Reduced Shrinkage Polyester–Montmorillonite Nanocomposite

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ABSTRACT: A new approach is described for utilizing the swelling characteristics of montmorillonite (MMT) to compensate for polymerization-induced shrinkage in unsaturated polyester. The naturally sorbed sodium cation, at the lamellar interface of the mineral, was exchanged with the onium salt of 12-aminolauric acid to produce organophilic MMT, which was compatible with the host resin. The latter, boosted by a small amount of dimethylformamide, swelled into a polymerizing polyester resin, thus reducing polymerization shrinkage. The incorporation of 5% 12-aminolauric MMT caused the shrinkage of the neat isophthalic polyester resin to be reduced from 8.7 to 2.6%. Wide-angle X-ray diffraction and high resolution scanning electron microscopy analyses showed that the shrinkage reduction was associated with increased interparticle spacing and uniform dispersion of the MMT domains on the nanoscale. Mechanical measurements indicated that the flexural strength of the new compound was comparable to that of the neat resin; however, a remarkable 100% increase in toughness was observed in association with a minor decrease in the modulus of elasticity. This increased toughness may be attributed to macromolecular changes associated with the monofunctional acid moiety of the 12-aminolauric acid. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 767–773, 2005

Key words: polyesters; polymerization; clay; shrinkage; nanocomposites

INTRODUCTION

Many polymers are known to undergo substantial polymerization shrinkage, particularly unsaturated polyesters. Shrinkage of the cured resin gives rise to residual stresses, which are likely to cause dimensional problems during manufacturing. This phenomenon is related to the development of residual stresses whose effects may contribute to premature failure of the product. Evidence suggests that curing-induced shrinkage and residual stresses are linearly related below the glass-transition temperature.[1] It has been further noted that the magnitude of residual stresses depends on the glass-transition temperature, thermal expansion coefficient, and elastic modulus of the resin, as well as on the curing conditions and degree of dimensional constraint during curing.[2] Inorganic fillers are traditionally used to decrease the effects of cure related shrinkage; however, they have the general tendency to decrease the ultimate elongation, tensile strength, and flexural strength.[3] Low profile additives, based on polymeric systems such as poly(vinyl ace-

tate) and saturated polyester, have been reported to result in an earlier volume expansion during curing and better shrinkage control.[4–6] More recently, the swelling characteristics of montmorillonite (MMT) have been manipulated to effect shrinkage control of concrete mixes,[7] epoxy compounds,[8] and poly(methyl methacrylate).[9,10] Preparations of unsaturated polyester/MMT nanocomposites have recently been reported[11,12]; however, these reports have not been concerned with shrinkage control.

Being known as "swelling clays" instigates the hypothesis of using MMTs as shrinkage-reducing agents. This class of minerals exhibits a lamellar structure, in which the lamellae are held together by relatively weak forces resulting from net negative charges on the lamellar surface, which cause them to attach by sorbed cations (Na or Ca). Irregular stacking of the lamellae and their limited size promotes assemblage into primary particles, which amass to form aggregates. Early evidence[13] indicated that the swelling of this mineral is due to increasing interparticle spacing rather than to the expansion of the primary particles. This leads to the hypothesis that, if the sorbed cation is exchanged with an appropriate organic cation, an organophilic MMT may swell into a polymerizing medium, thereby compensating for the polymerization shrinkage. This work examines the applicability of this hypothesis to unsaturated polyester resin, describing the prepara-

tion procedures and the characteristics of the resulting composites.

EXPERIMENTAL

Materials

The clay mineral used in this study was Na-MMT obtained from Southern Clay Products, Inc. (Gonzales, TX) as Mineral Colloid BP, which has a fine particle size of 75 μm in the dry state. The reported cation exchange capacity (CEC) was 114.8 mequiv/100 g. As stated by the supplier, the d_{001} (interlamellar) spacing was 12 Å when measured at ambient humidity and 9.6 Å after drying overnight in a vacuum oven at 100°C.

Aminolauric acid was obtained from Sigma–Aldrich Corp. (St. Louis, MO). The unsaturated polyester, isophthalic polyester resin (Crystic 272E), was obtained from Scott Bader Middle East Ltd. (Jebel Ali, Dubai, UAE). The resin viscosity was 4.5 P when measured at 25°C and 60 rpm in a Brookfield rotational viscometer. Its specific gravity at 25°C was 1.1, its volatile content was 40%, and its acid value was 18 mg KOH/g. The peroxide catalyst that was used was Butanox M-50, under the trade name M50 (Scott Bader Middle East Ltd.). With 2% catalyst, the gel time at 25°C was 18 min.

Methods

In the present study, three different polyester/MMT compounds were prepared, depending on the MMT treatment method. MMT was used either as received or after treatment. Two types of treatment methods were used. The first treatment entailed the removal of MMT impurities, ensuring that all the interlamellar ions were Na^+ (i.e., homoionic). The second treatment method involved the exchange of Na^+ ions with alkylammonium ions with organic tails that are perceived to be compatible with the polyester resin. The final product, an MMT/polyester compound, was prepared using the selected MMT. Details of the steps involved are described below.

Purification and homoionization of Na^+-MMT

To ascertain the purity and cationic homogeneity of MMT, the Mineral Colloid BP was subjected to the following treatment. The mineral was dispersed in distilled water and allowed to stand for several hours. Then the suspension was subsequently decanted and treated with 0.1M NaCl to produce homoionic Na-MMT. The mixture was filtered and repeatedly washed with distilled water until no chloride ions were detected in the filtrate. This was checked through a reaction with $AgNO_3$. The washed MMT was air-dried at 100°C for 24 h in a vacuum oven.

Alkylammonium-MMT (AMMT)

The cation exchange of Na^+ with the organic ammonium salt derivatives of 12-aminolauric acid was carried out according to a method reported earlier.[8] A batch of 100 g of the homoionic Na-MMT was swelled in 2500 mL of distilled water for 24 h with mechanical stirring. 12-Aminolauric acid (40 g) dissolved in 250 mL of hot distilled water was added slowly to the swelled Na-MMT under stirring. The pH of the suspension was adjusted to 5.5–6.0 by the addition of dilute HCl (1M) with stirring. The acidified suspension was then stirred overnight at room temperature. Subsequently, the temperature of the suspension was raised to 85–90°C and stirring was continued for 12 h. The product was filtered off, washed several times with hot distilled water, and dried under reduced pressure at 40°C to give 118 g of MMT–aminolauric acid intercalate.

The CEC of the intercalated alkylammonium ions was determined gravimetrically. A preweighed sample was exposed to ignition at 1000°C in a furnace, the inorganic residue was determined, and the milliequivalent of the organic substance was calculated. The resulting interlamellar spacing was calculated from wide-angle X-ray diffraction (WAXD) measurements.

Polyester/MMT compounds

Isophthalic polyester resin (100 g) was diluted with 5 mL of dimethylformamide in a 250-mL, round-bottomed flask and stirred at 30°C and 3000 rpm for 1 h with a mechanically propelled stirrer with square blades. Then, 5 g of the selected MMT, which was dried in a vacuum oven at 40°C for 2 h, was gradually added to the resin. The mixture was stirred for 2 h under a constant temperature of 30°C and then stirred at room temperature for an additional 24 h to achieve complete swelling of the MMT intercalate. Finally, 2 wt % peroxide curing agent (Butanox M-50) was added to the mixture with continuous stirring for 5 min.

The resin/MMT mixture was subsequently degased in a vacuum oven for 10 min and then poured into two different open molds. The first was an aluminum mold (127 × 12.7 × 3.2 mm) coated with mold release agent, and the second was a porcelain crucible with a volume of 11.8 cm^3. Samples molded in the aluminum mold were used for mechanical testing, and samples molded in the porcelain mold were used to measure shrinkage. The resin mixture was allowed to cure in the molds at room temperature for 24 h, followed by 5 h at 85°C. All samples were stored in a desiccator for further testing. This method was used to prepare polyester samples containing either 5% as-received MMT (UMMT), 5% homoionic MMT (HMMT), or 5% AMMT. Neat isophthalic polyester resin is denoted as unsaturated polyester resin.
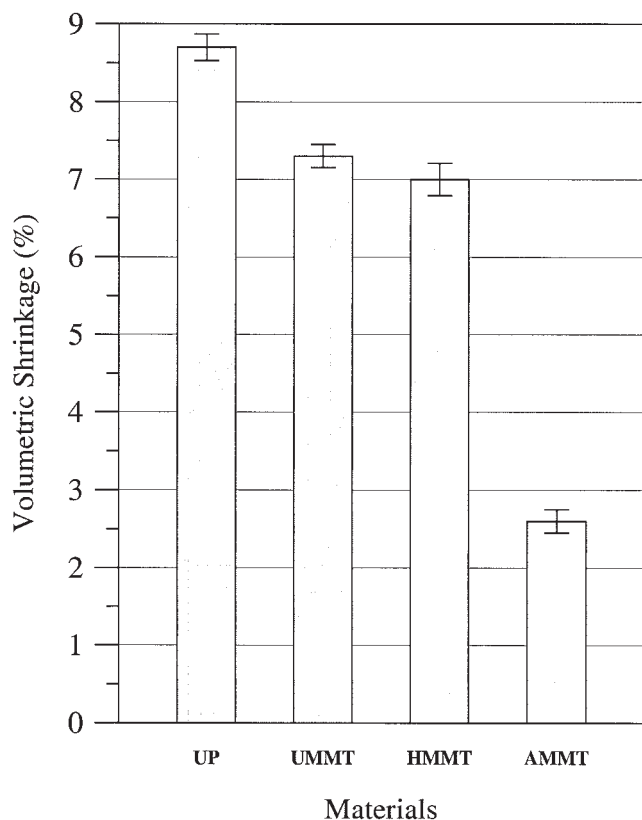
Figure 1 The volumetric shrinkage of unsaturated polyester and three different polyester/MMT compounds.

Characterization

The polyester/MMT compounds were characterized for volumetric shrinkage, interlamellar spacing, morphology, and mechanical properties. A brief description of the methods used for each is given below.

Volumetric shrinkage

We found that the most simple and straightforward method for determining the volumetric shrinkage was by measuring the change in volume of the curing resin in graduated porcelain vials. A known volume of the compounded resin was placed in a vial and allowed to cure. Once curing had been completed, the volume deficit resulting from polymerization shrinkage was compensated for by the addition of water from an automated dispenser.

Microstructural analysis

X-ray powder diffraction was performed using a Philips PW/1840, with an Ni filter and Cu Kα radiation (λ = 1.542 Å) at 40 kV and 30 mA and with a scanning speed 0.02°/s. The diffraction peaks between 2θ 2° and 25° were recorded. Measurements were made for the dried product to examine the interlayer activity in the as-prepared composite.

A Jeol JSM 5600 scanning electron microscope equipped with an energy dispersive X-ray detector was used to examine the morphology of fracture surfaces from three-point bend tests of the cured polyester/clay composite. The specimens were coated with gold for improved scanning electron microscopy (SEM) imaging.

Mechanical testing

The flexural properties of the polyester and nanocomposite samples were tested using a three-point bend test according to ASTM D790-00. The sample dimensions were 127 × 12.7 × 3.2 mm. The support span and the rate of crosshead motion were 50 mm and 1.3 mm/min, respectively. The specimen was deflected until rupture occurred. An MST testing machine was equipped with universal testing software (Test Works) capable of graphical and numerical analysis of the test data. The flexural stress, flexural modulus, and deflection were calculated according to the formulas reported in ASTM D790-00.

RESULTS AND DISCUSSION

Polymerization-induced shrinkage is primarily attributed to molecular packing that results from the formation of inter- and intrachain covalent bonds. To encounter this phenomenon, a polymerizing system must incorporate expanding entities that are uni-
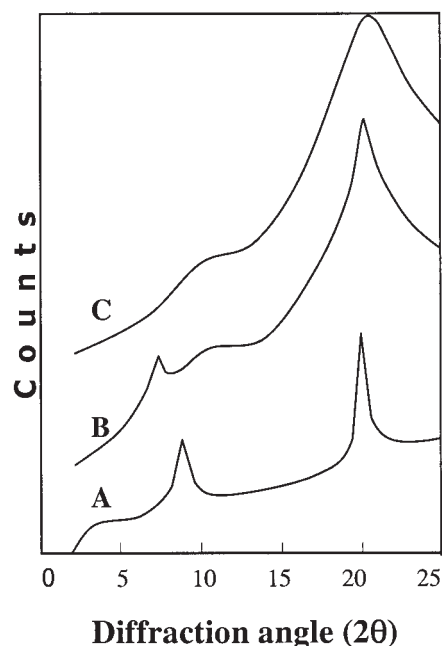
Figure 2 The X-ray diffraction behavior of HMMT (curve A), UMMT (curve B), and AMMT (curve C).
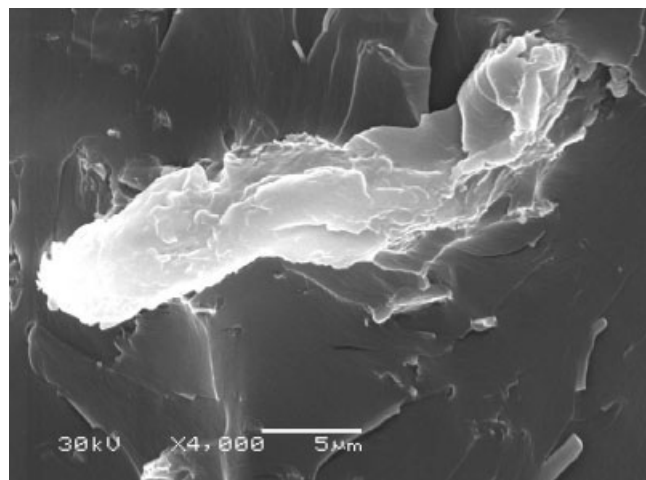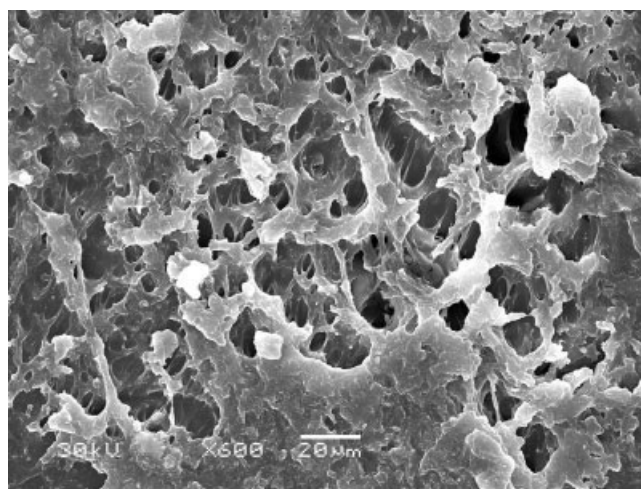
(a)
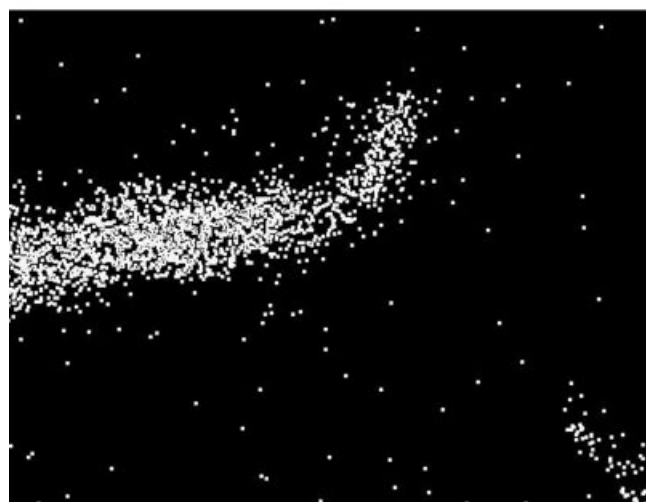
(b)

Figure 3　(A) An SEM micrograph of the fracture surface of the UMMT sample and (B) an X-ray scan for silicon in the same area.

formly networked within it. In this work, the oddity of the crystalline structure of MMTs is exploited to perform the desired function.

　Figure 1 displays the final volumetric shrinkage of the three different formulations, each containing 5% (by weight) MMT, compared to that of the neat resin. As expected, the incorporation of 5% as-received MMT caused a modest shrinkage reduction from 8.7 to 7.4%. As seen in the figure, similar behavior is displayed by HMMT, where incorporating 5% HMMT reduced the shrinkage to 7%. This reduction is attributed to the presence of MMT as a powdered solid, in addition to the effect of the expansion of the interlaminar galleries associated with resin adsorption within it. The slight improvement of HMMT over the as-received MMT may be thought of as the result of removing impurities. It was noteworthy that 5% AMMT brought the shrinkage down to 2.5%.

　To examine the factors contributing to the results presented above, WAXD and SEM evidence was examined. The former was used to gauge activity within the interlayer spacing and the latter was used to examine the dispersed morphology in each case.

　Figure 2 represents WAXD patterns of different samples. Curve A in Figure 2 shows the pattern associated with HMMT. Sodium activated MMT shows a sharpened first peak situated between 2θ 5° and 10°, corresponding to the (001) plane. The interlamellar spacing corresponding to d(001) was estimated using the Bragg relationship $n\lambda = 2d \sin \theta$ and was found to be 9.8 Å, in agreement with reported values.[11,14] Curve B in Figure 2 shows the HMMT powder diffraction behavior. The interlamellar spacing of the clay, corresponding to the (001) plane peak, shifted
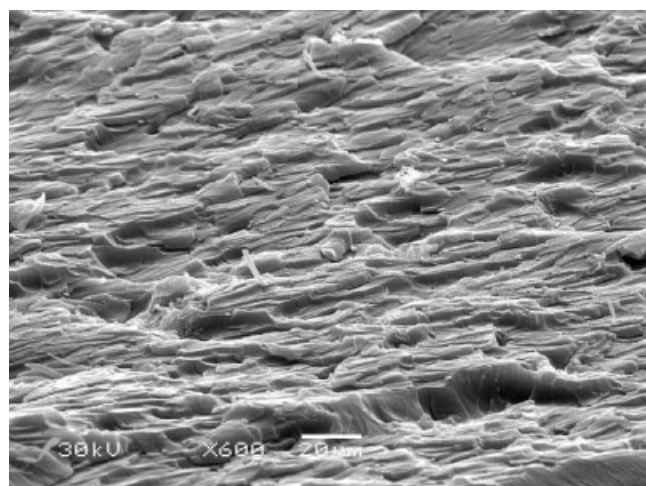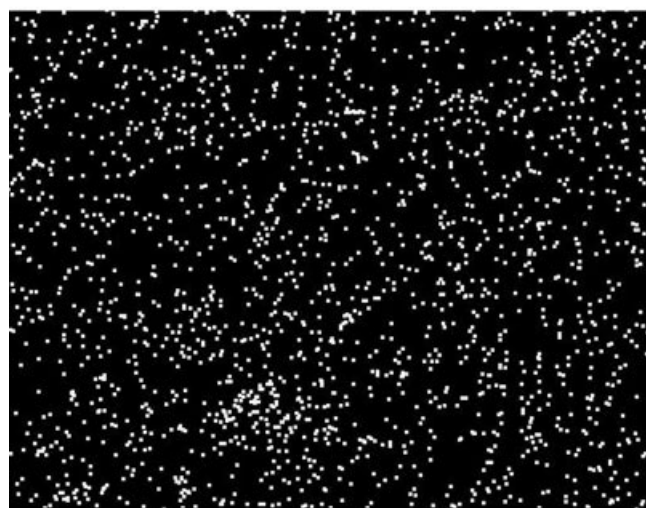

(a)
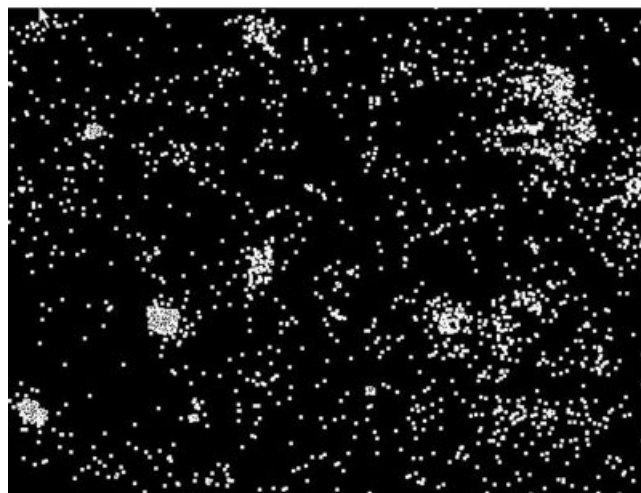
(b)

Figure 4　(A) A low magnification SEM micrograph of the fracture surface of the UMMT sample and (B) an X-ray scan for silicon in the same area, showing well-dispersed MMT agglomerates.
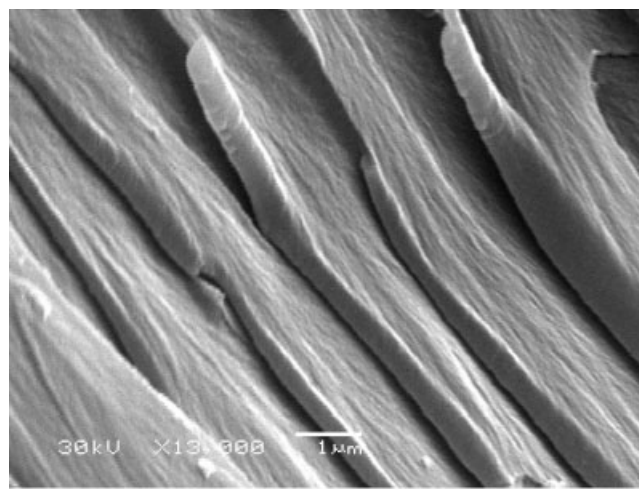
(a)

(b)

Figure 5 (A) An SEM micrograph of the fracture surface of the AMMT sample and (B) an X-ray scan for silicon in the same area.

The high angle peak at 2θ 20° and $d = 4.5$ Å remained in a similar position for all samples. This peak corresponds to crystallographic planes of the clay layer at (110) and (020), and its position is independent of the basal spacing.[16]

Figure 3(a) illustrates a selected area micrograph of the fracture surface of a UMMT sample. The image of intact mineral agglomerate in the range of 25 μm is shown. Figure 3(b) is an X-ray scan for elemental silicon of the same area imaged in Figure 3(a). The match between the two contours identifies the agglomerate as MMT. A repeat of this analysis at lower magnification (original magnification ×600) is shown in Figure 4(a,b). Note that the MMT agglomerates are well dispersed, but they continue to maintain their agglomerate identity.

(a)

(b)

Figure 6 (A) A high magnification SEM micrograph of the fracture surface of the AMMT sample and (B) an X-ray scan for silicon in the same area.
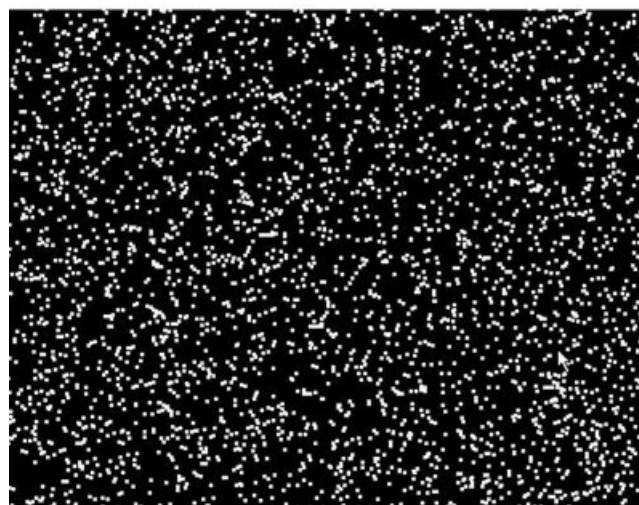
from 9.8 Å for the HMMT to 11.2 Å for HMMT (Fig. 2, curve B). This small shift of the interlayer distance is due to diffusion of the unsaturated polyester molecules between the silicate layers of the clay, indicating that the unsaturated polyester resin did not intercalate between the layers of HMMT. The negligible shift of the peak suggests that the basal spacing of the MMT is unaffected by the unsaturated polyester resin matrix and that the material formed is comparable to conventional filled polymer.[11,12,15] The d(001) peak for AMMT, which is typically observed at 17 Å,[16] was not observed for AMMT. The absence of the diffraction peak in the small angle region for AMMT suggests that the clay particles were exfoliated, an indication that the silicate layers were delaminated by the polymer molecules during the reaction.

An identical analysis of the fracture surface of an AMMT composite reveals a strikingly different mineral morphology, as shown in Figure 5(a,b). At the same magnification (original magnification ×600) used in Figure 4, the field appears unoccupied by any MMT domains and the corresponding elemental mapping for silicon does not reveal any agglomeration. Even at the higher (original) magnification of ×13,000, as seen in Figure 6, the MMT domains cannot be resolved from the image [Fig. 6(A)] or from the silicon mapping [Fig. 6(b)]. These observations suggest that the AMMT agglomerates have been dissociated to primary particles, whose size is below the SEM resolution. This conclusion, coupled with the significant shrinkage reduction observed for AMMT, is in accord with the early finding that MMT expansion occurs on the primary particle level.

It is also interesting to note that the general nature of the fracture surface morphologies of the two composites differ significantly. The UMMT composite displays a patchy appearance [Fig. 4(a)], which contrasts with the layered appearance displayed by the AMMT composite [Fig. 5(a)]. The former is reminiscent of the ductile fracture surfaces of linear polymers such as polyethylene and the latter appears to reflect a slip-stick mechanism on a submicroscale [Fig. 6(a)].

Figure 7 shows the flexural stress–strain behavior of the neat unsaturated polyester resin and that of the AMMT composite. The flexural strength of the composite (65 MPa) is nearly identical to that of the neat
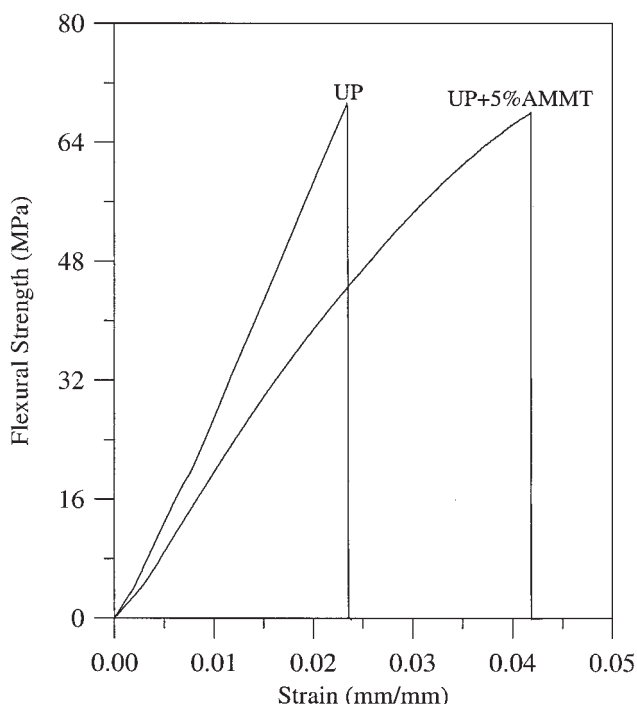
TABLE I
Mechanical Properties of Polyester/Montmorillonite Compounds

Mechanical Properties	UP	UMMT	HMMT	AMMT
Flexural strength (MPa)	67 (3.1)	52 (2.1)	62 (5.5)	65 (3.5)
Flexural modulus (GPa)	3.22 (0.4)	3.45 (0.37)	3.47 (0.4)	2.12 (0.2)
Deflection (%)	2.2 (0.3)	1.8 (0.01)	1.8 (0.1)	4.0 (7E-2)

Standard deviation are shown in parentheses.

resin (67 MPa). However, a one-third reduction in the flexural modulus appears to have produced a twofold increase in the ultimate strain, reported as the percent deflection.

Table I summarizes the mechanical properties of all tested materials. The slightly lower values of the flexural strength and the more significant reduction in the ultimate deflection because of the addition of 5% as-received or HMMT may be attributed to the agglomerate nature of the mineral, which most likely acted as sites of stress concentration, thus leading to strength reduction. The fact that the lowest strength observed was for UMMT may be due to impurities present in the as-received MMT.

The minor increase in the modulus displayed by the UMMT and HMMT composites is expected because of the addition of a mineral whose modulus is higher that that of the host resin. The one-third reduction of the modulus of the AMMT composite may be related to a possible reduction in the degree of polymerization that is imparted by the terminal acid group of the alkylammonium derived from 12-aminolauric acid. Such an effect apparently acted as an effective plasticizer to the matrix, giving rise to lower modulus and higher elongation.

CONCLUSIONS

The results demonstrate that a significant reduction in polymerization shrinkage of unsaturated polyester resin is achieved by incorporating AMMT. Microstructural analyses suggested that the observed shrinkage reduction resulted from the expansion of the MMT domains. A stoichiometric rationale was introduced to explain an associated increase in the ultimate flexural stain and a corresponding decrease in the flexural modulus.

Figure 7 The flexural stress–strain behavior of the unsaturated polyester resin (UP) and the AMMT composite.

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