Role of Epoxy Groups on Clay Surface in the Improvement of Morphology of Poly(L-lactide)/Clay Composites

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ABSTRACT: An organoclay containing epoxy groups, namely twice functionalized organoclay (TFC), was successfully synthesized by reacting (glycidoxypropyl)trimethoxysilane with Cloisite25A (C25A), which had previously been modified with an amine compound. The role of the epoxy groups on the clay surface in improving the morphology of the poly(L-lactide) (PLLA)/clay composites was investigated. The silicate layers in the PLLA/TFC composite were initially intercalated and became fully exfoliated as the epoxy content in the TFC was increased from 0 to 0.359 mmol/g, as confirmed by infrared spectra and TEM observations. However, the exfoliated morphology became an intercalated/exfoliated mixture when the clay content in the composites was in excess of 5 wt %. Not only was the tensile modulus and tensile strength enhanced by compounding with TFC but so was elongation at break of the PLLA. In contrast, the tensile properties of the PLLA/C25A were far inferior to those of the PLLA/TFC, and its elongation at break and tensile strength decreased sharply as the content of C25A increased. The higher degree of exfoliation in the silicate layers in PLLA/TFC and the improved mechanical properties compared with those of PLLA/C25A were attributed to the enhanced interfacial interaction through a chemical reaction between the epoxy groups of the TFC and the end groups of the PLLA.

Introduction

Recently, there have been several attempts to improve the end-use properties of poly(L-lactide) (PLLA) using PLLA/clay nanocomposites. Maiti et al.[1] produced intercalated PLLA/clay nanocomposites using an organically modified clay via melt compounding. They investigated the effects of the particle size and cationic exchange capacity (CEC) of the clay on the overall extent of intercalation. A mixture of intercalated/exfoliated silicate layers was obtained by Ray et al.[2] for the PLLA/clay composites. Krikorian et al.[3] prepared PLLA/clay composites using the exfoliation adsorption technique through the dispersion of organoclay, Cloisite 30B, in a suitable dilute solvent with subsequent mixing with PLLA. The favorable enthalpic interaction between the diols of the organic modifier with the C═O bonds present in the PLLA backbone was one of the most important driving forces for exfoliation.

Using theoretical models, Balazs[4,5] suggested that an increase in the chain length of the organic molecules tethered on clays is a promising approach to further promote the dispersion of the clay sheets in the polymer matrix. Recent studies[6−9] reported the various extent of clay dispersion using a variety of polymers grafted on the montmorillonite surface. The difference in the responses was attributed to the specific polymer−clay interactions.[10] A strong polymer−clay interaction destroyed and dispersed the clay layers, whereas a weak interaction preserved the clay tactoids.

The superior mechanical properties of the polymer/clay composites were attributed not only to the molecular level dispersion of the aluminosilicate layers but also to the strong interactions between the polymer matrix and the clay layers.[11] To improve the interaction between the polymer and clay, various cationic surfactants with functional groups were used to modify the clay using an ion-exchange reaction.[12] Another approach to improve the compatibility between the polymer and clay was introduction of polar functional groups such as maleic anhydride to the polymer matrix. Both intercalated and exfoliated structures coexisted in the polypropylene (PP)/clay composites with maleic anhydride-grafted-PP as a compatibilizer.[13] Manias and Chung[6] successfully obtained exfoliated PP/clay nanocomposites using amine-terminated PP as the organic modifier for montmorillonite. However, the window of the two approaches was limited due to the poor availability of the chemicals.

This study describes in detail the role of functional groups in the exfoliation of clay in a polymer matrix. For this purpose, was modified Cloisite25A (C25A) with (glycidoxypropyl)trimethoxysilane (GPS) to introduce epoxy groups into C25A, as shown in Figure 1.[14] The twice functionalized organoclay (TFC) thus prepared was compounded using poly(L-lactide) (PLLA). The silane compounds might contain various functional groups,[15] which can specially interact with the polymer matrix to improve the wetting properties between the phases. The morphology and mechanical properties were examined for the PLLA composites with the clay whose epoxy content was changed.

Experimental Section

Materials. Poly(L-lactide) (PLLA) was manufactured by Cargill Dow Co. (Minneapolis, MN) with a weight-average molecular weight of 2.4×10^5. It was dried in a vacuum oven at 50 °C for at least 2 days. The once organically modified clay, Cloisite25A (C25A), was purchased from the Southern Clay Product Inc. and was purified by dissolving it in ethanol at 70 °C for 4 h in order to remove any contaminants. The silane coupling agent, (glycidoxypropyl)trimethoxysilane (GPS), was supplied by Aldrich.

Preparation of Twice Functionalized Organoclay (TFC). After GPS (3.5 g) was hydrolyzed at pH 4.0 for 4 h in a solution of acetic acid in ethanol (90 wt %)/deionized water (10 wt %) mixture (200 mL), the C25A (10 g) was added and

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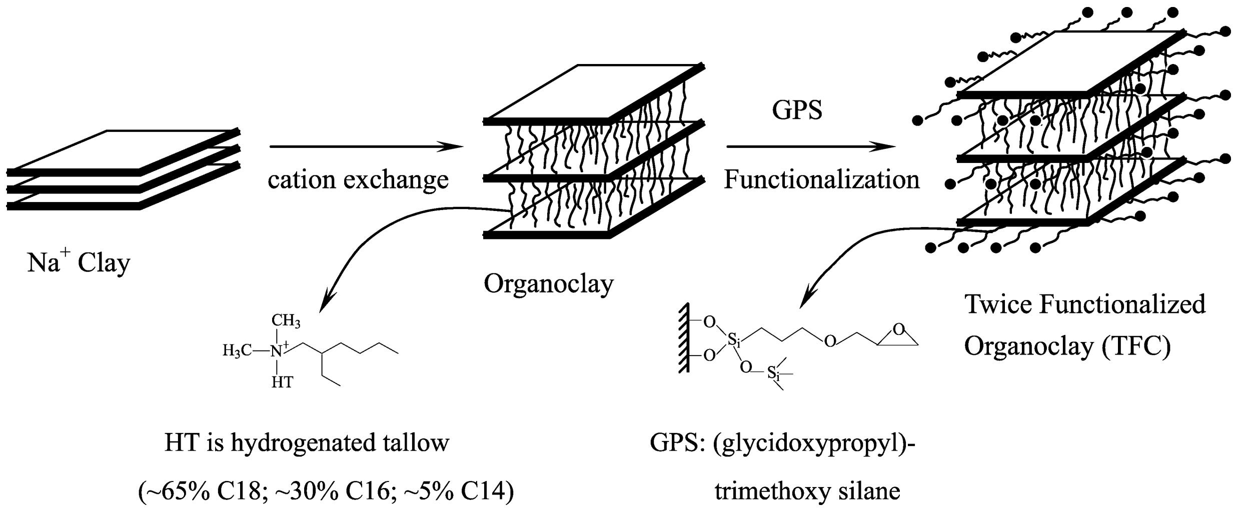

Figure 1. Schematic diagram for the preparation of the twice functionalized organoclay (TFC).

Table 1. Materials Properties of the Organoclays with a Different Epoxy Content

sample	C25A	TFC-1	TFC-2	TFC-3	TFC-4	TFC-5
d-spacing (Å)	18.46	18.54	18.49	18.65	18.56	18.63
epoxy content (mmol/g)	0	0.024	0.042	0.104	0.271	0.359

the mixture was then heated with reflux at 70 °C for different times. The product was diluted five times with 1-propanol to remove the soluble homocondensates. The resulting product was then filtered and repeatedly washed with ethanol at room temperature and dried in a vacuum oven at 50 °C for at least 48 h. The amount of epoxy groups grafted on the C25A was determined using the chemical titration method.[16] Briefly, TFC was suspended in 1,4-dioxane, and a solution of 1,4-dioxane/HCl was added. The resulting solution was stirred vigorously at 40 °C for 30 min to ensure complete mixing for a complete reaction with the epoxy groups. The epoxy content was determined by back-titrating with a methanolic NaOH solution employing cresol red as an indicator. The epoxy content was calculated using the following formula:

$$\text{epoxy (mmol/g)} = \frac{(V_{\text{NaOH(blank)}} - V_{\text{NaOH}})C_{\text{NaOH}}}{m_{\text{TFC}}}$$

where m_{TFC} is the mass of TFC in grams. $V_{\text{NaOH(blank)}}$ and V_{NaOH} are the volume of NaOH in milliliters added during the back-titration in the absence of TFC and in the presence of TFC, respectively. C_{NaOH} is the concentration of NaOH in the solution in mol/L used for the back-titration.

Nanocomposites Preparation. The nanocomposites of the PLLA/Clay were prepared by melt compounding of PLLA with the clays at 180 °C. The organoclays in the powder shape [Cloisite 25A (C25A) and twice functionalized organoclay (TFC)] were dispersed in methanol (10 g/mL) and sonicated for 10 min. Subsequently, the solution was scattered over the PLLA pellets and dried in a vacuum oven at 60 °C for 12 h. The mixture was melt compounded using a Brabender internal mixer at 180 °C for different times. The compounded and pelletized strands were dried under vacuum at 50 °C in order to remove the residual water. The dried pellets were then hot pressed at 180 °C for 1 min under 4 atm to prepare the sheets with a thickness of approximately 0.5 mm using a hot press. The molded sheets were then quickly cooled and annealed at 60 °C for 12 h prior to use for the various characterizations. The compositions and characteristic parameters of the PLLA and its composites are presented in Table 1.

Measurements. The grafting behavior of the silane was monitored by Bio-rad Fourier transformed infrared (FTIR) spectrophotometry. The determination of the bonded coupling agent was assessed by FTIR through the intensity of the Si–OH peak.

X-ray measurements were carried out by using a Philips PW1847 X-ray diffractometer with reflection geometry and Cu Kα radiation (wavelength $\lambda = 0.154$ nm) operated at 40 kV and 100 mA. The data were collected within the range of the scattering angles (2θ) of 2–30°.

Transmission electron microscopy (TEM) images were obtained using a TEM 2000 EX-II microscope (JEOL, Tokyo, Japan) operated at an accelerating voltage of 100 kV to observe the nanoscale structures of the various nanocomposites. All the ultrathin sections (less than 100 nm) were microtomed using a Super NOVA 655001 instrument (Leica, Swiss) with a diamond knife and were then subjected to TEM observations without staining.

The tensile specimens were prepared from hot pressed sheets of PLLA, PLLA/C25A, and PLLA/TFC. The specimens were subjected to uniaxial elongation at room temperature (below the T_g) or at 65 °C (above the T_g). All the measurements were carried out using UTM, Hounsfield test equipment at a cross-head speed of 50 mm/min.

Results and Discussion

The layered silicates contained silanol groups,[17] which remain intact even after the organophilic modification through a cation exchange reaction. GPS can react with these silanol groups to introduce epoxy functional groups on the silicate layers.[18] This would increase the hydrophobicity of the clay and enhance the wetting properties of the clay layers with PLLA. The chemical reaction between the epoxy groups and the end groups of the PLLA would further improve the mechanical properties of the PLLA/clay composites. The evidence of the grafting of GPS to C25A can be provided through the FTIR observations. Figure 2 shows the change in the FTIR difference spectra of the C25A as a function of the reaction time with GPS at pH 4. The chemical bonding of the silane molecules to C25A is expected to change the IR spectra significantly.[19] Figure 2 shows that the intensity of the peak at 3638 cm^{-1}, which is assigned to the stretching band of the terminal Si–OH on the surface of C25A, decreases as the reaction time of GPS with C25A increases. This confirms the chemical reaction between the hydrolyzed GPS monomers or oligomers with the silanol groups of C25A. Figure 1

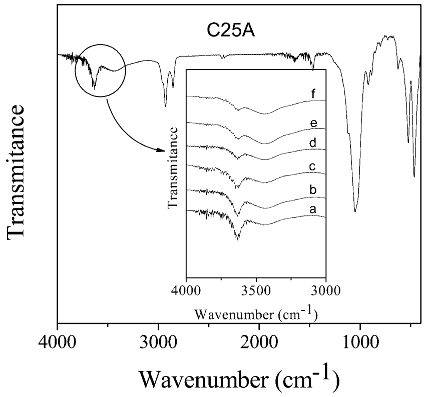

Figure 2. FTIR difference spectra of the Cloisite25A. The inset shows the variation in the peak intensity corresponding to the Si−OH groups of the Cloisite25A treated with GPS for different period of time at pH 4 with GPS/25A = 0.5 on weight basis: (a) Cloisite 25A, (b) 1 h, (c) 4 h, (d) 8 h, (e) 12 h, (f) 24 h.

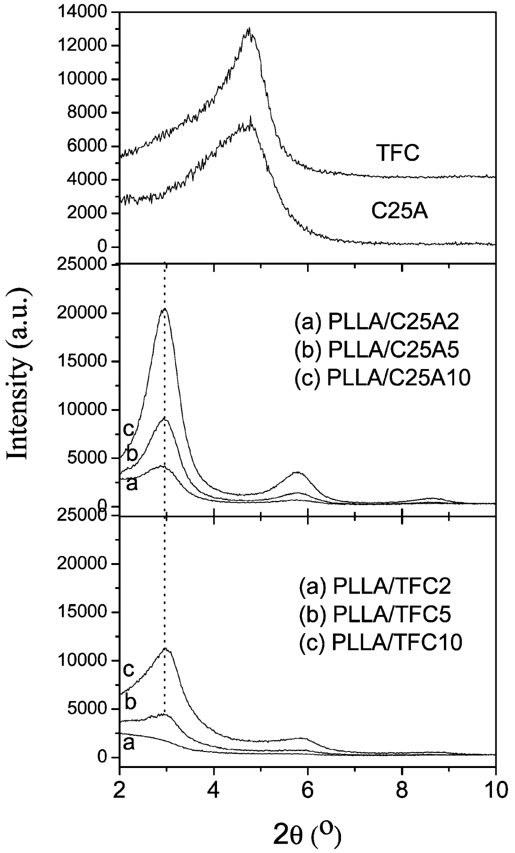

Figure 3. XRD patterns of the Cloisite25A, TFC, and PLLA composites with the two respective clays.

Table 2. Tensile Properties of the PLLA/Clay Nanocomposites at 65 °C

samples	modulus (MPa)	elongation at break (%)	strength (MPa)
PLLA	1583.8	7.5	59.3
PLLA/C25A2	1799.3	5.44	58.4
PLLA/C25A5	1956.1	4.95	57.5
PLLA/C25A10	2204.0	1.24	25.5
PLLA/TFC2	2099.6	6.1	68.6
PLLA/TFC5	2670.4	8.2	74.5
PLLA/TFC10	2805.3	12.9	81.9

shows a schematic of the grafting structure of the silane molecules on the clay surface.[20] It is believed that the silane molecules react mainly at the “broken” edges of the clay crystalline sheets because the hydroxy content at the edges of the clay sheets was much higher than that on the plain surface.[17,21,22] As a result of the cation exchange reaction, the interlayer of the clay was filled with organic molecules, which impeded diffusion of the silane molecules to penetrate into the inter-space and react with the hydroxy groups inside the clay sheets. This assumption was confirmed by XRD (Figure 3) in that the interlayer spacing, *d*(001), of the C25A (18.46 Å) was almost the same as the *d*(001) of TFC (18.62 Å). Therefore, the grafting reaction occurred mainly outside the clay layers. A similar phenomenon was also reported by Herrera et al.[23] More than 90% of the epoxy rings would remain intact without ring opening after 24 h of the reaction under similar conditions.[24] The epoxy content of the TFC was measured using the chemical titration method as demonstrated in Table 1. The epoxy groups of TFC could eventually react with the functional groups of PLLA.[25]

Figure 3 shows the XRD patterns corresponding to the C25A, TFC, PLLA/C25A, and PLLA/TFC composites. The number after the abbreviation is the weight percentage of the clay in the composite. This means that PLLA/C25A2, for example, is a composite composed of 98 wt % PLLA and 2 wt % C25A. The intercalation of the polymer chains would increase the interlayer spacing compared with that of C25A, which would shift the XRD peak toward a lower angle.

In the case of the composites containing 10 wt % of the respective clays, the *d* spacing between the layers expanded from 18.46 to 29.6 Å for PLLA/C25A10 and from 18.62 to 30.0 Å for PLLA/TFC10. The intensity of the *d*(001) peak decreased as the content of C25A in PLLA/C25A composite decreased and shifted slightly toward a lower diffraction angle For example, for PLLA/C25A5, the 2θ angle was 2.93° (30.1 Å) while for PLLA/C25A2 the 2θ angle was 2.89° (30.5 Å). The same trend was observed for the PLLA/TFC composites, and the interlayer spacing of the PLLA/TFC composites increased from 30.0 to 30.4 Å as the content of TFC decreased from 10 to 5 wt %. The small peak at $2\theta = 5.9°$ was assigned to the (002) plane of the clay. The increase in the *d* spacing of the composites compared with that of the corresponding neat organoclay indicates that the PLLA molecules were inserted into the interlayer of the organoclay.

The intensity of the peak of the TFC-based composite was much more attenuated than that of the C25A-based one. The lower intensity of the peak was attributed to the partial disruption of parallel stacking or layer registry of the TFC to give rise to some exfoliation of the clay platelets. The intercalation/exfoliation coexistence in the PLLA/TFC composite can be confirmed by the TEM image shown in Figure 4, where a typical TEM micrograph of the composites containing 5 wt % C25A was compared with that containing 5 wt % of TFC. The dark entities are the intercalated organophilic clay layers. Figure 4 shows that the stacks of the clay layers forming the clay crystallites are well dispersed in the polymer matrix, and the dispersion of the clay layers in the PLLA/TFC is better than in the PLLA/C25A. These results are in accordance with the XRD data shown in Figure 3.

It should be noted that both XRD peaks at $2\theta = 5.9°$ and $2\theta = 2.9°$ disappeared when the TFC content in PLLA/TFC was 2 wt % (Figure 3a, PLLA/TFC2), which is indicative of an absence of any ordered layer structure. This lack of intergallery clay diffraction is due to

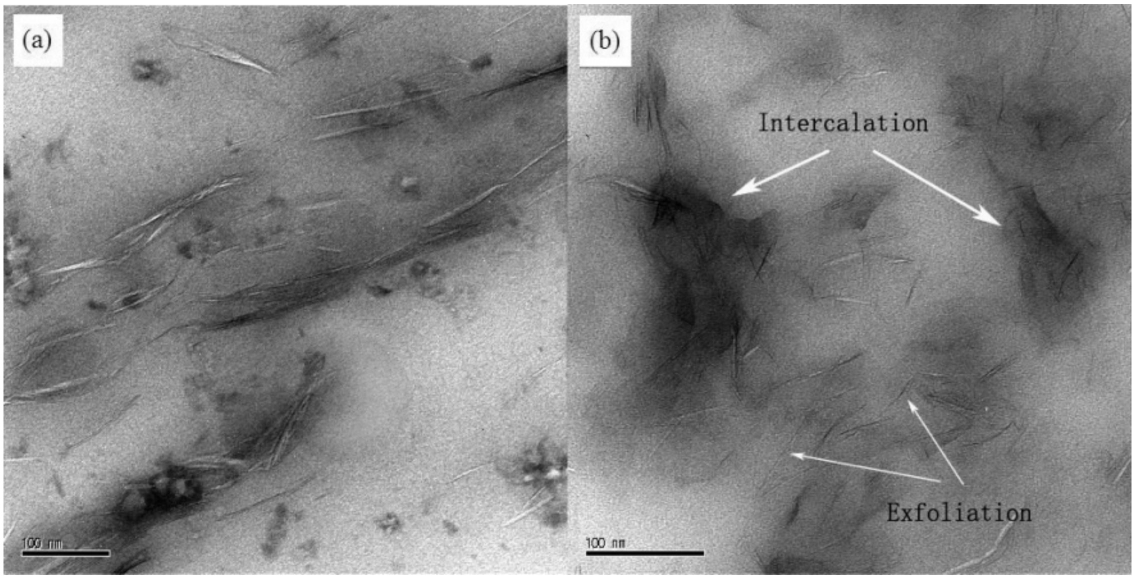

Figure 4. TEM images for PLLA composites with the two clays: (a) PLLA/C25A, (b) PLLA/TFC.The content of the clays was 5 wt %.

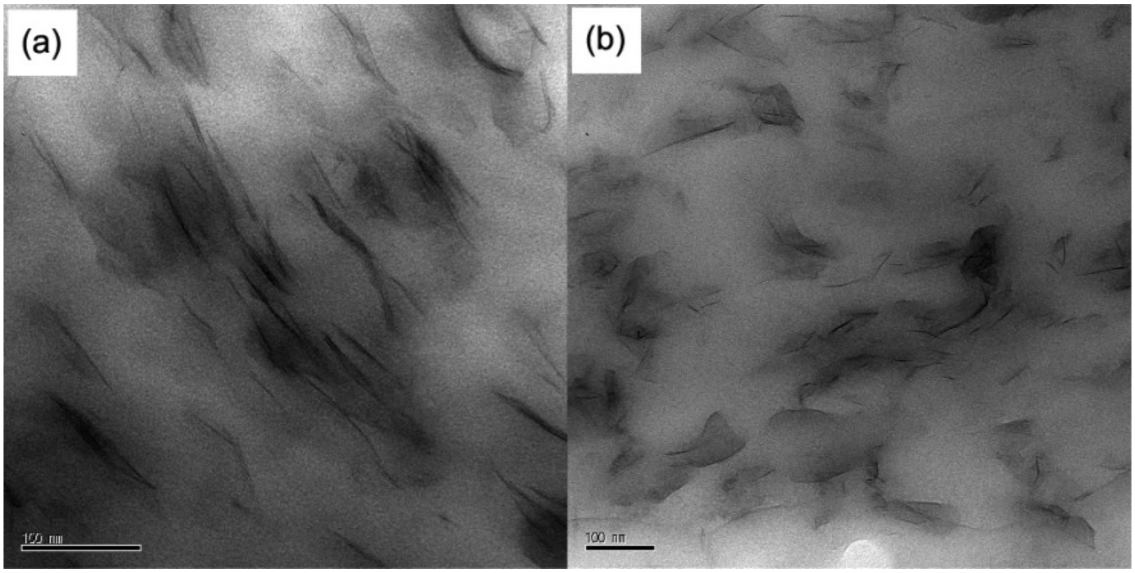

Figure 5. TEM images of PLLA composites with the two clays. (a) PLLA/C25A, (b) PLLA/TFC. The content of the clays was 2 wt %.

the exfoliation and random distribution of the clay platelets within the PLLA matrix.[14]

Typical TEM micrographs of the composites with a 2 wt % of C25A were compared with that having 2 wt % of TFC, as shown in Figure 5. Nanometer-range intercalated clay tactoids can be clearly seen in Figure 5a for the PLLA/C25A2 composite. The dark lines correspond to the cross section of the clay sheets of ca. 1 nm thickness, and the gap between two adjacent lines is the interlayer spacing or gallery. The measured distance between the two adjacent lines, i.e., the interlayer spacing of the intercalated tactoids, obtained from the TEM observations, is consistent with those from the XRD data. In contrast, TEM image of PLLA/TFC2 shown in Figure 5b demonstrates the presence of individual layers as well as a few packets of silicate consisting of 2−3 layers. Therefore, a higher degree of exfoliation of the silicate layers was obtained for the PLLA/TFC composite than for the PLLA/C25A composite. This is despite the fact that the XRD pattern of the neat TFC was almost identical to that of the neat C25A.

The role of the reactive functional groups of TFC in the intercalation and exfoliation of the clay layers in the PLLA matrix was examined by comparing the XRD and TEM data of the PLLA/TFC composite with those of the PLLA/C25A composite. The d spacings in the respective composites were similar (see the dotted lines in Figure 3), which means that the intercalation of the clay layers was governed mainly by the organic ammonium compound used for the cation-exchange reaction and that the grafted silane molecules did not make a significant contribution to PLLA molecules intercalating further into the clay interlayers. Instead, the epoxy groups played a key role in the exfoliation of the clay layers. This is because the XRD d_{100} peak for PLLA/TFC was much less intense than that for PLLA/C25A and because well-separated single clay layers were observed in the TEM image of the PLLA/TFC composites. On the other hand, many clay layer stacks were observed in the PLLA/C25A composites.

To further examine the effect of epoxy groups on the final morphology of the composites, the compounding

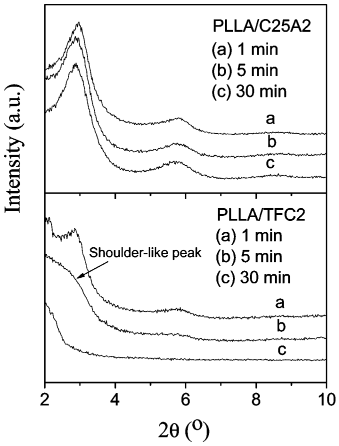

Figure 6. XRD patterns of the PLLA/clay composites at different mixing times at 180 °C. The content of the clays was 2 wt %.

time was changed, and the XRD patterns of the resulting composites were obtained, as shown in Figure 6. For the polymer composites with the reactive clays, the mixing time and shear force are the key factor controlling the morphological structure.[26] Applying a shear force should break up the primary particles and increase the uniformity. When PLLA/TFC was compounded in a Brabender mixer at 180 °C for 5 min, a shoulder-like profile around $2\theta \approx 2.8°$ was observed on the XRD pattern. However, the shoulder peak disappeared completely when the compounding time was increased to 30 min. The TEM micrograph in Figure 7 reveals a homogeneous dispersion of clay platelets throughout the PLLA/TFC composite without any aggregation or tactoid formation, which is indicative of a fully exfoliated clay structure of the PLLA/TFC composite when the compounding was carried out for 30 min. In sharp contrast, the intensity and position of the XRD peak remained almost constant for the PLLA/C25A system even though the compounding time was increased from 1 to 30 min. This clearly confirms that the functionalization of the clay played a key role in the exfoliation of the clay layers. The clay sheets are believed to exfoliate layer by layer in the PLLA matrix as the shear time increases. An underlying clay layer is peeled off after the clay layer adjacent to it reacts with the PLLA and is peeled off. The chemical reaction between the clay and PLLA takes place to form a PLLA−clay hybrid in situ and promotes peeling of the clay layers.

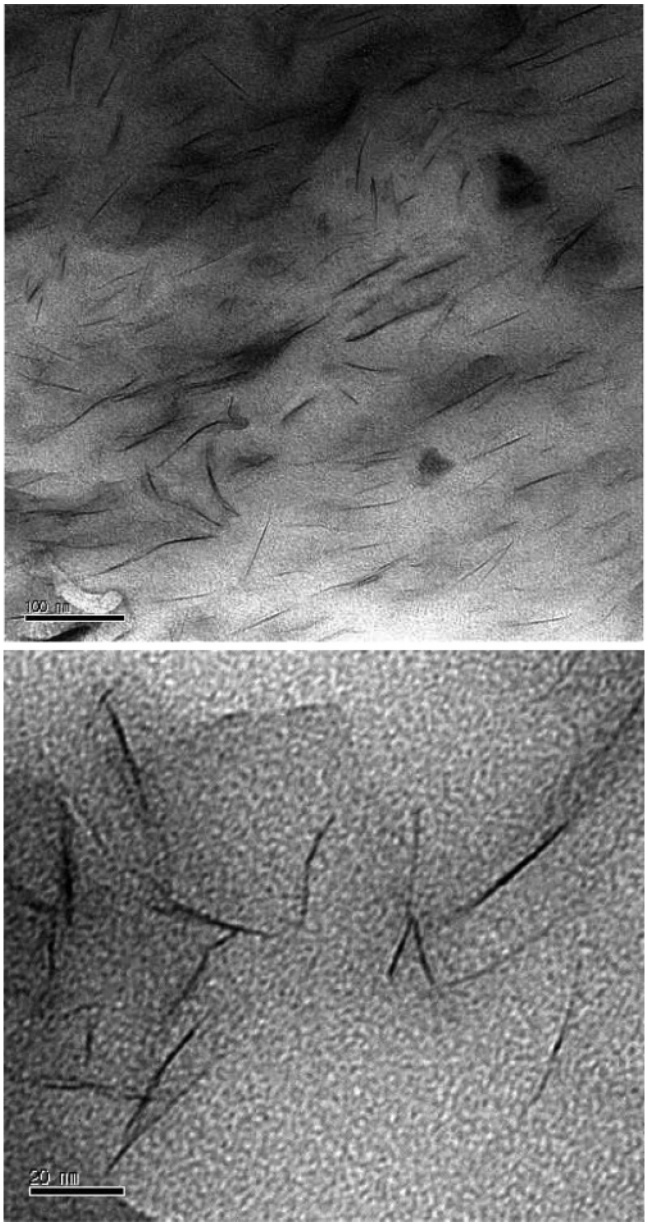

Figure 7. TEM images for PLLA/TFC composite with 2 wt % TFC after mixing for 30 min at 180 °C.

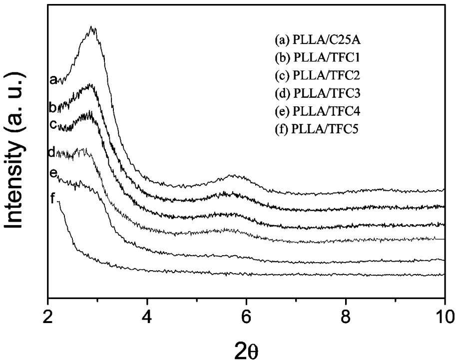

Figure 8. XRD patterns of the PLLA composites with C25A and TFC as a function of the epoxy content.The content of the clays was 2 wt %.

TFCs containing different levels of epoxy groups were synthesized to examine the effects of the epoxy content on the clay surface on the XRD pattern of the PLLA/TFC composites, as shown in Figure 8. Increasing the content of the epoxy groups on the clay surface did not obviously increase the *d* spacing of the organoclay. This is because few silane molecules permeate and react inside the clay layers, but they mainly grafted at the “broken” edges of the clay crystalline sheets. However, compounding the different clays with PLLA leads to a substantially different XRD pattern depending on the epoxy content of the clays. The XRD pattern of the nanocomposite derived from the neat C25A organoclay exhibited the most intense 2θ scattering peak, as shown in Figure 8a, suggesting that the clay layers were not exfoliated but intercalated. As the level of the epoxy groups increased, the intensity of the scattering peak became more attenuated, as demonstrated in Figure 8b−f, indicating that the ordered organoclay became broken up and delaminated. The scattering peak disappeared almost completely when the PLLA was compounded with the TFC-5 whose epoxy content was 0.359 mmol/g, which is indicative of a fully exfoliated morphology. The typical TEM photographs reported in a

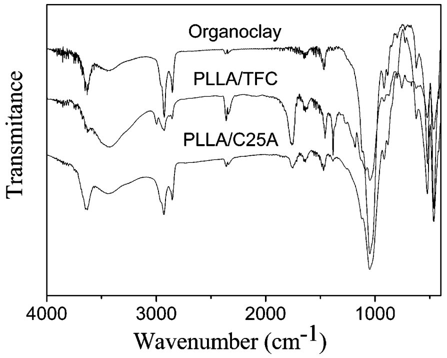

Figure 9. FTIR spectra of organoclay, PLLA/TFC, and PLLA/C25A composites after extraction with boiling chloroform for 1 week.

previous paper[14] confirmed the fully exfoliated morphology of the PLLA/TFC-5 composite. These results can be explained by the effect of the epoxy groups. The degree of exfoliation of the PLLA/TFC composites is determined mainly by the content of the epoxy groups. The chemical reaction between the epoxy groups and the end groups of the PLLA formed the PLLA−clay hybrid in situ during the compounding process. To the best of our knowledge, this study reports for the first time the fully exfoliated PLLA/clay composite via a melt compounding process. All previous studies finished with composites composed of an intercalated or at most intercalated/exfoliated mixture.[1−3,27−31]

The high degree of exfoliation of the silicate layers in the PLLA matrix can be attributed to the enhanced interaction of the TFC with PLLA. The reaction between the end groups of the PLLA and the epoxy groups of the TFC should have made a significant contribution to enhancing the compatibility. To verify the reaction for the in-situ formation of the clay−PLLA hybrid, the PLLA/TFC composites were Soxhlet extracted in boiling chloroform for 1 week. Figure 9 shows the infrared spectra of the PLLA/C25A and PLLA/TFC composites after extraction. The spectrum of the PLLA/TFC composite exhibited a strong absorbance peak at 1762 cm^{-1} due to the vibration of the PLLA carbonyl groups,[14] while the same peak was negligibly small in the spectrum of the PLLA/C25A composite, indicating that the PLLA molecules were chemically bound to the TFC and were not removed during extraction. In contrast, most of the PLLA molecules, which were physically adsorbed to the C25A, were extracted with boiling chloroform. The reaction mechanism between the end groups of the PLLA and epoxy groups is well established.[32,33]

A strong interaction between the consecutive clay platelets is expected due to the polar Si−OH groups on the surface of C25A. The clay platelets endure a shear during the compounding due to the strong interaction, and exfoliation of the intercalated structure of C25A can barely be realized (Figure 10a). In marked contrast, the clay surface of the TFC is more organophilic than that of C25A. Moreover, the terminal epoxy functional groups anchor the PLLA molecules on the clay surface, and the cohesive interaction between the PLLA tail and the PLLA matrix tears off the clay platelets effectively, as shown in the schematic in Figure 10b. Similar results were also reported by Manias and Chung,[6] who found that polypropylene (PP) chains anchored to the inorganic surface effectively exfoliated the clay platelets, and the exfoliated structure was maintained even after further mixing with neat PP.

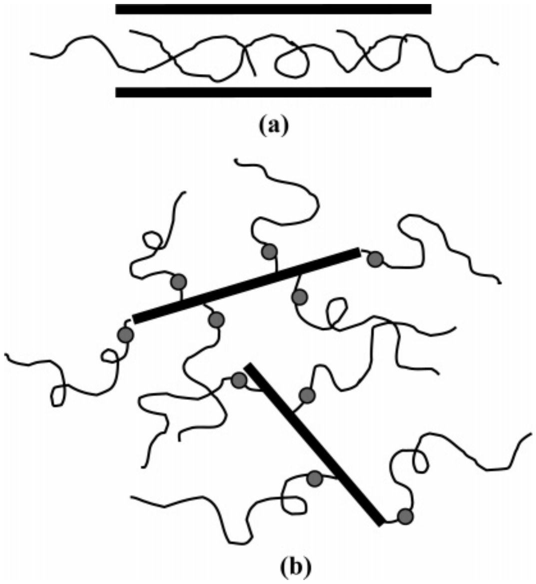

Figure 10. Schematic illustration of the molecular structures of (a) PLLA chains located between clay interlayers (PLLA/25A) and (b) exfoliated nanocomposite owing to the end group reaction (PLLA/TFC).

Table 3. Tensile Properties of the PLLA/Clay Nanocomposites at 65 °C

samples	modulus (MPa)	elongation at break (%)	strength (MPa)
PLLA	1.67	735	24.4
PLLA/C25A2	1.71	770	28.0
PLLA/C25A5	1.93	920	24.1
PLLA/C25A10	3.46	855	17.9
PLLA/TFC2	1.75	835	29.4
PLLA/TFC5	2.65	735	30.6
PLLA/TFC10	5.65	720	40.3

The improved mechanical properties and better barrier characteristics[34] are expected to be the result of a higher degree of exfoliation. According to Table 2, the addition of C25A to PLLA increased the tensile modulus, which suggests that C25A acted as reinforcing filler due to its high aspect ratio and platelet structure. However, the tensile strength and particularly the elongation at break of the PLLA/C25A composites decreased precipitously as the C25A content was increased.

The enhancement of the tensile modulus of the PLLA/TFC composites was more prominent than those with C25A. Table 3 demonstrates that the tensile modulus, tensile strength and elongation at break of the PLLA/TFC composites increased in order to uphold their toughness considerably as the TFC content was increased to 10 wt %. In many cases,[35−37] the increase in the tensile modulus of the polymers by compounding with clay sacrifices the elongation at break. The tensile properties of the PLLA and its composites with TFC at 65 °C are shown in Table 3 and Figure 11. It can be seen that the tensile modulus and tensile strength of the PLLA/TFC composites were superior to those of either the neat PLLA or PLLA/C25A composites above or below the T_g of PLLA.

The higher degree of exfoliation and the improved tensile properties of the PLLA/TFC composites are believed to be associated with the epoxy functional groups of the TFC, which promoted an interaction between the clay and the polymer via a chemical reaction.

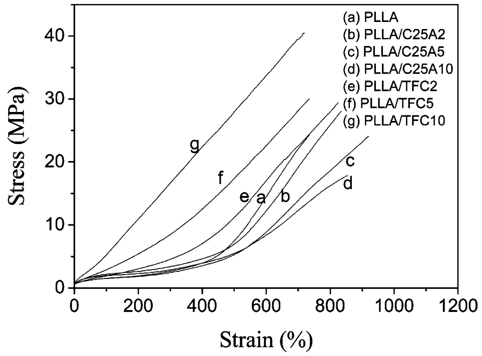

Figure 11. Stress−strain curves at 65 °C for PLLA and its composites with C25A and TFC.

Conclusions

This study developed a new and convenient method to prepare twice functionalized organoclay (TFC) by reacting (glycidoxypropyl)trimethoxysilane with the silanol groups of a commercially available organoclay, Cloisite 25A (C25A). TFC and C25A were melt-compounded with PLLA to prepare the PLLA/C25A and PLLA/TFC composites, respectively. The epoxy groups on the surface of TFC played a key role in the exfoliation of the composites and the improvement in their mechanical properties. A larger extent of exfoliation was observed for the PLLA/TFC composites as the epoxy content of the TFC increased, and a fully exfoliated morphology was eventually obtained by melt compounding when the epoxy content was 0.359 mmol/g. Elongation at break as well as the tensile modulus and tensile strength of the PLLA was greatly improved by compounding with TFC due to the increased interfacial interaction, which was attributed to a chemical reaction between the epoxy groups of the TFC and the end groups of the PLLA.

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References and Notes

(1) Maiti, P.; Yamada, K.; Okamoto, M.; Ueda, K.; Okamoto, K. *Chem. Mater.* **2002**, *14*, 4654.
(2) Ray, S. S.; Yamada, K.; Okamoto, M.; Ogami, A.; Ueda, K. *Chem. Mater.* **2003**, *15*, 1456.
(3) Krikorian, V.; Pochan, D. J. *Chem. Mater.* **2003**, *15*, 4317.
(4) Balazs, A. C.; Singh, C.; Zhulina, E. *Macromolecules* **1998**, *31*, 8370.
(5) Kuznetsov, D. V.; Balazs, A. C. *J. Chem. Phys.* **2000**, *113*, 2479.
(6) Wang, Z. M.; Nakajima, H.; Manias, E.; Chung, T. C. *Macromolecules* **2003**, *36*, 8919.
(7) Beyer, F. L.; Tan, N. C. B.; Dasgupta, A.; Galvin, M. E. *Chem. Mater.* **2002**, *14*, 2983.
(8) Huang, X. Y.; Brittain, W. J. *Macromolecules* **2000**, *34*, 3255.
(9) Viville, P.; Lazzaroni, R.; Pollet, E.; Alexandre, M.; Dubois, P. *J. Am. Chem. Soc.* **2004**, *126*, 9007.
(10) Vaia, R. A.; Giannelis, E. P. *Macromolecules* **1997**, *30*, 7990.
(11) Kawasumi, M. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 819.
(12) Okada, O.; Kawasumi, M.; Usuki, A.; Kojima, Y.; Kurauchi, T.; Kamigaito, O. *Mater. Res. Soc. Symp. Proc.* **1990**, *171*, 45.
(13) Manias, E.; Touny, A.; Wu, L.; Strawhecker, K.; Lu, B.; Chung, T. C. *Chem. Mater.* **2001**, *13*, 3516.
(14) Chen, G. X.; Choi, J. B.; Yoon, J. S. *Macromol. Rapid Commun.*, in press.
(15) Tesoro, G.; Wu, Y. In *Silanes and Other Coupling Agents*; Mittal, K. L., Ed.; VSP Publishers: Utretcht, 1992. Shen, Z.; Simon, G. P.; Cheng, Y. B. *Polymer* **2002**, *43*, 4251.
(16) Freeman, S. K. *Applications of Laser Raman Spectroscopy;* John Wiley & Sons: New York, 1974.
(17) Pinnavaia, T. J.; Beall, G. W. *Polymer-Clay Nanocomposites*; Wiley Series in Polymer Science; Wiley: New York, 2000.
(18) Chu, L.; Daniels, M. W.; Francis, F. *Chem. Mater.* **1997**, *9*, 2577.
(19) Dai, J. C.; Huang, J. T. *Appl. Clay Sci.* **1999**, *15*, 51.
(20) Leu, C. M.; Wu, Z. W.; Wei, K. H. *Chem. Mater.* **2002**, *14*, 3016.
(21) Theng, B. K. G. *Chemistry of Clay-organic Reactions;* Wiley: New York, 1974.
(22) Ray, S. S.; Okamoto, K.; Okamoto, M. *Macromolecules* **2003**, *36*, 2355.
(23) Herrera, N. N.; Letoffe, J. M.; Putaux, J. L.; David, L.; Bourgeat-Lami, E. *Langmuir* **2004**, *20*, 1564.
(24) Xue, G.; Koenig, J. L.; Ishida, H. *Rubber Chem. Technol.* **1991**, *64*, 162.
(25) Kim, H. Y.; Jeong, U.; Kim, J. K. *Macromolecules* **2003**, *36*, 1594.
(26) Huang, X.; Lewis, S.; Brittain, W. J.; Vaia, R. A. *Macromolecules* **2000**, *33*, 2000.
(27) Ray, S. S.; Maiti, P.; Okamoto, M.; Yamada, K.; Ueda, K. *Macromolecules* **2002**, *35*, 3104.
(28) Ray, S. S.; Maiti, P.; Okamoto, M.; Yamada, K.; Ueda, K. *Nano Lett.* **2002**, *2*, 423.
(29) Ray, S. S.; Yamada, K.; Okamoto, M.; Ueda, K. *Polymer* **2003**, *44*, 857.
(30) Chang, J. H.; An, Y. U.; Cho, D.; Giannelis, E. P. *Polymer* **2003**, *44*, 3715.
(31) Paul, M. A.; Alexandre, M.; Degee, P.; Calberg, C.; Jerome, R.; Dubois, P. *Macromol. Rapid Commun.* **2003**, *24*, 561.
(32) Ju, M. J.; Chang, F. C. *Appl. Polym. Sci.* **1999**, *73*, 2029.
(33) Ashcroft, W. R. *Chemistry and Technology of Epoxy Resins*; Ellis, B., Ed.; Blackie Academic & Professional: Glasgow, UK, 1993.
(34) Alexandre, M.; Dubois, P. *Mater. Sci. Eng.*, *R.* **2000**, *28*, 1.
(35) Lim, S. T.; Kim, J. W.; Chin, I.; Kwon, Y. K.; Choi, H. J. *Chem. Mater.* **2002**, *14,* 1989.
(36) Lim, S. T.; Hyun, Y. H.; Choi, H. J.; Jhon, M. S. *Chem. Mater.* **2002**, *14*, 1839.
(37) Lee, K. M.; Han, C. D. *Macromolecules* **2003**, *36*, 7165.

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