

# Thermal and Mechanical Properties of Plasticized Poly(L-lactide) Nanocomposites with Organo-Modified Montmorillonites

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**ABSTRACT:** Nanocomposites of poly(lactide) (PLA) and the PLA plasticized with diglycerine tetraacetate (PL-710) and ethylene glycol oligomer containing organo-modified montmorillonites (ODA-M and PGS-M) by the protonated ammonium cations of octadecylamine and poly(ethylene glycol) stearylamine were prepared by melt intercalation method. In the X-ray diffraction analysis, the PLA/ODA-M and plasticized PLA/ODA-M composites showed a clear enlargement of the difference of interlayer spacing between the composite and clay itself, indicating the formation of intercalated nanocomposite. However, a little enlargement of the interlayer spacing was observed for the PLA/PGS-M and plasticized PLA/PGS-M composites. From morphological studies using transmission electron microscopy, a finer dispersion of clay was observed for PLA/ODA-M compos-

ite than PLA/PGS-M composite and all the composites using the plasticized PLA. The PLA and PLA/PL-710 composites containing ODA-M showed a higher tensile strength and modulus than the corresponding composites with PGS-M. The PLA/PL-710 (10 wt %) composite containing ODA-M showed considerably higher elongation at break than the pristine plasticized PLA, and had a comparable tensile modulus to pure PLA. The glass transition temperature ( $T_g$ ) of the composites decreased with increasing plasticizer. The addition of the clays did not cause a significant increase of  $T_g$ . © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2594–2602, 2006

**Key words:** nanocomposites; polyesters; mechanical properties; thermal properties

## INTRODUCTION

Poly(lactide) (PLA) is a linear aliphatic thermoplastic polyester, mainly produced by the ring-opening polymerization of L-lactide,<sup>1,2</sup> which is converted from L-lactic acid produced by the fermentation of sugar feed stocks.<sup>3,4</sup> PLA has received much attention in the research of alternative biodegradable polymers produced from renewable resources. Recently, PLA has been used for the construction materials<sup>5,6</sup> because of its low price, in addition to biomedical applications.<sup>7,8</sup> However, the low deformation at break limits its application. Considerable efforts have been made to improve the brittle properties so as to compete with low-cost and flexible commodity polymers such as polyethylene, polypropylene, and poly(vinyl chloride). As plasticizers for PLA, various type of compounds such as citrate ester, poly(ethylene glycol) (PEG), glucose monoesters, partial fatty acid esters, oligomeric lactic acid, and glycerol have been used to improve the

flexibility of PLA.<sup>9–13</sup> However, the addition of plasticizer generally causes the lowering of strength and modulus, in addition to the increase of deformation. The PLA-based materials having a good balance of stiffness and high deformation are still required for wide applications. In recent years, polymer/layered silicate nanocomposites have received significant research attention, because they often exhibit remarkable improvement of mechanical, thermal, fire retardant, gas barrier, and optical properties, at low clay content. The PLA-based nanocomposites have already been prepared by melt intercalation method<sup>14–18</sup> and in situ polymerization method.<sup>19</sup> Also, PLA/PEG nanocomposites with organo-modified montmorillonites have been prepared by melt intercalation method, and their morphologies and thermal properties have been reported.<sup>20</sup>

The present article describes thermal and mechanical properties of the nanocomposites based on organo-modified montmorillonites and the PLA plasticized with diglycerine tetraacetate and PEG, prepared by melt intercalation method. Our attention is focused on the balance of tensile modulus and elongation at break of the plasticized PLA nanocomposites.

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## EXPERIMENTAL

### Materials

PLA (LACEA H-100, melt flow rate (190°C, 2.16 kg) 8 g/10 min, specific gravity 1.26, melting temperature ( $T_m$ ) 164°C (differential scanning calorimetry, DSC)) was supplied from Mitsui Chemical, (Tokyo, Japan). RIKEMAL PL-710 (diglycerine tetraacetate, Riken Vitamin (Tokyo, Japan)) and poly(ethylene glycol) (PEG, number-average molecular weight  $\sim$ 1000, Kanto Chemical (Tokyo, Japan)) were used as plasticizers of PLA. Sodium ( $\text{Na}^+$ ) montmorillonite (MMT, Kunipia F, cation exchange capacity (CEC): 115 mequiv/100 g) was supplied by Kunimine Industries (Tokyo, Japan). The amines used for the preparation of organophilic clays were *n*-octadecylamine (ODA) and polyethylene glycol stearylamine (PGS, *N,N*-bis[poly(ethyleneoxy)]stearylamine, total degree of polymerization of ethyleneoxy unit is  $\sim$ 15), which were supplied from Tokyo Kasei Kogyo (Tokyo, Japan). All the other chemicals used in this work were reagent grade and used without further purification.

### Preparation of organoclays

Each organoclay was prepared by cation exchange of natural counterions with organic ammonium compounds. A typical procedure in case of ODA is as follows: MMT (10.0 g, 11.5 mmol of the exchangeable cation) was dispersed in 1000 mL of deionized water at room temperature. ODA (4.03 g, 15.0 mmol) was dissolved in a mixture of deionized water (78 mL) and concentrated hydrochloric acid (1.93 mL, 22.4 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 ions were detected with a 0.14N  $\text{AgNO}_3$  solution. The filter cake was freeze-dried, crushed into a powder with a mortar and pestle, and screened with a 280-mesh sieve. The ODA-modified montmorillonite is denoted as ODA-M. Organic fraction and cation exchange rate (CER) of the ODA-M were 24.0 wt % and 98.5%, respectively.

When PGS-modified montmorillonite (PGS-M) was prepared following the same procedure as for ODA-M, the CER was very low ( $\sim$ 40%). Therefore, the PGS-M prepared by use of excess PGS 96.3 g (0.104 mol) and HCl 13.3 mL (0.155 mol) toward MMT 10.0 g (11.5 mmol) was used in this study. Organic fraction and CER of the PGS-M were 41.5 wt % and 65.4%, respectively.

### Preparation of composites

The sodium montmorillonite and organoclay particles and PLA pellets were dried in vacuo at 40°C for at

least 24 h before they were used. The melt mixing of PLA, plasticizer, and the clay particles was performed on a Laboplasto-Mill with a twin rotary roller mixer (Toyo Seiki, Tokyo, Japan). The plasticizer content was 10 and 20 wt %. The inorganic content of the blends was 3.0 wt %. The mixing was carried out for 5 min at a rotary speed of 50 rpm at 190°C. The mixture was crushed into small pieces, and it was dried at 40°C in vacuo for at least 24 h before injection molding. Each dumbbell-shaped specimen (5 mm wide, 2 mm thick, 32 mm long in its parallel part, and 72 mm long in all) was molded with a desk injection-molding machine (Little-Ace I Type, Tsubako, Chigasaki, Japan). The cylinder temperature and molding temperature during the injection molding were 190 and 45°C, respectively.

### Measurements

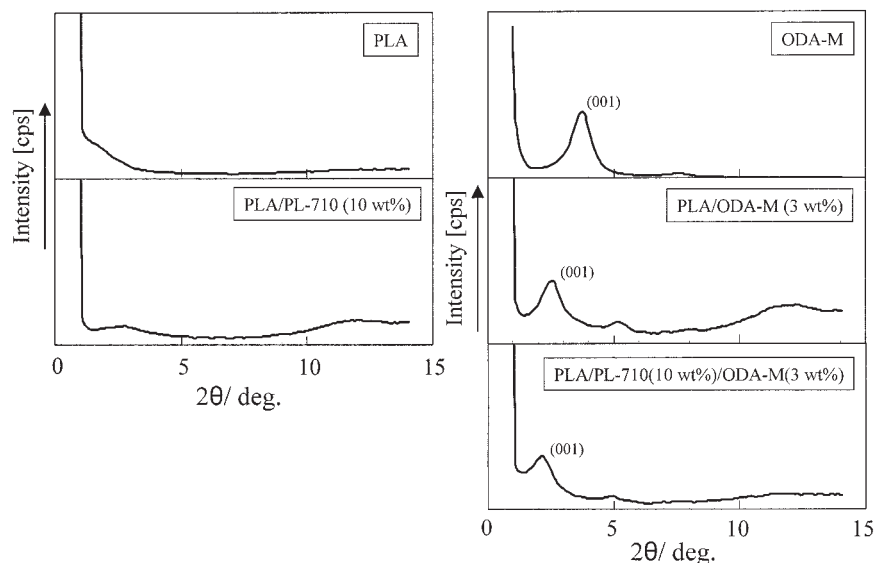
CER of organoclay was calculated from CEC (115 mequiv/100 g) of Kunipia F, and the weight decrease [ $W_1$  (g)] and remaining weight [ $W_2$  (g)] measured by thermogravimetric analysis (TGA) on a PerkinElmer TGA-7 instrument (Yokohama, Japan) when the organoclays were heated from room temperature to 700°C at a heating rate of 20°C/min in a nitrogen atmosphere. CER was calculated as follows: CER (%) =  $100 (W_1/MW)/[10^{-5} \text{CEC} (W_2 + 23.0W_1/MW)]$ , where MW is the molecular weight of the organic ammonium cation. The organic fraction (wt %) of each organoclay was  $100W_1/(W_1 + W_2)$ .

Tensile test of the composites was performed with an Autograph AGS-500C (Shimadzu, Kyoto, Japan), according to the standard method for testing the tensile properties of plastics (JIS K7113 (1995)). The 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 standard deviation were calculated.

The X-ray diffraction (XRD) analysis was performed at the ambient temperature on a Rigaku RINT-2100 X-ray diffractometer (Tokyo, Japan) at a scanning rate of 2.0°/min with Cu  $K\alpha$  radiation ( $\lambda = 0.154$  nm) at 40 kV and 14 mA. Sodium montmorillonite and freeze-dried organoclays were studied as powders. The blended materials were prepared in films about 400  $\mu\text{m}$  thickness via compression molding.

Dynamic viscoelastic measurements of the films were obtained on a Rheograph Solid (Toyo Seiki, Tokyo, Japan), with a chuck distance of 20 mm, a frequency of 10 Hz, and a heating rate of 2°C/min.

Transmission electron microscopy (TEM) was performed on a H-500 TEM (Hitachi, Tokyo, Japan) with a 75 kV accelerating voltage. The dumbbell-shaped samples were sectioned into roughly 100-nm thin sections at  $-70^\circ\text{C}$  with a ultramicrotome with a diamond



**Figure 1** XRD patterns of the composites containing ODA-M of inorganic content 3 wt % and their related samples.

knife and then were mounted on 200-mesh copper grids.

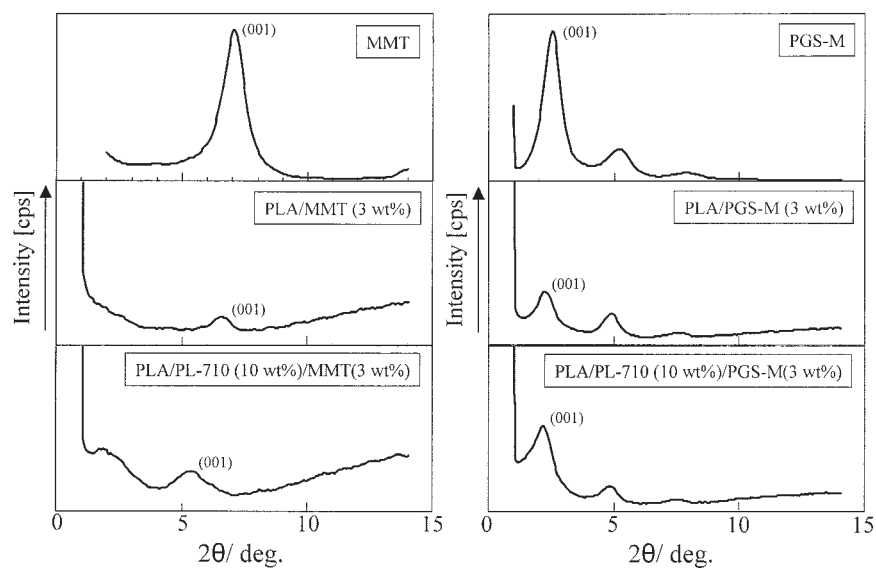
The DSC was performed on a PerkinElmer DSC Pyris 1 DSC in a nitrogen atmosphere. The glass transition temperature ( $T_g$ ), crystallization temperature from the glassy state ( $T_{g,c}$ ), and melting temperature ( $T_m$ ) of the PLA composite were determined from the first heating scan of the injection-molded sample at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Dispersion of the clays in the PLA-based composites

XRD analysis of the clays and PLA-based composites with inorganic content 3 wt % was performed to in-

vestigate the morphologies of the clays in the composites. As typical XRD patterns, the XRD charts for the composites containing ODA-M, MMT, and PGS-M of inorganic content 3 wt % are shown in Figures 1 and 2. The peaks at a small angle region on the XRD charts 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. Table I summarizes the results of interlayer spacing in the clays and composites with inorganic content 3 wt %. The difference in the interlayer spacing between the natural and organoclay is due to the intercalation of ammonium surfactant. In accordance with the bulkiness of the used surfactants, the order of higher interlayer spacing was PGS-M > ODA-M > MMT. The



**Figure 2** XRD patterns of the composites containing MMT and PGS-M of inorganic content 3 wt %.

**TABLE I**  
**Interlayer Spacing in the Clay and PLA-based Composites with Inorganic Content 3 wt % as Determined by XRD Analysis**

Clay	XRD peak position ( $2\theta$ )		Interlayer spacing [001] (nm)		$\Delta d$ (nm) <sup>a</sup>
	In clay	In composite	In clay ( $d_1$ )	In composite ( $d_2$ )	
PLA/clay composites					
MMT	7.02	6.52	1.26	1.35	0.09
ODA-M	3.96	2.70	2.23	3.27	1.04
PGS-M	2.72	2.52	3.25	3.50	0.25
PLA plasticized with 10 wt% PL-710/clay composites					
MMT	7.02	5.58	1.26	1.58	0.32
ODA-M	3.96	2.34	2.23	3.77	1.54
PGS-M	2.72	2.40	3.25	3.68	0.43
PLA plasticized with 10 wt % PEG/clay composites					
MMT	7.02	4.98	1.26	1.77	0.51
ODA-M	3.96	2.50	2.23	3.53	1.30
PGS-M	2.72	2.46	3.25	3.59	0.34

$$^a \Delta d = d_2 - d_1.$$

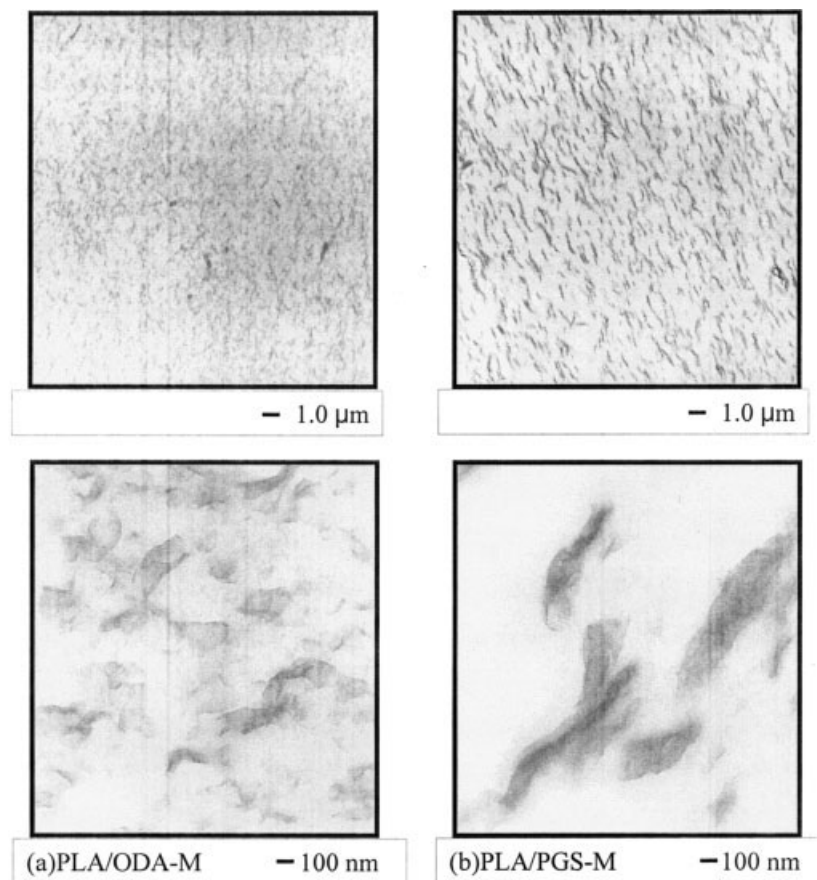
difference ( $\Delta d$ ) in interlayer spacing between the clay and composite with clay is related to the degree of intercalation. The higher order of  $\Delta d$  for all the PLA and plasticized PLA composites was ODA-M composites  $\gg$  PGS-M composites  $>$  MMT composites. It is obvious that intercalation occurs for all the composites with ODA-M. The plasticized PLA/ODA-M composites showed higher  $\Delta d$  than the PLA/ODA-M composites, indicating that intercalation of PL-710 or PEG in addition to matrix polymer PLA occurs for the plasticized PLA/ODA-M composites. The interlayer spacing of the PGS-M composites (3.5–3.7 nm) is not so different from that of the ODA-M composites (3.3–3.8 nm). However, because the interlayer spacing of PGS-M (3.25 nm) is higher than that of ODA-M (2.23 nm), the  $\Delta d$  of PGS-M composites (0.3–0.4 nm) was lower than that of ODA-M composites (1.0–1.5 nm). If the intercalation occurs for the plasticized PLA/PGS-M composites, there is a possibility of the reorganization of PGS intercalated between the aluminosilicate layers by the action of further intercalated PLA. Therefore, we can not conclude from a low  $\Delta d$  value (0.25 nm) of PLA/PGS-M composite that no intercalation occurs. The morphologies of the composites with PGS-M were investigated by means of TEM. The plasticized PLA/PGS-M composites showed a higher  $\Delta d$  than PLA/PGS-M composite, indicating that some intercalation of plasticizers occurs for PLA/PL-710/PGS-M and PLA/PEG/PGS-M composites. The  $\Delta d$  of PLA/MMT composite is 0.09 nm, indicating little intercalation occurs. The PLA/PEG/MMT (0.51 nm) and PLA/PL-710/MMT composites (0.32 nm) showed a little higher  $\Delta d$  than PLA/MMT composite, indicating some intercalation of PEG and PL-710 occurs. Vaia et al. have also reported on the occurrence of intercalation ( $\Delta d$

= 0.53 nm) for the composites of poly(ethylene oxide) and MMT.<sup>21</sup>

Figure 3 shows TEM images of PLA/ODA-M and PLA/PGS-M composites with inorganic content 3 wt %. It is obvious that ODA-M is more finely dispersed in PLA matrix than PGS-M. We have already reported that the composite with a higher  $\Delta d$  shows better and finer dispersion of clay for poly(butylene succinate) composites with various organo-modified MMT.<sup>22</sup> The similar trend was observed for PLA/ODA-M and PLA/PGS-M composites. Figure 4 shows TEM images of the plasticized PLA with 10 wt % PL-710/ODA-M and PGS-M composites, and the plasticized PLA with 10 wt % PEG/ODA-M composite. These three TEM images are alike in size and degree of dispersion of the stacked clays. The size of the stacked silicate layers of the PLA/PL-710/ODA-M and PLA/PEG/ODA-M composites were larger than that of PLA/ODA-M composite. The trend regarding dispersion of clays seems to be inconsistent with the fact that the former composites have larger  $\Delta d$  than the latter composite. Although we have no confirmation, it is thought that retardation of PLA intercalation accompanied by a preferential intercalation of plasticizer may cause deterioration of clay dispersion.

### Mechanical properties of the PLA-based composites

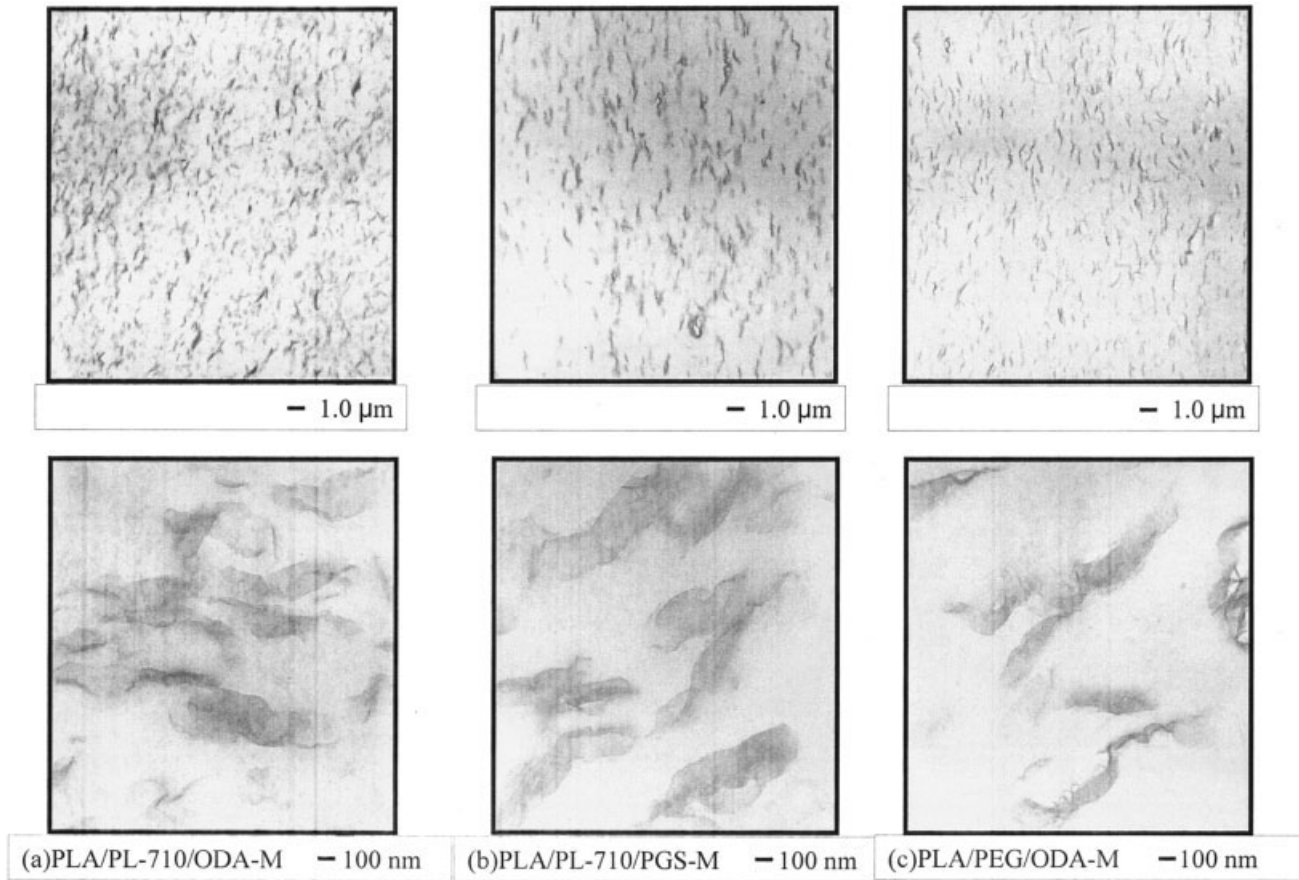
Figures 5–7 show tensile strength, tensile modulus, and elongation at break for PLA, plasticized PLA, and their composites with inorganic content 3 wt %. In the case without plasticizer, the PLA/MMT microcomposite had a lower tensile strength and modulus than pure PLA. In contrast to this, an interca-



**Figure 3** TEM images of the PLA composites with inorganic content 3 wt %: (a) PLA/ODA-M and (b) PLA/PGS-M.

lated PLA/ODA-M composite had the highest tensile strength, modulus, and elongation among PLA and PLA/clay composites. The PLA/PGS-M composite had a higher tensile modulus and lower tensile strength than pure PLA. These results are in agreement with the facts that the order of  $\Delta d$  is PLA/ODA-M  $\gg$  PLA/PGS-M > PLA/MMT, and that PLA/ODA-M composite has a finer and better dispersion of stacked clays than PLA/PGS-M composite. When PL-710 is added to PLA, tensile strength and modulus decreased with increasing PL-710 content as a whole. Although the addition of 10 wt % PL-710 to PLA resulted in no improvement in elongation, the addition of both 10 wt % PL-710 and 3 wt % organoclays (ODA-M and PGS-M) caused marked improvement in elongation. It is also noteworthy that the PLA/PL-710 (10 wt %)/ODA-M (3 wt %) composite has a comparable tensile modulus to pure PLA. When the PL-710 content is 20 wt %, the elongation of the plasticized PLA is sufficiently high, and is comparable to those of the plasticized PLA with organoclays. However, a considerable lowering of tensile modulus was observed when 20 wt % of PL-710 was added. Figure 8 shows

the comparison of stress–strain curves between PLA plasticized with 10 wt % PL-710 and its ODA-M composite. It is obvious that elongation at break of PLA/PL-710/ODA-M is much higher than that of PLA/PL-710, although the elongation at the highest stress is small for both the samples. We do not know the reason for that; however, it is thought that a higher PL-710 concentration at the interlayer than at the outside of clay causes a better elongation. The PLA plasticized with 10 wt % PEG has a higher elongation at break than the PLA plasticized with 10 wt % PL-710. However, the presence of the clays caused a lowering of the elongation for the PLA/PEG (10 wt %) composites. The lowering of elongation by the addition of clay is a reasonable result in general. The  $\Delta d$ 's of the PLA/PEG (10 wt %) composites is lower than those of the corresponding PLA/PL-710 (10 wt %) composites (Table I). Therefore, it is thought that PL-710 intercalates into the clay layers more preferentially than PEG. The less difference of plasticizer concentration between the inside and outside of clay layers may be a reason for the less elongation in case of the PLA/PEG (10 wt %) composites.

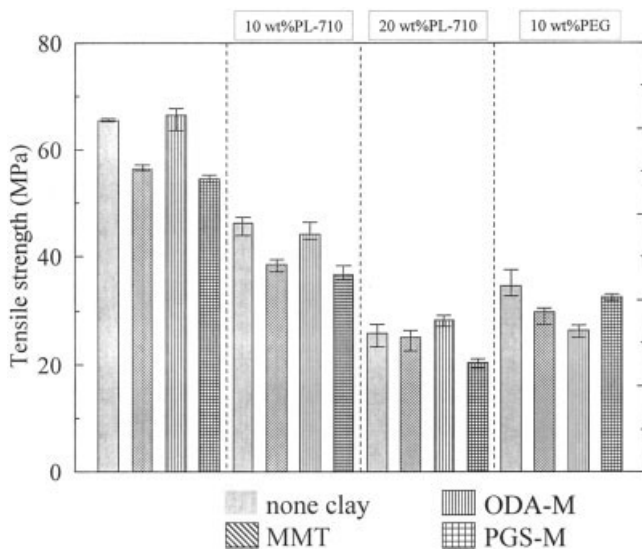


**Figure 4** TEM images of the PLA composites containing 10 wt % plasticizer and 3 wt % inorganic content: (a) PLA/PL-710/ODA-M, (b) PLA/PL-710/PGS-M, and (c) PLA/PEG/ODA-M.

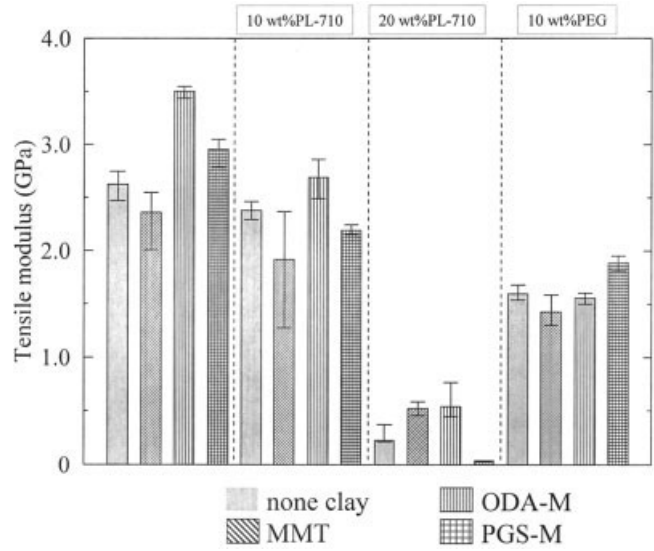
**Dynamic viscoelastic properties of the PLA-based composites**

Figure 9 shows dynamic viscoelastic curves of PLA and PLA composites. In agreement with the result of

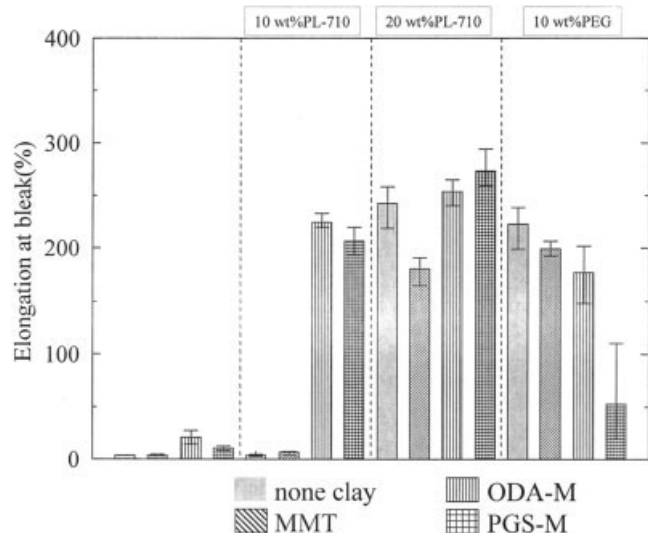
tensile modulus, the PLA/ODA-M composite showed the highest storage modulus over the temperature range of 30–90°C. The increase of storage modulus at about 80°C after the drop at about 60°C accompanied



**Figure 5** Tensile strength of PLA, plasticized PLA, and their composites with inorganic content 3 wt %.

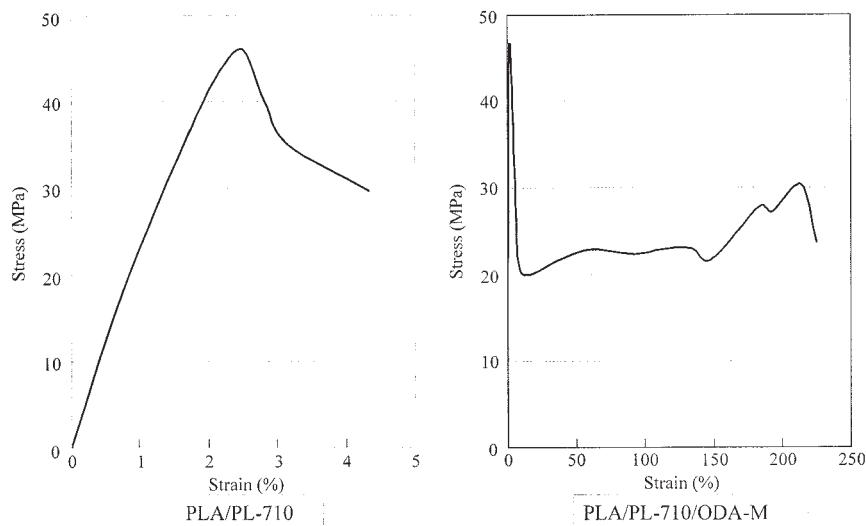


**Figure 6** Tensile modulus of PLA, plasticized PLA, and their composites with inorganic content 3 wt %.



**Figure 7** Elongation at break of PLA, plasticized PLA, and their composites with inorganic content 3 wt %.

by the glass transition for PLA/ODA-M composites is attributed to the crystallization of PLA component. The PLA/ODA-M composite showed a little higher  $\tan \delta$  peak temperature corresponding to  $T_g$  than the PLA/MMT and PLA/PGS-M composites. This result indicates that the intercalation of PLA into the gallery of silicate layers causes the interference of molecular motion for PLA/ODA-M composite. Figure 10 shows dynamic viscoelastic curves of PLA plasticized with 10 wt % PL-710 and its composites. Also, in case of using the plasticized PLA, ODA-M composite showed the highest storage modulus. However, the  $\tan \delta$  peak temperature of the PLA/PL-710/ODA-M composite was almost the same as that of PLA/PL-710.



**Figure 8** Stress-strain curves of PLA/PL-710 (10 wt %) and PLA/PL-710 (10 wt %)/ODA-M (3 wt %).

### Thermal properties of the PLA-based composites

The thermal properties of the PLA composites determined from the first heating DSC scans are summarized in Table II. When we discuss the mechanical properties of PLA nanocomposites in connection with the degree of intercalation, the influence of degree of crystallinity ( $\chi_c$ ) of the PLA component in the composites should be considered because  $\chi_c$  may change by the influence of the organoclay. The  $\chi_c$  was calculated based on the enthalpy of fusion of 100% crystalline PLA, equal to 93 J/g. The original degree of crystallinity ( $\chi_{c,o}$ ) of the injection-molded composite can be evaluated from the value of  $(\Delta H_m - \Delta H_{g,c})$ , where  $\Delta H_m$  and  $\Delta H_{g,c}$  are the heat of melting and heat of crystallization from the glassy state of the injection-molded sample in the first heating DSC scan, respectively. Also, the finally attained degree of crystallinity ( $\chi_{c,f}$ ) after the DSC heating scan was calculated from the value of  $\Delta H_m$ . When the clays are not added,  $\chi_{c,o}$  increased with PL-710 content. The PLA/PEG (10 wt %) showed considerably higher  $\chi_{c,o}$  than PLA/PL-710 (10 wt %). The addition of the clays caused more increase of  $\chi_{c,o}$ . The addition of the plasticizers also caused the increase of  $\chi_{c,f}$ . On the other hand, the addition of the clays did not have a significant effect on  $\chi_{c,f}$ . We can not strictly discuss the influence of additives on crystallization behavior from these results, because the thermal history of the injection molded samples is not strictly equal each other. However, these data roughly indicate that the plasticizers promote crystallization due to enhanced chain mobility. Also, it is thought that the clays accelerate the crystallization by acting as a nucleating agent, while do not largely affect the finally attained crystallinity. When the composites with the same amount of addi-

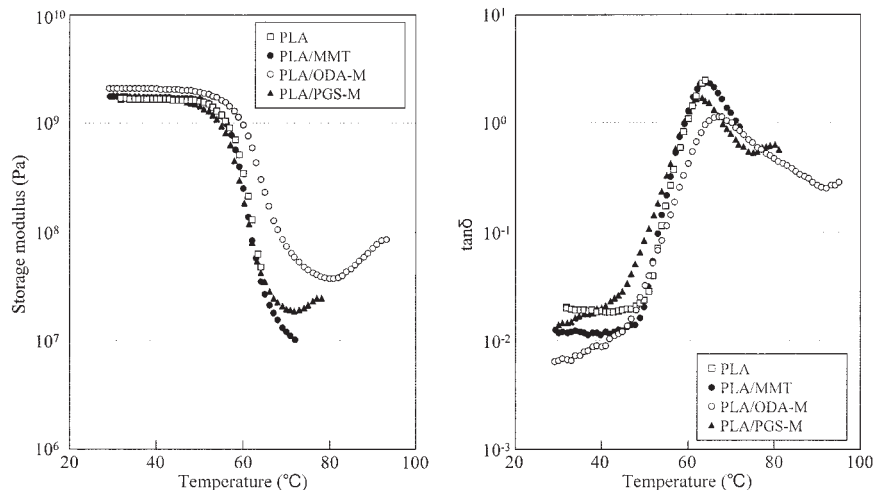


Figure 9 Dynamic viscoelastic curves of PLA/clay composites with inorganic content 3 wt %.

tives are compared, the difference of  $\chi_{c,o}$  due to the kind of clays is not significant. Therefore, the improvement of tensile properties of plasticized PLA/ODA-M composites should be attributed to the intercalated structure. The glass transition temperature ( $T_g$ ) decreased with increasing plasticizer. The addition of clays did not cause a significant increase of  $T_g$ .

CONCLUSIONS

PLA nanocomposites containing montmorillonites (MMT, ODA-M, and PGS-M) and plasticizers (PL-710 and PEG) were prepared by melt intercalation method. The XRD and TEM observations demonstrated that intercalation occurs for PLA/ODA-M composite and PLA/plasticizers/ODA-M composites, and that the former composite has a better dispersion. Regarding the composites containing

PGS-M, although the confirmation of intercalation was not obtained from the XRD observation, PLA/PL-710/PGS-M composite appeared to have a similar morphology to the intercalated PLA/PL-710/ODA-M composite on the TEM observation. The PLA and PLA/PL-710 composites with ODA-M showed a higher tensile strength and modulus than the corresponding composites with MMT and PGS-M. Although the addition of 10 wt % PL-710 to PLA resulted in no improvement in elongation, the addition of both 10 wt % PL-710 and 3 wt % ODA-M caused marked improvement in elongation without any change in the high tensile modulus compared with that of pure PLA. The plasticizers promote crystallization due to enhanced chain mobility. Also, the clays accelerate the crystallization by acting as a nucleating agent, while does not largely affect the finally attained crystallinity.

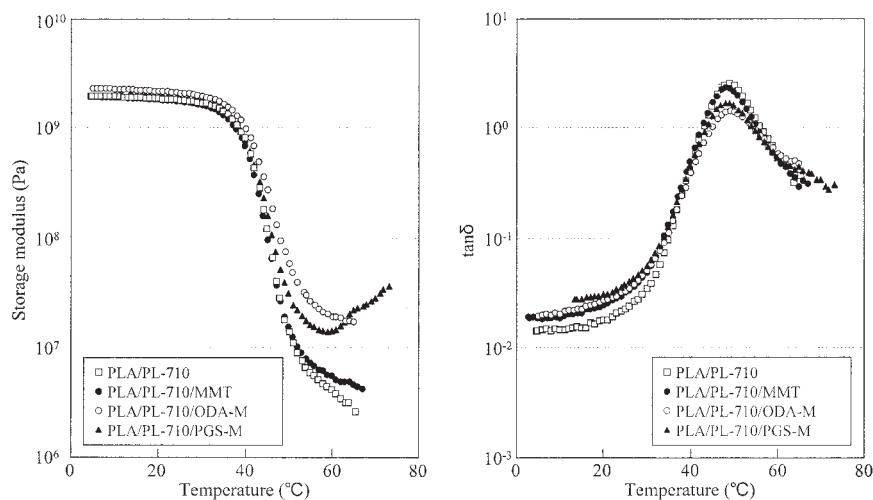


Figure 10 Dynamic viscoelastic curves of PLA/PL-710 (10 wt %)/clay composites with inorganic content 3 wt %.



TABLE II  
Thermal Properties of PLA and PLA Composites with Inorganic Content 3 wt %

Clay	Plasticizer [content (wt %)]	$T_g$ (°C)	$T_{g,c}$ (°C)	$\Delta H_{g,c}$ (J/g)	$T_m$ (°C)	$\Delta H_m$ (J/g)	$\chi_{c,o}$ (%)	$\chi_{c,f}$ (%)
None	None [0]	61.8	117.2	28.2	165.6	32.4	4.5	34.8
None	PL-710 [10]	42.4	121.7	33.5	160.8	39.1	6.0	42.0
None	PL-710 [20]	27.4	98.8	21.2	162.1	31.9	11.5	34.3
None	PEG [10]	41.3	95.2	14.5	166.5	38.5	25.8	41.4
MMT	None [0]	66.2	142.7	20.3	171.5	33.0	13.7	35.5
MMT	PL-710 [10]	43.5	116.8	21.1	163.1	36.5	16.5	39.2
MMT	PL-710 [20]	23.5	91.3	19.7	153.3	34.6	16.0	37.2
MMT	PEG [10]	40.2	95.4	18.7	163.3	45.0	28.3	48.4
ODA-M	None [0]	61.4	137.1	18.9	157.6	34.3	16.6	36.9
ODA-M	PL-710 [10]	42.1	107.2	20.9	158.9	34.6	14.8	37.2
ODA-M	PL-710 [20]	28.9	114.2	18.5	162.1	32.5	15.1	34.9
ODA-M	PEG [10]	42.0	94.2	14.8	163.9	40.9	28.1	44.0
PGS-M	None [0]	61.2	114.7	23.2	160.2	35.6	13.3	38.3
PGS-M	PL-710 [10]	42.6	96.9	22.5	160.9	35.5	14.0	38.2
PGS-M	PL-710 [20]	21.2	84.3	18.6	152.7	30.6	12.9	32.9
PGS-M	PEG [10]	39.1	92.9	17.0	164.9	43.4	28.5	46.7

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

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