IMPACT OF RECYCLING ON THE MECHANICAL AND THERMO-MECHANICAL PROPERTIES OF WOOD FLOUR/HIGH DENSITY POLYETHYLENE AND WOOD FLOUR/POLY LACTIC ACID COMPOSITES

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Title

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MASTER OF SCIENCE

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ABSTRACT

This research concentrates on the recyclability of two wood plastic composites (WPCs) - wood flour/HDPE and wood flour/PLA composites. Two different filler loadings (30 and 50 wt%) were considered for each polymer composite. Each composite formulation contained 3 wt% of a coupling agent, and was individually recycled up to six times by extrusion process. Samples for mechanical and thermo-mechanical tests were prepared by injection molding. All test results were statistically analyzed with a confidence level of 95%. Additional tests such as fiber length measurement, GPC, DSC, TGA, FTIR, and SEM were also performed at specific reprocessing cycles. After reprocessing six times, all formulations showed lower relative decrease in most stiffness properties but higher relative increase in most strain properties. In strength properties, both HDPE composites showed lower relative decrease after reprocessed six times; however, higher and lower filler PLA composites showed sharp decrease reprocessed at second and six times respectively.

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CHAPTER 1. INTRODUCTION

This chapter concentrates on the general information of wood plastic composites (WPCs) - definition, advantages, application, global market, and disadvantages. It then focuses on the problem statement (caused by WPC waste) followed by a proposed solution. In the end, this chapter discusses the materials and methods, and the objectives of this research.

1.1. Definition and Advantages of WPCs

Wood plastic composites (WPCs) are made of wood fiber or filler and a thermoplastic [6]. WPCs are considerably a new member in the composite family and are getting much attention of the researchers, at present, because of the better specific properties of its constituents (wood fiber and polymer). Wood fiber (or natural fiber) has a high specific strength and stiffness, low cost, ease of machinability, reduced health concern, biodegradability, and low density [2, 7, 9]. It is the most available renewable resource in the world [43]. Natural fibers are incorporated into polymers (composite formation) because the polymer alone cannot serve all the desired properties. Again, the incorporation of fibers reduces the cost of the composites compared to some plain polymers [45]. When natural fibers are added to the polymer, stress transfer takes place from the matrix to the fiber in the formulated composite. As a result, the composite shows higher mechanical, thermal, and physical properties, and hence could be used in different applications as an engineered material.

1.2. Global Market and Application of WPCs

WPCs are widely used in household apparatus (e.g. doors, decking, windows, furniture, railing, staircase handrails), and automotive industry (e.g. door panels, seat covers) [17]. These composites are now also used in aerospace applications [23]. Table 1.1 shows the global production of WPCs in 2010 and 2012, and Fig. 1.1 shows the global market of WPCs and plastic lumber in 2008 to 2011, and 2016 (predicted). It can be seen that WPCs are largely produced in North America and China worldwide. They are also produced, at comparatively lower rates, in Europe, Japan, Russia, and South East Asia (Nova Institute, 2014). However, WPC production is increasing in these countries (or continents). These composites are used in construction or building products on a grand scale. They also have applications, in comparatively lower amounts, in automotive, infrastructure, and industrial areas along with some other miscellaneous consumer needs (Fig. 1.1).

1.3. Disadvantages of WPCs

Along with a lot of advantages, WPCs have some limitations too. However, most of the limitations could be overcome by employing several methods such as fiber surface treatment (chemical), and/or addition of a coupling agent. For instance, the most important limitation (of formulating WPCs) is the incompatibility between the hygroscopic fiber and the hydrophobic polymer matrix. This incompatibility leads to poor fiber dispersion in the matrix, fiber agglomeration, less adhesion between fiber and matrix, and high stress concentration. As a result, the incompatibility causes lower stress transfer, void formation, and crack propagation which finally lead to lower mechanical, thermal, or physical properties of the composite. Nevertheless, this disadvantage could be diminished by incorporating a small amount of a coupling agent or a compatibilizer (in the composite) which increases the adhesion quality between the fiber and the matrix. The increased adhesion quality contributes to better stress transfer, less void formation, and less crack propagation, and finally results in better properties of the WPCs [17]. When the properties are improved, WPCs become competent to be used in different applications.

1.4. Problem Statement

As mentioned earlier, WPCs are largely produced each year all over the world. Along with a large volume of WPCs comes a proportionately huge amount of plastic waste (after the life time of WPCs) each year which is a critical environmental concern. For example, according to EPA (Environmental Protection Agency) report 2014, almost 32 million tons of plastic waste were generated in US in 2012. The huge amount of plastic waste creates a lot of environmental pollutions such as soil pollution, air pollution, and sea pollution. Most plastic waste (except bio-degradable polymer), such as polyethylene (PE) and polypropylene (PP), take a very long time (nearly one thousand year or more) to completely degrade in soil [44]. Plastic waste creates air pollution when they are disposed in landfills or incinerated. Moreover, Plastic waste, floating on the surface of the sea, destroys sea life. For example, the biggest ocean garbage site (the great pacific garbage patch) reduced sea life six to one in that area [71]. Because of these consequences, plastic waste management is becoming a concern for environmental protection [1, 6].

Table 1.1: Global production of WPCs in 2010 and 2012 [Source: Nova Institute, 2014].

Country (or Continent)	2010 (Ton)	2012 (Ton)
North America	900,000	1,100,000
China	300,000	900,000
Europe	220,000	260,000

1.5. Proposed Solution

To date, there are three established ways for plastic waste management- 1) disposal in landfill, 2) incineration, and 3) recycling. Among these three waste managing processes, recycling is getting more attention of the researchers because of its less impact on the environment. Disposal in landfills contaminates the soil and air. Similarly, incineration creates air pollution and causes global warming by producing noxious gases [13]. This process also completely destroys the material. On contrary, recycling creates no (or little) environmental pollution. In addition, it reserves the material for further use. Because of these two important advantages, recycling could be considered one of the best processes for plastic waste management. Along with these advantages, there are some other rationales to consider recycling. In recent years, the global oil price has been fluctuating. Since most of the polymers are petroleum-based, the price of these polymers has also been fluctuating which is undesirable [6]. And deforestation is creating an insufficient wood supply along with producing an environmental concern [13]. So global oil price fluctuation and deforestation also emphasize on considering recycling as a competent plastic waste management process.

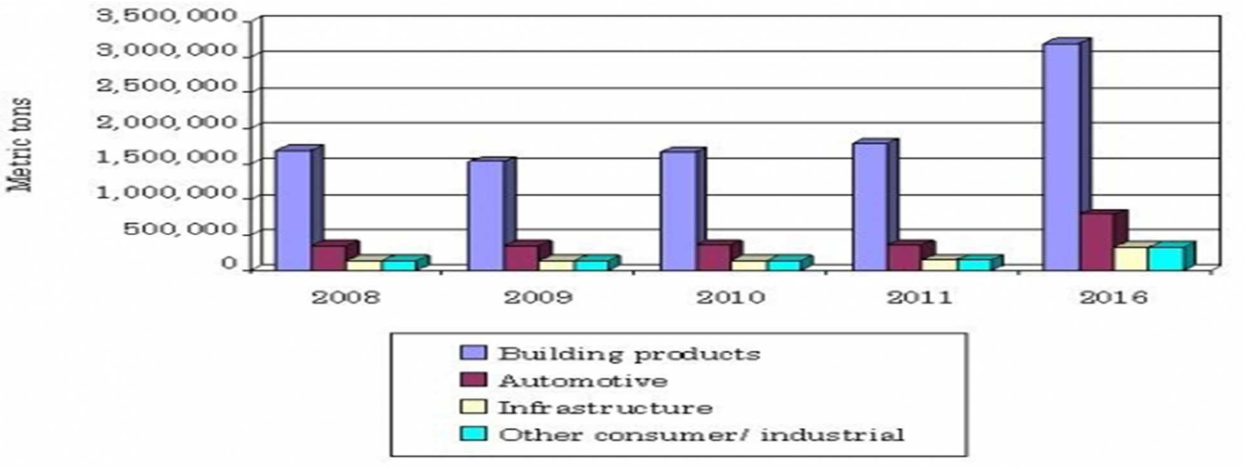

Fig. 1.1: Global market of WPCs and plastic lumber from 2008 to 2011, and in 2016 (expected values) [Source: BCC, Report PLS034B, June 2011].

1.6. Materials and Testing

In this regard, this research aims at investigating the effect of recycling on mechanical and thermo-mechanical properties of two important WPCs. That is to say, this research examines how much impact recycling causes on the properties of these composites. And based on the results, this research concludes how many times these WPCs could be recycled. In this respect, one WPC is made of oak wood flour (filler) and a petroleum-based polymer- high density polyethylene (HDPE) with MAPE (maleic anhydride grafted PE) as a coupling agent (CA). The other WPC is made of oak wood flour and a bio-based polymer- poly lactic acid (PLA) with PLA-g-MA (maleic anhydride grafted PLA) as a coupling agent. For each WPC two different formulations (30 and 50 wt% of WF) are considered. The particle size distribution of oak wood flour (WF) is given in Table 1.2. Table 1.3 and 1.4 respectively show some physical and mechanical properties of HDPE and PLA. Table 1.5 exhibits the considered testing with corresponding ASTM standards.

1.7. Rationale for Selecting Materials

There are certain reasons for selecting the filler, the polymers, and the specific formulations of the bio-composites in this research. The filler (wood flour) is selected, primarily because it is bio-degradable and it has higher specific strength and stiffness properties along with other advantages (mentioned earlier). HDPE is selected because it provides -1) lower melting point (around 130 ºC), 2) easier processing (relatively soft), 3) lower moisture absorption (near zero) at ambient temperature, and 4) higher abrasion and corrosion resistance (most environmentally stable polymer) [21]. And PLA is selected because it provides- 1) biodegradability, and 2) higher strength and stiffness [63]. The primary distinction between these two polymers is that HDPE is non-biodegradable and PLA is completely bio-degradable. In this way, this research focuses on two different types of bio-composites, although no comparison is made in their properties caused by recycling. Besides this, lower filler (30 wt% WF) and higher filler (50 wt% WF) HDPE composites are considered because they are respectively used in automobile and construction or building industry.

1.8. Methodology

In this research, extrusion was used as the recycling process and each formulation of both composites (WF/HDPE and WF/PLA) was recycled up to six times. Every recycled material, along

Table 1.2: Particle size distribution of oak wood flour (provided by Southern Wood Services, GA, USA)

Seive Size (mm)	Range (%)
0.841	0-5%
0.595	5-15%
0.400	35-42%
0.250	40-50%
0.177	6-9%
0.149	0-1%
< 0.149	0-2%

Table 1.3: Physical and mechanical properties of HDPE (provided by Chevron Phillips Chemical Company LP, TX, USA)

Properties	HDPE (Marlex 9012)	ASTM Method
Density (g/cm^3)	0.952	D 1505
Melt Flow Index (g/ 10 min)	11.5	D 1238 (190 ºC/ 2.16 Kg)
Melting Point (ºC)	130	
Tensile Yield Strength (MPa)	27	D 638 (5 mm/ min)
Elongation at Break (%)	900	D 638 (5 mm/ min)
Flexural Modulus (MPa)	1270	D 790 (1.3 mm/ min)

Table 1.4: Physical and mechanical properties of PLA (provided by NatureWorks LLC, MN, USA)

Properties	PLA (Ingeo 2003D)	ASTM Method
Density (g/cm^3)	1.24	D 792
Melt Flow Index (g/ 10 min)	6.0	D 1238 (190 ºC/ 2.16 Kg)
Melting Point (ºC)	210	
Tensile Yield Strength (MPa)	60	D 882
Tensile Modulus (MPa)	3500	D 882
Elongation at Break (%)	6.0	D 882
Heat Deflection Temperature (ºC)	55	E 2092
Impact Resistance (J/m)	16	D 256

with virgin material, was injection molded followed by testing. Extrusion and injection molding are the two most widely used manufacturing processes of WPCs. That is because extrusion (twin screw) provides a uniform fiber distribution (in composite) and injection molding shapes the material with very little degradation [55, 61]. That is why these processes have been selected in this research. Fig. 1.2 shows the manufacturing process and tests of the WPCs. During extrusion, a constant temperature profile was used for both formulations of WF/HDPE composite (detail in chapter 4) and another constant temperature profile for both formulations of WF/PLA composite (detail in chapter 5). Prior to extrusion, wood flour, CA (MAPE or PLA-g-MA), and polymer (HDPE or PLA) were dried at 80 ºC for 24 hours. The moisture content of the dried filler was found less than 0.5%. Then the materials (30 or 50 wt% of WF, 3 wt% of CA, and HDPE or PLA) were mixed and extruded followed by pelletizing. The pelletized material was named as ‘cycle 0’ (or virgin) material. This material was again dried at 80 ºC for 24 hours and a portion of it was injection molded. The rest of the pellets was passed through the extruder again at the same corresponding conditions. After extrusion, this material was named as ‘cycle 1’ material, a portion of which was dried and injection molded. The remaining pellets were again dried and extruded to get the ‘cycle 2’ material. This process continued up to six times to get the ‘cycle 6’ material. Therefore, in total there are 4 formulations (2 formulations for each WPC), each of which individually contains ‘cycle 0’ to ‘cycle 6’ material. All injection molded materials were taken for testing. Additionally, virgin WPCs without CA were produced for all four formulations to investigate the effect of CA. The effect of WF content was also explored. However, these materials were never reprocessed and completely kept outside the ‘Design of Experiment’ (chapter 3).

1.9. Objectives

The prime objectives of this research are outlined as follows-

1) To investigate the impact of recycling (individually) on the mechanical and thermo-mechanical properties of two formulations (30 and 50 wt% WF) of both WF/HDPE and WF/PLA composite.

2) To examine the change on fiber length, molecular structure of the polymer, crystallinity, thermal stability, and morphology of the composites caused by recycling so that the change in responses (test results) could be understood.

3) To inspect the effect of coupling agent and WF content on the responses for each formulation only at cycle 0 (virgin material).

Table 1.5: Name of tests and corresponding ASTM standard test methods

Name of Test	ASTM Method
Tensile	D 638
Flexural	D 790
Izod Impact Resistance	D 256
Heat Deflection Temperature (HDT)	D 648
Coefficient of Thermal Expansion (CTE)	
Dynamic Mechanical Analysis (Storage Modulus)	D 4065
Melt Flow Index (MFI)	D 1238
Scanning Electron Microscopy (SEM)	
Fourier Transform Infra-Red Spectroscopy (FTIR)	
Differential Scanning Calorimetry (DSC)	F 2625
Thermo-gravimetric Analysis (TGA)	E 1131

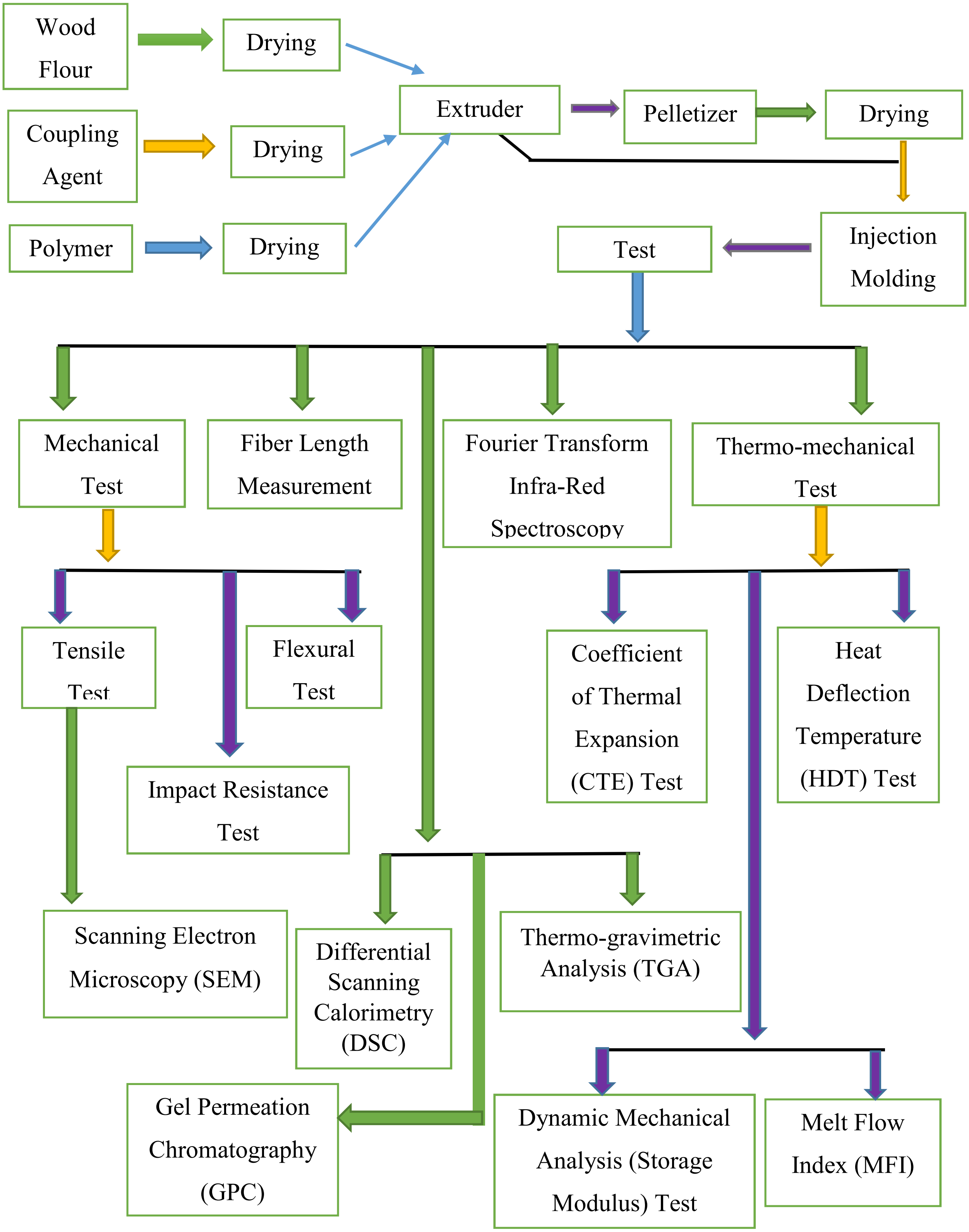

Fig. 1.2: Schematic diagram of manufacturing process and sample testing of WF/HDPE and WF/PLA composites.

1.10. Focus of Following Chapters

Similar to chapter 1, each following chapter, in this thesis, concentrates on a certain topic. Chapter 2 describes the literature review of natural fiber composites, especially on WF/HDPE and WF/PLA composites. Chapter 3 focuses on the 'Design of Experiment (DOE)' and data analysis of this research. Chapter 4 and 5 respectively concentrate on the recyclability of WF/HDPE and WF/ PLA composite. Chapter 6 briefly describes the conclusions found in the research with recommended future work. Finally, Appendix I and II respectively show the regression analysis (response vs. no. of reprocessing cycles) of WF/HDPE and WF/PLA composite.

CHAPTER 2. LITERATURE REVIEW

This chapter focuses on the literature review of the recycling of natural fiber/thermoplastic polymer composites, especially of HDPE and PLA bio-composites. At the beginning of the chapter, an overview of general composites has been briefly discussed to provide a preliminary background. The chapter then narrows down to the overview of a subtype of composite family-thermoplastic composites followed by wood plastic composites (WPCs) -a subtype of thermoplastic composites. Afterwards the chapter discusses the problem statement of the research (situation and consequences) along with the proposed solution. Finally, the chapter explores the important work of other researchers on the effect of recycling on different properties of natural fiber composites (especially HDPE and PLA composites) associated with the importance of the proposed research.

2.1. Composite Materials

Composite material is made of two or more constituents that are distinct in their chemical structures and physical properties along with a distinguishable interface between them. Composite material shows significantly different properties that to its constituents. The constituents could be classified in two categories- continuous and discontinuous. In general, the discontinuous constituent or phase significantly improves composite stiffness and hence is named as reinforcement. On contrast, the continuous phase acts as a matrix in which the reinforcement (fibers/fillers) is incorporated in directional or randomized way depending on the composite application. When a composite is subjected to load (or stress), the matrix first takes the load and then transfers it to the fibers or fillers that are considerably stiffer than the matrix [40]. Some examples of fibers are carbon fiber, glass fiber, and natural or wood fiber (e.g., oak fiber). And examples of matrix materials include thermosetting plastic (e.g., epoxy), thermoplastic (e.g., polyethylene), metals (e.g., aluminum), and carbon. Some commonly used composites are carbon fiber/epoxy composite, glass fiber/epoxy composite, metal matrix composite, and natural fiber/thermoplastic composite.

2.2. Classification of Composite Materials

Composite materials could be classified based on two points of view- reinforcement and matrix. Figs. 2.1 and 2.2 respectively show the classification of composites based on reinforcement and matrix. Based on reinforcement, composites are primarily divided into three groups such as- 1) fiber reinforced composites, 2) particulate composites, and 3) structural composites. Fiber reinforced composites consist of long fibers while particulate composites consist of particulate reinforcement (or fillers) [40]. Fiber reinforced composites can further be divided into two groups- 1) glass fiber composite, and 2) carbon fiber composite. The structural composites are sub-divided into two categories 1) laminated composite (having multi layers or plies), and 2) sandwich composite (having sandwich shape) [11].

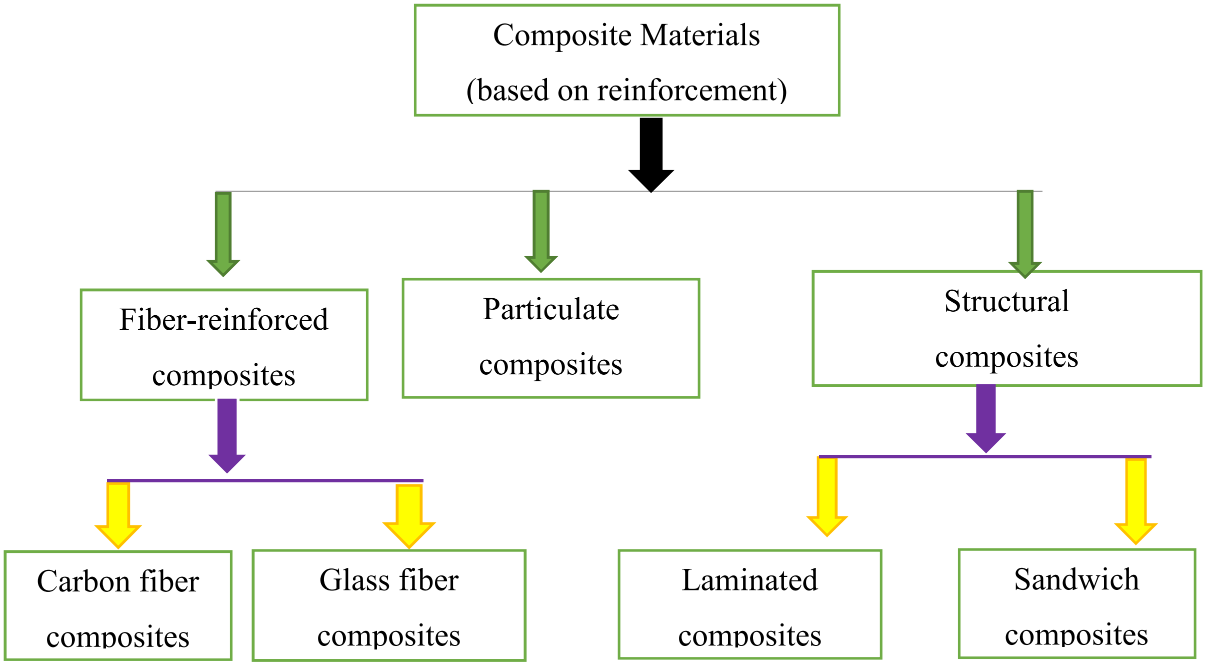

Fig. 2.1: Classification of composite materials (based on reinforcing element) [11].

Composites can also be divided, based on matrix material, into three groups -1) ceramic matrix composites (CMC), 2) organic matrix composites (OMC), and 3) metal matrix composites (MMC). The OMCs can further be divided into -1) polymer matrix composites (PMC), and 2) carbon matrix composites (CMC). PMCs can be subdivided into two groups -1) thermoset matrix composites (once cured matrix cannot be re-melted), and 2) thermoplastic matrix composites (matrix can be re-melted) [11].

According to the above classifications, WF/HDPE and WF/PLA composites could be categorized in both ways - particulate composite or thermoplastic composite. However, the term ‘thermoplastic composite’ would be used throughout this chapter.

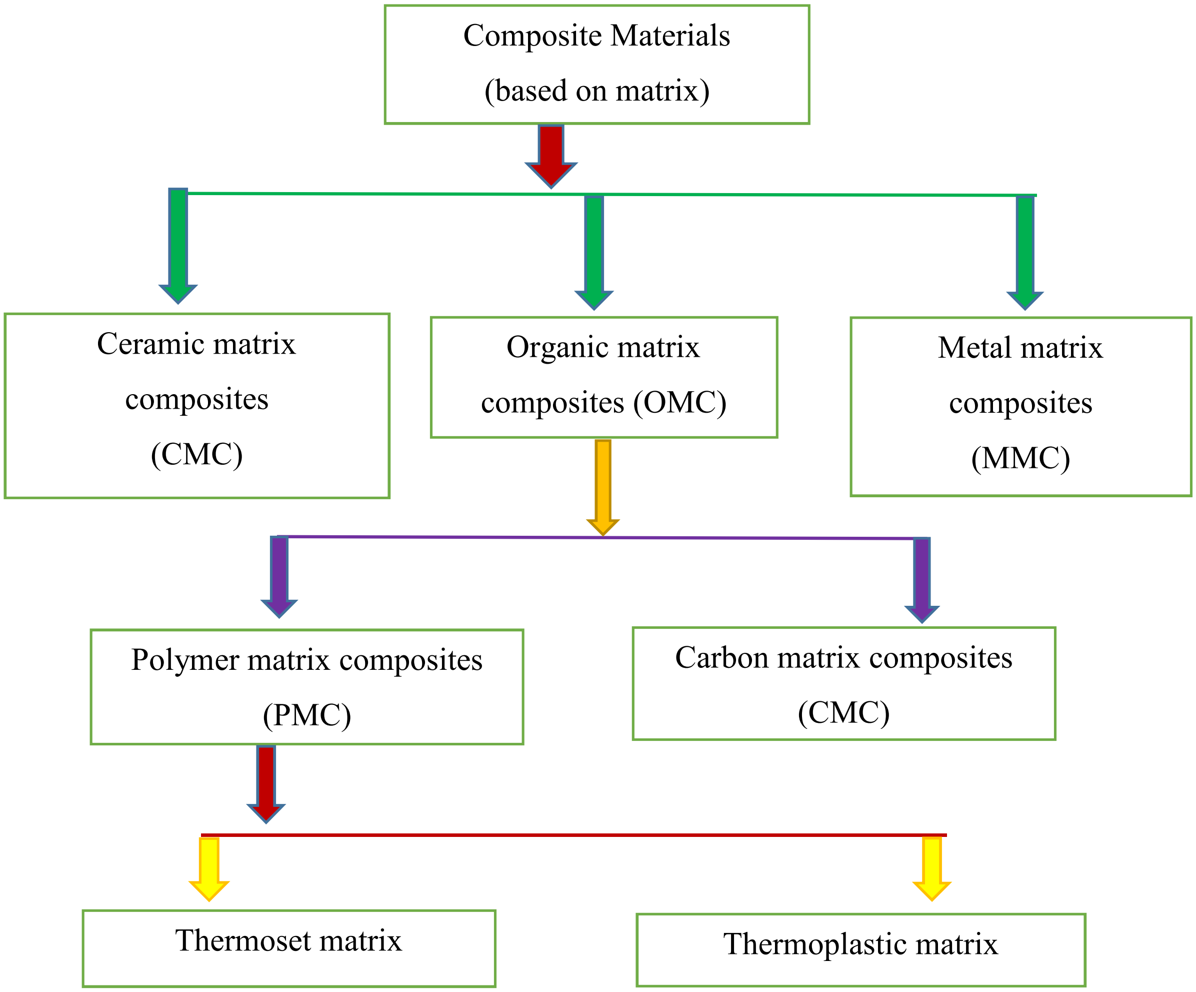

Fig. 2.2: Classification of composite materials (based on matrix) [11].

2.3. Characteristics of Composite Materials

Composites are preferred because of their two most important properties- specific strength (σ_u/ρ) and specific modulus (E/ρ), where σ_u is the ultimate strength, E is the Young's modulus, and ρ is the density of the material [37]. Most composites have lower density which results in higher specific strength and specific modulus. For example, graphite/epoxy unidirectional composite has an ultimate strength almost equal to that of steel. But this composite has a specific strength which is three times that of steel. That is to say, this composite would require only one third of the mass of steel for any particular application. This reduction in mass causes reduction in material cost, and for some applications, such as aerospace, reduction in mass causes large savings on fuel cost [37].

Along with a lot of advantages, composites have some drawbacks too. First, high performance composites require a high fabrication cost. Second, since most composites are anisotropic, the analysis of their mechanical and thermal behavior is more complex. Third, flaws in composite are difficult to find out and repair. Fourth, most composites cannot show higher fracture toughness which is a very important property [37]. However, composites are being widely accepted as engineered materials in a huge number of applications despite the associated difficulties.

2.4. Application of Composite Materials

Composites are being used in numerous applications in today's world. Some applications of them have been given below [37]-

Polymer matrix composites (PMC): military aircraft, commercial airlines (e.g., landing gear doors), helicopters (e.g., rotor blades), space shuttle (e.g., payload bay doors), sports (e.g., shafts of golf club, rackets of tennis and racquetball), automotive industry (e.g., leaf springs).

Metal matrix composites (MMC): space (e.g., tubes that support fuselage frame of space shuttle, mast of the Hubble Telescope), military (e.g., components of missile guidance system), automotive industry (e.g., in automotive engines), transportation (e.g., components of gas turbine engines).

Ceramic matrix composites (CMC): high temperature zones (e.g., cutting tool subjected to oxidizing environment with high temperature), space (e.g., monofilaments of future aircraft engines).

Carbon-carbon composites (CCC): space (e.g., nose cones of space shuttle, aircraft brakes), mechanical fasteners for high temperature.

2.5. Thermoplastic Composites

Thermoplastics are organic polymers that, once solidified, can be re-melted and given new shapes. Unlike thermosets, thermoplastics and their composites could be easily recycled. Some examples of thermoplastics are polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and poly lactic acid (PLA). Thermoplastic composites are produced with two types of fibers- non bio fiber and bio fiber. Non bio fibers (e.g., carbon fiber, glass fiber, aramid fiber) are synthesized from different chemical substances while bio fibers are naturally produced (e.g., wood, hemp, flax, and sisal fiber). Bio (or natural) fibers are now replacing non-bio (or synthetic) fibers, because of their good mechanical properties and biodegradability [2]. That is why bio fiber/thermoplastic composites are getting much attention in composite research.

2.6. Wood Plastic Composites (WPCs)

Wood plastic composites (WPCs) are thermoplastic composites with natural fiber or filler as reinforcement [6]. WPCs provide high specific strength and stiffness, biodegradability, and low fabrication cost with easier processing [2]. This research focuses on two different types of WPCs-

WPCs of HDPE and WPCs of PLA. WPCs made of HDPE are primarily used in building and construction industry. WPCs made of PLA have applications in medical devices and in disposable items.

2.7. Recycling of WPCs

As mentioned in chapter 1, higher WPC production every year (Table 1.1 and Fig. 1.1)- after their service life- finally results in a huge number of plastic waste, and this waste could be better managed by recycling rather than disposal in landfills and incineration. As a result, more research is going on the recycling of WPCs for plastic waste management. The next two sections respectively describe the research work done on the recycling of natural fiber/HDPE and natural fiber/PLA composites with some WPCs of other polymers such as PP and PVC (summarized in Table 2.1).

2.7.1. Effect of Recycling on WF/HDPE Composites

WPCs made of HDPE are widely used in numerous applications all over the world [17]. That is why a lot of research has been done on the effect of recycling on the properties of these composites. This section briefly refers to the common materials and methods along with the effect of reprocessing on important properties of WPCs of HDPE. However, a lot of differences exist in type of wood fiber, fiber loading, type and amount of coupling agent, grade of HDPE, way of reprocessing, and testing methods. Therefore, a general comparison or conclusion- in properties of separate composites- cannot be made.

In most research work, composites were prepared from virgin fiber (e.g., hemp, oak, and sisal) and virgin polymer [1, 5, 7, 17]. These composites were then successively reprocessed in various ways such as injection molding and grinding [1, 7], extrusion and milling [5], and grinding and extrusion [17]. The number of reprocessing cycles varied from 1 to 20. The results showed that mechanical properties of these WPCs remained constant or decreased with the increased no. of reprocessing cycles while failure strain, water uptake, and thermal stability increased.

In some research work, recycled composites were prepared from virgin fiber and recycled (post-consumer or extruded) HDPE, or recycled fiber and virgin HDPE [2, 3, 12, 26]. These composites were made by using plasticoder, compression molding or hot press molding. It was reported that mechanical properties and dimensional stability of the recycled composites were found equivalent or even better compared to that of the corresponding virgin composites.

Other research work focused on recycled composites that were made from recycled fiber and recycled polymer by using air-forming and hot press molding [4]. The results showed insignificant degradation in the mechanical properties of these recycled composites.

In many engineering applications, a certain amount of recycled composite is mixed with virgin composite to reduce cost. In this regard, some research work concentrated on recycled composites (of PVC) by adding WPC scrap into virgin WPC at a weight ratio of 30:70- the ratio that provided optimum mechanical properties [13]. This mixture of composites was then successively reprocessed up to 8 times by extrusion. It was reported that this WPC could be reprocessed without any significant degradation in the mechanical properties.

A few other research work considered preparing recycled composites by adding recycled fiber (waste paper sludge) into virgin WPC [25]. The results showed that the flexural properties and tensile modulus of the composite increased, and water uptake decreased with increased content of paper sludge.

2.7.2. Effect of Recycling on WF/PLA Composites

PLA is generally used in various applications such as in biomedical and electronic field, automotive industry, and disposable items [49, 50, 52, 58, 59]. However, unlike HDPE, PLA is yet to be widely used in engineering applications, primarily because of its higher production cost, and lower properties such as brittleness and lower heat deflection temperature [42, 44]. Therefore, limited amount of research work has been done on the effect of recycling on properties of PLA bio-composites. And as mentioned in the previous section, a general comparison cannot be made in the properties of individual composites due to the greater number of associated inconsistencies.

In some research work, composites were made by incorporating virgin fiber into virgin polymer, and then these composites were consecutively reprocessed by injection molding (up to six times) [41]. It was found that mechanical properties of the composites initially remained constant and then started decreasing with increasing no. of reprocessing cycles, mainly due to fiber length reduction and polymer degradation.

Other research work focused on preparing recycled composites by adding recycled fiber into virgin polymer [42, 43, 46]. In most cases, the recycled composites showed comparable mechanical properties to virgin composites.

2.8. Summary

It could be observed from the above discussion that recycling of WPCs are done in one or combination of these following ways- extrusion, grinding, injection molding, addition of recycled fiber to virgin polymer, and addition of virgin fiber to recycled polymer. It could also be seen that no prior research work has been reported so far where reprocessing was performed up to six times, only by extrusion process for any of WF/HDPE and WF/PLA composites. In this way, this research is distinctive compared to the other researches on the recycling of WPCs done till now.

Table 2.1: Research work done on recycling of WPCs (HDPE and PLA composites)

Serial No.	Title	Recycling Procedure	Properties & Findings	Reference No.
1	Reprocessing of wood fiber reinforced polypropylene composites, Part I: Effects on physical and mechanical properties	Injection molding and grinding. (recycled 8 times)	Mechanical properties decreased	[1]
2	Preparation and properties of recycled HDPE/natural fiber composites	Recycled HDPE and virgin fiber	Comparable mechanical properties with virgin composites	[2]
3	Dimensional stability and mechanical behavior of wood-plastic composites based on recycled and virgin high-density polyethylene	Recycled HDPE and virgin fiber	Equivalent mechanical properties to virgin ones	[3]
4	Characteristics of wood-fiber plastic composites made of recycled materials	Recycled fiber with recycled HDPE, or recycled PP	Insignificant degradation of mechanical properties	[4]
5	Influence of the wood fiber filler on the internal recycling of poly vinyl chloride based composites	Extrusion and milling (recycled 20 times)	Mechanical properties increased or remained almost constant	[5]
6	Effect of Thermo-Mechanical Degradation of Polypropylene on Hygroscopic Characteristics of Wood Flour Polypropylene Composites	Recycled PP (2 times by extrusion), and virgin fiber	Water absorption and thickness swallowing increased	[6]
7	Investigations on the recycling of hemp and sisal fiber reinforced polypropylene composites	Injection molding and grinding (recycled 7 times)	Comparable mechanical properties with virgin composites	[7]
8	Mechanical properties of composites from sawdust and recycled plastics	Virgin fiber with recycled HDPE, or recycled PP	Equivalent mechanical properties to virgin ones	[12]
9	Recycling of wood plastic composites prepared from poly vinyl chloride and wood flour	Virgin and scrap WPC at 70:30 by wt% (extruded 8 times)	Insignificant degradation in mechanical properties	[13]

Table 2.1: Research work done on recycling of WPCs (HDPE and PLA composites) (continued)

Serial No.	Title	Recycling Procedure	Properties & Findings	Reference No.
10	Effects of the accelerated freeze-thaw cycling on physical and mechanical properties of wood flour-recycled thermoplastic composites	Virgin fiber with recycled HDPE, or recycled PP	Lower water uptake with higher strength properties compared to virgin ones	[14]
11	Experimental investigation on reprocessing of extruded wood flour/HDPE composites	Grinding and extrusion (recycled once)	Strength properties decreased, flexural modulus and water uptake increased	[17]
12	Reprocessing of wood fiber reinforced polypropylene composites. Part II: Hygrothermal ageing and its effects	Grinding and injection molding (recycled 8 times)	Tensile and impact strength decreased, and failure strain increased	[18]
13	Effects of Waste Paper Sludge on the Physico-Mechanical Properties of High Density Polyethylene/ Wood Flour Composites	Virgin WF/HDPE composite with waste paper sludge	Flexural properties and tensile modulus increased, and water uptake decreased with increased sludge content	[25]
14	Mechanical Properties of Wood Plastic Composite Panels Made From Waste Fiberboard and Particleboard	Virgin HDPE with waste fiberboard or waste particleboard	Comparable or increased flexural and impact strength to conventional fiberboard	[26]
15	Effect of recycling on mechanical behavior of bio-compostable flax/poly (L-lactide) composites	Injection molding (6 cycles)	Tensile strength and failure strain decreased with increased no. of injection cycles	[41]
16	Polylactide-Recycled Wood Fiber Composites	Virgin PLA and recycled fiber	10 wt% fiber WPC did not degrade while 20 wt% fiber WPC degraded highly during processing	[42]
17	A Study on Biocomposites from Recycled Newspaper Fiber and Poly (lactic acid)	Virgin PLA and recycled fiber	Similar mechanical properties to virgin talc/PLA or talc/PP composites	[43]
18	Green composites from recycled cellulose and poly(lactic acid): Physico-mechanical and morphological properties evaluation	Virgin PLA and recycled fiber	Comparable physico-mechanical properties with high performance composites	[46]

CHAPTER 3. DESIGN OF EXPERIMENT

This chapter describes the 'Design of Experiment' (DOE) and data analysis of this research. In this regard, the DOE and data analysis have been carried out exactly the same way for both composites (WF/HDPE and WF/PLA). That is to say, this chapter individually focuses on each composite and no comparison is made between their properties.

3.1. Design of Experiment (DOE)

A single factor (recycling) experimental design was developed with 7 levels (cycle 0 to cycle 6). The effect of the factor was investigated on 10 responses. The responses are – a) strength properties- tensile and flexural strength, impact resistance, b) stiffness properties- tensile, flexural and storage modulus, heat deflection temperature, and c) strain properties- failure strain, coefficient of thermal expansion, and melt flow index. In this design, sample size was 8 for all responses except melt flow index (sample size -5) and confidence level was 95 % ($\alpha=0.05$). The design is completely randomized.

It should be noted that although each composite has two formulations (30 and 50 wt% WF), fiber loading has not been included as a factor in the DOE. This is because, the effect of the factor recycling has been individually investigated for each formulation and hence there is no interaction. The DOE is summarized in Table 3.1.

3.2. Data Analysis

The effect of the factor was examined by one way 'Analysis of Variance (ANOVA)' at all levels for each formulation. ANOVA is the appropriate method of analyzing equality of more than two means for any response. For comparing equality of higher no. of means, T-test is not appropriate since it requires a lot of work and time. In addition, T-test causes inflation of type I error that makes the analysis incorrect. [36]. Prior to conducting ANOVA, necessary assumptions were inspected. Box plots were made to get a preliminary guess followed by test for ‘normal probability’ and ‘equal variances.’ The latter two tests were found validated in most of the cases. However, few analyses showed some declinations for ‘equal variance’ test. In those cases, the logarithmic data transformation was not performed (assuming equal variances for all cases), since the data transformation would create dissimilarity in the whole data analysis.

Table 3.1: Design of Experiment for each of WF/HDPE and WF/PLA composite

No. of Factor	1 (Recycling)
No. of Levels	7 (Cycle 0 – Cycle 6)
Model Type	Fixed Effects Model
Sample Size	8 (All responses except MFI-5)
Confidence Level	95 % (α=0.05)
Responses	Tensile Strength, Flexural Strength, Impact Resistance, Tensile Modulus, Flexural Modulus, Storage Modulus, Heat Deflection Temperature (HDT), Failure Strain, Coefficient of Thermal Expansion (CTE), Melt Flow Index (MFI)

Although ANOVA can indicate difference among means, it cannot make pairwise comparisons. For pairwise comparison, Tukey test is the appropriate test method that has been used in this data analysis. However, rather than Tukey test, there are two other methods for pairwise comparisons- 1) Scheffe’s method, and 2) Fisher Least Significant Difference (LSD) method. Scheffe’s method does not show the highest level of sensitivity and Fisher LSD method (although can control error rate α) cannot control the family error rate for pairwise comparisons. On contrast, Tukey test can control family error rate at the level of significance α. That is why Tukey test has been chosen for pairwise comparisons in this research. This test uses the following formula [36]-

$$T_{\alpha} = q_{\alpha}\,(a, f)\ X\ \sqrt{(\frac{MS_E}{n})} \tag{3.1}$$

Here, α is level of significance, a is no. of levels, f is degree of freedom of error, n is sample size, MS_E is mean squares of error, and q is studentized range statistic. The value of q statistic is determined from the statistical chart. According to Tukey Test, the difference of means of two groups will be significant if the absolute value of mean differences exceeds the value of T_α [36].

After conducting Tukey test, regression analysis was carried out to relate expected mean and no. of reprocessing cycles for each response. That is to say, regression analysis was performed to develop empirical models. These models help not only find predicted or expected mean at all levels, but also provide a better understanding of the effect of recycling [36]. Significance of regression analysis was validated by ANOVA (Appendix I and II).

Finally, effect of CA and WF content (only for virgin material) was examined by two sample T-test. Prior to performing T-test, test for 'normal probability' and 'equal variances' were conducted. T-test is the appropriate statistical method to compare means of two groups when sample size is small. T-test is conducted in two ways- for equal and unequal variances. The equations of T-test for equal variances (equation 3.2 and 3.3) and unequal variances (equation 3.4) are as follows [36]-

$$t_0 = (\bar{y}_1 - \bar{y}_2)/\left(S_p\, X \sqrt{\frac{1}{n_1}+\frac{1}{n_2}}\right) \tag{3.2}$$

$$S_p^2 = \left((n_1 - 1)S_1^2 + (n_2 - 1)S_2^2\right)/(n_1 + n_2 - 2) \tag{3.3}$$

$$t_0 = (\bar{y}_1 - \bar{y}_2)/\surd\left(\frac{S_1^2}{n_1}+\frac{S_2^2}{n_2}\right) \tag{3.4}$$

Here, $\bar{y}_1$ and $\bar{y}_2$ are means, n_1 and n_2 are sample sizes, S_1^2 and S_2^2 are individual variances of sample 1 and 2 respectively. S_p^2 is an estimate calculated from sample variances and sample sizes. From the t-statistic, p-value was calculated.

Table 3.2 summarizes the data analysis methods (tests) with corresponding purposes. In this work, statistical software ‘Minitab 16’ was used for the data analysis of WF/HDPE composite and ‘Minitab 17’ for WF/PLA composite.

Table 3.2: Data analysis methods with corresponding purpose

Name of Test	Purpose of Test
One Way Analysis of Variance (ANOVA)	Investigating effect of recycling
Tukey Test	Inspecting comparison of means
Regression Analysis	Developing empirical models
Two Sample T-Test	Investigating effect of CA and WF content (only for virgin material)

CHAPTER 4. IMPACT OF RECYCLING ON THE MECHANICAL AND THERMO-MECHANICAL PROPERTIES OF WF/HDPE COMPOSITE

This chapter describes in detail the effect of recycling on the mechanical and thermo-mechanical properties of WF/HDPE composite.

4.1. Introduction

Wood Plastic Composites (WPCs) are made of a natural fiber or filler (e.g., oak, kenaf, hemp, and sisal fiber) and a thermoplastic (e.g., polyethylene and polypropylene) [6, 26], and they are widely accepted especially because of their biodegradability, higher specific strength and stiffness, and zero or very low health concern along with other advantages [2, 7, 9, 17]. Among all WPCs, wood fiber (WF)/ HDPE (high density polyethylene) composites are extensively used in household apparatus (e.g., doors, decking, windows, railing, and furniture), and automotive industry (e.g., door panels and seat covers) [17]. HDPE has a lower melting point (around 130 ºC) compared to the degradation temperature of most natural fibers (200-220 ºC) which helps easier processing of its composites [17]. HDPE also shows higher toughness, stiffness, chemical resistance, thermal stability, and electrical insulation [29]. However, HDPE alone cannot provide all desired properties of an engineered material and therefore, fiber incorporation becomes necessary. In general, wood fiber/filler has elastic modulus and strength that are respectively 40 and 20 times higher than that of HDPE [28, 31] and it is the most available renewable resource in the world [43]. In addition, wood flour is considerably cheap since a substantial amount of wood waste is generated in wood industry at different steps of processing [3]. Regarding these benefits, WF could be considered as an effective filler for HDPE that increases the mechanical and thermal properties of the polymer [9] and hence, WF/HDPE composites are widely used as an engineered material in today's world.

Along with a lot of advantages, WF/HDPE composites come with some imperfections. The major problem is the incompatibility between the two basic components- fiber and matrix, but this problem could be resolved by using some specific methods. Natural fibers or fillers are hydrophilic (prone to absorb water) while petroleum based polymers (in this case HDPE) are hydrophobic (reluctant to absorb water). This incompatibility causes poor interfacial adhesion between fiber and matrix when mixed together. Poor adhesion leads to less stress transfer from matrix to fibers that finally results in lower mechanical and thermal properties of the WPC. However, this problem could be worked out by adding a little amount of suitable coupling agent (CA) to the composite. The CA helps improve the interfacial adhesion quality that leads to higher composite properties. Besides the addition of CA, there are some other methods, such as fiber surface treatment, to improve the composite properties [5, 7, 16, 17]. Since the composite properties could be improved, despite the initial drawbacks, WPCs of HDPE are produced worldwide on a grand scale.

However, a higher WPC production finally leads to, after their lifetime, a higher amount of plastic waste that generate high environmental concern [1, 6]. Plastic waste cause soil and air pollution. All petroleum based plastics take a very long time to degrade in soil that greatly reduce the soil fertility [44]. In addition, plastic waste, floating on sea surface, reduce the sea life in a greater amount. Because of these environmental concerns, plastic waste management is now a very important issue all over the world.

At present, there are three well-known methods for plastic waste management- 1) disposal in landfills, 2) incineration, and 3) recycling. The first two processes cause environmental pollution while the third process is environment friendly and hence, could be considered the best way for plastic waste management. When disposed in landfills, plastic waste degrades the soil, and when incinerated, create noxious gases and thus help global warming [13]. On contrast, recycling causes no (or little) environmental pollution and saves the material without significant degradation of its properties (in most cases) that helps its further use. Although some countries, such as Germany, are hesitant to use the recycled plastic materials because of surface appearance and physico-mechanical properties, most countries are emphasizing on the recycling of plastic waste [1]. For example, according to US Environmental Protection Agency (2014) report, 31.75 million tons of plastic waste were generated in US in 2012, of which 17.4% was HDPE waste, and 2.8 million tons of plastics were recycled, of which 20.4% was recycled HDPE.

There are two other advantages that recycling could provide. In recent years, the crude oil price has been fluctuating, and since the petroleum based plastics are produced from the crude oil, the price of these plastics has also been fluctuating. This phenomenon has drawn the attention of the researchers, and industries on the recycled plastics [6]. In addition, deforestation, that creates inadequacy of new resources and thus causes environmental concern, is another important factor for considering recycling [13].

It can be seen that recycling is not only the best approach but an essential process for WPC waste management and therefore, lots of research have been going on the recycling of WPCs. Beg et al. have reprocessed WF/PP composites by injection molding and grinding up to eight times, and reported that the mechanical properties of the composite decreased with increased number of reprocessing cycles [1]. Lei et al. added pine or bagasse flour to recycled HDPE, and concluded that the mechanical properties of the recycled composites compared well with that of the virgin ones [2]. Adhikary et al. made recycled HDPE /virgin fiber WPC, and reported that the recycled WPCs have equivalent mechanical and dimensional properties to virgin ones [3]. Augier et al.

recycled virgin WPCs of PVC by extrusion and milling up to 20 times, and found that mechanical properties of the composite increased or remained almost constant with ascending no. of reprocessing cycles [5]. Bourmaud et al. recycled virgin WPCs of PP by injection molding and grinding up to 7 times, and found comparable mechanical properties of recycled WPCs with virgin WPCs [7]. Petchwattana et al. mixed virgin and scrap WPC at a weight ratio of 70:30, extruded that WPC 8 times, and reported insignificant degradation in mechanical properties of recycled WPCs [13]. Shahi et al. recycled virgin WPCs of HDPE once by grinding and extrusion, and reported decrease in strength properties but increase in water uptake of recycled WPCs [17].

According to the above discussion, it is evident that, in most cases recycled WPCs of HDPE are almost as good as virgin ones. However, it should be noted that the results are not exactly comparable. That is because, there are a lot of distinctions in the grades of the polymers, types of wood fibers/fillers, grades of coupling agents and their percentage content, presence of different contaminants (or additives) in recycled composites, and the manufacturing and recycling processes of the WPCs [2].

It can be observed that there are several ways of recycling the WPCs such as -1) using extrusion, injection molding, and grinding, 2) using extrusion and grinding, 3) adding virgin WF into recycled plastics and vice-versa, and 4) adding recycled WPC into virgin WPC. In this chapter, the influence of recycling has been investigated on the mechanical and thermo-mechanical properties of oak wood flour (WF) and HDPE composite with the presence of a coupling agent (MAPE). Two different filler loading formulations (30 and 50 wt% WF) were individually recycled up to six times by extrusion process. Test samples were made by injection molding. Virgin composites without MAPE (for both formulations) were made, in the same processing conditions, to inspect the impact of the coupling agent. In addition, the impact of WF loading, on the composite properties, was also measured only at cycle 0 (virgin composites).

4.2. Experimental Procedure

4.2.1. Materials

Oak wood flour were obtained from Southern Wood Services, GA, USA. The wood particle size distribution is given in Table 1.2. The polymer, high density polyethylene (Marlex 9012), was provided by Chevron Phillips Chemical Company, TX, USA. The polymer has a MFI of 11.5 g/10 min, density of 0.952 g/cm^3, and vicat softening temperature of 124 ^{o}C (Table 1.3). The coupling agent- maleic anhydride grafted PE (MAPE) was provided by Sigma-Aldrich, MO, USA.

4.2.2. Methods

4.2.2.1. Composite Preparation

Composite pellets were prepared from 30 and 50 wt% wood flour with HDPE and 3 wt% MAPE by using a twin-screw co-rotating extruder (Leistriz Micro 18 GL 40 D, NJ, USA). From the composite pellets, test samples were prepared by using a single screw injection molder (Model SIM- 5080, Technoplas Inc., Ohio, USA). The extruder has seven different temperature zones. The temperature of these zones, from feed section to melting section, was respectively maintained at 160 ^{o}C, 193 ^{o}C, 199 ^{o}C, 204 ^{o}C, 207 ^{o}C, 210 ^{o}C, and 213 ^{o}C. The temperature of the die and gate adapter was controlled at 213 ºC. The screw rpm of the extruder was set at 150. Prior to extrusion, wood flour, MAPE, and HDPE were dried in an oven at 80 ^{o}C for a minimum period of 24 hours to remove moisture. The dried wood flour had a moisture content of less than 0.5%. The extruded material (in the form of strands) was then passed through a water bath followed by pelletizing to make composite pellets. A portion of these pellets were dried in an oven at 80 ^{o}C for at least 24 hours and then molded by using an injection molder to make tensile and flexural testing samples. The samples for other tests- such as CTE, HDT, and storage modulus- were prepared from the flexural bar samples. This material was named as ‘cycle 0’ or ‘virgin’ material (individually for both composite formulations).

The remaining pellets of ‘cycle 0’ material were dried in an oven at 80 °C (24 hours) and again extruded at the same processing conditions (mentioned above). The extruded strands were cooled to room temperature followed by pelletizing. A quantity of these pellets were dried at 80 °C and again injection molded to make testing samples. This material was named as ‘cycle 1’ or ‘first time recycled’ material.

The remaining pellets of ‘cycle 1’ material were again consecutively dried, extruded, cooled, and pelletized. A portion of this pelletized composite was dried, and injection molded to get ‘cycle 2’ or ‘second time recycled’ material. This process was repeated up to six times, in total, to get ‘cycle 6’ or ‘sixth time recycled’ composite of both formulations (Fig. 1.3). Composites without MAPE were also prepared (for both filler loadings) at the same processing conditions that were never recycled.

4.2.2.2. Tensile Testing

Tensile testing was performed using an Instron universal testing machine (Model 5567, MA, USA) according to the ASTM D 638: Standard Test Method for Tensile Properties of Plastics. The load cell capacity was 2 KN and the crosshead speed was set at 5 mm/min. An extensometer was used (up to 0.5% strain) to measure the tensile modulus with more precision. The samples were kept at room temperature (25 °C). Eight samples were tested for each batch.

4.2.2.3. Flexural Testing

Flexural testing (three-point bend test) was performed using an Instron universal testing machine (Model 5567, MA, USA) according to the ASTM D 790: Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. The specimen dimensions were 75 mm x 12.7 mm x 3.2 mm with a support span of 52 mm (in the test). A 2 KN load cell was used with a crosshead speed of 1.4 mm/min. The samples were kept at room temperature (25 °C). Eight samples were tested for each batch.

4.2.2.4. Coefficient of Thermal Expansion (CTE)

Coefficient of thermal expansion test was carried out from 30 ºC to 50 ºC by using a Dynamic Mechanical Analyzer (TA Instruments, DMA Q800, DE, USA) with a tension film clamp. The ramp rate was 3 °C and no preload force was used. The specimen dimensions were 38.1 mm x 12.7 mm x 3.2 mm with the actual length of 12.74 mm (in the test). Eight samples were tested for each batch. The following equation was used to measure the CTE-

$$\alpha = \left(\frac{\Delta L}{\Delta T}\right) . \left(\frac{1}{L}\right) \tag{4.1}$$

Here, α is the coefficient of thermal expansion, ΔL is the change in length, ΔT is the change in temperature, and L is the initial length (12.74 mm).

4.2.2.5. Heat Deflection Temperature (HDT)

Heat deflection temperature test was carried out using a Dynamic Mechanical Analyzer (TA Instruments, DMA Q800, DE, USA) with a three point bending clamp according to the ASTM D 648: Standard Test Method for Deflection Temperature of Plastics Under Flexural Load in the Edgewise Position (pressure δ=0.455 MPa). The ramp rate was 3 °C/min. The specimen dimensions were 65 mm x 12.7 mm x 3.2 mm where the actual supported length was 50 mm. Eight samples were tested for each batch.

4.2.2.6. Dynamic Mechanical Analysis

Storage modulus was measured at 30 ºC with a frequency of 1 Hz and an amplitude of 15 μm by using the same Dynamic Mechanical Analyzer (mentioned above) with a dual cantilever beam clamp. The ramp rate was 3 °C/min. The soak time (at 28 ºC) was 5 minutes. The specimen dimensions were 65 mm x 12.7 mm x 3.2 mm where the actual supported length was 41.6 mm. Eight samples were tested for each batch.

4.2.2.7. Izod Impact Test

Izod impact test was carried out using an Izod Impact Tester (Tinius Olsen, Model Impact 104, PA, USA) according to the ASTM D 256: Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics. The specimen dimensions were 63.5 mm x 12.7 mm x 3.2 mm with a notch of 2 mm in depth. No additional weights were used with the pendulum. Eight samples were tested for each batch.

4.2.2.8. Melt Flow Index (MFI)

Melt Flow Index (MFI) was measured with an Extrusion Plastometer (Tinius Olsen, Model MP 600, PA, USA). This test was carried out according to the ASTM D 1238: Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer. The temperature was set at 190 ºC and the load was 2.16 Kg. Five samples were tested for each batch.

4.2.2.9. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was performed on the fracture surfaces of tensile specimens that were attached to aluminum mounts with colloidal silver paste. A gold-palladium coating was applied with a Balzers SCD 030 sputter coater (BAL-TEC RMC, Tucson, AZ, USA). A JEOL JSM-6490LV scanning electron microscope (JEOL USA, Peabody, MA, USA) was used at an accelerating voltage of 15 KeV.

4.2.2.10. Fiber Length Measurement

A small amount (3 g) of composite pellets were heated with toluene in a small jar (surrounded by a heating liquid) at 140 ºC with constant stirring for 96 hours. After the polymer dissolved in toluene, the fibers were separated by filtering. The fibers were then dried, and fiber length was measured by using a Zeiss microscope (Axiovart 40 Mat). The average length of 100 fibers has been reported.

4.2.2.11. Differential Scanning Calorimetry (DSC)

DSC was carried out using a differential scanning calorimeter (TA instruments, DSC, Q1000, DE, USA) in nitrogen (flow rate 50 ml/min) for the temperature range of -10 ºC to 180 ºC. The heating rate was 10 ºC/min. Hermetic Aluminum pans were used for holding the sample. The weight of each sample was approximately 10 mg.

4.2.2.12. Thermogravimetric Analysis (TGA)

TGA was carried out using a thermogravimetric analyzer (TA instruments, TGA, Q500, DE, USA) in air (sample gas, flow rate 60 ml/min) and nitrogen (balance gas, flow rate 40 ml/min). The scanned temperature range was from 25 ºC to 800 ºC. The heating rate was 10 ºC/min. The weight of each sample was approximately 10 mg.

4.2.2.13. Fourier Transform Infra-Red Spectroscopy (FTIR)

FTIR was conducted by using a Thermo Scientific Nicolet 8700 spectrometer in photoacoustic mode in the range of 700-3500 cm^{-1}. The samples were the small pieces of composites having an approximate thickness of 0.5 mm. FTIR data was analyzed by using OMNIC spectra software.

4.2.2.14. Gel Permeation Chromatography (GPC)

A small amount of composite pellets (3 g) were heated with toluene in a small jar (surrounded by a heating liquid) at 140 ºC for 96 hours. When the polymer completely dissolved in toluene, the solution was separated from the fibers that were precipitated on the bottom of the jar. HDPE was separated from toluene by drying the solution in open air at room temperature (25 °C). The dried HDPE was then dissolved in tetrahydrofuran (THF) by heating their solution with constant stirring for 20 minutes. This solution was cooled to ambient temperature and the concentration of this solution was 2 mg/ml. Molecular weight analysis was performed at 40 °C with a GPC apparatus (EcoSEC HLC-8320GPC, Tosoh Bioscience, Japan) by using two columns (TSKgel SuperHM-L 6.00 mm ID× 15 cm) with a differential refractometer detector (DRI). The eluent (THF) flow rate was 0.4 ml/min. The injection volume was 20 µl for each sample.

4.3. Results and Discussion

4.3.1. Effect of Coupling Agent

The coupling agent (MAPE) increased the strength properties (e.g., tensile and flexural strength) of both composites. The MAPE also increased the stiffness properties (e.g., tensile and flexural modulus) of WF 50 HDPE (50 wt% filler) composite but showed no improvement in that of WF 30 HDPE (30 wt% filler) composite (Table 4.1). The strength properties are mainly dependent on interfacial adhesion between the fiber and the matrix. These properties increased due to the increased interfacial adhesion between the WF and HDPE, caused by the coupling agent [1, 3, 4, 14]. On contrast, the stiffness properties are mainly dependent on the degree of mobility constrain of polymer molecular chains by the fiber [8, 10]. The coupling agent increased the polymer chain restriction of WF 50 HDPE composite that led to increased stiffness properties.

However, it could not increase the polymer chain constrain for WF 30 HDPE composite, possibly due to lower filler content.

4.3.2. Effect of WF Content

WF 50 HDPE composite showed higher strength and stiffness properties but lower strain properties (e.g., failure strain and melt flow index) that to WF 30 HDPE composite. This is because, more WF content creates more ester bonds with the polymer and hence more stress transfer takes place from the matrix to the fiber. This leads to higher strength and stiffness properties of WF 50 HDPE composite. As the higher filler composite becomes stiffer, it shows more resistance to elongate (by applied load) that finally results in its lower strain properties.

Table 4.1: Effect of coupling agent (MAPE) on the properties of WF/HDPE composites (by two sample T-test)

Properties	WF 30 HDPE Composite	WF 50 HDPE Composite
Tensile Strength (MPa)	9	17
Tensile Modulus (MPa)	0	550
Flexural Strength (MPa)	6	16
Flexural Modulus (MPa)	0	50
Storage Modulus (MPa)	0	100
Impact Resistance (J/m)	0	12
Heat Deflection Temperature (ºC)	0	5

4.3.3. Effect of Recycling

4.3.3.1. Effect of Recycling on Fiber Length

The fiber length of WF 50 HDPE composite was measured at cycle 0 and cycle 6. Fiber length decreased with increased no. of reprocessing cycles. From cycle 0 to cycle 6, the average fiber length (of 100 fibers) decreased from 433.66 μm to 348.26 μm. Figs. 4.1 and 4.2 respectively show the images of fiber at cycle 0 and cycle 6.

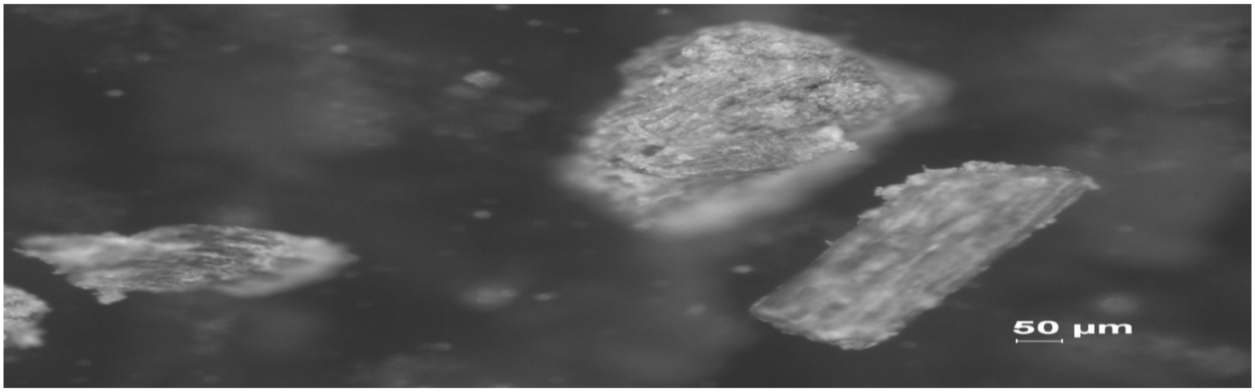

Fig. 4.1: Image of fibers of WF 50 HDPE composite at cycle 0.

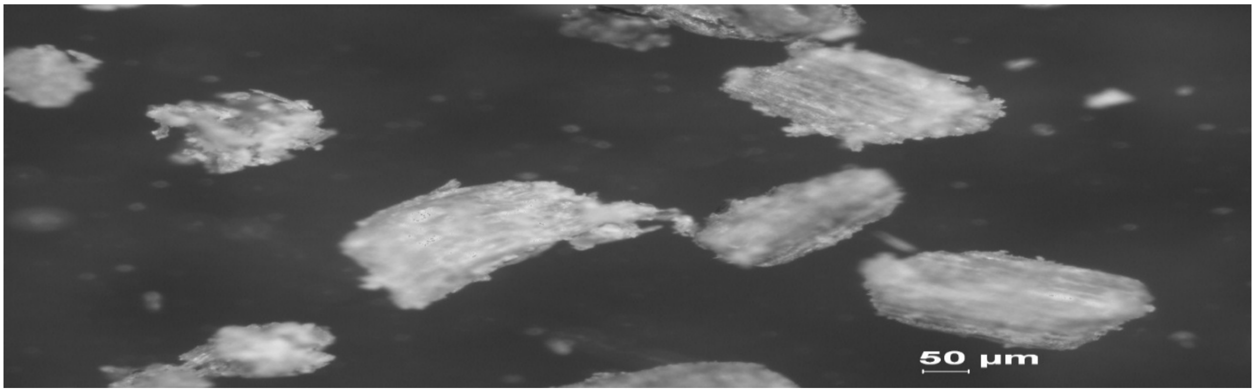

Fig. 4.2: Image of fibers of WF 50 HDPE composite at cycle 6.

4.3.3.2. Effect of Recycling on the Molecular Weight of the Polymer

The molecular weights of HDPE of WF 50 HDPE composite was measured at cycle 0 and cycle 6 by gel permeation chromatography (GPC). Both the weight averaged molecular weight (M_w) and the number averaged molecular weight (M_n) decreased with increased no. of reprocessing cycles. From cycle 0 to cycle 6, the M_w decreased from 116,113 to 110,360 and the M_n decreased from 110,602 to 102,198. The polydispersity index (PDI) also increased from 1.05 (cycle 0) to 1.08 (cycle 6) that denotes lower molecular weights of HDPE by reprocessing [13].

4.3.3.3. Effect of Recycling on Strength Properties

The effect of recycling was statistically found significant on the strength properties (tensile and flexural strength, and impact resistance) for both composites. All strength properties gradually

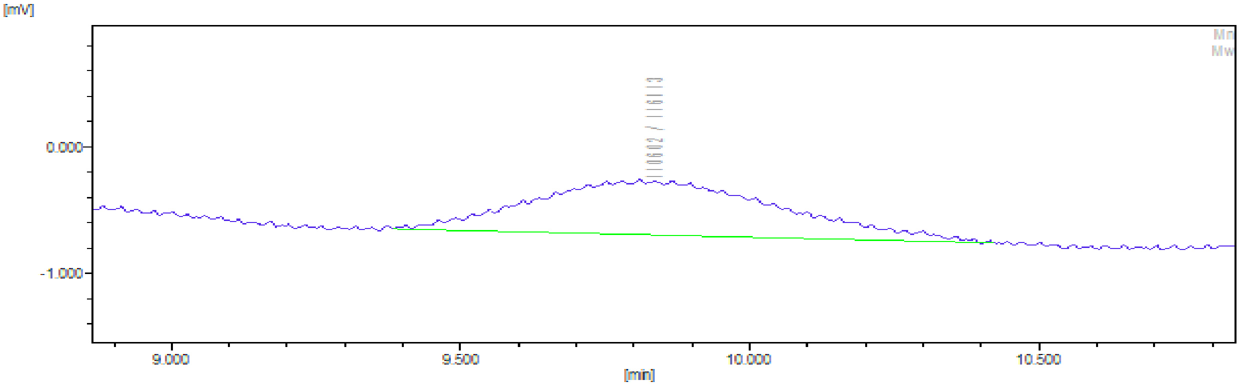

Fig. 4.3: Gel permeation chromatogram of WF 50 HDPE composite at cycle 0.

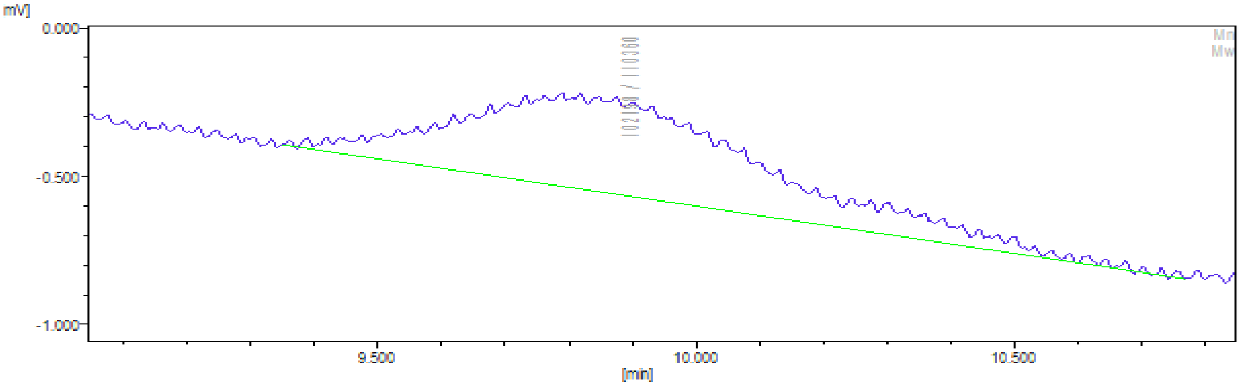

Fig. 4.4: Gel permeation chromatogram of WF 50 HDPE composite at cycle 6.

decreased with ascending no. of reprocessing cycles (figs. 4.7, 4.10, and 4.13). For example, from cycle 0 to cycle 6, the average tensile strength of WF 30 HDPE composite decreased from 25.79 MPa to 23.1 MPa, and the average flexural strength of WF 50 HDPE composite decreased from 45.7 MPa to 41.11 MPa (Table 4.16). This could be due to the reduction in fiber length (Figs. 3.1-3.2) and molecular weights of HDPE (Figs. 3.3-3.4) caused by the heat and shear stress history of successive extrusion (recycling) [1, 7, 17, 41]. Prior to recycling, both composites at cycle 0 show good interfacial adhesion between the fiber and matrix (Figs. 4.14 and 4.16). On contrast, composites at cycle 6 show lower interfacial adhesion along with bended fibers, fiber agglomeration, and a lot of pores (Figs. 4.15 and 4.17). The decrease in interfacial adhesion plays a vital role to reduce the strength properties of the composites. In addition, fiber agglomeration and pores (or micro-voids) help easier crack propagation that significantly decreases the strength properties of both composites at cycle 6. The corresponding box plots, ANOVA Tables, and regression equations of composite strength properties have been given below.

4.3.3.3.1. Data Analysis of Tensile Strength

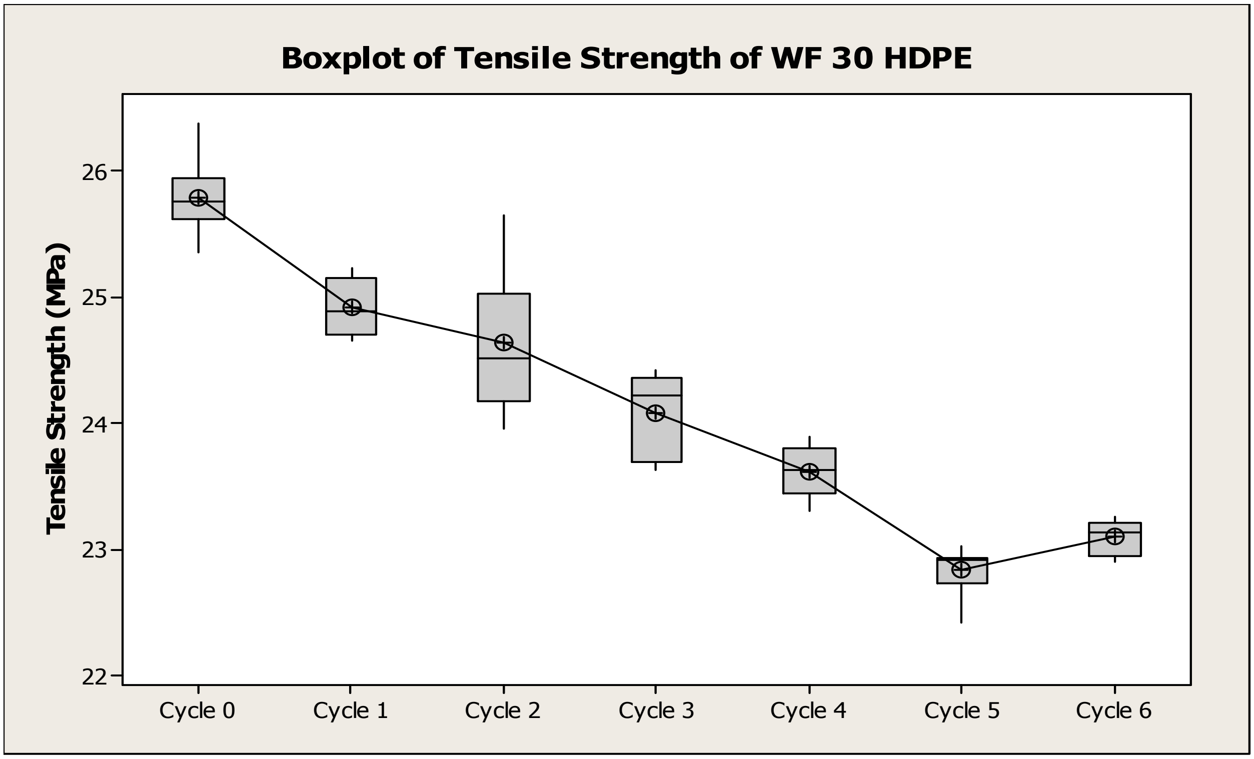

Fig. 4.5: Box plot of tensile strength of WF 30 HDPE composite.

Table 4.2: One way ANOVA of tensile strength of WF 30 HDPE composite

```
Source  DF       SS      MS      F      P
Factor   6  53.3199  8.8866  93.07  0.000
Error   49   4.6786  0.0955
Total   55  57.9985
S = 0.3090   R-Sq = 91.93%   R-Sq(adj) = 90.95%
```

Table 4.3: One way ANOVA of tensile strength of WF 50 HDPE composite

```
Source  DF       SS       MS       F      P
Factor   6  75.7758  12.6293  160.16  0.000
Error   49   3.8638   0.0789
Total   55  79.6396
S = 0.2808   R-Sq = 95.15%   R-Sq(adj) = 94.55%
```

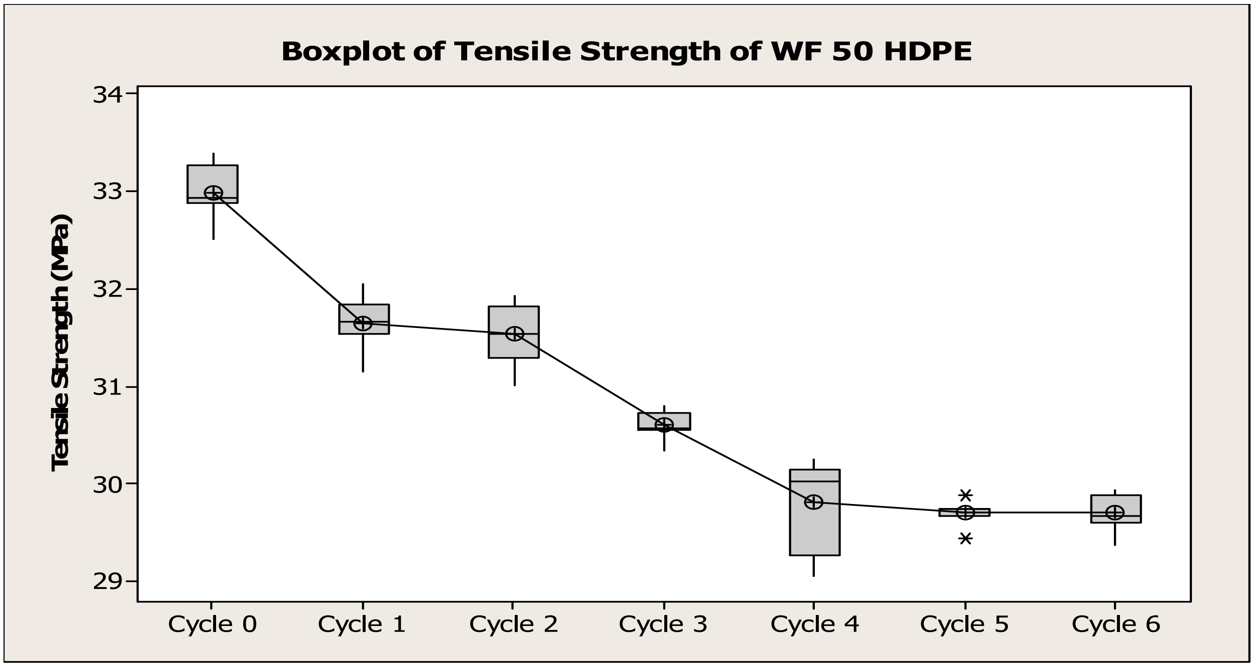

Fig. 4.6: Box plot of tensile strength of WF 50 HDPE composite.

The regression equations of expected mean of tensile strength (Y) vs. no. of reprocessing cycles (X) of WF 30 HDPE (eqn. 4.2) and WF 50 HDPE (eqn. 4.3) composite are as follows-

$$Y = 25.77 - 0.7167\ X + 0.04039\ X^2 \tag{4.2}$$

$$Y = 32.94 - 1.056\ X + 0.08380\ X^2 \tag{4.3}$$

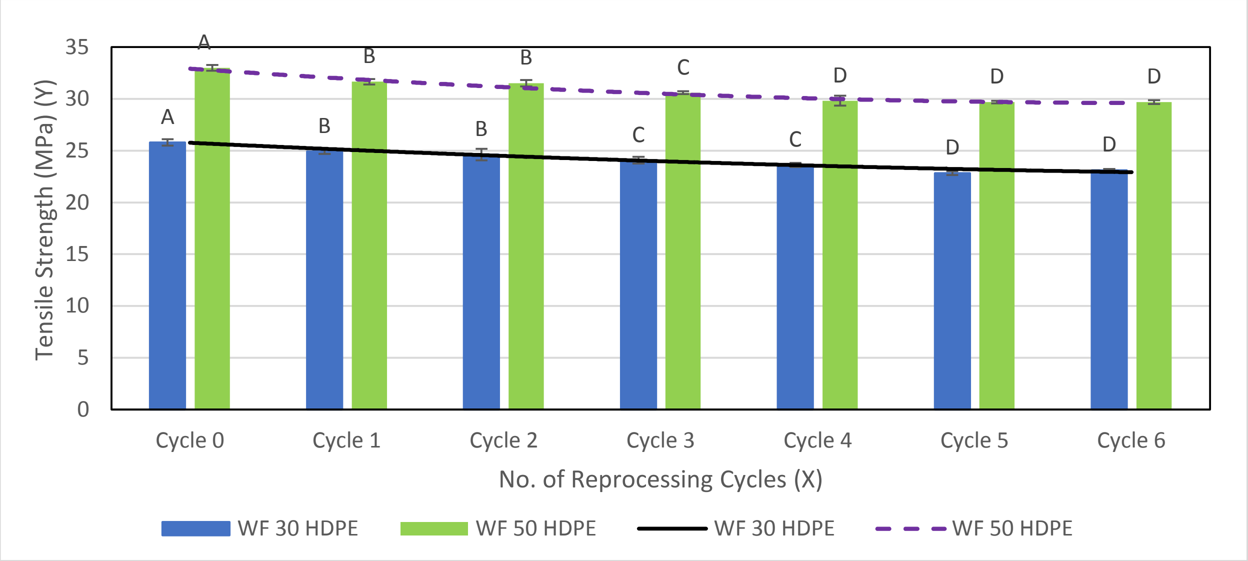

Fig. 4.7: Effect of recycling on the tensile strength of WF/HDPE composites. Means that do not have a common letter are significantly different.

4.3.3.3.2. Data Analysis of Flexural Strength

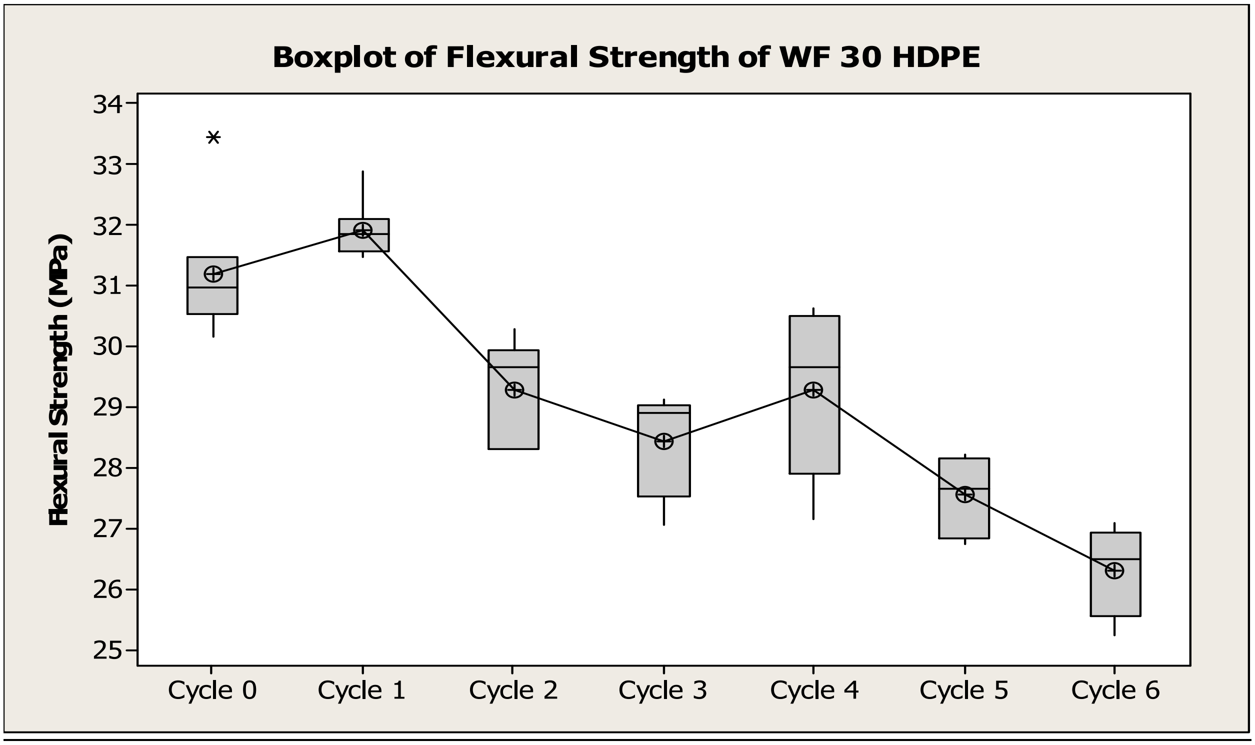

Fig.4.8: Box plot of flexural strength of WF 30 HDPE composite.

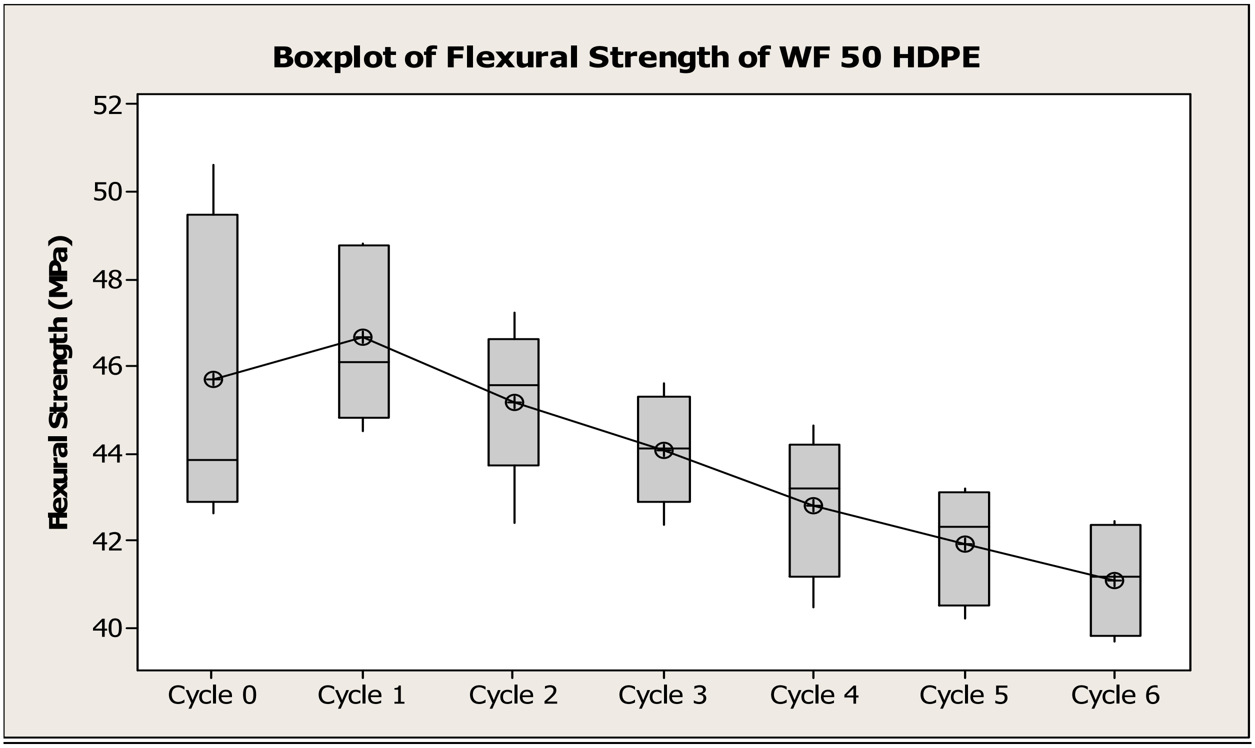

Fig. 4.9: Box plot of flexural strength of WF 50 HDPE composite.

Table 4.4: One way ANOVA of flexural strength of WF 30 HDPE composite

```
Source  DF       SS      MS      F      P
Factor   6  184.446  30.741  39.60  0.000
Error   49   38.040   0.776
Total   55  222.485
S = 0.8811   R-Sq = 82.90%   R-Sq(adj) = 80.81%
```

Table 4.5: One way ANOVA of flexural strength of WF 50 HDPE composite

```
Source  DF      SS     MS     F      P
Factor   6  203.05  33.84  8.97  0.000
Error   49  184.85   3.77
Total   55  387.90
S = 1.942   R-Sq = 52.35%   R-Sq(adj) = 46.51%
```

The regression equations of expected mean of flexural strength (Y) vs. no. of reprocessing cycles (X) of WF 30 HDPE (eqn. 4.4) and WF 50 HDPE (eqn. 4.5) composite are as follows-

$$Y = 31.65 - 0.8366 X \tag{4.4}$$

$$Y = 46.67 - 0.9142 X \tag{4.5}$$

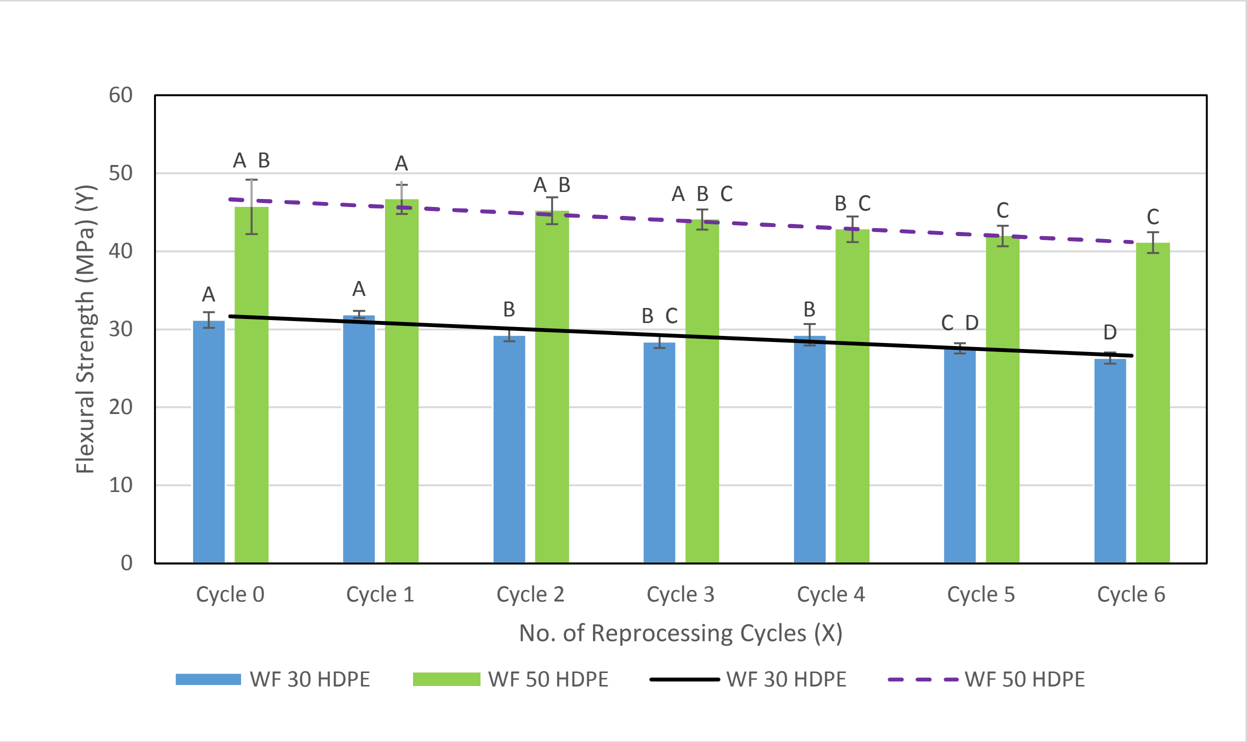

Fig. 4.10: Effect of recycling on the flexural strength of WF/HDPE composites. Means that do not have a common letter are significantly different.

4.3.3.3.3. Data Analysis of Impact Resistance

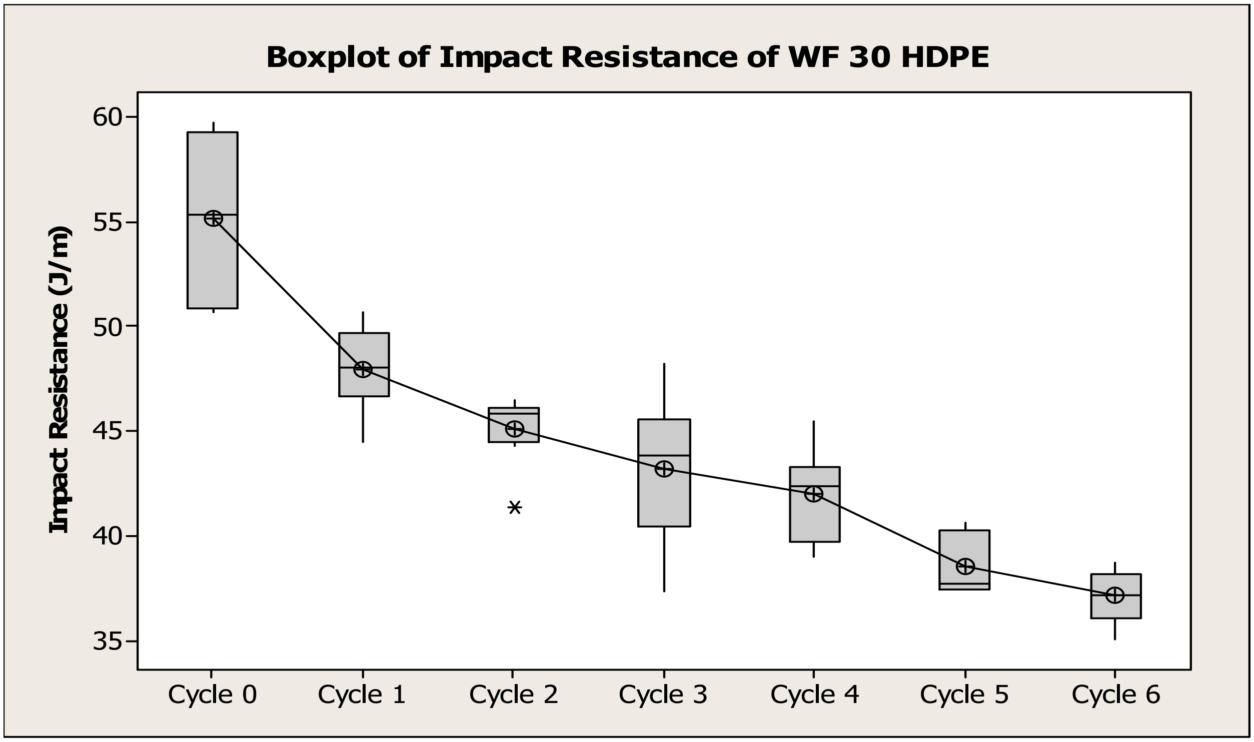

Fig. 4.11: Box plot of impact resistance of WF 30 HDPE composite.

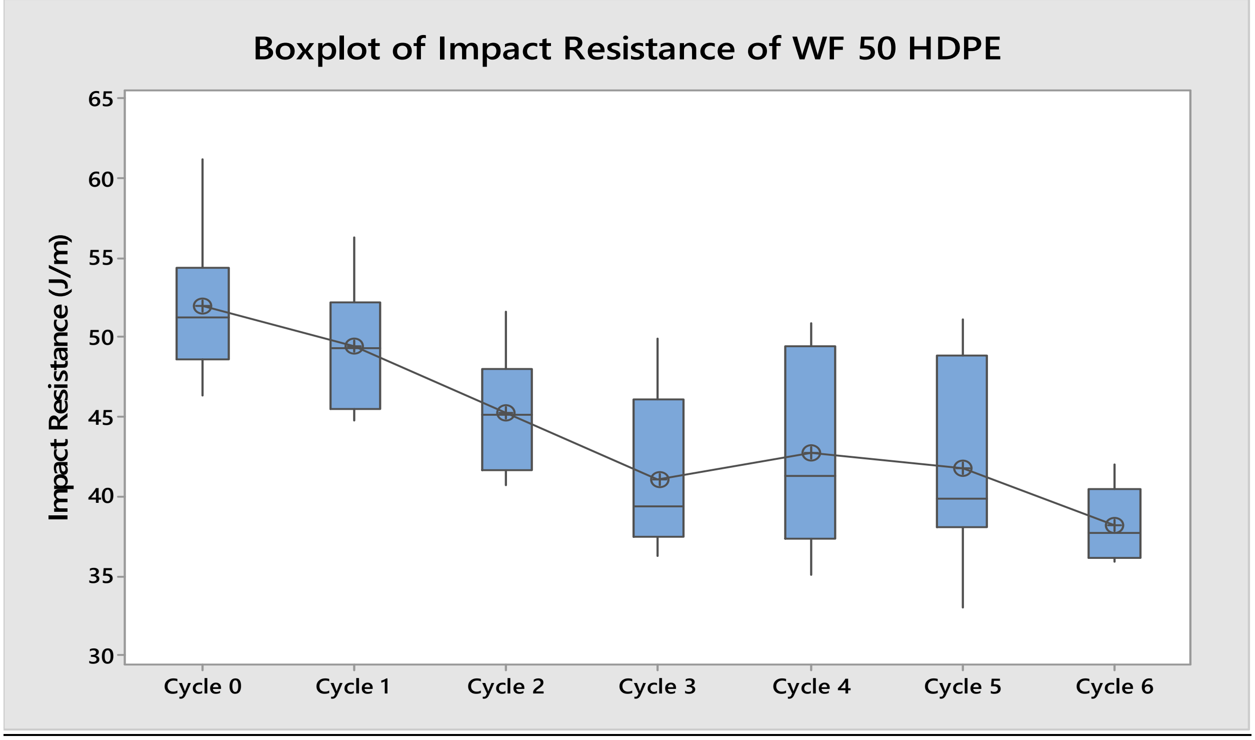

Fig. 4.12: Box plot of impact resistance of WF 50 HDPE composite.

Table 4.6: One way ANOVA of impact resistance of WF 30 HDPE composite

```
Source  DF       SS      MS      F      P
Factor   6  1780.70  296.78  46.40  0.000
Error   49   313.43    6.40
Total   55  2094.13
S = 2.529   R-Sq = 85.03%   R-Sq(adj) = 83.20%
```

Table 4.7: One way ANOVA of impact resistance of WF 50 HDPE composite

```
Source  DF  Adj SS  Adj MS  F-Value  P-Value
Factor   6    1137  189.53     8.31    0.000
Error   49    1117   22.80
Total   55    2254
      S    R-sq  R-sq(adj)  R-sq(pred)
4.77447  50.45%     44.38%      35.28%
```

The regression equations of expected mean of impact resistance (Y) vs. no. of reprocessing cycles (X) of WF 30 HDPE (eqn. 4.6) and WF 50 HDPE (eqn. 4.7) composite are as follows-

$$Y = 54.84 - 7.718\ X + 1.696\ X^2 - 0.1521\ X^3 \qquad (4.6)$$

$$Y = 50.70 - 2.109\ X \qquad (4.7)$$

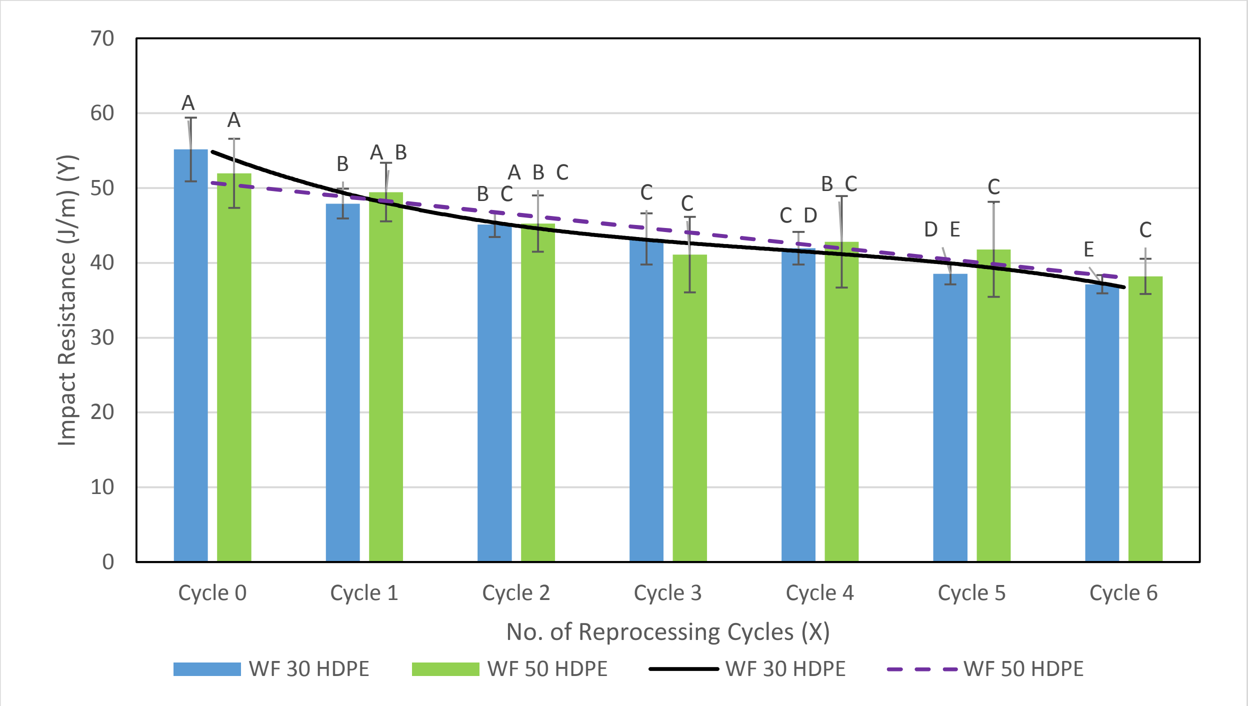

Fig 4.13: Effect of recycling on the impact resistance of WF/HDPE composites. Means that do not have a common letter are significantly different.

4.3.3.3.4. SEM Images

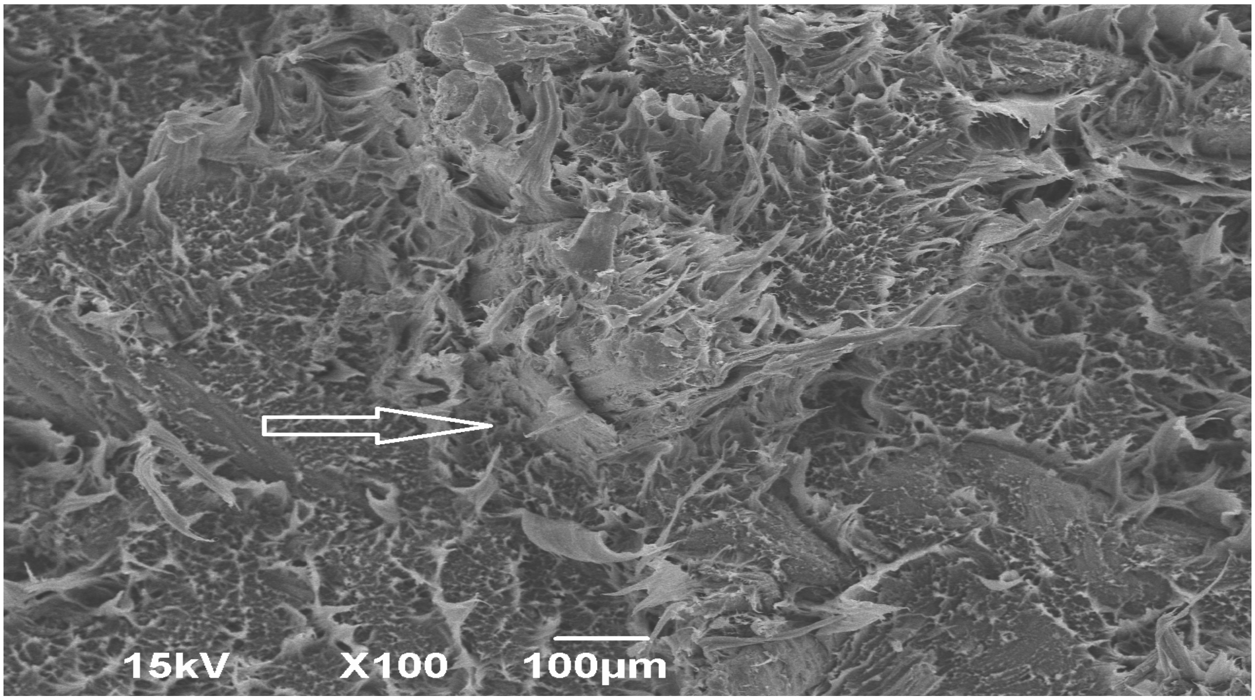

Fig 4.14: SEM micrographs of WF 30 HDPE composite at cycle 0 with magnification of 100X.

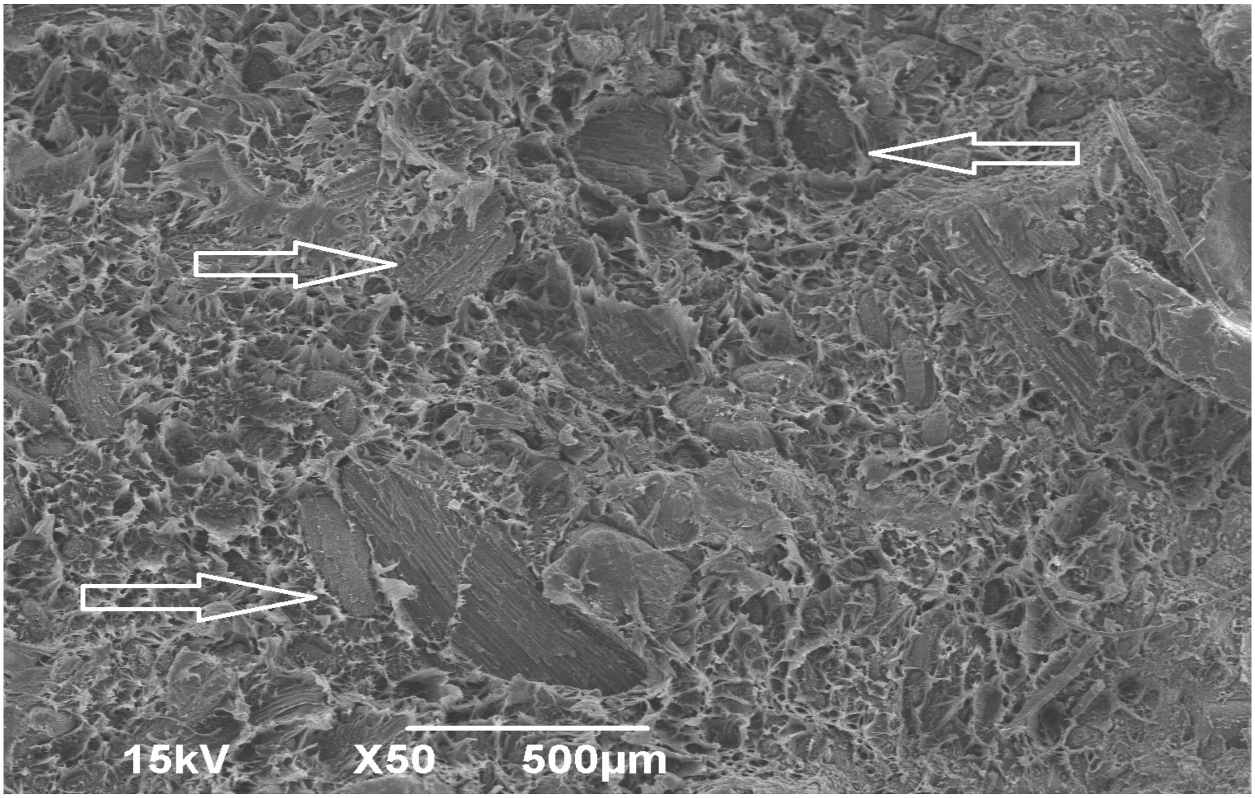

Fig. 4.15: SEM micrographs of WF 30 HDPE composite at cycle 6 with magnification of 50X.

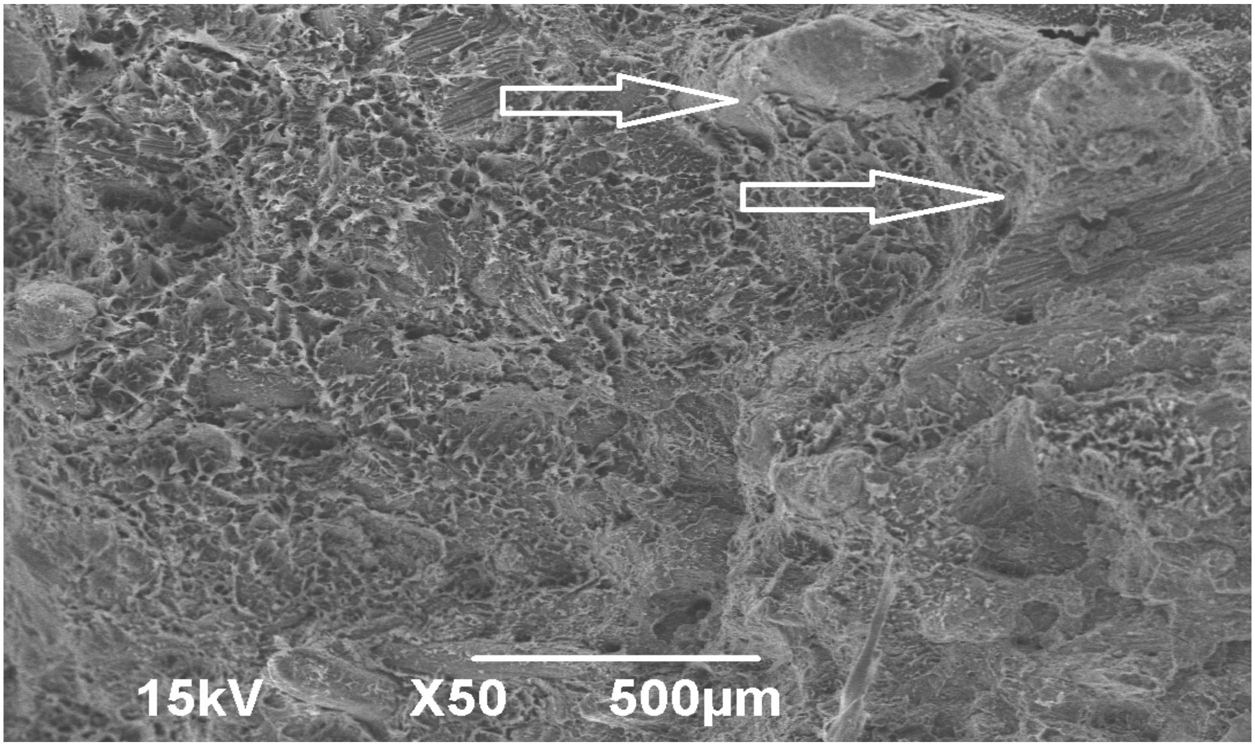

Fig. 4.16: SEM micrographs of WF 50 HDPE composite at cycle 0 with magnification of 150X.

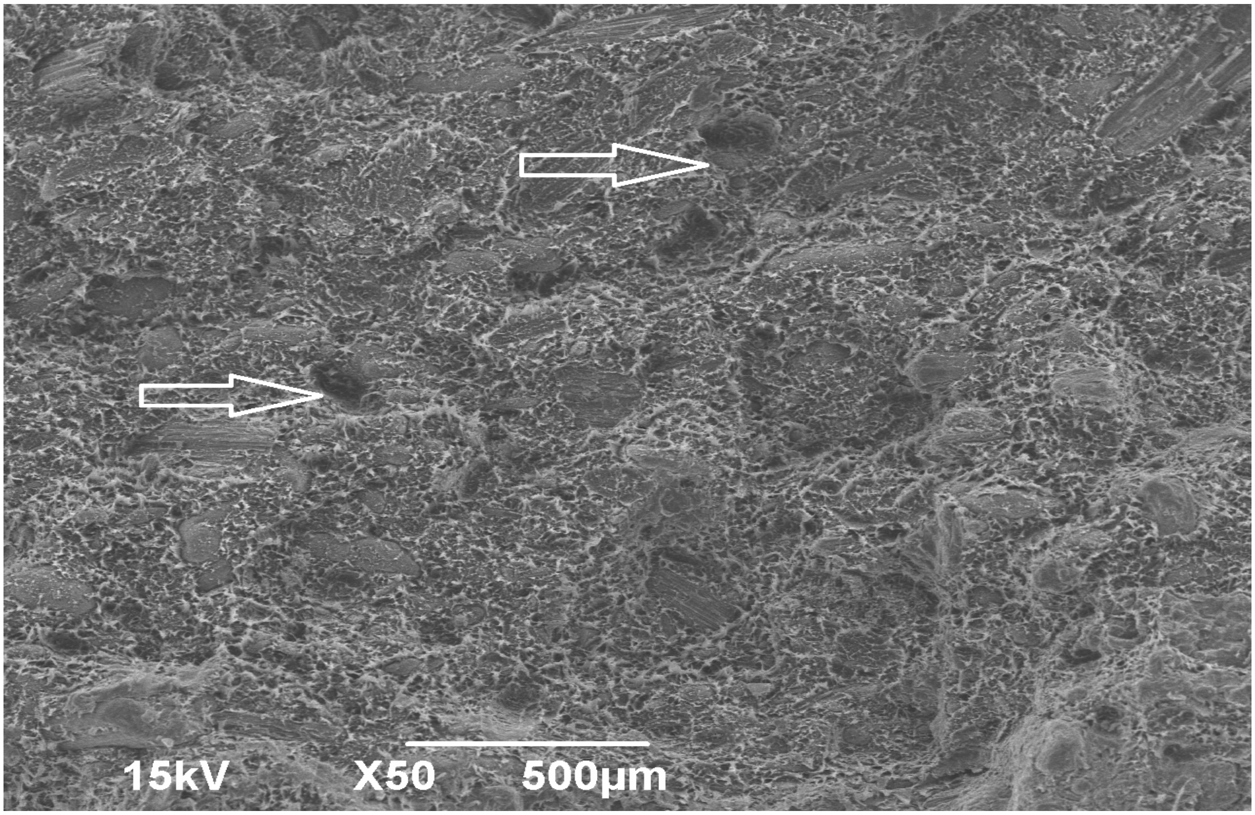

Fig. 4.17: SEM micrographs of WF 50 HDPE composite at cycle 6 with magnification of 50X.

4.3.3.4. Effect of Recycling on Stiffness Properties

The impact of recycling was also statistically found significant on all the stiffness properties (tensile, flexural, and storage modulus) and heat deflection temperature (HDT) for both composites. All these properties decreased with increased no. of reprocessing cycles (Figs. 4.20, 4.23, 4.26, and 4.29). For example, the flexural modulus of lower and higher filler composite respectively decreased 26% and 24 % (approx.) after reprocessing 6 times (Table 4.16). This could be due to the fiber and polymer degradation of the composites that causes lower stress transfer from the matrix to fiber with repetitive extrusion [1]. This less efficient stress transfer finally results in lower stiffness properties of the composites. In addition, lower fiber length at cycle 6 could provide less restriction to polymer chain mobility and thus cause lower stiffness. Furthermore, increased no. of pores could also lead to lower stiffness properties at cycle 6 (Figs. 4.14-4.17). Since heat deflection temperature (HDT) is a stiffness dependent property, it decreased with successive reprocessing for both composites. The corresponding box plots, ANOVA Tables, and regression equations of composite stiffness and HDT properties are given below.

4.3.3.4.1. Data Analysis of Tensile Modulus

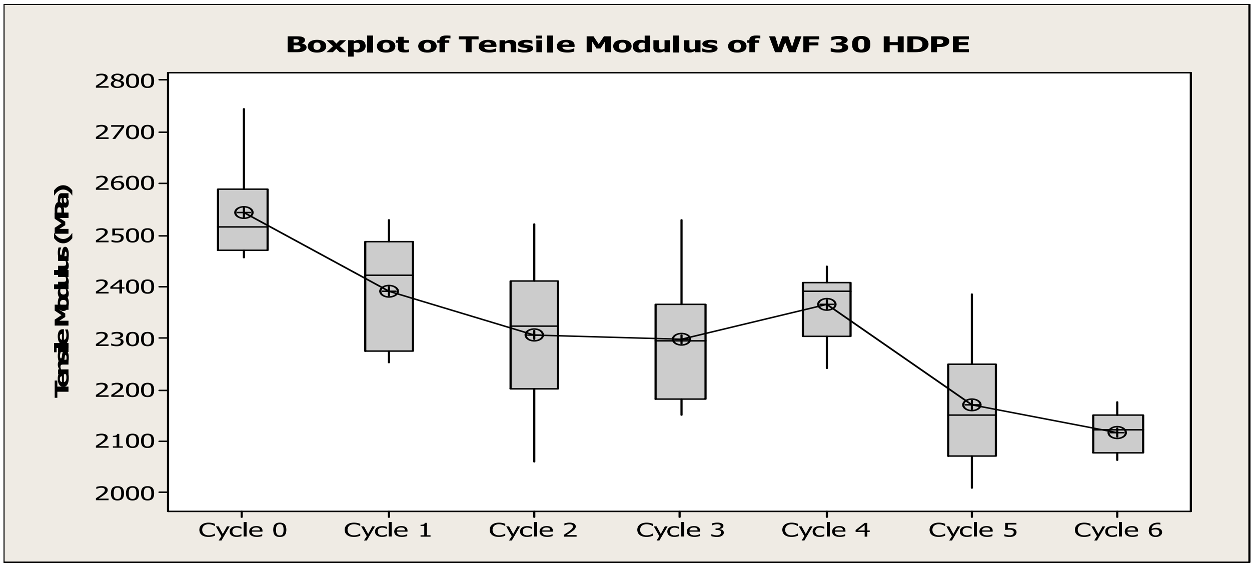

Fig. 4.18: Box plot of tensile modulus of WF 30 HDPE composite.

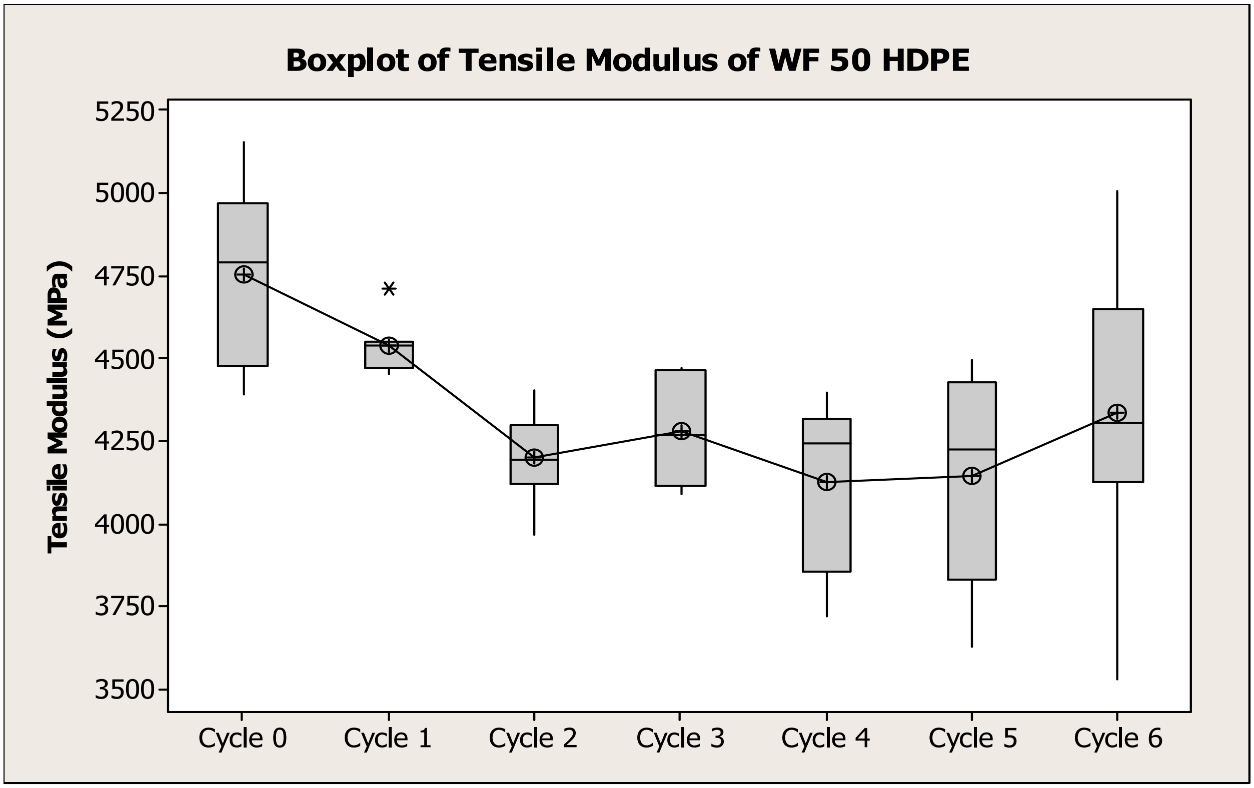

Fig. 4.19: Box plot of tensile modulus of WF 50 HDPE composite.

Table 4.8: One way ANOVA of tensile modulus of WF 30 HDPE composite

```
Source  DF       SS      MS      F      P
Factor   6   972144  162024  14.44  0.000
Error   49   549793   11220
Total   55  1521937
S = 105.9   R-Sq = 63.88%   R-Sq(adj) = 59.45%
```

Table 4.9: One way ANOVA of tensile modulus of WF 50 HDPE composite

```
Source  DF       SS      MS     F      P
Factor   6  2539062  423177  6.11  0.000
Error   49  3391920   69223
Total   55  5930982
S = 263.1   R-Sq = 42.81%   R-Sq(adj) = 35.81%
```

The regression equations of expected mean of tensile modulus (Y) vs. no. of reprocessing cycles (X) of WF 30 HDPE (eqn. 4.8) and WF 50 HDPE (eqn. 4.9) composite are as follows-

$$Y = 2492 - 59.46\ X \tag{4.8}$$

$$Y = 4766 - 315.4\ X + 40.03\ X^2 \tag{4.9}$$

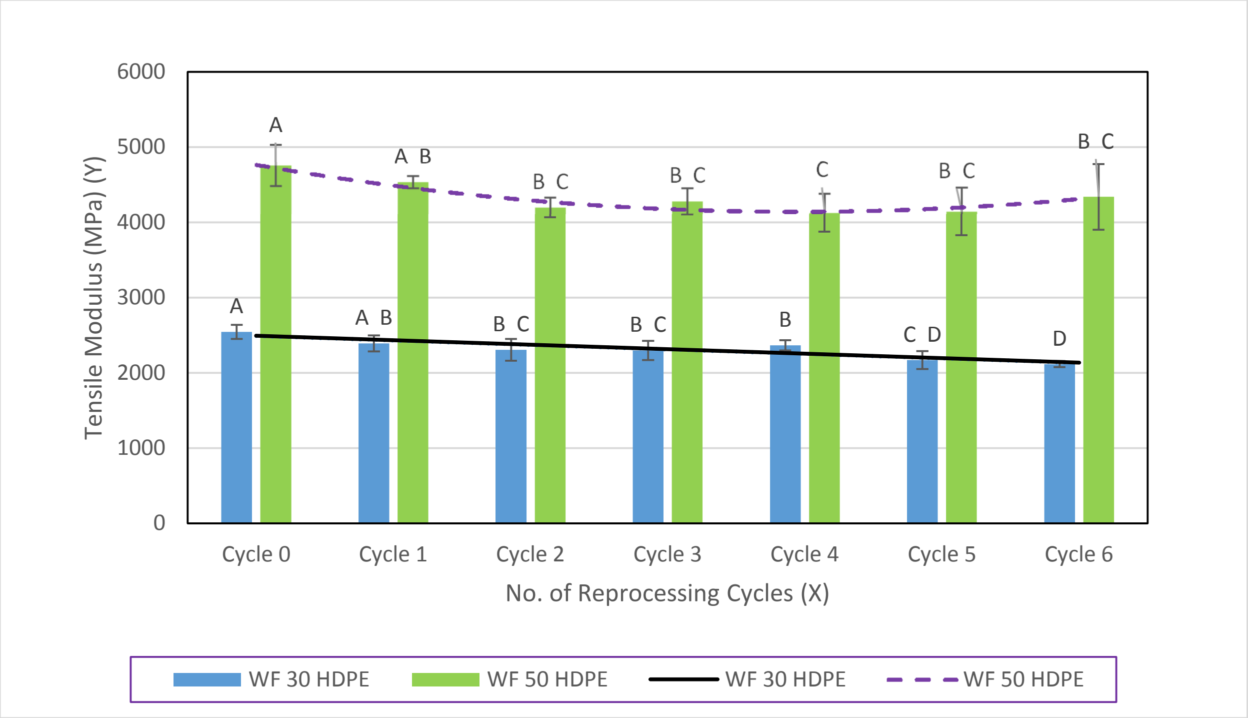

Fig. 4.20: Effect of recycling on the tensile modulus of WF/HDPE composites. Means that do not have a common letter are significantly different.

4.3.3.4.2. Data Analysis of Flexural Modulus

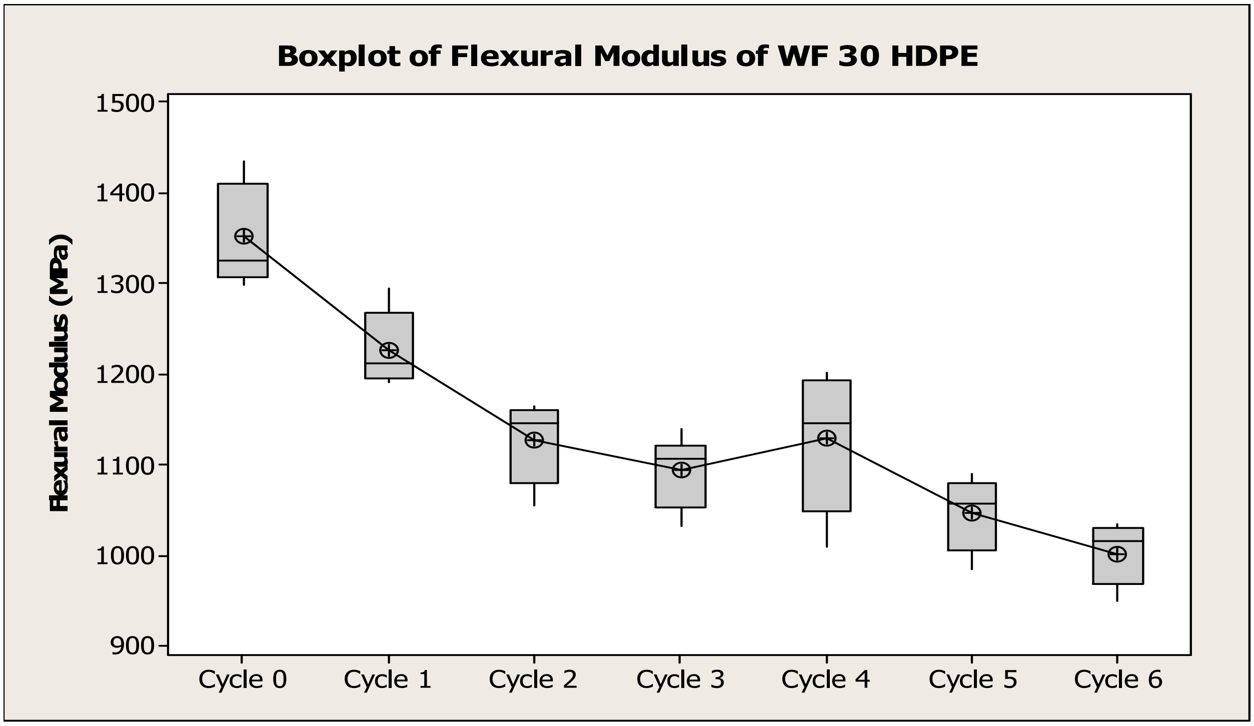

Fig. 4.21: Box plot of flexural modulus of WF 30 HDPE composite.

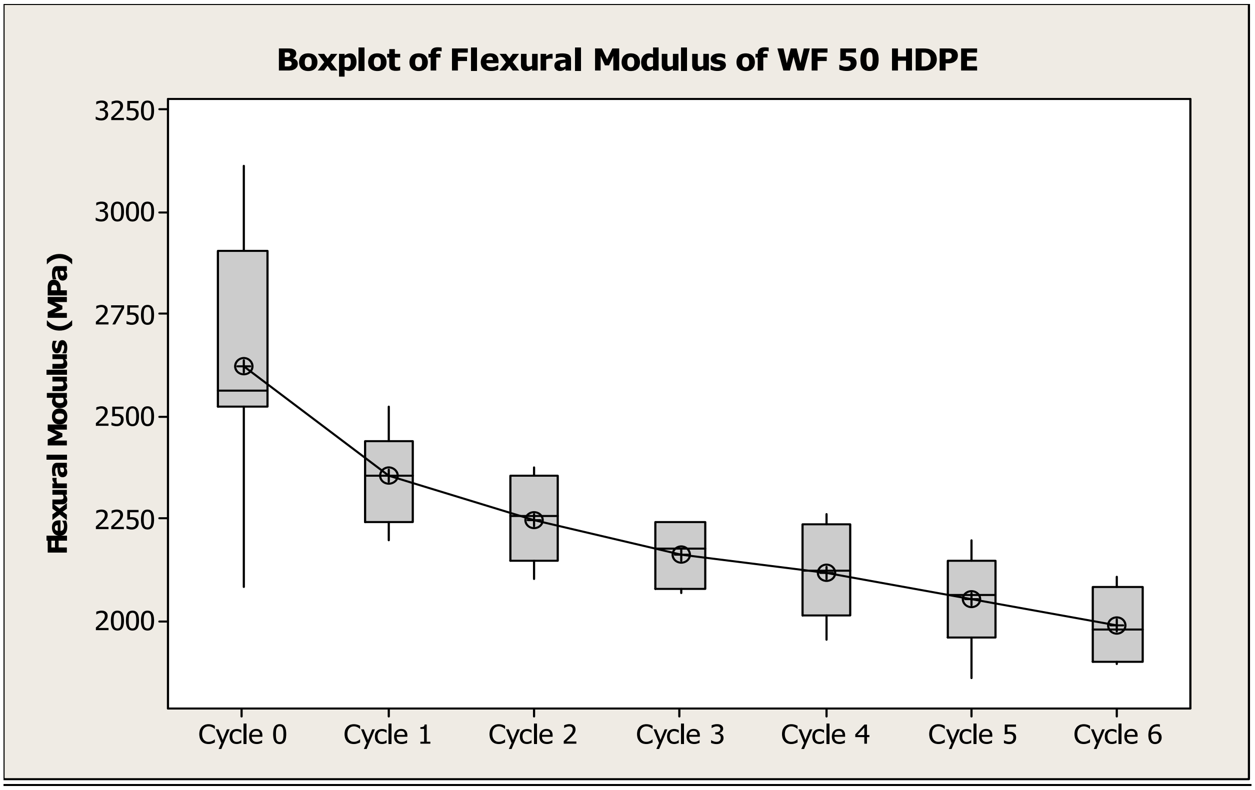

Fig. 4.22: Box plot of flexural modulus of WF 50 HDPE composite.

Table 4.10: One way ANOVA of flexural modulus of WF 30 HDPE composite

```
Source  DF      SS      MS      F      P
Factor   6  665702  110950  47.95  0.000
Error   49  113383    2314
Total   55  779085
S = 48.10   R-Sq = 85.45%   R-Sq(adj) = 83.66%
```

Table 4.11: One way ANOVA of flexural modulus of WF 50 HDPE composite

```
Source  DF       SS      MS      F      P
Factor   6  2206614  367769  15.32  0.000
Error   49  1176606   24012
Total   55  3383221
S = 155.0   R-Sq = 65.22%   R-Sq(adj) = 60.96%
```

The regression equations of expected mean of flexural modulus (Y) vs. no. of reprocessing cycles (X) of WF 30 HDPE (eqn. 4.10) and WF 50 HDPE (eqn. 4.11) composite are as follows-

$$Y = 1358 - 191.3\,X + 50.60\,X^2 - 4.788\,X^3 \tag{4.10}$$

$$Y = 2584 - 187.9\,X + 15.64\,X^2 \tag{4.11}$$

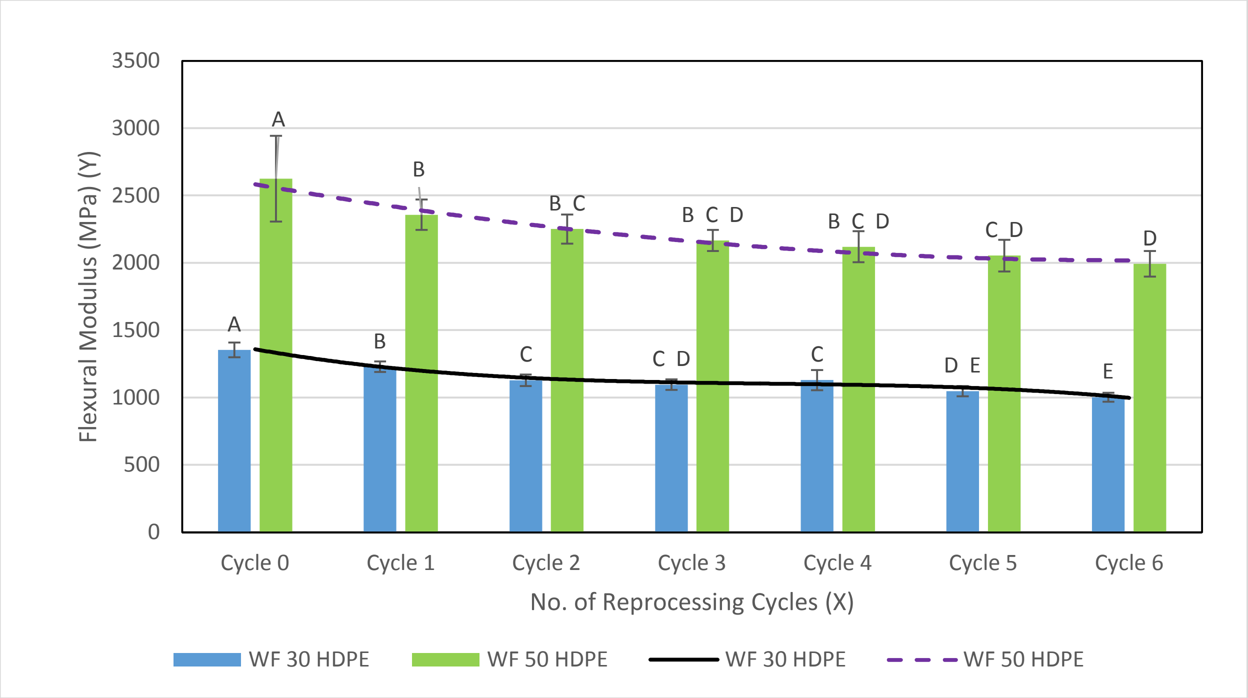

Fig 4.23: Effect of recycling on the flexural modulus of WF/HDPE composites. Means that do not have a common letter are significantly different.

4.3.3.4.3. Data Analysis of Storage Modulus

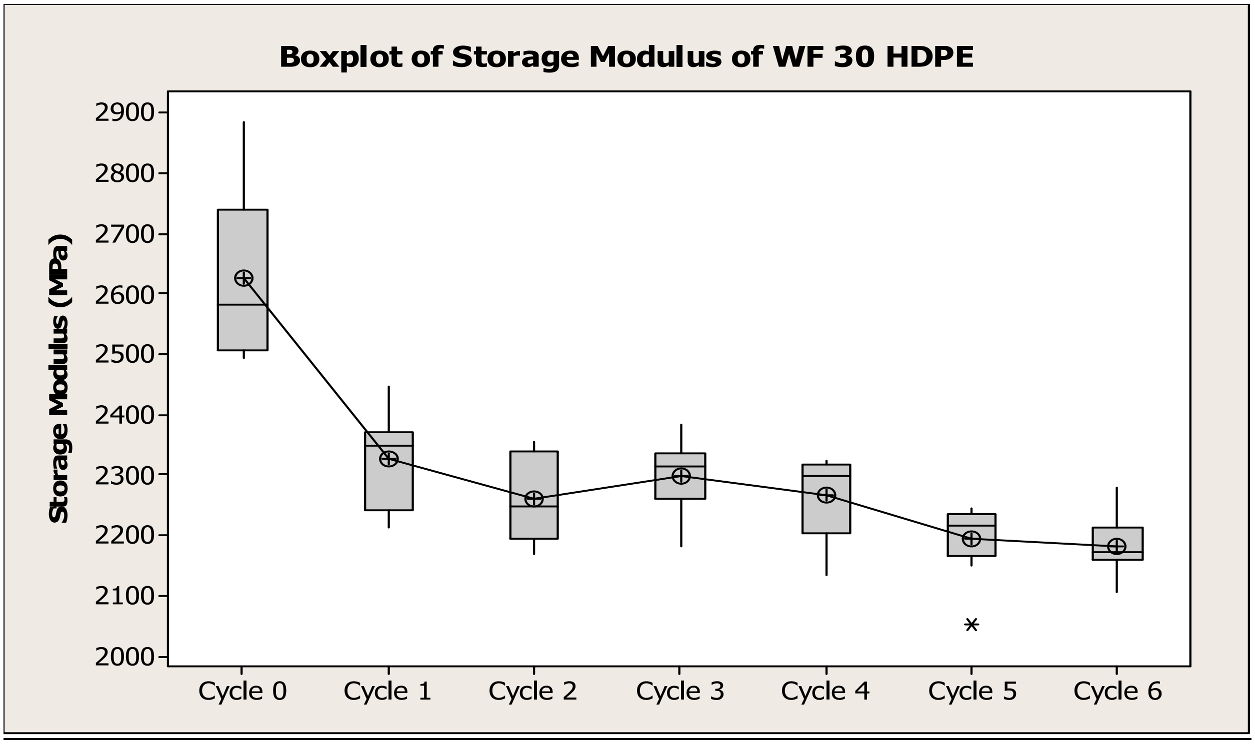

Fig. 4.24: Box plot of storage modulus of WF 30 HDPE composite.

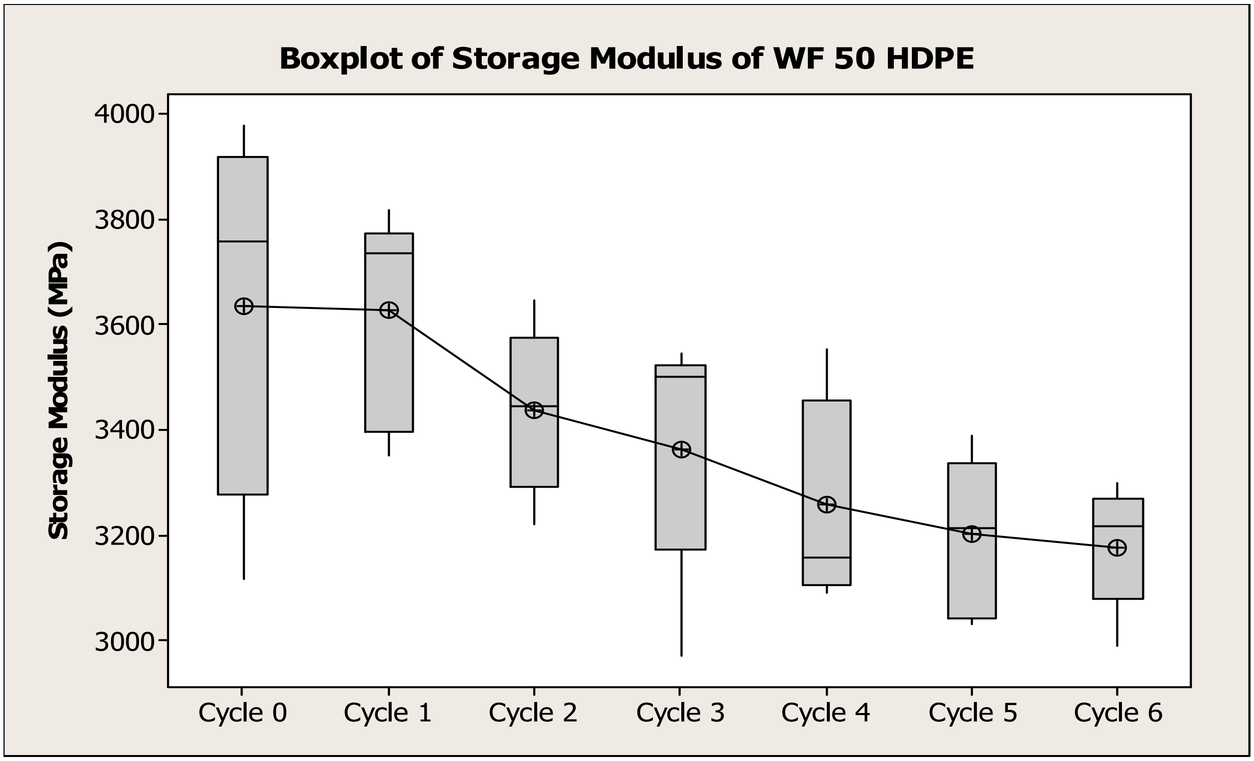

Fig. 4.25: Box plot of storage modulus of WF 50 HDPE composite.

Table 4.12: One way ANOVA of storage modulus of WF 30 HDPE composite

```
Source  DF       SS      MS      F      P
Factor   6  1079006  179834  26.99  0.000
Error   49   326478    6663
Total   55  1405484
S = 81.63   R-Sq = 76.77%   R-Sq(adj) = 73.93%
```

Table 4.13: One way ANOVA of storage modulus of WF 50 HDPE composite

```
Source  DF       SS      MS     F      P
Factor   6  1725522  287587  6.82  0.000
Error   49  2067002   42184
Total   55  3792523
S = 205.4   R-Sq = 45.50%   R-Sq(adj) = 38.82%
```

The regression equations of expected mean of storage modulus (Y) vs. no. of reprocessing cycles (X) of WF 30 HDPE (eqn. 4.12) and WF 50 HDPE (eqn. 4.13) composite are as follows-

$$Y = 2607 - 323.7 X + 94.49 X^2 - 8.830 X^3 \tag{4.12}$$

$$Y = 3643 - 85.55 X \tag{4.13}$$

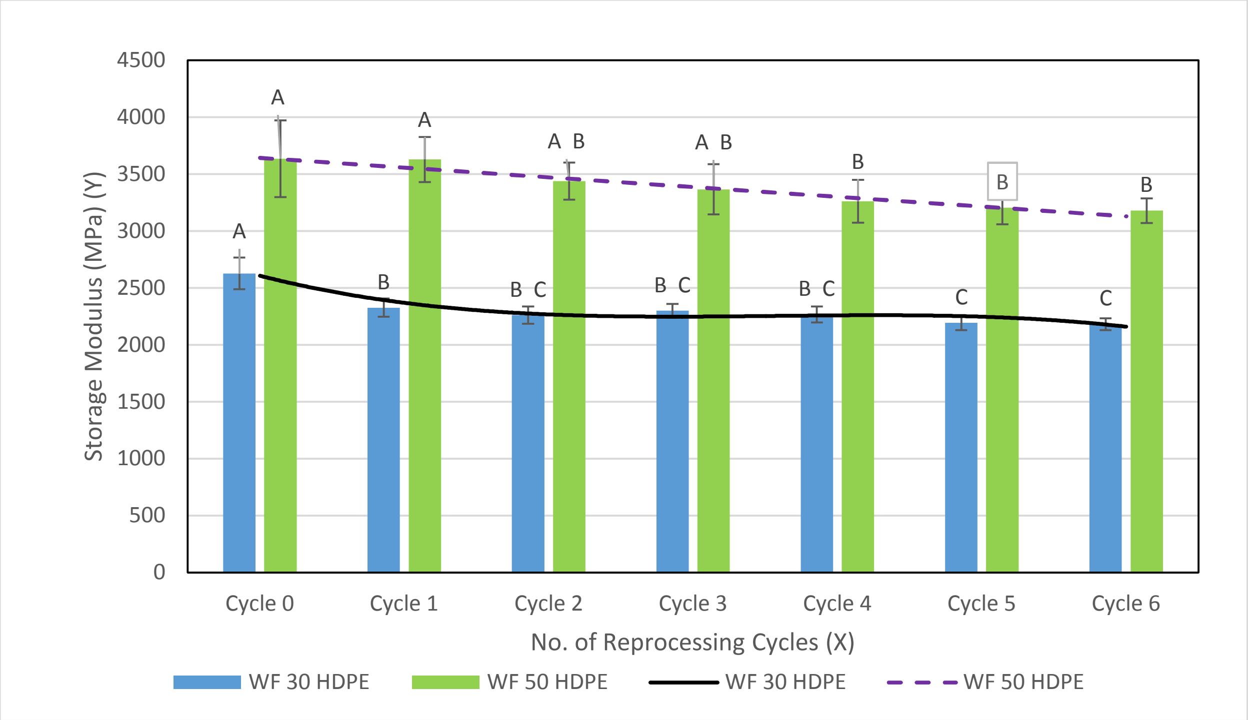

Fig 4.26: Effect of recycling on the storage modulus of WF/HDPE composites. Means that do not have a common letter are significantly different.

4.3.3.4.4. Data Analysis of Heat Deflection Temperature (HDT)

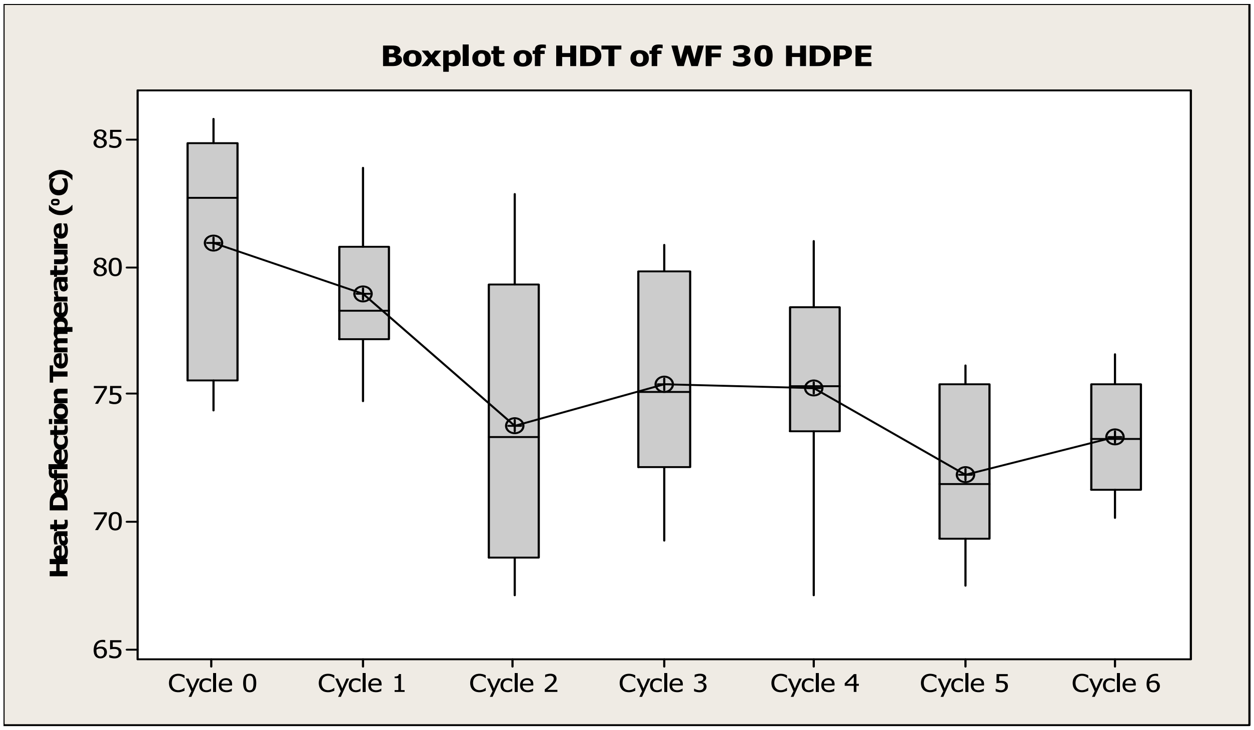

Fig. 4.27: Box plot of heat deflection temperature of WF 30 HDPE composite.

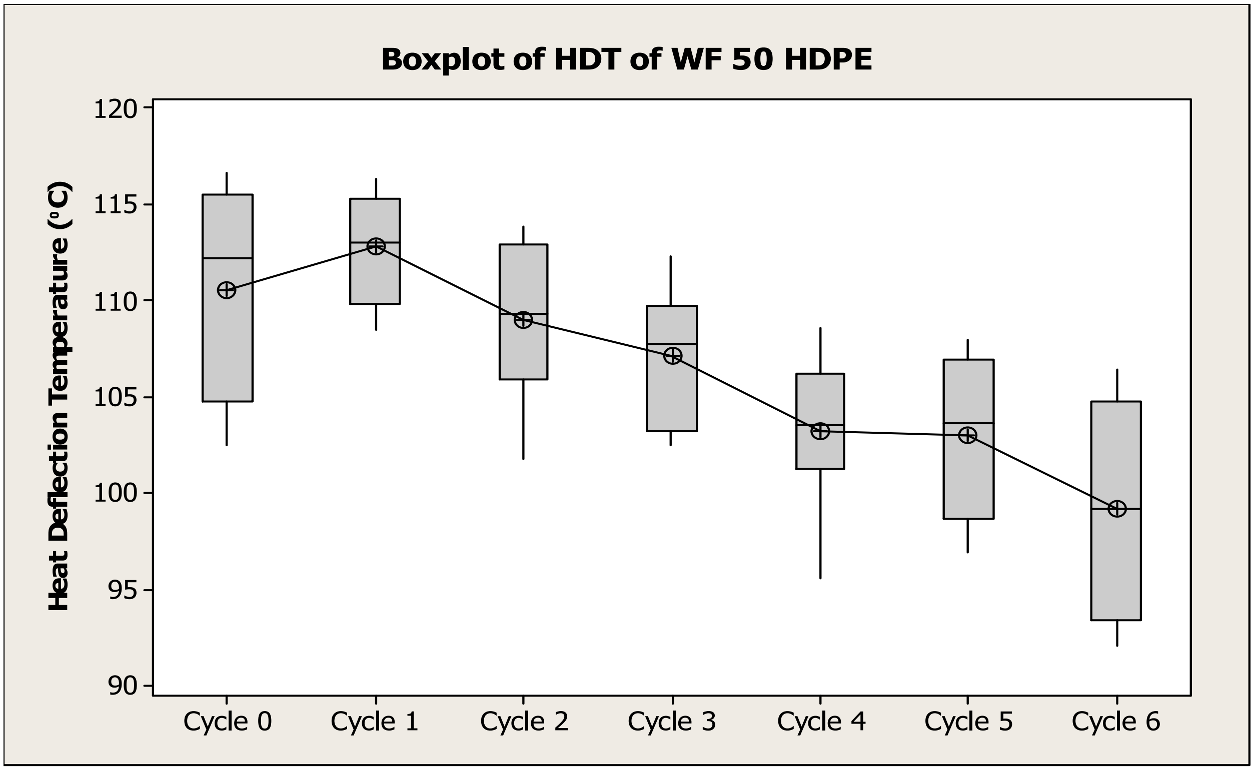

Fig. 4.28: Box plot of heat deflection temperature of WF 50 HDPE composite.

Table 4.14: One way ANOVA of HDT of WF 30 HDPE composite

```
Source  DF      SS    MS     F      P
Factor   6   493.5  82.3  5.16  0.000
Error   49   780.6  15.9
Total   55  1274.1
S = 3.991   R-Sq = 38.74%   R-Sq(adj) = 31.23%
```

Table 4.15: One way ANOVA of HDT of WF 50 HDPE composite

```
Source  DF      SS     MS     F      P
Factor   6  1112.2  185.4  9.36  0.000
Error   49   970.9   19.8
Total   55  2083.2
S = 4.451   R-Sq = 53.39%   R-Sq(adj) = 47.68%
```

The regression equations of expected mean of HDT (Y) vs. no. of reprocessing cycles (X) of WF 30 HDPE (eqn. 4.14) and WF 50 HDPE (eqn. 4.15) composite are as follows-

$$Y = 79.42 - 1.262\ X \tag{4.14}$$

$$Y = 112.8 - 2.120\ X \tag{4.15}$$

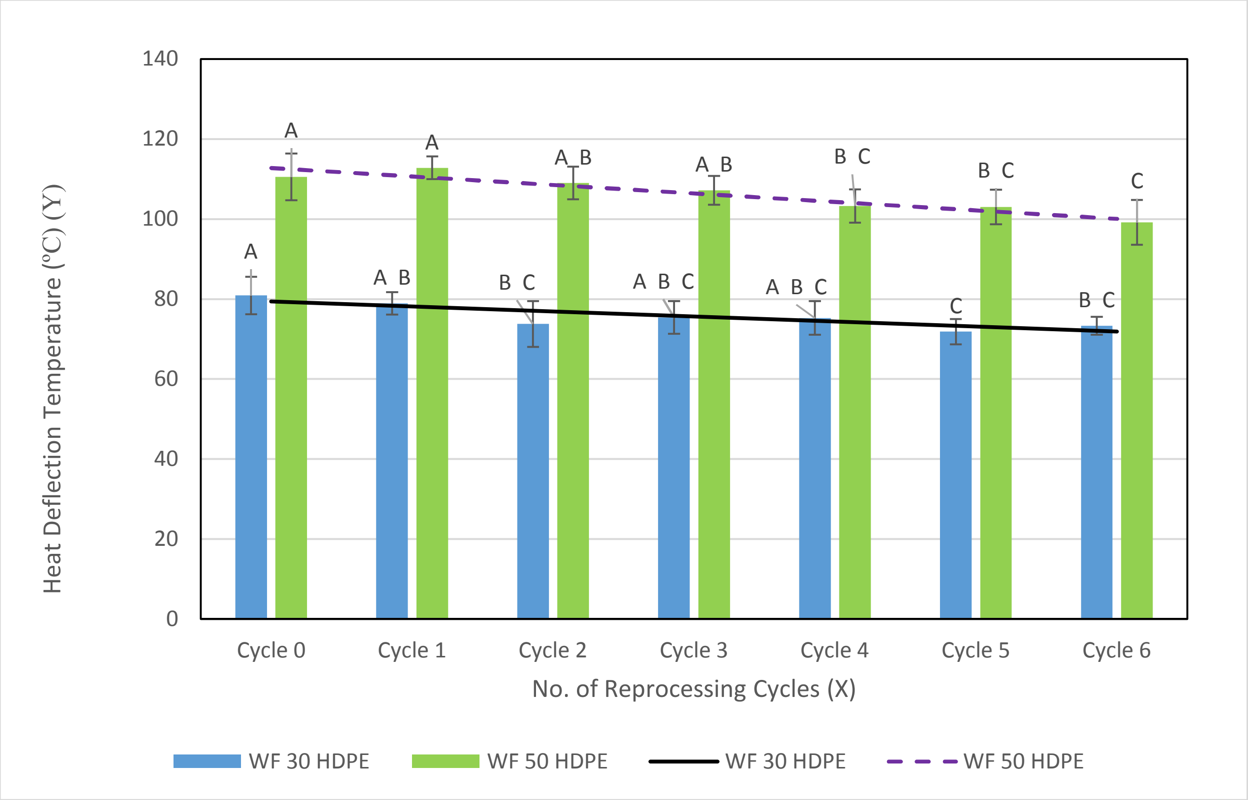

Fig. 4.29: Effect of recycling on the heat deflection temperature of WF/HDPE composites. Means that do not have a common letter are significantly different.

4.3.3.5. Effect of Recycling on Strain Properties

The impact of recycling was statistically found significant on the failure strain, coefficient of thermal expansion (CTE), and melt flow index (MFI) for both composites. On contrast to the strength and stiffness properties, these strain properties increased with increased no. of reprocessing cycles (Figs. 4.32, 4.35, and 4.38). This could be attributed to the fact that the fiber probably degrades higher than the polymer with repetitive extrusion [1]. From cycle 0 to cycle 6, the average fiber length of WF 50 HDPE composite decreased 19.7% while the M_w of HDPE decreased approximately 5% (Sec. 3.3.1-3.3.2). As the fiber degrades higher with successive reprocessing, the polymer properties become more dominant (than the fiber's) in the composite. And since the polymer shows much higher strain than the fiber, higher fiber degradation leads to higher strain properties of the composites at cycle 6. In other words, as the composites become less stiff with successive recycling, they show less resistance to strain (with applied load) that leads to higher strain properties at cycle 6. The associated box plots, ANOVA Tables, and regression equations have been given below for the strain properties of both composites.

Table 4.16: Relative difference of means in the properties of WF HDPE composites between cycle 0 and cycle 6 (values in parentheses are the corresponding standard deviations)

Properties	WF 30 HDPE Composite			WF 50 HDPE Composite		
	Cycle 0	Cycle 6	Relative Difference (%)	Cycle 0	Cycle 6	Relative Difference (%)
Tensile Strength (MPa)	25.80 (0.31)	23.10 (0.14)	-10.45	32.99 (0.28)	29.70 (0.19)	-9.97
Tensile Modulus (MPa)	2544.27 (94.28)	2116.42 (40.23)	-16.82	4755.36 (271.99)	4337.96 (437.34)	-8.78
Failure Strain (%)	8.43 (0.41)	14.05 (1.09)	66.67	4.44 (0.37)	6.16 (0.56)	38.74
Flexural Strength (MPa)	31.20 (1.01)	26.31 (0.72)	-15.67	45.70 (3.48)	41.11 (1.33)	-10.04
Flexural Modulus (MPa)	1353.80 (54.19)	1002.59 (33.43)	-25.94	2624.70 (319.13)	1992.67 (94.75)	-24.08
Impact Resistance (J/m)	55.16 (4.26)	37.14 (1.23)	-32.66	51.97 (4.62)	38.20 (2.34)	-26.51
Heat Deflection Temperature (ºC)	80.90 (4.67)	73.32 (2.27)	-9.37	110.54 (5.84)	99.19 (5.59)	-10.27
Storage Modulus (MPa)	2626.50 (139.17)	2181.38 (52.17)	-16.95	3634.38 (337.16)	3177.75 (109.38)	-12.56
Coefficient of Thermal Expansion (x10^5) (mm/mm/ ºC)	3.18 (0.84)	5.08 (0.62)	59.75	1.71 (1.26)	2.56 (0.95)	49.61
Melt Flow Index (g/ 10 min)	3.25 (0.17)	4.49 (0.06)	38.11	0.56 (0.04)	1.96 (0.04)	252.26

4.3.3.5.1. Data Analysis of Failure Strain

Table 4.17: One way ANOVA of failure strain of WF 30 HDPE composite

```
Source  DF      SS     MS      F      P
Factor   6  167.34  27.89  24.74  0.000
Error   49   55.24   1.13
Total   55  222.57
S = 1.062   R-Sq = 75.18%   R-Sq(adj) = 72.14%
```

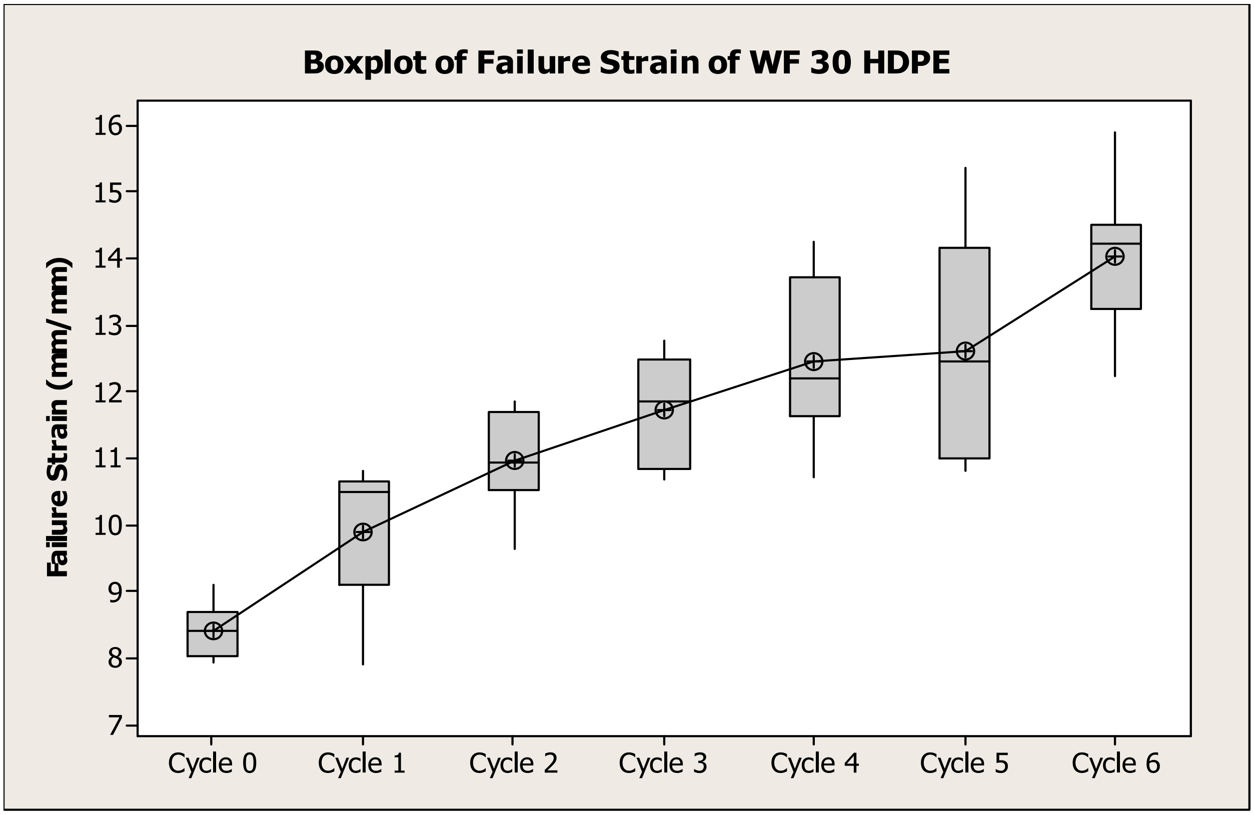

Fig. 4.30: Box plot of failure strain of WF 30 HDPE composite.

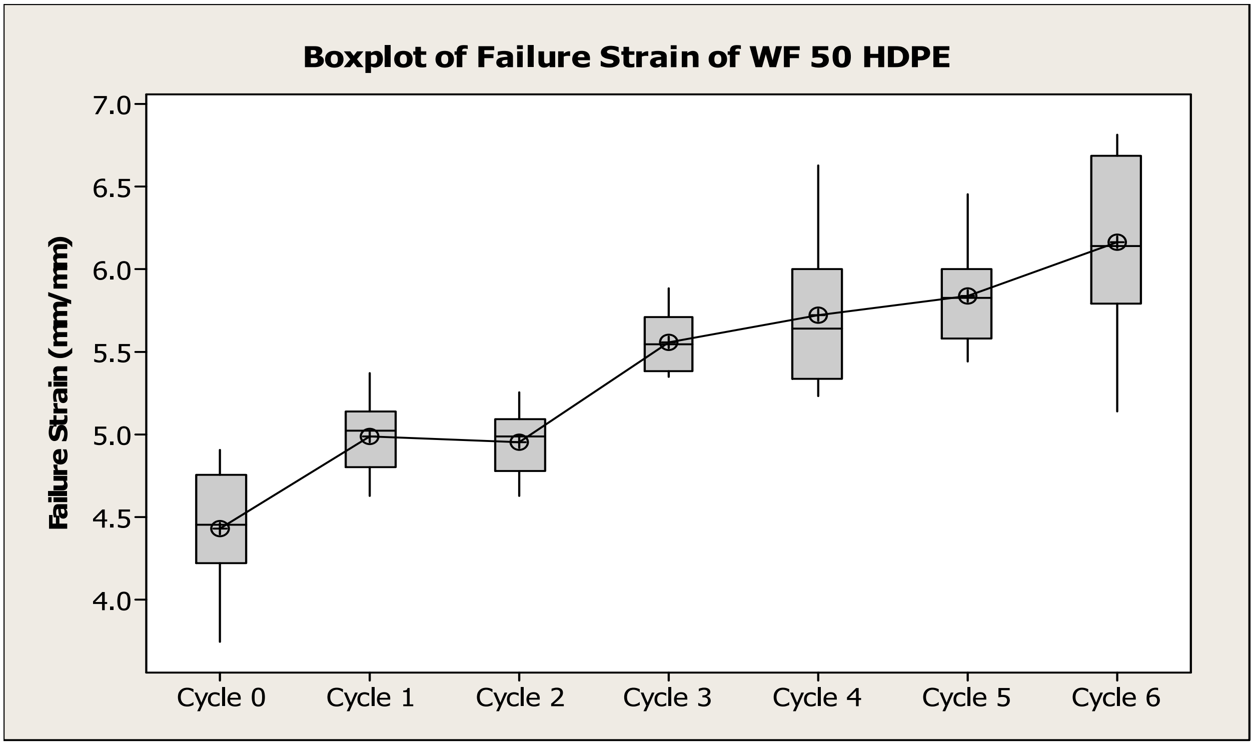

Fig. 4.31: Box plot of failure strain of WF 50 HDPE composite.

Table 4.18: One way ANOVA of failure strain of WF 50 HDPE composite

```
Source  DF      SS     MS      F      P
Factor   6  17.561  2.927  22.55  0.000
Error   49   6.359  0.130
Total   55  23.920
S = 0.3602   R-Sq = 73.42%   R-Sq(adj) = 70.16%
```

The regression equations of expected mean of failure strain (Y) vs. no. of reprocessing cycles (X) of WF 30 HDPE (eqn. 4.16) and WF 50 HDPE (eqn. 4.17) composite are as follows-

$$Y = 8.913 + 0.8479\ X \tag{4.16}$$

$$Y = 4.568 + 0.2729\ X \tag{4.17}$$

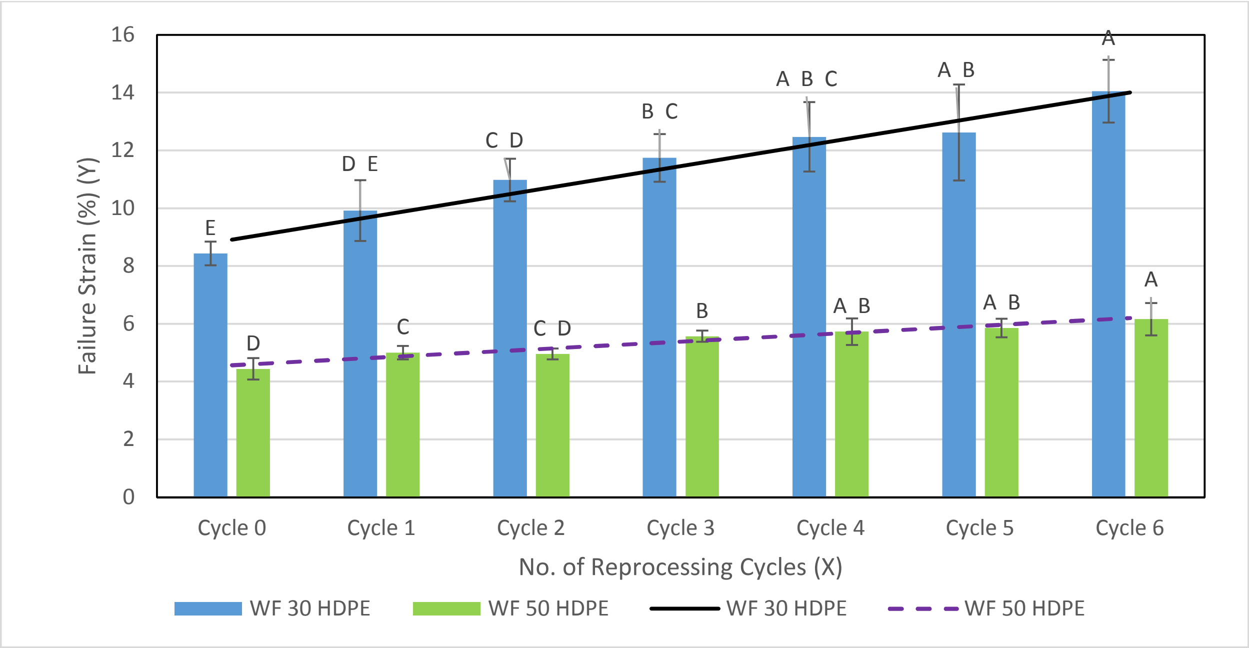

Fig. 4.32: Effect of recycling on the failure strain of WF/HDPE composites. Means that do not have a common letter are significantly different.

4.3.3.5.2. Data Analysis of Coefficient of Thermal Expansion (CTE)

Table 4.19: One way ANOVA of CTE of WF 30 HDPE composite

```
Source  DF          SS          MS     F      P
Factor   6  0.0000000  0.0000000  5.00  0.000
Error   49  0.0000000  0.0000000
Total   55  0.0000000
S = 0.000007986   R-Sq = 37.99%   R-Sq(adj) = 30.40%
```

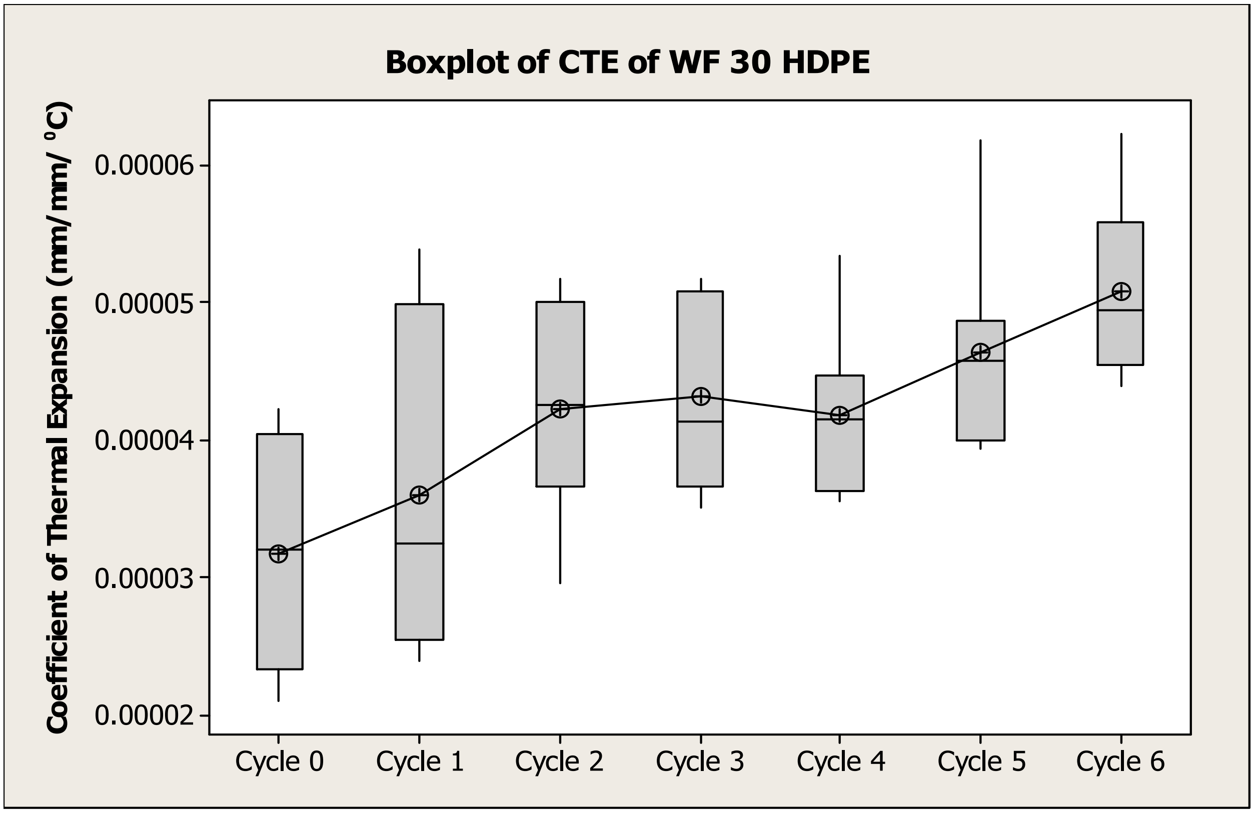

Fig. 4.33: Box plot of CTE of WF 30 HDPE composite.

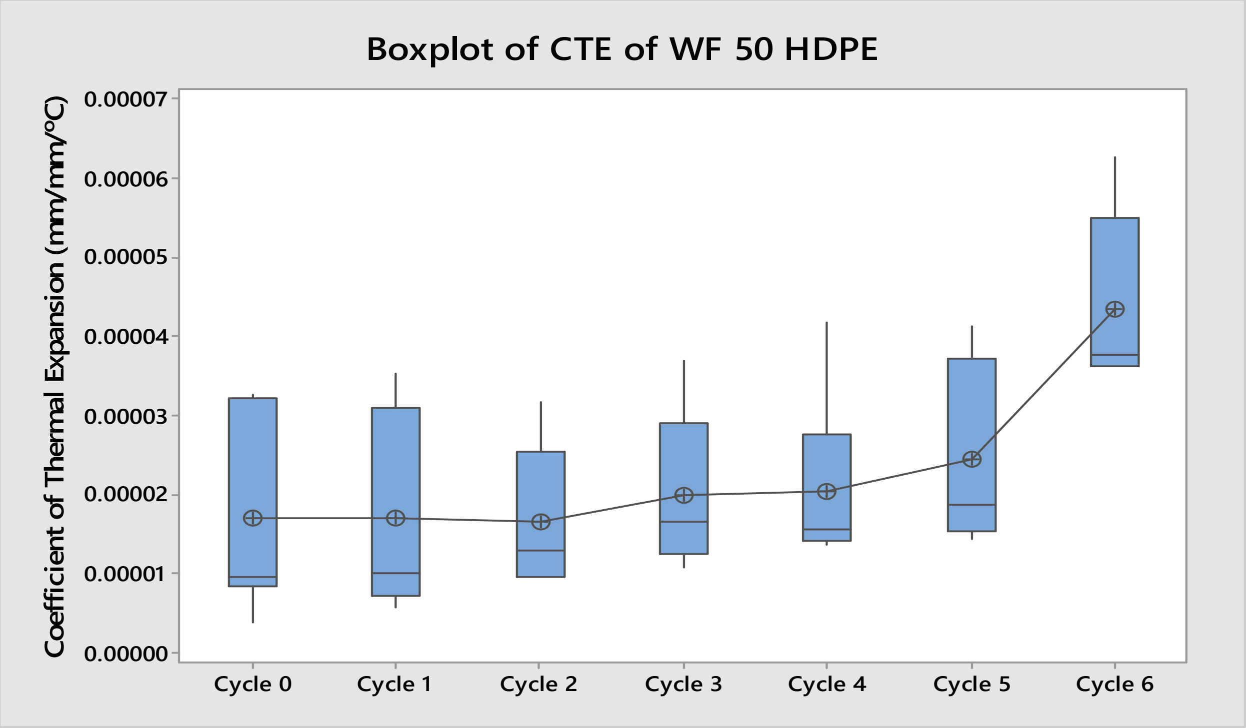

Fig. 4.34: Box plot of CTE of WF 50 HDPE composite.

Table 4.20: One way ANOVA of CTE of WF 50 HDPE composite

```
Source  DF    Adj SS    Adj MS  F-Value  P-Value
Factor   6  0.000000  0.000000     6.12    0.000
Error   49  0.000000  0.000000
Total   55  0.000000
Model Summary
        S    R-sq  R-sq(adj)  R-sq(pred)
0.0000110  42.82%     35.82%      25.32%
```

The regression equations of expected mean of CTE (Y) vs. no. of reprocessing cycles (X) of WF 30 HDPE (eqn. 4.18) and WF 50 HDPE (eqn. 4.19) composite are as follows-

$$Y = 0.000033 + 0.000003 X \tag{4.18}$$

$$Y = 0.000019 - 0.000005 X + 0.000001 X^2 \tag{4.19}$$

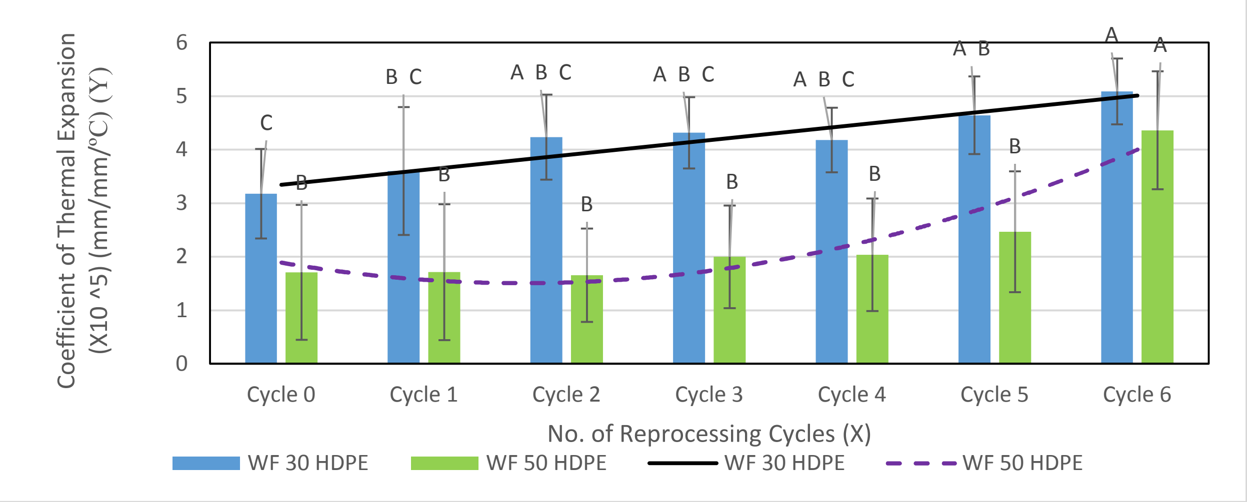

Fig. 4.35: Effect of recycling on the coefficient of thermal expansion of WF/HDPE composites. Means that do not have a common letter are significantly different.

4.3.3.5.3. Data Analysis of Melt Flow Index (MFI)

Table 4.21: One way ANOVA of MFI of WF 30 HDPE composite

```
Source  DF  Adj SS   Adj MS  F-Value  P-Value
Factor   6  5.8459  0.97432    92.31    0.000
Error   28  0.2955  0.01055
Total   34  6.1415
Model Summary
       S    R-sq  R-sq(adj)  R-sq(pred)
0.102736  95.19%     94.16%      92.48%
```

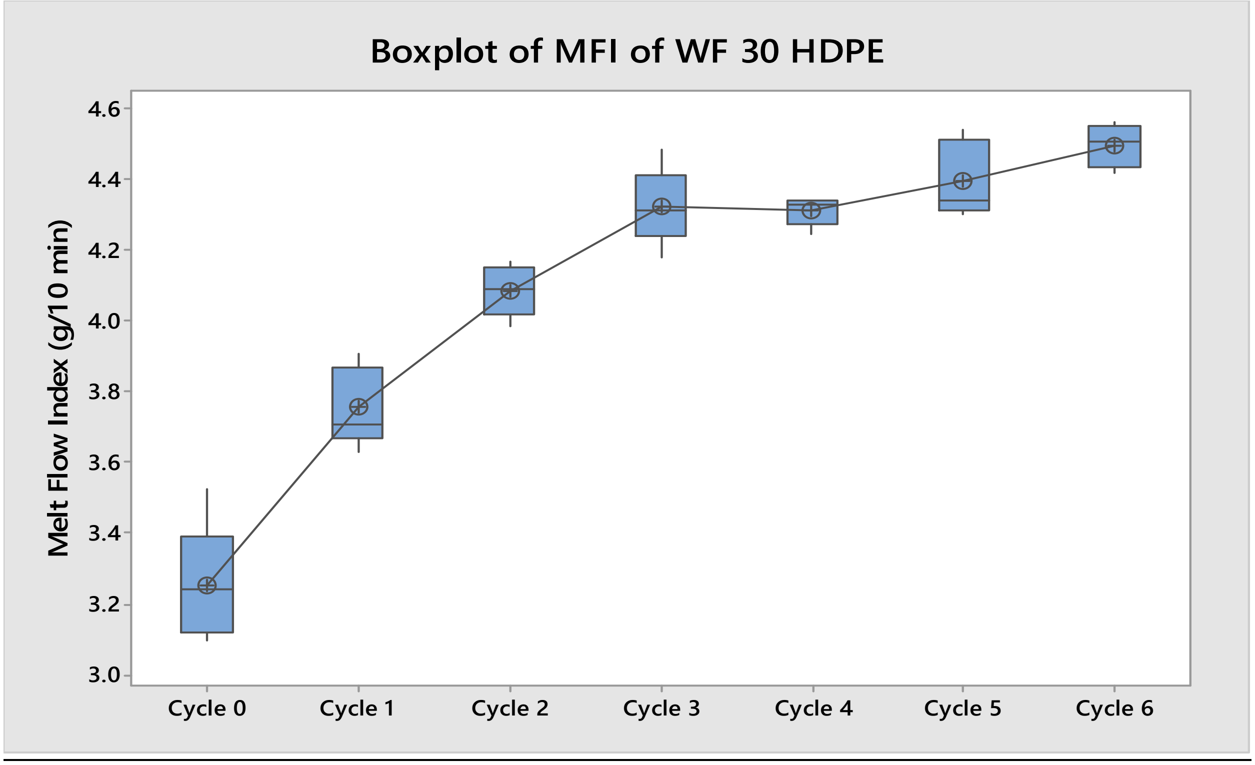

Fig. 4.36: Box plot of MFI of WF 30 HDPE composite.

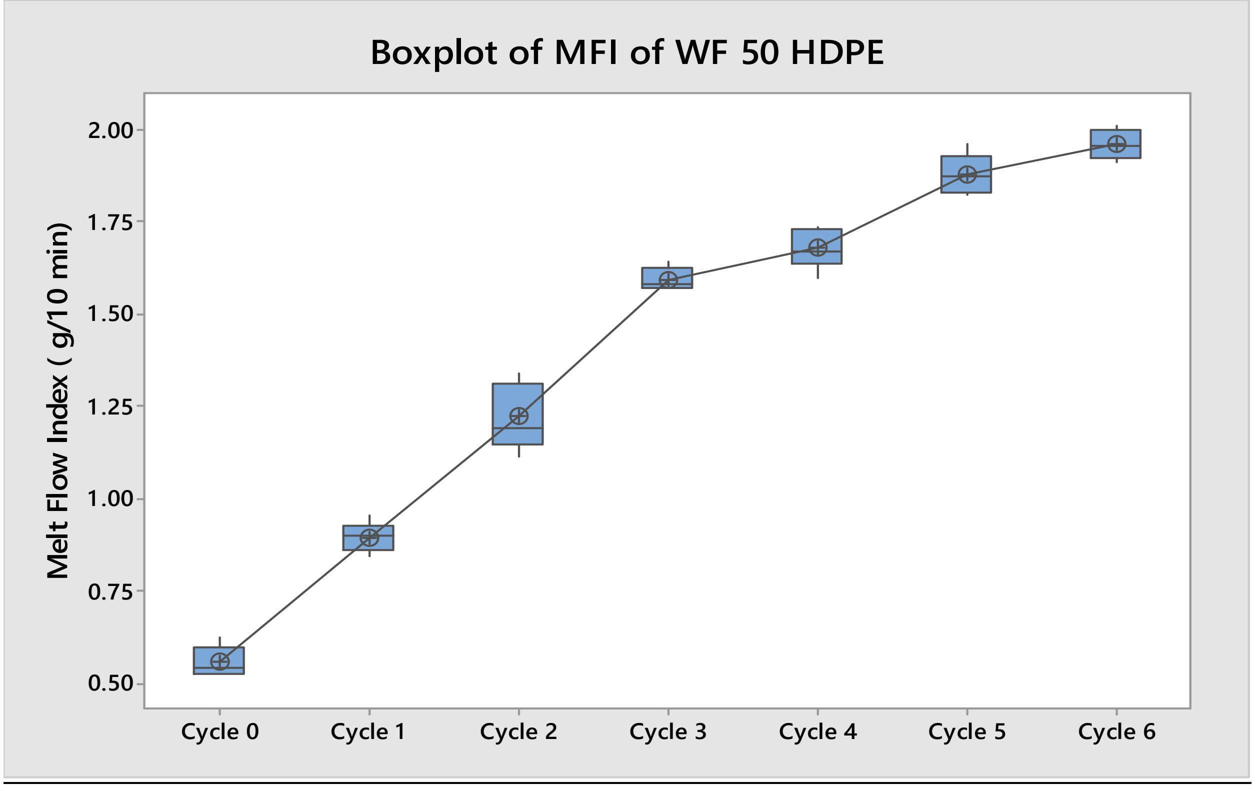

Fig. 4.37: Box plot of MFI of WF 50 HDPE composite.

Table 4.22: One way ANOVA of MFI of WF 50 HDPE composite

```
Source  DF   Adj SS   Adj MS  F-Value  P-Value
Factor   6  8.28545  1.38091   483.09    0.000
Error   28  0.08004  0.00286
Total   34  8.36549
Model Summary
        S    R-sq  R-sq(adj)  R-sq(pred)
0.0534651  99.04%     98.84%      98.51%
```

The regression equations of expected mean of MFI (Y) vs. no. of reprocessing cycles (X) of WF 30 HDPE (eqn. 4.20) and WF 50 HDPE (eqn. 4.21) composite are as follows-

$$Y = 3.243 + 0.6625\ X - 0.1385\ X\verb|^|2 + 0.01045\ X\verb|^|3 \qquad (4.20)$$

$$Y = 0.5387 + 0.4147\ X - 0.02961\ X\verb|^|2 \qquad (4.21)$$

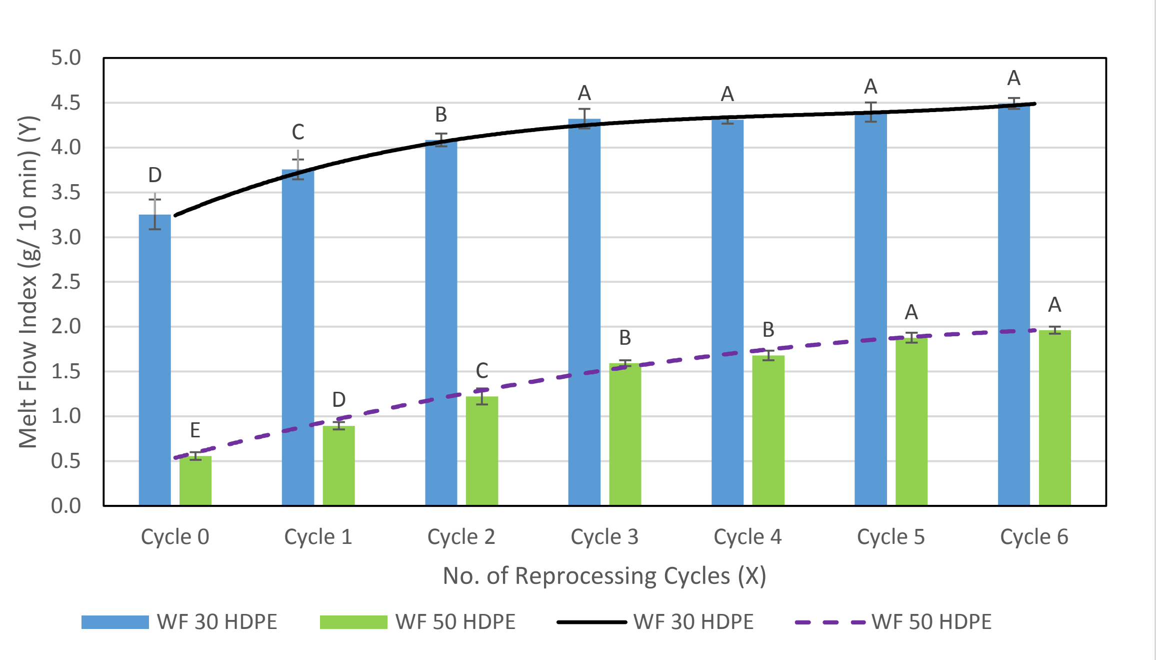

Fig. 4.38: Effect of recycling on the melt flow index of WF/HDPE composites. Means that do not have a common letter are significantly different.

4.3.3.6. FTIR Analysis

Fourier Transform Infra-Red Spectroscopy (FTIR) was performed at cycle 0 and cycle 6 of each formulation (Figs. 4.39 and 4.40). This experiment denoted continuing degradation of these composites during recycling. The characteristic absorptions, functional groups, type of vibration, and type of chemical reactions are given in Table 4.23 and 4.24. Some functional groups such as carboxylic acid, alcohol, ketone, aldehyde, and ether indicate oxidative product formation while others such as amine and double bond indicate weaker bond formation or unsaturation [38, 39]. These functional groups (oxidative and weaker bond) imply the ongoing degradation of the composites by successive recycling. Each composite shows almost the same characteristic absorptions at cycle 0 and cycle 6. However, the relative degradation- between cycle 0 and corresponding cycle 6- could not be compared due to the inconsistencies in the experiment such as thickness difference and heterogeneity of small composite samples.

Table 4.23: FTIR analysis of WF 30 HDPE composite at cycle 0 and cycle 6 [38, 39]. Left and right characteristic absorptions in the first column respectively indicate the wavenumber of cycle 0 and cycle 6. Otherwise, the wavenumbers are same for both cycles.

Characteristic Absorptions (cm^{-1})	Functional Group	Type of Vibration	Indication by Functional Group
1688 / 1700	Ketone or Aldehyde	Stretch	Oxidation
1649	Amine	Stretch	Weaker Bond
1508	Aromatic Double Bond	Bending	Weaker Bond
1464	Amine	Stretch	Weaker Bond
1368	Alcohols or Phenols	Bending	Oxidation
1239 / 1243	Carboxylic Acid	Stretch	Oxidation
1063 / 1059	Ether / Amine	Stretch	Oxidation / Weaker Bond
723	Amine	Bending	Weaker Bond

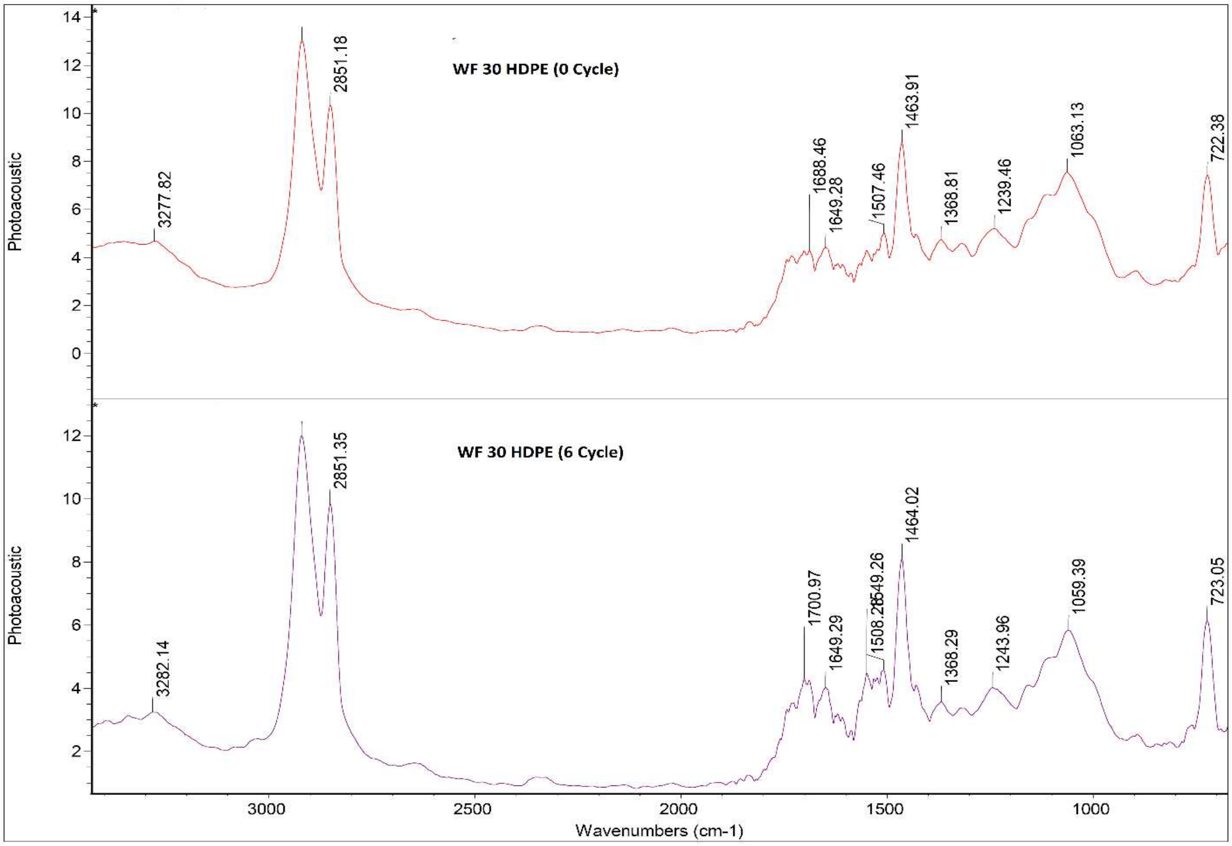

Fig. 4.39: FTIR spectra of WF 30 HDPE composite at cycle 0 (red) and cycle 6 (blue).

Table 4.24: FTIR analysis of WF 50 HDPE composite at cycle 0 and cycle 6 [38, 39]. Left and right characteristic absorptions in the first column respectively indicate the wavenumber of cycle 0 and cycle 6. Otherwise, the wavenumbers are same for both cycles.

Characteristic Absorptions (cm^{-1})	Functional Group	Type of Vibration	Indication by Functional Group
1605 / 1602	Amine	Bending	Weaker Bond
1506	Carboxylic Acid	Bending	Oxidation
1463	Amine	Stretch	Weaker Bond
1367 / 1325	Alcohols or Phenols	Bending	Oxidation
1242 / 1238	Carboxylic Acid	Stretch	Oxidation
1063	Ether / Amine	Stretch	Oxidation / Weaker Bond
723 / 721	Alcohols or Phenols	Bending	Oxidation

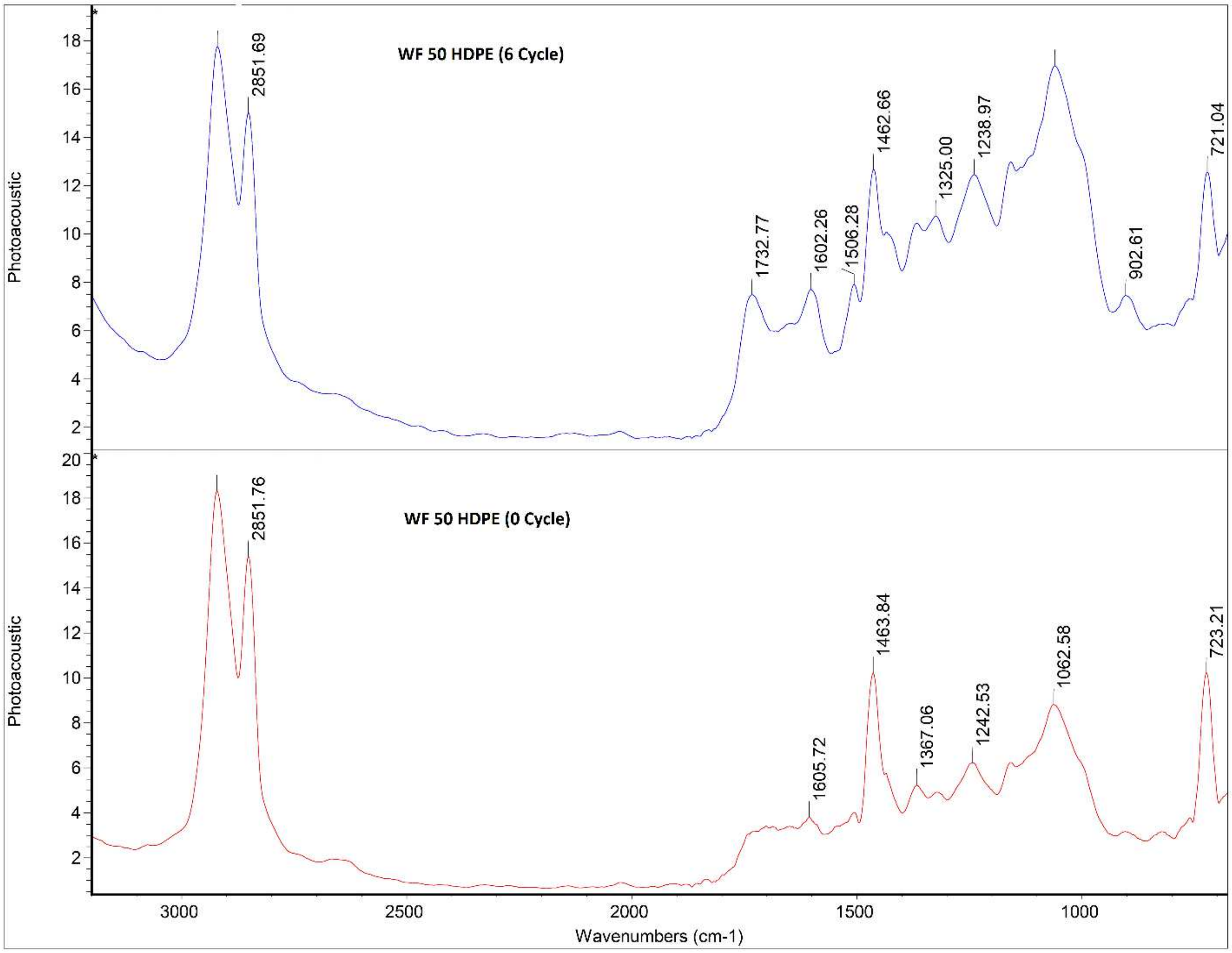

Fig. 4.40: FTIR spectra of WF 50 HDPE composite at cycle 0 (pink) and cycle 6 (blue).

4.3.3.7. Effect of Recycling on Crystallinity and Thermal Stability

Table 4.25 and Fig. 4.41 show the results of DSC analysis of WF 50 HDPE composite at cycle 0 and cycle 6. The percentage crystallinity of HDPE in composite was measured by the following equation [2]-

$$\% \text{ Crystallinity}=\left(\frac{\Delta H_{exp}}{\Delta H}\right) x \left(\frac{1}{W}\right) x100 \qquad (4.22)$$

Here, ΔH_{exp} is the experimental heat of fusion determined by DSC, ΔH is the heat of fusion of fully crystalline HDPE (289.3 J/g), and W is the weight fraction of HDPE in the composite. The crystallinity and crystalline temperature of HDPE (in composite) decreased but melting point increased with increased no. of reprocessing cycles. This could possibly be due to the higher degradation of fiber that to polymer with repetitive extrusion. Since fiber incorporation helps increase polymer crystallinity [1], higher fiber degradation at cycle 6 results in less crystallinity of HDPE. The crystalline temperature of HDPE decreased with successive reprocessing due to the molecular weight reduction of the polymer. However, the melting point of HDPE slightly increased from 132.67 °C (cycle 0) to 134.09 °C (cycle 6) probably because of the increase in thermal stability of the composite (discussed next).

Table 4.25: DSC analysis of WF 50 HDPE composite at cycle 0 and cycle 6

Property	Cycle 0	Cycle 6
Melting Point (ºC)	132.67	134.09
Crystalline Temperature (ºC)	114.67	114.40
Heat of Fusion (J/g)	85.97	78.64
Crystallinity (%)	63.23	57.83

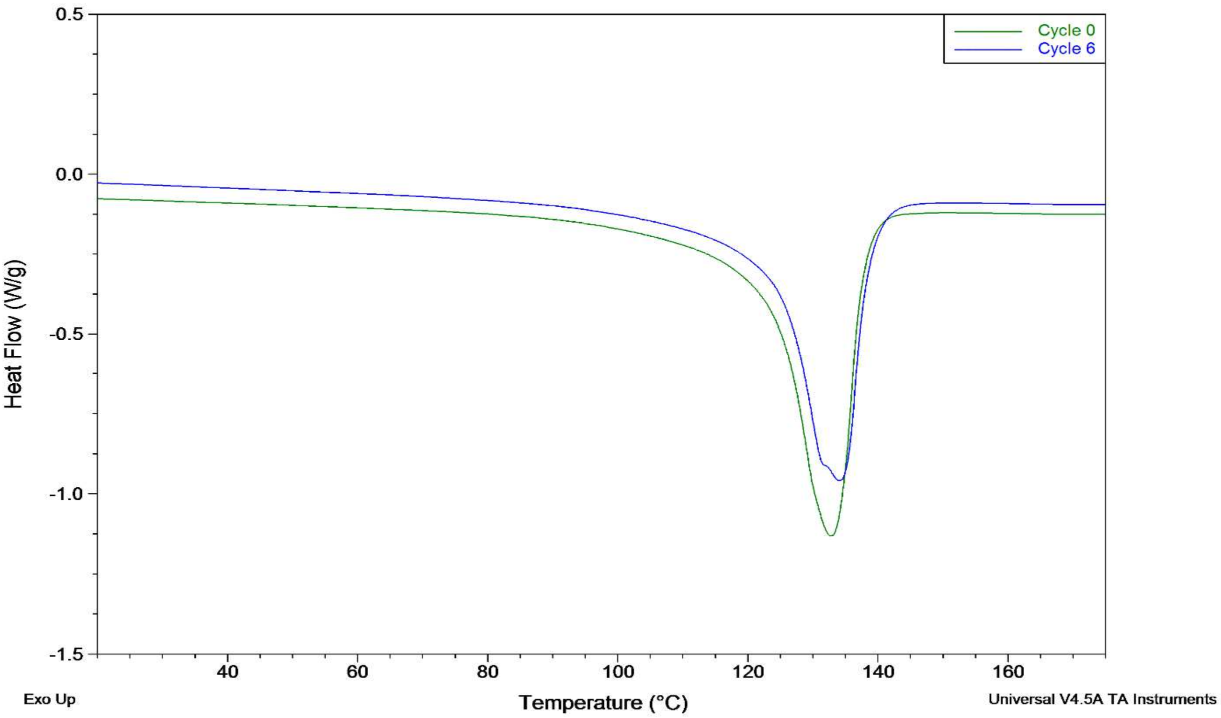

Fig. 4.41: DSC curves of WF 50 HDPE composite at cycle 0 and cycle 6.

Thermal stability of WF 50 HDPE composite increased with increased no. of reprocessing cycles (Table 4.26, and Figs. 4.42 and 4.43). Both the onset degradation temperature and fastest decomposition temperature increased from cycle 0 to cycle 6. This could be due to the molecular weight reduction of the polymer by repetitive extrusion [1]. Additionally, the amount of volatile materials in the composite was probably reduced due to reprocessing that led to higher thermal stability of the composite at cycle 6.

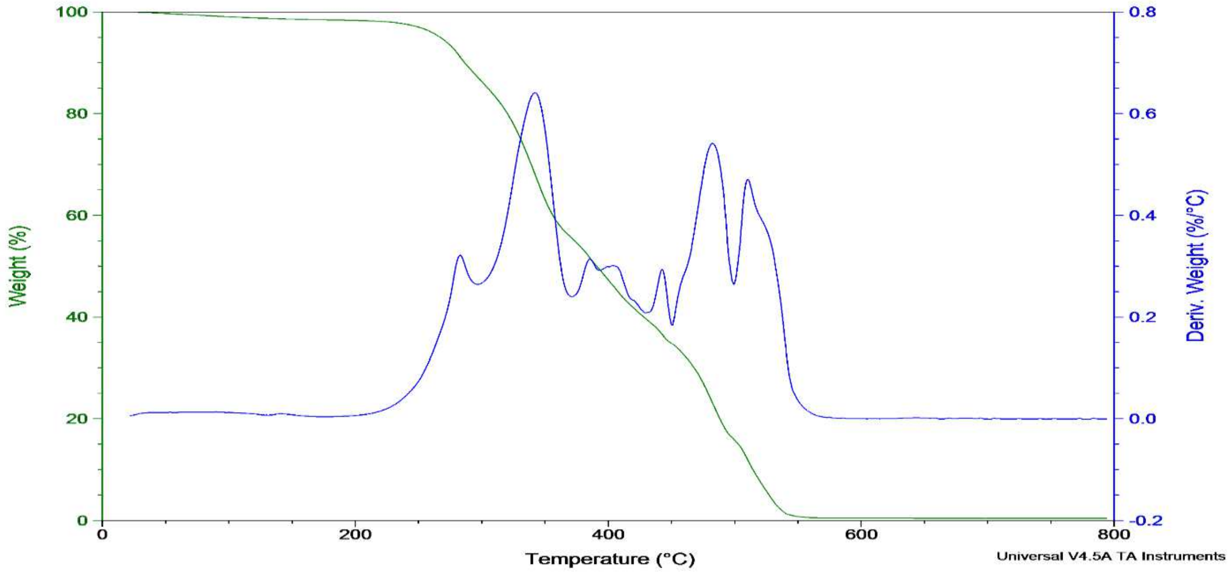

Fig. 4.42: TGA curve and 1st derivative of the curve of WF 50 HDPE composite at cycle 0.

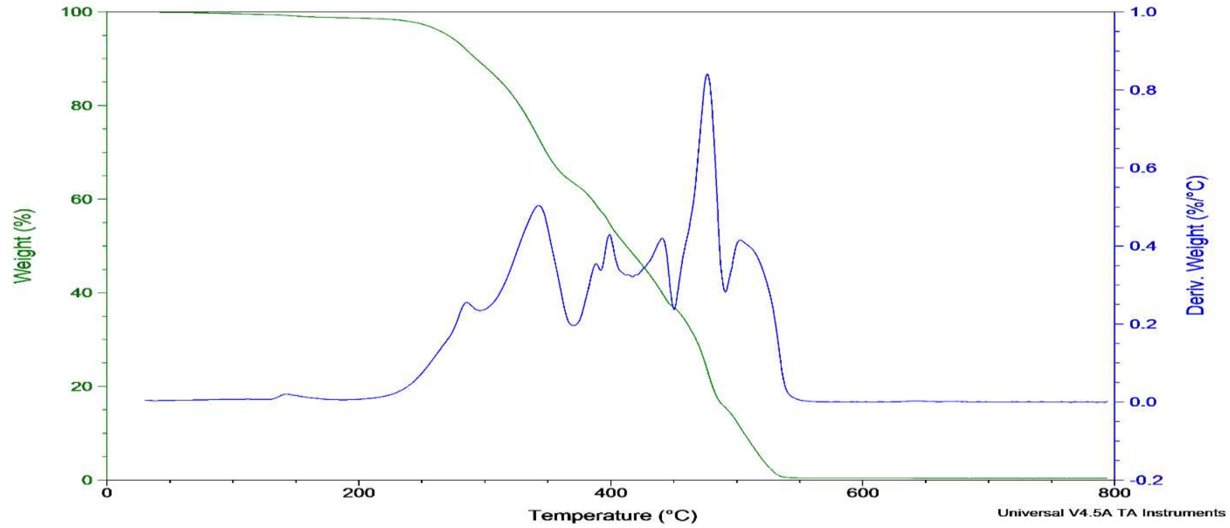

Fig. 4.43: TGA curve and 1st derivative of the curve of WF 50 HDPE composite at cycle 6.

Table 4.26: TGA of WF 50 HDPE composite at cycle 0 and cycle 6

Property	Cycle 0	Cycle 6
Onset Thermal Degradation Temperature (ºC)	294.12	362.63
Fastest Decomposition Temperature (ºC)	341.46	476.11
Residue (%)	0	0

4.4. Conclusion

WF/HDPE composites were made from oak wood flour, HDPE, and a coupling agent (MAPE). Two composite formulations- 30 and 50 wt% filler individually with 3 wt% MAPE- were prepared by extrusion. The coupling agent improved most strength and stiffness properties of both composites. Higher WF content increased strength and stiffness properties but decreased strain properties of the composite. Both composites were individually recycled up to 6 times by extrusion and test samples were made by injection molding. The effect of recycling was statistically found significant for all mechanical and thermo-mechanical properties of both composites. With successive recycling, strength and stiffness properties of the composites decreased but strain properties increased- mostly due to the fiber and polymer degradation. However, the relative change or degradation, produced by recycling, was found mild in all strength and stiffness properties of these composites.

CHAPTER 5. IMPACT OF RECYCLING ON THE MECHANICAL AND THERMO-MECHANICAL PROPERTIES OF WF/PLA COMPOSITE

This chapter describes in detail the effect of recycling on the mechanical and thermo-mechanical properties of WF/PLA composite.

5.1. Introduction

At present, biodegradable polymers and their natural fiber composites are preferred to non-biodegradable plastics and their composites all over the world [41, 42]. This is because, biodegradable polymers and their natural fiber composites are not only environment friendly but capable of higher properties. Non-biodegradable polymers and their composites need thousands of years to degrade [44] and create huge environmental pollution at the end of their life cycle (by disposal in landfills and incineration). In addition, these oil-based polymers could be produced in a limited amount since the reserved petroleum in the world would end up sometime [52, 53, 56, 61]. On contrast, biodegradable polymer, such as Poly Lactic Acid (PLA), takes only a few years to degrade. PLA is an aliphatic thermoplastic polyester generated by polymerization or poly condensation of monomers of lactic acid and these monomers can be produced from natural resources such as sugar, beet, wheat, and corn [61, 66]. PLA has higher strength and stiffness, and is regarded as the best of all environment friendly polymers [53]. It has a wide range of application such as in- biomedical field (e.g., drug delivery devices, sutures, scaffolds, and pins.) [49, 52], electronic field (e.g., portable device housings) [50], automotive industry and construction (e.g., interior panels and indoor furnishing) [58, 59], and disposable items (e.g., packaging, plastic bags, disposable cups and plates, planting, and compostable bottles) [49, 50, 52, 55, 59]. However, incorporation of fiber in PLA is necessary since the polymer alone could not meet all desired requirements of an engineered material [45]. Incorporation of fiber also reduces the manufacturing cost. Wood is the most available renewable resource all over the world [43]. Wood fiber is better in properties compared to many synthetic fibers (e.g., glass fiber) due to its lower density, lower cost, higher specific strength and stiffness, ease of processing, and biodegradability [42, 52-54, 56]. Regarding these benefits, WF/PLA composite could be considered a competent bio-compostable engineered material

Along with a lot of advantages, PLA and WF come with some drawbacks and so their composite. Even though these WPCs are creating position in the commercial market, PLA is yet to be used in extensive commercial engineering applications because of its lower impact resistance, lower softening temperature, higher brittleness, poor moisture resistance, and lower heat deflection temperature [42, 54, 63, 65, 66]. The manufacturing cost of PLA is comparatively higher, and the profitability in PLA manufacturing has not yet been established strong enough to trust [45]. Similarly, wood fiber (WF) also has some drawbacks such as lower bulk density, higher heat sensitivity, and its hygroscopic nature (absorbs moisture) [42]. When WF is compounded with PLA, the fiber could not possibly be uniformly dispersed in the matrix. This could result in less stress transfer from matrix to fiber and hence produce lower load carrying capacity of the composite [43]. However, despite these challenges, the amount of WPCs of PLA, at present, is increasing in the commercial market [53].

As the production of WF/PLA composites is increasing, primarily because of their biodegradability and renewability, the disposal of these WPCs after used only once would lead to a huge amount of material waste which is unnecessary and uneconomical. In this case, recycling could be a good processing method at the end of their (WPCs) service lives since this process would widen their life time and reduce the consumption on the new resources. As a result, the impact on the environment would reduce significantly [41]. In addition, the recycled materials could be less expensive and thus help improve the global economy. Because of these benefits, recycling could be considered a viable method for managing WF/PLA composite waste. And research work is going on to investigate the effect of recycling on the properties of these WPCs.

However, few research work have been reported on the recycling of WF/PLA composites, to date, since PLA is yet to be recognized as a fully commercial polymer such as PE or PP. In most research, recycling of PLA based WPCs has been done with virgin PLA and recycled fiber, or vice-versa. Duigou et al. recycled virgin Flax/PLA composite by injection molding up to six times, and concluded that the WPC could be recycled up to 3 times without major degradation in properties [41]. Pilla et al. formulated recycled composite of virgin PLA and recycled fiber, and found that 10 wt% fiber WPC did not degrade while 20 wt% fiber WPC degraded highly during processing [42]. Huda et al. also made recycled WPC of recycled newspaper fiber and virgin PLA, and reported equivalent mechanical properties of the recycled WPC to virgin talc/PLA or virgin talc/PP composite [43]. Huda el al. made another experiment on recycled WPC produced from virgin PLA and recycled cellulose fiber (of newsprint), and found comparable physico-mechanical properties of the recycled WPC with that of high performance composites [46].

The aim of this chapter is to investigate the effect of recycling on the mechanical and thermo-mechanical properties of oak WF/PLA composite. In this regard, two formulations- 30 and 50 wt% filler composites, each with 3 wt% PLA-g-MA (coupling agent) - were individually recycled up to six times by extrusion. Virgin composites without PLA-g-MA (for both formulations) were also made to investigate the impact of the coupling agent, and were never recycled.

5.2. Experimental Procedure

5.2.1. Materials

Oak wood flour were provided by Southern Wood Services, GA, USA. The particle size distribution of wood flour has been given in Table 1.2. Poly Lactic Acid (Ingeo Biopolymer 2003D) was provided by NatureWorks LLC, MN, USA. The polymer has a MFI of 6 g/10 min (210 ºC, 2.16 Kg), specific gravity of 1.24, and heat deflection temperature of 55 ºC (Table 1.4). PLA-g-MA was made by extrusion process in the laboratory and used as the coupling agent.

5.2.2. Methods

5.2.2.1. Composite Preparation

Composite pellets were prepared from 30 and 50 wt% wood flour (WF) with PLA and 3 wt% PLA-g-MA by using a twin screw co-rotating extruder (Leistriz Micro 18 GL 40 D, NJ, USA). Test samples were prepared from the composite pellets by using a single screw injection molder (Model SIM- 5080, Technoplas Inc., Ohio, USA). Prior to extrusion, WF, PLA-g-MA, and PLA were dried in an oven at 80 ºC for at least 24 hours. The moisture content of the dried filler was found less than 0.5%. All these dried materials were mixed and passed through the extruder. The extruder has seven different temperature zones. The temperature profile of these zones (from feed section to melting section) was 157 ºC, 180 ºC, 190 ºC, 200 ºC, 200 ºC, 202 ºC, 205 ºC. The temperature of the die and gate adapter was kept at 205 ºC. The screw rpm of the extruder was set at 200. After extrusion, composite strands were passed through a water bath to cool down to room temperature followed by pelletizing. A portion of these pellets were then dried at 80 °C for 24 hours and then injection molded to make tensile and flexural samples. Samples for other tests were made from the flexural bar samples. This material was named as ‘cycle 0’ or ‘virgin’ material (individually for both formulations).

The remaining pellets of 'cycle 0' material were dried at 80 ºC (24 hours) and then extruded at the same processing conditions. The extruded composite strands were again passed through a water bath followed by pelletizing. A portion of these pellets were dried at 80 ºC and then injection molded. This material was named as 'cycle 1' or 'first time recycled' composite.

The remaining pellets of 'cycle 1' material were successively dried, extruded, cooled, and pelletized. A portion of these pellets were again dried and injection molded to get 'cycle 2' or 'second time recycled' material. This process continued up to 6 times in total to get 'cycle 6' or 'sixth time recycled' material. Composites without PLA-g-MA were also made at the same processing conditions (for both formulations) to investigate the impact of the coupling agent.

5.2.2.2. Coupling Agent Preparation

The PLA-g-MA (maleic anhydride grafted PLA) coupling agent was prepared from PLA, maleic anhydride (provided by Sigma-Aldrich), and an initiator (Benzoyl Peroxide) by using the same twin screw co-rotating extruder (Sec. 2.2.1). The wt% of these ingredients in PLA-g-MA were respectively 91 %, 8%, and 1%. Prior to extrusion, only PLA was dried at 80 ºC for 24 hours while the maleic anhydride and the initiator were kept at room temperature (25 ºC). The extrusion temperature profile (from feed section to melting section) was 82 ºC, 88 ºC, 93 ºC, 100 ºC, 115 ºC, 127 ºC, and 140 ºC. The temperature of the die and the gate adapter was controlled at 140 ºC. The extruder screw rpm was set at 200.

5.2.2.3. Tensile Testing

Tensile test was carried out with an Instron universal testing machine (Model 5567, MA, USA) according to ASTM D 638: Standard Test Method for Tensile Properties of Plastics. In this case, the load cell capacity was 30 KN. The strain rate (of the tensile sample) was controlled at 5 mm/min and an extensometer was used to measure the initial strain. The samples were kept at room temperature (25 °C) before and at the time of testing. Eight samples were tested for each batch.

5.2.2.4. Flexural Testing

Flexural test was carried out by using an Instron universal testing machine (Model 5567, MA, USA) according to ASTM D 790: Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. The load cell capacity was 2 KN and the crosshead speed was 1.4 mm/min. The sample dimensions were 75 mm x 12.9 mm x 3.3 mm with an approximate support span of 53 mm (in the test). The samples were kept at room temperature (25 °C) before and at the time of testing. Eight replications were tested for each batch.

5.2.2.5. Coefficient of Thermal Expansion (CTE)

The coefficient of thermal expansion test was performed from 30 ºC to 50 ºC by using a Dynamic Mechanical Analyzer (TA Instruments, DMA Q800, DE, USA) with a tension film clamp and no preload force. The ramp rate was set at 3 ºC /min. The sample dimensions were 38.1 mm x 12.9 mm x 3.3 mm where the initial length was 12.74 mm. Eight samples were tested for each batch. The following equation was used to measure the CTE-

$$\alpha = \left(\frac{\Delta L}{\Delta T}\right) . \left(\frac{1}{L}\right) \tag{5.1}$$

Here, α is the coefficient of thermal expansion, ΔL is the change in length, ΔT is the change in temperature, and L is the initial length (12.74 mm).

5.2.2.6. Heat Deflection Temperature (HDT)

Heat deflection temperature was measured by using a Dynamic Mechanical Analyzer (TA Instruments, DMA Q800, DE, USA) with a three point bending clamp according to ASTM D 648: Standard Test Method for Deflection Temperature of Plastics under Flexural Load in the Edgewise

Position (pressure δ=0.455 MPa). The ramp rate was controlled at 3 ºC /min. The sample dimensions were 65 mm x 12.9 mm x 3.3 mm where the actual supported length was 50 mm. Eight samples were tested for each batch.

5.2.2.7. Dynamic Mechanical Analysis

Storage modulus was measured at 30 ºC by using the same Dynamic Mechanical Analyzer (mentioned above) with a dual cantilever beam clamp. The frequency and amplitude were 1 Hz and 15 μm respectively. The ramp rate was set at 3 ºC /min. The soak time was 5 minutes (at 28 ºC). The sample dimensions were 65 mm x 12.9 mm x 3.3 mm. The actual supported length was 41.6 mm. Eight samples were tested for each batch.

5.2.2.8. Izod Impact Test

The notched Izod impact test was carried out by an Izod impact tester (Tinius Olsen, Model Impact 104, PA, USA) according to the ASTM D 256: Standard Test Method for Determining the Izod Pendulum Impact Resistance of Plastics. No additional load was used with the pendulum. The sample dimensions were 63.5 mm x 12.9 mm x 3.3 mm with a notch of 2 mm. Eight samples were tested for each batch.

5.2.2.9. Melt Flow Index (MFI)

Melt flow index was measured by using an extrusion plastometer ((Tinius Olsen, Model MP 600, PA, USA) according to ASTM D 1238: Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer. The temperature and load were respectively 190 ºC and 2.16 Kg. Five replications were tested for each batch.

5.2.2.10. Scanning Electron Microscopy (SEM)

Fracture surfaces of tensile samples were examined by a JEOL JSM-6490LV scanning electron microscope (JEOL USA, Peabody, MA, USA) at an accelerating voltage of 15 KeV. The samples were attached to aluminum mounts with colloidal silver paste. A conductive gold-palladium coating was applied with a Balzers SCD 030 sputter coater (BAL-TEC RMC, Tucson, AZ, USA).

5.2.2.11. Fiber Length Measurement

A small amount of composite pellets (3 g) were heated with acetone in a small jar at 130 ºC with constant stirring for two hours. When the polymer completely dissolved in acetone, wood fibers were separated from the solution by filtering. The separated fibers were then dried and fiber length was measured by using a Zeiss microscope (Axiovart 40 Mat). The average length of 100 fibers has been reported.

5.2.2.12. Differential Scanning Calorimetry (DSC)

DSC was carried out using a differential scanning calorimeter (TA instruments, Q1000, DE, USA) in nitrogen (flow rate 50 ml/min) for a scanned temperature range of -10 ºC to 240 ºC. The heating rate was 10 ºC/min. Hermetic Aluminum pans were used for holding the samples. The weight of each sample was approximately 10 mg.

5.2.2.13. Thermo-gravimetric Analysis (TGA)

Thermogravimetric analysis was carried out by using a thermogravimetric analyzer (TA instruments, Q500, DE, USA) for a temperature range of 25 ºC to 800 ºC in air (sample gas, flow rate 60 ml/min) and nitrogen (balance gas, flow rate 40 ml/min). The heating rate was 10 ºC/min. The weight of each sample was approximately 10 mg.

5.2.2.14. Fourier Transform Infra-Red Spectroscopy (FTIR)

FTIR was carried out using a Thermo Scientific Nicolet 8700 spectrometer in photoacoustic mode and in the range of 700-3500 cm^{-1}. The composite samples had an approximate thickness of 0.5 mm. FTIR data was analyzed by using OMNIC spectra software.

5.2.2.15. Gel Permeation Chromatography (GPC)

A small amount of composite pellets (3 g) were heated with acetone in a small jar at 130 °C for two hours. When the polymer completely dissolved in acetone, the solution was separated from the precipitated fibers. PLA was then separated from acetone by drying it in open air at room temperature (25 °C). This dried PLA was dissolved in tetrahydrofuran (THF) to make a solution with a concentration of 2 mg/ml. The analysis of molecular weight was performed at 40 °C with a GPC apparatus (EcoSEC HLC-8320GPC, Tosoh Bioscience, Japan) by using two columns (TSKgel SuperHM-L 6.00 mm ID× 15 cm) with a differential refractometer detector (DRI). The eluent (THF) flow rate was 0.4 ml/min. The injection volume was 20 µl for each sample.

5.3. Results and Discussion

5.3.1. Effect of Coupling Agent

The coupling agent (PLA-g-MA) did not improve the properties for both formulations. Instead, the coupling agent created slightly negative effects in some cases. This could be attributed to the fact that- the melting point of the maleic anhydrite (50 ºC) and PLA (210 ºC) differs significantly. Therefore, during extrusion, the maleic anhydride was not possibly well grafted on PLA. This leads to insufficient functional sites on the polymer. Since the functional sites are necessary to create strong bonding between the fiber and the matrix, the coupling agent was not effective enough to improve composite properties. In addition, the initiator (Benzoyl Peroxide) could possibly play a role for producing insufficient functional sites on the polymer.

5.3.2. Effect of Wood Flour Content

Higher wood flour content did not improve strength properties (e.g., tensile and flexural strength) and heat deflection temperature (HDT), but increased stiffness properties (e.g., tensile and flexural modulus) and decreased strain properties (e.g., failure strain and melt flow index) of the PLA composite. Strength properties did not improve because, although the filler content increased, the interfacial adhesion between the fiber and matrix probably did not improve. Additionally, higher filler content could produce fiber agglomeration in the composite that results in stress concentration. Stress concentration helps easier crack propagation and thus leads to lower strength properties [59].

Similarly, higher filler content could not improve HDT of the composite. This is because, lower crystalline polymers show HDT nearly their glass transition temperature while higher crystalline polymers show HDT around their melting temperature [65]. Higher filler content does not play any role to make a change in HDT of lower crystalline polymers [67].

On contrary to strength properties and HDT, WF 50 PLA (50 wt% filler) composite showed increased tensile, flexural, and storage modulus respectively by 950 MPa, 450 MPa, and 450 MPa that to WF 30 PLA (30 wt% filler) composite. This is because, the stiffness properties of bio-composites mainly depend on wood flour content rather than other factors such as fiber length and fiber dispersion on the matrix [45, 61]. Higher filler content produced more restriction to the polymer chain mobility and hence increased the composite stiffness [42, 45, 50]. As the higher filler composite becomes stiffer, it produces more resistance to strain by applied load, and thus shows decrease in strain properties.

5.3.3. Effect of Recycling

5.3.3.1. Effect of Recycling on Fiber Length

Fiber length of WF 30 PLA composite was measured at cycle 0 and cycle 6. Fiber length of the composite decreased with increased no. of reprocessing cycles. The average length of 100 fibers was 253.24 μm and 111.15 μm respectively for cycle 0 and cycle 6. Figs. 5.1 and 5.2 respectively show the images of fiber at cycle 0 and cycle 6 of WF 30 PLA composite.

Fig. 5.1: Fibers of WF 30 PLA composite at cycle 0 (magnification 10 X).

Fig. 5.2: Fibers of WF 30 PLA composite at cycle 6 (magnification 10 X).

5.3.3.2. Effect of Recycling on Molecular Weight of PLA

The average molecular weights of PLA of WF 30 PLA composite were measured at cycle 0 and cycle 6 by gel permeation chromatography (GPC). Both the weight averaged molecular weight (M_w) and number averaged molecular weight (M_n) of PLA decreased with ascending no. of reprocessing cycles. From cycle 0 to cycle 6, the M_w of PLA decreased from 151,115 to 81,958 and the M_n of PLA decreased from 133,762 to 50,742 (Figs. 5.3 and 5.4). The polydispersity index (PDI) also increased from 1.13 (cycle 0) to 1.62 (cycle 6) that is an indication of lower molecular weights of PLA due to recycling [13].

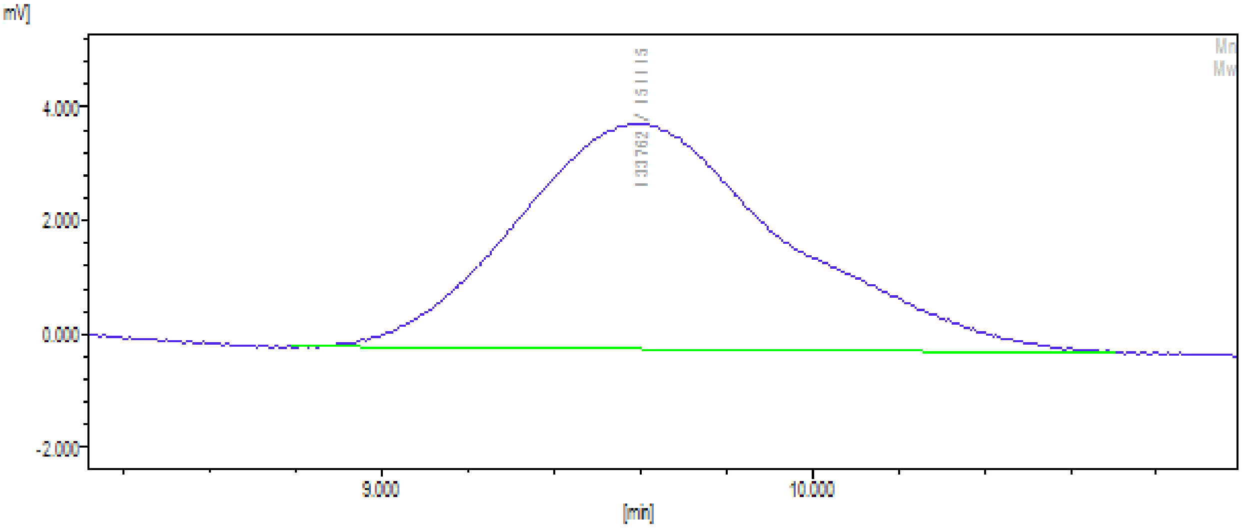

Fig. 5.3: Gel Permeation Chromatogram of PLA of WF 30 PLA composite at cycle 0.

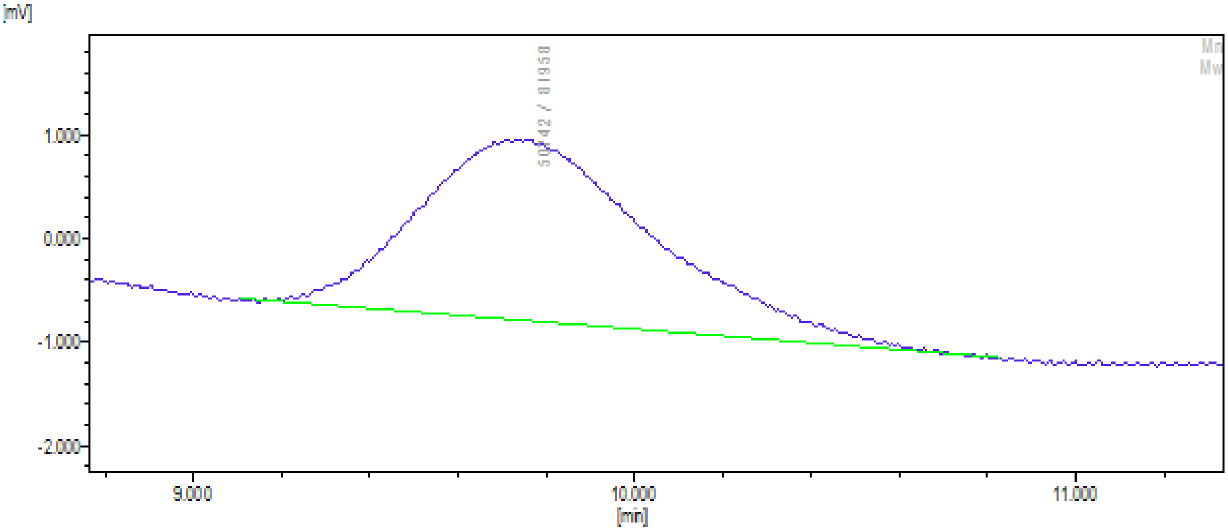

Fig. 5.4: Gel Permeation Chromatogram of PLA of WF 30 PLA composite at cycle 6.

5.3.3.3. Effect of Recycling on Strength Properties

The impact of recycling was statistically found significant on the strength properties (tensile strength, flexural strength, and impact resistance) of both composites. All strength properties of the composites decreased with increased no. of reprocessing cycles.

Strength properties of WF 30 PLA composite sharply decreased at cycle 6 while they were somewhat constant (or nearer) in the previous cycles (Figs. 5.7, 5.10, and 5.13). Strength properties of bio-composites primarily depend on fiber length (or aspect ratio), fiber content, void content, interfacial adhesion, and molecular weight of polymer. In this case, fiber length and molecular weight of polymer possibly decreased in a greater amount at cycle 6 than the previous cycles (Figs. 5.1-5.4). In addition, crack propagation and fiber pull-outs are observed at cycle 6 that indicates lower interfacial adhesion between the fiber and matrix (Figs. 5.14 and 5.15). This lower interfacial adhesion, due to heat and shear stress history, finally results in lower strength properties of the composite [41].

Similarly, strength properties of WF 50 PLA composite decreased highly at cycle 2 and became somewhat constant (or nearer) up to cycle 6 (Figs. 5.7, 5.10, and 5.13). This could be due to the same degradation mechanism of fiber and polymer along with lower interfacial adhesion at cycle 2. In addition, a lot of pores (or micro voids) are observed at cycle 2 (Figs. 5.16 and 5.17) that significantly contributed to lower strength properties. The amount of pores at cycle 2 is almost equivalent to that at cycle 6 (Figs. 5.17 and 5.18) and probably that is why, strength properties of WF 50 PLA composite are almost constant from cycle 2 to cycle 6.

It could also be observed that, strength properties of higher filler composite decreased much earlier (at cycle 2) that to lower filler composite (at cycle 6). This could happen since PLA degradation in the composite depends on filler content. More filler content helps degrade PLA more rapidly [41]. This is because, the chemical structure of PLA is very susceptible to hydrolytic degradation. Higher filler content contains higher amount of moisture, and thus degrades the PLA much earlier. In addition, higher fiber content creates higher shear stress during extrusion and causes more (or rapid) degradation of PLA [41].

The box plots, ANOVA Tables, and regression equations, corresponding to the strength properties of both composites, have been given below.

5.3.3.3.1. Data Analysis of Tensile Strength

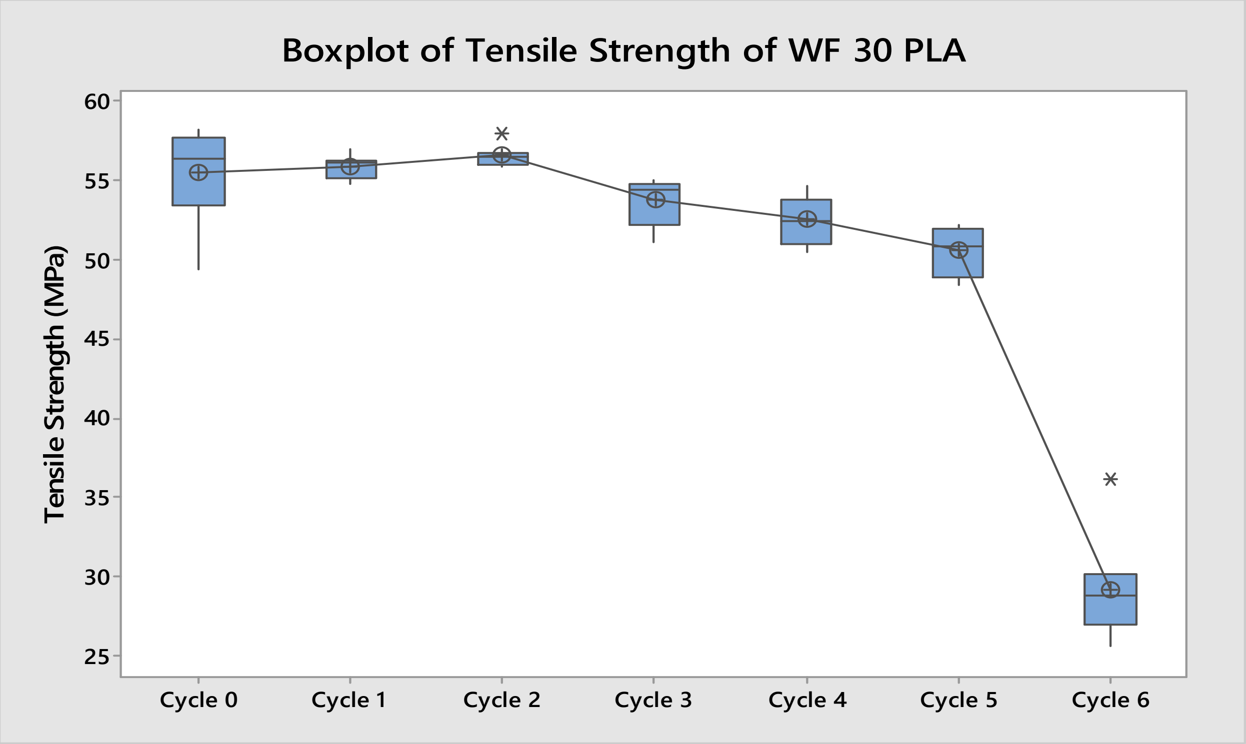

Fig. 5.5: Box plot of tensile strength of WF 30 PLA composite.

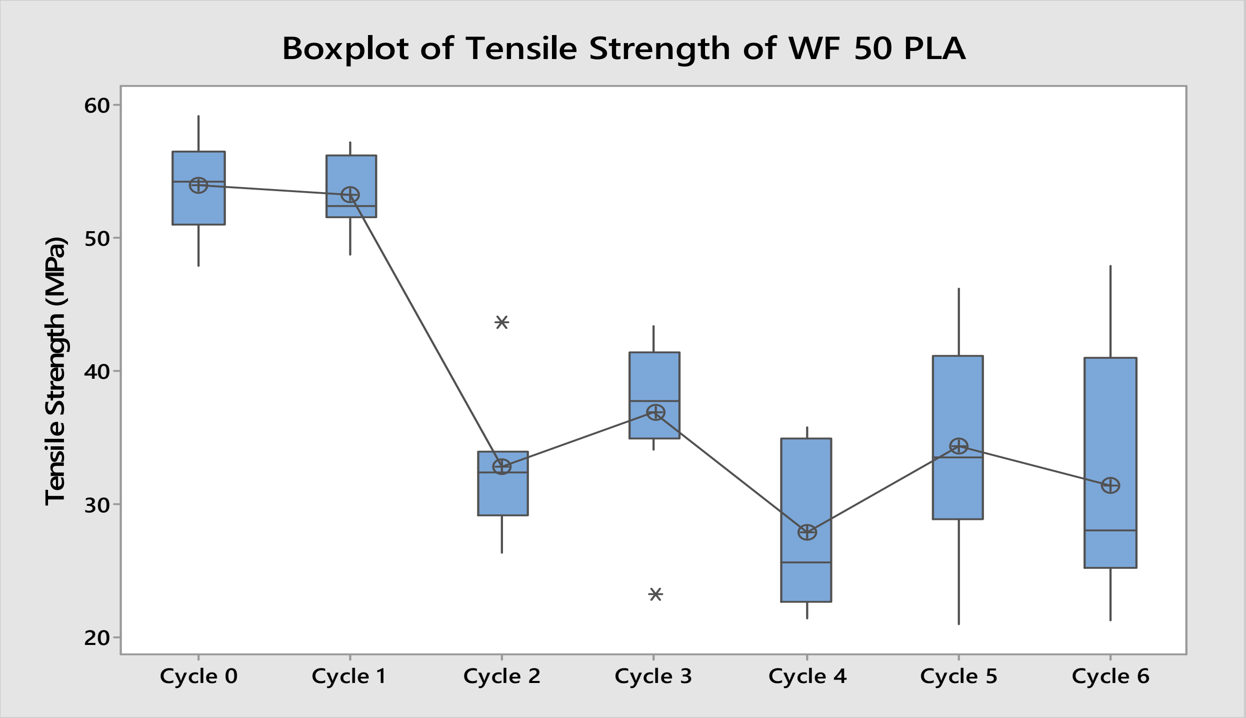

Fig. 5.6: Box plot of tensile strength of WF 50 PLA composite.

Table 5.1: One way ANOVA of tensile strength of WF 30 PLA composite

```
Source  DF  Adj SS   Adj MS  F-Value  P-Value
Factor   6  4466.2  744.358   192.37    0.000
Error   49   189.6    3.870
Total   55  4655.8
Model Summary
      S    R-sq  R-sq(adj)  R-sq(pred)
1.96711  95.93%     95.43%      94.68%
```

Table 5.2: One way ANOVA of tensile strength of WF 50 PLA composite

```
Analysis of Variance
Source  DF  Adj SS  Adj MS  F-Value  P-Value
Factor   6    5378  896.34    22.32    0.000
Error   49    1968   40.17
Total   55    7346
Model Summary
      S    R-sq  R-sq(adj)  R-sq(pred)
6.33765  73.21%     69.93%      65.01%
```

The regression equations of expected mean of tensile strength (Y) vs. no. of reprocessing cycles (X) of WF 30 PLA (eqn. 5.2) and WF 50 PLA (eqn. 5.3) composite are given below.

$$Y = 56.32 - 4.253\ X + 2.818\ X^2 - 0.4704\ X^3 \qquad (5.2)$$

$$Y = 56.27 - 10.91\ X + 1.161\ X^2 \qquad (5.3)$$

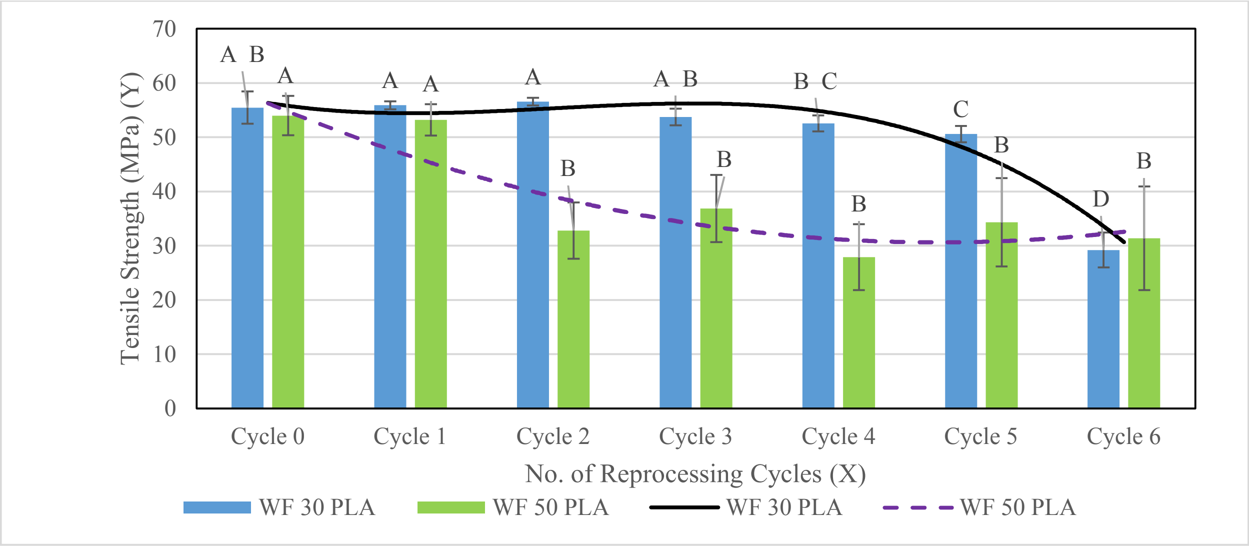

Fig 5.7: Effect of recycling on the tensile strength of WF/PLA composites. Means that do not have a common letter are significantly different.

5.3.3.3.2 Data Analysis of Flexural Strength

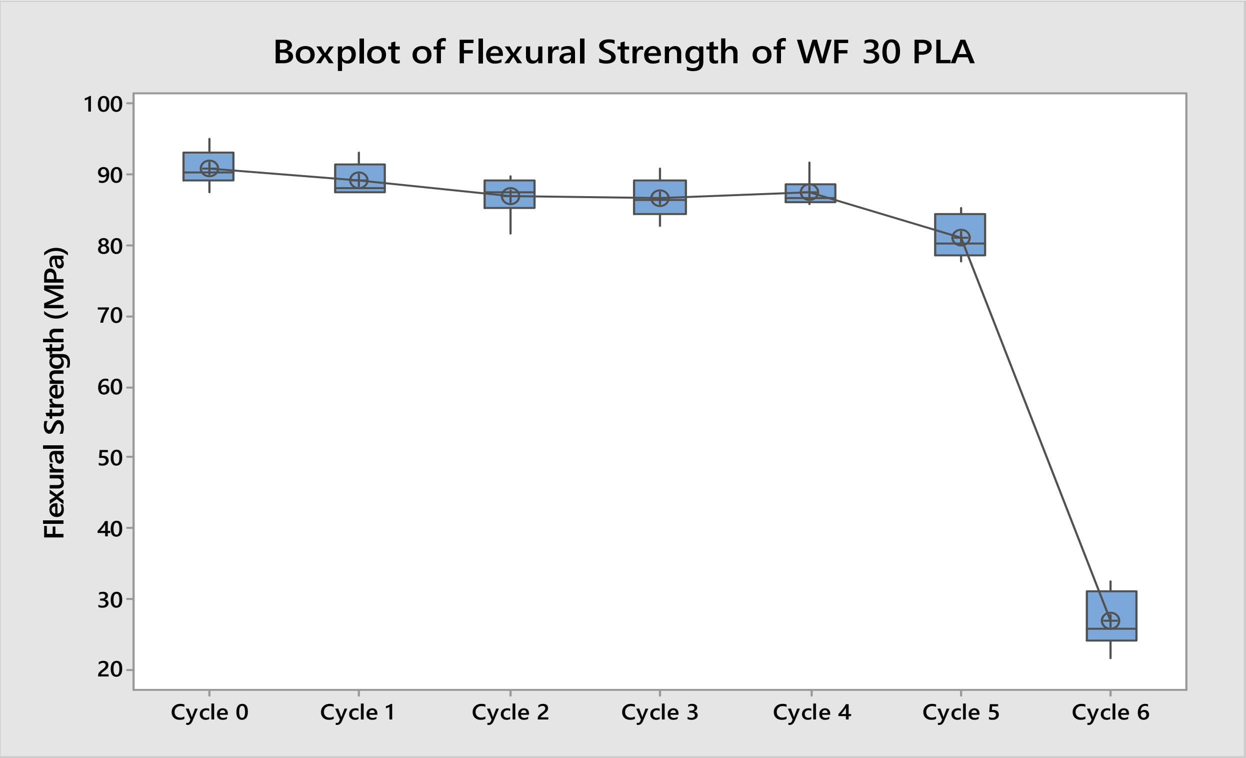

Fig. 5.8: Box plot of flexural strength of WF 30 PLA composite.

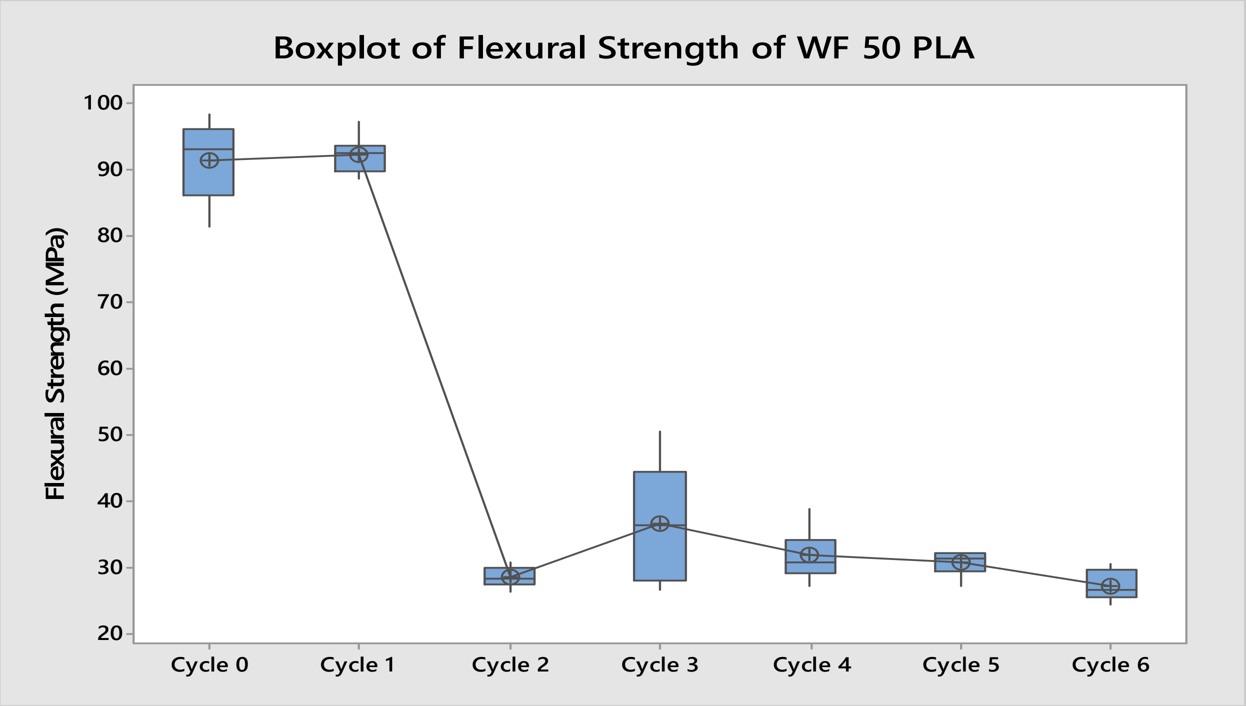

Fig. 5.9: Box plot of flexural strength of WF 50 PLA composite.

Table 5.3: One way ANOVA of flexural strength of WF 30 PLA composite

```
Source  DF   Adj SS   Adj MS  F-Value  P-Value
Factor   6  25349.8  4224.97   543.69    0.000
Error   49    380.8     7.77
Total   55  25730.6
Model Summary
      S    R-sq  R-sq(adj)  R-sq(pred)
2.78765  98.52%     98.34%      98.07%
```

Table 5.4: One way ANOVA of flexural strength of WF 50 PLA composite

```
Source  DF  Adj SS   Adj MS  F-Value  P-Value
Factor   6   42542  7090.34   346.42    0.000
Error   49    1003    20.47
Total   55   43545
Model Summary
      S    R-sq  R-sq(adj)  R-sq(pred)
4.52408  97.70%     97.41%      96.99%
```

The regression equations of expected mean of flexural strength (Y) vs. no. of reprocessing cycles (X) of WF 30 PLA (eqn. 5.4) and WF 50 PLA (eqn. 5.5) composite are as follows-

$$Y = 93.43 - 18.64 X + 10.73 X^2 - 1.565 X^3 \tag{5.4}$$

$$Y = 97.49 - 30.06 X + 3.155 X^2 \tag{5.5}$$

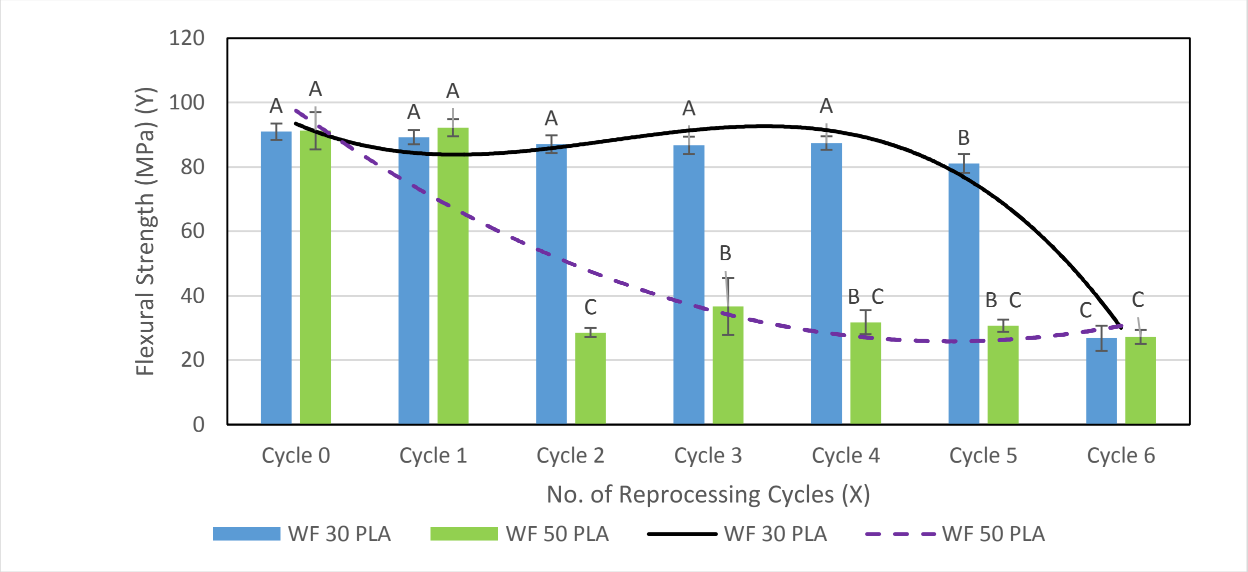

Fig. 5.10: Effect of recycling on the flexural strength of WF/PLA composites. Means that do not have a common letter are significantly different.

5.3.3.3.3. Data Analysis of Impact Resistance

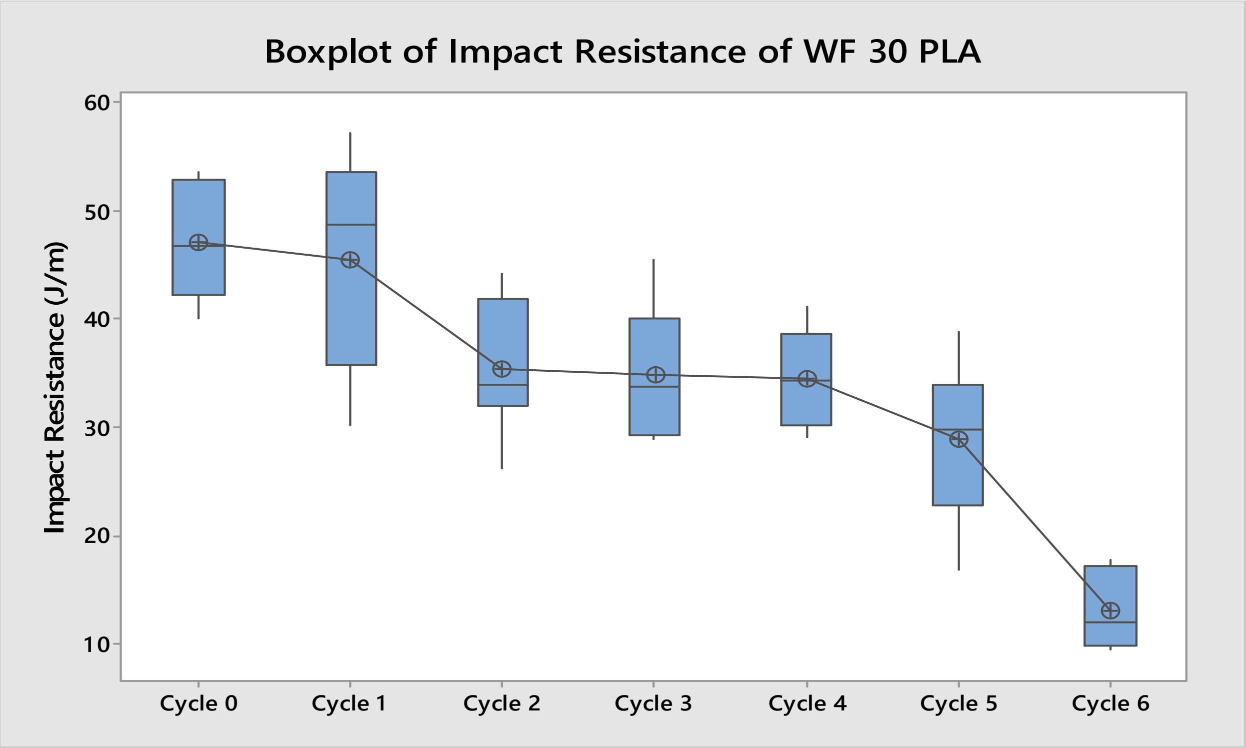

Fig. 5.11: Box plot of impact resistance of WF 30 PLA composite.

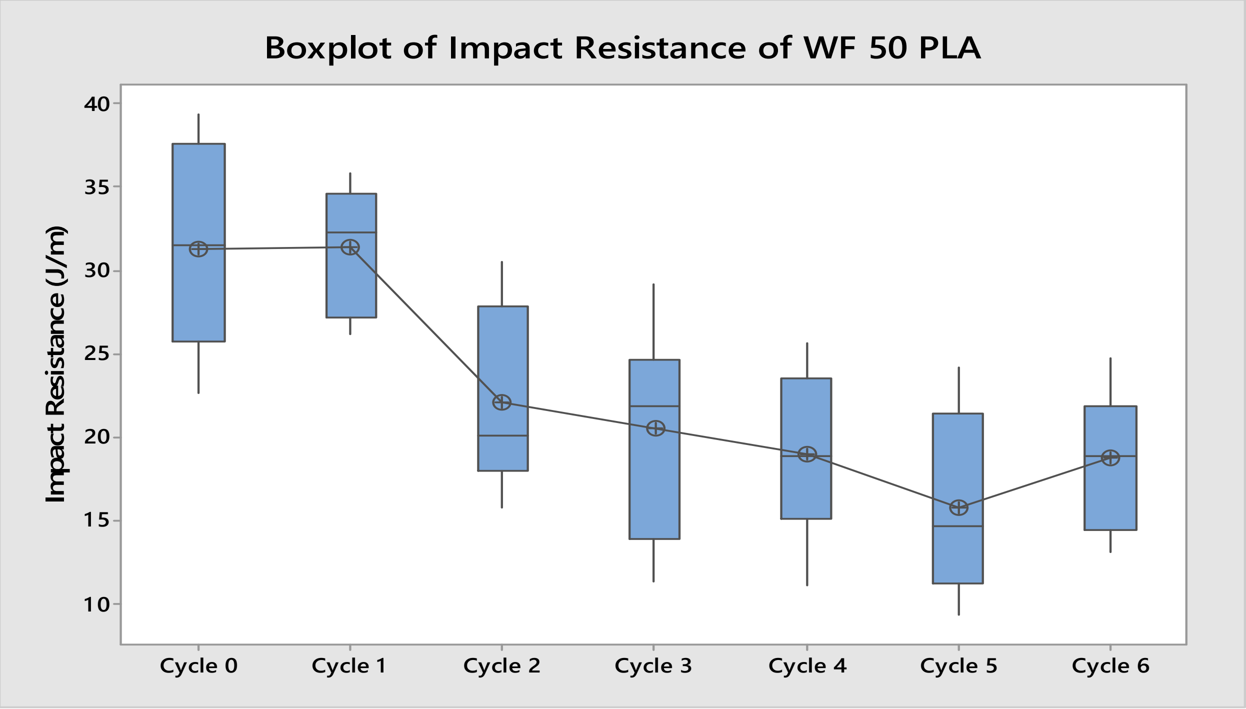

Fig. 5.12: Box plot of impact resistance of WF 50 PLA composite.

Table 5.5: One way ANOVA of impact resistance of WF 30 PLA composite

```
Source  DF  Adj SS   Adj MS  F-Value  P-Value
Factor   6    6174  1028.92    25.59    0.000
Error   49    1970    40.21
Total   55    8144
Model Summary
      S    R-sq  R-sq(adj)  R-sq(pred)
6.34093  75.81%     72.85%      68.40%
```

Table 5.6: One way ANOVA of impact resistance of WF 50 PLA composite

```
Source  DF  Adj SS  Adj MS  F-Value  P-Value
Factor   6    1861  310.13    11.42    0.000
Error   49    1330   27.15
Total   55    3191
Model Summary
      S    R-sq  R-sq(adj)  R-sq(pred)
5.21059  58.31%     53.21%      45.55%
```

The regression equations of expected mean of impact resistance (Y) vs. no. of reprocessing cycles (X) of WF 30 PLA (eqn. 5.6) and WF 50 PLA (eqn. 5.7) composite are as follows-

$$Y = 48.75 - 10.66 X + 3.571 X^2 - 0.4598 X^3 \tag{5.6}$$

$$Y = 33.08 - 5.820 X + 0.5411 X^2 \tag{5.7}$$

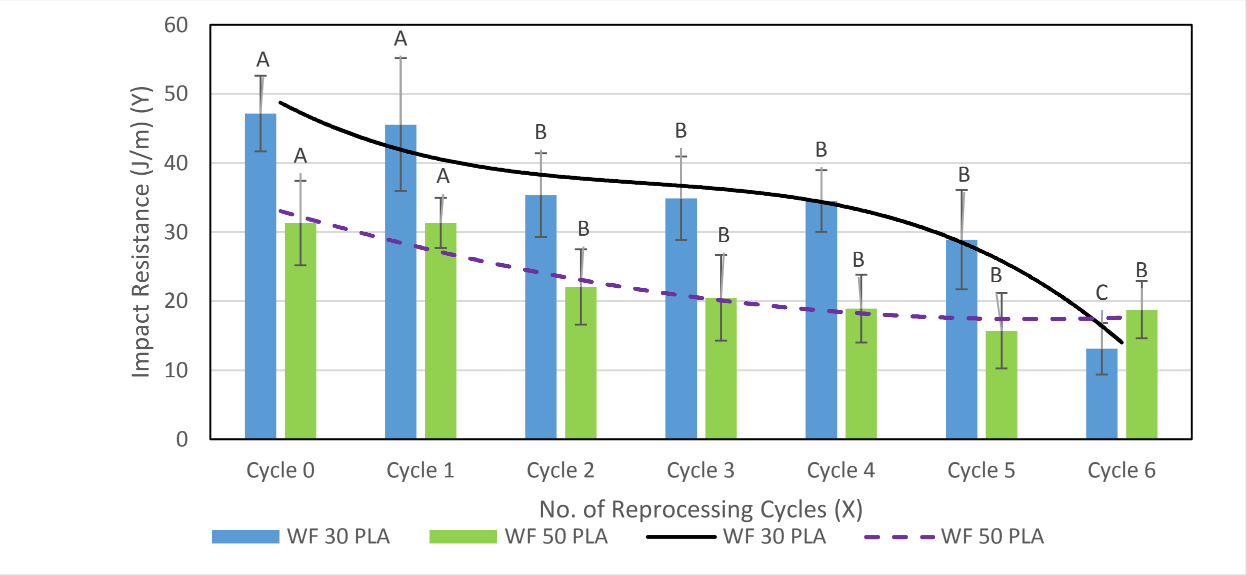

Fig. 5.13: Effect of recycling on the impact resistance of WF/PLA composites. Means that do not have a common letter are significantly different.

5.3.3.3.4. SEM Images

The SEM images of fracture surface of tensile samples at cycle 0 and cycle 6 for both composites have been given below.

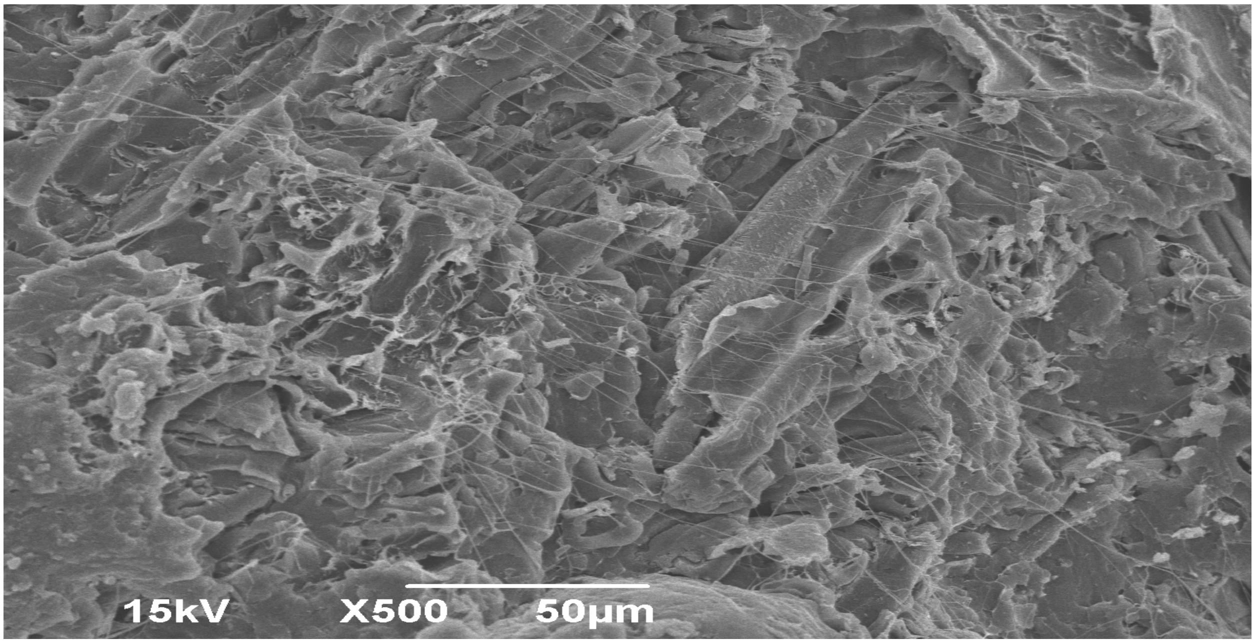

Fig. 5.14: SEM of WF 30 PLA composite fracture surface at cycle 0 with a magnification of 500X.

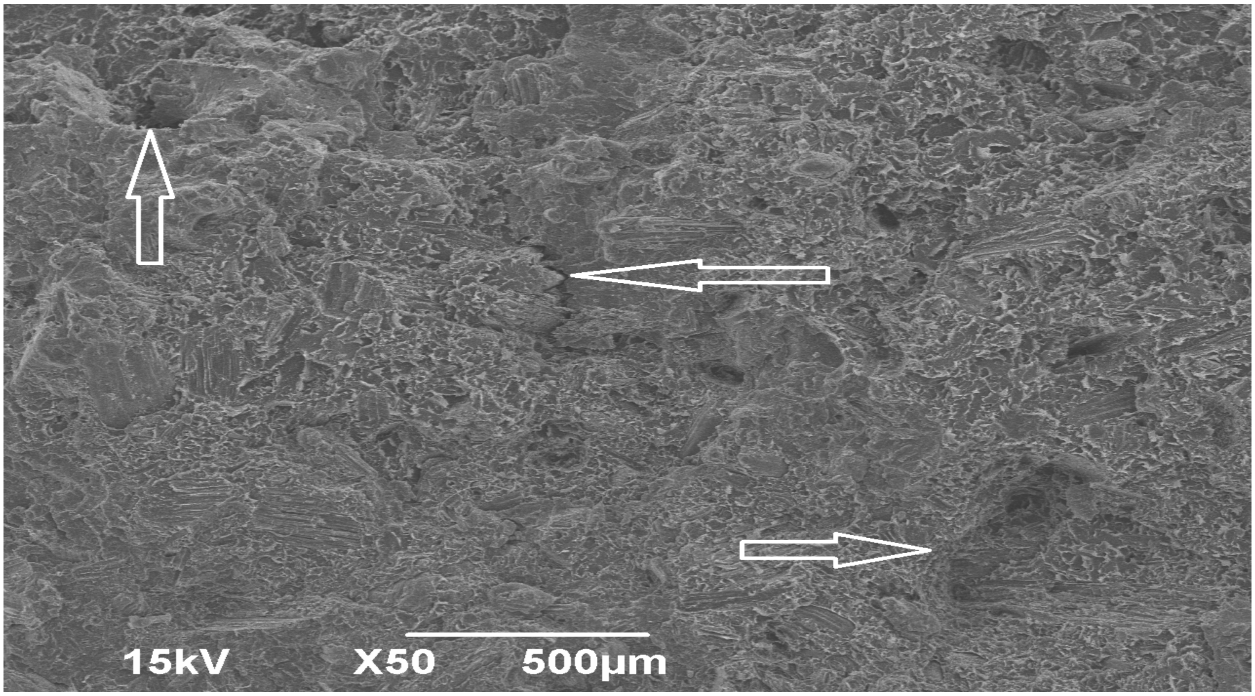

Fig. 5.15: SEM of WF 30 PLA composite fracture surface at cycle 6 with a magnification of 50X.

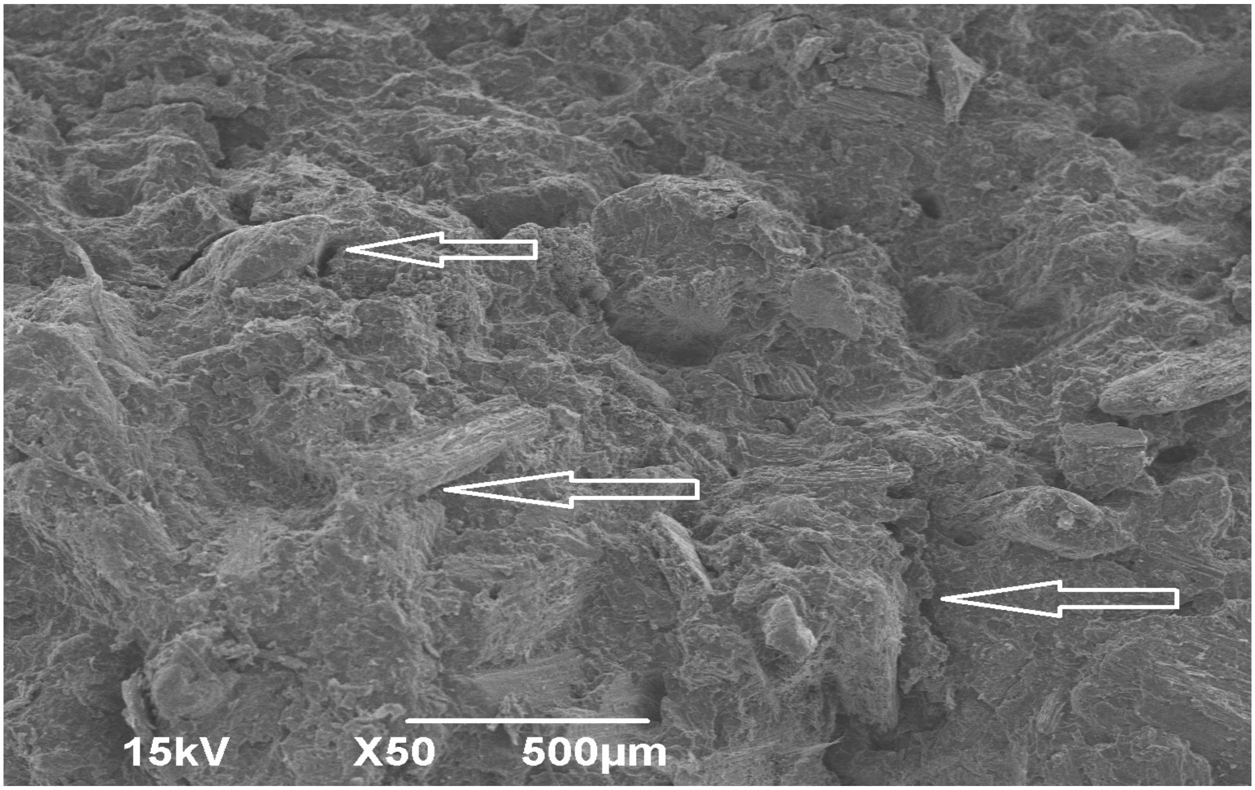

Fig. 5.16: SEM of WF 50 PLA composite fracture surface at cycle 0 with a magnification of 50X.

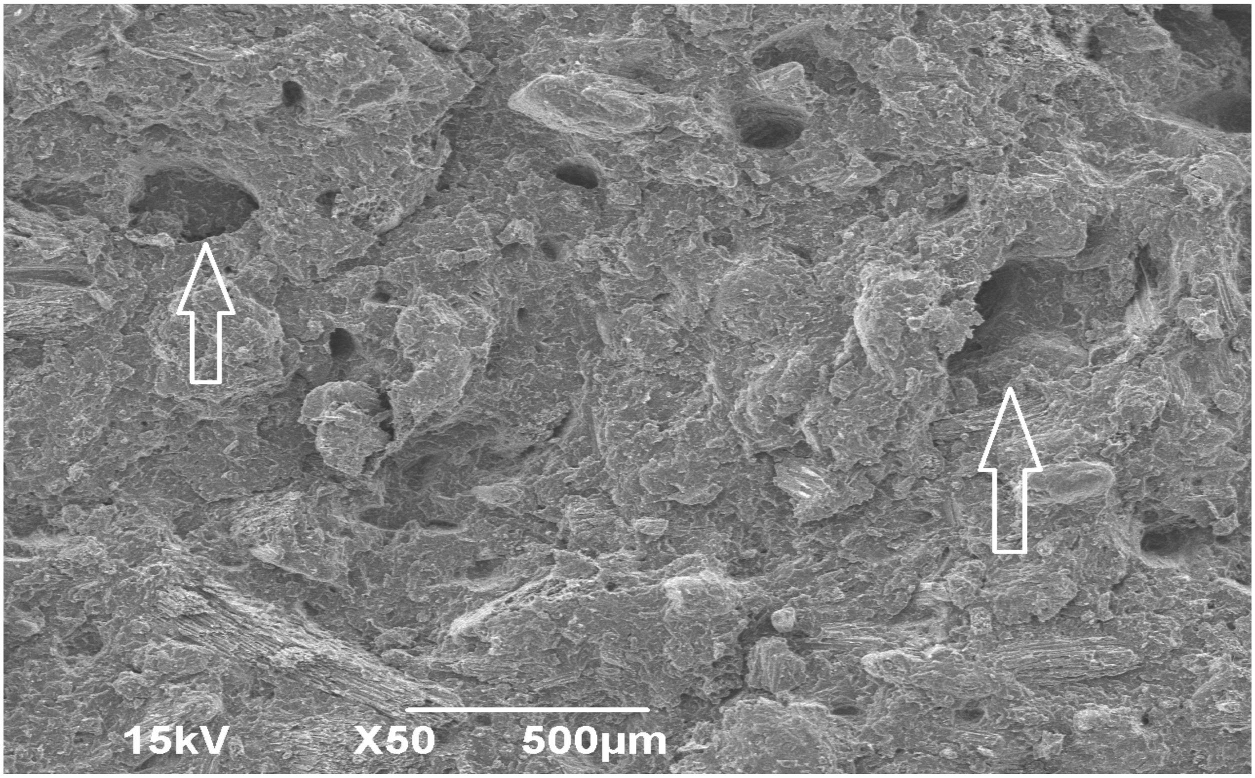

Fig. 5.17: SEM of WF 50 PLA composite fracture surface at cycle 2 with a magnification of 50X.

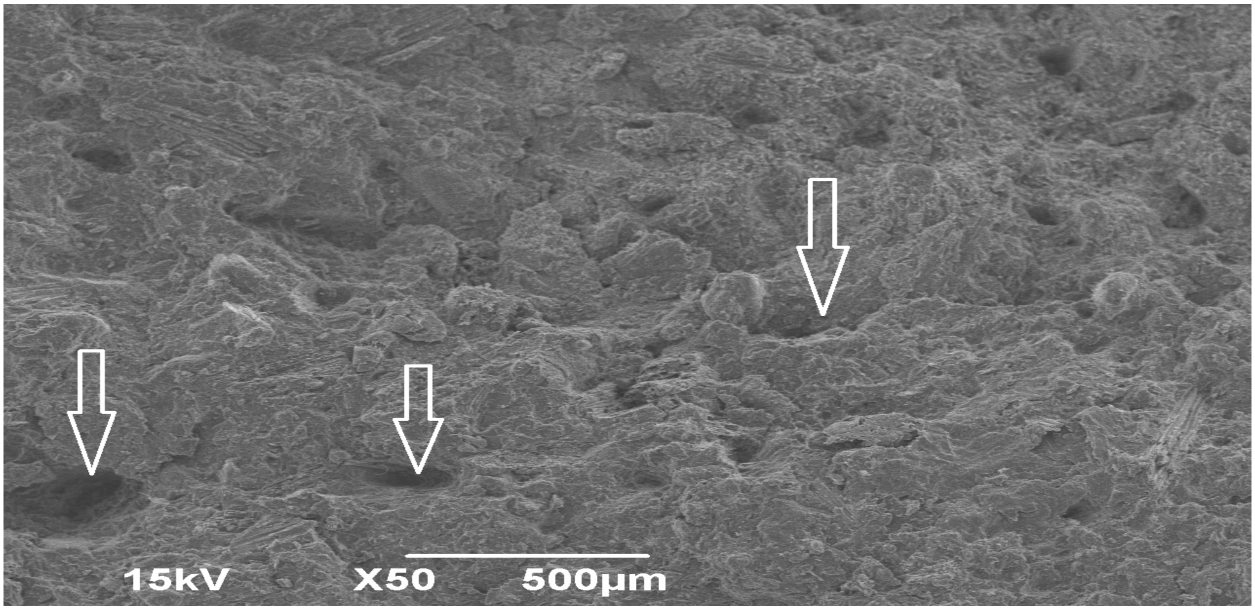

Fig. 5.18: SEM of WF 50 PLA composite fracture surface at cycle 6 with a magnification of 50X.

5.3.3.4. Effect of Recycling on Stiffness Properties

The impact of recycling was statistically found significant on the stiffness properties (tensile, flexural, and storage modulus) and heat deflection temperature (HDT) (Table 5.7-5.14) of both composites. All these properties gradually decreased with increased no. of reprocessing cycles (Figs. 5.21, 5.24, 5.27, and 5.30). This could be due to the fiber and polymer degradation (Figs. 5.1-5.4), increased no. of pores, and poor interfacial adhesion (between the fiber and matrix) with successive recycling.

However, most stiffness properties of both composites showed lower relative decrease, from cycle 0 to cycle 6, compared to the corresponding strength properties (Table 5.21). For example, after reprocessing 6 times flexural modulus decreased 6% and 28% respectively for higher and lower filler composite while both flexural strengths decreased approximately 70%. This is because, stiffness properties of bio-composites are mostly dependent on the fiber content that restricts polymer chain mobility. These properties are not highly dependent on other factors such as fiber length or aspect ratio [45, 61]. Since the fiber content was constant, the polymer chain entanglement (by the fiber) decreased less and that resulted in lower decrease in stiffness properties of the composites. HDT is a stiffness dependent property, and probably that is why HDT showed similar type of behavior.

For WF 50 PLA composite, flexural modulus slightly differed from tensile modulus in response to successive recycling (Figs. 5.21 and 5.24). This is because, the testing procedures of tensile and flexural tests are completely different for composite materials. For tensile test, the modulus is the result of the average properties thorough out the thickness (or cross section) while for flexural test, the modulus is highly dependent on the top and bottom surface properties of the specimen [46]. The associated box plots, ANOVA Tables, and regression equations of stiffness properties and HDT of these composites have been given below.

5.3.3.4.1. Data Analysis of Tensile Modulus

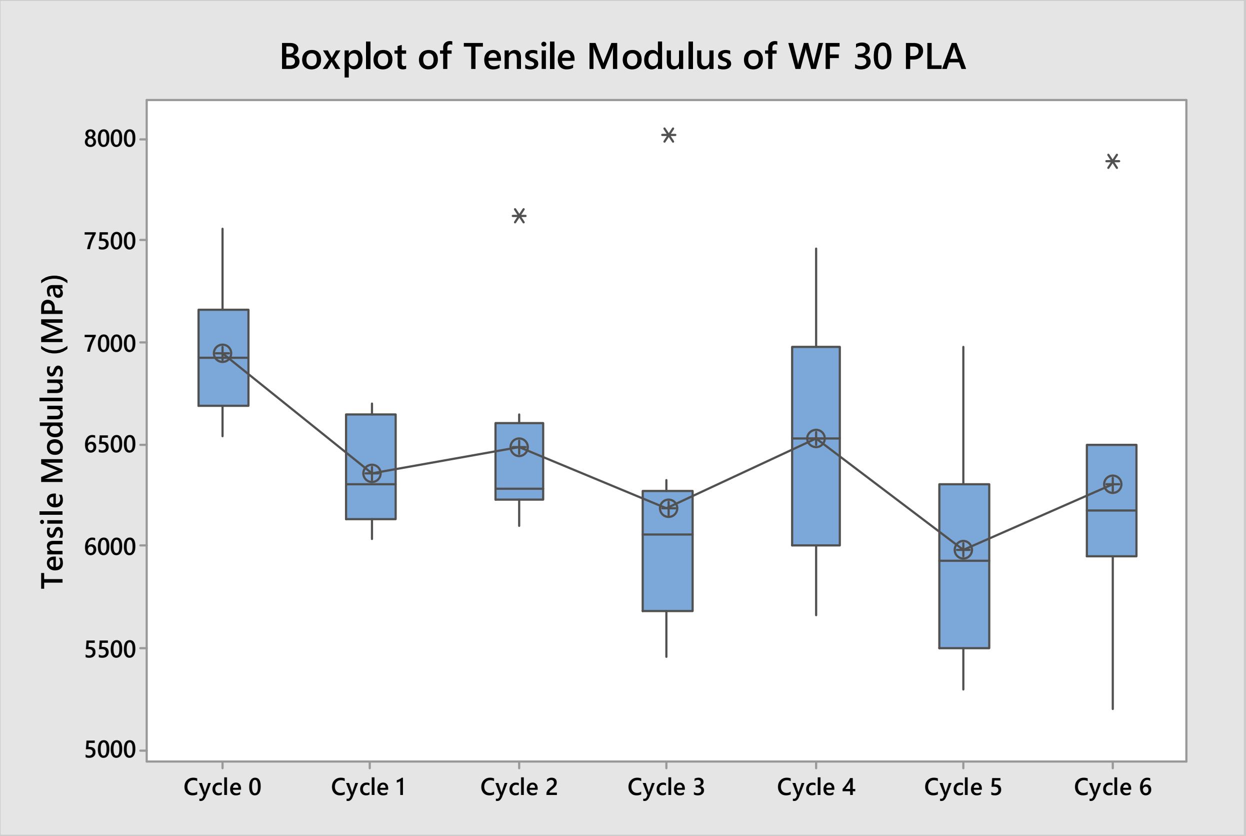

Fig. 5.19: Box plot of tensile modulus of WF 30 PLA composite.

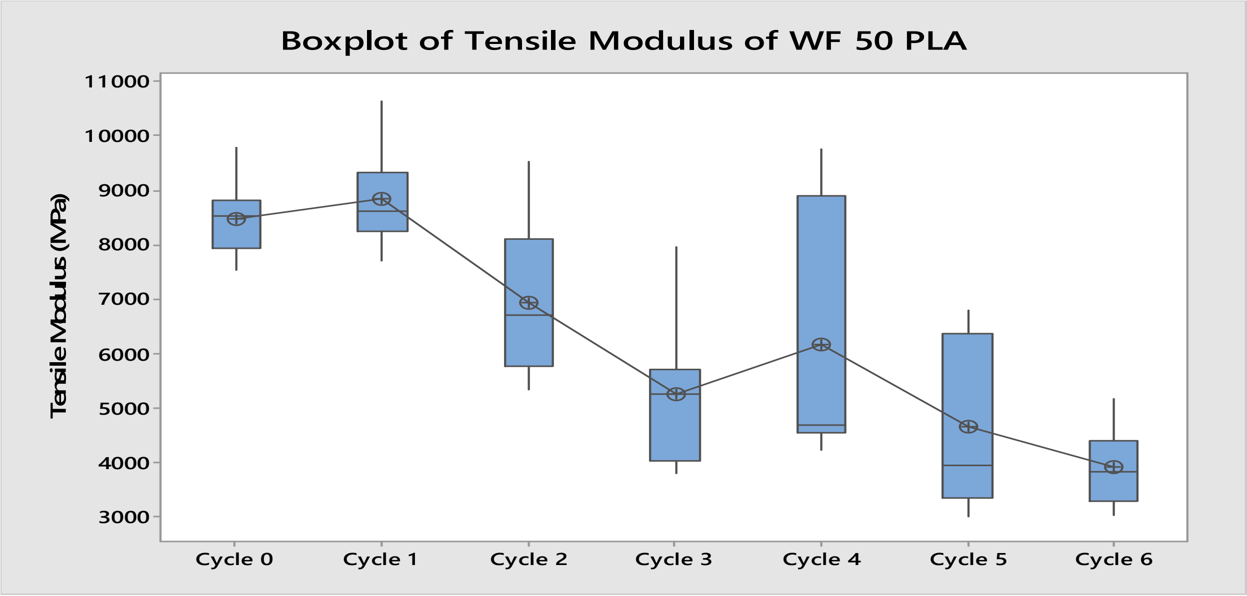

Fig. 5.20: Box plot of tensile modulus of WF 50 PLA composite.

Table 5.7: One way ANOVA of tensile modulus of WF 30 PLA composite

```
Source  DF    Adj SS  Adj MS  F-Value  P-Value
Factor   6   4493999  749000     2.31    0.049
Error   49  15913631  324768
Total   55  20407630
Model Summary
      S    R-sq  R-sq(adj)  R-sq(pred)
569.884  22.02%     12.47%       0.00%
```

Table 5.8: One way ANOVA of tensile modulus of WF 50 PLA composite

```
Source  DF     Adj SS    Adj MS  F-Value  P-Value
Factor   6  169571843  28261974    14.62    0.000
Error   49   94723231   1933127
Total   55  264295074
Model Summary
      S    R-sq  R-sq(adj)  R-sq(pred)
1390.37  64.16%     59.77%      53.19%
```

The regression equations of expected mean of tensile modulus (Y) vs. no. of reprocessing cycles (X) of WF 30 PLA (eqn. 5.8) and WF 50 PLA (eqn. 5.9) composite are as follows-

$$Y = 6684 - 94.85\ X \tag{5.8}$$

$$Y = 8771 - 817.3\ X \tag{5.9}$$

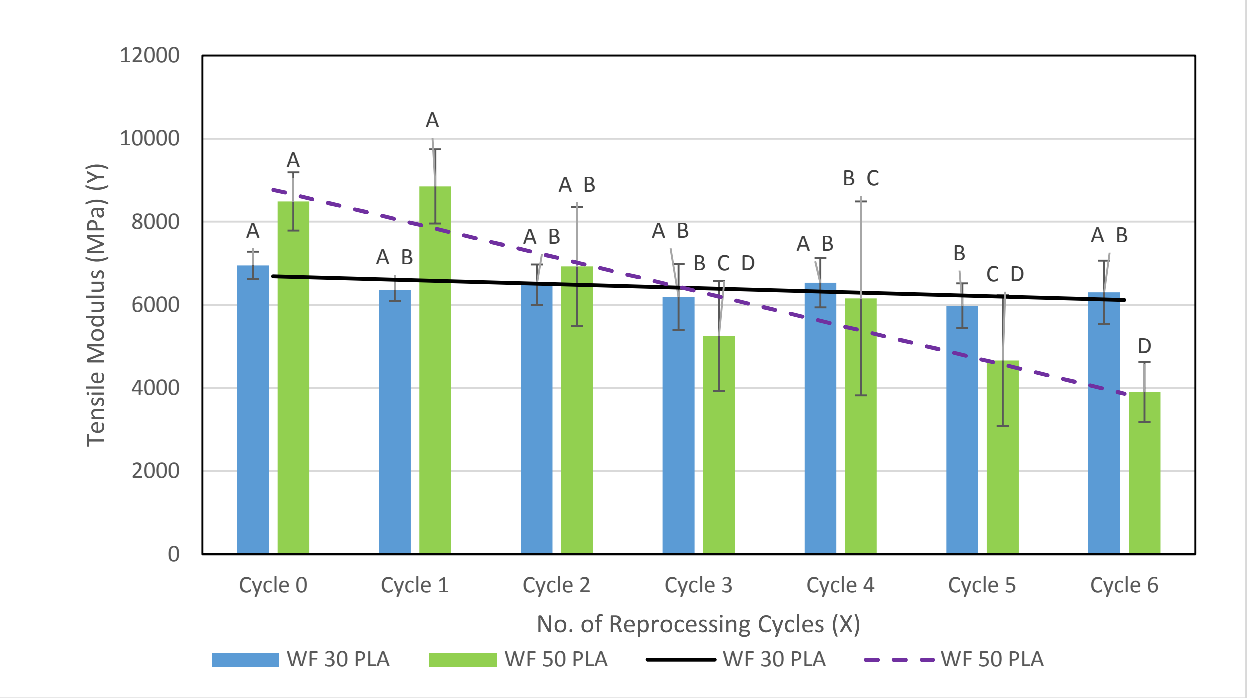

Fig. 5.21: Effect of recycling on tensile modulus of WF/PLA composites. Means that do not have a common letter are significantly different.

5.3.3.4.2. Data Analysis of Flexural Modulus

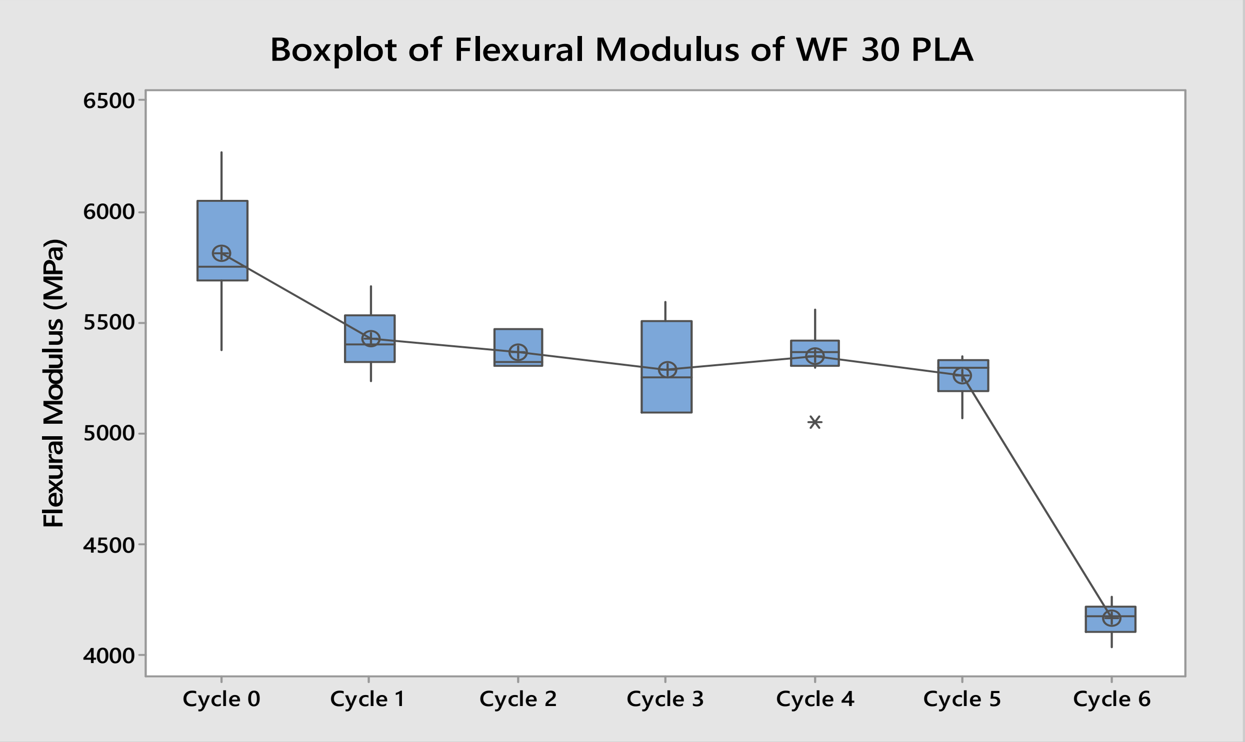

Fig. 5.22: Box plot of flexural modulus of WF 30 PLA composite.

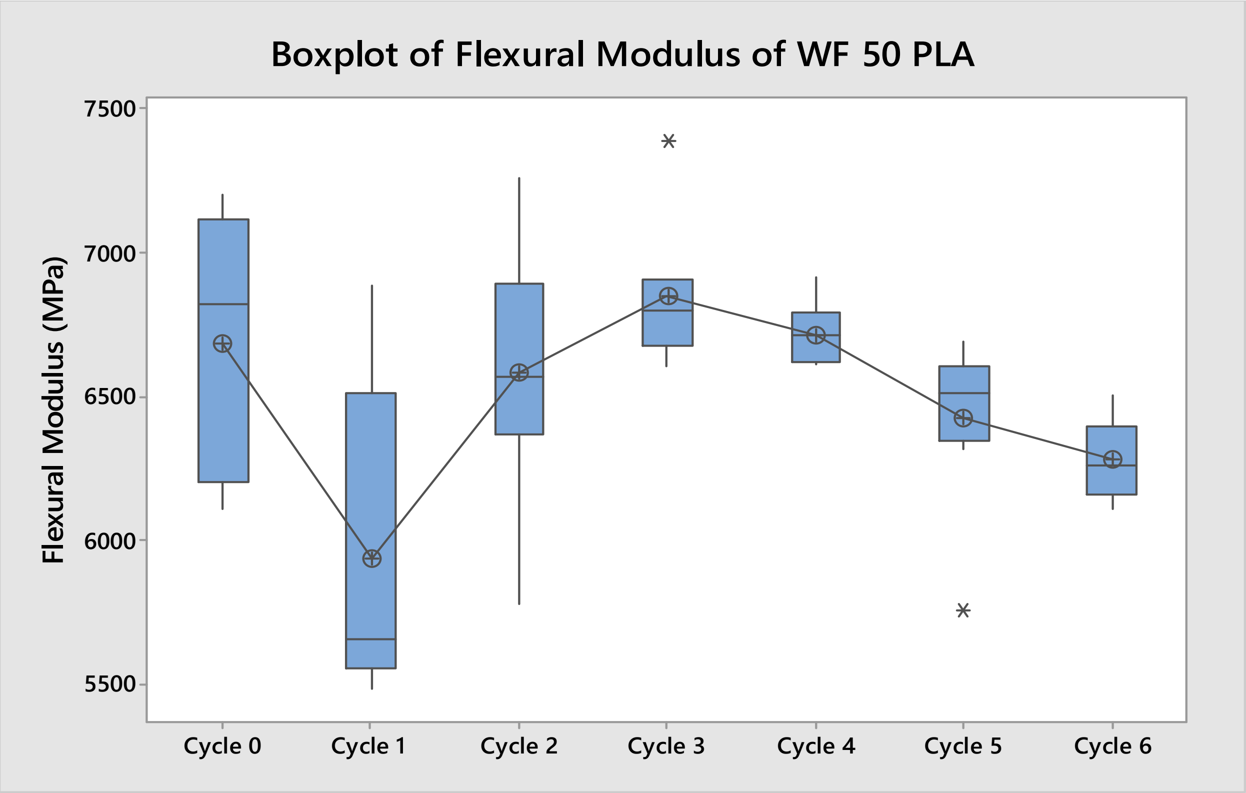

Fig. 5.23: Box plot of flexural modulus of WF 50 PLA composite.

Table 5.9: One way ANOVA of flexural modulus of WF 30 PLA composite

```
Analysis of Variance
Source  DF    Adj SS   Adj MS  F-Value  P-Value
Factor   6  12409585  2068264    81.21    0.000
Error   49   1247928    25468
Total   55  13657513
Model Summary
      S    R-sq  R-sq(adj)  R-sq(pred)
159.587  90.86%     89.74%      88.07%
```

Table 5.10: One way ANOVA of flexural modulus of WF 50 PLA composite

```
Source  DF    Adj SS  Adj MS  F-Value  P-Value
Factor   6   4632564  772094     6.20    0.000
Error   49   6100860  124507
Total   55  10733424
Model Summary
      S    R-sq  R-sq(adj)  R-sq(pred)
352.856  43.16%     36.20%      25.76%
```

The regression equations of expected mean of flexural modulus (Y) vs. no. of reprocessing cycles (X) of WF 30 PLA (eqn. 5.10) and WF 50 PLA (eqn. 5.11) composite are as follows-

$$Y = 5845 - 755.4\ X + 324.0\ X^2 - 40.53\ X^3 \qquad (5.10)$$

$$Y = 6532 - 396.8\ X + 226.7\ X^2 - 28.42\ X^3 \qquad (5.11)$$

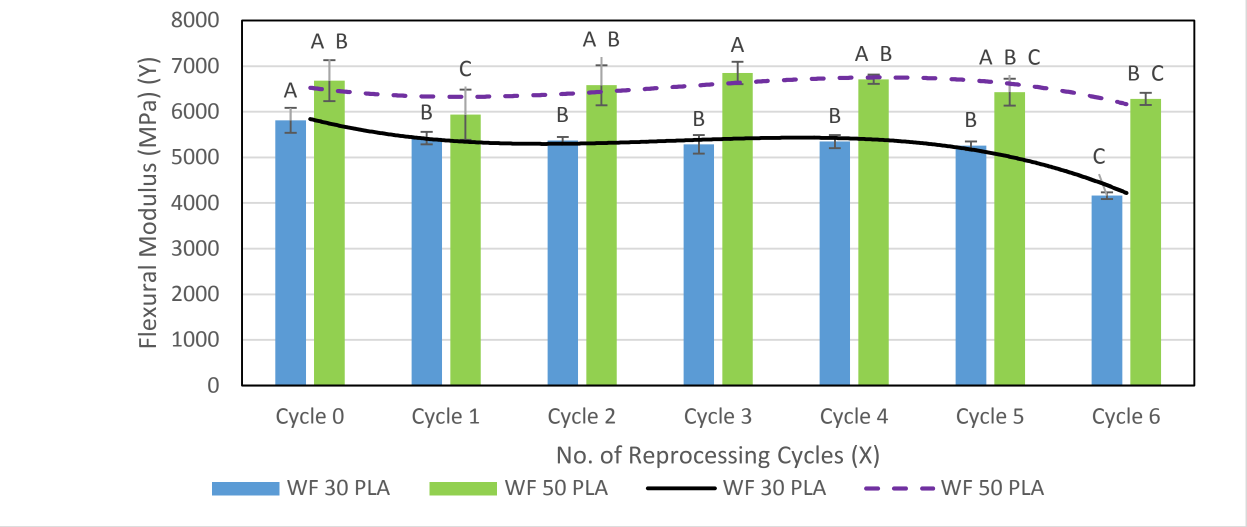

Fig. 5.24: Effect of recycling on the flexural modulus of WF/PLA composites. Means that do not have a common letter are significantly different.

5.3.3.4.3. Data Analysis of Storage Modulus

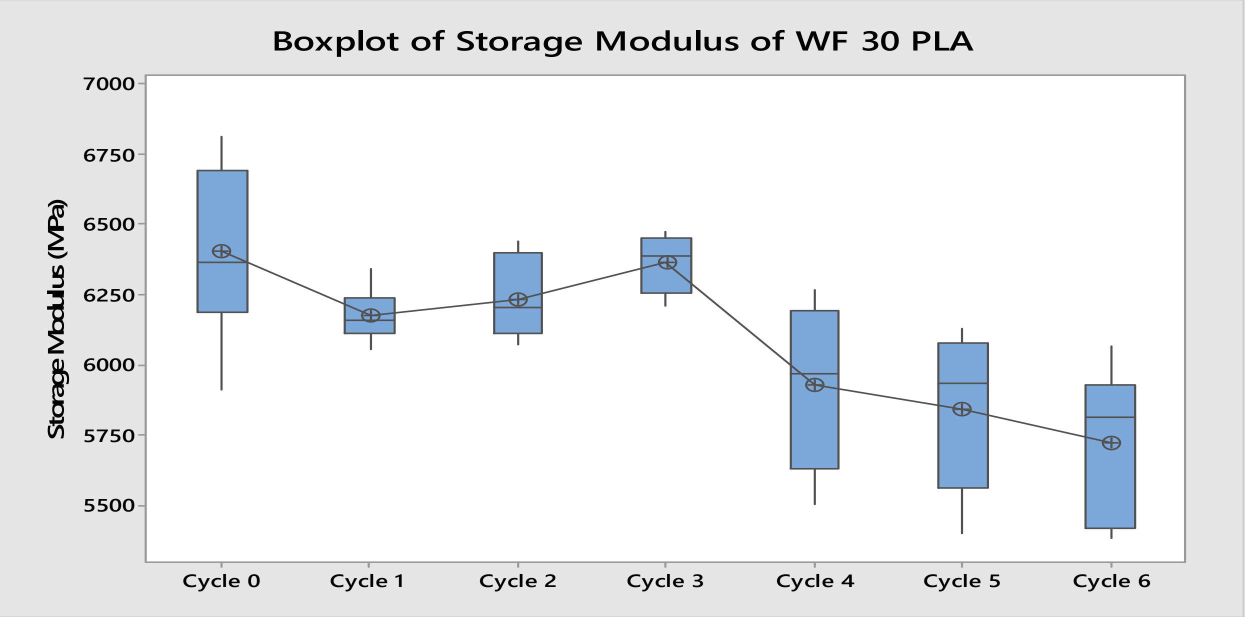

Fig.5.25: Box plot of storage modulus of WF 30 PLA composite.

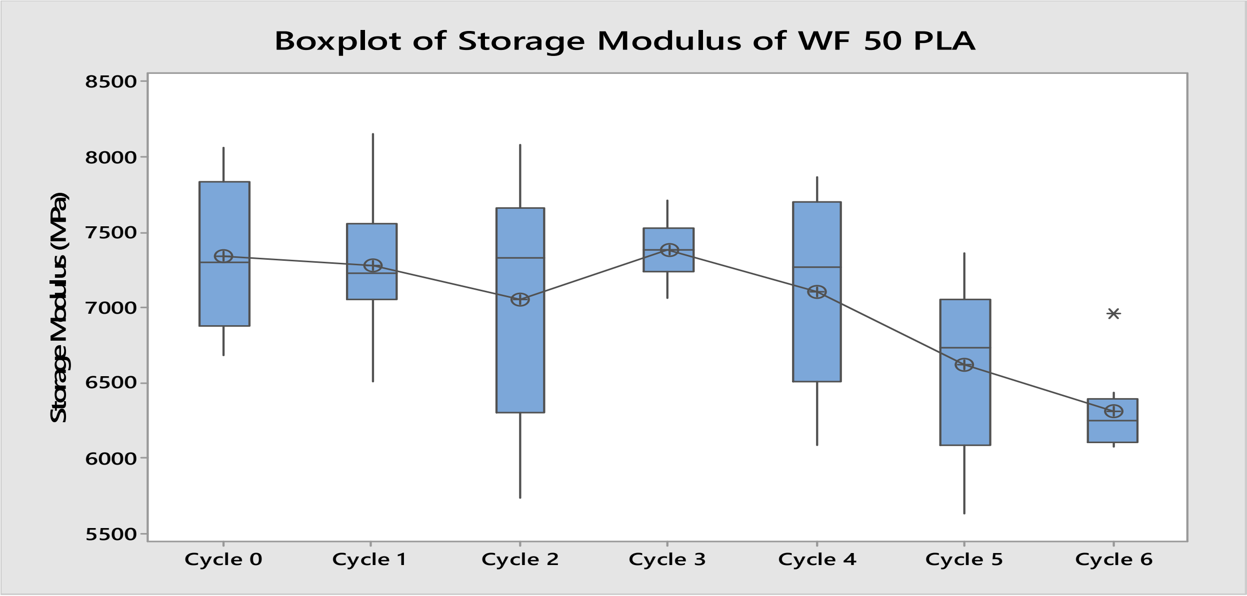

Fig. 5.26: Box plot of storage modulus of WF 50 PLA composite.

Table 5.11: One way ANOVA of storage modulus of WF 30 PLA composite

```
Source  DF   Adj SS  Adj MS  F-Value  P-Value
Factor   6  3418579  569763    10.73    0.000
Error   49  2602386   53110
Total   55  6020966
Model Summary
      S    R-sq  R-sq(adj)  R-sq(pred)
230.456  56.78%     51.49%      43.55%
```

Table 5.12: One way ANOVA of storage modulus of WF 50 PLA composite

```
Source  DF    Adj SS   Adj MS  F-Value  P-Value
Factor   6   7819154  1303192     4.44    0.001
Error   49  14388501   293643
Total   55  22207655
Model Summary
      S    R-sq  R-sq(adj)  R-sq(pred)
541.888  35.21%     27.28%      15.38%
```

The regression equations of expected mean of storage modulus (Y) vs. no. of reprocessing cycles (X) of WF 30 PLA (eqn. 5.12) and WF 50 PLA (eqn. 5.13) composite are as follows-

$$Y = 6422 - 108.3\ X \tag{5.12}$$

$$Y = 7516 - 162.7\ X \tag{5.13}$$

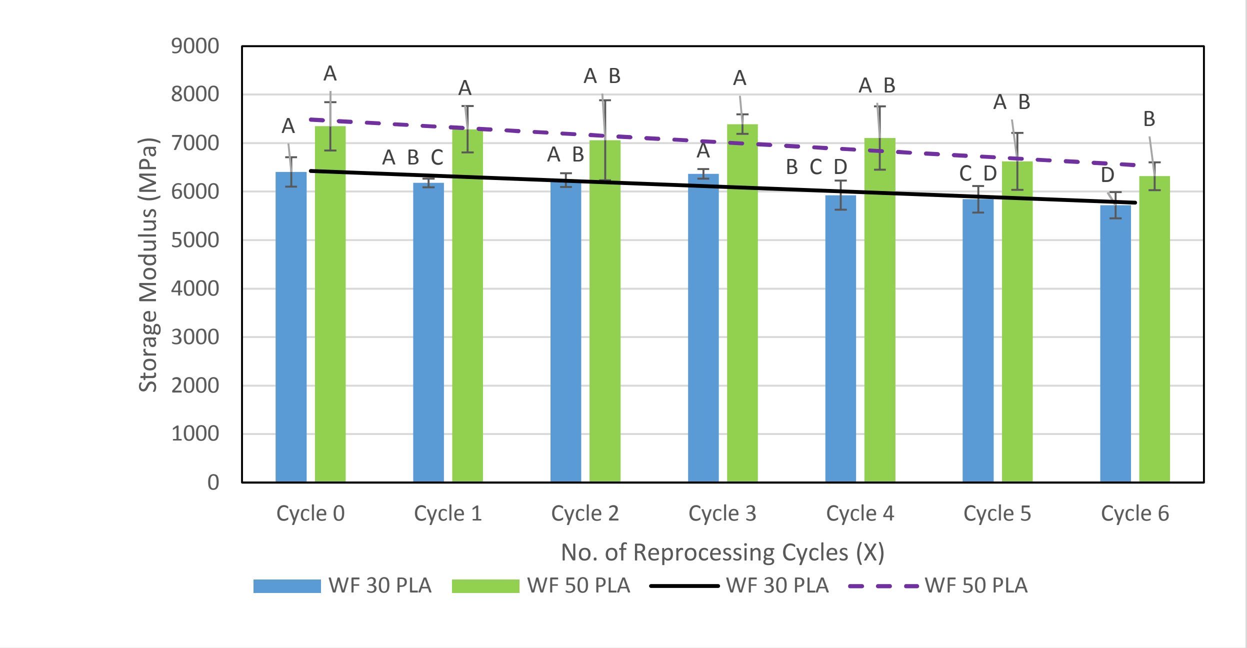

Fig. 5.27: Effect of recycling on the storage modulus of WF/PLA composites. Means that do not have a common letter are significantly different.

5.3.3.4.4. Data Analysis of Heat Deflection Temperature (HDT)

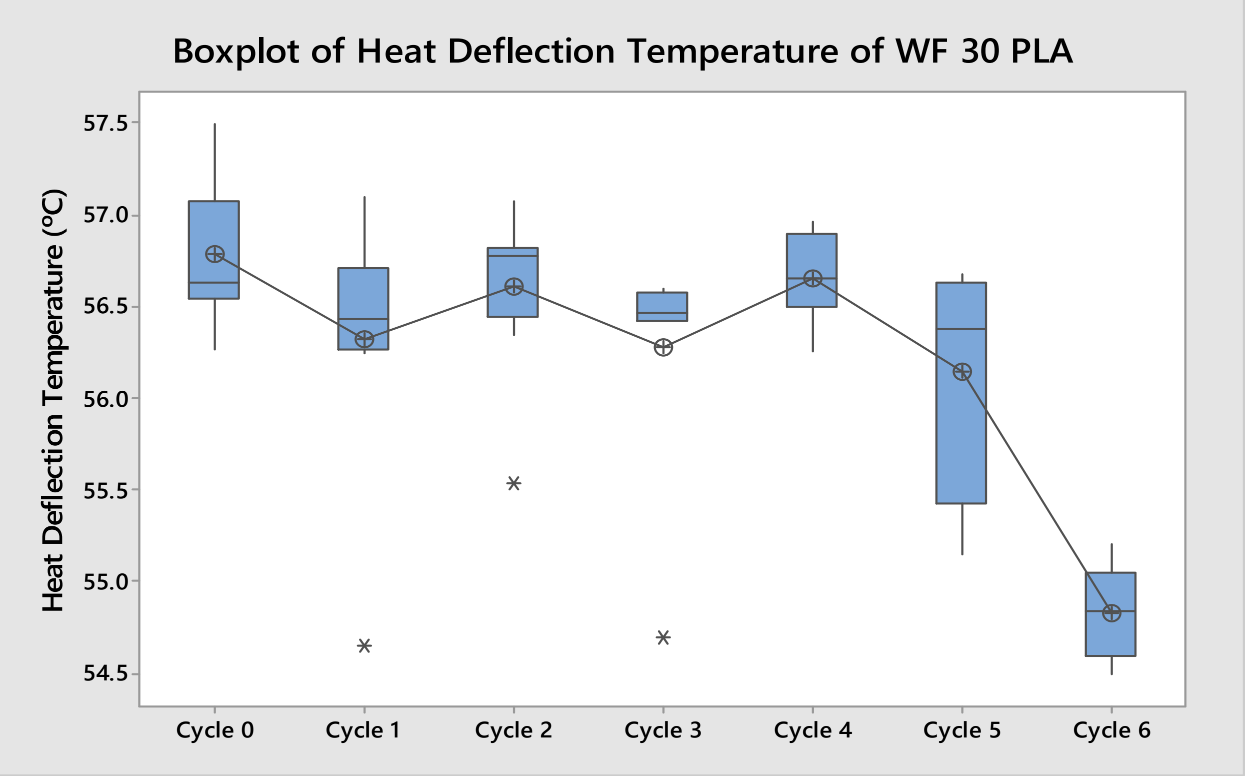

Fig. 5.28: Box plot of heat deflection temperature (HDT) of WF 30 PLA composite.

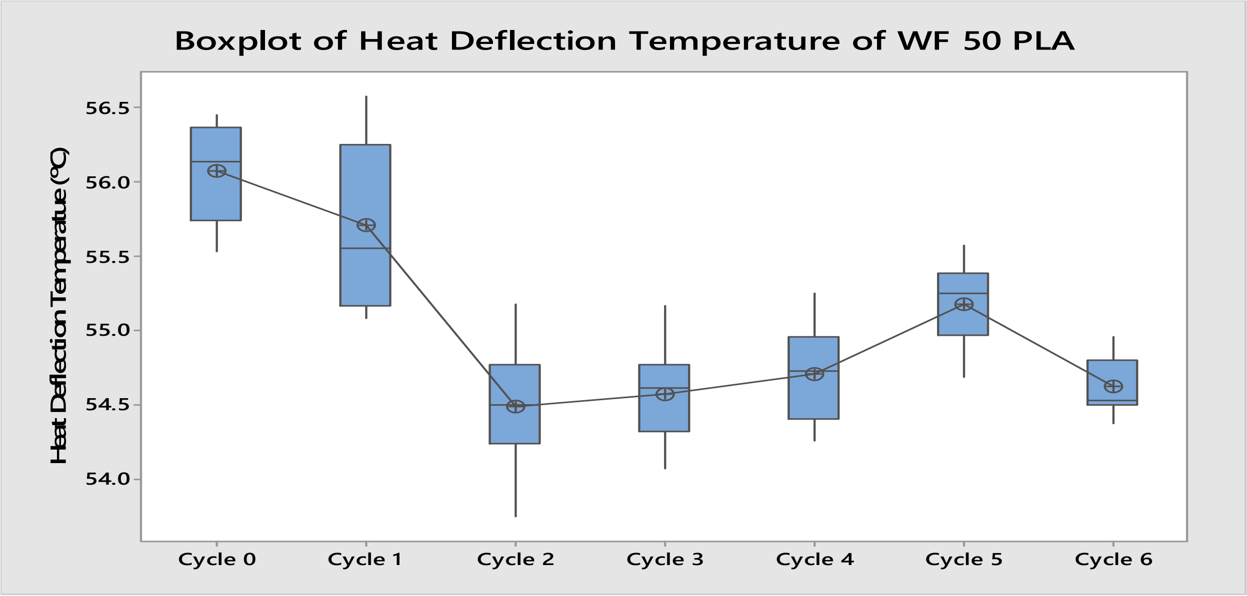

Fig. 5.29: Box plot of heat deflection temperature (HDT) of WF 50 PLA composite.

Table 5.13: One way ANOVA of heat deflection temperature of WF 30 PLA composite

```
Source  DF  Adj SS  Adj MS  F-Value  P-Value
Factor   6   20.79  3.4652    13.15    0.000
Error   49   12.92  0.2636
Total   55   33.71
Model Summary
       S    R-sq  R-sq(adj)  R-sq(pred)
0.513430  61.68%     56.99%      49.95%
```

Table 5.14: One way ANOVA of heat deflection temperature of WF 50 PLA composite

```
Source  DF  Adj SS  Adj MS  F-Value  P-Value
Factor   6  18.686  3.1143    22.26    0.000
Error   49   6.855  0.1399
Total   55  25.541
Model Summary
       S    R-sq  R-sq(adj)  R-sq(pred)
0.374035  73.16%     69.87%      64.94%
```

The regression equations of expected mean of HDT (Y) vs. no. of reprocessing cycles (X) of WF 30 PLA (eqn. 5.14) and WF 50 PLA (eqn. 5.15) composite are as follows-

$$Y = 56.79 - 0.742\ X + 0.3729\ X^2 - 0.05045\ X^3 \quad (5.14)$$

$$Y = 56.25 - 1.362\ X + 0.3757\ X^2 - 0.03170\ X^3 \quad (5.15)$$

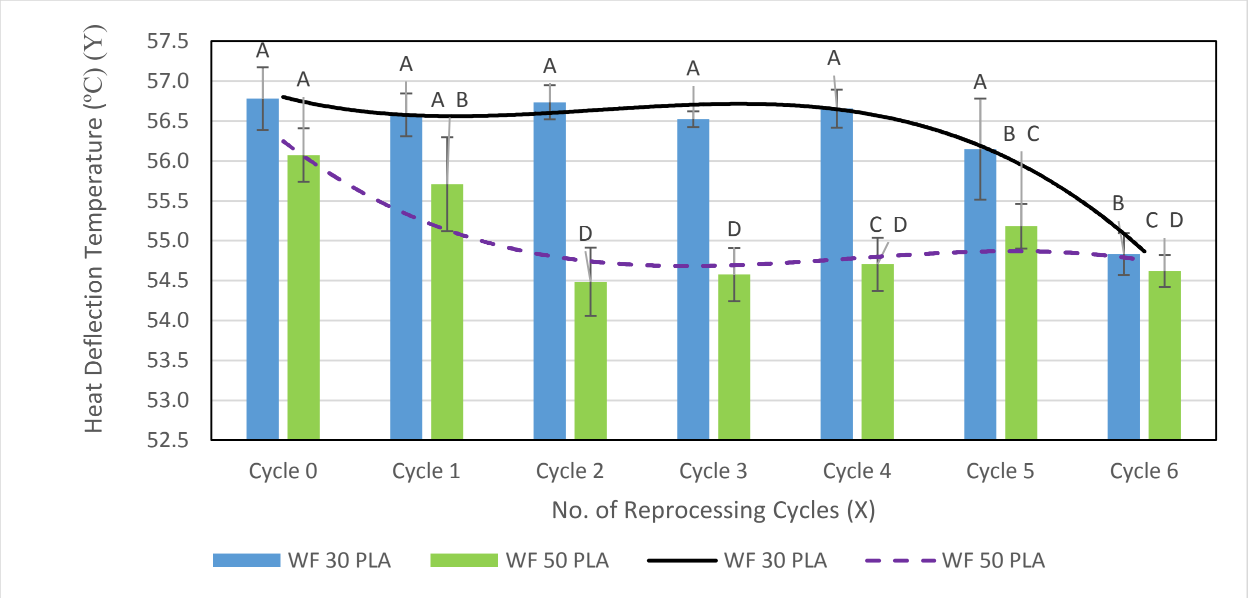

Fig. 5.30: Effect of recycling on the heat deflection temperature (HDT) of WF/PLA composites. Means that do not have a common letter are significantly different.

5.3.3.5. Effect of Recycling on Strain Properties

The impact of recycling was also statistically found significant on failure strain, coefficient of thermal expansion (CTE), and melt flow index (MFI) of both composites (Table 5.15-5.20). Most of these strain properties increased with increased no. of reprocessing cycles. This is because, as the composites become less stiff, they show more inclination to strain by applied load (and/or heat) with successive recycling.

For WF 30 PLA composite, although CTE increased with consecutive recycling, failure strain increased from cycle 0 to cycle 5 and then decreased sharply at cycle 6 (Figs. 5.33 and 5.36). This could be attributed to the fact that failure strain was measured with a tensile load while CTE was measured with no preload force. CTE increased only due to the increase in temperature. At cycle 6, the composite degraded so highly that it could not withstand higher load (Fig. 5.7) and it failed earlier compared to the previous cycles. As the composite failed earlier, its failure strain decreased instead of increasing. On contrast, CTE showed a higher value at cycle 6 due to the absence of external force that resulted in no failure of the composite.

5.3.3.5.1. Data Analysis of Failure Strain

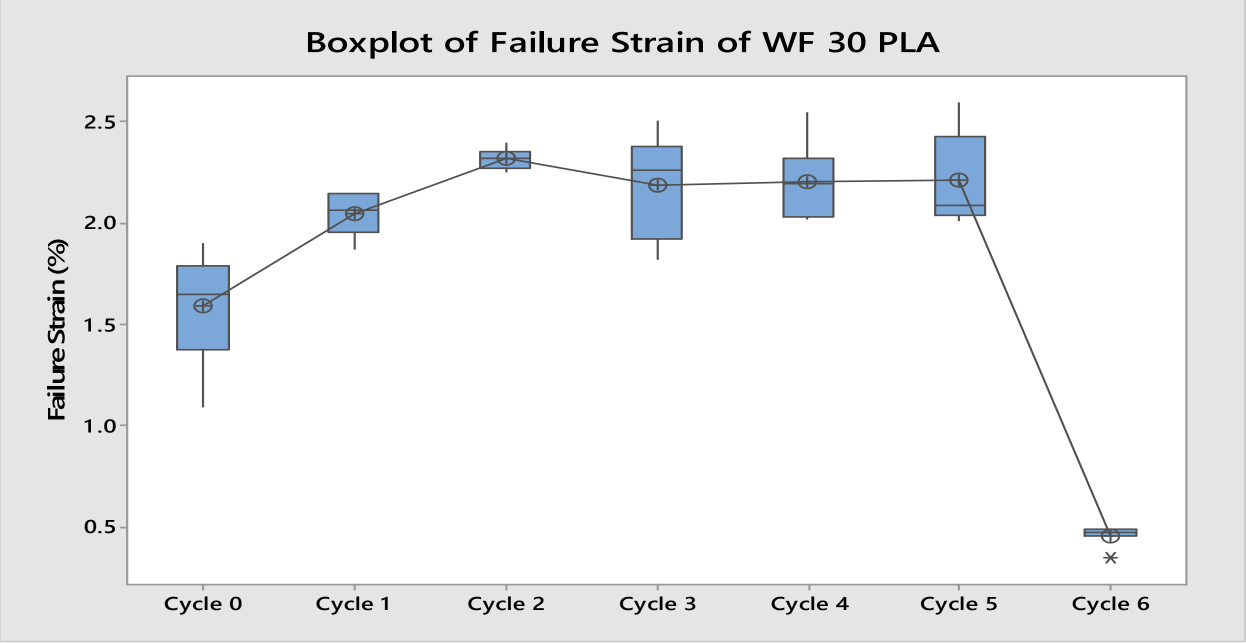

Fig. 5.31: Box plot of failure strain of WF 30 PLA composite.

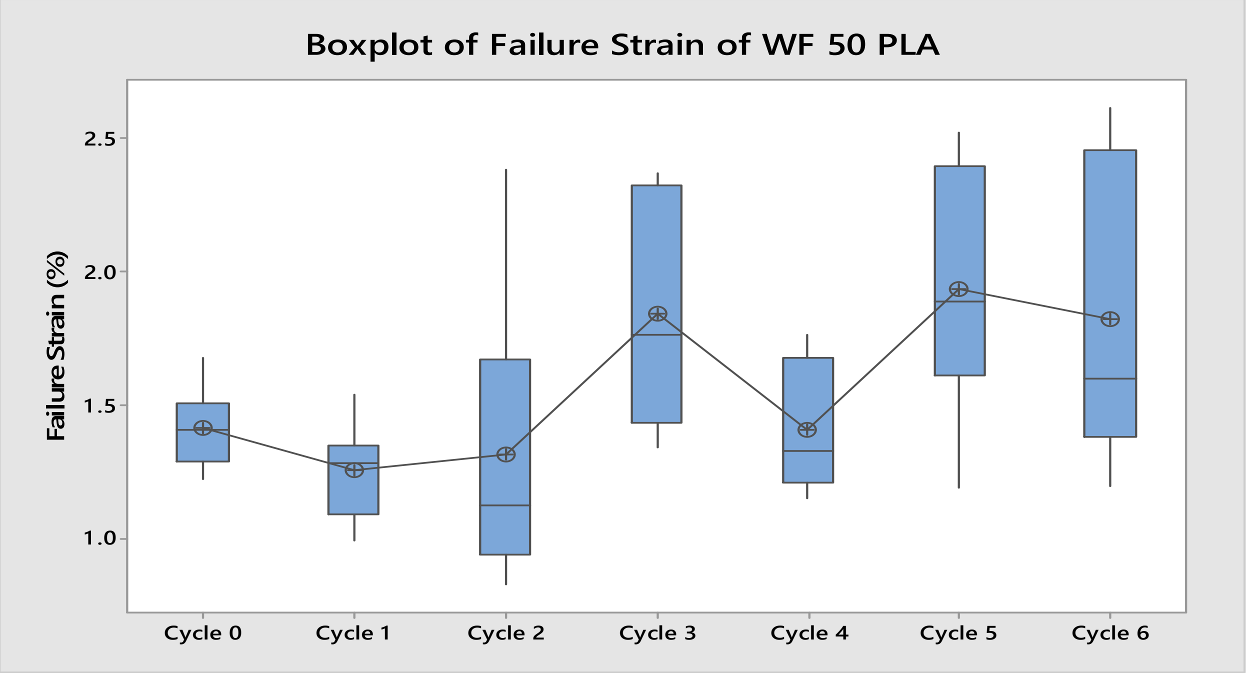

Fig. 5.32: Box plot of failure strain of WF 50 PLA composite.

Table 5.15: One way ANOVA of failure strain of WF 30 PLA composite

```
Source   DF  Adj SS   Adj MS  F-Value  P-Value
Factor    6  21.005  3.50077   104.23    0.000
Error    49   1.646  0.03359
Total    55  22.650
Model Summary
       S    R-sq  R-sq(adj)  R-sq(pred)
0.183263  92.73%     91.84%      90.51%
```

Table 5.16: One way ANOVA of failure strain of WF 50 PLA composite

```
Source   DF  Adj SS  Adj MS  F-Value  P-Value
Factor    6   3.886  0.6477     4.23    0.002
Error    49   7.497  0.1530
Total    55  11.383
Model Summary
       S    R-sq  R-sq(adj)  R-sq(pred)
0.391149  34.14%     26.08%      13.98%
```

The regression equations of expected mean of failure strain (Y) vs. no. of reprocessing cycles (X) of WF 30 PLA (eqn. 5.16) and WF 50 PLA (eqn. 5.17) composite are as follows-

$$Y = 1.682 + 0.0864\ X + 0.1538\ X^2 - 0.03302\ X^3 \tag{5.16}$$

$$Y = 1.283 + 0.09571\ X \tag{5.17}$$

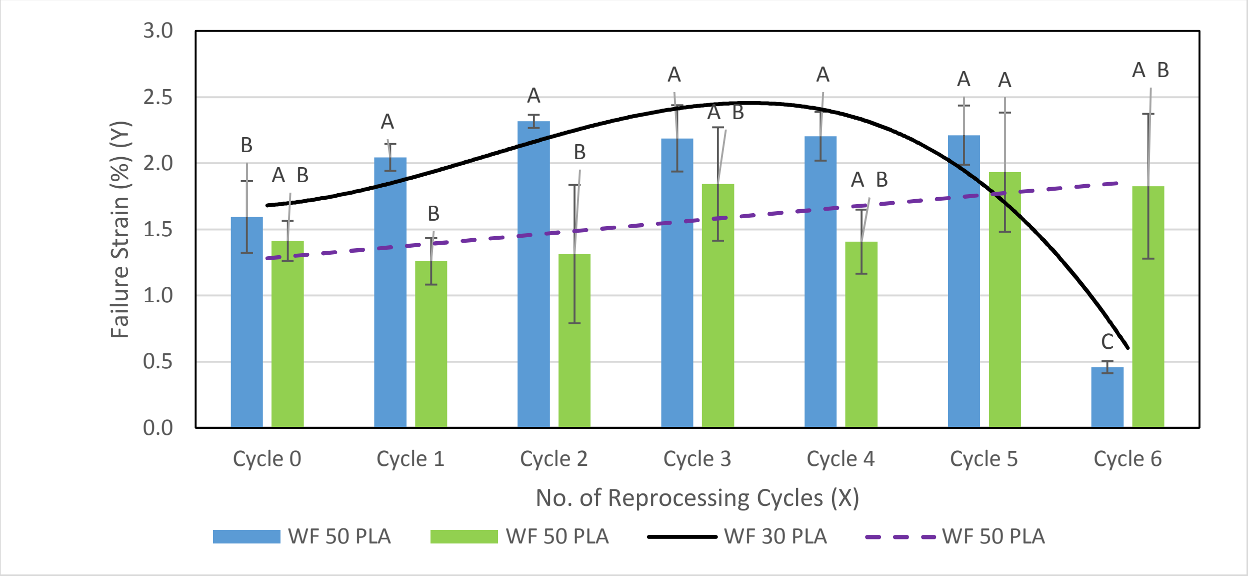

Fig. 5.33: Effect of recycling on the failure strain of WF/PLA composites. Means that do not have a common letter are significantly different.

5.3.3.5.2 Data Analysis of Coefficient of Thermal Expansion (CTE)

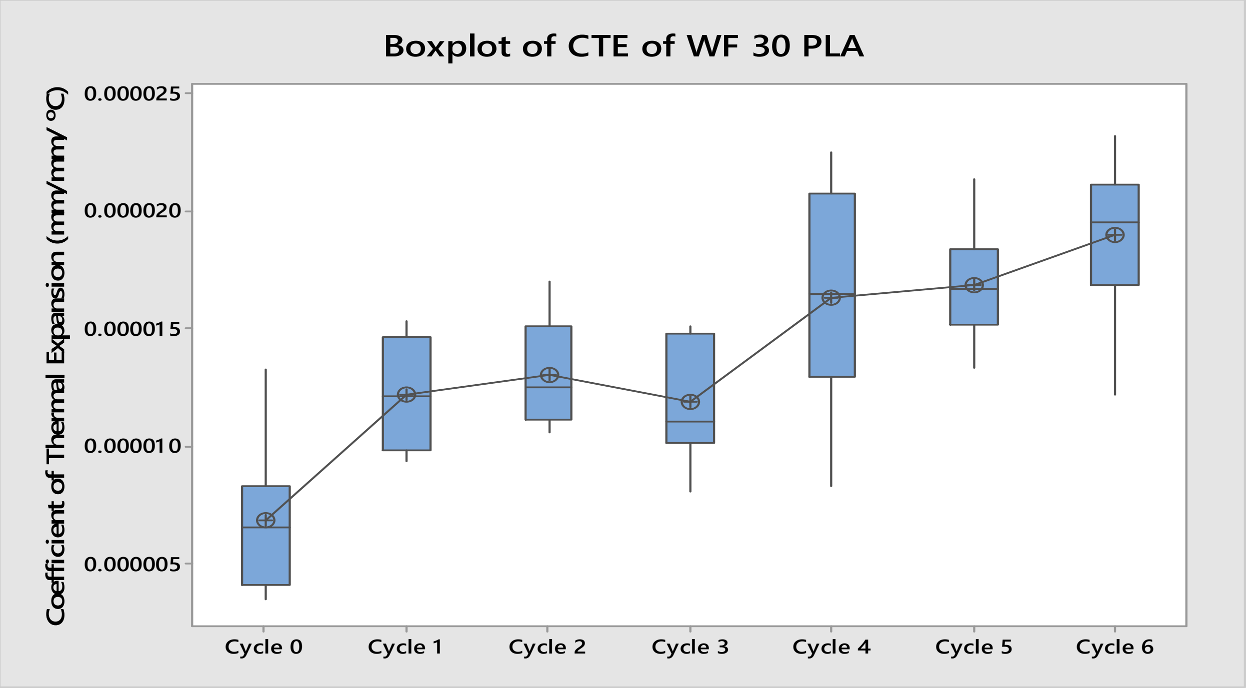

Fig. 5.34: Box plot of CTE of WF 30 PLA composite.

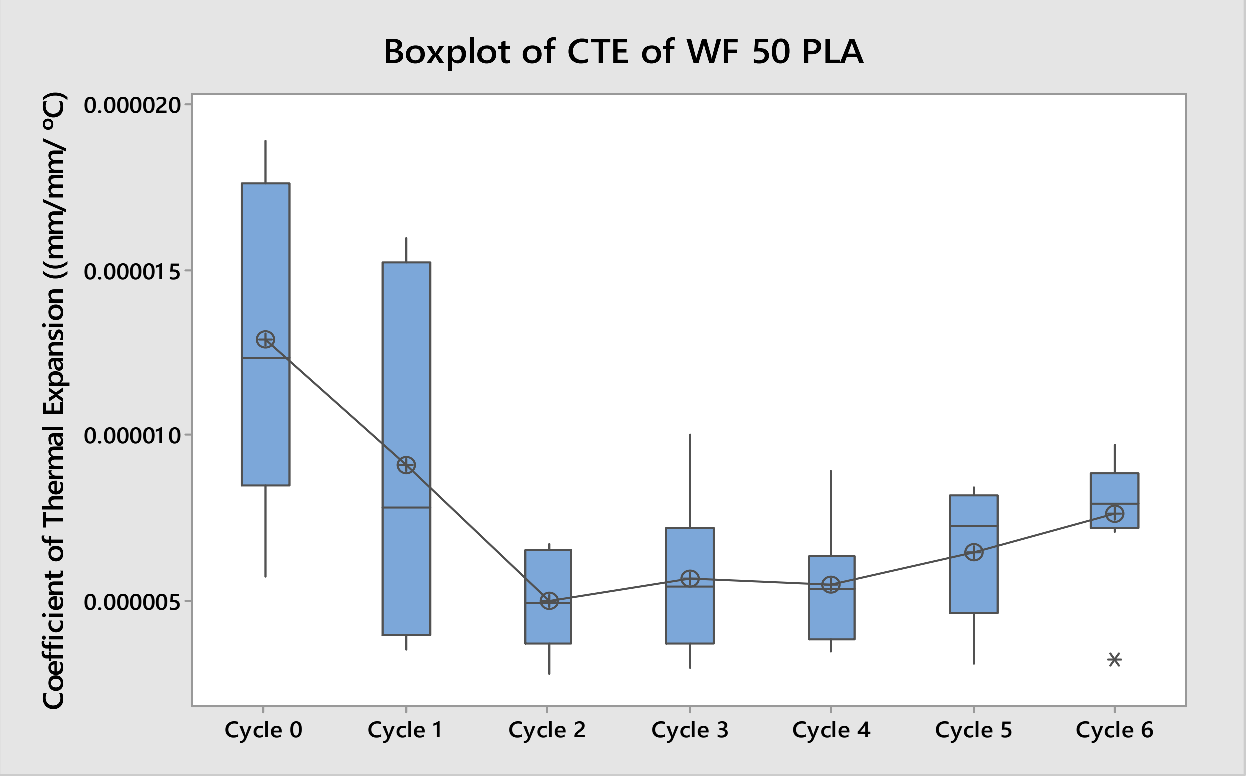

Fig. 5.35: Box plot of CTE of WF 50 PLA composite.

Table 5.17: One way ANOVA of CTE of WF 30 PLA composite

```
Source   DF    Adj SS    Adj MS  F-Value  P-Value
Factor    6  0.000000  0.000000    13.58    0.000
Error    49  0.000000  0.000000
Total    55  0.000000
Model Summary
        S    R-sq  R-sq(adj)  R-sq(pred)
0.0000031  62.45%     57.86%      50.96%
```

Table 5.18: One way ANOVA of CTE of WF 50 PLA composite

```
Source   DF    Adj SS    Adj MS  F-Value  P-Value
Factor    6  0.000000  0.000000     6.07    0.000
Error    49  0.000000  0.000000
Total    55  0.000000
Model Summary
        S    R-sq  R-sq(adj)  R-sq(pred)
0.0000032  42.64%     35.61%      25.08%
```

The regression equations of expected mean of CTE (Y) vs. no. of reprocessing cycles (X) of WF 30 PLA (eqn. 5.18) and WF 50 PLA (eqn. 5.19) composite are as follows-

$$Y = 0.000009 + 0.000002\ X \tag{5.18}$$

$$Y = 0.000013 - 0.000004\ X + 0.000001\ X^2 \tag{5.19}$$

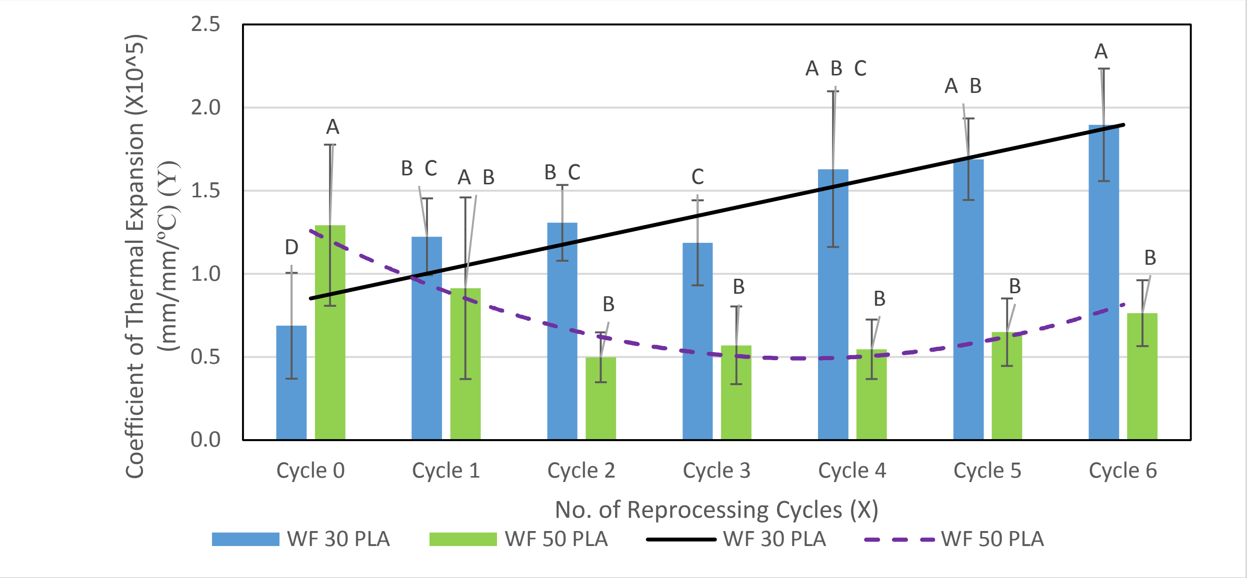

Fig. 5.36: Effect of recycling on the coefficient of thermal expansion (CTE) of WF/PLA composites. Means that do not have a common letter are significantly different.

5.3.3.5.3. Data Analysis of Melt Flow Index (MFI)

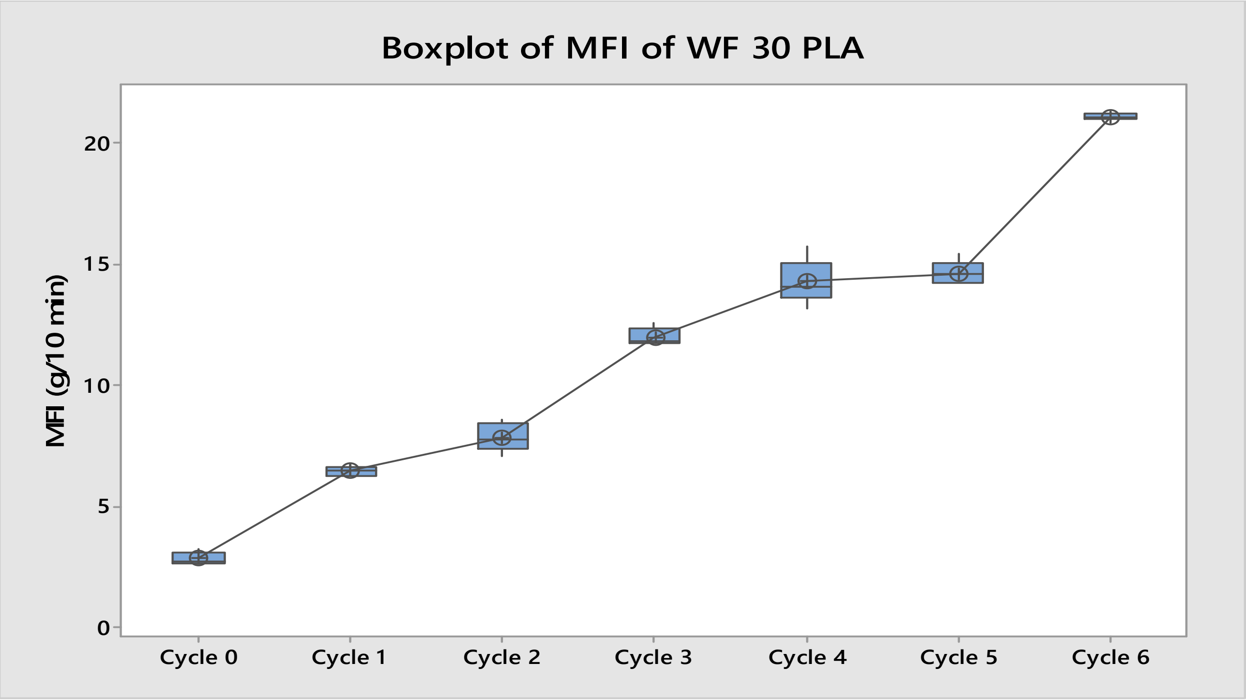

Fig. 5.37: Box plot of MFI of WF 30 PLA composite.

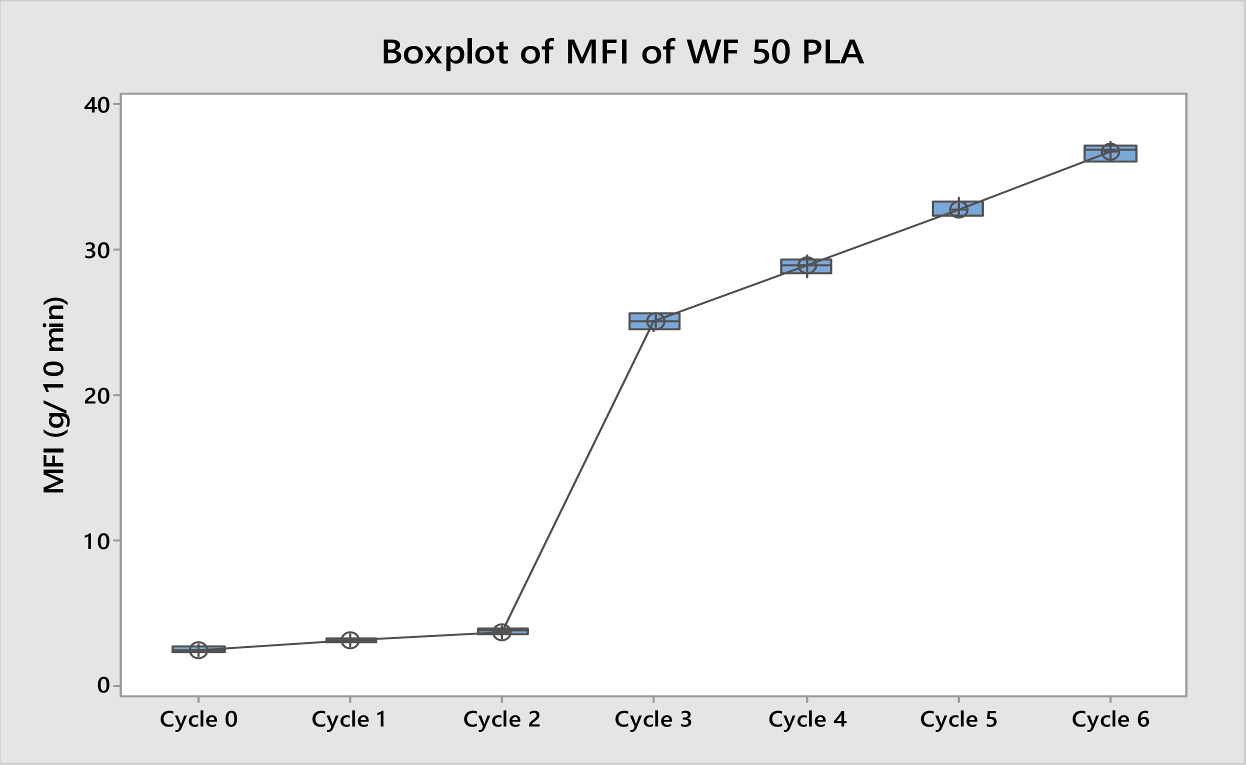

Fig. 5.38: Box plot of MFI of WF 50 PLA composite.

Table 5.19: One way ANOVA of MFI of WF 30 PLA composite

```
Source  DF   Adj SS   Adj MS  F-Value  P-Value
Factor   6  1115.27  185.878   765.94    0.000
Error   28     6.79    0.243
Total   34  1122.06
Model Summary
       S    R-sq  R-sq(adj)  R-sq(pred)
0.492624  99.39%     99.26%      99.05%
```

Table 5.20: One way ANOVA of MFI of WF 50 PLA composite

```
Source  DF   Adj SS   Adj MS  F-Value  P-Value
Factor   6  6954.82  1159.14  5812.51    0.000
Error   28     5.58     0.20
Total   34  6960.41
Model Summary
       S    R-sq  R-sq(adj)  R-sq(pred)
0.446566  99.92%     99.90%      99.87%
```

The regression equations of expected mean of MFI (Y) vs. no. of reprocessing cycles (X) of WF 30 PLA (eqn. 5.20) and WF 50 PLA (eqn. 5.21) composite are as follows-

$$Y = 2.712 + 4.411\ X - 0.8483\ X^2 + 0.1014\ X^3 \tag{5.20}$$

$$Y = 2.236 - 4.563\ X + 5.101\ X^2 - 0.5698\ X^3 \tag{5.21}$$

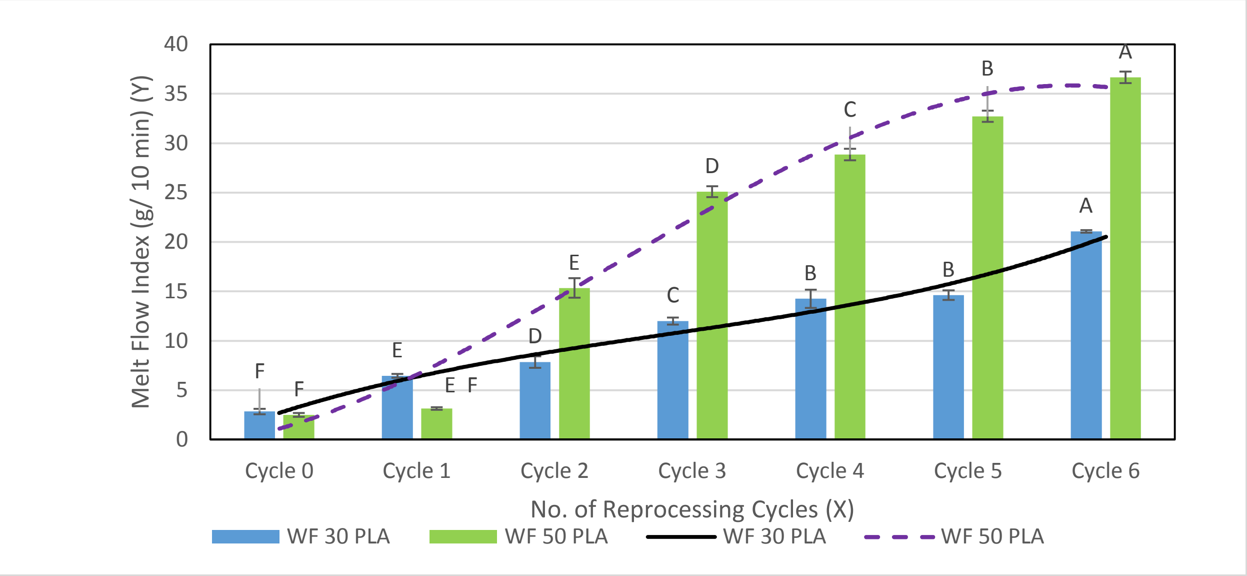

Fig. 5.39: Effect of recycling on the melt flow index (MFI) of WF/PLA composites. Means that do not have a common letter are significantly different.

Table 5.21: Relative difference in means of properties of WF/PLA composites between cycle 0 and cycle 6 (values in parentheses are the corresponding standard deviations)

Properties	WF 30 PLA Composite			WF 50 PLA Composite		
	Cycle 0	Cycle 6	Relative Difference (%)	Cycle 0	Cycle 6	Relative Difference (%)
Tensile Strength (MPa)	55.46 (2.95)	29.21 (3.23)	-47.34	53.98 (3.61)	31.38 (9.55)	-41.86
Tensile Modulus (MPa)	6949.95 (331.99)	6303.36 (759.82)	-9.30	8487.95 (698.60)	3907.93 (725.54)	-53.96
Failure Strain (%)	1.59 (0.27)	0.46 (0.04)	-71.22	1.41 (0.15)	1.83 (0.54)	29.20
Flexural Strength (MPa)	90.96 (2.543)	26.81 (3.929)	-70.53	91.24 (5.80)	27.26 (2.15)	-70.12
Flexural Modulus (MPa)	5811.89 (273.48)	4163.17 (74.57)	-28.37	6685.00 (450.84)	6284.67 (135.05)	-5.99
Impact Resistance (J/m)	47.18 (5.48)	13.13 (3.73)	-72.18	31.32 (6.13)	18.76 (4.15)	-40.10
Heat Deflection Temperature (ºC)	56.78 (0.39)	54.83 (0.26)	-3.43	56.07 (0.33)	54.62 (0.2)	-2.58
Storage Modulus (MPa)	6405.88 (303.47)	5721.88 (271.05)	-10.68	7347.88 (498.78)	6317 (288.39)	-14.03
Coefficient of Thermal Expansion (mm/mm/ ºC)	6.87E-06 (3.18E-06)	1.89E-05 (3.38E-06)	175.94	1.29E-05 (4.83E-06)	7.63E-06 (1.97E-06)	-40.93
Melt Flow Index (g/ 10 min)	2.85 (0.26)	21.09 (0.13)	640.37	2.50 (0.21)	36.67 (0.58)	1364.60

5.3.3.6. FTIR Analysis

Fourier Transform Infra-Red Spectroscopy (FTIR) was conducted- at cycle 0 and cycle 6 of both formulations- that showed ongoing degradation during reprocessing (Figs. 5.40 and 5.41). The characteristic absorptions, functional groups, type of vibration, and chemical reactions are shown in Table 5.22 and 5.23 [38, 39]. Some functional groups such as carboxylic acid, ether, alcohols, and phenols indicate oxidative reactions while other functional groups, such as Amine, indicate weaker bond formation. All these functional groups, produced by chemical reactions, imply the ongoing degradation of the composites during extrusion (recycling). Each composite formulation shows characteristic absorptions at almost the same wavenumbers for cycle 0 and cycle 6. However, due to the inconsistencies associated with FTIR experiment- unequal thickness and heterogeneity of small composite samples- the relative degradation between cycle 0 and corresponding cycle 6 could not be measured.

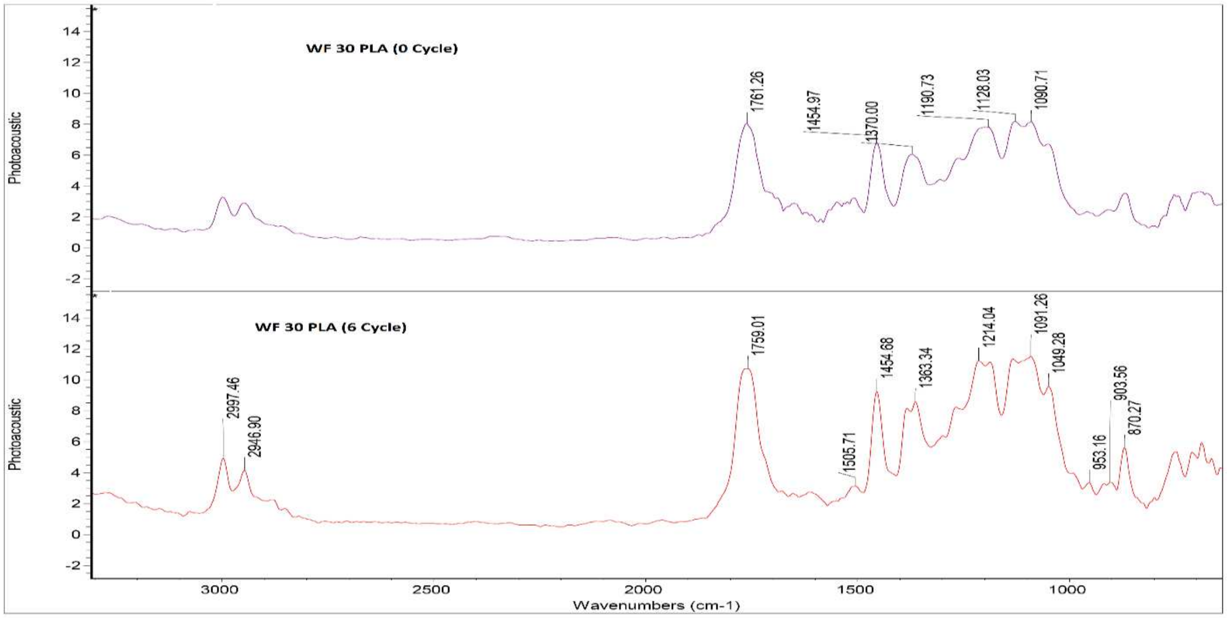

Fig. 5.40: FTIR Spectra of WF 30 PLA composite at cycle 0 (indigo) and cycle 6 (red).

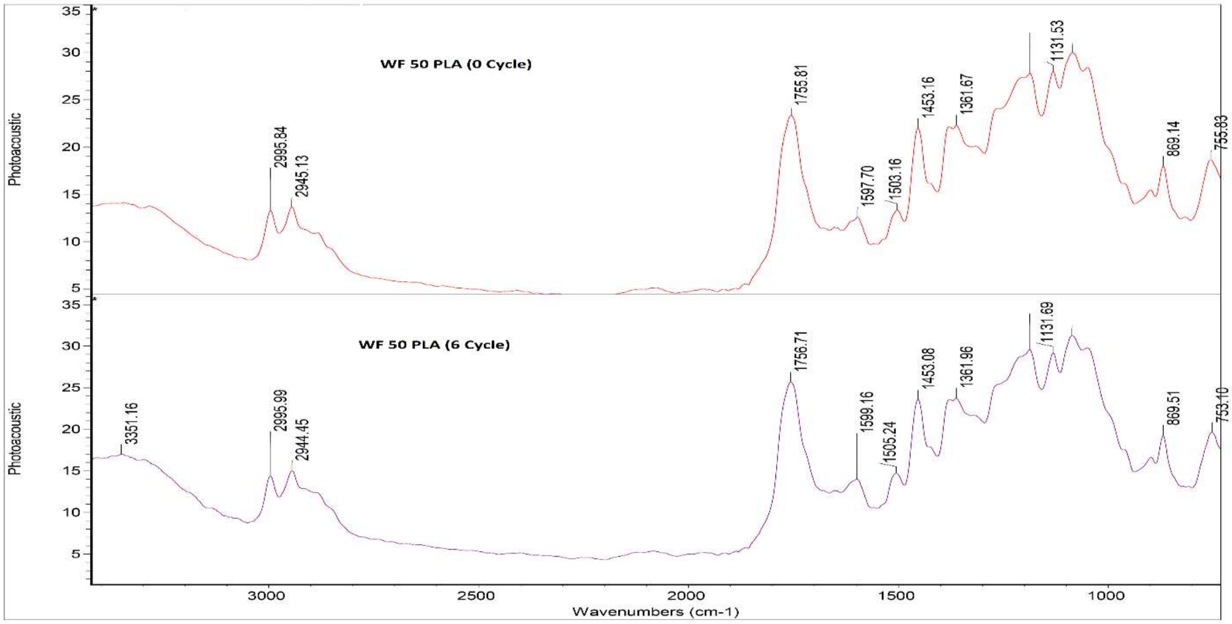

Fig. 5.41: FTIR Spectra of WF 50 PLA composite at cycle 0 (red) and cycle 6 (indigo).

Table 5.22: FTIR analysis of WF 30 PLA composite at cycle 0 and cycle 6 [38, 39]. Left and right characteristic absorptions in the first column are the wavenumbers respectively at cycle 0 and cycle 6. Otherwise, the characteristic absorptions are same for both cycles.

Characteristic Absorptions (cm^{-1})	Functional Group	Type of Vibration	Indication by Functional Group
1761 / 1769	Carboxylic Acid	Stretch	Oxidation
1505	Carboxylic Acid	Bending	Oxidation
1454	Amine	Stretch	Weaker Bond
1370 / 1363	Alcohols or Phenols	Bending	Oxidation
1190 / 1214	Ether / Amine	Stretch	Oxidation / Weaker Bond
1091	Ether / Amine	Stretch	Oxidation / Weaker Bond
1049	Ether / Amine	Stretch	Oxidation / Weaker Bond
870	Amine	Bending	Weaker Bond

Table 5.23: FTIR analysis of WF 50 PLA composite at cycle 0 and cycle 6 [38, 39]. Left and right characteristic absorptions in the first column are the wavenumbers respectively at cycle 0 and cycle 6. Otherwise, the characteristic absorptions are same for both cycles.

Characteristic Absorptions (cm^{-1})	Functional Group	Type of Vibration	Indication by Functional Group
1755	Carboxylic Acid	Stretch	Oxidation
1597 / 1600	Carboxylic Acid	Bending	Oxidation
1505	Carboxylic Acid	Bending	Oxidation
1453	Amine	Stretch	Weaker Bond
1361	Alcohols or Phenols	Bending	Oxidation
1131	Ether / Amine	Stretch	Oxidation / Weaker Bond
869	Amine	Bending	Weaker Bond
755	Amine	Bending	Weaker Bond

5.3.3.7. Effect of Recycling on Crystallinity and Thermal Stability

The percentage crystallinity of PLA (of WF 50 PLA composite) was measured by the following equation [2]:

$$\% \text{ Crystallinity}=\left(\frac{\Delta H_{exp}}{\Delta H}\right) x \left(\frac{1}{W}\right) x100 \qquad (5.22)$$

Here, ΔH_{exp} is the experimental heat of fusion determined by DSC, ΔH is the heat of fusion of fully crystalline PLA (93.1 J/g), and W is the weight fraction of PLA in the composite. The crystallinity of PLA (in composite) decreased with increased no. of reprocessing cycles (Fig. 5.42 and Table 5.24). This is because, the fibers probably degraded in a relatively higher amount that to PLA at cycle 6. From cycle 0 to cycle 6, the average fiber length decreased approximately 56% while the weight averaged molecular weight of PLA decreased 45.7% (Sec. 3.3.1-3.3.2). Although the molecular weight reduction of PLA is to increase the crystallinity of the composite, the higher relative fiber degradation, caused by reprocessing, results in lower crystallinity. Similarly, the melting temperature of PLA in composites decreased with reprocessing due to the molecular weight reduction [1].

However, thermal stability (of WF 50 PLA composite) increased with increased no. of reprocessing cycles (Table 5.25 and Figs. 5.43-5.44). This could be due to the molecular weight reduction of PLA at cycle 6 [1]. In addition, the amount of volatiles in the composite possibly decreased with successive recycling that resulted in increased thermal stability of the composite.

Table 5.24: DSC analysis of WF 50 PLA composite at cycle 0 and cycle 6

Properties	Cycle 0	Cycle 6
Melting Point (ºC)	152.15	149.64
Crystallization Temperature (ºC)	145.33	144.24
Heat of Fusion (J/g)	16.64	15.42
Crystallinity (%)	38.03	35.24

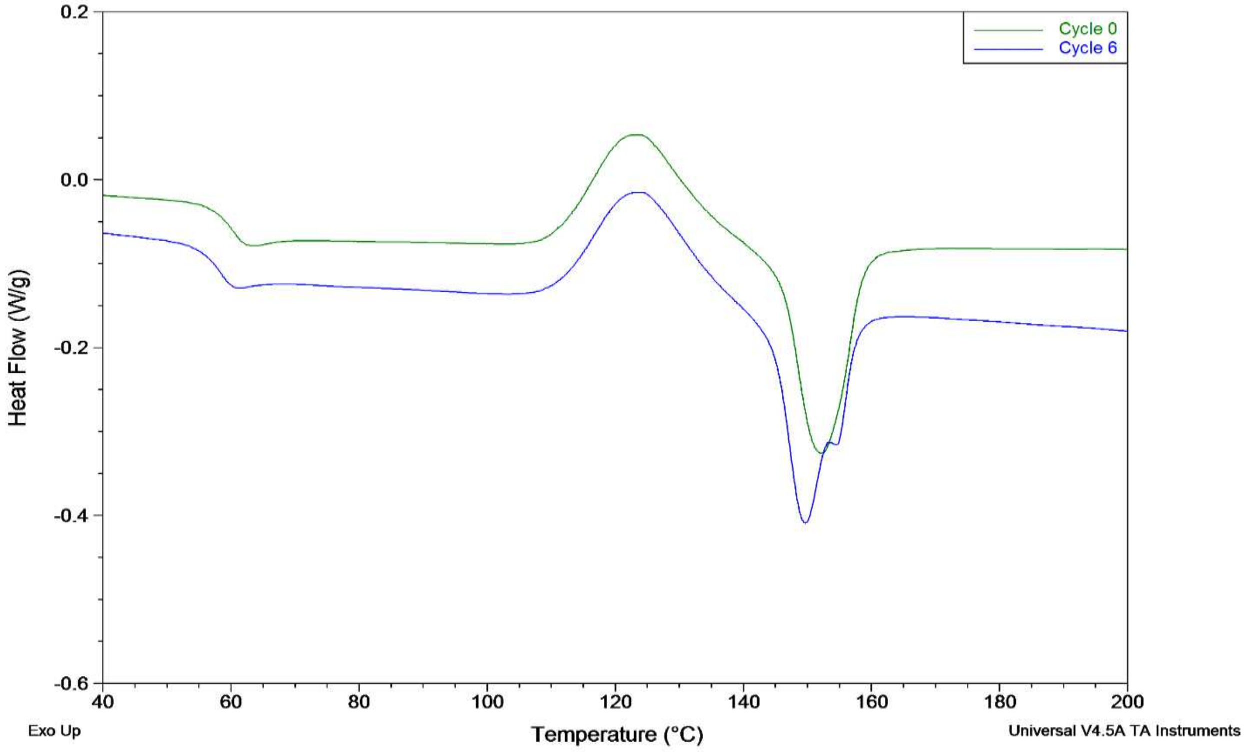

Fig. 5.42: DSC analysis curves of WF 50 PLA composite at cycle 0 and cycle 6.

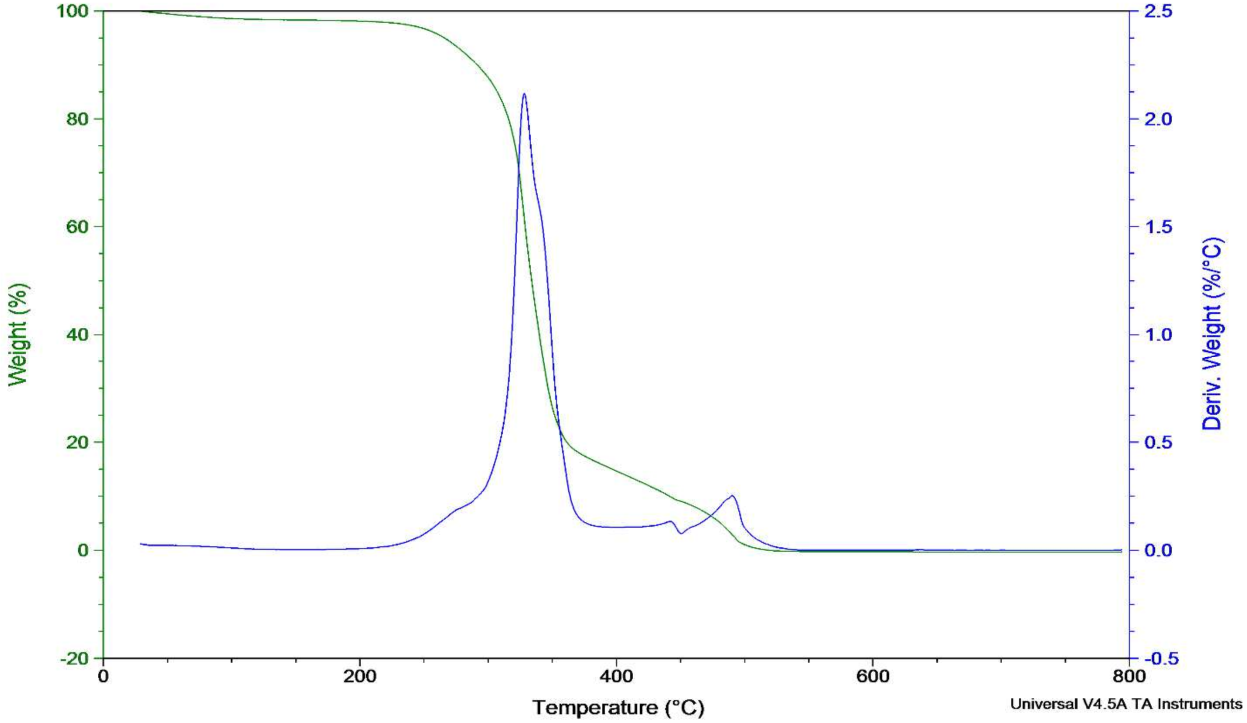

Fig. 5.43: TGA curve and 1st derivative of the curve (with respect to temperature) of WF 50 PLA composite at cycle 0.

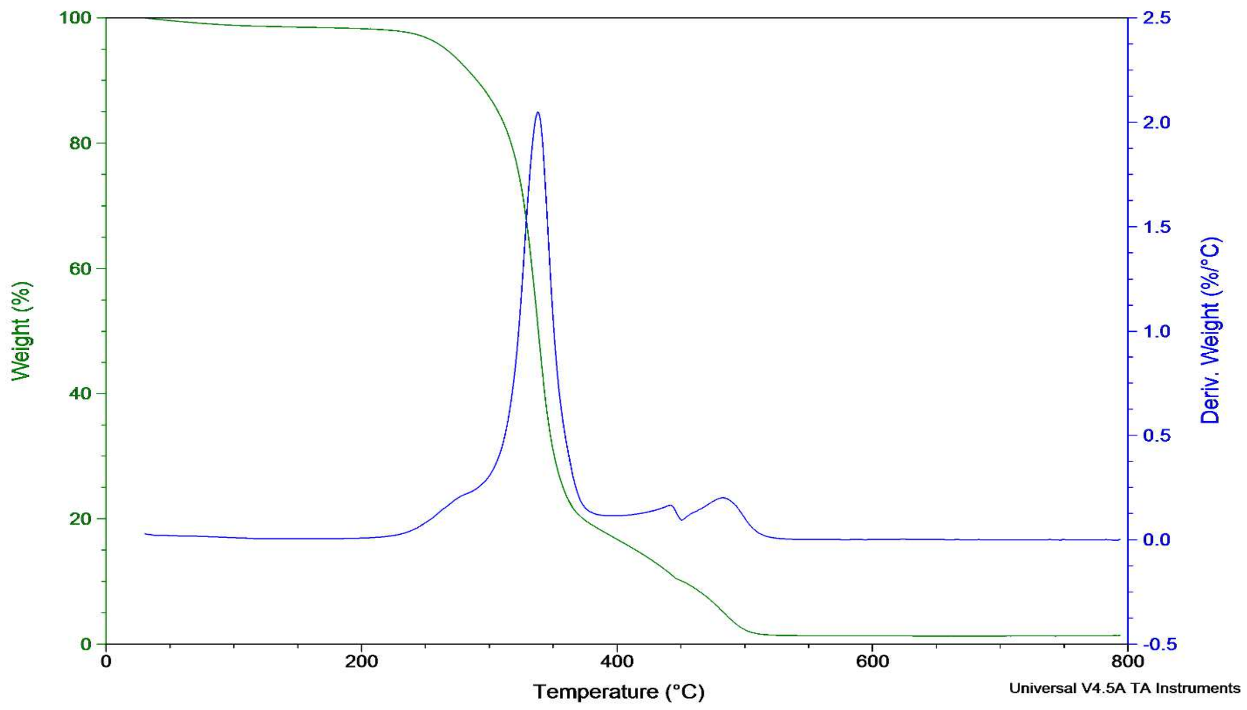

Fig. 5.44: TGA curve and 1st derivative of the curve (with respect to temperature) of WF 50 PLA composite at cycle 6.

5.3.3.8. Comparison of Fiber Lengths of HDPE and PLA Composite

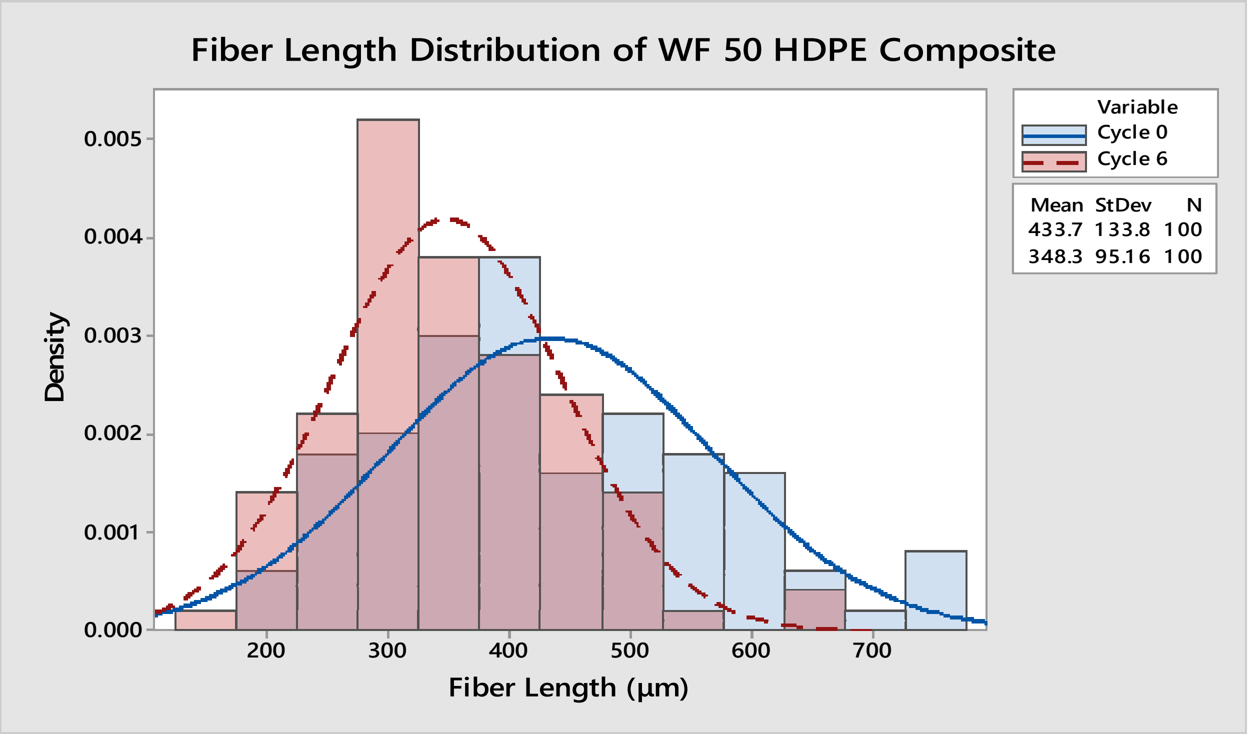

Fig. 5.45: Normal distribution plot of fiber length of WF 50 HDPE composite at cycle 0 and 6.

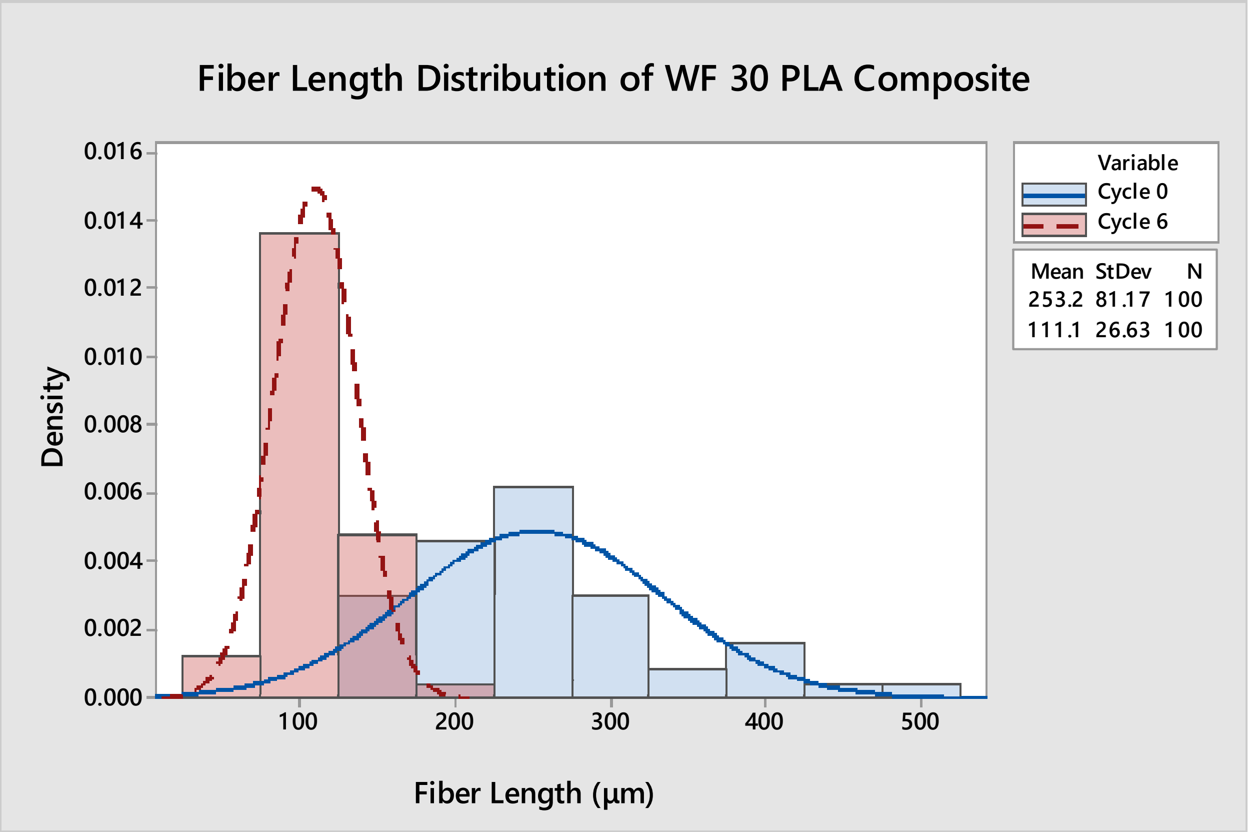

Fig. 5.46: Normal distribution plot of fiber length of WF 30 PLA composite at cycle 0 and 6.

Table 5.25: TGA of WF 50 PLA composite at cycle 0 and cycle 6

Property	Cycle 0	Cycle 6
Onset Thermal Degradation Temperature (ºC)	312.42	316.10
Fastest Decomposition Temperature (ºC)	327.06	337.22
Residue (%)	0	1.35

As mentioned earlier, most wood fiber lengths- before incorporating into polymer- were in the range of 250-400 µm (Table 1.2), and due to reprocessing or re-extrusion, the average fiber length of both composites decreased from cycle 0 to cycle 6. However, PLA composite showed smaller average fiber length that to HDPE composite at corresponding cycles (Figs. 5.45 and 5.46).

At cycle 0, the average fiber lengths of PLA and HDPE composite were respectively 253.2 µm and 433.7 µm; and at cycle 6, the values were 111.1 µm and 348.3 µm. This could be due to two probable reasons. First, PLA has a lower MFI (6 g/10min) that to HDPE (11.5 g/10 min), which led to higher shear stress for PLA composite during extrusion compared to that of HDPE composite, and finally resulted in lower average fiber length of PLA composite. And second, the screw rpm of extrusion for PLA and HDPE composite were 200 and 150 respectively. This higher screw speed produced higher shear stress (or shear rates), which could also result in lower average fiber length of PLA composite.

5.4. Conclusion

Wood flour/PLA composites were made by extrusion with a coupling agent (PLA-g-MA). Two filler loading composites (30 and 50 wt% WF) were formulated- each with 3 wt% PLA-g-MA. The coupling agent did not improve most mechanical and thermo-mechanical properties of both composites. Higher filler content increased stiffness properties (tensile, flexural, and storage modulus), decreased strain properties (failure strain, CTE, and MFI), and showed no impact on strength properties (tensile and flexural strength, and impact resistance) of the composite. Both composites were individually reprocessed up to six times by extrusion. For 30 wt% filler composite, strength properties sharply decreased at cycle 6 while these properties were somewhat constant in the previous cycles. On contrast, for 50 wt% filler composite, strength properties highly decreased at cycle 2 rather than cycle 6. However, for both composites, stiffness properties and HDT showed a lower relative decrease that to corresponding strength properties with successive recycling. Most strain properties of both composites increased with increased no. of reprocessing cycles.

CHAPTER 6. CONCLUSION AND FUTURE WORK

This research explores the impact of recycling on the mechanical and thermo-mechanical properties of two different types of WPCs- WF/HDPE and WF/PLA composite- each of which consists of two different filler loading formulations (30 and 50 wt% filler). Each formulation incorporated 3 wt% of a corresponding compatible coupling agent, and was individually reprocessed six times by extrusion. From extruded pellets, test samples were prepared by injection molding. Mechanical and thermo-mechanical tests were performed on every reprocessed cycle (cycle 0 to cycle 6) of each formulation. All these test results were statistically analyzed with a confidence level of 95%. Additionally, some other tests were also conducted to understand the changes in properties of composites produced by recycling. This chapter briefly discusses the findings of this research along with some suggested future work.

6.1. Impact of Recycling on the Properties of WF/HDPE Composite

The coupling agent (MAPE) improved most of the mechanical and thermo-mechanical properties of both virgin (cycle 0) composite formulations. At cycle 0, the coupling agent showed more improvement in properties of 50 wt% filler composite that to 30 wt% filler composite. Higher WF content increased the strength and stiffness properties but decreased the strain properties of the virgin composite. The effect of recycling was statistically found significant for all mechanical and thermo-mechanical properties of both formulations. Thermal stability of higher filler composite increased but crystallinity decreased with increased no. of reprocessing cycles. Both composite formulations showed lower relative decrease in strength and stiffness properties but higher relative increase in strain properties (between cycle 0 and cycle 6) with increased no. of reprocessing cycles, primarily due to the fiber and polymer degradation.

6.2. Impact of Recycling on the Properties of WF/PLA Composite

The coupling agent (PLA-g-MA) did not improve the properties of both composite formulations. Higher WF content increased the stiffness properties of the composite but did not improve the strength properties. The effect of recycling was statistically found significant for all mechanical and thermo-mechanical properties of both formulations. Most of the strength and stiffness properties (of both composites) decreased but strain properties increased with increased no. of reprocessing cycles, primarily because of the fiber and polymer degradation. Higher and lower filler composite showed a drastic decrease in strength properties respectively at second and sixth reprocessing cycle. Thermal stability of 50 wt% filler composite increased but crystallinity decreased with increased no. of reprocessing cycles.

6.3. Suggested Future Work

- A higher amount of CA (4 or 5 wt %) could provide better results for WF/PLA composites.
- Other extrusion temperature profiles could improve the impact of recycling for all composite formulations.
- All results and conclusions of this research are based on a laboratory scale. Therefore, the industrial use of these composites could show some variation in properties.
- Accelerated freeze-thaw cycling could be considered at each cycle for better understanding of the reprocessing effect on the composite properties.
- Rheological experiments could be added to make the research more worthwhile.

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APPENDIX A: REGRESSION ANALYSIS OF THE PROPERTIES OF WF/HDPE COMPOSITE

A.1. Tensile Strength

A.1.1. WF 30 HDPE

```
The regression equation is
Y = 25.77 - 0.7167 X + 0.04039 X^2
S = 0.349894   R-Sq = 88.8%   R-Sq(adj) = 88.4%
Analysis of Variance
Source      DF       SS       MS       F      P
Regression   2  51.5099  25.7550  210.37  0.000
Error       53   6.4886   0.1224
Total       55  57.9985
Sequential Analysis of Variance
Source     DF       SS       F      P
Linear      1  50.4137  358.92  0.000
Quadratic   1   1.0962    8.95  0.004
```

A.1.2. WF 50 HDPE

```
The regression equation is
Y = 32.94 - 1.056 X + 0.08380 X^2
S = 0.345897   R-Sq = 92.0%   R-Sq(adj) = 91.7%
Analysis of Variance
Source      DF       SS       MS       F      P
Regression   2  73.2984  36.6492  306.32  0.000
Error       53   6.3412   0.1196
Total       55  79.6396
Sequential Analysis of Variance
Source     DF       SS       F      P
Linear      1  68.5798  334.84  0.000
Quadratic   1   4.7186   39.44  0.000
```

A.2. Tensile Modulus

A.2.1. WF 30 HDPE

```
The regression equation is
Y = 2492 - 59.46 X
S = 116.271   R-Sq = 52.0%   R-Sq(adj) = 51.1%
```

```
Analysis of Variance
Source      DF       SS      MS      F      P
Regression   1   791910  791910  58.58  0.000
Error       54   730027   13519
Total       55  1521937
```

A.2.2. WF 50 HDPE

```
The regression equation is
Y = 4766 - 315.4 X + 40.03 X^2
S = 260.174   R-Sq = 39.5%   R-Sq(adj) = 37.2%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   2  2343392  1171696  17.31  0.000
Error       53  3587590    67690
Total       55  5930982
Sequential Analysis of Variance
Source     DF       SS      F      P
Linear      1  1266359  14.66  0.000
Quadratic   1  1077033  15.91  0.000
```

A.3. Failure Strain

A.3.1. WF 30 HDPE

```
The regression equation is
Y = 8.913 + 0.8479 X
S = 1.06744   R-Sq = 72.4%   R-Sq(adj) = 71.8%
Analysis of Variance
Source      DF       SS       MS       F      P
Regression   1  161.042  161.042  141.34  0.000
Error       54   61.529    1.139
Total       55  222.571
```

A.3.2. WF 50 HDPE

```
The regression equation is
Y = 4.568 + 0.2729 X
S = 0.366244   R-Sq = 69.7%   R-Sq(adj) = 69.2%
Analysis of Variance
Source      DF       SS       MS       F      P
Regression   1  16.6770  16.6770  124.33  0.000
Error       54   7.2433   0.1341
Total       55  23.9203
```

A.4. Flexural Strength

A.4.1. WF 30 HDPE

```
The regression equation is
Y = 31.65 - 0.8366 X
S = 1.10321   R-Sq = 70.5%   R-Sq(adj) = 69.9%
Analysis of Variance
Source      DF       SS       MS       F      P
Regression   1  156.763  156.763  128.80  0.000
Error       54   65.722    1.217
Total       55  222.485
```

A.4.2. WF 50 HDPE

```
The regression equation is
Y = 46.67 - 0.9142 X
S = 1.92790   R-Sq = 48.3%   R-Sq(adj) = 47.3%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   1  187.191  187.191  50.36  0.000
Error       54  200.708    3.717
Total       55  387.898
```

A.5. Flexural Modulus

A.5.1. WF 30 HDPE

```
The regression equation is
Y = 1358 - 191.3 X + 50.60 X^2 - 4.788 X^3
S = 50.1837   R-Sq = 83.2%   R-Sq(adj) = 82.2%
Analysis of Variance
Source      DF      SS      MS      F      P
Regression   3  648128  216043  85.79  0.000
Error       52  130957    2518
Total       55  779085
Sequential Analysis of Variance
Source     DF      SS       F      P
Linear      1  570618  147.81  0.000
Quadratic   1   37904   11.78  0.001
Cubic       1   39607   15.73  0.000
```

A.5.2. WF 50 HDPE

```
The regression equation is
Y = 2584 - 187.9 X + 15.64 X^2
S = 152.758   R-Sq = 63.4%   R-Sq(adj) = 62.1%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   2  2146469  1073234  45.99  0.000
Error       53  1236752    23335
Total       55  3383221
Sequential Analysis of Variance
Source     DF       SS      F      P
Linear      1  1982113  76.39  0.000
Quadratic   1   164355   7.04  0.010
```

A.6. Coefficient of Thermal Expansion (CTE)

A.6.1. WF 30 HDPE

```
The regression equation is
Y = 0.000033 + 0.000003 X
S = 7.844562E-06   R-Sq = 34.1%   R-Sq(adj) = 32.8%
Analysis of Variance
Source      DF         SS         MS      F      P
Regression   1  0.0000000  0.0000000  27.90  0.000
Error       54  0.0000000  0.0000000
Total       55  0.0000000
```

A.6.2. WF 50 HDPE

```
The regression equation is
Y = 0.000015 + 0.000002 X
S = 0.0000103558   R-Sq = 8.9%   R-Sq(adj) = 7.2%
Analysis of Variance
Source      DF         SS         MS     F      P
Regression   1  0.0000000  0.0000000  5.25  0.026
Error       54  0.0000000  0.0000000
Total       55  0.0000000
```

A.7. Heat Deflection Temperature (HDT)

A.7.1. WF 30 HDPE

```
The regression equation is
Y = 79.42 - 1.262 X
```

```
S = 4.12173   R-Sq = 28.0%   R-Sq(adj) = 26.7%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   1   356.73  356.732  21.00  0.000
Error       54   917.39   16.989
Total       55  1274.12
```

A.7.2. WF 50 HDPE

```
The regression equation is
Y = 112.8 - 2.120 X
S = 4.46375   R-Sq = 48.4%   R-Sq(adj) = 47.4%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   1  1007.21  1007.21  50.55  0.000
Error       54  1075.95    19.93
Total       55  2083.17
```

A.8. Storage Modulus

A.8.1. WF 30 HDPE

```
The regression equation is
Y = 2607 - 323.7 X + 94.49 X^2 - 8.830 X^3
S = 86.8267   R-Sq = 72.1%   R-Sq(adj) = 70.5%
Analysis of Variance
Source      DF       SS      MS      F      P
Regression   3  1013462  337821  44.81  0.000
Error       52   392021    7539
Total       55  1405484
Sequential Analysis of Variance
Source     DF      SS      F      P
Linear      1  727206  57.90  0.000
Quadratic   1  151530  15.25  0.000
Cubic       1  134726  17.87  0.000
```

A.8.2. WF 50 HDPE

```
The regression equation is
Y = 3643 - 85.55 X
S = 199.682   R-Sq = 43.2%   R-Sq(adj) = 42.2%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   1  1639378  1639378  41.11  0.000
```

```
Error       54  2153146    39873
Total       55  3792523
```

A.9. Impact Resistance

A.9.1. WF 30 HDPE

```
The regression equation is
Y = 54.84 - 7.718 X + 1.696 X^2 - 0.1521 X^3
S = 2.53246   R-Sq = 84.1%   R-Sq(adj) = 83.2%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   3  1760.64  586.879  91.51  0.000
Error       52   333.49    6.413
Total       55  2094.13
Sequential Analysis of Variance
Source     DF       SS       F      P
Linear      1  1648.71  199.88  0.000
Quadratic   1    71.94   10.21  0.002
Cubic       1    39.99    6.23  0.016
```

A.9.2. WF 50 HDPE

```
The regression equation is
Y = 50.70 - 2.109 X
S = 4.82624   R-Sq = 44.2%   R-Sq(adj) = 43.2%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   1   996.34  996.342  42.78  0.000
Error       54  1257.80   23.293
Total       55  2254.14
```

A.10. Melt Flow Index (MFI)

A.10.1. WF 30 HDPE

```
The regression equation is
Y = 3.243 + 0.6625 X - 0.1385 X^2 + 0.01045 X^3
S = 0.101759   R-Sq = 94.8%   R-Sq(adj) = 94.3%
Analysis of Variance
Source      DF       SS       MS       F      P
Regression   3  5.82047  1.94016  187.37  0.000
Error       31  0.32100  0.01035
Total       34  6.14147
```

```
Sequential Analysis of Variance
Source     DF       SS       F      P
Linear      1  4.87101  126.52  0.000
Quadratic   1  0.83153   60.62  0.000
Cubic       1  0.11794   11.39  0.002
```

A.10.2. WF 50 HDPE

```
The regression equation is
Y = 0.5387 + 0.4147 X - 0.02961 X^2
S = 0.0638216   R-Sq = 98.4%   R-Sq(adj) = 98.3%
Analysis of Variance
Source      DF       SS       MS        F      P
Regression   2  8.23514  4.11757  1010.89  0.000
Error       32  0.13034  0.00407
Total       34  8.36549
Sequential Analysis of Variance
Source     DF       SS       F      P
Linear      1  7.86698  520.78  0.000
Quadratic   1  0.36816   90.39  0.000
```

APPENDIX B: REGRESSION ANALYSIS OF THE PROPERTIES OF WF/PLA COMPOSITE

B.1. Tensile Strength

B.1.1. WF 30 PLA

```
The regression equation is
Y = 56.32 - 4.253 X + 2.818 X^2 - 0.4704 X^3
S = 2.89357   R-Sq = 90.6%   R-Sq(adj) = 90.1%
Analysis of Variance
Source      DF       SS       MS       F      P
Regression   3  4220.37  1406.79  168.02  0.000
Error       52   435.38     8.37
Total       55  4655.76
Sequential Analysis of Variance
Source     DF       SS      F      P
Linear      1  2492.51  62.22  0.000
Quadratic   1  1345.55  87.21  0.000
Cubic       1   382.31  45.66  0.000
```

B.1.2. WF 50 PLA

```
The regression equation is
Y = 56.27 - 10.91 X + 1.161 X^2
S = 7.46738   R-Sq = 59.8%   R-Sq(adj) = 58.3%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   2  4390.81  2195.40  39.37  0.000
Error       53  2955.37    55.76
Total       55  7346.18
Sequential Analysis of Variance
Source     DF       SS      F      P
Linear      1  3484.71  48.73  0.000
Quadratic   1   906.10  16.25  0.000
```

B.2. Tensile Modulus

B.2.1. WF 30 PLA

```
The regression equation is
Y = 6684 - 94.85 X
```

```
S = 583.612   R-Sq = 9.9%   R-Sq(adj) = 8.2%
Analysis of Variance
Source      DF        SS       MS     F      P
Regression   1   2015059  2015059  5.92  0.018
Error       54  18392571   340603
Total       55  20407630
```

B.2.2. WF 50 PLA

```
The regression equation is
Y = 8771 - 817.3 X
S = 1457.32   R-Sq = 56.6%   R-Sq(adj) = 55.8%
Analysis of Variance
Source      DF         SS         MS      F      P
Regression   1  149610102  149610102  70.44  0.000
Error       54  114684972    2123796
Total       55  264295074
```

B.3. Failure Strain

B.3.1. WF 30 PLA

```
The regression equation is
Y = 1.682 + 0.0864 X + 0.1538 X^2 - 0.03302 X^3
S = 0.278895   R-Sq = 82.1%   R-Sq(adj) = 81.1%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   3  18.6056  6.20186  79.73  0.000
Error       52   4.0447  0.07778
Total       55  22.6503
Sequential Analysis of Variance
Source     DF       SS       F      P
Linear      1   2.8984    7.92  0.007
Quadratic   1  13.8231  123.57  0.000
Cubic       1   1.8842   24.22  0.000
```

B.3.2. WF 50 PLA

```
The regression equation is
Y = 1.283 + 0.09571 X
S = 0.415685   R-Sq = 18.0%   R-Sq(adj) = 16.5%
```

```
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   1   2.0521  2.05211  11.88  0.001
Error       54   9.3309  0.17279
Total       55  11.3830
```

B.4. Flexural Strength

B.4.1. WF 30 PLA

```
The regression equation is
Y = 93.43 - 18.64 X + 10.73 X^2 - 1.565 X^3
S = 5.45783   R-Sq = 94.0%   R-Sq(adj) = 93.6%
Analysis of Variance
Source      DF       SS       MS       F      P
Regression   3  24181.6  8060.55  270.60  0.000
Error       52   1549.0    29.79
Total       55  25730.6
Sequential Analysis of Variance
Source     DF       SS       F      P
Linear      1  12412.5   50.33  0.000
Quadratic   1   7539.2   69.14  0.000
Cubic       1   4230.0  142.00  0.000
```

B.4.2. WF 50 PLA

```
The regression equation is
Y = 97.49 - 30.06 X + 3.155 X^2
S = 13.1150   R-Sq = 79.1%   R-Sq(adj) = 78.3%
Analysis of Variance
Source      DF       SS       MS       F      P
Regression   2  34428.7  17214.3  100.08  0.000
Error       53   9116.2    172.0
Total       55  43544.9
Sequential Analysis of Variance
Source     DF       SS      F      P
Linear      1  27740.0  94.78  0.000
Quadratic   1   6688.7  38.89  0.000
```

B.5. Flexural Modulus

B.5.1. WF 30 PLA

```
The regression equation is
Y = 5845 - 755.4 X + 324.0 X^2 - 40.53 X^3
S = 178.850   R-Sq = 87.8%   R-Sq(adj) = 87.1%
Analysis of Variance
Source      DF        SS       MS       F      P
Regression   3  11994174  3998058  124.99  0.000
Error       52   1663339    31987
Total       55  13657513
Sequential Analysis of Variance
Source     DF       SS      F      P
Linear      1  8037307  77.22  0.000
Quadratic   1  1117639  13.16  0.001
Cubic       1  2839229  88.76  0.000
```

B.5.2. WF 50 PLA

```
The regression equation is
Y = 6532 - 396.8 X + 226.7 X^2 - 28.42 X^3
S = 410.599   R-Sq = 18.3%   R-Sq(adj) = 13.6%
Analysis of Variance
Source      DF        SS      MS     F      P
Regression   3   1966680  655560  3.89  0.014
Error       52   8766744  168591
Total       55  10733424
Sequential Analysis of Variance
Source     DF       SS     F      P
Linear      1     2139  0.01  0.918
Quadratic   1   569098  2.97  0.091
Cubic       1  1395444  8.28  0.006
```

B.6. Coefficient of Thermal Expansion (CTE)

B.6.1. WF 30 PLA

```
The regression equation is
Y = 0.000009 + 0.000002 X
S = 3.227898E-06   R-Sq = 54.7%   R-Sq(adj) = 53.9%
```

```
Analysis of Variance
Source      DF         SS         MS      F      P
Regression   1  0.0000000  0.0000000  65.23  0.000
Error       54  0.0000000  0.0000000
Total       55  0.0000000
```

B.6.2. WF 50 PLA

```
The regression equation is
Y = 0.000013 - 0.000004 X + 0.000001 X^2
S = 3.167385E-06   R-Sq = 39.5%   R-Sq(adj) = 37.2%
Analysis of Variance
Source      DF         SS         MS      F      P
Regression   2  0.0000000  0.0000000  17.32  0.000
Error       53  0.0000000  0.0000000
Total       55  0.0000000
Sequential Analysis of Variance
Source     DF         SS      F      P
Linear      1  0.0000000   8.70  0.005
Quadratic   1  0.0000000  22.49  0.000
```

B.7. Heat Deflection Temperature (HDT)

B.7.1. WF 30 PLA

```
The regression equation is
Y = 56.79 - 0.7420 X + 0.3729 X^2 - 0.05045 X^3
S = 0.519814   R-Sq = 58.3%   R-Sq(adj) = 55.9%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   3  19.6577  6.55255  24.25  0.000
Error       52  14.0508  0.27021
Total       55  33.7084
Sequential Analysis of Variance
Source     DF       SS      F      P
Linear      1  10.8328  25.57  0.000
Quadratic   1   4.4265  12.72  0.001
Cubic       1   4.3984  16.28  0.000
```

B.7.2. WF 50 PLA

```
The regression equation is
Y = 56.25 - 1.362 X + 0.3757 X^2 - 0.03170 X^3
S = 0.452437   R-Sq = 58.3%   R-Sq(adj) = 55.9%
```

```
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   3  14.8967  4.96557  24.26  0.000
Error       52  10.6444  0.20470
Total       55  25.5411
Sequential Analysis of Variance
Source     DF       SS      F      P
Linear      1  7.66640  23.16  0.000
Quadratic   1  5.49372  23.52  0.000
Cubic       1  1.73660   8.48  0.005
```

B.8. Storage Modulus

B.8.1. WF 30 PLA

```
The regression equation is
Y = 6422 - 108.3 X
S = 250.645   R-Sq = 43.7%   R-Sq(adj) = 42.6%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   1  2628528  2628528  41.84  0.000
Error       54  3392438    62823
Total       55  6020966
```

B.8.2. WF 50 PLA

```
The regression equation is
Y = 7516 - 162.7 X
S = 558.256   R-Sq = 25.6%   R-Sq(adj) = 24.2%
Analysis of Variance
Source      DF        SS       MS      F      P
Regression   1   5690083  5690083  18.26  0.000
Error       53  16517462   311650
Total       54  22207546
```

B.9. Impact Resistance

B.9.1. WF 30 PLA

```
The regression equation is
Y = 48.75 - 10.66 X + 3.571 X^2 - 0.4598 X^3
S = 6.58036   R-Sq = 72.4%   R-Sq(adj) = 70.8%
```

```
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   3  5892.01  1964.00  45.36  0.000
Error       52  2251.66    43.30
Total       55  8143.67
Sequential Analysis of Variance
Source     DF       SS       F      P
Linear      1  5310.44  101.21  0.000
Quadratic   1   216.19    4.38  0.041
Cubic       1   365.37    8.44  0.005
```

B.9.2. WF 50 PLA

```
The regression equation is
Y = 33.08 - 5.820 X + 0.5411 X^2
S = 5.34055   R-Sq = 52.6%   R-Sq(adj) = 50.8%
Analysis of Variance
Source      DF       SS       MS      F      P
Regression   2  1679.50  839.752  29.44  0.000
Error       53  1511.64   28.521
Total       55  3191.14
Sequential Analysis of Variance
Source     DF       SS      F      P
Linear      1  1482.74  46.87  0.000
Quadratic   1   196.77   6.90  0.011
```

B.10. Melt Flow Index (MFI)

B.10.1. WF 30 PLA

```
The regression equation is
Y = 2.712 + 4.411 X - 0.8483 X^2 + 0.1014 X^3
S = 1.09176   R-Sq = 96.7%   R-Sq(adj) = 96.4%
Analysis of Variance
Source      DF       SS       MS       F      P
Regression   3  1085.11  361.703  303.46  0.000
Error       31    36.95    1.192
Total       34  1122.06
Sequential Analysis of Variance
Source     DF       SS       F      P
Linear      1  1072.29  710.98  0.000
Quadratic   1     1.72    1.15  0.292
Cubic       1    11.10    9.31  0.005
```

B.10.2. WF 50 PLA

```
The regression equation is
Y = 1.131 + 3.951 X + 1.787 X^2 - 0.2476 X^3
S = 2.18716   R-Sq = 97.4%   R-Sq(adj) = 97.2%
Analysis of Variance
Source      DF       SS       MS       F      P
Regression   3  5627.47  1875.82  392.13  0.000
Error       31   148.29     4.78
Total       34  5775.76
Sequential Analysis of Variance
Source     DF       SS       F      P
Linear      1  5479.44  610.23  0.000
Quadratic   1    81.79   12.20  0.001
Cubic       1    66.23   13.85  0.001
```