

Properties of Amylopectin/Montmorillonite Composite Films Containing a Coupling Agent

D. Nordqvist, M. S. Hedenqvist

School of Chemical Science and Engineering, Fibre and Polymer Technology, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

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ABSTRACT: The addition of clay to polymers has the combined effects of enhancing both the strength/stiffness and the barrier properties. This investigation presents a novel approach to further enhance the strength/stiffness of cast plasticized amylopectin (AP)/Na⁺-montmorillonite clay films using a water-soluble coupling agent, poly[(isobutylene-*alt*-maleic acid, ammonium salt)-*co*-(isobutylene-*alt*-maleic anhydride)], between the filler and the matrix. The addition of clay increased the strength and stiffness of the film and the addition of 0.4 parts of a coupling agent per 1 part clay further increased these properties. The trends were the same after each treatment, and there were always significant differences in stiffness and strength between the films without clay and with clay with 0.4 parts of the coupling agent.

The increase in stiffness/strength in the presence of a small amount of the coupling agent suggested that it had a bridging effect, presumably through strong secondary bonds to the clay and to the matrix. Infrared spectroscopy and moisture swelling experiments indicated that ester bonds were formed between the coupling agent and AP. X-ray spectroscopy and transmission electron microscopy revealed that the clay-particle/polymer structure was qualitatively independent of the presence of the coupling agent showing a mixture of intercalated clay stacks and exfoliated platelets. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 4160–4167, 2007

Key words: amylopectin; montmorillonite; composite; mechanical properties; coupling agent

INTRODUCTION

For several years, efforts have been made to develop renewable packaging materials and it is today more important than ever to find sustainable alternatives to the conventional petroleum-based packaging materials. Although, the amount of renewable packaging materials is so far very small, the introduction of e.g. polylactide¹ and starch/polymer blends² has meant that the future of renewables in packaging is beginning to look more promising. Starch is readily available and is among the cheapest biodegradable materials available on the market.³ However, to increase the use of starch-based packaging, several properties of the starch have to be improved. These include ductility and strength. The simplest way of improving the ductility is to add a plasticizer, but this unfortunately leads to a loss in strength and stiffness. The present investigation aims at finding a way of minimising the loss in strength and stiffness when a plasticizer is added.

There has been extensive research on starch-based films.^{4–7} Starch from most wild species is a mixture

of amylose (~ 30%) and amylopectin (AP) (~ 70%), both based on chains of (1 → 4) linked α -D-glucose.⁸ AP is highly branched whereas amylose is linear, and AP, in contrast to amylose, thus forms an amorphous transparent film,⁹ which is an attractive feature for packaging. Investigations of amylose and AP film properties have not been as intense as the studies of starch films.^{10–14} The major commercial starch source is maize, but potato, rice, and wheat are also major sources.¹⁵

AP granules from e.g. waxy maize are semicrystalline and insoluble in water at room temperature. However, when heated in an excess of water to above the gelatinisation temperature, the granules are destroyed and a continuous gel is formed which turns into a fully amorphous or semicrystalline glass when cooled to room temperature.¹⁶ The glass is not at equilibrium and it is therefore prone to crystallise on aging. This is especially the case for plasticized AP stored at a high relative humidity and at refrigerating temperatures.¹⁷ At low relative humidity ($\geq 50\%$ RH), however, even glycerol-plasticized AP films do not crystallise with time.

It was observed in the present investigation that relatively high plasticizer contents are needed to produce ductile AP films. At these high contents the film stiffness and strength are low. In addition the gas permeability of AP films increases with increasing

Correspondence to: M. S. Hedenqvist (mikaelhe@polymer.kth.se).

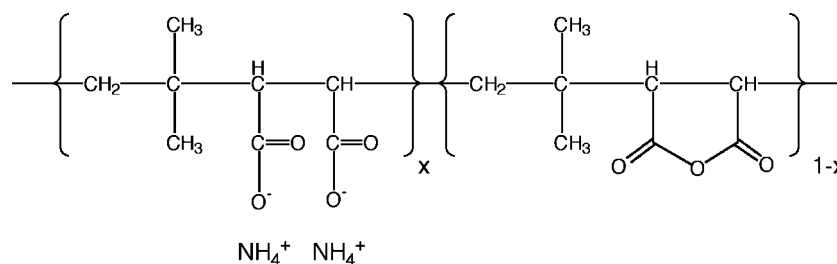


Figure 1 Structure of PIM, Poly[(isobutylene-*alt*-maleic acid, ammonium salt)-*co*-(isobutylene-*alt*-maleic anhydride)]. $x = 0.7$ – 0.8 according to the supplier.

glycerol content above 10 wt %.¹² A possible route to enhance the stiffness and strength is to blend the plasticized AP with clay particles. Clay may also help to reduce the increase in gas/liquid permeance that normally accompanies an increase in glycerol content. To achieve the optimal effects of the clay, the particles have to be well dispersed and well bonded to the polymer matrix.

The purpose of this investigation has been to see whether it is possible to enhance the strength and stiffness of a montmorillonite-clay/AP composite film through enhanced polymer-filler adhesion using a water-soluble coupling agent. The approach is based on a simple mixing technique. The hypothesis is that, even though the AP itself can form polar/hydrogen bonds with the clay, the water-soluble polar coupling agent will cover the clay surface more effectively during aqueous mixing, and hence form a larger number of strong secondary bonds with the clay than when AP is used alone. In this investigation, poly[(isobutylene-*alt*-maleic acid, ammonium salt)-*co*-(isobutylene-*alt*-maleic anhydride)] (PIM, Fig. 1), which is a commercial binder for e.g. ceramic powder,¹⁸ was used as coupling agent. The reasons for selecting PIM were its water solubility, polarity and content of reactive ring anhydride groups. The concept relies on the ability of PIM to form strong secondary (dipolar and hydrogen) bonds with the clay and at the same time form ester and strong secondary bonds with the AP (Fig. 2). The idea is that it is possible to produce linkages by exposing the clay to PIM in water before exposing it to AP. The mass content of PIM was 0.4 (4 wt % of total dry film mass) and 2.5 (25 wt % of total dry film mass) times the clay content, which, based on densities of $\rho = 2606 \text{ kg/m}^3$ for montmorillonite¹⁹ and $\rho = 1300 \text{ kg/m}^3$ for PIM,¹⁸ correspond to a PIM volume which is, respectively, ca. 80% and ca. 500% of the clay volume. The lower PIM content is similar to surfactant contents in commercial clay filler formulations and the higher PIM content was chosen to ensure more complete coverage of the clay.

To our knowledge, this is the first investigation in which a coupling agent has been used in composite

films containing starch, or starch components, and clay.

EXPERIMENTAL

Materials

Amylopectin (AP) from maize [CAS: 9037-22-3] and poly[(isobutylene-*alt*-maleic acid, ammonium salt)-*co*-(isobutylene-*alt*-maleic anhydride)] [CAS: 52032-17-4], M_w : $\sim 60,000 \text{ g/mol}$ (PIM) were purchased from Sigma-Aldrich and glycerol was kindly supplied by Karlshamn Tefac AB, Sweden. A natural sodium-rich montmorillonite (MMT), Cloisite[®]Na⁺, was obtained from Southern Clay Products (TX).

Methods

Film formation and composition

The films were produced by first mixing distilled water and MMT, with and without PIM, using an ultrasonicator (20 s, 40 A, pulser 5/1). The mixture

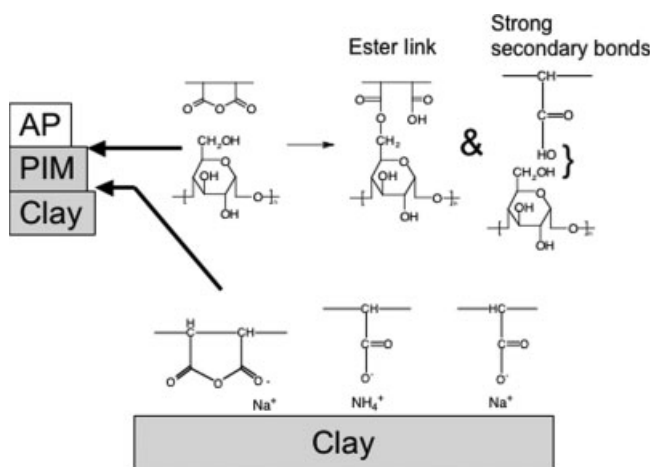


Figure 2 The concept of PIM as a coupling agent, including ester bond formation between AP and PIM (shown schematically). Also shown are examples of the strong secondary bond types that may exist between AP and PIM and between PIM and clay.

TABLE I
Composition of the Films

Sample	Amylopectin (wt %)	Glycerol (wt %)	On dry basis MMT (wt %)	PIM (wt %)	Cooking time (min)
70-30-0-0	70	30	0	0	15
60-30-10-0	60	30	10	0	14
56-30-10-4	56	30	10	4	13
35-30-10-25	35	30	10	25	10

was then added to a dispersion of distilled water, glycerol, and AP. The final dispersion was left on a stirrer at 100°C for a certain period of time (cooking time, see Table I) until the dispersion changed from milky to translucent. The gelatinised dispersion was poured into petri dishes and left to dry for at least 2 days at 30–40% RH. The petri dishes were coated with a layer of polytetrafluoroethylene supported by an aluminium foil (Bytac Type AF-21). The dried films were peeled off and stored in chambers at 30% RH. The AP concentration was 4 wt % with respect to the total dispersion and the amounts of MMT and glycerol were, respectively, 10 and 30 wt % with respect to the total film dry mass. The content of PIM was also expressed in relation to the total dry matter. A composite film here is denoted e.g.: 35-30-10-25, corresponding to wt % of AP-glycerol-MMT-PIM.

Infrared spectroscopy (IR)

Films were analyzed using a Perkin Elmer Spectrum 2000 FTIR spectrometer equipped with a single reflection ATR accessory from Specac (Kent, England). At least three measurements were performed on each sample.

Tensile testing

The tensile testing was performed at 23°C and 30% RH using an Instron 5566 tensile testing machine. Dumb-bell specimens, with a narrow-section width and length of respectively 4 and 20 mm, were used. The film thickness, measured with a Mitutoyo 10C-1128 micrometer (Mitutoyo Scandinavia AB, Sweden), was $90 \pm 10 \mu\text{m}$. The thickness was calculated as the average of four different measurements on each specimen. The crosshead speed was 10 mm/min.

Transmission electron microscopy (TEM)

Samples embedded in an epoxy resin were cryo-sectioned at -120°C using an RMC ultramicrotome and the 50–100 nm thick sections were collected and placed onto formvar/carbon-coated Cu-grids using a hairpin. The sections were subsequently viewed in a Philips Tecnai 10 electron microscope.

X-ray diffraction

X-ray diffractograms were obtained with an X'Pert PRO X-ray unit manufactured by PANalytical. It operates at 45 kV and 40 mA with Cu K α radiation. The scans were performed in the reflection mode in the 2θ range: 1–40°, and thereafter smoothed.

Moisture absorption measurements

The moisture absorption measurements were made by placing the film in a sealed flask with water at the bottom. The film was kept slightly above the water level by placing it on a steel-grid table that was standing in the water with its legs anchored on the flask bottom. The moisture uptake was determined by weighing the film before and after three days of exposure.

RESULTS AND DISCUSSION

In order to select a suitable clay content for the glycerol-AP films, films were cast with 1, 2, 5, and 10 wt % MMT. It was found that only the 10 wt % clay films were of sufficient ductility to be easily handled and 10 wt % clay was therefore used thereafter. It is possible that an even higher clay content would be satisfactory, but, in general, it is recommended to use as little clay as possible for e.g. exfoliation/dispersion and optical reasons. Therefore, a clay content above 10 wt % was not considered.

IR-measurements

Figure 3 shows the IR spectra in the region of interest for the composite films after different processing steps. In order to facilitate the comparison between the different IR curves their intensities were all normalised with respect to the 2930 cm^{-1} peak (not shown) corresponding to the methylene unit²⁰ present in AP and glycerol. The films were analyzed (1) after being stored at 30% RH at room temperature, (2) after being heat-treated at 150°C for 5 min and subsequently cooled to room temperature, and finally (3) after an additional two-day reconditioning at 30% RH at room temperature. These films are referred to, respectively, as untreated, heat-treated and reconditioned.

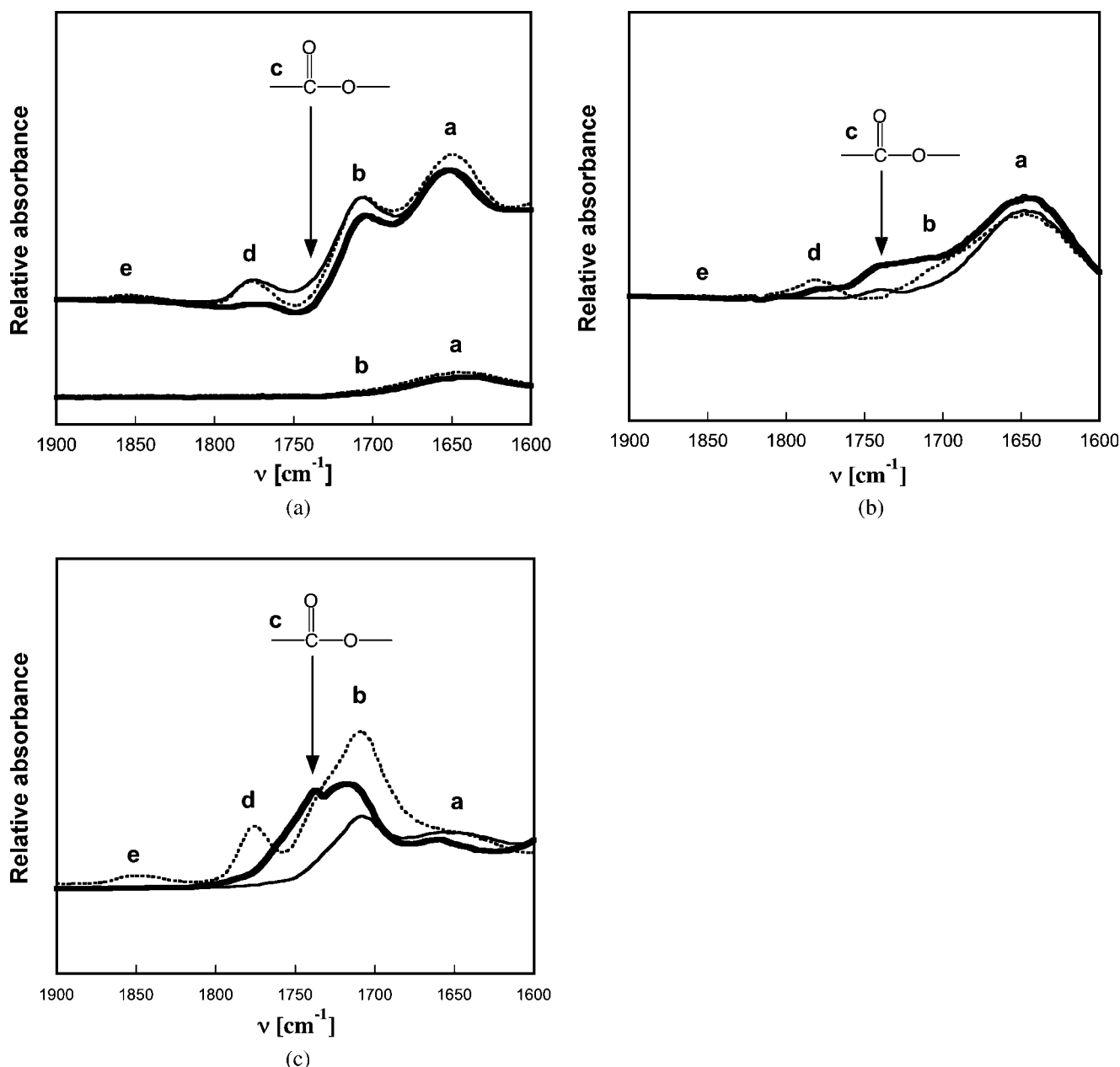


Figure 3 (a) IR spectra of the 0-30-0-70 (upper) and 60-30-10-0 (lower) samples, untreated (thin line), heat treated (broken line), and reconditioned (thick line). The spectral intensities were normalized with respect to the methylene 2930 cm^{-1} peak. The letters refer to (a) water H—O—H bend vibration (1650 cm^{-1}), (b) carboxylic acid ($\sim 1710\text{ cm}^{-1}$), (c) ester ($\sim 1740\text{ cm}^{-1}$), (d) ring anhydride asymmetric stretching vibration ($\sim 1780\text{ cm}^{-1}$), and (e) the corresponding symmetric band ($\sim 1865\text{ cm}^{-1}$). (b) Same as in (a) but for sample 56-30-10-4. (c) Same as in (a) but for sample 35-30-10-25.

To obtain IR information that relates solely to interactions between AP and PIM, it was necessary to first analyze separately the spectra of the PIM/glycerol and of the AP/glycerol/clay films. Figure 3(a) shows that the spectrum of the AP/glycerol/clay film was basically independent of the treatment. The main feature was a peak close to 1650 cm^{-1} , associated with the water H—O—H bending vibration,²¹ and a very weak shoulder at $\sim 1710\text{ cm}^{-1}$ corresponding to carboxylic acid.²⁰ In the PIM/glycerol film, two additional peaks were observed corre-

sponding to the presence of a ring anhydride (symmetric ($\sim 1865\text{ cm}^{-1}$) and asymmetric ($\sim 1780\text{ cm}^{-1}$) stretching vibration bands.²² The main effect of the heat-treatment on the PIM/glycerol film was a slight increase in the amount of anhydride groups [Fig. 3(a), peaks d and e]. This is expected since, when moisture is present, the ring anhydride actually exists, to a certain extent, as carboxylic acid. During drying, when moisture is removed, the ring anhydride is reformed.²² The changes due to heat treatment, with and without reconditioning, were greater when both

AP and PIM were present in the film [cf. Fig. 3(b,c) with Fig. 3(a)]. The untreated film containing 4 wt % PIM showed a new peak at $\sim 1740\text{ cm}^{-1}$ corresponding to the presence of an ester group [Fig. 3(b), peak c].²⁰ Ester-bond formation between a hydroxyl group on the starch glucose ring and an anhydride unit, e.g. on maleated polyethylene, has been documented by Yoo et al.²² and by Bikiaris and Panayiotou.²³ When the film was heat-treated, a weak, almost invisible, symmetric and a stronger asymmetric anhydride stretching-vibration peak appeared [Fig. 3(b), peaks d and e]. These two peaks were a natural consequence of the reformation of PIM anhydrides during the high temperature drying. In the reconditioned film, the ester peak (peak c) increased at the expense of the anhydride peaks.

The spectra representing the film with 25 wt % PIM were similar to those of the 4 wt % PIM film, except that the peaks were stronger. The ester peak [Fig. 3(c), peak c] was to a large extent hidden in the strong carboxylic acid peak [Fig. 3(c), peak b] in the untreated and heat-treated films, but it was prominent in the reconditioned film. The spectra of the 4 and 25 wt % PIM films showed a higher ester peak in the reconditioned films than in the untreated films [cf. peak c in Fig. 3(b,c); thick and thin curves]. This suggests that the heat-treatment and reconditioning increased the number of ester bonds.

It is possible that PIM also reacted with glycerol.²⁴ However, IR spectra on PIM with glycerol indicated only a very small "ester" shoulder (1740 cm^{-1}) on the carboxylic acid peak [Fig. 3(a)]. Thus, this reaction is here considered to be only of minor importance.

Moisture absorption

To obtain further evidence that AP reacted with PIM, the degree of swelling in moisture of films of pure AP, pure PIM and AP/PIM (50/50 w/w) was investigated. The pure PIM film was completely dissolved whereas the AP film sorbed 35 wt % moisture. Since pure PIM was completely dissolved, it was impossible to assess the degree of esterification between AP and PIM in the untreated blend based on sorption data. However it was possible to see whether the heat-treatment had any effect on the degree of esterification and thereby also to see whether esterification generally occurred. The untreated AP/PIM film sorbed 454 wt % moisture whereas the heat-treated film, subsequently conditioned in moist air during the three day-sorption experiment, sorbed only 150 wt %. The fact that the moisture uptake by the heat-treated and conditioned film was less than that of the untreated film indicated that further esterification took place between PIM and AP. It is

TABLE II
Tensile Properties of the Films, Values not Connected by the Same Letter are Significantly Different (Student's *t* test, $p = 0.1$)

Sample	Untreated	Heat-treated	Reconditioned
Strength [MPa]			
70-30-0-0	3.2 ^{EF}	3.2 ^{EF}	3.0 ^{EF}
60-30-10-0	4.4 ^{DE}	6.8 ^B	4.2 ^{DEF}
56-30-10-4	5.0 ^{CD}	13.0 ^A	7.0 ^{BC}
35-30-10-25	2.3 ^G	3.5 ^{DEF}	3.0 ^{FG}
Modulus [MPa]			
70-30-0-0	73 ^F	98 ^{EF}	66 ^F
60-30-10-0	169 ^{DE}	356 ^{BC}	207 ^D
56-30-10-4	221 ^{BCD}	633 ^A	444 ^B
35-30-10-25	188 ^D	250 ^{CD}	198 ^{DE}
Strain at break [%]			
70-30-0-0	22 ^{BC}	28 ^{BC}	26 ^{BC}
60-30-10-0	21 ^{BC}	8 ^D	24 ^{BC}
56-30-10-4	38 ^A	3 ^D	22 ^{BC}
35-30-10-25	28 ^B	22 ^C	24 ^{BC}

therefore probable that PIM-AP ester bonds were also present in the untreated film as a consequence of the first heating cycle associated with film formation, as indicated by the presence of an ester peak or shoulder ($\sim 1740\text{ cm}^{-1}$) in the IR spectra of the untreated films [Fig. 3(b,c)].

Tensile tests

The results of the tensile tests, presented in Table II, show that the strength and stiffness increased with the addition of 10 wt % clay, and even further with 4 wt % PIM. This was observed for all treatments, although the trends were in some cases within the limit of experimental error. The difference in strength and stiffness between the clay-free films and the clay films containing 4 wt % PIM was however always significant. The films with 25 wt % PIM were weaker and softer than the 4 wt % PIM films, which was a natural consequence of the fact that the strength and stiffness of PIM were lower than those of AP; the stress and stiffness of the PIM/glycerol film (sample 0-30-0-70) were, respectively, <2 and <35 MPa. The strain at break was of the order of 20–30% for all films and treatments, except for the heat-treated clay-containing films, with or without 4 wt % PIM, which were more brittle. The reason for this was not clear; a suggestion is that the presence of clay induces stress concentrations at the polymer-clay interface when the film is under stress, and that this leads to fracture when the matrix has dried and is less flexible (contain less moisture) to relax these stresses. Although X-ray and TEM (see below) showed no qualitative difference in the clay distribution among the films, it is still possible that fewer large "critical" clay-stacks were present in the 25 wt %

film than in the other clay-containing films. Large particles (intercalated stacks) initiate fracture more effectively than single exfoliated clay platelets, and it only takes a single "critically sized" particle to initiate fracture. Another plausible explanation of the ductility of the film with high PIM-content is that a large amount of PIM can resist extensive moisture loss during the heat treatment and thus make the composite tough. Interestingly, the ductility was not severely altered in the presence of clay and PIM in the untreated and reconditioned states. The changes in strength and stiffness with heat-treatment and reconditioning were also small, or absent, for the film without clay. Adding clay yielded a stiff and strong film after heat-treatment, but the effect vanished when the film was reconditioned. The heat-treated film with 4 wt % PIM had the highest strength and stiffness of all the films. The reconditioning reduced this effect, but, although the scatter was relatively large, it seemed that the reconditioned film was stronger and stiffer than the untreated film. Its strain at break was also significantly less than that of the untreated film, indicating that an irreversible change had occurred during the heat-treatment. The trend among the different treatments for the 25 wt % PIM film resembled the trend for the film with only clay more closely than that for the 4 wt % PIM film.

To verify the PIM bridging effect, a 4 wt % PIM film was also produced by first blending PIM with AP and glycerol before MMT was added. This yielded an untreated film which had a stiffness and strength that were, respectively, 25 and 28% lower than those of the original film in which PIM was first mixed with MMT. The strain at break was however, within the limit of experimental error, the same in both cases. This shows that the beneficial PIM effect was achieved by first mixing PIM with clay and then exposing the PIM/clay mixture to AP/glycerol. Thus, the enhanced strength and stiffness in the presence of a small amount of PIM seemed to be due primarily to its bridging effect between AP and clay, which leads to a more efficient clay-induced reinforcement (Fig. 2).

To see whether the cooking time (Table I) affected the final mechanical properties, an untreated film with AP and glycerol (70-30-0), gelatinized for 15 min, was compared with a film gelatinized for 10 min. The strength, stiffness, and strain at break of the 15 min film were, respectively, 80, 80, and 112%, of that of the 10 min film, which was within the limit of experimental error. Thus, the effect of cooking time, within the 10–15 min range, was of minor importance.

To conclude, it appeared that the addition of clay increased the strength and stiffness of plasticized AP. The addition of a small amount of PIM increased

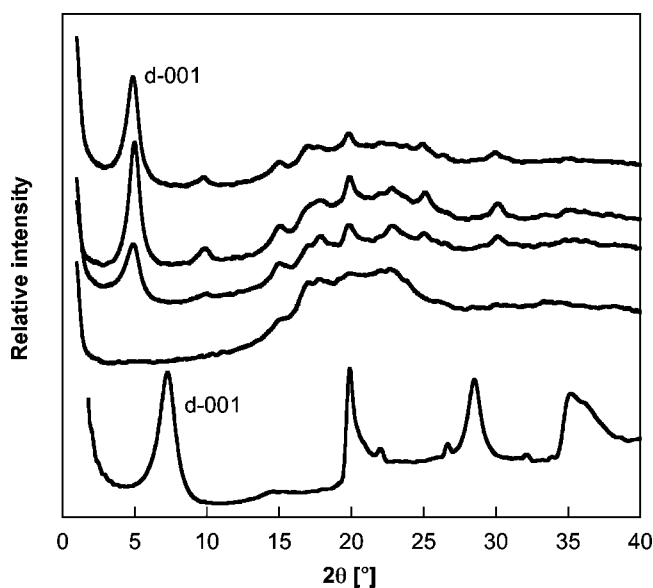


Figure 4 X-ray diffractograms representing, from top to bottom, samples: 60-30-10-0, 56-30-10-4, 35-30-10-25, 70-30-0-0, and MMT-Na⁺.

these properties further. Although the differences were in several cases within the limit of experimental error, it was observed that the trends were the same for all the treatments. Considering the low inherent strength and stiffness of PIM, the increase in strength and stiffness was probably due to efficient bonding between clay and AP achieved with PIM as coupling agent.

X-ray and TEM

The diffractograms in Figure 4 show that the d_{001} reflection of the pure clay was shifted to lower angles (larger distances) when the clay was incorporated in the composite films. The d_{001} distance increased from 1.2 nm in the clay to approximately 1.8 nm in all the composite films. Thus a considerable amount of the clay particles were only intercalated, which was not surprising considering the large concentration of clay. 10 wt % clay corresponds to a system where steric effects may prevent complete exfoliation.²⁵ Nevertheless, 10 wt % clay was chosen, as mentioned previously, because a lower clay content gave a poor ductility. In interpreting the X-ray diffractograms, the strength of the d_{001} peak was related to the $\sim 20^\circ$ MMT peak since the latter is due to the internal clay platelet structure and its position and strength are therefore insensitive to swelling of the clay tactoids.²⁶ The 25 wt % PIM diffractogram presented in Figure 4 indicated a less pronounced d_{001} peak, relative to the $\sim 20^\circ$ MMT peak, than that of the 4 wt % film. This would normally indicate a larger degree of exfoliation in the 25 wt % film, but

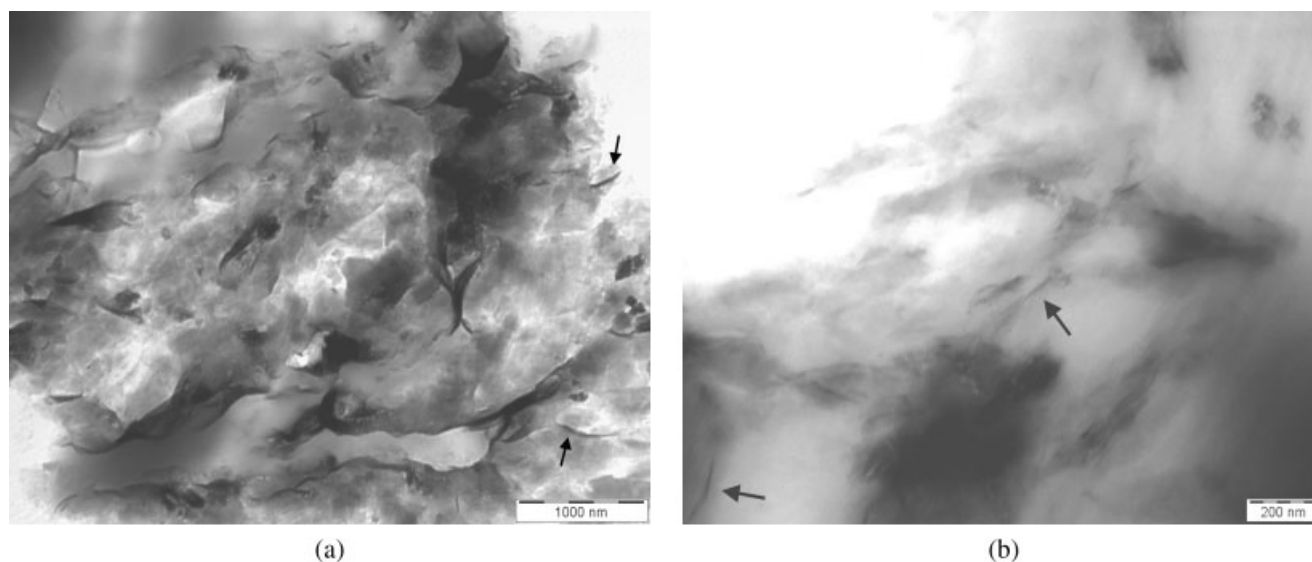


Figure 5 (a) TEM micrograph of 60-30-10-0 (low resolution). Arrows indicate clay platelets. (b) TEM micrograph of 35-30-10-25 (high resolution). Arrows indicate clay platelets.

repeated measurements showed that this was not the case. The relative d_{001} intensity varied in a non-systemic way between the films with different PIM contents. Thus, as suggested by others,²⁶ X-ray should be combined with TEM in order to reveal whether exfoliated clay does exist. Other X-ray peaks also changed in position and/or intensity from sample to sample, but the analysis of these effects was ignored here because the focus was entirely on the prominent d_{001} peak.

TEM showed, besides intercalated structures, that exfoliated clay particles were also present (Fig. 5). Intercalated stacks and exfoliated clay particles, observed at low magnification in Figure 5(a) (sample 60-30-10-0) and at high magnification in Figure 5(b) (sample 35-30-10-25), were also present in the other clay-AP films. Hence the same type of clay morphology was observed with or without PIM.

X-ray and TEM thus revealed that the addition of 10 wt % clay resulted in a mixture of intercalated and exfoliated clay-polymer structures in all the clay-containing systems.

CONCLUSIONS

The tensile tests showed that the addition of a small amount of PIM (4 wt % with respect to the total film dry mass) increased the strength and stiffness of the clay-AP film to the extent that the difference between the clay-free and PIM-clay films was always significant. The use of PIM, selected because of its water solubility, polarity and content of reactive ring anhydride groups, as a coupling agent thus seems to be a promising route for increasing the strength and

stiffness of clay-polymer composites without any severe loss of ductility. When the water-soluble PIM was mixed with clay before the plasticized AP was added, an efficient link was apparently achieved between the clay and the AP. The link was probably achieved with strong secondary bonds and, between PIM and AP, also ester bonds. The presence of the coupling agent had no significant effect on the type of clay-AP composite structure. The clay was present as exfoliated platelets and in intercalated stacks.

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