

## Property Enhancement in Unsaturated Polyester Nanocomposites by Using a Reactive Intercalant for Clay Modification

Sinan Şen,<sup>1</sup> Hatice Burçin Gündem,<sup>1</sup> Bülend Ortaç<sup>2</sup>

<sup>1</sup>Department of Polymer Engineering, Yalova University, 77100 Yalova, Turkey

<sup>2</sup>UNAM-Institute of Materials Science and Nanotechnology, Bilkent University, 06800 Ankara, Turkey

Correspondence to: S. Şen (E-mail: sinans@yalova.edu.tr)

**ABSTRACT:** Polymeric nanocomposites were synthesized from unsaturated polyester (UPE) matrix and montmorillonite (MMT) clay using an *in situ* free radical polymerization reaction. Organophilic MMT was obtained using a quaternary salt of coco amine as intercalant having a styryl group making it a reactive intercalant. The resultant nanocomposites were characterized via X-ray diffraction and transmission electron microscopy. The effect of increased nanofiller loading on the thermal and mechanical properties of the nanocomposites was investigated. All the nanocomposites were found to have improved thermal and mechanical properties as compared with neat UPE matrix, resulting from the contribution of nanolayer connected intercalant-to-crosslinker which allows a crosslinking reaction. It was found that the partially exfoliated nanocomposite structure with an exfoliation dominant morphology was achieved when the MMT loading was 1 wt %. This nanocomposite exhibited the highest thermal stability, the best dynamic mechanical performance and the highest crosslinking density, most probably due to more homogeneous dispersion and optimum amount of styrene monomer molecules inside and outside the MMT layers at 1 wt % loading. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3247–3254, 2013

**KEYWORDS:** clay; composites; mechanical properties; polyesters; thermal properties

Received 10 October 2012; accepted 21 January 2013; published online 20 February 2013

DOI: 10.1002/app.39055

### INTRODUCTION

In recent years, polymeric nanocomposites have attracted a great deal of attention because of the impressive enhancements of material properties due to nanometer size of filler dispersion compared with pure or conventionally filled polymers.<sup>1,2</sup> Both thermoplastics and thermosets have been widely used in preparation of polymer nanocomposites including layered silicates as nanosized reinforcers. Thermoset matrices have a wide range of industrial applications such as coatings and adhesives. Most common thermoset polymers used in polymer nanocomposites include phenol resins<sup>3</sup>, epoxy resins,<sup>4</sup> and unsaturated polyester (UPE) resins.<sup>5,6</sup> Among them, UPE resin exhibits relatively poor mechanical and thermal properties, which restricts its use in advanced composite systems. In order to enhance the performance of UPE resin, it has been reinforced with nanosized clays by *in situ* intercalative polymerization method in which polymer resin, dissolved in a polymerizable monomer such as styrene, is intercalated between clay layers via simultaneous mixing and then followed by crosslinking reaction.<sup>5–10</sup>

Montmorillonite (MMT) clay, having a high aspect ratio, is one of the most commonly used layered silicates in preparation of

polymeric nanocomposites. The surface of natural clay, in general, is hydrophilic and this inhibits its dispersion in the organic phase. To make a hydrophobic clay surface, mixing with quarternized alkyl ammonium ions as intercalants has been attempted because the ammonium ions can exchange easily with ions between the silicate layers, resulting in increases in the distances between the silicate layers.<sup>3,11</sup> Bharadwaj et al.<sup>5</sup> dispersed quaternary alkyl ammonium modified MMT clays in UPE resin by *in-situ* intercalative polymerization method. They obtained partially exfoliated nanocomposite structures and observed a decreasing trend in static and dynamic mechanical properties with increasing clay concentration. Suh et al.<sup>6</sup> also prepared the UPE nanocomposite with quarternized alkyl ammonium ions by both simultaneous and sequential mixing of UPE, styrene, and organophilic MMT at 60°C. It was reported that the nanocomposites obtained by simultaneous mixing resulted in intercalated structures with a lower glass transition temperature ( $T_g$ ) value in comparison with that of UPE itself. These results were attributed to insertion of relatively smaller styrene molecules in between MMT layers at high levels which lowers possibility of crosslinking reaction with reactive double bonds of UPE. On the other hand, the results of the sequential

mixing method, which involves the addition of styrene to UPE/MMT preintercalates showed a more homogeneous network and high crosslink density with increasing mixing time. Numerous other types of compatible agents have been used to obtain organophilic clays. Alternatively, silane coupling agents as modification agents for clay have been used in UPE<sup>7</sup> and urethane nanocomposites<sup>12</sup> because of their ability to react with hydroxyl groups situated at the surfaces and particularly at the edges of the clay layers. However, some exfoliation in predominantly intercalated nanocomposite structure was obtained due to insufficient intercalation or lack of ion-exchange reaction of clay layers in presence of only silane as modification agent.

Recently, in one of my own works, an alternative method for modification of the clay was reported in order to overcome abovementioned inhomogeneous crosslinking of reactive double bonds of UPE and its undesirable effects.<sup>13</sup> In that study, a “double” modified MMT clay, having intercalants of both cetyl trimethyl ammonium bromide and trimethoxy vinyl silane was used as organoclay. The exfoliated UPE nanocomposite structure exhibiting better thermal and dynamic mechanical properties was obtained when the MMT clay was modified in the presence of the two intercalants simultaneously even with 3 wt % clay loading. This result was ascribed to participation of reactive double bond in vinyl silane coupling agent in the polymerization reaction from both surface and edges of ammonium ion intercalated clay layers. The “double” modified MMT clay was prepared by using the two intercalants, simultaneously but using two different solutions; one including the ammonium salt dissolved in water which was then added to that of a mixture of ethanol and water including silane coupling agent and MMT clay.

In this study, unlike conventional ammonium salts or a two-intercalants system, incorporation of an ammonium salt containing a reactive double bond as only one intercalant for modification of MMT clay is thought to be an original solution to the drawbacks mentioned above. UPE nanocomposites were prepared by *in-situ* free-radical polymerization method. The MMT clay was rendered organophilic with a quaternary salt of coco amine having a styryl part as the reactive group for crosslinking reaction. The cocoamine salt is expected to intercalate between the clay layers via ionic interactions and participate in polymerization reaction via its reactive double bond. This may lead to exfoliated nanocomposite structure via existence of nanolayer connected intercalant-co-crosslinker serving to crosslink and enhance mechanical strength and thermal stability. The probable participation of reactive double bond in the polymerization reaction between ion-exchanged clay layers may make this intercalant more advantageous in delamination than aforementioned “double” modified clay<sup>13</sup> which participate in the crosslinking reaction only from its edges and surfaces. Differences in dynamic mechanical and thermal properties as well as the morphology of the resultant nanocomposites are all discussed as a function of degree of clay loading.

## EXPERIMENTAL

### Materials

UPE resin (orthophthalic) including 37% styrene is the product of Poliya Poliester A.Ş., Istanbul, Turkey, with a brand name of

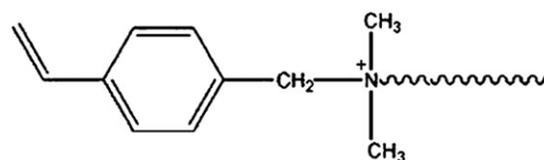


Figure 1. Molecular structure of quaternary coco amine.

Poliipol<sup>TM</sup> 3553. Methyl ethyl ketone peroxide (MEKP), which was in the form of 50% solution, as initiator and cobalt naphthenate (Co-naphthenate), which contains 6% cobalt, as promoter were purchased from Aldrich (Steinheim, Germany) and used as received. The clay, sodium montmorillonite (NaMMT) was kindly donated by Süd Chemie (Nanofil 1080, cationic [Na<sup>+</sup>] exchange capacity of 100 meq/100 g). The chemical structure of the modifier, quaternary cocoamine salt, having a vinyl group and a tail with up to 18 carbons composed of ca 6% C8, ca 4% C10, ca 48% C12, ca 21% C14, ca 11% C16, and ca 10% C18 alkyl chains<sup>14,15</sup> is depicted in Figure 1.

NaMMT (1 g) was dispersed in 200 mL of deionized water at 80°C and a separate solution of 1 g of quaternary coco amine salt, modifier, in 100 mL of deionized water was slowly added to the clay solution and mixed vigorously, while keeping the temperature of the solution at 80°C. After mixing, the total volume is brought up to 600 mL and stirred for 1 h. The organically modified MMT (CocoMMT) was recovered by centrifuging the solution, followed by repeated washings with deionized water to remove excess ions. The final product was dried at 50°C in a vacuum oven for 48 h.

### Preparation of Unsaturated Polyester Nanocomposites

All nanocomposites were prepared by mixing the modified clay, CocoMMT (1, 2, and 3 wt %, with respect to the resin), with the UPE resin which has 0.25% by weight of resin, Co-naphthenate promoter and 37% by weight of resin, styrene in it. After stirring the mixture at room temperature for 24 h, 2%, by weight of resin, MEKP initiator was added just before molding and mixed. Then the mixture was directly poured into silicone molds having necessary dimensions for the tests, and allowed to cure in the molds at room temperature for 24 h followed by 3 h at 120°C to complete curing reaction.

The resultant nanocomposites are referred as UPEXM-C, where X represents CocoMMT clay loading percent.

### Characterization

X-ray diffraction (XRD) measurements of NaMMT and OrgMMT clays as well as nanocomposites were conducted on a Rigaku D/Max 2200 Ultimat diffractometer (Rigaku, Tokyo, Japan) with CuK<sub>α</sub> radiation ( $\lambda = 1.54 \text{ \AA}$ ), operating at 40 kV and 40 mA with a scanning rate of  $2^\circ \text{ min}^{-1}$ .

Morphology of the nanocomposites was investigated by XRD, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) measurements. TEM analysis was performed using a FEI Tecnai<sup>TM</sup> G2 F30 (FEI, Hillsboro, OR, USA instrument operating at an acceleration voltage of 200 kV. About 100-nm ultrathin TEM specimens were cut by using cryo-ultramicrotome (EMUC6 + EMFC6, Leica) equipped with a

diamond knife. The ultrathin samples were placed on copper grids for TEM analyses. The fracture surfaces of the composites were investigated by scanning electron microscopy (SEM) analysis, using ESEM-FEG and EDAX Philips XL-30 microscope (Philips, The Netherlands).

Dynamic mechanical properties of the composites were measured with a dynamic mechanical analyzer (DMA Q800, TA Instruments, New Castle, DE) in single cantilever mode at a frequency of 1 Hz and at a heating rate of 3°C min<sup>-1</sup>. The average dimensions of the molded samples were 12 × 35 × 3.5 mm<sup>3</sup>.

Thermogravimetric analysis (TGA) was performed on a Seiko TG/DTA 6300 thermal analysis system instrument (Seiko Instruments, Tokyo, Japan) under nitrogen flow with a heating rate of 10°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Clay Modification

Modification of the MMT clay was followed with X-ray diffraction analysis. XRD analysis gave the values of the interlayer spacing or *d*-spacing of the NaMMT and CocoMMT which were obtained from the peak position of the *d*<sub>001</sub> reflection in the diffraction patterns (Figure 2). A 2θ angle of 7.28° and basal spacing of 12.13 Å was found for NaMMT clay. It can be seen from Figure 2 that diffraction angle of CocoMMT was found to be lower (3.4°) and its interlayer spacing was found to be 25.96 Å (Table I). Thus, a decrease in the diffraction angle and increase in interlayer distance indicates that intercalation of quaternary coco amine salt into MMT clay layers through the ion-exchange reaction was successful, resulting in an organophilic clay.

The existence of quaternary coco amine salt in the MMT structure was also confirmed by TGA. Figure 3 shows the TGA scans of NaMMT and CocoMMT clays. It is clear from Figure 3 that OrgMMT shows a lower decomposition onset temperature as well as higher degradation dependent weight loss compared to pure NaMMT. Pure MMT has only 7.20 % total weight loss indicating water removal. After the intercalation, this amount reaches almost 29% at higher temperatures, resulting from the degradation of intercalated and edge/surface attached coco amine salt. This result can be accepted as an indication of the successful modification of the MMT clay.

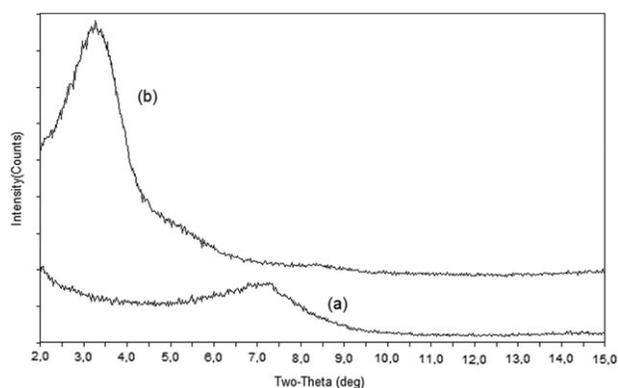


Figure 2. X-ray diffractograms of (a) NaMMT and (b) CocoMMT clays.

Table I. XRD Data for Clays and UPE Nanocomposites

Clays and nanocomposites	<i>d</i> <sub>001</sub> of clay, Å <sup>a</sup>
NaMMT	12.1 (7.28°)
CocoMMT	25.9 (3.40°)
UPE1M-C	No reflection
UPE2M-C	37.4 (2.35°)
UPE3M-C	36.4 (2.42°)

<sup>a</sup>Two-theta angles are given in parentheses.

The degree of dispersion of CocoMMT clay in unsaturated polyester nanocomposites was determined by XRD analyses. Figure 4 shows X-ray diffractograms of UPE nanocomposite samples. As it can be seen from the figure, there is no noticeable MMT clay peak (*d*<sub>001</sub> reflection) appearing in the diffraction peak of the UPE1M-C, leading to exfoliation. This result may be ascribed to the homogeneous dispersion of the clays, which does not present any more ordering, or a too large spacing between the layers in the case of exfoliated structure.<sup>1</sup> On the other hand, XRD curves of UPE2M-C and UPE3M-C nanocomposites exhibited a peak with a *d*-spacing value of 37.41 Å and 36.48 Å (Table I) in the relevant angle region representing the diffraction from the (001) crystal surface of the silicate layers as an indication of intercalated nanocomposite structure. This may result from some amount of multilayer tactoids of CocoMMT clay and polymer chains. Moreover, the relatively smaller and broader nature of these peaks could be accepted as proof of the existence of a partially exfoliated or intercalated structure.<sup>1</sup>

The nanoscale dispersion was also easily observed in TEM images. The dark lines seen in TEM images (Figure 5) represent individual silicate layers. As it can be seen from the images, all the nanocomposites have some irregular dispersions of the silicate layers. Some particles of the silicate layers were fully exfoliated as single platelets of CocoMMT clay (white circles) with an average thickness of 1 nm and orientation in different directions, while some kept an ordering of the expanded multilayers. As shown in Figure 5(a), Exfoliation is quite clear for UPE1M-C nanocomposite and the nanosized clays are separated from each other in a broad range of separation (30–115 Å). Even though the UPE1M-C nanocomposite showed no peak in its XRD pattern [Figure 4(a)], the TEM analysis shows a partially exfoliated structure with relatively more exfoliated silicate layers in comparison with other nanocomposites.

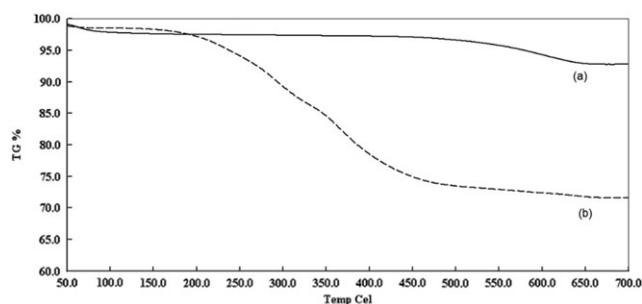
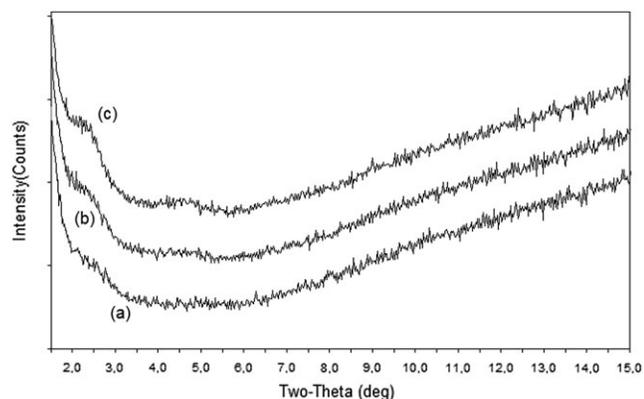


Figure 3. TGA thermograms of (a) NaMMT and (b) CocoMMT clays.



**Figure 4.** X-ray diffraction curves of (a) UPE1M-C, (b) UPE2M-C and (c) UPE3M-C nanocomposites.

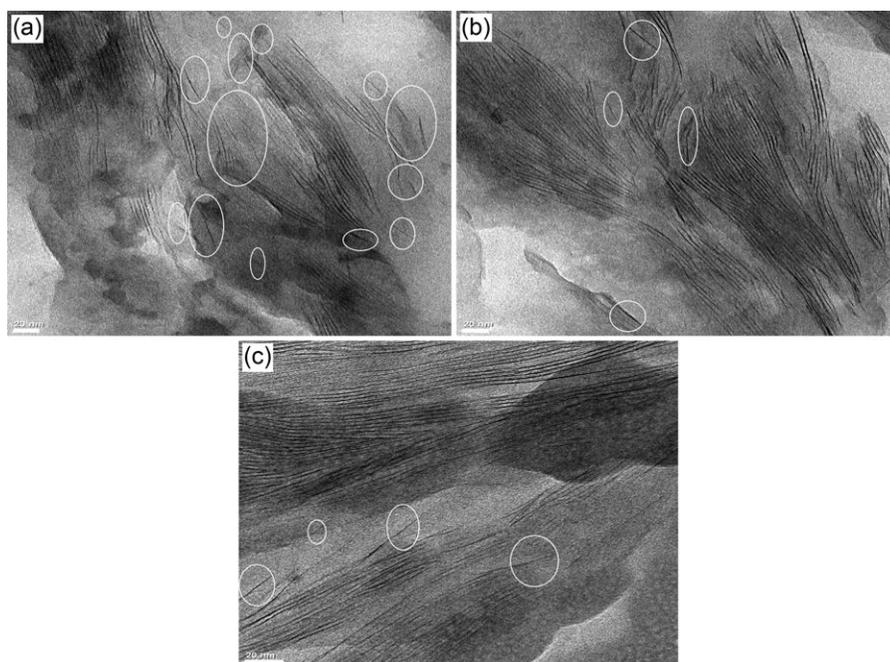
For the nanocomposites UPE2M-C and UPE3M-C, existence of multilayer “tactoids” of CocoMMT organophilic clay layers and polymer chains [Figure 5(b,c)] can be attributed to characteristic morphology of the intercalated and laminated silicate layers in UPE matrix. Moreover, in these figures exfoliated CocoMMT silicate layers (white circles) as single platelets with a thickness of of 1 nm can also be seen. For these nanocomposites, the separation between the dispersed platelets is also irregular and in the broad range of 38–112 Å and 39–82 Å, respectively which is in good agreement with their XRD results [Figure 4(b,c)]. Based on this information, one can postulate that UPE2M-C and UPE3M-C may also have a partially exfoliated/intercalated structure.<sup>1</sup>

Disappearance of XRD peak and presence of relatively high amount of exfoliated layered silicates in UPE1M-C [Figure 5(a)]

may be explained by presence of relatively less or optimum amount of styrene monomer with UPE chains inside the clay galleries in 1% clay loading. This may result in a more homogeneous crosslinking reaction inside and outside of the silicate layers. However, as clay loading increases, relative to UPE molecules, the probability of penetration of high amount of smaller styrene molecules into the clay galleries increases because the styrene monomers diffuse into the gallery of the organophilic MMTs much faster than the UPE chains.<sup>6</sup> Thus, relatively less amount of much bigger UPE molecules is found between clay layers and may lead to insufficient exfoliation in UPE2M-C and UPE3M-C.

The thermal stabilities of neat UPE and the nanocomposites were studied by thermogravimetric analysis (TGA) and shown in Figures 6 and 7. The onset degradation temperature at which 5% degradation occurs ( $T_{d5}$ ), representative of the onset temperature of degradation and the mid-point degradation temperatures ( $T_{d50}$ ) were all given in Table II.

As it can be seen from the TGA trace (Figure 6), although the differences in thermograms seem to be small, the UPE2M-C and UPE3M-C degrade at a slightly faster rate in the temperature range of 200–380°C compared with pure polymer and thereafter the situation reverses. For these nanocomposites, the weight loss in the above-mentioned temperature range most probably results from degradation of intercalant as well as water on clay surface and that between silicate layers. These nanocomposites display retardation of the thermal degradation above 380°C. On the other hand, it is clear from the figure and Table II, the onset temperature of degradation was found to increase by 13°C for the UPE1M-C nanocomposite whereas much lower values were observed for other nanocomposites compared with neat UPE. The mid-point degradation temperatures ( $T_{d50}$ ) of



**Figure 5.** TEM micrographs of (a) UPE1M-C, (b) UPE2M-C and (c) UPE3M-C nanocomposites (scale bar: 20 nm).

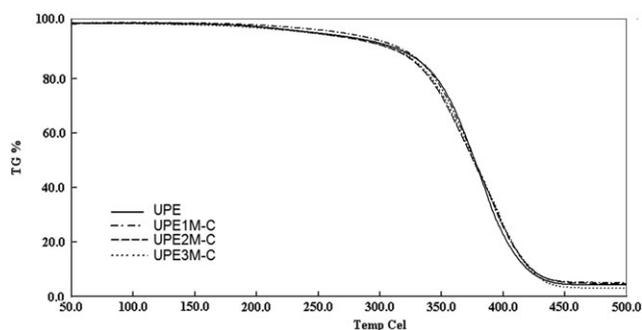


Figure 6. TGA thermograms of neat UPE matrix and its nanocomposites.

the nanocomposites were found to be very close to that of neat UPE (Table II).

The peak maximum temperature values from the first derivative (DTG) of weight loss (Figure 7), which is representative of the temperature at which maximum rate of weight loss occurs, were given in Table II. Although, the maximum temperatures of the derivative curves of the nanocomposites seems to be unchanged, all the nanocomposites exhibited a much slower degradation rate and relatively broad peak at their maximum weight loss temperature compared to neat UPE. This result may be attributed to the promotion of polymerization from inside the clay galleries and also from surface/edges of the clay with the help of reactive double bonds present in the intercalant bonded to the clay which leads to decrease in degradation rate of the polymer around clay surface.

The rate of decomposition at the maximum weight loss temperature was found to be the lowest for the UPE2M-C nanocomposite compared with neat UPE and other nanocomposites. The decrease in degradation rate of UPE2M-C and also in UPE3M-C, on the other hand, may be ascribed to a decrease in permeability or diffusivity of volatile degradation products because of more compact silicate matrix in multilayered intercalated systems [Figures 4(b,c) and 5(b,c)]. In other words, it may cause hindered out-diffusion of the volatile decomposition products or at least a slower escape from interlayer galleries.<sup>16</sup>

Although the nanocomposites, UPE2M-C and UPE3M-C seem to have relatively lower degradation rates for maximum weight loss, they were found to lose 5% of their weight losses at a much earlier temperatures compared to UPE1M-C (Table II). Therefore, it can be safely stated that UPE1M-C nanocomposite has the highest thermal stability relative to the neat UPE and other

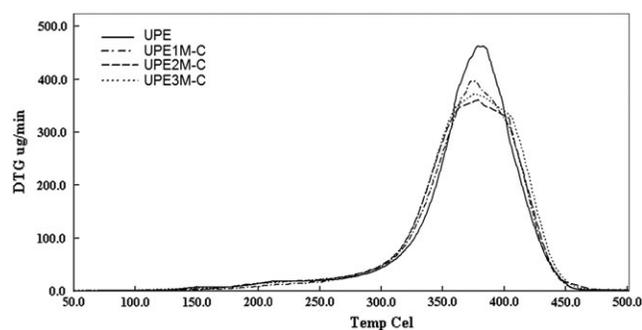


Figure 7. TGA derivative thermograms of neat UPE matrix and its nanocomposites.

nanocomposites. This enhanced thermal stability may be ascribed to presence of relatively high amount of exfoliated CocoMMT layers in UPE1M-C. This exfoliation dominant nature [Figure 5(a)] may lead to a “maximized” interaction between the clay and the polymer matrix because of a larger surface area of the clay interacting with the polymer, so leading to restricted molecular mobility of the polymer chains and resulting in inhibition of the diffusion of the decomposition products in the polymer matrix.<sup>17</sup>

The dynamic mechanical performances of UPE and its nanocomposites were investigated by DMA. Two different parameters were determined as a function of temperature. The tan delta versus temperature and storage modulus ( $E'$ ) versus temperature plots are all shown in Figures 8 and 9, respectively. The glass-transition temperature ( $T_g$ ) was taken as the maximum tan delta peak point which was calculated from the  $E''$  (loss modulus)/ $E'$  (storage modulus) ratio.<sup>16–18</sup> Compared with neat UPE, all the nanocomposites were found to have higher tan delta peak temperatures or  $T_g$  values. This may be probably due to the contribution of reactive styryl part of the modifier in the polymerization<sup>15</sup> leading to a strong interaction between clay layers and polymer matrix. The nanocomposite UPE1M-C displays the highest increase in the the tan  $\delta$  peak temperature, which is also in good agreement with the highest increase in the storage modulus (Figure 9). This may be ascribed to its exfoliation morphology [Figures 4(a) and 5(a)] leading to a large surface area of the clay interacting with the polymer which prevents the segmental motions of the polymer chains near organic–inorganic interfaces.<sup>19,20</sup>

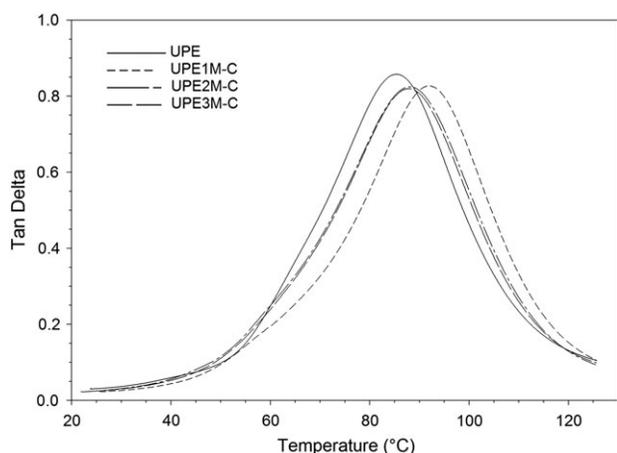
The storage moduli at 65 and 80°C were determined and reported in Table III. In DMA studies, it is well known that

Table II. TGA Data for Neat UPE and UPE Nanocomposites

Materials	$T_{d5}$ (°C) <sup>a</sup>	$T_{d50}$ (°C) <sup>a</sup>	Maximum rate of weight loss <sup>b</sup> ( $\mu\text{g min}^{-1}$ at °C)
Neat UPE	277.30 (2.08)	376.90 (3.43)	463.18 (3.46) at 380.00 (2.24) °C
UPE1M-C	290.30 (1.93)	377.00 (2.01)	397.42 (2.25) at 376.30 (3.58) °C
UPE2M-C	273.70 (2.46)	375.70 (0.92)	362.18 (2.62) at 377.40 (1.72) °C
UPE3M-C	273.00 (1.26)	376.40 (1.70)	386.51 (1.29) at 375.90 (1.13) °C

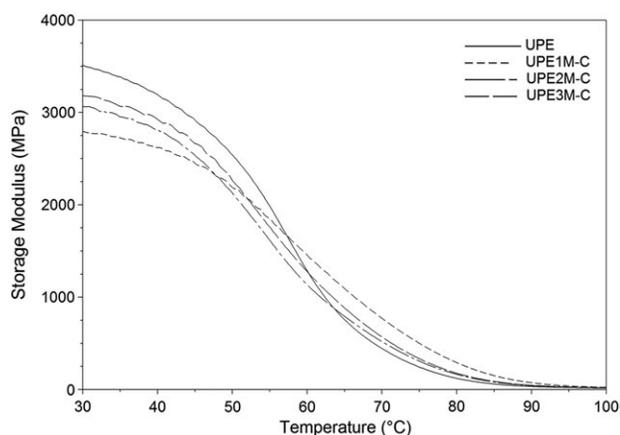
<sup>a</sup>Calculated from weight loss versus temperature curve of TGA thermogram.

<sup>b</sup>Calculated from derivative thermograms. Data in parentheses represent standard deviations



**Figure 8.** Tan  $\delta$  versus temperature plots of neat UPE matrix and its nanocomposites.

whether in static or dynamic tests, the modulus change under  $T_g$  is not very clear and sensitive because of the highly restricted motion of the chains with very low energies. In Figure 9, as a much more meaningful comparison, the moduli of all the nanocomposites around  $T_g$  (65°C) and above  $T_g$  (80°C), were observed to be higher than that of the neat UPE (Table III) which is consistent with lower the maximum tan delta peak values (Figure 8). About 44% increase in storage modulus around  $T_g$  was achieved as a result of incorporation of 1 wt % of CocoMMT clay into the UPE matrix. Moreover, the rubbery plateau modulus at 80°C of the nanocomposite UPE1M-C is about 2.5 times higher than that of neat UPE. This is a strong advantage of nanocomposite material that it is able to retain a high modulus even at temperatures above the glass transition temperature ( $T_g$ ). This behavior can be attributed to the extraordinarily large aspect ratio of exfoliated silicate layers with good dispersion of organoclay particles in the polymer matrix. This increases the polymer–clay interactions, making the entire surface area available for the polymer and leading to dramatic changes in mechanical properties. Above 2 wt % loading of CocoMMT,  $T_g$ , and storage modulus values were found to be



**Figure 9.** Storage modulus versus temperature plots of neat UPE matrix and its nanocomposites.

**Table III.** DMA Data for Neat UPE and UPE Nanocomposites

Material	$E'$ at 65°C (MPa)	$E'$ at 80°C (MPa)
UPE	757.10 (5.68)	121.00 (4.12)
UPE1M-C	1093.00 (12.63)	291.10 (5.88)
UPE2M-C	792.80 (6.37)	164.00 (1.99)
UPE3M-C	883.90 (3.72)	176.30 (3.55)

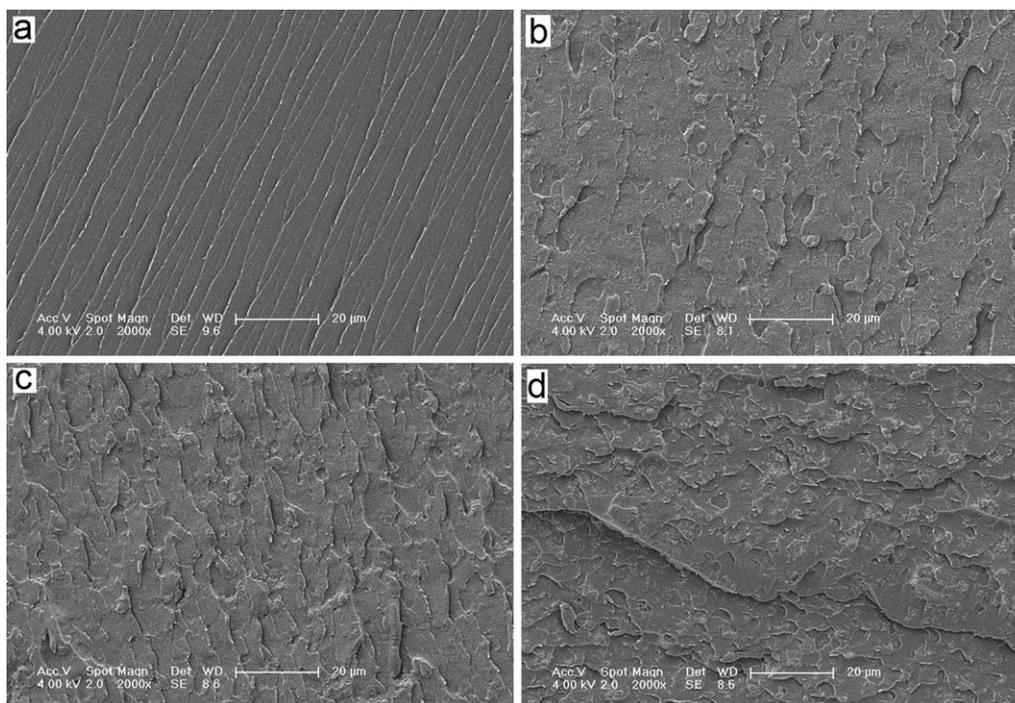
Data in parentheses represent standard deviations.

lower compared to UPE1M-C but still higher than those of neat UPE. This may probably be due to presence of relatively more styrene monomer between silicate layers which cause unreacted UPE chains outside the clay layers and heterogeneous crosslinking density as well as intercalated nanocomposite structure confirmed by XRD and TEM analyses (Figures 4 and 5). As a result, the highest increase in tan  $\delta$  peak temperature and in storage modulus is observed for the UPE1M-C nanocomposite. This indicates that 1 wt % clay loading is more effective in strengthening polymer matrix than 2 and 3 wt % loading degree.

Crosslinking density of the samples was evaluated based on the theory of rubber elasticity<sup>6,21</sup> in which the number-average molecular weight between crosslinks ( $M_c$ ) is correlated with the rubber plateau modulus<sup>22</sup> and inversely related to each other. According to this theory, it is also well known that crosslink density ( $\nu_c$ ) is proportional to the rubber plateau modulus since  $\nu_c$  is inversely proportional to  $M_c$ . It can be stated that the all the UPE nanocomposites prepared at room temperature have higher crosslinking density than neat UPE due to their increased rubber plateau moduli values (Table III). This result may be ascribed to the presence of reactive intercalant in the clay galleries and at edge/surface of the clay participating in the polymerization reaction<sup>15</sup> which may lead to an increased crosslinking density. The reason for the highest rubber plateau modulus value and crosslinking density of UPE1M-C in comparison with other nanocomposites may be due to relatively much more homogeneous dispersion of styrene monomers and thereby homogeneous crosslinking reaction of UPE chains inside and outside of the silicate layers at 1 wt% loading.<sup>6</sup>

In case of UPE2M-C and UPE3M-C nanocomposites, a probable decrease in mechanical and thermal properties may be expected due to high amount of styrene inside the clay layers and thus inhomogeneous crosslinking reaction of UPE. This disadvantage, however, may be compensated by contribution of the modifier in the crosslinking reaction of UPE through its reactive styryl double bond which can be accepted as an indication of significant effect of the reactive intercalant on the properties of the resultant nanocomposites.

Fracture surfaces of UPE and its nanocomposites were investigated by SEM analyses (Figure 10). Figure 10(a) shows the pure UPE with a brittle fracture surface having large cracks, which is a typical of glassy material. The images of the UPE nanocomposites [Figure 10(b–d)], on the other hand, show a fracture surface with a crack propagation along a more tortuous path and



**Figure 10.** SEM micrographs of the fracture surfaces of (a) neat UPE, (b) UPE1M-C (c) UPE2M-C, and (d) UPE3M-C nanocomposites.

with much smaller-sized cracks. It may be caused by the presence of organoclay layers as reinforcing phase and their good dispersion in the matrix.<sup>13</sup> This result is highly consistent with higher dynamic  $T_g$  and stiffness values for the nanocomposites compared to neat UPE matrix (Figures 8 and 9).

## CONCLUSIONS

Unsaturated polyester-montmorillonite nanocomposites were successfully prepared by *in situ* free radical crosslinking polymerization of UPE in the presence of styrene monomer. Organically and functionally modified montmorillonite clay was used as nanosized reinforcer in different loading degrees. All the nanocomposites showed a partially exfoliated structure and the UPE1M-C nanocomposite was found to have relatively higher degree of delamination of more silicate layers as thin platelets in the matrix. It was also found to have the highest thermal stability and better dynamic mechanical properties. This result is most probably due to more homogeneous dispersion and optimum amount of styrene monomer molecules inside and outside the MMT layers, even with a clay content as low as 1 wt %. Also, the improvements in both thermal and mechanical properties for all the nanocomposites were ascribed to the polymerization reaction occurring in between silicate layers and from the edge/surface of the modified clay through the intercalated and edge/surface attached reactive intercalant. The rubbery plateau modulus and crosslinking density of UPE1M-C nanocomposite having an exfoliation dominant morphology showed the maximum values % loading. SEM images of the nanocomposites indicated that presence of CocoMMT clay with a homogeneous and nanosized dispersion in the polymer matrix, led to crack propagation along a more “rougher” path compared with

brittle neat UPE. As a result it can be safely concluded that partially exfoliated UPE nanocomposites with different degrees of exfoliation can be prepared as thermally stable and high strength materials by using a functionally and organically modified clay in 1–3 wt % clay loadings.

## ACKNOWLEDGMENTS

Supports given by Yalova University Scientific Research Projects Coordination Department (Projects no. 2012-042) are gratefully acknowledged.

## REFERENCES

- Alexandre, M.; Dubois, P. *Mater. Sci. Eng. R: Reports* **2000**, *28*, 1.
- Ray, S. S.; Okamoto, M. *Prog. Polym. Sci.* **2003**, *28*, 1539.
- Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. *Chem. Mater.* **1995**, *7*, 2144.
- Lee, D. C.; Jang, L. W. *J. Appl. Polym. Sci.* **1998**, *68*, 1997.
- Bharadwaj, R. K.; Mehrabi A. R.; Hamilton, C.; Trujillo, C.; Murga, M.; Fan, R.; Chavira, A.; Thompson, A. K. *Polymer* **2002**, *43*, 3699.
- Suh, D. J.; Lim, Y. T.; Park, O. O. *Polymer* **2000**, *41*, 8557.
- Kornmann, X.; Berglund, L. A.; Sterte, J. *Polym. Eng. Sci.* **1998**, *38*, 1351.
- Jo, B. W.; Park, S. K.; Kim, D. K. *Constr Build Mater.* **2008**, *22*, 14.
- Al-Khanbashi, A.; El-Gamal, M.; Moet, A. *J. Appl. Polym. Sci.* **2005**, *98*, 767.

10. Zhou, Y.; Yang, X.; Jia, D. M. *Polym. Int.* **2007**, *56*, 267.
11. Wang, Z.; Pinnavaia, T. J. *Chem. Mater.* **1998**, *10*, 1820.
12. Dean, K. M.; Bateman, S. A. Simons, R. *Polymer* **2007**, *48*, 2231.
13. Şen, S. *Polym. Compos.* **2010**, *31*, 482.
14. Memeş, M.; Mencilođlu, Y.; Nugay, T.; Nugay N. *Polym. Preprint. Am. Chem. Soc. Div. Polym. Chem.* **2004**, *45*, 806.
15. Helvaciođlu, E.; Aydin, V.; Nugay, T.; Nugay, N.; Uluocak, B. G. Şen, S. *J. Polym. Res.* **2011**, *18*, 2341.
16. Şen, S.; Nugay, N.; Nugay, T. *Polym. Int.* **2006**, *55*, 552.
17. Leszczynska, A.; Njuguna, J.; Pielichowski, K.; Banerjee, J. R. *Thermochim. Acta* **2007**, *453*, 75.
18. Kim, H. G.; Oh, D. H.; Lee, H. B.; Min, K. E. *J. Appl. Polym. Sci.* **2004**, *92*, 238.
19. Noh, M. W.; Lee, D. C. *Polym. Bull.* **1999**, *42*, 619.
20. Landry, C. J. T.; Coltrain, B. K.; Landry, M. R.; Fitzgerald, J. J.; Long, V. K. *Macromolecules* **1993**, *26*, 3702.
21. Ferry, J. D. *Viscoelastic Properties of Polymer*, 3rd ed., Wiley: New York, **1980**.
22. Vandersanden, M. C. M.; Meijer, H. E. H. *Polymer* **1993**, *34*, 5063.