

Mechanical and Thermal Characterization of Compression Moulded Polylactic Acid Natural Fiber Composites Reinforced with Hemp and Lyocell Fibers

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ABSTRACT: This research evaluates the effects of PLA/PP blend ratio and Lyocell/hemp mixture ratio on the morphology, water absorption, mechanical and thermal properties of PLA-based composites. The composites were fabricated with 30 mass % hemp using compression moulding. As a reference composites made from PP were also studied. Combining of hemp and Lyocell in PLA composite leads to the reduction of moisture absorption and can improve the impact, tensile, flexural properties when compared with PLA/hemp. Composite based on the PLA/PP blend-matrix could not improve the tensile and flexural properties compared with PLA/hemp, however; the lighter composite with better impact properties was obtained. The crystallization temperature of the PLA-PP/hemp increased compared with pure PLA. This result was also confirmed by the SEM micrographs. The moisture absorption of PLA-PP/hemp was higher than PLA/hemp. Based on theoretical analysis of DMTA data, there was favorable adhesion in all composites. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40534.

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INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable polymer produced from lactic acid, which is made by fermentation of carbohydrate sources, such as corn. It is considered as one of the most promising biomedical and packing materials with a broad market prospect.¹ Many of the PLA properties are compared to those polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) (such as stiffness, tensile strength, and gas permeability), turning PLA into a potential substitutes to petroleum-based products.² However, to date the use of PLA in the engineering field is limited due to hydrophobicity, brittleness, low impact resistance, high cost as well as to sensitivity to the temperature. To enhance the thermal stability and mechanical properties of PLA, chemical modification, physical blending with some polymers such as poly(glycolic acid), poly(hydroxyalkanoates), and poly(caprolactone), and using natural fiber reinforcements can be done.^{1,3,4}

Several researches on PLA blends with other polymers have been carried out in order to modify the properties for PLA^{5–10} or to reduce the cost.^{11,12} Because PLA is biodegradable, blending of PLA with nonbiodegradable polymers, such as PP, HDPE, LDPE, PS, and PET can improve the resistance of PLA to

hydrolysis, also the degradability of conventional polymers can be improved by blending with PLA.^{13,14} PLA and PP are two quite different candidate matrix materials with different advantages, where PLA is a renewable biopolymer, and PP is a more hydrophobic low-cost commodity thermoplastic and has high toughness, and low density.^{15,16} In addition, PLA and PP have similar processing temperatures (200–230°C).¹⁷ A brief attempt has been made to blend and produce products such as fibers from PLA and PP.^{14,18} However, there are limited numbers of studies on the mechanical properties of the composites produced from PLA/PP blend.¹⁹

Low weight, low cost, recyclability, and biodegradability are advantages of natural fibers compared to synthetic compounds.^{20,21} These are also renewable and have relatively high strength and stiffness. The reinforcement of PLA with lignocellulosic fibers seems to be a viable alternative to increase their mechanical performance and to preserve the environmentally friendly character of the outcome.²²

Hemp fibers can be considered an appropriate choice for reinforcing polymer composites due to their high stiffness, strength, and aspect ratio.²³ They also have an extremely high fiber yield per unit density, and they are disease and pest-resistant,

Table I. Tenacity, Modulus, Elongation, and Linear Density for Hemp and Lyocell Fibers Before and After Heat Treatment

Treatment	Fibre	Tenacity (cN/dtex)	E-modulus (cN/dtex)	Elongation (%)	Linear density (dtex)
As received	Hemp	4.66 (1.43)	97.71 (24.92)	3.93 (0.66)	4.15
	Lyocell	3.27 (0.63)	55.87 (23.06)	8.70 (2.01)	1.36
After hot pressing	Hemp	3.75 (1.10)	84.62 (26.60)	3.37 (0.88)	4.27
	Lyocell	2.12 (0.92)	48.46 (20.29)	4.75 (1.84)	1.38

enabling production methods with a low impact on the environment.²⁴ There are already some studies aimed at optimizing hemp-fibers-reinforced PLA composites. Researchers have investigated the effects of different manufacturing processes, fiber pre-treatments, fiber loading and fiber orientation on PLA/hemp composites.^{25,26} It was found that PLA/hemp composites mostly have good stiffness and tensile characteristics. However, the impact properties are often worse than those of the pure matrix, which is typical for a natural fiber-reinforced PLA composite. Bax et al.²⁷ investigated PLA/flax composites and observed that the impact strength increased with increased flax fiber content, but the impact strength of the composites was clearly lower than that of the pure PLA sample. Oksman et al.²⁸ studied the Charpy impact behavior of PLA/flax composites (40 wt % fiber), it was found that the composite impact strength decreased by >25% compared to pure PLA. This effect was also observed by Müssig.²⁹ He investigated the mechanical properties of hemp fiber (40 wt %) reinforced PLA. The impact strength was halved compared with pure PLA.

In contrast with bast fibers (like hemp fibers) with an elongation at break of approximately 5%,¹⁷ man-made cellulose fibers have a higher elongation at break (>8–10%).³⁰ Because of the high elongation at break for the regenerated cellulose fibers such as Rayon, Cupro or Lyocell, compared to the elongation at break for the matrix, composites with high impact strength values can be created. Lyocell fibers are known to have good mechanical properties, wettability, high tenacity, and good drapability as well as being environmentally friendliness. Therefore, they have potential applications as reinforcements for composites and can improve mechanical and physical properties.³¹

In the context of this study, the mechanical characteristics of composites in terms of the reinforcing fiber and matrix characteristics were examined. Composites of PLA and hemp fibers, PLA and hemp-Lyocell fiber mixtures, a PLA/PP blend and hemp fibers, PLA and Lyocell fibers as well as PP and hemp were investigated. The aim was to manufacture several composites based on two different kinds of reinforcing fiber and two different matrices to investigate the characteristics of the composites related to the fiber and matrix used. Different constituents can be used to tailor the composite characteristics for diverse requirements, for instance the high stiffness of the hemp fibers with the high elongation at break and resin wetting and tenacity of the Lyocell fibers also, by combining the good mechanical properties of PLA, including stiffness and strength with the positive characteristics of polypropylene, including high toughness and being cheap polymer.

MATERIALS AND METHODS

Materials

The PLA staple fibers, provided by Trevira GmbH (Hattersheim, Germany), had a fineness of 1.7 dtex and a mean fiber length of 38 mm. Based on the manufacture's information, the PLA fibers were made from PLA Polymer 6202D from NatureWorks®, Cargill Dow LLC (Minnetonka, USA). It had a density of 1.24 g cm⁻³, a melt temperature of 160–170°C, a glass transition temperature of 60–65°C, 98% L-lactide, and a molecular weight of 97,000. The hemp, in the form of baled loose staple fibers (genus species *Cannabis Sativa L*) was supplied by Hemptage AG (Adelsdorf, Germany). According to the manufacture's info, the average diameter of the hemp fiber was 20–40 μm and had a mean fiber length of 30 mm. The Lyocell staple fibers were supplied by Lenzing AG (Lenzing, Austria). The average length and diameter of the fibers were 38 mm and 13.4 μm, respectively. The PP fibers were supplied by FiberVisions (Varde, Denmark) and had a fineness of 3.3 dtex and a mean fiber length of 66 mm.

Single Fiber Tensile Test. The hemp and Lyocell fibers were tested on a Favigraph single-fiber tensile tester from Textechno GmbH (Mönchengladbach, Germany) equipped with a 20-cN load cell and with gauge length of 20 mm. The test speed was 20 mm min⁻¹ and the averages from 20 tests are reported in Table I. To evaluate the effect of the composite processing conditions on the hemp and Lyocell characteristics, single fibers were treated in a hot press machine at 190°C and 1.7 MPa for 15 min, identical to the conditions used for the fabrication of the composites, and then tested for tensile properties.

Table I summarizes the measured properties of the hemp and Lyocell fibers used in this investigation.

Methods

Preparation of Prepreg and Composites. Five prepreg mats with different fiber compositions were prepared:

- 70 mass % PLA + 30 mass % hemp
- 70 mass % PLA + 30 mass % Lyocell
- 70 mass % PLA + 15 mass % hemp + 15 mass % Lyocell
- 35 mass % PLA + 35 mass % PP + 30 mass % hemp
- 70 mass % PP + 30 mass % hemp

The needed amount of PLA, PP, Lyocell and the hemp staple fibers were first weighed in their loose form and then they were manually mixed, and fed to a carding machine from Mesdan S.P.A (Bresciana, Italy). During carding, the longer PLA and PP fibers supported the shorter hemp and Lyocell fibers and

provided the fiber-to-fiber cohesion which resulted in a web suitable for further processing. The blended fiber web was carded three times to parallelize the fibers and to achieve mat uniformity.

The obtained prepreg mats were dried in a vacuum chamber (0.9 mbar; 70°C) for at least 18 h before compression molding. After drying the mats were stored under dry conditions. The prepreg was covered by a Teflon sheet to prevent sticking of the matrix to the surface of the mould before it was placed into a preheated steel mould with a $20 \times 20 \text{ cm}^2$ cavity and 10-mm depth. The steel mould was of own design, and machined by a local machine shop. The mould was then placed in a hydraulic compression-molding machine from Rondol Technology (Staffordshire, UK). Compression molding was done at a temperature of 195°C and a pressure of 1.7 MPa for 20 min. Neat PLA sheets, to be used as reference material, were made by melting PLA fibers under the same processing conditions.

Test Methods. The specimens were stored at ambient conditions after processing. Then, before testing, the specimens were conditioned for at least 24 h at 23°C and 50% relative humidity according to DIN EN ISO 291. The test specimens were cut by laser according to the standard dimensions, given below.

Composite density and porosity. The densities of the composites were determined by the buoyancy method (Archimedes' principle), using ethanol as the displacement medium. Before the specimens were immersed in ethanol, they had been covered by a varnish containing paraffin to avoid absorption during immersion. The fiber volume fraction was calculated from the fiber weight fraction with allowance for porosity using the method proposed by Madsen et al.³²

Water absorption test. Water absorption analysis was done on composite specimens according to ASTM D570-98. The specimen dimension was $\sim 36 \times 10 \text{ mm}^2$. The specimens were first dried in an oven for 24 h at 60°C, and then put in a desiccator in order to cool down to room temperature. The measured weights of these specimens were denoted as W_0 . The specimens were then immersed in two different baths, one of distilled water at room temperature and one of hot water at 80°C. The amount of water absorbed was measured every 24 h for 10 days. At each measuring point the specimen was removed from the bath, and the surface was wiped dry and the weight was recorded as W . The percentage of apparent weight gain (W_G) was calculated using eq. (1).

$$W_G = [(W - W_0) / W_0] \times 100\% \quad (1)$$

Tensile test. The tensile testing was done according to ISO 527 in a universal H10KT testing machine equipped with a mechanical extensometer (model 100R long travel extensometer), attached to the central part of the specimen by clips. The testing parameters were a loading rate of 10 mm min^{-1} and a loading range of 1 kN. The average tensile values were collected from six separate measurements. The testing machine and the extensometer were supplied by Tinius Olsen (Salford, UK).

Dynamic mechanical thermal analysis. The viscoelastic properties of the specimens were measured using a dynamic mechanical analyser (DMTA Q-series TA instrument supplied by Waters

LLC, Newcastle, DE). Rectangular specimens with the dimensions $50 \text{ mm} \times 8 \text{ mm}$ and 1–2 mm thickness were used using the dual cantilever method. The measurements were performed at a frequency of 1 Hz and amplitude of $15 \mu\text{m}$. The temperature range was from 30 to 150°C at a scanning rate of 3°C min^{-1} . The storage modulus (E') and loss factor ($\tan \delta$) of the specimens were measured as a function of temperature.

Flexural testing. The flexural test was performed using the same testing machine as for tensile testing according to ISO 14125 standard test method for fiber-reinforced plastic composites. At least five specimens were assessed for each batch of samples. The loading rate was 10 mm min^{-1} and the load range was 1 kN. The specimen dimension was $80 \times 15 \text{ mm}^2$ (length \times width), and the thickness varied depending on the sample. The outer span was 64 mm and the range of displacement was 20 mm. At least five specimens were assessed for each sample reported the average values.

Impact testing. The Charpy impact strength of the composites was tested according to ISO 179. A pendulum type Zwick test instrument from Zwick GmbH (Ulm, Germany) was used to measure the unnotched, rectangular specimens ($80 \text{ mm} \times 10 \text{ mm} \times 1\text{--}2 \text{ mm}$). For each material, ten specimens were tested edgewise.

Differential scanning calorimetry. The DSC analysis was done on a DSC Q2000 supplied by TA Instruments, New Castle, DE. Samples of $\sim 10 \text{ mg}$ were heated at a rate of $10^\circ\text{C min}^{-1}$ in a nitrogen-purge stream from 20 to 200°C, then cooled to 0°C, and heated again from 20 to 200°C. The data from the first scan were used. For each sample, three replicates were scanned in order to get average values. The percentage crystallinity (X_{DSC}) of PLA and PP was calculated using eq. (2)³³:

$$X_{\text{DSC}} \% = \frac{\Delta H_f - \Delta H_{\text{cc}}}{\Delta H_f^0} \times \frac{100}{w} \quad (2)$$

where $\Delta H_f^0 = 93 \text{ J g}^{-1}$ for 100% crystalline PLA and 209 J g^{-1} for 100% crystalline PP ΔH_f is the enthalpy of melting, ΔH_{cc} is the cold crystallization enthalpy, and w is the weight fraction of PLA in the composite.

Scanning electron microscopy (SEM). Composite fracture surface morphologies were studied using low-vacuum scanning-electron microscopy, a JEOL JSM 6610LV instrument, JEOL (Tokyo, Japan) with an operating voltage of 5–10 kV. For low vacuum imaging, no specific preparation was required.

RESULTS AND DISCUSSION

Single Fiber Tensile Test

To evaluate the effect of the high temperature compression molding conditions, the tensile properties of heat treated hemp and Lyocell staple single fibers were determined and compared to untreated single fibers, see Table I. Heat treatments greatly reduce the mechanical properties. Cellulosic fibers are mixtures of organic materials (cellulose, hemicellulose, and lignin) and heat treatment at elevated temperatures can cause physical and chemical changes. The physical changes are associated with enthalpy, weight, color, strength, crystallinity, and orientation of microfibril angle.³⁴ The chemical changes are related to the

Table II. Composition of the Fabricated Composites Calculated from the Density Measurements

Sample	Density (g cm ⁻³)	Fibre mass fraction (%)		Fibre volume fraction (%)	Matrix volume fraction (%)	Porosity volume fraction (%)
		Hemp	Lyocell			
PLA	1.2490 (0.0002)	-	-	0.0	100.0	-
PLA/hemp	1.0914 (0.0154)	30.0	-	23.0 (0.6)	61.2 (0.9)	10.8 (0.2)
PLA/Lyocell	1.2765 (0.0112)	-	30	25.2 (0.2)	71.5 (0.6)	3.3 (0.9)
PLA/hemp-Lyocell	1.1222 (0.0169)	15.0	15.0	22.4 (0.3)	76.4 (1.2)	2.1 (0.1)
PLA-PP/hemp	1.0171 (0.0402)	30	-	20.6 (0.8)	65.9 (12.6)	11.9 (3.5)
PP/hemp	0.8758 (0.0154)	30	-	17.8 (0.4)	67.4 (1.4)	14.9 (1.8)
PP	0.9103 (0.0019)	-	-	0.0	100.0	-

Note: Data in the brackets are mean (SD).

decomposition of the molecular structure. Heat treatment results in the weight loss of moisture plus weight loss due to thermal degradation. The thermal degradation of cellulosic fibers results in change in color and deterioration in mechanical properties of the fibers.^{35,36}

Influence of Different Natural Fibers

In this study, five different composites were produced by compression molding of prepregs containing 30 mass % reinforcement (hemp respective Lyocell) and 70 mass % matrix, (PP respective PLA). The physical characteristics of the composites made are summarized in Table II. The porosity ranged from 2.1 to 14.9 vol %, and the higher porosity was seen for the PP/hemp and PLA-PP/hemp composites. The porosity fraction is rather high even if the fiber volume fraction was as low as 30 mass %, and this could be due to several factors. The complexity of the surface chemistry and the irregularity of the morphology of plant fibers is one of the most important considerations as well as to the presence of luminal cavities.³² It can be observed that the Lyocell-based composite had the lower void content which is obviously due to the higher interfacial adhesion.

Water Absorption Characteristics

Figure 1 shows the apparent weight gain (W_G) as a function of the immersion time at different temperatures for the manufactured composites. In Figure 1(a), it can be seen that for all the composites investigated, W_G increases monotonically with time. This increase in W_G is consistent with other studies of natural fiber composites.^{37–39} The absence of the induction period characterized by zero weight gain at the initial stage of water immersion treatment, could be explained by the different material packing between the skin and core regions, which indicates that the hemp and Lyocell fibres were uniformly dispersed in the PLA and PP matrix.¹⁶

It can also be seen that the slopes of the W_G vs. time plots were steeper for all composites compared with the slopes for neat PP and PLA. It can be observed that the composites exhibited significantly higher water absorption than for neat PLA and PP due to the hydrophilic nature of Lyocell and hemp because of the presence of polar groups such as —OH and —COOH in the fibers. These results are in accordance with published data

showing that the lignocellulosic fibres displayed a higher tendency to absorb water than does the PLA and PP.^{39–41} Among all composites in this study, PLA/Lyocell and PLA/hemp-Lyocell showed the lowest water absorptions (up to 6.7 and 10.3 wt %, respectively), which may be due to their lower porosity and also better interfacial adhesion which decreases the thickness of the interphase area between the fibers and the matrix, thus decreasing the water absorption through the interphase and further into inner parts of the structure.^{42,43} From the results, it can be

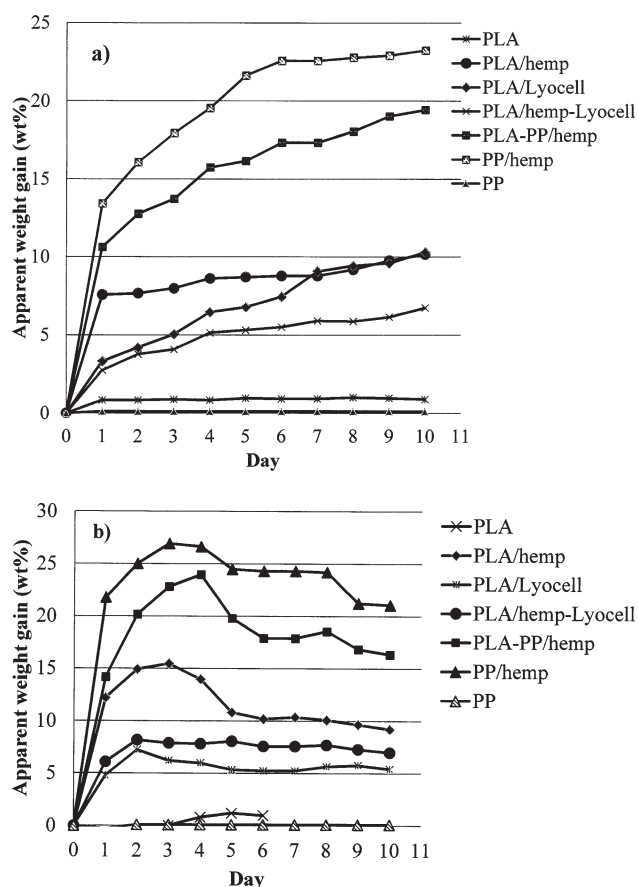


Figure 1. Apparent weight gain against time for the manufactured composites at: (a) room temperature and (b) 80°C.

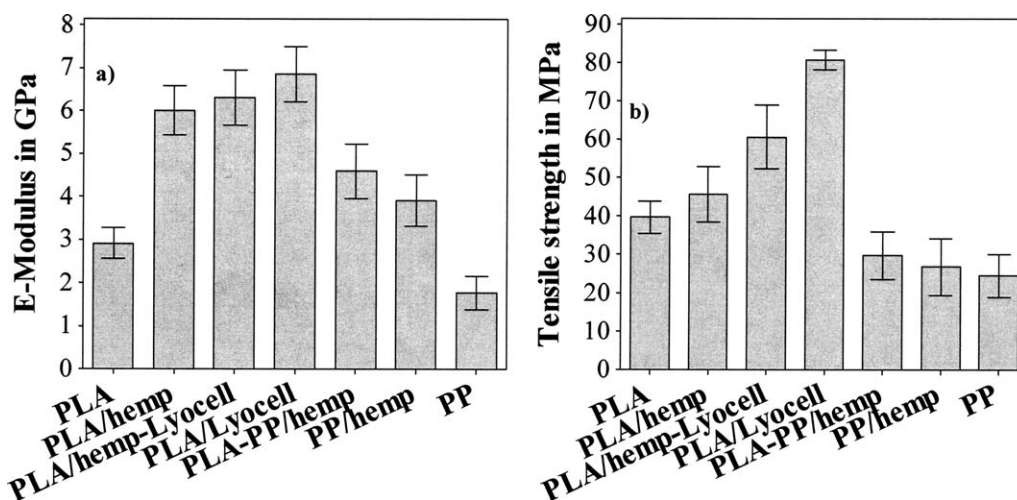


Figure 2. Tensile properties of the manufactured composites: (a) tensile modulus, and (b) tensile strength.

concluded that the PP/hemp had higher moisture absorption compared with PLA/hemp. It could be explained by the lower interfacial compatibility between hemp fiber and PP matrix, which can result in incomplete wetting resulting in microcracks, offering channels for better moisture transport.⁴⁴ The PLA-PP/hemp composite showed higher moisture absorption than PLA-hemp composite.

As shown in Figure 1(b), after 5 days at 80°C, the neat PLA sample was very soft and it was difficult to decant water and rinse the sample without losing some material. The experiment for neat PLA was therefore discontinued after 5 days. Furthermore, it can be seen that the water immersion temperature influences the water absorption curves. Increasing the immersion temperature from room temperature to 80°C increased the water absorption of the neat PLA and composites, as well as shortened the saturation time. The immersion temperature affected PLA/hemp-Lyocell more than it did for PLA/Lyocell composites. The weight gain was found to decrease after passing through a maximum. For PLA composites, this was due to the formation of a neat resin peel on the surface resulting from degradation and dissolving with time together with the removal of some substances from the hemp and Lyocell fiber during the immersion.^{45–47} In contrast, even though the apparent weight gain for the PP composite also decreased after passing through a maximum, the PP dissolution did not take place. In fact, it has been reported that the PP is very resistant to moisture attack within even at elevated temperature.^{37,39,46} It is of interest to understand the mechanisms that cause the decrease in weight gain. The hemp fibers are responsible for the weight loss observed, which is due to the removal of certain fractions from the hemp fibers during the water immersion.

Tensile Properties

An overview of the tensile strength and modulus of the composites compared with the values of the neat PLA and PP matrix is given in Figure 2(a,b). Compared with the tensile modulus of the pure PLA matrix [Figure 2(a)], there is an improvement of 138% for PLA/Lyocell, 117% for PLA/hemp-Lyocell, 106% for PLA/hemp and 59% for the PLA-PP/hemp composites. The tensile

modulus have been decreased by the admixture of the PP fibers in the PLA/hemp composite compared with the PLA/hemp composite since the tensile modulus of PP is lower than that of PLA.

As can be seen in Figure 2(b), the tensile strength of PLA composites was significantly higher than the tensile strength of the neat PLA and neat PP matrix, which was 39.7 and 24.6 MPa, respectively. Neat PLA has better mechanical properties than neat PP.²⁸ In the comprehensive outline, the highest tensile strength values were reached by PLA/Lyocell with 80.9 MPa, PLA/hemp-Lyocell with 60.6 MPa, followed by PLA/hemp with 45.7 MPa, PLA-PP/hemp with 29.8 MPa and PP/hemp with 26.9 MPa.

The improvement of the tensile properties of hemp-reinforced PLA composites by addition of Lyocell fibers could be attributed to the lower amount of porosity in the composite and the much higher fineness of the Lyocell fibers, which promote a better fiber–matrix adhesion.

Flexural Properties

The results of the flexural testing are shown in Figure 3(a,b). The flexural modulus of the composites were all higher than for neat PLA and neat PP, which is especially evident for the PLA/Lyocell which had a flexural modulus (5.8 GPa) three times higher than that of neat PLA (1.9 GPa) [Figure 3(a)]. Moreover, the superior flexural properties of the PLA composites with hemp-Lyocell compared with the PLA composites with hemp can be attributed to the better adhesion between Lyocell fibers with PLA matrix as well as lower porosity. It is also obvious from the results that composites made from PLA-PP/hemp showed an evident improvement in flexural modulus across the PP/hemp composite, but lower than that of PLA/hemp composite. As shown in Figure 3(b), the flexural strength showed an increase of 43.5% for the PLA/Lyocell composite and 23.5% for the PLA/hemp-Lyocell composite compared with neat PLA. However, the flexural strengths of the other composites were all lower than of neat PLA.

Impact Resistance

The results of the Charpy impact test are shown in Figure 4. For the neat PLA matrix, an impact strength value of 11.5 kJ m⁻²

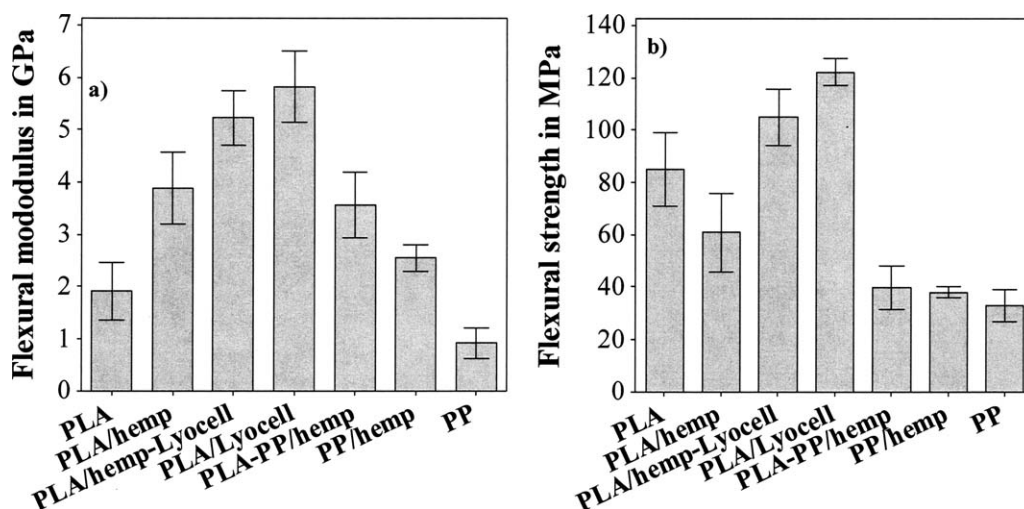


Figure 3. Flexural properties of the composites: (a) flexural modulus, and (b) flexural strength.

was measured. Similar values have also been seen in other studies.^{27,28} A significant reinforcement effect was determined for the PLA/Lyocell composites with an impact value of 26 kJ m^{-2} and for the PLA/hemp-Lyocell composite with an impact value of 21.7 kJ m^{-2} , while the value of the PLA/hemp composites (9.7 kJ m^{-2}) was lower than for the neat PLA matrix. This can be explained by a higher elongation at break of Lyocell compared with hemp fibers resulting in an improvement of the impact strength in the composites.^{48,49} Hence, the highest impact value was reached by PLA/hemp-Lyocell due to the higher elongation characteristics of the Lyocell fibers, while using hemp fibers resulted in a brittle character of the PLA composites. The behavior of the hemp fiber is in accordance with the known behavior of natural fibers under an impact load.

The impact strength of pure PP was around 18.9 kJ m^{-2} . Similar values have also been seen in other studies.^{50,51} However, the impact strength of PP-based composites was lower than that of neat PP. It has been reported that the un-notched impact resistance of thermoplastic natural fibers composites generally show a decreasing trend. The behavior of fiber reinforcement under impact load is more complicated than under bending and tensile load since the impact strength is attributed to the energy consumption during failure, and also attributed to the addition of fibers which probably creates regions of stress concentration which require less energy to initiate a crack.

A mixture of PLA-PP/hemp resulted in a further improvement of the impact strength up to 9.8 kJ m^{-2} compared with PLA/hemp with 8.8 kJ m^{-2} .

Dynamic Mechanical Thermal Testing

Figure 5(a,b) shows the dynamic viscoelastic curves for neat PLA and composites made from PLA. The storage modulus (at 30°C) increased from 2.5 GPa for pure PLA, up to 3.7 GPa for PLA/Lyocell followed by 3.2 GPa for PLA/hemp-Lyocell, 3.1 GPa for PLA/hemp and 2.6 GPa for PLA-PP/hemp composite [Figure 5(a)]. The storage modulus increased when hemp and Lyocell fibers were introduced into PLA. The increase in the stiffness of fiber-containing samples, which reveals effective

stress transfer from the fiber to the matrix at the interface, can be interpreted as good adhesion between the fibers and the matrices.^{1,52–54} The sharp decrease in the storage modulus (around $57\text{--}61^\circ\text{C}$ for most of the samples) corresponds to the α -relaxation of the amorphous regions in PLA.⁵⁵

The storage modulus started to increase again at temperatures of around $90\text{--}100^\circ\text{C}$, which is a result of the cold crystallization of PLA and this peak shifted to a lower temperatures with the addition of PP. The cold crystallization was also observed in the DSC curves. This result suggested that the incorporation of PP increased the cold-crystallization ability of PLA.⁵⁶

The dampening, or $\tan \delta$, is the ratio between the loss modulus and the storage modulus and provides information about the internal friction of the material and the adhesion of the interface. For a composite, the molecular motion in the interphase will contribute to the dampening. A larger area under the α -relaxation peak in the $\tan \delta$ curves of a polymer indicates that the molecular chains exhibit a higher degree of mobility thus better damping properties.⁵⁷ The area under this peak for PLA-based composites [Figure 5(b)] seems to be smaller compared with neat PLA. A possible explanation is that there is a good interaction between the fiber and the matrix. Adding

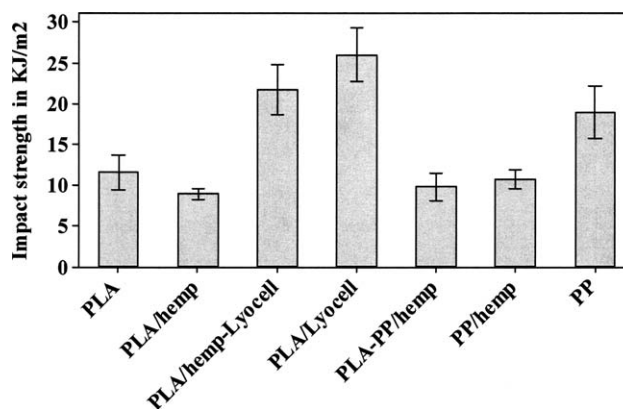


Figure 4. Impact strength of the manufactured composites.

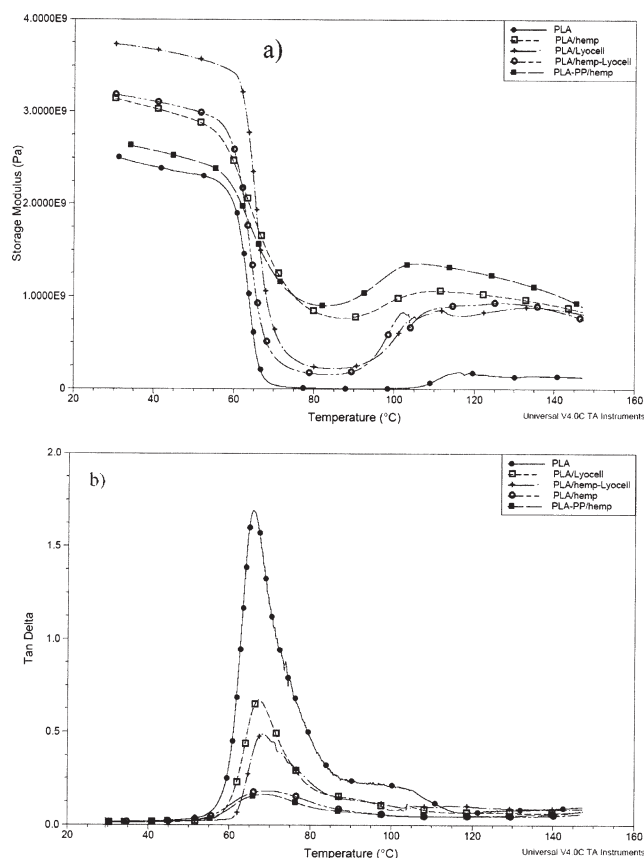


Figure 5. DMTA analysis of PLA and PP reinforced with hemp and Lyocell fibers. (a) Storage modulus vs. temperature; (b) $\tan \delta$ curves.

fibers to the matrix will decrease the mobility of the polymer chains, and consequently reduce the dampening, as reported by Pothan et al.⁵⁸ The glass-transition temperature is often recorded at the maximum of the $\tan \delta$. The recorded T_g of the samples were 65.6°C for pure PLA, 67.5°C for PLA/Lyocell, 68°C for PLA/hemp-Lyocell, 68.8°C for PLA-PP/hemp and 69.7°C for PLA/hemp. It is obvious that incorporating fibers increases the T_g for both PLA and PP. The slight shift in T_g to a higher temperature (by a few degrees) indicates that the mobility of polymer chains is affected. Mathew et al.⁵⁹ discussed that the shift to higher temperature usually indicates restricted movement of molecules because of better interaction between the fiber and the polymer matrix.

The broad transition (between 90 and 110°C) for all the fiber-reinforced PLA relates to the cold crystallization of PLA in this temperature region.

Differential Scanning Calorimetry

To examine the effect of the added fibers on the crystallinity of PLA, DSC analysis was performed. The DSC heating and cooling thermograms for all composites produced are shown in Figure 6(a,b). The glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) obtained from the DSC studies are summarized in Table III. The data indicates that T_g and T_m was slightly affected by the introduction of hemp and Lyocell fibers with a few decrease. Furthermore the T_c decreased

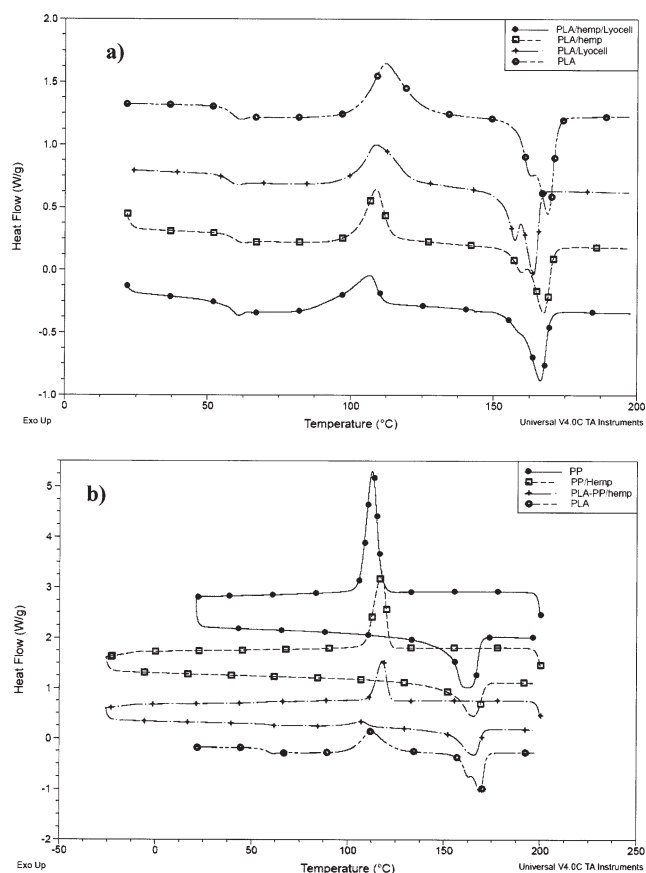


Figure 6. DSC thermograms from the cooling and the second heating run for the fabricated composites.

from 112.1°C of pure PLA to 106.4°C of composite containing hemp-Lyocell fibers. It can be clearly seen that the degree of crystallization increases from 4.6% for neat PLA up to 8.3% for PLA/hemp, 16.9% for PLA/Lyocell and 11.8% for PLA/hemp-Lyocell. It is noteworthy to see that the above increase in the crystallinity of PLA with respect to fiber content is consistent with other studies of natural fiber/PLA composites.^{3,60,61} The double melting peaks suggest that occurrence of the crystal's reorganization during the heating run.^{62–64}

In comparison with PP, the incorporation of hemp fibers shifts the crystallization temperature to the higher temperature. This

Table III. Differential Scanning Calorimetric Data for the Composites from the Cooling and Second Heating Run (10°C min⁻¹)

Sample	X_{DSC} (%)	T_g (°C)	T_c (°C)	T_m (°C)
PLA	4.6	59.2	112.1	167.4
PLA/hemp	8.3	59.4	108.6	166.8
PLA/Lyocell	16.9	57.6	108.7	166.7
PLA/hemp-Lyocell	11.8	57.5	106.4	166.3
PLA-PP/hemp	5.3	58.8	117.9	166.5
PP/hemp	1.4	–	117.3	164.4
PP	0.6	–	112.5	166.6

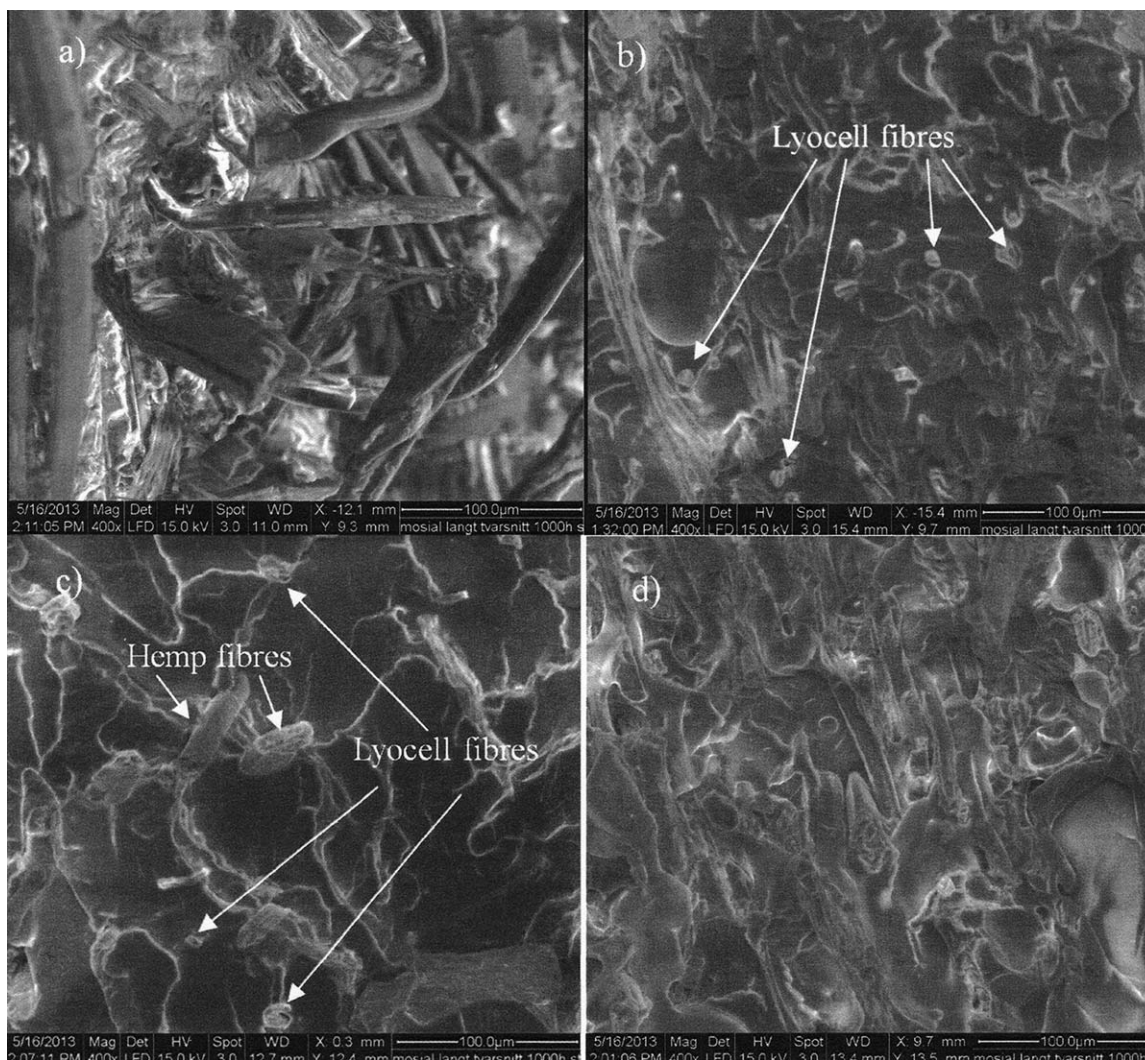


Figure 7. SEM images of tensile fracture surfaces of (a) PLA/hemp, (b) PLA/Lyocell, (c) PLA/hemp-Lyocell, and (d) PLA-PP/hemp composites.

increase suggests that hemp fibers possibly act as heterogeneous nucleating agents causing the PP to crystallize at higher temperature.⁶⁵ As evident from the crystallization thermogram T_c [Figure 6(b)], the incorporation of PP within the PLA matrix increased T_c of the PLA from 112 to 117.9°C. Moreover, the crystallinity of the PLA in its blend with PP slightly increased.

Scanning Electron Microscopy Analysis

Figure 7 shows the SEM micrographs of the fracture surface for tensile specimens for different composites. Compared to PLA/hemp composites [Figure 7(a)], less pulled-out fibers and corresponding holes are visible for the PLA/Lyocell-hemp and PLA/Lyocell composites [Figure 7(b,c)]. These observations suggest that the adhesion between the PLA matrix and the Lyocell fiber is quite good. It should be noted that the finer Lyocell fibers were used which lead to the bigger specific surface between fiber and matrix and better adhesion between them.

As shown in Figure 7(d) the PP and PLA polymers do not have the well-defined spherical shapes and the separation of the two components or pores.

CONCLUSIONS

The effects of the choice of matrix and reinforcing filler on the structure and properties of PLA-based composites have been studied, focusing on the water absorption, mechanical and thermo-mechanical properties. Based on the mechanical tests, the obtained results showed that combining hemp and Lyocell in a PLA-based composite can improve significantly the impact strength at ambient temperature, flexural and tensile strength and modulus, compared with hemp fiber reinforced PLA. Moreover, the moisture absorption was reduced by up to 47.4%. From the DMTA results, it is evident that incorporation of the hemp and Lyocell fiber gives a considerable increase in storage modulus and a decrease in $\tan \delta$ values. The study performed using DSC revealed that the melting point of PLA was not affected significantly after reinforcement with the hemp-Lyocell mixture but the glass transition temperature increased a few degrees. The PLA in the composites had high orientation degree and crystallinity which was attributed to effective heterogeneous nucleation induced by hemp and Lyocell fibers, however, the degree of crystallinity of PLA/hemp composite was higher.

Although Lyocell is expensive, it is reproducible by artificial production and the admixture of Lyocell fibers to hemp fibers leads to less quality variation in the fabricated composites.⁴⁸

On the contrary, the combination of PP and PLA had a destructive effect on the mechanical properties. Composites based on the PLA/PP blend-matrix containing hemp had only enhanced impact strength of the composite, compared with the PLA/hemp composite but not the flexural, tensile and damping properties. The crystallization temperature of the hemp-reinforced PLA-PP composites decreased compared with pure PLA indicating that the incorporation of PP improved the cold-crystallization ability of PLA. The changes in the crystal structure and melting points PLA-PP/hemp composite indicate partial compatibility between the two polymers. This result was also confirmed by the SEM micrographs, in which no well-defined spherical shapes and separation of the two polymers were observed. The PLA-PP/hemp composite showed higher water absorption than the PLA/hemp did. In addition to improving the impact properties of PLA, the PLA-PP/composite are lighter, with relatively lower price and can be engineered to have controlled degradability for different applications.

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