Morphological, Rheological and Mechanical Properties of Pla-Typha Based Biocomposites

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Abstract

Due to the demand from society for the consumption of ecological polymeric materials, one of the polymers that have satisfied this request is the poly (lactic acid) (PLA). This polymer is derived from renewable resources, it is recyclable and biodegradable. It presents a good understanding between the promising properties and the cost. However, a route to increase the mechanical properties and reduce the cost of PLA is the elaboration of PLA based biocomposites by using fillers from natural waste. In this work, The effect of *Typha* content on the morphological, rheological, thermal and mechanical properties of PLA matrix was studied. Four formulations were produced with different mass concentrations. The results showed an increase in the viscoelastic properties, as a function of the *Typha* stem powder concentration. The DSC analysis showed an increase in the crystallinity rate of the various composites confirming the nucleating effect provided by the filler. TGA analysis indicated a decrease in the decomposition temperature of the composites. Mechanical tensile tests have shown a significant improvement in the mechanical properties mainly for the samples containing 45% (w/w) of *Typha* powder.

Keywords

1. Introduction

The demand by consumers of wood polymer composites (WPC) is having an important increase. At the same time, there was a consequent increase in the products manufactured from WPC and this phenomenon has aroused interest

on the part of plastic manufacturing companies [1]. The main advantage of using WPC composites is a reduction in the cost of final products. In addition to their biodegradability, they have other important properties, such as high specific stiffness, low density, renewal capacity [2] [3] [4]. Furthermore, an increasingly important interest takes into consideration the aesthetic values of these composites. In fact, the products made with a composite having a large fraction of fillers have an appreciated appearance of the surface and particular sensation to the touch. This characteristic distinguishes them compared to traditional polymers. At the same time, due to their much higher resistance to atmospheric factors compared to wood, the WPCs materials are very widely used as a wood substitute for making terraces, platforms or building facades [1]. Due to their ecological nature, the polymers from renewable resources have received considerable attention; in addition to the risks of futuristic shortages has been increased demand by the consumer society for environmentally friendly products. It is within this framework, that biodegradable poly (lactic acid) (PLA) seems to be one of the best alternatives among all biopolymers with its promising thermal and mechanical properties as well as its low cost [5] [6] [7]. This bioplastic can be produced from renewable resources such as maize and cassava and can be biodegraded naturally into H_2O and CO_2 [8] [9]. However, these composites have a limited number of applications because of different factors as slow crystallization kinetic, easy aging, low rigidity and high product cost. To solve these problems different types of fillers have been combined with polymer matrices to increase the thermal and mechanical properties of biocomposites [10] [11]. This work focuses on the study of *Typha australis* stem powder biocomposite material without the use of any kind of chemical compatibilizers. *Typha australis* is an aquatic plant, found on wetlands, and belongs to the family Typhaceae. It is particularly widespread in the valley of the Senegal River. This plant can reach a height of 3 meters [12] and moreover, it turns out to be harmful for agricultural production because of its invasive nature and source of pests [13]. It is used for the construction of wetlands for ecological restoration, wastewater treatment and is also the raw material for weaving paper because of its fiber length, toughness, and heat preservation performance [14] [15] [16] [17]. In this work, the morphological, thermal, rheological, and mechanical properties of biocomposites based on Typha stem powder (TSP) and Poly (lactic acid) (PLA) were studied. The relationship between the powder-mass ratio and the properties of biocomposites was analyzed.

2. Experimental

2.1. Materials

Poly (lactic acid) (PLA) is a thermoplastic polyester produced by fermentation of renewable agricultural raw materials followed by polymerization. In this study, it has been used the PLLA (PLA4032D), which contained ~2 wt% D-lactic acid and the average molecular weight was 190,000. It was purchased by Nature Works

LLC. The density, melting point (Tm) and glass transition temperature of the PLA4032D were 1.24 g/cm^3, 170°C, and 59.2°C, respectively. The natural filler used was the *Typha* stem powder. It was collected on the Senegal River banks, in Bango in the region of Saint Louis. The plant was been cut and dried in the air then it undergoes mechanical grinding to transform the stems into powders.

2.2. Compounding and Processing

The *Typha* stem powder was oven-dried at 105°C and the PLA at 60°C for 24 hours to remove moisture. The composites were elaborated in a HAAKE Mini-lab twin-screw extruder (Thermo Scientific), operated at a screw speed of 100 rpm, at a temperature of 180°C for 5 min. Four formulations of the composites were prepared with different content of filler equal to 0%, 25%, 35%, 45% in mass of TPS. The composites were then compression molded using a Carver laboratory press at 180°C and 200 bar for 1 minute to obtain a film of about 150 μm. The film is used for the mechanical test.

3. Characterization

3.1. Morphological Characterization

A HIROX SH4000M scanning electron microscope (SEM) was used. The samples were fractured in liquid nitrogen and after sputter-coated with gold under an argon gas flow for 15 min. The coated samples were left to dry at room temperature before SEM could be performed. The SEM analyses were done at 20 kV and at a range of magnification equal at ×80 to ×150.

3.2. Thermal Analysis

3.2.1. Thermogravimetric Analysis (TGA)

To study the thermal degradation process of biocomposites, a TGA analysis was performed. A Mettler Toledo machine operating under a nitrogen atmosphere (20 ml/min) has been used for this purpose. The samples were analyzed at 30°C - 600°C with a heating rate of 10°C/min and a mass of ≈20 mg was used for each sample.

3.2.2. Differential Scanning Calorimetry Analysis

Thermal analysis of the biocomposite samples was carried out on a differential scanning calorimeter (METTLER TOLEDO DSC 3). All DSC measurements were performed with powdered samples of about 10 ± 0.2 mg under a nitrogen atmosphere with a flow rate of 20 ml/min. All samples were subjected to the same thermal experiment with the following thermal protocol:

1) First, the samples were heated from 25°C to 210°C at a heating rate of 10°C/min to eliminate any thermal history effect;

2) Second, the samples were cooled from 210°C to 40°C at a cooling rate of 10°C/min to detect the crystallization temperature (Tc);

3) Finally, the samples were heated from 25°C to 210°C at a heating rate of

10°C/min to determine T_m. T_m and the heat of fusion (ΔH_m) were obtained from the thermograms during the second heating. The values of ΔH_m were used to estimate the crystallinity degree (X_c). The degree of crystallinity (X_c) of the PLA component was determined from the following equation [16] [17]:

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_0 \times (1 - w\% TSP)} \times 100$$

where ΔH_m, ΔH_c and ΔH_0 are the heat of fusion of the composites, cold crystallization and PLA 100% crystalline, respectively. The $w\%$ *TSP* is the percentage of *Typha* stem powder. For the PLA ΔH_0 is taken to be 93 (J/g) [18].

3.3. Rheological Characterization

The viscoelastic behavior of molten polymers can be determined using oscillatory rheological experiments such as dynamic mechanical testing, which offers a convenient way to assess the frequency dependence of mechanical properties of polymers. A useful representation is to plot the experimental frequency sweep data points in the complex plane. That means that imaginary part (of the complex viscosity) η' values are reported along the abscissa (X axis) and the real ones (η'') on the ordinate (Y axis) as schematized in **Figure 1**; where η' is the loss viscosity, η'' is the storage viscosity and ω is the pulsation of the frequency: $\omega = 2\pi N$. Usually, the experimental points are located on an arc of circle characteristic for a Cole-Cole distribution. The extrapolation of this arc of circle to the zero ordinate value gives the Newtonian viscosity which is related to the average molecular weight Mw of the considered polymer through a power law: ($\eta_0 = K (Mw)^{3.4}$) [17].

Melt rheological measurements of neat PLA and PLA composites were carried out with an ARES Rheometer Scientific mechanical spectrometer in oscillatory frequency sweep mode with a parallel-plates measuring cell. The diameter of the plates was 8 mm and the gap was 1 - 1.5 mm. The frequency was ranged from 0.1 rad/s to 100 rad/s. Deformation was kept constant at 5% over the entire frequency range to ensure linearity. This strain was selected from a dynamic strain sweep test, in which, within 1% to 10% of strains, at a fixed frequency of 10 rad/s, the drift deviation from linearity was followed; the frequency sweep test was then carried out at a constant temperature at 180°C.
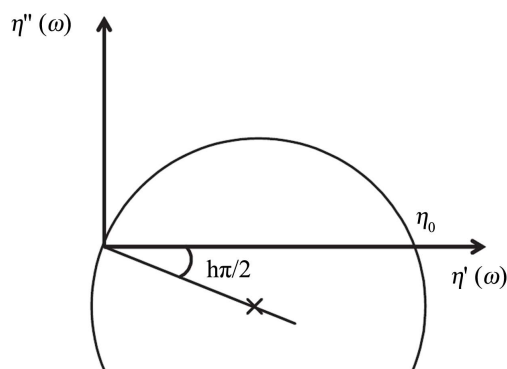

Figure 1. Cole-cole scheme.

3.4. Mechanical Properties

The apparatus used is a Lloyd EZ 50 traction bench. The results are analyzed using the software: NEXYGEN. The tensile strength and elongation at break of the composite were measured according to the ASTM D638-10 method at a crosshead speed of 30 mm/min. Each sample was subjected to at least 5 repetitive tests to obtain an average.

4. Results and Discussions

4.1. Morphological Characterization

The cross-sectional topography of PLA/TSP composites and TSP were observed by scanning electron microscopy. It can be observed from Figure 2(a) the differences in shape and size of the particles which constitute the TSP. The shape of powder ranges from particles of approximately spherical geometry lower than 50 microns, going up to filaments more than 1 mm. The large distribution of the particles, in terms of size and shape, reflects on the dispersion in the PLA matrix. As shown in Figures 2(b)-(d) a randomly orientation in the three directions of space and a phase separation between the TSP and matrix was rough with grooves and holes. In fact, in the tensile test, some TSP fibers could be extracted directly from the PLA matrix, indicating that the poor mechanical properties mainly resulted from the poor interfacial adhesion (mechanical test-Section 4.4). In addition, the presence of gaps between the pores and the two phases indicated that the motion of PLA molecules was restricted by poor interfacial compatibility [19].
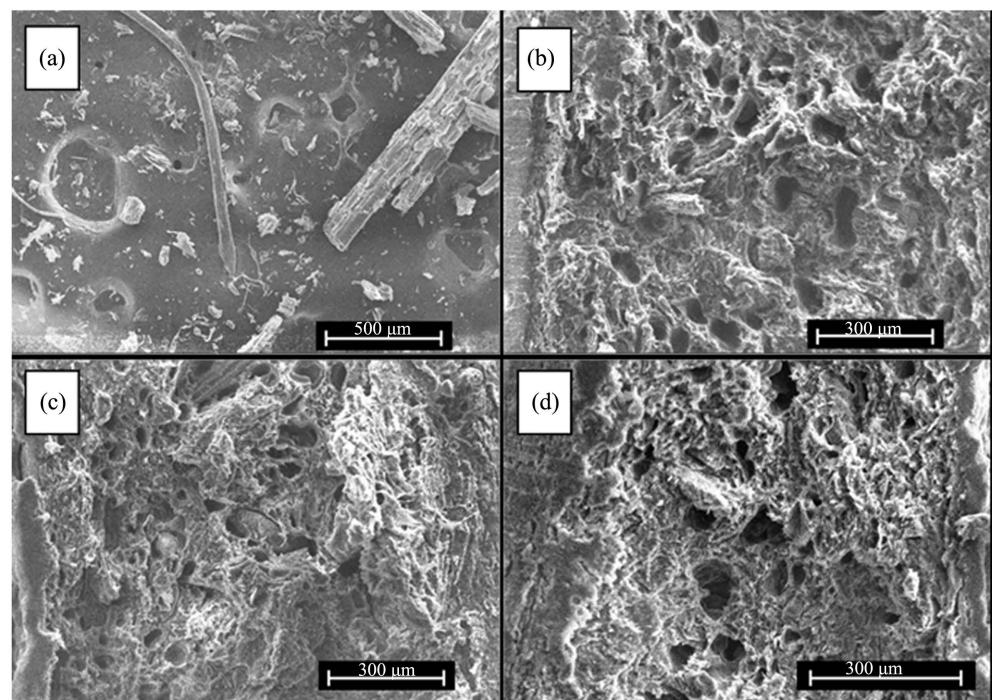
Figure 2. SEM images of PLA biocomposites: (a) TSP; (b) PLA 25TSP; (c) PLA 35TSP; (d) PLA 45TSP.

4.2. Thermal Analysis

4.2.1. Thermogravimetric Analysis

In order to better understand the effect of the TSP on the thermal degradation of the samples, thermogravimetric analysis was used. The thermogravimetric curves for all the samples are shown in **Figure 3**.

TSP loses moisture around 100˚C. The onset of the degradation of TSP is around 240˚C, this degradation is mainly due to the thermal scission of hemicellulose and the glycosidic linkages of cellulose. The total mass loss percentage for TSP at 600˚C is 70%. Pure PLA demonstrates one-step degradation and the onset of the degradation was observed around 340˚C. The elaborated biocomposites presented an intermediate thermal behavior, the onset of the mass loss decrease by increasing the TSP content. The onset of degradation for the composites containing 25%, 35% and 45% TSP is respectively 285˚C, 295˚C, 302˚C. Finally, carbonization of composites was observed at 600˚C [20] [21] [22].

### 4.2.2. Differential Scanning Calorimeter (DSC) Method Analysis

Figure 4 shows the thermograms corresponding to all samples, obtained from the heating and cooling cycles. The glass transition temperature (T_g) and melting temperature (T_m) of PLA were around 61˚C and 170˚C, respectively. A decrease in the cold crystallization temperature to 100˚C was noted (**Table 1**). The decrease of the cold crystallization temperature can be connected with the increase of polymer chains uniformity due to the presence of the TSP.

The T_g does not present variations and the T_m is very slightly reduced in the presence of TSP, however, the double melting-peak phenomenon is reduced after the adding of the powder is usual for polyesters to show the double melting-peak since the presence of crystals with different uniformity. The presence of
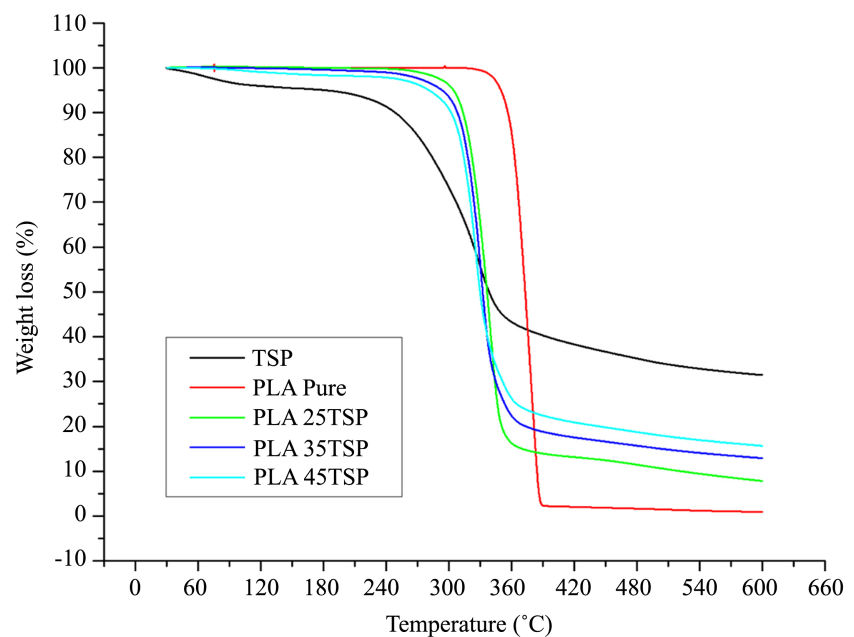
Figure 3. ATG thermograms of PLA, TSP and its composites.
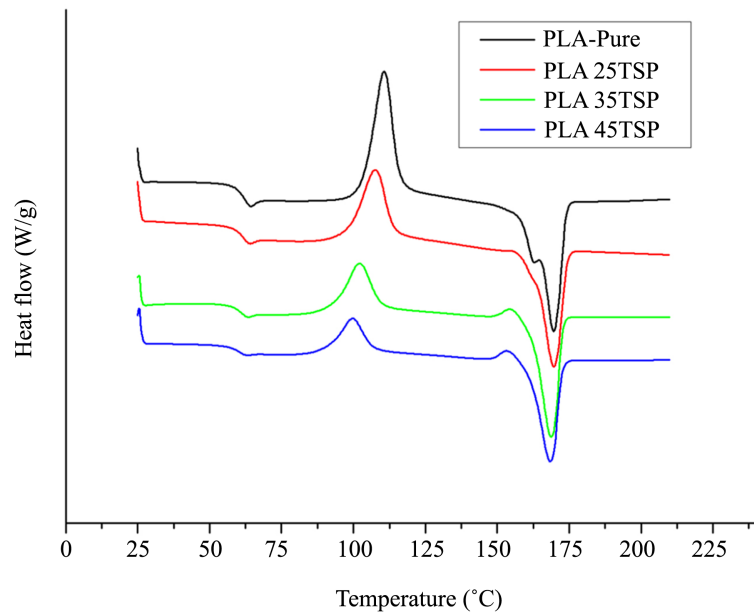
Figure 4. Fusion thermograms of biocomposites.

Table 1. Neat PLA thermal properties and its composites.

Samples	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	X_C (%)
PLA Pure	61	111	170	27	31	4%
PLA 25TSP	61	108	170	18	27	12%
PLA 35TSP	61	102	169	13	26	22%
PLA 45TSP	61	100	168	8	23	30%

a single peak in the biocomposites can be explained by the lowering of the mobility of PLA chains, compared with neat PLA. Moreover, this explanation is also consistent with the reduction of the temperature of cold crystallization and the increase of the degree of crystallinity (**Table 1**), which highlights an increase in the order of PLA chains [21].

4.3. Rheological Behavior

Figure 5 represents the complex plane variations for the neat PLA and the PLA composites. As introduced above, an extrapolation of the circle arc constructed on the complex graph allows us to determine the Newtonian viscosity. **Table 2** reports the Newtonian values determined for all the samples. These values show an increase in the viscosity of PLA 25TSP that is 76% higher than virgin PLA. Though, an increase in the quantity of the charge causes a reduction of the viscosity, reaching a Newtonian viscosity value, for the sample PLA 45TSP, comparable with that measured for PLA Pure with a difference of about 6% more. The changing of the viscosity is caused by the perturbation of the normal polymer flow since the filler particles hinder the mobility of chain segments. Moreover, great changes are observed for the samples loaded regarding the reference
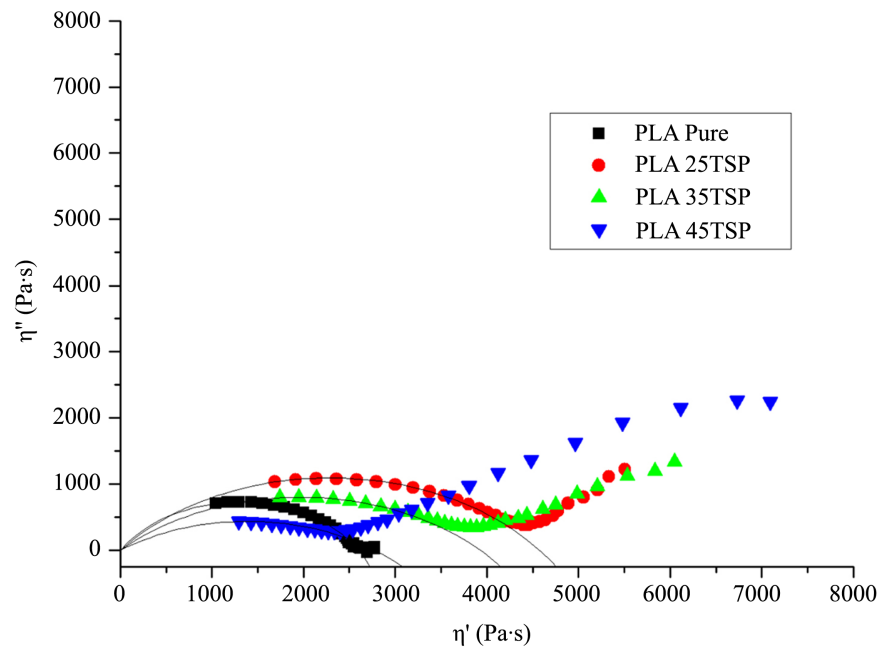
Figure 5. Complex plane diagrams for all the composites at T = 180˚C.

Table 2. Newtonian viscosity values.

Samples	η_0 (Pa s)
PLA Pure	2606
PLA 25TSP	4576
PLA 35TSP	3929
PLA 45TSP	2780

PLA Pure. All the samples with the natural fillers exhibit a deviation to the circular behavior promoting the shift of the Newtonian plateau to the low frequencies. This is characteristic of a gel behavior, indicating that at different concentrations of the powder, the level of interaction between the matrix and the filler is different at different frequencies applied [23]. In fact, at low frequencies, the viscosity strongly increases with the *Typha* powder content, as evidenced by the storage module of composites (G') (**Figure 6**) since G' is higher than pure matrix due to the intrinsic rigidity of TSP. Shear-thinning behavior of the molten mass was observed, the viscosity of the composites is strongly influenced by the shear rate. The storage modulus, especially for the highest powder content, shows that the matrix transfers great stress to the filler and based on G' data, serving as the measure of elastic behavior, we can conclude that with the addition of the TSP the solid-like behavior for all the samples clearly increases [21].
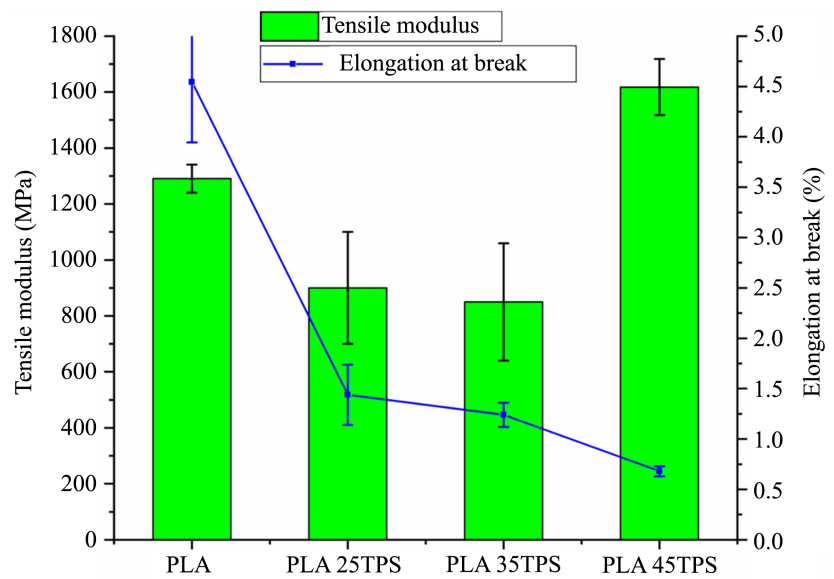
4.4. Mechanical Properties of Biocomposites PLA/*Typha* Stem

The mechanical tensile properties (Young's modulus, maximum strain, ultimate tensile strength) of the biocomposites are presented in **Table 3** and **Figure 7**. It
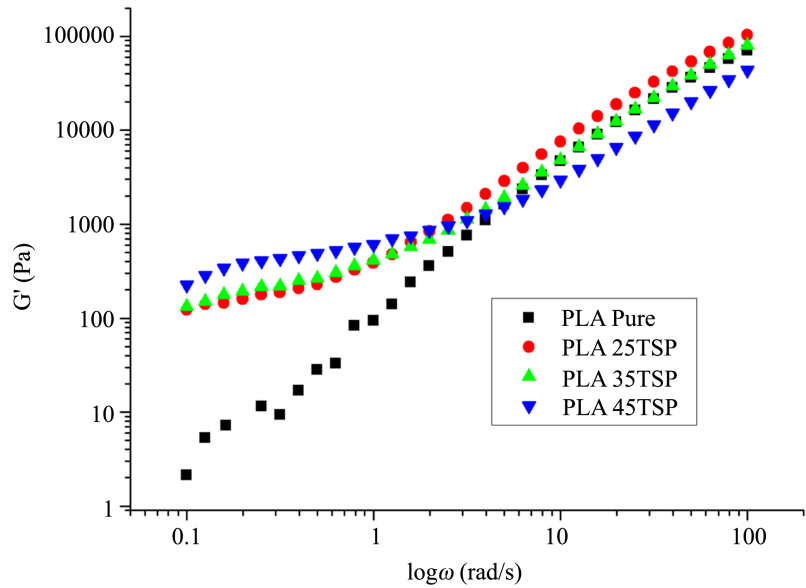
Figure 6. Frequency variations of storage G' for pure PLA and its composites at T = 180˚C.

Figure 7. The tensile modulus and elongation at break as a function of TSP concentration.

Table 3. The results of tensile mechanical tests.

Samples	Young's modulus	Ultimate Tensile Strength	Breaking Strength	Deformation at break	Maximum strain
	MPa	MPa	MPa	%	%
PLA Pure	1291.0 ± 45	38.0 ± 3.1	4.0 ± 1.1	4.6 ± 0.6	15.0 ± 0.9
PLA 25TPS	900.0 ± 198	8.0 ± 4.1	1.4 ± 0.6	1.4 ± 0.3	0.5 ± 0.5
PLA 35TPS	850.0 ± 211	6.0 ± 3.5	1.1 ± 1.8	1.2 ± 0.1	2.2 ± 0.1
PLA 45TPS	1618.0 ± 112	6.0 ± 2.6	0.6 ± 0.1	0.7 ± 0.1	1.3 ± 0.3

is noted a decrease in Young's modulus of biocomposites containing 25% and 35% of TSP compared to virgin polymer. However at 45%, there is a clear increase of the module due to the intrinsic rigidity of TSP and also with the high wood content (the latter having high tensile properties), these tensile properties of the composite were improved. Decreases in the modulus observed for samples containing 25% and 35% could be caused by the inhomogeneity of the powder consisting of particles as observed in the morphological characterization section. This lowering is certainly related to the formation of aggregates and the piling up of the fibers against each other, phenomena that favor the formation of defects. At high fiber proportions, the molten mixture is very viscous and appears as "dry" and this promotes friction between fibers and contributes to the creation of pores and cavities at the interface. As a result, the fiber/matrix contact area is reduced resulting in poorer stress transfer.

5. Conclusion

This work has shown that the *Typha* stem powder can be used in PLA matrix as a reinforcing agent. Experimental results showed an increase in rheological properties after the addition of the TSP. In fact, the viscosity increase compared with pure matrix, mainly at low frequencies. The results of the thermal analysis also revealed an increase in the degree of crystallinity without a significant change in melt properties and transition temperature. The SEM morphology exhibited the presence of pores between the two phases indicating that the motion of PLA molecules was restricted by poor interfacial compatibility. The morphologic results are congruent with the mechanical characterization that not show a clear improvement of the mechanical properties for the samples containing the 25 and 35 (wt%), however, the biocomposite containing 45% of *Typha* powder have tensile properties superior to virgin PLA that could be explained by the intrinsic rigidity of TSP that with a high percentage allows the reduction of the gap between the TSP powders and the polymer matrix.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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