

Effect of thermal annealing on the mechanical and thermal properties of polylactic acid–cellulosic fiber biocomposites

A. A. Pérez-Fonseca,^{1,2} J. R. Robledo-Ortiz,³ R. González-Núñez,² D. Rodrigue¹

¹Department of Chemical Engineering and CERMA, Université Laval, Quebec City, Quebec G1V 0A6, Canada

²Departamento de Ingeniería Química, Universidad de Guadalajara, Guadalajara, Jalisco 44430, México

³Departamento de Madera, Celulosa y Papel, Universidad de Guadalajara, Zapopan, Jalisco 45510, México

Correspondence to: D. Rodrigue (E-mail: Denis.Rodrigue@gch.ulaval.ca)

ABSTRACT: Polylactic acid (PLA) biocomposites were produced by a combination of extrusion and injection molding with three cellulosic reinforcements (agave, coir, and pine) and contents (10, 20, and 30%). In particular, some samples were subjected to thermal annealing (105 °C for 1 h) to modify the crystallinity of the materials. In all cases, morphological (scanning electron microscopy) and thermal (differential scanning calorimetry, dynamical mechanical thermal analysis) characterizations were related to the mechanical properties (Charpy impact, tensile and flexural tests). The results showed that annealing increased the crystallinity for all the materials produced, but different mechanical behaviors were observed depending on fiber type and content. For example, annealing increased the impact strength and flexural modulus of PLA and PLA biocomposites (agave, coir, and pine), while decreasing their flexural strength. But the main conclusion is that fiber addition combined with thermal annealing can substantially increase the thermal stability of the studied materials. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43750.

KEYWORDS: biopolymers & renewable polymers; cellulose and other wood products; composites; crystallization; thermal properties

Received 26 August 2015; accepted 5 April 2016

DOI: 10.1002/app.43750

INTRODUCTION

Cellulosic fiber–reinforced polymers have received a substantial increase in interest in recent years because of their low cost and high specific properties. Cellulosic fibers offer good opportunities as reinforcements for composites because of their ecological and environmental advantages, as well as attractive mechanical properties. Several publications have focused on the use of cellulosic fibers as reinforcement for polypropylene (PP) and polyethylene (PE).^{1,2} Nevertheless, petroleum-based polymers have the disadvantage of not being biodegradable, at least in a limited timescale. For this reason, the demand for biodegradable polymers such as polylactic acid (PLA) and polyhydroxyalcanoates (PHA) has recently increased.^{3–6} PLA is a versatile thermoplastic produced from a lactic acid monomer mainly coming from the fermentation of corn, potatoes, sugar beets, and sugar cane.⁷ It is currently the most-used biopolymer owing to its high mechanical strength and easy processability.⁸ But PLA has some disadvantages, such as brittleness, sensitivity to high temperature and humidity, low impact strength, and relatively high cost. Nevertheless, some of these drawbacks could be improved by the addition of fibers as reinforcement.⁹

The reinforcement of PLA with cellulosic fibers results in biocomposites that are sustainable and biodegradable in nature.

These materials reduce the dependence on petroleum resources, which are depleting rapidly.¹⁰ Most of the research on PLA biocomposites was devoted to improving the mechanical properties (stiffness) to a level that would satisfy specific applications and where PLA could replace synthetic polymers like PP.¹¹ Bledzki and Jazkiewicz¹² made a comparative study on biopolymers such as PLA and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) reinforced with cellulosic fibers versus PP, reporting significant increases in tensile stiffness and strength with fiber content. However, depending on the fiber type, different levels of improvement were reported. In order to increase the general mechanical properties of PLA biocomposites, investigations were performed on improving fiber–matrix interactions using different additives. Csizmadia *et al.*¹³ used wood impregnated with a phenolic resin to reinforce PLA and reported increased strength and decreased water absorption. Awal *et al.*¹⁴ prepared PLA–wood biocomposites with bioadimide and reported improvements in the flexural (17%) and impact (25%) strengths compared to biocomposites without bioadimide.

However, PLA's main limitation is its mechanical and thermal properties, which are not stable at higher temperature because of its low softening point around 60 °C.¹⁵ To overcome this drawback, some studies focused on improving PLA crystallinity

Table I. Characteristics of the Fibers Used

Component	Agave	Coir	Pine
Extractives (%)	6	4	19
Lignin (%)	23	37	31
Holocellulose (%)	70	59	50
Length (mm)	1.1	0.9	0.7
Diameter (mm)	0.2	0.2	0.3

by adding nucleating agents. This reduces the surface free-energy barrier for nucleation and enables crystallization to take place faster and at higher temperature upon cooling.¹⁶ Another technique to increase PLA crystallinity is thermal annealing (postprocessing treatment), which consists of submitting the samples to a controlled temperature for a limited time. Mofokeng *et al.*¹⁷ applied an annealing process after the extrusion of PLA–sisal biocomposites. They placed the samples in an oven at 120 °C for 3 h for recrystallization, and afterward the samples were dried in an oven at 85 °C, followed by injection molding at 190 °C. They reported that PLA biocomposites showed a better interaction between the fibers and PLA than other polymers like PP. However, the material lost its ability to sustain stresses as soon as the glass-transition temperature was exceeded. Mathew *et al.*¹⁸ treated neat PLA, PLA–cellulose, and PLA–wood biocomposites by heating for 3 days at 80 °C. The treatment improved the crystallinity of PLA, PLA–cellulose, and PLA–wood from 19, 35, and 45% to 57, 53, and 52%, respectively, and the dynamic modulus at 80 °C increased from 2.2, 46.7, and 24.5 MPa to 720, 2160, and 2150 MPa, respectively. Pantani and Sorrentino¹⁹ prepared PLA samples by injection molding and kept the samples in an oven at 105 °C for 8 h to increase crystallinity (the maximum crystallinity reached was 30%) to study its effect on material degradation in a homemade respirometric system. Higher crystallinity was found to decrease the PLA degradation rate: the amorphous samples reached 60% degradation in about 35 days, whereas the semicrystalline samples just reached 30% in 60 days.

In this study, a commercial grade of PLA was used to produce biocomposites based on agave, coir, and pine. Three concentrations (10, 20, and 30%) were used to produce the biocomposites via twin-screw extrusion coupled with injection molding. Since injection molding is a process with a fast cooling rate, thermal annealing was applied to determine its effect on the mechanical behavior of these biocomposites. The main applications of these materials could be for packaging and material handling (boxes, trays, bins, and so on).

EXPERIMENTAL

Materials

PLA 3251D from NatureWorks LLC (Minnetonka, MN) was used as the matrix. This biopolymer has a melt flow index (MFI) of 80 g/10 min (190 °C/2.16 kg), a density of 1.24 g/cm³, a melting temperature of 188–210 °C, and a crystalline melting temperature of 155–170 °C. Agave fibers (*A. tequilana* Weber var. Azul) were obtained from a local tequila company (Jalisco, Mexico), coir fibers were provided by Agrocoir S.A. de C.V.

(Colima, Mexico), and pine sawdust was supplied by Aserraderos Gómez Farias (Jalisco, Mexico). The chemical composition and the aspect ratio (L/D) of the particles after injection molding are reported in Table I.

Biocomposite Preparation

The agave and coir fibers were treated before being used. The fibers were soaked in water for 24 h and then passed through a Sprout-Waldron D2A509NH refiner (Andritz Inc., Muncy, PA) with two 30 cm diameter discs, one fixed and the other rotating at 1770 rpm to separate the pith from the fibers. The fibers were then placed in a centrifuge to remove excess water and were finally dried outdoors. Pine sawdust did not receive any previous treatment and was used as received from the sawmill. The particles were milled and sieved to keep only the range between 50 and 70 mesh. Three contents were used: 10, 20, and 30 wt %. The materials were first processed in a twin-screw extruder, a Leistritz (Remscheid, Germany) Micro 27 GL/GG 32D, with a temperature profile set to 150/160/160/170/180/180/170/160 °C. The extruder had a die with three circular holes, each one being 2 mm in diameter. The screw rotational speed was set at 100 rpm. The biocomposites were cooled in a water bath and then pelletized. The pellets were then oven-dried for 24 h at 75 °C to be injection molded on a NISSEI (Nagano, Japan) model PS 60E9ASE with a mold temperature of 30 °C and a screw temperature profile of 165/185/190/185 °C. The samples molded were of different dimensions: 80 × 12.7 × 3.1 mm³ and 126 × 12.7 × 3.1 mm³ rectangular bars, as well as type IV dog-bone specimens (ASTM D638). Thermal annealing was performed on the injection-molded samples for 1 h in an oven at 105 °C and after leaving the samples to cool down at room temperature (23 °C). For composite sample identification, the code “XX F” was used, where “XX” is the fiber content (10, 20, or 30 wt %) and “F” is the fiber type (A: agave; C: coir; P: pine). Treated samples (T) and untreated samples (U) were characterized as described next.

Morphology

Samples were submerged in liquid nitrogen and then fractured. Micrographs of the exposed surfaces were obtained with a JEOL (Tokyo, Japan) JSM-840A scanning electron microscope (SEM) with a high-vacuum gun and a voltage of 15 kV to characterize the morphology (the state of fiber adhesion or dispersion in the matrix). Samples were sputter-coated with a thin layer of gold and were viewed perpendicular to the fractured surface (cross section).

Thermal Properties

The glass-transition (T_g), crystallization (T_c), and melting (T_m) temperatures were measured by differential scanning calorimetry (DSC). The samples used for DSC were cut from the injected specimens in order to have a weight between 7 and 9 mg. The equipment, a Perkin Elmer (Waltham, MA) DSC-7, was programmed to work in the temperature range between 50 and 160 °C under a nitrogen flow of 50 mL/min. The heating rate was 10 °C/min. The melting temperature and melting enthalpy (ΔH_m) were calculated using MATLAB software, while the crystallinity level (X_c) was determined as^{15,18}

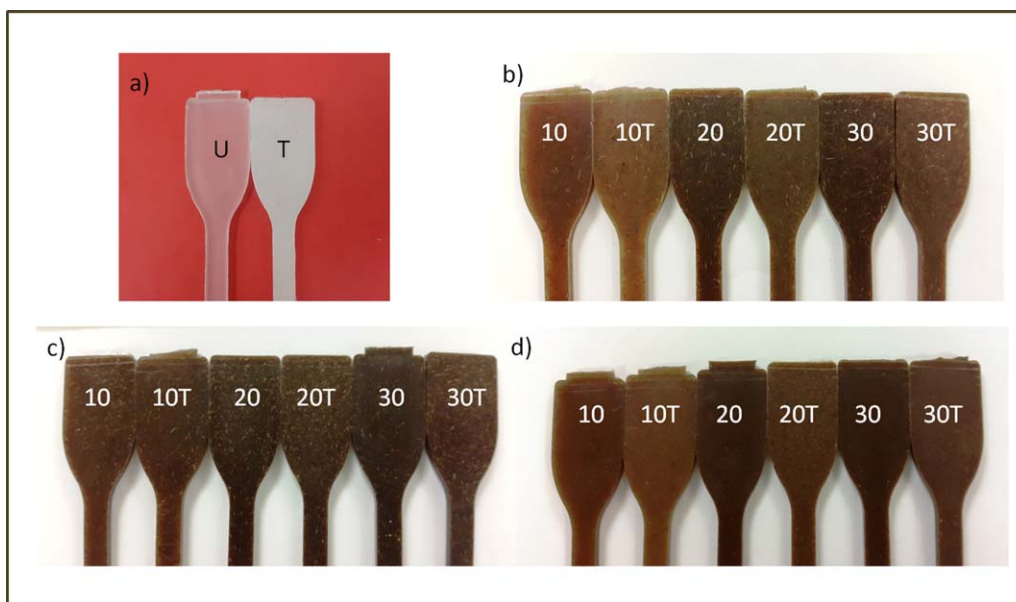


Figure 1. Effect of annealing on the color of neat PLA and the composites: (a) PLA, (b) PLA–agave, (c) PLA–coir, and (d) PLA–pine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$X_c = \frac{\Delta H_{m,exp}}{\Delta H_{ref}} \times \frac{1}{x} \times 100\% \quad (1)$$

where $\Delta H_{m,exp}$ is the experimental heat of fusion determined from DSC, ΔH_{ref} is the theoretical heat of fusion of fully crystalline PLA (93 J/g),¹⁸ and x is the weight fraction of PLA in the biocomposites.

Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis (DMTA) was performed on a TA Instruments (New Castle, DE) RSA3 equipped with a three-point bending fixture. The temperature was increased from 35 to 110 °C with a heating rate of 1.5 °C/min and using a frequency of 1 Hz under the auto-tension mode (0.02% deformation). The test specimen dimensions were 50.0 × 12.7 × 3.1 mm³, and the span used was 40 mm.

Mechanical Properties

The impact strength of the biocomposites was determined with a Tinius Olsen (Horsham, PA) Model 104 impact tester. The specimens were prepared according to ASTM D6110, and each value represents the average of 10 notched (ASN automatic sample notcher from Dynisco, Franklin, MA) samples. The flexural and tensile properties were evaluated using a universal machine Instron (Norwood, MA) model 4411. Flexural tests were carried out according to ASTM D790, and the sample dimensions were 80 × 12.7 × 3.1 mm³ with a span length of 40 mm. Six samples per composition were tested at a crosshead speed of 10 mm/min. Tensile tests were carried out using a 1 kN load cell, and the specimens were tested according to ASTM D638 (type IV specimen). Testing was performed at a crosshead speed of 5 mm/min with seven specimens per composition. All of the tests were performed at room temperature (23 °C). An analysis of variance (ANOVA) was performed (Statgraphics software) for all mechanical properties to ensure statistically significant differences.

RESULTS AND DISCUSSION

Morphology

Figure 1 presents typical images of the materials before and after thermal annealing. It can be seen that the treatment produced changes in the sample colors (darker and opaque), which indicate possible modifications that are due to the formation of small crystals in the samples.¹⁹ Figure 2 presents images at different magnifications of the biocomposites with 30% of each fiber. In the first six micrographs (a–f), it is observed that a good fiber distribution in the matrix was achieved. In the other micrographs (g–l), it can be observed that the fiber–matrix interface quality is good. These characteristics were very similar for the three types of fibers. PLA is a polymer with polar oxygen atoms, which could form hydrogen bonds with the hydroxyl groups of the cellulosic fibers.²⁰ As a consequence, PLA–fiber interactions are expected to be much better than most polymers, which are generally hydrophobic (nonpolar). Figure 2 also shows that annealing did not modify the material's morphology.

Thermal Properties

Typical DSC curves are presented in Figure 3, and the results are compiled in Table II. According to these data, T_m and T_g values for PLA and the biocomposites are around 166 °C and 60 °C respectively, which are typical values.¹⁶ Despite the amount of fiber added, the T_g values for the biocomposites were similar to neat PLA (around 60 and 61 °C). The same behavior is observed for the T_m values. Similar results were found by Teymoorzadeh and Rodrigue,²¹ who worked with PLA–maple wood biocomposites. Also, the same behavior was observed for treated samples.

The curves presented in Figure 3 also show that the cold crystallization peak is not observed for treated samples of neat PLA and PLA biocomposites (agave, coir, and pine), which indicates that the crystalline region in the system was not detectable

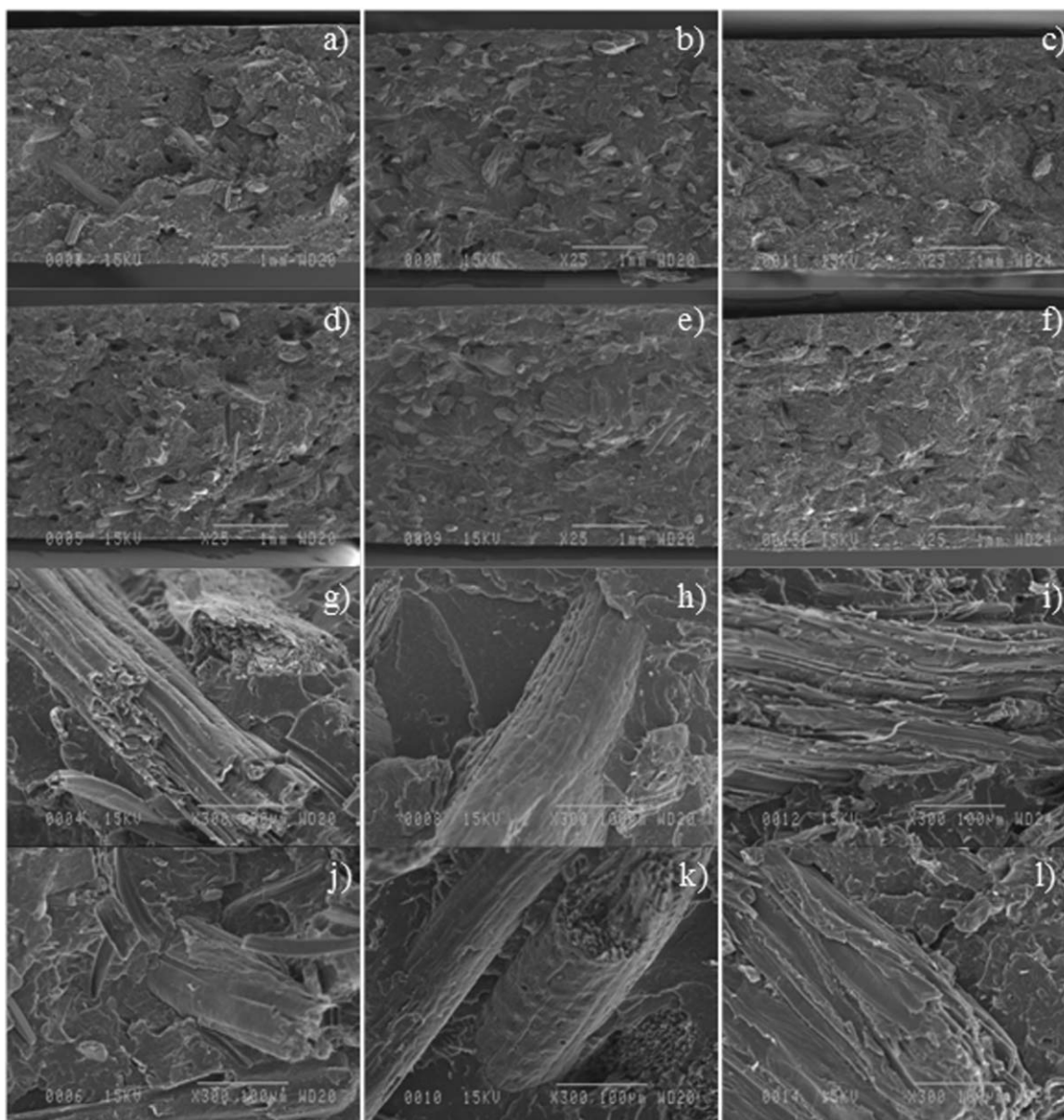


Figure 2. Morphology of the composites with 30% fiber: (a and g) PLA–agave, (b and h) PLA–coir, (c and i) PLA–pine, (d and j) PLA–agave (T), (e and k) PLA–coir (T), (f and l) PLA–pine (T).

because of crystallinity modification that was due to thermal annealing. Similar results were reported by Mathew *et al.*¹⁸ in biocomposites of PLA with cellulose and wood fibers. For untreated PLA, the cold crystallization peak appears around 96 °C, while for PLA–agave this peak is shown at 93.5 °C for all fiber compositions. In PLA–coir biocomposites, the values of T_c are around 94 and 92 °C, the lower being obtained for the highest amount of fiber (30%). When fibers are used as reinforcement, crystal formation can be initiated at different locations: at the fiber surface or at defects in the biocomposites (interface), depending on the fiber type.¹⁸ The reduced induction time for semicrystalline polymers with fibers is due to the fact that the surface roughness of the fibers plays a key role in increasing crystal nucleus density.²² Dong *et al.*²³ prepared PLA–coir biocomposites and confirmed that these fibers played

an effective nucleating role to accelerate the PLA crystallization process and thus improved the crystal growth rate. Way *et al.*²⁴ prepared PLA–maple and PLA–cotton biocomposites and found that the PLA crystallization peak decreased with fiber addition, which could be related to the nature of the fiber used. For PLA–pine biocomposites, the crystallization peak shifted from 96 to 97.5 °C when the fiber content was increased. This behavior can be associated with the fibers either acting as nucleation sites for crystallization or restricting the mobility of the polymer chains. Mofokeng *et al.*¹⁷ reported that increasing the amount of fibers made the immobilization effect dominant. The ΔH and crystallinity values for untreated PLA were 44.4 J/g and 47.7%, respectively. After annealing, these values increased to 47.9 J/g and 51.5%, which confirmed that annealing increased the PLA crystallinity. The crystallinity of the biocomposites also

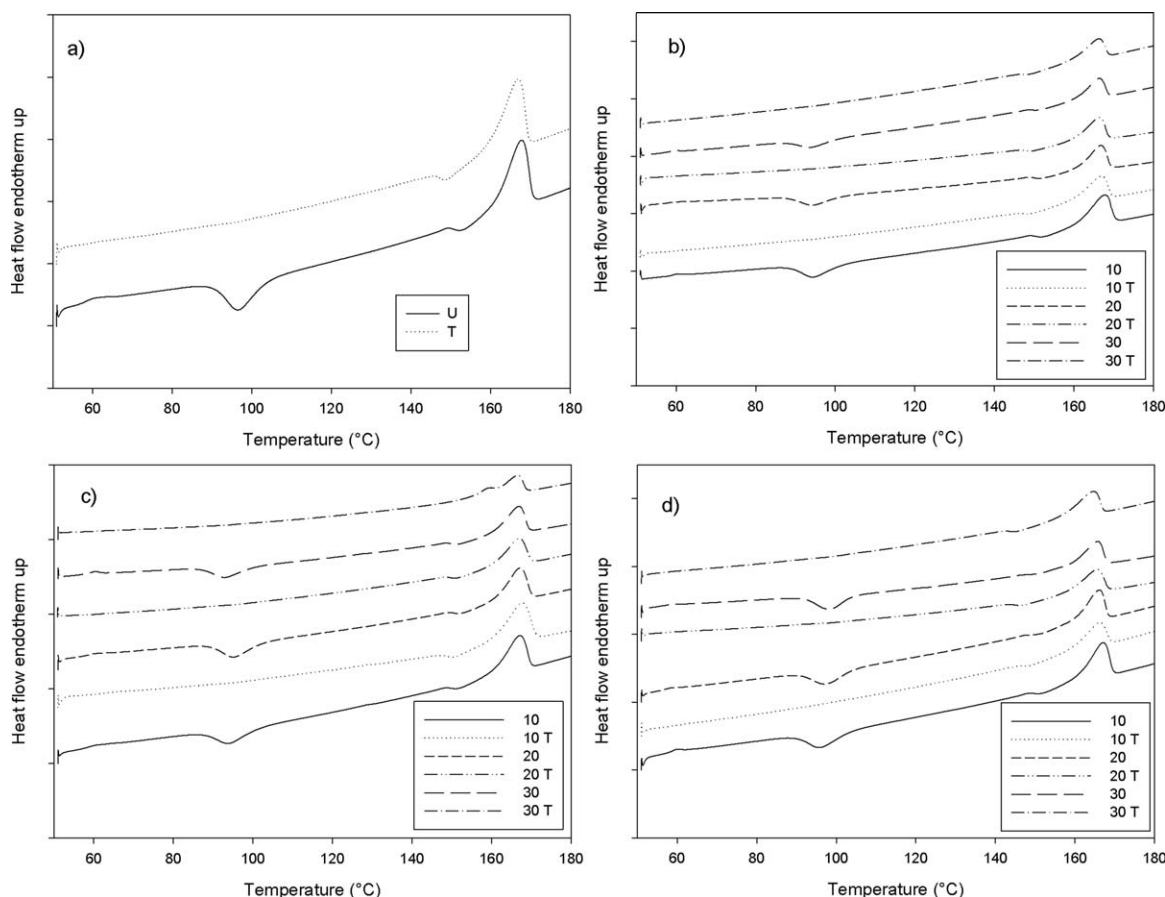


Figure 3. Typical DSC curves before and after thermal annealing: (a) PLA, (b) PLA–agave, (c) PLA–coir, and (d) PLA–pine.

increased due to annealing (2–9%) for all the fibers used, but the maximum crystallinity level was achieved for PLA–agave biocomposites (57%).

Dynamic Mechanical Thermal Analysis

Figure 4 shows the dynamic storage modulus of neat PLA and the biocomposites as a function of temperature. As expected, the storage modulus of PLA biocomposites increased with fiber

content and type. For example, at 40 °C, neat PLA has a modulus of 1278 MPa, while the maximum values for agave, coir, and pine biocomposites were 1990, 1835, and 2171 MPa, respectively. These increases were due to the reinforcement imparted by the fibers and their good interface with the PLA matrix, allowing for stress transfer within the composite.²⁵ But the thermal treatment at 40 °C slightly decreased the moduli for the biocomposites.

Table II. Thermal Characteristics of PLA and Composites before (U) and after (T) Thermal Annealing

Samples	Fiber content (%)	T_g (°C)		T_m (°C)		T_c (°C)		ΔH_m (J/g)		Crystallinity (%)	
		U	T	U	T	U	T	U	T	U	T
PLA	0	59.9	61.3	167.2	166.9	96.0	—	44.4	47.9	47.7	51.5
Agave	10	60.2	61.3	167.5	166.9	93.5	—	37.1	39.7	44.3	47.4
	20	59.8	61.3	166.7	166.2	93.5	—	33.6	38.1	45.2	51.1
	30	60.0	61.7	166.4	166.2	93.5	—	33.2	37.1	51.1	56.9
Coir	10	61.0	60.6	167.2	166.7	94.0	—	37.3	41.2	44.6	49.3
	20	60.6	60.9	167.0	166.3	94.0	—	35.4	36.4	47.5	48.9
	30	60.3	60.6	166.8	166.7	92.0	—	30.3	31.3	46.6	48.1
Pine	10	60.1	61.0	166.7	166.0	96.0	—	38.4	42.4	45.9	50.7
	20	58.9	61.0	166.6	165.6	97.0	—	30.9	38.5	41.5	51.8
	30	59.7	60.6	165.4	164.4	97.5	—	29.0	34.1	44.6	52.4

Table III. Dynamic Modulus of PLA and Composites before and after Thermal Annealing

Sample	Fiber content (%)	Dynamic modulus at 40 °C (MPa)		Dynamic modulus at 70 °C (MPa)		Temperature for 30% of modulus at 40 °C (°C)	
		U	T	U	T	U	T
		PLA	0	1278	1243	7	483
Agave	10	1511	1740	18	787	56	78
	20	1682	1715	49	871	58	94
	30	1990	1556	99	886	59	110
Coir	10	1401	1271	16	613	57	85
	20	1835	1454	30	848	56	110
	30	1704	1341	42	1053	58	110
Pine	10	1648	1175	11	628	55	78
	20	2171	1326	25	717	57	90
	30	1489	1416	7	793	57	110

As the temperature increased, a sharp modulus reduction was observed around 55–80 °C, which is associated with matrix softening and the α -relaxation of the amorphous regions of PLA.¹⁸ Nevertheless, this drop was much less important when fibers were added

to the matrix [Figure 4(b–d)]. Way *et al.*²⁴ mentioned that this lower decrease is directly associated with the reinforcing effect of the fibers, which have higher stiffness. Also, increases in storage modulus can be related to an effective stress transfer from the fiber to the matrix (good fiber–matrix adhesion).²⁰ Figure 4 shows that the dynamic modulus was even more improved by annealing. It can be seen that the decrease in storage modulus above 55 °C was almost eliminated in treated PLA and PLA biocomposites. In Table III the values of storage modulus at 70 °C are presented. It is clear that the values considerably increased (by around two orders of magnitude). In general, samples without treatment have 30% of the initial dynamic modulus (value at 40 °C) for temperatures around 55 °C, while for treated samples this value was reached at much higher temperatures (110 °C) for all the biocomposites with 30% fiber. Mathew *et al.*¹⁸ also reported that heat treatment substantially improved the dynamic modulus and thermal stability of their biocomposites. This improvement means that the treated biocomposites can be used at much higher temperatures than untreated ones.

Impact Strength

Figure 5 shows that PLA impact strength (30 J/m) increases with the addition of agave or coir fiber, reaching values of 35 and 40 J/m for fiber contents of 20 and 30%, respectively. For agave and coir biocomposites, the impact strength increased with fiber content, while for pine biocomposites, a constant value was obtained (around 30 J/m). This behavior can be related to fiber length: agave and coir fibers are much longer

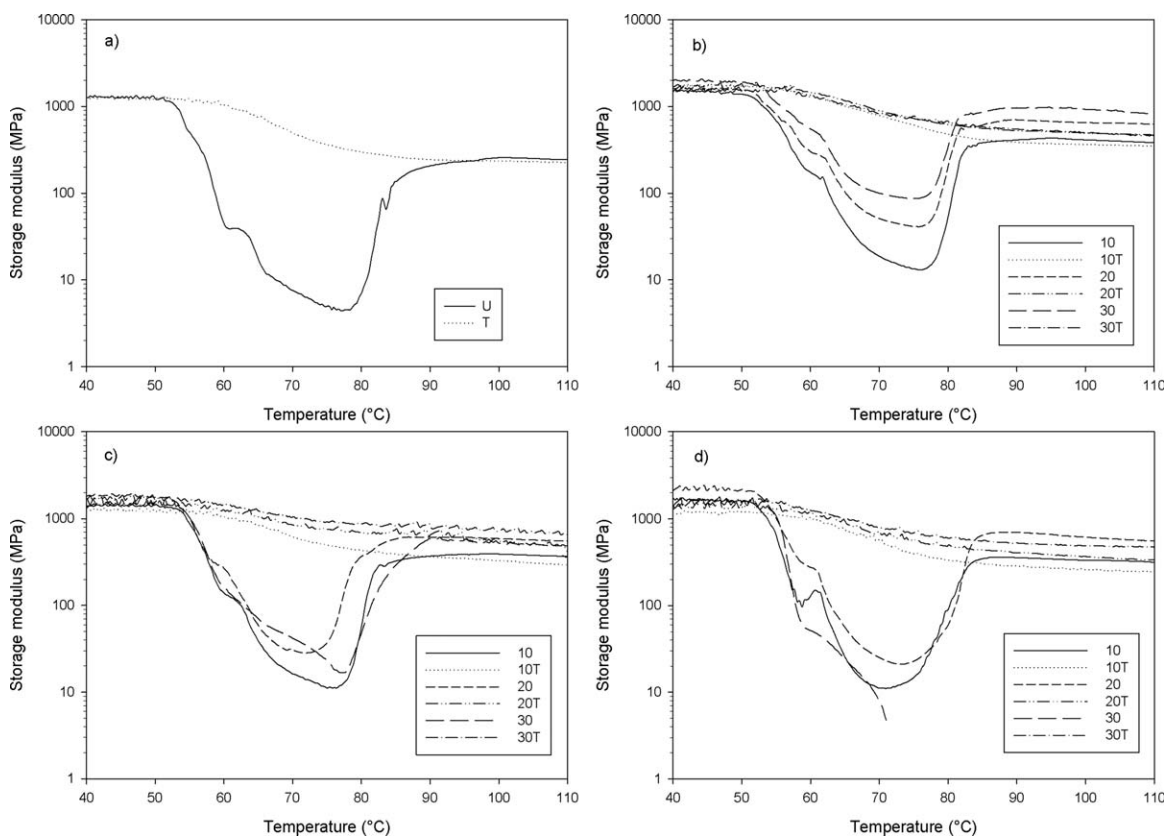


Figure 4. Storage modulus before and after thermal annealing: (a) PLA, (b) PLA–agave, (c) PLA–coir, and (d) PLA–pine.

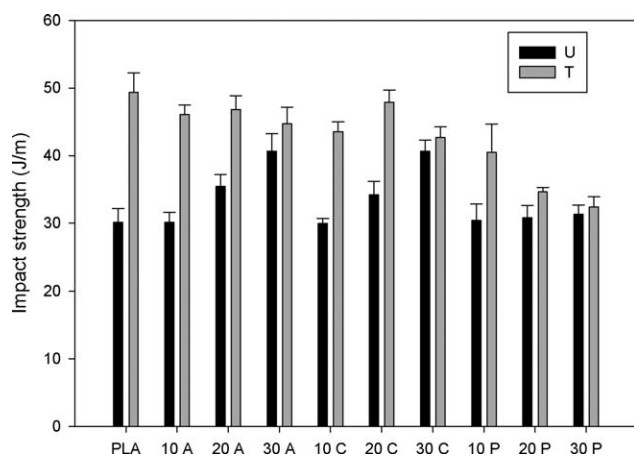


Figure 5. Impact strength before (U) and after (T) thermal annealing.

than pine (see Table I). In fact, previous studies reported that the composite impact strength can increase because of higher mechanical energy dissipated during failure (longer fiber pull-out distance) and possible fiber–fiber interaction (entanglements), as long as no fiber breakup occurs.²⁰ When longer fibers are introduced into the PLA matrix, the impact strength greatly increased because of a high number of long fiber pull-outs.²⁶ The results obtained for the treated samples showed that the impact strength of PLA increased by 64% because of annealing. PLA–agave biocomposites showed increases of 52, 32, and 10% for 10, 20, and 30% fiber, respectively. In coir biocomposites, the increases were 45, 40, and 5% for 10, 20, and 30% fiber, respectively. For pine biocomposites, with only 10% fiber the impact strength increased significantly (33%), while at 20% it was 12%, and there was no change at 30% fiber. Again, the results can be related to matrix crystallinity. Perego *et al.*²⁷ annealed PLA and observed that the impact strength of amorphous PLA (26 J/m) could be increased to 70 J/m (169%) by thermal treatment.

Flexural Properties

Figure 6(a) shows that PLA flexural strength (95 MPa) decreases with fiber addition. For agave fiber biocomposites, the flexural strength increased with the amount added up to a maximum of 89 MPa (30% of fiber). In coir biocomposites, the flexural strength for 10 and 30% fiber was 91 MPa, while at 20% fiber a small decrease to 88 MPa was observed. In contrast, in pine biocomposites the decrease depended on fiber content: 85, 80, and 73 MPa for 10, 20, and 30% of fiber, respectively. A good fiber–matrix interface lead to good load transfer to the fibers and improved strength. Nevertheless, without the use of coupling agents to improve interfacial adhesion, it is common that flexural strength decreases.^{24,28} Awal *et al.*¹⁴ prepared PLA–wood biocomposites and found that the neat PLA flexural strength was higher than that of the PLA–wood biocomposites, assigning this behavior to poor interfacial adhesion between wood fibers and PLA. Table I shows that pine fibers have lower cellulose (50%) and the highest wax (19%) contents compared to agave and coir fibers. Waxes are on the fiber surfaces, strongly influencing the surface properties of cellulose-based materials. In some cases, it is recommended to treat the fibers to remove

these noncellulosic components to increase the accessibility of surface functional groups.²⁹ Also, a higher cellulose content gives more strength to the fibers,³⁰ as is the case for agave and coir. In order to improve the fiber–matrix adhesion in PLA–fiber biocomposites, some studies focused on using coupling agents. Kim *et al.*²⁸ used maleic anhydride–PLA (MAPLA) as a coupling agent for PLA–pineapple fiber biocomposites and reported increases in flexural strength from 73 to 88 MPa and tensile strength from 33 to 43 MPa. Csiskos *et al.*³¹ studied the effect of the MAPLA concentration on the properties of PLA–wood biocomposites and reported that tensile strength increased from 47 to 56 MPa. Here, no coupling agent was used in order to focus on the annealing effect. The effect of annealing resulted in lower flexural strength for PLA and PLA biocomposites by around 15 to 20% for all the fiber contents. Nevertheless, the flexural modulus of all the biocomposites increased because of fiber addition, going from 2300 MPa (neat PLA) to values around 3000 MPa (biocomposites with 30% of all fibers), with the maximum being for PLA with 30% of coir fibers (3110 MPa), as shown in Figure 6(b). After annealing, the flexural modulus of neat PLA and biocomposites increased by 5 to 10%, which it is not a considerable value.

Tensile Properties

The tensile strength results are presented in Figure 7(a) and show trends similar to flexural strength [Figure 6(a)]: the values

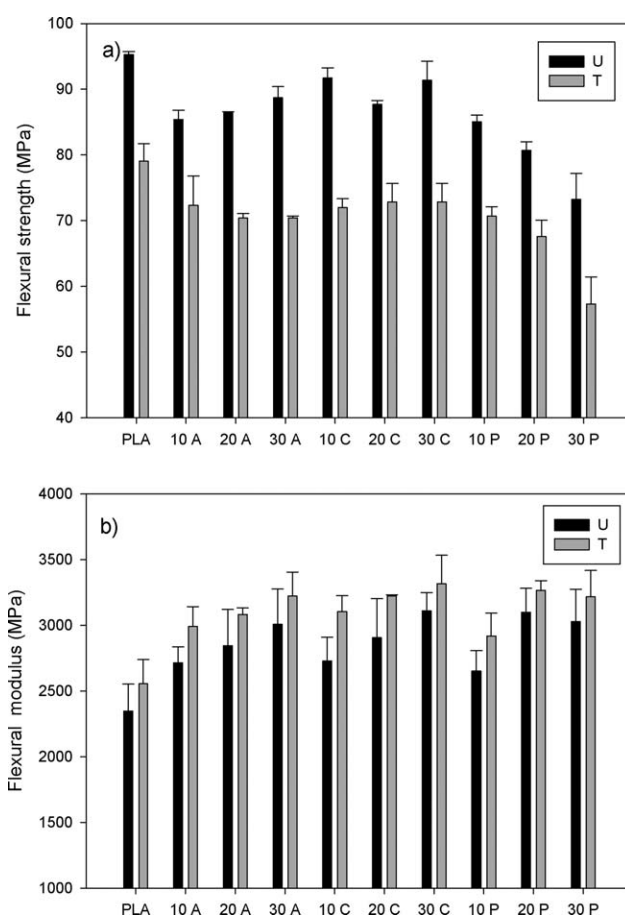


Figure 6. Flexural properties before (U) and after (T) thermal annealing: (a) strength and (b) modulus.

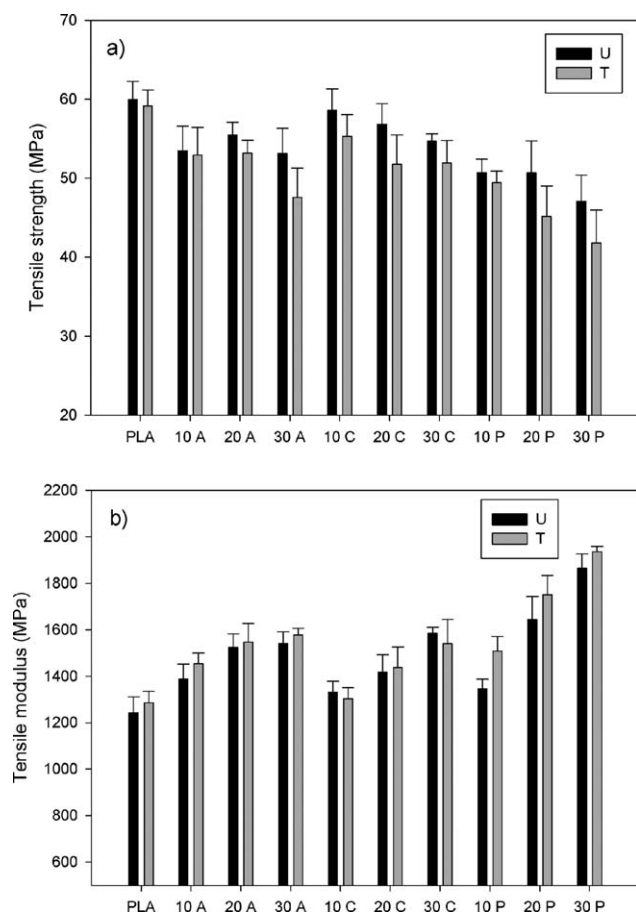


Figure 7. Tensile properties before (U) and after (T) thermal annealing: (a) strength and (b) modulus.

decreased with increasing fiber content. In most cases where tensile strength decreases with increasing fiber content, this is an indication of limited adhesion between the fibers and the matrix, leading to low interfacial stress transfer.³² The tensile strength of neat PLA (60 MPa) decreased to 53, 55, and 47 MPa for agave, coir, and pine (30% fiber), respectively. For biocomposites with coir and pine, the tensile strength decreased with fiber content, while for agave biocomposites, a maximum value of 55 MPa at 20% of fiber was obtained. As observed in Figure 7(a), the highest tensile strength values were obtained for coir biocomposites with 10% of fiber (59 MPa). Haque *et al.*³³ prepared PP–palm and PP–coir biocomposites and found that coir biocomposites presented higher tensile strength than palm biocomposites. This behavior was related to the lower cellulose and higher lignin contents in coir. As a result of higher lignin content, the fibers are more resilient and stronger.²⁹ The results after annealing show that the treatment decreased the tensile strength of all the samples. As reported in Table II, annealing of the biocomposites increased crystallinity and brittleness of the PLA, and these changes affect the tensile properties.³⁴ The tensile modulus results [Figure 7(b)] show that this property increased with fiber content: from 1242 MPa for neat PLA to 1540, 1585, and 1865 MPa for agave, coir, and pine biocomposites (30% fiber), respectively. This increase was expected because of the higher modulus of cellulosic fibers compared to

PLA. Annealing did not have an effect on the tensile modulus of neat PLA or on the agave or coir biocomposites, where the tensile modulus values remained in the same range for untreated and treated samples: around 1200 MPa for neat PLA and 1300, 1400, and 1500 for 10, 20, and 30% of agave or coir fiber content. For PLA–pine biocomposites, a small increase was observed from 1350, 1650, and 1865 MPa to 1500, 1750, and 1935 MPa for 10, 20, and 30% of fiber content, respectively.

CONCLUSIONS

In this work, PLA biocomposites were produced using different fiber types (agave, coir, and pine) and content (10, 20, and 30 wt %). The materials were produced via extrusion and injection molding. In particular, annealing (105 °C for 1 h) was applied to determine the effect of a thermal treatment on the mechanical behavior of these biocomposites. Based on the results obtained, several conclusions can be made.

First, the morphology was studied via SEM images, which showed that interfacial contact between PLA and the reinforcements (agave, coir, or pine) was good without any coupling agent (no voids at the interface). Nevertheless, the tensile and flexural strengths decreased with increasing fiber content, which is an indication of limited fiber–matrix adhesion.

Second, the DSC analysis showed that PLA crystallinity was decreased when fibers were added. Thermal annealing on neat PLA and PLA–fiber biocomposites (for all the fibers used) increased the crystallinity of the materials, achieving increases up to 10% for PLA–pine biocomposites. The DMTA results showed that the addition of agave, coir, or pine fibers improved the dynamic modulus of neat PLA, and annealing can substantially increase the maximum use temperature of these materials.

Finally, the mechanical characterization showed that chemical composition and fiber dimensions are important parameters for the mechanical behavior. In our case, longer fibers such as coir and agave produced biocomposites with higher impact strength compared to neat PLA. But higher wax contents like in pine fibers produced biocomposites with lower tensile and flexural strength. Annealing also increased the impact strength and flexural modulus of neat PLA and all the biocomposites.

ACKNOWLEDGMENTS

One of the authors (A.A.P.F.) acknowledges the financial support of the Mexican National Council for Science and Technology (CONACyT #266256) for a scholarship. Technical help from Yann Giroux and Erick Cisneros was highly appreciated.

REFERENCES

- Gwon, J. G.; Lee, S. Y.; Chun, S. J.; Doh, G. H.; Kim, J. H. *Korean. J. Chem. Eng.* **2010**, *27*, 651.
- Faruk, O.; Bledzki, A. K.; Fink, H. P.; Sain, M. *Prog. Polym. Sci.* **2012**, *37*, 1552.
- Armentano, I.; Bitinis, N.; Fortunati, E.; Mattioli, S.; Rescignano, N.; Verdejo, R.; Lopez-Manchado, M. A.; Kenny, J. M. *Prog. Polym. Sci.* **2013**, *38*, 1720.

4. Bhatt, R.; Shah, D.; Patel, K. C.; Trivedi, U. *Bioresour. Technol.* **2008**, *99*, 4615.
5. Faludi, G.; Dora, G.; Renner, K.; Móczó, J.; Pukánszky, B. *Compos. Sci. Technol.* **2013**, *89*, 77.
6. Loureiro, N. C.; Esteves, J. L.; Viana, J. C.; Ghosh, S. *Composites Part B* **2014**, *60*, 603.
7. Porras, A.; Maranon, A. *Composites Part B* **2012**, *43*, 2782.
8. Arrieta, M. P.; López, J.; Rayón, E.; Jiménez, A. *Polym. Degrad. Stabil.* **2014**, *108*, 307.
9. Teymoorzadeh, H.; Rodrigue, D. J. *Renew. Mater.* **2014**, *2*, 270.
10. Bajpai, P. K.; Singh, I.; Madaan, J. *Wear* **2013**, *297*, 829.
11. Huda, M. S.; Mohanty, A. K.; Drzal, L. T.; Schut, E. J. *Mater. Sci.* **2005**, *40*, 4221.
12. Bledzki, A. K.; Jaszkievicz, A. *Compos. Sci. Technol.* **2010**, *70*, 1687.
13. Csizmadia, R.; Faludi, G.; Renner, K.; Móczó, J.; Pukánszky, B. *Composites Part A* **2013**, *53*, 46.
14. Awal, A.; Rana, M.; Sain, M. *Mech. Mater.* **2015**, *80*, 87.
15. Baheti, V.; Militky, J.; Marsalkova, M. *Polym. Compos.* **2013**, *34*, 2133.
16. Lim, J. S.; Park, K.; Chung, G. S.; Kim, J. H. *Mater. Sci. Eng. C* **2013**, *33*, 2131.
17. Mofokeng, J. P.; Luyt, A. S.; Tabi, T.; Kovacs, J. J. *Thermoplast. Compos. Mater.* **2011**, *25*, 927.
18. Mathew, A. P.; Oksman, K.; Sain, M. *J. Appl. Polym. Sci.* **2006**, *101*, 300.
19. Pantani, R.; Sorrentino, A. *Polym. Degrad. Stabil.* **2013**, *98*, 1089.
20. Baghaei, B.; Skrifvars, M.; Berglin, L. *Compos. Part A* **2013**, *50*, 93.
21. Teymoorzadeh, H.; Rodrigue, D. J. *Biobased Mater. Bioenergy* **2015**, *9*, 1.
22. Arias, A.; Heuzey, M. C.; Huneault, M. A. *Cellulose* **2013**, *20*, 439.
23. Dong, Y.; Ghataura, A.; Takagi, H.; Haroosh, H.; Nakagaito, A.; Lau, K. T. *Composites Part A* **2014**, *63*, 76.
24. Way, C.; Wu, D. Y.; Cram, D. J. *Polym. Environ.* **2013**, *21*, 54.
25. Bledzki, A. K.; Gassan, J. *Prog. Polym. Sci.* **1999**, *24*, 221.
26. Tokoro, R.; Vu, D. M.; Okubo, K.; Tanaka, T.; Fujii, T.; Fujiura, T. *J. Mater. Sci.* **2008**, *43*, 775.
27. Perego, G.; Cella, G. D.; Bastlo, C. J. *Appl. Polym. Sci.* **1996**, *59*, 37.
28. Kim, K. W.; Lee, B. H.; Kim, H. J.; Sriroth, K.; Dorgan, J. R. *J. Therm. Anal. Calorim.* **2012**, *108*, 1131.
29. Mohanty, A. K.; Misra, M.; Drzal, L. T.; Selke, S. E.; Harte, B. R.; Hinrichsen, G. In *Natural Fibers, Biopolymers, and Biocomposites*; Mohanty, A.; Misra, M.; Drzal, L.; Eds.; Taylor & Francis: Boca Raton, FL, **2005**; Chapter 1, pp 16–51.
30. Pérez-Fonseca, A. A.; Robledo-Ortíz, J. R.; Ramirez-Arreola, D. E.; Ortega-Gudiño, P.; Rodrigue, D.; González-Núñez, R. *Mater. Design* **2014**, *64*, 35.
31. Csikos, A.; Faludi, G.; Domján, A.; Renner, K.; Móczó, J.; Pukánszky, B. *Eur. Polym. J.* **2015**, *68*, 592.
32. Oksman, K.; Skrifvars, M.; Selin, J. F. *Compos. Sci. Technol.* **2003**, *63*, 1317.
33. Haque, M.; Hasan, M.; Islam, S.; Ali, E. *Bioresour. Technol.* **2009**, *100*, 4903.
34. Ma, H.; Jo, C. W. *J. Compos. Mater.* **2010**, *45*, 1451.

SGML and CITI Use Only
DO NOT PRINT

