Preparation and characterization of biodegradable aliphatic polyester/thermoplastic starch/organoclay ternary hybrid nanocomposites

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Abstract—Biodegradable aliphatic polyester (APES)/thermoplastic starch (TPS)/Cloisite 30B ternary hybrid nanocomposites were prepared via melt intercalation. The dispersion of the silicate layers in the APES/TPS hybrids were characterized by using X-ray diffraction and transmission electron microscopy. Tensile and barrier properties of the APES/TPS/Cloisite 30B hybrids were also studied. Adding APES to the TPS/Cloisite 30B hybrids leads to higher tensile strength and improved barrier property.

Keywords: Biodegradable; aliphatic polyester; thermoplastic starch; organoclay; nanocomposites; hybrid.

1. INTRODUCTION

Biodegradable polymers have been extensively investigated since the 1970s in order to protect the environment from non-biodegradable plastic wastes [1, 2]. Among such compounds, starch has received much attention in its use as biodegradable packing materials because it is readily available at a low cost and has very fast biodegradability [3–9]. The potential advantages of starch polymers, apart from their environmental gains, are the abundant availability of the raw materials from renewable sources. Starch promotes the biodegradability of a non-biodegradable plastic, and starch can also be used together with a fully biodegradable synthetic plastic producing cheaper biodegradable blends [4–9].

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Unfortunately, one major problem with the existing starch polymer is its limited processability because its melting temperature is higher than the decomposition temperature of the composite. Therefore, it is difficult to make blown thin film for package application. To enable melting below decomposition temperature of starch polymer, thermoplastic starch (TPS) has been developed by gelatinizing starch with 6–10% moisture with heat and pressure [10]. Poor water resistance and low strength are limiting factors, however, for the use of materials manufactured only from TPS, and hence it is often blended with other polymers. Some of the thermoplastics investigated until now include low density polyethylene (LDPE), linear low density polyethylene (LLDPE), poly (ε-caprolactone; PCL), poly (butylene succinate-co-adipate: PBSA), cellulose acetate, and so on [11–18]. However, blending of starch with these plastics does not necessarily make them totally biodegradable [19, 20]. Therefore, a more ideal situation would be to use totally biodegradable materials.

Polymer-layered silicate (PLS) nanocomposites can be used to improve mechanical strength and water resistance while preserving total biodegradability of TPS. Melting intercalating polymers into the layered silicates of clay has been proven to be an excellent technique to prepare PLS nanocomposites [21–23]. With only a few percent of clay, PLS exhibits greatly improved mechanical, thermal and barrier properties compared with the pristine polymers [24]. Since silicate itself is harmless to the environment, these nanocomposites can preserve environmental gains and improve the mechanical strength and water sensitivity.

In this aspect, studies on thermoplastic starch/clay nanocomposites have been reported from our group [25, 26]. These nanocomposites give higher tensile strength and better barrier properties to water vapor as compared to the pristine TPS. In the present work, to further improve barrier properties and mechanical strength, synthetic biodegradable aliphatic polyesters (APES) with good water resistance and high mechanical strength were blended with the TPS/organoclay nanocomposites. APES/TPS/organoclay ternary nanocomposites were prepared via melt intercalation.

The objective of this research is to investigate the influence of compositions and the nanostructure on the tensile and barrier properties of APES/TPS/organoclay hybrid nanocomposites. The nanocomposites were characterized by wide-angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM).

2. EXPERIMENTAL

2.1. Materials

Biodegradable aliphatic polyester (APES) was kindly supplied by Sunkyong Co. Korea under the trade name of Skygreen-2109. It is prepared by polycondensation of aliphatic glycols (ethylene glycol and 1,4-butanediol) and aliphatic dicarboxylic acids (succinic acid and adipic acid) with weight-average molecular weight of 60,000.
Potato starch (PS: Katayama Co.), glycerol (95%, Junsei Chemical Co. Ltd), and water were used in preparing the TPS. The premixture containing native potato starch/water/glycerol (ratio 5/2/3 by wt) was retained for 1 h to let plasticizers (water and glycerol) swell the granular starch molecules. These swelled mixtures were transferred to the Haake mixer (Rheocord 600 system) and the starch was gelatinized at 110°C with 100 rpm for 25 min. The temperature and torque were monitored during the processing. After processing, the TPS was cooled down and then cut up into small particles in order to be premixed with clay powder easily.

The identification of TPS prepared in this work was performed using wide-angle X-ray diffraction (WAXD) and a scanning electron microscopy (SEM: JEOL 35CF). The TPS exhibited amorphous X-ray diffraction pattern with fine morphology and no granules, while natural potato starch granules show a typical β-type crystalline structure, as reported in the literature [27, 28].

Organically modified montmorillonite (organoclay) was purchased from Southern Clay Products under the trade name of Cloisite 30B. Organic modifier of Cloisite 30B is methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium.

2.2. Preparation of APES/TPS/organoclay nanocomposites

Cloisite 30B, TPS and APES were dried under vacuum at 80°C for at least 24 h. Dried TPS, APES and Cloisite 30B were mixed in a Haake Rheocord mixer at 130°C with 50 rpm for 15 min. The final ratios of APES/TPS/Organoclay were 75/20/5, 45/50/5, and 15/80/5. The organoclay content was fixed at 5 wt%. The hybrids were then injection molded using a CS-183 MMX Mini-MAX molder (Custom Scientific Instruments Inc.) to get dog-bone shaped specimens for characterization and property measurements. The melting and molding temperatures were 115°C and 25°C, respectively. The specimens were placed in tightly sealed polyethylene bags to prevent moisture absorption.

2.3. Measurements

2.3.1. Characterization of the nanocomposites. XRD patterns were taken with a Rigaku D/max 2200H X-ray diffractometer (40 kV, 50 mA). The scanning rate is 0.5°/min. The basal spacing of the silicate layer, d, was calculated using the Bragg equation, \( n\lambda = 2d \sin \theta \). TEM images were taken from cryogenically microtomed ultra thin sections using a Hitachi H-800 TEM.

2.3.2. Measurements of properties. A Universal Testing Machine (Model UL25, Hounsfield Co.) was used to obtain the tensile properties of the nanocomposites at room temperature. The crosshead speed was 10 mm/min. All measurements were performed for five replicates of dog-bone shaped specimens and averaged to get the final result.

The apparatus and methodology described in the ASTM E96-80 [29] were used to measure the water vapor transmission rate (WVTR) of the films. Four films, 1.7 cm diameter discs, were prepared with 110 µm thickness and tested at 24 ± 2°C.
Each specimen was sealed by a rubber O-ring on Plexiglas cups containing 60 ml saturated magnesium nitrate solution (54% relative humidity (RH)). There was an air gap of 17.95 mm between the solution and the underside of the specimen, and the test cups were placed in an air-tight plastic desiccators containing CaSO$_4$ desiccant (0% RH). The cups were 1.70 cm (inner diameter), 2.30 cm (outer diameter) and 7.65 cm (depth) with an exposed film area of 2.26 cm$^2$. The cups were weighed to the nearest 0.1 mg at 4 h intervals during 24 h. Regression analysis of weight loss as a function of time was performed to ensure that accurate steady state slopes were obtained. WVTR was calculated by dividing the slope by the exposed film area.

Dynamic mechanical analysis (DMA) was carried out on a Rheovibron DDV-25F (Orientec Co.) in the tension mode with the following parameters: frequency = 1 Hz; scan rate = 4°C/min; temperature range = −150°C to 130°C. Specimens were cut out from the central part of the dog-bone shaped samples.

3. RESULTS AND DISCUSSION

3.1. Characterization of APES/TPS/organoclay hybrids

Figure 1 shows the XRD patterns of the APES/TPS/Cloisite 30B hybrids containing 5 wt% of Cloisite 30B prepared through different mixing procedures. The XRD patterns of the APES/Cloisite 30B hybrid, TPS and Cloisite 30B are also included. It was reported in our previous work that the APES/Cloisite 30B hybrid exhibited intercalated structure [30].

For APES/Cloisite 30B (95/5) hybrid, the original peak of Cloisite 30B (2θ = 4.7°) shifted to around 2θ = 2.7°, indicating the great extent of intercalation of APES into the gallery of the silicate layers. Different mixing methods were used for curve b and c. For curve b, APES, TPS and Cloisite 30B were mixed together.

![Figure 1. Effect of Cloisite 30B contents and mixing process on the XRD patterns of APES/TPS/Cloisite 30B nanocomposites.](image-url)
For curve c, APES was blended with Cloisite 30B, and then this APES/Cloisite 30B hybrid was mixed with TPS. For both of the final hybrids, the original peak of Cloisite 30B ($2\theta = 4.7^\circ$) shifted to around $2\theta = 2.8^\circ$. This is mainly due to the intercalation of APES into the gallery of Cloisite 30B layers, since the increase of the interlayer spacing in the TPS/Cloisite 30B nanocomposite was not so large [25].

The nanostructure of the polymer/clay hybrids depends on the compatibility and interaction among the polymer, the silicate layer, and the ammonium cations located in the gap of the silicate layers. Due to the strong polar interactions between a small amount of polar hydroxyl group of water in the TPS chain and the silicate layer of the inorganic natural clay (i.e. Cloisite Na$^+$), it was reported that the TPS chains can intercalate into the interlayer of the Cloisite Na$^+$ [25]. The Cloisite 30B was also rendered hydrophobic but due to the existence of hydroxyethyl groups, the methyltallowbis-2-hydroxyethyl ammonium cation in the Cloisite 30B interlayer has polar interactions with TPS, favoring the intercalation of TPS chains and the formation of TPS/Cloisite 30B hybrids. However, the introduction of these polar hydroxyethyl groups also enhances the interaction of the ammonium cation with the silicate surface. As a result, replacement of the surface contacts by TPS chains will be less favorable, impeding the extensive intercalation.

It was also suggested that any component (starch, glycerol, and water if remaining) may escape from the TPS matrix and swell the clay, which favors the intercalation of the TPS chains in the case of TPS based hybrids. Since the TPS/Cloisite 30B hybrid, unlike the TPS/Cloisite Na$^+$ hybrid, did not exhibit any intercalation behavior, the possibility of the swelling of clays by any of the parent component residues must be negligible, if any [25].

Figure 2 shows the XRD patterns of various APES/TPS/Cloisite 30B hybrids with different contents of APES and TPS prepared by 2 step mixing procedures. In Fig. 2, the TPS/Cloisite 30B hybrid (e) shows a weak peak at 4.3°, while the Cloisite 30B exhibits a peak at 4.7°, indicating the formation of the intercalated nanocomposites, although the degree of intercalation does not seem to be large. It should be noted from pure TPS (Fig. 1(d)) and TPS/Cloisite 30B hybrid (Fig. 2(e)) that broad featureless peaks observed around 7–15° are due to the amorphous character of TPS [25–28].

In the XRD patterns, the APES/TPS/Cloisite 30B ternary hybrids show decreasing intensity of peak around 2.8°, with increasing the TPS content. Since this peak is mainly due to the intercalation of APES into the gallery of Cloisite 30B layers, the intensity of peak decreases with increasing TPS content. Therefore, two different degrees of intercalation may exist in the APES/TPS/Cloisite 30B ternary hybrids. One is the intercalation of APES into the silicate layers causing the shift of original peak of Cloisite 30B ($2\theta = 4.7^\circ$) to around $2\theta = 2.8^\circ$ and the other is the intercalation of TPS into the silicate layers causing the shift of original peak of Cloisite 30B ($2\theta = 4.7^\circ$) to around $2\theta = 4.3^\circ$.

To further confirm the dispersion states of the Cloisite 30B in the APES/TPS matrix, TEM studies at varying compositions of APES and TPS were carried out.
Figure 2. Effect of blend compositions on the XRD patterns of APES/TPS/Cloisite 30B nanocomposites.

Figure 3. TEM images of APES/TPS/Cloisite 30B hybrids: (a) APES 75%/30B 5%/TPS 20%, (b) APES 45%/30B 5%/TPS 50%, (c) APES 15%/30B 5%/TPS 80%; upper: low magnification; lower: high magnification.

Figure 3 presents the TEM images of the APES/TPS/Cloisite 30B hybrids exhibiting multilayer morphologies with alternating polymeric and inorganic silicate layers. Obviously interlayer distances are not uniform in the multilayer morphologies.
Perhaps the smaller interlayer distance is due to the intercalation of TPS into the silicate layers and larger interlayer distance is due to the intercalation of APES into the silicate layers.

3.2. Tensile properties

The tensile properties of APES/TPS/Cloisite 30B hybrids are shown in Table 1. The content of Cloisite 30B was fixed at 5 wt%. Tensile strength increases but the elongation at break decreases with the increase in APES content. When the content of APES increases from 0 to 15 wt%, the tensile strength increases sharply. However, when the content of APES increases from 15 to 50 wt%, there is no increase in the tensile strength. A possible explanation for this result will be discussed in the thermo-mechanical analysis. Since APES is more expensive than TPS, it is important to find the optimal composition of APES for APES/TPS/Cloisite 30B nanocomposites. In order to improve tensile strength of the TPS/Cloisite 30B hybrid, adding more than 15 wt% APES to the TPS/Cloisite 30B hybrid is not necessary.

3.3. Water vapor transmission rate (WVTR)

Since one of the objectives of this research is to improve the water resistance, water vapor transmission rate (WVTR) of hybrid films with different compositions was examined. Figure 4 shows WVTR of the nanocomposite films. WVTR decreases with increasing APES contents. Comparing WVTR of TPS and APES, the WVTR of TPS films are much higher than APES films. The high hydrophilicity of TPS molecules favorable to the adsorption of water molecules could contribute to the increase in WVTR of the films. The permeability of APES/TPS/Cloisite 30B nanocomposite with only 15 wt% APES was reduced significantly compared with TPS/Cloisite 30B hybrid.

The observed dramatic decrease in WVTR is of great importance in evaluating TPS and APES composites for use in food packaging, protective coatings, and other applications where efficient polymeric barriers are needed. For these applications, significant reduction in WVTR can result in either increased barrier efficiency, or reduced thickness of the barrier layer for the same efficiency. Furthermore, reduced

Table 1.

<table>
<thead>
<tr>
<th>Hybrids composition</th>
<th>Property</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APES 95%/Cloisite 30B 5%</td>
<td></td>
<td>3.45</td>
<td>10.3</td>
</tr>
<tr>
<td>APES 75%/Cloisite 30B 5%/TPS 20%</td>
<td></td>
<td>3.40</td>
<td>10.4</td>
</tr>
<tr>
<td>APES 45%/Cloisite 30B 5%/TPS 50%</td>
<td></td>
<td>3.35</td>
<td>10.4</td>
</tr>
<tr>
<td>APES 15%/Cloisite 30B 5%/TPS 80%</td>
<td></td>
<td>3.37</td>
<td>18.0</td>
</tr>
<tr>
<td>TPS 95%/Cloisite 30B 5%</td>
<td></td>
<td>2.8</td>
<td>44.5</td>
</tr>
</tbody>
</table>
WVTR in biodegradable polymer composite films may have the added benefit of modifying degradation rates, because hydrolysis of matrix polymer is likely to depend on the transport of water from the surface into the bulk of the material [31].

3.4. Thermo-mechanical analysis

DMA analysis has been studied to track the temperature dependence of storage modulus and tanδ behaviors of the APES/TPS/Cloisite 30B nanocomposites. Figures 5 and 6 show the temperature dependence of storage modulus and tanδ for pure TPS, APES and the APES/TPS/Cloisite 30B ternary nanocomposites. The storage modulus of nanocomposites at −60°C and 20°C is listed in Table 2. At a given temperature, the storage modulus of the hybrids increases with the increase in APES content as shown in Fig. 5 and Table 2. The storage modulus of hybrids is significantly higher than that of pure TPS, even at the lower APES composition. Therefore, the flexible TPS matrix is significantly reinforced by the introduction of 5 wt% Cloisite 30B and 15 wt% APES.

In Fig. 6(e), the α-relaxation processes associated with the glass transition of the amorphous phase of TPS could be clearly determined. The relaxation temperatures can be taken at the maximum of the respective tan δ peak in Fig. 6. The TPS shows two transition peaks around 8.0°C and −62°C due to the α-relaxation associated with the glass transition of the amorphous phase of starch (Tα) and the β-relaxation (Tβ) attributed to the glass transition of glycerol, respectively [32]. The Tα of APES was observed around −30°C (Fig. 6(a)). Each Tα peak of TPS and APES could be identified for the 45/50/5 hybrid composition of APES/TPS/Cloisite 30B. However, for the 15/80/5 composition of APES/TPS/Cloisite 30B hybrids, both Tα peaks of TPS and APES shift between the Tα of pure components and as a result, Tα peaks
Figure 5. Effect of compositions on the storage modulus behavior of APES/TPS/Cloisite 30B hybrid nanocomposites at 1 Hz frequency.

Figure 6. Effect of compositions on the tan δ behavior of APES/TPS/Cloisite 30B hybrid nanocomposites at 1 Hz frequency.

become broad. Therefore, partial miscibility may be inferred. This result may explain the sharp increase in tensile strength of APES/TPS/Cloisite 30B hybrid, when the content of APES increases from 0 to 15 wt%, and no increase in the tensile strength, when the content of APES increases from 15 to 45 wt%.

Before concluding, it should be mentioned that there exist many complex problems in an alloy nanocomposites, simultaneously or independently, including the clay dispersion in matrix, domain coalescence and interfacial tension change by adding organoclays, and the migration of the clay particle from one phase to another due to the interfacial tension, etc. Furthermore, a more systematic experimental approach is needed to monitor compatibility change except to presenting intercalation behavior through multi-technique experiments including more systematic XRD and TEM experiments [33]. The properties of polymer/clay nanocomposites would be
Table 2.
Storage modulus of APES/TPS/30B clay nanocomposites at $-60^\circ$C and $20^\circ$C

<table>
<thead>
<tr>
<th>Hybrids composition</th>
<th>$E'$, Storage modulus (Dyne/cm$^2$) $\times 10^{-9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature $-60^\circ$C</td>
</tr>
<tr>
<td>APES 100%</td>
<td>47</td>
</tr>
<tr>
<td>APES 95%/Cloisite 30B 5%</td>
<td>59</td>
</tr>
<tr>
<td>APES 75%/Cloisite 30B 5%/TPS 20%</td>
<td>53</td>
</tr>
<tr>
<td>APES 45%/Cloisite 30B 5%/TPS 50%</td>
<td>41</td>
</tr>
<tr>
<td>APES 15%/Cloisite 30B 5%/TPS 80%</td>
<td>39</td>
</tr>
<tr>
<td>TPS 95%/Cloisite 30B 5%</td>
<td>26</td>
</tr>
<tr>
<td>TPS 100%</td>
<td>22</td>
</tr>
</tbody>
</table>

highly governed by a change in the intercalation behavior. Whenever we have an intercalated structure of ternary polymer blend/clay nanocomposites, it is worthwhile to consider the compatibility between polymers and clay. Depending on this value, one of two polymers will have better intercalation into the clay gallery than the other [34, 35]. However, the properties of the mixture system of the present work cannot be simply understood only in terms of intercalation behavior, since an increase of clay gallery by polymer intercalation may be found even for an incompatibility situation, such as melt intercalation of clay with polystyrene [36]. In addition, the polymer intercalation behavior also depends on the preparation method of the nanocomposites [37]. Therefore, further research on more detailed and theoretical interpretation on the polymer blend based nanocomposites including the present APES/TPS/organoclay nanocomposites is now underway and will be reported elsewhere.

4. CONCLUSIONS

In this work, biodegradable aliphatic polyester (APES)/thermoplastic starch (TPS)/Cloisite 30B ternary nanocomposites were prepared via melt intercalation. Two different degrees of intercalation were observed in the APES/TPS/Cloisite 30B ternary hybrids. One is the intercalation of APES into the silicate layers causing the shift of original peak of Cloisite 30B ($2\theta = 4.7^\circ$) to around $2\theta = 2.8^\circ$ and the other is the intercalation of TPS into the silicate layers causing the shift of original peak of Cloisite 30B ($2\theta = 4.7^\circ$) to around $2\theta = 4.3^\circ$. Adding APES to the TPS/Cloisite 30B hybrids leads to higher tensile strength and improved barrier property. In order to improve tensile strength of the TPS/Cloisite 30B hybrid, adding more than 15 wt% APES to the TPS/Cloisite 30B hybrid is not necessary.

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REFERENCES


