Preparation of Cassava Starch/ Montmorillonite Nanocomposite Film

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Cassava starch/montmorillonite nanocomposite films were prepared using solution casting techniques. This research was focused on the exploitation of an intercalating agent (cationized diethanolamine) to delaminate the layered silicate of montmorillonite in order to homogeneously disperse the nanoparticles in a starch matrix. A mixture of cassava starch, montmorillonite (MMT), diethanolamine (DEA) (calculated from the optimum cation exchange capacity of MMT:DEA of 2:1), glycerol as a plasticizer, and distilled water was well mixed with a homogenizer before adjusting the mixture with acetic acid to pH 7 and heated to gelatinize at a temperature between 70-80°C. The obtained homogeneous starch solution was cast onto acrylic mold and allowed to dry in the open air. The dried film was peeled off and subjected to property investigation and characterization.

A change in the montmorillonite structure from layered platelets to individually delaminated sheet was revealed by X-ray diffraction (XRD). The starch/montmorillonite nanocomposite film exhibited the complete disappearance of XRD reflection at $2\theta = 5.590^{\circ}$, indicating the nanoscale dispersion of montmorillonite. Transmission electron microscopy (TEM) results further supported the occurrence of blend composite at the nanoscale level. Even though the nanocomposite between starch and montmorillonite was achieved, tensile strength and Young's modulus were opposite to the expected results. These properties were adversely affected by the presence of DEA due to its hygroscopicity. A significant increase in the percent of elongation was also related to the plasticizing effect of DEA. The strongly hygroscopic nature of DEA led to subsequent disappointment in that other physical properties such as water vapor transmission rate (WVTR) and moisture absorption increased. These traits which are not desirable properties for packaging films.

Key words: Cassava starch, biodegradable nanocomposite, starch-based polymer, biodegradable film.

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การเตรียมฟิล์มนาโนคอมโพสิตของแป้งมันสำปะหลัง/ มอนต์มอริลโลไนต์

ปียะพร คามภีรภาพพันธ์ กาวี ศรีกูลกิจ และควงหทัย เพ็ญตระกูล (2547) วารสารวิจัยวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย **29(2)**

การเตรียมฟิล์มนาโนคอมโพสิตของแป้งมันสำปะหลัง/มอนต์มอริลโลไนต์ทำโดยเทคนิค การหล่อจากสารละลาย ในงานวิจัยนี้ เป็นการใช้สารอินเตอร์คาเลต (intercalating agent) (ไดเอทา-โนลามีนแคทไอออน) ในการลอกชั้นซิลิเกตของแร่มอนต์มอริลโลไนต์ เพื่อให้เกิดการกระจาย ด้วอย่างสม่ำเสมอของอนุภาคระดับนาโนในเมทริกซ์ของแป้งมันสำปะหลัง วิธีการทดลองคือ นำ ของผสมระหว่างแป้งมันสำปะหลังมอนต์มอริลโลไนต์ไดเอทาโนลามีน (อัตราส่วนระหว่างมอนต์ มอริลโลไนต์ต่อไดเอทาโนลามีนเป็น 2:1 ซึ่งคำนวณจากความสามารถในการแลกเปลี่ยนแคท ใอออนที่เหมาะสมที่สุด) กลีเซอรอลซึ่งเป็นพลาสติไซเซอร์และน้ำกลั่นมาผสมด้วยเครื่องปั่นให้ เป็นเนื้อเดียวกันแล้วปรับค่าความเป็นกรดค่างให้เท่ากับ 7 ด้วยกรดอะซิติก และให้ความร้อนถึง อุณหภูมิเจลลาติไนซ์ (70-80 องศาเซลเซียส) จากนั้นนำสารละลายแป้งที่เป็นเนื้อเดียวกันมาหล่อ ในแม่แบบอะคริลิกและทิ้งให้แห้งในบรรยากาศปกติ เมื่อฟิล์มแห้งสนิทจึงลอกฟิล์มออกจาก แม่แบบเพื่อทดสอบสมบัติและวิเกราะห์ผลต่อไป

จากการวิเคราะห์ด้วยเทคนิคเอ็กซเรย์ดิฟแฟรกชัน (XRD) พบการเปลี่ยนแปลง โครงสร้างของมอนต์มอริลโลในต์จากแผ่นที่ซ้อนกันไปเป็นแผ่นเดี่ยว ฟิล์มนาโนคอมโพสิตของ แป้ง/มอนต์มอริลโลในต์ยังแสดงถึงการหายไปของพิก XRD ที่ตำแหน่ง 20 = 5.590° อันเป็น การบ่งซี้การเกิดการกระจายตัวในระดับนาโนของมอนต์มอริลโลในต์ นอกจากนี้ภาพจากกล้อง จุลทรรศน์อิเล็กตรอนแบบส่องผ่าน (TEM) ยังสนับสนุนการเกิดการผสมในระดับนาโนของ กอมโพสิตอีกด้วย ถึงแม้จะเตรียมนาโนคอมโพสิตได้ แต่ความทนแรงดึงและยังก์มอดูลัสกลับมีผล ตรงกันข้ามกับที่คาดไว้ เนื่องจากผลของการพลาสติไซซ์ของไดเอทาโนลามีน ซึ่งส่งผลให้กวาม สามารถในการยืดดึง ฉ จุดขาดที่เพิ่มขึ้นอย่างเด่นชัด นอกจากนี้การที่ไดเอทาโนลามีนเป็นสาร ชอบน้ำมาก จึงทำให้สมบัติทางกายภาพ เช่น อัตราการซึมผ่านของไอน้ำและการดูดซึมความชื้น ของฟิล์มเพิ่มขึ้น ซึ่งถือเป็นข้อด้อยของการนำไปประยุกต์เป็นฟิล์มบรรจุภัณฑ์

ี้ คำสำคัญ แป้งมันสำปะหลัง นาโนคอมโพสิตที่ย่อยสลายทางชีวภาพ ฟิล์มที่ย่อยสลาย ทางชีวภาพ

INTRODUCTION

In recent years there has been a growing interest in the use of biodegradable polymers for packaging materials in order to reduce the environmental pollution caused by plastic wastes.⁽¹⁾ Starch is known to be completely biodegradable in soil and water and is potential an effective packing material because it is cheap and has very fast biodegradability.⁽²⁾ However, high viscosity and poor melt properties make starch difficult to process. Also products made from starch are often brittle and water sensitive.⁽³⁾ To alleviate this problem, starch is modified by several methods such as blending with $synthetic^{(4,5)}$ or natural polymers,⁽⁶⁾ preparing in a composite form⁽⁷⁾ and by cross-linking.⁽⁸⁾

In addition, to improve the mechanical properties of the starch composites at the same time, a small percent age of inorganic fillers are commonly added to a polymer matrix.

For example the addition of polymerlayered silicate (PLS) exhibits greatly improved mechanical, thermal, and barrier properties as compared with the pristine polymer.⁽⁹⁾ The clay, montmorillonite (MMT), is one of the attractive fillers utilized due to its great surface area (as high as 750 m²g⁻¹), large aspect ratio (greater than 50), and platelet thickness of 10Å. Generally, the inorganic surface of the clay is modified by organic treatment to make the platelet more compatible with the polymer. Their composites are normally referred to as tactoids with MMT being blended into a polymer and no separation of their layersshown as conventional composite in Figure 1. Intercalation occurs when a small amount of polymer moves into the gallery spacing between the clay platelets. Exfoliation occurs when silicate layers are substantially expanded and no longer parallel.



Figure 1. Three possible types of polymer-clay composites.⁽¹⁰⁾

In this research, cassava starch/ montmorillonite nanocomposite films were prepared, with the goal being to produce starch based biodegradable plastic. To obtain the starch/clay nanocomposite, the montmorillonite was treated with an intercalant which, in this study, was an aminoalcohol, diethanolamine neutralized by acetic acid to become quaternary ammonium salt. The casting process was carried out by the thermal gelatinization of starch/

intercalated montmorillonite dispersion under applied shear force. The cast film with the thickness of 60-80 microns was then characterized using X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Its physical properties (thickness, transparency, water absorption, and water vapor transmission rate), and mechanical property (tensile strength) were determined.

EXPERIMENTAL

Materials

Cassava starch was purchased from E.T.C. International trading Co., Ltd. Commercial grade montmorillonite clay under the trade name of Mac-gel was provided from Thai Nippon Chemical Industry Co., Ltd., Thailand. An analytical grade of diethanolamine and a commercial grade of glycerol were purchased from Merck, Germany. An analytical grade of acetic acid was purchased from BDH, Poole, England.

Sample preparation

Montmorillonite/diethanolamine ratio determination

The determination of ion exchange capacity of the montmorillonite was undertaken by viscosity measurement. The montmorillonite was treated with various amounts of diethanolamine in a range of 0–8 grams dispersed in 150 ml of distilled water in the reactor and stirred at 60°C for 1 hour. Various amounts of acetic acid was added into montmorillonite dispersions until constant viscosity was achieved. The mixtures were further stirred at 600 rpm for 10 minutes to allow the complete ion exchange reaction prior to testing.

Preparation of organoclay

Twenty grams of montmorillonite clay were added to 800 ml of distilled water. The mixture was well stirred mechanically to obtain full dispersion. Diethanolamine neutralized with acetic acid was added to the clay suspension in a weight ratio equivalent to the cation exchange capacity of the clay (determined in the previous section). The ion exchange reaction was equilibrated for 10 minutes at 60°C. The supernatant was discarded. The slurry was filtered and washed with distilled water. The collected organoclay was dried at ambient temperature.

Preparation of cassava starch/ montmorillonite nanocomposite film

Cassava starch/montmorillonite nanocomposite films were prepared by the casting technique. The gelatinized starch solution containing well-dispersed nanoparticles of exfoliated montmorillonite was prepared by mixing 5 grams of oven dried cassava starch with various weight ratio of clay and 1 gram of glycerol. Distilled water was then added to obtain 5wt% starch dispersion. Diethanolamine was added into the dispersion. The weight ratio of montmorillonite to diethanolamine in the dispersion was held at 2:1 which was calculated from the obtained optimum cation exchange capacity value. Diethanolamine was converted to cation by the addition of acetic acid. The dispersion was mechanically stirred at 1000 rpm and heated to the gelatinized temperature of starch (70–80°C). The starch solution was cast onto acrylic sheet molds with a wet thickness of 2-3 mm. The cast film was dried overnight at ambient temperature. After the water completely evaporated, the films were removed. Note that 5 grams of cassava starch, 1 gram of glycerol and 95 cm³ of water were used with various amounts of clay and acetic acid as presented in Table 1.

Preparation of Cassava Starch/Montmorillonite Nanocomposite Film.....

Formula	Sample code	MMT	DEA	Acetic acid
1	St-C0,D0	_	_	_
2	St-C2,D1	2.0	1.0	0.6
3	St-C4,D2	4.0	2.0	1.2
4	St-C6,D3	6.0	3.0	1.8
5	St-C8,D4	8.0	4.0	2.2
6	St-C10,D5	10.0	5.0	2.8
7	St-C12,D6	12.0	6.0	3.4
8	St-C0,D1	_	1.0	0.6
9	St-C0,D2	_	2.0	1.2
10	St-C0,D3	_	3.0	1.8
11	St-C0,D4	_	4.0	2.2
12	St-C0,D5	_	5.0	2.8
13	St-C0,D6	—	6.0	3.4
14	St-C2,D0	2.0	_	_
15	St-C4,D0	4.0	_	_
16	St-C6,D0	6.0	_	_
17	St-C8,D0	8.0	_	_
18	St-C10,D0	10.0	_	_
19	St-C12,D0	12.0	_	_

Table 1. The composition of each formula.

Remarks: The composition of MMT, DEA, and acetic acid are presented in term of weight percent (based on starch).

Characterization

Viscosity

Viscosity of the montmorillonite dispersion was measured by Brookfield viscometer model RVT 111588. Five specimens were tested for each determination.

X-ray diffraction (XRD)

X-ray diffraction was performed using a PW 3710 Philips diffractometer with CuK_{α} radiation ($\lambda = 0.1542$ nm) in a sealed tube operated at 40 kV and 30 mA. The diffraction curves were obtained from 2 to 30° at a scanning rate 1°min⁻¹. The basal spacing of the silicate layer, *d*, was calculated using the Bragg's equation, $\lambda = 2d \sin\theta$ (where θ is the diffraction position and λ is the wavelength).

Transmission electron microscopy (TEM)

All cassava starch/montmorillonite nanocomposite solution samples were

diluted with distilled water (nanocomposite solution:distilled water ratio = 1:20). 300-mesh Cu grids were dipped in these solutions and dried at ambient temperature. TEM images of films were obtained with J200CX TEM, using an acceleration voltage of 100 kV. Highmagnification images were taken at 30,000 and 85,000 times of the origin specimen size.

Scanning electron microscopy (SEM)

SEM samples were prepared from nanocomposite and conventional composite plates. The samples were mounted on stub with double-sided adhesive tape and coated with a thin layer of gold. Images were taken using a JEOL scanning electron microscope, JSM-5410LV, using an accelerating voltage of 15 kV, and a magnification 350 times the origin specimen size.

Tensile properties

The tensile strength, percent of elongation, and modulus values were investigated using a Zwick Z010 universal testing machine according to the ASTM D882 standard.⁽¹¹⁾ Samples were cut to 200×15 mm and conditioned at 50 \pm 5% RH, 23 \pm 2°C for 24 hours. The gauge length and crosshead speed were 100 mm and 10 mm/min, respectively. The tests were carried out at 23 \pm 2°C and 50 \pm 5% RH. Each determination was taken from an average of five specimens.

Transparency

Transparency of the cassava starch/montmorillonite nanocomposite film was obtained using an Instrument Color System (I.C.S.), Macbeth UV-Vis spectrophotometer, mode transmittance wavelength was from 360 to 750 nm.

Moisture absorption

The moisture absorption of the cassava starch/montmorillonite nanocomposite film was determined using test specimens of 76.2×25.4 mm. The test specimens were dried in a 50°C oven for 24 hours, then cooled in a desiccator, and immediately weighed to obtain the initial weight. The specimens were conditioned in a container at 100% RH for 24 hours. After 24 hours, the specimens were removed from the container, dried by wiping with cloth, and then weighed immediately to obtain the final weight. The percentage of sample weight increase was calculated by using the below formula.

$$Moisture \ absorption(\%) = \frac{final \ weight - initial \ weight}{initial \ weight} \times 100$$

Water vapor transmission rate (WVTR)

The water vapor transmission rate of the cassava starch/montmorillonite nanocomposite film was carried out according to the specification of ISO2528-1995E.⁽¹²⁾ A minimum of three 90 mm diameter circular test specimens were prepared from each film sample. The test specimens were fastened to a deep dish containing 15 mm of distilled water using a condition B (temperature 38 \pm 1°C and relative humidity 90 \pm 2%). The dishes were weighed every hour. The total mass increase graphically as a function of time of exposure, the test being completed when three or four points lie on a straight line. The WVTR for each test piece was then calculated, in grams per square meter per 24 hours, from the equation.

$$WVTR = \frac{240 \times m_1}{S}$$

- where m_1 is the rate of increase in mass, in mg h⁻¹, determined from the graph
 - S is the area, known to within 1%in cm² (normally 50 cm²), of the tested surface of the test piece.

RESULTS AND DISCUSSIONS

Viscosity

The montmorillonite suspension was treated with diethanolamine in cationic form [$^{+}NH_2(CH_2CH_2OH)_2$], obtained by neutralization with acetic acid (pH = 7) and in weight ratios of montmorillonite to diethanolamine varying from 10:0–10:8. The measured viscosity expressed in

centipoises (cps) was recorded and the results are shown in Figure 2.

It can be seen that viscosity of diethanolamine treated montmorillonite increases rapidly from 10:0 to 10:3, then increases gradually from 10:3 to 10:5 and tends to be constant from 10:5 onward. At the optimum viscosity, the ratio between

montmorillonite and diethanolamine was calculated to determine the maximum cation exchange capacity, which was found to be 2:1. This ratio then was used throughout the experiment for the preparation of starch/montmorillonite nanocomposite film.



Figure 2. The viscosity of montmorillonite dispersion at various amounts of diethanolamine neutralized with acetic acid to pH 7.

X-ray diffraction (XRD)

The wide angle X-ray diffraction (XRD) patterns of montmorillonite (MMT) and diethanolamine modified montmorillonite (MMT-DEA) in the region between $2\theta = 2^{\circ}$ and $2\theta = 20^{\circ}$ are shown in Figure 3 (a) and (b), respectively. Each curve shows only one peak at $2\theta = 5.975^{\circ}$ for MMT and $2\theta = 5.590^{\circ}$ for MMT-DEA. The peaks assigned to the 001 lattice spacing of

silicate layer in montmorillonite as suggested by Usuki *et al.*⁽¹³⁾ The interlayer spacing corresponding of these peaks increases from 14.78 to 15.80 Å. In general, the higher degree of basal spacing expansion usually results in the higher chance of polymer intercalation which leads to a higher possibility of layered-silicate delamination in the polymer matrix.



Figure 3. XRD patterns of montmorillonite and diethanolamine modified montmorillonite.

Figure 4 shows the XRD pattern of cassava starch film (a) and the clay nanocomposite film (b). Both films display a broad band in the region between $2\theta = 15^{\circ}$ and $2\theta = 30^{\circ}$. The broad bands indicate that the films contain amorphous regions or partially ordered structures. The XRD pattern of the nanocomposite also shows a peak at

 $2\theta = 5.015^{\circ}$. The interlayer spacing corresponding of these peaks increases up to 17.62 Å. An increase in the interlayer spacing from 15.80 Å in the organoclay to 17.62 Å in the nanocomposite film resulted from some intercalation occurring during the component blending above the gelatinization temperature of cassava starch.



Figure 4. XRD patterns of films.

From the XRD results, it can be concluded that montmorillonite was dispersed in the starch matrix at the nanoscale level based on the complete disappearance of the XRD peak at $2\theta =$ 5.015 due to the exfoliation of aminosilicate layer.

Transmission electron microscopy (TEM)

Figure 5 shows the transmission electron micrographs of starch films containing (a) pristine montmorillonite (MMT) and (b) diethanolamine modified montmorillonite (MMT-DEA).



(a) Virgin MMT

(b) Intercalated MMT

Figure 5. TEM photographs of montmorillonite present in starch film at 85,000 magnification (a) containing virgin MMT and (b) containing intercalated MMT.

In the case of starch film containing pristine montmorillonite [Figure 5(a)], interspacing between aminosilicate layers could not be observed, indicating the remaining original structure similar to the sole montmorillonite as shown in Figure $6.^{(14)}$ This result indicates that there was no intercalation taking place with pristine montmorillonite due to the absence of cationic exchangeable species. On the other hand, starch films containing diethanolamine modified montmorillonite in Figure 5(b) shows the individual alumino-silicate layers. The clay morphology is very different from the pristine montmorillonite. These results showed the existence of an intercalated pattern of the clay because diethanolamine is an exchangeable cationic species which is consistent with the XRD pattern. However, the silicate layers have a very strong electrostatic interaction through intergallery cations make it extremely difficult to achieve complete exfoliation of the layers.



Figure 6. TEM micrograph of sole montmorillonite at 140,000 magnification by Wang *et al.*⁽¹⁴⁾

Scanning electron microscopy (SEM)

The surface morphology of starch films at the microscopic level was examined by SEM. Figures 7(a) and (b) represent the surface morphology of the nanocomposite film and the conventional composite film, respectively. In the conventional composite film, the population of larger clay particles around 10 μ m in the diameter was commonly observed. In contrast, the clay particles [Figure 7 (a)] are more finely dispersed in the nanocomposite indicated by the

significant reduction of the large clay particles. The difference could be attributed to the treatment of the clay by cationized DEA. The alkylammonium ions rendered the separation of the aminosilicate layer, resulting in the breakage of the clay particle into individual sheet plates. Consequently, better dispersion of exfoliated clay could be obtained in the case of nanocomposite film.



Figure 7. SEM micrographs [Formula 3].

Tensile properties of starch/ montmorillonite nanocomposite film

According to the viscosity measurement, the ratio 2:1 of MMT:DEA was applied to all the tensile properties by varying the amount from 0,0 to 12,6 w/w of starch. Furthermore, in this work the tensile properties of nanocomposite films contained MMT-DEA compared with their DEA and MMT were investigated. From Figures 8 and 9, starch films containing various amounts of pristine montmorillonite exhibit insignificant differences in tensile strength. Young's modulus shows insignificant changes in the mechanical properties. The ineffective reinforcement of the clay particles probably was due to the phase separation between the starch matrix and the clay filler.



Figure 8. Tensile strength of nanocomposite films.



Figure 9. Young's modulus of nanocomposite films.



Figure 10. Elongation at break of nanocomposite films.

In the case of intercalated montmorillonite, it was generally expected that an increase in tensile strength and Young's modulus should be observed by the largely increased surface area of montmorillonite due to the intercalation by DEA. However, it was disappointing that the resulting evidence presented in Figures 8 and 9 were totally opposite. Tensile strength and Young's modulus of the nanocomposite film gradually decrease with the increased content of montmorillonite. Furthermore, it can be seen that tensile strength and Young's modulus tend to decrease as MMT-DEA increases implying that diethanolamine adversely affects the tensile strength and Young's modulus of the film. A possible reason for the large decrease in tensile strength and Young's modulus is the hygroscopic nature of DEA. The nanocomposite films were prone to absorb more moisture consequently contributing to the plasticizer effect of the DEA.

Figures 8 and 9 show that there is a sharp decrease in tensile strength and Young's modulus as DEA increased from 0 to 6 wt%. In addition, the elongation at breaks of the hybrid films is shown in Figure 10. The elongation at breaks of nanocomposite starch was clearly seen to increase with increasing MMT-DEA content. The explanation of this phenomenon may be the fact that the diethanolamine behaved like glycerol which is a typical plasticizer for starch products.

Transparency

Figure 11 shows the percentage of transmittance of cassava starch/ montmorillonite nanocomposite film at a wavelength of 500 nm and containing pristine montmorillonite (MMT) and diethanolamine modified montmorillonite (MMT-DEA) prepared by casting process. The results show that the films were off-white in color but highly translucent. The results suggest that the translucency slightly decreased with increasing montmorillonite content because of agglomeration of the clay Compared to the films with particles. diethanolamine modified montmorillonite, the films that contained pristine montmorillonite were cloudier. The translucency of the hybrid films was due to the degree of clay particle dispersion in the matrix polymer.



Figure 11. Transmittance of cassava starch/montmorillonite nanocomposite film at wavelength 500 nm.

Moisture absorption

From Figure 12, it can be observed that moisture absorption of the nanocomposite film increases gradually with an increase in the amount of MMT as well as DEA (since the latter is proportional to MMT content). Therefore, it is no doubt that the moisture uptake capability of the nanocomposite film is largely influenced by the presence of DEA due to its hygroscopic nature. However, it was to reduce the amount of DEA since the optimum intercalation of montmorillonite would be affected.



MMT-DEA weight percent (based on starch)

Figure 12. Plot of percentages of moisture absorption of nanocomposite films at various formulations.

Water vapor transmission rate (WVTR)

WVTR values for a 70-micron thickness are given in Figure 13. The cassava starch/montmorillonite nanocomposite film was found to be superior in its permeability property to ordinary cassava starch film. For nanocomposite films, the results showed that the higher content of MMT-DEA resulted in higher water vapor permeability. The explanation of this phenomenon is based on the fact that diethanolamine is a plasticizer like glycerol. When the plasticizer content (water, glycerol and diethanolamine) increased in the nanocomposite film, the WVTR increased. The increase in WVTR could be either attributed to greater interchain distances in the presence of the plasticizer or to a denser packing of the polymer chains.



Figure 13. Effect of MMT-DEA content on water vapor transmission rate of various films.

CONCLUSIONS

A starch/clay nanocomposite consisting of montmorillonite at the molecular level was synthesized by using cassava starch and montmorillonite intercalated with an ammonium salt of diethanolamine. The cation-exchange capacity of the montmorillonite was of importance in the synthesis of cassava starch/ montmorillonite nanocomposite films because it determined the amount of alkylammonium ions that can be intercalated between the layers. In this context, the optimum cation exchange capacity was 2:1 montmorillonite to diethanolamine ratio.

Both cassava starch and starch/clay nanocomposite films were subsequently prepared by means of solution casting techniques. As seen from the XRD patterns and TEM micrographs of the nanocomposite film, this hybrid had a special structure in which montmorillonite dispersed homogenously. These results suggested that starch-clay nanocomposite can be classified as a intercalated nanocomposite.

On the microscale, SEM micrographs demonstrate a finer dispersion of the clay particles in the nanocomposite as compared with the conventional composites based on the same constitutes. The difference may be due to the treatment of the clay in which hydroxyammonium ions render the clay in organophilic and allow a better dispersion of the clay in an organic medium.

Tensile strength and Young's modulus of starch/clay nanocomposite films decreased, but their percentage elongation increased with increasing MMT-DEA contents. The explanation to this phenomenon is based on the fact that diethanolamine is a plasticizer like glycerol.

Films were highly translucent, but the translucency of nanocomposite films slightly decreased with increasing montmorillonite to diethanolamine ratio contents. At the same ratio, the films that contained pristine montmorillonite were cloudier than those of diethanolamine modified montmorillonite. The translucency of the hybrid films was due to the degree of clay particle dispersion in the matrix polymer. Moisture absorption and water vapor transmission rates of nanocomposite films increased with increasing MMT and DEA content because diethanolamine is a plasticizer for nanocomposite film.

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REFERENCES

- 1. Rakeuchi, H. and Cohen, C. (1999) "Reinforcement of poly(dimethylsiloxane) elastomers by chain-end anchoring to clay particles" *Macromolecules*, **32**, 6792-6799.
- 2. Oya, A., Kurokawa, Y. and Yasuda, H. (2000) "Factors controlling mechanical properties of clay mineral/polypropylene nanocomposites" *Journal of Materials Science*, **35**, 1045-1050.
- 3. Bhattacharya, M. (1998) "Stress relaxation of starch/synthetic polymer blends" *Journal of Materials Science*, **33**, 4131-4139.
- 4. Arvanitoyannis, I., Biliaderis, C. G., Ogawa, H. and Kawasaki, N. (1998) "Biodegradable films made from low density polyethylene (LDPE), rice starch, and potato starch for food packaging applications: Part 1" *Carbohydrate Polymers*, **36**, 89-104.
- 5. Psomiadou, E., Arvanitoyannis, I., Biliaderis, C. G., Ogawa, H. and Kawasaki, N. (1997) "Biodegradable films made from low density polyethylene (LDPE), wheat starch and soluble starch for food packaging applicants: Part 2" Carbohydrate Polymers, **33**, 227-242.
- Fishman, M. L., Coffin, D. R., Konstance, R. P. and Onwulate, C. I. (2000) "Extrusion of pectin/starch blends plasticized with glycerol" *Carbohydrate Polymers*, 41, 317-325.

- Abdul-Hatiz, S. A. (1997) "Synthesis and characterization of hypochlorite oxidized poly (methacrylic acid)-starch composite" *Polymer Degradation and Stability*, 55 (1), 9-16.
- Simkovic, N., Laszlo, J. A. and Thompson, A. R. (1996) "Preparation of a weakly basic ion exchange by crosslinking starch with epichlorohydrin in the presence of NH₄OH" *Carbohydrate Polymers*, **30(1)**, 25-30.
- Hasebawa N., Kawasumi M., Kato M., Usuki A. and Okada A. (1998) "Preparation and mechanical properties of polypropylene-clay hybrids using a maleic anhydride-modified polypropylene oligomer" *Journal of Applied Polymer Science*, 67(1), 87-92.
- 10. Khayankarn, O. (1999) Adhesion and permeability of polyimide-clay nanocomposite as protective coating for microelectronic gas sensor, M.Sc. Thesis in Polymer Science, The Petroleum and Petrochemical College, Chulalongkorn University.
- 11. ASTM standard D882. (1995) *Standard test method for tensile properties of thin plastic sheeting*, American Society for Testing and Material. U.S.A.
- 12. ISO standard 2528. (1995) Sheet materials-Determination of water vapour transmission rate-gravimetric (dish) method, International Organization for Standardization.
- Usuki, A., Kawasumi, M., Kojima, Y., Okada, A., Kurauchi, T. and Kamigaito, O. (1992) "Swelling behavior of montmorillonite cation exchanged for ωamino acids by ε-caprolactam" *Journal* of Materials Research, 8(5), 1174-1180.
- 14. Wang, S., Hu, Y., Tang, U., Wang, Z., Chen, Z. and Fan, W. (2003) "Preparation of polyethylene-clay nanocomposites directly from Na⁺ montmorillonite by a melt intercalation method" *Journal of Applied Polymer Science*, **89**, 2583-2585.

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