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Mechanical Properties of Polylactic Acid/Montmorillonite/Chitin Nanowhiskers Composite films

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GRAPHICAL ABSTRACT

(a) (b)

(a) Chitin nanowhisker
(b) PLA/MMT5/CHW Film

ABSTRACT

In this work, polylactic acid (PLA) is an aliphatic polyester which has good biodegradability and commonly used in food packaging industry. Regarding to its drawback such as brittleness, poor water vapour or gas barrier properties and low thermal stability, this study focuses on mechanical and thermal properties. One of the ways to enhance the properties of the polymer is through the incorporation of additives or filler. Montmorillonite at optimum content is 5 phr, (MMT5) and various chitin nanowhisker (CHW) content (1, 2, 3, 4 phr) was used as filler in PLA through solution casting method. The mechanical and thermal properties of PLA/MMT5 and PLA/MMT5/CHW composite films were investigated using tensile test and Thermogravimetric Analysis (TGA) respectively. The result for tensile test focused on tensile strength, elongation at break and Young's modulus. Tensile strength of PLA/MMT5 decreased when addition of CHW content. While for the Young's modulus and elongation at break, the composite films increased when 1 and 2 phr CHW content were added into the PLA/MMT5. In TGA, the result showed that the thermal stability increased upon addition of CHW. In addition, Fourier transform infrared spectroscopy (FTIR) was used to identify functional group and positive interaction in the composites. The IR spectrum affirmed that there are no significant different when added CHW content into the PLA/MMT5 films.

Keywords: polylactic acid, chitin nanowhisker, montmorillonite, incorporation of filler

1. INTRODUCTION

Nowadays, many societies are concern about the preservation of our ecological system. Various materials such as plastics are produced from polymers that are made from fossil sources and are usually non-biodegradable. Plastics packaging waste may therefore pollute the environment if its disposal is not well planned. An alternative solution is to use biodegradable plastics. Currently, many researchers are interested to contribute in producing polylactic acid (PLA) film due to its biodegradability properties and therefore has the tendency to reduce environmental pollution. Hence, the latest research has been exploited to apply biodegradable material instead of petroleum based synthetic polymer commonly used for packaging food stuffs, synthetic and other materials [1]. Polylactic acid (PLA) is an important aliphatic polyester and most popular among the other polymers due to its good biodegradability [2]. Apart from the properties, it is suitable for many applications such as in medicine, food packaging and agriculture [3]. Nevertheless, these PLA films have limitations such as its brittleness, poor water vapour or gas barrier properties and low thermal stability [1]. Thus, in order to overcome some if not all of these problems, PLA may require the incorporation of either organic or inorganic fillers to make PLA films as a more competitive bio-plastics [3].

Pure PLA is difficult to use due to its low strain at break coupled with high modulus of elasticity [4], thus some strategies for overcoming the limitation of PLA involves blending with other polymers to improve the overall mechanical properties. Alternatively, adding nanofillers from chitin, clays or other sources are added to form PLA-based nanocomposites [5, 6]. In certain applications, chemical additives or modified polymers are purposely added to biodegradable polymers when durability is needed [7]. Thus, the presence of other polymers or nanofillers that can impact biodegradation of PLA have been reported [8] Chitin has a huge potential to reinforce many bio-based polymer matrixes [9] and converted into individual nano-fibrils called chitin nanowhiskers (CHW) [10] since it has good biodegradability, nanosized dimension, high surface area and easy to modify. The functional films can be applied in many applications such as reinforcing additives for high performance environmentally friendly, biomedical for drug deliver or in tissue engineering [10]. Thus, CHW can act as filler in PLA films to enhance the properties of biopolymer [11]. Besides that, the usage of organoclay such as montmorillonite (MMT) has also been used to improve the PLA film [12]. It can also act as filler besides chitin nanowhisker, cellulose nanowhisker and

microcrystalline cellulose. The modification with MMT will provide greater compatibility with the polymer and the hydrolytic degradation process show faster activation compared to neat PLA as has been reported by Stloukal *et al*. (2005) [12].

2. EXPERIMENTAL

2.1 Materials

PLA in pellet form was obtained from Nature Work™ PLA 300ID, Minnetonka (MN USA) with a density of 1.24 gcm^{-3} and melt flow index (MFI) of *ca*. 15 g/10 min (190°C, 2.16 kg^{-1}). Commercial chitin powder was obtained from Sigma (Chemical Company, Iceland). The solvent used was hydrochloric acid and chloroform which is purchase from Merck (Malaysia). Organo-modified MMT (Nanomer 1.30TC) was obtained from Nanocor Inc. (Arlington Heights IL, USA). Nanomer 1.30TC is organically modified with approximately 30 wt % of octadecylamine and has a mean dry particle size 16-22 mm.

2.2 Preparation of CHW, PLA/MMT5 and PLA/MMT5/CHW

CHW (1.0 g) was fully dissolved in boiling 3M hydrochloric acid (30 mL) and it was heated in a water bath for 90 min under vigorous stirring. After treatment, the suspension was diluted with distilled water (50 mL), followed by centrifugation (3200 rpm, 15 min). This process was repeated three times. For each 15 min, the solution was decanted and replaced with new distilled water in the centrifuge tube. The supernatant was obtained and take a rest for a while before proceeding to next step. Then, the suspension was transferred to a cellulose tubing and dialysed against flowing tap water for 2 h. The tubing was immersed in a beaker containing distilled water and was left for 24 h at room temperature to allow the solvent to evaporate. The sample was transferred into a bottle and was sonicated for four times (5 min sonication, 5 min rest). Finally, the CHW suspension was weighed, stored in a sample bottle and kept at 4°C in a refrigerator until further use.

The PLA/MMT5 were prepared by mixing of PLA pellets (10.0 g) with MMT (5 phr) as described in previous publication [14]. The control PLA/MMT5 mixtures were placed in chloroform (64 mL) for 2 h at 60°C until all the PLA pellets dissolved. The suspension was then sonicated for 5 min using ultrasonic bath to ensure a dispersion of MMT fillers, as well as to remove bubbles produced during stirring. The solution was immediately cast onto a clean and dry glass plate with spreader to get nanocomposites films with thickness ~100 µm. The solvent evaporation was carried out at vacuum temperature for 24 h before analyses. The film kept in the desiccator before proceed for characterization using IR spectroscopy, TGA and tensile test.

The PLA/MMT5/CHW hybrid were prepared by mixing of PLA pellets (10.0 g) with MMT (5 phr) and different amount of CHW which is (1, 2, 3, 4 phr) as describe in previous publication [14]. The CHW filler in water suspension form. Solvent exchange and then carry out through centrifuge. Then, exchange water with acetone and continue with chloroform. The CHW was sonicated using an ultrasonic bath for 5 min to ensure a homogenous dispersion of CHW inside the chloroform. Next, CHW was transferred into a reaction flask containing PLA pellets and MMT. Subsequently, the various PLA/MMT5/CHW mixtures was placed in chloroform (64 mL) for 2 h at 60°C until the PLA pellets was fully dissolved. The dissolved PLA that contained MMT5/CHW and was sonicated for another 5 min. Lastly, the solution was cast onto a clean and dry glass plate with spreader immediately before proceeding to analyses [14].

3. RESULTS AND DISCUSSION

3.1. Tensile test

Mechanical properties of PLA/MMT5 and PLA/MMT5/CHW films can be differentiated using tensile test. Results of the tensile strength, elongation at break and Young's modulus were shown in Figure 1, 2 and 3 respectively.

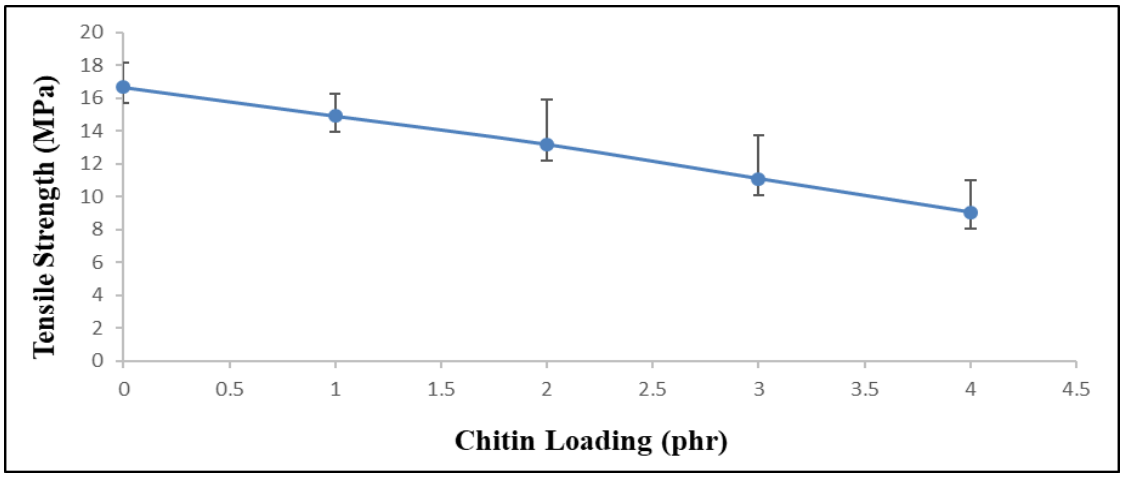

Figure 1 Effect of CHW content on tensile strength of PLA/MMT5 and PLA/MMT5/CHW.

In the present work, Figure 1 shows that tensile strength of PLA/MMT5 decreased upon the addition of CHW at 1 phr (~14 MPa) and it indicate that there was no improvement in interaction between the PLA/MMT5 and CHW. This was due to the less interaction of the matrix itself as presence in the large particles of CHW which lead a reduction in any interaction force between the hydrogen bonding. Besides that, the drastic drop in tensile strength of PLA/MMT5/CHW4 probably due to filler agglomeration which increases in stress concentration transfer [13]. Thus, it leads to a reduction in mechanical properties of the composite.

As can be seen in Figure 2, elongation at break of composite films decreased with addition of CHW content. The percent of elongation at break of PLA/MMT5/CHW decreased by 16 % as CHW increased from 1 to 4 phr. Generally, the elongation at break of PLA composite are lower than PLA/MMT5. The reduction of elongation at break in this case due to stiffening effect of the fillers by corresponding to chain movement of PLA during tensile strength. Further addition of filler with 4 phr CHW has led to decrease the elongation at break due to the less interaction and dispersion of filler in PLA matrix.

The PLA/MMT5 and PLA/MMT5/CHW were given a negative impact in Young's modulus. As can be seen in Figure 3, when 1 phr CHW was added in PLA/MMT5, the result of Young's modulus was slightly increased from ~6.3 to ~6.4 GPa. It was expected that stiffening effect from both fillers play an important role in Young's modulus of the composites that correspond to increase in hydrogen bonding. The drops in Young's modulus at value of 2 phr for PLA/MMT5/CHW due to filler agglomeration which reduce the interaction force.

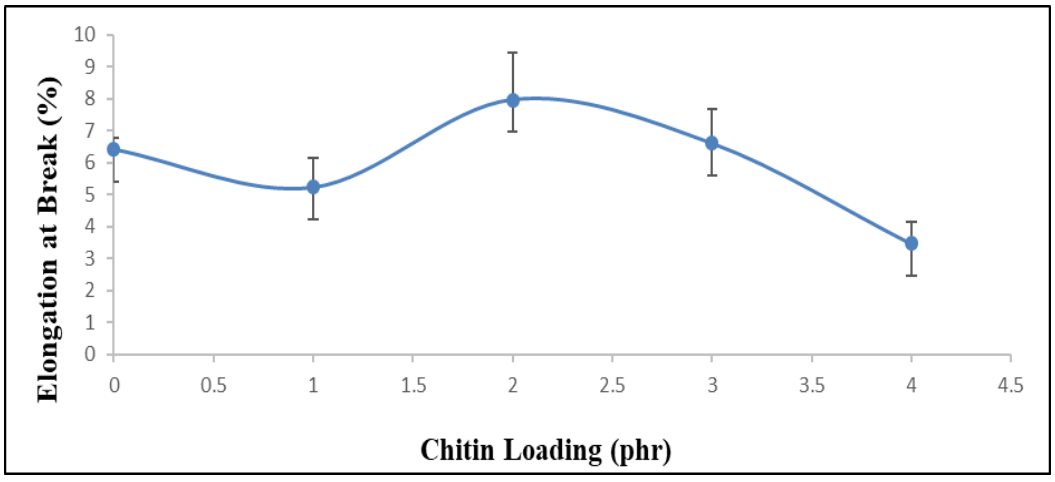

Figure 2 Effect of CHW content on tensile strength of PLA/MMT5 and PLA/MMT5/CHW.

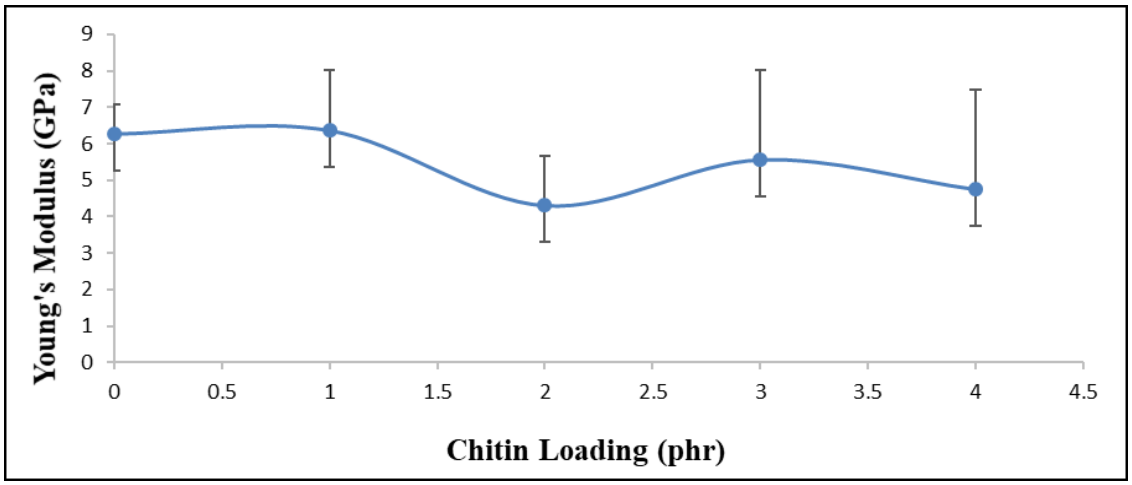

Figure 3 Effect of CHW content on Young's modulus of PLA/MMT5 and PLA/MMT5/CHW.

3.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) gives an information on the structure of the intercalating molecules by the weight loss steps. The characteristics thermal parameters selected were the onset temperature, which is the initial weight loss temperature, and maximum degradation temperature, which is the highest thermal degradation rate temperature obtained from the peak of derivative thermograms (DTG) [14].

The TGA and DTG curves of the PLA/MMT5 and PLA/MMT5/CHW films under nitrogen atmosphere gas. For easy interpretation, the characteristic temperatures such as temperature of 10% of weight loss ($T_{10\%}$), it corresponded to the maximum rate of thermal degradation (T_{max}) from DTG. The temperature of 50% weight loss ($T_{50\%}$) are used to compare the thermal stability of PLA/MMT5 and PLA/MMT5/CHW. Therefore, $T_{10\%}$ is often considered as measurement of the initial degradation temperature.

The result at Table 1 shows clearly that $T_{10\%}$ of each composite is higher than the PLA/MMT5 when addition of CHW fillers in the system. $T_{10\%}$ increased dramatically from 290 to 300ºC when added of CHW at 1 phr. However, with further addition of CHW loading content at 3 phr, the $T_{10\%}$ decrease is lower compared to 4 phr, which show an increment to 329ºC. The decrease of $T_{10\%}$ of MMT5 composite is due to the loss of water in MMT. The reason why the sample should be kept in the desiccator before characterisation is to reduce absorption of water or moisture which can affect the thermal properties.

Table 1 Thermal Properties of PLA/MMT5, PLA/MMT5/CHW

Samples	Degradation Temperature (ºC)			DTG Peaks (ºC)	Residual Weight (%) at 600 ºC
	$T_{10\%}$	$T_{20\%}$	$T_{50\%}$	T_{max}	
PLA/MMT5	290	330	350	360	3.95
PLA/MMT5/CHW1	300	335	355	362	4.65
PLA/MMT5/CHW2	310	340	368	362	3.92
PLA/MMT5/CHW3	300	335	354	362	4.56
PLA/MMT5/CHW4	329	340	358	362	7.53

3.3 FTIR Spectroscopy

The FTIR spectroscopy was used to observe the interaction of intermolecular and phase behaviour between the CHW, PLA/MMT5 and PLA/MMT5/CHW composite films respectively. Based on the IR spectrum, the peak appeared at 3263.37 cm^{-1} is attributed to hydroxyl group. The absorption peak at 2961.74 cm^{-1} and 2932.41 cm^{-1} are corresponded to –CH alkanes. The C=O amide and N-H bend show the stretching vibration at 1661.53 cm^{-1} and 1554.43 cm^{-1} respectively. The peak at 1379.00 cm^{-1} corresponds to $–CH_3$ bending vibration, while C-O of alcohol appears as a peak at 1074.71 cm^{-1} and 1025.80 cm^{-1}. The absorption peak at 1314.15 cm^{-1} for C-N amine. The spectrum of CHW shown as below in Figure 4.

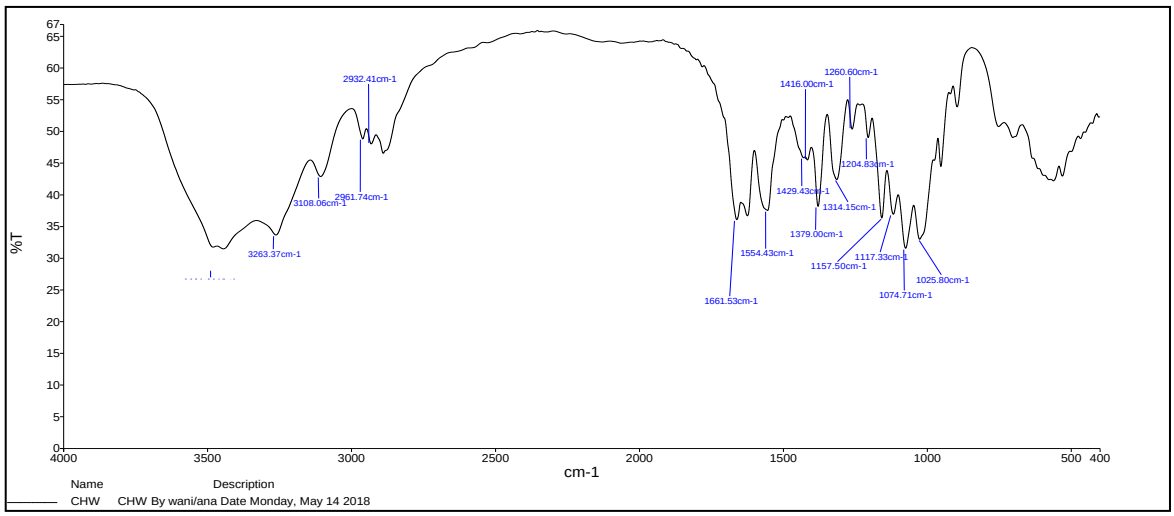

Figure 4 FTIR spectrum of CHW.

In Figure 5, the peaks at 3646.78 cm^{-1} and 3507.99 cm^{-1} correspond to bending vibrations of two terminal hydroxyl groups. The peak at 2999.00 cm^{-1} and 2948.00 cm^{-1} are attributed to an asymmetrical stretching vibration of a –CH alkanes. The absorption peak at 1759.00 cm^{-1} is attributed to the stretching vibration of C=O ester group. The peak at 1453.00 cm^{-1} correspond to $–CH_3$ bending vibration, and C-O group stretching vibration is represented as a peak at 1163.00 cm^{-1}. Furthermore, two peaks appeared at 518.32 and 465.06 cm^{-1} attributed to stretching vibration of the Si-O groups of the MMT filler. The spectrum shows that a good interaction between PLA and MMT5 filler through the formation of polar interactions between the functional groups of both components [15]. In addition, MMT5 filler contain a large number of polar sites uniformly distributed along the structure indicated an

electron density content around the interlayer spaces and surfaces. According to Feijoo *et al*. (2005), the IR spectrum of PLA nanocomposites might be due to the formation of polar interaction between hydroxyl groups of the PLA with Si-O groups of the MMT5 [16].

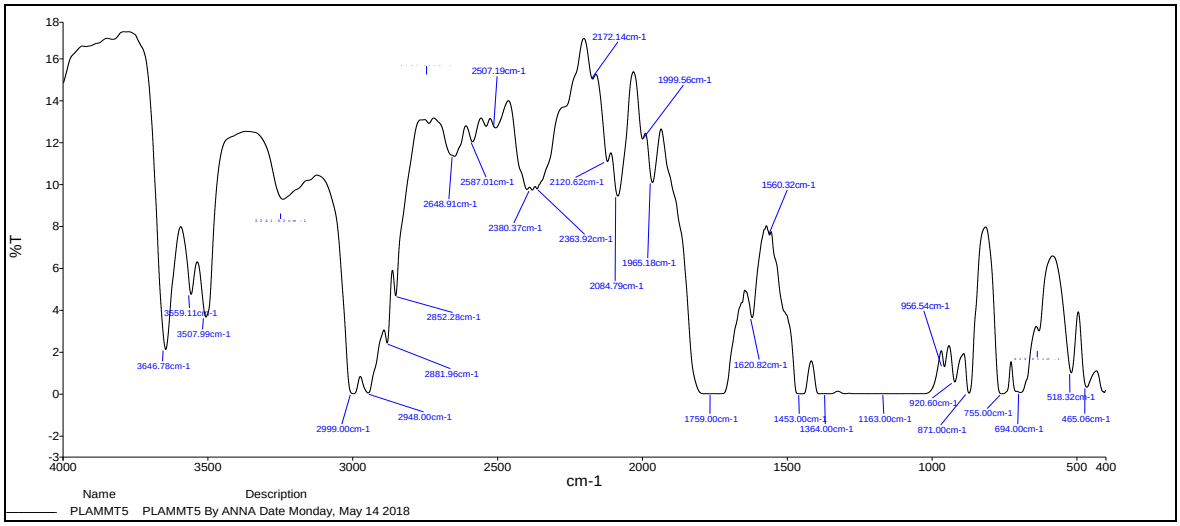

Figure 5 FTIR Spectrum of PLA/MMT5.

The PLA/MMT5/CHW film was also characterized using IR spectroscopy. The spectrum of these film did not show any differences in peaks profile even though the amount of CHW content is different. The spectrum of PLA/MMT5 and PLA/MMT5/CHW were combined together and the different coloured of bands corresponded to varying CHW content (1, 2, 3 and 4 phr). The band showed quite similar even the CHW content is different in the Figure 6. This is because it only involved incorporation of different content of CHW and therefore it only has changes in physical interaction rather than chemical. Besides that, IR can only detect the interaction of functional group in the compound and not the amount of compound. Hence, the significance difference in IR spectrum cannot be observed.

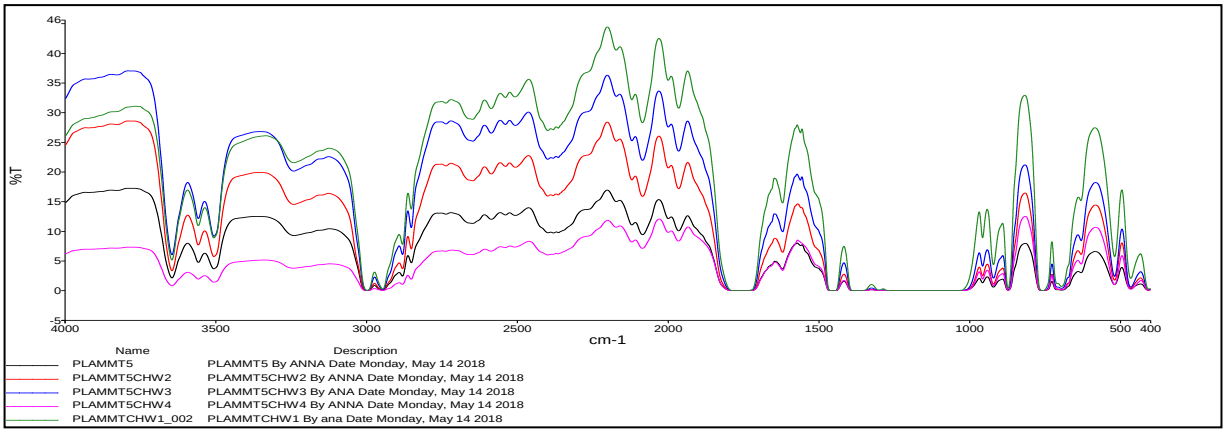

Figure 6 Combination spectrum of PLA/MMT5 and PLA/MMT5/CHW.

4. CONCLUSION

As a conclusion, PLA/MMT5 and PLA/MMT5/CHW composite films were successfully synthesized using solution casting method. All the characterizations were done and the result revealed the effect of PLA/MMT5 and PLA/MMT5/CHW on thermal and mechanical properties. The tensile strength of PLA/MMT5/CHW was decreased when CHW content was increased up to 4 phr. While for Young's modulus and elongation at break showed an increasing for 1 and 2 phr, respectively, before a decline was observed. The hybrid composite PLA/MMT5 showed an increase in thermal properties with increasing CHW content. Therefore, it clearly shows that the incorporation with filler-filler interaction can improve the thermal stability of polymer matrix.

REFERENCES

[1] Shariatinia, Z., and Fazli, M. (2015) Mechanical Properties and Antibacterial Activities of Novel Nanobiocomposite Films of Chitosan and Starch. Food Hydrocolloids. 46, 112-124.
[2] Neppalli, R., Causin, V., Mareja, C., Adhikari, R., Scholtyssek, S., Ray, S. S., and Marigo, A. (2014). The Effect of Different Clays on The Structure, Morphology and Degradation Behaviour of Poly(lactic acid).
[3] Djidi, D., Mignard, N., and Taha, M. (2015). Thermosensitive Polylactic-Acid-Based Networks. Industrial Crops and Products. 72, 220-230.
[4] Cong, D. V., Hoang, T., Giang, N. V., Ha, N. T., and Lam, D. T. (2012). A Novel Enzymatic Biodegradable Route for PLA/EVA blends under agricultural soil of Vietnam. Material Science and Engineering C. 32, 558-563.
[5] Balakrishnan, H., Hassan, A., Imran, M., and Wakit, M. U. (2012). Toughening of Polylactic Acid Nanocomposites: A Short Review. Polymer-Plastics Technology and Engineering. 51, 175-192.
[6] Raquez, J. M., Habibi, Y., Murariu, M., and Dubois, P. (2013). Polylactide (PLA)-based Nanocomposites. Progress in Polymer Science. 38, 1504-1542.
[7] Yamano, N., Kawasaki, N., Oshima, M., and Nakayama, A. (2014). Polyamide 4 with Long-Chain Fatty Acid group-Suppresing the Biodegradable Polymers. Polymer Degradation and Stability. 108, 116-122.
[8] Garrison, T. F., Murawski, A., and Quirino, R. L. (2016). Bio-Based Polymers with Potential for Biodegradability. Polymers. 8(262), 1-22.
[9] Mushi, N.E., Butchosa, N., Zhou, Q., and Berglund, L.A. (2014). Nanopaper Membranes from Chitin- Protein Composite Nanofibers Structure and Mechanical Properties. Journal of Applied Polymer Science. 131.
[10] Villanueva, M. E., Salinas, A., Eduardo, D. L., and Copello, G. J. (2014). Chitin Nanowhiskers as Alternative Antimicrobial Controlled Release Carriers. Royal Society of Chemistry. 17, 1-7.
[11] Liqing, W., and Mcdonald, A.G. (2016). A Review on Grafting of Biofibers for Biocomposites. Materials. 9, 303.
[12] Stloukal, P., Kalendova, A., Mattausch, H., Laske, S., Holzer, C., Chitu, L., Bodner, S., Maier, G., Slouf, M., and Koutny, M. (2015). Kinetics and Mechanism of the Biodegradation of PLA/clay Nanocomposites during Thermophilic Phase of Composting Process. Waste Management. 42, 31-40.
[13] Manan, S. N.A., and Mohamad, Z. (2014) The Effect of Blending Ratio on Mechanical Properties of Polylactic Acid (PLA) / Ethylene Vinyl Acetate (EVA). Applied Mechanics and Material. 554, 194-198.
[14] Chen, N. L., Feng, H. X., Guo, J. W., Luo, H. M., and Qiu, J. H. (2011b). Biodegradable Poly(lactic acid)/TDI-Montmorillonite Nanocomposites: Preparation and Characterization, In Advanced Material Research. 221, 211-215.
[15] Silverajah, V. S. G., Ibrahim, N. A., Yunus, W. M. Z. W., Hassan, H. A., and Woei, C. B. (2012). A Comparative Study on the Mechanical, Thermal and Morphology Characterization of Poly(lactic acid)/Epoxidized Palm Oil Blend, International Journal of Molecular Sciences. 13, 5878-5898.