



CHARACTERIZATION OF PALM KERNEL SHELL FILLED POLYLACTIC ACID COMPOSITES

B. Y. Lim¹, C. H. Voon², H. Salmah¹ and A. Nadiatul Husna¹

¹ School of Materials Engineering, Universiti Malaysia Perlis, Taman Muhibah, Jejawi, Perlis, Malaysia

² Institute of Nanoelectronic Engineering, Universiti Malaysia Perlis, Tingkat, Malaysia
 Indah, Jalan Kangar-Alor Setar, Seriab, Kangar, Perlis, Malaysia

E-Mail: bylim@unimap.edu.my

ABSTRACT

In this study, the mechanical properties, morphological studies and thermal properties of the PLA/PKS composites were investigated. The palm kernel shell (PKS) filled polylactic acid (PLA) composites were prepared at different PKS loading by using melt mixing compounding at 180 °C. The 3-aminopropyltriethoxysilane (3-APE) was selected as coupling agent. The incorporation of PKS into PLA had decreased the tensile strength and elongation at break of the PLA/PKS composites. However, the composites' modulus of elasticity was increased with increase of PKS loading. The PLA/PKS composites treated with 3-APE had higher tensile strength and elongation at break but lower modulus of elasticity. This improvement was attributed to the enhanced PKS-PLA interaction. The better interaction of PKS and PLA was proven through scanning electron microscopy and Fourier transform infrared analysis. The thermal stability of PLA/PKS composites was enhanced with 3-APE treatment.

Keywords: polylactic acid, palm kernel shell, surface treatment.

INTRODUCTION

The increasing awareness on preserving the earth has encouraged the development of green composites, with the aim to reduce consumption of non-degradable petroleum based polymer (Awal *et al.* 2009, Faruk *et al.* 2012, Peltola *et al.* 2014). Polylactic acid (PLA) is one of the aliphatic polyesters that are well known for its biodegradability. Other examples of aliphatic polyesters include polyglycolic acids (PGA), polycaprolactone (PCL), and poly-hydroxybutyrate (PHB). PLA is a type of fully degradable polymer that can be derived from the fermentation of corn, starch and sugar beet (Awal *et al.* 2015). Due to its high mechanical properties which are comparable to many other thermoplastic such as polyethylene, polystyrene and polypropylene, together with its good process ability, PLA is a promising polymer for many applications (Lu *et al.* 2014). However, PLA possesses some drawback such as brittle, low gas barrier and low water resistance, which limit its usage in certain applications (Tawakkal *et al.* 2012).

Natural fillers obtained from plant based have been widely used as alternative to synthetic filler. Bledzki *et al.* (1999) and Faruk *et al.* (2012) had done thorough reviews on the composites filled with natural fillers. Generally, the natural fillers offer many advantages such as low density, low cost, easy processing, cause less skin irritation or respiratory problems to human and lesser machine wear in production process (Oksman *et al.* 2003, La Mantia *et al.* 2011, Sdrobiş *et al.* 2012). There are many studies reported on the utilization of natural fillers in PLA composites. Some of the examples are oat husk and cocoa shells (Lezak *et al.* 2008), kenaf (Taib *et al.* 2010), bamboo (Ma *et al.* 2011) and coconut shells (Chun *et al.* 2013).

In Malaysia, the production of palm oil has generated plenty of biomass every year. The biomass

includes empty fruit bunch, mesocarp fibre, palm kernel shell and palm oil mill effluent (Ng *et al.* 2012). Palm kernel shell (PKS) is hard stony endocarp that surrounds the kernel and it is attained by breaking the palm kernel (Salmah *et al.* 2012). Based on 88.74 million tonnes of fresh fruit bunch processed in 2010, there were 4.98 million tonnes of PKS available from palm oil industry (Ng *et al.* 2012). The PKS is comprised of 50.70% lignin, 22.70% hemicellulose, 20.80% cellulose and others (Ng *et al.* 2012). Therefore, PKS can be potential filler in polymer matrix. In our previous studies, we had reported the thermal studies of PKS filled low density polyethylene composites (Salmah *et al.* 2012).

Despite the advantages of natural fillers, the poor adhesion of hydrophilic natural filler to hydrophobic polymer has caused some drawbacks. It is believed that the hydrophilic natural filler tends to agglomerate due to the filler-filler interaction. The agglomeration of fillers may cause uneven distribution and poor dispersion in the composites processing (Rasidi *et al.* 2014). Thus, the properties of the composites produced will be affected and compromised. In order to improve the interfacial bonding between filler and matrix, a coupling agent is commonly added. Silanes are known as an efficient coupling agent that are used in the production of natural filler reinforced polymer composites (Xie *et al.* 2010). The silane molecules have bifunctional groups that can react with two phases of filler and matrix, respectively, thereby forming a bridge in between them.

In present study, 3-aminopropyltriethoxysilane (3-APE) was selected as coupling agent in PLA/PKS composites. The effect of PKS loading and 3-APE on the mechanical properties, morphological studies and thermal properties of PLA/PKS composites were investigated.



EXPERIMENTAL

Materials

The Poly(lactic acid) (PLA) granulate was supplied by TT Biotechnologies Sdn. Bhd., Penang, Malaysia. The palm kernel (PKS) was received from Malpom Industries Sdn. Bhd., Nibong Tebal, Malaysia. The PKS was cleaned and dried in an oven at 80 °C for 24 hours to remove the moisture. Then, the dried PKS was ground into fine particles. After sieving process, the powder with particle size that smaller than 75 μm was selected. The 3-aminopropyltriethoxysilane (3-APE) was obtained by Aldrich Chemical Company Inc, Penang, Malaysia.

Surface treatment

The liquid 3-APE was dissolved in ethanol by the ratio of 3% (v/v). The PKS was added slowly into the 3-APE solution. The mixture was mechanically stirred for 1 hour at room temperature. The treated PKS was filtered and dried at 80 °C for 24 hours to evaporate the ethanol.

Preparation of composites

The PLA/PKS composites were prepared by using the Z-blade mixer at temperature 180 °C and 30 rpm of rotor speed. First, the PLA was loaded into the mixer for 5 minutes then PKS was added and the mixing was continued for 10 minute. Finally, the composites were removed from the mixer and underwent hot press process. The hot press process was carried out at 180 °C with 6 minutes of pre heat, 4 minutes of compression and 4 minutes of cooling under pressure. A similar procedure was conducted for the treated PLA/PKS composites with 3-APE. Table-1 shows the formulation of treated and untreated PLA/PKS composites.

Table-1. Formulation of treated and untreated PLA/PKS composites with 3-APE.

Materials	Untreated Composites	Treated Composites with 3-APE
PLA (php)	100	100
PKS (php)	0, 10, 20, 30, 40	10, 20, 30, 40
3-APE (%)*	-	3

php = parts per hundred of polymer

*3% from weight of PKS

Tensile testing

The tensile test was conducted according to ASTM D638 by using an Instron 5569. A crosshead speed of 20 mm/min was selected. For each formulation of the composites, three samples were selected and tested. Tensile strength, elongation at break and modulus of elasticity for the composites were determined.

Scanning electron microscopy

The fracture surfaces of PLA/PKS composites were examined by using scanning electron microscope (SEM) with an acceleration voltage of 5 kV. In order to avoid charging, the composite surfaces were sputter coated with a thin layer of platinum.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out by using Perkin Elmer Pyris Diamond TG-DTA. The samples were weighed about 15–25 mg. The thermal degradation of the composites was studied in the temperature range of 30 °C to 600 °C under nitrogen flow of 50 ml/min. A heating rate of 20 °C/min was selected.

Fourier transform infrared (FTIR)

Fourier transform infrared spectra of the PLA/PKS composites were acquired by using Perkin Elmer Spectrum 400 series FTIR in ATR (Attenuated Total Reflectance) mode. Four consecutive scans with 4.0 cm⁻¹ resolution were used for each spectrum. The scan range was 650 - 4000 cm⁻¹.

RUSULTS AND DISCUSSION

Tensile properties

Figure-1 shows the tensile strength of treated and untreated PLA/PKS composites at different filler loading. It was noticed that addition of PKS into PLA matrix did not improved the tensile strength of neat PLA. The tensile strength of PLA/PKS composites decreased with the increase of PKS loading. This is an indication of poor interfacial bonding between neat PLA and PKS particles. The hydrophilic PKS was not compatible with the hydrophobic PLA. Besides, PKS with irregular shape (as shown in Figure-2) may act as weakening point that hinder the stress being transferred from PLA matrix to PKS. Salmah et al. (2013) reported similar finding in the study of coconut shell powder (CSP) filled PLA ecocomposites. The addition of CSP had reduced the tensile strength of the composites.

However, with the treatment of 3-APE, the treated composites showed higher tensile strength as compared to untreated composite at similar loading. The tensile strength of treated PLA/PKS composite at 10 php PKS loading is comparable to that of neat PLA. It was believed that the 3-APE treated PKS had better interfacial bonding with PLA. Thus, the stress transfer between the matrix and filler was enhanced.

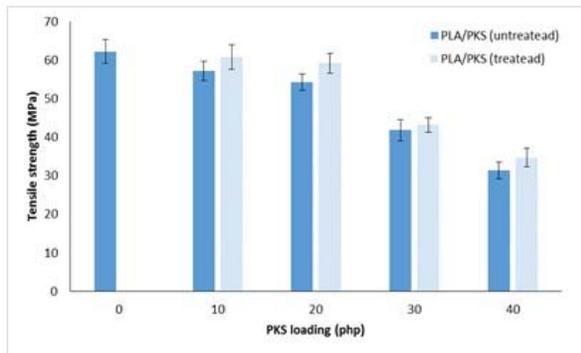


Figure-1. Effect of PKS loading on tensile strength of PLA/PKS composites.

Figure-3 illustrates the elongation at break of treated and untreated PLA/PKS composites. The presence of PKS decreased elongation at break of the composites. This observation was attributed to the stiffening effect of PKS that restricted the mobility of PLA chains. The plastic deformation process of the PLA was suppressed. The better interfacial adhesion established between filler and matrix further lower the PLA chain mobility. Similar observation was reported in a study of chitosan filled polypropylene composites (Salmah *et al.* 2011).

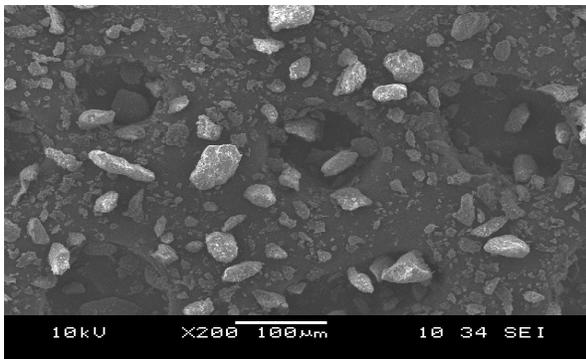


Figure-2. SEM micrograph of PKS at 200X magnification.

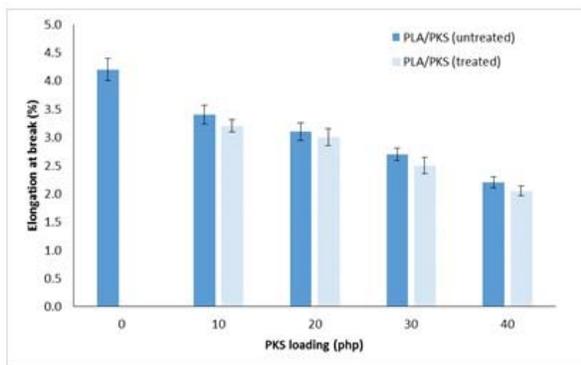


Figure-3. Effect of PKS loading on elongation at break of PLA/PKS composites.

The modulus of elasticity of the treated and untreated PLA/PKS composites is presented in Figure 4. The modulus of elasticity of PKS is higher than that of PLA, thus led to the increase in modulus of elasticity of composites. In addition, the restriction of PLA polymer chain mobility due to the presence of PKS can also contributed to the increasing of modulus of elasticity of the composites. This result was in agreement with the study of polylactic acid/ cellulose composites reported by Shumigin and co-workers (2011).

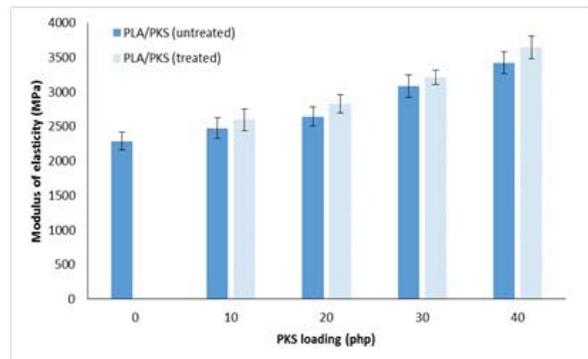


Figure-4. Effect of PKS loading on modulus of elasticity of PLA/PKS composites.

Morphological study

The SEM micrograph of the fracture surface for the untreated composites with 20 and 40 php PKS loading are presented in Figure-5 and Figure 6, respectively. The rough surface and voids indicated the detachment of PKS during the tensile testing. This can be attributed to the poor interfacial bonding between PLA and PKS. The higher PKS loading resulted in rougher fracture surface and more voids were observed. Figure-7 and Figure-8 show the micrograph of the treated PLA/PKS composites at 20 and 40 php, respectively. It can be seen that PKS was embedded in the PLA matrix, thus led to lower surface roughness. By using 3-APE as coupling agent, the interaction between filler and matrix was enhanced. It was believed that 3-APE was capable to enhance the filler-matrix interaction by improving the wettability of coconut shell powder as filler in PLA matrix (Chun *et al.* 2012).

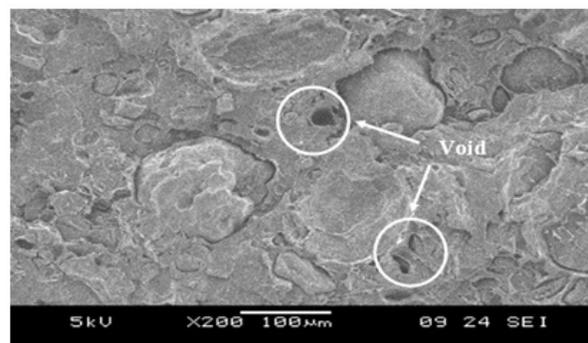


Figure-5. SEM micrograph of tensile fracture surface of untreated PLA/PKS composite at 20 php of PKS loading.

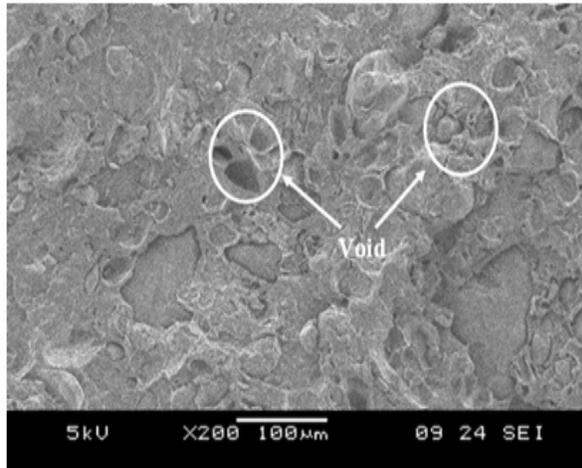


Figure-6. SEM micrograph of tensile fracture surface of untreated PLA/PKS composite at 40 php of PKS loading.

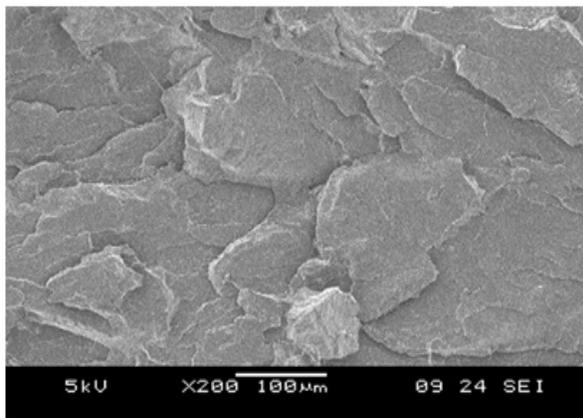


Figure-7. SEM micrograph of tensile fracture surface of treated PLA/PKS composite at 20 php of PKS loading.

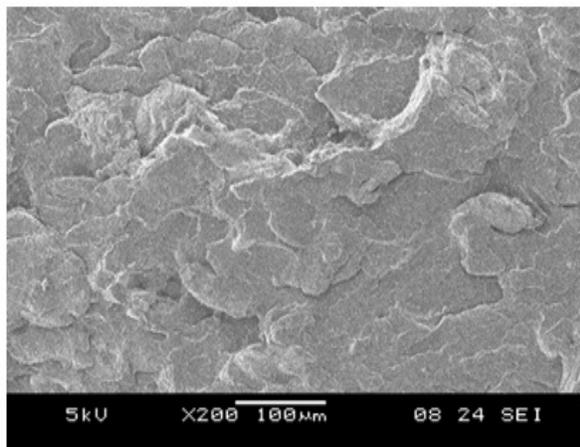


Figure-8. SEM micrograph of tensile fracture surface of treated PLA/PKS composite at 40 php of PKS loading.

Thermogravimetric analysis (TGA)

Figure-9 shows the thermal degradation of PKS, PLA and treated and untreated PLA/PKS composites at different filler loading. The initial weight loss of PKS was due to the evaporation of volatile and moisture content. The rapid weight loss of PKS only took place at temperature higher than 240 °C. Therefore, it proved that the PKS was remained stable during the processing of PLA/PKS composites. It can be seen that the incorporation of PKS into PLA reduced the final weight loss. The char residue contributed by PKS was believed to be capable of forming protective barrier that hindered the decomposition of composites. Therefore, the PLA/PKS composites at higher PKS loading had better resistivity towards thermal decomposition, thus, produced lower final weight loss. At similar filler loading, the treated PLA/PKS composites with 3-APE had lower weight loss as compared to that of the untreated composites. The 3-APE treatment promoted better wettability of PKS that improved interfacial bonding between PLA and PKS. Hence, the thermal degradation of composites was suppressed and resulted in higher residue.

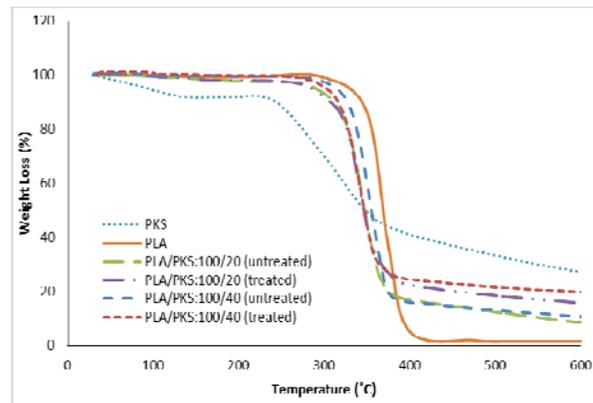


Figure-9. TGA curves of PKS, PLA, treated and untreated PLA/PKS composites.

The derivative thermogravimetric (DTG) curves of PKS, PLA, treated and untreated PLA/PKS composites are illustrated in Figure 10. A two-step thermal degradation was observed in PKS as indicated by the two peaks at 270 °C and 341 °C, respectively. The decomposition was attributed to the degradation cellulose and lignin, which were the main component in PKS. In the case of PLA, only one peak was observed, which showed single step degradation took place at 300-400 °C. The treated and untreated PLA/PKS composites both underwent single step degradation. The decomposition of PKS was suppressed as it was covered by PLA at the initial step of composites degradation. Then the degradation of composites took place at lower temperature as compared to that of neat PLA. This result was in agreement to the thermal study of coconut shell filled polylactic acid composites (Chun *et al.* 2013).

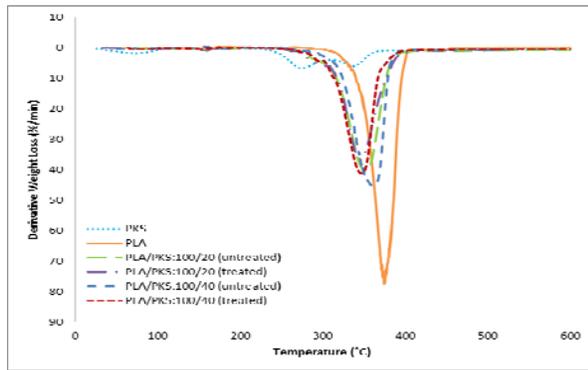


Figure-10. DTG curves of PKS, PLA, treated and untreated PLA/PKS composites.

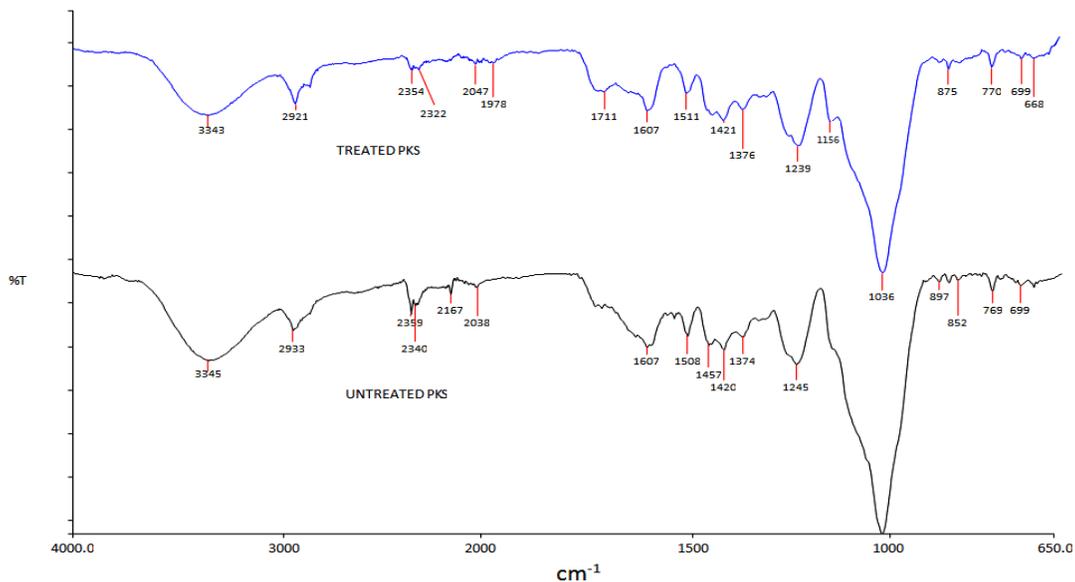


Figure-11. FTIR spectra of treated and untreated PKS with 3-APE.

CONCLUSIONS

The presence of PKS reduced the tensile strength and elongation at break of PLA/PKS composites. However, the modulus of elasticity and thermal stability of the composites increased with PKS loading. The treated composites with 3-APE exhibited higher tensile strength and elongation at break, but lower modulus of elasticity. The thermal stability of the composites was enhanced due to the better interfacial bonding between PKS and PLA. This is in good consistent with the SEM micrograph of fracture surfaces. The FTIR analysis confirmed the 3-APE had successfully modified the surface of PKS.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the funding support for this work from the Fundamental Research Grant Scheme (FRGS 9003-00440) under Ministry of Education Malaysia (MOE).

Fourier transform infrared spectroscopy (FTIR) analysis

Figure X shows that FTIR spectra of the treated untreated PKS with 3-APE. The 3000 – 3800 cm^{-1} was contributed by the hydroxyl group in PKS. After the treatment, it was found that the corresponding peak of hydroxyl groups was shifted from 3345 cm^{-1} to 3343 cm^{-1} , accompanied by the reduction in intensity. A new peak was found at 1156 cm^{-1} , which was believed to be assigned to the cellulose-Si-O or Si-O-Si linkage. A similar result was reported by Rasidi *et al.* (2014) in the study of silanized nypa fruticans filled polylactic acid/recycled low density polyethylene biocomposites.

REFERENCES

- [1] Awal, A., Ghosh, S. and Sain, M. (2009). Thermal properties and spectral characterization of wood pulp reinforced bio-composite fibers. *Journal of thermal analysis and calorimetry* 99(2), pp 695-701.
- [2] Awal, A., Rana, M. and Sain, M. (2015). Thermorheological and mechanical properties of cellulose reinforced PLA bio-composites. *Mechanics of Materials* 80, Part A(0), pp 87-95.
- [3] Bledzki, A. K. and Gassan, J. (1999). Composites reinforced with cellulose based fibres. *Progress in Polymer Science* 24(2), pp 221-274.
- [4] Chun, K. S., Husseinayah, S. and Osman, H. (2012). Mechanical and thermal properties of coconut shell powder filled polylactic acid biocomposites: effects of



www.arpnjournals.com

- the filler content and silane coupling agent. *Journal of Polymer Research* 19(5), pp 1-8.
- [5] Chun, K. S., Husseinsyah, S. and Osman, H. (2013). Properties of coconut shell powder-filled polylactic acid ecomposites: Effect of maleic acid. *Polymer Engineering & Science* 53(5), pp 1109-1116.
- [6] Faruk, O., Bledzki, A. K., Fink, H.-P. and Sain, M. (2012). Biocomposites reinforced with natural fibers: 2000–2010. *Progress in Polymer Science* 37(11), pp 1552-1596.
- [7] La Mantia, F. and Morreale, M. (2011). Green composites: A brief review. *Composites Part A: Applied Science and Manufacturing* 42(6), pp 579-588.
- [8] Lezak, E., Kulinski, Z., Masirek, R., Piorkowska, E., Pracella, M. and Gadzinowska, K. (2008). Mechanical and thermal properties of green polylactide composites with natural fillers. *Macromolecular bioscience* 8(12), pp 1190-1200.
- [9] Lu, T., Liu, S., Jiang, M., Xu, X., Wang, Y., Wang, Z., Gou, J., Hui, D. and Zhou, Z. (2014). Effects of modifications of bamboo cellulose fibers on the improved mechanical properties of cellulose reinforced poly (lactic acid) composites. *Composites Part B: Engineering* 62, pp 191-197.
- [10] Ma, H. and Joo, C. W. (2011). Influence of surface treatments on structural and mechanical properties of bamboo fiber-reinforced poly (lactic acid) biocomposites. *Journal of composite materials*, pp 0021998311401096.
- [11] Ng, W. P. Q., Lam, H. L., Ng, F. Y., Kamal, M. and Lim, J. H. E. (2012). Waste-to-wealth: green potential from palm biomass in Malaysia. *Journal of Cleaner Production* 34, pp 57-65.
- [12] Oksman, K., Skrifvars, M. and Selin, J.-F. (2003). Natural fibres as reinforcement in polylactic acid (PLA) composites. *Composites science and technology* 63(9), pp 1317-1324.
- [13] Peltola, H., Pääkkönen, E., Jetsu, P. and Heinemann, S. (2014). Wood based PLA and PP composites: Effect of fibre type and matrix polymer on fibre morphology, dispersion and composite properties. *Composites Part A: Applied Science and Manufacturing* 61, pp 13-22.
- [14] Rasidi, M. S., Salmah, H. and Teh, P. L. (2014). Properties of silanized nypa fruticans filled polylactic acid/recycled low density polyethylene biocomposites. *Polymer Engineering & Science*, pp n/a-n/a.
- [15] Salmah, H., Faisal, A. and Kamarudin, H. (2011). Chemical modification of chitosan-filled polypropylene (PP) composites: The effect of 3-aminopropyltriethoxysilane on mechanical and thermal properties. *International Journal of Polymeric Materials* 60(7), pp 429-440.
- [16] Salmah, H., Koay, S. and Hakimah, O. (2013). Surface modification of coconut shell powder filled polylactic acid biocomposites. *Journal of Thermoplastic Composite Materials* 26(6), pp 809-819.
- [17] Salmah, H., Lim, B. Y. and Teh, P. L. (2012). Melt rheological behavior and thermal properties of low-density polyethylene/palm kernel shell composites: Effect of polyethylene acrylic acid. *International Journal of Polymeric Materials* 61(14), pp 1091-1101.
- [18] Salmah, H., Lim, B. Y. and Teh, P. L. (2012). Rheological and thermal properties of palm kernel shell-filled low-density polyethylene composites with acrylic acid. *Journal of Thermoplastic Composite Materials* 26(9), pp 1155-1167.
- [19] Sdrobiş, A., Darie, R. N., Totolin, M., Cazacu, G. and Vasile, C. (2012). Low density polyethylene composites containing cellulose pulp fibers. *Composites Part B: Engineering* 43(4), pp 1873-1880.
- [20] Shumigin, D., Tarasova, E., Krumme, A. and Meier, P. (2011). Rheological and mechanical properties of poly (lactic) acid/cellulose and LDPE/cellulose composites. *Materials Science* 17(1), pp 32-37.
- [21] Taib, R. M., Ramarad, S., Ishak, Z. A. M. and Todo, M. (2010). Properties of kenaf fiber/polylactic acid biocomposites plasticized with polyethylene glycol. *Polymer composites* 31(7), pp 1213-1222.
- [22] Tawakkal, I. S. M., Talib, R. A., Abdan, K. and Ling, C. N. (2012). Mechanical and physical properties of kenaf-derived cellulose (KDC)-filled polylactic acid (PLA) composites. *BioResources* 7(2), pp 1643-1655.
- [23] Xie, Y., Hill, C. A. S., Xiao, Z., Militz, H. and Mai, C. (2010). Silane coupling agents used for natural fiber/polymer composites: A review. *Composites Part A: Applied Science and Manufacturing* 41(7), pp 806-819.