

## Reinforcing Mechanical, Water Absorption and Barrier Properties of Poly(Lactic Acid) Composites with Kenaf-Derived Cellulose of Thermally-Grafted Aminosilane

Tee, Y. B.<sup>1</sup>, Rosnita, A. T.<sup>1,2\*</sup>, Khalina, A.<sup>3</sup>, Chin, N. L.<sup>1</sup>, Roseliza, K. B.<sup>1</sup>, and Khairul Faezah, M. Y.<sup>1</sup>

<sup>1</sup>Department of Process and Food Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

<sup>2</sup>Halal Products Research Institute, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

<sup>3</sup>Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.

### ABSTRACT

The effects of filling poly(lactic acid) (PLA) composites with cellulose thermally-grafted with hydrolysed 3-aminopropyltriethoxysilane (APS) were investigated. Composites containing 30 wt% of kenaf-derived cellulose (C) and silane-grafted cellulose (SGC) were melt-blended into a PLA matrix before being hot-pressed into 0.3 mm sheets. The tensile strength of neat PLA was 47 MPa. With addition of C and SGC, the tensile strength was improved by 13% and 23%, respectively. The tensile modulus was approximately doubled for both of the composites. PLA/C and PLA/SGC composites remained brittle with marginally lowered elongation at break. The addition of C and SGC significantly increased the oxygen barrier of PLA with the reduction of oxygen transmission rate (OTR) of PLA at 76.6 cc/m<sup>2</sup>/day to 42.2 cc/m<sup>2</sup>/day and 40.3 cc/m<sup>2</sup>/day, respectively. This was due to the tortuous path created and crystallites induced by the fillers. The water vapour transmission rate (WVTR) for PLA, PLA/C and PLA/SGC was in the range of 21-23 g/m<sup>2</sup>/day. From the water absorption test, PLA/SGC reported slightly better water resistance as

compared to PLA/C. The reinforcing results from these bio-based materials may suggest contribution towards packaging oxygen and moisture sensitive food.

**Keywords:** Cellulose, kenaf, mechanical barrier, poly(lactic acid), silane coupling agent, water absorption

### ARTICLE INFO

#### Article history:

Received: 5 January 2015

Accepted: 25 May 2015

#### E-mail addresses:

tee.yee.bond@outlook.com (Tee, Y. B.),

rosnita@upm.edu.my (Rosnita, A. T.),

khalina@upm.edu.my (Khalina, A.),

chinnl@upm.edu.my (Chin, N. L.),

roseliza@upm.edu.my (Roseliza, K. B.),

kfaezah@upm.edu.my (Khairul Faezah, M. Y.)

\* Corresponding author

## INTRODUCTION

When environmental conservation had not yet become an issue, many manufacturers used manmade fibres as fillers in composites due to their superior composite reinforcing ability (Mohanty *et al.*, 2000). It was not until the late 1980s that research into natural fibres as composite fillers became important (Westman *et al.*, 2010). Specifically in the plastic packaging field, research works on natural fibre reinforced petroleum-derived plastics, the so called “big four” polyethylene (PE), poly(propylene) (PP), polystyrene (PS) and poly(vinyl chloride) (PVC), became prevalent (Mohanty *et al.*, 2000). In recent years, with the intensifying environmental concern and stringent government regulations especially in the Asian and European countries, development of packaging materials that are attuned to the environment such as bio-derived polymers, recyclable materials and reusable packaging have become a main focus (Holbery & Houston, 2006; Satyanarayana *et al.*, 2009; Johansson *et al.*, 2012).

Noticing the increasing demand of “greener” products, it became the impetus of the present research to produce an entirely bio-sourced composite specifically for food packaging applications. Kenaf-derived cellulose and poly(lactic acid) (PLA) were chosen as the filler and matrix for the present research. However, as was agreed by various authors, the major drawback of using natural fibres as composite filler is their marked hydrophilicity and polar nature (Khan & Hassan, 2006; Masirek *et al.*, 2007; Xie *et al.*, 2010; Pang & Ismail,

2013) as this leads to other problems, such as poor interfacial adhesion with the non-polar polymeric matrixes (Abdelmouleh *et al.*, 2007; Lu *et al.* 2008; Kalia *et al.*, 2009), agglomeration and uneven dispersion of fibres within the matrix (Kazayawoko *et al.*, 1999; Masirek *et al.*, 2007) and poor resistance towards moisture (Bisanda & Ansell, 1991; Castellano *et al.*, 2004; Kalia *et al.*, 2009).

To improve the compatibility of natural fibres and polymer matrix, fibre and/or matrix modification with physical or chemical treatments can be done (George *et al.*, 2001). Among other modifications, treating fillers with a silane coupling agent was frequently practised by various authors (Khan & Hassan, 2005; Huda *et al.*, 2008; Lee *et al.*, 2009). However, thermal grafting of the hydrolysed silane or silanol onto the fillers before addition into matrix was comparatively little. Thermal grafting was highlighted in this research as a procedure to enable chemical condensation of the silanol and siloxane (-Si-O-Si-) polymer networks onto the fibres, which was initially only hydrogen bonded (Si-OH). Unlike hydrogen bonding, the siloxane bridges (Si-O-C) from the condensation cannot be hydrolysed off and thus desorption of the coupling agent is diminished (Brochier Salon *et al.*, 2005). An in-depth review with regards to this study was done by Xie and co-workers (2010).

Recently, the authors reported elsewhere the thermal properties of PLA composites that were reinforced with aminosilane-grafted cellulose derived from kenaf fibres (Tee *et al.*, 2013). As the composites

were characterised towards packaging applications, the barrier properties of the material became customary in maintaining the quality and shelf life of the food product (Siracusa, 2012). At least to our knowledge, little work on the barrier properties of a thermoplastic composite was published. Thus, the objective of the present work was to investigate the mechanical, water absorption and barrier properties of the PLA composites reinforced with silane grafted cellulose.

## MATERIALS AND METHOD

### *Materials*

Poly(lactic acid) (PLA) resin (Ingeo 2003D, with MFI of 6 g/10 min at 210°C and bulk density of 0.85 g/cm<sup>3</sup>) was purchased from NatureWorks LLC, USA. Kenaf bast fibre (KBF) was provided by the Institute of Tropical Forestry and Forest Products (INTROP), Malaysia. Reagent-grade acetic acid (CH<sub>3</sub>COOH) and sodium hydroxide (NaOH), technical-grade sodium chlorite (NaClO<sub>2</sub>) of 80% purity and 3-aminopropyltriethoxysilane (APS) of 99% purity were purchased from Fisher Chemicals Sdn. Bhd., Malaysia.

### *Preparation of Fillers and PLA Composites*

A detailed methodology of preparations was reported elsewhere (Tee *et al.*, 2013). Derivation of cellulose (C) from kenaf bast fibres was done via chlorination followed by 2 h of soaking in 5% w/v of NaOH solution. Preparation of silane-grafted cellulose (SGC) was done via treatment with 5 wt%

of APS coupling agent followed by thermal treatment at 120°C under vacuum of 2 mm Hg for 2 h. Preparation of PLA/C and PLA/SGC composites at 70:30 w/w loading with 0.3-mm thickness was done via melt blending and hot pressing.

### *Characterisation*

#### **Tensile testing**

A rectangular strip with 100 mm x 15 mm x 0.3 mm dimensions was cut from each film specimen and was subjected to tensile measurement using a Universal Testing Machine (Instron Model 4301, USA) with a load cell of 1 kN. The test was performed at a cross-head speed of 5 mm/min. The average values of seven repetitions of each specimen were reported with standard error.

#### **Scanning electron microscope**

The fracture surface of the PLA and composite films after the tensile test was observed using a variable pressure scanning electron microscope (LEO, 1455 VP SEM, England) at an accelerated voltage of 20 kV. Each sample was sputter-coated with gold before scanning.

#### **Water absorption**

Five rectangular strips with 30 mm x 10 mm x 0.3 mm dimension were cut from each film specimen and oven dried at 50°C for 24 hours to a constant weight and measured as the initial weight,  $W_1$ . Then, they were immersed in distilled water at room temperature. At regular time intervals (every 24 h), each strip was taken out,

pressed dry with a cloth and subsequently weighted for up to 70 days. The amount of water absorbed by the specimen was calculated using Equation [1],

$$W_t(\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad [1]$$

where  $W_t$  the total water absorbed by the specimen, and  $W_1$  and  $W_2$  are the weights of the specimen before and after immersion in the water respectively. The average values of five repetitions of each specimen were reported.

**Oxygen transmission rate.** Oxygen transmission rate (OTR) of the film specimens was acquired using Oxygen Permeability Analyser (Mocon®, Oxtran 2/21, USA) in accordance with ASTM D 3985-05. The test area of the films was 5cm<sup>2</sup>. The test was run at 23.0°C, 0% RH, barometric pressure of 755 to 759 mmHg with nitrogen flow rate of 10 sscm.

**Water vapour transmission rate.** Water vapour transmission rate (WVTR) of the film specimens was acquired using Water Vapour Permeability Analyser (Mocon®, Permatran W3/33B, USA) in accordance with ASTM F 1249-06. The test area of the films was 5cm<sup>2</sup>. The test was run at 37.8°C with 90± 2% RH at the permeant side.

## RESULTS AND DISCUSSION

### *Tensile Properties*

Table 1 shows the tensile properties of PLA, PLA/C and PLA/SGC films. The tensile strength of neat PLA was 47 MPa. The addition of 30 wt% of C increased 13% of the tensile strength while the addition of

SGC further improved the tensile strength to 58 MPa, with 23% of total increment. The improvement of tensile strength indicated effective stress transfer from the good interfacial bonding between the fillers and PLA matrix (El-Shekeil *et al.*, 2012). For PLA/C, this could be due to the rough and grooved surface topography of the cellulose derived through alkali treatment as was previously defined elsewhere (Tee *et al.*, 2013); which enabled the formation of mechanical interlocking to the PLA matrix (Avella *et al.*, 2009; Tawakkal *et al.*, 2012). As for PLA/SGC, the tensile strength was further improved from the enhanced interfacial adhesion between the silane-grafted cellulose and PLA matrix (Khan & Hassan, 2006; Lee *et al.*, 2008). The amine groups of the hydrolysed APS could have formed hydrogen bonds with the carboxylic sites on the hydrolysed PLA backbone (Ghosh *et al.*, 2010) while siloxane bridges (S-O) were formed between the hydrolysed APS and the hydroxyl groups of cellulose (Brochier Salon *et al.*, 2005; Zhao *et al.*, 2012). Authors have reported an increase in tensile strength of composites in the range of 0.5 MPa to 8 MPa from the silane treatment (Abdelmouleh *et al.*, 2007; Khan & Hassan, 2006; Pang & Ismail, 2013; Wang *et al.*, 2011; Zhao *et al.*, 2012). Compared with the current research, the increase in composites' tensile strength from the silane grafting was rather high at 5 MPa and this could be further changed with different amounts of silane. Zhao *et al.* (2012) treated poly(butylene succinate)/rice straw fibre composites with different amount of APS

coupling agent and reported an increase in tensile strength in the range of 4 MPa to 6 MPa.

The tensile modulus of neat PLA was 7 GPa. With C added, the tensile modulus of PLA almost doubled at 13 GPa. With SGC, the tensile modulus was further increased to 15 GPa. The increase in stiffness of the composites was contributed by the comparatively higher stiffness of the cellulose (Luz *et al.*, 2008). El-Shekeil and co-workers (2012) termed it as a 'logical trend' that a composite becomes stiffer with the addition of natural fibres. The further increment in stiffness with silane treatment was also reported by several authors (Abdelmouleh *et al.*, 2007; Huda *et al.*, 2008; Lee *et al.*, 2009). This could be due to the better adhesion from the treatment which restricts the polymer chain mobility and further hinders the ability of the polymer to deform.

TABLE 1  
Tensile Properties of PLA, PLA/C, and PLA/SGC Films

Samples	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PLA	47(±1.0)	7(±0.1)	1.6(±0.09)
PLA/C (70/30)	53(±2.3)	13(±0.3)	0.6(±0.02)
PLA/SGC (70/30)	58(±1.8)	15(±0.1)	0.6(±0.02)

Standard error in parenthesis ( )

As seen in Table 1, the elongation at break of neat PLA was 1.6%, which was, as expected, low due to its brittle nature. Both

PLA/C and PLA/SGC composites further lowered the elongation at break to 0.6%. As the rigid fillers were added to the PLA, they suppressed the PLA matrix to elongate further (Tawakkal *et al.*, 2012). The voids between the fillers and matrix interface may cause an early rupture or premature composite failure, thus decreasing the elongation at break (Luz *et al.*, 2008).

The micrographs of tensile fracture surface of the film samples are shown in Fig.1 to Fig.3. The fracture surface for PLA was clear cut and smooth, representing its brittle nature. As for the composites, the cellulose was rod shaped with different diameters and randomly dispersed in the matrix. From the PLA/SGC micrograph in Fig.3b, it can be seen that the cellulose was surface-coated, which could be the grafted silane (Koga *et al.*, 2011; Tee *et al.*, 2013). From the PLA/C micrograph in Fig.3, aside from some good physical interlocking between the cellulose and the matrix, there were quite a number of filler-related failures such as cellulose pullout, gaps between cellulose and PLA matrix interface and cellulose-matrix debonding, which resulted in voids. Although the filler-related mechanisms similar to PLA/C were also seen in the PLA/SGC micrographs, it was significantly less in comparison. Moreover, good interfacial adhesion and compatibility between the interfaces was seen as there was better wetting out of the PLA matrix onto the SGC and this improved the tensile properties.

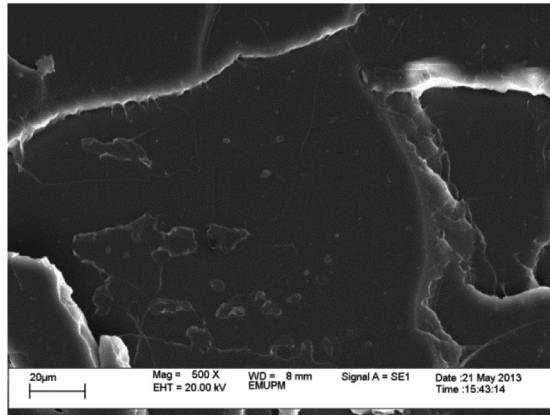


Fig.1: Tensile fracture surface of PLA film at 500× magnification.

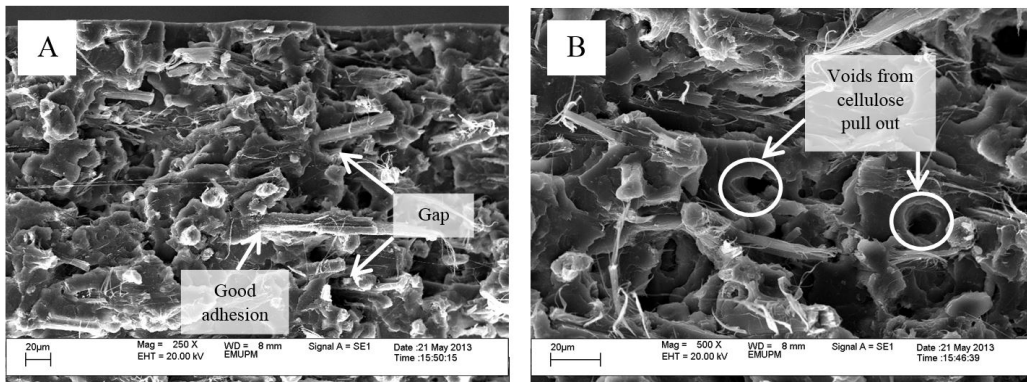


Fig.2: Tensile fracture surface of PLA/C composite films at A) 250× magnification, and B) 500× magnification.

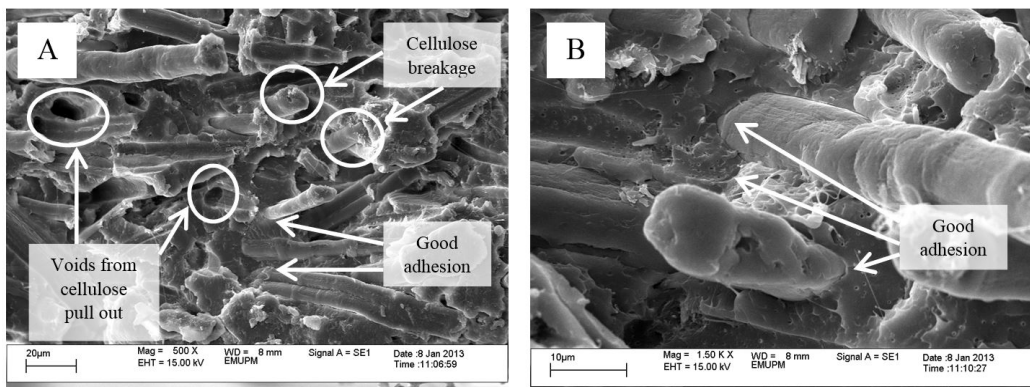


Fig.3: Tensile fracture surface of PLA/SGC composite films at A) 500× magnification, and B) 1500× magnification.

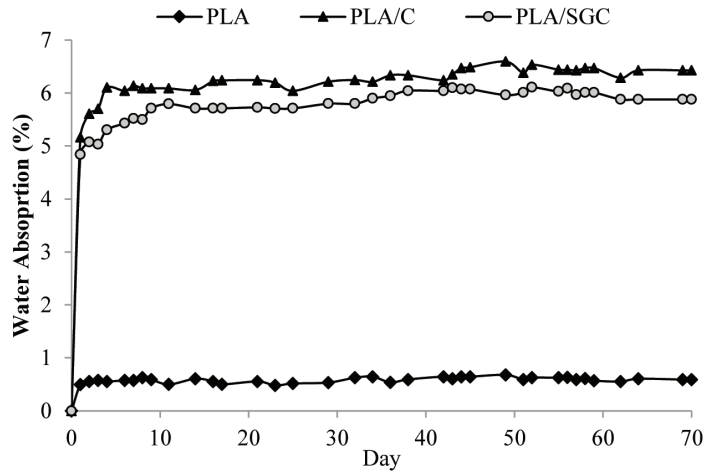


Fig.4: Water absorption of PLA, PLA/C and PLA/SGC composite films.

#### Water Absorption

Fig.4 shows the water absorption of the PLA and composite films measured throughout 70 days of water immersion. For the PLA film, equilibrium was reached within 2 days with low water absorption of 0.6%. For the composite films, there was a rapid increase in water absorption in the first 2 days. The following days showed a gradual increase until equilibrium was reached. PLA/C absorbed 6.5% of moisture. Comparatively, PLA/SGC slightly improved the water resistance with 5.9% of water absorption. Few authors have reported the effect of silane treatment on the water absorption of natural fibre-related composites. The range of water reduction was reportedly low at the range of 0.2 to 1.3% by the authors (Abdelmouleh *et al.*, 2007; Zhao *et al.*, 2012; Pang *et al.*, 2013).

Water can penetrate into composite materials via three mechanisms whereby water molecules can either diffuse through

micro gaps between polymer chains, capillary transported into gaps between the fillers-matrix interfaces from incomplete wetting or transported through the matrix micro cracks or pores formed during compounding (Zhao *et al.*, 2012). The free hydroxyl groups in cellulose readily form hydrogen bonds with the water molecules and this expands the cells until they are saturated with water (Rampinelli *et al.*, 2010; Zhao *et al.*, 2012). The cell expansion may generate even more micro cracks and fibre-matrix debonding, which causes further water penetration (Mat Taib *et al.*, 2008). At similar filler loadings, composites with SGC had lower water absorption, which indicated the presence of the silane coupling agent in enhancing the filler-matrix interfacial adhesion. Lee *et al.* (2009) called it better wetting out of the polymer matrix onto the fibres. From the previous finding via Fourier transform infrared spectroscopy (FTIR), silane-grafted cellulose had comparatively fewer free -OH

groups as they were chemically grafted with the silanol of the ethoxysilane (Tee *et al.*, 2013). This also contributed to the decreased amount of equilibrium water absorption by PLA/SGC.

### Barrier Properties

Table 2 shows the barrier properties of PLA, PLA/C and PLA/SGC films. The average oxygen and water vapour transmission rate of the PLA films was 76.6 cc/m<sup>2</sup>/day and 23.05 g/m<sup>2</sup>/day. The incorporation of 30 wt% of cellulose resulted in OTR of 42.2 cc/m<sup>2</sup>/day, with 45% reduction. The incorporation of similar loading of SGC further reduced the OTR to 40.3 cc/m<sup>2</sup>/day. As for WVTR, it was reported that PLA/C only slightly reduced 2% of PLA films' WVTR. PLA/SGC further reduced 8% of the WVTR, resulting 20.85 g/m<sup>2</sup>/day. While the incorporation of cellulose had more influence as compared to the effect of silane grafted onto the cellulose in retarding the oxygen permeation of the film, it was vice versa in terms of water vapour. At least to our knowledge, not many authors reported the barrier properties of polymer-cellulose composites. Laxmeshwar and co-workers (2012) reported the trend of OTR and WVTR of PLA reinforced with treated microcrystalline cellulose at different loading. They had the same finding whereby the fillers had more significant influence in increasing the oxygen barrier properties of the composites as compared to the water vapour barrier properties. The slight reduction of WVTR could be due to the initial PLA's WVTR that was already

low. The reduction of OTR and WVTR from the addition of fillers was due to the decrease in the polymer chain flexibility (Laxmeshwar *et al.*, 2012). Similar to stiffness, the polymer chain flexibility was further reduced with SGC due to the improved interfacial adhesion, and thus further improved the barrier properties. The addition of fillers also created a blocking effect as they forced the permeant to follow the tortuous pathway during diffusion (Majeed *et al.*, 2013). According to Shogren *et al.* (1997), crystallites impose barriers to permeant diffusion, which also explains the improved barrier properties of PLA/C and PLA/SGC as cellulose is known to be highly crystalline (Mwaikambo & Ansell, 2002). Other studies report that cellulose and SGC were shown to be crystal nucleating agents, which further supports the role of these fillers in increasing the barrier of the composite films (Tee *et al.*, 2013).

TABLE 2  
Barrier properties of PLA, PLA/C, and PLA/SGC Films

Samples	Oxygen transmission rate (cc/m <sup>2</sup> /day)	Water vapour transmission rate (g/m <sup>2</sup> /day)
PLA	76.6(±6.5)	23.1(±0.5)
PLA/C (70/30)	42.2(±4.6)	22.7(±0.2)
PLA/SGC (70/30)	40.3(±1.8)	20.9(±1.8)

Standard error in parenthesis ( )

### CONCLUSION

In the current work, improvement in tensile properties was attained with the addition of cellulose into a PLA matrix and they



were further enhanced with silane-grafted cellulose. The rigidity of the fillers slightly reduced the elasticity of PLA, which was brittle in nature. Increment in water absorption was reported in PLA/C. However, composites with silane-grafting reported slightly better water resistance from the improved interfacial compatibility and reduced free –OH groups in the cellulose. While the incorporation of C and SGC into the PLA matrix increased the oxygen and water vapour barrier properties, in particular, SGC was more effective in improving the water vapour barrier properties of the composites. This may suggest the potential of these bio-based materials for packaging oxygen and moisture-sensitive food.

#### ACKNOWLEDGEMENTS

The authors wish to express their thanks to the Institute of Tropical Forestry and Forest Products (INTROP), Malaysia for the supply of kenaf bast fibres. The authors also acknowledge Universiti Putra Malaysia (Malaysia) for providing financial support under grant No. 9199816.

#### REFERENCES

- Abdelmouleh, M., Boufi, S., Belgacem, M. N., & Dufresne, A. (2007). Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibres loading. *Composites Science and Technology*, 67(7-8), 1627-1639.
- Avella, M., Buzarovska, A., Errico, M. E., Gentile, G. & Grozdanov, A. (2009). Eco-challenges of bio-based polymer composites. *Materials*, 2(3), 911-925.
- Bisanda, E. T. N., & Ansell, M. P. (1991). The effect of silane treatment on the mechanical and physical properties of sisal-epoxy composites. *Composites Science and Technology*, 41(2), 165-178.
- Brochier Salon, M. C., Abdelmouleh, M., Boufi, S., Belgacem, M. N., & Gandini, A. (2005). Silane adsorption onto cellulose fibres: Hydrolysis and condensation reactions. *Journal of Colloid and Interface Science*, 289(1), 249-261.
- Castellano, M., Gandini, A., Fabbri, P., & Belgacem, M. N. (2004). Modification of cellulose fibres with organosilanes: Under what conditions does coupling occur? *Journal of Colloid and Interface Science*, 273(2), 505-511.
- El-Shekeil, Y. A., Sapuan, S. M., Abdan, K., & Zainuddin, E. S. (2012). Influence of fibre content on the mechanical and thermal properties of kenaf fibre reinforced thermoplastic polyurethane composites. *Materials and Design*, 40(11), 299-303.
- George, J., Sreekala, M. S., & Thomas, S. (2001). A review on interface modification and characterization of natural fibre reinforced plastic composites. *Polymer Engineering and Science*, 41(9), 1471-1485.
- Ghosh, S. B., Bandyopadhyay-Ghosh, S., & Sai, M. (2010). Composites. In R. Auras, R., Lim, L. T., Selke, S. E. M., & Tsuji, H. (Eds.), *Poly(lactic acid): Synthesis, structures, properties, processing, and applications* (2nd ed.). (pp. 239-310). United States: John Wiley & Sons.
- Holbery, J., & Houston, D. (2006). Natural-fibre-reinforced polymer composites in automotive applications. *JOM*, 58(11), 80-86.
- Huda, M. S., Drzal, L. T., Mohanty, A. K., & Misra, M. (2008). Effect of fibre surface treatments on the properties of laminated biocomposites from poly(lactic acid) (pla) and kenaf fibres. *Composites Science and Technology*, 68(2), 424-432.

- Johansson, C., Bras, J., Mondragon, I., Nechita, P., Plackett, D., Simon, P., Svetec, D. G., Virtanen, S., Baschetti, M. G., Breen, C., Clegg, F., & Aucejo, S. (2012). Renewable fibres and bio-based materials for packaging applications - A review of recent developments. *BioResources*, 7(2), 2506-2552.
- Kalia, S., Kaith, B. S., & Kaur, I. (2009). Pretreatments of natural fibres and their application as reinforcing material in polymer composites - A review. *Polymer Engineering and Science*, 49(7), 1253-1272.
- Kazayawoko, M., Balatinez, J. J., & Matuana, L. M. (1999). Surface modification and adhesion mechanisms in woodfibre-polypropylene composites. *Journal of Materials Science*, 34(24), 6189-6199.
- Khan, M. A., & Hassan, M. M. (2006). Effect of  $\gamma$ -aminopropyl trimethoxy silane on the performance of jute-polycarbonate composites. *Journal of Applied Polymer Science*, 100(5), 4142-4154.
- Koga, H., Kitaoka, T., & Isogai, A. (2011). In situ modification of cellulose paper with amino groups for catalytic applications. *Journal of Materials Chemistry*, 21(25), 9356-9361.
- Laxmeshwar, S. S., Viveka, S., Kumar, D. J. M., & Nagaraja, G. K. (2012). Preparation and properties of composite films from modified cellulose fibre-reinforced with PLA. *Der Pharma Chemica*, 4(1), 159-168.
- Lee, B.-H., Kim, H.-S., Lee, S., Kim, H.-J., & Dorgan, J. R. (2009). Bio-composites of kenaf fibres in polylactide: Role of improved interfacial adhesion in the carding process. *Composites Science and Technology*, 69(15-16), 2573-2579.
- Lee, S. Y., Kang, I. A., Doh, G. H., Yoon, H. G., Park, B. D., & Wu, Q. (2008). Thermal and mechanical properties of wood flour/talc-filled polylactic acid composites: Effect of filler content and coupling treatment. *Journal of Thermoplastic Composite Materials*, 21(3), 209-223.
- Lu, J., Askeland, P., & Drzal, L. T. (2008). Surface modification of microfibrillated cellulose for epoxy composite applications. *Polymer*, 49(5), 1285-1296.
- Luz, S. M., Del Tio, J., Rocha, G. J. M., Gonçalves, A. R., & Del'Arco Jr., A. P. (2008). Cellulose and cellulignin from sugarcane bagasse reinforced polypropylene composites: Effect of acetylation on mechanical and thermal properties. *Composites: Part A*, 39(9), 1362-1369.
- Majeed, K., Jawaid, M., Hassan, A., Abu Bakar, A., Abdul Khalil, H. P. S., Salema, A. A., & Inuwa, I. (2013). Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. *Materials and Design*, 46(1), 391-410.
- Masirek, R., Kulinski, Z., Chionna, D., Piorkowska, E., & Pracella, M. (2007). Composites of poly(L-lactide) with hemp fibres: Morphology and thermal and mechanical properties. *Journal of Applied Polymer Science*, 105(1), 255-268.
- Mat Taib, R., Ramarad, S., Ishak, M., & Todok, M. (2008, 15-19 June 2008). *Water absorption and tensile properties of kenaf bast fibre-plasticized poly(lactic acid) biocomposites*. Paper presented at the Polymer Society 24th Annual Meeting (PPS-24), Salerno, Italy.
- Mohanty, A. K., Misra, M., & Hinrichsen, G. (2000). Biofibres, biodegradable polymers and biocomposites: An overview. *Macromolecular Materials and Engineering*, 276-277(1), 1-24.
- Mwaikambo, L. Y., & Ansell, M. P. (2002). Chemical modification of hemp, sisal, jute, and kapok fibres by alkalization. *Journal of Applied Polymer Science*, 84(12), 2222-2234.
- Pang, A. L., & Ismail, H. (2013). Tensile properties, water uptake, and thermal properties of polypropylene/waste pulverized tire/kenaf (PP/

- WPT/KNF) composites. *BioResources*, 8(1), 806-817.
- Rampinelli, G., Landro, L. D., & Fujii, T. (2010). Characterization of biomaterials based on microfibrillated cellulose with different modifications. *Journal of Reinforced Plastics and Composites*, 29(12), 1793-1803.
- Satyanarayana, K. G., Arizaga, G. G. C. & Wypych, F. (2009). Biodegradable composites based on lignocellulosic fibres - An overview. *Progress in Polymer Science*, 34(9), 982-1021.
- Shogren, R. (1997). Water vapor permeability of biodegradable polymers. *Journal of Environmental Polymer Degradation*, 5(2), 91-95.
- Tawakkal, I. S. M. A., Talib, R. A., Abdan, K., & Chin, N. L. (2012). Mechanical and physical properties of kenaf-derived cellulose (KDC)-filled polylactic acid (PLA) composites. *BioResources*, 7(2), 1643-1655.
- Tee, Y. B., Talib, R. A., Khalina, A., Chin, N. L., Kadir Basha, R., & MdYunos, K. F. (2013). Thermally grafting aminosilane onto kenaf-derived cellulose and its influence on the thermal properties of poly(lactic acid) composites. *BioResources*, 8(3), 4468-4483.
- Wang, Y., Qi, R., Xiong, C., & Huang, M. (2011). Effects of coupling agent and interfacial modifiers on mechanical properties of poly(lactic acid) and woodflour biocomposites. *Iranian Polymer Journal*, 20(4), 281-294.
- Westman, M. P., Fifield, L. S., Simmons, K. L., Laddha, S. G., & Kafentzis, T. A. (2010). *Natural fibre composites: A review*. (No. 19220). Springfield, U.S.A.: Pacific Northwest National Laboratory.
- Xie, Y., Hill, C. A. S., Xiao, Z., Militz, H., & Mai, C. (2010). Silane coupling agents used for natural fibre/polymer composites: A review. *Composites: Part A*, 41(7), 806-819.
- Zhao, Y., Qiu, J., Feng, H., & Zhang, M. (2012). The interfacial modification of rice straw fibre reinforced poly(butylene succinate) composites: Effect of aminosilane with different alkoxy groups. *Journal of Applied Polymer Science*, 125(4), 3211-3220.

