

Nanocomposites Based on Poly(butylene adipate-co-terephthalate) and Montmorillonite

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ABSTRACT: Nanocomposites based on biodegradable poly(butylene adipate-co-terephthalate) (PBAT) and layered silicates were prepared by the melt intercalation method. Nonmodified montmorillonite (MMT) and organo-modified MMTs (DA-M, ODA-M, and LEA-M) by the protonated ammonium cations of dodecylamine, octadecylamine, and *N*-lauryldiethanolamine, respectively, were used as the layered silicates. The comparison of interlayer spacing between clay and PBAT composites with inorganic content 3 wt % measured by X-ray diffraction (XRD) revealed the formation of intercalated nanocomposites in DA-M and LEA-M. In case of PBAT/ODA-M (3 wt %), no clear peak related to interlayer spacing was observed. From morphological studies using transmission electron microscopy, the ODA-M was found to be finely and homogeneously dispersed in the

matrix polymer, indicating the formation of exfoliated nanocomposite. When ODA-M content was increased, the XRD peak related to intercalated clay increased. Although the exfoliated ODA-M (3 wt %) nanocomposite showed a lower tensile modulus than the intercalated DA-M and LEA-M (3 wt %) composites, the PBAT/ODA-M composite with inorganic content 5 wt % showed the highest tensile modulus, strength, and elongation at break among the PBAT composites with inorganic content 5 wt %. Their tensile properties are discussed in relation to the degree of crystallinity of the injection molded samples. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 386–392, 2005

Key words: nanocomposites; biodegradable; polyesters; organoclay; mechanical properties

INTRODUCTION

Nanocomposites based on biodegradable polyesters and layered silicate have been attracting attention because the layered clay is environmentally friendly, naturally abundant, and economic, and the improvement of various properties in comparison with neat biodegradable polymers can enlarge the application fields of the polymer. In general, polymer-layered silicate nanocomposites can be prepared by four different methods: solution intercalation, *in situ* intercalative polymerization, polymer melt intercalation, and template synthesis.¹ Polymer melt intercalation has been proven to be an excellent technique because of its versatility, its compatibility with current polymer processing techniques, and its environmentally benign character due to the absence of solvent.² Regarding the biodegradable polyester nanocomposites prepared by the polymer melt intercalation, the nanocomposites based on poly(lactic acid) (PLA),^{3–7} poly(ϵ -caprolactone) (PCL),^{8,9} and poly(butylene succinate) (PBS)^{10–12} have been already studied by several groups. Poly(butylene adipate-co-terephthalate) (PBAT) is a new type of biodegradable polyester supplied by BASF¹³ and

Eastman Chemical Company.¹⁴ PBAT is more flexible and has a higher elongation at break than other biodegradable polyesters such as PLA and PBS, and therefore is more suitable for food packaging and agricultural films. To the best of our knowledge, so far there is no report on the PBAT nanocomposite. The present article describes an investigation of the nanocomposites based on PBAT and organo-modified montmorillonites. Our attention is focused on the relationship between the morphology of the composites and tensile properties.

EXPERIMENTAL

Materials

PBAT(Ecoflex®, melt flow rate (190°C, 2.16 kg) 3.3–6.6 g/10 min, specific gravity 1.26, glass transition temperature (T_g) –30°C [differential scanning calorimetry (DSC), melting temperature (T_m) 115°C (DSC)] was supplied BASF Japan Ltd. (Japan). Sodium (Na⁺) montmorillonite (MMT, Kunipia F, cation exchange capacity(CEC): 115 mEq/100 g) was supplied by Kunimine Industries Co. Ltd. (Tokyo, Japan). The amines used for the preparation of organophilic clays were dodecylamine (DA), octadecylamine (ODA), and *N*-lauryldiethanolamine (LEA), which were supplied from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). All other chemicals used in this work were reagent grade and used without further purification.

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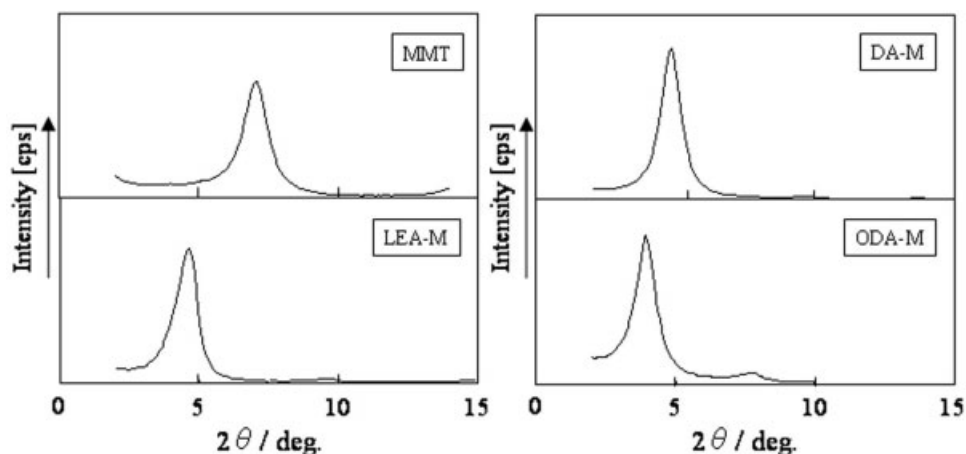


Figure 1 XRD patterns of MMT and organo-modified MMTs.

Preparation of organoclays

Organoclay was prepared by cation exchange of natural counterions with organic ammonium compounds. In all cases, the molar ratio of exchangeable cation calculated from CEC value, amine, and hydrochloric acid is 1.00 : 1.50 : 2.25. A typical procedure in case of LEA is as follows: MMT (10.0 g, exchangeable cation 11.5 mmol) was dispersed in 1,000 mL of deionized water at room temperature. LEA (4.73 g, 17.3 mmol) was dissolved in a mixture of deionized water (78 mL) and concentrated hydrochloric acid (2.24 mL, 26.0 mmol) and slowly poured into the clay suspension. The suspension was stirred for 1 h at 80°C. The exchanged clay was filtered, washed with a 1 : 1 mixture of water and ethanol, and redispersed in deionized water. This procedure was repeated several times until no chlorine ion was detected with 0.14N AgNO₃ solution. The filter cake was freeze-dried, crushed into powder using a mortar and pestle, and screened with a 280-mesh sieve. The LEA-modified montmorillonite is denoted as LEA-M.

The cation exchange rates of DA-M, ODA-M, and LEA-M organoclays were 115.6, 117.3, and 96.7%, respectively. Their organic fractions were 20.4, 27.4, and 23.9 wt %, respectively.

Preparation of composites

The sodium montmorillonite and organoclay particles and PBAT pellets were dried under vacuum at 40°C for at least 24 h before use. Melt mixing of PBAT with the clay particles was performed on a Laboplasto-Mill with a twin rotary roller-mixer (Toyo Seiki Co. Ltd., Japan). The inorganic content of the blends varied from 3.0 to 10.0 wt %. The mixing was carried out for 5 min with a rotary speed 50 rpm at 140°C. The mixture was crushed to small pieces after immersion in liquid nitrogen and dried at 40°C *in vacuo* for at least 24 h prior to injection molding. The dumbbell-shaped

specimen (width 5 mm, thickness 2 mm, length of parallel part 32 mm, total length 72 mm) was molded using a desktop injection molding machine (Little-Ace I Type, Tsubako Co. Ltd., Japan). The cylinder temperature and molding temperatures during the injection molding were 200 and 60°C, respectively.

Measurements

Cation exchange rate (CER) of organoclay was calculated from cation exchange capacity (CEC: 115 mEq/100 g) of Kunipia F, and the weight decrease [W_1 (g)] and remaining weight [W_2 (g)] measured by thermogravimetric analysis (TGA) on a Perkin-Elmer TGA-7 instrument when the organoclay was heated from room temperature to 700°C with a heating rate of 20°C/min in a nitrogen atmosphere. CER is calculated from the following equation: CER (%) = $100(W_1/MW)/[10^{-5}CEC(W_2 + 23.0W_1/MW)]$, where MW is the molecular weight of organic ammonium cation. Organic fraction (wt %) of organoclay is $100W_1/(W_1 + W_2)$.

TABLE I
Interlayer Spacing as Determined by XRD Analysis
for Clays and PBAT Composites
with Inorganic Content 3 wt %

Clay	XRD peak position(2θ)		Interlayer spacing [001] (nm)		Δd (nm) ^b
	In clay	In composite	In clay (d ₁)	In composite (d ₂)	
MMT	7.02	6.76	1.26	1.31	0.05
DA-M	5.00	3.22, 6.46 ^a	1.77	2.74	0.97
ODA-M	4.84	—	1.82	—	—
LEA-M	4.86	2.76, 5.62 ^a	1.82	3.20	1.38

^a The weak peak with a higher 2θ value is due to [002] plane of the silicate layers.

^b Δd = d₂ - d₁ (nm).

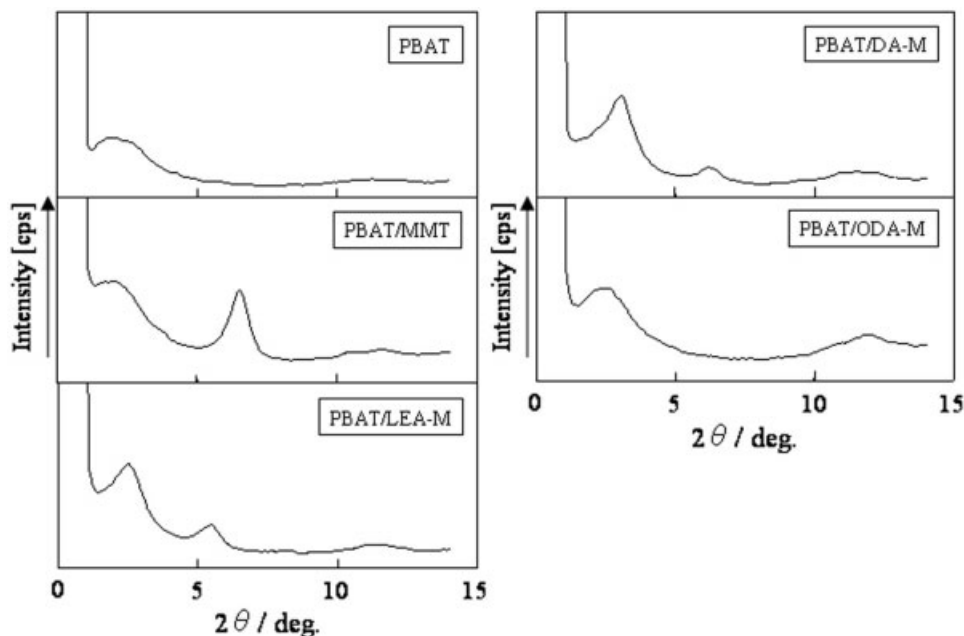


Figure 2 XRD patterns of PBAT and PBAT/clay composites with inorganic content 3 wt %.

Tensile tests of the composites were performed using an Autograph AG-I (Shimadzu Co. Ltd., Japan) based on the standard method for testing the tensile properties of plastics (JIS K7113(1995)). Span length was 50 mm and the testing speed was 10 mm/min. Five composite specimens were tested for each set of samples, and the mean values and the standard deviation (σ) were calculated.

X-ray diffraction (XRD) analysis was performed at ambient temperature on a Rigaku RINT-2100 X-ray diffractometer at a scanning rate of $2.0^\circ/\text{min}$, using $\text{CuK}\alpha$ radiation (wavelength, $\lambda = 0.154 \text{ nm}$) at 40 kV and 14 mA. Sodium montmorillonite and the freeze-dried organoclay were studied as powders. The blended materials were prepared in films of 0.40 mm thickness by compression molding.

Dynamic viscoelastic measurements of the rectangular plates (length 30 mm, width 5 mm, thickness 2 mm) cut from the dumbbell-shaped composites were performed on a Rheograph Solid (Toyo Seiki Co., Ltd, Japan) with a chuck distance of 20 mm, a frequency of 10 Hz, and a heating rate of $2^\circ\text{C}/\text{min}$.

The DSC was performed on a Perkin-Elmer DSC Pyris 1 DSC in a nitrogen atmosphere. The crystallization temperature from the glassy state ($T_{g,c}$) and melting temperature (T_m) of the PBAT composite were determined from the first heating scan of the injection-molded sample at a heating rate of $10^\circ\text{C}/\text{min}$.

Transmission electron microscopy (TEM) was performed on an electron microscope with a 75-kV accelerating voltage. The dumbbell-shaped samples were sectioned into roughly 100 nm thin sections at -70°C using a ultramicrotome with a diamond knife and then mounted on 200-mesh copper grids.

RESULTS AND DISCUSSION

Dispersion of clays in PBAT

Three kinds of amine compounds (DA, ODA, and LEA) that were effective for the formation of intercalated PBS nanocomposites¹² were used for the preparation of organo-modified MMT in this study. Figure 1 shows the XRD patterns of MMT and organoclays. The peaks correspond to the [001] basal reflection of the montmorillonite aluminosilicate. From the angular location of the peaks and the Bragg condition, the interlayer spacing (d_1) of each of the clays was determined. The computed values are summarized in Table I. The difference in the interlayer spacing between the

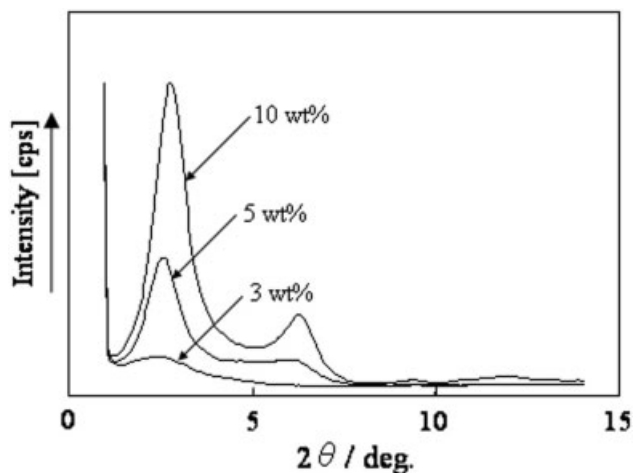


Figure 3 XRD patterns of PBAT/ODA-M composites with various inorganic content.

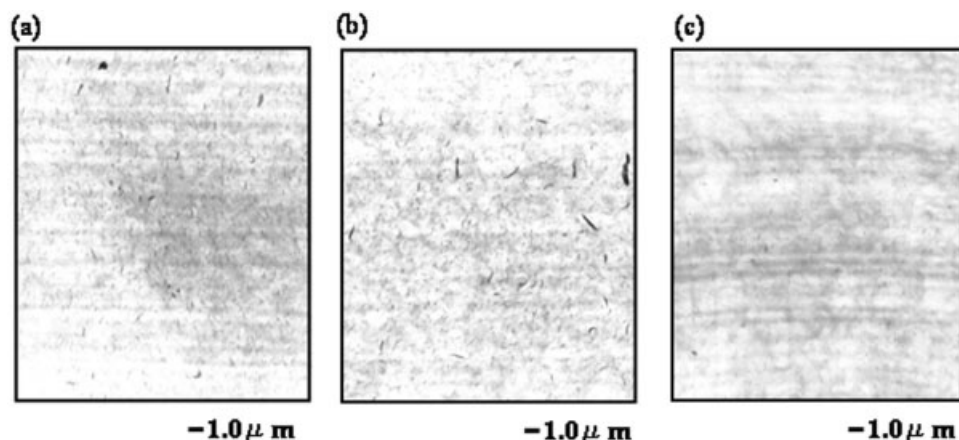


Figure 4 TEM images (10,000 power) of PBAT composites with inorganic content 3 wt %: (a) PBAT/DA-M, (b) PBAT/LEA-M, and (c) PBAT/ODA-M.

natural and organoclay is due to the intercalation of ammonium surfactant. The surfactant having bulkier substituent on the nitrogen atom shows a higher interlayer spacing. Figure 2 shows the XRD patterns of PBAT and PBAT composites with inorganic content 3 wt %. The difference (Δd) in interlayer spacing between clay and PBAT/clay relates to the degree of intercalation. The Δd of PBAT/MMT is nearly zero, indicating that little or no intercalation occurs. The values of Δd for PBAT/DA-M and PBAT/LEA-M are 0.97 and 1.38 nm, respectively, indicating that PBAT is intercalated into the gallery of silicate layers in these composites (Table I). The PBAT/ODA-M composite showed only a broad peak around $2\theta = 3^\circ$. However, the peak is thought to mainly relate to the PBAT component, because neat PBAT and PBAT/MMT composite show a similar peak around 3° . Even if the peak of the PBAT/ODA-M composite contains the [001] basal reflection of the silicate plates, the contributing proportion would be small. Also, although clear peaks corresponding to the [002] plane are observed at

5.6 and 6.4° for PBAT/LEA-M and PBAT/DA-M composites, respectively, there is no peak corresponding to the [002] plane for PBAT/ODA-M composite. We suppose that the main peak corresponding to the silicate layer is hidden in a smaller angle region than 1° of the XRD curve of PBAT/ODA-M composite with inorganic content 3 wt %. In that case, there is a possibility of the formation of partially exfoliated nanocomposite. For the PBAT/ODA-M composites with inorganic content 5 and 10 wt %, a couple of clear diffraction peaks corresponding to the [001] and [002] planes was observed around 3 and 6° (Fig. 3). The Δd of PBAT/ODA-M (5 wt %) is calculated to be 1.20 nm, indicating that the increase of ODA-M caused the formation of intercalated nanocomposite.

Figure 4 shows 10,000-power TEM images of PBAT composites with inorganic content 3 wt %. It is obvious that ODA-M is more finely dispersed in the matrix than DA-M and LEA-M. The PBAT/DA-M and PBAT/LEA-M composites contained some clusters of clays. The 100,000-power TEM images are shown in

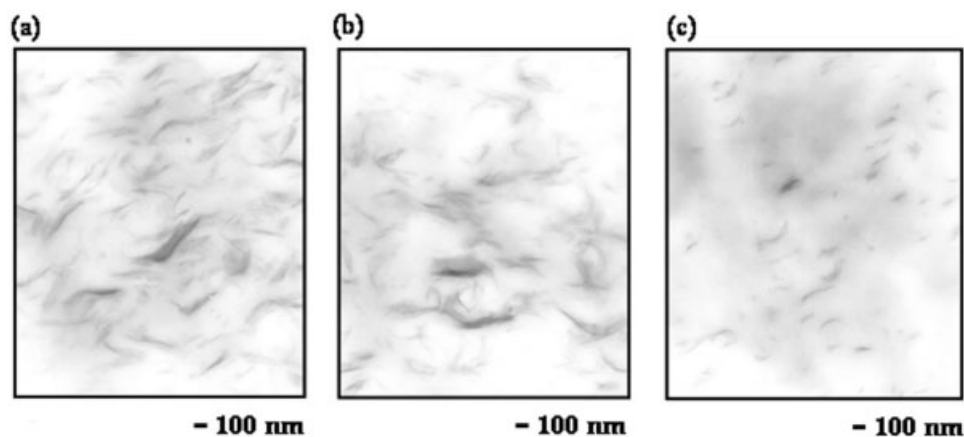


Figure 5 TEM images (100,000 power) of PBAT composites with inorganic content 3 wt %: (a) PBAT/DA-M, (b) PBAT/LEA-M, and (c) PBAT/ODA-M.

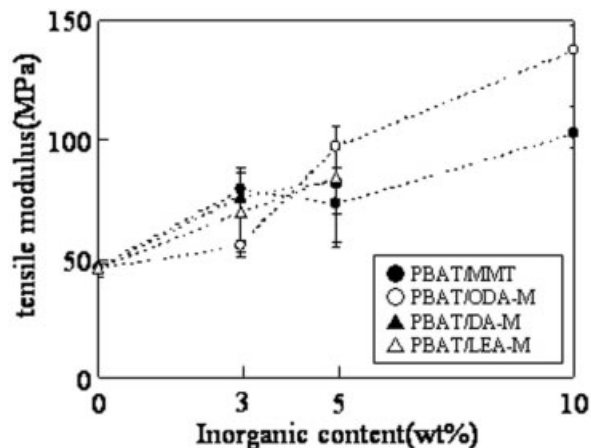


Figure 6 Relation between tensile modulus and inorganic content of PBAT composites.

Figure 5. It is obvious that PBAT/DA-M and PBAT/LEA-M composites are mainly composed of a stacked intercalated structure. In the case of PBAT/ODA-M composite, a smaller amount of stacked plates appeared in the broad- and obscure-shaded region. Judging from this result in addition to XRD studies, it is concluded that exfoliation mainly occurs in the broad-shade region.

Mechanical properties of PBAT composites

Figures 6–8 show the tensile properties of PBAT composites. As a whole, tensile modulus increased by the addition of clays, while tensile strength and elongation at break are rather lowered. Among the PBAT/organoclay composites with inorganic content 3 wt %, the intercalated DA-M composite showed the highest modulus, and the exfoliated ODA-M composite showed the lowest modulus (Fig. 6). The reason why the exfoliated PBAT/ODA-M composite showed the lowest modulus is discussed on the section of thermal properties of PBAT composites in relation to the degree of crystallinity. When the inorganic content is 5 wt %, ODA-M composite showed the highest modulus, while the PBAT/MMT microcomposite showed the lowest modulus. The tensile modulus of ODA-M composites considerably increased with inorganic content. Among the PBAT/organoclay composites with inorganic content 3 wt %, the exfoliated ODA-M composite showed the highest strength (Fig. 7). However, the value of strength was slightly higher than neat PBAT. Therefore, the exfoliation is thought to be effective for the maintenance of the tensile strength. In the intercalated DA-M and LEA-M composites, the strength decreased with inorganic content. In a previous paper, we reported that the tensile strength decreased with increasing LEA-M in the intercalated PBS/LEA-M composite.¹² Almost the same tendency was observed in the PBAT/DA-M and PBAT/LEA-M

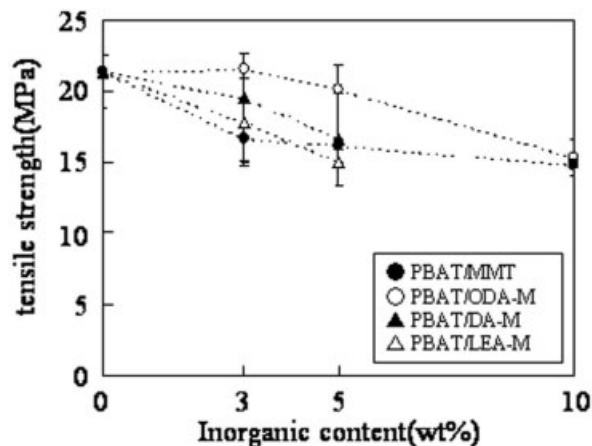


Figure 7 Relation between tensile strength and inorganic content of PBAT composites.

nanocomposites. In ODA-M composites, the tensile strength decreased with increasing inorganic content. This result should be again attributed to the occurrence of intercalation rather than exfoliation by the increase of ODA-M. It appears that elongation at break is somewhat lowered by the addition of clays (Fig. 8). When the PBAT composites with inorganic content 5 wt % are compared, the PBAT/ODA-M composite showed the highest tensile modulus, strength, and elongation.

Dynamic viscoelastic properties of PBAT composites

Figure 9 shows dynamic viscoelastic curves of PBAT and PBAT composites with inorganic content 3 wt %. All of the samples showed a primary dispersion around -20°C and a secondary dispersion around 60°C in the $\tan \delta$ curves. The former corresponds to the motion of the poly(butylene adipate) unit, and the latter corresponds to the motion of poly(butylene

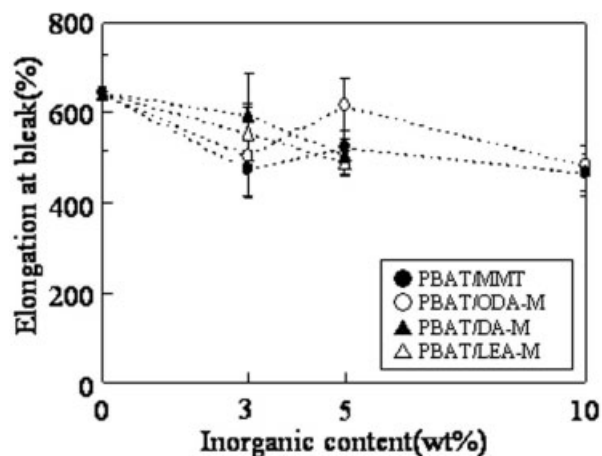


Figure 8 Relation between elongation at break and inorganic content of PBAT composites.

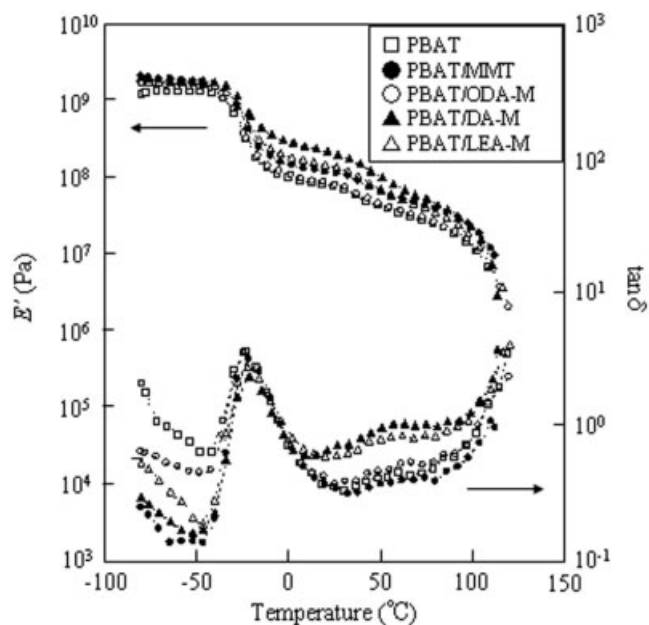


Figure 9 Dynamic viscoelastic curves of PBAT and PBAT/clay composites with inorganic content 3 wt %.

terephthalate). The $\tan \delta$ peak temperature corresponding to glass transition temperature (T_g) of the poly(butylene adipate) unit of all the PBAT/clay composites was slightly higher than that of neat PBAT. In agreement with the result of the tensile modulus, the intercalated DA-M or LEA-M composite showed a higher storage modulus (E') than the exfoliated ODA-M composite and neat PBAT over the temperature range of -30 to 70°C . When materials become soft above T_g , the reinforcement effect of the clay particles becomes prominent, due to restricted movement of the polymer chains, hence strong enhancement of modulus appears.¹⁵ There was no significant improvement of storage modulus in the glassy state when the temperature is lower than -30°C .

Thermal properties of PBAT composites

The thermal properties of the PBAT composites determined by DSC measurements are summarized in Ta-

ble II. When we discuss the mechanical properties of PBAT nanocomposites in connection with the degree of intercalation/exfoliation, the influence of degree of crystallinity (χ_c) of PBAT component in the composites should be considered because the χ_c may change by the influence of the organoclay. The original degree of crystallinity of the injection-molded composite can be evaluated from the value of $(\Delta H_m - \Delta H_{g,c})$, where ΔH_m and $\Delta H_{g,c}$ are the heat of melting and crystallization from the glassy state of the injection-molded sample in the first heating DSC scan, respectively. When the composites with inorganic content 3 wt % are compared, the $(\Delta H_m - \Delta H_{g,c})$ value of the PBAT/ODA-M composite is considerably lower than other composites, indicating that the injection-molded PBAT/ODA-M composite has a lower χ_c . The reason of a lower tensile modulus of the exfoliated PBAT/ODA-M composite with inorganic content 3 wt % should be attributed to the lower χ_c . The exfoliation may influence the retardation of the crystallization of the PBAT component during the injection molding. The $(\Delta H_m - \Delta H_{g,c})$ values of the PBAT/ODA-M composite with inorganic content 5 and 10 wt % are higher than that of the PBAT/ODA-M composite with inorganic content 3 wt %. The fact that the PBAT/ODA-M composites with inorganic content 5 and 10 wt % showed considerably higher tensile modulus than the composite with inorganic content 3 wt % may be attributed to the fact that the former composites have a higher χ_c and higher inorganic content than the latter composite.

CONCLUSIONS

Nanocomposites based on PBAT and layered silicates (MMT, DA-M, ODA-M, and LEA-M) were prepared by melt intercalation and subsequent injection molding. From the TEM and XRD observations of PBAT/organoclay composites with inorganic content 3 wt %, it was revealed that the intercalation occurs in case of DA-M and LEA-M, and the exfoliation in addition to some intercalation occurs in case of ODA-M. The ODA-M was more finely dispersed in the matrix than

TABLE II
Thermal Properties of PBAT and PBAT Composites

	Inorganic content (wt %)	$T_{g,c}$ ($^\circ\text{C}$)	$\Delta H_{g,c}$ (J/g)	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	$\Delta H_m - \Delta H_{g,c}$ (J/g)
PBAT	0	64.3	0.36	115.3	13.3	12.9
PBAT/MMT	3	60.6	1.40	115.1	12.8	11.4
PBAT/DA-M	3	57.3	0.74	115.4	12.5	11.8
PBAT/LEA-M	3	59.3	0.62	114.5	14.2	13.6
PBAT/ODA-M	3	57.3	0.99	114.4	9.9	8.9
PBAT/ODA-M	5	60.1	0.83	116.7	11.1	10.3
PBAT/ODA-M	10	60.5	0.69	117.5	10.2	9.5

$T_{g,c}$ is the crystallization-temperature from the glassy state; T_m is melting temperature; $\Delta H_{g,c}$ and ΔH_m are the heat of crystallization from the glassy state and heat of melting per 1 g of PBAT contained in the composite, respectively.

the DA-M and LEA-M. When ODA-M content was increased, the XRD peak related to intercalated clay increased. Among the PBAT composites with inorganic content 3 wt %, the exfoliated PBAT/ODA-M composite showed the lowest tensile modulus. This result was reasonably related to the retardation of crystallization of the PBAT component in the presence of exfoliated ODA-M. When the tensile properties of the PBAT composites with inorganic content 5 wt % are compared, the PBAT/ODA-M composite showed the highest tensile modulus, strength, and elongation at break.

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