Biodegradable Polymer /Clay Nanocomposites Based on Poly(Butylene Adipate-co-Terephthalate) and Poly(Lactic Acid)

Mahin Shahlari and Sunggyu Lee
Department of Chemical and Biological Engineering
Missouri University of Science and Technology, Rolla, MO 65409, U.S.A.

Abstract

Poly(butylene adipate-co-terphthalate) (PBAT) is a biodegradable polymer with high ultimate elongation but low modulus. This paper demonstrates that the addition of nano-sized clay can improve the modulus without significantly decreasing the tensile strength and biodegradability of the PBAT , while offering enhanced blendability with a rigid biodegradable polymer as a conceivable means to improve the PBAT's modulus.

Poly(butylene adipate-co-terephthalate) was melt mixed with 3 wt.% and 5 wt.% Cloisite 15A which is organically modified Montmorillonite. This process resulted in nanocomposites with higher moduli than those of the neat PBAT samples. A further increase in the modulus of the PBAT was achieved by blending it with poly(lactic acid) (PLA) in addition to Cloisite 15A. Samples containing 10, 20, or 50% PLA and 5 % clay were melt compounded with a twin screw extruder. The samples were then prepared as films and injection molded parts. The morphologies of the blends were examined using scanning electron microscopy (SEM), and the thermal properties of the blends were tested using Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analyzer (TGA). X-Ray Diffraction (XRD) was used to investigate the intercalation and dispersion of clay layers in the polymer matrix.

The addition of 5 wt. % and 3 wt. % Cloisite 15A increased the Young's modulus and flexural modulus of PBAT by 57.5% and 36.5%, respectively. DSC results revealed slight changes in the melting temperature of PBAT nanocomposites but significant changes in PLA melting and cold crystallization upon presence of clay particles in the blend. According to the XRD results, the clay layers were intercalated in both the PBAT and the PBAT and PLA blend. Finally, the addition of clay to the PBAT and PLA blend decreased the PLA phase domain size significantly, thus providing morphological evidence for enhanced compatibility.

Introduction

Methods for modifying biodegradable plastics and expanding their application without adversely affecting the biodegradability of the material are increasingly important in the world intent on the development of environmentally friendly polymeric products. Advancements in processing and modification make biodegradable plastics more capable of competing with non-biodegradable materials.

PBAT is a random copolymer of butylene adipate and Terphthalate which has shown to be fully biodegradable when composted. This polymer owes its biodegradability to butylene adiapte group and owes its stability and mechanical properties to the therphthalate part.[1] Due to the random structure of the copolymer, PBAT generally cannot crystallize to a significant degree, hence it has a wide melting peak unlike that of either the aliphatic or the aromatic homopolymers, poly(butylenb adipate) and poly(butylene terphthalate), respectively.[2]

Due to its low crystallization, PBAT has low modulus and stiffness. In order to modify these properties, this polymer has been compounded with inorganic compounds such as talc[1] and montmorillonites (MMTs) organically modified with the protonated ammonium cations of dodecylamine, octadecylamine, and N-laurydiethanolamine[3].

Recently, many researchers in both acadamia and industry have studied polymer nanocomposites containing clay. Incorporation of layered organically modified clay into thermoplastic polymer composites has caused significant improvements over neat polymers and conventional composites. Incorporation of layered silicates of clay into thermoplastic polymers could enhance mechanical properties. This process could also change barrier properties, reduce flammability and modify polymer's thermal stability.[4] Since all these unique improvements require only a very low percentage of clay (due to its high aspect ratio) the density of products made with such polymeric nanocomposites would be dramatically lower than that of products made with traditional composites which generally use more than 30% percent of inorganic materials.

MMT is one the most commonly used clays for the production of commercial clay polymer nanocomposites, An MMT with the chemical formula of $M_x(Al_4\text{-}Mg_x)Si_8O_{20}(OH)_4$ is first purified, then chemically treated. To increase the d-spacing between the layers, ion exchanging reactions are produced, and hydrocarbon groups of varying sizes are grafted on the clay layers.[5]

In this study, PBAT was compounded with silicate layers organically modified with dimethyl dehydrogenated tallow quaternary ammonium and was melt blended with polylactide (PLA). PLA is the most commonly studied[6,7,8,9,10,11,12] and relatively inexpensive bio-based, biodegradable polymer which can be produced from renewable resources such as corn starch, sugar and wheat. At room temperature, PLA is a rigid thermoplastic with very low strain at break (3.8%) and high modulus (3.4 GPa), which makes this polymer an appealing choice to increase the overall modulus of the polymer PLA/PBAT blend. Since PBAT is produced from petroleum resources, addition of PLA which is synthesized form renewable resources enhances the renewability of the final compound.

Jiang *et al.* have studied the PBAT and PLA blend, with PLA as the dominant phase.[6] Their rheological studies show that PBAT has higher elasticity and viscosity than PLA, and a shorter Newtonian region. To the best of the authers' knowledge, there has not been any published work on PLA and PBAT blend with PBAT being the dominant phase nor has any work been published on the effect of clay on this blend.

Experimental

Materials

The PLA 4042D used in this study was a product by NatureWorks LLC (United States) with 1.24 g/cm^3 as density. The PBAT was a DuPont product marketed as Ecoflex® with mass density of 1.25g/cm^3 and melt flow rate of 2.5 to 4.9 grams per 10 min at 190 °C Cloisite® 15A were supplied by Southern Clay Products and is an MMT modified with dimethyl, dehydrogenated tallow, quaternary ammonium.

Sample preparation

Twin screw extruder was used for compounding PBAT with clay and blending it with PLA. The twin screw extruder is a Brabender model D6/2 with an L/D ratio of 7:1 and 42 diameter counter-rotating screw. The extruder temperature was controlled at 3 heating zones and the die and the temperature was at 180, 180, 190 and 190 respectively. A gravity hopper was used to feed the extruder and the feed throat was equipped with cooling channel which enabled water circulation to avoid premature melting of the pellets in the feed throat of the extruder.

Characterization

Crystallization and melting behaviors of the samples were studied using TA Instruments DSC 2010 Differential scanning calorimeter. The DSC experiments were conducted in a nitrogen atmosphere with a nitrogen flow rate of 10mL/min. The samples were initially heated to 190°C to remove any thermal history, then cooled to 35°C then reheated to 190°C with a heating rate of 10°C/min. The melting and crystallization temperature (T_m and T_c), along with heat of fusion and crystallization (ΔH_m and ΔH_c), were determined using TA universal analysis software. The samples and their replications were tested in a random order to avoid any systematic error in the results.

Scanning electron microscopy (SEM) was done using a Hitachi S 4700 FESEM at an accelerating voltage of 5KV, ultra-high resolution mode and low working distance of 3-5 mm. The samples were merged in liquid nitrogen and then fractured. Subsequently the samples were sputter-coated with gold-palladium. Although the samples were coated, low accelerating voltage was chosen to avoid charging the sample and a short working distance was adopted to assist acquiring vivid images.

For measuring tensile properties, dumbbell and rectangular samples were prepared using MI Morgan-press laboratory size injection molder. Tensile and flexural tests were conducted according to ASTM D6338 standards using an Instron 4469 Universal Testing Machine.

All XRD measurements were conducted using a Philips X-Pert Diffractometer at ambient temperature, 45 KV and 40 mA. The scanning step was 0.03 degree and time per each step was 10 seconds.

Results and Discussion

PBAT nanocomposites

X-ray diffractometry was used to investigate the state of organoclay dispersion within the polymer matrix. The XRD results are shown in figure 1. The low-angle peaks correspond to the {001} basal reflection of the silicate layers. From the angular location of the peaks and the Bragg's relation[4], the interlayer spacing, d001, of each sample were determined. These are shown in table 1. Larger d-spacing for the particles compounded with polymer, indicated that silicate layers had been intercalated by the PBAT chains.

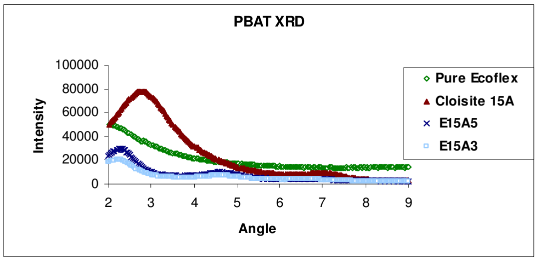

Figure 1-X-ray differaction patterns of Cloisite 15A, PBAT-3% Cloisite 15A and PBAT 5% Cloisite 15A

Table 1- XRD peak positions and interlayer spacing of Cloisite 15A and PBAT with 35 and 5%

	2Θ	d-spacing	2Θ	d-spacing
PBAT5%15A	2.245	3.932	4.65	1.901
Cloisite 15A	2.83	3.125	6.97	1.268
PBAT3%15A	2.275	3.880	4.672	1.890

The tensile properties of the PBAT samples containing 3% and 5% Cloisite 15A are shown in table 2. The addition of 3% Cloisite 15A to PBAT increased the elastic modulus of the samples by 24.89% and the flexural modulus by 15.56%. Adding 5% Cloisite 15A increased these two properties by 57.46% and 36.49%, respectively.

Table 1- Modulus of the PBAT nanocomposites containing 3% and 5% Cloisite 15A

	Modulus of Elasticity	Flexure Modulus
PBAT	13925	15045.71
PBAT 15A 3%	17390.4	17387.29
PBAT 15A 5%	21926.5	20536

The DSC results for the PBAT samples compounded with Cloisite 15A showed no significant changes in melting temperature, crystallization temperature or degree of crystallinity of the compounds compared to the pure polymer.

PBAT/PLA nanocomposites

XRD results of the blend with 90% PBAT-10% PLA and 50%PBAT-50%PLA blends containing 3% and 5% Cloisite 15A are compared the Cloisite 15A powder in Figure 2 and table 2. The angular location of the peaks and the interlayer spacing indicate better dispersion of the silicate layers in the 90% PBAT blend. This result may be due either to the higher compatibility of Cloisite 15A with PBAT or the relatively lower compatibility of the clay with PLA. The better dispersion of silicate layers in the 50% blend may also be due to the tendency of the silicate layers to remain in the interface.

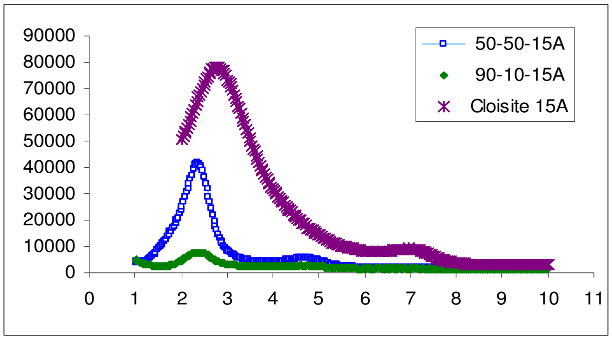

Figure 2-Xray diffraction patterns of Cloisite 15A, PBAT-3%Cloisite 15A and PBAT-5%Cloisite 15A

Table 3- XRD peak positions and interlayer spacing of Cloisite 15A in PBAT 90%-PLA 10% with 5% Cloisite 15A and PBAT 50%-PLA 50% with 5% Cloisite 15A

	2Θ	d-spacing	2Θ	d-spacing
90-10-15A5%	2.4	3.69	4.62	1.91
50-50-15A5%	2.37	3.73	4.67	1.89
Cloisite 15A	2.83	3.13	6.97	1.27

The SEM images show a distinct two-phase morphology in the absence of nano-size silicate layers. The addition of silicate layers significantly changes the morphology of the blend. As shown in figure 3, in the presence of silicate layers, the deformation of PLA phase dose not create defect cavities observable around the PLA phase in the neat blend. The stretched PLA phase in the nanocomposite case may indicate ductile fracture of the PLA in the presence of Cloisite 15A versus the brittle fracture PLA exhibited in the neat blend.

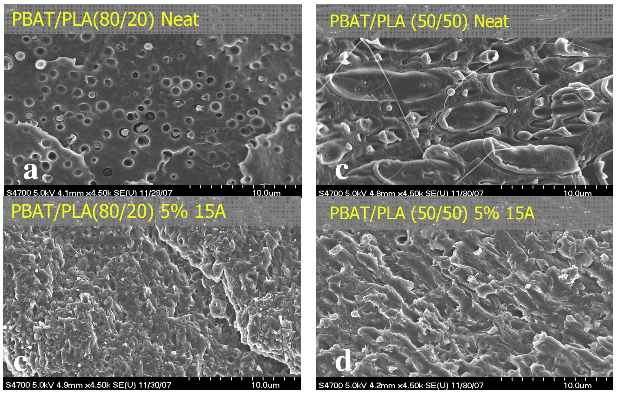

Figure 3- SEM micrographs of PBAT/PLA blend nanocomposites; (a) PBAT80/PLA20, (b) PBAT80/PLA20/5% C15A,(c) PBAT50/PLA50, d) PBAT50/PLA50/5%C15A

The DSC graph for pure PLA in the second heating did not show any peak beside glass transition (T_g). The lack of a peak indicates that the polymer chains were not able to form any crystalline structure at the heating rate of 10°C/min. On the other hand, results for PBAT /PLA blends show a wide peak for PBAT melting and a small peak for PLA melting. Upon addition of Cloisite 15A to the blend, the melting graph for the 80/20 and 50/50 blends shows an additional peak for cold crystallization which did not appear for the neat blends. This additional peak makes measurement of the area under the PBAT melting peak difficult; however, the melting point for the nanocomposites appear to be the same as that for the neat blends. In the nanocomposite case, the PLA shows two close melting peaks instead of a single peak that appears in the neat blend, indicating the possibility of different crystalline structures in presence of clay particles. Thermal properties of the samples are reported in table 4 and DSC graphs are depicted in figure 4.

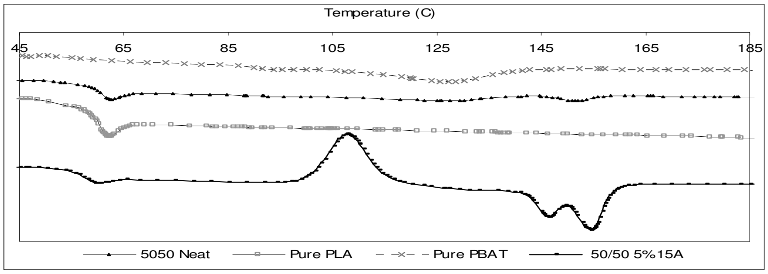

Figure 4- DSC graphs of melting pure PLA, pure PBAT, PBAT50/PLA50 and PBAT/PLA50/5%C15A

Table 4-Glass transition, cold crystallization temperature, melting temperatures and the crystallization temperature of PBAT80/PLA20 and PBAT50/PLA50 with and without 5% Cloisite 15A.

	PBAT	80-20 Neat	80-20 5%15A	50-50 Neat	50-50 5%15A	PLA
Tg	-	55.42	53.54	57.68	54.5	57.58
Tcc	-	-	106.77	-	107.9	-
Tm 1	127.2	128.48	129.17	127.46	127.36	-
Tm 2	-	149.87	146.52	152.1	146.06	-
Tm 3	-	-	154.42	-	154.42	-
Tc	87.53	89.1	94.86	88.16	93.54	-

Tensile testing of the PBAT-PLA films show that the modulus of the sample, as it was predicted, improved significantly as the PLA percentage increased. The PBAT/PLA blend samples mechanical properties are shown in table 5.

Table 5- Tensile Modulus of PBAT, PBAT80/PLA20, PBAT50/PLA50 and PLA

Samples	Modulus MPa/%
PBAT	0.99
80-20	1.22
50-50	5.55
PLA	13.12

Conclusion

PBAT was compounded with PLA and nano-size clay and the dispersion of clay in the pure PBAT and PBAT/blend was studied using XRD which showed that clay was intercalated in all cases and it was better dispersed when the PLA content was lower. SEM images showed that presence of clay in the PBAT/PLA blend changed the morphology of the compound. The clay presence also had significantly affected the crystallization rate of the PLA in the blend and finally, modulus of PBAT was enhanced due to compounding with clay and PLA.

References

1- Raquez, M., Nabar, Y., Narayan, R. And Dubois, P. Macromolecular materials and engineering, (2008) 310-320
2- Shi, X.Q., Ito, H. and Kikutan, T., polymer (2005) 11442-11450
3- Someya, Y., Sugahara, Y. and Shibata, M. Applied polymer science (2005) Vol 95. 386-392
4- Chow W, Mohd. Ishak Z, Ishiaku U, Karger-Kocsis J, Apostolov A. Journal of Applied polymer Science 2004. 91, 175-189.
5- Utracki L.A. clay-containing polymeric nanocomposites, rapra technology, (2004)
6- Jiang, L.; Wolcott, M. and Zhang, J. Biomacromolecules, 2006, 199-207
7- Pluta, M. J. of Polymer Science: PArtB: Polymer Physics, 2006, 3392-3405
8- Chen, G.; Choi, J. and Yoon, J. Macromolecular Rapid Communication, 2005, 183-187
9- Bhardwaj, R. and Mohanty, A. Biomacromolecules, 2007, 183-187
10- Oksman, K. and Selin, J. Plastics and Composites from Polylactic acid 150-165
11- Ajayqn, P.; Schadler, L,; Braun, P,; *Nanocomposite Science and Technology* Wiley VCH, (2003)
12- Lee, S.; Lee, Y. and Lee, J. Macromolecular Research, 2007, 44-50