

Using Maleic Anhydride Grafted Poly(lactic acid) as a Compatibilizer in Poly(lactic acid)/Layered-Silicate Nanocomposites

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ABSTRACT: The goal of this work was to prepare exfoliated poly(lactic acid) (PLA)/layered-silicate nanocomposites with maleic anhydride grafted poly(lactic acid) (PLA-MA) as a compatibilizer. Two different layered silicates were used in the study: bentonite and hectorite. The nanocomposites were prepared by the incorporation of each layered silicate (5 wt %) into PLA via solution casting. X-ray diffraction of the prepared nanocomposites indicated exfoliation of the silicates. However, micrographs from transmission electron microscopy showed the presence of intercalated and partially exfoliated areas. Tensile testing showed improvements in both the tensile modulus and yield strength for all the prepared nanocomposites. The results from the dynamic mechanical ther-

mal analysis showed an improvement in the storage modulus over the entire temperature range for both layered silicates together with a shift in the $\tan \delta$ peak to higher temperatures. The effect of using PLA-MA differed between the two layered silicates because of a difference in the organic treatment. The bentonite layered silicate showed a more distinct improvement in exfoliation and an increase in the mechanical properties because of the addition of PLA-MA in comparison with the hectorite layered silicate. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1852–1862, 2006

Key words: mechanical properties; nanocomposites; transparency

INTRODUCTION

Layered silicates have been used as fillers in polymers for a long time, and in recent years, attention has been focused on using these materials to fabricate nanocomposites.¹ The main driving force behind the preparation of nanocomposites is the remarkable improvement in the mechanical properties, thermal stability, flame retardancy, and reduced permeability at low reinforcement concentrations (~ 5 wt %).^{2–4} Layered silicates are able to provide a large interfacial area for matrix/reinforcement interactions, which gives rise to this remarkable improvement in the properties. A large variety of polymer matrices together with different types of unmodified and organically modified layered silicates have been investigated for the production of nanocomposites.^{1–6} The dispersion of the layered silicates can differ in nanocomposites, depending on the extent of the interaction with the polymer and the processing method used. The morphology can vary from tactoids to intercalated, partially exfoliated structures to fully exfoliated structures.^{4–6} Today, several organically modified layered silicates are available that

are tailored to suit different polymers and solvent systems. It is therefore becoming easier to design and control the morphology and properties of nanocomposites.

Currently, there is increased interest in developing biobased materials to reduce environmental pollution and increase the use of natural and renewable resources. Biopolymers such as cellulose esters (CA, CAB, and CAP), poly(hydroxyalkanoate)s, and poly(lactic acid) (PLA) are increasingly being studied as replacements for petroleum-based polymers.^{7–10} The potential of these materials in medical devices, packaging, and automotive applications is continuously being explored by researchers and industry. Studies have compared the performances of biopolymers and synthetic polymers in packaging applications.^{8,10} Petersen et al.,⁸ for example, compared films made of different biodegradable polymers with films made of polyethylene, polypropylene, and polystyrene. They concluded that biodegradable polymers have high potential in the packaging of highly respiring food, such as fruits and vegetables, because of their high O_2/CO_2 permeability ratio. However, they found that a major drawback of using biopolymers as packaging materials is their high water vapor permeability.⁸ The preparation of nanocomposites has been considered a promising method to improve these properties along with the mechanical properties without affecting the transparency of the polymers.¹¹ As this is a very

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new field, more research has to be carried out before these materials can be used as replacements for conventional packaging materials.

PLA is a biodegradable, thermoplastic polyester produced from L-lactic acid derived from the fermentation of corn starch.⁹ PLA is becoming increasingly popular as a biodegradable engineering plastic because of its high mechanical strength and easy processability in comparison with other biopolymers.⁹ However, PLA has lower thermal stability [glass-transition temperature (T_g) \approx 58°C], water vapor, and gas barrier properties than petroleum-based polymers used in packaging applications.^{8,10} Recently, work has been ongoing to prepare nanocomposites of layered silicates and PLA. Most studies have tried to combine PLA with organically modified montmorillonite.^{12–20} These studies report the use of both compounding extrusion^{12–16} and solution casting^{17–20} to exfoliate the layered silicate inside the PLA matrix. The results show that intercalation is possible, but it is difficult to develop a system that is completely exfoliated. Mica,^{14,16,19} saponite,¹⁶ and smectite¹⁴ have also been incorporated into PLA. The smectite layered silicate has shown quite promising results. A few studies have used a compatibilizer to improve the exfoliation of the layered silicates within the polymer matrix. Ray et al.¹² used oligo (ϵ -caprolactone) in their study to improve the exfoliation of layered silicates in PLA. Their results showed that using a compatibilizer improved the parallel stacking of the silicate sheets. Paul et al.¹⁵ used poly(ethylene glycol) (PEG) in their study to plasticize PLA to make the polymer chains more mobile and thereby improve the intercalation. Their study showed that PEG chains penetrated the layered silicates, leaving less PEG available to plasticize the remaining PLA.

Maleic anhydride (MA) is a polar monomer and has been used to modify nonpolar polymers to improve the exfoliation of layered silicates.^{21–23} The results show that using MA grafted polymers as compatibilizers can improve the exfoliation in, for example, cellulose acetate,²¹ polypropylene,²² and thermoplastic polyolefin²³ nanocomposites. It has also been used in PLA/starch composites to improve the compatibility between these two immiscible phases.²⁴ It is therefore believed that grafting MA onto PLA and using this as a compatibilizer will help to improve the exfoliation of layered silicates inside a PLA matrix.

The goal of this work was to prepare exfoliated PLA/layered-silicate nanocomposites with maleic anhydride grafted poly(lactic acid) (PLA-MA) as a compatibilizer. Two different layered silicates were used in the study, bentonite and hectorite, which were both able to swell in chloroform. The structural details of the system were studied with X-ray analysis, field emission scanning electron microscopy (FESEM),

and transmission electron microscopy (TEM). The mechanical performance was evaluated with conventional tensile testing and dynamic mechanical thermal analysis (DMTA). Ultraviolet-visible (UV-vis) spectroscopy and measurements of the water contact angle were also carried out because these two parameters are important for packaging applications.

EXPERIMENTAL

Materials

Matrix

PLA (Nature Works 4031 D) was supplied by Cargill Dow LLC (Minneapolis, MN). The material had a density of 1.25 g/cm³, a T_g of 58°C, and a melting point of 160°C. The molecular weight of the material was between 195,000 and 205,000 g/mol.

Reinforcements

Bentonite and hectorite were supplied by Elementis Specialties (New Jersey). These two smectite layered silicates were organically modified and were commercially available as Bentone 107 (bentonite) and Bentone 2004 (hectorite). The characteristics of the two layered silicates are listed in Table I.

Chemicals

MA, purchased from Merck-Schuchardt (Germany), and dicumyl peroxide, purchased from Sigma-Aldrich (Norway), were used to graft MA onto PLA. Chloroform, purchased from Lab-Scan (Dublin, Ireland), was used to swell the layered silicates and to dissolve both the pure and grafted PLA. Silicon 100 from Novatio Europe N.V. was used to grease the Petri dishes before the casting.

MA grafting

The grafting of MA onto PLA supplied by Cargill Dow was carried out according to the guidelines given by Shiraishi and Ajioka.²⁵ PLA pellets (3 kg) were first dried at 40°C overnight. The dried PLA pellets were blended with 300 g of melted MA and 10.5 g of dicumyl peroxide. The blend was compounded with a Coperion Werner and Pfleiderer ZSK 25 WLE twin-screw extruder with a throughput of 5 kg/h and a torque of 40%. The temperature zones of the extruder had settings ranging from 170 to 200°C. The extrudate was collected and pelletized into granulates. The grafting percentage was determined to be 2.3 wt % MA by titration procedures described by Shiraishi and Ajioka. The chemical reaction between PLA and MA has been described by others.²⁴

TABLE I
Characteristic Parameters of the Layered Silicates

Characteristic	Bentonite	Hectorite
Commercial name	Bentone 107	Bentone 2004
Central sheet	Aluminum oxide	Magnesium oxide
Organic treatment	Dimethyl dihydrogenated tallow treatment	Dimethyl benzyl hydrogenated tallow treatment
Density (g/cm ³)	1.7	1.8
Sheet dimensions (nm)	800 × 800 × 1	800 × 80 × 1
Surface area per sheet (m ²)	1.28 × 10 ⁻¹²	1.30 × 10 ⁻¹³
Surface area per g (m ² /g) ^a	1180	1130

^a Calculated on the basis of full exfoliation.

Processing of the nanocomposites

Swelling of the layered silicates

Solutions (1 wt %) of the layered silicates were prepared by the addition of the layered silicates to chloroform. The solutions were stirred for 24 h with a magnetic stirrer at room temperature. This procedure was followed by 15 min of sonification.

Film preparation

The nanocomposites were prepared via solution casting. PLA and PLA-MA were dissolved in chloroform. PLA formed a 15 wt % solution, whereas PLA-MA formed a 10 wt % solution. The solutions were stirred on a hot plate at 50°C until the pellets were fully dissolved (~ 5 h). The formulations (see Table II) were mixed and then sonified for 15 min before casting. The formulations were then cast in Petri dishes greased with silicon and left to evaporate at room temperature for a week. The prepared films had a thickness of approximately 0.15 mm and a total dry weight of 5 g.

Characterization

Wide-angle X-ray diffraction (WAXD)

WAXD (D5005 diffractometer, Siemens) was used to study the morphology of the prepared nanocomposites. The samples were exposed for a period of 11 s for each angle of incidence (θ) with a Cu K $\alpha_{1,2}$ X-ray source with a wavelength (λ) of 1.541 Å. θ was varied from 1.5 to 40 by steps of 0.06°. Bragg's law ($n\lambda = 2d \sin \theta$) was used to calculate the d -spacing of the layered silicates.

Electron microscopy

Two different types of electron microscopes were used to analyze the structure of the produced nanocomposites. First, the fracture surface of PLA/bentonite was analyzed in a Zeiss Supra 55VP low-vacuum field emission scanning electron microscope to determine the size of the intercalations present in

the material. An accelerating voltage of 1.16 kV was applied together with a high vacuum in the chamber. Second, the nanostructure of the prepared nanocomposites was investigated with a Philips CM30 transmission electron microscope at an acceleration voltage of 100 kV. A small sample with a cross-sectional area of 2 × 7 mm² was embedded in epoxy and cured overnight in room temperature. The final ultramicrotoming was performed with a diamond knife at room temperature generating electron transparent foils, which were approximately 50 nm thick. These foils were gathered on a 300-mesh Cu grid.

Tensile testing

Tensile testing was carried out with a Rheometric Scientific MiniMat 2000 miniature material tester with a 1000 N load cell at a crosshead speed of 2 mm/min. The samples were prepared by strips being cut from the films with a width of 5 mm. The length between the grips was 15 mm, and seven samples were used to characterize each material. The results obtained from the MiniMat 2000 could be used only for comparison because the strain values were based on the rotational movement of the drive shaft.

DMTA

The dynamic mechanical properties of the nanocomposite films were measured with a Rheometric Scientific DMTA V in the tensile mode. The measurements were carried out at a constant frequency of 1 Hz, a strain amplitude of 0.05%, a temperature range of 15–100°C, a heating rate of 3°C/min, and a gap distance of 20 mm. All samples were placed in a

TABLE II
Prepared Formulations (wt %)

Material	PLA	PLA-MA	Bentonite	Hectorite
PLA	100	—	—	—
PLA/bentonite	95	—	5	—
PLA/hectorite	95	—	—	5
PLA/PLA-MA/bentonite	85	10	5	—
PLA/PLA-MA/hectorite	85	10	—	5

vacuum oven at room temperature for 4 days before the testing to remove the last remaining chloroform. The samples were prepared by strips being cut from the films with a width of 5 mm. Four samples were used to characterize each material.

Water contact angle

The water contact angles were measured on a KSV Instruments optical contact-angle meter with a static setup. Five samples were used to characterize each material.

UV-vis spectrometry

Transparency measurements were carried out on a Varian Cary 5 UV-vis/near-infrared spectrophotometer. λ was varied between 600 and 200 nm, and a spectral bandwidth of 2 was used together with a scanning rate of 50 nm/min. Five samples were used to characterize each material.

RESULTS AND DISCUSSION

Material structure

The structure of layered-silicate nanocomposites is often divided into different categories depending on the degree of exfoliation of the layered-silicate sheets. The morphology can vary from a microcomposite (tactoidal) to an intercalated structure to a partially

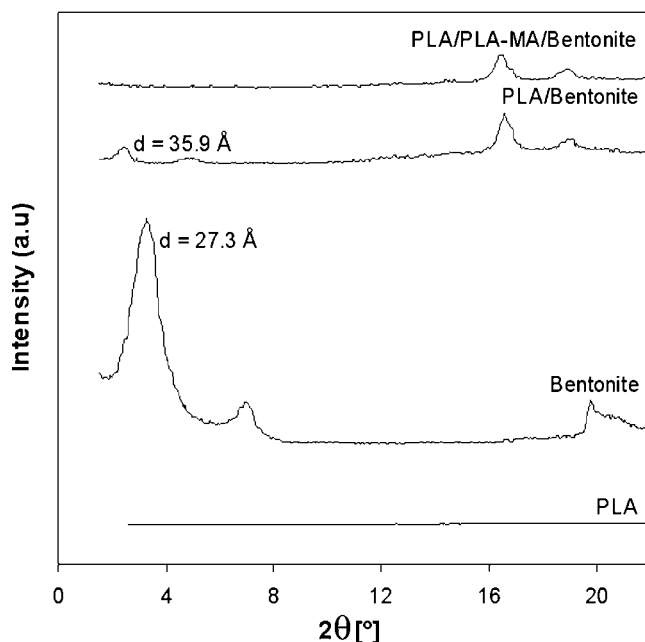


Figure 1 WAXD results for the bentonite nanocomposites. The graph indicates that intercalation occurred in the PLA/bentonite system and that full exfoliation occurred in the PLA/PLA-MA/bentonite system.

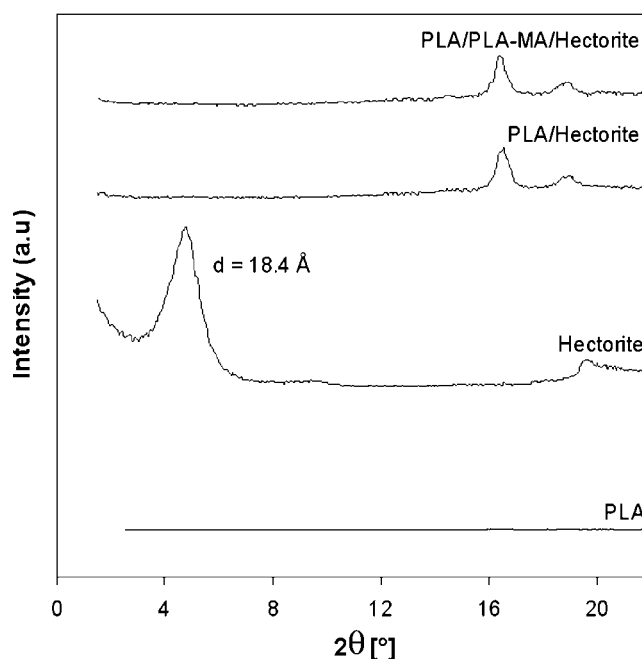


Figure 2 WAXD results for the hectorite nanocomposites. The graph indicates that full exfoliation occurred in both systems, PLA/hectorite and PLA/PLA-MA/hectorite.

exfoliated structure to a fully exfoliated structure. The degree of exfoliation will have a large impact on the mechanical properties, and it is therefore important to conduct a thorough investigation of the morphology. In this study, the morphology was investigated with WAXD, FESEM, and TEM.

The results from WAXD are shown in Figures 1 and 2. In Figure 1, peaks for bentonite are identified at $2\theta = 3.24^\circ$ and $2\theta = 7.02^\circ$, which correspond to d -spacings of 27.3 and 12.6 Å. In the PLA/bentonite material, these peaks have shifted to the left, giving $2\theta = 2.46^\circ$ ($d = 35.9$ Å) and $2\theta = 4.92^\circ$ ($d = 18.0$ Å). In the nanocomposite containing bentonite and PLA-MA, the peaks are absent. Generally, increasing d -spacing is considered an indication of intercalation, and the absence of peaks indicates exfoliation.²⁶ In Figure 2, a peak for hectorite is identified at $2\theta = 4.8^\circ$; this corresponds to a d -spacing of 18.4 Å. In both nanocomposites containing hectorite, this peak is absent. This indicates that hectorite is easier to exfoliate in PLA than bentonite. There are two reasons that can explain this behavior. First, there is a difference in the sheet sizes of the clays. The width of hectorite is 10 times smaller than that of bentonite, and this makes it less difficult to peel the hectorite sheets apart. Second, there is a difference in the organic modification of the two clays: the hectorite clay is more polar. WAXD showed that even though the initial d -spacing of the bentonite sheets was larger than that of the hectorite sheets (≈ 9 Å), hectorite was still able to achieve exfoliation. The WAXD study also indicated that PLA-MA was necessary to achieve

exfoliation of the bentonite sheets in the PLA matrix. From the WAXD study, it is not possible to see an effect of PLA-MA on the hectorite nanocomposite.

An FESEM study was performed on a fracture surface of the PLA/bentonite nanocomposite. This specific nanocomposite was chosen to study the size distribution of the tactoids and intercalated areas present in the produced nanocomposites. The WAXD study showed that the PLA/bentonite nanocomposite was the least exfoliated of the four nanocomposites produced, and analyzing this structure would therefore show the largest tactoids/intercalations present in the four nanocomposite materials. Intercalation was defined by Lan and Pinnavaia²⁷ as an area in which one or more polymer chains have penetrated the clay structure, but the properties are still determined by the silicate. This is different from a tactoid, for which no penetration of the clay structure has occurred by the polymer.²⁷ Exfoliation is said to have occurred when individual silicate sheets are evenly distributed throughout the polymer matrix.²⁷ Exfoliation can occur as ordered or disordered exfoliation, and ordered exfoliation can be identified by X-ray diffraction studies.²⁸ Figure 3 shows that the size distribution of the tactoids present in the PLA/bentonite nanocomposite was very large and that not only the thickness of the tactoids varied. Even the length and width of the tactoids varied. There were a few tactoids that had dimensions up to $7 \times 4 \times 1.5 \mu\text{m}^3$, which were much larger than the first, but most of the tactoids were on the order of $2.5 \times 1.5 \mu\text{m}^3$.

TEM micrographs of the nanocomposites are shown in Figures 4 and 5. The four nanocomposites were very similar. The figures show a nonhomogeneous structure with mixed regions of tactoids [black arrow in Fig. 4(a)], intercalations [dark gray arrow in Fig. 4(a)], and exfoliation [light gray arrow in Fig. 4(a)]. The PLA/PLA-MA/bentonite nanocomposite [Fig. 4(c)] had a more exfoliated structure than the PLA/bentonite nanocomposite [Fig. 4(a)]. This indicated that PLA-MA had the ability to improve the

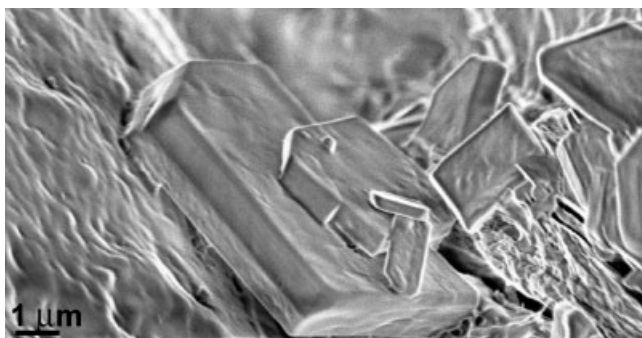


Figure 3 FESEM analysis of a fracture surface of the PLA/bentonite nanocomposite. The image shows the size distribution of the tactoids present in the material.

exfoliation of the bentonite sheets. In the detailed image of the PLA/bentonite material [Fig. 4(b)], it is possible to see an intercalated area with polymer chains between the silicate sheets. The detailed image of the PLA/PLA-MA/bentonite system [Fig. 4(d)] shows an exfoliated structure. The detailed images of the two hectorite systems [Fig. 5(b,d)] show a larger degree of exfoliation than that of the two bentonite systems. Here it is possible to identify single well-dispersed layered-silicate sheets. The TEM analysis indicates that PLA-MA had the largest effect on the bentonite layered silicate. This will be reflected in the mechanical properties because there is a strong link between the degree of exfoliation and the improvements in the mechanical properties. The TEM analysis also indicates that there was a slight increase in the exfoliation of the hectorite layered silicate with the use of PLA-MA.

The structure of the prepared nanocomposites could on the whole be described as intercalated and partially exfoliated. This experiment has shown that it is difficult to obtain full exfoliation with solution casting even if a compatibilizer is used. The PLA-MA did improve the exfoliation of both layered silicates, but not to the degree of full exfoliation. The layered silicates used were chosen together with a supplier to find clays that would swell and exfoliate in chloroform, but this was not enough to obtain full exfoliation in the PLA matrix. One possible reason for this can be found by the study of the entropic and energetic factors of the system.²⁹ It is known that the entropy gain is small when organically modified layered silicates are intercalated, so to succeed with full exfoliation, other driving forces are needed. For example, strong silicate-polymer interactions can be created or extra energy can be provided to the system with extrusion or other production methods that can supply heat or shear forces.

The disappearance of the response from the (001) plane is often seen as an indication of a fully exfoliated layered-silicate system. This does not have to be the case because only a few percent of clay is added to the material and WAXD is sensitive to the quantity of the material measured. It is also difficult to measure below 1.5° . This is why TEM also should be performed. It is important to understand that WAXD and TEM do not have to give the same results. WAXD is normally seen as a bulk analysis method, but when layered silicates are being investigated, this might not be true. A low angle has to be used to identify the response from the (001) plane of the layered silicates, and as a result, the diffraction pattern will be generated closer to the surface of the material than what is normal. TEM, on the other hand, is performed on cross sections of the polymer films. These two methods therefore complement each other.

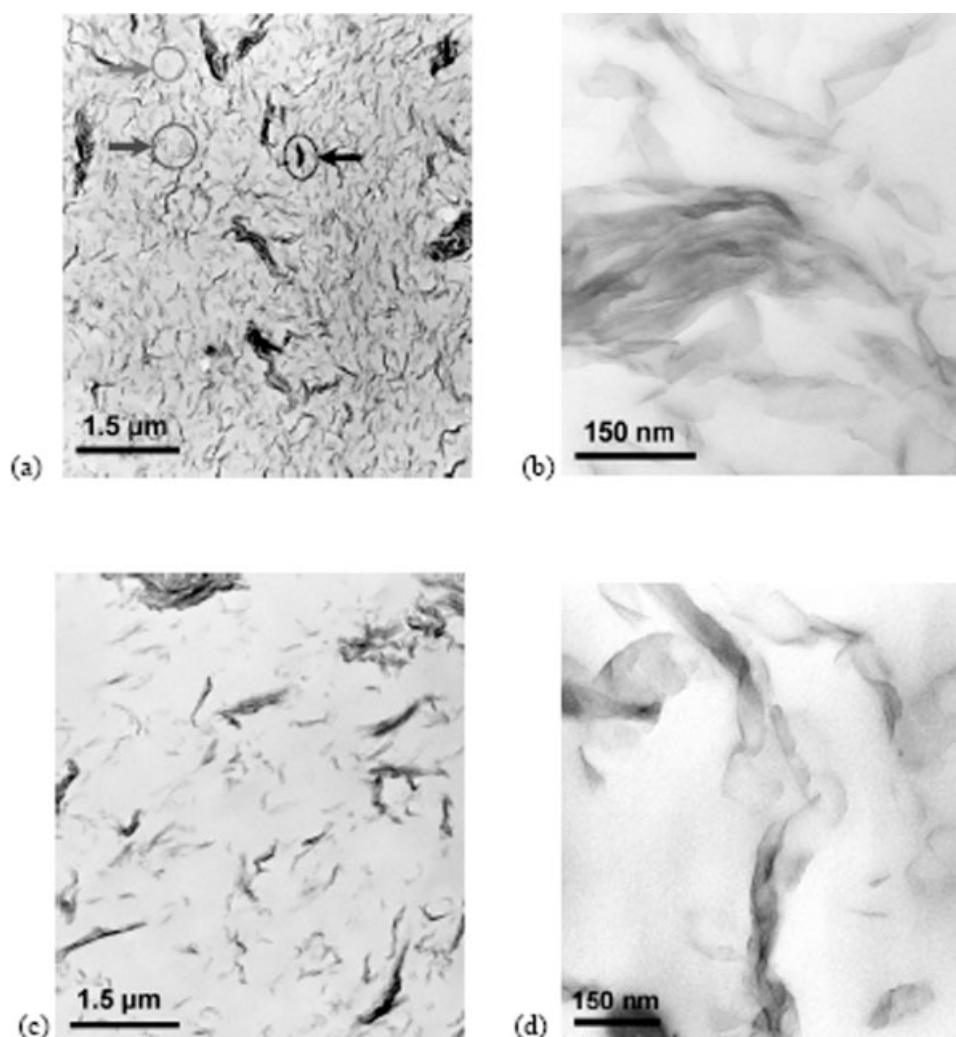


Figure 4 TEM analysis of the bentonite nanocomposites: (a,b) PLA/bentonite and (c,d) PLA/PLA-MA/bentonite. The figures show a nonhomogeneous structure with mixed regions of tactoids (black arrow), intercalations (dark gray arrow), and exfoliation (light gray arrow).

Mechanical properties

The mechanical properties of the prepared nanocomposite films are presented in Table III. All the prepared nanocomposite materials showed improvements in both the tensile modulus and yield strength in comparison with pure PLA. Table III shows that the PLA/PLA-MA/bentonite nanocomposite showed the largest improvements in both the tensile modulus and yield strength of all the prepared materials: 82 and 63% in comparison with those of pure PLA. The two bentonite nanocomposites had a larger increase in both the tensile modulus and yield strength than the two hectorite nanocomposites. This can be explained by a difference in the volume fraction between the two layered silicates used. The 5 wt % bentonite used corresponds to a volume fraction of 3.7%, whereas the 5 wt % hectorite used corresponds to a volume fraction of 3.5%. The difference in the

degree of exfoliation between the two systems did not seem to contribute to the mechanical properties in the same proportion as the volume fraction. The PLA/hectorite nanocomposite was better exfoliated than the PLA/bentonite nanocomposite, but the tensile modulus and yield strength of the PLA/hectorite nanocomposite was lower than that of the PLA/bentonite nanocomposite.

Figure 6 shows that the elongation to break was reduced by the addition of bentonite and hectorite to PLA. The bentonite clay had a more negative effect on the elongation to break than the hectorite clay. In regular composites, the elongation to break is affected by the volume fraction and dispersion of the reinforcement inside the matrix. It is well known that the addition of stiff reinforcements can reduce the elongation to break of the matrix because the reinforcements will cause stress concentrations. The bentonite nanocomposites contained both a higher

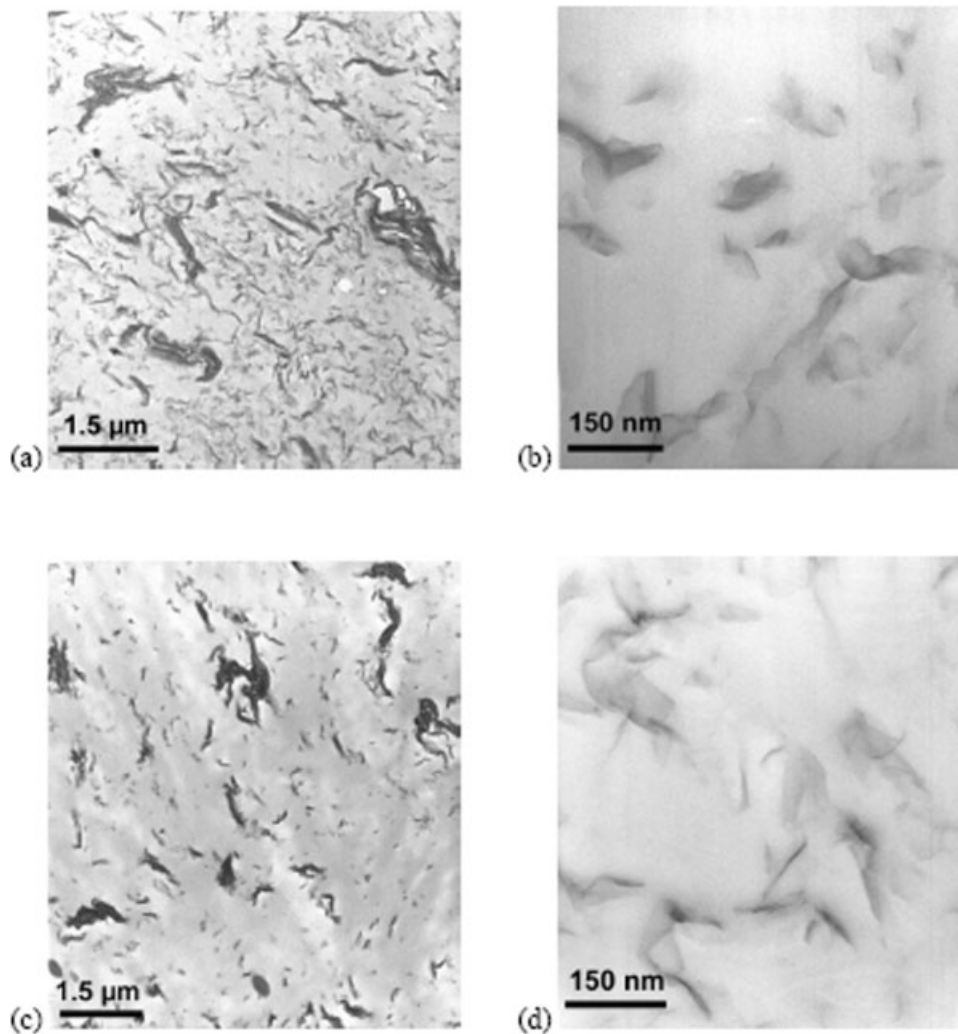


Figure 5 TEM analysis of the hectorite nanocomposites: (a,b) PLA/hectorite and (c,d) PLA/PLA-MA/hectorite. The figures show a nonhomogeneous structure with mixed regions of tactoids, intercalations, and exfoliation. The detailed images show that the hectorite nanocomposites were more exfoliated than the bentonite nanocomposites.

volume fraction and less exfoliated layered silicates than the hectorite nanocomposites. As a result, the elongation to break was more reduced in the bentonite nanocomposites than in the hectorite nanocomposites.

PLA-MA had an effect on the mechanical properties of the bentonite nanocomposite. Table III shows that there was a slight increase in both the tensile modulus and yield strength when PLA-MA was added to the nanocomposite. This can be explained

by the improved exfoliation of the bentonite sheets inside the PLA matrix. The degree of exfoliation was important for the improvements in the mechanical properties because it was linked to the available interfacial area. PLA-MA also had a negative effect on the elongation to break of both layered silicates. Table III shows that the elongation to break of the bentonite nanocomposite was more affected than the elongation to break of the hectorite nanocomposite. Earlier, it was concluded that exfoliation had a posi-

TABLE III
Properties of the Nanocomposites

Material	Tensile modulus (GPa)	Yield strength (MPa)	Elongation to break (%)	Water contact angle (°)
PLA	1.7 ± 0.2	28.5 ± 3.8	186 ± 30	81 ± 5
PLA/bentonite	2.6 ± 0.3	42.0 ± 4.3	46 ± 20	94 ± 3
PLA/hectorite	2.3 ± 0.4	39.1 ± 4.7	70 ± 14	92 ± 5
PLA/PLA-MA/bentonite	3.1 ± 0.3	46.5 ± 4.0	9 ± 2	95 ± 4
PLA/PLA-MA/hectorite	2.4 ± 0.4	40.9 ± 2.7	32 ± 2	91 ± 1

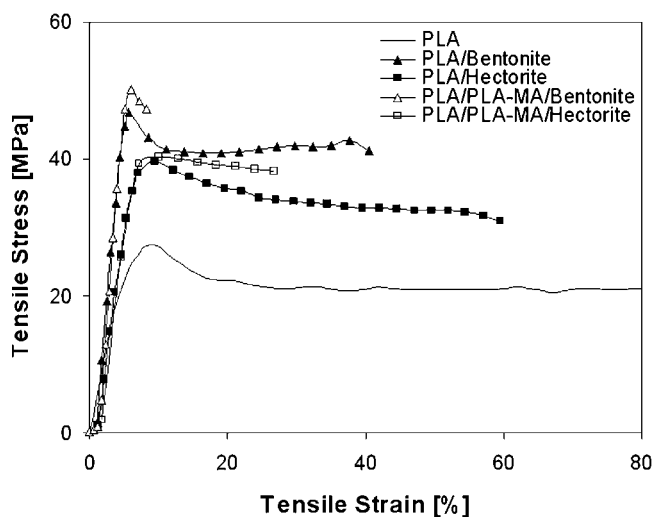


Figure 6 Stress-strain curves indicating improvements in both the tensile modulus and yield strength of the nanocomposites in comparison with those of pure PLA.

tive effect on the elongation to break. As a result, the addition of PLA-MA must also have affected the interfacial adhesion between the layered silicates and the PLA matrix. Improved interfacial adhesion will allow good stress transfer to take place between the layered silicate and the polymer matrix. The improvements in the mechanical properties of the bentonite nanocomposite could therefore be a combination of improved exfoliation and interfacial adhesion to the PLA matrix.

Comparing the tensile modulus measured for pure PLA in this experiment (1.7 ± 0.2 GPa) to the tensile modulus of the same grade of PLA when it had been extruded without the use of chloroform (2.0 ± 0.2 GPa),³⁰ we do not believe that large quantities of chloroform were still remaining in these materials. On the other hand, it is important to remember that the testing equipment used to generate the mechanical properties cannot be used for quantitative analysis.

Dynamic mechanical properties

The storage modulus for the nanocomposite materials as a function of temperature is given in Figure 7. The storage modulus of the nanocomposites improved over the entire temperature span in comparison with that of pure PLA. This indicates that the nanocomposite materials were able to increase the temperature of use of PLA. The improvement in the storage modulus was most significant above 50°C, at which molecular relaxation occurred for PLA. T_g of pure PLA was reported by Cargill Dow to be 58°C. The storage modulus curve for PLA showed a significant drop in the modulus after 45°C, and then the curve flattened out at 75°C. For the nanocomposite

films, the drop was more gradual and occurred at higher temperatures. The PLA/PLA-MA/bentonite nanocomposite showed the highest storage modulus over the entire temperature span in comparison with the other three nanocomposites.

At higher temperatures at which the PLA matrix softens, the reinforcing effect of the layered silicates will increase because of their ability to restrict the motions of the PLA chains. At 70°C, the PLA/PLA-MA/bentonite nanocomposite showed a 560% increase in the storage modulus compared with that of pure PLA (see Table IV). The other three nanocomposites showed an improvement of 230–300% in the storage modulus at 70°C compared with that of pure PLA (see Table IV). The difference in the reinforcement effect at 70°C between PLA/PLA-MA/bentonite and the other three nanocomposites could be due to increased adhesion between the bentonite and the PLA matrix caused by the PLA-MA.

The $\tan \delta$ peak recorded for the nanocomposites shifted to higher temperatures compared with the $\tan \delta$ peak for pure PLA (see Fig. 8). This indicates that the layered silicates were able to affect the segmental motions of the PLA matrix. The shifts in the $\tan \delta$ peak were on the whole quite small, except for one nanocomposite material, PLA/PLA-MA/bentonite, for which the shift was significant (10°C; see Table IV). This could be an indication of improved interfacial adhesion between the bentonite layered silicate and the PLA matrix due to the addition of PLA-MA. The intensity of the $\tan \delta$ peak for all the nanocomposites also decreased compared with the $\tan \delta$ peak for pure PLA, and this indicated that fewer polymer chains were participating in this transition. It is possible to see a correlation between the intensity of the $\tan \delta$ peak and the degree of exfolia-

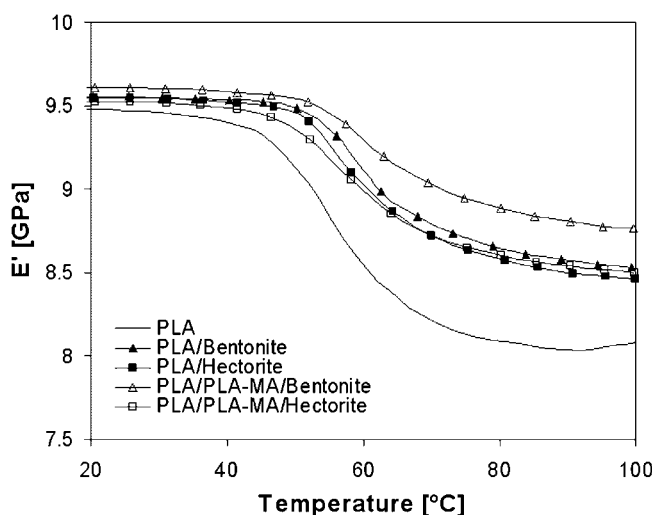


Figure 7 Storage modulus (E') curves from DMTA indicating improvements in E' of the nanocomposites over the entire temperature span in comparison with that of pure PLA.

TABLE IV
Storage Modulus (E') and $\tan \delta$ Peaks of
the Nanocomposites

Material	E' (GPa)		Tan δ peak ($^{\circ}$ C)
	25 $^{\circ}$ C	0 $^{\circ}$ C	
PLA	2.9 \pm 0.1	0.15 \pm 0.03	59 \pm 1
PLA/bentonite	3.6 \pm 0.1	0.60 \pm 0.03	65 \pm 0
PLA/hectorite	3.5 \pm 0.0	0.50 \pm 0.09	65 \pm 1
PLA/PLA-MA/bentonite	4.0 \pm 0.0	1.00 \pm 0.02	69 \pm 0
PLA/PLA-MA/hectorite	3.4 \pm 0.0	0.53 \pm 0.02	65 \pm 1

tion of the layered silicates. The PLA/bentonite material showed the highest $\tan \delta$ peak of the nanocomposites and was less exfoliated than the other three nanocomposites. The intensity of the $\tan \delta$ peaks was also decreasing because of the addition of PLA-MA. This was due to improved exfoliation of the layered silicates. The $\tan \delta$ peak for all the nanocomposites except the PLA/bentonite material broadened compared with the $\tan \delta$ peak for pure PLA. A broadening of the $\tan \delta$ peak indicates that the temperature span needed for the transition has increased. This can be explained by the layered-silicate sheets hindering the PLA chains to different extents.

The observed increase in the storage modulus as well as a broadening and shift in the $\tan \delta$ peak to higher temperatures for the nanocomposite materials indicated an altered chain mobility of the PLA matrix. This can be explained by PLA chains penetrating the structure of the layered silicates, so these chains would not be able to move as freely as the PLA chains in the pure material. As a result, the nanocomposites showed an increased temperature of use compared with that of pure PLA.

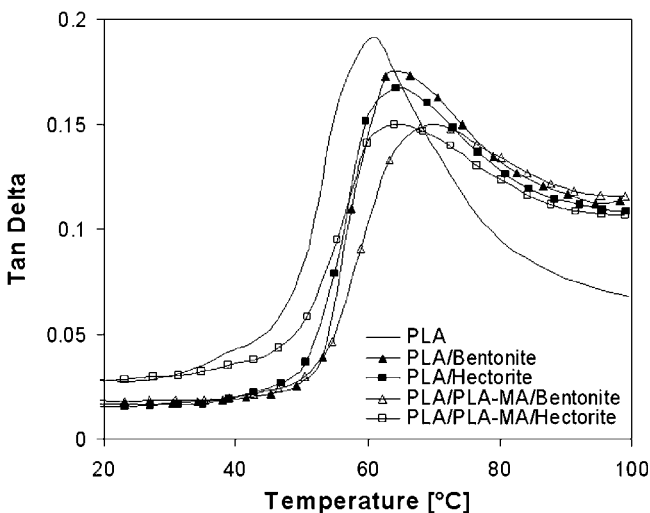


Figure 8 Tan δ peaks from DMTA indicating altered chain mobility of the PLA matrix in the produced nanocomposites.

Water contact angle

The results from the measurements of the water contact angles can be seen in Table III. All nanocomposites registered higher water contact angles than pure PLA. This indicates that the nanocomposites were more hydrophobic than PLA. All four nanocomposite systems showed similar results, and it was not possible to distinguish any specific effect due to the use of PLA-MA. This can be explained by the high margin of error for this analysis method. As an example, the hydrophobic character of the PLA/PLA-MA/bentonite system was improved by 16% compared with that of pure PLA. The measurements of the water contact angles give an indication of the attraction between the nanocomposites and water. If the water contact angle increases, the permeability of water vapor should therefore theoretically decrease because of the increased hydrophobic nature of the material. Most packaging applications demand that the polymer be able to withstand moist conditions, so the water vapor permeability is of great importance in extending the use of PLA in packaging applications.

UV-vis spectrometry

The results from the UV-vis spectrometry scans are shown in Figure 9. This figure shows that there was a large reduction in the amount of light being transmitted through the nanocomposites compared with pure PLA. This was unexpected. A transparent matrix containing a low volume percentage of the exfoliated nanoreinforcement is said to obtain good optical clarity,³¹ and the nanocomposites should therefore have shown properties similar to those of the transparent matrix in the spectrometry study.

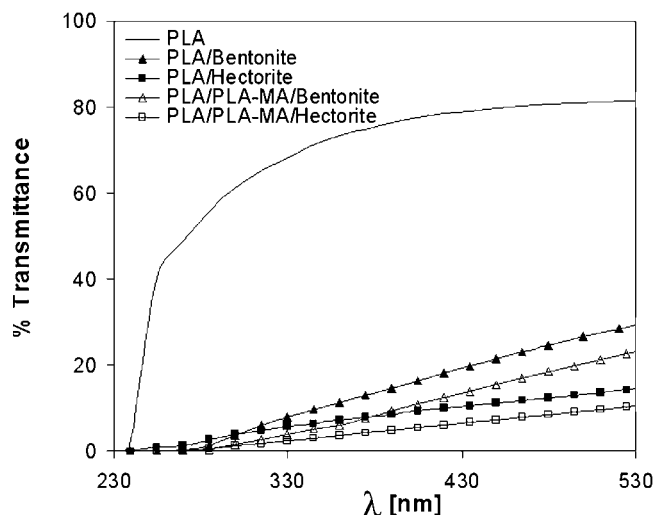


Figure 9 Transparency measurements indicating decreased transmission of UV and visible light through the nanocomposites in comparison with that of pure PLA.

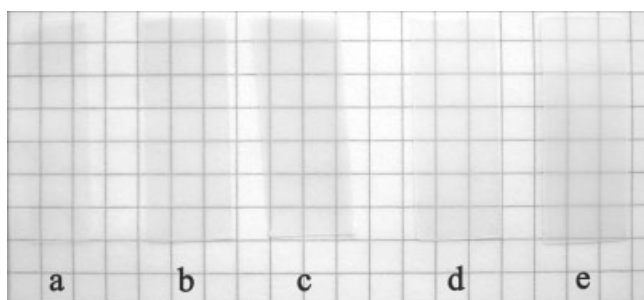


Figure 10 Optical clarity of the prepared materials: (a) PLA, (b) PLA/bentonite, (c) PLA/PLA-MA/bentonite, (d) PLA/hectorite, and (e) PLA/PLA-MA/hectorite.

The layered silicates in this study were not fully exfoliated, and this caused a reduction in the amount of light being transmitted through the nanocomposites. However, Figure 9 shows that exfoliation had a negative effect on the amount of light being transmitted through the nanocomposites. The two hectorite nanocomposites were more exfoliated and contained a lower volume fraction of layered silicates than the bentonite nanocomposites, but the hectorite nanocomposites still showed a larger reduction in the amount of transmitted light. All the prepared nanocomposite films were transparent (see Fig. 10), but the films containing bentonite had a beige tone because of the color of the layered silicates. The addition of PLA-MA, which had a positive effect on the degree of exfoliation, had a negative effect on the transmission of light (see Fig. 9). This can be explained by PLA-MA not being a completely clear material. The produced PLA-MA material had a light yellow tone that seemed to have had a negative effect on the transmission of light. It is difficult to explain the results obtained in this UV-vis spectrometry study. There have to be factors other than the degree of exfoliation affecting the results.

As mentioned earlier, the bentonite nanocomposites had a beige tone because of the color of the layered silicate. This is unfortunately not accepted in packaging applications.

CONCLUSIONS

The goal of this work was to prepare exfoliated PLA/layered-silicate nanocomposites with PLA-MA as a compatibilizer. Two different layered silicates were used in the study, bentonite and hectorite, which both swelled in chloroform. The nanocomposites were prepared by the incorporation of each layered silicate (5 wt %) into PLA via solution casting.

The study showed that the results from WAXD and TEM did not correspond. WAXD indicated full exfoliation for three of the nanocomposites, whereas TEM indicated a morphology of intercalated and partially exfoliated layered silicates in all the nano-

composites. All materials showed an improvement in the mechanical properties. The PLA/PLA-MA/bentonite nanocomposites showed an 82% improvement in the tensile modulus and a 63% improvement in the yield strength in comparison with pure PLA. Unfortunately, the elongation to break decreased for all the nanocomposites compared with that of pure PLA. DMTA showed that the storage modulus of the nanocomposites films improved most significantly above 50°C, with the PLA/PLA-MA/bentonite nanocomposite showing the best results. The $\tan \delta$ peak also shifted to higher temperatures for all the nanocomposites prepared, indicating altered polymer chain mobility of the PLA matrix. The surface of the nanocomposite films also became more hydrophobic, and the nanocomposites transmitted less UV and visible light than pure PLA.

The two layered silicates used in this study had different organic treatments. The WAXD study of the nanocomposites showed that the organic treatment of the hectorite layered silicates made it easier to exfoliate the layered silicate in chloroform, whereas the analysis of the mechanical properties showed that the organic treatment of the bentonite layered silicates resulted in better interaction with the PLA matrix. The organic treatment of the bentonite was also more compatible with the compatibilizer, PLA-MA, than the organic treatment of the hectorite. The bentonite layered silicate showed more distinct improvements in the exfoliation and mechanical properties because of the addition of PLA-MA as a compatibilizer. This experiment showed that only a small amount of MA (0.23 wt %) was needed to improve the degree of exfoliation of the layered silicates and the mechanical properties of the nanocomposites.

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