM in asphalt and their respective effect on each performance related properties of asphalt will enable us to develop modified asphalt with superior properties. It is also possible to develop modified asphalts with customized properties based on the environmental and design needs and requirements.

Objectives

The main objective of this research is to characterize the activities of CRM particles, at molecular level, during interaction with asphalt, and to understand the effect of these changes on developing each of binder’s performance related properties. Moreover, in this study, to control the interaction between CRM and asphalt, factors that regulate each activity of the CRM in asphalt are investigated and identified.

The changes in structure and composition of CRM are monitored during the interaction as well as aging process of the modified binder. And, eventually, the effect of these changes on high and low temperature properties of asphalt and its aging mechanism is investigated.

Scope and Approach

To achieve the objectives of this study, several interactions are performed under different conditions. Activities of the CRM (swelling and dissolution) in asphalt are monitored. The effect of different parameters, such as interaction temperature, mixing rate, CRM concentration, and CRM type is defined. The state of dissolved portion of the CRM in asphalt matrix, under each of the conditions, is studied through molecular characterization. To investigate the effect of each of the CRM activities on final physical properties of the modified asphalt, the viscoelastic analysis is conducted on modified asphalt and its liquid phase, CRM removed condition. The effect of aging on status of CRM is studied through aging the CRMA and investigating the changes on composition of CRM and its dissolution in asphalt. Finally, the effect of CRM activities on glass transition temperature of the asphalt binder and its low temperature performance is studied using Differential Scanning Calorimetry (DSC) method and Bending Beam Rheometer (BBR).

Organization of the Thesis

The thesis summarizes the research work done between August 2009 and February 2014. In Chapter 2 detailed literature review is presented. General aspects and theories of interaction between asphalt and CRM are reviewed. Current state of art of analytical techniques used to characterize asphalt and modified asphalt is also presented. The experimental design of this work and materials and methods utilized during the experimental stage of the research are presented in Chapter 3. The effect of different parameters on dissolution mechanism of CRM in asphalt is discussed in Chapter 4. The molecular status of dissolved portion of CRM and its effect on internal structure of asphalt and its time temperature dependent physical properties is also presented in Chapter 4. In Chapter 5, the effect of CRM interaction and its exchange of components with asphalt are discussed on oxidative aging mechanism of asphalt binder.

Moreover, the age hardening of CRM modified asphalt with different levels of CRM dissolution is explained in this chapter. The effect of long-term aging on status of CRMA is investigated in Chapter 6. Additionally, the effect of CRM dissolution on low temperature properties of asphalt binder and its glass transition temperature is explained in this chapter. Summary of findings, conclusions, and recommendations for future research are presented in Chapters 7.

CHAPTER 2. LITERATURE REVIEW

Asphalt Binder

Asphalt is a byproduct of the distillation process of crude oil and consequently composed of various hydrocarbons including the most polar, most aromatic, and highest molecular weight components of crude oils. It has a complex chemical structure that results in its complex physical and rheological behavior [2, 36].

Asphalt typically composed of two distinct groups of materials, asphaltene and maltene [37]. Asphaltene is the most complex part of asphalt that is developed by agglomeration of the most polar components of asphalt, and is responsible for viscosity development of the asphalt. This part also has the highest tendency for association to other particles. Maltene on the other hand, composed of resins, waxes, aliphatic, and aromatic compounds. Asphaltene particles are micelle parts dispersed and stabilized in the maltene [38]. Asphaltene is an insoluble portion of asphalt in aromatic solvents. Several researchers tried to investigate its physical structure using Atomic Force Microscopy (AFM) and X-ray diffraction (XRD) [39-42]. It is claimed that asphaltene consist of a layered structure with layer distance of approximately 3.6 Å.

According to Petersen et al., asphalt can be categorized into two main groups, “Gel-type” asphalts and “Sol-type” asphalts [10]. According to this classification “Sol-type” asphalts are those, which consist of enough aromatic components and resins to well, peptize (disperse) the asphaltene particles and consequently they cannot form an extensive microstructure. On the other hand, “Gel-type” asphalts do not contain enough aromatic and maltene fractions to fully peptize the asphaltene fraction. Thus, in Gel-type asphalts, asphaltene form large agglomerations which in extreme cases can form a continuous network throughout the asphalt [10].

According to Petersen et al., different physical properties of asphalts are governed with the dispersion state of the asphaltene in asphalt matrix that is consequently determines the type of the asphalt. It is speculated that “Sol-type” asphalts mostly show high temperature susceptibility, high ductility, and low rates of age hardening whereas, the “Gel-type” asphalts show exactly a converse physical behavior. However these two types of asphalts are two extremes and mostly asphalts are fitted in between [10].

Complex chemical composition of asphalt and internal association of its components to each other leads to viscoelastic behavior of asphalt. Also, asphalt's physical properties highly depend on loading rate and temperature. Asphalt is very fluid at high temperatures or low loading rates and very brittle and stiff at low temperatures or high loading rates [43-44]. This susceptibility causes the asphalt pavement to be affected by traffic load in varying climatic environments. The flexible pavements need to be stiff enough at high temperatures to prevent rutting or permanent deformation and flexible enough at very low temperatures to prevent thermal cracking by dispersing the energy through deformation rather than micro cracking. These functionalities are required for pavements to accommodate increasing traffic in different climatic environments. The physical performance of conventional asphalts is not ideal for the increasing demand of today's roads, considering the increased traffic loads and volume which and, therefore different types of modification is utilized to improve its performance based on current needs [26].

Tire Rubber

Tire rubber is a complex engineered vulcanized compound that is mainly comprised of Natural Rubber (NR), Polyisoperene, and Synthetic Rubber (SR), Styrene-Butadiene Rubber and/or Butadiene Rubber, and highly cross-linked with sulfur and reinforced with Carbon Black

(CB). Also, other additives like aromatic hydrocarbons and antioxidants have been added to improve its workability and softness and prevent it from aging and oxidization, respectively [7]. The average amount of each of these components in tire rubber is presented in Table 2-1. The tire rubber has been engineered in a manner to tolerate the toughest weathering and loading conditions and to be durable. All these conditions make it almost impossible to recycle [4].

Table 2-1: Typical Composition of CRM

Component	Weight %
Natural rubber	19. 4
Synthetic rubber	37. 5
Carbon black	20. 8
Fabric, fillers, accelerators, antiozonants, etc.	22. 2

In 2005, approximately 300 Million Scrap tires generated in US, 14% of which have been disposed in landfills [Scrap Tire Markets 5]. Disposing scrap tires in landfills poses two major problems: waste of valuable materials and environmental pollution. To eliminate these problems several approaches have been followed in waste management system to create market for scrap tires [4].

Major portion of scrap tires have been used in several markets that mainly include: Tire derived fuel, civil engineering materials and ground rubbers. Each of these markets roughly consumed 52%, 16% and 12% of generated scrap tires respectively in 2005 [5]. Among all these approaches, Tire derived fuel market shows a very significant capacity to use scrap tires, but it is still a very low value recovery process of waste rubbers and suffering from air pollution problem. Therefore, using tires in other two markets seems more economical and environmental friendly and show substantial potential of growth [6, 23].

The concept of using ground tire, known as Crumb Rubber Modifier (CRM), in asphalt for surface treatment was initially introduced in the mid 1960s and the application of CRM expanded to hot mix asphalt industry as an asphalt modifier in 1970s [6].

Crumb rubber is shredded tire rubber into small particle sizes less than 6.3 mm. The shredding is typically carried out in two methods; ambient and cryogenic. In both methods the tire rubber is reduced to smaller manageable pieces and the steel fraction and fiber fraction are separated from the other components of tire. In ambient method, the tires are shredded into fine particles using ground mill at ambient temperature and in the cryogenic method, the tire is converted into fine particles using grinder at freezing temperature.

Processing methods of CRM define the morphology of the CRM particles and its surface characteristics [23, 45]. According to Heitzman et al. CRM that is processed with cryogenic method has very smooth and regular surface in comparison to the one produced by ambient method and therefore, has a lower interaction rate with asphalt [8].

In addition to the processing method, the gradation of CRM particles is also important in defining the average surface area of the particles and consequently the rate of reaction between asphalt and rubber. Several researchers state that finer CRM react faster with asphalt due to higher contact surface area [12].

Other than the production method of the CRM, the source of the tire rubber is important in defining the type and characteristics of the CRM. CRM can be produced from passenger car tires, truck tires or a mix of these two sources. Truck tires contain more natural rubber in their composition comparing to the passenger car tires. Therefore, the CRM produced from each of these sources vary in its composition. It is shown that the compatibility of the CRM produced from each of these tire sources is different with asphalt due to their different chemical composition. This is explained further in subsequent sections.

CRM Modification of Asphalt

Crumb rubber can be added into the asphalt in two different methods: “Dry process” and “Wet process”. These two methods are both initially developed in late 1960s [6]. In Dry process, Crumb rubber is added into the aggregates before introducing the hot asphalt binder and it substitute part of fine aggregate in the mix. This process initially developed in Sweden by the trade name of Rubit and subsequently registered in US under the trade name of Plusride. Research showed this method substantially increases amount of asphalt needed for the mix that adversely affects the construction cost.

The “Wet process” covers all those processes in which CRM is added into the asphalt binder prior to its introduction to aggregate [9]. In this method Crumb rubber and asphalt are interacted at high temperatures for certain amount of time. During this process the CRM swell and modify the properties of the asphalt.

Both explained methods need rubber tires to be grinded into very small particles from 425 micron to 25 micron sieve. Thus, the preprocessing of the rubber tires is necessary [6]. Among these two processes, wet process got the attention of researchers and industries due to its better performance and relatively lower production cost along with more application for its final product [6, 9].

Addition of CRM to the asphalt can be conducted at different interaction conditions. Charles McDonald, who initiated the wet process in early 1960s, added the CRM to the asphalt at 170°C for 45 min [23]. But, other researchers considered different interaction temperatures and mixing speeds to interact the CRM with asphalt to understand the effect of interaction parameters on interaction mechanism between CRM and asphalt and property development of modified asphalt.

Effective parameters

Different parameters are involved in interacting the asphalt and CRM. The effect of each these parameters have been investigated by several researchers. In general the effective parameters in interaction between the CRM and asphalt can be categorized into two main groups; material parameters and interaction parameters.

Material parameters include different properties of CRM and asphalt as follow:

- ✓ Asphalt properties
- ✓ Asphalt source
- ✓ Asphalt grade
- ✓ CRM properties
- ✓ CRM concentration
- ✓ CRM size
- ✓ CRM source
- ✓ CRM processing method

According to Bahia et al. the asphalt properties is more effective in defining the final properties of the modified asphalt than the CRM type [12]. However, their study was limited to low interaction temperature and speed. Also, it is shown that ambient processed CRM and finer CRM particles have higher rate of interaction with asphalt that is attributed to their higher specific surface area level. More surface area of the particles facilitates the contact of the asphalt and particles and therefore accelerates the interaction process. The source of tires affects the composition and cross-linked structure of CRM particles which defines its swelling extent [46].

Heitzman et al. stated that the CRM from truck tire source has higher compatibility with asphalt than the CRM from passenger car tires due to their higher Natural rubber content [8, 47]. However, comparing the solubility parameter of the CRM components and asphalt components indicates that synthetic polymer components should have better compatibility with aromatics of asphalt than the natural rubber [25].

Interaction parameters include all parameters that contribute in interacting the asphalt and CRM. These parameters are as follow:

- ✓ Temperature
- ✓ Mixing Speed
- ✓ Time

Typically, in asphalt industry, the CRM is interacted with asphalt at temperatures around 170˚C and 10Hz for 45 min to 60 min. However, it is proven that this interaction condition is not optimum production condition [17]. Abdelrahman et al. investigated the effect different interaction parameters on property development of asphalt rubber. According to their results, the physical properties of the asphalt rubber improve by time at very low interaction temperatures (i.e. 160˚C and 10Hz) whereas, at higher interaction conditions (i.e. 190˚C and 30Hz) the properties enhances at early stages of interaction and then start to degrade. And, finally at very high interaction conditions (i.e. 220˚C and 50Hz) the physical properties of the asphalt rubber degrades by starting the interaction.

Interaction Mechanism

The interaction between CRM and asphalt is not a chemical reaction [12, 48]. At low interaction conditions CRM particles absorb the light molecular components of asphalt and swell up to 3 to 5 time their original size [8]. By increasing the interaction conditions to higher temperature, mixing speeds and time, the CRM particles start to degrade and dissolve into the asphalt matrix [17, 26, 28].

Abdelrahman in his research investigated the effect of interaction conditions on swelling and degradation of the CRM particles in the matrix. He stated that at low interaction conditions the CRM continues to swell throughout the interaction time and consequently improves the high temperature physical properties of asphalt. This is also proven by other researchers [23]. By increasing the interaction temperature and mixing speed to higher levels the CRM particles star swelling at early stages of the interaction and then degrades by increasing the interaction time.

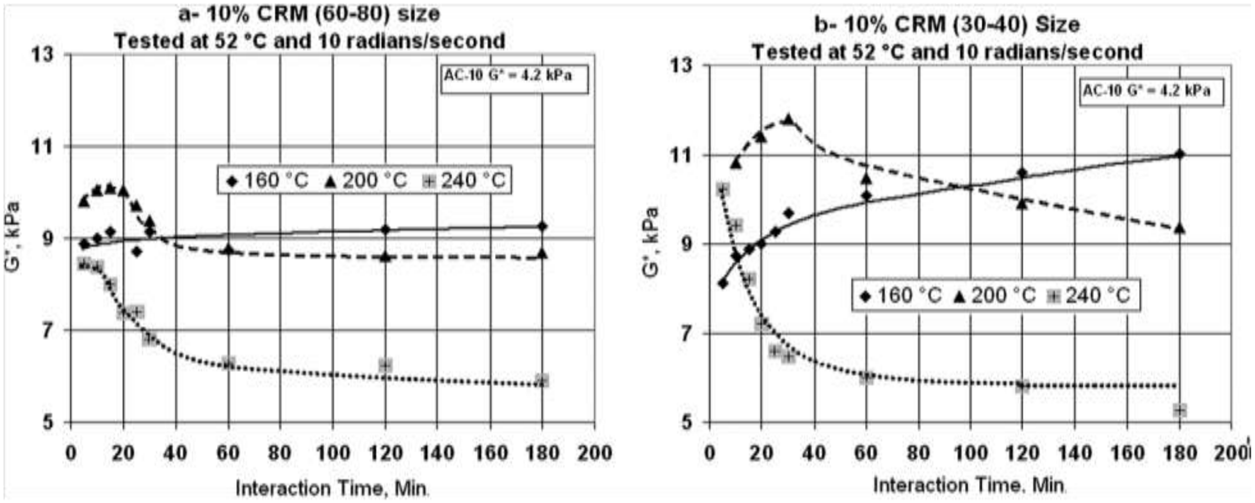

Figure 2-1: Trends of asphalt rubber interaction under different conditions [1-2]

And finally at very high interaction conditions, the CRM particles start degradation instantly and therefore, the high temperature physical properties of the asphalts degrades throughout the entire interaction and levels finally [26, 28]. The General trend of asphalt rubber behavior under different interaction conditions, developed by Abdelrahman, is presented in Figure 2-1.

It needs to be noted that swelling of polymers in presence of solvent is due to diffusion of small molecules of solvent into the structure of polymers. In the case of amorphous polymers, at first stage, the small molecules of solvent diffuse into the polymer. The polymer turn into a gel state and after that, polymers molecules start diffusing into the solvent. In cross-linked polymers the swelling stage happens in the same manner as amorphous polymers and the state of cross-linked polymer changes to gel. But, the swelling process in cross-linked polymers reaches to equilibrium and remains in that condition without diffusion of polymer chains into the solvent. CRM particles are highly cross-linked polymers which in presence of asphalt go through the same process of swelling. However, due to relatively high molecular weight of asphalt the swelling process takes much longer. Also, it needs to be noted that the dissolution of CRM in asphalt is not as same as diffusion of amorphous polymeric components into the solvent. Green et al. studied the swelling process of CRM in asphalt in details [23]. The dissolution of cross-linked polymers, like CRM, usually happens along with their devulcanization and partial depolymerization. This type of behavior of CRM is studied in this research in detail.

Airey et al. investigated the absorption process of light molecular components of asphalt by rubber particles. They concluded that the viscosity of the asphalt is highly important in defining the rate of swelling of the CRM particles. Asphalts with lower viscosity are absorbed faster by CRM particles and lead to their faster swelling rate. Also, they showed after the swelling of CRM particles, the Asphaltene content of the residual binder increases significantly which indicates that Asphaltene portion of the asphalt does not contribute in swelling process of the CRM particles [46]. Gawel et al. investigated the component exchange between the CRM and asphalt during interaction. They showed that the aliphatic compounds of the asphalt with linear chain structure penetrate to the CRM particles and fatty acids are release into the asphalt matrix from CRM particles [25].

Billiter et al. stated that presence of the CRM particles in asphalt in swollen condition is not optimal in developing the asphalt physical properties. They investigated the disintegration and devulcanization/depolymerization of CRM in asphalt under different interaction conditions. They showed that by increasing the temperature and time of interaction of asphalt and rubber, the CRM start to disintegrate and release its components in asphalt in the form of polymeric chains. They stated that increasing the interaction mixing speed accelerates the disintegration process of CRM and leads to depolymerization of released polymeric chains [13, 27]. Moreover, Billiter et al. and Zanzotto et al. in two different studies showed that intensive increase in the interaction temperature (i.e. to above 240˚C) leads to high disintegration of CRM particles in asphalt matrix. Also, increasing the interaction time at the given temperature leads to cleavage of the polymeric chains, which showed itself by decrease in average molecular weight of asphalt [17, 24].

Billiter et al. showed that the chemical composition of asphalt is also important in devulcanization/depolymerization of CRM particles in asphalt. They showed CRM dissolve faster in asphalts with higher amount of aromatics [27]. They attributed this observation to the higher diffusion rate of aromatics in CRM particles. They also showed that depolymerization of the released polymeric components of the CRM occurs faster in asphalts with higher asphaltene and polar components content [17].

Performance Related Properties of Asphalt

In order to develop specification for grading and characterizing asphalt, Strategic Highway Research Program (SHRP) was launched in 1987 which established performance based specification of asphalt, called Superpave specifications. In this specification all tests were designed for both modified and unmodified asphalt binders. Also, this specification addresses and measures those properties of asphalt, which are directly related to the distresses of the asphalt pavements [48-49].

These tests consist of Rotational Viscometer (RV), Dynamic Shear Rheometer (DSR), Bending Beam Rheometer (BBR), Tensile strength, Rolling Thin-Film Oven (RTFO), and Pressure Aging Vessel (PAV). All these tests designed to measure the performance related properties of asphalt. RV is used to measure the viscosity of asphalt in mix and compaction temperature. DSR is used to measure the complex modulus, elasticity, viscosity and the loss tangent of asphalt in its high and intermediate service temperature. These properties are showing the ability of asphalt to resist permanent deformation and fatigue cracking, respectively. BBR measures the stiffness and m-value of asphalt in minimum service temperature of asphalt pavement. The results would indicate the ability of the asphalt to resist cracking in very cold environment. Also, the RTFO and PAV are simulate the short-term aging and long term aging of the asphalt respectively [50]. There are two assumptions in Superpave test method which are required to be met in order to be applicable for any binder.

1. Binder behavior is independent of film thickness and sample geometry; and
2. The binder is evaluated based on the properties within the linear viscoelastic range in which its behavior is independent of the strain or stress level.

Accordingly, several researchers analyzed the applicability of Superpave test methods on modified asphalts and especially CRM modified asphalts [13, 49, 51]. Several difficulties have been reported in various researches regarding to application of Superpave test methods on modified asphalts. For instance aging the modified asphalt through RTFO and PAV may cause degradation of modifier in asphalt or initiation of more interaction between them as they are all being conducted at higher temperature than the temperatures asphalt face within its service life in order to accelerate the test [52]. Also, modified asphalt does not roll appropriately in the RTFO bottles or creep out because of their high viscosity [53]. Moreover, most of the modified asphalts behave non-linearly and this may cause difficulty in the use of Superpave test protocols. In addition, there are CRM particles in CRM asphalts, which make the use of DSR more complicated. Billiter claims that using stress control test method may cause a relatively huge strain which will affect the asphalt rubber interface and consequently affect the repeatability of the test [13]. In spite of all these problems, still lots of researchers use these methods to characterize modified asphalt and some of them apply minor modification to omit aforementioned problems. Huang et al. suggest using lower temperature for aging the modified asphalt in PAV while using longer time (i.e. 60°C and 48 hr) [15]. In order to, solve the RTFO problem, Bahia et al. suggest to use metal bars with specific sizes inside the RTFO bottles to facilitate the rolling of the modified binder and also prevent them from flowing out [49]. And, in the case of linearity of modified asphalt, Billiter suggests to find the linearity limits of the modified asphalt before applying the test and also use strain control test instead of conventional stress control one. Also, to resolve the presence of the CRM particles in CRM asphalts, he suggests using a larger gap between the plates.

Effect of CRM on Performance Related Properties of Asphalt

Rutting

Rutting is permanent deformation of the pavement under the load and mainly happens at hot summer days during first or second year after laying down the flexible pavement. Different parameters can cause creation of rutting, including misusing the pavement by overloading it or failures in designing the pavement surface and subsurface layers of the pavement. The main component that handles the load on the pavement is aggregate. For asphalt pavement it is very important to select crushed surface aggregates with create great interlock and prevent aggregates from slipping. Failure in selecting quality aggregates leads to rutting. The second important material in flexible pavement is asphalt binder, which works as glue and binds the aggregates to each other. The properties of asphalt binder changes by temperature and, therefore, it is crucial to select the asphalt binder based on the environment temperature. To resist rutting most of the energy that is being applied to the pavement by passing traffic, needs to be recovered through elastic rebound of the pavement rather than dissipating through permanent deformation. In general the amount of total work that is being dissipated in each loading cycle needs to be minimized. According to SHRP program, the amount of energy that being dissipated in each loading cycle can be mathematically calculated using the following equation:

$$W_c = \pi \times \sigma^2 \times \frac{\sin \delta}{G^*} \qquad \text{Eq. 2-1}$$

Where

W_c = Work dissipated per load cycle,

σ = Stress applied during the load cycle,

G* = Complex modulus

δ = Phase angle

As it is indicated in Eq. 2-1, the work that is being dissipated in each load cycle is inversely proportional to G*/sin(δ) . According to this equation we can minimize the energy dissipated in each loading cycle by increasing the G* and decreasing the phase angle for asphalt binder.

Asphalt is a viscoelastic thermoplastic material which turns in to a fluid at high temperatures (above 120°C) and gets very brittle at very low temperatures (below 10°C). Also, at temperatures in between it shows viscose and elastic behavior at the same time. Changing the temperature changes the elasticity and viscosity in asphalt, the proportion of which is measured by phase angle (δ). At high temperatures, asphalt is more of a viscose material and deform under the load. This behavior cause permanent deformation on flexible pavements at high service temperatures like hot summer days. Base on viscoelastic properties of asphalts and energy dissipation in the road according to Eq. 2-1, asphalts with higher elasticity (G') and lower viscosity (G") and in total higher stiffness (G*) are more rutting resistance. To evaluate this property of asphalt in Performance Grading system of asphalt the following equation is suggested:

$$Rutting\ parameter = \frac{G^*}{\sin(\delta)} \qquad \text{Eq. 2-2}$$

Where the G* is complex modulus of the asphalt binder and the δ is the phase angel. These parameters are defined with following equations:

$$G^* = \frac{maximum\ Shear\ Stress}{Maximum\ Shear\ Strain} = \frac{\tau_{max}}{\gamma_{max}} \qquad \text{Eq. 2-3}$$

$$\delta = Time\ lag\ between\ Shear\ Strain\ and\ Shera\ stress$$

In performance Grading (PG) system the rutting parameters of the asphalt binder is measured in two stages; tank or original asphalt and short-term aged asphalt. For original asphalt, the rutting parameter should be greater than 1 kPa and for short-term aged asphalt the rutting parameters should be greater than 2.1 kPa at a given temperature to be able to use the asphalt binder in pavements with such high service temperatures. To measure the rutting parameter, the Superpave program suggested the Dynamic Shear Rheometer.

The rutting resistance property of asphalt binder is one of the most studied properties. Several researchers have studied this property of the asphalt for several years and suggested different methods to improve this property. Various modification methods have been suggested to improve the high service temperature performance of asphalt binder from air blowing the asphalt binder to polymer modification of the asphalt.

The effect of CRM on high service temperature performance of the asphalt is widely studied and proved. Possibly the first time that the effect of CRM on high service temperature performance of the asphalt was studied was by McDonald who for the first time introduced the CRM as a modifier. After introduction of the PG grading system by Superpave program, Bahia et el, investigated the effect of the CRM on high service temperature performance of the asphalt, using DSR [12]. They stated that the DSR test method, suggested by Superpave program to measure the rutting performance of the asphalt, is applicable for the CRM modified asphalt. However, the settings need minor adjustments due to granular nature of the CRMA which has CRM particles in it. In another research they suggested increasing the gap between the plates in the DSR based on the size of the modifier particles in asphalt [54]. Other researchers also showed that addition of CRM into the asphalt increases its complex modulus and elasticity [55-56]. However, the extent of the increase is highly depends on interaction and material parameters that introduced previously [12-13, 28]. Billiter et al. investigated the effect of complete degradation of CRM particles under extensive interaction conditions on rutting properties of asphalt binder. They concluded that degradation of the CRM particles still result in higher complex modulus of the asphalt, however, it is lower than the CRMA with swollen CRM particles in it [13, 17, 27]. Abdelrahman et al. investigated the progress in rutting performance of the CRMA as a function of the interaction conditions and time. They concluded that at low interaction conditions where the swelling of the CRM particles happen, the rutting performance of the CRMA enhances. However, by increasing the interaction temperature and time, the rutting performance of the CRMA deteriorates gradually, however, it is still performs superior in comparison with the unmodified asphalt binder [28].

Short-term aging

One of the most critical stages in flexible pavement construction is the mixing and compaction process during which the asphalt binder goes through substantial aging, known as short-term aging [57]. Different parameters affect the aging process of the asphalt during this stage including but not limited to: asphalt type and its content in the mix, nature of the aggregate and their gradation and production related parameters [57]. Asphalts from different sources can go through different aging process and therefore, their physical properties changes accordingly. Consequently, Superpave program intensively studied the aging of asphalt binder and considered it as a part of grading system. In order to measure and compare the physical properties of the asphalt binder after the aging process, the Superpave program studied different methods to simulate the aging of the asphalt binder, which happens during mixing and construction. Based on these studies they suggested two instruments; Thin Film Oven (TFO), and Rolling Thin Film Oven (RTFO). The two methods are producing the same samples, however, the RTFO method produce the samples in a shorter time and therefore is more interesting for asphalt industry.

During the short-term aging process, asphalt binder goes through different physical and chemical changes which results in its hardening and leads to premature failures in asphalt pavements [57-58]. Wu et al. investigated the changes in the micro-phases of asphalt binder during the aging. They showed that the multi-phase state of the neat asphalt binder tends to transform into a single-phase during the aging and the aging eliminates the borders between different phases [59]. Siddiqui et al. investigated the aging of asphalt binder using different analytical methods. They stated that carbonyl and sulfoxide groups increase considerably during the aging and there is a good correlation between their formation rate and the hardening rate of asphalt binders [41]. They also, stated that during the aging, aromatization and dehydrogenation of Asphaltene occurs [60]. Isacsson et al. and Glover et al., in two different studies, investigated the effect of aging on chemical composition of asphalt, including the formation of functional groups like carbonyl and sulfoxide, transformation of generic fractions of asphalt, and changes in the large molecular size components of asphalt [57, 61]. They stated that during the aging, the functional groups of asphalt oxidize and form carbonyl and sulfoxide groups. Also, part of the aromatic fraction of asphalt transform into the resins and part of the resins transform into the asphaltene [57, 61].

Several researchers also investigate the changes in average molecular weight of asphalt. In general it is shown that during the aging the average molecular weight of the asphalt increases [62]. Amirkhanian et al. investigated the changes in large molecular weight components of asphalt. They showed that increases and the medium and small molecular components of asphalt decreases during the aging of the asphalt [62]. This also has been proven by Cortizo et al. They showed that this changes in average molecular weight of asphalt is related to the oxidation of resins and polar components and their transformation to asphaltene [63].

In general, the aging of the asphalt is related to two main mechanisms; oxidization of functional groups in asphalt that increase its polarity, and volatilization of the light molecular components of the asphalt which function as peptizing agent. These two mechanisms lead to increase in the asphaltene and resins concentration in asphalt and consequently increase the stiffness of the asphalt [57].

Aging is still a fact in the case of modified asphalt. However, modification of asphalt can change its aging mechanism. For several years, researchers have studied the effect of different modifiers, from acids and antioxidants to polymers and fillers, on asphalt properties and its aging mechanism. It is shown that addition of antioxidants can retard the oxidization of the asphalt components during the aging [35]. Oliver et al. investigated the effect of two different types of antioxidants on the aging of the asphalt binder; diamyldithiocarbamate (LDADC) and hydrated lime (HL) [64]. They showed that both antioxidants are effectively retarding the oxidization of the asphalt component and prevent asphalt from hardening. However, HL is losing its effectiveness in long term whereas, LDADC effectively retards the oxidization process under long term period of exposure [64]. Apeagyei et al. also, studied the effect of different antioxidants on age hardening of the asphalt. They concluded that a combination of LDADC and Furfural is the most effective antioxidant which reduces the age hardening of asphalt up to 40% [31].

Polymer modifiers are also change the mechanism of aging of asphalt. As one of the most common modifiers in asphalt industry, the effect of polymer modifiers on aging of asphalt has been investigated by several researchers [35, 65-67]. Lu et al. investigated the effect of aging on different types of polymer modifiers including; styrene butadiene styrene (SBS), styrene ethylene butylene styrene (SEBS), ethylene vinyl acetate (EVA), and ethylene butyl acrylate (EBA) copolymers [65]. They concluded that polymer modifiers prevent formation of Sulfoxide in asphalt binder, however, they couldn't comment on formation of the carbonyl groups due to overlap of its spectrum with the spectrum of polymer modifiers. Moreover, they stated that aging of the polymer modified asphalt binder leads to degradation of the polymer chains in asphalt as well as oxidization of the asphalt binder. The degradation of the polymer chains are more significant in the case of the SEBS in comparison with other polymer modifiers [65]. The same degradation of polymer chains is reported in other studies too [35, 67].

Aging of the CRMA is much more sophisticated and complex than the neat asphalt and also modified asphalt by other modifiers due to complex composition of asphalt and crumb rubber and also the dynamic nature of the interaction between these two components and effect of the time and temperature on enhancement of the physical properties of the composite [54]. CRM particles absorb aromatics in asphalt and swell up to 3 to 5 times their original size at elevated temperatures however, never reaching to the maximum level of swelling during the interaction period [28]. Since mixing and construction of asphalt is conducted at high temperatures, close to the asphalt and CRM interaction temperature, the swelling of CRM particles can continue during this time in addition to the other conventional aging mechanisms of asphalt binder and lead to more changes in final physical properties of CRMA after its aging [15].

Depending on interaction parameters, CRM particles exchange their components, including antioxidants and polymeric components, with asphalt during the interaction. It is shown that each of these components individually affects the aging mechanism of asphalt. Antioxidants can retard the reactive groups of asphalt and prevent them from reacting with oxygen [35]. Also, polymeric chains function as retardant and inhibit the oxygen molecules penetrating into the asphalt and react with its functional groups. Moreover, it is shown that the polymeric chains may degrade during the aging and consequently neutralize part of the physical hardening happens due to oxidization and volatilization of asphalt components [35, 63].

Raad et al. investigated the short-term aging of CRMA. They stated that the RTFO affects modified binder more intensively in comparison with unmodified asphalt [68]. They showed that under the same condition of RTFO aging, the high temperature viscosity of the CRMA increases to higher extents than the unmodified asphalt binder. Also, the reported that the weight loss of the CRMA is lower than the unmodified asphalt during the aging, however, they didn’t provide sufficient data. Wang et al. in another study investigated the activities of the CRM particles during the short-term aging of asphalt [55]. They stated that CRM particles absorb the light molecular weight components of the asphalt during the interaction and prevent them from transforming to higher molecular weight components during the aging, which is happening in the case of unmodified asphalt. In this way the actual aging effect of RTFO on oxidization and aging of the asphalt binder is decreases [55].

Thermal cracking

Among several types of distresses on pavement, thermal cracking is of considerable concern and interest to highway engineers especially in Canada and the northern region of the United States. High cooling rate and very low temperatures result in shrinkage of the pavement and consequently develop tensile stresses on pavement. When these stresses exceed the fracture stress of the surface layer of the pavement, thermal cracking develops. Stiff asphalt pavements are more prone to low temperature cracking. Stiffness of the asphalt pavement primarily depends on stiffness of the asphalt binder used in it. Therefore, high stiffness of asphalt binder is the predominant cause of thermal cracking of pavement. Hence, measuring and controlling the stiffness of the asphalt at very low temperatures is crucial to construct durable pavements.

Superpave specification for grading asphalt has suggested the bending beam rheometer (BBR) test to determine the performance of asphalt binder at very low temperatures. This test measures the load and deflection, and calculates the creep stiffness, S(t), and m-value of asphalt samples. Creep stiffness represents how the asphalt binder resists the constant creep loading and the m-value represents the rate of stress relaxation by asphalt binder flow and is calculated based on the changes in creep stiffness of asphalt binder by the loading time. These properties of asphalt change by its modification.

Crumb rubber modification of asphalt is a well-established practice in the asphalt industry. Therefore, the effect of CRM on low temperature performance of asphalt and its resistance to thermal cracking has been widely studied. Bahia et al. and Billiter et al. in two different studies investigated the effect of CRM on low temperature of different binders. They stated that CRM improves the stiffness of the binder at low temperatures but degrades its m-value [12-13]. Billiter et al. also, investigated the effect of high curing conditions on low temperature properties of CRM modified asphalt. They concluded that high curing conditions improve the homogeneity of the modified binder as well as its creep stiffness at low temperatures [17]. However, they didn’t test the m-value of the modified asphalt.

The changes in low temperature properties of CRM modified asphalt have been attributed to different effects of CRM in asphalt. Billiter et al. stated that tire rubber has very low sensitivity to temperature and keeps its elastic properties at these temperatures. Therefore, tire rubber can function as elastic filler in asphalt at very low temperatures, close to asphalts glass transition temperature, and improves its flexibility [13]. On the other hand, Hesp et al. speculated that improvement in low temperature of asphalt in presence of CRM happens due to crack pining and crack blunting effect of these particles which lead to higher toughness of the binder [69-70]. Moreover, it is stated that CRM can improve the aging susceptibility of the asphalt binder which results in lower stiffness of asphalt after aging and consequently better physical properties at low temperatures.

Effect of CRM on Non-performance Related Properties of Asphalt

Storage stability

Modification of asphalt binder is a very common practice these days in order to improve its physical properties and performance. Modification of asphalt decreases its temperature susceptibility and this enables asphalt to withstand more load and more severe environments [71-72]. Also, asphalt modification changes the composition of asphalt and its homogeneity, depending on the type of modifier [73].

In practice, asphalt binders are stored at high temperatures, to facilitate handling and mix production process [54, 72]. Therefore, it is of great importance that asphalt stays stable during its storage time. However, in the case of most modified asphalts, severe phase separation occurs during storage at high temperatures. The mechanism of separation significantly depends on the type of modifier and its interaction with asphalt [54].

Since the modified asphalts consist of two distinct phases, its phase separation can be theorized based on Stoke's law. Based on this theory the phase separation in modified asphalt is governed by the terminal velocity of dispersed phase in Newtonian liquid. The terminal velocity is the velocity of the displacement of the particles when the gravity force on particles equals the drag force on particles in a Newtonian liquid and can be quantified by the following equation [74]:

$$v_t = \frac{2a^2\Delta\rho g}{9\eta} \qquad \text{Eq. 2-4}$$

Where a is the radius of the dispersed particle, $\Delta\rho$ is the difference of density between the particle and the Newtonian liquid medium, g is the gravitational acceleration and η is viscosity of the liquid medium.

Based on this theory, terminal velocity of the particles is directly related to the square of the radius of the particles and inversely related to the viscosity of the medium. Decreasing the terminal velocity in the system will decrease the displacement velocity of the particles. This theory has been utilized by several researchers to understand the mechanism of separation in modified asphalts, containing different modifiers, and the effective parameters that can prevent the separation from happening [72-73, 75-77].

The same concept can be considered about the CRM modified asphalt where there are CRM particles with various sizes suspended in liquid asphalt at high temperatures [72]. CRM particles have a relatively higher density (1.15±0.05 g/cm^3) than asphalt (1.02 g/cm^3) and consequently have the tendency to descend due to the gravitational forces, which depends on the volume of the CRM particles and difference between the density of the particles and asphalt [8]. On the other hand, asphalt at very high temperatures, shows Newtonian liquid behavior with a finite viscosity and therefore shows resistance to displacement of CRM particles by applying the drag force, which depends on the volume of CRM particles and the viscosity of the liquid. Manipulating these forces enable us to reduce the terminal velocity of the particles (displacement velocity of particles when the two forces are equal) and consequently reduce the sedimentation rate of CRM particles. To do this it is necessary to understand the changes in the size and density of CRM and the viscosity of the liquid phase of CRM modified asphalt and their effect on storage stability of the CRM modified asphalt. In CRM modified asphalt, terminal velocity defines the sedimentation velocity of CRM particle and therefore, we denote it sedimentation velocity throughout this work.

Storage stability of CRM modified asphalt has been investigated in several studies considering different parameters, including CRM particle size, asphalt type and interaction conditions [1, 21, 24, 72, 78]. It is stated that decreasing the CRM particle size, increasing the interaction mixing speed or extending interaction time improve the storage stability of asphalt [1, 21, 72]. Also, compatible asphalts have shown better storage stability in the case of modification.

In this study the effect of dissolution of CRM on storage stability of CRM modified asphalt was investigated using the Stoke's law theory.

Glass transition of asphalt

Glass transition is a result of decreasing the molecular mobility upon cooling the component at a fast rate. Molecular mobility principally depends on temperature and slows down by decreasing the temperature. Decreasing the temperature at high rates freeze the molecules and prevent them from structural rearrangement and reaching the equilibrium. Transition to glassy state changes the rubbery and plastic properties of polymeric components to glass and brittle.

Transition to glassy state also happens to asphalt at very low temperatures. However, due to complex composition of asphalt it shows more than one glass transition during its cooling down [79]. Several researchers have studied the glass transition of asphalt and investigated its effect on low service temperature performance of asphalt in pavement [79-86].

Wesolowski et al. investigated the glass transition temperature of petrolume products using as Differetial Sacning Calorimetry (DSC) [80]. They speculated that presence of parafinic components has marginal effect on glass transition temperature of petrolume products.

Brule et al. investigated the glass transition of asphalt using DSC, they stated that asphaltene and resin portion of asphalt has limited effect on glass transition temperature whereas saturates and aromatics highly contribute in glass transition of asphalt [81]. Also, they stated that there is a good correlation between the glass transition temperature of asphalt and its low temperature performance which is measured using Frass Brittle Point, not a standard method to measure the performance of asphalt. Ehrburgera et al. also, investigated the effect of paraffinic material on glass transition of asphalt [83]. They stated that presence of paraffinic components in asphalt interfere with glass transition of saturate components in asphalt and consequently decreases the glass transition temperature. They showed that storing the asphalt at room temperature leads to crystallization of paraffinic components that leads to its separation from saturates in asphalt.

Characterization Methods of Asphalt Binder

Spectroscopy

Several researchers in asphalt characterization field have used spectroscopy methods. FTIR method is an established method to investigate the aging mechanism and extent of asphalt binder [87]. The list of asphalt's IR characteristic bands is presented in Table 2-2. Lamontagne et al. [2],and Zhang et al. [32] developed several indices (e.g. Carbonyl and Sulfoxide) to measure the changes in composition of asphalt binder and trace any chemical interaction in it. They developed an empirical equation to compare the changes in the carbonyl content of asphalt. They measured the area under the each band valley to valley and calculated the percentage of the area under the characteristic band as an index as presented in Figure 2-2.

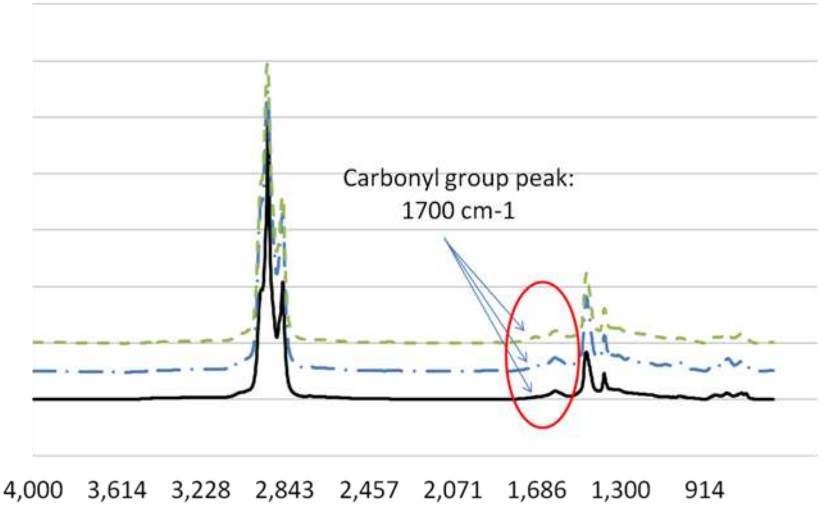

Figure 2-2: Developing different indices on the area under each characteristic band

Table 2-2: Band Assignments For Asphalt

Band Position (cm^{-1})	**Band Assignment**	**References**
1032	S=O stretching	Masson et al. Zhang et al. Abbas et al. [89-91]
1376	C—H symmetric bending of CH3	Zhang et al. Fang et al. Yao et al. [90, 92-93]
1419	C—H bending of —(CH2)n—	Socrates [94]
1437	C—H asymmetric bending of —(CH2)n—	Yao et al. [92]
1448	C—H asymmetric bending of —(CH2)n—	Socrates [94]
1458	C—H asymmetric bending of —(CH2)n—	Zhang et al. Yao et al. [90, 92]
1603	C=C stretching (aromatic)	Zhang et al. Fang et al. Yao et al. [90, 92-93]
1730	C=O Carbonyl	Zhang et al. [90, 92]
2853	C—H symmetric stretching (aliphatic)	Zhang et al. [90, 92]
2870	C—H symmetric stretching (aliphatic)	Socrates [94]
2924	C—H asymmetric stretching (aliphatic)	Yao [92]
2954	C—H asymmetric stretching (aliphatic)	Socrates [94]

Lamontagne et al. measured oxidization of asphalt binder during the aging [2] by embedding an aging chamber on FTIR equipment and monitoring the development of Carbonyl index as function of aging time. They showed that during the aging of asphalt the carbonyl index of asphalt increases constantly, however, the sulfoxide index of asphalt increases at early stages and then decreases by continuing aging process. They suggested that carbonyl index is more reliable in measuring the extent of oxidization of asphalt during its aging process. Also, in a different research they utilized FTIR in their simulator to directly investigate the aging of polymer modified asphalt [95]. They presented that the polymer modifiers degrade during the aging of polymer-modified asphalt and the carbonyl content of the asphalt increases significantly. They also showed that the presence of polymer modifier has negligible effect on increase of carbonyl content of asphalt. This aspect also was presented by Zhang et al. in their research. They showed that the ethylene index of polymer modified asphalt declines during aging process of asphalt, which is an indication of degradation of polymer structure [32].

Also, FTIR has been used to investigate status and amount of modifiers in asphalt binder and to measure the storage stability and compatibility of the modified asphalt [54]. Xiaohu Lu et al. used FTIR method to measure the phase separation of modified asphalt after Cigar tube test to investigate the modified asphalt storage stability [96]. They measured the intensity of the polymer bands for the samples extracted from the top and bottom fraction of a tube and compared them. The FTIR results show that the top samples have higher content of polymer modifiers than the bottom sample.

Masson et al. developed a method, using FTIR, to quantify the amount of polymer modifiers in asphalt binder, using the average absorptivity for the Poly-Styrene and Poly-Butadyne present in polymer modifiers of asphalt [89]. Also, in a different study they showed that oxidized asphalt show higher reactivity with asphalt modifiers due to its higher sulfoxide content [97]. Using FTIR method, Yao et al. stated that addition of Nano-clay modifiers and Carbon microfibers, may delay oxidization process of asphalt binder during the aging. They showed that the intensity of the carbonyl band in asphalt spectra increases to lower extends, comparing to the control sample (neat asphalt binder) [92].

Chromatography

"Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary (stationary phase) while the other (the mobile phase) moves in a definite direction" [98].

Chromatography method gives much information about the molecular structure of the material such as; weight average molecular weight, number average molecular weight, polydispersity, and molecular size distribution. Its capacity, simplicity and rapidness make it a very useful method in characterization of petroleum materials. Therefore, different chromatography methods have been used by several researchers to characterize the neat and modified asphalt. Petersen et al. used Ione Exchange Chromatography (IEC) and Gel Permeation Chromatography (GPC) to separate the neat asphalt into meaningful chemically fractions and investigate the effect of them on asphalt mechanical and physical behavior [43]. Using this method, researchers speculate that aging increases average molecular weight of the asphalt and on the other hand asphalts with lower molecular weight are more prone to aging [60, 62]. Also, it has been speculated that CRM and polymeric modifiers are swell and dissolve faster in asphalts with lower molecular weight [25].

The effect of addition of the CRM into the asphalt and different curing parameters on the molecular weight distribution of final product is another aspect which has been investigated in different works using Chromatography methods [24, 27, 99]. It is stated that increasing the rubber concentration or decreasing the CRM particle sizes would increase the rate of mass transfer from rubber to asphalt. Another aspect of the modified asphalt that has been investigated using the GPC method is the storage stability [54]. According to the definition of the storage stability and also the chromatography method, this method mostly has been used to analyze the phase separation of the modified asphalt after long storage time.

One of the short comes of Chromatography method is that the asphalt should be diluted to be able to be characterized with this method. Therefore, in almost all the studies, asphalt is diluted with solvents like tetrahydrofuran (THF). It has been claimed that solving the asphalt in solvent affect the asphalt microstructure and may cause some of the weak intermolecular bonds to break [54].

In asphalt industry the chromatography method has been used in comparative mode, due to its chemical complexity and wide range of molecular weight of its components. The most common method in interpreting the chromatography results of the asphalt is to divide its chromatogram into different sections and use the amount of each of the sections to investigate the changes. One of the most common methods in this regard is to partition molecular weight distribution of the asphalt into 3 semi-equal sections based on their elution time: Large Molecular Size (LMS), Medium Molecular Size (MMS) and Small Molecular Size (SMS) [100-101], as presented in Figure 2-3. Several researchers have tried to correlate the amount of each of these sections to final performance of the asphalt [60, 99, 101-102]. It is shown that the LMS fraction of asphalt shows the most correlation with the final physical properties of the asphalt binder [103].

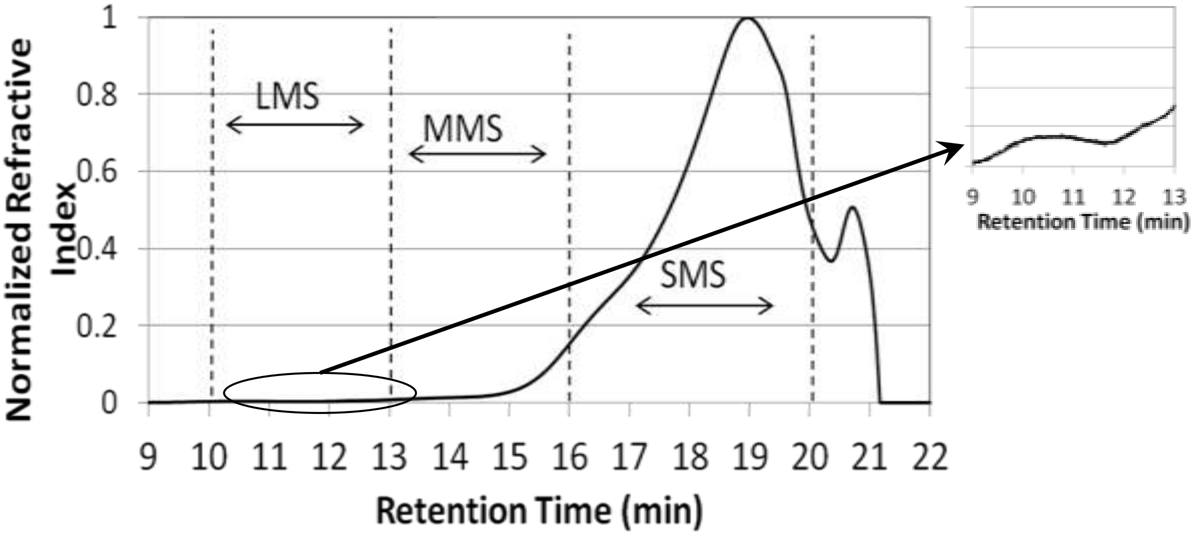

Figure 2-3: Different fractions in chromatogram of a asphalt binder sample

Isacsson et al. used GPC in their research to investigate the relation between the chemical composition of asphalt and its low temperature performance. They stated that the asphaltene has the highest molecular weight among all components in asphalt and therefore, they have the shortest elution time. Also, they reported that aging of asphalt leads to higher asphaltene content in asphalt which degrades it low temperature performance.

Thermal analysis

Thermal analysis is a characterization method in which materials' properties are measured as function of temperature [104]. This method has three advantages relative to other characterization methods; first, thermal analysis is a very accurate method with a high sensitivity to materials changing properties, second, it needs very small amount of samples which significantly reduces the cost and effort of sample preparation, third, it can be done in a very short time, therefore, it is possible to analyze several samples with one equipment in same time [105]. However, it only indicates the physical and chemical changes in the material, therefore, still there is need to test mechanical function of material to find out the relationship between these two. Thermal analysis has been used in several studies to characterize polymeric and petroleum materials. The two common thermal analysis methods are Thermo-gravimetric analysis and Differential Scanning Calorimetry.

Thermo-gravimetric analysis (TGA)

TGA is one of the most basic but still common methods of thermal analysis. In this method change of the weight of the material is measured accurately as a function of temperature. In this method the decomposition temperature of each component is used as a fingerprint of that component.

Researchers use TGA analysis to investigate the composition of multi-component samples [106-111]. Different methods of TGA analysis can be utilized to investigate the composition of a multi-component material, depending on the complexity of material. The most conventional method of TGA analysis is the ramp method in which the sample is heated up to a certain temperature with constant heating rate and the mass loss of the sample is measured by the instrument as a function of temperature [112]. The weak point of this method is that it cannot distinguish the components with close decomposition temperature.

A more sophisticated TGA method is the Isothermal Stepwise Thermo-Gravimetric (ISTG) analysis. In this method a programmed heating method is applied to the sample in order to be able to separate the decomposition process of different components that have close decomposition temperatures [112-114].

TGA analysis has been used widely in asphalt and rubber industry. Using this method Dong et al. analyzed the decomposition of the asphaltene fraction of asphalt [115]. They found that regardless to the heating rate, asphaltene decompose in a very narrow temperature (350 C to 450 C). Also, TGA have been used to measure the starting point of oxidation of the asphalt and modified asphalt [116]. It is shown that asphalt modification with polymers shifts the oxidation and decomposition starting points to the right (higher temperatures). TGA also have been used to measure the mass loss during the curing the blend of polymer modifier and asphalt. Adedeji et al. state that mass loss during curing the blend of asphalt and polymer modifier is negligible at 200°C for 90 min [34].

In polymer industry and more specifically in tire rubber industry the TGA method is utilized to characterize the composition of multi-component samples. Lee et al. suggest TGA as very powerful method to determine the proportion of natural rubber and synthetic rubber in binary blend of polymers. However, this method is not able to distinguish between different types of synthesized polymers like styrene-butadiene rubber (SBR) and butadiene rubber (BR) [107]. Moreover, the TGA is utilized in several studies to investigate the pyrolysis of waste tire rubbers [106, 109-111, 117]. Based on these studies, the composition of the waste tire rubber can be divided into oily components which decomposes at temperatures below 200°C, natural rubber which decomposes at temperatures between 300°C and 350°C and synthetic rubber which is decomposes at temperatures between 350°C and 400°C and finally the fillers like carbon black which decompose at temperatures above 400°C.

Differential scanning calorimetry (DSC)

DSC is one of the thermo-analytical techniques, which measures the amount of heat needed to increase the temperature of the unit weight of a sample in compare with the reference. This method can be used to measure several thermal events in a material, such as glass transition temperature, crystallization temperature, melting temperature. Also, it can give very useful information about the phases of material and their composition.

Accordingly, different researchers utilized this method to characterize asphalts and modified asphalts. Using this method it is shown that neat asphalt contains waxes which are not fully crystalline, nor amorphous. But, they can crystallize by time and consequently induce physical hardening into the asphalt binder [118].

It is shown that glass transition temperature of asphalt has a good correlation with its low temperature performance. Memon et al. showed glass transition temperature measurement could be a good alternative for SHRP low temperature test method in which asphalt is required to be in aged condition. In this research they used DSC method to measure glass transition temperature of various asphalt [119]. In other research the glass transition and thermal susceptibility of the polymer modified asphalt has been investigated through DSC. It is concluded that polymer modification of asphalt improves it thermal susceptibility while decrease its glass transition temperature due to absorption of aromatics of asphalt by polymers [116].

CHAPTER 3. MATERIALS AND METHODS

Introduction

In this chapter, materials and test methods are presented. The type of material, their sources, and basic properties are presented in Table 3-1. The test methods and material treatment methods are mainly adapted from current Superpave guidelines. Also, the experiment methods that are specifically developed for this research are presented in this chapter. Finally, the experimental method that used in this research and the tasks and subtasks that performed to fulfill the objectives of this research is presented in the form of a flowchart in Figures 3-3 to 3-5.

Materials

Two asphalts from two different sources, Flint Hill Resources and Murphy Oil Corporation, with the same PG grade of 58-28 were utilized in this research and denote NF and M, respectively. Also, to consider the effect of CRM composition, two different CRM batches, one from truck tire (TR) and one from passenger car tires (WTG), were utilized. Both CRM batches were produced by ambient method and were provided by Liberty Tire Recycling. CRM samples sieved and divided into different sizes, according to US standard system. For each interaction a certain size of CRM was utilized. The size of CRM, used in each interaction, is denoted by its sieve size in the code (higher sieve size - lower sieve size). For instance CRM size (30-40) indicates that the CRM particles are smaller than the mesh#30 (0.599mm) and larger than the mesh#40 (0.422mm).

In order to eliminate the variability in the row materials, all materials were obtained at once and as a batch for whole research.

Table 3-1: Properties of the Materials Under Study

Asphalt Type	PG grade	Physical properties @ 58˚C (Before aging)	Physical Properties @-18˚C (Before aging)	
		G*/sin(δ)	S(60) (mpa)	m-value
Flint Hill (NF)	PG58-28	1643.2	121	0.474
Murphy (M)	PG58-28	1233.2	103	0.455

CRM Type	Source	Process Method	%Acetone Extract	%Polymer	%Carbon Black	%Other
TR	Truck tire	Ambient	3.85	57.42	30.84	7.89
WTG	Passenger car tire	Ambient	5.59	55.45	31.41	7.55

Interactions

All interactions were conducted using 1200±100 g of asphalt in 1 gal paint cans, an aluminum heating mantle (100B TM634) attached to a bench top temperature controller and a J-type thermocouple. Nitrogen gas was applied on top of the all interactions to prevent any oxidization. Appendix 1 shows the list of interactions, their related code and parameters. The interaction parameters were selected based on the results of the preliminary studies by this research group to control the dissolution of CRM in asphalt and develop a set of samples with a wide variety of CRM dissolution percentages. The reliability of all interactions and testing was proved by running replications on limited number of samples based on feasibility.

CRM Extraction Method

CRM particles do not dissolve completely and remain in particulate form during interaction with asphalt. The CRM size in all interactions in this research controlled larger than 77µm (retained on Sieve #200), therefore their extraction from asphalt can be done through a mesh #200 (75 µm). To extract CRM particles, 10 g of modified asphalt is diluted in 100 g of Trichloroethylene (TCE) for 25 min and then passed through mesh #200 (75µm). The retained

CRM particles are washed with extra TCE until the filtrate gets colorless. The washed CRM particles are kept in oven at 65°C for 12 hrs. to assure complete solvent removal.

Extraction of Liquid Phase of Modified Asphalt

To obtain the liquid phase of the CRMA, required amount of CRMA was heated to 165˚C and drained through a mesh #200 (75µm) in the oven at 165˚C for 25min. The extracted liquid phase was stored at -12˚C immediately to prevent any unwanted aging or reaction

Dynamic Shear Rheometer (DSR)

Dynamic Shear Rheometer, Figure 3-1, from Bohlin Instruments CVO, (Worcestershire, UK) was used for viscoelastic analysis of neat asphalt, CRMA samples and their liquid phase. All single point tests were performed using 25mm diameter parallel plates at 64˚C and 1.59Hz to follow the Superpave guideline. The gap between plates for CRMA samples was selected to be 2mm, the minimum gap size that doesn't affect the results due the presence of CRM particle. And, for neat asphalt and the liquid phase it was selected to be 1mm. To avoid nonlinear viscoelasticity, all tests were performed in a strain control mode with strain less than 1%.

For temperature sweep analysis the test was performed at temperature range of 10°C to 70°C with 6°C increments. Plates with 25mm diameter were used for tests that performed above 45°C, and plates with 8mm diameter were used for the ones performed bellow 45°C. For the 25mm plate a gap size of 2mm was selected for CRMA samples and 1mm was selected for liquid phase samples and neat asphalt. All tests with 8mm diameter plates were performed using 2mm gap size.

Figure 3-1: Dynamic shear rheometer and plate geometry

Short-term Aging

In this study all samples were aged utilizing the rolling thin film oven (RTFO) by following the ASTM D2872-12 standard, except otherwise stated. To assure a complete flow of the samples in the RTFO bottles (specially in the case of CRM modified asphalt samples), the suggested method by Bahia et al. was applied [54]. Based on this method, a stainless steel rod by the size of 127 mm by 6.4 mm was placed in each bottle to ease the flow of the samples and prevent them from rolling out, which were observed during the preliminary studies by the others and also reported in other literatures [54, 120]. For consistency the rods were used for all samples, including the unmodified asphalt and modified asphalts. For reliability, at least two replication of RTFO was conducted on each sample. The RTFO, bottle and the special rode is shown in Figure 3-2.

Figure 3-2: RTFO and the bottle and rode configuration

In this study, the aged CRM modified asphalt samples have been noted as CRMA-RTFO and the aged CRMA-AC (the liquid phase of CRM modified asphalt that was extracted before aging) have been noted as CRMA-AC-RTFO. Moreover, after aging the CRM modified asphalt, its liquid phase was extracted from the whole matrix and denoted CRMA-RTFO-AC throughout this research.

To investigate the age hardening of the samples the following equation was utilized:

$$Aging\ Susceptibility = \frac{\frac{G^*}{\sin(\delta)}_{after\ aging}}{\frac{G^*}{\sin(\delta)}_{before\ aging}} \qquad \text{Eq. 3-1}$$

The G*/sin(δ) in Eq. 3-1 represents the rutting parameter of the samples before and after aging. For the aging susceptibility of the CRM modified asphalt, the G*/sin(δ) of the CRM modified asphalt after RTFO aging was divided by its G*/sin(δ) before aging. For the aging susceptibility of the CRMA-AC, the G*/sin(δ) of CRMA-AC-RTFO was divided by the

G*/sin(δ) of CRMA-AC and finally for the aging susceptibility of CRMA-RTFO-AC, its G*/sin(δ) was divided by the G*/sin(δ) of CRMA-AC.

Long Term Aging

To age the neat as and modified asphalt binder the standard method suggested by Superpave specification was followed. The samples were short-term aged RTFO, following the ASTM D2872-12e1. Then the RTFO residue was long term aged using the Pressure Aging Vessel (PAV), following the ASTM standard D6521-08. Based on this test method, the 50±0.5 grams of sample purred into special plates and placed in the PAV preheated chamber and sealed. The samples in the chamber were heated to 100°C and pressurized with hot air for 20 hours under 2.07 MPa. The samples (PAV residue) were taken out of the chamber and were stored in separate small containers at room temperature for further testing.

Bending Beam Rheometer

Bending beam rheometer from Applied Test Systems was utilized to determine the flexural creep stiffness and m-value of the CRMA samples and their liquid phase at low service temperatures. All tests were performed following the ASTM standard D 6648-08. Samples were prepared using aluminum molds. Aged and unaged samples were preheated up to 165˚C and then poured into the mold, which was covered with clear plastic sheets. The filled mold was kept on the bench until its temperature decreased bellow 60˚C. Then the exposed face of the mold was trimmed with a hot spatula and the sample was cooled to -5˚C for less than 5 min. Then the sample was demolded and kept in methanol bath at -18˚C for 60±5 min. for temperature equilibration. All BBR tests were conducted at -18˚C and test results were recorded for loading after 60 sec. All tests have been replicated three times for reliability reasons.

Thermo-Gravimetric Analysis (TGA)

In this study, TGA was used with two objectives and therefore, two different methods were utilized. The first objective was to monitor the changes in CRM composition during interaction with asphalt. The second was to measure the asphalt mass loss during short-term aging of asphalt rubber. For the first objective the stepwise isothermal (SITG) analysis was utilized and for the second objective the isothermal analysis was utilized.

Stepwise Isothermal Thermo-Gravimetric (SITG) analysis was utilized in this study to monitor the type and amount of dissolved components. In this respect a TA Instruments' Q500 TGA was utilized to run SITG analysis. This method prevents overlapping between decomposition temperature of different constitutes in the sample, due to a programmed heating process, and as a result has higher accuracy in comparison with the conventional method, in which a constant heating rate is applied to the sample. In the SITG method, 20 to 25 mg of sample was heated at a constant rate (20˚C/min) until the mass loss rate of the sample, measured automatically with the instrument, reached above a predefined constant (>1%/min). At this point the temperature of the sample was kept constant until the mass loss rate of the sample reached below a predefined constant (<0.5%/min). The sample was heated again, at the predefined rate, to the new temperature where the mass loss criteria, mentioned above, was satisfied again. This process was repeated until the temperature of the sample reached a predefined temperature (420˚C). The type and concentration of each component in the sample was defined based on its specific decomposition temperature and the amount of decomposing mass at that temperature, respectively [113].

During aging of the asphalt, part of its aromatics volatilize and result in higher concentration of resins and asphaltene and consequently higher stiffness of aged asphalt. In order to accurately investigate the effect of CRM modification on aromatics volatilization, TGA analysis was conducted on CRMA samples and their liquid phase in isothermal mode. In this method, 45±5 mg of sample was loaded on an aluminum sample holder and heated to 163˚C at a heating rate of 20˚C/min and then the temperature was kept constant for 85 min. The testing temperature and duration was selected in order to simulate the RTFO aging conditions. The total mass of the sample was monitored by the instrument during this period and any mass loss was recorded.

Modulated Differential Scanning Calorimetry (MDSC)

In this research the DSC was utilized in modulated set up, called Modulated DSC (MDSC), in which in addition to heating the sample in a linear mode, the temperature oscillates in a sinusoidal fashion to separate the glass transition, as reversible thermal phenomenon, from crystallization and melting, as non-reversible thermal phenomenon [121]. The MDSC test was performed by using a Q1000 differential scanning calorimeter from TA Instruments (USA). Samples with a mass of 10±2 mg were sealed in the hermetic aluminum pans. The thermal history of all samples was deleted by heating them to their melting point and then quenching them to -90°C with the same cooling rate of 2°C/min. The MDSC setup was selected based on the extensive research of Kriz et al. on application of MDSC on neat and modified asphalt binder [86]. The modulation amplitude was 2°C, the modulation period was 60 sec, and the linear heating rate was 2°C/min.

Fourier Transform Infrared (FTIR) Spectroscopy

A FTIR spectrometer, Nicolet 8700 from Thermo Scientific, was used in transmission mode to determine the chemical composition of the liquid phase of the CRMA in wave-numbers ranging from 4000cm^{-1} to 400cm^{-1}. Binders were dissolved in toluene with 5% concentration by toluene weight. 20 drops of the solution were dropped on the KBr disk and dried for 15 minutes to assure complete solvent removal. After removal of all solvent, the KBr disk was placed in the FTIR chamber and the chamber was purged for 15 min with Nitrogen gas. The experiment was performed by running 32 scans at 4 cm^{-1} resolution.

To quantify the growth of the carbonyl groups during the aging, carbonyl index was calculated as using Eq. 3-2, adapted from other researchers [2, 32]. In Eq. 3-2 the area under the band around 1700cm-1, attributed to the carbonyl group in asphalt, measured valley to valley and divided by the area under all asphalt's characteristic bands. Table 2-2 in Chapter 2 presents the list of characteristic IR bands found in asphalt.

$$\text{Carbonyl Index} = (A_{1700}/\sum A) * 100 \qquad \text{Eq. 3-2}$$

$$\sum A = A_{1700} + A_{1603}+A_{1458}+ A_{1448}+A_{1437}+A_{1419}+A_{1376}+A_{1032}+A_{(2954,2924,2870)}$$

Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) analyses were performed using a Waters 712 sample processor and a Waters 600E multisolvent delivery system. A Waters 410 differential refractometer was used to monitor sample elution. One column with mixed bed size, able to measure molecular size from 1000 to 10^7 mu, was used. Samples were prepared by dissolving liquid phase of CRMA in to Tetrahydrofuran (THF) with ratio of 1 to 500, asphalt to solvent. All prepared samples were tested within 20 to 60 minutes after preparation to assure complete dispersion of asphalt in solvent and prevent any aging that may occur to the diluted asphalt sample. The resulting solution was injected to the system using a PTFE syringe filter with a membrane pore size of 0.2 µm (0.2 micron).

Experimental Design

The following experiments were designed to fulfill the objectives of this research using the test methods explained earlier in this Chapter. The experimental design is divided into three main sections; experimental design for interactions, experimental design for sample treatment, and experimental design for analytical tests. Each of these experimental designs is explained in a form of flowchart as follow:

Interactions

The interactions in this research were conducted based on the flowchart in Figure 3-3.

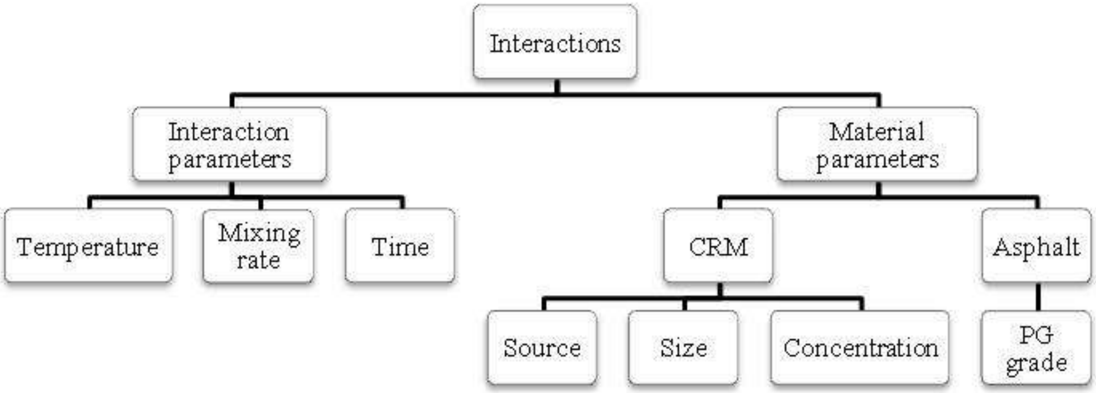

Figure 3-3: Experimental design for interactions

Sample treatment

The obtained samples from interactions will be treated based on the chart in Figure 3-4.

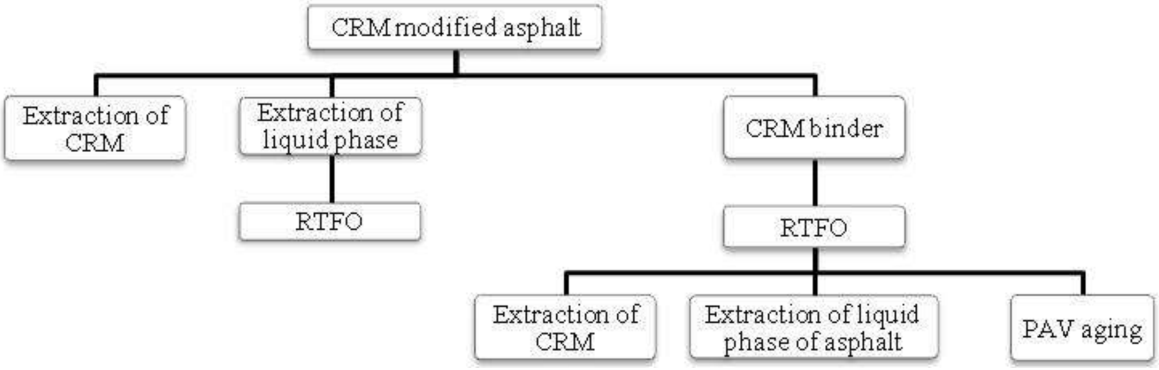

Figure 3-4: Experimental design for sample treatment

Analytical tests

The analytical tests were conducted on each of the obtained samples from sample treatment section in Figure 3-4. The analytical tests were conducted based on chart in Figure3-5.

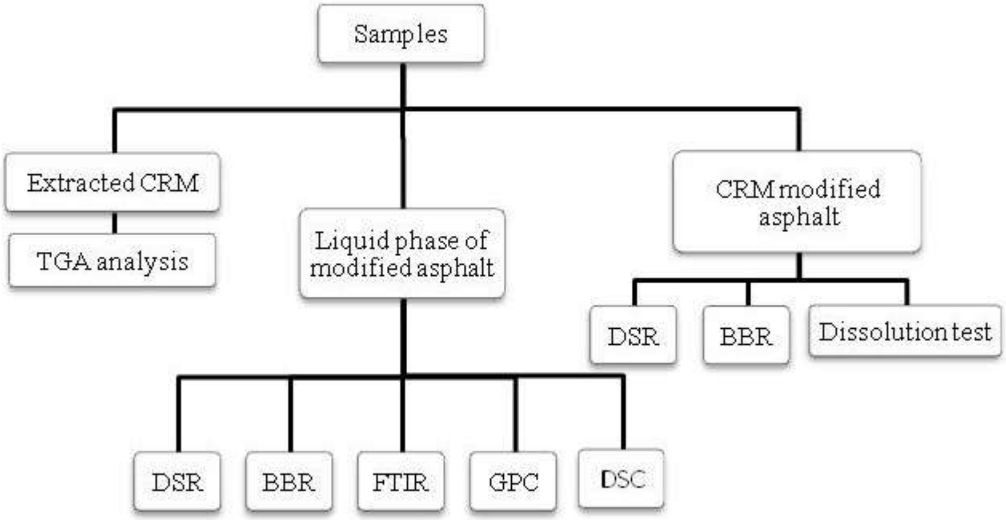

Figure 3-5: Experimental design for analytical tests

CHAPTER 4. MECHANISM OF CRM DISSOLUTION IN ASPHALT AND ITS EFFECT ON HIGH TEMPERATURE PERFORMANCE OF ASPHALT

Introduction

CRM modification of asphalt improves its rutting resistant properties through increasing the stiffness and elasticity of asphalt at high service temperatures [12]. Also, CRM modification extends the asphalt's fatigue life through thickening of asphalt film around aggregates and accordingly decreasing the asphalt's aging rate. Moreover, CRM reduce the stiffness of asphalt at very low service temperatures, which is in favor of its low service temperature performance; however, the deflection rate stays constant or decreases depending on the interaction condition [12, 17, 117]. All these improvements are due to evolution of the CRM particles in asphalt which leads to changes in asphalt composition and microstructure [12].

CRM is a complex engineered vulcanized compound which has different activities in asphalt depending on interaction conditions [28]. CRM is mainly comprised of natural rubber and synthetic rubber, which are cross linked with sulfur and reinforced with Carbon Black. Also, other additives like aromatic hydrocarbons and antioxidants have been added to improve its workability and prevent it from aging, respectively [7]. CRM never dissolves completely in asphalt, due to its cross linked structure [24], but its structure and integrity changes depending on interaction conditions [28].

Several researchers have investigated the nature of CRM activities and their effect on final properties of CRMA as a function of different interaction conditions [8, 17, 99]. It is shown that CRM absorbs light molecular components of asphalt and swells up to 3 to 5 times its original volume at low interaction temperatures (i.e. 160°C) [8]. Amirkhanian et al. showed that during the swelling of CRM particles in asphalt two different parameters influenced the final properties of modified asphalt: absorption of light molecular weight components of asphalt and swollen CRM particles [99]. However, the swollen particles played dominant role in defining the final properties of asphalt. Also, Abdelrahman et al. concluded that the stiffness of asphalt increased through swelling of the CRM while it is decreased when the CRM started dissolving into the asphalt binder and decreasing in their size [28]. In other research, Billiter et al. completely dissolved the CRM in asphalt utilizing high interaction temperature and shearing rate to find the effect of CRM dissolution on physical properties of asphalt [17]. They stated that the dissolved portion of CRM went through farther depolymerization at very high interaction temperatures and decreased in its average molecular weight.

Swelling and complete dissolution of CRM are two ends of interaction of CRM and asphalt. Depending on interaction conditions, a combination of both can happen which adds to the complexity of the CRM and asphalt interaction [27]. Moreover, depending on interaction conditions, the mechanism of dissolution may vary. In this chapter the mechanisms of CRM dissolution in asphalt and their effect on property development of modified asphalt were studied using several analytical techniques including dissolution test, DSR, TGA, and GPC.

CRM Dissolution in Asphalt

CRM dissolution was measured using CRM extraction method, mentioned in Chapter 3. The portion of the CRM particles that passed through mesh #200 (particles smaller than 0.075mm) was considered as dissolved portion. Statistical analysis on the results showed a standard deviation of 0.75 that indicates high repeatability of this test method. Figure 4-1 represents the effect of different parameters on CRM dissolution.

Effect of interaction parameters (temperature, mixing speed and time)

Figure 4-1 presents effect of interaction temperature, mixing speed and time on CRM dissolution. The lines are indicators of different interaction temperatures and the symbols are indicators of the different mixing speeds. Figure 4-1 indicates that CRM does not show a substantial dissolution in asphalt at the lowest mixing speed (10Hz) at 190°C while keeping the mixing speed at the same level and increasing the interaction temperature to 220°C significantly increases the CRM dissolution.

Also, Figure 4-1 shows that the effect of mixing speed and time is highly temperature dependent. At 160˚C increasing the mixing speed does not affect the trend and extent of the CRM dissolution. Also, the CRM dissolution trend is a flat line which indicates the negligible effect of time. But, at 190˚C and 220˚C, increasing the mixing speed significantly changes the extent and rate of the dissolution.

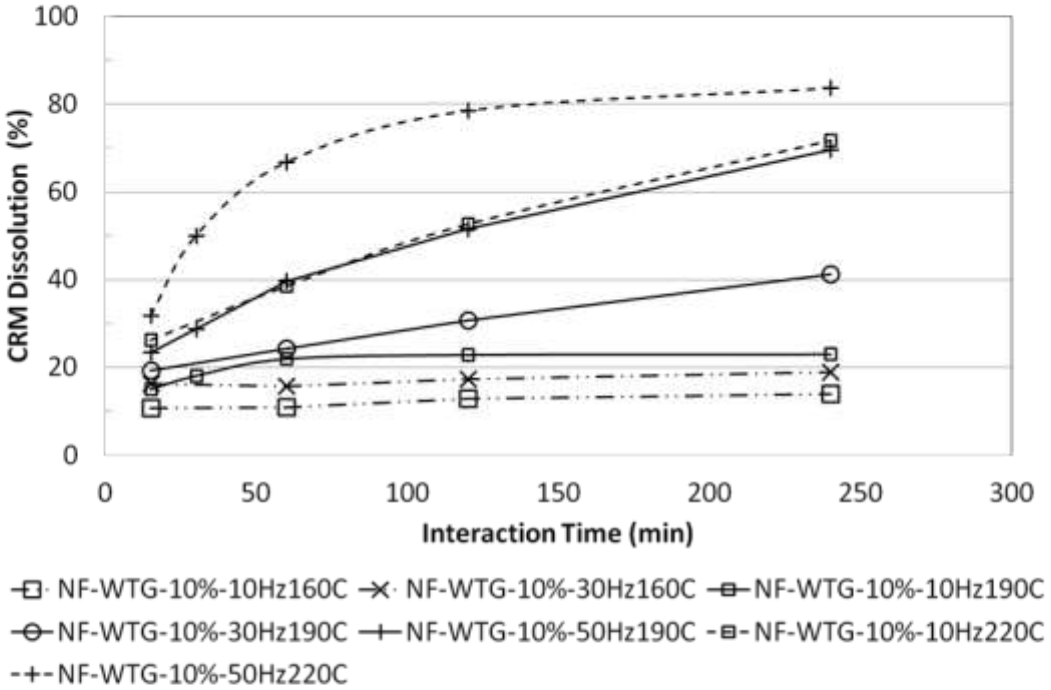

Figure 4-1: Effect of interaction conditions on dissolution of CRM in asphalt

Results in Figure 4-1 illustrate that temperature is the dominant parameter, among all interaction parameters, in dissolving the CRM in asphalt. The other parameters only facilitate the dissolution process depending on the interaction temperature.

Effect of CRM concentration

Figure 4-2 shows the effect of three CRM concentrations (10%, 15%, and 20% by the weight of original asphalt) on the rate and extent of CRM dissolution under different interaction conditions. The lines are representing the interaction conditions while the symbols are representing the CRM concentrations. Results in Figure 4-2 show that increasing the concentration of CRM to 20%, by the asphalt's weight, at 190˚C slightly decreases the CRM dissolution which can be attributed to lack of aromatics to diffuse into the CRM structure and facilitate its dissolution however, at 220˚C and 50Hz dissolution of CRM is independent from CRM concentration [27].

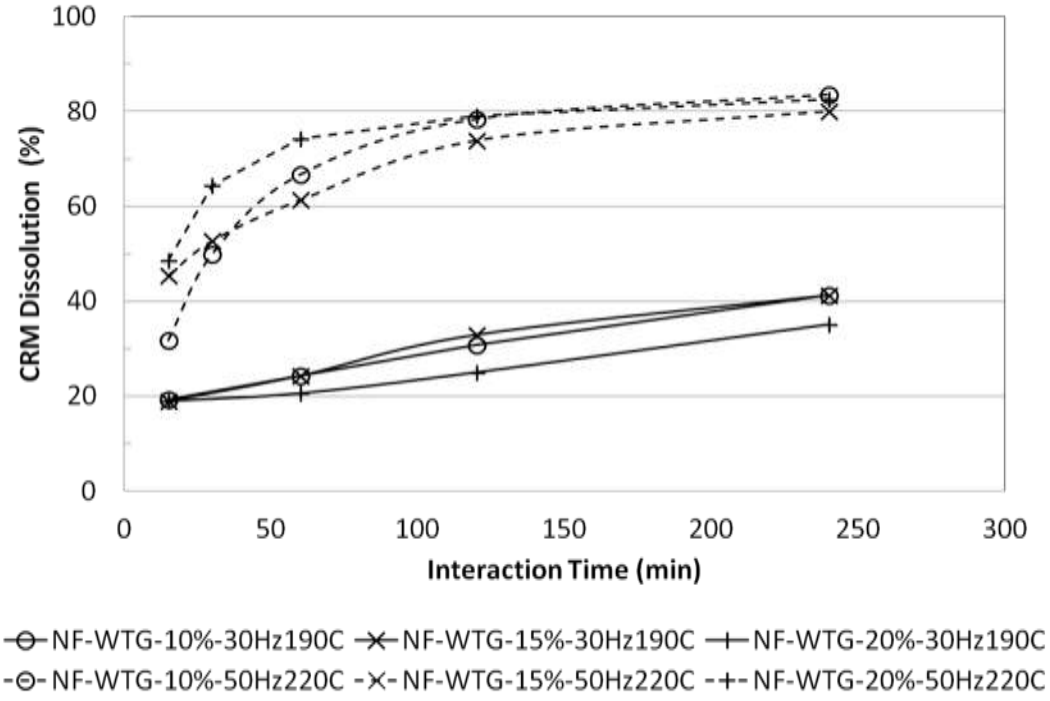

Figure 4-2: Effect of CRM concentration on dissolution of CRM in asphalt

Moreover, the negligible effect of CRM concentration on dissolution at 220˚C and 50Hz, in Figure 4-2, indicates that at this condition, the interaction parameters (temperature and mixing speed) are the dominant parameters which regulate the CRM dissolution is asphalt.

Effect of material type

To investigate the effect of material sources on dissolution behavior of CRM in asphalt several interactions were performed using different source of materials. Two CRM samples from two entirely different tire rubber sources, one from passenger car tire (WTG) and one from truck tire (TR), were interacted with same asphalt to study the effect of CRM composition, Figure 4-3. Also, two asphalt sources with the same PG grade were used to study the possible effect of asphalt composition on dissolution trend of CRM, Figure 4-4.

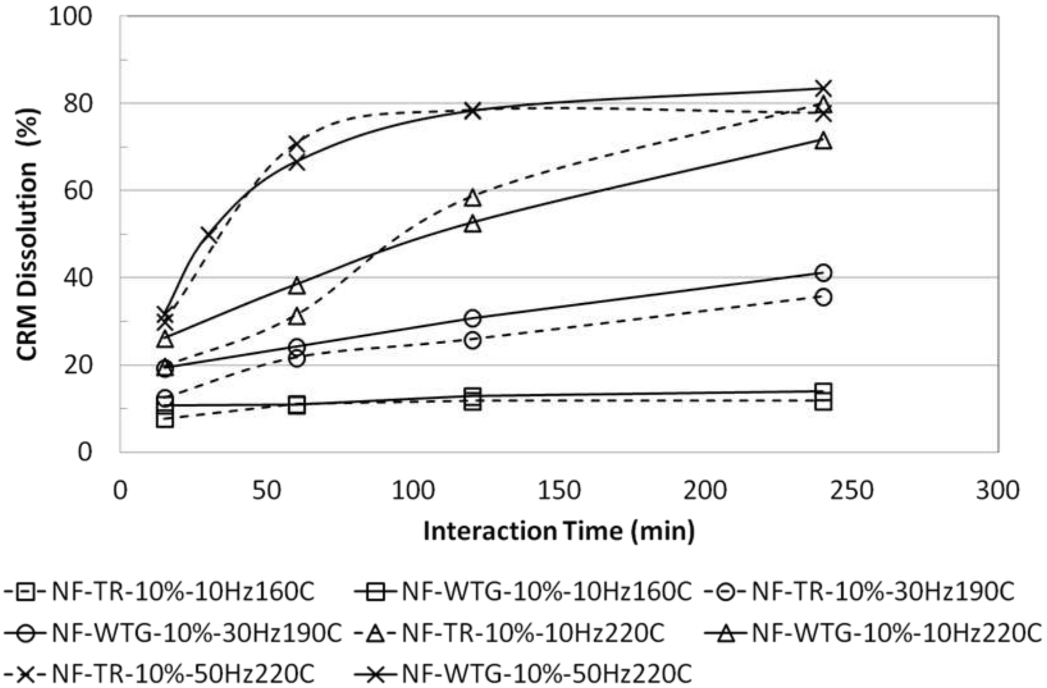

Figure 4-3: Effect of CRM type on dissolution trend of CRM in asphalt

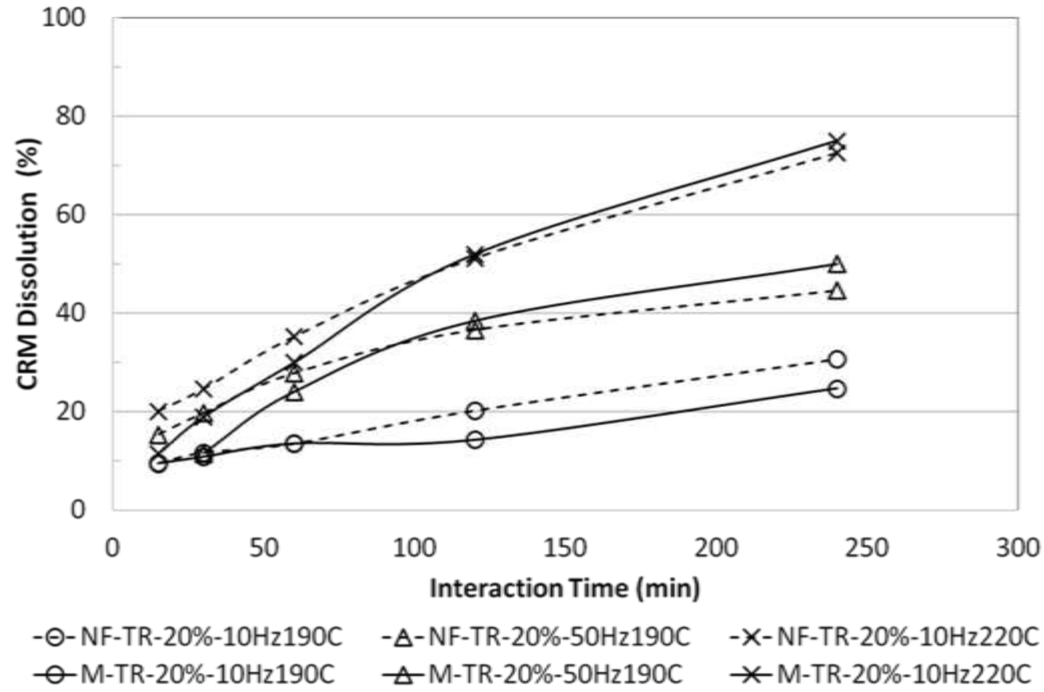

Figure 4-4: Effect of Asphalt source on dissolution trend of CRM

The results show that the dissolution trend of CRM is not significantly influenced by the source of the material at the interaction conditions under study. This is in spite of the result of other studies which show higher compatibility of truck tires with asphalt in comparison with passenger car tires, due to different natural rubber content. This indicates that during the short period of interaction between CRM and asphalt and in presence of heat and mixing speed, the main effective parameters that affect the behavior of CRM is interaction conditions.

Viscoelastic Analysis as Function of CRM Dissolution

The effect of interaction time on viscoelastic peroperties of asphalt is comprehensiveley studied by Abdelrhaman [26, 28]. This study is based on the findings of the research by Abdelrahman and therefore, most of the findgs in that research were developed again here to be able to expand on it. The replicated results are presented in Appendix 2 which includes the effect of different factors like; interaction temperature, mixing speed, CRM concentration, and etc. on viscoelatsic properties of CRMA and its liquid phase as a function of interaction time.

In this section to expand the undrestanding of the effect of CRM activities on the property development of CRMA, the viscoelastic properties of CRMA are superpositioned on top of each other as a function of CRM dissolution.

Viscoelastic analysis of CRMA

Development of complex modulus and phase angle of the CRMA, with 10% and 20% CRM concentration, as a function of CRM dissolution percentage is depicted in Figure 4-3. The lines in these two graphs indicate the general trend of the related parameters as a function of CRM dissolution while the symbols are representing the interaction conditions.

Figure 4-5 depicts that at low dissolution percentages, that occur at 160˚C or early stages of the interaction at 190˚C, the stiffness and phase angle of the CRMA improve (increase and decrease, respectively) which can be attributed to the swelling of the CRM particles [28, 122]. However, by increasing the dissolution of CRM, the physical properties of the CRMA start degrading which is in agreement with other studies [28]. This can be attributed to partial breakage of the 3D structure of CRM particles and shrinkage in their size [28]. This trend continues to a steady state condition, where more than 80% of the CRM was dissolved. In subsequent sections it will be illustrated that at this stage the liquid phase of the asphalt, including the dissolved portion of the CRM, is playing the dominant role in defining the physical properties of the whole sample.

Figure 4-5 also shows that the breakage of the 3D structure of CRM starts when the dissolution of the CRM reaches above 20%. Based on TGA analysis presented in subsequent sections, at this stage the CRM particles start releasing their polymeric components into the asphalt.

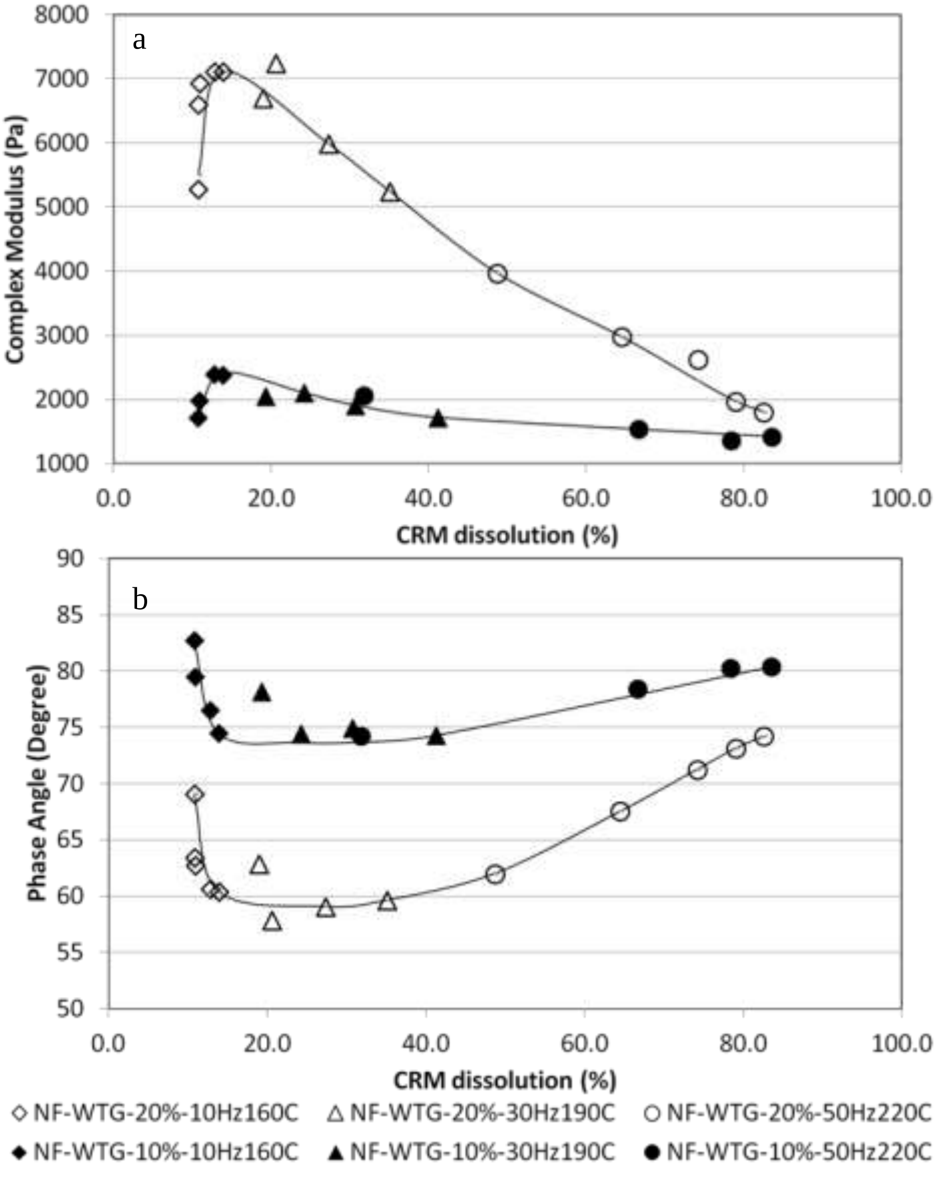

Figure 4-5: Physical properties of CRMA as a function of CRM dissolution by the weight of original CRM (a) complex modulus (b) phase angle

Comparing the results of the samples with 10% CRM concentration with the ones with 20% CRM concentration, it can be seen that both samples are fallowing the same trend. However, the sample with 20% CRM concentration shows much higher sensitivity to CRM dissolution and the complex modulus of the sample decreases with higher rate by increasing the CRM dissolution.

Viscoelastic analysis of liquid phase of CRMA

To better understand the changes in physical properties of the CRMA's liquid phase through absorption and desorption of light molecular weight components of asphalt as well as the release of CRM components, the liquid phase of the CRMA samples were extracted and tested using DSR.

The complex modulus and phase angle of the liquid phase of different CRMA were investigated in Appendix 2 as a function of interaction time. To investigate the effect of dissolved portion of the CRM on physical properties of the liquid phase of CRMA, their physical properties are superpositioned in Figure 4-6 and 4-7 as a function of the dissolved percentage of CRM by the asphalt's weight. The effect of interaction condition is presented in Figure 4-6. The symbols' shape is representative of the interaction mixing speed and the lines are representative of the interaction temperature.

Figure 4-6 shows that at 190˚C, the change of complex modulus and phase angle shows higher dependency on dissolved percentage of the CRM while at 220˚C, this dependency decreases significantly (comparing the slope of the corresponding trends). This indicates that the mechanism of dissolution of the CRM in asphalt varies at different interaction temperatures.

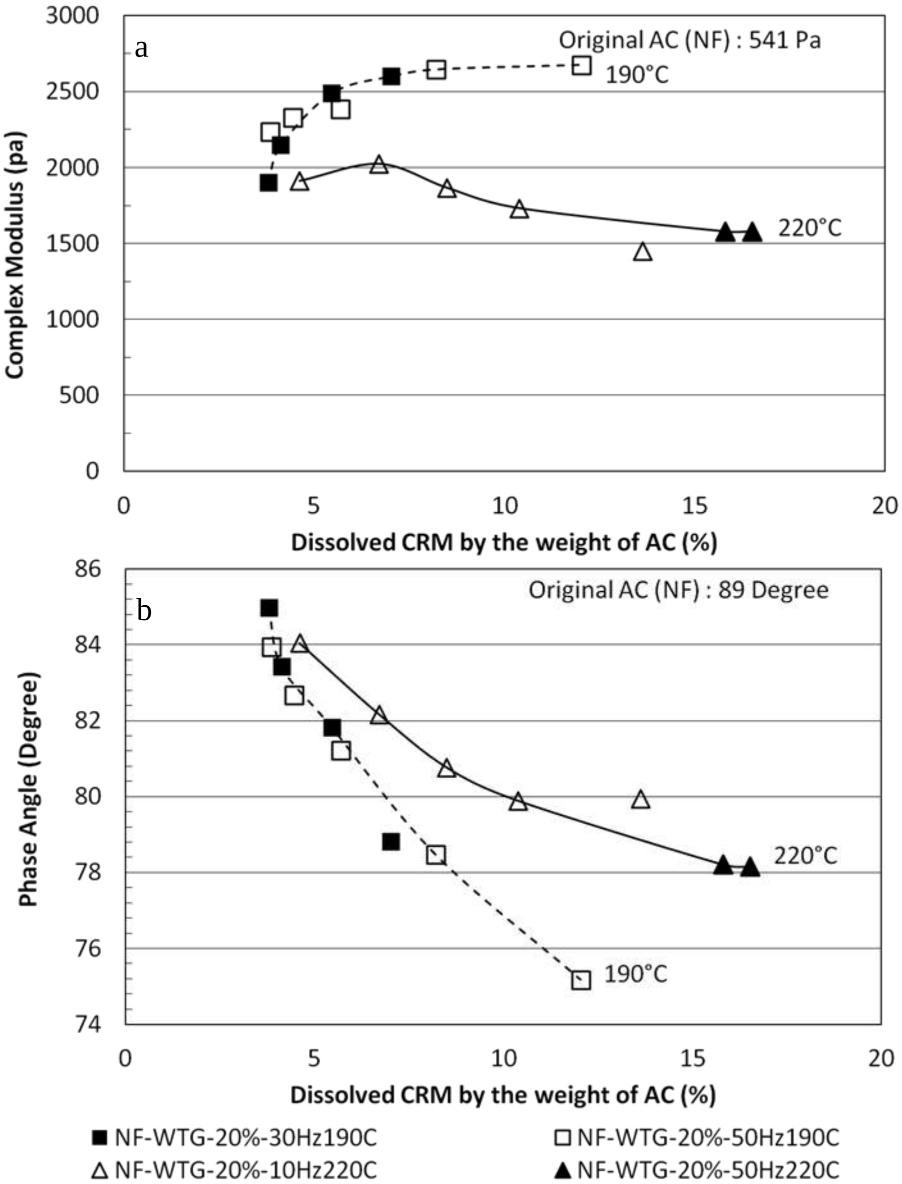

Figure 4-6: Development of physical properties of the liquid phase of CRMA as a function of the dissolved percentage of the CRM by the weight of asphalt (a) complex modulus (b) phase angle

Also, at each interaction temperature (190˚C or 220˚C), the complex modulus and phase angle of the liquid phase follow the same trend regardless of the mixing speed. Considering this observation, it is clear that the mechanism of dissolution is mostly defined by the interaction temperature rather than interaction mixing speed and that mixing speed only effective in accelerating this mechanism, which is in agreement with dissolution test results in Figure 4-1.

Comparing the results of interactions at two different interaction temperatures (190˚C and 220˚C) shows that in spite of the same amount of dissolved CRM, the CRMA interacted at 190˚C and 50Hz shows better physical properties than the one interacted at 220˚C and 50Hz. This indicates that increasing the mixing speed at 190˚C leads to release of polymeric components with higher molecular weights into the asphalt matrix which i more effective on asphalt's property development. These observations are in agreement with the research work by other researchers [24] and also proved by GPC test results in subsequent sections.

Figure 4-7 represents the effect of the CRM concentration on property development of the liquid phase of CRMA under different interaction conditions, shape of the symbols indicating the interaction conditions and the numbers in front of each line indicating the CRM concentration. Results show that for the CRMA interacted at 190˚C and 30Hz with 20% original CRM concentration, increasing the dissolved portion of the CRM significantly increases the complex modulus of the liquid phase of the CRMA. Based on the effect of the absorbed portion of the asphalt, discussed before, it can be speculated that the improvement in physical properties at this level is a result both; the dissolved portion of the CRM in the liquid phase of the CRMA and the absorption of the light molecular components by remaining, non-dissolved, CRM particles.

At 20% concentration, increasing the interaction conditions to 220˚C and 50Hz, which increases the dissolution of the CRM, deteriorates the physical properties of the liquid phase of the CRMA. This behavior can be attributed to the extensive breakage of the CRM structure which leads to desorption of light molecular components of asphalt along with CRM components to the asphalt matrix. Also, based on these results, the mechanism of dissolution that happens at higher interaction conditions is different than the ones that occur at lower interaction temperature and therefore, the activity of dissolved components at this condition is different than the ones at the lower interaction temperature (190˚C).

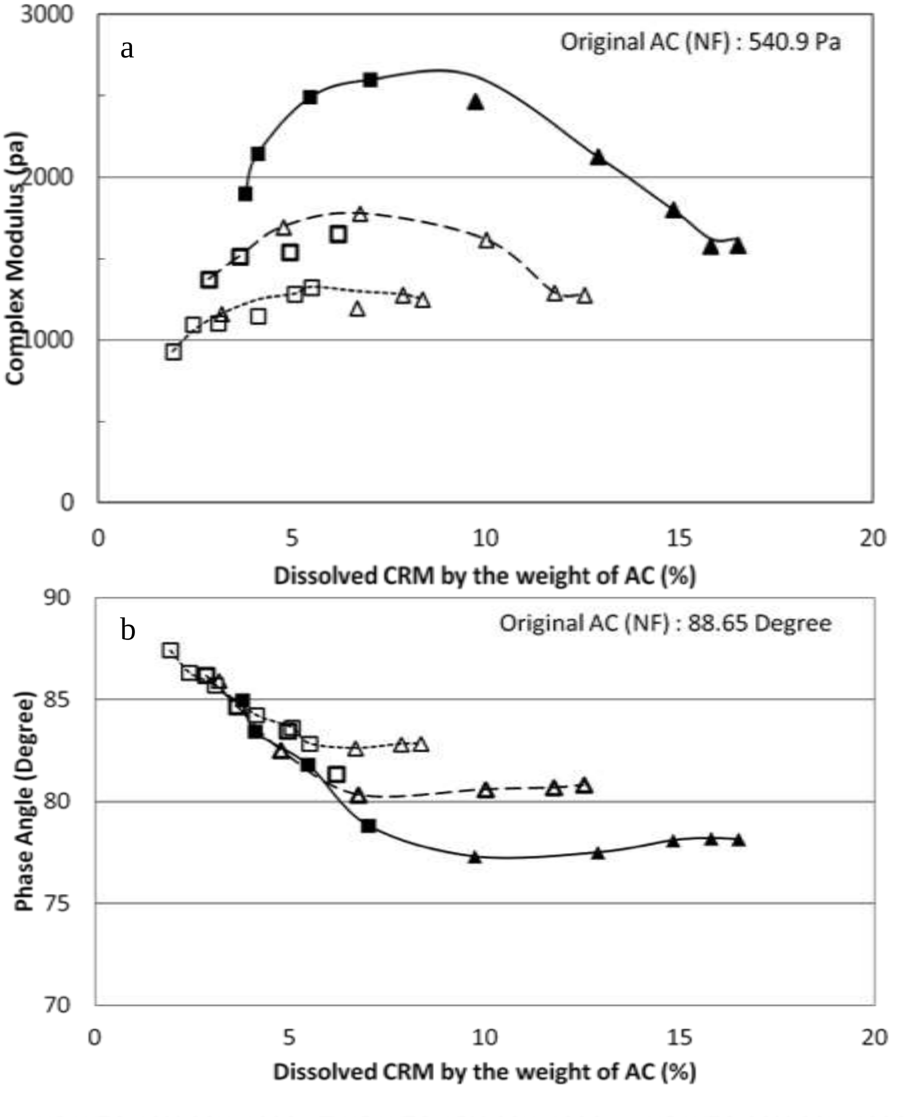

Figure 4-7: Effect of CRM concentration on development of physical properties of the liquid phase of CRMA (a) complex modulus (b) phase angle

The viscoelastic analysis on the liquid phase of CRMA in Figure 4-7 and composition analysis of the extracted CRM, explained in the next section, suggest that at the final stages of interaction at 220˚C and 50Hz, all absorbed light molecular weight components are released back into the asphalt matrix. Composition analysis of extracted CRM at this stage shows that there is no polymeric components left in remaining particles due to the high dissolution percentage of the CRM by its original weight (>80%) and therefore, the non-dissolved portion of CRM particles are incapable of swelling and absorbing light molecular components of asphalt. As a result, the main active modifier which causes the improvement in the physical properties of the liquid phase of CRMA, relative to the neat asphalt, is the dissolved portion of the CRM.

Figure 4-7 shows that the dependence of the physical properties of the liquid phase of CRMA to dissolved percentage of the CRM, by asphalt weight, decreases by decreasing the original CRM concentration. For instance, for the interaction with 20% original CRM concentration at 190˚C and 30Hz, increasing the dissolved percentage of the CRM by the asphalt's weight from 3% to 7%, increases the complex modulus of the liquid phase of the related CRMA by 60%; however, the same increase in dissolved percentage for the same interaction condition but with 15% of CRM concentration results in only 17% increase in its complex modulus and for the interactions with 10% of CRM concentration, this number decreases to almost zero. This behavior can be attributed to the amount of the absorbed light molecular components of asphalt by the remaining, non-dissolved, CRM particles in the matrix. The amount of remaining CRM particles is significantly higher in the samples with 20% original CRM concentration than the samples with 15% or 10% CRM concentration and therefore, the amount of absorbed asphalt by remaining CRM particles at higher concentrations (15%, 20%) is much higher. This situation leads to different actual concentration of the dissolved portion of the CRM in the liquid phase of CRMA, in spite of equal dissolved percentage by the weight of original asphalt, shown in Figure 4-7. This higher actual concentration leads to its higher effectiveness and better physical properties of the liquid phase of CRMA.

Temperature Dependent Viscoelastic Analysis

Temperature dependant viscoelastic properties of CRMA samples and their liquid phase were also investigated as a function of the CRM dissolution, using the DSR in tempreture sweep mode. The concentration of released components for the samples with 10% CRM is not enough to show any distinguishable changes in physical properties of the liquid phase (CRM removed) samples and therefore their results are not shown here. Figures 4-8 and 4-9 illusrate the results related to the samples with 20% CRM.

The results in Figures 4-8 and 4-9 are in agreemnet with other studies [8] which show that the CRM modification of asphalt mainly affects its high temperature properties and by decreasing the testing temperature the effect of CRM modification on physical properties of asphalt diminishes.

Results in Figure 4-8b show that by addition of CRM to asphalt, a distinct plateau region appears on the phase angle graph of the CRMA samples. The apearance of the plateau region is an indication of creation of internal network in asphalt [123-124]. The plateau region is intensified for the samples interacted at 190°C. By increaing the interaction temperature to 220°C, it can be seen that the plateau region start diminishing. The same type of behavior is also illustrated in Figure 4-9b, where the phase angle of the liquid phase of CRMA samples are presented. It can be seen that the sample "NF-WTG-20%-50Hz190C-240 (60%)" shows the most distinct plateau region comparing to the other samples interacted at higher temperatures. This indicates that the released components of the CRM in asphalt at certain interaction temperature (i.e. 190°C) are capable of forming internal network in the asphalt matrix. The composition and status of these components are invetigated and discussed in the sections hereafter.

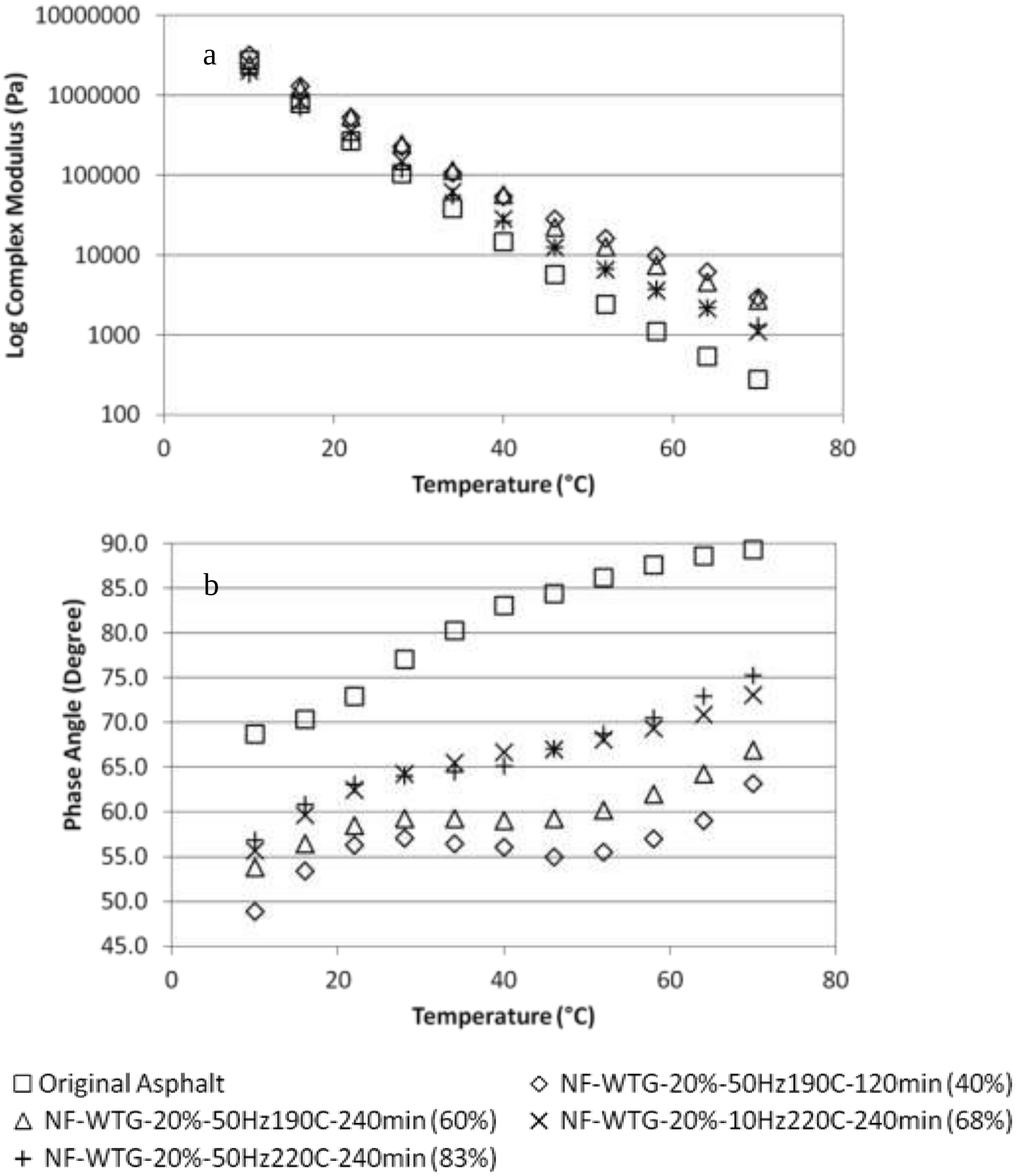

Figure 4-8: Temperature sweep viscoelastic properties of CRMA samples (a) complex modulus (b) phase angle

Note: The number in parenthesis shows the CRM dissolution percentage.

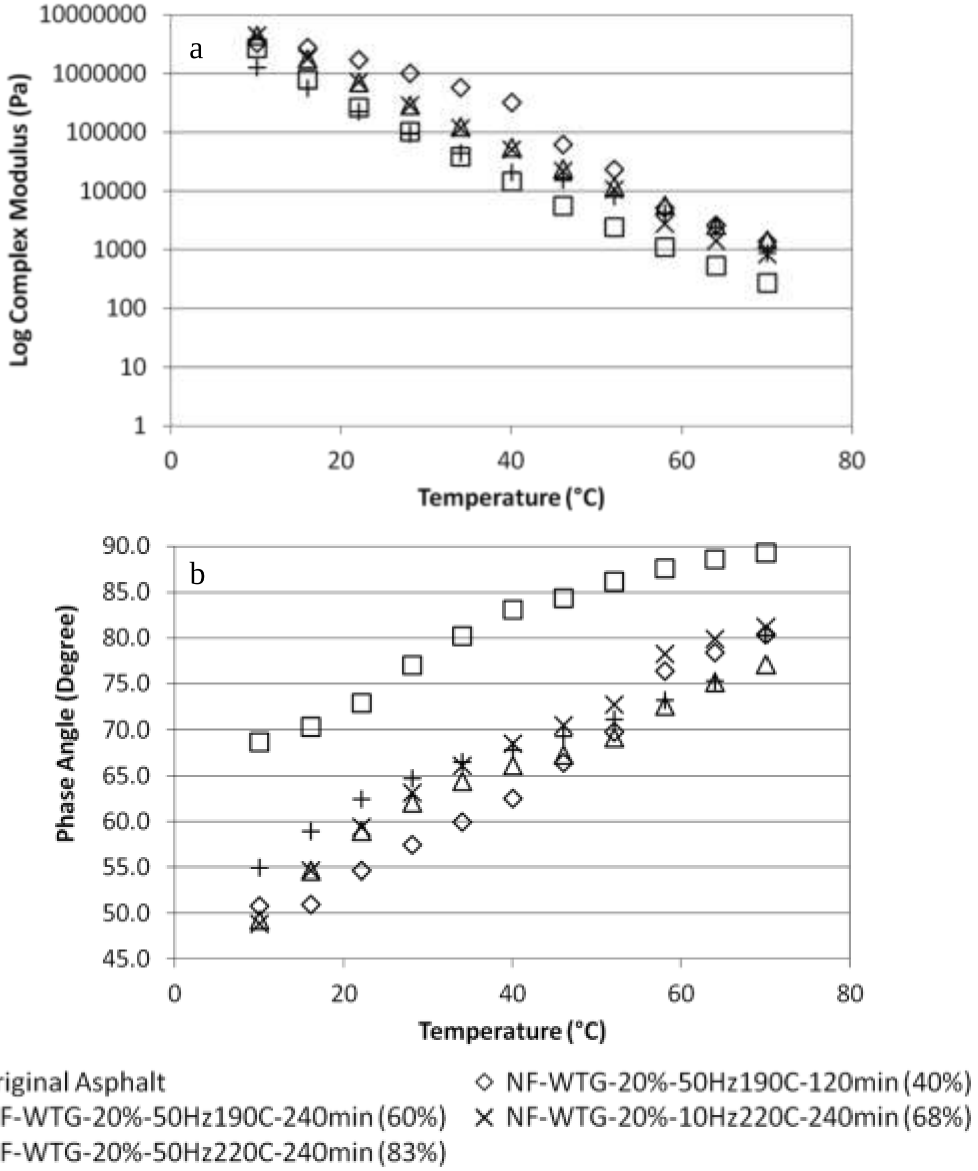

Figure 4-9: Temperature sweep viscoelastic properties of CRMA-AC (a) complex modulus (b) phase angle

Note: The number in parenthesis shows the CRM dissolution percentage.

Thermo-Gravimetric Analysis (TGA)To accurately measure the concentration of each component, stepwise isothermal TGA analysis was conducted on different CRM types and extracted CRM particles from different interactions, as explained in Chapter 3. Figure 4-10 illustrates the TGA results on two CRM sources; TR and WTG. As explained before, the TR CRM is obtained from truck tire sources which have higher content of natural rubber comparing to WTG CRM which is obtained from passenger car tires. Also, as explained in Chapter 3, several researchers have investigated the decomposition temperature of CRM components, individually or in a mix. It is shown that the oily components of the CRM are being decomposed at temperatures below 300°C. The decomposition temperature of the natural rubber is between 300°C to 350°C and the decomposition of synthetic rubber in CRM is between 350°C and 400°C. Finally the carbon black and other inorganic fillers in CRM decompose at temperatures much higher than 400°C.

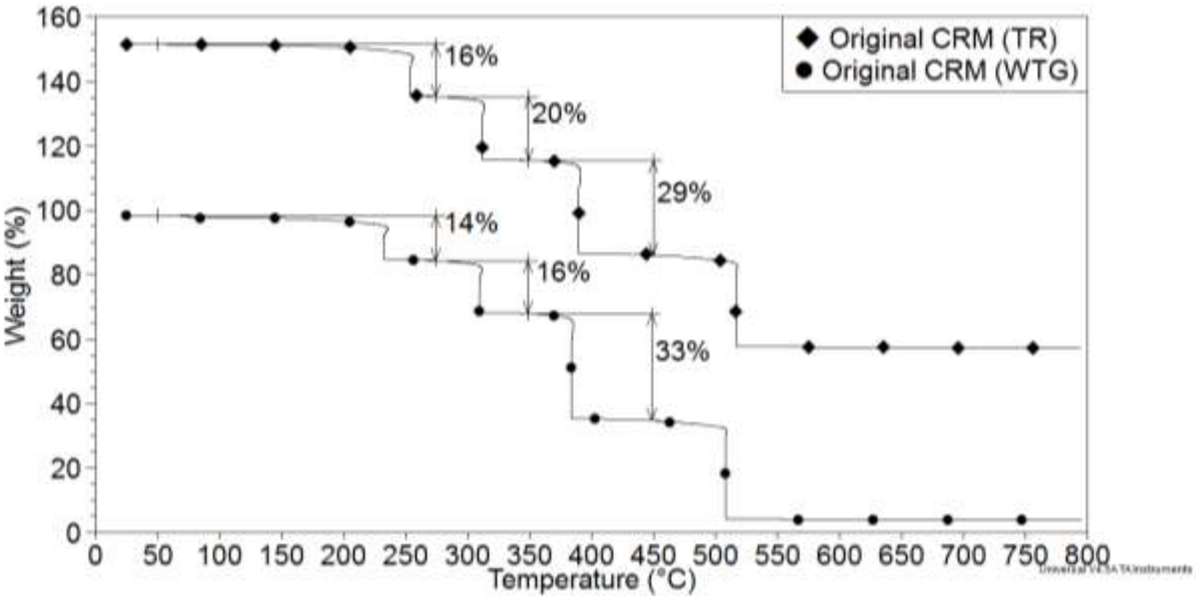

Figure 4-10: Thermographs of original CRM samples from two different sources; truck tire (TR) and passenger car tire (WTG)

Results in Figure 4-10 show that there are three steps on the thermograph of the original CRM samples which is attributed to the three main components in CRM, oily component, natural rubber and synthetic rubber based on their decomposition temperatures [107]. The residue of the sample at temperatures higher than 400˚C is attributed to the carbon black portion of the CRM and also the residual ashes of decomposition of other component. As the results show in Figure 4-10, the TR CRM contains higher percentage of natural rubber comparing to the WTG CRM. This proves the validity of the test method.

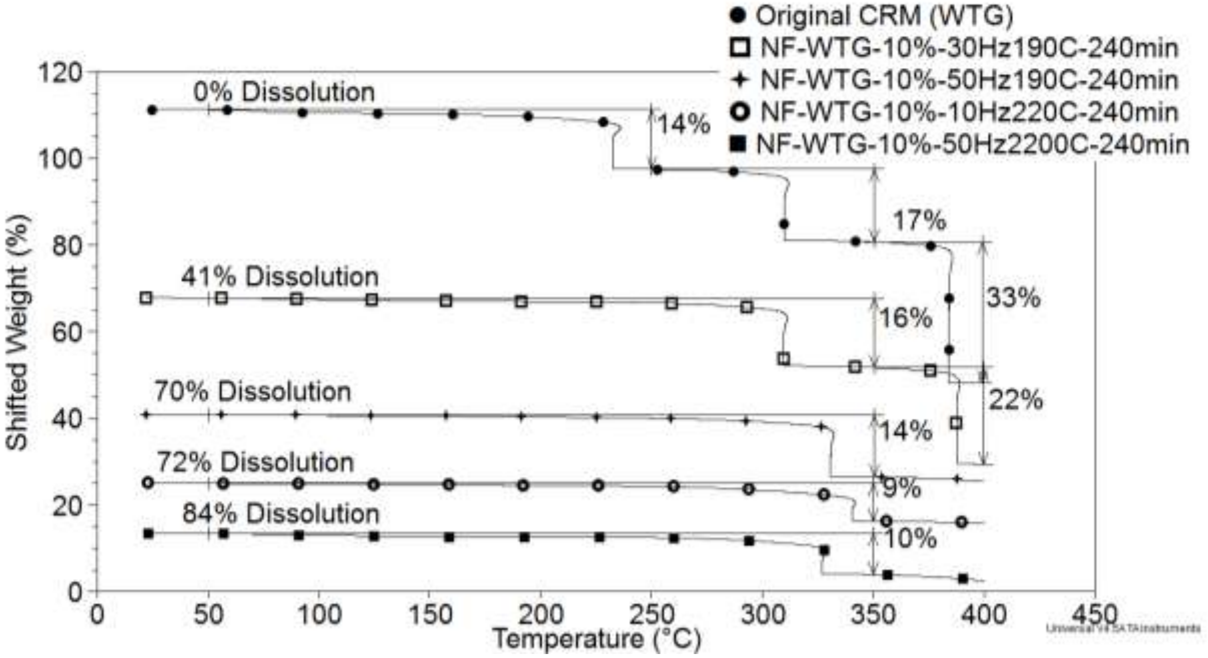

Figure 4-11: Thermographs of extracted CRM comparing to the original CRM

Figure 4-11 illustrates thermographs obtained from SITG analysis on extracted CRM samples from different interactions in comparison to the original CRM. As the results in Figure 4-11 depict the number of steps and also their height are changed for the extracted CRM samples depending on interaction condition. This indicates the changes in the composition of the CRM during the interaction with asphalt. The extracted CRM from the interaction with intermediate interaction parameters (190˚C and 30Hz) with 41.2% dissolution extent shows two steps with lower heights and higher amount of residue at 400˚C in comparison with the original CRM. This indicates that the CRM releases part of both types of polymeric components and its entire oily components into the asphalt matrix while still considerable amount of polymeric components in remaining portion of CRM particles. This result illustrate that the residual CRM particles at this stage still have the ability to absorb the light molecular components of asphalt and swell.

However, at the other extreme, at 220˚C and 50Hz, where 83.6% of CRM was dissolved in asphalt, only one step, with significantly lower height, remains in thermograph of the sample. This indicates the release of substantial portion of the polymeric components of CRM into the asphalt matrix. This also indicates, not much of polymeric compounds, which are responsible for absorption of light molecular components of asphalt and swelling action of CRM particles, was left in the remaining particles [125-126]. This justifies desorption of light molecular components and incapability of these particles in swelling at this stage of interaction. These results are in agreement with the viscoelastic results in Figure 4-7.

Gel Permeation Chromatography (GPC) Analysis

In order to study the status of the released components of CRM in the liquid phase of the asphalt under different interaction conditions, the extracted liquid phase of CRMA samples were tested under Gel Permeation Chromatography (GPC). This test is commonly used in polymer and asphalt industry to study the molecular size distribution of the samples.

In this study the chromatogram of the samples were normalized, based on their highest peak, and then divided into three sections based on the elusion time, as presented in Figure 2-3. The area underneath of each section was calculated using slice integration, suggested by Siddiqui et al. [60]. The area under the LMS section is the only section used in this study, as it is the main section that is expected to contain the released components of CRM.

The amount of LMS fraction for each sample, under different interaction conditions, was calculated, following the method presented in Figure 2-3. The results are presented in Figure 4-12 as a function of interaction time.

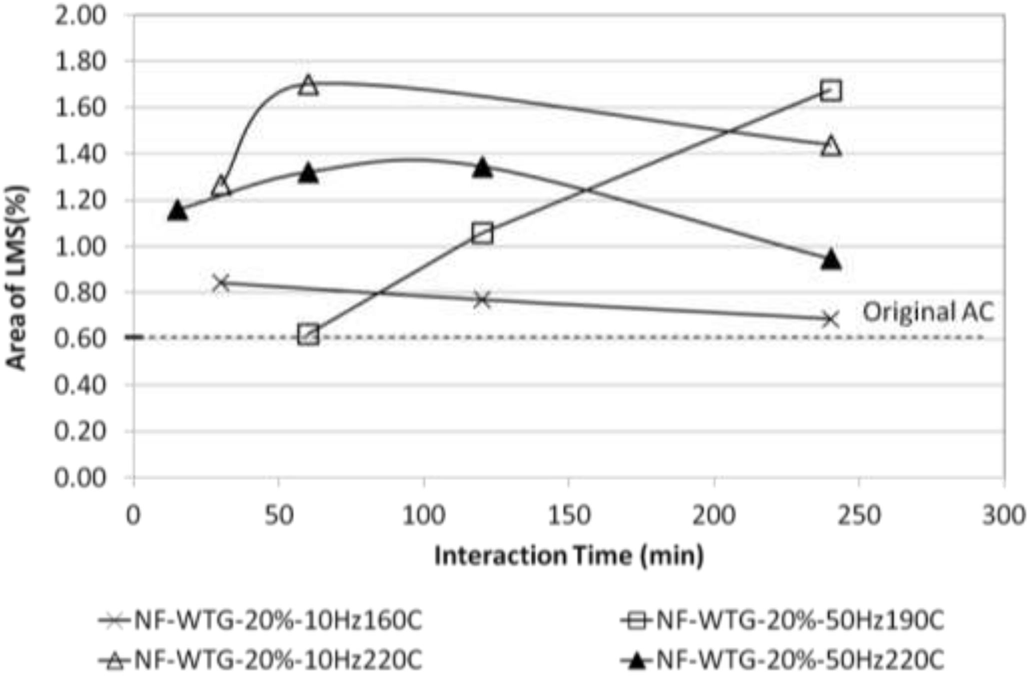

Figure 4-12: LMS content of liquid phase of CRMA samples under different interaction conditions

The LMS content, in Figure 4-12, stays almost constant throughout the interaction at 160°C and 10Hz, where the dissolution of the CRM is minimal and is limited to CRM's oily component. The LMS content of the samples interacted at 190°C and 50Hz increases by interaction time. Given the CRM dissolution results and physical properties of these samples, presented in previous sections, it is obvious that the increase in LMS content of the asphalt binder is mainly due to the release of polymeric components of CRM in asphalt. The results for the samples interacted at 220°C indicate that the LMS content of the samples under this condition increase first and then start decreasing, regardless of mixing speed. This can be related to the depolymerization of released polymeric components of the CRM in asphalt binder at high temperatures at extended interaction time. As can be seen the depolymerization of polymeric components is independent from interaction mixing speed. These results are in agreement with viscoelastic analysis that was conducted and presented in earlier sections. It is necessary to note that the release of polymeric components of CRM is not due to diffusion of polymer chains into the asphalt, like what happens for amorphous polymers in solvent. But tit is more is results of breakage of cross-links and also part of backbone of the polymer chains (partial depolymerization). And therefore, in all interaction conditions, the released polymeric chains are much smaller than actual polymer molecular. Our results show that these partially broken polymeric chains are larger when released at 190°C comparing to the ones released at 220°C.

Summary

Activities of crumb rubber modifier during interaction with asphalt and its effect on physical properties of liquid phase were investigated under different interaction conditions using DSR, TGA and GPC.

Based on the results it appears that for the material used in this research (asphalt type, CRM type and CRM size) the main interaction parameter that affect the CRM dissolution and its mechanism is the interaction temperature, while the effect of the other two interaction parameters, time and mixing speed, on CRM dissolution is highly temperature dependent and they have no effect on the mechanism of the dissolution.

Based on the TGA, it appears that at190˚C, remaining CRM particles in the matrix after 240min still are capable of absorbing the light molecular components of asphalt and swelling, but after 240min at 220˚C, the remaining particles are incapable of swelling and absorption activities.

Viscoelastic analysis reveals that a combination of different activities of CRM is responsible for developing or degrading the physical properties of CRMA and its liquid phase. The results show that at 190˚C, partial release of CRM components and also absorption of light molecular components of asphalt by remaining CRM particles are responsible in property development of the liquid phase of the CRMA while decreasing the size of CRM particles due to partial dissolution is responsible in degradation of physical properties of CRMA. On the other hand, at 220˚C, complete breakage of the 3D structure of CRM and desorption of asphalt's light molecular components along with depolymerization of released CRM components are responsible for degradation of physical properties of both CRMA and its liquid phase.

The temperature sweep viscoelastic analysis shows that at interaction temperature of 190°C, the released components of the CRM are active in the asphalt and are able to create internal network structure, which is illustrated by the plateau region on the phase angle of the sample. However, higher interaction temperature (i.e. 220°C), depolymerize the released polymeric components in asphalt and consequently degrades the physical properties of the liquid phase of the CRMA samples.

The GPC analysis further confirms the presence of polymeric components of CRM in liquid phase of CRMA through higher LMS content of the samples. The GPC analysis also confirms that the LMS content of the liquid phase of CRMA decreases by increasing the interaction temperature, which is an indication of depolymerization that happens to the released polymeric components at that high temperature. It appears that controlling the interaction at certain temperature (i.e. 190°C) leads to devulcanization of the polymeric components of the

CRM into the asphalt matrix and minimize their depolymerization. Therefore, the released polymeric components act as modifier and develop internal structure in liquid phase of asphalt.

The current study suggests that CRM dissolution in asphalt under an intermediate interaction temperature (i.e.190˚C) and a high mixing speed (i.e.50Hz) produces a more homogenous CRMA with enhanced high service temperature properties.

CHAPTER 5. EFFECT OF CRUMB RUBBER MODIFICATION ON AGING AND OXIDIZATION OF ASPHALT

Introduction

As explained before CRM interacts with asphalt in different manners and develops its properties accordingly, depending on interaction parameters. CRM particles are active in asphalt during and after the interaction and can go through changes which adds to the complexity of the CRMA [12]. This complexity makes it crucial to understand and control the activities of CRM in asphalt during different stages, from CRMA production to hot mix asphalt production.

One of the most critical stages in flexible pavement construction is the mixing and compaction process during which the asphalt binder goes through substantial aging, known as short-term aging [57]. During this period, asphalt binder goes through different physical and chemical changes which results in its hardening and leads to premature failures in asphalt pavements [57-58]. Wu et al. investigated the changes in the micro-phases of asphalt binder during the aging [59]. They showed that the multi-phase state of the neat asphalt binder tends to transform into a single-phase during the aging and the aging eliminates the borders between different phases. Siddiqui et al. investigated the aging of asphalt binder using different analytical methods [41]. They stated that carbonyl and sulfoxide groups increase considerably during the aging and there is a good correlation between their formation rate and the hardening rate of asphalt binders. They also, stated that during the aging, aromatization and dehydrogenation of Asphaltene occurs. Lu et al. [57] and Glover et al. [61] in two different studies, investigated the effect of aging on chemical composition of asphalt, including the formation of functional groups like carbonyl and sulfoxide, transformation of generic fractions of asphalt, and changes in the large molecular size components of asphalt. They stated that during the aging, the functional groups of asphalt oxidize and form carbonyl and sulfoxide groups. Also, part of the aromatic fraction of asphalt transforms into the resins and part of the resins fraction transform into the asphaltene. In general, the aging of the asphalt is related to two main mechanisms; oxidization of functional groups in asphalt that increase its polarity, and volatilization of the light molecular components of the asphalt which function as peptizing agent. These two mechanisms lead to increase in the Asphaltene and resins concentration in asphalt and consequently increase the stiffness of the asphalt [57].

Aging of the CRMA is much more sophisticated and complex than the neat asphalt due to its dynamic nature and effect of the time and temperature on enhancement of its physical properties [54]. CRM particles absorb aromatics in asphalt and swell up to 3 to 5 times their original size at elevated temperatures however, never reaching to the maximum level of swelling during the interaction period [28]. Since mixing and construction of asphalt is conducted at high temperatures, close to the asphalt and CRM interaction temperature, the swelling of CRM particles can continue during this time in addition to the other conventional aging mechanisms of asphalt binder and lead to more changes in final physical properties of CRMA after its aging [15].

Moreover, depending on interaction parameters, CRM particles exchange their components, including antioxidants and polymeric components, with asphalt during the interaction. It is shown that each of these components individually affects the aging mechanism of asphalt. Antioxidants can retard the reactive groups of asphalt and prevent them from reacting with oxygen [35]. Also, polymeric chains function as retardant and inhibit the oxygen molecules penetrating into the asphalt and react with its functional groups. Moreover, it is shown that the polymeric chains may degrade during the aging and consequently neutralize part of the physical hardening happens due to oxidization and volatilization of asphalt components [35, 63].

In this chapter the effect of CRM particles and their exchange of components with asphalt were investigated on the aging mechanisms of the Crumb Rubber Modified Asphalt (CRMA). In this regards, the CRMA and its liquid phase (CRM removed), called CRMA-AC throughout this research, were prepared at different interaction conditions and aged through Rolling Thin Film Oven (RTFO). The aging susceptibility of different samples was calculated comparing their rutting parameter ($G^*/\sin(\delta)$) before and after aging. Also, the oxidization of CRMA and CRMA-AC was studied by conducting FTIR analysis on asphalt samples. Then, the effect of CRM modification on volatilization of light molecular components of the samples during the aging was studied by conducting Thermo-Gravimetric Analysis on CRMA and CRMA-AC samples.

The long term aging of the CRMA is not considered in this research since the conditions of its laboratory method is considerably different from what happens in the field and its applicability on modified asphalt is controversial [15].

For coding purposes, the aged CRMA is noted as CRMA-RTFO and the aged CRMA-AC (Liquid phase of CRMA) is noted as CRMA-AC-RTFO. Moreover, after aging the CRMA, its liquid phase was extracted from the whole matrix, following the same extraction method mentioned earlier which is denoted CRMA-RTFO-AC throughout this research. Note that in the coding, the sequence of CRMA, AC, and RTFO defines the sequence of the job. For instance, CRMA-RTFO-AC indicates that the modified asphalt was aged first and then its liquid phase was extracted. But, CRMA-AC-RTFO indicates that the liquid phase of modified asphalt was extracted first (before aging) and then the liquid phase was aged using RTFO.

Effect of Short-term Aging on CRM Dissolution

In Chapter 4 it is shown that CRM particles partially dissolve into the asphalt matrix and release part of their components into the asphalt matrix, mainly depending on interaction temperature. At very low interaction temperatures (i.e. 160°C), the dissolution of CRM is minimized and is limited to its oily components. However, at higher interaction temperatures (greater than 190°C) the dissolution extends to polymeric components of CRM. In this section, the effect of RTFO aging on continuation of CRM dissolution is studied by comparing the dissolution percentage of CRM before and after aging, Figure 5-1.

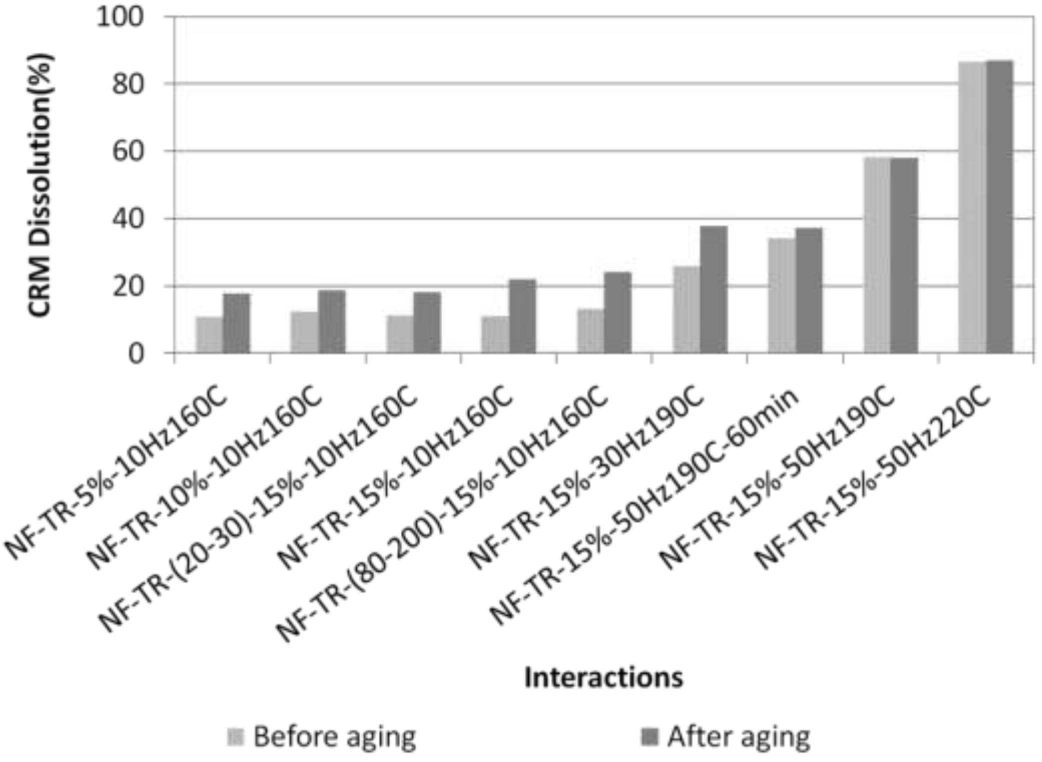

Figure 5-1: Effect of short-term aging on CRM dissolution

Results in Figure 5-1 show that the CRM dissolution progress during the aging, however, the progress diminishes by increasing the original CRM dissolution (before aging). In other words, intact CRM particles, with low dissolution before aging process, are more prone to disintegrate during the short-term aging. Also, the results show that CRM with lower sieve size (80-200), dissolve more during the aging of the sample than the CRM with higher sieve size (20-30). In the next sections the effect of dissolution of particles during the aging is considered in age hardening results of the CRMA samples.

Effect of CRM size and concentration

To investigate the effect of swollen CRM particles on short-term aging of CRMA, several CRMA samples with different CRM concentrations and CRM sizes were produced. To limit the activity of the CRM to swelling and minimized the dissolution, the interaction condition was controlled at 160°C and 10Hz and the interaction time was limited to 2 hrs. Figure 5-2 and Figure 5-3 show the changes in physical properties of CRMA and its liquid phase before and after aging and their aging susceptibility as a function of CRM concentration and CRM size, respectively.

In Figures 5-2a and 5-3a, the aging susceptibility is calculated based on Eq. 3-2. The results in these Figures show that the aging susceptibility of the CRMA-AC doesn't change as a function of the CRM concentration or CRM size, even though increasing the CRM concentration increases the absorption of light molecular components of asphalt and consequently enhances the physical properties of the CRMA-AC before aging, shown in Figure 5-2b. This indicates that absorption of light molecular weight components of asphalt by CRM particles has no remarkable effect on the extent of its age hardening and consequently its aging susceptibility.

Figure 5-2a shows that aging susceptibility and rutting parameters of the CRMA-RTFO-AC increases much faster than the ones for CRMA-AC-RTFO as a function of CRM concentration. This indicates that the liquid phase of the CRMA ages at a higher rate and to a higher extent in the presence of the CRM particles. Therefore, it can be concluded that in addition to the conventional aging mechanisms of neat asphalt (oxidization, volatilization, and polymerization) other aging mechanisms are also involved in the case of CRMA which is discussed in subsequent sections.

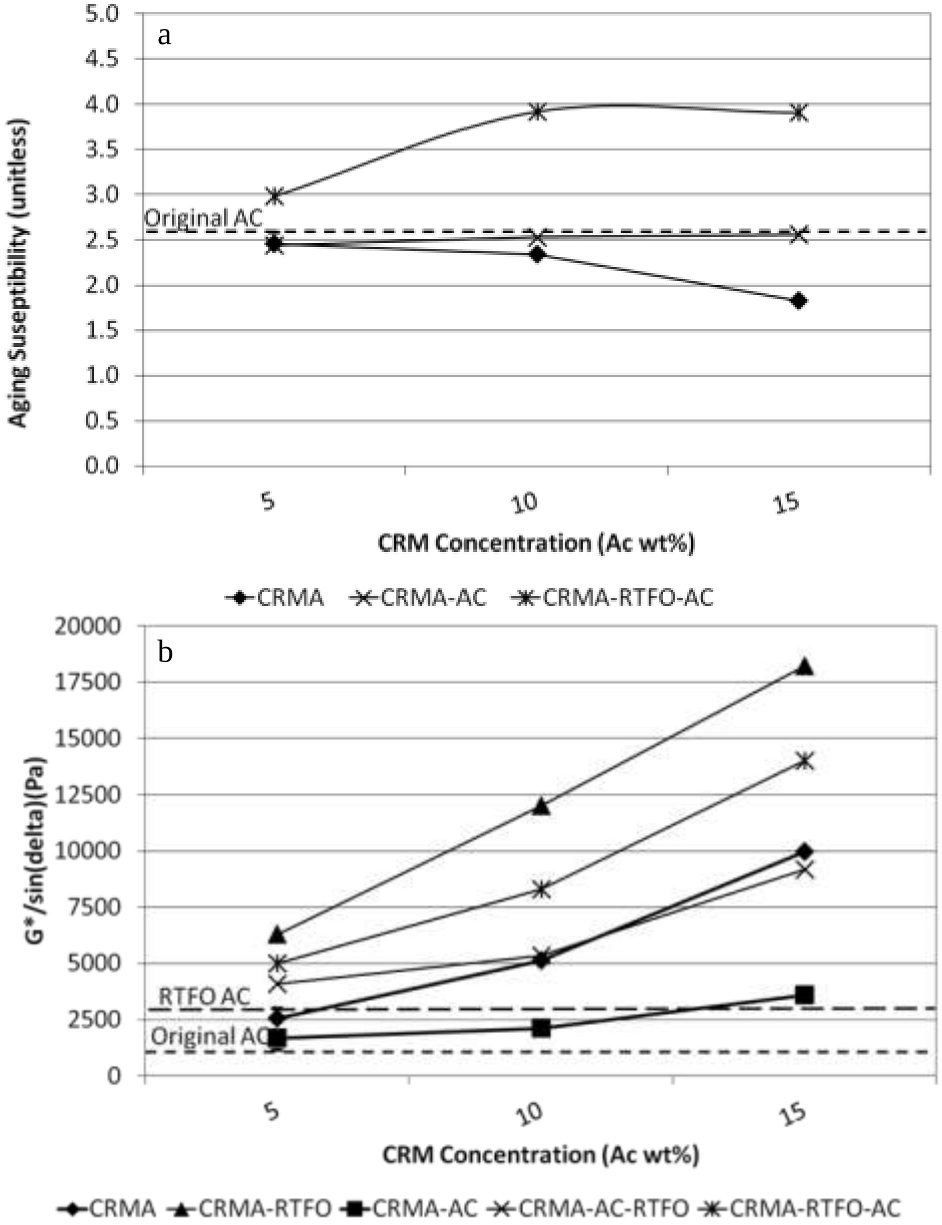

Figure 5-2: (a) Aging susceptibility (b) Physical properties of samples as a function of CRM concentration

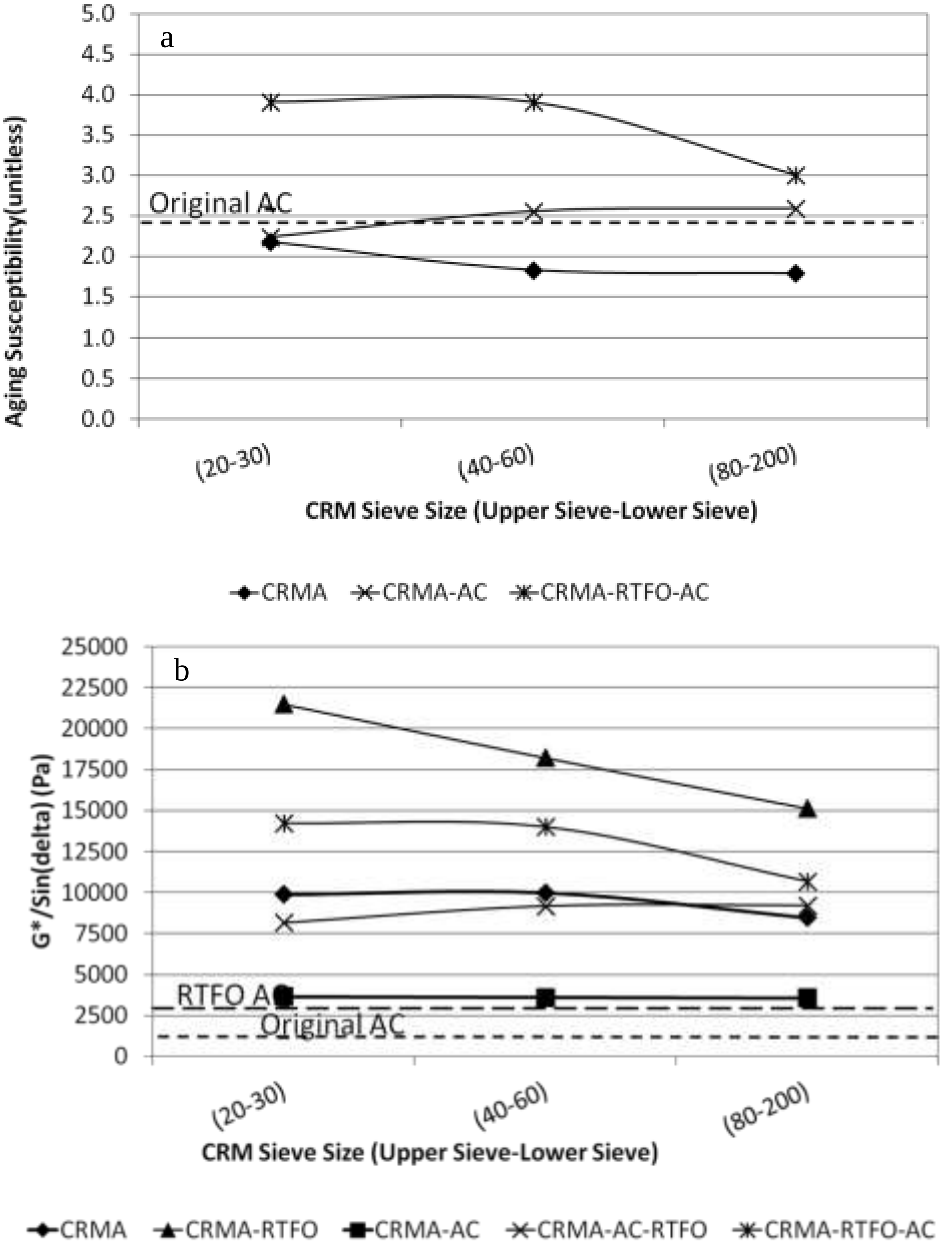

Figure 5-3: (a) Aging susceptibility (b) Physical properties of samples as a function of CRM size

The aging index and rutting parameter of the CRMA-RTFO-AC increases by increasing the CRM concentration (Figure 5-2a and 5-2b), and decreases by decreasing the CRM size (Figures 5-3a and 5-3b). This indicates that two phenomena are involved in hardening process of asphalt during the aging. The first phenomenon is the continued absorption of light molecular weight components of asphalt by CRM particles, which intensifies by increasing the CRM concentration, Figure 5-2a and 5-2b. The second phenomenon is the oxidization and volatilization of the liquid phase during the aging which is expected to depress by improving the CRM dispersion in asphalt through reducing its particle size, Figure 5-3a and 5-3b, and is further investigated in the subsequent sections.

Moreover, in Figure 5-2a, it can be seen that even though the aging susceptibility of the CRMA-RTFO-AC increases by increasing the CRM concentration, the aging susceptibility of the CRMA itself decreases. This is attributed to the dominant role of CRM particles in defining the physical properties of the CRMA at high CRM concentrations, which due to their marginal susceptibility to aging, reduce the aging susceptibility of the CRMA in total.

Effect of CRM dissolution

In this section, the effect of CRM dissolution on short-term aging of the modified asphalt is investigated. In this regard, the dissolution of CRM in asphalt was controlled through monitoring the interaction conditions. Figure 5-4 shows the changes in aging susceptibility and physical properties of samples as a function of CRM dissolution percentage.

As Figure 5-4a presents, the rutting parameter of the CRMA deteriorates by increasing the CRM dissolution, however, the complex modulus of the CRMA-AC increases slightly first and then deteriorates, which are both in accordance with the results presented in Chapter 4. Figure 5-4b shows that the aging susceptibility of the CRMA-AC and CRMA-RTFO-AC decreases significantly by increasing the CRM dissolution and finally reaches to the aging susceptibility of the CRMA. The decrease in aging susceptibility of the CRMA-AC can be attributed to the partial release of the CRM components in asphalt. These components are proven to interfere with age hardening mechanisms that are happening to the asphalt [127]. The decrease in aging susceptibility of the CRMA-RTFO-AC can be explained by the reduction in swelling capacity of the remaining CRM particles after partial dissolution and also the effect of released components of CRM into the asphalt matrix as explained in the case of the CRMA-AC.

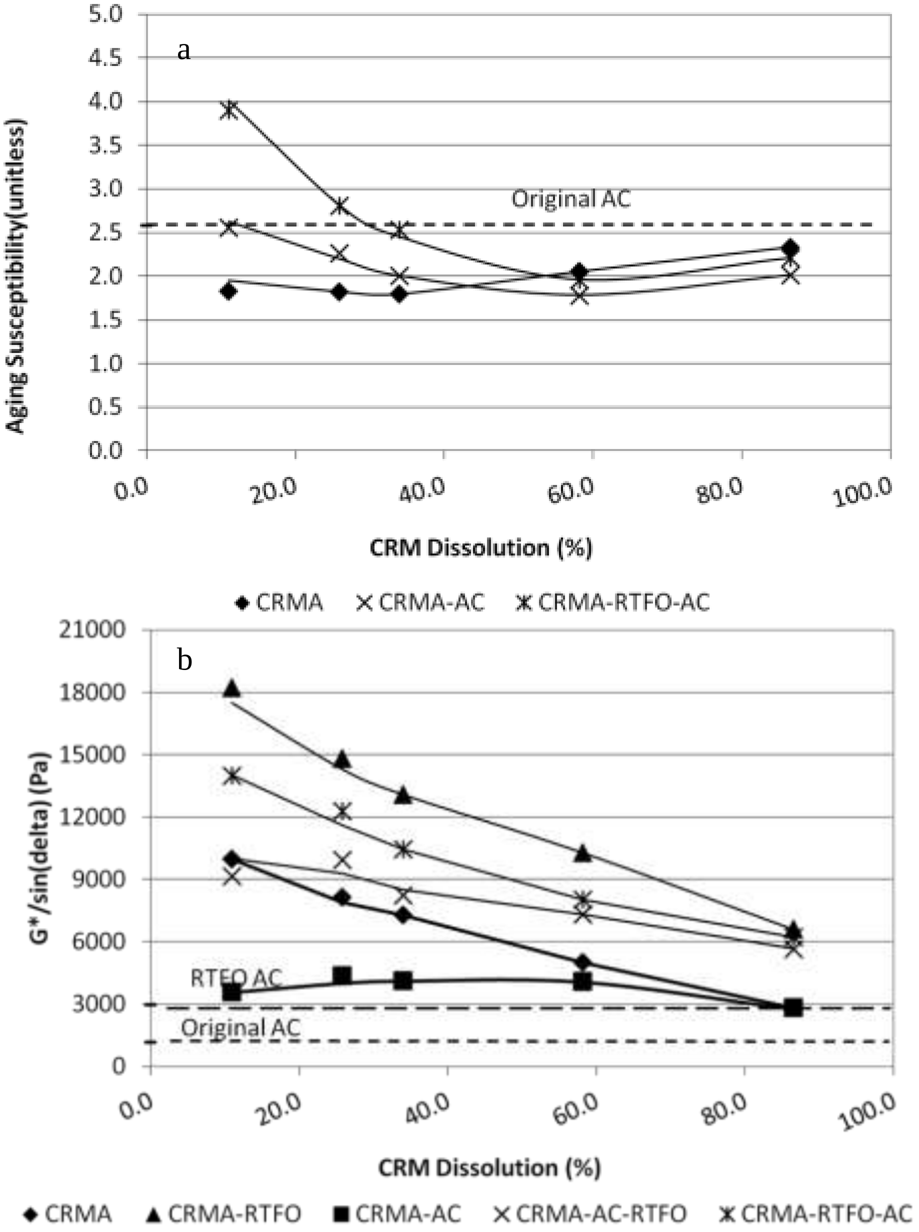

Figure 5-4: (a) Physical properties (b) Aging susceptibility of CRMA as a function of CRM dissolution

Moreover, Figure 5-4b shows that the aging susceptibility of the CRMA stays relatively constant by increasing the CRM dissolution up to 35% and then starts to increase slightly by further CRM dissolution and reaches to the aging susceptibility of the CRMA-AC and CRMA-RTFO-AC, higher than the aging susceptibility of the CRMA with low CRM dissolution. This indicates that the dominated role of CRM particles in defining the mechanical behavior of CRMA matrix diminishes by CRM dissolution, and the physical properties of the CRMA and its aging mechanism are being defined by the liquid phase of the CRMA rather than the particles.

Effect of aging temperature

CRM modification of asphalt remarkably increases its high temperature viscosity which drastically affects the handling of the binder as well as the mixing and compaction process of hot mix asphalt. Therefore, in different research works and technical reports it has been suggested to increase the temperature to remediate this problem. This increase in temperature highly affects the aging of the modified binder. To investigate the effect of the increased mixing temperature on aging of the CRMA, the standard RTFO test was conducted at four different temperatures, 163˚C, 170˚C, 180˚C and 190˚C and the results are presented in Figure 5-5 and 5-6.

Figure 5-5 shows that increasing the aging temperature significantly affects CRM particles' integrity in asphalt and leads to their dissolution during aging. As it is illustrated in this figure, at conventional aging temperature of the asphalt (163°C) the dissolution of CRM increases to 2 folds. By increasing the aging temperature to 190°C, the CRM dissolution increases more than four times of its original dissolution extent.

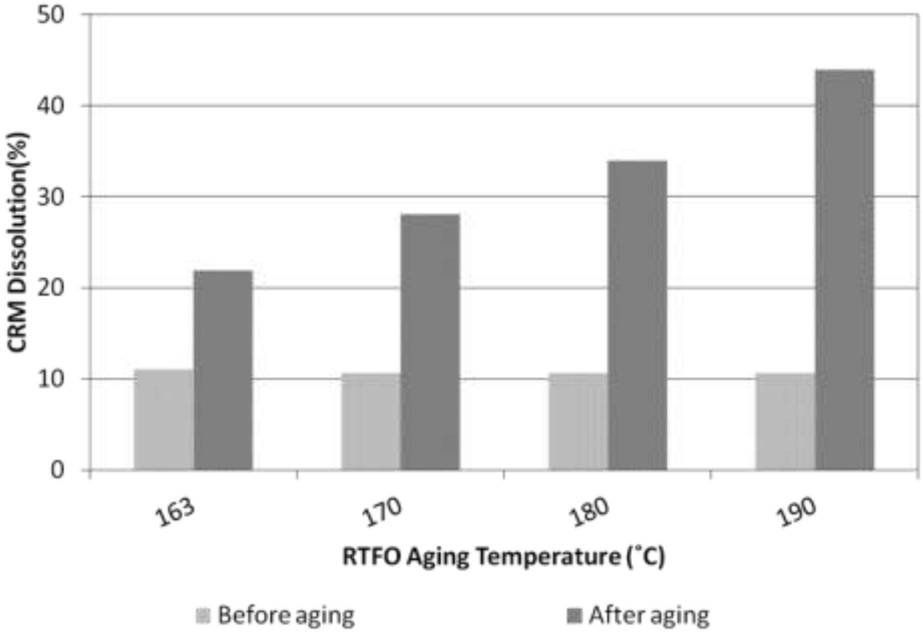

Figure 5-5: Effect of aging temperature on dissolution of CRM during the aging process

Figure 5-6a shows that the rutting parameter of the CRMA-AC-RTFO as a function of aging temperature increases constantly, whereas, the rutting parameter of the CRMA and CRMA-RTFO-AC increases much slower and then starts to decrease by increasing the aging temperature to 190˚C. Figure 5-6b shows the same trend for aging susceptibility index of the three components.

These results illustrate that increasing the aging temperature leads to disintegration of CRM particles in asphalt during aging and consequently desorption of the light molecular components of asphalt back into its matrix. These two phenomena, in spite of the hardening that happens due to faster oxidization of the liquid phase, presented in next section, result in deterioration of the rutting parameter of the CRMA and CRMA-RTFO-AC, as presented in Figures 5-6a. The reduction in rutting parameter leads to lower aging susceptibility, in Figure 5-6b.

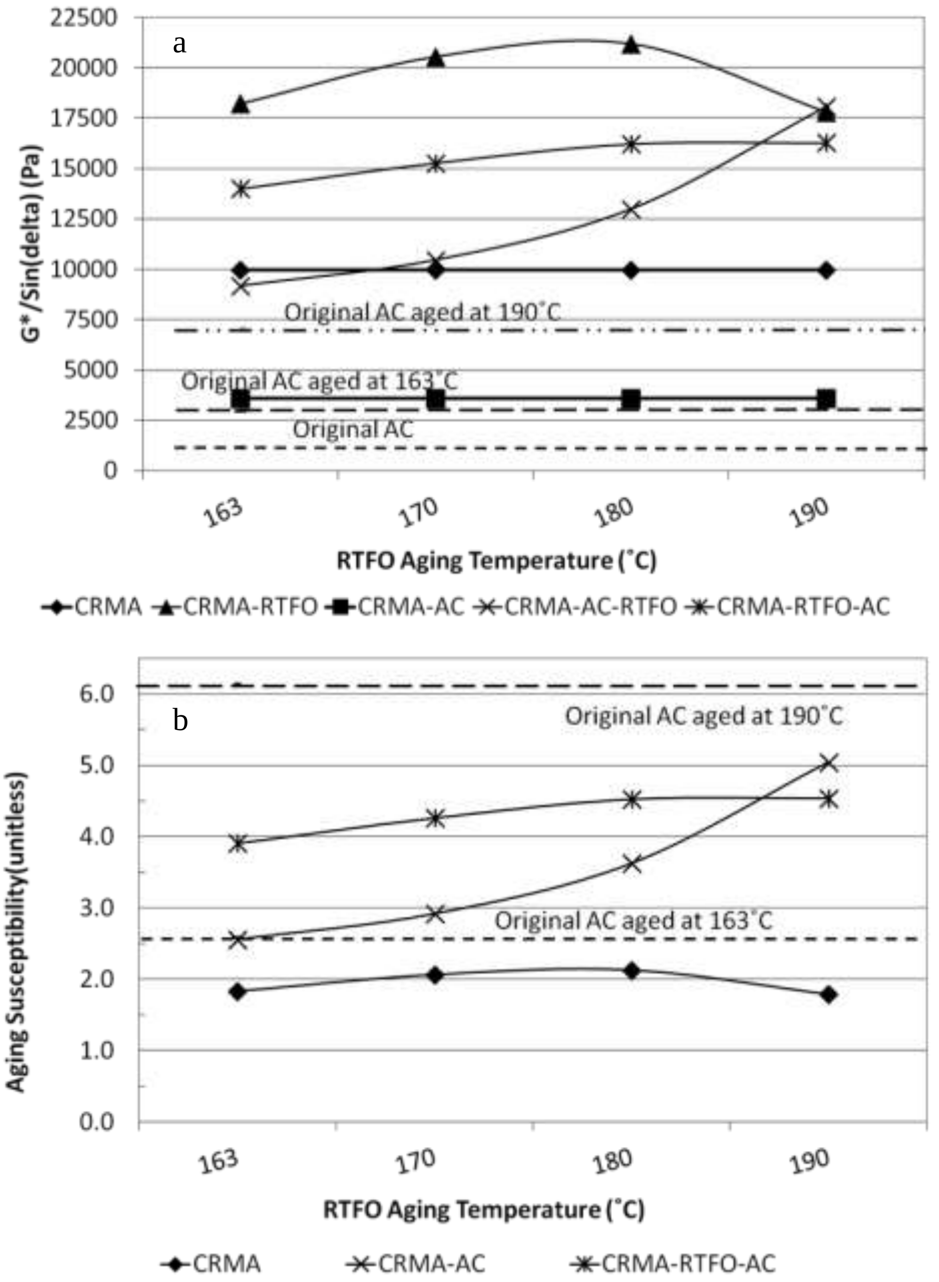

Figure 5-6: Effect of aging temperature on (a) rutting parameter of CRMA and its liquid phase (b) aging susceptibility of CRMA and its liquid phase

Moreover, Figure 5-6b shows that the aging susceptibility of CRMA-AC-RTFO that aged at 190˚C is much lower than the original asphalt, aged at the same condition. This indicates that independent from the presence of the CRM particles in the matrix, released components of the

CRM in the asphalt, even at very low original CRM dissolutions, improve its aging susceptibility and prevent it from oxidization.

It can be concluded that increasing the mixing temperature in hot mix asphalt production in order to reach the appropriate viscosity of asphalt, will significantly changes the integrity of CRM particles inside the matrix and consequently changes the nature and properties of the CRMA [128].

Effect of CRM on oxidization

One of the main mechanisms that are governing the age hardening of asphalt is oxidization of its polar components. During this process oxygen molecules are penetrate into the asphalt binder matrix and interact with its most polar components like resins and Asphaltene and creates carbonyl. This mechanism has been widely studied for neat asphalt binder by Lamontagne et al.[95], Zhang et al. [90] and Peterson et al [44].

The effect of CRM on oxidization of the CRMA samples was investigated by conducting FTIR. Due to the high absorption of IR beam by CRM particles, the FTIR was performed on the liquid phase of CRMA samples (CRM removed). The results of the FTIR are presented in Figure 5-7. Figure 5-7 illustrates the IR spectra of the liquid phase of selected CRMA sample before and after aging. It can be seen that the carbonyl band intensifies by aging the CRMA sample, which is an indication of oxidization of the sample during the aging. The IR spectra of all CRMA samples were obtained in the same manner.

To monitor the increase in the carbonyl content of the samples, an empirical method that was developed by Lamontagne et al. [95] and Zhang et al [90] was utilized here. It is necessary to note that the developed model is an empirical model and is just for comparing the amount of carbonyl at different stages of aging. For quantitative analysis, Fourier self-deconvultion analysis is required in order to analyze the area under the bands that have overlap with each other. However, in this work, to be able to utilize the empirical model that was developed by Lamontagne et al. and Zhange et al the areas under each band was calculated valley to valley.

The carbonyl index of each sample was calculated using the Eq. 3-2 and presented in Figure 5-8. Comparing the carbonyl index of the liquid phase of CRMA with 15% CRM concentration (NF-TR-15%-10Hz-190C) with the one with 5% CRM concentration (NF-TR-5%-10Hz-190C) and original asphalt shows that addition of CRM decreases the oxidization rate of the binder during the aging.

The carbonyl index for all the CRMA-AC-RTFO and CRMA-RTFO-AC samples are relatively the same. This indicates that the reduction in oxidization of the liquid phase is due to release of the oily components of CRM, which contain antioxidants [129], into the asphalt matrix.

The results also show that increasing the dissolution of CRM in asphalt has negligible impact on oxidization rate of the liquid phase of the CRMA. Combining the FTIR results (Figure 5-8) with the aging index results (Figure 5-4), reveals that the decreased aging index of the CRMA-AC as a function of CRM dissolution has other reasons than retarding the oxidization, which needs further investigation.

The FTIR results for the the CRMA that was aged at 190°C show that increasing the aging temperature significantly increases the oxidization of the liquid phase of the CRMA however, based on the results in Figure 5-5, the aging susceptibility and rutting parameter of the CRMA decreases. This result proves that dissolution of the CRM during the aging at higher tempeture offsets the hardening that happens due to the oxidization.

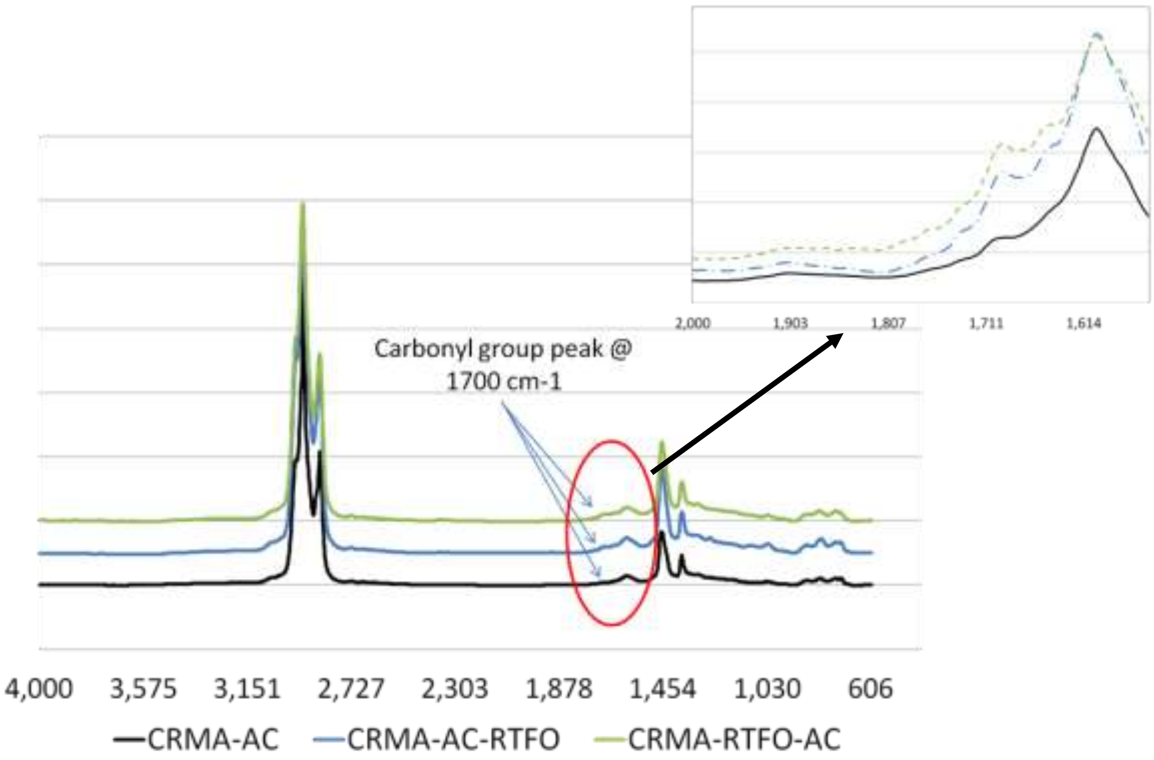

Figure 5-7: Transmission FTIR spectra of liquid phase of CRMA samples before and after aging

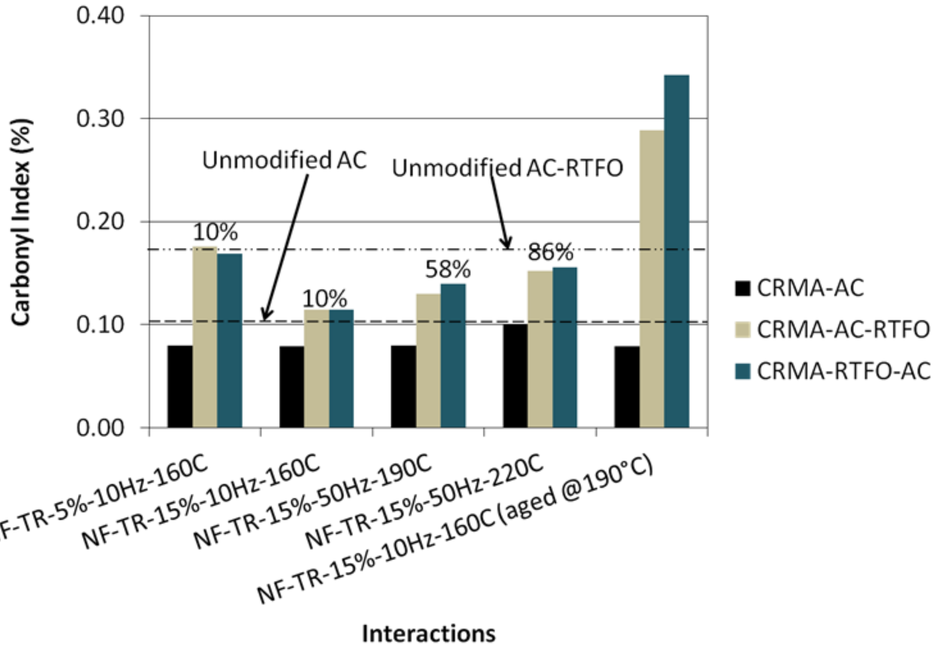

Figure 5-8: Carbonyl index of liquid phase of CRMA before and after aging

Effect of CRM on Mass Loss of Asphalt

The effect of CRM modification on mass loss of the samples during the aging was investigated by conducting TGA tests and the results are presented in Figure 5-9.

The results in Figure 5-9 show that all MA samples and their liquid phase show slightly lower mass loss at aging conditions comparing to the original asphalt, and as the interaction conditions (temperature and mixing speed) increases, the mass loss of the samples relatively decreases. This can be attributed to the partial volatilization of the light molecular components of asphalt during the interaction and also their absorption by CRM particles.

Moreover, comparing the results of the interaction "NF-TR-15%-10Hz160C" and its liquid phase "NF-TR-15%-10Hz160C (CRMA-AC)" in Figure 5-9 indicates that the presence of the CRM particles has no significant effect in preventing the aromatics of asphalt from volatilization.

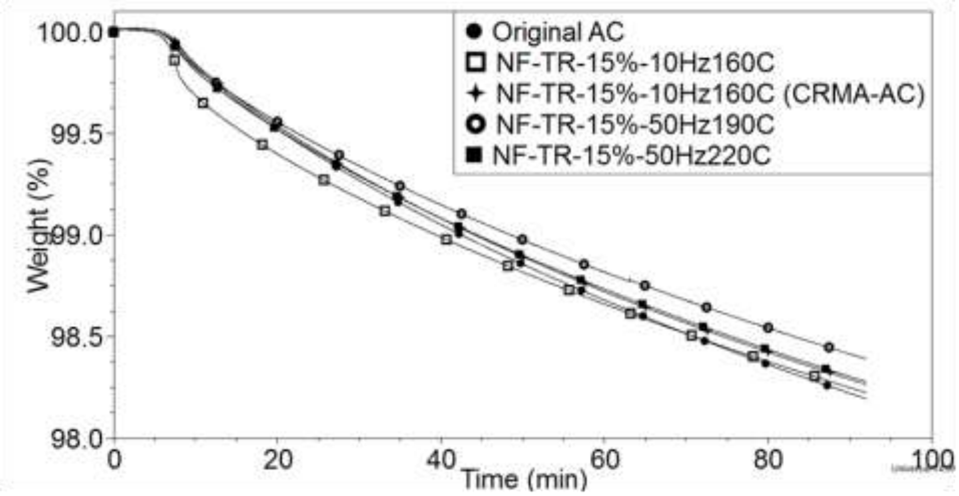

Figure 5-9: Effect of CRM on mass loss during the aging

Effect of Asphalt and CRM Type

In order to verify the effect of the asphalt and CRM source on the general trends that were observed in this chapter, a limited number of interactions were conducted using different sources of the CRM and asphalts. The effect of changing the sources of the material on the aging mechanism of the CRMA is presented in Figure 5-10.

Results in Figure 5-10 indicate that, however, the different types of CRM and asphalt leads to different values in aging susceptibility and rutting parameters, but they have no effect on the general trends that are explained in this study. The differences in the values can be attributed to different swelling capacity of CRM samples and also to different stiffness of the original asphalt samples under study.

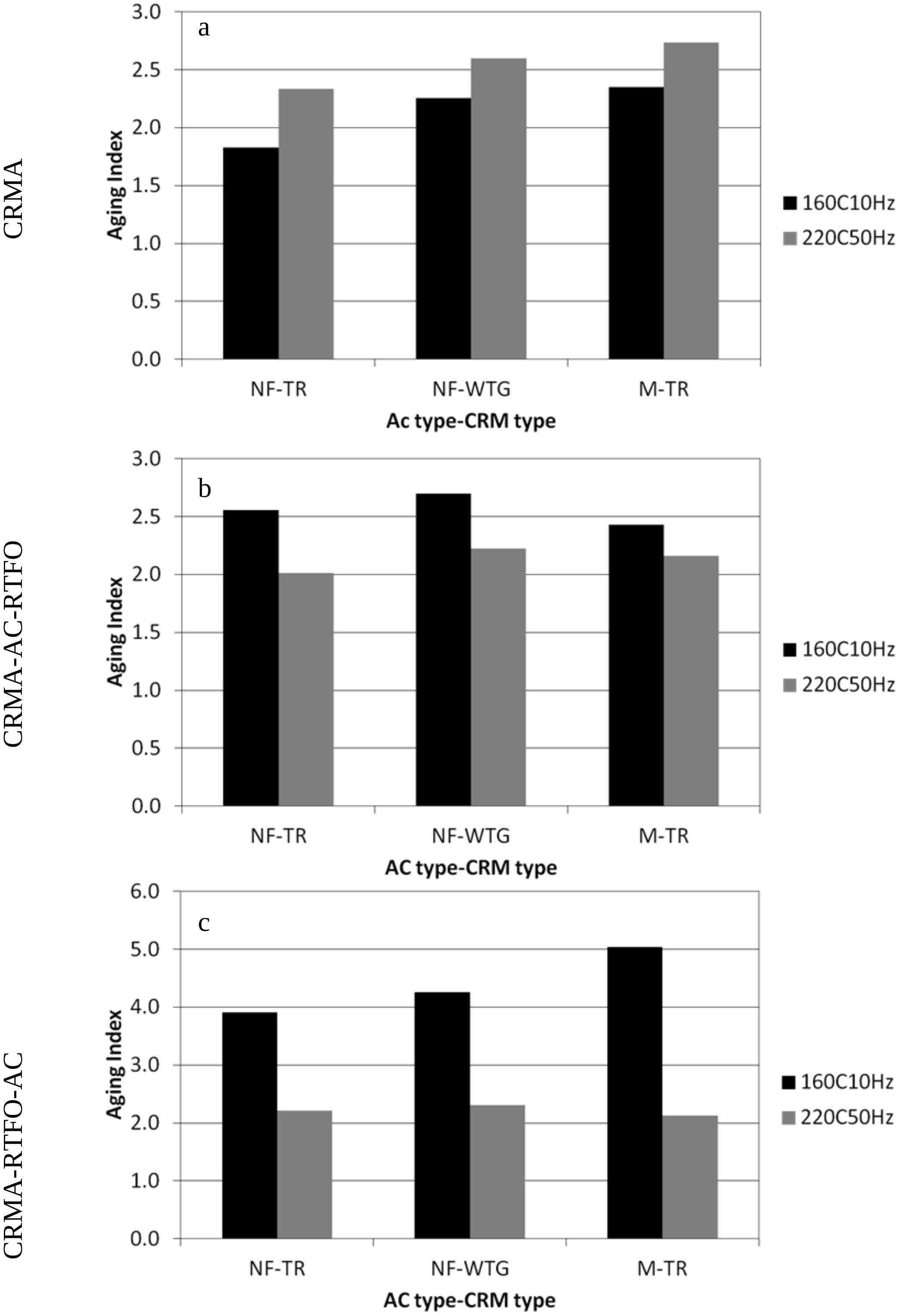

Figure 5-10: Effect of asphalt type and CRM type on aging index of (a) CRMA (b) CRMA-AC-RTFO (c) CRMA-RTFO-AC

Summary

The effect CRM dispersion in asphalt matrix and the exchange of components between asphalt and CRM were studied on the short-term aging mechanism of CRM modified asphalt. In this respect the CRMA samples and their liquid phase were aged utilizing RTFO. The physical aging susceptibility and oxidization indices were calculated using DSR and FTIR tests, respectively. Also, to study the effect of CRM on volatilization of aromatics of the asphalt the samples, TGA test was conducted.

The results in this chapter show that the presence of CRM particles or their extensive dissolution has no significant effect on oxidization of the liquid phase of CRMA, however, the release of the oily components of CRM, which contain antioxidants and can happen at early stages of any interaction, relatively retards the oxidization of the liquid phase of the CRMA. Moreover, the CRM particles have no significant role in depressing the volatilization of the liquid phase of the CRMA during the aging and the CRMA samples and their liquid phase show no remarkable difference in mass loss comparing to the neat asphalt.

The results also revealed that the CRM particles, when not dissolved, continue to absorb the aromatics and light molecular weight components of asphalt and swell in the asphalt matrix which leads to high aging susceptibility of the liquid phase of CRMA. But the dominant role of CRM particles in defining the mechanical behavior of the CRMA, especially at high CRM concentration (i.e. 10%, 15%), keeps the aging susceptibility of the CRMA matrix low.

Partial dissolution of the CRM particles into the asphalt matrix leads to superior stability of the whole matrix and its liquid phase in regards to mechanical behavior, due to inability of the CRM particles to change during the aging process. This will help to assure the similarity of the nature of the binder before and after mixing and compaction process of the hot mix asphalt.

Finally, the results show that increasing the aging temperature decreases the aging susceptibility of the CRMA in spite of the significant increase in the oxidization of the related liquid phase. Decreases in aging susceptibility are attributed to the disintegration of the CRM particles during the aging at higher temperatures (i.e. 190°C) which offsets the hardening of the liquid phase due to oxidization. These results reveal that increasing the mixing and compaction temperature of the CRMA leads to major changes in its nature and composition, and consequently different mechanical behavior.

CHAPTER 6. EFFECT OF CRM DISSOLUTION ON LOW TEMPERATURE PERFORMANCE OF THE CRMA

Introduction

Asphalt is a viscoelastic and thermoplastic material and its physical properties significantly change as a function of environment temperature. Therefore, asphalt is viscose liquid at very high temperatures and viscoelastic paste at intermediate temperatures and finally it is brittle glassy materials at very low temperatures. The temperature dependent properties of the asphalt can cause different distresses on pavement including rutting, which was discussed in Chapter 4, and thermal cracking. High cooling rate and very low temperatures result in instant shrinkage of the pavement and consequently developing of tensile stresses along the pavement. When these stresses exceed the fracture stress of the surface layer of the pavement, thermal cracking develops. Stiff asphalt pavements are more prone to low temperature cracking. Stiffness of the asphalt pavement at high service temperatures are primarily depends on aggregate structure whereas at low service temperature it highly depends on stiffness of the asphalt binder used in it. Therefore, high stiffness of asphalt binder is the predominant cause of thermal cracking of pavements and measuring and controlling the stiffness of the asphalt at very low temperatures is crucial to construct durable pavements.

Superpave specification for grading asphalt has suggested the bending beam rheometer (BBR) test to determine the performance of asphalt binder at very low temperatures. This test measures the load and deflection, and calculates the creep stiffness, S(t), and m-value of asphalt samples. Creep stiffness represents how the asphalt binder resists the constant creep loading and the m-value represents the rate of stress relaxation by asphalt binder flow and is calculated based on the changes in creep stiffness of asphalt binder by the loading time. These properties of asphalt change by its modification.

Crumb rubber modification of asphalt is a well-established practice in the asphalt industry. Therefore, the effect of Crumb Rubber Modifier (CRM) on low temperature performance of asphalt and its resistance to thermal cracking has been widely studied. Bahia et al. [12] and Billiter et al. [13] in two different studies investigated the effect of CRM on low temperature performance of different binders. They stated that CRM improves the stiffness of the binder at low temperatures but degrades its m-value. Billiter et al. also investigated the effect of high temperature curing conditions on low temperature properties of CRM Modified Asphalt (CRMA) [17]. They concluded that high curing conditions improve the homogeneity of the modified binder as well as its creep stiffness at low temperatures. However, they did not test the m-value of the modified asphalt.

The changes in low temperature properties of CRMA have been attributed to different effects of CRM in asphalt. Billiter et al. stated that tire rubber has very low sensitivity to temperature and keeps its elastic properties at these temperatures [17]. Therefore, tire rubber can function as elastic filler in asphalt at very low temperatures, close to asphalts glass transition temperature, and improves its flexibility. On the other hand, Hesp et al. speculated that improvement in low temperature of asphalt in presence of CRM happens due to crack pining and crack blunting effect of these particles which lead to higher toughness of the binder [69-70]. Moreover, it is stated that CRM can improve the aging susceptibility of the asphalt binder, which results in lower stiffness of asphalt after aging and consequently better physical properties at low temperatures.

In spite of all these studies, the exact contribution of CRM particles in developing the low temperature properties of asphalt is not well understood. In previous chapters it is shown that CRM goes through different changes during interaction with asphalt. CRM swells in asphalt through absorbing its light molecular components at low interaction temperatures (i.e. 160˚C) and dissolves in asphalt at higher interaction temperatures (i.e. 190˚C, 220˚C). Also, the mechanism of dissolution is different depending on interaction temperature. Each of these activities affects the nature of the liquid phase of the asphalt binder as well as the CRM particles and accordingly changes the physical properties of modified asphalt. The CRM activities lead to two types of changes in the CRMA; first, the changes in 3D structure and composition of CRM particles through swelling and dissolution of particles, second, the changes in the composition of the liquid phase of the asphalt through process of exchanging components between CRM and asphalt.

The complex dynamic nature of the CRMA and the variety of CRM activities in asphalt make it necessary to investigate the effect of each of the CRM activities on the low temperature properties of asphalt. Therefore, in this chapter the activities of CRM in asphalt was controlled by regulating the interaction condition, and a set of samples with wide range of CRM dissolution was developed. In order to distinguish and separate the effect of CRM modification on aging mechanism of CRMA from its effect on the low temperature performance of the CRMA, the low temperature performance of the samples were investigated before and after aging. Before aging, the low temperature properties of the CRMA samples and their liquid phase (CRM removed condition) were measured as a function by using BBR of CRM dissolution. The effect of CRM modification on glass transition temperature of the liquid phase of CRMA samples, which has important role in defining its low temperature mechanical behavior, was investigated through

Modulated Differential Scanning Calorimetry (MDSC). The low temperature properties of the CRMA samples were also measured after aging them through Pressure Aging Vessel (PAV).

Dissolution of CRM in Asphalt

Trend of CRM dissolution and the exchange of the materials between the CRM and asphalt were previously elaborated in Chapter 4. As explained in Chapter 4, dissolution of CRM in asphalt mainly depends on interaction temperature, and the effect of time and mixing speed is temperature dependent parameter. Also, the mechanism of dissolution varies by changing the temperature even though the extent of dissolution may stay the same. In this chapter, selected number of samples from Chapter 4 were obtained to conduct low temperature performance analysis on them and to investigate the effect of dissolution of CRM and its mechanism on low temperature properties of asphalt binder.

Low Temperature Properties of CRMA Before Aging

To determine the low temperature performance of the CRMA, a BBR test was conducted on each sample. Figure 6-1 presents the creep stiffness, s(60), and m-value of the CRMA samples as a function of CRM dissolution.

Based on the results in Figure 6-1, it can be seen that addition of CRM and increasing its concentration decreases both stiffness and m-value of the modified binder at very low CRM dissolutions, which is in accordance with the results in other studies [12, 17, 27]. The decrease in stiffness is advantageous while the decrease in m-value is disadvantageous to the low temperature performance of the CRMA. These changes in stiffness and m-value, at low level of CRM dissolution, indicate that the presence of flexible CRM particles in the asphalt matrix lowers its resistance to deflection but deteriorates the asphalt’s flow capacity and consequently its stress relaxation. These effects intensify by increasing the CRM concentration.

Also, at higher CRM concentration (20%), increasing the CRM dissolution improves the low temperature properties of the CRMA in regards to stiffness. But, no such trend is observable in the case of the lower CRM concentration (10%). This fact can be attributed to the tradeoffs between the reduction in flexibility of the remaining CRM particles in the matrix due to their dissolution and the decrease in the stiffness of the liquid phase (explained in the next section) due to the release of CRM components into the asphalt matrix. The former happens as the CRM particles lose their polymeric components (their flexible portion) into the asphalt matrix and become non-elastic fillers. The latter happens because of the changes in composition of the liquid phase that consequently alters its low temperature properties.

In the case of the samples with 10% CRM concentration, these two phenomena completely offset each other; therefore, increasing the dissolution of CRM does not change the stiffness of the total matrix. But in the case of samples with 20% CRM concentration, the lower stiffness of the liquid phase due to release of CRM components, dominates the stiffening that was gained due to the loss of the flexibility of CRM particles and consequently the stiffness of the whole matrix of CRMA decreases.

Figure 6-1b illustrates that increasing the CRM concentration significantly decreases the m-value of the CRMA at low dissolution levels. Also, increasing the CRM dissolution improves the m-value of the CRMA and finally at extensive CRM dissolution, the modified asphalt regains its original m-value. This reveals that the m-value is highly governed by the properties of the liquid phase of the matrix, which is in accordance with its definition; it represents the rate of stress relaxation by asphalt binder flow.

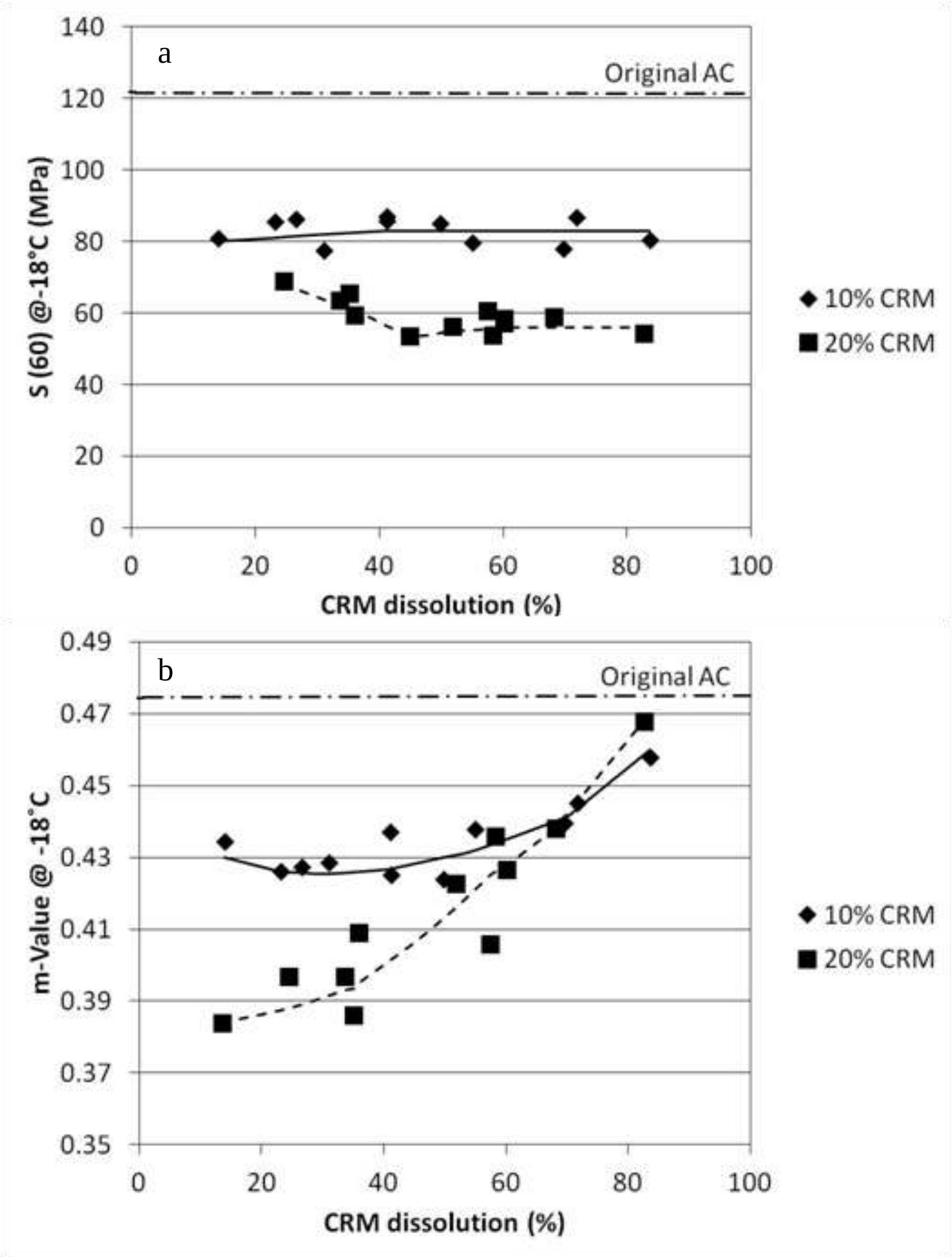

Figure 6-1: Effect of CRM dissolution on (a) stiffness (b) m-value of CRMA before aging

To further investigate the causes behind these trends, the BBR and DSC tests were conducted on the liquid phase of the CRMA (CRM removed condition) and the results are presented in subsequent sections.

Low Temperature Properties of Liquid Phase of CRMA Before Aging

Figure 6-2 presents the BBR test results on the liquid phase of the CRMA before aging. To investigate the effect of CRM particles and their dissolved portion, the changes in their stiffness and m-value are presented in two different illustrations. Results in Figures 6-2a and 6-2b show the changes in stiffness and m-value of the liquid phase, respectively, as a function of CRM dissolution percentage (calculated based on the weight of original CRM). Results in Figures 6-3a and 6-3b show the changes in stiffness and m-value of the liquid phase as a function of percentage of released rubber in the asphalt (percentage of dissolved CRM based on the weight of asphalt).

Results in Figure 6-2a show that at low levels of CRM dissolution (lower than 40%) the stiffness of the liquid phase of CRMA with 20% CRM concentration is higher than the one with 10% CRM concentration and both are higher than original asphalt. This indicates that at this level of CRM dissolution, absorption of light molecular components of asphalt is the cause of the increased stiffness of the liquid phase of the binder. Therefore, the liquid phase of CRMA with 20% CRM shows higher stiffness than the one with 10% CRM.

By increasing the CRM dissolution, the stiffness of the liquid phase of CRMA decreases remarkably. The results in Figure 6-2a show that the stiffness of the liquid phase of the CRMA with 20% CRM concentration decreases faster as a function of CRM dissolution than the one with 10% CRM concentration. The stiffness of the liquid phase of CRMA with 20% CRM concentration is higher than the one with 10% CRM concentration at low CRM dissolutions (below 40%) and it is lower at high CRM dissolutions (above 40%). Improvement in stiffness is inversely correlated with the amount of released CRM in the asphalt. The combination of the results in Figures 6-2a and 6-3a indicates that two different phenomena are involved in modifying the stiffness of asphalt at low temperatures. First, absorption and desorption of the light molecular weight components of asphalt by CRM particles; second, the release of polymeric and filler components of CRM into the asphalt matrix. Absorption of light molecular components at low dissolution levels increases the stiffness of the liquid phase significantly higher than the original binder, as explained before. Increasing the dissolution of CRM leads to desorption of these components back into the asphalt matrix and consequently decrease the stiffness of the liquid phase. The release of polymeric and filler components of CRM into the asphalt matrix changes the composition of the liquid phase of the CRMA and consequently changes its behavior at low temperatures.

Figure 6-2b shows the effect of CRM dissolution on m-value of the liquid phase of CRMA samples with two different CRM concentrations. At both CRM concentrations, the m-value of the liquid phase decreases first and then increases by increasing the CRM dissolution. The m-value of the liquid phase of the CRMA with 20% CRM concentration is significantly lower than the one with 10% CRM concentration and both are significantly lower than the original binder. Increasing the CRM dissolution in asphalt, above 40%, increases the m-value of the liquid phase of CRMA with both CRM concentrations. Figure 6-3b shows that at high CRM dissolutions (above 70%) the liquid phase of the CRMA with 20% CRM concentration has the same m-value as the one with 10% CRM concentration even though the amount of the released CRM components in asphalt is much higher in the case of samples with 20% CRM concentration [130].

Moreover, comparing the results in Figure 6-2b with the results in Figure 6-1b reveals that the m-value of all CRMA samples are very close to the m-value of their related liquid phase at very high CRM dissolution levels.

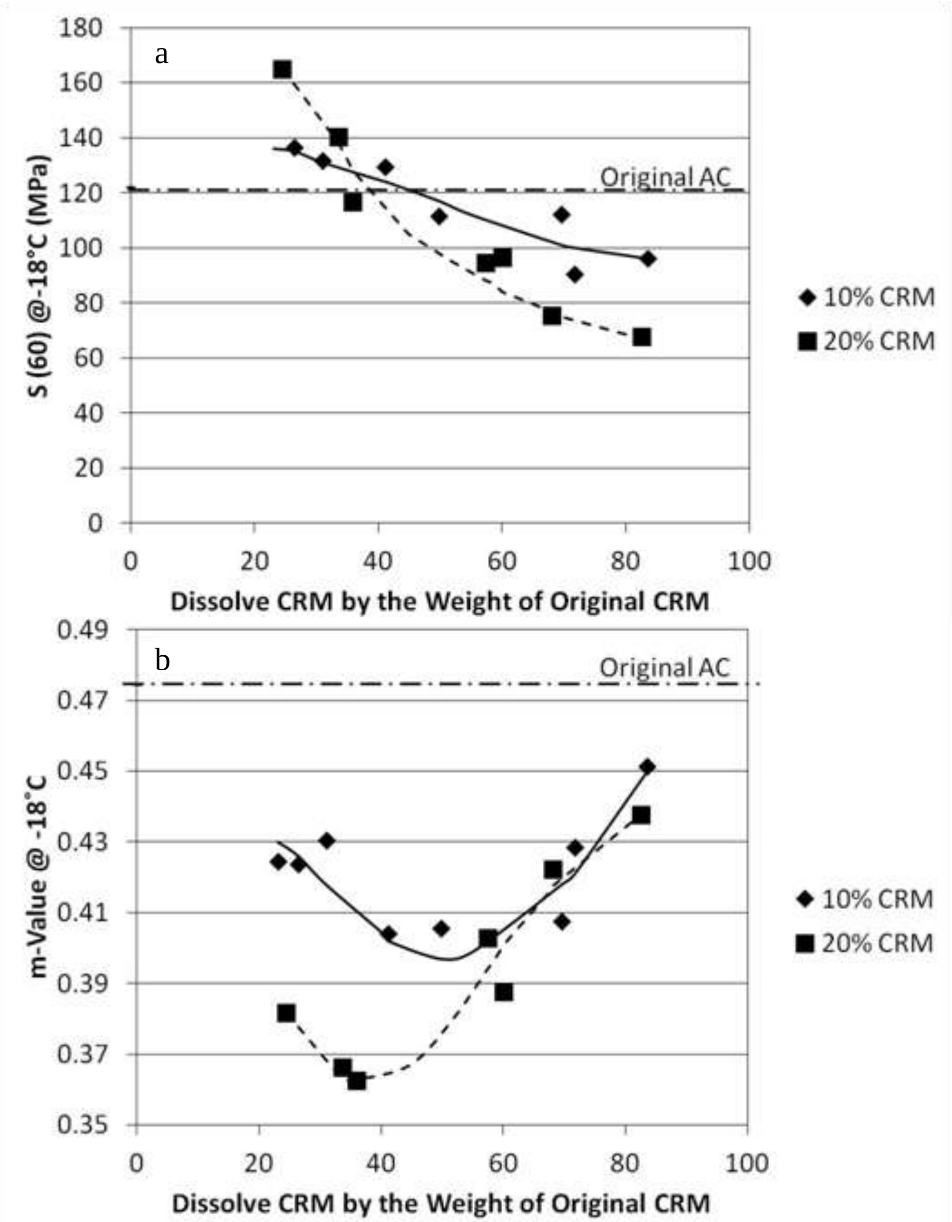

Figure 6-2: (a) stiffness (b) m-value of liquid phase of CRMA as a function of dissolved CRM by the weight of original CRM

All these results prove the statement in the previous section that the m-value of the binder is mainly governed by the liquid phase of the asphalt and the effect of CRM particles and released CRM components are marginal. In addition, these results reveal that the m-value of the liquid phase of the asphalt depends on the aromatics and oily phase of the asphalt that can be absorbed and desorbed by the CRM particles rather than the high molecular weight components.

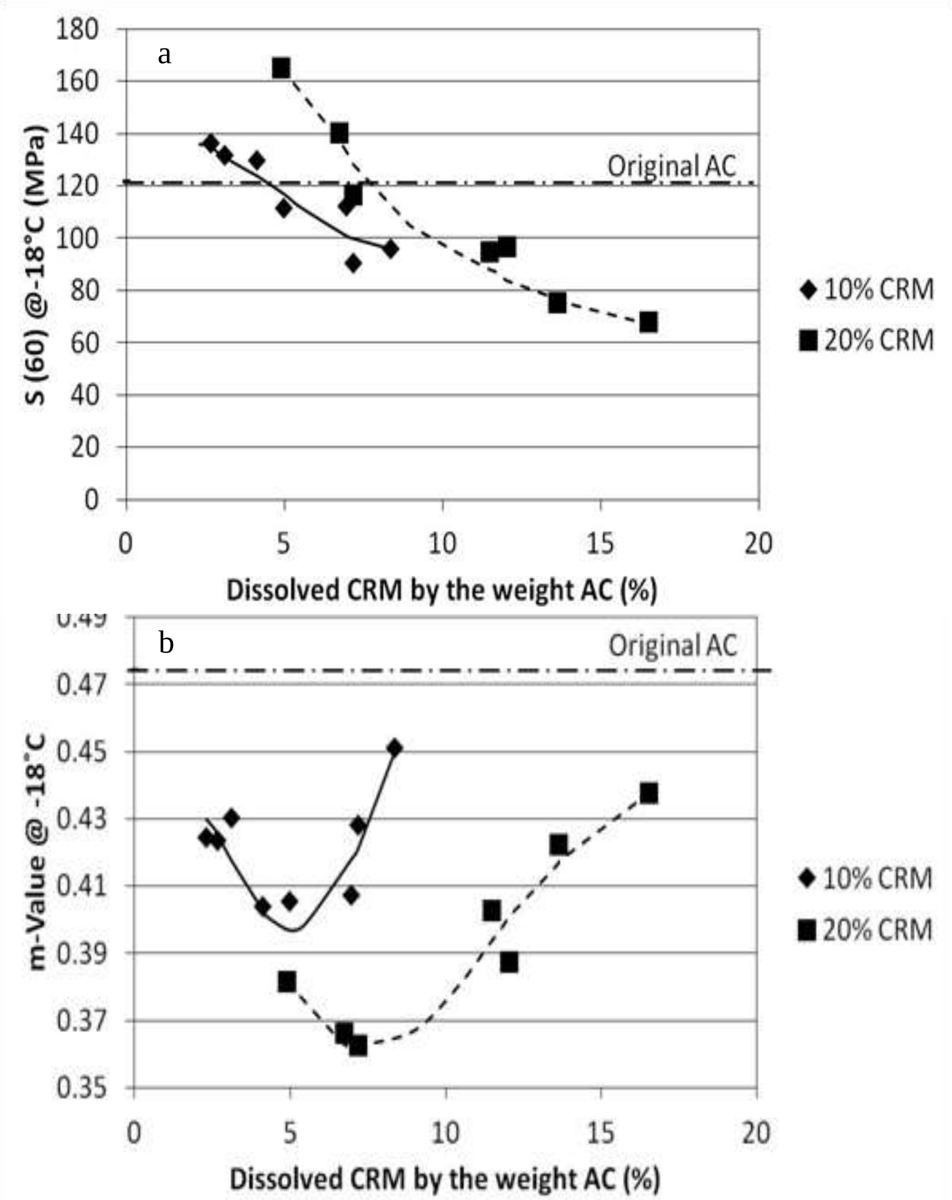

Figure 6-3: (a) stiffness (b) m-value of liquid phase of CRMA as a function of dissolved CRM by the weight of asphalt

Low Temperature Properties of CRMA After Aging

The PAV residue samples were tested by BBR and the results are presented in Figure 6-4 as a function of CRM dissolution. Note that the CRM dissolution, in this Figure, was calculated after the samples were aged through PAV and therefore, the dissolution values are different from the ones that are presented in Figures 6-1 and 6-2. The dissolution test results on PAV aged samples show that standard PAV procedure leads to extensive dissolution of CRM in asphalt and consequently changes the nature of the CRMA samples significantly. This needs further investigation, which is not in the scope of this work.

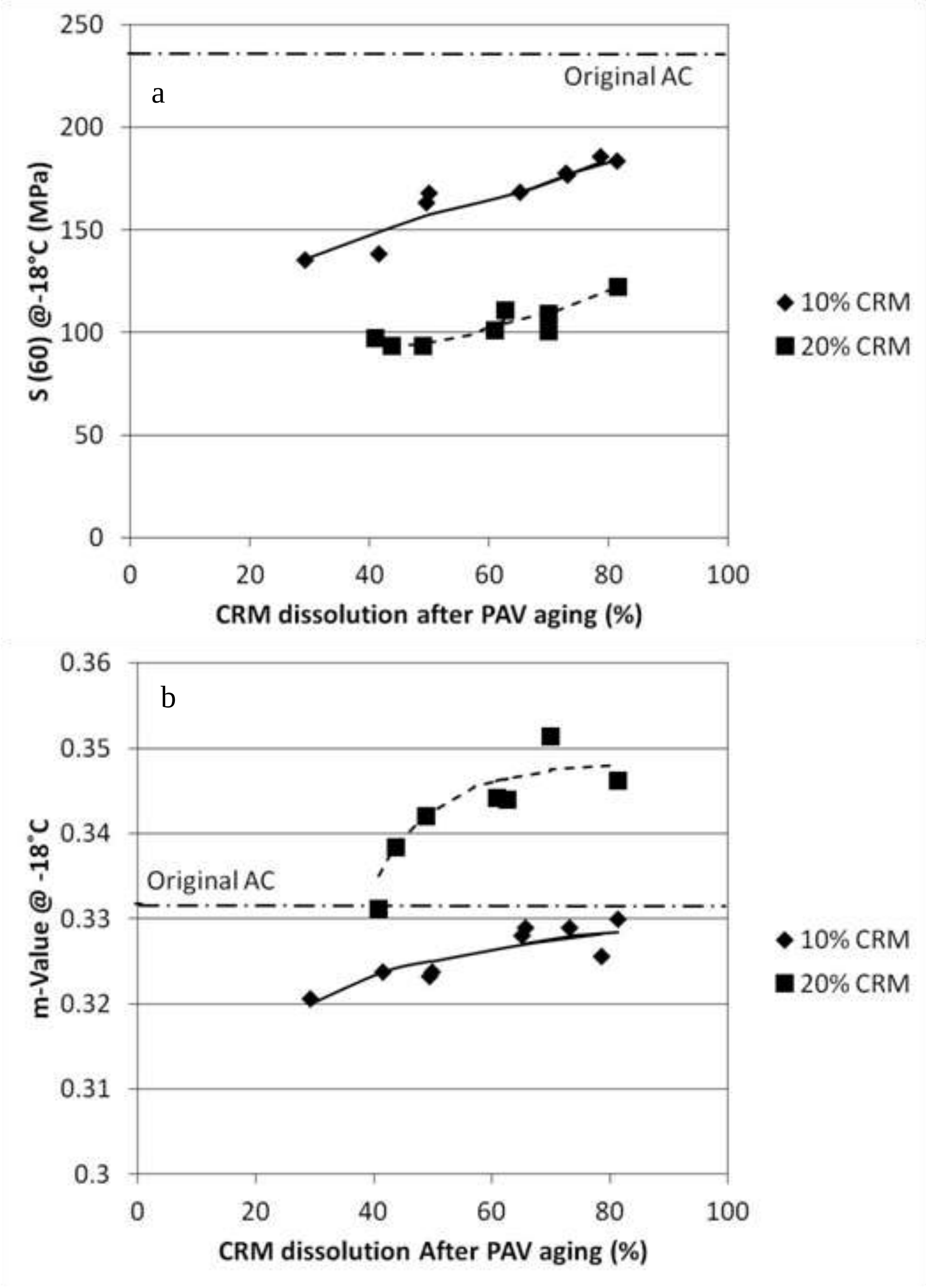

Figure 6-4: Effect of CRM dissolution on (a) stiffness (b)m-value of the CRMA in long term aged condition

As can be seen in Figure 6-4a, the stiffness of the aged samples is lower than the aged unmodified asphalt. The samples with the higher CRM concentration (20%) have lower stiffness than the one with the lower CRM concentration (10%). Moreover, the stiffness of the CRMA increases by increasing the dissolution percentage of CRM. This trend is different from what was observed in the case of CRMA samples before aging in Figure 6-1a. The difference can be attributed to the effect of CRM particles on aging mechanism of asphalt.

The changes in m-value of the aged CRMA as a function of CRM dissolution is presented in Figure 6-4. Results indicate that the m-value of the CRMA with 20% CRM concentration is higher than the one with 10% CRM concentration and the aged unmodified asphalt. Also, increasing the CRM dissolution increases m-value of the CRMA at both CRM concentrations (10% and 20%). This can be again attributed to the abundance of the aromatics and light molecular weight components in the asphalt matrix at this level of CRM dissolution.

A comparison between the results in Figures 6-4 and 6-1 indicates that the aging has remarkably less effect on low temperature properties of the CRMA samples comparing to the original asphalt and increasing the CRM concentration decreases this effect. This observation indicates that CRM can enhance the low temperature properties of asphalt in two different manners; first, improving its mechanical behavior at low temperatures, second, changing its aging process and making it less susceptible to aging, which is discussed in Chapter 5.

Glass Transition Temperature of Liquid Phase of CRMA

To understand the effect of CRM dissolution on glass transition of the liquid phase of the CRMA samples, the MDSC test was conducted on the liquid phase of selected number of them. Figure 6-5 represents the changes in glass transition of the liquid phase of CRMA samples with different CRM dissolution percentages. The glass transition temperature range was determined through specifying the starting and ending points of the stepwise drop in reversible heat flow of the sample using the TA Universal Analysis software, as presented in Figure 6-5.

Results in Figure 6-5 show that the glass transition temperature of the asphalt narrows significantly at low levels of dissolution of CRM, where the activities of the CRM is limited to absorption of the aromatics and other light molecular components of asphalt and swelling. But, by increasing the dissolution of CRM the glass transition temperature range of the liquid phase widens again, approaching to the same range of the neat asphalt, which can be attributed to the desorption of the aromatics and light molecular weight components by CRM. These results agree with the other research works that conclude that the glass transition temperature of the asphalt is governed by the aromatics and light molecular weight components of asphalt [81, 131].

A comparison of the trend of the changes in glass transition temperature range of the liquid phase with its stiffness and m-value, explained previously in Figure 6-2, indicates that the pattern of changes in glass transition temperature is more similar to the patter of changes in m-value than the stiffness. This can be attributed to the fact that the both parameters (m-value and glass transition) are governed by the aromatics and light molecular weight components in asphalt, whereas, the stiffness is governed by the amount of released components of CRM in the liquid phase. However, because of the different nature of the two measurement methods (BBR and MDSC), developing a direct correlation between the results is not possible in this research.

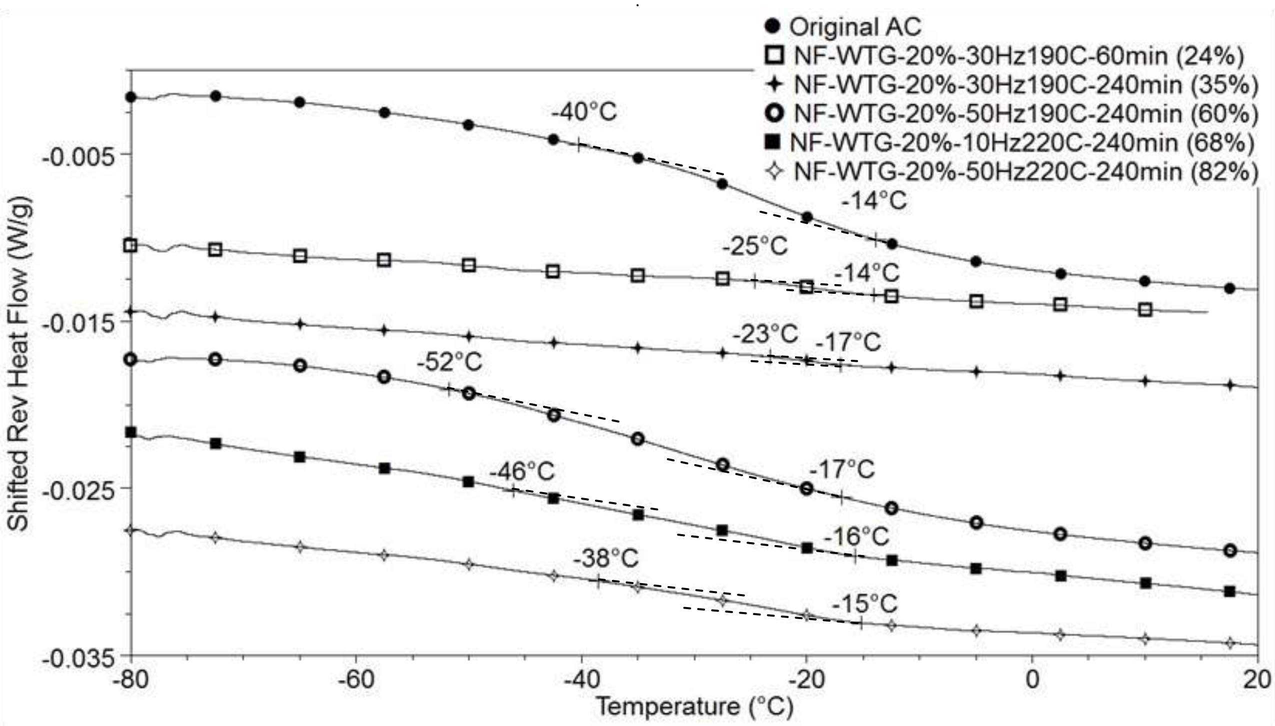

Figure 6-5: Glass transition of the liquid phase of the CRMA samples with different CRM dissolution percentages

Summary

A set of samples with wide range of CRM dissolutions was prepared at two levels of CRM concentrations (10% and 20%). The activities of CRM in asphalt and the material exchange between these two substances were controlled by regulating the interaction conditions (temperature, mixing speed, and time). In order to investigate the effect of these activities on the low temperature performance of the CRMA, the CRMA samples and their liquid phase were tested by BBR. Also, to investigate the effect of CRM dissolution and exchange of materials on the glass transition temperature of the liquid phase of the binder, the MDSC test was conducted. Finally, to investigate the effect of aging on development of the low temperature performance of CRMA, the CRMA samples were aged through RTFO and PAV, based on Superpave guidelines.

The BBR results show that addition of CRM to asphalt can enhance (decrease) the stiffness of the asphalt at very low temperatures and this enhancement intensifies by increasing the CRM dissolution in asphalt. At very low CRM dissolution levels (below 40%) the low stiffness of the CRMA matrix is attributed to the flexible behavior of the elastic CRM particles in brittle and glassy medium of asphalt. At higher levels of CRM dissolution (above 40%), where the rubbery component of the CRM released in to the asphalt matrix, the low stiffness of the CRMA is attributed to the lower stiffness of the liquid phase of CRMA due to the changes in its composition. BBR results also show that the m-value of the CRMA samples are mainly governed by the aromatics and light molecular weight components in the liquid phase of the CRMA. Therefore, at low levels of CRM dissolution, where the aromatics and light molecular weight components of asphalt are absorbed by the CRM particles, the CRMA shows a deteriorated m-value. But, by increasing the CRM dissolution and consequently desorption of the aromatics and light molecular weight components from CRM particles back into the asphalt matrix the m-value improves back to its original value and even higher. These results proved by running the BBR test on the liquid phase of the CRMA samples.

MDSC results proved that the glass transition temperature of the liquid phase of CRMA is mainly governed by the aromatics and other light molecular weight components of asphalt and therefore, its changes show a similar trend to the m-value of the CRMA samples. The changes in composition of the liquid phase of CRMA have no significant effect on its glass transition temperature.

Finally, the BBR test on PAV aged CRMA samples show that samples with 20% CRM concentration show a superior low temperature performance in comparison with the original asphalt. These results can be attributed to the effect of CRM on low temperature performance of the asphalt as well as the aging mechanism of it, which needs further investigation and is being studied by this research group. The BBR results on aged CRMA samples show that it is possible to enhance the low temperature performance of the CRMA through controlling the CRM concentration and the level CRM dissolution by regulating the interaction conditions.

CHAPTER 7. SUMMARY OF FINDINGS AND RECOMMENDATIONS

Summary of Findings

The interaction between CRM and asphalt studied in this research and the changes in physical and chemical nature of the CRM particles during interaction with asphalt were investigated. In this regard, the CRM binder was decomposed into its main components (CRM and liquid phase of binder) and each of those components studied separately. Each of these components was analyzed using several analytical techniques. The exchange of material between CRM and asphalt and the effect of changes in composition CRM on final properties of modified binder were studied. The followings are the Summary of findings in this research.

Interaction with asphalt changes the state of the CRM particles and consequently changes the final physical properties of modified asphalt. The changes in state of CRM particles highly depend on interaction temperature. The effect of time and mixing speed are temperature dependent.

CRM swells at early stages of interaction with asphalt at low and intermediate interaction temperatures (for instance temperatures lower than 190°C) and then start dissolving and disintegrating into the asphalt matrix. However, this swelling and dissolution does not follow the classical swelling and dissolution that is presented for amorphous polymers. In amorphous polymers dissolution of the polymers in the solvent happens as the polymer chains start diffusing into the solvent after its complete swelling. In the case of CRM, because of it highly cross-linked structure, dissolution happens along with breakage of cross-linked bonds and also backbone of polymer chains. Therefore, the released components of CRM into the asphalt have much smaller average molecular weight than actual polymer molecules.

TGA results indicated that CRM particles release their polymeric components into the asphalt at certain interaction conditions. The released polymeric components can act as modifiers in the liquid phase of asphalt and create internal network at certain stage of interaction at temperatures round 190°C. This indicates that under this interaction condition, it is possible to transfer the modification to the nature of the binder and produce a homogenous modified binder with better workability and superior performance.

Increasing the interaction temperature leads to a faster dissolution of CRM particles and depolymerization of the released polymeric components. Depolymerization of released polymeric components of CRM prevents creation of any internal structure in asphalt binder. In these circumstances the marginal improvement in physical properties of the asphalt is attributed to release of fillers like carbon black from CRM into the asphalt matrix.

GPC and TGA results in combination with viscoelastic analysis revealed that a combination of different activities of CRM is responsible for developing or degrading the physical properties of CRMA and its liquid phase. The results show that at 190˚C, partial release of CRM components as well as absorption of light molecular components of asphalt by remaining CRM particles are the two governing factory in property development of the liquid phase of the CRMA. Whereas, reduction in CRM particles size, due to their partial dissolution, is cause of degradation of physical properties of CRMA. At 220˚C, complete breakage of the 3D structure of CRM and desorption of asphalt's light molecular components along with depolymerization of released CRM components are responsible for degradation of physical properties of both CRMA and its liquid phase.

The effect CRM dispersion in asphalt matrix and the exchange of components between asphalt and CRM were studied on the short-term aging mechanism of CRM modified asphalt. In this respect the CRMA samples and their liquid phase were aged through RTFO. The physical aging susceptibility and oxidization indices were calculated using DSR and FTIR experiments, respectively.

The results indicated that the presence of CRM particles or their extensive dissolution has no significant effect on oxidization of the liquid phase of CRMA, however, the release of the oily components of CRM, which contain antioxidants and can happen at early stages of any interaction, relatively retards the oxidization process of asphalt binder and prevent it from corresponding stiffening. Moreover, the TGA results showed that the CRM particles have no significant role in depressing the volatilization of the liquid phase of the CRMA during the aging. The difference between the mass loss of the CRMA samples, their liquid phase and neat asphalt binder is insignificant.

The results also revealed that the CRM particles, when not dissolved, continue to absorb the aromatics and light molecular components of asphalt and swell in the asphalt matrix which leads to higher aging susceptibility of the liquid phase of CRMA comparing to the neat asphalt. But, the dominant effect of CRM particles in defining the mechanical behavior of the CRMA, especially at high CRM concentrations (i.e. 10%, 15%), keeps the aging susceptibility of the CRMA matrix low, as the CRM particles are not susceptible to any aging.

Partial dissolution of the CRM particles leads to lower susceptibility of CRMA and its liquid phase to aging, due to inability of the CRM particles to change during the aging process. This will help to assure similarity of the nature of the binder before and after mixing and compaction process of the hot mix asphalt.

The BBR results on CRMA and its liquid phase showed that addition of CRM to asphalt can enhance (decrease) the stiffness of the asphalt at very low temperatures and this enhancement intensifies by increasing the CRM dissolution in asphalt. At very low CRM dissolution levels (below 40%) the low stiffness of the CRMA matrix is attributed to the flexible behavior of the elastic CRM particles in brittle and glassy medium of asphalt. At higher levels of CRM dissolution (above 40%), where the rubbery component of the CRM released into the asphalt matrix, the low stiffness of the CRMA is attributed to the lower stiffness of the liquid phase of CRMA due to the changes in its composition.

BBR results also showed that the m-value of the CRMA is mainly governed by the aromatics and light molecular weight components in the liquid phase of the CRMA. Therefore, at low levels of CRM dissolution, where the aromatics and light molecular weight components of asphalt are absorbed by the CRM particles, the CRMA shows a deteriorated m-value. By increasing the CRM dissolution and consequently desorption of the aromatics and light molecular weight components from CRM particles back into the asphalt matrix the m-value increases to its original value and even higher.

MDSC results proved that the glass transition temperature of the liquid phase of CRMA is mainly governed by the aromatics and other light molecular weight components of asphalt and therefore, its follows the similar trend as the m-value of the CRMA samples. The release of polymeric components of CRM into the asphalt matrix does not interfere with glass transition temperature of the liquid phase of CRMA.

Finally, the BBR test on PAV aged CRMA samples showed that samples with 20% CRM concentration show a superior low temperature performance in comparison with the original asphalt. These results can be attributed to the effect of CRM on low temperature performance of the asphalt as well as the aging mechanism of it.

The BBR results on aged and unaged CRMA samples showed that it is possible to enhance the low temperature performance of the CRMA through controlling the CRM concentration and the level of CRM dissolution by regulating the interaction conditions.

Recommendations

Based on presented research, the following recommendation for future research is made.

Current study shows that CRM particles have very dynamic nature and continuously evolve interacting with asphalt. Considering this property, it is necessary to investigate evolution of mechanical behavior of CRM modified asphalt throughout its life cycle.

The current technology for simulation of long-term aging of the asphalt is not applicable for modified asphalt due to its harsh condition, which significantly affect the nature of modifiers in asphalt. Therefore, a new protocol needs to be developed considering the characteristics of asphalt modifiers and the mechanism of long-term aging that happens on the pavement.

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APPENDIX A. LIST OF INTERACTIONS AND RELATED PARAMETER

No.	Interaction Code	Asphalt Type	CRM Type	CRM Size	CRM %	Temp (°C)	Shear (Hz)	Sample Time (min.)	BBR	Dissolution Test	DSR	FTIR	GPC	MDSC	PAV	RTFO	Separation test	TGA
1	TR Rubber		TR	(30-40)														*
2	WTG Rubber		WTG	(30-40)														*
4	Flint Hill Asphalt	NF5828							*		*	*	*	*	*	*	*	*
5	H-TR(30-40)-10%-200C30hz	H6422	TR	(30-40)	10	200	30	10		*	*							*
6	H-TR(30-40)-10%-200C30hz	H6422	TR	(30-40)	10	200	30	120		*	*		*					*
7	H-TR(30-40)-10%-200C30hz	H6422	TR	(30-40)	10	200	30	240		*	*		*					*
8	H-TR(30-40)-10%-160C10hz	H6422	TR	(30-40)	10	160	10	10		*	*							*
9	H-TR(30-40)-10%-160C10hz	H6422	TR	(30-40)	10	160	10	120		*	*							
10	H-TR(30-40)-10%-160C10hz	H6422	TR	(30-40)	10	160	10	240		*	*							*
11	M-TR(30-40)-10%-190C30hz	M58	TR	(30-40)	10	190	30	120		*	*						*	
12	M-TR(30-40)-20%-220C10hz	M58	TR	(30-40)	20	220	10	240	*	*	*							
13	M-WTG(30-40)-10%-190C30hz	M58	WTG	(30-40)	10	190	30	120	*		*					*	*	
14	NF-TR(60-80)-10%-190C30hz	NF5828	TR	(60-80)	10	190	30	15		*	*							
15	NF-TR(60-80)-10%-190C30hz	NF5828	TR	(60-80)	10	190	30	60		*	*							
16	NF-TR(60-80)-10%-190C30hz	NF5828	TR	(60-80)	10	190	30	120		*	*							
17	NF-TR(30-40)-20%-160C10hz	NF5828	TR	(30-40)	20	160	10	15			*							
18	NF-TR(30-40)-20%-160C10hz	NF5828	TR	(30-40)	20	160	10	30			*							
19	NF-TR(30-40)-20%-160C10hz	NF5828	TR	(30-40)	20	160	10	60			*							
20	NF-TR(30-40)-20%-160C10hz	NF5828	TR	(30-40)	20	160	10	120			*							
21	NF-TR(30-40)-20%-160C10hz	NF5828	TR	(30-40)	20	160	10	240			*							
22	NF-TR(30-40)-20%-190C50hz	NF5828	TR	(30-40)	20	190	50	15		*	*							
23	NF-TR(30-40)-20%-190C50hz	NF5828	TR	(30-40)	20	190	50	30		*	*							
24	NF-TR(30-40)-20%-190C50hz	NF5828	TR	(30-40)	20	190	50	60		*	*							

No.	Interaction Code	Asphalt Type	CRM Type	CRM Size	CRM %	Temp (°C)	Shear (Hz)	Sample Time (min.)	BBR	Dissolution Test	DSR	FTIR	GPC	MDSC	PAV	RTFO	Separation test	TGA
25	NF-TR(30-40)-20%-190C50hz	NF5828	TR	(30-40)	20	190	50	120		*	*							
26	NF-TR(40-60)-15%-160C10hz	NF5828	TR	(40-60)	15	160	10	120		*	*			*		*		
27	NF-TR(40-60)-15%-160C10hz	NF5828	TR	(40-60)	15	160	10	120		*		*				*		
28	NF-TR(40-60)-10%-160C10hz	NF5828	TR	(40-60)	10	160	10	120		*	*					*		
29	NF-TR(40-60)-20%-160C10hz	NF5828	TR	(40-60)	20	160	10	120			*					*		
30	NF-TR(30-40)-20%-220C50hz	NF5828	TR	(30-40)	20	220	50	15		*	*							
31	NF-TR(30-40)-20%-220C50hz	NF5828	TR	(30-40)	20	220	50	30		*	*							
32	NF-TR(30-40)-20%-220C50hz	NF5828	TR	(30-40)	20	220	50	60		*	*							
33	NF-TR(30-40)-20%-220C50hz	NF5828	TR	(30-40)	20	220	50	120		*	*							
34	NF-TR(30-40)-20%-220C10hz	NF5828	TR	(30-40)	20	220	10	15			*							
35	NF-TR(30-40)-20%-220C10hz	NF5828	TR	(30-40)	20	220	10	30			*							
36	NF-TR(30-40)-20%-220C10hz	NF5828	TR	(30-40)	20	220	10	60			*							
37	NF-TR(30-40)-20%-220C10hz	NF5828	TR	(30-40)	20	220	10	120			*							
38	NF-TR(30-40)-20%-190C10hz	NF5828	TR	(30-40)	20	190	10	15		*	*							
39	NF-TR(30-40)-20%-190C10hz	NF5828	TR	(30-40)	20	190	10	30		*	*							
40	NF-TR(30-40)-20%-190C10hz	NF5828	TR	(30-40)	20	190	10	60		*	*							
41	NF-TR(30-40)-20%-190C10hz	NF5828	TR	(30-40)	20	190	10	120		*	*							
42	NF-TR(30-40)-20%-190C10hz	NF5828	TR	(30-40)	20	190	10	240	*	*	*						*	
43	NF-TR(40-60)-15%-190C30hz	NF5828	TR	(40-60)	15	190	30	120		*	*					*		
44	NF-TR(40-60)-15%-220C50hz	NF5828	TR	(40-60)	15	220	50	120		*	*					*		
45	NF-TR(40-60)-10%-190C30hz	NF5828	TR	(40-60)	10	190	30	120		*	*					*		
46	NF-TR(80-200)-15%-160C10hz	NF5828	TR	(80-200)	15	160	10	120			*					*		
47	NF-TR(20-30)-15%-160C10hz	NF5828	TR	(20-30)	15	160	10	120			*					*		
48	NF-TR(40-60)-15%-190C10hz	NF5828	TR	(40-60)	15	190	10	120			*					*		

No.	**Interaction Code**	**Asphalt Type**	**CRM Type**	**CRM Size**	**CRM %**	**Temp (°C)**	**Shear (Hz)**	**Sample Time (min.)**	**BBR**	**Dissolution Test**	**DSR**	**FTIR**	**GPC**	**MDSC**	**PAV**	**RTFO**	**Separation test**	**TGA**
49	NF-TR(80-200)-20%-190C10hz	NF5828	TR	(80-200)	20	190	10	15			*							
50	NF-TR(80-200)-20%-190C10hz	NF5828	TR	(80-200)	20	190	10	30			*							
51	NF-TR(80-200)-20%-190C10hz	NF5828	TR	(80-200)	20	190	10	60			*							
52	NF-TR(80-200)-20%-190C10hz	NF5828	TR	(80-200)	20	190	10	120			*							
53	NF-TR(60-80)-10%-190C30hz	NF5828	TR	(60-80)	10	190	30	240		*	*						*	
54	NF-TR(30-40)-20%-190C50hz	NF5828	TR	(30-40)	20	190	50	240	*	*	*		*				*	
55	NF-TR(30-40)-20%-220C50hz	NF5828	TR	(30-40)	20	220	50	240		*	*				*	*	*	
56	NF-TR(30-40)-20%-220C10hz	NF5828	TR	(30-40)	20	220	10	240			*						*	
57	NF-TR(80-200)-20%-190C10hz	NF5828	TR	(80-200)	20	190	10	240			*						*	
58	NF-TR(30-40)-10%-190C30hz	NF5828	TR	(30-40)	10	190	30	120		*	*						*	
59	NF-TR(30-40)-10%-200C30hz	NF5828	TR	(30-40)	10	200	30	240		*	*		*					*
60	NF-TR(30-40)-10%-220C10hz	NF5828	TR	(30-40)	10	220	10	240		*	*		*				*	*
61	NF-TR(30-40)-10%-220C50hz	NF5828	TR	(30-40)	10	220	50	240		*	*		*				*	
62	NF-TR(30-40)-10%-190C30hz	NF5828	TR	(30-40)	10	190	30	240		*	*						*	
63	NF-TR(40-60)-5%-160C10hz	NF5828	TR	(40-60)	5	160	10	120		*	*					*		
64	NF-TR(40-60)-15%-190C50hz	NF5828	TR	(40-60)	15	190	50	120		*				*		*		
65	NF-TR(40-60)-15%-190C50hz	NF5828	TR	(40-60)	15	190	50	60								*		
66	NF-TR(80-200)-20%-160C10hz	NF5828	TR	(80-200)	20	160	10	15			*							
67	NF-TR(80-200)-20%-160C10hz	NF5828	TR	(80-200)	20	160	10	30			*							
68	NF-TR(80-200)-20%-160C10hz	NF5828	TR	(80-200)	20	160	10	60			*							
69	NF-TR(80-200)-20%-160C10hz	NF5828	TR	(80-200)	20	160	10	120			*							
70	NF-TR(80-200)-20%-160C10hz	NF5828	TR	(80-200)	20	160	10	240			*							
71	NF-TR(30-40)-10%-190C30hz	NF5828	TR	(30-40)	10	190	30	240		*	*						*	
72	NF-TR(30-40)-10%-190C30hz	NF5828	TR	(30-40)	10	190	30	60		*	*							

No.	Interaction Code	Asphalt Type	CRM Type	CRM Size	CRM %	Temp (°C)	Shear (Hz)	Sample Time (min.)	BBR	Dissolution Test	DSR	FTIR	GPC	MDSC	PAV	RTFO	Separation test	TGA
73	NF-TR(30-40)-10%-160C10hz	NF5828	TR	(30-40)	10	160	10	240		*	*						*	
74	NF-TR(30-40)-10%-200C30hz	NF5828	TR	(30-40)	10	200	30	60		*	*		*					*
75	NF-TR(30-40)-10%-200C30hz	NF5828	TR	(30-40)	10	200	30	120		*	*		*					*
76	NF-TR(30-40)-10%-220C10hz	NF5828	TR	(30-40)	10	220	10	15		*	*							
77	NF-TR(30-40)-10%-220C10hz	NF5828	TR	(30-40)	10	220	10	60		*	*		*					*
78	NF-TR(30-40)-10%-220C10hz	NF5828	TR	(30-40)	10	220	10	120		*	*		*					*
79	NF-TR(30-40)-10%-220C50hz	NF5828	TR	(30-40)	10	220	50	60		*	*		*					
80	NF-TR(30-40)-10%-220C50hz	NF5828	TR	(30-40)	10	220	50	120		*	*		*					
81	NF-TR(30-40)-10%-190C30hz	NF5828	TR	(30-40)	10	190	30	15		*	*							
82	NF-TR(30-40)-10%-190C30hz	NF5828	TR	(30-40)	10	190	30	60		*	*							
83	NF-TR(30-40)-10%-190C30hz	NF5828	TR	(30-40)	10	190	30	120		*	*							
84	NF-TR(30-40)-10%-160C10hz	NF5828	TR	(30-40)	10	160	10	15		*	*							
85	NF-TR(30-40)-10%-160C10hz	NF5828	TR	(30-40)	10	160	10	60		*	*							
86	NF-TR(30-40)-10%-160C10hz	NF5828	TR	(30-40)	10	160	10	120		*	*							
87	NF-WTG(30-40)-20%-190C30hz	NF5828	WTG	(30-40)	20	190	30	15		*	*							
88	NF-WTG(30-40)-20%-190C30hz	NF5828	WTG	(30-40)	20	190	30	60		*	*							
89	NF-WTG(30-40)-20%-190C30hz	NF5828	WTG	(30-40)	20	190	30	120		*	*							
90	NF-WTG(30-40)-15%-220C50hz	NF5828	WTG	(30-40)	15	220	50	15		*	*							
91	NF-WTG(30-40)-15%-220C50hz	NF5828	WTG	(30-40)	15	220	50	30		*	*							
92	NF-WTG(30-40)-15%-220C50hz	NF5828	WTG	(30-40)	15	220	50	60		*	*							
93	NF-WTG(30-40)-15%-220C50hz	NF5828	WTG	(30-40)	15	220	50	120		*	*							

No.	Interaction Code	Asphalt Type	CRM Type	CRM Size	CRM %	Temp (°C)	Shear (Hz)	Sample Time (min.)	BBR	Dissolution Test	DSR	FTIR	GPC	MDSC	PAV	RTFO	Separation test	TGA
94	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	15		*	*							
95	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	30		*	*							
96	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	60		*	*							
97	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	120			*							
98	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	240		*	*							
99	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	360		*	*							
100	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	15			*							
101	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	30			*							
102	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	60			*							
103	NF-WTG(30-40)-10%-190C10hz	NF5828	WTG	(30-40)	10	190	10	15		*	*							
104	NF-WTG(30-40)-10%-190C10hz	NF5828	WTG	(30-40)	10	190	10	30		*	*							
105	NF-WTG(30-40)-10%-190C10hz	NF5828	WTG	(30-40)	10	190	10	60		*	*							
106	NF-WTG(30-40)-10%-190C10hz	NF5828	WTG	(30-40)	10	190	10	120		*	*							
107	NF-WTG(30-40)-20%-220C50hz	NF5828	WTG	(30-40)	20	220	50	15		*	*		*					
108	NF-WTG(30-40)-20%-220C50hz	NF5828	WTG	(30-40)	20	220	50	30		*	*							
109	NF-WTG(30-40)-20%-220C50hz	NF5828	WTG	(30-40)	20	220	50	60		*	*		*					

No.	Interaction Code	Asphalt Type	CRM Type	CRM Size	CRM %	Temp (°C)	Shear (Hz)	Sample Time (min.)	BBR	Dissolution Test	DSR	FTIR	GPC	MDSC	PAV	RTFO	Separation test	TGA
110	NF-WTG(30-40)-20%-220C50hz	NF5828	WTG	(30-40)	20	220	50	120		*	*		*					
111	NF-WTG(30-40)-10%-190C50hz	NF5828	WTG	(30-40)	10	190	50	15		*	*							
112	NF-WTG(30-40)-10%-190C50hz	NF5828	WTG	(30-40)	10	190	50	30		*	*							
113	NF-WTG(30-40)-10%-190C50hz	NF5828	WTG	(30-40)	10	190	50	60		*	*		*					*
114	NF-WTG(30-40)-10%-190C50hz	NF5828	WTG	(30-40)	10	190	50	120		*	*		*					*
115	NF-WTG(30-40)-10%-190C50hz	NF5828	WTG	(30-40)	10	190	50	240	*	*	*			*	*	*		*
116	NF-WTG(30-40)-30%-220C50hz	NF5828	WTG	(30-40)	30	220	50	15		*	*							
117	NF-WTG(30-40)-30%-220C50hz	NF5828	WTG	(30-40)	30	220	50	30			*							
118	NF-WTG(30-40)-30%-220C50hz	NF5828	WTG	(30-40)	30	220	50	60		*	*							
119	NF-WTG(30-40)-30%-220C50hz	NF5828	WTG	(30-40)	30	220	50	120		*	*							
120	NF-WTG(30-40)-30%-220C50hz	NF5828	WTG	(30-40)	30	220	50	240		*	*							
121	NF-WTG(40-60)-15%-160C10hz	NF5828	WTG	(40-60)	15	160	10	120			*					*		
122	NF-WTG(30-40)-20%-160C10hz	NF5828	WTG	(30-40)	20	160	10	15			*		*					
123	NF-WTG(30-40)-20%-160C10hz	NF5828	WTG	(30-40)	20	160	10	30			*							
124	NF-WTG(30-40)-20%-160C10hz	NF5828	WTG	(30-40)	20	160	10	60			*							
125	NF-WTG(30-40)-20%-160C10hz	NF5828	WTG	(30-40)	20	160	10	120			*							

No.	Interaction Code	Asphalt Type	CRM Type	CRM Size	CRM %	Temp (°C)	Shear (Hz)	Sample Time (min.)	BBR	Dissolution Test	DSR	FTIR	GPC	MDSC	PAV	RTFO	Separation test	TGA
126	NF-WTG(30-40)-20%-160C10hz	NF5828	WTG	(30-40)	20	160	10	240	*				*	*				
127	NF-WTG(30-40)-20%-190C50hz	NF5828	WTG	(30-40)	20	190	50	15		*	*							
128	NF-WTG(30-40)-20%-190C50hz	NF5828	WTG	(30-40)	20	190	50	30		*	*							
129	NF-WTG(30-40)-20%-190C50hz	NF5828	WTG	(30-40)	20	190	50	60		*	*		*					
130	NF-WTG(30-40)-20%-190C50hz	NF5828	WTG	(30-40)	20	190	50	120			*		*					
131	NF-WTG(40-60)-15%-190C50hz	NF5828	WTG	(40-60)	15	190	50	15			*							
132	NF-WTG(40-60)-15%-190C50hz	NF5828	WTG	(40-60)	15	190	50	120			*							
133	NF-WTG(40-60)-15%-190C50hz	NF5828	WTG	(40-60)	15	190	50	240			*					*		
134	NF-WTG(30-40)-20%-220C10hz	NF5828	WTG	(30-40)	20	220	10	15		*	*							
135	NF-WTG(30-40)-20%-220C10hz	NF5828	WTG	(30-40)	20	220	10	30		*	*		*					
136	NF-WTG(30-40)-20%-190C50hz	NF5828	WTG	(30-40)	20	190	50	360	*	*	*							
137	NF-WTG(30-40)-10%-220C10hz	NF5828	WTG	(30-40)	10	220	10	15		*	*							
138	NF-WTG(30-40)-10%-220C10hz	NF5828	WTG	(30-40)	10	220	10	30		*	*							
139	NF-WTG(30-40)-20%-190C30hz	NF5828	WTG	(30-40)	20	190	30	60	*	*				*	*	*		
140	NF-WTG(30-40)-20%-190C30hz	NF5828	WTG	(30-40)	20	190	30	120	*	*					*	*		
141	NF-WTG(30-40)-20%-190C10hz	NF5828	WTG	(30-40)	20	190	10	15			*							

No.	Interaction Code	Asphalt Type	CRM Type	CRM Size	CRM %	Temp (°C)	Shear (Hz)	Sample Time (min.)	BBR	Dissolution Test	DSR	FTIR	GPC	MDSC	PAV	RTFO	Separation test	TGA
142	NF-WTG(30-40)-20%-190C10hz	NF5828	WTG	(30-40)	20	190	10	30			*		*					
143	NF-WTG(30-40)-20%-190C10hz	NF5828	WTG	(30-40)	20	190	10	60			*							
144	NF-WTG(30-40)-20%-190C10hz	NF5828	WTG	(30-40)	20	190	10	120			*		*					
145	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	60	*	*	*				*	*	*	
146	NF-WTG(30-40)-20%-190C30hz	NF5828	WTG	(30-40)	20	190	30	240	*	*	*	*	*	*	*	*	*	
147	NF-WTG(30-40)-15%-220C50hz	NF5828	WTG	(30-40)	15	220	50	240					*				*	
148	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	480	*	*	*	*	*		*	*	*	
149	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	120	*	*	*				*	*	*	
150	NF-WTG(30-40)-10%-190C10hz	NF5828	WTG	(30-40)	10	190	10	240	*	*	*				*	*	*	
151	NF-WTG(30-40)-20%-220C50hz	NF5828	WTG	(30-40)	20	220	50	240	*	*	*	*	*	*	*	*	*	*
152	NF-WTG(30-40)-20%-190C50hz	NF5828	WTG	(30-40)	20	190	50	240	*	*	*		*	*	*	*	*	*
153	NF-WTG(30-40)-20%-220C10hz	NF5828	WTG	(30-40)	20	220	10	60		*	*		*				*	
154	NF-WTG(30-40)-20%-220C10hz	NF5828	WTG	(30-40)	20	220	10	120	*	*	*			*			*	
155	NF-WTG(30-40)-20%-220C10hz	NF5828	WTG	(30-40)	20	220	10	240	*	*	*		*	*		*	*	
156	NF-WTG(30-40)-10%-220C10hz	NF5828	WTG	(30-40)	10	220	10	60		*	*						*	
157	NF-WTG(30-40)-10%-220C10hz	NF5828	WTG	(30-40)	10	220	10	120	*	*	*				*	*	*	

No.	Interaction Code	Asphalt Type	CRM Type	CRM Size	CRM %	Temp (°C)	Shear (Hz)	Sample Time (min.)	BBR	Dissolution Test	DSR	FTIR	GPC	MDSC	PAV	RTFO	Separation test	TGA
158	NF-WTG(30-40)-10%-190C50hz	NF5828	WTG	(30-40)	10	190	50	120	*	*					*	*	*	
159	NF-WTG(30-40)-20%-220C10hz	NF5828	WTG	(30-40)	20	220	10	60	*	*	*				*	*		
160	NF-WTG(30-40)-20%-220C10hz	NF5828	WTG	(30-40)	20	220	10	120	*	*	*				*	*		
161	NF-WTG(30-40)-10%-160C10hz	NF5828	WTG	(30-40)	10	160	10	15		*	*							
162	NF-WTG(30-40)-10%-160C10hz	NF5828	WTG	(30-40)	10	160	10	60		*	*							
163	NF-WTG(30-40)-10%-160C10hz	NF5828	WTG	(30-40)	10	160	10	120		*	*							
164	NF-WTG(30-40)-20%-190C10hz	NF5828	WTG	(30-40)	20	190	10	240	*		*		*					
165	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	15		*	*	*						
166	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	60		*	*	*	*					*
167	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	120		*	*	*	*					*
168	NF-WTG(30-40)-10%-160C10hz	NF5828	WTG	(30-40)	10	160	10	240	*	*	*				*	*	*	
169	NF-WTG(30-40)-10%-160C30hz	NF5828	WTG	(30-40)	10	160	30	15		*	*							
170	NF-WTG(30-40)-10%-160C30hz	NF5828	WTG	(30-40)	10	160	30	60		*	*							
171	NF-WTG(30-40)-10%-160C30hz	NF5828	WTG	(30-40)	10	160	30	120		*	*							
172	NF-WTG(30-40)-10%-190C30hz	NF5828	WTG	(30-40)	10	190	30	240	*	*	*	*	*		*	*	*	*
173	NF-WTG(30-40)-10%-220C10hz	NF5828	WTG	(30-40)	10	220	10	15		*	*							

No.	Interaction Code	Asphalt Type	CRM Type	CRM Size	CRM %	Temp (°C)	Shear (Hz)	Sample Time (min.)	BBR	Dissolution Test	DSR	FTIR	GPC	MDSC	PAV	RTFO	Separation test	TGA
174	NF-WTG(30-40)-10%-220C10hz	NF5828	WTG	(30-40)	10	220	10	60		*	*							
175	NF-WTG(30-40)-10%-220C10hz	NF5828	WTG	(30-40)	10	220	10	120		*	*		*					*
176	NF-WTG(30-40)-10%-160C30hz	NF5828	WTG	(30-40)	10	160	30	240		*	*						*	
177	NF-WTG(30-40)-10%-220C10hz	NF5828	WTG	(30-40)	10	220	10	240	*	*	*		*		*	*	*	*
178	NF-WTG(30-40)-15%-190C30hz	NF5828	WTG	(30-40)	15	190	30	15		*	*							
179	NF-WTG(30-40)-15%-190C30hz	NF5828	WTG	(30-40)	15	190	30	60		*	*							
180	NF-WTG(30-40)-15%-190C30hz	NF5828	WTG	(30-40)	15	190	30	120		*	*							
181	NF-WTG(30-40)-15%-190C30hz	NF5828	WTG	(30-40)	15	190	30	240		*	*		*				*	
182	NF-WTG(40-60)-10%-190C30hz	NF5828	WTG	(40-60)	10	190	30	15		*	*							
183	NF-WTG(40-60)-10%-190C30hz	NF5828	WTG	(40-60)	10	190	30	60		*	*							
184	NF-WTG(40-60)-10%-190C30hz	NF5828	WTG	(40-60)	10	190	30	120		*	*							
185	NF-WTG(40-60)-10%-190C30hz	NF5828	WTG	(40-60)	10	190	30	240		*	*						*	
186	NF-WTG(30-40)-10%-220C50hz	NF5828	WTG	(30-40)	10	220	50	15		*	*							*
187	NF-WTG(30-40)-10%-220C50hz	NF5828	WTG	(30-40)	10	220	50	60		*	*		*					
188	NF-WTG(30-40)-10%-220C50hz	NF5828	WTG	(30-40)	10	220	50	120		*	*		*					
189	NF-WTG(30-40)-10%-220C50hz	NF5828	WTG	(30-40)	10	220	50	240	*	*	*	*	*	*	*	*	*	*

APPENDIX B. EFECT OF DIFFERENT PARAMETERS ON PROPERTY DEVELOPMENT OF CRMA AS FUNCTION OF INTERACTION TIME

Viscoelastic Analysis of CRMA as Function of Interaction Time

In this section the development of physical properties of CRMA is investigated as a function of interaction time. The effect of different interaction and material parameters is considered as follow:

Effect of interaction conditions

Figure B-1 illustrates the effect of interaction temperature on development of physical properties of CRMA. Results in this Figure indicate that interaction temperature highly affect the development of physical properties of the CRMA. As can be seen, at 160°C the complex modulus of the CRMA increases constantly throughout the interaction time whereas, its phase angle decreases (elasticity increases). At 190°C, the complex modulus of the CRMA increases by increasing at early stages of the interaction and then start to deteriorate. At 220°C both the complex modulus and the phase angle deteriorate throughout the interaction period. These results are in complete agreement with the research done by Abdelrahman et al [28].

The effect of interaction mixing speed under different interaction temperatures is illustrated in Figure B-2 to Figure B-4. The results in these Figures reveal that the effect of mixing speed on property development of the CRMA is highly temperature dependant.

As can be seen in Figure B-2, at 160°C, the effect of mixing speed is negligible and the complex modulus and the phase angle of the both samples (NF-WTG-10%-10Hz160C and NF-WTG-10%-30Hz160C) are reaching to the same numbers in a same trend.

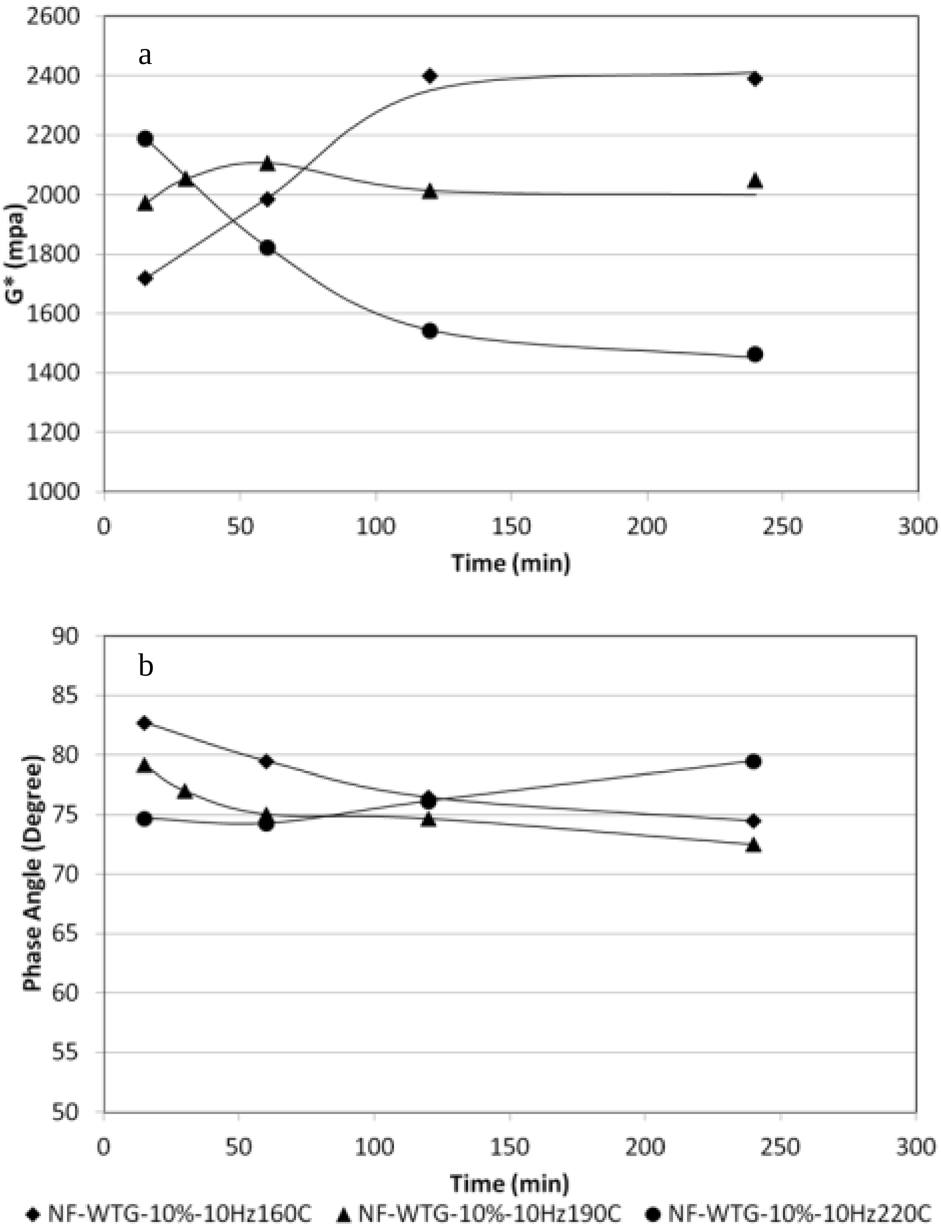

Figure B-1: Development of physical properties of CRMA under different interaction temperature (a) complex modulus (b) phase angle

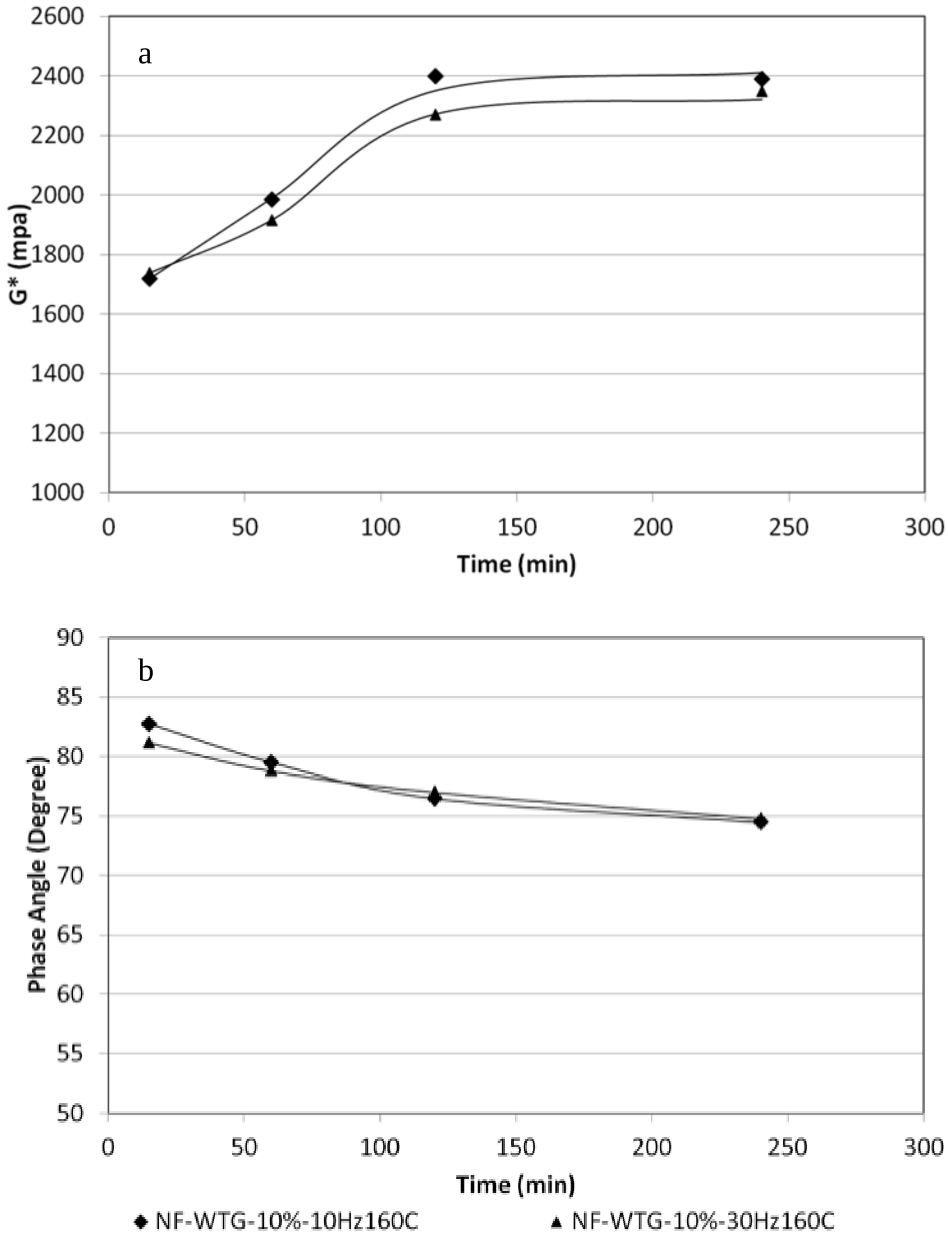

Figure B-2: Development of physical properties of CRMA at 160°C and under different interaction mixing speed (a) complex modulus (b) phase angle

Figure B-3 illustrate that at 190°C, altering the mixing speed can significantly influence the trend of property development of the CRMA. As can be seen at low mixng speed (10Hz) the complex modulus increase and the phase angle decreases constantly throughout the interaction time. By increasing the mixing speed to 30Hz, this trend changes.

The complex modulus increases at early stages of the interaction and then start to decrease (diteriorate) whereas the phase angle decreases first and then stays constant. At 50Hz, the complex modulus of the sample decreases constantly throughout the interatcion time. Also, the phase angle decreases first and then slightly increases by extending the time of interaction.

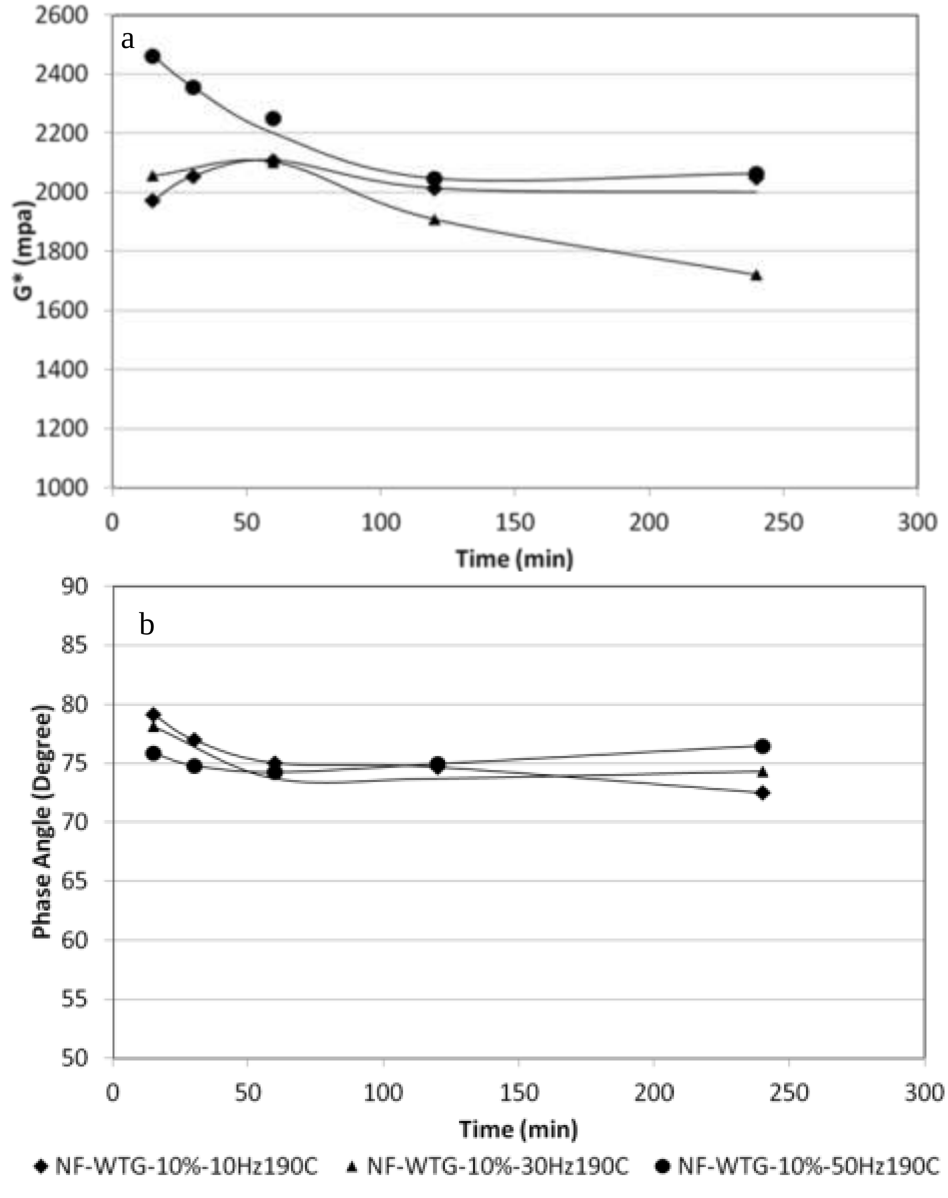

Figure B-3: Development of physical properties of CRMA at 190°C and under different interaction mixing speed (a) complex modulus (b) phase angle

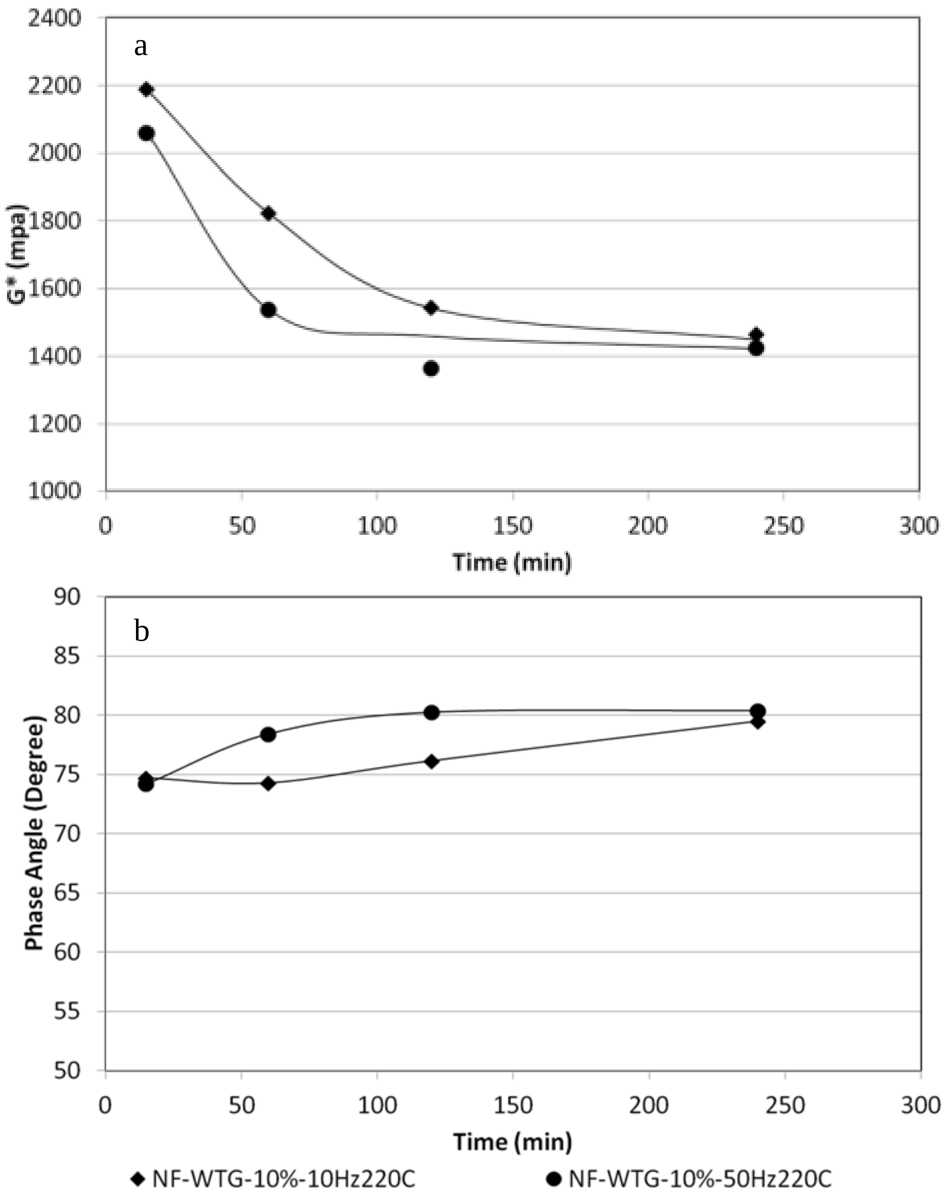

Figure B-4: Development of physical properties of CRMA at 220°C and under different interaction mixing speed (a) complex modulus (b) phase angle

In Figure B-4 it can be observed that, at 220°C, the mixing speed works as an accelerator for the interaction. At both speeds (10Hz and 50Hz) the complex modulus of the samoples decreases and the phase angle increases. At 50Hz the rates are faster than the ones at 10Hz. However, at both speeds the complex modulus and the phase angle finally reache to the same extend. This indicates that the mixing speed just affect the property development rate (here deterioration) without affecting its extent. These results are also in agreement with the results obtained by Abdelrahman et al. [28].

Effect of CRM concentration

The effect of CRM concentration on the trend of the property development of CRMA is investigated in this study at three CRM concentration levels; 10%, 15% and 20%. Figure B-5 illustrates the trend of physical property development as a function of interaction time at single interaction condition, 190°C and 30Hz.

As the results in Figure B-5 indicate, the trend of the physical property development is independent from the range of CRM concentrations, understudied. However, as expected CRM concentration has significant effect on the extent of modification. As can be seen in Figure B-5, higher CRM concentration results in higher complex modulus and lower phase angle for the modified asphalt.

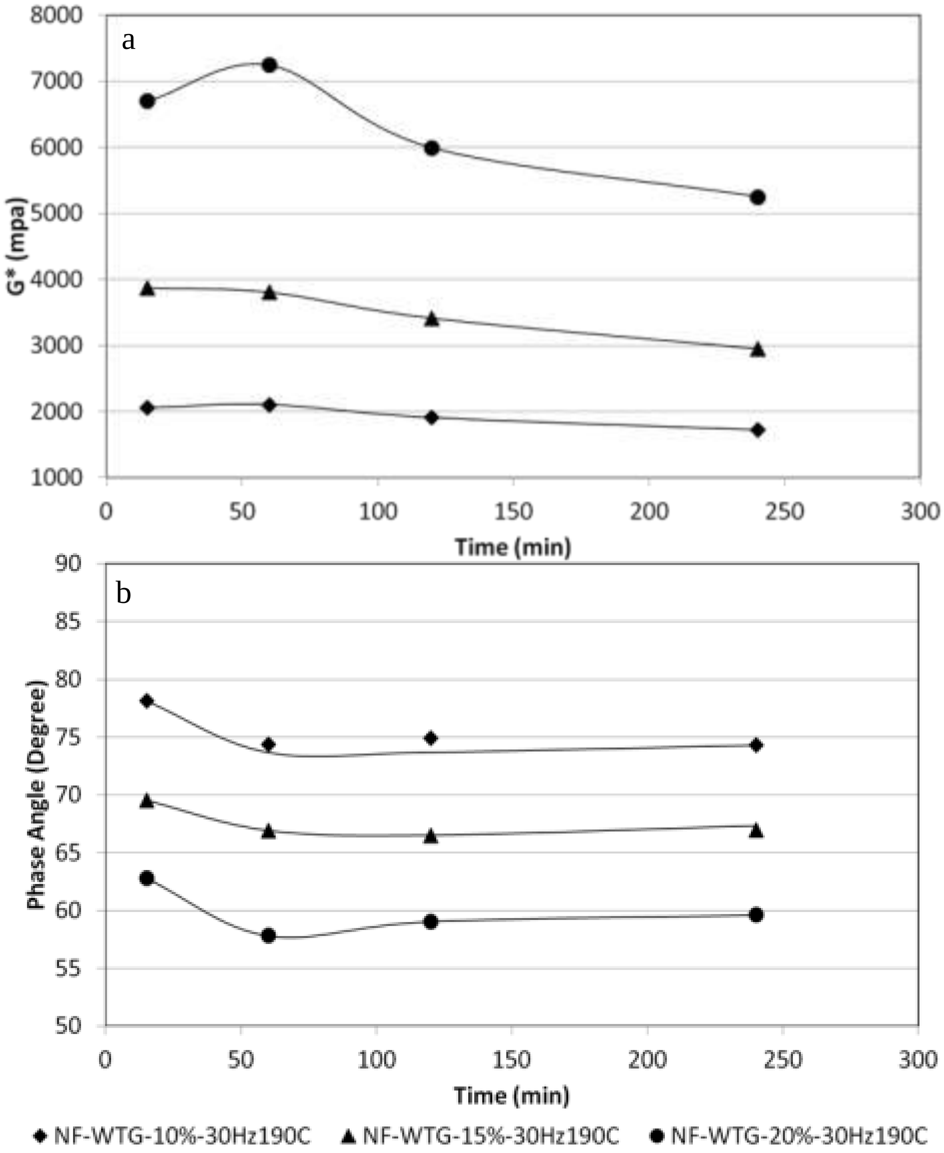

Figure B-5: Effect of different CRM concentrations on development of physical properties of CRMA at 190°C and 30Hz (a) complex modulus (b) phase angle

Also, comparing the results in Figure B-5 and B-6, it can be observed that CRMA with higher CRM concentration show more sensitivity to the interaction time. This will be more discussed in the subsequent sections.

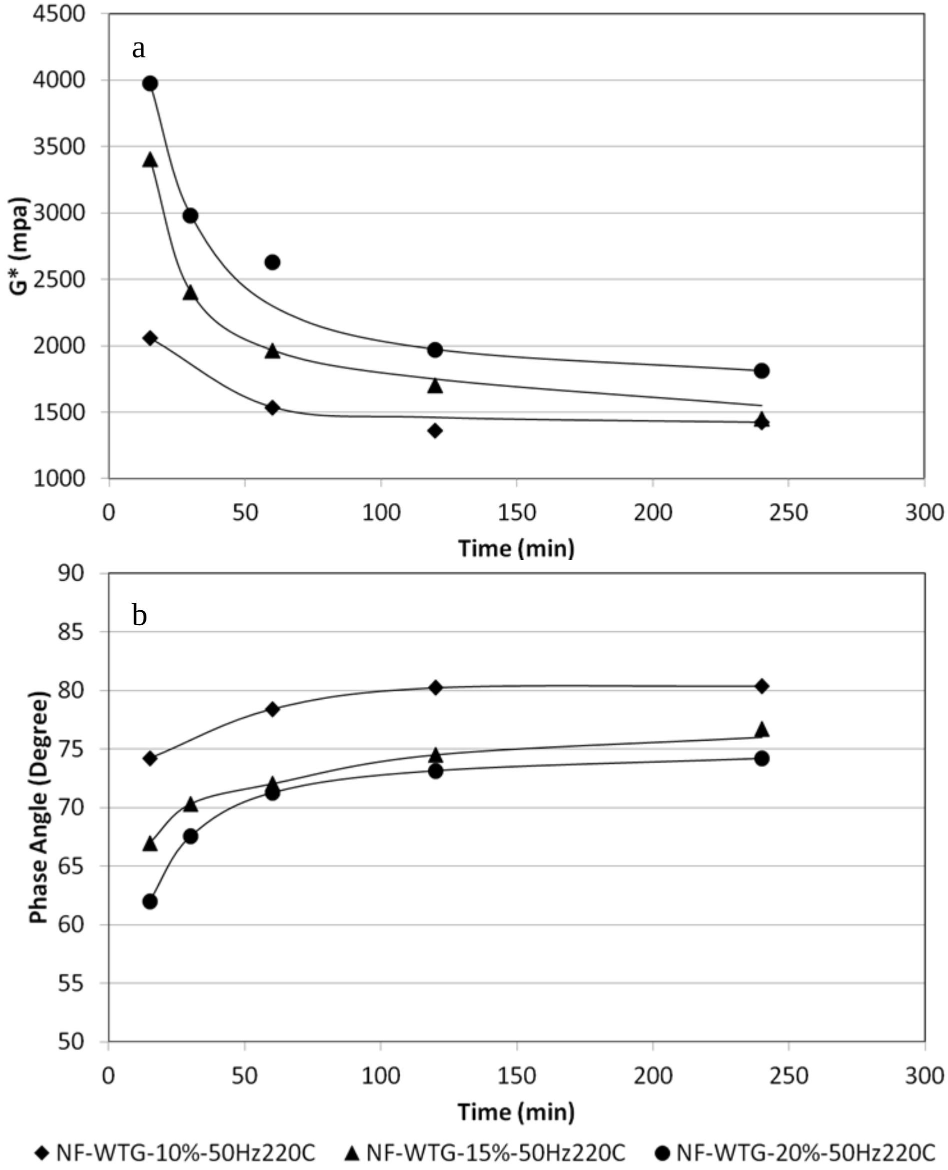

Figure B-6: Effect of different CRM concentrations on development of physical properties of CRMA at 220°C and 50Hz (a) complex modulus (b) phase angle

Effect of CRM type

In order to investigate the effect of CRM type on property development of the CRMA as a function of interaction time, two CRM batches were obtained from two different tire sources, passenger car tire (WTG) and truck tire (TR), as mention in Chapter 3. It is known that truck tires containe higher natural rubber content in comparison with the passenger car tires. Natural rubber is reported to have higher compatibility with asphalt aromatic components [8]

Figure B-7 illustrates the physical property developent of the CRMA with two different CRM types under several interaction conditions. In order to emphesise on the effect of the CRM sourceonlt the rsults for th CRMA with 20% CRM concentration is presented in this section. However, as discussed before, the CRM concentration has no considerable effect on the trend of property development of the CRMA and it only affects the extent of property development.

As the rsults in Figure B-7 illustrate, CRMA with TR CRM shows higher complex modulus and lower phase angle at low interaction conditions (160°C and 10Hz), where CRM paticles only swelle and there is no disintegration and dissolution of the particles. This can be related to the higher capacity of the TR CRM particles to swell and therefore improve the complex modulus and phase angle to higher extents.

At higher interaction conditions (190°C and 10Hz), where the CRM starts to disintegrate and dissolve into the asphalt in addition to swelling, it can be seen that CRMA with TR CRM shows better physical propeties than the CRMA with WTG CRM, at early stages of interaction. However, the differnces between the physical properties are decreasing by increasing the interaction time.

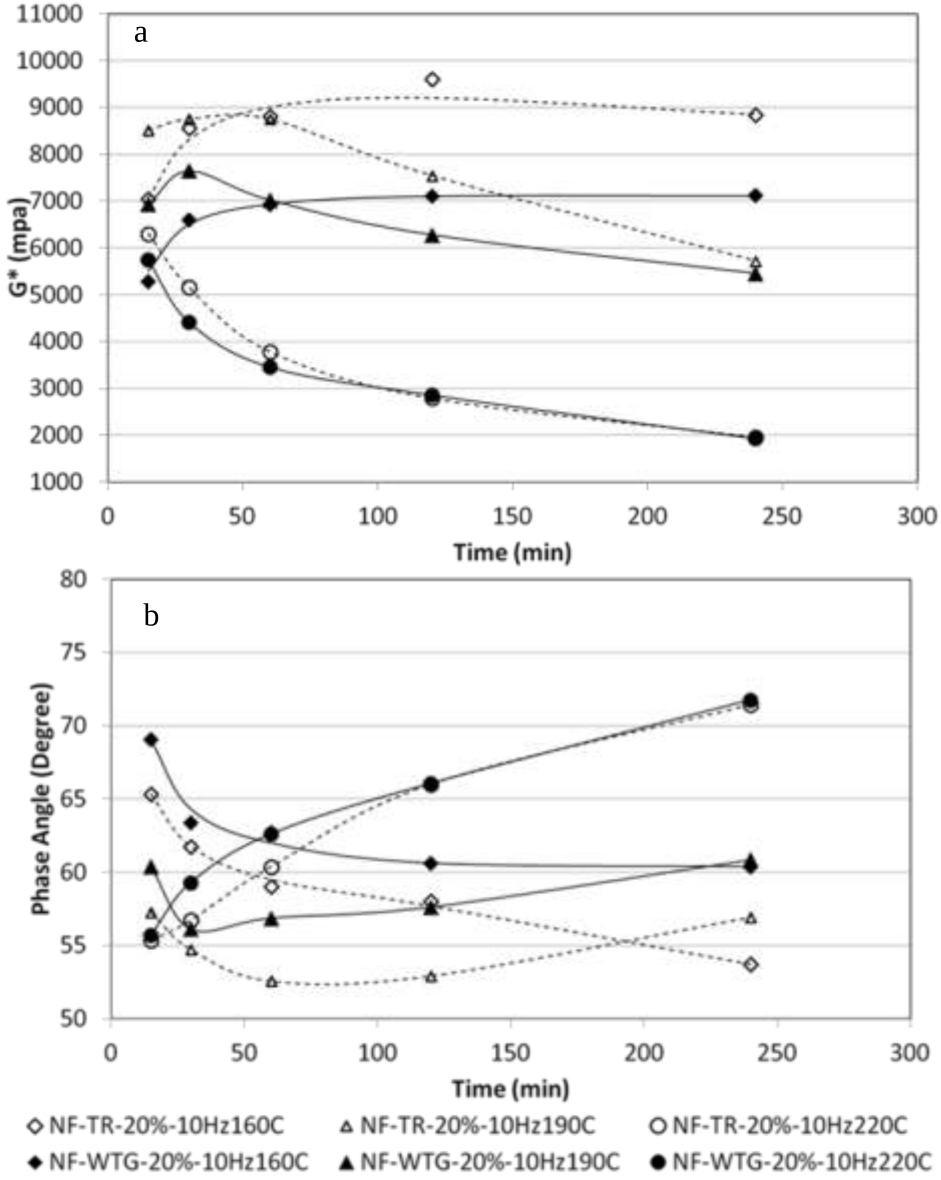

Figure B-7: Effect of CRM source on development of physical properties of CRMA at different interaction conditions (a) complex modulus (b) phase angle

The differences in physical peroperties of the CRMA with two different CRM types are marginal for the inetarctiosns at 220C and 10Hz. These results indicate that two sources of CRM are different in extend of swelling in asphalt however, their dissolution and the effect of their dissolved portion is not signifacntly differrent. The effect of CRM type on dissolution trend of CRM particles is disscussed in previous sections and the effect of the dissolved portion of different CRM types will be explained later in subsequent sections.

Effect of asphalt type

The effect of asphalt source on the property development of the CRMA was studied using two asphalts with same performance grade (PG 58-28), but from different refinery. The properties of asphalt and their sources are presented in the Chapter 3. Figure B-8 represents the results of this study.

As can be seen in Figure B-8, the asphalt source has no effect on the trend of the property development of the CRMA. However, the extend of the property development is different for different asphalts. This results is in accordance with the results reported in other studies [12-13].

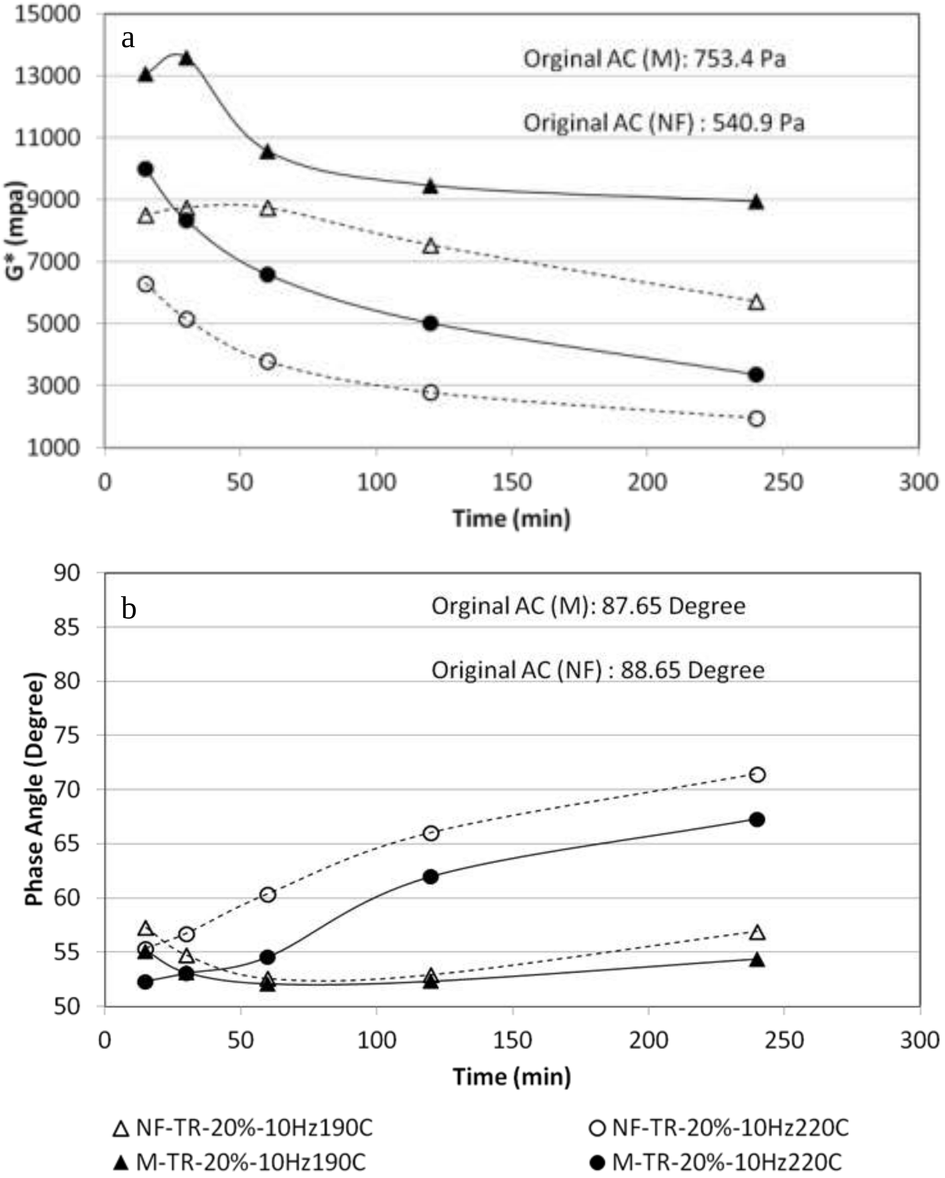

Figure B-8: Effect of asphalt source on development of physical properties of CRMA at different interaction conditions (a) complex modulus (b) phase angle

Viscoelastic Analysis of Liquid Phase of CRMA as a Function of Interaction Time

In order to invetigate the absorption and desorption of the aromatics in asphalt by CRM particls and also effect of dissolved portion of CRM on physical properties of CRMA, the liquid phase of the CRMA smaples extracted as explained in the Chapter 3. In this section the changes in physical properties of the liquid phase of the CRMA samples are studied as a function of interaction time. Combination of these results with the viscoelatic analysis results of the CRMA can rveals the mechanism of evolution of the CRM particles in asphalt binder during interaction.

Effect of CRM concentration

In this section the effect of CRM concentration on viscoelastic properties of the liquid phase of CRMA is studied at different interatcion conditions.

Figures B-9 to B-12 present the viscoelastic properties of the liquid phase of CRMA interacted at different interaction conditions. These interaction conditions have been selected based on the dissolution results. The objective was to underestand the difference between the effect of swelling of CRM particles than the effect of dissolution of the CRM particles on the viscoelastic properties of the liquid phase of CRMA.

The results in Figures B-9 and B-10, show that at very low interaction conditions where most of CRM activities are limited to absorbtion of light molecular weight components of asphalt and swelling, based on dissolution results presented in earlier sections, the complex modulus of the liquid phase CRMA increases and reaches to a stability toward the end of interaction time. However, as the results present, higher CRM concntration leads to higher complex modulus. This finding indicates that the stabilization of the complex modulus at final stages of interaction time is caused by limited capacity of the CRM particles swelling rather than the scracity of light molecular weight components of asphalt. The same trend can be obsereved ragrding to the phase angle of the samples.

Comparing the results in Figure B-9 with the ones in Figure B-10 reveals that at 190°C, Sewlling of CRM happens at faster rates and therefore, the complex modulus of the samples increases and reaches to stability faster than the samples interacted at 160°C. It can be concluded that higher temperature accelerates the swelling process of the CRM particles.

The viscoleastic properties of the liquid phase of CRMA, interacted at higher interaction conditions, are presented in Figures B-11 and B-12. At these high interaction conditions, CRM particles are significantly dissolved into the asphalt matrix, according to the dissolution results presented in earlier sections.

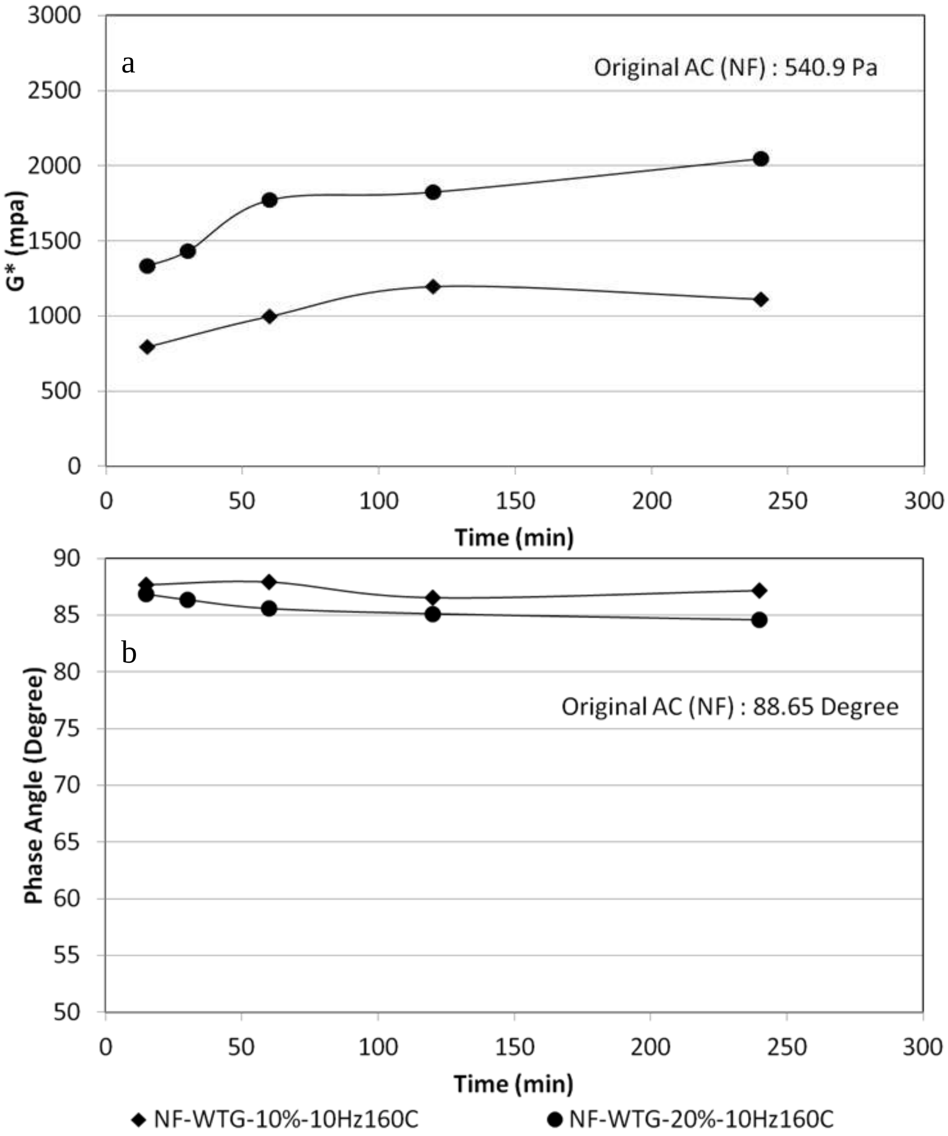

Figure B-9: Effect of CRM concentration on property development of liquid phase of CRMA at 160°C and 10Hz (a) complex modulus (b) phase angle

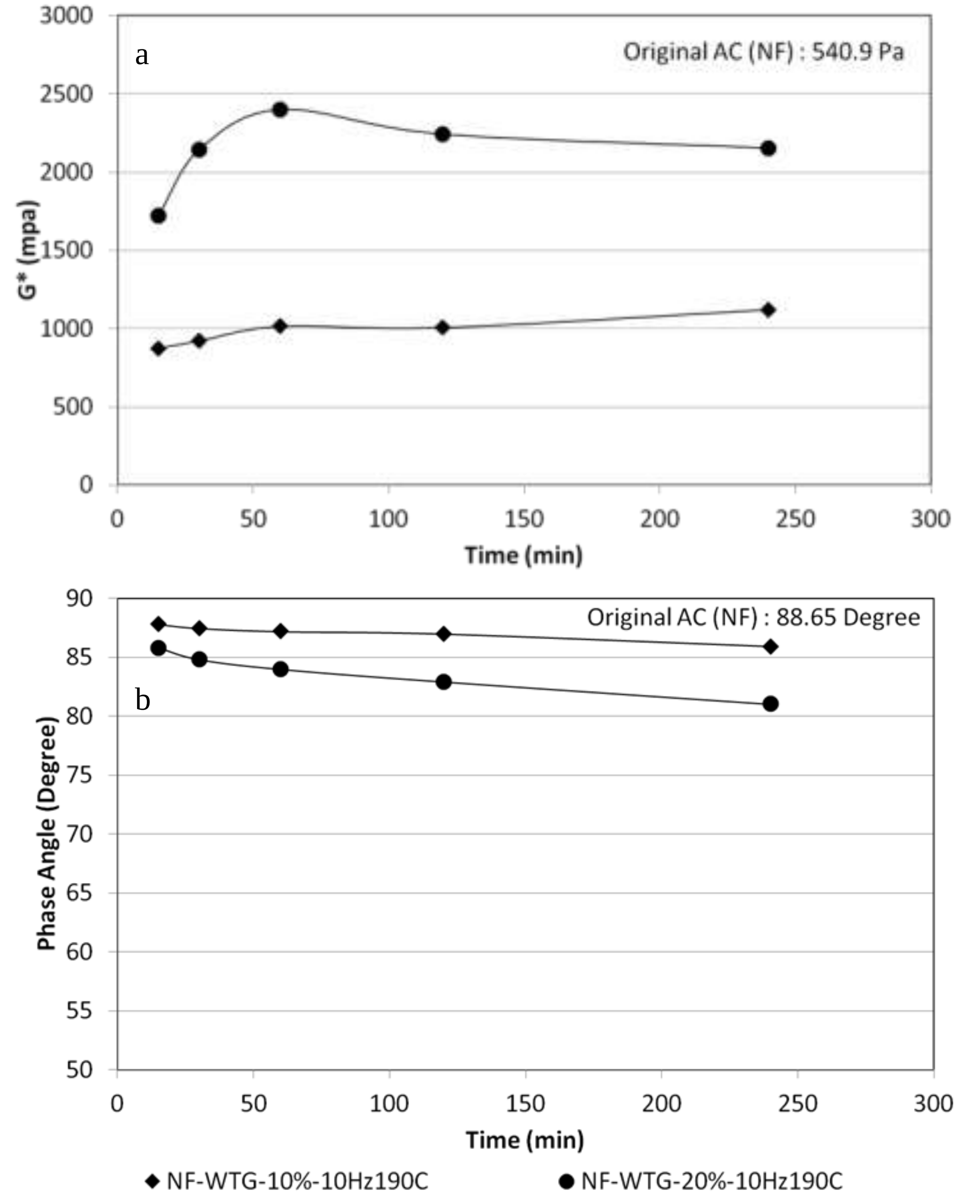

Figure B-10: Effect of CRM concentration on property development of liquid phase of CRMA at 190°C and 10Hz (a) complex modulus (b) phase angle

Comparing the results in Figure B-11 (interacted at 190°C and 50Hz) with results in Figure B-10 (interacted at 190°C and 50Hz) reveals that dissolution of CRM in asphalt increases the complex modolus of the liquid phase of the CRMA to higher lavels than what it gets in the case of swelling of the CRM particles.

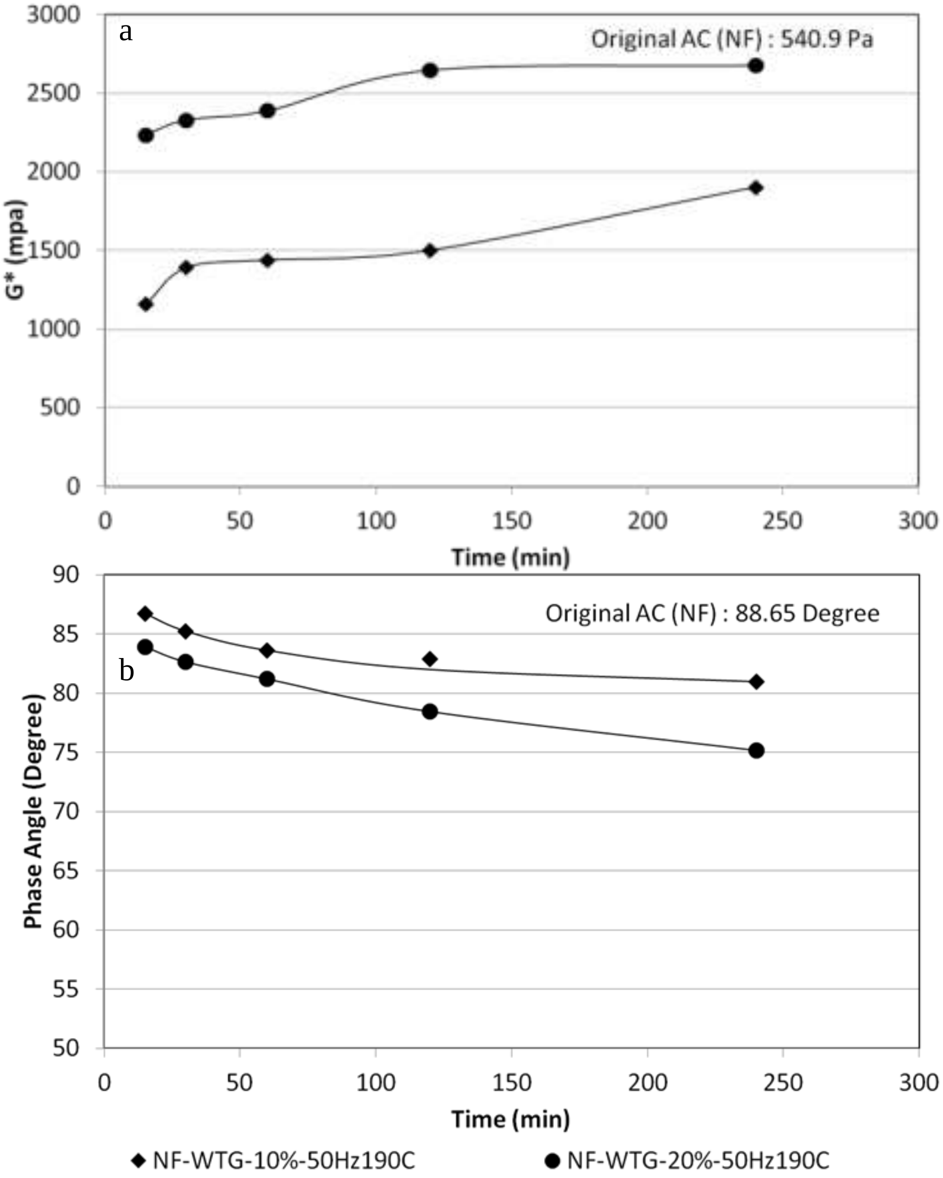

Figure B-11: Effect of CRM concentration on property development of liquid phase of CRMA at 190°C and 50Hz (a) complex modulus (b) phase angle

On the other hand, comparing the results in Figure B-11 (interacted at 190°C and 50Hz) with results in Figure B-12 (interactions at 220°C and 50Hz) reveals that at very high interaction temperatures (ie 220°C), the improved physical properties of the liquid phase of the CRMA deteriorates during the interaction time. This can be related to different mechanism of dissolution of CRM particles in asphalt which is discussed in subsequent sections.

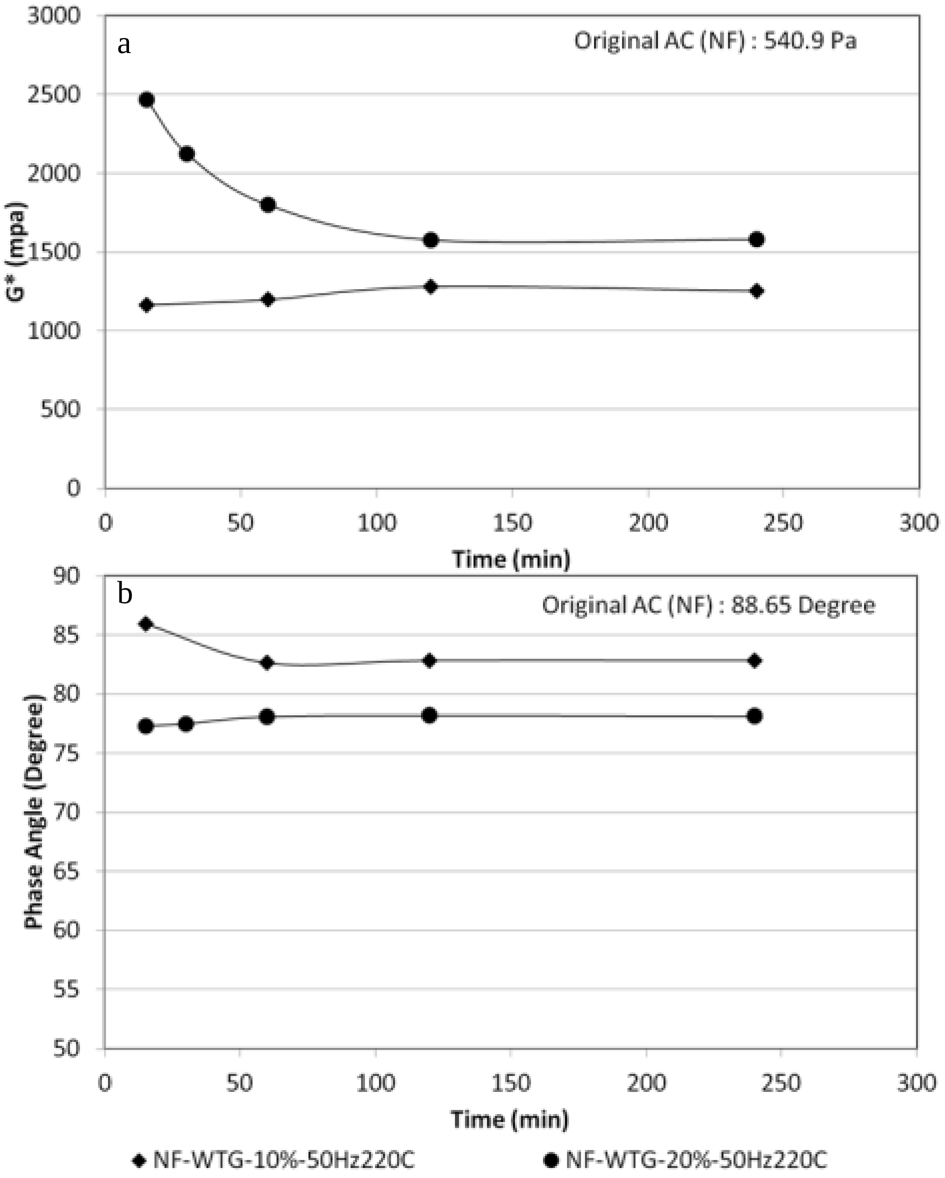

Figure B-12: Effect of CRM concentration on property development of liquid phase of CRMA at 220°C and 50Hz (a) complex modulus (b) phase angle

Effect of CRM type

The effect of swelling and dissolution of CRM particles, from different sources, is investigated in this section as a function of interaction time. The viscoelastic properties of the CRMA containing different CRM types are presented in Figure B-7. There, it is showed that the TR CRM has higher capacity to swell and swells to higher extents.

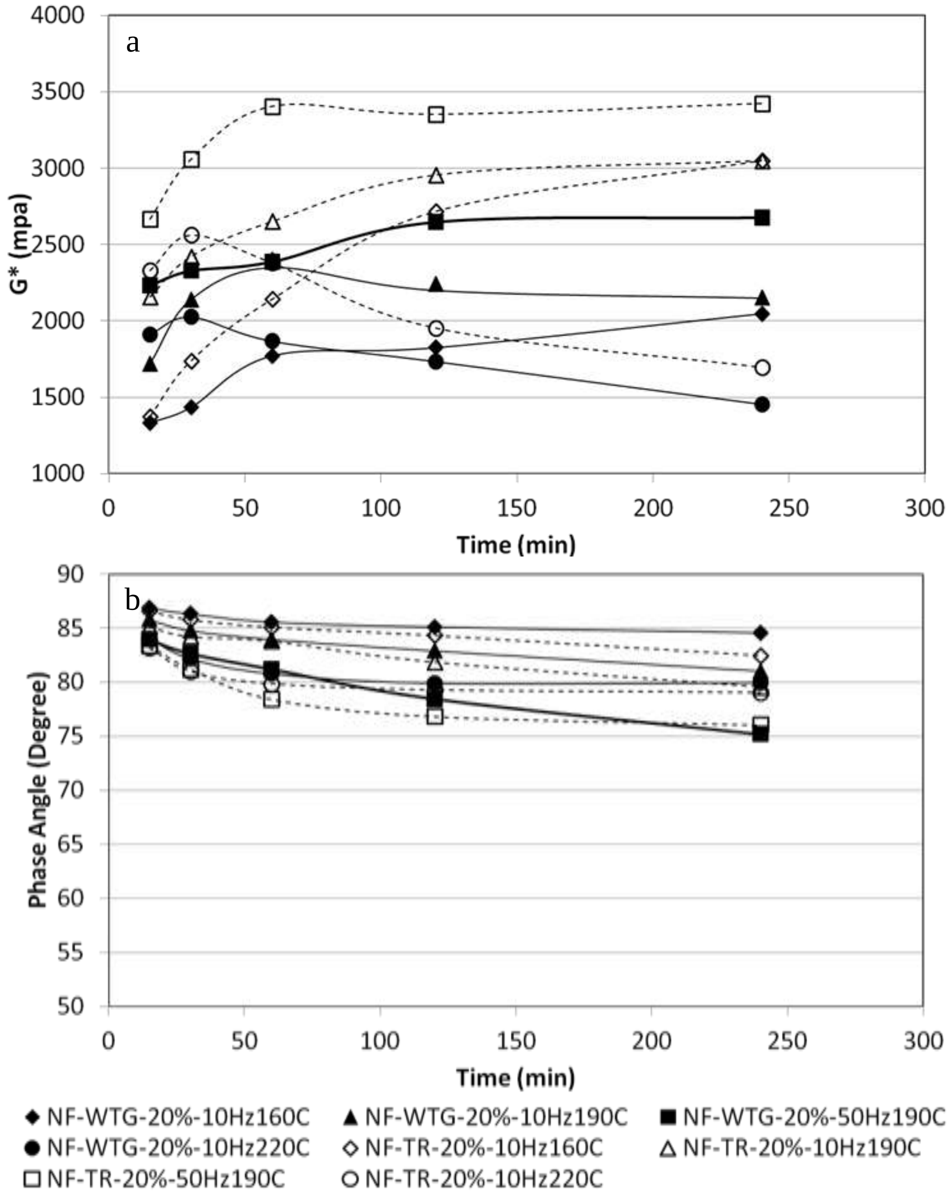

Figure B-13: Effect of CRM type on property development of liquid phase of CRMA (a) complex modulus (b) phase angle

The Figure B-13 shows physical behavior of the liquid phase of the CRMA containing different CRM types under a range of interaction conditions. As can be seen in Figure B-13, at low interaction conditions, where the activity of CRM is limited to absorption of light molecular weight components of asphalt and swelling, the samples with TR CRM show much higher complex modulus than the samples with WTG CRM. This again proves higher capacity of swelling in TR CRM comparing to the WTG CRM.

At higher interaction conditions, where the CRM particles start dissolving into the asphalt matrix, the liquid phase of CRMA with TR CRM type show slightly more enhanced physical properties in comparison with the CRMA with WTG CRM, interacted at the same interaction conditions. However, at very high interaction temperature (220˚C and 10Hz), the differences between physical properties of the samples with both CRM types diminish by extending the time of interaction.

Effect of asphalt type

The effect of asphalt type on property development of CRMA is explained in previous sections. In this section, the changes in physical properties of the liquid phase of CRMA are investigated using two different asphalt types.

Figure B-14 illustrates the complex modulus and phase angle of liquid phase of CRMA using two different asphalt sources. As can be seen in this Figure, at both interaction conditions the CRMA with Morphy (M) asphalt shows better high temperature physical properties than the Flint Hill (NF) asphalt.

The difference between the properties of samples is independent from the interaction condition. Also, in dissolution test results, explained in earlier sections, the asphalt type had marginal effect on CRM dissolution trend and extent. Combination of these results reveals that the differences in physical properties comes from the original asphalt properties rather than differences in asphalt rubber interaction

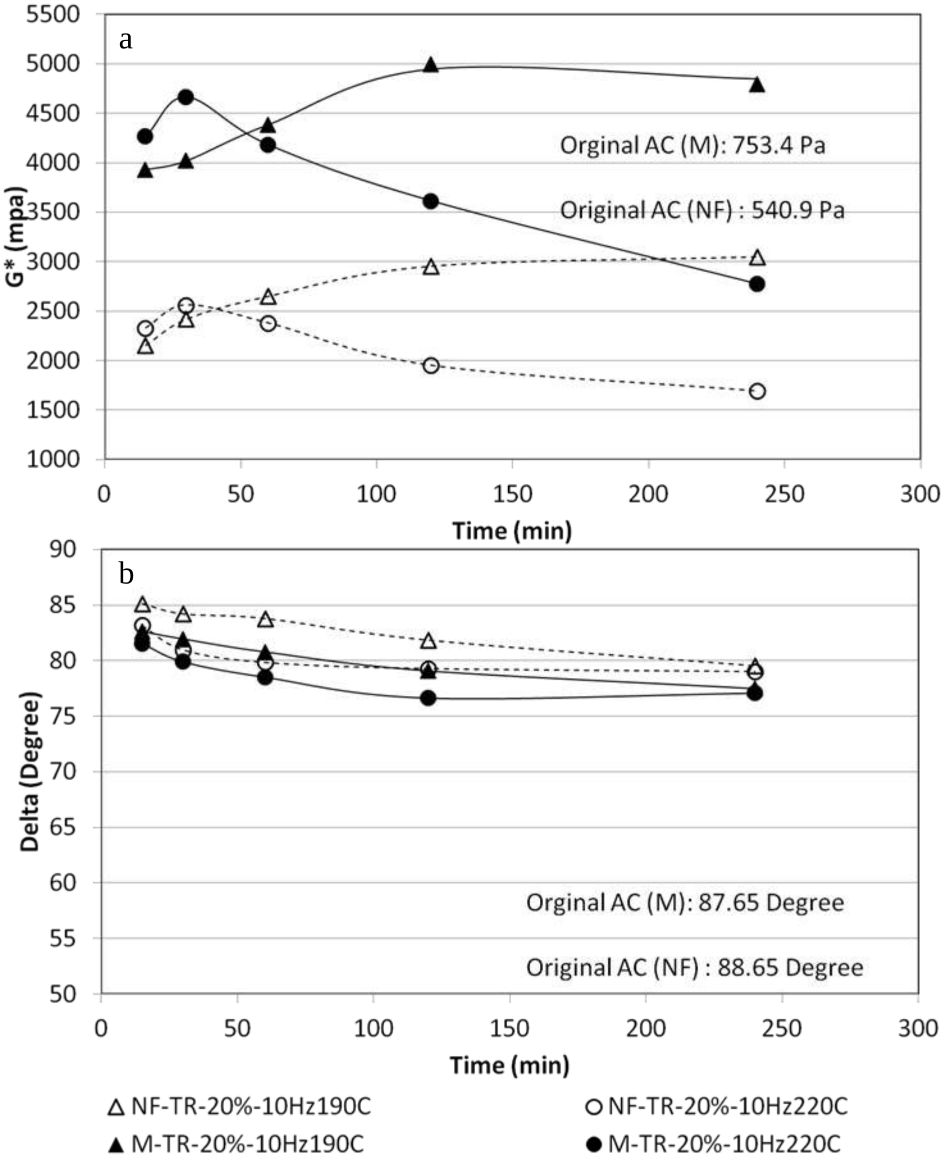

Figure B-14: Effect of asphalt type on property development of liquid phase of CRMA (a) complex modulus (b) phase angle