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Study on water absorption and biodegradation of polylactic acid/poly (butylene adipate-co-terephthalate) nanocomposite

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Abstract : The combination of Polylactic acid (PLA), a hydrophobic polymer, with polybutylene adipate co-terephthalate (PBAT), a hydrophilic polymer, results in a change in the properties of PLA from hydrophobic to hydrophilic. This was confirmed by testing water absorption properties of PLA/PBAT blends with different PBAT. The introduction of unmodified (MMT) and organomodified monmorillonite (OMMT) changed the hydrophilic-hydrophobic profile of the sample. PLA/PBAT nanocomposite was prepared by blending PLA/PBAT (85:15) with 1% introduction MMT and different type OMMT. The results revealed that the water absorption and biodegradation properties increase in

the present of MMT. Water absorption rate are dependable on the nature of nanocomposites (hydrophilic-hydrophobic) and tortuous path created in the present of silicate layer. Modification of MMT with different class of ammonium structure influenced the hydrophobicity of the nanocomposites. TEM pictured the increased tortuous path present in PLA/PBAT nanocomposite.

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Keywords : Polylactic acid/Poly (butylene adipate-co-terephthalate) nanocomposite; Water absorption; Biodegradability.

INTRODUCTION

Though petrochemical-based polymer has benefited the mankind in many ways, the use of non-biodegradable plastic materials is a cause for concern on earth's ecosystem. Incineration of plastic wastes produces a large amount of carbon dioxide and other toxic gases that contribute to global warming. Limited suitable landfill sites compounded the problem faced by the already fragile ecosystem.

To counter this problem, scientists have been researching and developing renewable and environmentally friendly polymeric materials (biodegradable polymers). These polymers are meant for use in short-term packaging and disposable application.

Biodegradable polymers are plastics capable of being decomposed by microorganism to become a simple mineral. Most of biodegradable polymers originate naturally from plant. Most of biodegradable polymers are originate naturally from plant. However, there is a class

of biodegradable polymer derived from petroleum source^[1].

PLA is linear aliphatic polyester synthesized through ring-opening polymerization of lactides or corn starch fermentation. It existed as enantiomers: L- and D-lactic acid^[1,2]. PLA is found to degrade through a two-step process. First, under an appropriate temperature and humidity, the high molecular weight polyester chain hydrolyses to lower molecular weight oligomers. Next, microorganisms convert the low molecular weight components to carbon dioxide, water and humus^[2].

Even as a biodegradable polymer, PLA has high mechanical properties, thermoplastic process ability and biological properties such as biocompatibility and biodegradability, all of which are crucial for industrial applications. Efforts to modify PLA to have a certain characteristics according to demanded properties^[3,4] have been successful. PBAT is an example of fully biodegradable aliphatic-aromatic copolyester where, with the aid of natural occurring enzyme^[2], it has the ability to degrade within a few weeks. Rasquez reported that PBAT polymer owes its biodegradability to butylene adipate group and its stability and mechanical properties to terephthalate^[5].

Polymer blending is widely used to produce new materials with different properties currently unattainable because of its practical and economical production method^[6]. Blending PLA with other polymers can significantly modify its water absorption and degradation rate. Alternatively, PLA's water absorption and biodegradability properties can be modified via the introduction of silicate layers using MMT. Hydrophilicity is a common feature of silicate layer due to the existence of water molecules. Development of polymer-layered silicate has drawn significant research interests in recent years because of its effectiveness in improving PLA properties^[7].

EXPERIMENTAL

Materials

In this study, PLA 4042D and PBAT (Ecoflex FBX 7011) were respectively acquired from USA Natureworks LLC, Minnetonka USA and BASF Plastic Technologies USA. The Sodium Montmorillonite (Na-MMT) with cation exchange capacity of 119 meq/100 g clay was obtained from Kunimine Ind. Co. Japan. Sur-

factant used was octadecylammonium (ODA) and dimethyl dioctadecyl ammonium (DDOA). ODA was brought from Merck Schuchardt OHG, Hohenbrunn, Germany whereas DDOA from Acros Organic, New Jersey USA. The commercialized clay used was Closite 20A (C20A) from Southern Clay, USA.

Preparation of PLA/PBAT blends nanocomposite

The organoclay was prepared according to the published method with slight modification^[8-10] in a 5000 ml beaker equipped with mechanical stirrer and thermometer. The beaker filled with 600 ml distilled water was heated to 80 °C and 20.00 g of Na-MMT was slowly added. Continuous stirring was maintained at 200 rpm for one hour.

Surfactant of ODA was prepared by adding 13.276 g ODA into 300 ml distilled water, followed by 4.8 ml concentrated hydrochloric acid. Once ready, the surfactant was added into hot montmorillonite dispersion with continuous stirring for another one hour. The resultant white precipitate was collected using suction filtration.

To remove the ammonium salt residue absorbed into the clay, the precipitate was washed with 3000 ml of hot distilled water. This process was repeated until no chloride ion can be detected in the filtrate using 0.1 N AgNO₃ as the indicator. The ODA-MMT was subsequently placed in a vent oven at 60 °C for 24 hours for drying. Next, the ODA-MMT was ground in a mortar and later, sieved into 75 µm size. ODA-MMT was stored in an airtight container to prevent moisture absorption.

Similar method was carried out to prepare modified montmorillonite DDOA. The DDOA solution was prepared by adding 32.00 g DDOA into 300 ml of distilled water followed by 4.8 ml of concentrated hydrochloric acid. In this report organomodified montmorillonite refers to OMMT.

PLA/PBAT nanocomposites with different MMT and OMMT were prepared through melt blending technique. The starting materials (PLA, PBAT, Na-MMT, DDOA-MMT, ODA-MMT and Closite 20A) were dried before weighing. The ratio of both PLA/PBAT used was 85/15 and the compounding of organoclay was 1.0 wt%. The materials were premixed before loaded into mixing chamber, which was already heated and stabilized at 180 °C. The mixture was blended at 180 °C, 50 rpm rotor speed for 6 minutes. Blended

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PLA/PBAT went through the same preparation method but without the addition of MMT or OMMT.

Next the compression moulding was carried out by preheating the sample at 180 °C for 2 minutes followed by full pressed at 110 kg/cm² for 8 minutes. The sample was left to cool at room temperature for 8 minutes under the same pressure to produce the sample sheet with dimension of 150x150x1 mm.

CHARACTERIZATION

Water absorption test

The moulded samples (size 3 cm x 3 cm x 0.1 cm) were immersed in water at room temperature. They were then taken out at specific time intervals and gently blotted with paper towel to remove surface excess water before weighing. The percentage of water absorbed was calculated using the formula below:

$$\% \text{ of water absorbed} = \frac{M_x - M_o}{M_o} \times 100\%$$

where, M_x and M_o indicate the weights of the collected sample and the initial weight of the sample respectively.

Biodegradable test

The percentage of weight loss represents the percentage of sample biodegradability. Mounded samples (size 3 cm x 3 cm x 0.1 cm) were then laid at a depth of 30 cm in the ground soil within the compound of the Faculty of Science, Universiti Putra Malaysia. The samples were later collected at a specific time intervals, gently rinsed with distilled water and blotted with paper towel to remove surface dirt. Samples were dried until the weight is constant indicating no moisture effect. These processes were repeated at several time intervals. The percentage weight loss was calculated using the formula below:

$$\% \text{ of weight loss} = \frac{W_x - W_o}{W_o} \times 100\%$$

where, W_x and W_o indicate the weights of the collected sample and the initial weight of the sample respectively.

Transmission electron microscopy

The nanoscale structure of the nanocomposites was examined by means of a high resolution TEM

(Hitachi H-7100), operated at an accelerating voltage of 100 kV. The ultrathin sample was prepared by dissolving 0.50 g of the nanocomposite into 100 ml chloroform and one drop of the dissolved solution was transferred onto a 200-mesh copper grids.

RESULTS

Water absorption nanocomposites

The water uptake in polymer may affect its mechanical properties, degradability, and dimensional stability. Water exposure and uptake may decrease the life of a polymer due to hydrolysis and micro crack formation^[11].

The percentages of water absorption for PLA/PBAT blends are shown in TABLE 1. From the result, pure PLA shows the lowest percentage of water absorption whereas PBAT show the highest percentage of weight gained. As more PBAT is blended with PLA, (5w% PBAT, 15w% PBAT and w% 25PBAT) the percentage of water absorbed increases. Highest percentage of water absorbed was PLA blending with 25wt% PBAT which is at 2.94% after 16 days.

TABLE 1 : Percentage of water absorbed for PLA/PBAT blends with various amount of PBAT

Sample	Time (days)				
	0	2	4	8	16
Neat PLA	0	1.11	1.15	1.15	1.15
95PLA/5PBAT	0	1.18	1.27	2.01	2.01
85PLA/15PBAT	0	1.22	2.82	2.84	2.84
75PLA/25PBAT	0	1.25	2.91	2.93	2.94
Neat PBAT	0	1.37	3.00	3.15	3.15

This trend was to be expected since PBAT is hydrophilic (containing more polar group) while PLA (aliphatic polyester) is hydrophobic^[12,13]. This phenomenon is a consequence of increased difficulty in the formation of polymer chain arrangements due to the greater amount of PBAT present. In addition, the hydrophilic character of PBAT causes poor adhesion to the hydrophobic PLA^[14].

Natural clay (MMT) is known form hydrogen bond with water. These water was located between MMT clay galleries. Its hydrophilic feature may influenced the water absorption of a sample when MMT blended together with PLA/PBAT. TABLE 2 shows the weight

gained for PLA/PBAT blended with 1.0 wt% MMT and OMMT (ODA-MMT, DDOA-MMT and C 20A). The result revealed the addition of MMT gives the highest percentage of water absorbed by the PLA/PBAT matrix which is 3.12% after 16 days. The introduction of OMMT decreased the amount of water uptake into the matrix when compared with the introduction of MMT. Among all OMMT, C 20A shows the lowest amount of water uptake which is 2.40% after 16 days. The amount of water absorbed into PLA/PBAT matrix increases following a pattern C 20A < DDOA-MMT < ODA-MMT.

TABLE 2 : Percentage of water absorbed for PLA/PBAT incorporation with different type of clay

Sample	Time (days)				
	0	2	4	8	16
PLA/PBAT	0	1.22	2.82	2.84	2.84
PLA/PBAT/Na-MMT	0	1.32	3.11	3.12	3.12
PLA/PBAT/ODA-MMT	0	1.20	2.47	2.50	2.50
PLA/PBAT/DDOA-MMT	0	1.21	2.43	2.44	2.44
PLA/PBAT/C 20A	0	1.21	2.40	2.40	2.40

Alkylammonium ion enables the interior clay surface conversion from hydrophilic to hydrophobic and increases the layer distance^[15]. C 20A structure is 4° ammonium salt structure with hydrogenated tallow (65% C₁₈, 30% C₁₆, 5% C₁₄). DDOA-MMT is a 3° of ammonium salt with the formula structure of (CH₃(CH₂))₁₇N⁺(CH₃)₂ and ODA-MMT is a 1° ammonium salt with the formula structure of C₁₈H₃₇N⁺H₃. Generally, modification of MMT with 4° ammonium structure makes the OMMT more hydrophobic compared to 1° ammonium salt.

Other factor affecting the water uptake in the case of nanocomposites was the increased in tortuous path (Figure 1). It is possible that the decrease in the free path of water molecules leads to the lower water uptake in the samples^[16].

Biodegradability

The weight loss of PLA/PBAT blended with 1.0 wt% of Na-MMT, ODA-MMT, DDOA-MMT and C 20A is presented in TABLE 3. The test indicates that twelve weeks are not enough to make the entire sample degraded.

The incorporation of MMT into PLA/PBAT matrix increases both the biodegradation and water absorption

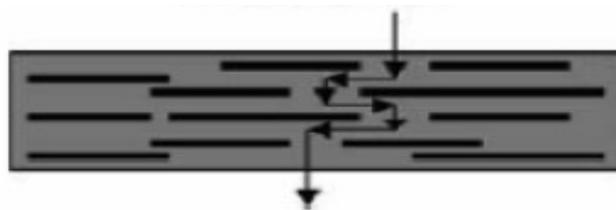


Figure 1 : Tortuous path in layered silicate nanocomposites^[9]

TABLE 3 : Percentage of weight loss for PLA/PBAT incorporation with different type of clay

Samples	Time (weeks)				
	0	3	6	9	12
PLA/PBAT	0.00	2.33	3.32	6.69	8.76
PLA/PBAT/Na-MMT	0.00	2.59	3.62	6.95	9.02
PLA/PBAT/ODA-MMT	0.00	2.13	3.16	5.65	7.96
PLA/PBAT/DDOA-MMT	0.00	2.07	3.07	5.23	7.62
PLA/PBAT/C 20A	0.00	2.00	2.96	4.81	7.41

rates. The 9.02% weight loss after 12 weeks is the highest recorded of all samples. On the other hand, the addition of OMMT tends to reduce biodegradation rate in the samples. At 7.41% after 12 weeks, C 20A shows the lowest biodegradation rate between all OMMT. The similar observation in water absorption may influenced biodegradability of polymer was discussed in the previous study^[14,17].

These findings suggest the rate of degradation of PLA/PBAT nanocomposites was subjected to the amount of water absorbed. The biodegradation of PLA involves four main phases. The four phases was water absorption, ester cleavage and formation of oligomer fragments, stabilization of oligomer fragments and diffusion of soluble oligomer by bacteria^[18].

The incorporation of modified MMT in nanocomposites results in a different mode of attack on the PLA component of the sample. Since PLA is aliphatic polyester, the attack disrupts of some ester linkages due to the presence of hydroxyl group^[19] which may influence the degradation rate. PLA/PBAT's greater biodegradation rate may have been caused by the same factor that leads to its higher water absorption.

TEM study

An objective of TEM analysis was to study the clay distribution inside PLA/PBAT. Clear distribution refers to the existence of good interaction between the organoclay and the matrix. It might due to the hydrogen

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bonding (Figure 2) between carbonyl group of both polymer and the hydroxyl group from the organoclay organic modifier. The number of alkyl chain in the modifier affected the hydrogen bonding between OMMT and polymer. Fukushima suggested that the fewer alkyl chain of organic modifier make $-OH$ group more available for interaction with the polymer^[20].

Figure 3 shows TEM images for PLA/PBAT/MMT/

OMMT. The dark lines represent the intersection of silicate layers while the grey background corresponds to PLA/PBAT matrix^[21]. From the images, PLA/PBAT/Na-MMT exhibits poor dispersion of clay platelets. Intercalated clay layers stack observed in addition of large clay agglomerates in TEM image for PLA/PBAT/Na-MMT. This may be attributed to the presence of strong electrostatic forces between clay layers^[21]. The

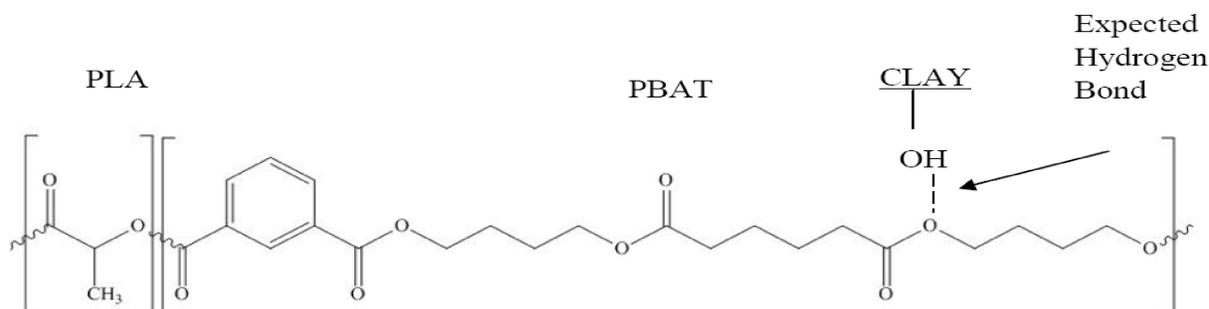
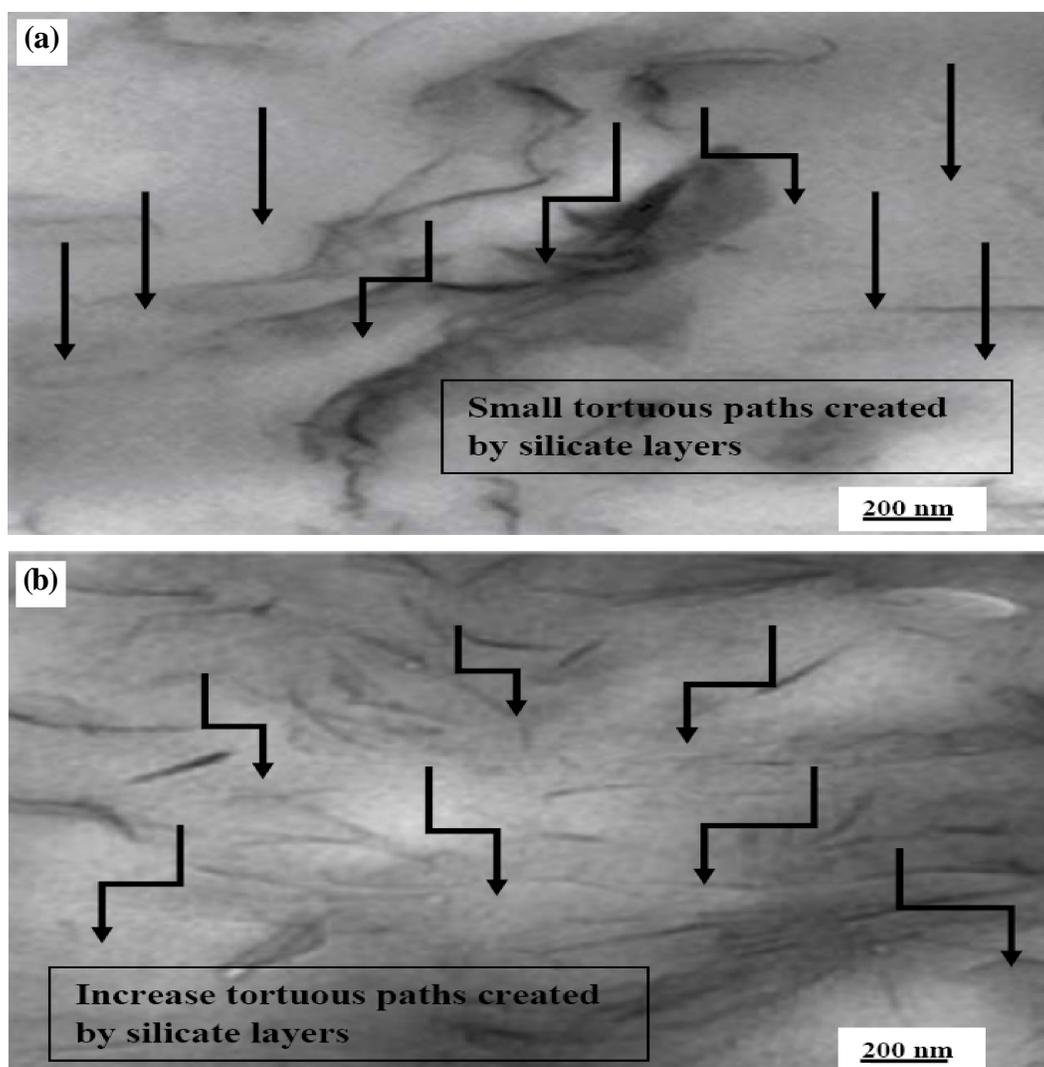


Figure 2 : Expected hydrogen bonding between the OMMT and PLA/PBAT blends



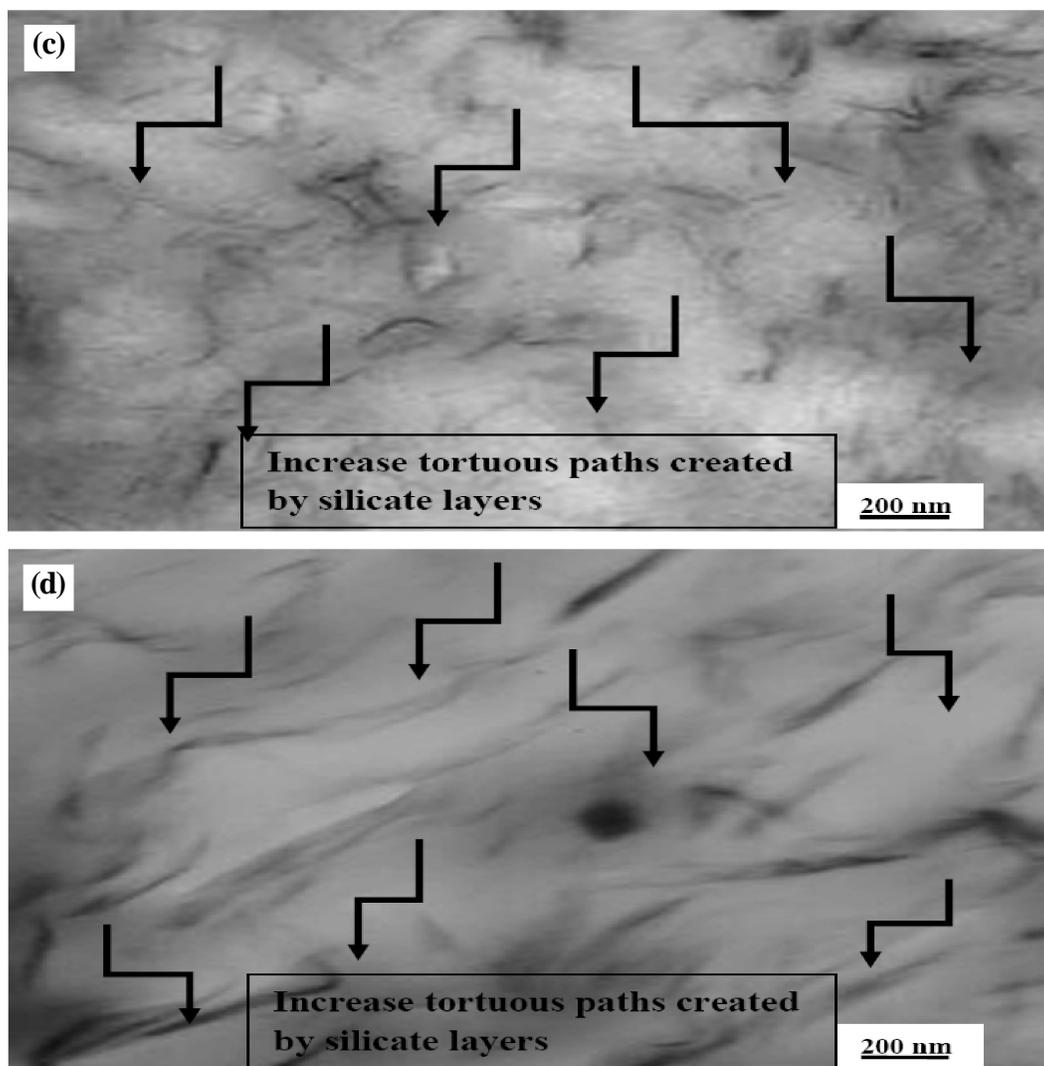


Figure 3 : TEM images for a) PLA/PBAT/MMT, b) PLA/PBAT/ODA-MMT, c) PLA/PBAT/DDOA-MMT and d) PLA/PBAT/C 20A nanocomposites at 1% clay (Magnification 10000x)

intercalated and agglomerates represent the inefficient free path. As a consequence, water will be absorbed more in the PLA/PBAT/MMT.

For PLA/PBAT/ODA-MMT, PLA/PBAT/DDOA-MMT and PLA/PBAT/C 20A, the absence of aggregates confirms the high exfoliation of the layer silicate. Increase in the number of alkyl group of organoclay results in an increased in interlayer spacing. The larger initial layer spacing may lead to easier exfoliation since attraction between platelets is reduced^[22]. According to Fornes, this situation implies that the diffusion of polymer chains inside clay galleries is less hindered due to the increased spacing which eventually leads to improved exfoliation. Improved exfoliations represent an increase in tortuous path in PLA/PBAT/OMMT and further reduce the nanocomposite's water absorption^[23].

CONCLUSION

This paper reports on the findings of the relationship between water absorption and biodegradation rate of PLA/PBAT nanocomposite. Blending PBAT to the PLA increases water absorption of the samples due to the high polarity of PBAT. Poor adhesion between PLA and PBAT causes change in sample behaviour from hydrophobic to hydrophilic as PBAT content is increased. Water absorption and biodegradability of PLA/PBAT nanocomposite increased as the MMT was introduced due to the hydrophilic nature of MMT and the small tortuous path present in the samples. Increase in water uptake in the sample disrupted some ester linkages present in PLA and influenced the samples degradation

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rate. However, addition of OMMT has resulted in reversed properties. Addition of OMMT decreases the water uptake in the samples due to the hydrophobic nature of OMMT and an increased tortuous path. TEM revealed the silicate layers (black line) formed tortuous path which are present in the samples after the addition of MMT and OMMT.

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