

**PHISICO-CHEMICAL PROPERIES OF ENVIRONMENTAL FRIENDLY STARCH-MMT
NANOCOMPOSITES FOR FILM MAKING**

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ABSTRACT: The synthesis of starch-clay nanocomposites has been carried out for making biodegradable packaging films and to investigate the effects of chemical compatibility of starch, plasticizer and nanoclay on the composite films. Starch-montmorillonite (MMT) hybrids showed an intercalated nanostructure due to the compatibility of the two components and led to cast film with higher tensile strength and better water vapor barrier properties as compared to starch-organically modified montmorillonite (I30E) hybrids, as well as native starch only. With increase in clay content (0-21 wt%), significantly higher (15-92%) tensile strength (TS) and lower (22-67%) water vapor permeability (WVP) were obtained. The results indicated that nanocomposite technology could be applied to improve the properties of starch-based packaging films. The barrier and mechanical properties of nanocomposite films did not vary significantly with different starch sources (corn, wheat and potato starch), whereas films from regular corn starch showed better properties than either high amylopectin or high amylose-based nanocomposite films.

Key words: Starch, MMT, nano composites, biodegradation

INTRODUCTION

Petrochemical-based plastics dominate today's society because they are cheap, lucrative, colored, and lightweight; possess high strength; can be easily processed; and have good water-barrier properties. But most of these materials are nondegradable, creating global environmental problems. Hence the persistence of plastics in the environment, the shortage of landfill space, concerns over emissions during incineration, entrapment, and ingestion hazards from these materials—concerns that have spurred efforts to develop biodegradable plastics. The development of biodegradable plastics from renewable resources, to replace conventional synthetic plastic products, provides opportunities for reducing waste through biological recycling to the biosystem. The recent challenge is to design materials that exhibit structural and functional stability during storage, yet are susceptible to microbial and environmental degradation upon disposal without any adverse environmental impact(1-4)

For these reasons, throughout the world today, the development of biodegradable materials with controlled properties has been a subject of great research challenge to the community of materials scientists and engineers. Among biodegradable polymers, synthetic biodegradable polymers derived from petroleum sources, such as polybutylene succinate and polycaprolactone, have been commercialized due to their good processibility with fairly good mechanical and physical properties. But the cost of petrobased aliphatic polyesters is high, which restricts their extensive application. Soy protein is regarded as an alternative material to nondegradable petroleum plastics because it is abundant, renewable, inexpensive, and biodegradable. But, the application of soy protein plastic is limited because of its low strength and high moisture absorption.[2,3] Therefore, blending of the petrobased aliphatic polyesters with agro-based soy protein is an effective way to reduce the, cost of the biodegradable materials(5-8) Packaging materials based on polymers that are derived from renewable sources may be a solution to the above problems.

Such polymers include naturally existing ones such as 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.

Among all the biopolymers, starch is one of the leading candidates as it is abundant and cheap. The cost of regular and specialty starches compares well with that of synthetic polymers such as LDPE, polystyrene (PS) and polyethylene terephthalate (PET) (9). Moreover, starch is completely and quickly biodegradable and easy to process because of its thermoplastic nature(10). Starch consists of two polysaccharides, the linear amylose and the highly branched amylopectin. The relative amounts of amylose and amylopectin depend upon plant sources and 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 addition of plasticizers such as glycerol, urea and formamide, which 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 its hydroxyl groups (11) addition of other polymers or biodegradable polymers, like poly (vinyl alcohol) (PVOH), and polylactide (PLA), to produce materials with properties intermediate to the two components (12-13). The resultant blends can be better processed via extrusion or film blowing, and have mechanical and/ or barrier properties superior to starch alone; and addition of compatilizers to lower the interfacial energy and increase miscibility of two incompatible phases (starch and synthetic biodegradable polymers), leading to a stable blend with improved characteristics(14). However, none of the above mentioned methods can adequately meet the requirements of a cost effective biopolymer-based film that has properties close to those of synthetic plastic packaging. High costs of compatilizers and synthetic biodegradable polymers, such as PLA and PVOH, limit the level of their incorporation in starch. The resultant improvement in barrier and mechanical properties is also not very satisfactory. Therefore, there is a significant need for exploring new techniques to meet the challenges of developing high quality starch based packaging films. The unique properties of nanostructured substances have opened windows of opportunity for the creation of high performance materials with a critical impact on food manufacturing, packaging, and storage (15). An example is polymer-layered silicate (PLS) nanocomposites, a promising class of new materials that represent polymers filled with small inorganic silicate clays with a high aspect ratio. These PLS nanocomposites have been the focus of academic and industrial attention in recent years because they often exhibit substantially enhanced physical and/or chemical properties relative to the original polymer matrix(16)

The clays used in PLS nanocomposites include montmorillonite (MMT), hectorite and saponite, and their various modifications. These clays are environmentally friendly, naturally abundant and economical. Like talc and mica, which are better known minerals, these layered silicates belong to the general family of 2:1 layered silicates (or phyllosilicates) (17). Their crystal structure consists of layers made up of two silica tetrahedral 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. The nanocomposites can be obtained by several methods, including in-situ polymerization, intercalation from solution or melt intercalation(16). Once clay intercalation or exfoliation has been achieved, improvement in properties can manifest as increase in tensile properties, as well as enhanced barrier properties, decreased solvent uptake, increased thermal stability and flame retardance. A diverse array of polymers have been used in PLS nanocomposite formation, ranging from synthetic non-degradable polymers, such as nylon(18), polystyrene (19), and polypropylene (20), to biopolymers, such as polylactide(16).

Recently, there have been several attempts to enhance the end-use properties of starch in biodegradable packaging by fabricating starch-clay nanocomposites. De Carvalho et al (21) provided a first insight in the preparation and characterization of thermoplasticized starch-kaolin composites by melt intercalation techniques. Park et al (22-23) reported an increase in elongation at break and tensile strength by more than 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 (24)(2003) observed a 70% increase in tensile strength of Cará root starch/hectorite nanocomposite films at 30% clay level. However, the percentage of elongation decreased by 50%. Very recently, Avella et al (25)(2005) reported the preparation of potato starch/MMT nanocomposite films for food packaging applications. Results showed an increase in mechanical properties. Furthermore, the conformity of the resulting material samples with actual packaging regulations and European directives on biodegradable materials was verified by migration tests and by putting the films into contact with vegetables and stimulants. Success of the studies above indicates that clays show much promise in improving the mechanical and barrier properties of starch-based packaging materials.

The present investigation describes the fabrication of starch-clay nanocomposites via melt extrusion processing. The study sets out to investigate the influence of clay type (natural and organically modified clay), clay content, starch source and amylose content on the formation of nanostructure and properties of the starch-clay composite films.

MATERIALS AND METHODS

Materials

Two types of nanoclay were obtained from Nanocor Inc. (Arlington Heights, IL): natural montmorillonite (MMT) and onium ion modified MMT (Nanomer I30E). Regular corn starch, wheat starch and potato starch, and waxy corn starch were obtained from Cargill Inc. (Cedar Rapids, IA). High amylose corn starches Hylon V (~55% amylose), Hylon VII (~70% amylose) and 100% amylose were obtained from National Starch (Bridgewater, NJ). Glycerol Sigma, St. Louis, MO) was used as a plasticizer for all studies.

Preparation of the starch-nanoclay composites

A laboratory-scale co-rotating twin screw extruder (Micro-18, American Leistritz, Somerville, NJ) with a six head configuration, and screw diameter and L/D ratio of 18 mm and 30:1, respectively, was used for the preparation of starch-nanoclay composites. The screw configuration and barrel temperature profile (85-90-95-100-110-120 °C). Dry starch, glycerol (15 wt%), clay (0-21 wt%) and water (19 wt%) mixtures were extruded at screw speed of 200 RPM. The extrudates were ground using a Wiley mill (model 4, Thomas- Wiley Co., Philadelphia, PA) and an Ultra mill (Kitchen Resource LLC., North Salt City, UT) for further use.

Structural characterization of starch-nanoclay composites

X-ray diffraction (XRD) studies of the samples were carried out using a Bruker D8

Advance X-ray diffractometer (40kV, 40mA) (Karlsruhe, Germany). Samples were scanned in the range of diffraction angle $2\theta=1-10^\circ$ at a step of 0.01° and a scan speed of 4 sec/step. The clay basal spacing (d-spacing) can be estimated by Bragg's law:

$$d = \frac{\lambda \cdot \sin \theta}{2}$$

Where λ = wavelength of X-ray beam, θ = the angle of incidence.

Transmission electron microscopy (TEM) studies were performed using a Philips CM100 electron microscope (Mahwah, NJ) operating at 100kV. Powder samples were placed onto a carbon-coated copper grid by physically interacting the grid and powders and analyzed to see the dispersion of clay platelets.

Film casting

Powder samples (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 into petri dishes to make the films. The suspension in petri dishes was dried at 23°C and 50% relative humidity (RH) for 24 hrs, after which the films were peeled off for further testing.

Properties of starch-nanoclay composite films

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 then were placed in a relative humidity chamber at 25°C and 75% relative humidity (RH). The weight of test cells was measured every 12 hours over three days and the changes in the weight were plotted as a function of time. The slope of each line was calculated by linear regression ($R_2 > 0.99$), and the water vapor transmission rate (WVTR) was calculated from the slope of the straight line (G/t) divided by the transfer area (A):

$$WVTR = \frac{\left(\frac{G}{t}\right)}{A} \quad \text{g/h}\cdot\text{m}^2$$

where G = weight change (g), t = time (h) and A = test area (m^2),

WVP was then calculated using equation (3):

$$WVP = \frac{WVTR \times d}{\Delta p} \quad \text{g}\cdot\text{mm/kPa}\cdot\text{h}\cdot\text{m}^2 \quad (3)$$

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

Tensile properties of the films were measured using a texture analyzer (TA-XT2, Stable Micro Systems Ltd., UK), based on standard method ASTM D882-02 (ASTM 2002). Films were cut into 1.5 cm wide and 8 cm long strips and conditioned at 23°C and 50% RH for three days before testing. The crosshead speed was 1 mm/min. Tensile strength (TS) and elongation at break (%E) were calculated using equations (4) and (5):

$$TS = \frac{L_p}{a} \times 10^{-6} \quad \text{MPa} \quad (4)$$

where L_p = peak load (N), and a = cross-sectional area of samples (m^2).

$$\%E = \frac{\Delta l}{l} \times 100 \quad (5)$$

where Δl = increase in length at breaking point (mm), and l = original length (mm).

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 the 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). According to Bragg's law, this would cause a shift of the diffraction peak towards 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).

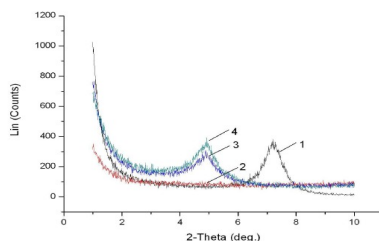


Figure 1 XRD patterns of (1) natural montmorillonite (MMT), (2) corn starch blank (0% MMT), and (3 and 4) corn starch/nanoclay hybrids with 3 and 6% MMT, respectively.

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.

Figure 1 shows 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 $2\theta = 7.21^\circ$, whereas the starch/MMT hybrids showed prominent peaks at $2\theta = 4.98^\circ$ (Figure 3.4). It also can be seen from Figure 1 that starch blank exhibited a featureless curve in the range of $1-10^\circ$ due to the amorphous character of gelatinized starch. The appearance of the new peak at 4.98° (d-spacing = 1.77 nm) with disappearance of the original peak of the nanoclay at $2\theta = 7.21^\circ$ (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. From Figure 1, it can be seen that the organically modified nanoclay I30E alone exhibited an intensive peak in the range of $2\theta = 3.930- 4.16^\circ$ (d-spacing ~ 2.25 nm), 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. Original MMT is usually hydrated sodium cations and Nanomer I30E is the modified clay which alkylammonium cations replaced the sodium cations in the clay galleries and thus render the normally hydrophilic silicate surface organophilic. The added functional groups lower the surface energy of the silicate surface and increase the gallery spacing (from 1.77 to 2.25nm) of the modified clay.

Therefore, compared with natural MMT, I30E doesn't show appreciable miscibility in the hydrophilic starch matrix. It might have a good compatibility with polycaprolactone (PCL) (26). On the other hand, in the case of 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), the starch chains combined with glycerol molecules can intercalate into the interlayers of the nanoclay.

TEM micrographs of typical starch-MMT and starch-I30E composites are presented in Figure 2. The TEM results corresponded well with the XRD patterns. Starch-MMT composites exhibited a multilayered nanostructure (Figure 2-a), whereas starch-I30E composites showed almost no intercalated multilayered morphology, but instead had particle agglomerates or tactoids. Figure 3 shows the effects of clay content (up to 21 wt% MMT) on the structure of the nanocomposites. It can be seen that 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.

Figure 1 shows XRD patterns of corn starch-clay composites before and after film formation. The data indicated that film making procedure didn't have a significant effect on XRD results.

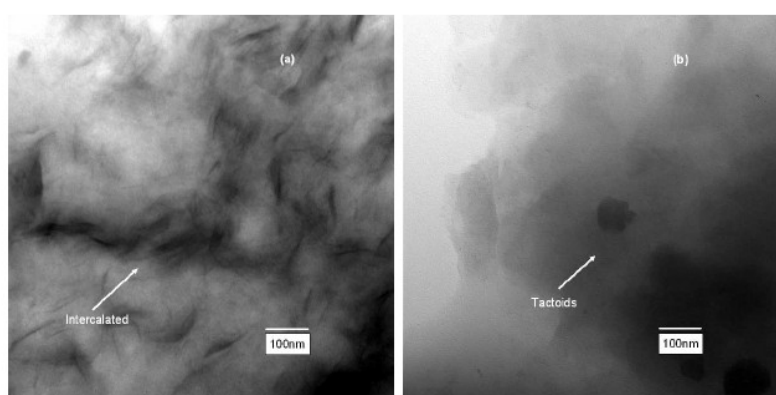


Figure 2 TEM images of (a) starch-6% MMT and (b) starch-6% I30E composites.

XRD curve is related to the distribution of clay interlayer spacing. We saw a constant structure at $2\theta=5^\circ$ (d-spacing=1.77nm), indicating that most clay interlayer spacing is in the range of 1.77nm. This interlayer spacing can be related to the thickness of starch molecular chain (about 0.5nm) and, thus, to its intercalation as a monolayer covering the interlayer surface of the clay. There do exist some other structures containing two starch molecular chains or half of starch chain inside the clay galleries, leading to the wider XRD distribution.

Water vapor permeability (WVP)

Table 1 and 2 show the moisture barrier properties of the starch nano clay composite films. Water vapor permeability (WVP) of the films was examined at a RH difference of 0/75% across the films. Table 1 shows the effects of clay type on WVP of corn starch based composite films. First, it can be clearly seen that, 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 from 0 to 9%, while WVP decreased significantly with the addition of 3 to 9% MMT. It was obvious that the addition of I30E did not help in improving the barrier properties of the films, which indicated that improvement in film properties depended on the occurrence of the intercalation or exfoliation (formation of nanocomposites).

Table -1 Effect of clay type on WVP of starch-based films

Clay content	WVP (g·mm/kPa·h·m ²)	
	Starch-MMT	Starch-I30E
0% clay	1.61 ± 0.08 ^a	1.61 ± 0.08 ^{ae}
3% clay	1.42 ± 0.04 ^b	1.63 ± 0.12 ^e
6% clay	1.06 ± 0.09 ^c	1.58 ± 0.08 ^e
9% clay	0.77 ± 0.04 ^d	1.56 ± 0.14 ^e

Mean ± standard deviation of each analysis

Means with the same letters are not significantly different (P<0.05).

Comparisons are made within the same row and column; n=3 for all treatments

Table2.Effect of starch type on WVP of starch-MMT nanocomposite films

MMT content	WVP (g·mm/kPa·h·m ²)		
	Corn starch	Wheat starch	Potato starch
0%	1.61±0.08 ^a	1.73±0.12 ^{ae}	1.81±0.15 ^{ah}
3%	1.42±0.04 ^b	1.35±0.09 ^{bf}	1.22±0.10 ^{bi}
6%	1.06±0.09 ^c	0.94±0.04 ^{cg}	0.98±0.06 ^{cij}
9%	0.77±0.04 ^d	0.82±0.08 ^{dg}	0.84±0.05 ^{dj}

Mean ± standard deviation of each analysis

Means with the same letters are not significantly different (P<0.05).

Comparisons are made within the same row and column; n=3 for all treatments

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 the case of starch-MMT composites, reduced the WVP. On the other hand, addition of I30E did not lead to intercalated structure thus there were no improvements in WVP of films made from starch-I30E composites. Figure 3 shows the effect of 0-21% MMT on WVP of wheat starch-nanoclay composite films. WVP decreased sharply as clay content increased from 0 to 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·h·m², which was almost 70% lower than WVP of the wheat starch blank. The observed dramatic decrease in WVP is of great significance for use of starch-based films in food packaging and other applications where good barrier properties are needed.

Table 2 shows the effects of starch source and amylose content on WVP. Literature suggests that films made from different types of starches have different properties. These differences are generally related to the content of amylose and amylopectin (27) reported better barrier properties of high amylose films as compared to high-amylopectin films. Higher amylopectin led to higher WVP. They suggested that the effect of 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 amylopectin films were completely amorphous. In general, diffusion of moisture is easier in amorphous systems than in crystalline ones. However, from Table 3, it can be seen that no significant difference in WVP was found between corn, wheat and potato starch-based nanocomposite films using MMT, although there are some slight differences in amylose content between corn, wheat and potato starches. It should be noted that irrespective of starch sources, the WVP decreased with increase in clay content from 0 to 9%. In Figure 3, normal corn starch based films presented better barrier properties than either amylopectin or high amylose based nanocomposite films. When amylose content reached 50%, the WVP almost remained constant. This may be related to XRD patterns and be possibly explained for the following reasons. First, the highest temperature used for extrusion processing was 120 °C, which probably was not high enough for complete gelatinization of high amylose starch. Lower gelatinization means a lower amount of starch chains available for interlayer penetration, thus affects the degree of clay exfoliation. Second, the presence of plasticizer (glycerol) may affect the properties of the high amylose films. Amylopectin was more sensitive than amylose to glycerol plasticization (27). They reported the properties of plasticized films were not improved by the presence of glycerol and remained constant when amylose content was higher than 40%. Third, the presence of mineral clay might affect the starch network structure and crystallization of amylose films.

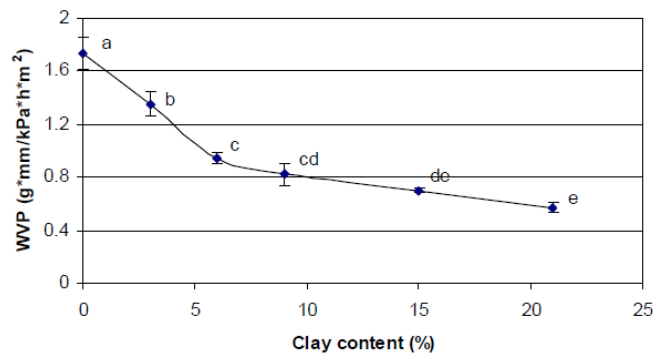


Figure 3 Effect of clay (MMT) content on water vapor permeability (WVP) of wheat starch-based nanocomposite films.

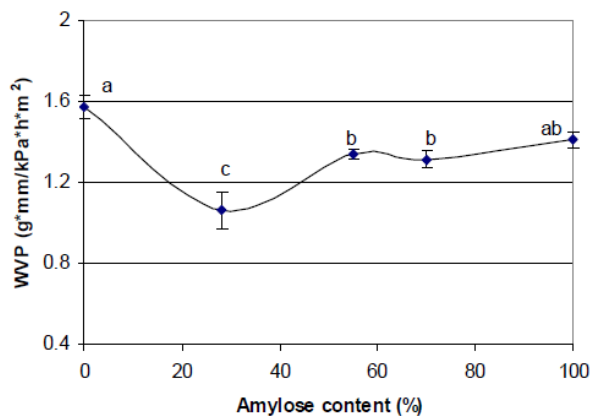


Fig 4: Water Vapor Permeability of Amylose

Tensile properties

Tables 3-4 shows the tensile properties of the starch nanoclay composite films. Tensile properties such as tensile strength (TS) and elongation at break (%E) have been evaluated from the experimental stress-strain curves obtained for all prepared nanocomposite films. Variability of TS and %E data exist due to several reasons: mixing procedure, the dispersion of nanoparticles, film casting, and also testing instrument. Tables 2 and 3. show the effects of clay type and clay content on tensile properties. When comparing Tensile strength of the starch/MMT and starch/I30E films, it was obvious that addition of natural MMT helped improve the tensile strength of the films. TS increased with the increasing of clay content. Similar to WVP, I30E still did not give any help to the tensile strength of the films. For Elongation at break (Table 3), no trends and no significant difference could be found here for starch/MMT the tensile strength of the films. For Elongation at break (Tables 3-4), no trends and no significant difference could be found here for starch/MMT and starch/I30E films. With increasing MMT content (Figure 3.), the TS increased rapidly from 14.05 to 27.02 MPa. However, %E did not exhibit much improvement. It even decreased with the increasing of MMT content.

Theoretically, the complete dispersion of clay layers 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 3 and 4 show the tensile strength and elongation at break of different starch source based nanocomposite films. No significant differences of TS and %E were seen between corn, wheat and potato based nanocomposite films. Figure 5 shows the effects of amylose content on tensile properties. As is known, amylose helps improve the mechanical properties of the films(20) reported that for unplasticized films, a continuous increase in tensile strength was observed as amylose increased from 0 to 100%. However, the results presented here were quite similar to WVP discussed above; regular corn starch-based nanocomposite films presented the highest tensile strength (TS); Elongation at break (%E) decreased with the increased amylose content; when amylase content reached above 50%, both TS and %E did not change significantly.

Table-3 Effect of clay % on the percentage Elongation

Clay content	Elongation at break (%)	
	Starch-MMT	Starch-I30E
0% clay	5.26±0.83 ^{abc}	5.26±0.83 ^c
3% clay	6.27±1.20 ^a	3.20±0.81 ^d
6% clay	4.44±0.52 ^b	4.51±0.91 ^{bcd}
9% clay	4.82±0.35 ^{ab}	4.99±0.85 ^{ac}

Mean ± standard deviation of each analysis

Means with the same letters are not significantly different (P<0.05).

Comparisons are made within the same row and column; n=5 for all treatments

Table 4 Effect of starch type on tensile strength

Clay content	Tensile Strength (MPa)		
	Corn starch	Wheat starch	Potato starch
0% clay	14.22±0.98 ^{cd}	14.05±0.42 ^{dg}	14.57±0.41 ^{dk}
3% clay	16.68±2.32 ^{bc}	16.21±1.4 ^{cf}	16.39±0.30 ^{ci}
6% clay	18.60±0.63 ^b	17.87±1.4 ^{bf}	18.66±0.50 ^{bi}
9% clay	23.58±0.58 ^a	21.27±0.44 ^e	22.25±1.07 ^{eh}

Mean ± standard deviation of each analysis

Means with the same letters are not significantly different (P<0.05).

Comparisons are made within the same row and column; n=5 for all treatments

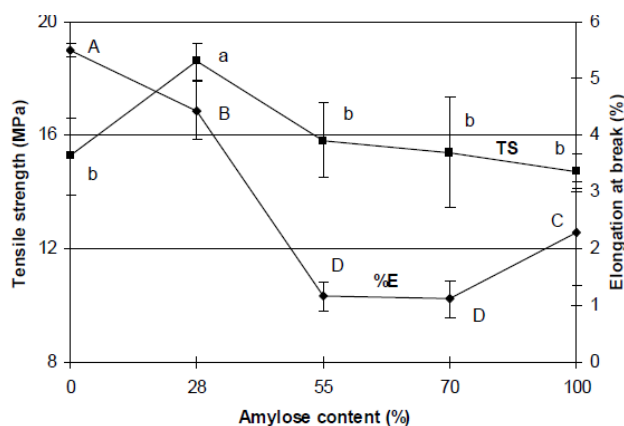


Fig 5 : Effect of amylose content on tensile strength

Conclusion

Biodegradable starch-clay nanocomposites were prepared by dispersing clay particles into the starch matrix via 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 nanoclays in the starch matrix depended on the compatibility and the polar interactions among the starch, glycerol, and the silicate layers. The starch/MMT composite films showed higher tensile strength and better barrier properties showed higher tensile strength and better barrier properties to water vapor than the starch/I30 hybrids, as well as starch blank, due to the formation of intercalated or exfoliated nanostructure. The clay content had great effects on the properties of the nanocomposite films. With the increasing of clay content, higher tensile strength and better barrier properties were obtained. Normal corn starch-based films presented better barrier and mechanical properties than either amylopectin or high amylose-based nanocomposite films. WVP, TS and elongation at break of the films did not change significantly as amylose content increased beyond 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 packaging materials. However, better performance is still needed for extending its application. Further studies including influence of plasticizers and extrusion processing conditions on starch-MMT nanocomposites are under investigation.

REFERENCES

1. Nayak PL, (2000) *Macromol Sci Rev Macromol Phys* 40:1(2000)
2. Swain SN, Biswal SM, Nanda PK, Nayak PLJ (2004) *Polym Enviorn* 12:35(2004)
3. Swain SN, Rao KK, Nayak PLJ (2004) *Thermal Anal Cal* 33:79(2004)
4. Swain SN, Rao KK, Nayak PLJ (2004) *Appl Polym Sci* 93:2590 (2004)
5. Swain SN, Rao KK, Nayak PL (2005) *Polym Int* 54:739 (2005)
6. Nanda PK, Rao KK, Nayak PLJ (2007) *Appl Polym Sci* 103:3134(2007)
7. Nanda PK, Rao KK, Nayak PLJ (2006) *Thermal Anal Cal* 95:2093(2006)
8. Nanda PK, Rao KK, Nayak PL (2007) *Polym Plast Technol Engg* 46:207 (2007)
9. Krochta, J.M., and De Mulder-Johnston, C., (1997) Edible and biodegradable polymer films: challenges and opportunities. *Food Technology*. 51(2): 61-74.
10. In *Annual Book of ASTM Standards*, Philadelphia, PA. American Society for Testing and Material, 2005

11. Doane, W. M. (1994) Opportunities and challenges for new industrial uses of starch. *Cereal Foods Worlds*. 39(8): 556-563.
12. Chen, L., Iman, S. H., Stein, T. M., Gordon, S. H., Hou, C. T., and Greene, R. V.(1996) Starch-polyvinyl alcohol cast film-performance and biodegradation. *Polym. Prepr.* 37: 461-462
13. Ke, T., and Sun, X., (2000) Physical properties of poly(lactic acid) and starch composites with various blending Ratios. *Cereal Chem.* 77(6): 761-768.
14. De Carvalho, A. J. F., Curvelo, A. A. S., and Agnelli, J. A. M. 2001. A first insight on composites of thermoplastic starch and Kaolin. *Carbohydrate Polymers*. 45: 189-194.
15. Avella, M., De Vlieger, J. J., Errico, M. E., Fischer, S., Vacca, P., and Volpe, M. G.(2005). Biodegradable starch/clay nanocomposite films for food packaging applications. *Food Chemistry*. 93: 467-474.
16. Giannelis, E. P. (1996) Polymer layered silicate nanocomposites. *Advanced Materials*.8(1): 29-35.
17. Kojima, Y., Usuki, A., Kawasumi, M., Okada, A., Fukushima, Y., Kurauchi, T., and Kamigaito, O.. (1993a). Mechanical properties of nylon 6-clay hybrid. *J. Mater. Res.* 8: 1185-1189.
18. 1189.
19. Vaia, R. A., Jandt, K. D., Kramer, E. J. & Giannelis, E. P. (1995). Kinetics of polymermelt intercalation. *Macromolecules*, 28, 8080-8085.Vaia, R. A. & Giannelis, E. P. (1997). Polymer melt intercalation in organically-modifiedlayered silicates: Model predictions and experiment. *Macromolecules*, 30, 8000-8009.
20. Kurokawa, Y., Yasuda, H., and Oya, A.,(1996). Preparation of a nanocomposite of polypropylene and smectite. *J. Mater. Sci. Lett.* 15: 1481-1483.
21. Mani, R., Tang, J., and Bhattacharya, M. (1998). Synthesis and characterization of starchgraft-polycaprolactone as compatibilizer for starch/polycaprolactone blends. *Macromolecular Rapid Communications*. 19(6): 283-286.
22. McGlashan, S. A., and Halley, P. J.(2003). Preparation and characterization of biodegradable starch-based nanocomposite materials. *Polymer International*. 52: 1767-1773
23. Moraru, C. I., Panchapakesan, C. P., Huang, Q., Takhistov, P., Liu, S., and Kokini, J. L. (2003), *Nanotechnology: A new frontier in food science*. *Food Technology*. 57(12): 24-29.
24. Park, H., Li, X., Jin, C., Park, C., Cho, W., and Ha, C. (2002) Preparation and properties of biodegradable thermoplastic starch/clay hybrids, *Macromol. Mater. Eng.* 287: 553-558.
25. Park, H., Lee, W., Park, C., Cho, W., and Ha, C. (2003). Environmentally friendly polymer hybrids part 1 Mechanical, thermal and barrier properties of thermoplastic starch/clay nanocomposites, *Journal of Materials Science*. 38: 909-915.
26. Phan, D., Debeaufort, F., LUU, D., and Voilley, A.(2005.) Functional properties of edible agar-based and starch-based films for food quality preservation. *J. Agric. Food Chem.* 53: 973-981
27. Lourdin, D., Della Valle, G., and Colonna, P. (1995). Influence of amylose content on starch films and foams. *Carbohydrate Polymer*. 27: 261-270.
28. Wilhelm, H. M., Sierakowski, M. R., Souza, G. P. & Wypych, F. (2003). Starch films reinforced with mineral clay. *Carbohydrate Polymers*, 52, 101-110.