

Poly(lactic acid) Hemp Composites Combined with Nano-silica

Izan Roshawaty Mustapa¹, M.N.M.Ansari^{1,2}, Robert A. Shanks¹

¹School of Applied Sciences, RMIT University,
Box 2476 GPO, Melbourne, VIC 3001, Australia.

²Mechanical Engineering, College of Engineering,
Universiti Tenaga Nasional, Malaysia.

ABSTRACT

Poly(lactic acid) (PLA)–hemp composites have been prepared by impregnation of hemp woven fabric with PLA solution. Nano-silica was dispersed in the PLA solution to introduce a matrix reinforcing nano-phase within the composite. The nano-silica can bridge between matrix PLA and hemp fibers, though their contribution to properties combines with the hemp fibers to produce high performance composites derived from natural resources. The thermal stability, morphology and mechanical performance of the composites demonstrated that the biocomposites produced are suitable for structural application where renewable resource and high performance are required.

Keywords: biodegradable, film stacking, nanocomposites, thermal stability, mechanical properties.

1 INTRODUCTION

Poly(lactic acid) (PLA) is a biopolyester prepared from renewable resources and biodegradable. PLA has received much attention due to its synthesis in commercial scale and adaptable properties where fibers, films, moldings and composites have been prepared. PLA has been plasticized, blended with related polymers [1] and used to prepare composites reinforced with natural fibers [2]. PLA composites have been modified to increase the interface between hydrophilic cellulose fibers and relatively hydrophobic PLA and to reduce the variability of properties caused by moisture absorption [3]. Glyceryl triacetate and tributyl citrate are suitable plasticizers, derived from natural resources, that address brittleness of PLA and can replace moisture in cellulose fibers and increasing their compatibility with PLA [4]. An important issue for all composites is reduction of creep. The reinforcing fibers dramatically reduce creep [5], however nano-composites can improve tensile properties and toughness [6].

The aim of this research was to prepare and characterize composites prepared from natural resources consisting of PLA combined with hemp-fiber and including nano-silica reinforcement of the matrix PLA. Objectives include determination of structure and morphology, and measurement of mechanical performance.

2 EXPERIMENTAL

2.1 Materials

Poly (lactic acid) (PLA 2002D, extrusion grade) was purchased in pellet form from Natureworks Co., Minnetonka, USA. Hemp Fibre was purchased from hemp store Auckland, New Zealand. Fumed Silica Cab-O-Sil M5, were purchased from Cabot Corporation USA. Chloroform (purity 99.0-99.4%, lab grade) was obtained from Merck KGaA, Darmstadt, Germany.

2.2 Sample preparation

The nano-silica was dispersed in the matrix PLA phase to enhance properties. Nano-silica particles of 8–12 nm exist as aggregates of about 20 particles fused together during the high temperature furnace nebulation. The silica aggregates then form larger agglomerates that were separated by ultrasonication during dispersion in a PLA solution in chloroform. The sonicated PLA–silica dispersion was added to a woven hemp fiber mat. Three layers of PLA–hemp composites was stack by using film stacking method, solvent was evaporated, then the composites was consolidated by compression molding at 180 °C for 10 min under a load of 2 t.

Table 1: Identification of abbreviations for PLA–hemp composites combined with nanosilica.

Samples	PLA / %·w/w	Silica /%·w/w
PSH0.0	100.0	0.0
PSH2.5	97.5	2.5
PSH7.5	92.5	7.5

2.3 Characterization

Composites were characterized using field-emission scanning electron microscopy (FEI Quanta 200 ESEM), thermogravimetry (Perkin-Elmer Pyris 1 TGA, 30-850 °C at 10 °C·min⁻¹) and Fourier transform infrared spectroscopy (Perkin-Elmer Spectrum 1 FTIR, diffuse reflectance mode) and wide-angle X-ray scattering (Bruker Nanostar). Mechanical properties were determined via modulated-force thermomechanical analysis (Perkin-Elmer DMA 8000, single cantilever bend mode, 1 Hz, 50.0 µm deformation, 30 to +180 °C at 2 °C·min⁻¹).

3 RESULTS AND DISCUSSION

TGA curves for neat PLA and PLA-Hemp composites under nitrogen are shown in Figure 1, and the data are summarized in Table 1. All PLA composites were thermally stable, corresponding with silica loading. This shows that thermal decomposition for PSH0.0 shifted to lower temperature. Silica increased thermal decomposition of composites. Thermal decomposition for PSH2.5 and PSH7.5 shifted significantly to higher temperatures than neat PLA and neat hemp, and decomposition temperature was dependent on silica content. The temperature corresponding to the onset of decomposition (T_{onset}) for a polymer is essential for evaluating its thermal stability and guiding melt processing. Refer to the data in Table 1, T_{onset} for PSH2.5 and PSH7.5 gradually increased as the content of silica increase in the composites. PSH7.5 exhibited highest T_{onset} , which is shifted approximately 15 °C towards higher temperature compared with T_{onset} for neat PLA.

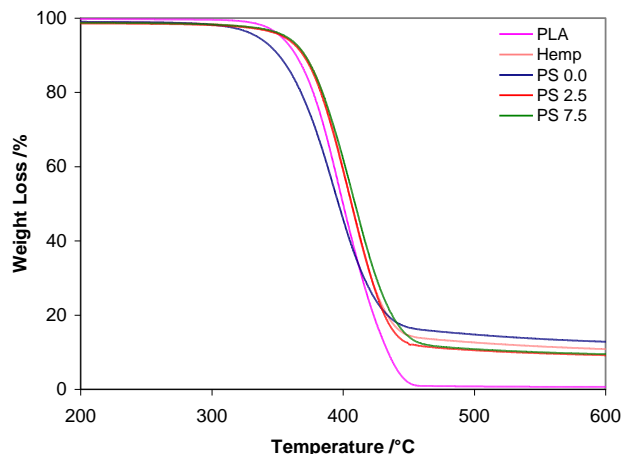


Figure 1. TGA curve of PLA-hemp composites.

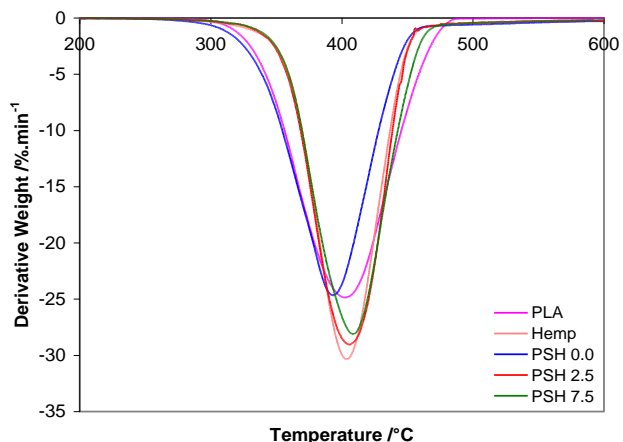


Figure 2. DTG curve of PLA-hemp composites.

The thermal characteristic parameter for a polymer can be investigated with the maximum rate of weight loss (T_{max}), which is defined as the peak temperature of the derivative TGA curve. T_{max} analysed from the derivative curve of PLA-hemp composites are shown in Table 1 and Figure 2.

All curves exhibit a single peak, indicating that thermal degradation of PLA composites occurs in one step. Results show that T_{max} of PSH0.0 decrease then gradually increase for PSH2.5 and PSH7.5 compared with the neat PLA and hemp, indicating better thermal stability for PLA-hemp composite combined with nano-silica. The addition of nano-filler particles in this study, clearly played an important role in the nanocomposites and was responsible for improvement in properties of the PLA matrix.

Table 2: Thermal decomposition of PLA-hemp composites.

Sample	T_{onset} (°C)	T_{max} (°C)	Residue at 700 °C (wt%)
PLA	334.0	406.1	0.5
Hemp	345.6	406.6	9.3
PSH0.0	315.2	395.3	11.6
PSH2.5	350.6	409.4	6.4
PSH7.5	355.5	412.3	6.6

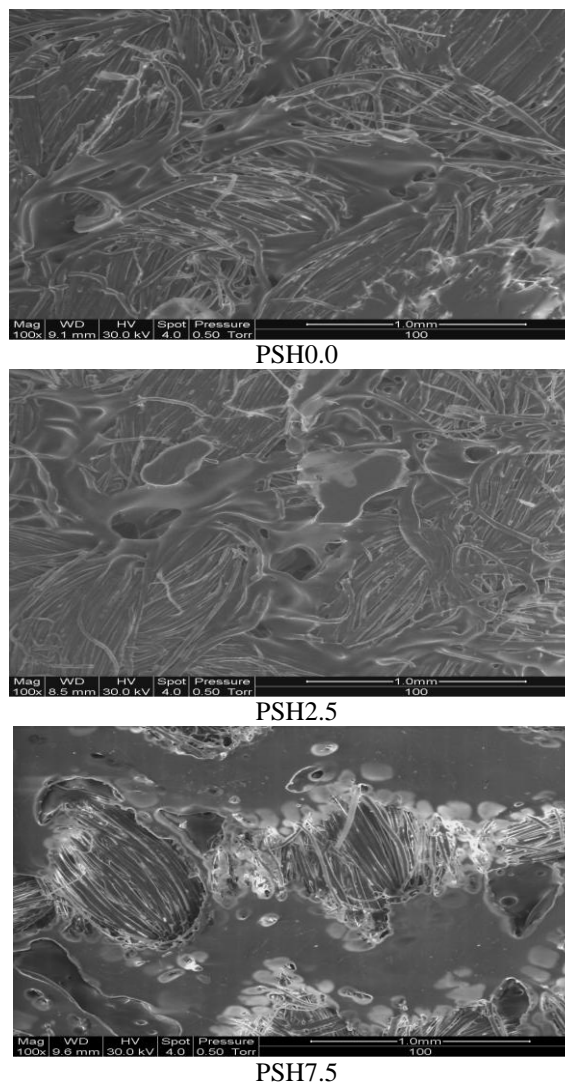


Figure 3. ESEM images of PLA-hemp composites.

Figure 3 represents surface morphology for PLA-hemp composites. Dispersion of nanofillers in a composite will influence on the properties and performances of the composites such as thermal stability and mechanical properties. Refer to Figure 3, PSH0.0 shows a smooth and uniform surface. The dispersion of silica in PSH2.5 and PSH7.5 shows them to be uniformly distributed in the PLA matrix, and this is considered as good dispersion of silica in the composites. The change in fibre orientation of all PLA-hemp composites were studied using X-ray scattering as shown in Figure 4.

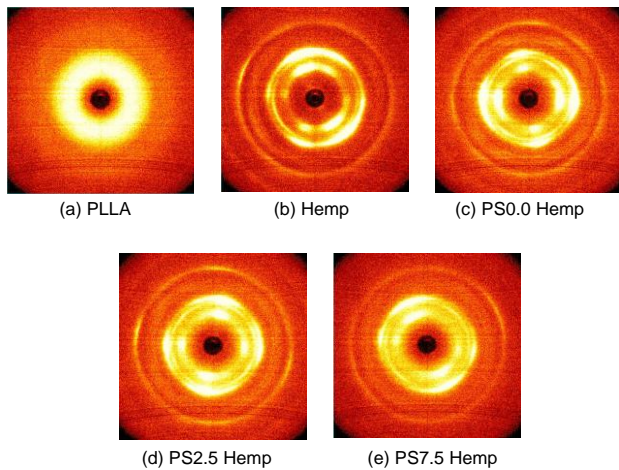


Figure 4. 2D WAXS images of PLA-hemp composites.

PLA shows an amorphous nature. PSH0.0, PSH2.5 and PSH7.5 show the same X-ray crystal diffraction patterns compared with PLA and hemp. The intensity was varied, but still remain the same trend. PSH0.0, PSH2.5 and PSH7.5 show peaks at around $2\theta = 16^\circ$ and $2\theta = 24^\circ$, indicating a crystalline structure. Figure 5 shows the FTIR spectrum for all PLA-hemp composites. FTIR analysis provides important evidence for reaction because it is sensitive and effective for structural characterization.

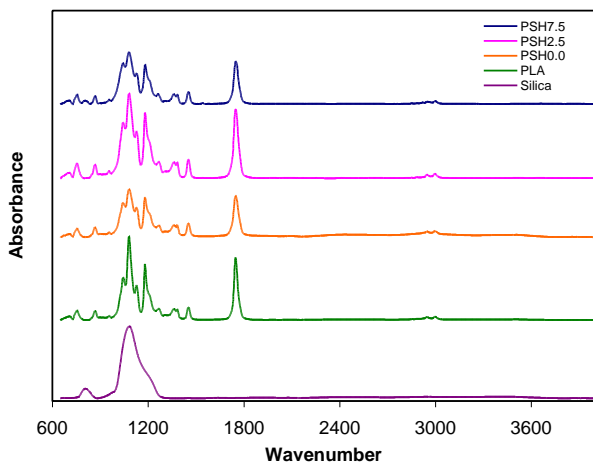


Figure 5. FTIR spectra for PLA-hemp composites.

The band at 1759 cm^{-1} is assigned to stretching vibration of carbonyl group, and the weak band at 1454 cm^{-1} due to the stretching vibration of $-\text{CH}_3$. The bands at 2850 to 2960 cm^{-1} are corresponding to the stretching vibration of CH_2 . These bands are consistent with the characteristic bands of original PLA for samples PSH0.0, PSH2.5 and PSH7.5. There are addition bands for samples PSH7.5, which appear at 804 cm^{-1} , indicating of silica in the composites. However, peaks were not detected for PSH2.5.

Figure 6 shows the dynamic storage modulus for PLA-hemp composites as a function of temperature. The addition of fumed silica in PLA and in combination of hemp had strong influence on the storage modulus. The storage modulus of PLA-hemp composites increased by addition of fumed silica indicating better interfacial bonding between fibers and matrix. The highest modulus is represented by PSH7.5, followed by PSH2.5 and PSH0.0. The storage modulus at 30°C , was increased by 14 % from 1.74 GPa to 1.98 GPa with the addition of 2.5 %·w/w of silica. Further increase in storage modulus up to 19 % was observed with increasing 7.5 %·w/w silica loading.

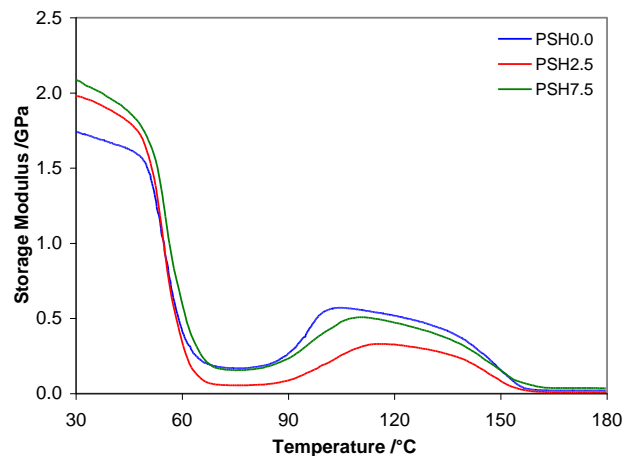


Figure 6. Storage modulus of PLA-hemp composites.

The increase in the storage modulus attributed to the reinforcement effect in the PLA-hemp composites imparted by silica that allow better stress transfer from the PLA matrix to the hemp fibres. These effects are related to the improvement of the thermo-mechanical stability in PLA-hemp composites. The same behaviour also observed in the preparation of PLA and silica with melt blending study [7].

Refer to Figure 6, the storage modulus showed a sharp decrease around 60°C , and then increases at 100°C in agreement with loss modulus for PLA-hemp composites shown in Figure 7. A decreasing trend was observed with the increasing temperature due to softening of polymer. On the other hand, the increase of modulus refers to the cold crystallization of the PLA. The glass transition temperature (T_g) were derived from the loss modulus curves to study the effect of fibre-silica on mobility of polymer chain. The T_g of PLA-hemp composites slightly shift to higher

temperature with addition of silica. As the content of silica increases, the T_g is increase with highest T_g for PSH7.5 at 59.0 °C compared with 57.4 °C for PSH2.5 and 57.0 °C for PSH0.0. Mathew et al. [8] discuss the shift to higher temperature usually indicates restricted molecule movement because of better interaction between the fibre and polymer matrix. Besides, the α -relaxation involves the movement of polymer chains. The present of crystalline structures or reinforcement could also act as a physical crosslink, decrease the mobility of amorphous regions and consequently increase the composite's stiffness.

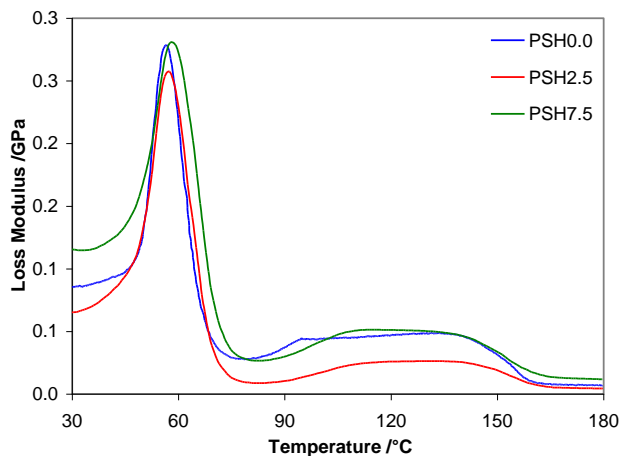


Figure 7. Loss modulus of PLA Hemp composites.

The damping factor or $\tan \delta$ peak intensity is indicate of the number of polymer chains involved in the relation process as shown in Figure 8. The $\tan \delta$ peak for all PLA-hemp composites was observed at 100 °C, in agreement with cold crystallization shown in loss modulus curve in Figure 7.

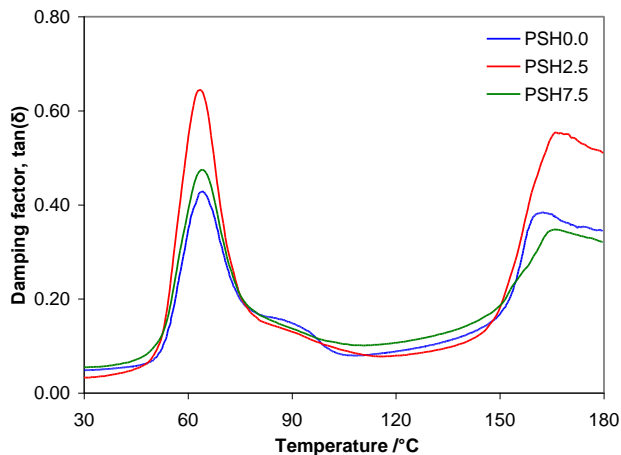


Figure 8. Damping factor of PLA Hemp composites.

The melting peak of PLA-hemp composites were observed in a temperature range 150 to 170 °C. Mechanical properties show a better thermal stability in PLA-hemp composites with addition of silica. PLA is an unique biodegradable polymer with very promising applications,

and this improvement is highly significant. Therefore, film stacking of PLA-silica matrix with hemp fibers can be considered as a possible way to improve the thermal stability of PLA based composites.

4 CONCLUSIONS

PLA-hemp composites of high modulus and strength were prepared, however they exhibited improved properties when combined with silica nano-particles in the matrix. These composites with bi-modal filler size provide traditional composite properties with the advantages of nano-composites combined. The micron-sized fibres have long fibres that are inter-woven facilitating stress transfer from the matrix. Within the PLA matrix the structure has been modified by nano-silica reinforcement resulting in physical crosslinks. The matrix is thus less ductile than a thermoplastic, approaching a thermoset via the physical crosslinks, though with a continued ability to be thermoformed into various shapes. PLA-silica nano-composites were found to enhance the properties of PLA, however inclusion of typical micro-fibers has provided composites with higher volume fraction of fillers than available from nano-fillers alone.

REFERENCES

- [1] L.M.W.K. Gunaratne and R.A. Shanks, Miscibility, melting, and crystallization behavior of poly(hydroxybutyrate) and poly(L-lactic acid) blends, *Polym. Eng. and Sci.*, 48 (2008) pp. 1683-1692.
- [2] S. Wong, R.A. Shanks and A. Hodzic, Effect of additives on the interfacial strength of poly(L-lactic acid) and poly(3-hydroxy butyric acid)-flax fibre composites, *Comp. Sci. and Tech.*, 67 (2007) pp. 2478-2484.
- [3] R.A. Shanks, A. Hodzic, and D. Ridderhof, Composites of poly(lactic acid) with flax fibers modified by interstitial polymerization, *J. Appl. Polym. Sci.*, 99 (2006) pp. 2305-2313.
- [4] S. Wong, R.A. Shanks, A. Hodzic, Poly(L-lactic acid) composites with flax fibers modified by plasticizer absorption, *Polym. Eng. and Sci.*, 43 (2003) pp. 1566-1575.
- [5] S. Wong and R. Shanks, Creep behaviour of biopolymers and modified flax fibre composites, *Composite Interfaces*, 15 (2008) pp. 131-145.
- [6] M.N.M.Ansari, H.Ismail and S.H.S.Zein. (2009) Effect of Multi-walled Carbon Nanotubes on Mechanical Properties of Feldspar Filled Polypropylene Composites. *Journal of Reinforced Plastics and Composites*, Vol. 28, No. 20, pp.2473-2485.
- [7] K. Fukushima, D. Tabuani, C. Abbate, M. Arena, P. Rizzarelli. (2011). Preparation, characterization and biodegradation of biopolymer nanocomposites based on fumed silica. *European Polymer Journal*. 47: 139-152.
- [8] Mathew AP, Oksman K, Sain M. (2005). The effect of morphology and chemical characteristics of cellulose reinforcement on the crystallinity of polylactic acid. *J Appl Polym Sci*. 101:300-310.