# Degradation in the mechanical and thermo-mechanical properties of natural fiber filled polymer composites due to recycling

Sujal Bhattacharjee, Dilpreet S Bajwa [⇑]

Department of Mechanical Engineering, North Dakota State University, Fargo, ND 58108-6050, USA

## highlights

- Wood flour and high density polyethylene based composites (WPC) can be efficiently recycled.
- Six reprocessing cycles showed relative decrease in strength and stiffness properties of WPC.
- The strain properties of WPC increased with recycling.
- The crystallinity of WPC decreased after recycling.
- The thermal stability of composites slightly increased after six reprocessing cycles.

## article info

## abstract

To manage the plastic waste, recycling is recognized as the most environment-friendly and non-destructive method. The aim of this research is to investigate the recyclability of oak wood flour (WF) filled high density polyethylene (HDPE) composites. Two different composite formulations (30 and 50 wt% filler) were considered, each with 3 wt% coupling agent maleic anhydride (MA). Both composites were individually reprocessed six times by extrusion. Test samples were injection molded, to measure mechanical and thermo-mechanical properties. Fiber length measurement and gel permeation chromatography (GPC) were performed respectively to examine the change on fiber length and molecular weight of polymer. Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), and Fourier Transform Infra-Red Spectroscopy (FTIR) were also carried out to better understand the impact of recycling on composite properties. After reprocessing six times, WF-HDPE composites showed relative decrease in strength and stiffness properties and slight increase in strain properties as compared to corresponding virgin composite. The strain properties saw an increase in their value with recycling. The crystallinity of HDPE decreased but thermal stability of the composite increased with reprocessing.

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## 1. Introduction

Wood Plastic Composites (WPCs) are typically manufactured from two fundamental constituents a natural fiber or filler, and a thermoplastic resin [1,2]. Nowadays, WPCs are widely accepted as building materials especially because of their durability, higher specific strength and stiffness, and zero or very low health concern along with other advantages [3–5]. Among all WPCs, wood fiber or filler (WF) based high density polyethylene (HDPE) 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) [6]. HDPE is preferred because it has

a lower melting point around 130 °C as compared to the degradation temperature of most natural fibers that varies between 200 and 220 °C, which helps in processing of its composites [6]. HDPE also shows higher toughness, stiffness, chemical resistance, thermal stability, and electrical insulation [7]. For improved properties incorporation of WF in HDPE becomes necessary since elastic modulus and strength of WF, in general is 40 and 20 times respectively higher than that of HDPE [8,9]. WF is also considerably cheap since a substantial amount of wood waste is generated in wood industry [10].

Along with a lot of advantages, WF-HDPE composites come with some imperfections. The major problem is the incompatibility between the fiber and matrix. Natural fibers are hydrophilic while thermoplastic polymers are hydrophobic. This incompatibility causes poor interfacial adhesion between fiber and matrix when

⇑ Corresponding author.
E-mail address: dilpreet.bajwa@ndsu.edu (D.S Bajwa).

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 resolved by adding specialty additives such as coupling agent (CA) or compatibilizers in the composites [11,12]. The CA helps to improve the interfacial adhesion that leads to improved bonding in the interface region. For improved properties of WF/HDPE composites, maleated polyethylene (MAPE) has been reported the better CA compared to other CA such as maleated polypropylene (MAPP) and carboxylated polyethylene (CAPE). This is due to the better wetting and higher compatibility of MAPE in HDPE polymer. In general, the typical amount of MAPE in the WF/HDPE composite-ranges from 1.5 wt% to 4.5 wt%. However, 3 wt% of MAPE has been reported the optimum level of CA for improved properties of WPCs made of HDPE polymer [3,7]. That is why incorporation of 3 wt% of MAPE has been considered for WF/HDPE composites in this research.

Another way to solve this problem is to separately modify the fiber surface and polymers, especially with silane CA. Surface modification of natural fibers improves the fiber surface functionalization for better chemical bonding and increases the fiber surface roughness for better mechanical interlocking. Silane treatment of polymers improves the chemical resistance and physico-mechanical properties of the polymers [13–15]. Therefore, a composite formulated by silane treated natural fibers and polymers also have higher thermal, chemical, and mechanical properties.

However, one major issue with WPC's are that they are not fully biodegradable at the end of their useful life and can raise an environmental concern if discarded in the landfills [1,16]. Plastic waste can cause soil and air pollution. All petroleum based plastics take a very long time to degrade in soil and impact the soil fertility [17]. 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.

There are several traditional methods that are used for plastic waste management. But most of these methods are detrimental to environment and destructive to material. For example, when disposed in landfills, plastic waste creates soil and air pollution; and when incinerated, this waste creates noxious gases that helps global warming [18]. On the contrary, recycling is the most environment friendly and undamaging process that can help to reuse the material without significant degradation in properties. The other advantages of recycling is the fluctuating price of crude oil based plastics which can add risk to pricing strategy. In addition, the need for landfills for discarding plastic is an environmental concern [18].

Considering all these advantages, recycling is acknowledged as best alternative for WPC waste management. To date, a lot of research have been done on the recycling of WPCs but the information is somewhat conflicting. Lei et al. added pine or bagasse flour to recycled HDPE, and concluded that the mechanical properties of the recycled composites compared fairly well with virgin composites [3]. 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 [4]. 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 [6]. Adhikary et al. made recycled HDPE/virgin fiber WPC, and reported that the recycled WPCs showed only a marginal change in mechanical and dimensional properties as compared to virgin ones [10]. 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 [11]. Beg et al. 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 [16]. Petchwattana et al. mixed virgin and post-consumer WPC at a weight ratio of 70:30, extruded that WPC eight times, and reported insignificant degradation in mechanical properties of recycled WPCs [18].

However, it should be noted that the all these studies are not exhaustive and comparable, due to multiple grades of the polymers, type of wood fibers/fillers, grade of coupling agents and their percentage content, presence of other specialized additives, and the manufacturing and recycling processes of the WPCs itself [3]. Since there is a lot of discrepancy in the literature, an in-depth study was conducted to understand the influence of reprocessing on the mechanical and thermo-mechanical properties of oak wood flour (WF) filled HDPE composites containing coupling agent (MAPE) with two different filler loadings. The material was individually recycled up to six times by extrusion, and test samples were injection molded after each reprocessing cycle.

## 2. Experimental

### 2.1. Materials

Oak wood-flour was provided by Southern Wood Services (Macon, GA). It is widely produced by the furniture industry as an operational waste. Wood particle size was in the range of 250 lm–400 lm. The thermoplastic polymer was high density polyethylene (Marlex 9012), manufactured by Chevron Phillips Chemical Company, TX. The polymer has a MFI of 11.5 g/10 min, density of 0.952 g/cm$^3$, and vicat softening temperature of 124 °C. The coupling agent-maleic anhydride grafted polyethylene (MAPE), with density 0.92 g/mL, $T_m$ of 107 °C was purchased by Sigma-Aldrich, St. Louis, MO.

### 2.2. Methods

#### 2.2.1. Composite manufacturing

Fig. 1 shows the manufacturing process of WF-HDPE composites. Composite pellets were manufactured from 30% nd 50 wt% wood flour, HDPE resin and 3 wt% MAPE, labelled at WF 30 HDPE and WF 50 HDPE respectively. The material was processing by using a twin-screw co-rotating extruder (Leistriz Micro 18 GL 40 D, NJ, USA). Test samples were prepared from pellets by using a single screw injection molder (Model SIM-5080, Technoplas Inc., OH). The extruder had seven different temperature zones. The temperature of these seven zones, from feed section to melting section, was 160 °C, 193 °C, 199 °C, 204 °C, 207 °C, 210 °C, and 213 °C respectively. The temperature of the die and gate adapter was controlled at 213 °C. 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 °C for a minimum period of 24 h 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 cooled bypassing it through a water bath followed by pelletizing. A portion of these pellets were dried in an oven at 80 °C for at least 24 h and then molded to make tensile and flexural testing samples. This material was named as 'cycle 0' or 'virgin' material. The remaining pellets of 'cycle 0' material were dried in an oven at 80°C for 24 h and again extruded at the same processing conditions as mentioned above and was named as 'cycle 1' or 'first time recycled' material. The remaining pellets from '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' composites.
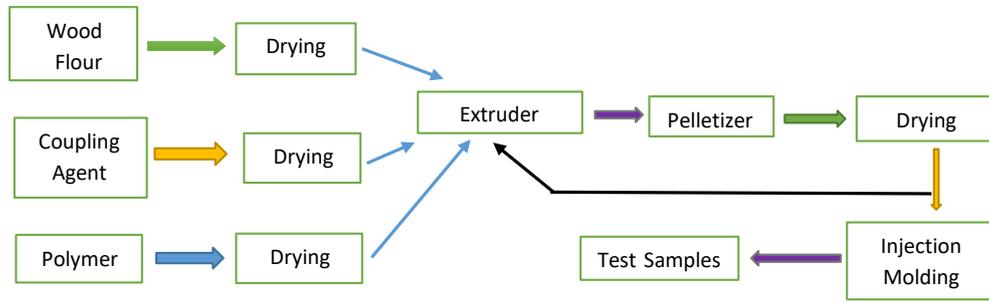
Fig. 1. Schematic diagram of the manufacturing process of WF-HDPE composites.
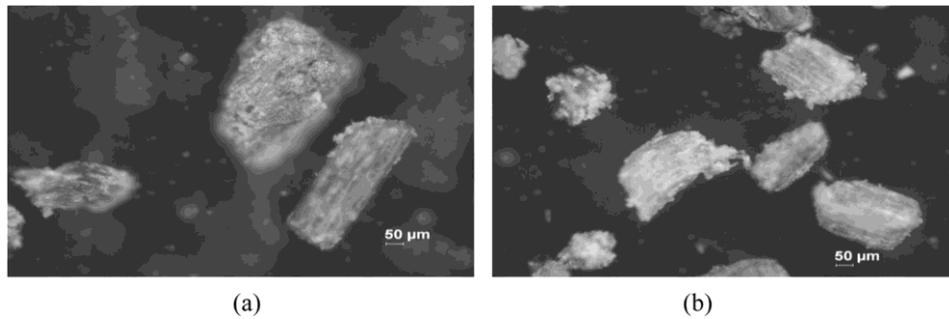


Fig. 2. Images of wood particle size of WF 50 HDPE composite at (a) cycle 0 and (b) cycle 6.
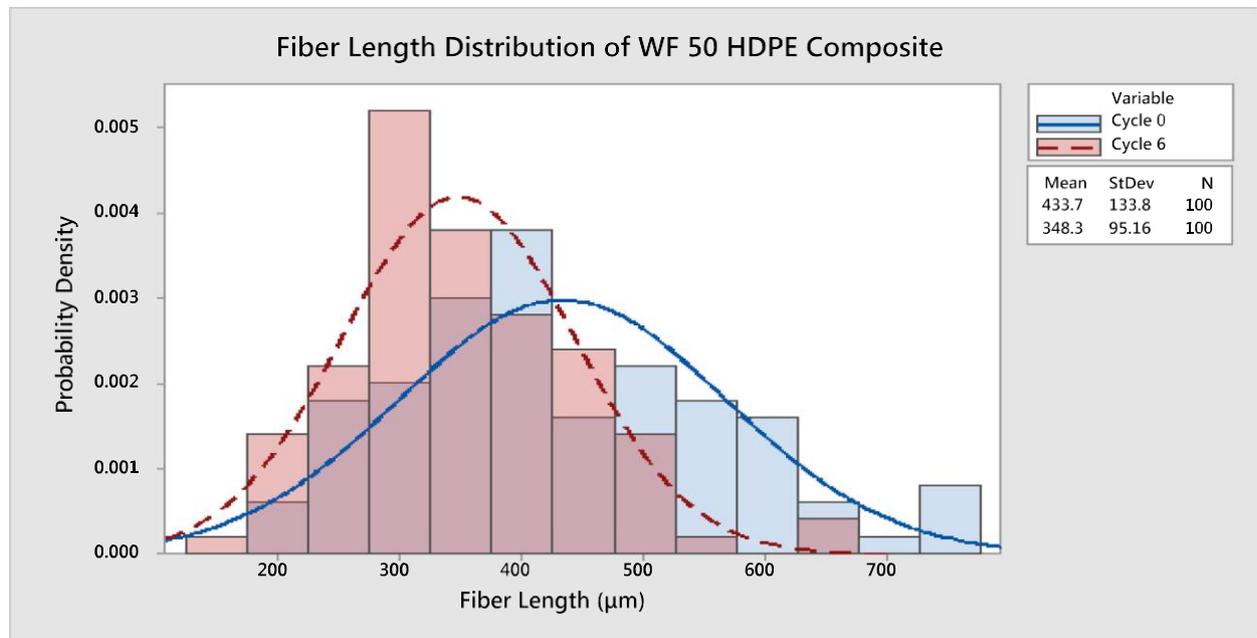


Fig. 3. Normal distribution plot of wood particle length of WF 50 HDPE composite at cycle 0 and 6.

## 2.2.2. Tensile testing

Tensile testing was performed using a universal testing machine Instron Model 5567 (Norwood, MA) following 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. The samples were conditioned at 23 °C and eight replicates were tested from each cycle.

Table 1
Molecular weight of HDPE of WF 50 HDPE composite at cycle 0 and cycle 6.

| Properties | Cycle 0 | Cycle 6 |
|---|---|---|
| $M_w$ (g/mol) | 116,113 | 110,360 |
| $M_n$ (g/mol) | 110,602 | 102,198 |
| Polydispersity Index (PDI) | 1.05 | 1.08 |

Table 2
Physical and mechanical properties of WF-HDPE composites after reprocessing cycles.

**a. Composite with 30% wood flour**

| Properties | WF 30 HDPE | | | | | | |
|---|---|---|---|---|---|---|---|
| | Cycle 0 | Cycle 1 | Cycle 2 | Cycle 3 | Cycle 4 | Cycle 5 | Cycle 6 |
| Tensile Strength (MPa) | 25.80 (0.31)[A] | 24.92 (0.23)[B] | 24.64 (0.56)[B] | 24.08 (0.33)[C] | 23.62 (0.21)[C] | 22.83 (0.19)[D] | 23.10 (0.14)[D] |
| Flexural Strength (MPa) | 31.20 (1.01)[A] | 31.92 (0.45)[A] | 29.30 (0.84)[B] | 28.44 (0.83)[BC] | 29.29 (1.38)[B] | 27.55 (0.65)[CD] | 26.31 (0.72)[D] |
| Impact Resistance (J/m) | 55.16 (4.26)[A] | 47.92 (1.99)[B] | 45.14 (1.67)[BC] | 43.18 (3.42)[C] | 41.97 (2.17)[CD] | 38.55 (1.42)[DE] | 37.14 (1.23)[E] |
| Tensile Modulus (MPa) | 2544.27 (94.28)[A] | 2391.56 (107.53)[AB] | 2307.14 (145.26)[BC] | 2297.19 (128.44)[BC] | 2366.40 (68.93)[B] | 2171.29 (118.85)[CD] | 2116.42 (40.23)[D] |
| Flexural Modulus (MPa) | 1353.80 (54.19)[A] | 1227.79 (39.35)[B] | 1127.44 (42.96)[C] | 1095.20 (39.34)[CD] | 1129.31 (75.33)[C] | 1047.06 (39.08)[DE] | 1002.59 (33.43)[E] |
| Storage Modulus (MPa) | 2626.50 (139.17)[A] | 2326.75 (79.04)[B] | 2260.75 (75.13)[BC] | 2299.25 (60.93)[BC] | 2266.25 (69.78)[BC] | 2194.00 (63.85)[C] | 2181.38 (52.17)[C] |
| Heat Deflection Temperature (°C) | 80.90 (4.67)[A] | 78.93 (2.79)[AB] | 73.78 (5.70)[BC] | 75.38 (4.09)[ABC] | 75.28 (4.20)[ABC] | 71.88 (3.16)[C] | 73.32 (2.27)[BC] |
| Failure Strain (%) | 8.43 (0.41)[E] | 9.92 (1.05)[DE] | 10.98 (0.74)[CD] | 11.74 (0.83)[BC] | 12.47 (1.20)[ABC] | 12.62 (1.66)[AB] | 14.05 (1.09)[A] |
| Coefficient of Thermal Expansion (mm/mm/ °C) x 10^5 | 3.18 (0.83)[C] | 3.60 (1.19)[BC] | 4.23 (0.79)[ABC] | 4.32 (0.66)[ABC] | 4.18 (0.61)[ABC] | 4.64 (0.72)[AB] | 5.09 (0.62)[A] |
| Melt Flow Index (g/ 10 min) | 3.25 (0.17)[D] | 3.76 (0.11)[C] | 4.09 (0.07)[B] | 4.32 (0.11)[A] | 4.31 (0.04)[A] | 4.40 (0.11)[A] | 4.49 (0.06)[A] |

**b. Composite with 50% wood flour**

| Properties | WF 50 HDPE | | | | | | |
|---|---|---|---|---|---|---|---|
| | Cycle 0 | Cycle 1 | Cycle 2 | Cycle 3 | Cycle 4 | Cycle 5 | Cycle 6 |
| Tensile Strength (MPa) | 33.00 (0.28)[A] | 31.66 (0.26)[B] | 31.54 (0.31)[B] | 30.60 (0.14)[C] | 29.82 (0.48)[D] | 29.71 (0.13)[D] | 29.71 (0.19)[D] |
| Flexural Strength (MPa) | 45.70 (3.49)[AB] | 46.67 (1.87)[A] | 45.19 (1.72)[AB] | 44.08 (1.30)[ABC] | 42.82 (1.63)[BC] | 41.95 (1.31)[C] | 41.11 (1.33)[C] |
| Impact Resistance (J/m) | 51.97 (4.62)[A] | 49.46 (3.91)[AB] | 45.25 (3.76)[ABC] | 41.11 (5.04)[C] | 42.82 (6.13)[BC] | 41.81 (6.35)[C] | 38.20 (2.34)[C] |
| Tensile Modulus (MPa) | 4755.36 (272)[A] | 4536.30 (79.66)[AB] | 4198.68 (132.68)[BC] | 4280.54 (174.73)[BC] | 4128.51 (254.43)[C] | 4144.84 (316.37)[BC] | 4337.96 (437.34)[BC] |
| Flexural Modulus (MPa) | 2624.70 (319.13)[A] | 2356.65 (112.49)[B] | 2250.67 (107.43)[BC] | 2165.68 (78.05)[BCD] | 2119.48 (115.18)[BCD] | 2053.34 (117.10)[CD] | 1992.67 (94.75)[D] |
| Storage Modulus (MPa) | 3634.38 (337.16)[A] | 3627.25 (197.22)[A] | 3436.88 (162.41)[AB] | 3364.88 (220.44)[AB] | 3259.88 (187.59)[B] | 3203.00 (143.49)[B] | 3177.75 (109.38)[B] |
| Heat Deflection Temperature (°C) | 110.54 (5.84)[A] | 112.82 (2.83)[A] | 109.05 (4.10)[AB] | 107.20 (3.58)[AB] | 103.26 (4.12)[BC] | 103.04 (4.32)[BC] | 99.19 (5.99)[C] |
| Failure Strain (%) | 4.44 (0.37)[D] | 5.00 (0.23)[C] | 4.96 (0.20)[CD] | 5.57 (0.19)[B] | 5.73 (0.46)[AB] | 5.85 (0.32)[AB] | 6.16 (0.56)[A] |
| Coefficient of Thermal Expansion (mm/mm/ °C) x 10^5 | 1.71 (1.26)[B] | 1.71 (1.27)[B] | 1.66 (0.87)[B] | 2.00 (0.96)[B] | 2.04 (1.05)[B] | 2.47 (1.13)[B] | 2.56 (0.94)[A] |
| Melt Flow Index (g/ 10 min) | 0.56 (0.04)[E] | 0.89 (0.04)[D] | 1.22 (0.09)[C] | 1.59 (0.03)[B] | 1.68 (0.05)[B] | 1.88 (0.05)[A] | 1.96 (0.04)[A] |

Values are shown as the mean standard deviation. Means with different letters are significantly different (P < 0.05).

Table 3
Relative difference in the means of the properties of WF-HDPE composites between cycle 0 and cycle 6.

| Properties | WF 30 HDPE composite | WF 50 HDPE composite |
|---|---|---|
| Tensile Strength (MPa) | -10.45 | -9.97 |
| Tensile Modulus (MPa) | -16.82 | -8.78 |
| Failure Strain (%) | 66.67 | 38.74 |
| Flexural Strength (MPa) | -15.67 | -10.04 |
| Flexural Modulus (MPa) | -25.94 | -24.08 |
| Impact Resistance (J/m) | -32.66 | -26.51 |
| Heat Deflection Temperature (°C) | -9.37 | -10.27 |
| Storage Modulus (MPa) | -16.95 | -12.56 |
| Coefficient of Thermal Expansion (x10^5)(mm/mm/°C) | 59.75 | 49.61 |
| Melt Flow Index (g/10 min) | 38.11 | 252.26 |

### 2.2.3. Flexural testing

Flexural testing (three-point bend test) was carried out using an Instron 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. The support span was 52 mm in the test. A 2 kN load cell was used with a crosshead speed of 1.4 mm/min. The samples were conditioned at room temperature (23 °C). Eight replicates were tested for each cycle.

### 2.2.4. Coefficient of thermal expansion (CTE)

Coefficient of thermal expansion was measured from 30 °C to 50 °C by using a Dynamic Mechanical Analyzer, (DMA) Q800 (TA Instruments, New Castle, DE) with a tension film clamp. The ramp rate was 3 °C and no preload force was used. The specimen dimensions were 12.74 mm x 12.7 mm x 3.2 mm. All samples were kept at room temperature (23 °C) before testing. Eight samples were tested for each batch. The following equation was used to measure the CTE-

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

Here, $\alpha$ is the coefficient of thermal expansion, DL is the change in length, DT is the change in temperature, and L is the initial length.

### 2.2.5. Heat deflection temperature (HDT)

Heat deflection temperature test was carried out using a DMA Q800 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 $d$ = 0.455 MPa). The ramp rate was 3 °C/min. The specimen dimensions were 65 mm x 12.7 mm x 3.2 mm with a supported length of 50 mm in the test. All samples were conditioned at 25 °C before testing. Five replicates were tested for each batch.

### 2.2.6. Storage Modulus

Storage modulus was measured at 30 °C by using a DMA Q800 with a dual cantilever beam clamp. The frequency and amplitude were respectively set at 1 Hz and 15 lm. The ramp rate was 3 °C/min. The soak time (at 28 °C) was 5 min. Eight replicates were tested with the specimen dimension 65 mm (length) x 12.7 (width) mm x 3.2 mm (thickness) where the actual supported length was 41.6 mm.

### 2.2.7. Izod impact test

Izod impact test was carried out using an Izod Impact Tester (Tinius Olsen, Model Impact 104, PA) 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. Eight replicates were tested at 25 °C.

### 2.2.8. Melt Flow Index (MFI)

Melt Flow Index (MFI) test was conducted by using an Extrusion Plastometer (Tinius Olsen, Model MP 600, Norwood, PA). 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 °C and the load was set at 2.16 kg. Before testing, composite pellets were dried at 80 °C for 24 h. Five replications were tested for each batch.

### 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.

### 2.2.10. Fiber length measurement

A small amount (3 g) of composite pellets were dropped in toluene solution set at 140 °C with constant stirring for 96 h. 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, Thornwood, NY). The average length of 100 fibers has been reported.

### 2.2.11. Differential Scanning Calorimetry (DSC)

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

### 2.2.12. Thermogravimetric Analysis (TGA)

TGA was carried out using a thermogravimetric analyzer Q500 (TA instruments, New Castle, DE) 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 °C to 800 °C. The heating rate was 10 °C/min. The weight of each sample was approximately 10 mg.

### 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.

### 2.2.14. Gel permeation chromatography (GPC)

A small amount of composite pellets (3 g) were heated with toluene in a small jar at 140 °C for 96 h. 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 min. 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 (Eco-SEC HLC-8320GPC, Tosoh Bioscience, Japan) by using two columns (TSKgel SuperHM-L 6.00 mm ID x 15 cm) with a differential refractometer detector (DRI). The eluent (THF) flow rate was 0.4 ml/min. The injection volume was 20 ll for each sample.

### 2.2.15. Statistical analysis

The data from the mechanical and thermo-mechanical tests were statistically analyzed with a confidence level of 95% for both composites. The average values have been reported. One-way analysis of variance (ANOVA), Tukey test, and regression analysis were performed by using software Minitab 16 statistical software (College Park, PA). Results of mean comparison from Tukey test are presented by denoting different alphabetic letters. Means that do not have a common letter are significantly different.

## 3. Results and discussion

### 3.1. Effect of reprocessing on fiber length

The wood fiber particle length of WF 50 HDPE composite was measured at cycle 0 and cycle 6. Fiber length decreased with increased number of reprocessing cycles. From cycle 0 to cycle 6, the average fiber length (of 100 fibers) decreased from 433.66 lm to 348.26 lm. Figs. 2 and 3 show the images of wood fiber particle and the normal distribution plot of fiber lengths respectively.

### 3.2. Effect of reprocessing on the molecular weight of the polymer

The molecular weights of HDPE used in 50% WF-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 number 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 (Table 1). The polydispersity index (PDI) ratio of $M_w/M_n$ also increased from 1.05 (cycle 0) to 1.08 (cycle 6) that denotes lower molecular weights of HDPE by reprocessing [18].

### 3.3. Effect of reprocessing on strength properties

For both 30 and 50% wood fiber filled composites, the effect of reprocessing was statistically found to be significant for tensile strength, flexural strength, and impact resistance. All these properties decreased with increased number of reprocessing cycles (Tables 2a, b and 3). For example, from cycle 0 to cycle 6, tensile strength of WF 30 HDPE composite decreased from 25.79 MPa to 23.1 MPa (10.45%) while flexural strength decreased from 31.2 MPa to 26.31 MPa (15.67%) (Table 3). This degradation in strength properties could be attributed to the fact that WF and HDPE are susceptible to a higher temperature (around 200 °C), especially in the presence of mechanical stress. In extrusion, both heat and shear stress are produced simultaneously that degrade the fiber and the polymer. Repetitive extrusion (or reprocessing) creates a
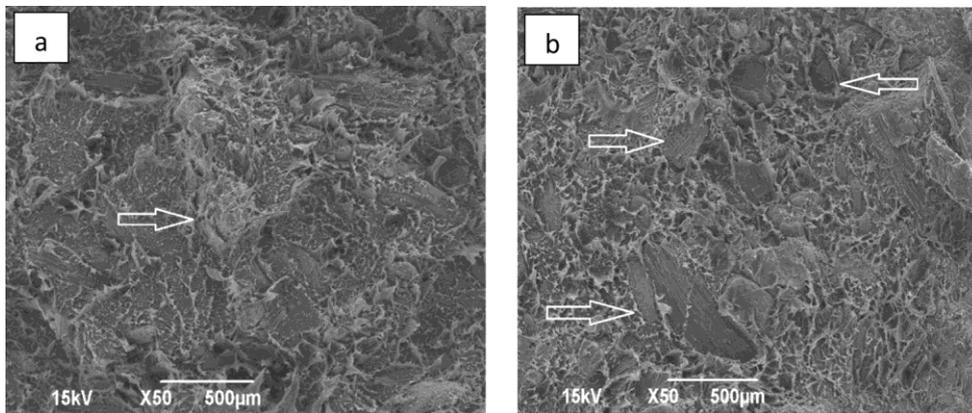
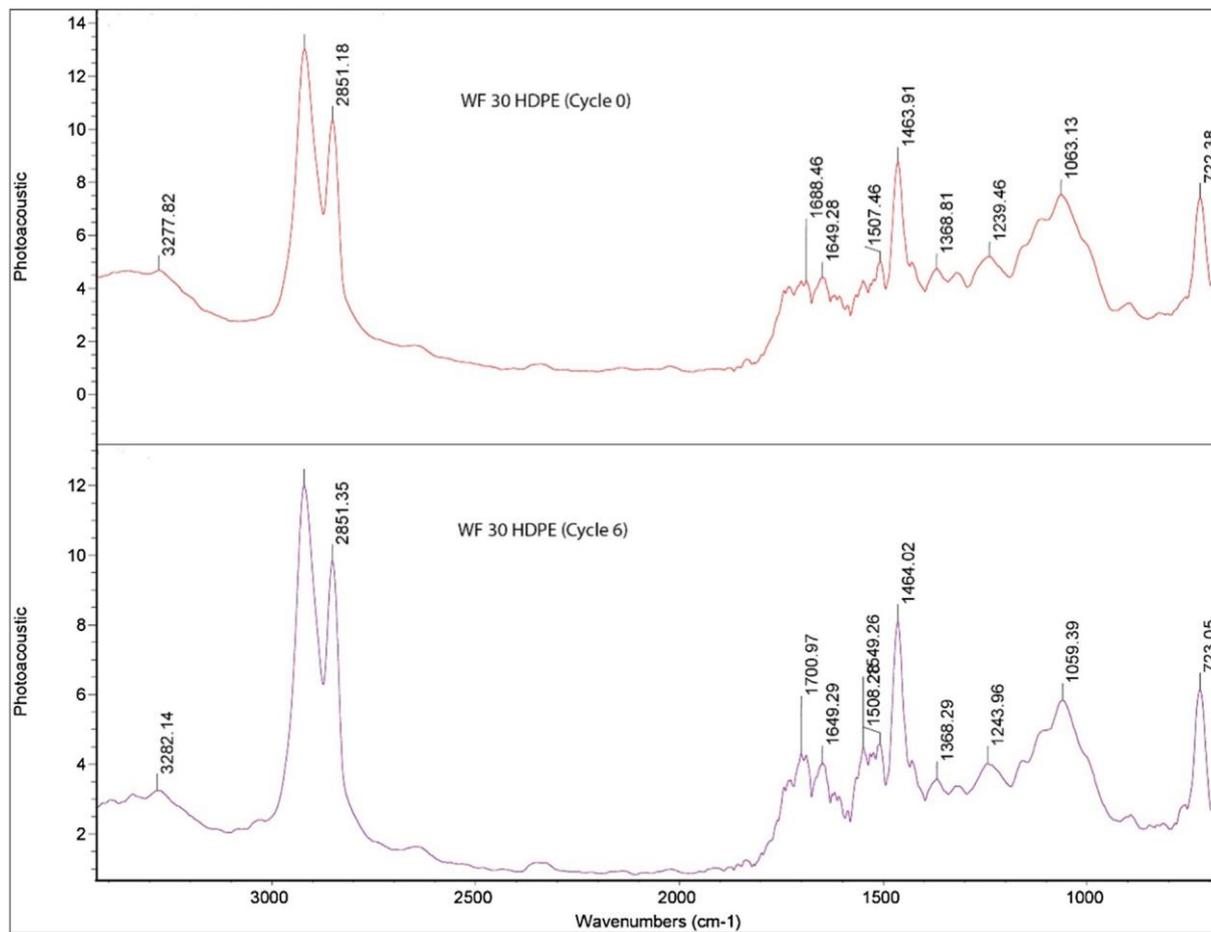Fig. 4. SEM of WF 30 HDPE composite at (a) cycle 0 and (b) cycle 6.



Fig. 5. FTIR spectra of WF 30 HDPE composite at cycle 0 and cycle 6.

noticeable reduction in fiber length (Section 3.1) and molecular weight of HDPE (Table 1) that finally result in a decrease in composite strength properties [4,6,16,19].

In addition, interfacial adhesion between the fiber and matrix plays a vital role to determine the strength properties. Improved interfacial adhesion leads to higher composite strength, and vice-versa. It is observed that, at cycle 0, WF 30 HDPE composite shows good interfacial bonding (Fig. 4a). However, at cycle 6, it shows lower interfacial adhesion along with shorter fibers, fiber agglomeration, and the presence of pores (Fig. 4b). This decrease in

interfacial adhesion leads to a decrease in composite strength. Moreover, fiber agglomeration and pores (or micro-voids), at cycle 6, aid in crack propagation that significantly decreases the strength properties of the composites [10,16].

### 3.4. Effect of reprocessing on stiffness properties

Similar to strength properties, a significant impact of reprocessing was found on all stiffness properties such as tensile modulus, flexural modulus, storage modulus, and heat deflection

Table 4
DSC analysis of WF 50 HDPE composite at cycle 0 and cycle 6.

| Property | Cycle 0 | Cycle 6 |
|---|---|---|
| Melting Point (°C) | 132.93 | 132.40 |
| Crystalline Temperature (°C) | 114.67 | 114.40 |
| Heat of Fusion (J/g) | 85.97 | 78.64 |
| Crystallinity (%) | 63.23 | 57.83 |

Table 5
Thermogravimetric analysis of WF 50 HDPE composite at cycle 0 and cycle 6.

| Property | Cycle 0 | Cycle 6 |
|---|---|---|
| Onset Thermal Degradation Temperature (°C) | 253.30 | 279.58 |
| Fastest Decomposition Temperature (°C) | 338.51 | 341.46 |
| Residue (%) | 0 | 0 |

temperature (HDT). These properties also decreased with successive recycling (Table 2a, b). For instance, after reprocessing six times, the flexural modulus of low and high filler loading composite reduced by 25.94% and 24.08% respectively (Table 3). The key reason for the reduction in these properties is the fiber and polymer degradation of the composites with repetitive extrusion [16]. As the interfacial adhesion between WF and HDPE continue to degrade with reprocessing, the stress transfer from the matrix to the fiber decreases. This less efficient stress transfer finally contributes to lower stiffness properties of the composites [10,16]. Besides, at cycle 6, lower fiber length and shorter polymer chain provide less restriction to polymer chain mobility and thus cause lower composite stiffness [6]. Since heat deflection temperature (HDT) is closely related to stiffness properties, it also decreased with successive reprocessing for both composites.

### 3.5. Effect of reprocessing on strain properties

Strain properties evaluated are failure strain, coefficient of thermal expansion (CTE), and Melt Flow Index (MFI). In contrast to the strength and stiffness properties, all strain properties increased with increasing number of reprocessing cycles (Table 2a, b). These properties increased probably due to higher fiber degradation than the polymer with repetitive extrusion [16]. From cycle 0 to cycle 6, the fiber length of WF 50 HDPE composite decreased 19.7% while the $M_w$ of HDPE decreased approximately 5% as discussed in Sections 3.1 and 3.2. As the fiber degrades higher with successive reprocessing, the polymer properties become more dominant than

the fibers 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 leading to higher strain properties at cycle 6.

### 3.6. FTIR analysis

FTIR analysis was performed on samples from cycle 0 and cycle 6 with 30% WF (Fig. 5). The experiment exhibited continued composite degradation during reprocessing by showing the formation of several functional groups. 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 [20,21]. These functional groups (oxidative and weaker bond) imply the ongoing degradation of the composite by successive recycling. The characteristic absorptions were found almost the same at cycle 0 and cycle 6 of the composite. However, the relative degradation between cycle 0 and cycle 6 could not be directly compared due to the associated inconsistencies in the experiment such as thickness difference and heterogeneity of small composite samples.

### 3.7. Effect of reprocessing on crystallinity and thermal stability

Table 4 and Fig. 6 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 [3]
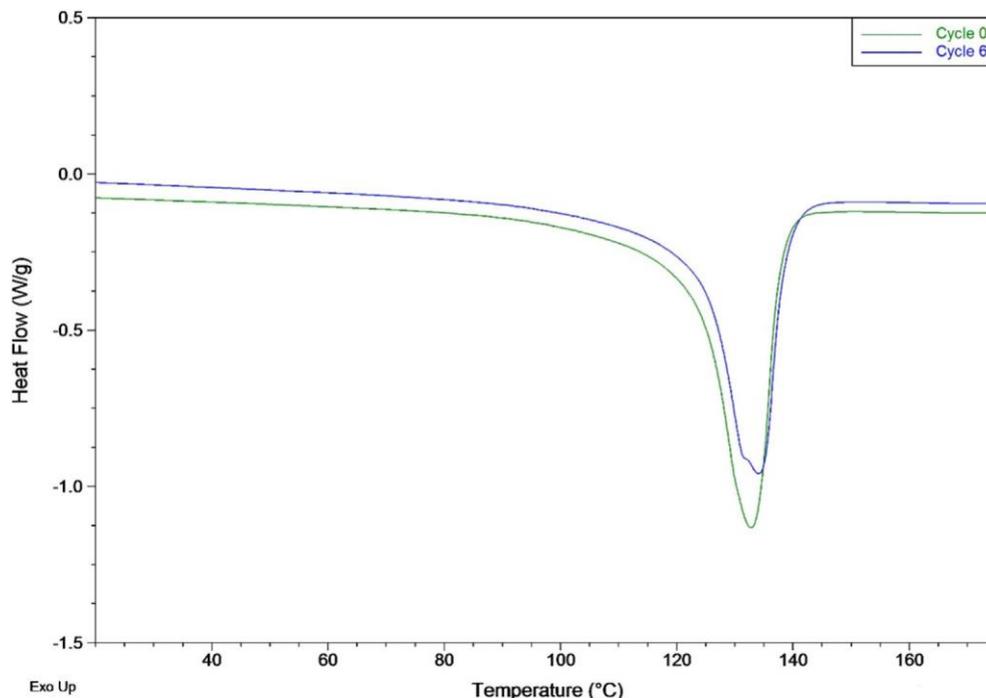


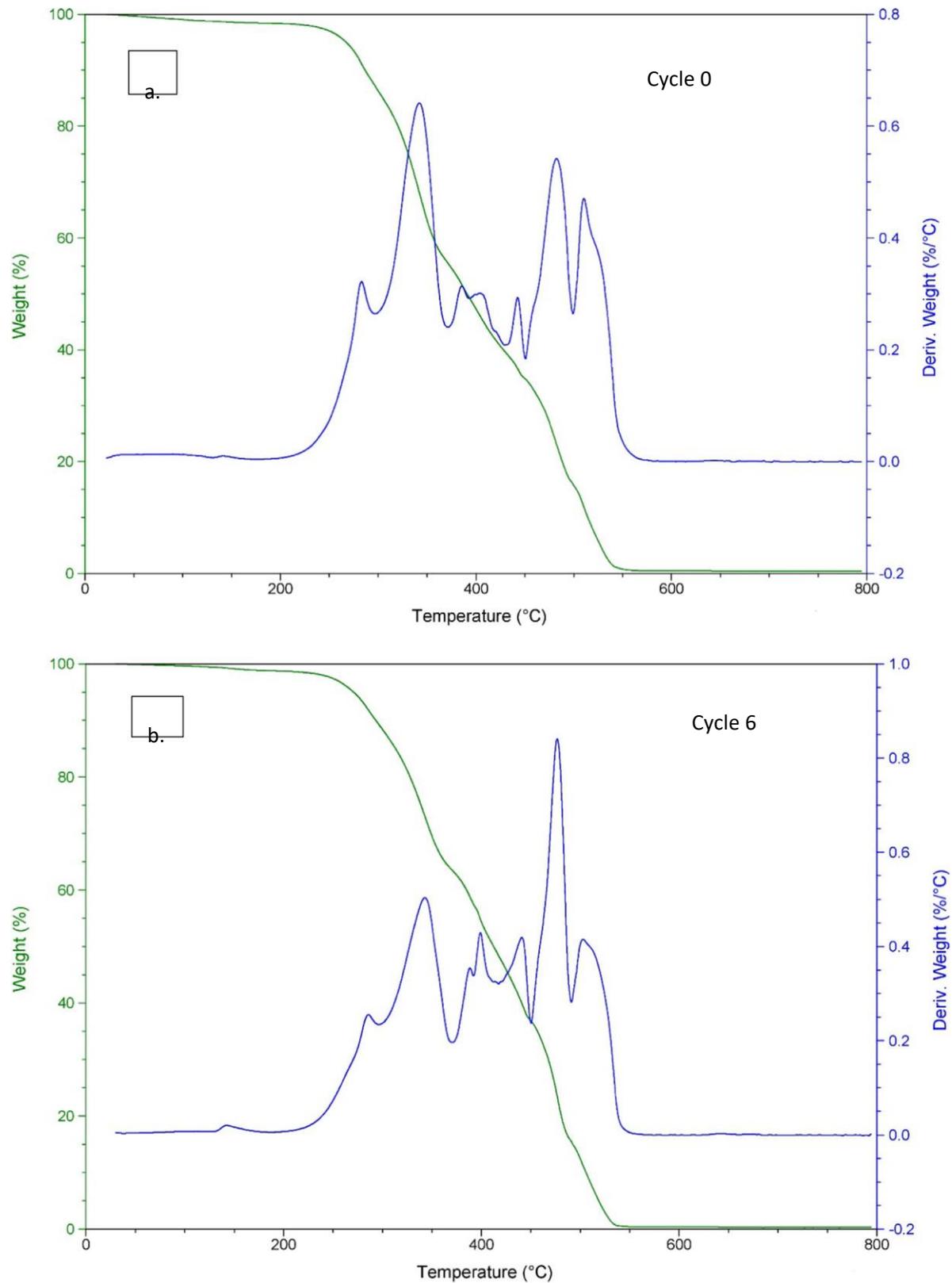Fig. 6. DSC curves of WF 50 HDPE composite at cycle 0 and cycle 6.

Fig. 7. TGA curve with 1st derivative of WF 50 HDPE composite at (a) cycle 0 and (b) cycle 6.

$$\% \text{ Crystallinity} = \left(\frac{\Delta H_{exp}}{\Delta H}\right) \times \left(\frac{1}{W}\right) \times 100 \qquad (2)$$

Here, $DH_{exp}$ is the experimental heat of fusion determined by DSC, $DH$ 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 decreased but melting point increased with increased number 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 [16], 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 composite slightly increased from 132.67 °C (cycle 0) to 134.09 °C (cycle 6) that can be attributed to slight charring of wood flour due to repeated heat cycles.

Thermal stability of WF 50 HDPE composite also increased with increasing number of reprocessing cycles (Table 5 and Fig. 7). 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 as well as stabilization of wood particles [16]. 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.

## 4. Conclusions

WF-HDPE composites with 30% and 50% oak wood flour, HDPE, and 3% coupling agent MAPE were manufactured in the laboratory and reprocessed up to six times by extrusion followed by injection molding. The effect of reprocessing was found to be statistically 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 mainly due to the decrease in fiber length and molecular weight reduction of the polymer. Other possible reasons for the changes in these properties include – 1) decreased interfacial adhesion between the wood fiber and polymer, 2) less efficient stress transfer from the matrix to fiber, and 3) increased polymer chain mobility with consecutive reprocessing cycles. The crystallinity of HDPE decreased but thermal stability of the composite increased with increased number of reprocessing cycles. Although recycling produced a negative effect, from cycle 0 to cycle 6 the relative change or degradation was found mild in all strength and stiffness properties of composites.

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