Barrier and Mechanical Properties of Starch-Clay Nanocomposite Films

Xiaozhi Tang,1 Sajid Alavi,2,3 and Thomas J. Herald1

ABSTRACT

The poor barrier and mechanical properties of biopolymer-based food packaging can potentially be enhanced by the use of layered silicates (nanoclay) to produce nanocomposites. In this study, starch-clay nanocomposites were synthesized by a melt extrusion method. Natural (MMT) and organically modified (130E) montmorillonite clays were chosen for the nanocomposite preparation. The structures of the hybrids were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Films were made through casting using granulate produced by a twin-screw extruder. Starch/MMT composite films showed higher tensile strength and better water vapor barrier properties than films from starch/130E composites, as well as pristine starch, due to formation of intercalated nanostructure. To find the best combinations of raw materials, the effects of clay content (0–21 wt% MMT), starch sources (corn, wheat, and potato), and amylose content (>0, 28, 55, 70, 100%) on barrier and mechanical properties of the nanocomposite films were investigated. With increase in clay content, significantly higher (15–92%) tensile strength (TS), and lower (22–67%) water vapor permeability (WVP) were obtained. The barrier and mechanical properties of nanocomposite films did not vary significantly with different starch sources. Nanocomposite films from regular corn starch had better barrier and mechanical properties than either high amylopectin or high-amylose-based nanocomposite films. WVP, TS, and elongation at break (%E) of the films did not change significantly as amylose content increased beyond 50%.

Plastics are widely used packaging materials for food and non-food products due to desirable material properties and low cost. However, the merits of plastic packaging have been overshadowed by its nondegradable nature, thereby leading to waste disposal problems. The public is also gradually coming around to perceive plastic packaging as something that uses up valuable and scarce nonrenewable natural resources like petroleum. Moreover, the production of plastics is relatively energy intensive and it results in the release of large quantities of carbon dioxide as a by-product, which is often believed to cause, or at least contribute to, global warming. Some recent research findings have also linked plastic packaging to some forms of cancer (El Amin 2005; Kirsch 2005).

Packaging materials based on polymers that are derived from renewable sources may be a solution to the above problems. Such polymers include naturally existing proteins, cellulose, starches, and other polysaccharides, with or without modifications, and those synthesized chemically from naturally derived monomers such as lactic acid. These renewable polymers (or biopolymer) are not only important in the context of petroleum scarcity, but are also generally biodegradable under normal environmental conditions.

Interest and research activity in the area of biopolymer packaging films have been especially intensive over the past 10 years (Krochta and De Mulder-Johnston 1997; Tharanathan 2003). For food packaging, important characteristics include mechanical properties such as tensile strength and elongation at break (%E), and barrier properties such as moisture and oxygen permeabilities. To compete with synthetic plastics, biopolymer materials should have comparable mechanical or barrier properties. This is especially difficult with moisture barrier properties because of the hydrophilic nature of most biopolymers compared with hydrophobic synthetic polymers such as low-density polyethylene (LDPE). Moreover, mechanical and oxygen barrier properties of most biopolymer-based packaging materials are moderate to good at low relative humidity (rh), but deteriorate exponentially with increased rh (Krochta and De Mulder-Johnston 1997).

Among all biopolymers, starch is one of the leading candidates as it is abundant and cheap. The cost of the regular and specialty starches ($0.20–0.70/lb) compares well with that of synthetic polymers such as LDPE, polystyrene (PS), and polyethylene terephthalate (PET) ($0.50–0.75/lb) (Krochta and De Mulder-Johnston 1997). Moreover, starch is completely and quickly biodegradable and easy to process because of its thermoplastic nature (Doane 1994). Starch consists of two polysaccharides: linear amylose and highly branched amylpectin. The relative amounts of amylose and amylpectin depend on the plant source which affect the material properties and gelatinization behavior of the starch.

Many strategies have been developed to improve the barrier and mechanical properties of starch-based biodegradable packaging films. These include 1) addition of new plasticizers such as urea and formamide that aid in the thermoplastic process and also increase flexibility of the final product by forming hydrogen bonds with starch that replace the strong interactions between hydroxyl groups (Ma et al. 2004); and 2) addition of synthetic biodegradable polymers like poly(vinyl alcohol) (PVOH) and polylactide (PLA) to produce materials with properties intermediate to the two components (Chen et al. 1996; Ke and Sun 2000), resultant blends can be better processed by extrusion or film blowing and have mechanical and barrier properties superior to those of starch alone; and 3) addition of compatibilizers to lower the interfacial energy and increase miscibility of two incompatible phases, leading to a stable blend with improved characteristics (Mani et al. 1998).

Recently, the application of polymer-layered silicate (PLS) nanocomposites has proven to be a promising option to improve barrier and mechanical properties (Sinha Ray and Okamoto 2003). Such PLS nanocomposites represent a new class of hybrid materials from inorganic silicate clays and organic polymer matrix. The clays used in PLS nanocomposites include montmorillonite (MMT), hectorite, saponite, and various modifications. These clays are environmentally friendly, naturally abundant, and economical. Like the better known minerals talc and mica, these layered silicates belong to the general family of 2:1 layered silicates (or phyllosilicates) (Giannelis 1996). Their crystal structure consists of layers made up of two silica tetrahedrals fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery. In pristine layered silicates, the interlayer cations are usually hydrated Na+ or K+, showing hydrophilic surface properties.

For real nanocomposites, the clay layers must be uniformly dispersed in the polymer matrix (intercalated or exfoliated), as opposed to being aggregated as tactoids (Fig. 1).

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The nanocomposites can be obtained by several methods including in situ polymerization, intercalation from solution, or melt intercalation (Sinha Ray and Okamoto 2003). Once clay intercalation or exfoliation has been achieved, improvement in properties can be manifested as an increase in tensile properties, as well as enhanced barrier properties, decreased solvent uptake, increased thermal stability, and flame retardance. A diverse array of polymers has been used in PLS nanocomposite formation, ranging from synthetic nondegradable polymers such as nylon (Kojima et al. 1993a,b), polystyrene (Vaia et al 1995; Vaia and Giannelis 1997), and polypropylene (Kurokawa et al. 1996; Usuki et al. 1997) to biopolymers such as polylactide (Sinha Ray et al. 2002a,b).

Several studies have been performed based on starch-clay nanocomposites. De Carvalho et al. (2001) provided first insight to the preparation and characterization of thermoplasticized starch-kaolin composites by melt intercalation techniques. Park et al. (2002 and 2003) reported an increase in %E and tensile strength by 20 and 25%, respectively, and a decrease in water vapor transmission rate by 35% for potato starch/MMT nanocomposites on addition of 5% clay. Wilhelm et al. (2003) observed a 70% increase in tensile strength of Cará root starch/hectorite nanocomposite films at a 5% clay. Avella et al. (2005) reported the preparation of potato starch/MMT nanocomposites through melt-extrusion processing. We set out to investigate the influence of clay type (natural and organically modified clay) and water (19 wt%) mixtures were extruded at a screw speed of 200 rpm. The extrudates were ground using a Wiley mill (model 4, Thomas-Wiley, Philadelphia, PA) and an Ultra mill (Kitchen Resource, North Salt City, UT) for further use. X-ray diffraction (XRD) studies of the samples were conducted using a Bruker D8 Advance X-ray diffractometer (40 kV, 40 mA) (Karlsruhe, Germany). Samples were scanned at diffraction angle 2θ = 1–10° at a step of 0.01° and a scan speed of 4 sec/step. Transmission electron microscopy (TEM) studies were performed using a Philips CM100 electron microscope (Mahwah, NJ) operating at 100 kV. Films were made from ground extrudates by casting. Powders (4%) were dispersed in water and then heated to 95°C and maintained at that temperature for 10 min with regular stirring. Subsequently, the suspension was cooled to 65°C and poured onto petri dishes to make the films. The suspension in petri dishes was dried at 23°C and 50% rh for 24 hr, after which the films were peeled off for further testing.

Water vapor permeability (WVP) was determined gravimetrically according to the standard method E96-00 (ASTM 2000). The films were fixed on top of test cells containing a desiccant (silica gel). Test cells were then placed in a relative humidity chamber with controlled temperature and relative humidity (25°C and 75% rh). After steady-state conditions were reached, the weight of test cells was measured every 12 hr over three days. The water vapor transmission rate (WVTR) was determined as

\[ \text{WVTR} = \frac{G}{t} \frac{A}{A} \text{g/hr} \times m^2 \]

where \( G \) = weight change (g), \( t \) = time (hr) and \( A \) = test area (m²).

WVP was then calculated as

\[ \text{WVP} = \frac{\text{WVTR} \times d}{\Delta p} \text{g/mm/kPa/hr} \times m^2 \]

where \( d \) = film thickness (mm) and \( \Delta p \) = partial pressure difference across the films (kPa).

Tensile properties of the films were measured using a texture analyzer (TA-XT2, Stable Micro Systems, UK) based on standard method ASTM D882-02 (ASTM 2002). Films were cut into strips 1.5 cm wide and 8 cm long and conditioned at 23°C and 50% rh for three days before testing.

**Experimental Design and Statistical Analysis**

WVP tests were replicated three times, while tensile tests were replicated five times. All the data were analyzed using scientific graphing and statistical analysis software (OriginLab, Northampton, MA). Statistical significance of differences was calculated using the Bonferroni LSD multiple-comparison method at \( P < 0.05 \).
RESULTS AND DISCUSSION

Structure of Starch-Nanoclay Composites

The XRD studies provided information on the intercalation and exfoliation processes and the short-range order of the molecular constituents in clay-polymer composites. It is generally thought that during the intercalation process, the polymer enters the clay galleries and forces apart the platelets, thus increasing the gallery spacing (d-spacing) (McGlashan and Halley 2003). According to Bragg’s law, this would cause a shift of the diffraction peak toward a lower angle. As more polymers enter the gallery, the platelets become disordered and some platelets are even pushed apart from the stacks of clay particles (partial exfoliated). This will cause XRD peaks with a wider distribution or even further shift to the left side. TEM images provide further evidence for the occurrence of intercalation and exfoliation processes. TEM allows a qualitative understanding of the internal structure, spatial distribution, and dispersion of nanoparticles within the polymer matrix through direct visualization.

Figures 3 and 4 show the XRD patterns of composites with different nanoclay type and content. It should be noted that Lin (counts) refers to intensity of diffracted X-rays. It is clear that the dispersion states of nanoclays in the starch matrix depended on the type of clay used. The natural MMT exhibited a single peak at 2θ = 7.21°, whereas the starch/MMT hybrids showed prominent peaks at 2θ = 4.98° (Fig. 3). Also, the starch blank (Fig. 3) exhibited a featureless curve in the range of 1–10° due to the amorphous character of gelatinized starch. The appearance of the new peak at 4.98° (d-spacing = 1.77 nm) with the disappearance of the original nanoclay peak at 2θ = 7.21° (d-spacing = 1.23 nm) and increase of d-spacing indicated the formation of nanocomposite structure with intercalation of starch in the gallery of the silicate layers of MMT. The organically modified nanoclay I30E alone exhibited an intensive peak in the range of 2θ = 3.93–4.16° (d-spacing = 2.23 nm) (Fig. 4), whereas starch-I30E hybrids showed weak peaks just under the original peak of the I30E. This implied that little or no intercalation/exfoliation was achieved in the starch matrix.

The above results clearly showed that compatibility and optimum interactions between starch matrix, organic modifiers (if any), and the silicate layer surface were crucial to the formation of intercalated or exfoliated starch-layered silicate nanocomposites. Nanomer I30E is an onium ion surface modified montmorillonite mineral. Compared with natural MMT, I30E is more surface hydrophobic and therefore is not very miscible in the hydrophilic starch matrix. On the other hand, in natural MMT, due to the strong interactions between small amounts of polar hydroxyl groups of starch and glycerol and the silicate layers of the nanoclay (inorganic MMT Na⁺), the starch chains and glycerol molecules can intercalate into the interlayers of the nanoclay.

TEM micrographs of typical starch-MMT and starch-I30E composites are shown in Fig. 5. TEM results corresponded well with XRD patterns. Starch-MMT composites exhibited a multilayered nanostructure (Fig. 5A), whereas starch-I30E composites showed almost no intercalated morphology but instead had particle agglomerates or tactoids (dark spots in Fig. 5B).

Figure 6 shows the effects of clay content (<21 wt% MMT) on the structure of the nanocomposites. The only change was the intensity of peak, which increased with higher clay content. There was no shift in any of the peaks with varying clay contents, indicating that the clay content did not have any significant effect on the occurrence of intercalation or exfoliation. Figures 7 and 8 show the XRD patterns of 6 wt% MMT-based nanocomposites made from different starches. The data indicated that whatever the starch source (corn, wheat, or potato) or amylose content (0, 28, 55, 70, and 100%), complete disruption of the original nanolayer spacing of MMT was achieved, accompanied by starch-MMT intercalation at a higher d-spacing. Starch source or type did not have any effect on d-spacing of the nanocomposites. Although the MMT level was constant (6%) for all nanocomposites, interestingly, the intensity of the XRD peaks appeared to increase with amylose content with a maximum at 70% amylose. This may suggest the occurrence of partial exfoliation of clay platelets with the

![Fig. 2](image2.jpg)

**Fig. 2.** Screw configuration and temperature profile for laboratory-scale extruder. Superscripts a) SE screw elements: number of flights – pitch (mm) – element length (mm) (2-30-60); b) all screws are forward and intermeshing; c) KB kneading block: number of disks – disk length (mm) – total block length (mm) – staggering angle of disks (F) or reverse (R) (4-4-20-45 F).

![Fig. 3](image3.jpg)

**Fig. 3.** XRD patterns of (1) natural montmorillonite (MMT), (2) corn starch blank (0% MMT), and (3 and 4) corn starch/nanoclay hybrids with 3 and 6% MMT, respectively.

![Fig. 4](image4.jpg)

**Fig. 4.** XRD patterns of (1) original nanomer I30E, (2) corn starch blank (0% I30E), and (3 and 4) corn starch/nanoclay hybrids with 3 and 6% I30E, respectively.
penetration of starch biopolymers into the silicate layers leading to their dispersal. It was hypothesized that as amylose content increased to >50%, the degree of exfoliation decreased with more of the starch-MMT nanocomposite present in the intercalated state, leading to greater intensity of XRD peaks.

Water Vapor Permeability (WVP)

Tables I and II and Figs. 9 and 10 show the moisture barrier properties of the starch-nanoclay composite films. Water vapor permeability (WVP) of the films was examined at a difference of 0–75% rh across the films. Table I shows the effects of clay type on WVP of corn starch-based composite films. At the same clay level, WVP of the starch-MMT composite films was significantly lower than that of films made from starch-I30E composites. Second, there was no significant difference in WVP when the I30E content increased 0–9%, while WVP decreased significantly with the addition of 3–9% MMT. It was obvious that the addition of I30E did improve the barrier properties of the films, which indicated that improvement in film properties depended on the occurrence of intercalation or exfoliation (formation of nanocomposites).
Generally, water vapor transmission through a hydrophilic film depends on both diffusivity and solubility of water molecules in the film matrix. When the nanocomposite structure is formed, the impermeable clay layers mandate a tortuous pathway for water molecules to traverse the film matrix, thereby increasing the effective path length for diffusion. The decreased diffusivity due to formation of intercalated nanostructure in starch-MMT composites reduced the WVP. On the other hand, addition of 130E did not lead to intercalated structure, thus there were no improvements in WVP of films made from starch-I30E composites.

Figure 9 shows the effect of 0–21% MMT on WVP of wheat starch-nanoclay composite films. WVP decreased sharply as clay content increased 0–6%. With further increase in MMT content to 21%, the WVP continued to decrease, although more gradually. WVP of wheat starch with 21% clay was 0.57 g × mm/kPa × hr × m², which was ≈70% lower than WVP of the wheat starch blank.

Table II and Fig. 10 show the effects of starch source and amylose content on WVP. Literature suggests that films made from different types of starches have different properties. Rindlav-Westling et al (1998) reported better barrier properties of high-amylose films compared with high-amylpectin films. Phan et al (2005) reported that the WVP of films is directly proportional to the amylose content. They suggested that the effect of the amylose content on the WVP of the starch could be attributed to the crystallization of amylose chains in the dried films. Amylose films showed B-type crystalline structure, whereas amylpectin films were completely amorphous. In general, diffusion of moisture is easier in amorphous systems than in crystalline systems. However, Table II shows that no significant difference in WVP was found between corn, wheat, and potato starch-based nanocomposite films using MMT, although there are some differences in starch granule size and shape, and amylose content between corn, wheat, and potato starches (Deis 1998). Regardless of starch sources, the WVP decreased with increase in clay content of 0–9%. In Fig. 10, normal corn starch-based films presented better barrier properties than either amylpectin or high-amylose-based nanocomposite films. When amylose content reached 50%, the WVP almost remained constant. This may be related to the XRD patterns. One reason is that the highest temperature used for extrusion processing was 120°C, which probably was not high enough for a higher degree of gelatinization of high-amylose starch. Knutson (1990) and Varavinit et al (2003) reported that gelatinization temperatures increased with the increasing amounts of amylose. Bhattacharya and Hanna (1987) found that as the extruder barrel temperature increased from 116 to 164°C, % gelatinization increased from 73.6 to 98.4 in the waxy corn (1% amylose), while it increased from 40 to 55.2 in the ordinary corn samples (30% amylose) at the moisture content range of 17.8–42.2% (db). A higher degree of gelatinization means more disruption of starch granules and more leaching of amylose and amylpectin from the granule, thus facilitating the starch chains entering the clay galleries.

In addition, the presence of plasticizer (glycerol) may affect the film properties. Amylopectin was found to be more sensitive to glycerol plasticization than amylose in Lourdin et al (1995), who reported that the properties of plasticized films were not improved by the presence of glycerol and remained constant when amylose content was >40%. In addition, the presence of mineral clay may affect the starch network structure and crystallinity of amylose films.

### Tensile Properties

Tables III–VI and Figs. 11 and 12 show the tensile properties of the starch-nanoclay composite films. Tensile properties such as TS and %E were evaluated from the experimental stress-strain curves obtained for all prepared nanocomposite films. Tables III and IV show the effects of clay type and clay content on tensile properties. When comparing TS of the starch/MMT and starch/I30E films (Table III), it was obvious that addition of natural MMT helped improve the TS of the films. TS increased with

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**TABLE I**

Effects of Clay Type on WVP of Corn Starch-Based Films

<table>
<thead>
<tr>
<th>Clay Content</th>
<th>Starch-MMT</th>
<th>Starch-I30E</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% clay</td>
<td>1.61 ± 0.08a</td>
<td>1.61 ± 0.08ae</td>
</tr>
<tr>
<td>3% clay</td>
<td>1.42 ± 0.04b</td>
<td>1.63 ± 0.12e</td>
</tr>
<tr>
<td>6% clay</td>
<td>1.06 ± 0.09c</td>
<td>1.59 ± 0.08e</td>
</tr>
<tr>
<td>9% clay</td>
<td>0.77 ± 0.04d</td>
<td>1.56 ± 0.14e</td>
</tr>
</tbody>
</table>

* Mean ± standard deviation of each analysis. Means within the same row and column followed by the same letters are not significantly different (P < 0.05); n = 3 for all treatments.

**TABLE II**

Effects of Starch Type on WVP of Starch-MMT Nanocomposite Films

<table>
<thead>
<tr>
<th>MMT Content</th>
<th>Corn Starch</th>
<th>Wheat Starch</th>
<th>Potato Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% MMT</td>
<td>1.61 ± 0.08a</td>
<td>1.73 ± 0.12ae</td>
<td>1.81 ± 0.15ah</td>
</tr>
<tr>
<td>3% MMT</td>
<td>1.42 ± 0.04b</td>
<td>1.35 ± 0.09bf</td>
<td>1.22 ± 0.10bs</td>
</tr>
<tr>
<td>6% MMT</td>
<td>1.06 ± 0.09c</td>
<td>0.94 ± 0.04cg</td>
<td>0.98 ± 0.06c–j</td>
</tr>
<tr>
<td>9% MMT</td>
<td>0.77 ± 0.04d</td>
<td>0.82 ± 0.08dg</td>
<td>0.84 ± 0.05dj</td>
</tr>
</tbody>
</table>

* Mean ± standard deviation of each analysis. Means within the same row and column followed by the same letters are not significantly different (P < 0.05); n = 3 for all treatments.
the increasing of clay content. Similar to WVP, I30E still did not increase the TS of the films. For %E (Table IV), no trends and no significant difference could be found for the starch/MMT and starch/I30E films.

With increasing MMT content (Fig. 11), the TS increased rapidly from 14.05 to 27.02 MPa. However, %E did not exhibit much improvement. It even decreased with increased MMT content. This was coincident with the report by Lee et al. (2005), which suggested that good dispersion of the clay platelets in the polymer reduced tensile ductility and increased tensile strength compared with neat polymer.

Theoretically, the complete dispersion of clay nanolayers in a polymer optimizes the number of available reinforcing elements for carrying an applied load and deflecting cracks. The coupling between the tremendous surface area of the clay and the polymer matrix facilitates stress transfer to the reinforcement phase, allowing for such tensile and toughening improvements.

Tables V and VI show TS and %E of different starch-based nanocomposite films. No significant differences of TS and %E were seen in nanocomposite films based on corn, wheat, and potato. Figure 12 shows the effects of amylose content on tensile properties. Amylose helps improve the mechanical properties of the films (Wolff et al. 1951; Lourdin et al. 1995). However, the results presented here were quite similar to those for WVP discussed above: regular corn-starch-based nanocomposite films presented the highest TS; the %E decreased with the increased amylose content; when amylose content was >50%, neither TS nor %E changed significantly.

CONCLUSIONS

Biodegradable starch-clay nanocomposites were prepared by dispersing clay particles into the starch matrix through melt extrusion processing. Two types of clay, MMT and I30E, were chosen for the hybrid preparation. Starch/MMT showed better clay dispersion in the starch matrix. The dispersion of nanoclay in the starch matrix depended on the compatibility and the polar interactions among the starch, the silicate layers, and glycerol.

The starch/MMT composite films showed higher tensile strength and better barrier properties to water vapor than the starch/I30E hybrids, as well as the starch blank, due to the formation of intercalated or exfoliated nanostructure. Clay content had great effects on the properties of nanocomposite films. Higher TS and better barrier properties were obtained with increased clay content.

**TABLE III**

<table>
<thead>
<tr>
<th>Clay Content</th>
<th>Starch-MMT</th>
<th>Starch-I30E</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% clay</td>
<td>14.22 ± 0.98cd</td>
<td>14.22 ± 0.98d</td>
</tr>
<tr>
<td>3% clay</td>
<td>16.68 ± 2.32bc</td>
<td>12.41 ± 4.19cd</td>
</tr>
<tr>
<td>6% clay</td>
<td>18.60 ± 0.63b</td>
<td>13.73 ± 3.01d</td>
</tr>
<tr>
<td>9% clay</td>
<td>23.58 ± 0.58a</td>
<td>13.22 ± 1.35d</td>
</tr>
</tbody>
</table>

* Mean ± standard deviation of each analysis. Means within the same row and column followed by the same letters are not significantly different (P < 0.05); n = 5 for all treatments.

**Fig. 11.** Effects of clay content (MMT) on tensile properties of wheat starch-based nanocomposite films. Error bars ± SD. Data points with different letters imply significant difference (P < 0.05).

**TABLE IV**

<table>
<thead>
<tr>
<th>Clay Content</th>
<th>Starch-MMT</th>
<th>Starch-I30E</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% clay</td>
<td>5.26 ± 0.83abc</td>
<td>5.26 ± 0.83c</td>
</tr>
<tr>
<td>3% clay</td>
<td>6.27 ± 1.20a</td>
<td>3.20 ± 0.81d</td>
</tr>
<tr>
<td>6% clay</td>
<td>4.44 ± 0.52b</td>
<td>4.51 ± 0.91bcd</td>
</tr>
<tr>
<td>9% clay</td>
<td>4.82 ± 0.35ab</td>
<td>4.99 ± 0.85ac</td>
</tr>
</tbody>
</table>

* Mean ± standard deviation of each analysis. Means within the same row and column followed by the same letters are not significantly different (P < 0.05); n = 5 for all treatments.

**Fig. 12.** Effect of amylose content on tensile properties of corn starch-based nanocomposite films with 6% MMT. Error bars ± SD. Data points with different letters imply significant difference (P < 0.05).

**TABLE V**

<table>
<thead>
<tr>
<th>Clay Content</th>
<th>Corn Starch</th>
<th>Wheat Starch</th>
<th>Potato Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% clay</td>
<td>14.22 ± 0.98cd</td>
<td>14.05 ± 0.42dg</td>
<td>14.57 ± 0.41dk</td>
</tr>
<tr>
<td>3% clay</td>
<td>16.68 ± 2.32bc</td>
<td>16.21 ± 1.4cf</td>
<td>16.39 ± 0.30cj</td>
</tr>
<tr>
<td>6% clay</td>
<td>18.60 ± 0.63b</td>
<td>17.87 ± 1.4bf</td>
<td>18.66 ± 0.50bi</td>
</tr>
<tr>
<td>9% clay</td>
<td>23.58 ± 0.58a</td>
<td>21.27 ± 0.44e</td>
<td>22.25 ± 1.07ch</td>
</tr>
</tbody>
</table>

* Mean ± standard deviation of each analysis. Means within the same row and column followed by the same letters are not significantly different (P < 0.05); n = 5 for all treatments.

**TABLE VI**

<table>
<thead>
<tr>
<th>Clay Content</th>
<th>Corn Starch</th>
<th>Wheat Starch</th>
<th>Potato Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% clay</td>
<td>5.26 ± 0.83abc</td>
<td>6.08 ± 0.6cde</td>
<td>5.47 ± 0.67e</td>
</tr>
<tr>
<td>3% clay</td>
<td>6.27 ± 1.20af</td>
<td>5.66 ± 1.49df</td>
<td>5.91 ± 0.73ef</td>
</tr>
<tr>
<td>6% clay</td>
<td>4.44 ± 0.52bh</td>
<td>7.86 ± 1.86cg</td>
<td>6.49 ± 0.61egh</td>
</tr>
<tr>
<td>9% clay</td>
<td>4.82 ± 0.35abj</td>
<td>5.09 ± 0.42dj</td>
<td>6.06 ± 0.58e</td>
</tr>
</tbody>
</table>

* Mean ± standard deviation of each analysis. Means within the same row and column followed by the same letters are not significantly different (P < 0.05); n = 5 for all treatments.
Normal corn starch-based films we studied here presented better barrier and mechanical properties than either the amylopectin or high-amylose-based nanocomposite films. WVP, TS, and %E values of the films did not change significantly as amylose content increased to >50%.

The results presented here for starch-MMT nanocomposites proved that the concept of nanocomposite technology can be applied to improve the properties of starch-based biopolymer. However, even better performance will be needed for extending its application. Further studies including influence of plasticizers and extrusion processing conditions on starch-MMT nanocomposites are currently underway.

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LITERATURE CITED

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