MECHANICAL AND THERMAL CHARACTERIZATION OF A FLAX FIBRE REINFORCED BIOBASED HIGH-DENSITY POLYETHYLENE COMPOSITE

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ABSTRACT

Growing concerns on the climate change are leading many manufacturing sectors to be more environmentally conscious, valuing renewable materials and reusing resources and waste. Along the same trend, bio-based polymer composites and natural fibre reinforcements are considered widely as an alternative to the synthetic and nonrenewable composites, while targeting similar or even superior physical properties. This study aims to investigate the mechanical and thermal performance of a new flax fibre reinforced green high-density polyethylene (G-HDPE), made by compression molding. Using 30wt% flax fibres in the G-HDPE showed an increase up to 225% in the biocomposite's tensile strength, and a 250% increase in its Young's modulus, when compared to the neat G-HDPE, despite increasing the density by 10% only. Thermogravimetric analysis showed a reduction from 440 °C to 300 °C in the initial thermal degradation temperature of the biocomposite, relative to the neat matrix. Differential scanning calorimetry showed that both melting and crystallization enthalpy decreased as the flax fibre content increased from 0 to 30wt%. Melting and crystallization temperature peaks were not affected by the natural fibre addition. Of note, the composite studied is 100% biobased and it does not use any additives, increasing its potential for recyclability and circular economy applications.

1 INTRODUCTION

Polymers reinforced by natural fibres have been used in recent decades as an alternative to synthetic and non-renewable composite materials, owing to their renewable and abundant sourceability, in addition to the ease of processability, low cost and non-toxicity [1]–[8]. To exemplify, natural fibre reinforced composites can be 25-30% stronger than glass fibre composites of the same weight, while requiring less energy consumption even when compared to traditional construction materials such as wood, steel, and concrete [9], [10]. Following this trend, the natural fibre composites world market has been evaluated at USD 4.46 billion in 2016, and it is estimated to achieve a compound annual growth rate under 12% by 2024 [9].

Natural plant fibres have been used to reinforce polymeric composites in several applications. Among these fibres, flax is known for its low density, high strength and stiffness, next to being renewable and low-cost [11]. Presently, flax fibre reinforced composites are employed extensively in molding automotive components [12], [13]. In particular, in Germany, Hemp and Flax composites are rapidly substituting glass, while reducing material and maintenance costs in the production of automotive interior molding components [13]–[15]. Though at a slower pace, natural fibre reinforced polymers have also been applied in the aerospace, chemical, electronic and sporting goods sectors [9].

Although the development of natural fibre reinforced polymers inherently provides a socioeconomic potential in generating more agricultural-based economies in the manufacturing sector, the main source of the polymeric resin in the material system is still petroleum-based [16]. To address the latter, the Green High-Density Polyethylene (G-HDPE), among other bioresins, has been recently developed as a bio-based polymer synthesized from sugarcane-derived ethanol, with a minimum bio-based carbon content of 95%. In addition to the minimal harm to the environment, G-HDPE has physical and mechanical properties comparable to traditional petroleum-based high-density Polyethylene [16].

The present case study aims to investigate the mechanical and thermal performance of a new green high-density polyethylene reinforced with flax fibres. The biocomposites samples with 0 to 30wt% flax fibre content were made through compression molding. The mechanical properties of the biocomposites were evaluated through tensile and hardness tests. Scanning Electron Microscopy (SEM) was performed to gain insight into the biocomposite's fibre/matrix adhesion. Thermal properties were characterized through Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

2 MATERIALS AND METHODS

2.1 Materials

A 367gsm dry flax fibre fabric with a 2x2 twill weave supplied by Rock West Composites (San Diego, CA, USA) was used as the reinforcement. SGF4950HS green high-density polyethylene pellets donated by Braskem (Pennsylvania, PA, USA) was used as the matrix.

2.2 Sample preparation

Flax fibre reinforced G-HDPE samples were made through compression molding using a Carver Auto Series hydraulic press. First, the as-received flax fibre fabrics were cut to fit to an aluminum mold of 108x278mm^2 and dried at 105 °C for 2 hours (Thermotron SM-4-8200) to remove the room humidity effect. G-HDPE pellets were compressed into thin sheets for 20 minutes, under 1 ton and 170 °C. Then, layers of flax fibre and G-HDPE sheets were sandwiched (Table 1) and compression molded for 40 minutes, under the same pressure and temperature conditions. Finally, the hydraulic press was cooled to room temperature before the samples were removed from the mold.

Table 1. Specifications of the biocomposite sample groups fabricated.

Material (group)	Flax fibre fabrics (number of layers)	Flax fibre (%wt)	G-HDPE (%wt)
Neat G-HDPE	0	0	100
G-HDPE/10%FF	1	10	90
G-HDPE/20%FF	2	20	80
G-HDPE/30%FF	3	30	70

2.3 Mechanical analysis

Three specimens of each biocomposite group (Table 1) were tensile tested using an Instron 5969 device at 6mm/min, in accordance with ASTM D3039 [17]. Specimens' dimensions were 3.5x25x250 mm^3 (Figure 1). A W-E404-F extensometer was used to record transverse displacement and thereby estimate the Poisson's ratio of the samples. A Qualitest HPE II Digital Barcol Durometer was used to measure the hardness shore D, in accordance with ASTM D2240 [18]. The Analysis of the variance (ANOVA) and Tukey's test with statistical significance of α=5% were performed in Minitab.

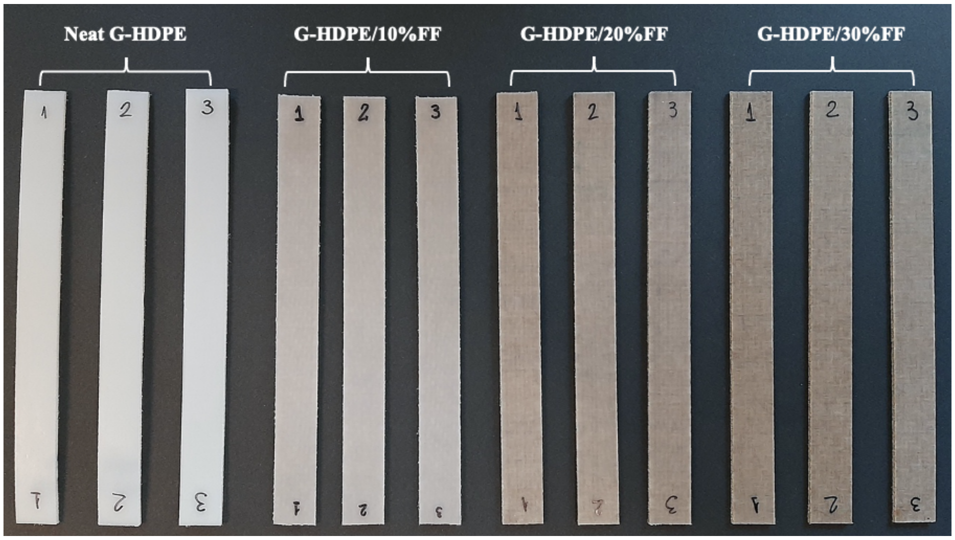

Figure 1. Specimens of the flax fibre reinforced G-HDPE composites for tensile testing.

2.4 Scanning electron microscopy

After tensile fracture, a Tescan Mira 3 XMU scanning electron microscope was employed to visualize the biocomposites' fibre/matrix adhesions. Samples were coated with a 10nm layer of platinum and analyzed at 200x magnitude, with an acceleration voltage of 5 kV.

2.5 Thermal analysis

Thermogravimetric analysis was performed using a TA TGA 5500 and a 100ul platinum pan. The temperature range was set from room temperature to 800 °C, at 10 °C/min. For differential scanning calorimetry, a TA DSC Q2000 and an aluminum crucible were used. Samples were cooled from room temperature to -90 °C at 40 °C/min, and then heated to 300 °C at a rate of 5 °C/min two times. An isothermal state of 10 min was kept between the cycles to eliminate the thermal history. Both TGA and DSC tests were performed with samples' masses ranging between 10mg and 20mg and under Nitrogen flow of 25mL/min.

3 RESULTS AND DISCUSSION

3.1 Mechanical analysis

The obtained tensile stress-strain curves are shown in Figure 2. The tensile strength of the biocomposite increased proportionally as the flax fibre content increased. Using 30wt% flax fibres in G-HDPE showed a tensile strength increase up to 225% and a Young's modulus increase of 250%, when compared to the neat G-HDPE. This improvement occurred while increasing the density only by 10%. As the flax content was increased, the composite material became more brittle. Accordingly, a significant increase in the tensile strength and Young's modulus were expected to occur. On the other hand, 20 and 30wt% flax reinforcement showed statistically no significant change in tensile strain, Young's modulus and Poisson's ratio (Table 2). This may indicate the occurrence of fibre-to-fibre interactions, which can lead to premature failure due to non-uniform stress transfer [19].

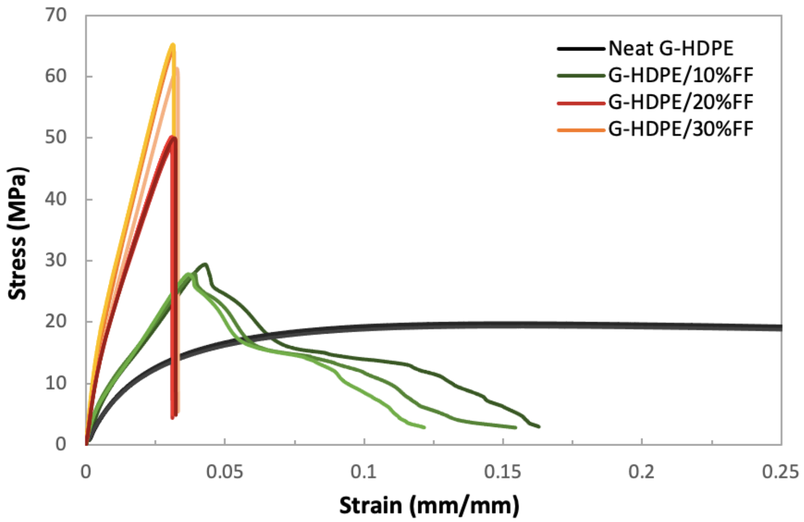

Figure 2. Tensile stress-strain curves of neat and flax fibre reinforced G-HDPEs. Note that each test was repeated three times per material group (groups are color-coded in the graph).

Table 2. Mechanical properties of neat and flax fibre reinforced G-HDPEs.

Material formulation	Strength (MPa)	Strain (%)	Young's modulus (MPa)	Density (kg/m^3)	Poisson's ratio	Hardness shore D
Neat G-HDPE	19.5 ± 0.3^{a}	15.3 ± 0.3^{a}	861.64 ± 13.5^{a}	939.4 ± 8.1^{a}	0.29 ± 0.02^{a}	62.1 ± 0.2^{a}
G-HDPE/10%FF	28.4 ± 0.9^{b}	3.9 ± 0.3^{b}	1284.5 ± 138.6^{a}	942.2 ± 0.7^{a}	0.14 ± 0.03^{b}	62.5 ± 0.1^{b}
G-HDPE/20%FF	49.6 ± 0.9^{c}	3.1 ± 0.1^{c}	2591.3 ± 57.5^{b}	990.0 ± 2.5^{b}	0.11 ± 0.01^{b}	61.4 ± 0.1^{c}
G-HDPE/30%FF	63.5 ± 1.9^{d}	3.2 ± 0.1^{c}	3007.0 ± 378.2^{b}	1025.9 ± 4.7^{c}	0.09 ± 0.01^{b}	63.0 ± 0.2^{d}
R-sq	99.7%	99.9%	96.6%	98.8%	94.8%	95.7%

For each column, means with different superscripts indicate significant differences caused by flax reinforcement at a 95% confidence level.

It is worth noting that the present study found superior mechanical properties to those reported earlier in the literature for Flax/HDPE composites made through injection molding [20], [21]. Although the mechanical properties of neat HDPE results were comparable to those of G-HDPE, only a 17% increase in tensile strength had been reported when using 30wt% flax fibre [21]. Recently, a tensile strength of 31 MPa while adding 20% flax fibre in HDPE was reported in the study [20]. However, it is still 60% lower than the reported value in the present study.

Hardness shore D results indicated that both the neat G-HDPE and its biocomposites can be categorized as "hard". Statistical results indicated slightly better performance of G-HDPE/30%FF (Table 2). Finally, R-square correlations indicate that the flax fibre content strongly affects the mechanical performance of the G-HDPE. Therefore, G-HDPE/FF formulation can be optimized in practice to meet the desired ductility/tensile strength ratio given an industry application's requirements.

3.2 Scanning electron microscopy

The morphology of tensile fractured surfaces of 20 and 30wt% flax fibre reinforced G-HDPE samples are presented in Figure 3. The SEM images showed an intense presence of fibre pull-out, especially for G-HDPE/20%FF biocomposite (Figure 3a).

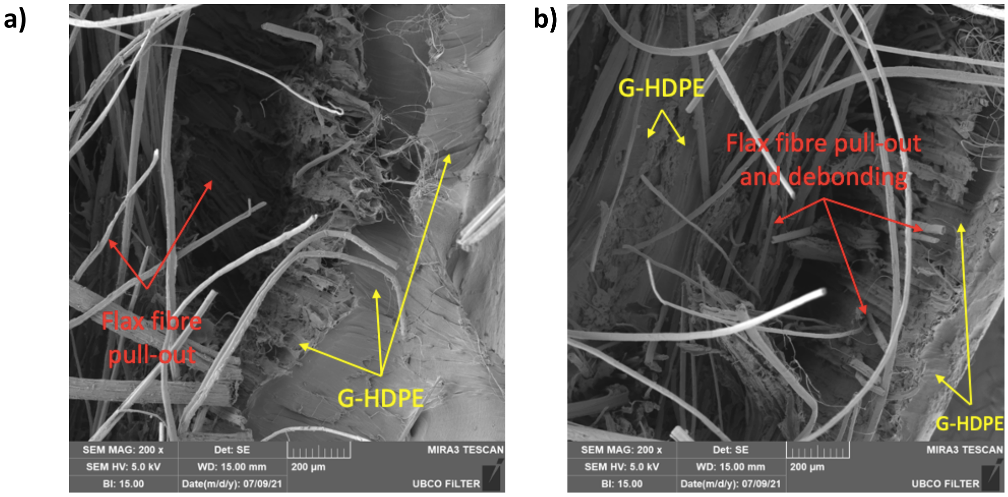

Figure 3. SEM images of a) G-HDPE/20%FF and b) G-HDPE/30%FF.

Samples with a higher amount of flax fibres seemed to show a lower amount of flax fibre pull-out (Figure 3b). This may be explained due to the use of thinner G-HDPE sheets in the biocomposite manufacturing process. According to the literature, the observed pull-out can indicate a weak interfacial bonding between the polymer matrices (hydrophobic) and the flax fibre (hydrophilic)[19]. Fibre treatment or the addition of maleic anhydride to the polymer matrix could improve the fibre/matrix interface and lead to higher tensile strength values [19]. However, the addition of such chemicals would also reduce the ecological and recycling potential of the biocomposite.

3.3 Thermal analysis

The neat G-HDPE and its biocomposites were analyzed by TGA (Figure 4) and DSC (Figure 5) to determine the effect of flax fibre on the thermal stability of the samples. Figure 4 shows the weight loss percentage and its derivative thermogravimetric (DTG) curves obtained by TGA.

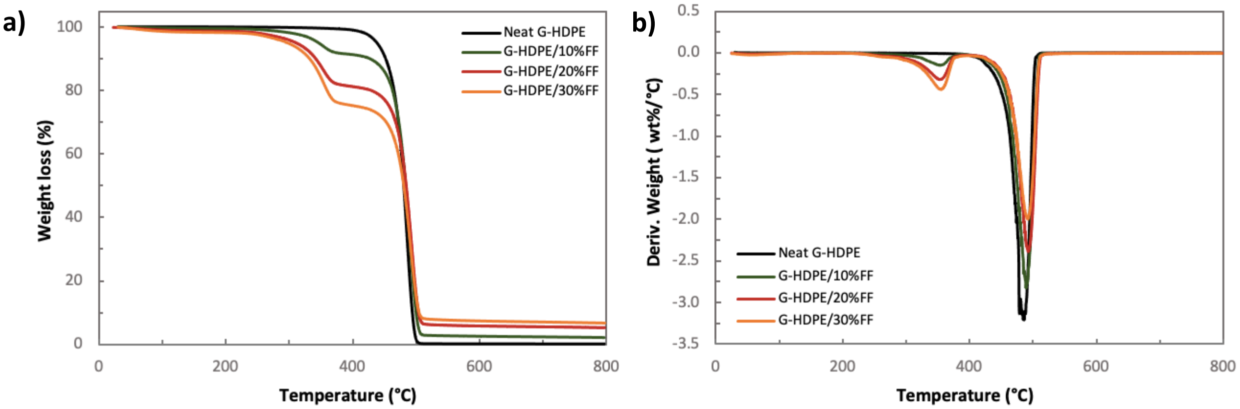

Figure 4. TGA and DTG curves of neat G-HDPE and flax fibre reinforced G-HDPE.

Onset temperatures were considered at 5% weight loss, where the G-HDPE showed a higher thermal stability (440 °C) compared to its biocomposites (347 - 300°C). The first weight loss stage at 200 – 400 °C was attributed to hemicellulose, cellulose and lignin decompositions of the flax fibre. Aligned with the literature, the decomposition of hemicellulose occurred first at 220 – 315 °C, followed by cellulose with a peak around 350 °C and finally by lignin [20], [22]. The second decomposition peak occurred at 490 °C. This weight loss was attributed to the breakage of

C-C bonds in the main chain of the G-HDPE matrix, which was completely degraded at 550 °C (Figure 4a). All biocomposite samples still had up to 7% residue left even at 800 °C, which can be attributed to the hemicellulose and lignin [22].

DSC results (Figure 5) showed that the melting and crystallization temperature peaks are not significantly affected by the flax fibre fabric addition, even though natural fibre has a lower thermal stability than the G-HDPE. The melting and crystallization peaks for the neat G-HDPE and its biocomposites were found at 129 °C and 105 °C, respectively. However, both melting (Figure 5a) and crystallization (Figure 5b) enthalpies decreased as the flax fibre content increased. Similar results has been reported in the literature, where the addition of natural fibre acts to weaken bonds and restrict the motions of polymer chains, requiring less heat to melt HDPE [23].

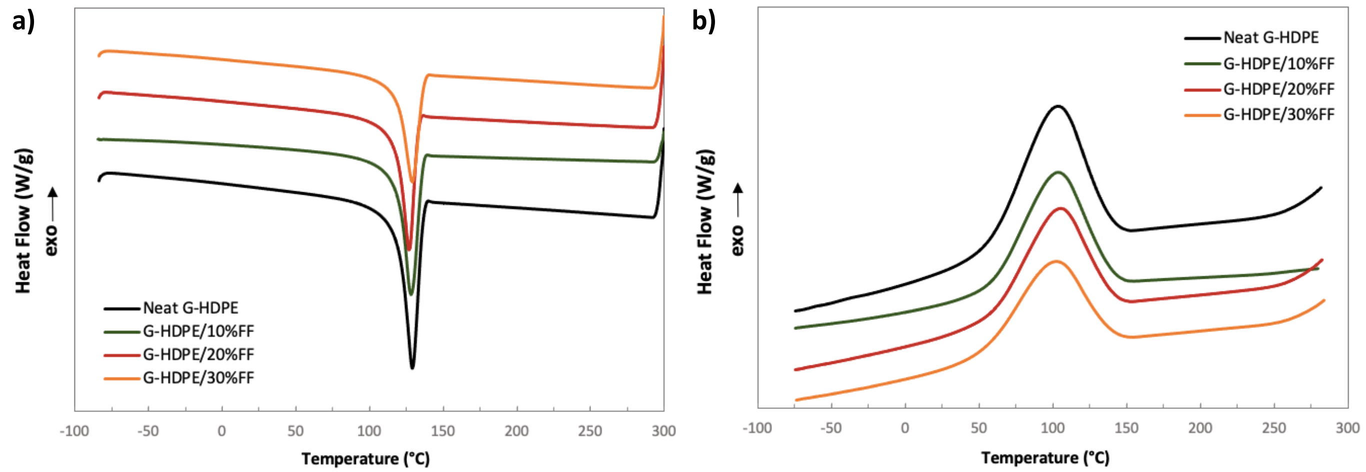

Figure 5. DSC curves of the second a) heating and b) cooling cycles obtained for the neat G-HDPE and its biocomposites.

4 CONCLUSION

The main objective of this study was to mechanically and thermally characterize a new flax fibre reinforced green high-density polyethylene. Tensile strength, Young's modulus and hardness shore D properties were significantly improved by the flax fibre reinforcement. The biocomposite G-HDPE/30%FF showed the best performance, obtaining the tensile strength of 63.5 MPa and the Young’s modulus of 3 GPa. The Poisson’s ratio and tensile strain were similar for all biocomposite formulations, showing reductions of at least 75% and 52%, respectively, relative to the neat matrix. SEM images indicated a weak fibre/matrix adhesion, suggesting that the mechanical potential of flax fibre reinforcement was not fully exploited. Additives to improve fibre/matrix chemical compatibility should be investigated in the future work. The thermal stability of biocomposites were lower than the neat G-HDPE (440 °C) due to hemicellulose, cellulose and lignin decompositions. Therefore, only temperatures below 300 °C must be considered when processing such flax fibre reinforced composites. The DSC results showed a decrease of melting and crystallization enthalpies as the flax fibre content increased, while not significantly affecting the peak temperatures.

5 ACKNOWLEDGMENT

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