Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

ELSEVIER

Polymer 44 (2003) 3715–3720

polymer

www.elsevier.com/locate/polymer

Poly(lactic acid) nanocomposites: comparison of their properties with montmorillonite and synthetic mica (II)

Jin-Hae Chang[a,*], Yeong Uk An[a], Donghwan Cho[a], Emmanuel P. Giannelis[b]

[a]*Department of Polymer Science and Engineering, Kumoh National University of Technology, Kumi 730-701, South Korea*
[b]*Department of Material Science and Engineering, Cornell University, Ithaca, NY 14853-1501, USA*

Received 18 December 2002; received in revised form 12 March 2003; accepted 17 March 2003

Abstract

Our study was to clarify the intercalation of polymer chains to organoclays and to improve the thermo-mechanical properties. Two organoclays were synthesized. One was a montmorillonite modified with hexadecylamine (C_{16}-MMT); the other was a fluorinated-mica modified with hexadecylamine (C_{16}-Mica). Dispersions of organoclays with poly(lactic acid) (PLA) were by using the solution intercalation method at different organoclay contents to produce nano-scale composites. The maximum ultimate tensile strength was observed for blends containing 4 wt% of either of the two organoclays and decreased with further increases in the organoclay content. The initial modulus increased with increasing organoclay content up to 4 wt% for C_{16}-MMT. When the C_{16}-MMT content was greater than this critical wt%, the modulus of the hybrids started to decrease. In contrast, the initial modulus of the hybrids using C_{16}-Mica increased continually with increasing clay content from 2 to 8 wt%. The tensile properties of the C_{16}-Mica hybrids were higher than those of the hybrids containing C_{16}-MMT. The optical translucency was not affected by the organoclay content up to 6 wt%; however, the films containing 8 wt% organoclays were slightly more cloudy.

Keywords: Poly(lactic acid) nanocomposite; Organoclay; Thermo-mechanical properties

1. Introduction

Poly(lactic acid) (PLA) is a linear aliphatic thermoplastic polyester. Generally, commercial grades of PLA are copolymers of poly(L-lactide) and poly(DL-lactide). PLA is produced from renewable resources, has excellent properties which are comparable to many petroleum-based plastics, and is readily biodegradable. Consequently, it has been proposed as a renewable and degradable plastic for use in service ware, grocery bags, waste-composting bags, films, and controlled release materials for pesticides and herbicides [1–4]. PLA has high mechanical properties, thermal plasticity, fabric ability, and biocompatibility [5,6]. However, PLA is more expensive than the majority of commodity polymers. Moreover, the processibility of PLA is rather poor, and its biodegradation rate is not easy to control of PLA [7,8]. In spite of these difficulties, considerable efforts have been made to improve the properties of PLA so that it can as to compete with low-cost, flexible commodity polymers. These attempts modified PLA with biocompatible plasticizers or blended PLA with other polymers [9–13].

Nanocomposites are class of composites derived from ultrafine inorganic particles with sizes in the order of nanometers that are homogeneously dispersed in a polymer matrix. Because of their nanometer sizes, nanocomposites possess properties that are superior to those of conventional composites because of the interfacial adhesion being maximized. Recently, nano-scale composites of polymers with clays or organoclays have been studied extensively [14–18].

Clays have sandwich types of structures with one octahedral Al sheet and two tetrahedral Si sheets, the so called philo-silicate. There are many types of philo-silicates: kaolinite, montmorillonite, hectrite, saponite, synthetic mica, etc. For our purposes, montmorillonite and synthetic mica were chosen for syntheses of the nanocomposites. These clays consist of stacked silicate sheets with lengths of about 218 nm for montmorillonite and 1,230 nm

---

[*] Corresponding author. Tel.: +82-54-467-4292; fax: +82-42-483-6155.
E-mail address: changjinhae@hanmail.net (J.H. Chang).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00276-3

for synthetic mica. They have the same sheet thickness of 1 nm. Therefore, the only difference among them is the lengths of the silicate sheets [19–20].

In this study, hexadecylamine was used as an alkylamine in organoclays in a starch-blended PLA matrix. This paper deals with the influences of organoclays, such as hexadecylamine-montmorillonite (C_{16}-MMT) and hexadecylamine-synthetic mica (C_{16}-Mica), on the thermo-mechanical properties, morphologies, and film translucencies. These properties of PLA/C_{16}-MMT hybrid films compared with those of similar films prepared from C_{16}-Mica. We also describe the properties of PLA hybrids films as functions of the organoclay content.

2. Experimental

2.1. Materials

The source clay, Kunipia-F (Na^+-montmorillonite), was obtained from Kunimine Co. By screening the Na^+-montmorillonite (Na^+-MMT) with a 325-mesh sieve to remove impurities, we obtained clays with a cationic exchange capacity of 119 mequiv./100 g. Na^+-type fluorinated synthetic mica (Na^+-Mica) with the free OH group of the mica replaced by fluorine was supplied by CO-OP Ltd., Japan. Its cationic exchange capacity was in the range of 70–80 mequiv./100 g.

The hexadecylamine was purchased from Aldrich Chemical Co. and was used as received. All reagents were purchased from TCI and Aldrich Chemical Co. Commercially available solvents were purified by distillation. *N*,*N*′,-dimethylacetamide (DMAc) was purified and dried over molecular sieves before use. Common reagents were used without further purification. The PLA had a high starch content (43%). This resin was supplied by Kolon Company, Korea, with a weight-average molecular weight of 160,000. The pure PLA films were characterized by a broad intensity maximum, indicating an amorphous structure, appearing approximately at $2\theta = 16–17°$ in Wide-angle X-ray diffraction (WAXD).

2.2. Preparation of organophilic-MMTs and PLA/organophilic-MMT hybrid films

Dispersions of Na^+-MMT and Na^+-Mica were added to solutions of ammonium salts of hexadecylamine (C_{16}-). Organophilic clays were obtained through a multi-step process and were called C_{16}-MMT [21] and C_{16}-Mica [19], respectively.

In a 500 ml beaker, 4.0 g of hexadecylamine, 2.5 ml of concentrated HCl, and 200 ml of water were placed. This solution was heated at 80 °C. In 400 ml of water, 10 g of clay was dispersed at 80 °C. This dispersion of clay was added to the ammonium salt of the hexadecylamine solution, and the mixture was stirred vigorously for 1 h. The precipitate was isolated by filtration, placed in a 250 ml beaker with 300 ml of hot water, and stirred for 1 h. The product was then filtrated and freeze-dried. C_{16}-Mica was made using the same procedure of that used for C_{16}-MMT.

Since the synthesis procedures for polymer/organoclay nanocomposites with different weight percents (wt%) of organoclays are very similar, only a representative example for the preparation of PLA/C_{16}-MMT (2 wt%) is given [10, 18,22]. A mixture of 50.0 g of a DMAc dispersion containing 0.08 g of C_{16}-MMT, 4.0 g of a PLA solution, and excess DMAc was stirred vigorously at room temperature for 4 h. The solution was spread onto a $10 \times 10\ cm^2$ glass plate, and the solvent was evaporated in a vacuum at 70 °C for 1 day. The films were then cleaned in an ultrasonic cleaner three times for 5 min each. These films, with the solvent removed, were dried again in a vacuum oven at 70 °C for 1 day. The thickness of the film were 10–15 μm.

2.3. Characterization

Thermogravimetric analyses of the hybrids were carried out with a Du Pont model 910 thermogravimetric analyzer (TGA) at a heating rate of 20 °C/min under a N_2 flow. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature using a Rigaku (D/Max-IIIB) X-ray diffractometer with Ni-filtered Co Kαradiation. The scanning rate was 2°/min over a range of $2\theta = 2–15°$

The tensile properties of the solution cast films were determined using an Instron Mechanical Tester (Model 5564) at a crosshead speed of 5 mm/min at room temperature. The specimens were prepared by cutting strips 5 mm wide by 70 mm long. The experimental uncertainties in the tensile strength and the modulus were ± 2 and ± 10 MPa, respectively. An average of ten individual determinations was obtained.

The samples for the transmission electron microscope (TEM) were prepared by putting PLA hybrid films into epoxy capsules and then curing the epoxy at 70 °C for 24 h in vacuum. After that, the cured epoxies containing the PLA hybrids were microtomed into 9 mm thick slices, and a layer of carbon, about 3 nm thick, was deposited on each slice on a mesh 200 copper net. TEM photographs of ultrathin sections of the polymer/organoclay hybrid samples were taken on an EM 912 OMEGA transmission electron microscope at an acceleration voltage of 120 kV.

3. Results and discussion

3.1. Dispersibility of organoclay in PLA

The XRD results for the PLA/C_{16}-MMT hybrid films are shown in the Fig. 1. The measured d_{001}-spacing of Na^+-MMT is 11.99 Å ($2\theta = 8.60°$). After cation exchange with hexadecylamine (C_{16}), the d_{001}-spacing is 25.96 Å ($2\theta =$

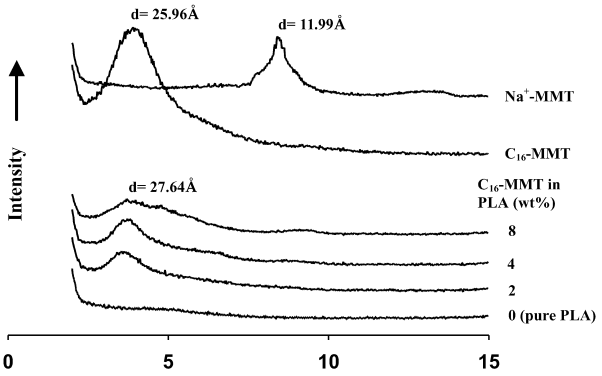

Fig. 1. WAXD patterns of Na^+-MMT, C_{16}-MMT, PLA, and their hybrids.

3.95°). It appears that Na cations are replaced exactly by C_{16} cations in the organic modification and that the C_{16}-MMT prepared in this study is well dispersed in water. When PLA/C_{16}-MMT hybrids are formed, an organoclay peak at $2\theta = 3.68°$ ($d = 27.64$ Å) appears in the diffraction pattern of PLA/C_{16}-MMT. Further increases in the basal interlayer spacing imply that polymer chains are intercalated within the clay galleries [23–25]. With increasing organoclay content from 2 to 8 wt%, PLA/C_{16}-MMT hybrid films showed the same diffraction pattern.

Fig. 2 shows the XRD curves for PLA/C_{16}-Mica hybrid films. The d_{001} reflection for the mica was found at $2\theta = 10.64°$, which corresponds to an interlayer distance of 9.65 Å. It is clear that the XRD data shift to smaller angles for the modified clay. Surface modification by alkylamine afforded substantially increased interlayer distances for mica. The XRD peak for the surface-modified clay was found at $2\theta = 2.77°$, corresponding to an interlayer distance of 37.03 Å. As would be expected, the ion exchange between the clay (Na^+-Mica) and the alkylamine (C_{16}) results in an increase in the basal interlayer spacing in comparison with pristine Na^+-Mica and leads to a big shift of the diffraction peak toward lower values of the 2θ compared to C_{16}-MMT. The d_{001} reflection of Na^+-Mica at $2\theta = 10.64°$ is seen in the modified clay (C_{16}-Mica), as well as in the hybrids with the organoclay. This means that pristine mica remains in the final materials, as well as in the PLA/C_{16}-Mica hybrids, for C_{16}-Mica contents up to 8 wt%. In all samples, the peaks observed around $d = 19$, 17, and 11 Å or $2\theta = 5.33°$, 6.17°, and 9.14°, respectively, correlate to the 002 and the 003 planes of the clay layers.

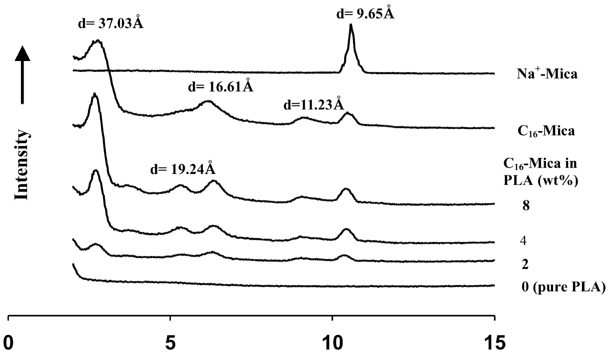

Fig. 2. WAXD patterns of Na^+-MMT, C_{16}-Mica, PLA, and their hybrids.

From the above results, a substantial increase in the intensities of the XRD peaks is observed for clay loading from 2 to 8 wt%. The presence of the organoclay, however, had no effect on the location of the peak. This indicates that perfect exfoliation of the clay layer structure of the organoclay in PLA does not occur. Organoclay dispersion in PLA will be cross-checked further by using the TEM data, which are discussed in the next section.

3.2. Morphology

WAXD is a conventional method to determine the interlayer spacing of clay layers in the original clay and in the intercalated polymer/clay nanocomposites. On the other hand, the internal structures of the nanocomposites on a nanometer scale are observed by using TEM. TEM allows a qualitative understanding of the internal structure through direct observation.

Typical TEM photographs for the hybrids with organoclays are displayed in Fig. 3. Fig. 3(a) and (b) are for PLA hybrids containing 4 wt% organoclays. The dark lines in the pictures are 1 nm thick clay layers, the spaces between the

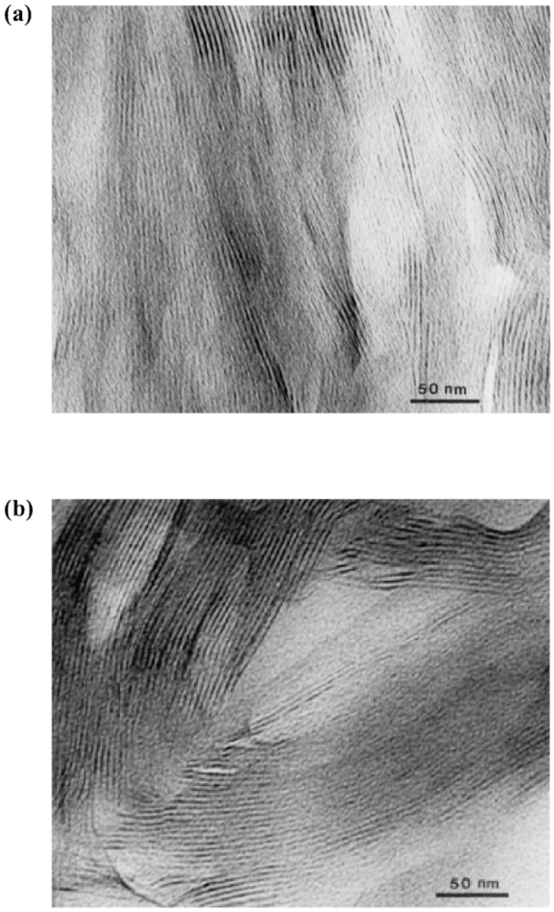

Fig. 3. TEM photographs of PLA hybrids containing 4 wt% organoclay: (a) C_{16}-MMT and (b) C_{16}-Mica.

dark lines are interlayer spaces, and the gray bases are the PLA matrix. For the C_{16}-MMT hybrid films in Fig. 3(a), some of the clay is dispersed well in the PLA matrix, and some of it is agglomerated to a size of approximately 5–10 nm.

In the case of the nanocomposite containing the same wt% C_{16}-Mica, the TEM micrograph, Fig. 3(b), show region with individual dispersion of partially delaminated sheets in the matrix and regions where a regular stacking of sheets being maintained with a layer of polymer between the sheets. This is consistent with the XRD results shown in Figs. 1 and 2.

3.3. Thermal stabilities

The thermal stabilities of pure PLA and its hybrids are listed in Table 1. In the cases of the C_{16}-MMT and the C_{16}-Mica hybrids, the initial degradation temperatures (T_D^i) (at 2% weight loss) of the PLA hybrid films decreased with increasing amount of organoclay, with a maximum decrease of 49 °C from the value for pure PLA for 8 wt% C_{16}-MMT and of 16 °C for the same wt% loading of C_{16}-Mica. Based on the fact that inorganic species have good thermal stabilities, it is generally believed that the introduction of inorganic components into organic materials can improve their thermal stabilities. This increase in the thermal stability can be attributed to the high thermal stability of clay and to the interaction between the clay particles and the polymer matrix [26–29]. Ogata et al. [12] reported that the clays seemed to hinder the deformation of the crystalline structures of PLA hybrids at low temperatures, but they also observed that the clays acted as deformation accelerators at higher temperatures. In any event, in contrast to pure PLA, the onsets of initial decomposition for PLA/C_{16}-MMT and C_{16}-Mica shift towards lower temperatures with increasing clay content, indicating a lowering of their thermal stabilities upon intercalation at higher temperatures. Similar results have also been observed in other studies of polymer nanocomposites [30].

A comparison of the thermal stabilities leads to the conclusion that the C_{16}-Mica hybrids are thermally more stable than the C_{16}-MMT hybrids because the free OH groups in the pristine mica are replaced by fluorine atoms in synthetic mica. This effect increases the initial decomposition temperature of the mica hybrid, leading to a higher relative thermal stability. However, the thermal insulation effect did not occur in our system at higher temperatures.

Table 1
Thermogravimetric analyses of PLA/organoclay hybrid films

Clay wt%	C_{16}-MMT		C_{16}-Mica	
	$T_D^{i\,a}$ (°C)	wt_R^{600b} (%)	T_D^i (°C)	wt_R^{600} (%)
0 (pure PLA)	370	2	370	2
2	343	4	363	3
4	336	6	361	5
6	331	6	356	7
8	321	8	354	7

[a] Initial weight reduction onset temperature.
[b] Weight percent of residue at 600 °C.

The weight of the residue at 600 °C (wt_R^{600}) linearly increased, ranging from 2 to 8% for clay loadings from 0 to 8 wt%, for all PLA/organoclay hybrids (see Table 1). The onset of initial degradation of the hybrids decreased, but the char residue at 600 °C increased, due to the incorporation of the organoclay. This enhancement of the char formation is ascribed to the high heat-resistance due to the clay itself [31]. Only representative examples of the TGA curves for the PLA hybrids with 4 wt% organoclay content are shown in Fig. 4.

3.4. Tensile properties

Fig. 5 shows the mechanical property of hybrid films with different organoclay contents. The ultimate strengths of the hybrids increased remarkably with the organoclay content and possessed a maximum value for clay content loading of 4 wt%. The ultimate tensile strengths of the hybrids increased from 19 to 28 MPa with increasing C_{16}-MMT content up to 4 wt% and from 19 to 44 MPa with increasing C_{16}-Mica content up to 4 wt%. Above the critical wt% clay loadings corresponding to the ultimate strengths, the strength values of all the hybrids started to decrease due mainly to the agglomeration of clay particles, as we described in other articles [10,22,31]. Dispersion is very important because failure to disperse can induce agglomerations. Failure initiated many clay agglomerates, which meant that cracks were initiated on and propagated inside the agglomerates [32]. In short, a high organoclay content leads to agglomeration of clay particles, which reduces the tensile strength.

Fig. 6 shows the dependence of the initial modulus on the organoclay content. The modulus increased linearly with increasing organoclay content up to a critical value of 4 wt% for C_{16}-MMT. When the organoclay content was greater than this critical value, the modulus started to

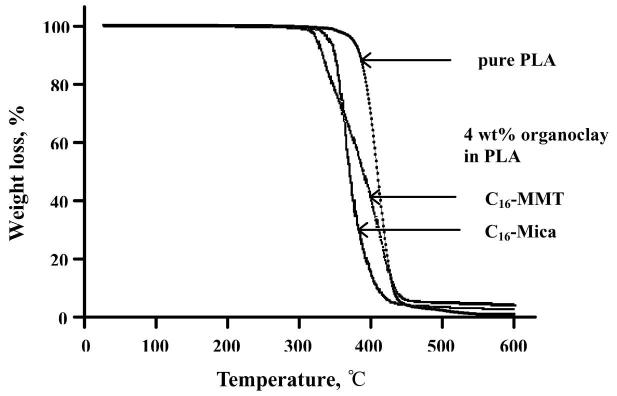

Fig. 4. TGA thermograms of PLA and its hybrids containing 4 wt% organoclay.

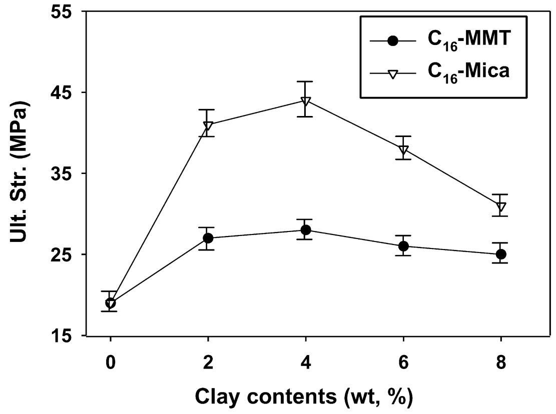

Fig. 5. Effects of the clay loading on the ultimate tensile strength of the hybrid films.

decrease. In contrast, the initial modulus of the hybrids using C_{16}-Mica increased linearly with increasing clay content from 2 to 6 wt%. As the amount of organoclay was increased to 8 wt%, the modulus of the hybrid significantly increased to 633 MPa, a three-fold increase over pure PLA (Table 2) (208 MPa). Compared to the C_{16}-MMT hybrids, this big enhancement of the modulus is ascribed to the resistance exerted by the clay itself, as well as to the orientation and the higher aspect ratio of the mica layers [19]. Additionally, the stretching resistance of the oriented backbone of the polymer chain in the gallery also contributed to enhancing the modulus.

Table 2
Tensile properties of PLA/organoclay hybrids films

Clay wt%	C_{16}-MMT			C_{16}-Mica		
	Ult. str. (MPa)	Ini. mod. (MPa)	E.B. (%)[a]	Ult. str. (MPa)	Ini. mod. (MPa)	E.B. (%)
0 (pure PLA)	19	208	845	19	208	845
2	27	254	981	41	252	1272
4	28	285	1146	44	270	1150
6	26	276	1054	38	311	1100
8	25	274	1060	31	633	569

[a] Elongation percent at break.

The elongation at breaks of the hybrid films with organoclays are shown in Fig. 7. The elongation at breaks of PLA is clearly seen to increase with the introduction of an organoclay and with increasing organoclay content. However, a certain wt% of organoclay loading corresponds to a maximum value, giving a 36–49% increase in the elongation at break. Thus, it can be concluded from the above observations that in a certain organoclay content range, the introduction of organoclay will lead to both a strengthening and a toughening of the PLA matrix. This may be regarded as a feature of nanocomposites. A further increase in the organoclay content leads to a decrease in the elongation at break, with the elongation break of 8 wt% C_{16}-MMT being much higher than that of pure PLA and that of 8 wt% C_{16}-Mica being much lower than that of pure PLA.

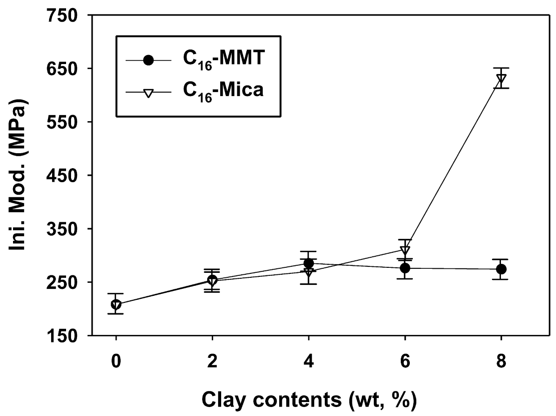

Fig. 6. Effects of the clay loading on the initial tensile modulus of the hybrid films.

From the above results, it appears that there is an optimal amount of organoclay needed in a hybrid to achieve the greatest improvements in its properties. The properties of the C_{16}-Mica hybrids were better than those of the C_{16}-MMT hybrids in ultimate tensile strength and initial modulus. We suggest that C_{16}-Mica in nanocomposites not only induces a stronger interfacial interaction between PLA and the organoclay but also imparts the higher rigidity of the clay structure.

3.5. Optical translucency

Optical nanocomposites are translucent so as to reduce light scattering and to obtain high values of optical purity. For high translucency, the dispersed phase should have an average size smaller than the wavelength of visible light (i.e. 400–800 nm) [16].

The PLA/organoclay hybrid films prepared by using a solvent–casted process were off-white in color, but highly translucent. Moreover, the levels of translucency were not affected by the organoclay contents up to 6 wt% as shown in Fig. 8. Because hybrid films may have phase domains smaller than these wavelengths of light, the materials may be translucent even though the clay loading is increased.

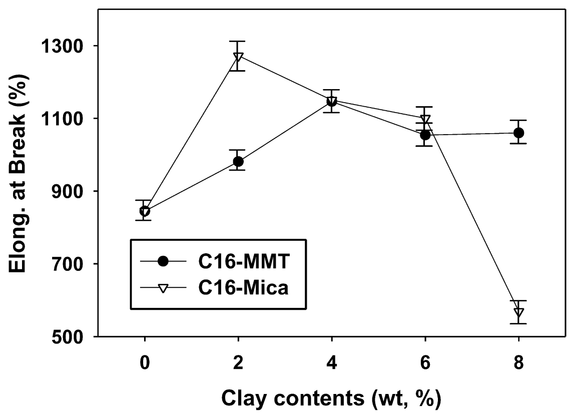

Fig. 7. Effects of the clay loading on the elongation at break of the hybrid films.

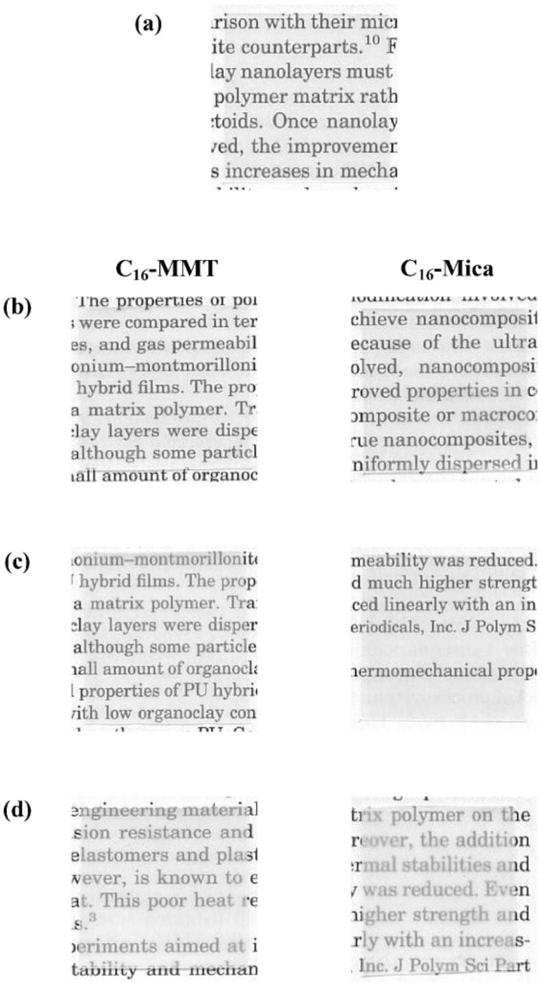

Fig. 8. Translucency of PLA hybrid films containing (a) 0 (pure PLA), (b) 4, (c) 6, and (d) 8 wt% organoclays.

However, the translucency slightly decreased with increasing organoclay content because of agglomerations of the clay particles. Compared to the films with 4–6 wt% organoclays, the films containing 8 wt% were cloudier in Fig. 8, but there was still no problem in reading a letter through the film. The translucency of the hybrid films was due the degree of dispersion of the clay particles in the matrix polymer.

4. Conclusions

Considering effort has been expended to improve the thermo-mechanical properties of common thermoplastics by blending them with organoclays. In this investigation, we tried to clarify the structural effect of alkylamine-type organoclay reinforcement in a PLA matrix in the form of films. We demonstrated that a small amount of added organoclay was enough to improve the tensile properties of the PLA films. This suggested that so-called nanocomposites were attained.

By comparing the two tested organoclays, we found that C_{16}-Mica was more effective in improving the physical strength of PLA films. C_{16}-Mica is believed to enhance the interfacial interaction between the clay and the PLA matrix. In this study, the combination of the high aspect ratio of the mica and the improved interaction between the clay and the PLA certainly made C_{16}-Mica a better reinforcing filler than C_{16}-MMT. Also, this observation agreed with the tendency for the tensile properties of these hybrids to change with the organoclay loading.

References

[1] Vert M, Schwach G, Coudane J. J Macromol Sci Pure Appl Chem 1995;A32:787.
[2] Bigg DM. SPE ANTEC Tech Papers 1996;2028.
[3] Tsuji H, Ikada Y. J Appl Polym Sci 1998;67:405.
[4] Martin O, Averous L. Polymer 2001;42:6209.
[5] Engelberg I, Kohn J. Biomaterials 1991;12:292.
[6] Naitove MH. Plast Technol 1998;44:13.
[7] Hong HW, Moony DJ. Synthetic biodegradable polymer scaffolds. Boston: Birkhauser; 1997. Chapter 4.
[8] Perego G, Cella GD, Bastioli C. J Appl Polym Sci 1996;195:1649.
[9] Ramsay BA, Langlade V, Carreau PJ, Ramsay JA. Appl Environ Microbiol 1993;59:1242.
[10] Chang J-H, An YU, Sur GS. J Polym Sci, Part B: Polym Phys 2003; 41:94.
[11] Jacobson S, Fritz HG. Polym Engng Sci 1996;36:2799.
[12] Ogata N, Jimenez G, Kawai H, Ogihara T. J Polym Sci, Part B: Polym Phys 1997;35:389.
[13] Zhang L, Goh SH, Lee SY. Polymer 1998;39:4841.
[14] Lagaly G. Appl Clay Sci 1999;15:1.
[15] Usuki A, Koiwai A, Kojima Y, Kawasumi M, Okada A, Kurauchi T, Kamigaito O. J Appl Polym Sci 1995;5:119.
[16] Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito O. J Polym Sci, Part A: Polym Chem 1993;31:2493.
[17] Giannelis EP. Adv Mater 1996;8:29.
[18] Chang J-H, Seo B-S, Hwang D-H. Polymer 2002;43:2969.
[19] Yano K, Usuki A, Okada A. J Polym Sci, Part A: Polym Chem 1997; 35:2289.
[20] Garcia-Martinez JM, Laguna O, Areso S, Collar EP. J Polym Sci, Part B: Polym Phys 2000;38:1564.
[21] Yang Y, Zhu Z, Yin J, Wang X, Qi Z. Polymer 1999;40:4407.
[22] Chang J-H, Park KD, Cho D, Yang HS, Ihn KJ. Polym Engng Sci 2001;41(9):1514.
[23] Hsiao SH, Liou G-S, Chang L-M. J Appl Polym Sci 2001;80:2067.
[24] Zilig C, Mulhaupt R, Finter J. Macromol Chem Phys 1999;200:661.
[25] Ke Y, Lu J, Yi X, Zhao J, Qi Z. J Appl Polym Sci 2000;78:808.
[26] Wen J, Wikes GL. Chem Mater 1996;8:1667.
[27] Fischer HR, Gielgens LH, Koster TPM. Acta Polym 1999;50:122.
[28] Petrovic XS, Javni L, Waddong A, Banhegyi GJ. J Appl Polym Sci 2000;76:133.
[29] Zhu ZK, Yang Y, Yin J, Wang X, Ke Y, Qi Z. J Appl Polym Sci 1999; 3:2063.
[30] Bharadwaj RK, Mehrabi AR, Hamilton C, Trujillo C, Murga M, Fan R, Chavira A, Thompson AK. Polymer 2002;43:3699.
[31] Chang J-H, An YU. J Polym Sci, Part B: Polym Phys 2002;40:670.
[32] Masenelli-Varlot K, Reynaud E, Vigier G, Varlet J. J Polym Sci, Part B: Polym Phys 2002;40:272.