Influence of organoclay on behaviour of polylactic acid (PLA)/polypropylene (PP) blend

Noor Hafizah Abdul Halim, Engku Zaharah Engku Zawawi, Ahmad Zafir Romli, Rozana Mohd Dahan, Nor Yuliana Yuhana

Faculty of Applied Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

Abstract. In this study, thermoplastic composite by blending of Polylactic acid (PLA) and Polypropylene (PP) was prepared with fixed ratio of 75:25 % by weight. Varying content of organoclay were studied with different loading of 1,3,5 and 7 wt.% in order to study the potential of this nanofiller in the composite. The composites were prepared by using twin screw extruder. Characterizing of PLA/PP-Clay (PLA/PP-C) composites were analyzed by focusing on physical, thermal and morphological properties. Water absorptions was analyze to observe the percentage of water uptake when percentage loading of organoclay added were increased. Differential scanning calorimetry (DSC) was performed to analyze the thermal stability and thermal sensitivity of the composite. Meanwhile, x-ray diffraction (XRD) were observed to study the fracture surfaces of PLA/PP-Clay composites. In water absorptions analysis it was found that the percentage of water uptake were decreased when organoclay added at 7 wt.%. DSC results showed that melting temperature (Tm) were decreased when the loading of organoclay increased and the thermal stability was improved by addition of organoclay. Morphological analysis by XRD showed that exfoliation and intercalation happened in the system. It is suggested that these combination of PLA/PP-Clay have a good potential for the fabrication of nanocomposites.

1. Introduction

Polymer nanocomposites was investigated intensively by using nanoparticles which is only small loading of silicates needed but can exhibit better properties in nanocomposites fabrication. Development of composites by using microfiller have reached their limitation in optimization. The previous study found that their performance in strength, resistance to corrosion and thermal stability by using microfiller has a lot of trade off [1]. Nanocomposites was discovered in 1990s where Toyota was applied these polymer nanocomposites in the parts of their car’s brand then these application was widely used during 2000s and above. Even though the era of nanocomposites was started to be used a long time ago, but the dispersion state of nanoparticles at low filler loading remain being challenges for the researchers to study their full potential of performance [2]. The performance of nanocomposites depends on their features such as their size, aspect ratio, surface area, volume fraction and also their compatibility with the other types of matrix. Nanocomposites was extensively investigate to develop enhancement in mechanical properties, improvement in thermal stability and sensitivity, gas barrier performance and reduce flammability to be used in variation of applications at low filler loading. The types of clay filler play the important role in order to develop better properties.
Montmorillonite clay (MMT) was one of the organically silicate that commonly used to study the effects on the plastic blends to fabricate nanocomposite. Clay minerals can be categorized by 4 different types which is kaolinite group, smectite group, illite group and also chlorite group [3]. MMT was under smectite group which is its particle in sheets formed and has layers with a layer thickness about 0.96nm and the lateral dimension of 100-200nm. The layers divided into two types which are octahedral and tetrahedral structural of sheets which is content of aluminium or magnesium octahedral sheets between two silica-oxygen tetrahedral sheets. MMT is low cost and readily available. MMT was studied by other researchers in fabrication of MMT with other polymeric materials such as Poly(vinyl) alcohol (PVA), Polyethylene (PE), Polycaprolactone (PCL) and also Polypropylene (PP).

Polylactic acid (PLA) was gained attraction from researchers to investigate their functions and properties to produce biodegradable plastics composite in order to reduce the usage of conventional plastic sources from fossil-based polymers materials. PLA was identified as biogradable material which is it was derived from renewable sources such as potato, yarn, and sugar cane. PLA has good performance in mechanical strength, thermal stability and also eco-friendly material. But PLA also has high brittleness and stiff polymer with low elongation[4]. Because of this disadvantages in PLA properties, it was required to combine with the other type of polymer material in order ro develop it properties. For example blending of PLA with polypropylene (PP), High density polyethylene (HDPE) and PCL. Polypropylene (PP) is synthetic plastics material which is synthesized from petroleum-based sources. This material was widely used in the industry applications due to their flexible properties and also one of fastest growing types of thermoplastics. Based on the Department of Statistics in 2012, about 19,000 metric tons of waste from solid waste and plastic waste were produced from all the households in Malaysia [5]. The increment of plastics waste at the landfill was critical and most of plastics were dumped are from petroleum-based materials and eventually end up as nondegradable waste at the end. Therefore, the using of biopolymer materials such as PLA in product application is among the solution to reduce these problems.

Blending of plastics was gained attention from researchers since it can enhance the properties of composites and can reduce the cost of production. PLA is a hydrophilic aliphatic polyester material meanwhile PP is hydrophobic material behaviour. The blending of both materials will tend to cause of immiscibility between these two materials and the blending of matrix with filler also exhibit the problem. Afterwards it will cause low adhesion between materials and contribute to the low mechanical properties of the composite performance. In this case, compatibilizer was important to overcome that problem. Compatibilizer was functional as an aid during the processing then can exhibit development of adhesion bonding between all materials during blending process. Among of the compatibilizer that usually used in this blending process was maleic anhydride grafted polypropylene (MAgPP). The objective of this study to prepared and study the effect of organoclay filler on the thermal and morphological properties of PLA/PP blend.

2. Materials and method
2.1. Materials
PLA resin grade 2003D was purchased from Nature Works LLC with specific gravity of 1.24 g/cc, MFR 6.0 g/10 min and have transparent appearance. PP with melt flow index of 2.1 g/10 min with density of 0.9 g/cm³ was produced by Lotte Chemical Titan Holding Sdn Bhd. Organoclay (Nanomer® I.44P) and maleic anhydride grafted polypropylene (MAgPP) were purchased from Aldrich.

2.2. Preparation of PLA/PP nanocomposite
PLA and PP blend with organoclay was melt blended in twin screw extruder TSE 16TC with fix ratio of 75 wt.% PLA and 25 wt.% PP. The loading of organoclay was varied at 1,3,5 and 7 wt.% and namely as PLA/PP-C1 until PLA/PP-C7. All materials were predried in oven at temperature 80°C for
8 hours prior of blending. Afterwards, all materials were premixing at the outside then blend in the twin screw extruder. The extrudate produced were crushed by using crusher in order to produce granulate shaped. Then, all materials were prepared according to the testing required.

2.3. Testing and characterization

Water absorption analysis were done to observe the water uptake of the nanocomposites when organoclay filler were added in the PLA/PP blends. All samples were cut and dried in oven for 24 hours at 70°C. The samples were weighed by using electronic weight balance to record the dry weight of samples. Then, all samples were submerged in distilled water and immersed for 24 hours. The samples were taken out for weight measurement and wiped with tissue to remove water on the sample’s surface. The weight gain percentage were calculated using equation 1.

\[
\text{Water uptake \%} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100
\]

For thermal analysis, differential scanning calorimetry (DSC) analysis were conducted by using Netzsch DSC 200 F3 to study the thermal behaviour of the composites. The samples weight of 8-10mg were heated from 30°C to 250°C under nitrogen atmosphere with the heating rate of 10°C/min and then held at this temperature for 5 min before proceed to second heating process in order to remove the thermal history and to ensure the materials melted uniformly. Then the samples heated again to 250°C at the same heating rate under nitrogen atmosphere for the second heating process. The glass transition temperature (Tg), crystallization temperature (Tc) and melting temperature (Tm) were determined and recorded at the heating curves.

Meanwhile for morphological analysis was done to analyse the dispersion of organoclay. The fracture surface of samples was observed by using x-ray diffraction (XRD) to analyze the fracture behaviour of nanocomposite. All datas were recorded by using XRD machine (PANalytical). The diffractometer were scanned in 20 ranges from 0° until 40°. The peaks were plotted and analyzed.

3. Results and discussion

3.1. Water absorptions

Water absorptions refer to the immersion of nanocomposites samples in the dionized water at room temperature. All the samples were immersed in water for 10 days. Figure 1 shows the percentage of water uptake for all samples at different compositions. The organoclay is hydrophilic properties which is easier to absorb water. This can be observed when the organoclay added at 1% by weight, the percentage of water uptake was increased. Based on the graph, organoclay at 3 wt.% has high percentage of water uptake as compared to the other compositions. As we can observed that when the organoclay loading added above than 5 wt.%, the percentage of water uptake were decreased. This is might be due to the tortuosity pathway of the organoclay in the composite systems which is hindered the water fusion in the nanocomposites. Besides that, the decreased percentage of water uptake might be due to the presence of organoclay which act as nucleating agent could develop the nucleation efficiency and the crystallinity in nanocomposite system then cause the water absorption is less in the composites [6].
Figure 1. Percentage of water absorptions in nanocomposites of PLA/PP and PLA/PP-C at different loading

3.2. Thermal properties
Differential scanning calorimetry (DSC) were analysed to study the thermal behaviour of nanocomposite. The table 1 shows the tabulated data for glass transition temperature (Tg), melting temperature (Tm) for second heating process which has two peaks Tm₁ and Tm₂ besides crystallization temperature (Tc) during cooling process for this PLA/PP blends with and without organoclay. MAgPP has no effect on the Tm of PLA material. Based on the table 1, Tg₁ values were no significant changes for all compositions even organoclay was added.

Table 1. The thermal properties of PLA/PP and PLA/PP-Clay nanocomposites.

| Sample        | First heating Tg₁ (°C) | Second heating Tg₂ (°C) | Tm₁ (°C) | Tm₂ (°C) | Tc (°C) |
|---------------|------------------------|-------------------------|----------|----------|---------|
| PLA/PP        | 62.3                   | 54.1                    | 139.9    | 149.7    | 113.9   |
| PLA/PP-C1     | 62.2                   | 51.8                    | 143.6    | 148.2    | 111.3   |
| PLA/PP-C3     | 62.6                   | 51.8                    | 136.7    | 147.4    | 111.6   |
| PLA/PP-C5     | 62.6                   | 51.6                    | 146.6    | 161.3    | 111.5   |
| PLA/PP-C7     | 61.9                   | 49.1                    | 143.1    | 159.5    | 112.3   |

Figure 2 and 3 shows the DSC curve for first and second heating respectively. It was observed that, during the second heating the Tg₂ was shifted to lower temperature from 54.1°C to 51.8°C. The molecular weight loss during the processing due to the polymer chains composition has more free volume compared with neat matrix exhibit the decreasing of Tg in second heating process [7]. Double melting temperature Tm₁ and Tm₂ can clearly seen in both figure 3. It caused by the formation of different structure of crystal which is at high temperature (α-form) and lower temperature (β-form) by the high content of PLA in the composites [8]. The α-form corresponds to most common polymorph and β-form is the imperfect crystal structure. The formation of two peaks at melting temperature also might be due to the corresponds for melting temperature of PLA and also PP material. As shown in
figure 3, Tm values for nanocomposite were slightly decreased when organoclay was added at 1 wt.% and 3 wt.% because the presence of organoclay could induced the crystallization ability of PLA matrix [9].

![Figure 2. DSC curve first heating for PLA/PP and PLA/PP-C at different loading](image1)

![Figure 3. DSC curve second heating for PLA/PP and PLA/PP-C at different loading](image2)

DSC cooling curve for PLA/PP and PLA/PP-C nanocomposites are shown in figure 4. The Tc was shifted to lower temperature when organoclay loading was added at 1 wt.% into PLA/PP from 113.9°C to 111.3°C. This might be due to the crystallization happened too slow in PLA matrix to form crystallinity because nanocomposites rapidly cooled from the molten state [10]. The reduction of Tc also can be affected by the compatibilizer which is restricted the formation of crystal of PLA and crystallization process of nanocomposites [11].

![Figure 4. DSC curve for cooling of PLA/PP and PLA/PP-C at different loading](image3)
3.3. Morphological properties
The level of exfoliation and intercalation can be analysed by using XRD analysis. Figure 5 shows the X-ray diffraction pattern of pure organoclay silicate and also the combination of PLA/PP-C with various loading of 1, 3 and 7 wt.%. As shown in the figure 5, actually there were two peaks were found in pure organoclay at 2θ reading under 40°. The diffraction peak which clearly can be seen were at 2θ=7.34° which corresponds to d-spacing 12.05Å and at 2θ=20.26° (4.39Å). In the PLA/PP-C nanocomposites, the diffraction peaks were shifted to the lower degrees of 2θ. The peaks were recorded at 17.68° (5.02Å) for 1 wt.%, 17.45° (5.08Å) for 3 wt.% and 17.5° (5.07Å) for 7 wt.% of organoclay loading as compared to pure organoclay at diffraction peak 2θ=20.26°. This might be due to the factor of intercalation happened with polymer material chains in the clay galleries [12]. The disappearance peak at 2θ below than 10° for the PLA/PP nanocomposites for 1, 3 and 7 wt.% of organoclay might be due to the exfoliated or intercalated structure of organoclay silicates in the specimens.

![Figure 5. XRD images of PLA/PP-organoclay nanocomposites with (a) 1 wt.% organoclay (b) 3 wt.% organoclay and (c) 7 wt.% organoclay.](image)

4. Conclusions
It was found that, the percentage of water absorptions were increased when organoclay was added at 1 wt.% and when the organoclay loading increased until 7 wt.%, the percentage were decreased. This happened due to the formation of turtuosity pathway of layered silicate which hindered the diffusion of water in the nanocomposites. Meanwhile, in DSC analysis there are formation of two peaks at melting temperature for all compositions. These peaks corresponds to the melting temperature for PLA and PP materials. The crystallization temperature slightly decreased after addition of organoclay. This might be due to the crystallization happened too slow in PLA matrix to form crystallinity because nanocomposites rapidly cooled from the molten state. For XRD analysis, it was found that the reading of 2θ shifted from 20.26° for pure organoclay to the lower degree for organoclay loading at 1, 3 and 7 wt.%. The disappearance peak for all compositions under 10° might be due to the exfoliated and intercalated structure for the organoclay in the PLA/PP blends. In order to develop better behaviour of nanocomposites, it is suggested that the optimum amount of organoclay suitable to be used is within the range 1 until 5% by weight.
5. References

[1] Olalekan S T, Muyibi S A, Shah Q H, Alkhatib M F, Yusof F and Qudsieh I Y 2010 Improving the Polypropylene-Clay Composite Using Carbon Nanotubes as Secondary Filler Energy Res. J 1 68–72

[2] Müller K, Bugnicourt E, Latorre M, Jorda M, Sanz Y E, Lagaron J M, Miesbauer O, Bianchin A, Hankin S, Bolz U, Perez G, Jedinszki M, Linder M, Scheurerer Z, Castello S and Schmid M 2017 Review on the Processing and Properties of Polymer Nanocomposites and Nanocoatings and Their Applications in the Packaging, Automotive and Solar Energy Fields Nanomaterials 74

[3] Uddin F 2018 Montmorillonite: An Introduction to Properties and Utilization Web of Science

[4] Mohsen A H and Ali N A 2018 Mechanical, Color and Barrier, Properties of Biodegradable Nanocomposites Poly(lactic acid)/Nanoclay J. Bioremediat. Biodegrad. 9

[5] Afroz R, Rahman A, Masud M and Akhtar R 2016 The Knowledge, Awareness, Attitude and Motivational Analysis of Plastic Waste And Household Perspective in Malaysia Environ. Sci. Pollut. R

[6] Kord B, Hemmali A H and Ghasemi I 2011 Properties of PP / wood flour / organomodified montmorillonite nanocomposites Wood Sci. Technol. 45 111–19

[7] Perez J G, Nascimento L, Bou J J, Urquiza E F, Santana O O, Carrasco F and Maspoch M Ll 2010 Influence of Crystallinity on the Fracture Toughness of Poly (lactic acid)/Montmorillonite Nanocomposites Prepared by Twin-Screw Extrusion J. Appl. Polym. 120 896-905

[8] Fukushima K., Tabuani D and Camino G 2009 Nanocomposites of PLA and PCL based on montmorillonite and sepiolite Mater. Sci. Eng. C 29 1433–41

[9] Luo Y, Liu H Y, Zhang G Z and Qu J P 2017 Morphological and thermal properties of PLA / OMMT nanocomposites prepared via vane extruder Mater. Sci. Eng. 213

[10] Fukushima K, Tabuani D, Arena M, Gennari M and Camino G 2013 Effect of clay type and loading on thermal , mechanical properties and biodegradation of poly (lactic acid) nanocomposites React. Funct. Polym. 73 540–49

[11] Jamshidian M, Tehrany E A, Imran M, Jacquot M and Desobry S 2010 Poly-Lactic Acid: Production, Applications, Nanocomposites, and Release Studies Comp. Rev. Food Sci Food Saf. 9 552–71

[12] Salehiyan R, Ray S S, Bandyopadhyay J and Ojijo V 2017 The Distribution of Nanoclay Particles at the Interface and Their Influence on the Microstructure Development and Rheological Properties of Reactively Processed Biodegradable Polylactide/Poly(butylene succinate) Blend Nanocomposites Polymers 350

Acknowledgements

The authors would like to thank Universiti Teknologi MARA, Malaysia and the Institute Research Management & Innovative (IRMI) for the support for this research. This project was funding under the Fundamental Research grant Scheme (FRGS), 600-IRMI/FRGS 5/3 (070/2019).