Structure and properties of organically modified poly(butylene adipate-co-terephthalate) based nanocomposites

A Rasvida1,2, K Fukushima3, M-C Yang2
1Department of Materials and Metallurgical Engineering, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember (ITS) Surabaya, Indonesia
2Department of Materials Science and Engineering, National Taiwan University of Science and Technology, 43, Sec. 4, Keelung Rd, Taipei, Taiwan 106

E-mail: amaliyarasyida@gmail.com; amaliya@mat-eng.its.ac.id

Abstract. Poly (butylene adipate-co-terephthalate (PBAT) nanocomposites were prepared by melt blending PBAT with 5 wt.% of modified or unmodified montmorillonites (MMT). The effect of the presence of organic modifiers in MMT on the morphological, crystalline, thermal, and mechanical properties of PBAT nanocomposites was evaluated. The dispersion and distribution of the clays were studied by using wide angle X-ray analysis (WAXS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) analysis. Materials characterization techniques included: contact angle measurements, differential scanning calorimetry (DSC), thermogravimetry (TGA) and surface hardness analysis. As general results, nanocomposites exhibited different level of clay dispersion depending on the clay/organic modifier’s chemical affinity with the polymer. Contact angle measurements show increases in the hydrophobicity level of PBAT based CLO30B, this could depict its high potential for packaging applications. In addition, Thermal analysis showed that clays partially hindered kinetics and extent of PBAT crystallization on cooling. In general, thermal properties of PBAT were improved by addition of clays, for a barrier effect of the nanoparticle towards polymer decomposition products ablation. In parallel, addition of clays led to enhancements in polymer hardness. These properties were found to be apparently influenced by clay dispersion level and chemical compatibility between the organic modifier and polymer matrix.

1. Introduction

In the last decade, biodegradable polymers have received much attention because of their wide range of promising applications in packaging, agriculture, and biomedical fields. The most often used biodegradable polymers have been polylactide (PLA), polyhydroxyalkanoate (PHA), polycaprolactone (PCL), and poly(butylene adipate terephthalate) (PBAT) [1]. Among these, PBAT has been widely studied due to its high commercial availability, biodegradability, and aromatic structure. The aromatic structure brings to this polymer an excellent pattern of physical properties such as: high performance properties and strong resistance to hydrolysis, and to bacterial and fungal attack [2]. Moreover, PBAT is flexible and has a higher elongation at break than most biodegradable polyesters, such as PLA to render them more suitable for packaging films [3]. The main limitations toward its wider industrial applications are its relatively insufficient thermal and mechanical resistance. However, it has been found that the above drawbacks can be overcome through filling techniques. In this way, the use of nano-sized
fillers can potentially confer to polymer matrices multifunctional enabling properties (magnetic, optical, thermal, and mechanical properties) when compared to conventional polymer formulations [4–7].

Among the various nanoparticles studied, montmorillonites (MMT) have been one of the most studied layered silicates for the preparation of polymer nanocomposites due to their high availability, versatility and respectability towards the environment [8]. These nanoparticles are phyllosilicate clays of the 2:1 type. In their unmodified form usually contain Na⁺ or K⁺ ions [9], and they are only miscible with hydrophilic polymers [10]. Consequently, in order to increase their compatibility with polymers, it is sometimes necessary to convert the normally hydrophilic silicate interlayer environment into an organophilic one, for instance by ion-exchange reactions of the inter-gallery inorganic cations with primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations [11], thus making possible high interfacial interactions between these organic modified clays and the polymer matrix.

Only few articles reported studies of PBAT/clay nanocomposites. Someya et al., (2004,2005) [12,13] obtained certain level of clay intercalation and exfoliation in several compositions of PBAT/clay nanocomposites prepared by melt intercalation. Chivrac et al., (2006, 2007) [14,15] have tested some commercial montmorillonites in PBAT compositions, revealing that higher intercalation degrees could be obtained by using particular preparation techniques and that the stiffness of PBAT matrix could increase with clay content due to the important interactions between PBAT and nanoparticles. In a recent work [16-18], we studied the morphology and properties of PBAT nanocomposites prepared by melt-mixing and by using different amount and types of nanoparticles including montmorillonite, fluorohectorite, and sepiolite.

The aim of this work is therefore to study whether the presence of organic modifiers can affect considerably the morphological, crystalline, thermal, and mechanical properties of PBAT. A comparative study of the properties of PBAT nanocomposites with and without any kind of clay modifier was performed in order to check whether the resulting nanocomposites could present potentially interesting properties for some industrial applications such as packaging applications.

2. Materials and Methods

PBAT (Mw = 140 kDa) with 44 mol% BT, was supplied by BASF AG (ECOFLEX* F BX 7011). Nanoparticles were supplied by Rockwood Additives Ltd. The characteristics of these clays are listed in Table 1. Nanocomposite preparation is based on our previous research [18]

Wide Angle X-ray Spectra (WAXS) were recorded at room temperature using Thermo ARL diffractometer X-tra 48 in the range 1-30° (2θ) (step size = 0.02°, scanning rate = 2 s/step) by using filtered Cu Kα radiation (λ = 1.54 Å).
Scanning electron microscopy (SEM) was carried out on the cryogenic fracture surface of the specimens using an SEM apparatus equipped with energy dispersive spectroscopy (EDS).

Transmission electron microscopy (TEM) was performed using a field emission transmission electron microscope (FE-TEM) (Philips TECNAI G2 F20) using an accelerator voltage of 120 kV. Ultrathin sections about 100 nm thick were cut with a Power TEOMEX microtome with a diamond knife and placed on a 200-mesh copper grid.

Table 1. Characteristics of nanoparticles

| Type of nanoparticle | Commercial name | Modifier structure | Notation in text |
|----------------------|-----------------|--------------------|------------------|
| Montmorillonite      | NANOFIL 116     | None               | NANO             |
| Montmorillonite\(^a\) | CLOISITE 20A    |                    | CLO20A           |
| Montmorillonite\(^b\) | CLOISITE 30B    |                    | CLO30B           |

HT = Hydrogenated linear alkyl chains: C\(_{8-18}\)

\(^a\) = Organic modifier content ca. 38 wt.% according to technical data sheet.

\(^b\) = Organic modifier content ca. 30 wt.% according to technical data sheet.

Measurements of static water contact angle were performed according to the standard procedure in an air-conditioned laboratory at 25°C. A small drop of deionized water (~7 µL) was put onto the flat sample surfaces using a syringe such that the drop volume at the surface expands.

Differential scanning calorimetry (DSC) tests were carried out using a Perkin Elmer DSC 4000, under nitrogen atmosphere at a scanning rate of 10°C/min, sample size 5-6 mg in aluminium pans. Thermal history of samples was erased by a preliminary heating-cooling cycle at 10°C/min from 20 to 200°C. The crystallinity (χ) of the polymer and nanocomposites was evaluated taking into account the amount of clay present in nanocomposites by using the following expression [19]:

\[
X = \left( \frac{\Delta H_m(t)}{\Delta H_m^0 \times \frac{\% \text{ filler}}{100}} \right) \times 100
\]

where \(\Delta H_m(t)\) is the specific melting enthalpy of the sample, \(\Delta H_m^0\) is the melting enthalpy of the 100% crystalline PBAT (114 J/g) [14] and \% filler is the weight percentage of the clay (5%).

Thermogravimetric analysis (TGA) was carried out on 10 mg samples using a thermogravimeter (TGA Q500, TA) at 10°C/min from 50 to 800 °C under air flow.
The surface hardness was determined using a Durometer Type A (PTC instruments, model 306L, ASTM 2240-85). Three readings for each sample were taken for statistical purposes.

3. Results and Discussions

3.1. Morphology

3.1.1. Wide Angle X-Ray Analysis (WAXS)

The WAXS pattern of neat PBAT was characterized by five diffraction peaks (Figure 1) observed at 2θ = 16.1°, 17.3°, 20.2°, 23.1°, and 25.0°, corresponding to the interlayer distance of 0.55, 0.52, 0.44, 0.38, and 0.36 nm respectively, and indicating a crystalline structure for PBAT. These peaks were also observed at the same intensity for PBAT nanocomposites, indicating that no significant changes in the PBAT crystal structure was obtained by nanofiller incorporation. This behavior was in agreement with previously results obtained on PBAT based nanocomposites [14,16,17], as an unimportant transcrystallinity at the nanofillers/PBAT interface upon clay addition was observed.

![Figure 1. WAXS patterns of neat PBAT and nanocomposites](image)

The WAXS patterns of NANO, CLO20A and CLO30B based nanocomposites in the lower angle range are presented in Figure 2. NANO was characterized by a single diffraction peak at 2θ = 7.0° corresponding to the basal reflection (001), and accounting for 1.3 nm interlayer distance (Figure 2a). On the other hand, CLO20A was characterized by two diffraction peaks at 2θ = 4.5° and 2.0° which corresponded to the interlayer distance 2.0 and 4.4 nm, respectively (Figure 2b) and related to the basal reflection (001) [17,19]. In parallel, CLO30B was characterized by a single diffraction peak at 2θ = 5.0°, corresponding to the interlayer distance of 1.8 nm (Figure 2c). Since the three clays had a similar chemical structure (Table 1), the higher interlayer distance found by pristine CLO20A and CLO30B as
compared to NANO could be attributed to the presence of the organic modifier between their clay platelets (Table 1).

NANO based materials showed a slight shift of the clay diffraction peak to lower angles corresponding to an increase of the interlayer distance of around 0.1 nm for nanocomposites, and indicating the obtainment of certain intercalation level in these nanocomposites without organo-modifying the nanofiller. Similar results were found by Chivracet et al., (2006) [14], obtaining intercalated-nanocomposites of PBAT with non-organo-modified nanofillers. Even more, it was also observed an almost complete disappearance of the peak for NANO based nanocomposites, suggesting extensive dispersion of the clay in the polymer matrix.

![Figure 2. WAXS patterns of pristine clays and PBAT nanocomposites with 5% of (a) NANO, (b) CLO20A, and (c) CLO30B.](image)

In the case of CLO20A based materials (Figure 2b), the main WAXS diffraction peak of CLO20A (ca. 0.6 nm) got lower after mixing with PBAT, suggesting less intercalation of the clay in PBAT. Another difference observed was a slight broadening of both WAXS peaks, indicating the possible occurrence of a disordered structure of CLO20A in PBAT.
On the other hand, CLO30B based nanocomposites (Figure 2c) exhibited a higher interaction/intercalation level with PBAT matrix. Indeed an important shift of the clay diffraction peak to lower angles was observed, corresponding to an increase of ca. 1.7 nm. Moreover, a significant decrease of the clay peak intensity was also observed in CLO30B based nanocomposites, which could account for the formation of an exfoliated/disordered structure.

3.1.2. Transmission Electron Microscopy (TEM)

Figure 3a shows that PBAT/NANO nanocomposites exhibited certain level of intercalation together with the presence of clay micro-aggregates in agreement with XRD results. It was also possible to observe the presence of single clay layers in the polymer matrix (Figure 3b). When correlating these observations with the results obtained by WAXS analysis, it was possible to conclude that the significant decrease of the WAXS peak intensity of NANO could be associated to the attainment of a disordered structure in this system by intercalation and exfoliation.

Figure 3. TEM patterns of PBAT + 5% NANO at 97 Kx of magnification: intercalated- and micro-structures (a) and exfoliated particles (b) PBAT/CLO20A (c) and PBAT/CLO30B (d) at 97Kx of magnification

Figure 3a shows that CLO20A formed micro-aggregation of the silicate layers in PBAT matrix, confirming non-extensive intercalation of this clay in PBAT as previously observed through WAXS analysis. Nevertheless, it is important to highlight that the presence of several single CLO20A layers in the polymer matrix (circles in Figure 3c) indicated the attainment of partially exfoliated nanocomposites, which could explain the broadening of the peak observed for these nanocomposites.

Figure 3d shows that PBAT/CLO30B nanocomposites exhibited a high concentration of single clay layers distributed along the polymer matrix as well as a high amount of intercalated structures of silicate particles in accordance with WAXS results.

3.1.3. Scanning Electron Microscopy (SEM)

Figure 4 shows the SEM micrographs of the fractured surfaces of PBAT and nanocomposites, revealing that all clays were highly distributed in the entire polymer matrix (see EDS images). PBAT/NANO nanocomposites (Figure 4a1 and 4a2) exhibited a good dispersion of clay particles, however some
microaggregates (ca. 5-10 μm) were still visible (circles in Fig. 4a1), in agreement with the clay aggregates observed by TEM.

In the case of PBAT/CLO20A nanocomposites, SEM images (Figure 4b) revealed the occurrence of micro-aggregation of clay particles (circles in Figure 4b1), confirming that the dispersion of this clay was less extensive in PBAT matrix, in accordance with XRD and TEM results.

![SEM and EDS images of fractured surface of PBAT/NANO (a1 and a2), PBAT/CLO20A (b1 and b2), and PBAT/CLO30B (c1 and c2).](image)

**Figure 4.** SEM and EDS images of fractured surface of PBAT/NANO (a1 and a2), PBAT/CLO20A (b1 and b2), and PBAT/CLO30B (c1 and c2).

In the case of PBAT/CLO20A nanocomposites, SEM images (Fig. 4b) revealed the occurrence of micro-aggregation of clay particles (circles in Figure 4b2), confirming that the dispersion of this clay was less extensive in PBAT matrix, in accordance with XRD and TEM results.

Figure 4c shows that PBAT/CLO30B nanocomposites exhibited no aggregates in the micron range (only very few aggregates of about 1-2 μm were observed in certain zones of the polymer matrix), in
agreement with the high dispersion of these particles previously detected by WAXS and TEM analysis. The results from WAXS, TEM and SEM pointed out that PBAT/CLO30B nanocomposites presented higher degree of dispersion and intercalation than PBAT/NANO and PBAT/CLO20A. This was probably due to higher interactions between the carbonyl groups (>C=O) of PBAT and the surface hydroxyl groups of CLO30B layers and of its organic modifier [21]. Although NANO and CLO20A also had hydroxyl groups on the surface of their silicate layers, the absence of an organic modifier in NANO as well as the absence of hydroxyl groups in the organic modifier of CLO20A (see Table 1) could be able to hinder high interactions between these clays and PBAT, resulting thus in a lower clay dispersion level than that observed for PBAT/CLO30B.

3.2. Contact Angle Measurements
Wettability can be expressed by the contact angle of a liquid on a solid substrate. Figure 5 shows the contact angle photographs and measurements obtained from PBAT and its nanocomposites. These results show that the addition of NANO and CLO20A increases the surface wettability of PBAT, especially NANO. The higher wettability level observed for PBAT nanocomposites based on NANO and CLO20A can be attributed to the presence of surface hydroxyl groups on its clay layers, making the PBAT more hydrophilic. CLO30B also presents a high concentration of hydroxyl groups on its clay layers. However, its high level of dispersion in the polymer matrix could considerably decrease the wettability level of PBAT.

![Contact angle measurements of PBAT and its nanocomposites](image)

**Figure 5.** Contact angle measurements of PBAT and its nanocomposites

In this way, the presence of highly exfoliated and intercalated layers of CLO30B into the PBAT matrix, in agreement with morphological analyses, could act as a barrier against water through the bulk material, compensating the possible higher hydrophilicity effect of CLO30B particles on PBAT matrix, thus observing no increase in the hydrophilicity of PBAT upon addition of this clay [22-23].
3.3. Differential Scanning Calorimetry (DSC)

Table 2 reports the results obtained from the DSC thermograms of PBAT and nanocomposites during cooling and second heating. The results showed that the addition of 5% of layered silicate clays in PBAT matrix decreased the temperature of crystallization ($T_c$) by 6-11°C, enthalpy of crystallization ($\Delta H_c$) by 5-7 J/g, melting temperature ($T_m$) by 1-5°C, enthalpy of melting ($\Delta H_m$) by 9-11 J/g, and crystallinity ($\chi$) of PBAT by 7-9%.

The decreases in $T_c$, $\Delta H_c$, $T_m$, $\Delta H_m$ and $\chi$ for PBAT nanocomposites indicated that the addition of 5% NANO, CLO20A and CLO30B could slightly hinder kinetics and extent of crystallization of PBAT on cooling, as well as promote the formation of largely imperfect crystals [14], which melted at lower temperatures than PBAT crystals. These last phenomena were probably caused by an increase in the polymer viscosity upon clay addition, which reduced the mobility of the macromolecular chains to the crystal growth front [16]. No particular differences in the trend of crystallization and melting were observed between nanocomposites.

| Sample              | Cooling  | Second heating |
|---------------------|----------|----------------|
|                     | $T_c^*$ (°C) | $\Delta H_c$ (J/g) | $T_m^*$ (°C) | $\Delta H_m$ (J/g) | $\chi$ (%) |
| PBAT                | 109      | 31             | 133         | 32             | 28          |
| PBAT + 5 % NANO     | 103      | 24             | 132         | 22             | 20          |
| PBAT + 5% CLO20A    | 98       | 26             | 128         | 21             | 19          |
| PBAT + 5% CLO30B    | 104      | 24             | 131         | 23             | 21          |

3.4. Thermo-Gravimetric Analysis (TGA)

Figure 6 reports the TGA curves for PBAT and nanocomposites in air. The thermal stability properties of PBAT were improved by the presence of the clays. Indeed, an increase of $T_{max}$ of PBAT ($T_{max} = 400°C$) was observed, being these increases similar for all nanocomposites ($ca. 3$-10°C). This behaviour was attributed to a barrier effect of the clay towards polymer decomposition products ablation, which enhanced the overall thermal stability of the system, as well as assisted in the formation of char during thermal decomposition, thus tending to increase the maximum weight loss temperature of PBAT [1,16].
3.5. **Surface Hardness**

Figure 7 shows the hardness measurements for pristine PBAT and nanocomposites. The addition of nanoparticles brought some enhancements in the surface hardness of PBAT. These enhancements seemed to be independent of the clay type and dispersion level, observing similar increases upon addition of all nanofillers. These increases in hardness of PBAT matrix were associated to the inherent rigid nature of clays [24] and to the general good interaction/dispersion level between these clays and the polymer. Moreover, we have reported that the presence of clays increased thermo-mechanical properties as well as compressive strength and modulus elasticity of PBAT [18].

**Figure 7.** Hardness measurements for pristine PBAT and nanocomposites

4. **Conclusions**

All nanocomposites showed different levels of clay distribution and dispersion into PBAT matrix. According to WAXS, TEM, and SEM analysis, CLO30B exhibited higher dispersion and intercalation
with PBAT than NANO and CLO20A related to higher interactions between the carbonyl groups of PBAT with the hydroxyl groups of CLO30B layers and its organo-modifier. Although NANO and CLO20A also had hydroxyl groups on the surface of their silicate layers, the absence of an organic modifier in NANO as well as the absence of hydroxyl groups in the organic modifier of CLO20A could elicit lower interactions between these clays and PBAT as compared to CLO30B.

Higher level of clay dispersion in the polymer matrix could considerably decrease the wettability level of PBAT. Concerning to industrial application, increases in the hydrophobicity level of PBAT based CLO30B could present a high potential for packaging applications, as a low hydrophilicity level is a requirement for materials with this final use.

Thermal analysis showed that there were no particular differences in the trend of crystallization and melting between nanocomposites, indicating that clay/organic modifier structure and clay dispersion level did not considerably affect the thermal properties of PBAT nanocomposites. Similar conclusions were obtained by TGA results, observing a similar improvement in the thermal stability of PBAT after addition of all nanoparticles.

The addition of all nanofillers also leaded to some enhancements in the surface hardness of PBAT which seemed to be independent of the type and dispersion level of clay, and associated to the inherent rigid nature of clays and to the general good interaction between clays and the polymer matrix.

Considering all results, it would be possible to predict a possible wide range of industrial applications for these PBAT based nanocomposites (such as packaging), however, it is important to consider that depending on the final use of these nanocomposites the organic modifier structure and clay dispersion level in the polymer matrix could play or not a key role in the desired properties to achieve for some determined used.

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References

[1] Sinha Ray S, Bousmina M 2005 Progress in Mater. Sci. 50 962-1079.
[2] Li F et al 2007 Polym. Degrad. Stab. 92 1053–1060.
[3] Bordes P et al 2009 Prog. Polym. Sci. 34 125–155.
[4] Qin X Y et al 1999 Nanostruct. Mater. 11 259–270.
[5] Ferrari M 2005 Nat. Rev. Cancer 5 161–171.
[6] Vasir J K et al 2005 Curr. Nanosci. 1 47–64.
[7] Webster T J et al 1999 Biomaterials 20 1221–1227.
[8] Sinha Ray S, Okamoto M 2003 Progress in Polym. Sci. 28 1539 - 1641.
[9] Krishnamoorti L et al 1996 Chem. Mater. 8 1728.
[10] Webster T J et al 2000 Biomaterials 21 1803–1810.
[11] Utracki L A et al 2007 Polym. Adv. Technol. 18 1.
[12] Someya Y et al 2005 J. Appl. Polym. Sci. 95 386–392.
[13] Someya Y et al 2004 J. Appl. Polym. Sci. 91 1463–1475.
[14] Chivrac F et al 2006 J. Polym. Environ. 14 393–401.
[15] Chivrac F et al 2007 J. Polym. Sci. Polym. Phys. 45 1503–1510.
[16] Fukushima J et al 2012 Mater. Sci. and Engineering:C 32 1331 - 1351.
[17] Fukushima K et al 2013 J. Polym Res 20 302
[18] Fukushima K et al 2013 Appl. Clay Science 80-81 291-298
[19] Fukushima K et al 2009 Mater. Sci. and Eng. C 29 1433-1441.
[20] Mohanty S, Nayak S 2009 Int. J. Plastics Technol. 13 163-185.
[21] Mohanty S, Nayak S 2010 Int. J. Plastics Technol. 14 192-212.
[22] Alexandre B et al 2009 J. Membrane Sci. 328 186-204.
[23] Anadão P et al 2010 Appl. Clay Sci. 48 127-32.
[24] Ramanand A J, Badal D 2009 Reinforced Plastic and Composite 28 343.