

Vinylester Resin-Clay Hybrids Using Various Intercalating Agents

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ABSTRACT: Vinylester resin-clay hybrids were prepared by the mixing different types of organically-modified montmorillonite (OMMT) with vinylester resin (VER) prepolymer, followed by thermal polymerization. VER prepolymer was synthesized from the reaction of diglycidylether of bisphenol-A (DGEBA) with acrylic acid. Various types of organic ammonium salts have been used as intercalating agents for montmorillonite, including *N,N*-dimethyl-*N*-(4-vinylbenzyl)stearyl ammonium chloride (VSA), *N*-allyl-*N,N*-dimethyl-stearyl ammonium chloride (ASA) and *N,N*-dimethyl-stearyl ammonium chloride (SA). The dispersion of OMMT into VER matrix was studied by XRD, which indicates the dependence of the morphology

mainly on the OMMT content. UV-vis spectra of the hybrids were used to give a quantitative value of the effect of OMMT content on the transparency of VER/OMMT hybrid films. Also, the Vickers test has been performed to study the effect of OMMT content on the surface hardness of the hybrid films. In addition, the thermal properties of the hybrids have been characterized by measuring the softening points and thermogravimetric analyses of the hybrids in comparison with the pure resin. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2060–2068, 2010

Key words: vinylester resin; montmorillonite; intercalating agent; nanocomposites; hardness; softening point

INTRODUCTION

Polymer nanocomposites are attractive, because they often show an improvement in mechanical, thermal, barrier, and optical properties, as well as fire retardancy.^{1,2} The use of layered silicate clays as precursors to prepare organic-inorganic nanocomposites has been extensively studied with various types of polymers.^{3,4} The most commonly used clay type for preparation of nanocomposites is montmorillonite (MMT), which is an aluminosilicate mineral. The lattice structure of MMT consists of layers organized in stacks with periodic interlayers space. The thickness of each layer is ~ 0.96 nm. The interlayer, referred to as gallery, is normally 0.3–0.5-nm thick. Because of the hydrophilic nature of MMT, the diffusion of nonpolar polymer into the clay galleries is not possible. The best approach to increase the compatibility of MMT with nonpolar polymers is surface modification of MMT to produce a hydrophobic environment within the galleries of the organically modified

MMT. This modification process is achieved by an ion-exchange reaction of the inter-gallery inorganic cations with long chain organic cations to make the interlayer galleries hydrophobic in nature. Most clay modifications have been carried out by using organic ammonium salts. In addition, the organic ammonium cations can provide functional groups that react with the monomer or polymer to improve the interfacial strength between organoclay as a reinforcing agent and polymer matrix.^{5,6}

Polymer-clay nanocomposites can be prepared by the dispersion of organically modified MMT (OMMT) into the monomers or prepolymers with or without the presence of solvent followed by polymerization. A variety of polymer clay nanocomposites have been synthesized and studied using thermoplastic, thermoset and elastomeric polymers. Some examples of thermoplastic polymers include nylon 6^{7,8} and styrene.⁹ Examples of thermosets are epoxy,^{10–13} benzoxazine resin¹⁴ and phenolic resin,¹⁵ and for elastomers are amine-terminated butadiene nitrile (ATBN),¹⁶ silicon rubber,¹⁷ and polyurethane.¹⁸

Vinylester resin (VER) attracted much attention due to its easy of preparation and attractive properties.¹⁹ The nature of VER backbone structure offers toughness and flexibility to the cured resin as well as chemical resistance.²⁰ Also, the presence of secondary hydroxyl groups impairs polarity which improves its adhesion and wetting properties.

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Furthermore, it has an excellent reactivity due to the terminal vinyl groups which can be homopolymerized or copolymerized with other vinyl monomers or prepolymers.^{21,22} Thus, VER is widely used as a matrix for fiber reinforced plastics (FRP) applications in which unsaturated polyester resins are less suitable due to low strength, moderate environmental resistance and low glass transition temperature (T_g).²³ There are a few studies reported for VER-clay nanocomposites.^{24–26} The objective of the current study is to investigate the influence of various types of organoclay on the morphology, thermal and mechanical properties of VER nanocomposites.

EXPERIMENTAL

Materials

Sodium montmorillonite (MMT) with cation exchange capacity (CEC) of ca. 119 mEq/100 g was supplied from Kunimine Industry, Japan, under trade name Kunipia-F. Diglycidyl ether Bisphenol-A (DGEBA) was kindly received from Dow Chemical, Japan and dried under vacuum before use. Acrylic acid was purchased from Aldrich and dried under vacuum at 100°C before use. Vinylbenzyl chloride was obtained from Aldrich and used without further purification. Dimethylstearyl amine, hydroquinone, imidazole, diethyl ether, benzoyl peroxide, and ethanol were purchased from Kishida, Japan and used as received. Allyl bromide, dioxane and tetrahydrofuran (THF) were used as received from Tokyo Kasei.

Preparation of 2,2-di[4-(3-acryloyloxy-2-hydroxy-n-propoxy)phenyl]propane (VER prepolymer)

VER prepolymer was prepared according to the reported methods.^{27,28} DGEBA (100 g, 266 mmol) was charged into a 500 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser. To this flask, acrylic acid (38.30 g, 532 mmol), imidazole (0.45 g, 6.10 mmol) and hydroquinone (0.14 g, 1.64 mmol) were added. The mixture was stirred and gradually heated to 60, 70, 80, 90, 100, and 120°C at 1 h intervals. The amber-colored viscous resin was then cooled and stored at low temperature in a refrigerator until use.

Preparation of Organically-Modified Clays

Preparation of *N,N*-dimethyl-stearyl ammonium modified clay (SA-MMT)

Into a 1-L beaker, conc. HCl (0.045 g, 1.19 mmol) was added to *N,N*-dimethylstearyl amine (0.353 g, 1.19 mmol) suspended in 200 mL of distilled water. The mixture was heated with stirring at 80°C until a

clear solution was obtained. To this solution of *N,N*-dimethyl-stearyl ammonium chloride (SA), a homogeneous suspension of 10 g of MMT in 200 mL distilled water was added under mechanical stirring at 80°C. The stirring was continued for 10 h, followed by filtration of the precipitated organoclay. The organoclay was suspended in hot distilled water and stirred mechanically for 1 h followed by filtration. This process was repeated until no white precipitate of AgCl was detected in the filtrate by addition of 0.1N AgNO₃. Finally, the precipitate was washed once by ethanol, followed by drying under vacuum at 80°C for 2 days. The powder was sieved to get particles less than 63 μm.

Preparation of *N,N*-dimethyl-*N*-(4-vinylbenzyl)-stearyl ammonium modified clay

N,N-dimethyl-*N*-(4-vinylbenzyl)stearyl ammonium modified clay (VSA-MMT) was prepared by adding a solution of freshly prepared VSA (11.7 g, 26 mmol) to the clay suspension (20 g, 23 mmol) according to the reported method.⁹

Preparation of *N*-allyl-*N,N*-dimethylstearyl ammonium modified clay

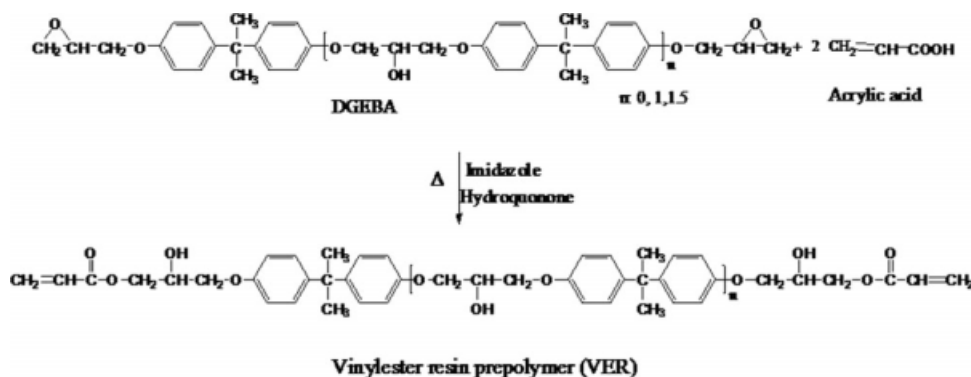
N-allyl-*N,N*-dimethylstearyl ammonium modified clay (ASA-MMT) was prepared following the reported method²⁹ by the addition of a suspension of 10 g Na-MMT to a salt solution of *N,N*-dimethylstearyl amine (3.86 g, 13 mmol) and allyl bromide (1.57 g, 13 mmol).

Preparation of VER/clay hybrids

Nanocomposites were prepared by mixing of VER with various ratios of different organoclays. The typical adopted method for hybrid preparation is as follows: 0.03 g of MMT was added to 2.97 g of VER prepolymer dissolved in 4 mL dioxane, followed by stirring overnight. Benzoyl peroxide was added as an initiator followed by stirring for 30 min. The mixture was cast over pretreated glass plate followed by drying at 60°C for 5 h to remove the solvent. The hybrid film as fixed on glass plate was cured at 80°C, 100°C, 120°C and finally at 160°C for 2 h each to give transparent film of VER/3% OMMT. Similarly, VER-clay hybrids with different OMMT loading were also prepared.

Measurements

Infrared spectra (IR) were recorded on a JASCO spectrophotometer model FT/IR-420, by casting a thin film of hybrid on KBr disk. Proton nuclear magnetic resonance (¹H-NMR) spectra were measured



Scheme 1 Preparation of vinyl ester resin (VER)-clay prepolymer.

on a Varian Mercury 300 (300 MHz) instrument. Thermogravimetric analysis (TGA) was done with Rigaku Thermo Plus 2 TG-DTA TG8120 under air at a heating rate of 5°C/min and under argon at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was conducted using a Rigaku Plus 2 DSC8230 at a heating rate of 10°C/min under nitrogen. XRD was measured using X-ray diffractometer, Rigaku, RINT2000 using CuK α radiation (30 kV, 20 mA). The experiments were performed in a 2 θ range of 2–10° with scan rate of 0.3°/min and scan step of 0.01°. The Vickers hardness was measured using a AKASHI AVK-A machine. UV-vis absorption spectra were measured using Shimadzu UV-2101 PC spectrophotometer for films with thickness about 0.3 mm for all hybrid films. Softening points of hybrids were measured by the penetration method under a constant indentation load for rising temperature scanning with heating rate of 10°C/min. The penetration depth as a function of temperature was continuously detected by an electro-optical extensometer (Model 200X, Zimmer) with a precision of 0.5 μm via monitoring the gap made by a pair of silicon nitride tabs mounted at sample stage and indenter.

RESULTS AND DISCUSSION

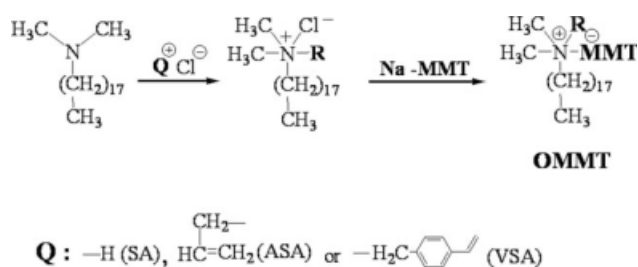
Preparation of VER/clay hybrids

VER prepolymer was prepared from the reaction of acrylic acid and DGEBA using imidazole as a catalyst and hydroquinone as an inhibitor, Scheme 1. The formation of VER was followed by IR spectra as shown in Figure 1. The disappearance of absorption at 917 cm^{-1} due to the epoxide group and the presence of the absorption bands at 830 cm^{-1} and 1635 cm^{-1} corresponding to the vinyl group ($\text{CH}_2=\text{CH}-$) indicates the formation of VER.^{27,30} Further confirmation of VER prepolymer structure was performed by $^1\text{H-NMR}$, Figure 2. The characteristic peaks assigned to hydroxyl group ($-\text{OH}$) at 5.8 ppm and double bond ($\text{CH}_2=\text{CH}-$) at 6.2–6.4 ppm were observed, confirming the structure of VER.³¹

The use of reactive intercalating agent for clay modification is known to play an important role in promoting the compatibility between organoclay and the polymer matrix.^{32,33} In this study, three different kinds of intercalating agents were used, two of them contain reactive sites toward the reaction with VER as shown in Scheme 2. The intercalating agents for clay are *N,N*-dimethyl-*N*-(4-vinylbenzyl)-stearyl ammonium chloride (VSA), *N*-allyl-*N,N*-dimethyl-stearyl-ammonium chloride (ASA), and *N,N*-dimethyl-stearyl ammonium chloride (SA). The produced OMMTs were named VSA-MMT, ASA-MMT, and SA-MMT, respectively.

XRD is frequently used to monitor the change in the gallery spacing of clay after modification. XRD patterns of MMT and the various OMMT derivatives (Fig. 3) show that the typical diffraction peak due to *d*-spacing of MMT is shifted to lower Bragg angles by modification with organic cations, suggesting the increase of interlayer spacing. The original *d*-spacing of MMT (1.28 nm) increased to 1.97, 2.22, and 2.34 nm for SA-MMT, ASA-MMT, and VSA-MMT, respectively, due to the replacement of smaller Na^+ ions by large size organic cations. The *d*-spacing of clay derivatives increased in the following order; MMT < SA-MMT < ASA-MMT < VSA-MMT. This order suggests that the intercalating agent of a bulky aromatic ring led to organoclay having a higher interlayer spacing.

The amount of intercalating agent grafted onto clay layers was investigated by TGA under air



Scheme 2 Preparation of organoclays (OMMTs).

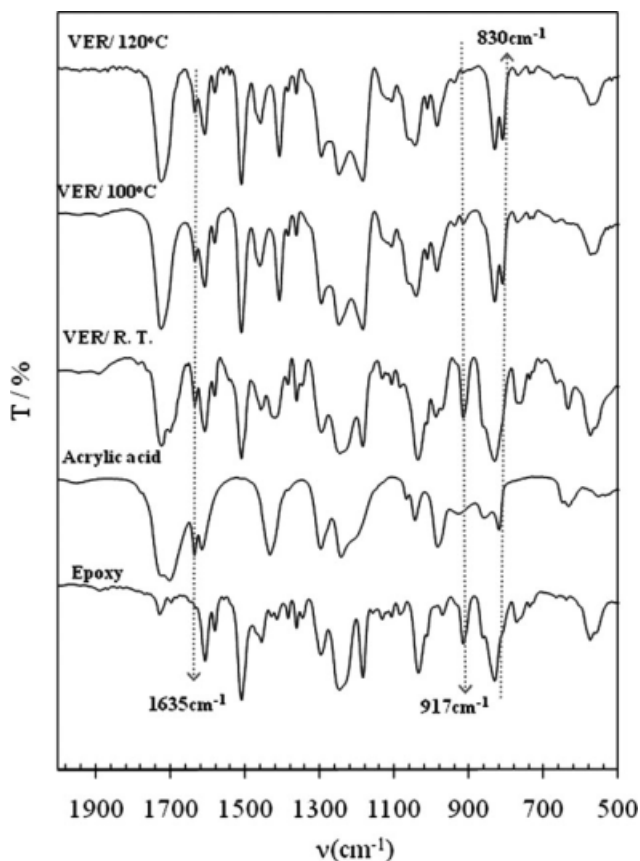


Figure 1 IR Spectra of epoxy and acrylic acid reaction at different temperature.

atmosphere for OMMT derivatives. The unmodified MMT lost 5% of its initial weight while heating the material to 800°C. The slight weight loss between 400°C and 700°C corresponds to the loss of the water and the collapse of the crystallographic structure. In case of the organoclays, the weight loss due to degradation of the surfactant is observed at temperature range between 200°C and 700°C.³⁴ The weight loss for SA-MMT, ASA-MMT, and VSA-MMT determined from the TGA is 29, 32, and 28 wt %, respectively. Also, the amount of surfactant grafted onto clay layers was determined by elemental analysis and the data are summarized in Table I. The results of elemental analysis agree with the theoretical amount of clay modifier.

VER-clay nanocomposites were prepared by blending VER with organoclays using dioxane as a solvent to assist the dispersion of organoclay into VER due to the high viscosity of VER. Dioxane was preferred as a solvent because the dispersion of neat organoclays in dioxane gives a stable suspension without any precipitation. Other solvents such as dimethylformamide, dimethylacetamide and dimethylsulfoxide are also good candidates for organoclay dispersion in VER. However, they were not chosen because of their high boiling points, which

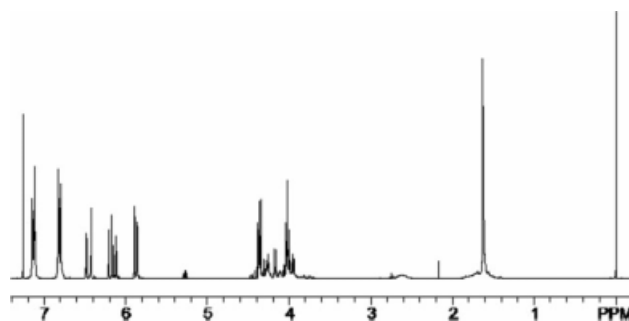


Figure 2 NMR Spectra of VER prepolymer.

may lead to residual solvent in the hybrids. The thermal polymerization of VER in presence of organoclay was studied by DSC. The nonisothermal polymerization thermograms are shown in Figure 4. For neat VER an exotherm was observed with onset at ca.75°C and maximum at 116°C due to free radical polymerization of olefinic group. The onset of the exothermic peak due to polymerization of VER slightly shifted to higher temperature with the inclusion of VSA-MMT. This shift is attributed to the restriction of VER mobility by the dispersed organoclay into the matrix, leading to increase the cure temperature. VER/5% VSA-MMT blend as an example was studied by DSC after each polymerization temperature. As shown in Figure 3, the exothermic peak decreases gradually and disappeared by the

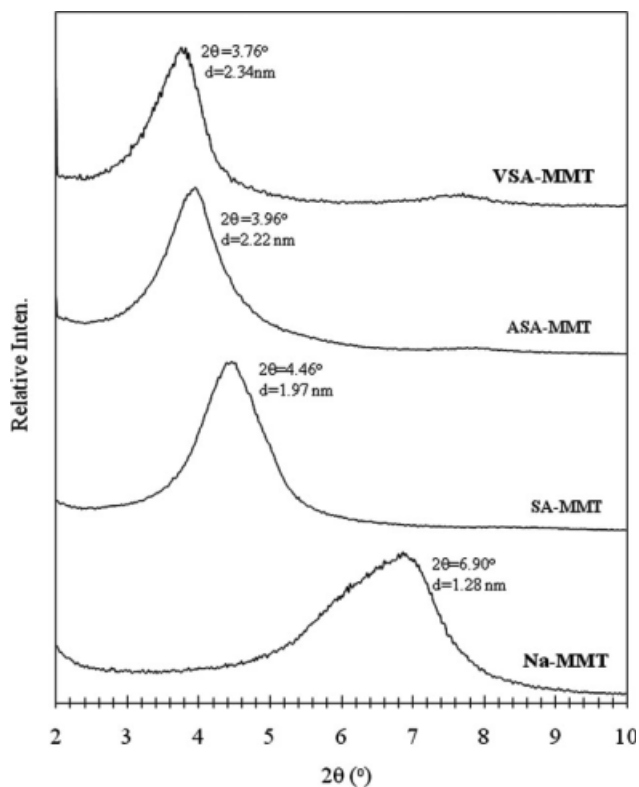


Figure 3 XRD of Na-MMT and OMMTs.

TABLE I
MMT and Modified OMMT

Code	Theoret. (Organic Part) (%) ^a	TGA under air		Elemental analysis						
		wt % (Inorganic Part) ^b	wt % (Organic Part) ^b	%C		%H		%N		% Organic Part ^c
				Calc.	Found	Calc.	Found	Calc.	Found	
SA-MMT	26.75	71	29	20.02	20.69	3.67	4.11	1.16	1.24	26.04
ASA-MMT	29.35	68	32	22.28	22.31	3.87	4.37	1.13	1.13	27.81
VSA-MMT	33.62	72	28	26.47	26.03	3.95	4.41	1.06	1.07	31.51

^a The amount of organoclay used in preparation of hybrid.

^b wt % at 800°C.

^c This obtained from elemental analysis.

end of the thermal treatment at 160°C, suggesting the complete polymerization of VER.

IR spectra shown in Figure 5 for VER/10% VSA-MMT were also measured after each thermal treatment stage. IR spectra indicate a significant decrease of the characteristic absorption band due to C=C at 1639 cm⁻¹ after 160°C. In addition, the band at 1040 cm⁻¹ is due to Si—O of silicates framework of clay. Thus, both DSC and IR spectra indicate that the polymerization of VER effectively completed by the end of 160°C treatment cycle.

Morphology study of VER/OMMT hybrids

XRD is highly sensitive to the degree of order within the silicate layer stacks in the polymeric matrix. Generally, the change in the *d*-spacing or nonparallel ori-

entation of layers due to the collapse of the clay leads to broadening, weakening or disappearance of the XRD maxima. Figure 6 shows XRD patterns of the VER/VSA-MMT hybrids. At lower VSA-MMT content (1–3%), the XRD pattern is featureless with the absence of any diffraction peaks corresponding to VSA-MMT. This suggests that the possibility of complete exfoliation or intercalation-exfoliation of VSA-MMT into VER matrix.³⁵ This is attributed firstly to the intercalation of VER into the interlayer clay gallery, leading to expansion of the interlayer spacing. This expansion allows an excessive amount of VER to penetrate into the interlayer spacing, leading to the collapse of clay lattice structure upon polymerization. At 5% of VSA-MMT loading, a small broad diffraction appeared at $\sim 2\theta = 4.52^\circ$

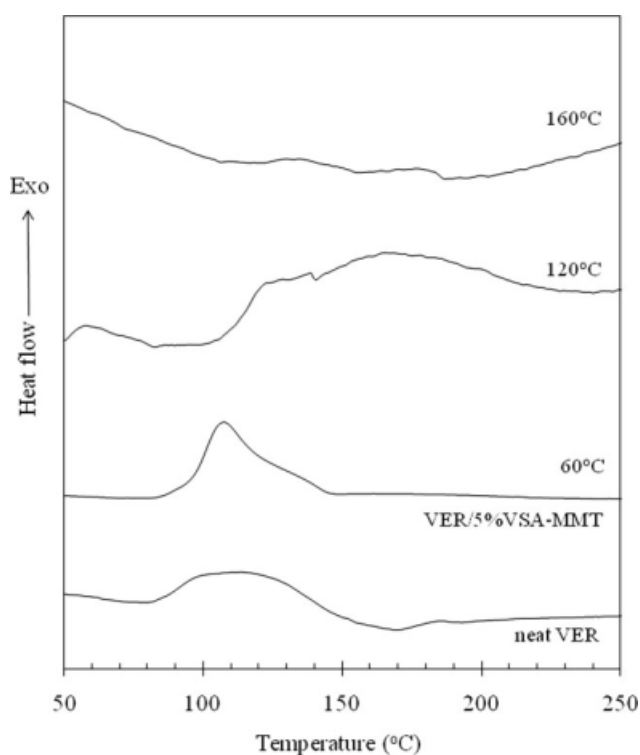


Figure 4 DSC of neat VER and VER/5% VSA-MMT after different polymerization temperatures.

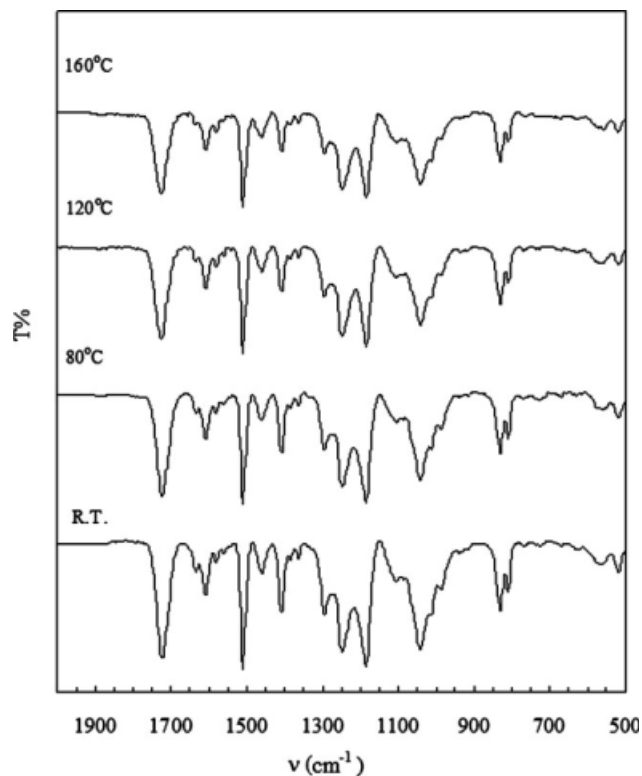


Figure 5 IR spectra of VER/10% VSA-MMT hybrid after different curing temperatures.

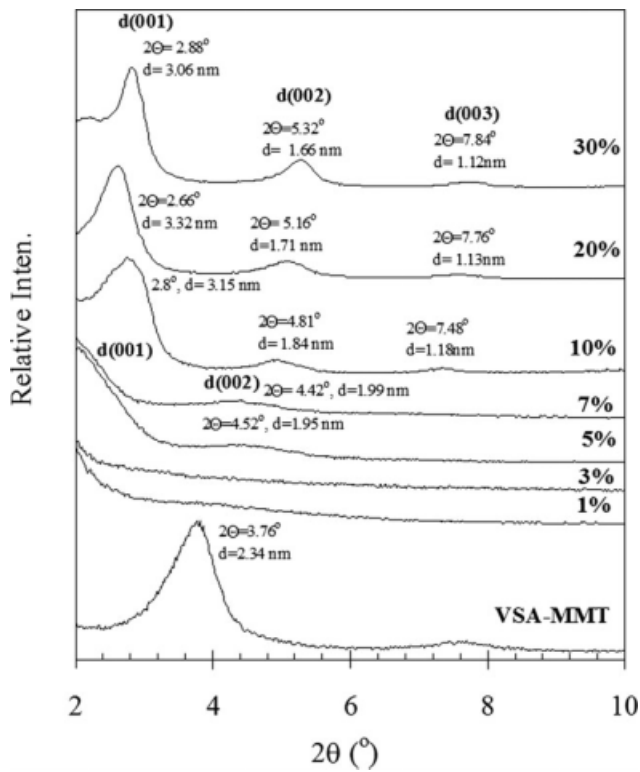


Figure 6 XRD of VER/VSA-MMT hybrids.

corresponding to a *d*-spacing of 1.9 nm. The intensity of this diffraction slightly increased with VSA-MMT content of 7%. This diffraction peak is likely

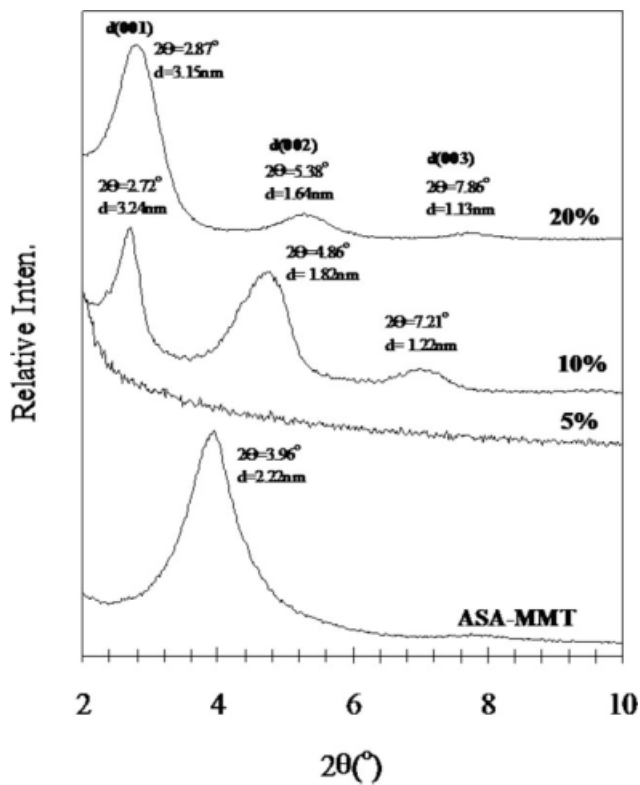


Figure 7 XRD of VER/ASA-MMT hybrids.

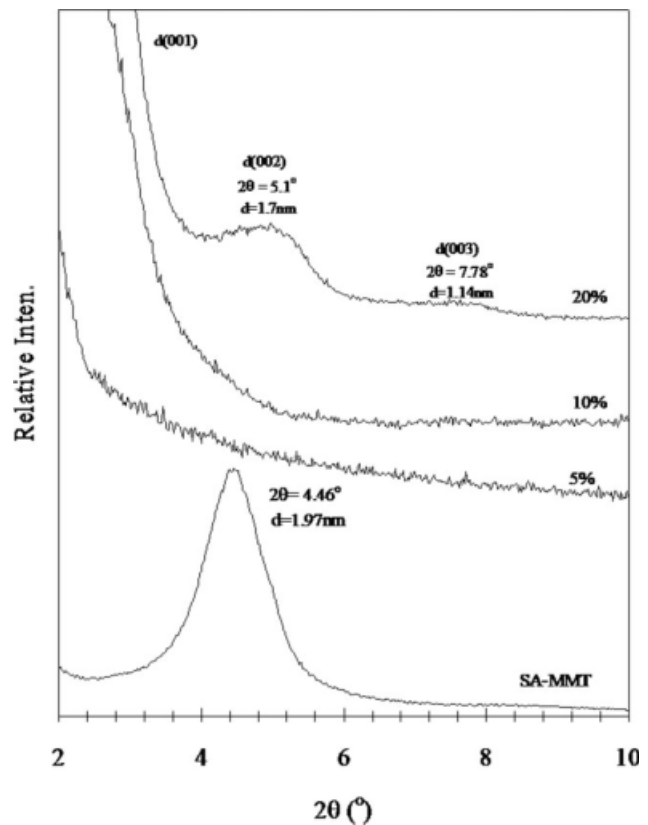


Figure 8 XRD of VER/SA-MMT hybrids.

to be due to a higher order from *d*(002) plane.³⁶ At higher VSA-MMT content (10, 20, and 30 wt %), three diffraction peaks were observed which are attributed to *d*(001), *d*(002), and *d*(003), suggesting

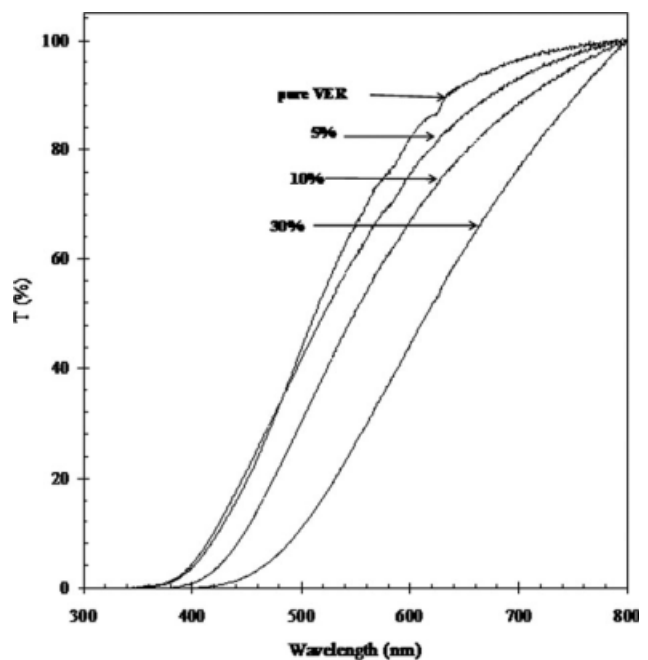


Figure 9 UV Study of VER and VER/VSA-MMT hybrids with different ratios of VSA-MMT.

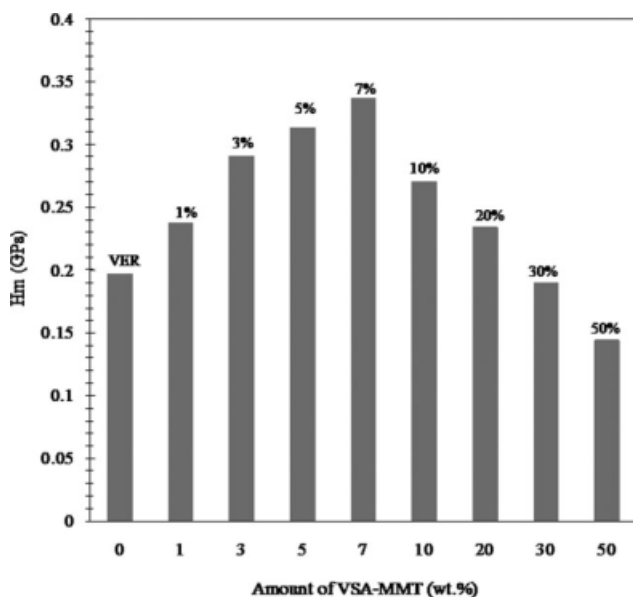


Figure 10 Microhardness of pure VER and VER/VSA-MMT hybrids with different ratios of VSA-MMT.

the formation of a well organized intercalated structures.

For VER/ASA-MMT hybrids, XRD patterns showed no peak up to 5 wt % loading, as shown in Figure 7. This indicates that the organoclay is exfoliated into VER forming exfoliated nanocomposites or a mixed morphology of intercalation-exfoliation is obtained. At 10 and 20% loading of ASA-MMT, $d(001)$, $d(002)$, and $d(003)$ reflections were observed that fit in respect to their position and intensity to that of VER/VSA-MMT hybrids. In case of VER/SA-MMT hybrids, however, reflections due to intercalated order structures were clearly observed at 20% SA-MMT as shown in Figure 8. These results of XRD demonstrate that the solution intercalation process for VER/OMMT hybrids exhibits intercalated morphology with well ordered structures as suggested by the presence of $d(001)$, $d(002)$, and $d(003)$ reflections.^{37,38}

The dispersion of the organoclays into VER matrix produced hybrids with different characteristic transparency. Generally, the transparency decreased with increase of the organoclay content due to the increase of the particle size of the organoclay. UV-vis spectra for the neat resin and the VER/VSA-MMT hybrids were measured to get a quantitative evidence for the effect of organoclay on the transparency of the hybrids. A thin film of neat VER has a very good optical transparency; its transmittance was 96% at 700 nm as shown in Figure 9. However, at 5, 20, and 30% of organoclays content, the transmittance is decreased to 93, 88, and 76% at 700 nm, respectively. This decrease in optical transmittance can be used as a criterion to indicate the increase of

organoclay particle size that leads to maximize the scattering of visible light and hence decreases the transparency.³⁹

Properties of VER/ clay hybrids

The hardness of the hybrids was carried out to evaluate the effect of the inclusion of the clay into VER matrix. The hardness of a hybrid film mostly depends on the crosslinking density of the respective polymer and the filler content.⁴⁰ As shown in Figure 10, the hardness of the neat VER was 0.190 GPa which increased to 0.237, 0.290, 0.313 and 0.337 GPa by the inclusion of 1%, 3, 5, and 7% of VSA-MMT, respectively. This could be attributed to two main factors; the first is the reinforcement effect of the homogeneously dispersed and fully exfoliated rigid clay layers into VER matrix.⁴¹ The second factor is the strong interfacial bonding between VER and clay layers through the double bond grafted on the clay.⁴² It was observed that the increase of the clay content more than 7 wt % has led to decrease the hardness of the hybrid materials. This may be attributed to decreasing the crosslinking density of the VER network structure and the aggregation of clay. The comparison of the hardness values of hybrids with different type of OMMT with the same loading (5 wt %), revealed that VSA-MMT (0.313 GPa) and ASA-MMT (0.236 GPa) have higher hardness values than SA-MMT (0.226 GPa), which may be attributed to the strong interfacial bonding between VER matrix and silicate layers through the common double bond polymerization in both organoclay and VER.

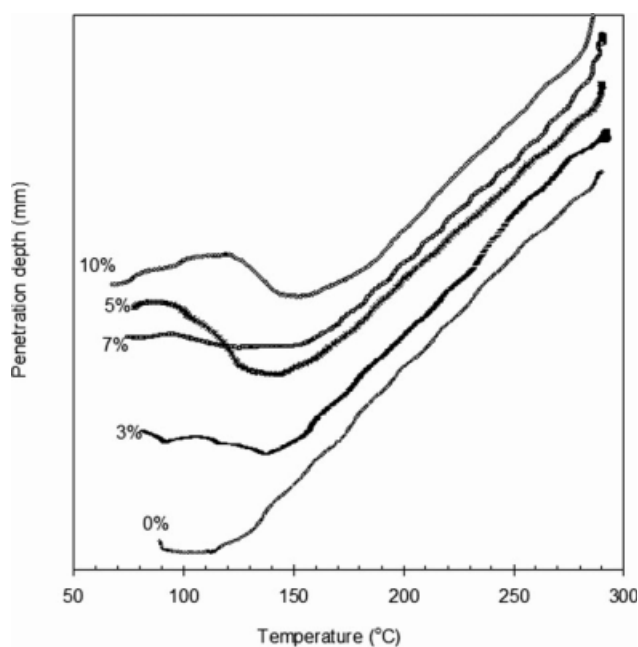


Figure 11 Softening points-temperature relationship of pure VER and VER/VSA-MMT hybrids.

TABLE II
Thermal Properties of VER-Clay Hybrids

Code	TGA under Air			TGA under Argon			Softening Temp. (°C)
	T_5 (°C)	T_{10} (°C)	Char yield (%)	T_5 (°C)	T_{10} (°C)	Char yield (%)	
VER	289	355	–	331	368	11	123
VER/ 1% VSA-MMT	–	–	–	352	374	14	–
VER/ 3% VSA-MMT	346	369	3	350	375	15	148
VER/ 5% VSA-MMT	350	376	4	350	375	19	154
VER/ 7% VSA-MMT	–	–	–	361	377	22	161
VER/ 10% VSA-MMT	352	379	9	340	372	26	144
VER/ 20% VSA-MMT	–	–	–	335	358	30	–
VER/ 30% VSA-MMT	332	362	21	334	357	34	–
VER/ 50% VSA-MMT	–	–	–	314	342	44	–
VER/ 10% SA-MMT	348	374	7	–	–	–	–
VER/ 20% SA-MMT	329	357	15	–	–	–	–
VER/ 10% ASA-MMT	333	366	10	–	–	–	–
VER/ 20% ASA-MMT	329	359	15	–	–	–	–

The softening temperatures of the hybrids were examined to estimate the glass transition temperatures (T_g) of the VER with different VSA-MMT content.⁴³ Figure 11 shows the effect of the clay content on the softening temperature of the VER/VSA-MMT hybrids. Generally, the softening points increased by increasing the clay contents: 123, 148, 154, and 161°C at clay content of 0, 3, 5, and 7 wt %, respectively (Table II). This increase in softening temperature is attributed to the maximized adhesion between the VER and OMMT layers due to the nanometer size of the dispersed organoclay. The rigid clay nanolayers restrict the VER segmental motion near the organic-inorganic interface which is a typical effect of clay dispersed into a polymer system.¹⁴ By increasing the amount of clay up to 10 wt %, the softening point decreased to 144°C, which is due to the aggregation of clay particles. This indicates that the amount of clay is not only the reason for improvement of the thermal stability, but also the manner of clay dispersion in VER matrix.²⁵

The TGA thermograms of VER/VSA-MMT under air atmosphere are shown in Figure 12. The neat VER was decomposed through two steps; the first step was in the range of 160–450°C due to the decomposition of the aliphatic part. The second step was in the range of 500–600°C due to the decomposition of the more thermally stable aromatic component.⁴⁴ The char yield at 800°C represents the clay content in VER matrix, which is in accordance with the theoretical content. The inclusion of VSA-MMT into VER matrix increased the thermal stability as shown in Table II. The temperature of 5 and 10% weight loss (T_5 and T_{10}) are dramatically increased from 289 and 355°C for neat resin to 350 and 376°C for VER/VSA-MMT hybrid with 5% organoclays content, respectively. This enhancement in thermoxidative stability is due to the barrier effect of the dispersed layered silicates

which minimize the permeability of oxygen into the bulk of the material.^{45,46} As a result, the hybrid showed a delayed decomposition behavior than the neat resin. The thermal stability decreased, however, with the increase of organoclay content above 10 wt % due to the aggregation of clay.²⁵ Similarly, at 10 wt % of clay loading, the T_5 and T_{10} were 348 and 374°C for VER/10% SA-MMT; and were 333 and 366°C for VER/10% ASA-MMT. This may be attributed to the

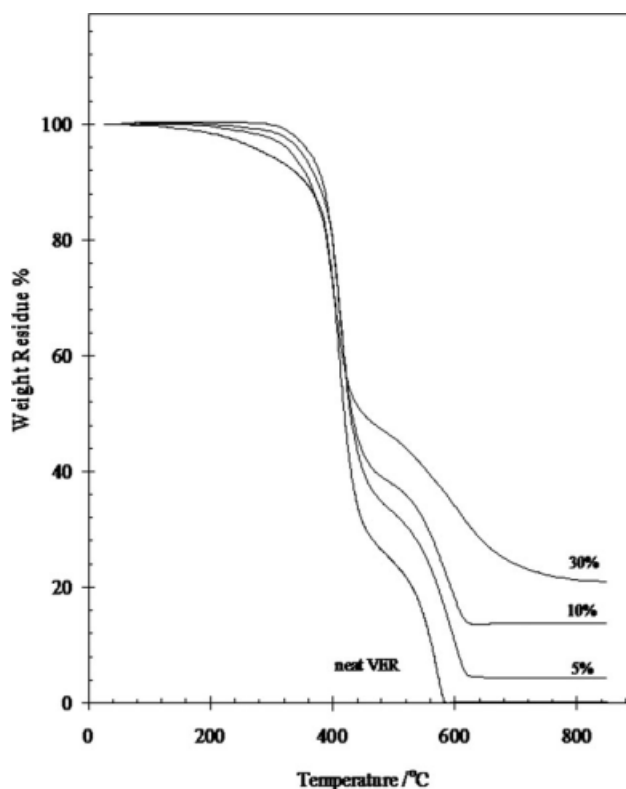


Figure 12 TGA under air atm. for pure VER and VER/VSA-MMT hybrids with different ratios of VSA-MMT.

lower thermal stability of the intercalating agent of clay than the polymer and the restriction of VER polymerization by the action of high content of organoclay.

Thermal degradations of VER/VSA-MMT hybrids were also studied by TGA under argon atmosphere. Weight loss under argon gas occurred in one-step between 350 and 500°C, different from the two-step mode under air gas. The temperature of 5% and 10% weight loss, and char yield at 800°C are summarized in Table II. The increase in thermal stability by the inclusion of the clay is apparently observed. The improvement of thermal stability is significant at low clay loading, where it was higher up to 7% organoclay loading. The temperatures of T_5 and T_{10} for neat resin were increased from 331 and 368°C to 361 and 377°C for VER/7% VSA-MMT hybrid. This may be attributed to the full dispersion of organoclay into VER matrix, which significantly increases the thermal stability of the resulting hybrid by hindering the degradation volatiles from exiting from the hybrid during its thermal degradation.

CONCLUSIONS

A series of novel nanocomposites was prepared by the inclusion of different organoclays into VER prepolymer matrix. XRD results demonstrated that the solution intercalation process for VER/OMMT hybrids formation exhibit an intercalated morphology with well ordered structures as suggested by the presence of $d(001)$, $d(002)$, and $d(003)$ reflections. The transparency of the film did not change with low clay content as indicated by UV study. Thermal stability and softening point were enhanced by the inclusion of organoclay. This improvement in the properties is not only related to the clay content, but also to the manner of clay dispersion in VER matrix.

References

- Ajayan, P. M.; Schadler, L. S.; Braun, P. V. *Nanocomposite Science and Technology*; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, 2003.
- Wing, M. Y.; Yu, Z. *Polymer Nanocomposites*; Woodhead Publishing Limited, CRC Press, 2005.
- Pinnavaia, T. J.; Beall, G. W. *Polymer-Clay Nanocomposites*; John Wiley & Sons Ltd: Cambridge, England, 2000.
- Ke, Y. C.; Stroeve, P. *Polymer-Layered Silicate and Silica Nanocomposites*; Elsevier B.V.: Amsterdam, 2005.
- Moet, A.; Akelah, A. *Mater Lett* 1993, 18, 97.
- Su, S.; Wilkie, C. *J Polym Sci Part A: Polym Chem* 2003, 41, 1124.
- González, T. V.; Salazar, C. G.; Rosa, J. R.; González, V. G. *J Appl Polym Sci* 2008, 108, 2923.
- Song, L.; Hu, Y.; He, Q.; You, F. *Colloid Polym Sci* 2008, 286, 721.
- Akelah, A.; Rehab, A.; Agag, T.; Betiha, M. *J Appl Polym Sci* 2007, 103, 3739.
- Kelly, P.; Akelah, A.; Qutubuddin, S.; Moet, A. *J Mater Sci* 1994, 29, 2274.
- Park, J.; Jana, S. C. *Macromolecules* 2003, 36, 8391.
- Zammarano, M.; Franceschi, M.; Bellayer, S.; Gilman, J. W.; Meriani, S. *Polymer* 2005, 46, 9314.
- Qi, B.; Zhang, Q. X.; Bannister, M.; Mai, Y. W. *Compos Struct* 2006, 75, 514.
- Agag, T.; Takeichi, T. *Polymer* 2000, 41, 7083.
- Manfredi, L. B.; Puglia, D.; Kenny, J. M.; Vázquez, A. *J Appl Polym Sci* 2007, 104, 3082.
- Moet, A.; Akelah, A.; Salahuddin, N.; Hiltner, A.; Baer, E. *Mater Lett* 1995, 22, 97.
- Ma, J.; Yu, Z.; Kuan, H.; Dasari, A.; Mai, Y. *Macromol Rapid Commun* 2005, 26, 830.
- Rehab, A.; Akelah, A.; Agag, T.; Shalaby, N. *Polym Adv Technol* 2007, 28, 108.
- Cassis, F.; Talbot, R. In: *Polyester and Vinyl Ester Resins*; Peters, T., Ed.; Chapman & Hall Publishing: London, 1998.
- Yang, H.; Lee, L. *J Appl Polym Sci* 2001, 79, 1230.
- Ullet, J.; Chartoff, R. *Polym Eng Sci* 1995, 35, 1086.
- Oprea, S.; Vlad, S.; Stanciu, A.; Macoveanu, M. *Eur Polym J* 2000, 36, 373.
- White, M. N.; Henson, C. In: *International Encyclopedia of Composites*, Lee, S. M., Ed.; VCH: New York, 1991; Chapter 6, p 489.
- Yebassa, D.; Balakrishnan, S.; Feresenbet, E.; Raghavan, D.; Start, R.; Hudson, D. *J Polym Sci Part A: Polym Chem* 2004, 42, 1310.
- Someya, Y.; Shibata, M. *Polym Eng Sci* 2004, 44, 11.
- Ray, D.; Sengupta, S.; Sengupta, S. P.; Mohanty, A. K.; Misra, M. *Macromol Mat Eng* 2006, 291, 1513.
- Gawdzik, B.; Matynia, T. *J Appl Polym Sci* 2001, 81, 2062.
- Rosu, L.; Cascaval, C.; Rosu, D. *J Optoelectron Adv Mat* 2006, 8, 690.
- Agag, T.; Takeichi, T. *Polym Comp* 2007, 29, 750.
- Bajpai, M.; Shukla, V.; Kumar, A. *Prog Org Coat* 2002, 44, 271.
- Ziaee, S.; Palmese, G. *J Polym Sci Part B: Polym Phys* 1999, 37, 725.
- Fu, X.; Qutubuddin, S. *J. Polymer* 2001, 42, 807.
- Fu, X.; Qutubuddin, S. *J. Colloid Interface Sci* 2005, 283, 373.
- Qutubuddin, S.; Meneghetti, P. Ph.D. Thesis, Case Western Reserve University, School of Graduate Studies, Cleveland, Ohio, 2004.
- Yu, Y. H.; Yeh, J. M.; Liou, S. J.; Chen, C. L.; Liaw, D. J.; Lu, H. Y. *J Appl Polym Sci* 2004, 92, 3573.
- Gatos, K.; Szazdi, L.; Pukanszky, B.; Karger-Kocsis, J. *Macromol Rapid Commun* 2005, 26, 915.
- Zhu, J.; Wang, X.; Tao, F.; Xue, G.; Chen, T.; Sun, P.; Jin, Q.; Ding, D. *Polymer* 2007, 48, 7590.
- Xu, L.; Reeder, S.; Thopasridharan, M.; Ren, J.; Shipp, D.; Krishnamoorti, R. *Nanotechnology* 2005, 16, S514.
- Cho, J.; Sul, K. *Polymer* 2001, 42, 727.
- Starr, B.; Burts, E.; Upson, J.; Riffle, J. *Polymer* 2001, 42, 8727.
- Yi, G.; Yan, F. *Wear* 2007, 262, 121.
- Ranade, A.; Souza, A.; Gunade, B. *Polymer* 2002, 43, 3759.
- Takeichi, T.; Nakamura, K.; Agag, T.; Muto, H. *Des Monom Polym* 2004, 7, 727.
- Camino, G.; Tartaglione, G.; Frache, A.; Manfredi, C.; Costa, G. *Polym Degrad Stab* 2005, 90, 354.
- Takeichi, T.; Zeidam, R.; Agag, T. *Polymer* 2002, 43, 53.
- Agag, T.; Takeichi, T. *High Perform Polym* 2002, 14, 115.