Biocomposites of Flax Fiber and Polylactic Acid: Processing and Properties

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ABSTRACT: This work investigates the effect of the addition of flax fiber (15, 25, and 40 wt%) on the mechanical, morphological, rheological, and thermal properties of polylactic acid (PLA). In the first step, no coupling agent was used to produce fully biodegradable and biobased composites. In particular, flexural tests were performed on the composites to evaluate their mechanical properties, while density, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and rheological tests were also carried out. Scanning electron microscopy images (SEM) show good flax fiber dispersion in the PLA matrix along with good contact between both phases, leading to improved stress transfer. Based on the results obtained, the addition of 40 wt% flax fiber resulted in a 142% increase in flexural modulus. It was also found that flax fiber significantly decreased the glass transition, crystallization, and melting temperatures of PLA.

KEYWORDS: Polylactic acid, flax fiber, composites, processing, properties

1 INTRODUCTION

Recently, the use of biofibers as substitutes for glass and carbon fibers in the production of reinforced polymer composites has been extensively increased due to ever-increasing environmental concerns. Biofibers are abundant, cost-effective and low density, with good specific mechanical properties comparable to glass and carbon fibers [1,2]. One of the most widely used biofibers is flax (*Linum Usitatissimum*), and Canada has been the world's largest producer and distributer of flax since 1994. In 2005/2006, Canada produced approximately 1.035 million tons of flax.

Flax is known to have superior mechanical properties compared to other biofibers such as kenaf, sisal, jute, hemp, etc. Among all the natural fibers, flax has the best performance considering its low cost, low weight, and its high strength and stiffness. For instance, the maximum tensile strength of flax, hemp, kenaf, and jute is 2000, 900, 930, and 800 MPa, respectively. In addition, the specific modulus of flax is about 45 (GPa cm^3/g), which is significantly higher than 29 (GPa cm^3/g) for E-glass [3].

Most recently, the use of biobased and biodegradable polymers reinforced with natural biofibers in the production of "green" composites has increased due to environmental concerns. The use of biofibers as reinforcement in biodegradable polymers such as polylactic acid (PLA) and polyhydroxyalkanoates (PHA) has been established as a new pathway toward the production of more sustainable materials with fewer or negligible hazardous effects on the environment. Among the different types of biodegradable polymers, PLA is considered as the best example due to its vast application range. Overall, biodegradable and biocompostable polymers can be used in packaging and agriculture, but PLA applications are even wider, i.e., in the electronic, automotive, and construction industries [4]. The mechanical and physical properties of PLA are also acceptable compared to petroleum-based and other biodegradable polymers. For instance, compared to polypropylene (PP), PLA has higher tensile strength and tensile modulus with a similar melting temperature of 170°C [5,6]. In addition, the tensile strength, tensile modulus, impact resistance, and barrier properties of PLA are comparable to polyethylene terephthalate (PET), the main

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polyester thermoplastic resin from petroleum-based monomers [7].

Although PLA has good mechanical and physical characteristics, it also has some disadvantages such as brittleness, sensitivity to high temperature/humidity, low impact strength, and high cost [8]. As a solution to these problems, addition of biofibers is well known to positively improve the weak thermal stability and mechanical properties of PLA [2,9]. Several investigations have been reported on the mechanical, thermal, and physical characteristics of various types of PLA composites reinforced with different biofibers. Some studies have suggested that these composites have comparable or even higher properties than conventional composites such as PP/natural fiber-reinforced composites [2,5,10,11]. Meanwhile, several studies have shown that for biofiber-reinforced composites based on PLA, the mechanical properties (tensile and flexural moduli) increased due to the presence of natural fibers [12,13]. The reason behind these improvements is the polar nature of PLA, which results in good interaction with biofibers, leading to enhanced mechanical properties [6]. It has also been claimed that interfacial adhesion between PLA and biofibers is rather strong by nature [4,14].

Some studies on the mechanical and physical properties of flax/PLA composites have been published. Oksman *et al.* [2] reported that the introduction of 30 wt% flax fiber in PLA increased the tensile modulus from 3.4 to 8.3 GPa. However, increasing fiber content from 30 to 40 wt% did not further improve the modulus of the composites, which dropped to 7.3 GPa. They also reported that the glass transition temperature of their PLA/flax composites increased from 50°C for neat PLA to 60°C for PLA/flax composites. Bax and Mussig studied the mechanical properties of PLA/flax composites at different fiber contents (10 to 30 wt%) [15]. It was shown that flax fiber increased tensile strength from 43 MPa at 10 wt% flax to 54 MPa at 30 wt% flax. Tensile modulus and impact strength were enhanced and their maximum values were 6.3 GPa and 72.2 kJ/m^2, respectively. Increasing fiber content from 10 wt% to 30 wt% increased both tensile strength and modulus from 42.7 MPa and 3.9 GPa to 72.2 MPa and 6.3 GPa, respectively. Arias *et al.* [16] prepared composites of PLA/flax and evaluated their mechanical and thermal properties. Their results showed that the addition of 20 wt% of flax fiber increased the Young's modulus by 50%. Results of differential scanning calorimetry revealed that the glass transition temperature did not change after the flax fiber addition and remained close to 60°C. Yuan *et al.* [17] showed that the interaction between flax fiber and PLA seemed to be efficient as a result of good wetting of flax fibers by PLA. Flax fiber addition from 30 to 40 wt% increased both flexural strength and modulus from 28.7 MPa to 37.0 MPa and from 3.2 to 4.7 GPa, respectively.

Since there is limited published work on the manufacture of PLA/flax fiber composites via injection molding, the aim of this work is to produce PLA composites by this process and to further investigate the effect of flax fiber on the mechanical and thermal properties of PLA/flax fiber composites. In the first step, no coupling agent or surface treatments were used to produce the composites. The results are completed with rheological measurements to study the effect of flax on PLA in the melt state.

2 MATERIALS AND METHODS

The matrix used in this study was PLA grade 3251D from NatureWorks LLC. This polymer has a MFI of 80 g/10 min (190°C/2.16 kg), a density of 1.24 g/cm^3, a melting temperature of 188–210°C and a crystalline melting temperature of 155–170°C. Flax fibers obtained from Biolin Research Inc. (Saskatoon, SK, Canada) were used and sieved between 125 and 250 microns. Three different flax contents were used: 15, 25, and 40 wt%.

2.1 Composite Preparation

Both PLA pellets and flax fibers were dried in an oven at 80°C for 24 h prior to extrusion. Compounding was performed in a HAAKE co-rotating twin-screw extruder (Polylab OS) with a flow rate of 500 g/h and a circular die diameter of 3 mm at 100 rpm. The materials were then pelletized and dried in an oven at 80°C for 24 h before being injection molded. The injection molding machine was a NISSEI (model PS 60E9ASE) with a mold temperature of 30°C. The materials were molded into rectangular bars having dimensions of 115 mm in length, 25 mm in width, and 3.1 mm in thickness.

The temperature profiles for extrusion and injection molding are shown in Table 1. For characterization, the samples were cut directly from the molded parts.

2.2 Mechanical Characterization

Flexural testing (three-point bending with a span of 50 mm) was performed on specimens with dimensions of 60.0 × 12.5 × 3.1 mm^3 on an Instron universal tester model 5565 with a speed of 2 mm/min. At least five samples were tested to get an average.

Table 1 Extrusion and injection molding temperature profile used.

Extrusion Temperature Profile (°C)	Injection Molding Temperature Profile (°C)
T_1: 195	T_1: 195
T_2: 200	T_2: 200
T_3: 200	T_3: 195
T_4: 175	T_4: 190
T_5: 150	–
T_6: 140	–

2.3 Thermal Properties

The glass transition (T_g), crystallization (T_c), and melting (T_m) temperatures were measured by differential scanning calorimetry (DSC). The tests were performed using a METTLER DSC 7. Samples of approximately 10 mg were analyzed in aluminum pans by heating from 25 to 200°C at a rate of 10°C/min under nitrogen. To obtain the decomposition temperature of the composites, thermogravimetric analysis (TGA) was performed using a TA Instruments model Q5000 IR. Between 1 and 5 mg of composite was heated from 50 to 600°C at a heating rate of 10°C/min under nitrogen.

2.4 Scanning Electron Microscopy (SEM)

Fractured surfaces of the composites (from notched Izod impact tests) were selected to investigate the PLA-flax fiber interface. Sample surfaces were studied with a JEOL JSM-840A scanning electron microscope (SEM) with a high vacuum gun and a voltage of 15 kV. Samples were first sputter coated with a thin layer of gold.

2.5 Density

Density of the composites was measured using a gas (nitrogen) pycnometer ULTRAPYC 1200e (Quantachrome instruments).

2.6 Rheology

The melt rheological properties of PLA and PLA/flax fiber biocomposites were measured using a Rheometeric Scientific ARES rheometer. Dynamic oscillatory tests were performed using a 25 mm parallel plate geometry with gaps of about 2 mm. The tests were performed under nitrogen at two temperatures spanning the range of processing conditions (170 and 190°C). First, strain sweep tests were made to determine the effect of deformation. Then, frequency sweeps between 0.1 and 400 rad/s were performed in the linear viscoelastic zone of each material.

3 RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM)

Figure 1(a–f) shows SEM images of PLA/flax fiber composites with different fiber contents and magnifications. As can be seen in images (a, c, and e), good dispersion of flax fiber in PLA is obtained. SEM images at higher magnification (b, d, and f) show the interfacial contact between flax fibers and PLA. It is revealed that flax fiber surface is well coated with PLA as lack of any gaps between both phases seems to imply good interaction and adhesion [18]. As reported earlier, the polar and hydrophilic nature of both flax and PLA is believed to be the reason for good dispersion and uniformity inside the composites [15,19,20].

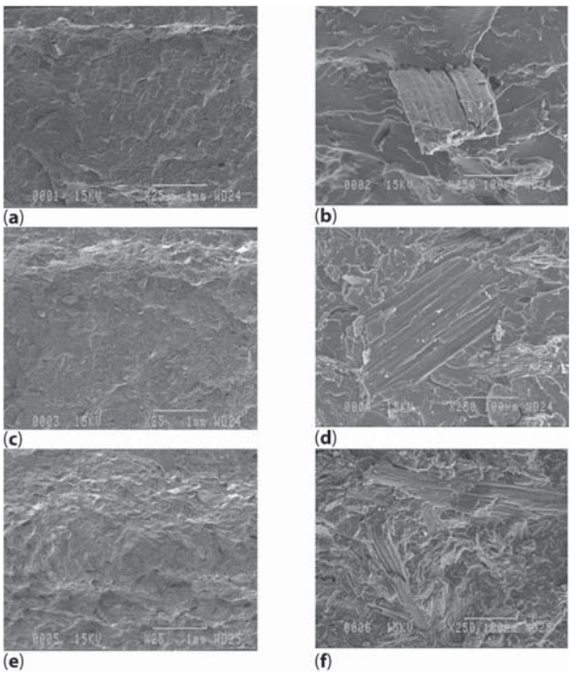

Figure 1 SEM images of: **a)** PLA/15% flax (x25), **b)** PLA/15% flax (x250), **c)** PLA/25% flax (x25), **d)** PLA/25% flax (x250), **e)** PLA/40% flax (x25), **f)** PLA/40% flax (x250).

Table 2 Density of the materials.

Sample	Flax content (wt%)	Density (g/cm^3)
Flax fiber reinforced PLA	15	1.332 (0.001)
	25	1.343 (0.001)
	40	1.410 (0.001)
Neat PLA	–	1.300 (0.010)
Flax fiber	–	1.500 (0.010)

Values in parentheses represent standard deviations

3.2 Density

Density of the PLA/flax fiber composites is presented in Table 2. It is shown that as a result of flax fiber addition (density of 1.50 g/cm^3), the density of PLA/flax fiber composites increased from 1.30 (neat PLA) to 1.41 g/cm^3 for 40 wt% flax fiber-reinforced PLA composites. Increasing flax fiber content from 15 to 25, and 40 wt% resulted in a density increase of about 2.3, 3.1, and 8.5%, respectively. Teymoorzadeh and Rodrigue have also reported similar increases for PLA/wood flour composites [18].

3.3 Mechanical Properties

Figure 2 shows the flexural modulus of PLA/flax composites. The addition of flax significantly increased the flexural modulus of the composites. As can be seen, the flexural modulus increased from 2.5 GPa for neat PLA (0 wt% flax fiber) to 6.0 GPa at 40 wt% flax fiber. This value is much higher than the 4.7 GPa reported by Yuan *et al.* [17]. Actually, increasing flax content from 15 to 25, and 40 wt% increased the flexural modulus by 38, 96, and 142%, respectively. In a similar study [18], a flexural modulus increase from 2.4 GPa for neat PLA to 5.9 GPa at 40 wt% wood flour was reported.

3.4 Thermal Properties

Figure 3 presents the DSC plots for PLA and PLA/flax composites. As can be seen, addition of flax to PLA decreased glass transition (T_g), crystallization (T_c), and melting (T_m) temperatures. In a work by Lee *et al.* [21], a slight decrease in T_g, T_c, and T_m, was also reported for PLA/wood flour composites. They claimed that in the case of glass transition temperature, this value is dependent on molecular characteristics, composition, and compatibility of the components in the amorphous matrix. The results for T_g were also in agreement with studies performed earlier on PLA/flax composites [2,16]. Table 3 shows DSC and TGA results for neat PLA and PLA/flax composites. It is shown that by increasing flax content from 0 to 15, and 25 wt%, T_g decreased by about 3 and 2°C, respectively. Furthermore, as fiber content increased from 25 to 40 wt%, the T_g value remained unchanged. In the case of T_c and T_m, increasing flax content changed these values by about 2 to 6°C. For instance, the T_c value as a function of fiber content decreased from 99°C to 93°C. As can be seen in Table 3, T_m decreased from 170 to 166°C. Lee *et al.* [21] claimed that the presence of voids within the PLA structure is the reason for the reduction of melting temperature. Results of TGA analysis show an increase in decomposition temperature (T_d) from 282°C for neat PLA to 340°C for the composites with 40 wt% flax fiber.

3.5 Rheology

As is the case for most filled polymers, the linear viscoelastic range (onset of strain dependence) is shorter. Based on the results obtained, strain amplitude for frequency tests were selected as 15, 4, 0.7, and 0.02% for 0, 15, 25, and 40 wt% flax composites, respectively. Based on these values, Figures 4 and 5 present the dynamic viscosity curves for neat PLA and PLA composites at two temperatures (170 and 190°C). As expected, a shear-thinning behavior was obtained as viscosity decreases with increasing frequency. Also, dynamic viscosity increased with flax content and decreased with increasing temperature. By increasing the flax fiber content from 0 to 40 wt%, the dynamic viscosity at 100 rad/s increased from 0.3 to 1.9 kPa.s at 170°C, while the increase is from 0.1 to 1.7 kPa.s at 190°C. The dynamic viscosity at 100 rad/s for 40 wt% flax at 170°C was around 1.9 kPa.s, which decreased to 1.6 kPa.s by increasing temperature at 190°C. Shumigin *et al.* [22] pointed out that for PLA filled with cellulose fibers, the dynamic viscosity increased compared to the neat polymer matrix as a result of cellulosic fiber addition. They showed that the zero shear viscosities (η_0^*) for PLA reinforced with 10 wt% cellulose fiber was about 16% higher for neat PLA. They also claimed that the viscosity increase is related to concentration, particle size, distribution, and filler shape. It is obvious that the presence of rigid fillers in the matrix restrict polymer

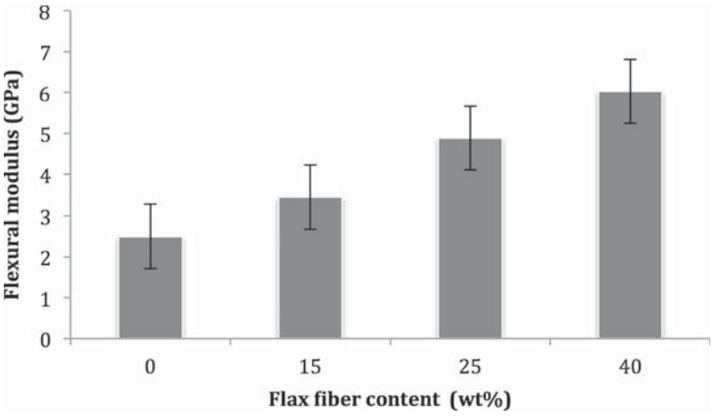

Figure 2 Effect of flax fiber content on the flexural modulus of PLA.

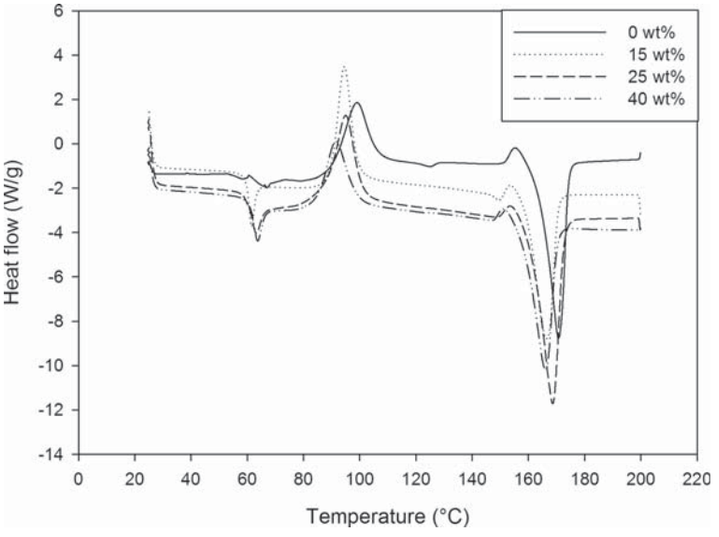

Figure 3 DSC thermographs for PLA and PLA/flax fiber composites.

Table 3 Effect of flax content on the thermal properties of PLA.

Sample No.	Flax content (wt%)	Decomposition Temperature (°C)	Glass Transition (°C)	Crystallization Temperature (°C)	Melting Temperature (°C)
1	0	282	62	99	170
2	15	332	59	95	166
3	25	332	60	95	168
4	40	340	60	93	167

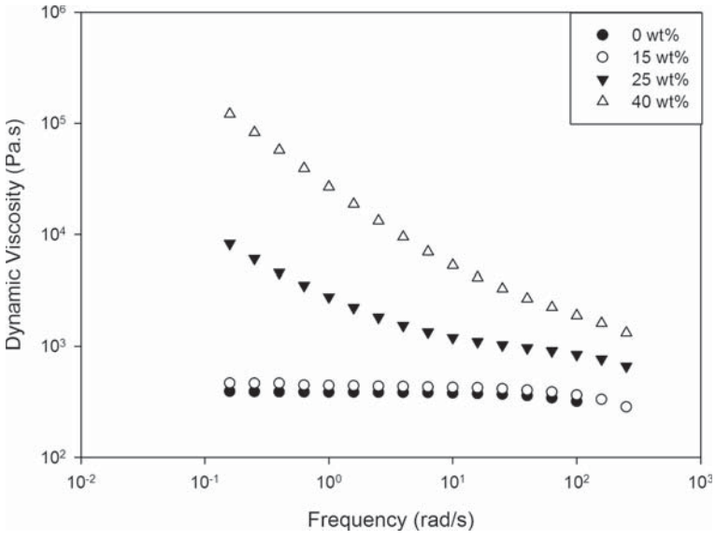

Figure 4 Dynamic viscosity as a function of frequency and flax fiber content (170°C).

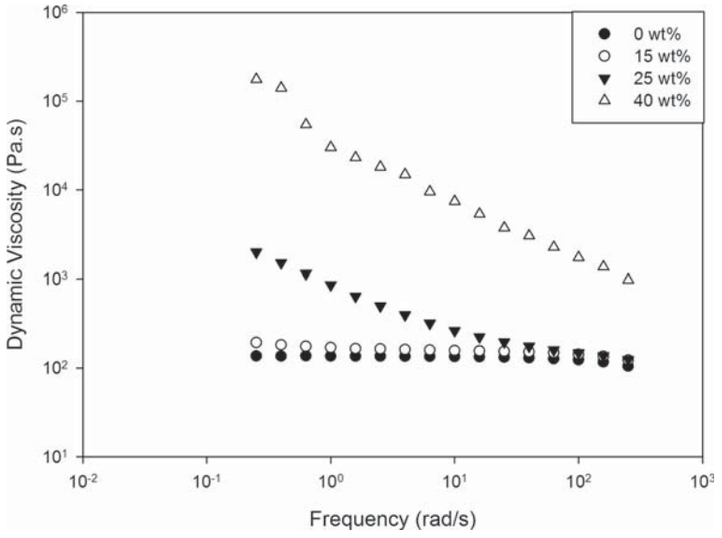

Figure 5 Dynamic viscosity as a function of frequency and flax fiber content (190°C).

chain mobility. Moreover, they showed that as cellulose fiber content increased from 0 to 10 wt%, dynamic viscosity increased from 1.7 kPa.s for neat PLA to 2.1 kPa.s for PLA polymer filled with 10 wt% cellulose fiber.

On the other hand, Figures 6 and 7 show the storage modulus as a function of frequency and fiber content. Based on these results, the storage modulus of PLA increased with flax fiber addition and decreased with temperature. It is believed that the presence of rigid flax fibers within the PLA structure results in improved stress transfer from the polymer matrix to the flax fibers and hinders polymer chain deformation. It can be seen that by increasing the flax fiber content from 0 to 40 wt% at 170°C, the storage modulus at 100 rad/s increased from 8 to 78 kPa. At 190°C, the storage modulus at 100 rad/s increased from 1.5 to 360 kPa as flax fiber content increased from 0 to 40 wt%. Moreover, it is noticeable that the slope of the elastic moduli curve at low frequency decreases as flax fiber content increases [22]. As flax fiber content increases, the presence of a plateau at low frequency represents an apparent yield stress, which can also be detected in viscosity curves by the

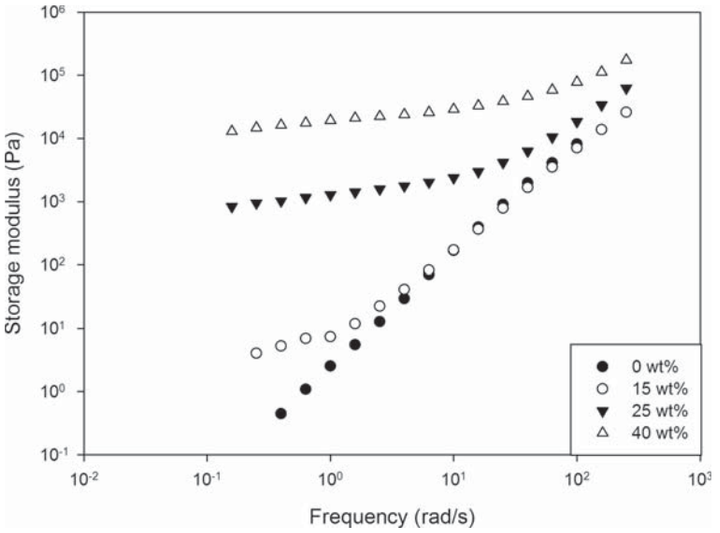

Figure 6 Storage modulus as a function of frequency and flax fiber content (170°C).

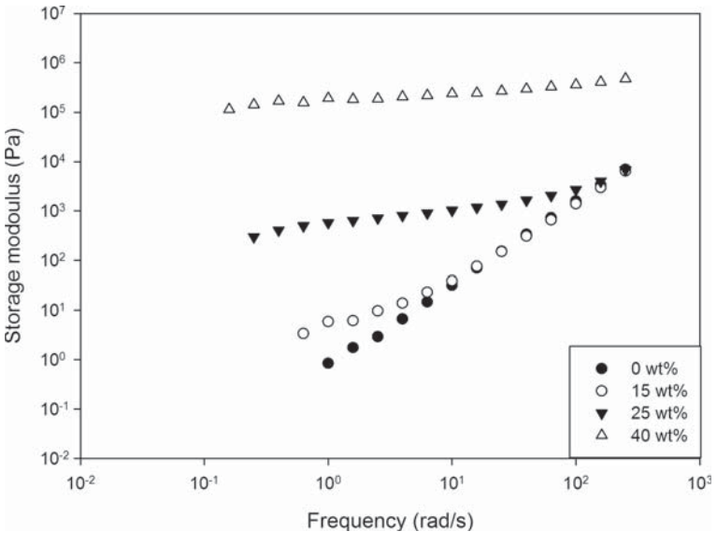

Figure 7 Storage modulus as a function of frequency and flax fiber content (190°C).

disappearance of the Newtonian plateau between 15 and 25 wt% flax.

Based on the results obtained from the rheological properties of PLA and PLA/flax composites, it is highly noticeable that the increase in mechanical properties of PLA/flax composites is similar to that of rheological properties. As the rheological studies revealed, the storage modulus of PLA and PLA composites increased due to flax fiber addition. Therefore, one could relate both types of properties to each other.

4 CONCLUSION

Composites based on PLA and flax fibers were prepared to investigate the effect of flax fiber content (0–40 wt%) on the mechanical, morphological, rheological, and thermal properties of biocomposites. In particular, injection molding was used to prepare the samples.

First, based on SEM images, good flax fiber dispersion within the PLA matrix was observed. Moreover, good adhesion between flax fibers and PLA without the use of any coupling agent was shown. Second,

mechanical characterization tests revealed that flax fibers significantly improved the flexural modulus of PLA/flax composites. Based on the results obtained, PLA flexural modulus increased from 2.4 to 6.0 GPa at 40 wt% flax. Third, thermogravimetric analysis showed an increase in the decomposition temperature of the composites from 282°C for neat PLA to 340°C at 40 wt% flax fiber. The DSC results revealed a reduction in glass transition, crystallization, and melting temperatures. Glass transition temperature decreased from 62 to 59°C for neat PLA and PLA with 15 wt% flax fiber, respectively. There was also a reduction in melting temperature from 170°C for neat PLA to 166°C for PLA with 40 wt% flax fiber. Finally, rheological characterizations showed a non-Newtonian behavior for PLA and its composites. Dynamic viscosity and storage modulus of PLA can be substantially increased as a result of the flax fiber addition.

Based on the results obtained, reinforcing PLA with flax fibers without any coupling agent or surface modification resulted in composites with acceptable mechanical, physical, and thermal properties comparable to their conventional counterparts.

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