Polymer/Clay Nanocomposite Plasticization: Elucidating the Influence of Quaternary Alkylammonium Organic Modifiers

Erin Pavlacky, Dean C. Webster

Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota 58108
Correspondence to: D. C. Webster (E-mail: dean.webster@ndsu.edu)

ABSTRACT: The potential of nanoclay organic modifiers to induce plasticizing effects in resin and coatings systems was studied. In previous work, it was found that while low amounts of incorporation of organomodified clays significantly improved the physical and mechanical properties of a ultraviolet (UV)-curable nanocomposite, further increasing the organomodified clay content could result in the reduction of properties. To investigate the potential impact of the organic modifier composition and concentration on polymer properties, a series of experiments were carried out using only the organic modifier. Methyl, tallow, bis-2-hydroxyethyl ammonium (MTEtOH), the organic modifier used in montmorillonite clay Cloisite® 30B, was dispersed with precursor polyester oligomers at 1–10 wt % through an *in situ* synthesis process and via sonication, and UV-curable coatings were prepared from these MTEtOH-containing resins. The organic modifier cetyltrimethylammonium bromide (CTAB) was also studied to examine the impact of the organic modifier structure. According to differential scanning calorimetry, small decreases in the glass transition temperatures (T_g) of the MTEtOH-containing polyesters were observed, but CTAB-containing polyesters had small T_g increases. Polyester molecular weight and viscosity were also affected by both the structure of the organic modifier as well as its concentration. The mechanical performance of the UV-curable coatings diminished with increased MTEtOH concentration for the films containing the organic modifier compared to a control film. Furthermore, the crosslink density was found to reduce $\sim$ 50% with increased MTEtOH loading into the UV-curable films. The cure characteristics, thermal stability, and optical clarity were also studied. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 324–333, 2013

INTRODUCTION

Polymer/clay nanocomposites are described as the introduction of nanoscale fillers into a polymer matrix. The incorporation of low quantities (1–5 wt %) of layered silicates in polymer matrices to produce composites with drastically improved material properties has become a heavily researched topic since the introduction of Nylon-6/clay nanocomposites by Toyota.[1–3] Research involving polymer/clay nanocomposites has ranged from improving barrier properties to explore their biodegradation in coatings systems.[4–8] Nanosized additives offer advantages over traditional, micron-sized composite fillers by decreasing weight, cost, and brittleness.

The most widely used family of clays used in the production of polymer/clay nanocomposites are the 2 : 1 phyllosilicates, also referred to as layered silicates.[9] The phyllosilicate structure is composed of two silicon tetrahedral sheets fused to one aluminum or magnesium hydroxide octahedral sheet to form a single clay layer. Montmorillonite clays belong to the class of smectite 2 : 1 phyllosilicates and are formed from the crystallization of

solution containing silicon and magnesium. The clay layer possesses a negative charge as a result of the isomorphic substitutions that replace Al^{3+} for Mg^{2+} ions. To balance these negative charges, alkali or alkaline earth metal cations will adsorb to the clay sheet surfaces, leading to face-to-face stacking of clay platelets with cations between the layers.[10] The space occupied by these cations forms a van der Waals gap referred to as the interlayer or gallery. The interlayer cations are critical to the final dispersion of layered silicates within a polymer matrix as the cations will dictate the affinity of the clay to the polymer as well as provide a source for organic modification to the clay sheet.

Organic modification of layered silicates is commonly performed to render the inorganic clay platelets more organophilic to facilitate their incorporation into a polymer matrix. The alkali or alkaline earth cations situated within the clay interlayer will increase compatibility with hydrophilic polymers, such as polyvinyl alcohol.[11] To increase layered silicate organophilicity, ion exchange reactions are conducted to replace the interlayer

earth cations with various organic surfactants, which increases clay/polymer affinity. Interlayer cations are referred to as exchangeable cations due to the ease of replacement as the cations are not covalently incorporated into the clay sheet structure.[12]

Quaternized alkylammonium cations are commonly exchanged with cations to modify clay platelets. The impact of alkylammonium ion modifiers on the properties of epoxy/clay nanocomposites was studied by Xidas and Triantafyllidis.[13] The structure, functionality, polarity, and hydrophobicity of the modifiers resulted in varying degrees of clay dispersion as well as changes in mechanical, thermomechanical, and thermal properties of the nanocomposite films. Fornes et al.[14] examined how the length of the alkyl chain attached to the nitrogen atom of various organic modifiers affected the final clay dispersion in Nylon-6 nanocomposites. Modifiers with one alkyl chain provided the highest degree of exfoliation compared to modifiers with zero or two alkyl chains. Two alkyl chains showed poorer dispersion than one alkyl chain due to the increased repulsive interactions between the modifier hydrocarbon chains and the polyamide matrix. The superiority of quaternary ammonium modifiers over primary, secondary, and tertiary ammonium clays was reported by Kim and White[15] in a study on the impact of organic modifiers on montmorillonite clays in the formation of polymer/clay nanocomposites. The quaternary ammonium modifiers demonstrated the best compatibility with polar polymers. This observation was attributed to the greatest surface area interaction between the long alkyl chains of the modifier, and the polar polymeric material as the quaternary ammonium modifier will cover more of the clay platelet than shorter alkyl chains. Additionally, the longer alkyl chains permitted a higher degree of intercalation of the polymer into the montmorillonite clay interlayer.

In addition to increasing the affinity of primarily hydrophilic clay to polymer matrices, the organic modifier may also serve as an initiation source or reaction site in a wide variety of polymerization reactions. Fan et al.[16,17] described a technique for ionically binding organic modifiers to clay platelets that may be activated to initiate polymerization reactions. The surface-initiated polymerizations were performed by cationic free radical initiators to synthesize polystyrene/clay nanocomposites. Free-radical grafting was also performed by Mansoori et al.[18] in the preparation of polyacrylamide/clay nanocomposites. A silylation reaction was used to modify montmorillonite clay with vinyltrichlorosilane, followed by chemical grafting of polyacrylamide to the clay surface to produce intercalated nanocomposites. Photo-induced polymerizations have also been successfully performed with the utilization of layered silicate organomodification as a photoinitiation source.[19–22] Recently, living radical polymerization methods have been used to produce nanocomposites exhibiting well-defined polymer functionality and architecture. The modification of layered silicates has been used to facilitate atom transfer radical polymerization,[23–26] nitroxide-mediated polymerization,[27–29] and reverse addition–fragmentation chain transfer[30–33] in multiple studies.

Organic modifiers provide crucial alterations to an unmodified layered silicate structure by increasing clay interlayer distance, providing functionality for polymerization reactions, lowering the surface energy of the silicate sheets, and improving the affinity between the clay and polymer. The volume fraction of the modified silicates will have a profound impact on the final properties of both polymeric materials and their coatings. Interestingly, increasing the clay volume fraction within a polymeric matrix has not always been shown to increase the mechanical or thermal properties of a coatings system. Miyagawa et al.[34] reported an unexpected decrease in the glass transition temperature (T_g), determined from the maximum point of the tan δ curve from dynamic mechanical testing, of epoxy/clay nanocomposites with increased clay loading. With increases in the clay volume fraction, the T_g decreased from 131 to 117°C instead of increasing, a trend commonly observed with increased clay content due to chain restriction. One explanation given for this phenomenon was the organic modifier, containing a long-chain fatty alkyl amine, was thermally dissociated during polymerization. This dissociation would then allow the low-molecular weight alkyl amine to act as a plasticizer. As the clay volume fraction was increased, the concentration of the organic modifier, and thus the alkyl amine, would also increase. Therefore, the alkyl amine could potentially have plasticized the nanocomposite coating to a high enough extent that the T_g would decrease. Shah and Paul[35] explored the impact of organoclay degradation on melt-processed polyethylene–clay nanocomposites with varying melt process temperatures. Decreases in d-spacing from X-ray diffraction analysis for the nanocomposites prepared at higher temperatures (180–200°C) were observed, a phenomenon attributed to higher concentrations of alkylammonium surfactants leaving the clay interlayer. Cervantes et al. studied the thermal degradation of commercially available organomodified clays using thermogravimetric analysis (TGA) coupled with Fourier transform infrared spectroscopy to study the evolved gases during clay thermal decomposition.[36] The thermal decomposition of the organomodified clays was attributed to different mechanisms, depending on the quaternary ammonium surfactant structure, including Hofmann eliminations, nucleophilic substitutions, tallow residue thermal degradation, and unexchanged quaternary ammonium surfactant thermal degradation.

Another instance of decreased T_g values with increased organoclay filler has been reported for polylactide-based nanocomposites.[37] Again, the unexpected trend was hypothesized to be a result of plasticization from the organic modification of the montmorillonite clay. Conversely, Fu and Qutubuddin[38] and Kim et al.[39] have attributed this trend to the increased viscosity of the polymer system and the decreased polymer density around the silicate fillers, respectively. Although the impact of organic modification of layered silicates has been widely shown to influence several resin and material properties, the influence of the organic modifier, independent of the clay, has not yet been reported.

Our previous work with ultraviolet (UV)-curable nanocomposite barrier coatings produced through a novel *in situ* preparation technique had shown unexpected decreases in mechanical and thermal properties with increased clay loading.[40] To explore these unanticipated results, the goal of this study was to isolate the impact of alkylammonium ions used in layered silicate
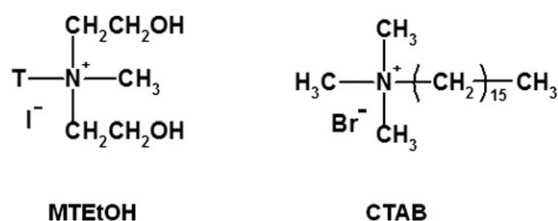
Figure 1. Structures of the Cloisite® 30B organic modifier (MTEtOH) and cetyltrimethylammonium (CTAB), two common quaternary alkylammonium cations.

modification on the properties of the same polyester and coatings systems previously developed. By incorporating just the organic modifiers, without layered silicates, into the polyester resins, the impact of these modifiers on the final resin and film properties may be studied. The organic modifier concentrations used in this study were equivalent to the methyl, tallow, bis-2-hydroxyethyl ammonium (MTEtOH) concentration in Cloisite® 30B clay and cetyltrimethylammonium bromide (CTAB) concentration in the CTAB-modified Cloisite® Na+ clay used in our previous study. The organic modifiers were once again dispersed by the *in situ* preparation technique and by a process of mixing and sonication. The impact of the organic composition and concentration on the resulting polyesters and their coatings were studied and compared to the clay-containing polyesters and nanocomposite coatings.

EXPERIMENTAL

Materials

The monomers maleic anhydride, 1,6-hexanediol, and diethylene glycol were purchased from Sigma Aldrich (Milwaukee, WI), and monomer 1,4-cyclohexanedicarboxylic acid (1,4-CHDA) was obtained from Eastman Chemical Company (Kingsport, TN). Tri(ethylene glycol) divinyl ether (TEGDVE), the reactive diluent used for creating UV-curable films, was also purchased from Sigma Aldrich, as was the CTAB organic modifier and iodomethane. Photoinitiator Darocur® 1173, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, was supplied from CIBA (Basel, Germany). Ethomeen T/12, a bis(2-hydroxyethyl) tallow alkyl amine, was generously supplied from AkzoNobel (Houston, TX).

Preparation of Organic Modifiers

The organic modifier of Cloisite® 30B, MTEtOH, was reproduced by a quaternization reaction of a tallow amine ethoxylate, similar to a procedure reported by Chen et al.[41] Ten grams of Ethomeen T/12 was added to 79 mL of dimethylsulfoxide and 11.95 g of iodomethane. The solution was stirred at room temperature (23°C) for 16 h, precipitated with ice-cold diethyl ether, filtered, and dried in a vacuum oven at 25°C. The CTAB organic modifier was used without further modification. Structures of the both alkylammonium organic modifiers are displayed in Figure 1.

Organic Modifier Dispersion—*In Situ* Technique and Sonication

The concentrations of MTEtOH and CTAB were selected to be equivalent to the modifier concentrations of Cloisite® 30B and CTAB-modified clays were used in our previous study. TGA

determined the organic modifier content of Cloisite® 30B and CTAB-modified Cloisite® Na+ to be ~ 30 and 48 wt %, respectively. These values were used to disperse the equivalent amount of organic modifier as would be found in the dispersion of 1, 2, 5, and 10 wt % Cloisite® 30B and CTAB-modified Cloisite® Na+ clays. For example, 1 wt % Cloisite® 30B clay in the *in situ* preparation technique of clay dispersion is 1.20 g (≈120 g total monomer weight), and so 30% of 1.20 g or 0.36 g was the organic modifier weight incorporated into the polyester resin to maintain equivalent organic modifier concentration to our previous study. The *in situ* technique was used to disperse the organic modifiers in the liquid monomer diethylene glycol before unsaturated polyester synthesis. Organic modifiers MTEtOH or CTAB were dispersed at high shear with diethylene glycol to achieve homogeneity and then mixed overnight at room temperature with a magnetic stir bar. To examine the utility of this *in situ* technique, MTEtOH was also dispersed into the polyester resin through mixing and sonication to compare the properties achieved.

Synthesis of Unsaturated Polyesters

The unsaturated polyesters were synthesized by standard melt polyesterification according to the composition previously reported.[40] Briefly, monomers maleic anhydride (1.000 mol), 1,6-hexanediol (0.625 mol), and 1,4-CHDA (0.172 mol) were combined with the diethylene glycol (0.824 mol)/organic modifier dispersion in a 250-mL three-necked RBF equipped with mechanical stirrer, nitrogen inlet, temperature probe/controller, condenser, water collection flask, and heating mantle. The reaction mixture was ramped to 60, 120, and 180°C and then stopped once an acid value of ~ 20 mg KOH/g of sample was achieved. With the sonication-dispersion technique, the organic modifiers were dispersed in virgin polyester resin by mixing with a metal spatula and then placing each sample in an ultrasonic bath for 8 h. Polyester compositions are detailed in Table I, where the MTEtOH and CTA weights are based on the total monomer weight for the *in situ* preparation technique or based on 10 g of polyester for the mixing and sonication-dispersion technique. The control polyester contained no organic modifier.

Coating Preparation

UV-curable coatings were prepared by combining the unsaturated polyesters with the reactive diluent TEGDVE and Darocur® 1173. The polyester and TEGDVE were mixed in a 1 : 1 ratio based on reactive functional groups: maleate to vinyl ether. The photoinitiator was added based on 6 wt % of the polyester, modifier, and reactive diluent. The coating formulations were hand-mixed to achieve uniformity and then left undisturbed until air bubbles had dissipated. Next, these formulations were cast with a Gardco bar-coater onto glass and aluminum substrates with a five-mil clearance. The cast formulations were subjected to UV-irradiation (Dymax 200 EC silver lamp (UV-A, 365 nm, intensity ≈ 40 mW/cm^2) for 60 s to achieve tack-free films. Coatings were left undisturbed for 24 h to allow for film equilibration.

Nomenclature

The names of the unsaturated polyesters were designated based on the organic modifier, the wt % of the organic modifier, and

Table I. Unsaturated Polyester Compositions

Polyester	Organic modifier	Organic modifier weight (g)	Dispersion technique
Control	None	–	–
Q1_MTEtOH_in situ	MTEtOH	0.36	In situ
Q2_MTEtOH_in situ	MTEtOH	0.72	In situ
Q5_MTEtOH_in situ	MTEtOH	1.80	In situ
Q10_MTEtOH_in situ	MTEtOH	3.60	In situ
Q1_MTEtOH_sonic	MTEtOH	0.03	Mixing/sonication
Q2_MTEtOH_sonic	MTEtOH	0.06	Mixing/sonication
Q5_MTEtOH_sonic	MTEtOH	0.15	Mixing/sonication
Q10_MTEtOH_sonic	MTEtOH	0.30	Mixing/sonication
Q1_CTAB_in situ	CTAB	0.58	In situ
Q2_CTAB_in situ	CTAB	1.15	In situ
Q5_CTAB_in situ	CTAB	2.88	In situ

the dispersion method (*in situ* or sonication technique). The polyester name is as follows: wt % modifier (derived from the wt % modifier on the modified clay samples)_type (MTEtOH or CTA)_dispersion method (*in situ* or sonic). The prefix "Q" is used to distinguish the polyesters and coatings containing only the quaternary ammonium modifier, instead of the modified clay. *In situ* indicates that the *in situ* polymerization technique was used in the dispersion of the organic modifiers, and "sonic" represents that the organic modifier was dispersed by mixing and sonication. For example, Q1_MTEtOH_*in situ* describes a polyester containing 1 wt % MTEtOH, the Cloisite® 30B organic modifier, dispersed through the *in situ* process. Polyesters and coatings without the "Q" suffix refer to the unsaturated polyesters and coatings containing clay from our previous study and are shown for comparison of properties.

Characterization

Each unsaturated polyester was characterized to determine molecular weight, viscosity, T_g, and isomerization of the polyester backbone. The polyester molecular weight was determined using a Waters 2410 Gel Permeation Chromatograph equipped with a refractive index detector. Polyester samples were dissolved in tetrahydrofuan to produce a 1% sample solution. Calibration was performed with polystyrene standards, and the flow rate was 1 mL/min. The viscosity measurements were performed with an ICI cone and plate viscometer at 100°C. The T_g of each polyester was determined from differential scanning calorimetry (DSC) using TA Instruments Q1000 Series DSC with a heat–cool–heat testing cycle. The polyester samples were equilibrated at −90°C, heated to 100°C at a rate of 10°C/min, cooled to −90°C at a rate of 10°C/min, and then heated once again to 100°C at a rate of 10°C/min. The T_g was determined from the inflection point in the second heating scan. The percent isomerization observed from maleate to fumarate in the unsaturated polyester backbone was determined from [1]H-nuclear magnetic resonance (NMR) spectroscopy using a JEOL ECA Series 400 MHz NMR spectrometer with procedure followed from Curtis et al.[42]

Coatings derived from the unsaturated polyesters were cured by UV-irradiation with a Dymax 200 EC silver lamp (UV-A, 365 nm, intensity ≈ 40 mW/cm^2). The cure characteristics were determined by a Thermo Nicolet Magna-IR 850 spectrometer with a detector-type DTGS KBr to perform real-time IR measurements. The UV-radiation source was a LESCO Super Spot MK II UV-curing lamp equipped with a fiber-optic light guide for curing the samples. Each formulation was spin-coated at 3000 RPM onto a KBr window before being placed in the spectrometer chamber, ∼ 20 mm from the end of the fiber-optic cable with a 10 mW/cm^2 light intensity. The samples were subjected to UV and IR irradiation simultaneously. The degree of conversion was calculated based on the disappearance of the vinyl ether double bonds. The conversion was calculated from

$$\% \ conversion = \{[(A_{1639})_0 - (A_{1639})_t]/(A_{1639})_0\} \times 100$$

where $(A_{1639})_0$ is the absorbance at time $= 0$ and $(A_{1639})_t$ is the absorbance at time $= t$.

Dynamic mechanical thermal analysis (DMTA) was performed using a TA Instrument Q800 Dynamic Mechanical Analyzer to examine the dynamic mechanical properties of each coating. Free films of the cured coatings were removed from a glass substrate and cut to dimensions of ∼ 15 mm × 5 mm × 0.070–0.080 mm thickness. These films were characterized using 1 Hz frequency, a constant strain of 0.05%, a heating rate of 5°C/min over a temperature range of −50 − 150°C. The organic modifier weight percent and the coating thermal stability were tested using TGA with a TA Instruments Q500 Thermogravimetric Analyzer. Samples were heated under nitrogen atmosphere from 25 to 800°C at a rate of 20°C/min. The optical clarity of the coatings was examined with a Varian Cary 5000 UV–vis spectrometer by determining transmittance at 400 nm.

RESULTS AND DISCUSSION

Unsaturated Polyester Characterization

In our previous study, we reported the development of a novel *in situ* preparation technique to create highly dispersed clays in a precursor oligomer before the formation of UV-curable nanocomposite coatings. During the characterization of these nanocomposites, several coating properties reached a maximum, but then decreased or diminished with higher clay concentrations (5–10 wt %). For example, the storage modulus, degradation temperature, and film hardness increased with the addition of 1–2 wt % clay, but higher levels of clay led to decreases in these properties. One possible explanation for this phenomenon is that the organic modifier of the layered silicate may plasticize the precursor oligomer and coating. When the clay content increases, the organic modifier concentration will also increase, leading to a greater degree of plasticization. Additional theories have also been considered, including decreased polymer density surrounding the clay fillers and increased polymer viscosity. With this study, we explore the impact of layered silicate organic modifiers on both polyester and coating properties by synthesizing unsaturated polyester resins in the presence of MTEtOH and CTAB to isolate the impact of each organic modifier. Throughout the discussion of results, the properties

Table II. Unsaturated Polyester Properties

Polyester	Acid number	M_n (g/mol)	M_w (g/mol)	PDI	Viscosity (Poise)	T_g (°C)	% Fumarate
Control	21	1100	2400	1.9	2.4	−42	33
Q1_MTEtOH_in situ	21	1100	2400	1.9	1.2	−41	37
Q2_MTEtOH_in situ	22	1300	2900	1.9	1.8	−40	40
Q5_MTEtOH_in situ	21	1500	2800	1.9	3.4	−38	37
Q10_MTEtOH_in situ	22	1700	3400	2.0	6.4	−37	42
Q1_MTEtOH_sonic	21	1300	2400	1.8	1.4	−43	35
Q2_MTEtOH_sonic	21	1300	2400	1.8	1.8	−45	34
Q5_MTEtOH_sonic	21	1300	2400	1.8	1.8	−45	34
Q10_MTEtOH_sonic	21	1300	2400	1.8	1.8	−49	38
Q1_CTAB_in situ	20	1500	3000	2.0	3.2	−39	50
Q2_CTAB_in situ	21	1300	2700	2.1	3.2	−39	59
Q5_CTAB_in situ	22	2800	4200	1.5	7.0	−34	57
1_30B_in situ[a]	21	1800	3500	1.9	3.3	−36	46
2_30B_in situ	22	1500	3800	2.5	5.4	−39	39
5_30B_in situ	21	1800	3900	2.2	5.8	−41	41
10_30B_in situ	21	4000	7300	1.8	8.8	−43	64
1_30B_sonic	21	1900	3600	1.9	3.5	−37	19
2_30B_sonic	21	2000	3600	1.8	3.7	−37	17
5_30B_sonic	21	1400	3500	2.4	4.8	−41	24
10_30B_sonic	21	1900	3800	2.0	5.4	−42	18
1_CTAB_in situ	20	2800	6900	2.4	6.0	−32	53
2_CTAB_in situ	21	2400	4700	2.0	6.5	−33	62
5_CTAB_in situ	22	1800	4800	2.7	7.3	−36	52

[a]This data and following are reported in Ref. 40.

obtained from both the clay-containing unsaturated polyesters and UV-curable nanocomposites from our previous study will be shown for comparison.

The characterization of the organic modifier-containing unsaturated polyesters was critical to understanding the impact of the organic modification on the final coating properties. Table II contains a summary of the unsaturated polyester properties. In accordance with our previous study, the two organic modifiers were incorporated into the polyester during polyesterification through the *in situ* technique as well as after polyester synthesis via sonicating the organic modifier with a control polyester resin. With each polyester resin, the target acid number was 20 mg of KOH/g of polyester. Careful monitoring of the acid number was important to ensure similar acid number values; therefore, comparable degrees of polymerization were maintained.[43]

GPC was used to examine the molecular weight and polydispersity index (PDI) for the organic modifier-containing polyester resins. The M_n and M_w values obtained for each polyester were less than the molecular weights recorded for the clay-containing polyester counterpart. Increased clay weight led to large increases in polyester molecular weight, whereas increasing the organic modifier concentration produced only slightly larger molecular weight values. The introduction of the MTEtOH organic modifier to a polyester resin via sonication did not change

the molecular weight; each polyester sample had a M_n value of 1300 g/mol and an M_w value of 2400 g/mol. With the *in situ* preparation technique, slight increases in the molecular weight values were observed; however, the organic modifier did not affect the molecular weight or polydispersity to the degree observed with the clay-containing polyesters. Without the addition of the clay fillers into the polyester resin, the hydrodynamic volume of the polyester oligomers was rather consistent. Lower PDI values were observed with the organic modifier-containing polyesters (1.8–2.1) compared to the clay-containing polyesters (1.8–2.7).

The viscosities of the organic modifier-containing polyesters were lower than the control polyester at lower concentrations (1–2 wt %) of the organic modifiers. Q1_MTEtOH_*in situ*, Q2_MTEtOH_*in situ*, and the polyesters prepared through sonication had viscosities ranging from 1.2 to 1.8 Poise, whereas the control polyester viscosity was 2.4 Poise. This trend demonstrates the effect of the organic modifier of the polyester oligomers; even small additions of the organic modifier can affect the polyester properties. Because the molecular weights of these polyesters were comparable to the control polyester, the introduction of the organic modifier may be reducing the viscosity due to plasticization of the polyester oligomers. Once the organic modifier concentration was increased to the 5–10 wt % range, the viscosities of Q5_MTEtOH_*in situ* and

Table III. Cure, Mechanical, Thermal, and Optical Clarity Characterization Data of Cured Coatings

Coating name	Conversion (%)	E' (MPa, 25°C)	XLD (mol/cm^3)	T_{10}% (°C)	Transmittance (%)
Control	72	370	0.022	240	98
Q1_MTEtOH_in situ	69	440	0.019	300	96
Q2_MTEtOH_in situ	73	530	0.031	305	98
Q5_MTEtOH_in situ	80	285	0.026	305	99
Q10_MTEtOH_in situ	78	280	0.011	300	97
Q1_MTEtOH_sonic	70	240	0.011	300	99
Q2_MTEtOH_sonic	73	340	0.022	300	97
Q5_MTEtOH_sonic	73	320	0.016	265	99
Q10_MTEtOH_sonic	72	280	0.010	250	93
Q1_CTAB_in situ	77	730	0.030	305	95
Q2_CTAB_in situ	79	790	0.031	290	94
Q5_CTAB_in situ	77	780	0.029	295	94
NC1_30B_in situ[a]	80	890	0.041	255	94
NC2_30B_in situ	81	1020	0.042	245	92
NC5_30B_in situ	80	1250	0.086	250	85
NC10_30B_in situ	83	1500	0.033	230	84
NC1_30B_sonic	79	810	0.017	270	95
NC2_30B_sonic	87	910	0.014	290	95
NC5_30B_sonic	87	625	0.024	300	82
NC10_30B_sonic	77	390	0.015	280	62
NC1_CTAB_in situ	83	610	0.023	270	98
NC2_CTAB_in situ	80	495	0.016	280	98
NC5_CTAB_in situ	80	340	0.014	260	97

[a]This data and following are reported in Ref. 40.

Q10_MTEtOH_in situ were increased to 3.4 and 6.4 Poise, respectively, but still remained lower than their clay-containing counterparts. The polyesters containing the CTAB modifier also showed slight increases in viscosity, ranging from 3.2 to 7.0 Poise. The viscosity increases may be attributed to the higher molecular weights for these polyester oligomers.

The organic modifier did not affect the glass transition temperature (T_g) of each polyester to the extent of the molecular weights and viscosities, but small variations were observed. The sonication dispersion technique produced organic modifier-containing polyesters with T_g values slightly lower (1–7°C) than the control polyester, possibly a sign of oligomer plasticization. The in situ preparation technique, conversely, resulted in the T_g values slightly higher (1–8°C). Higher concentrations of the organic modifier resulted in more significant changes to the T_g. Both Q10_MTEtOH_sonic ($T_g = -49$°C) and Q5_CTAB_in situ ($T_g = -34$°C) had T_g values ranging further from the control polyester ($T_g = -42$°C).

Unlike the clay-containing unsaturated polyesters, the MTEtOH organic modifier did not greatly impact the final maleate-fumarate isomerization of the polyester backbone. Without the steric hindrance from the clay fillers, the hydroxy-functional monomers may have exhibited less preference to react with the transisomer.[42,44] Polyesters dispersed with the CTAB organic modifier had higher degrees of maleate-fumarate isomerization,

ranging from 50 to 59% fumarate isomers. Once again, higher percentages of fumarate isomers with the CTAB-modified polyester systems may be a consequence of higher resin viscosity.

Cure Characteristics

The final conversion of the UV-curable coatings derived from the organic modifier-containing polyesters had a direct correlation to the polyester viscosity. The extent of the reaction was characterized using RTIR by monitoring the disappearance of the vinyl ether double bond (1639 cm^{-1}) from the reactive diluent TEGDVE (values reported in Table III). Disappearance of this vinyl ether double bond indicated the degree of conversion of the maleate-vinyl ether-coating system. The coating formulations containing polyesters with viscosities similar to the control formulation had comparable conversions. As discussed previously, the polyesters Q1_MTEtOH_in situ, Q2_MTEtOH_in situ, and polyesters prepared with sonication had viscosities similar to the control polyester resin. Each coatings system derived from these low-viscosity polyesters had comparable conversions (69–73%) to the control coatings system (72%). The more viscous Q5_MTEtOH_in situ, Q10_MTEtOH_in situ, and the CTAB-organic modifier polyesters also possessed higher conversions (78–80%). This same trend was observed with the clay-containing polyesters: higher viscosity resins produced a higher degree of double-bond conversion. Figure 2 displays RTIR curves representing the difference in conversion of the
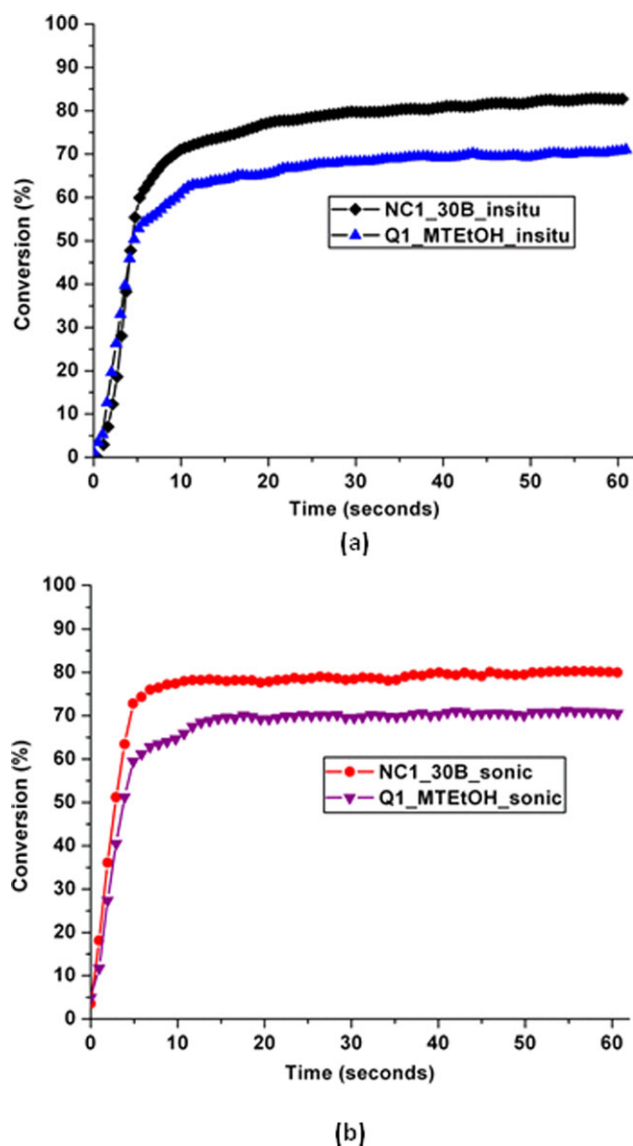
Mechanical Properties

The viscoelastic properties of the UV-curable coatings were influenced by the concentration and the compositions of the MTEtOH and CTAB organic modifiers, as seen in the results obtained from DMTA. A summary of these mechanical properties are compiled in Table III and shown in Figure 3. The coatings containing Q1_MTEtOH_*in situ* and Q2_MTEtOH_*in situ* had higher storage moduli than the control coating with values of 440 and 530 MPa, respectively. At the 5 and 10% incorporation, the modulus decreased and was lower than that of the control coating. In contrast, the MTEtOH-containing coatings, where the modifier was incorporated using sonication, had lower storage moduli than the control coating (240–340 MPa). The CTAB-containing coatings showed significantly different behavior and were not similarly affected by the organic modifier, and
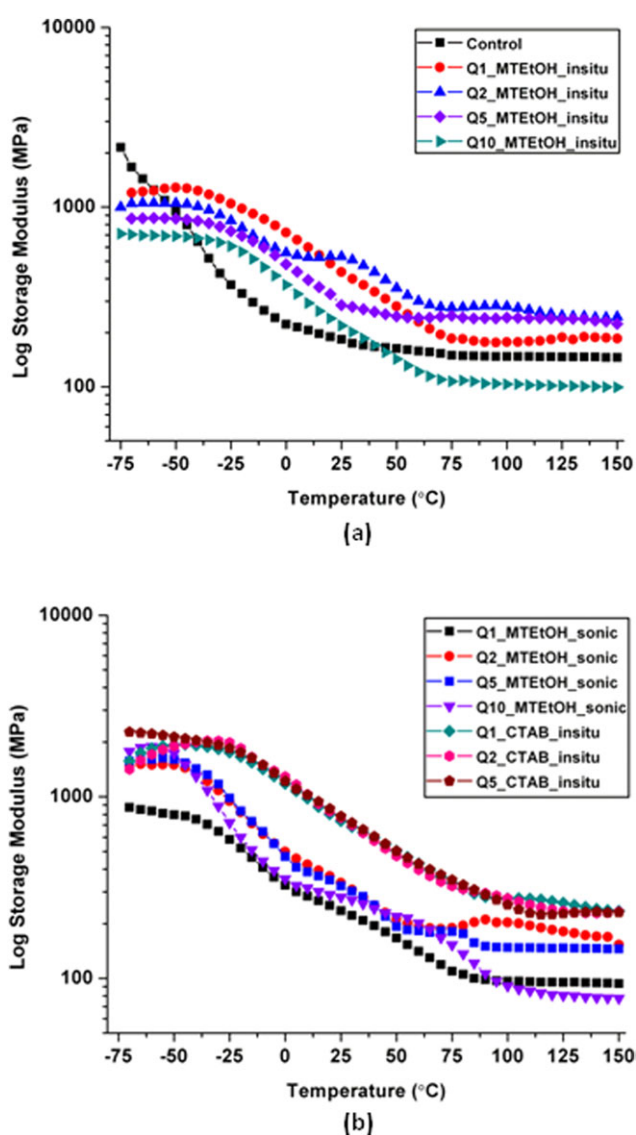

Figure 2. Real-time infrared spectroscopy conversion of 1 wt % clay and MTEtOH-containing formulations prepared through (a) the *in situ* synthesis technique and (b) the mixing and sonication dispersion route after 60 s of UV exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

higher viscosity clay-containing polyesters and the lower viscosity MTEtOH-containing polyesters. Higher viscosity coatings formulations may exhibit decreased rates of termination, a consequence of the difficulty of reactive chain ends to diffuse through the system, leading to an autoacceleration effect. Because this phenomenon was observed with polyesters containing both the organically modified clay as well as just the organic modifier, the conversion of these coatings systems appears to be dependent on the viscosity of the precursor polyester resin. In addition, the clay-containing polyesters exhibited higher viscosities than the organic modifier-containing polyesters, thus contributing to the higher conversions seen in the polyesters containing organomodified clay.

Figure 3. DMTA storage modulus plots for (a) *in situ* preparation MTEtOH-containing coatings and (b) sonication MTEtOH-containing coatings and *in situ* preparation CTAB-containing coatings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the storage moduli for these systems were all highly similar between 730 and 790 MPa, higher than that of the control coating.

As these results are compared to the results of the corresponding nanocomposites, it is apparent that the role of the organic modifier depends on its chemical structure and method of incorporation. In our previous study, we reported decreases in the storage modulus of the nanocomposite coatings made using Cloisite® 30B via sonication with 5–10 wt % organically modified clays (these results are also reported in Table III), a trend that is repeated with the coatings made using only the organic modifier. From these trends, the organic modifier appears to be a contributing factor to the final mechanical performance of these coatings. Decreases in the storage moduli and crosslink density were observed in the coatings containing polyesters prepared through sonication of the MTEtOH; the storage moduli of each coating was 30–130 MPa lower than the control coating. The decreases in the mechanical performance of coatings containing Cloisite® 30B clay and the MTEtOH organic modifier at higher concentrations (5–10 wt %) may be a result of plasticization and decreased crosslink density. Although the incorporation of 1–2 wt % Cloisite® 30B organic modifier did not significantly affect the storage moduli and crosslink densities, the coatings containing 5–10 wt % Cloisite® 30B organic modifier had lower storage moduli and crosslink densities compared to the control coating. From these results, it is apparent that increasing the MTEtOH organic modifier content decreased the mechanical performance of these coatings.

The case of the *in situ* incorporation of the Cloisite® 30B and the corresponding *in situ* incorporation of the MTEtOH modifier follow a different pattern. For the nanocomposites made using the *in situ* incorporation of the organomodified clay (NC1 through NC10), the storage modulus systematically increases as the amount of organomodified clay is increased. As discussed in our previous publication (and seen in Table III), this contrasts with the properties found for the samples prepared by sonication, indicating better interaction of the clay with the polymer using the *in situ* approach. The coatings prepared using the *in situ* incorporation of the MTEtOH show an interesting behavior. At low levels of incorporation (1 and 2%), the coatings exhibit a somewhat higher modulus than the control. However, at higher amounts of incorporation, the coatings Q5_MTEtOH_*in situ* and Q10_MTEtOH_*in situ* had storage moduli of 285 and 280 MPa, respectively, which was ∼ 100 MPa lower than the control coating (370 MPa). In addition, the crosslink density of Q5_MTEtOH_*in situ* (0.026 mol/cm³) was similar to the control coating, but the crosslink density of Q10_MTEtOH_*in situ* was reduced by 50% (0.011 mol/cm³). Thus, while the *in situ* incorporation of the organic modifier may have a plasticizing effect on the matrix resin, the reinforcing effect of the incorporation of the nanoclay overcomes the effect of the organic modifier leading to a higher modulus in the nanocomposites as the amount of organic modified clay is increased. This further supports the previous results that the *in situ* incorporation of the organic modified clay imparts better interaction between the clay and the polymer matrix resin, leading to higher moduli at all levels of clay incorporation.
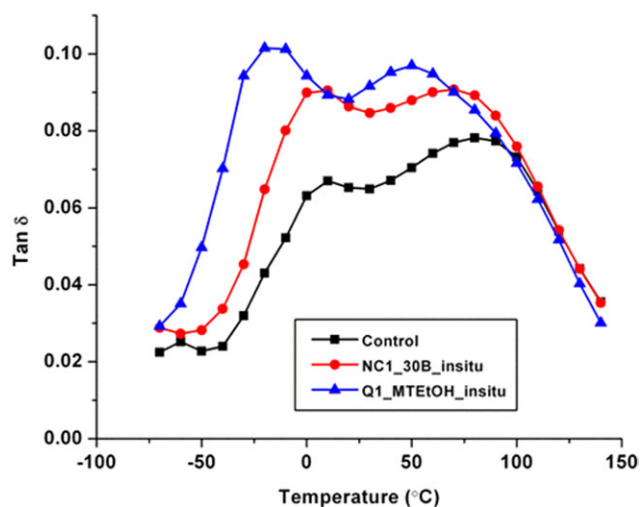

Figure 4. Tan δ plots from dynamic mechanical analysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conversely, the coatings containing the CTAB-organic modifier had storage moduli ranging from 730 to 790 MPa, ∼ 400 MPa greater than the control coating, as well as higher crosslink densities (0.029–0.031 mol/cm³). These trends are somewhat in contrast to the results of the MTEtOH organic modifier as the CTAB organic modifier did not diminish the coating mechanical properties. However, the nanocomposite coatings containing the CTAB-modified clay had decreased storage moduli and crosslink density with increased clay loading. As the organic modifier does not appear to be influencing the mechanical performance of the coatings, another explanation may be the inability of the coatings system to adequately surround the clay with higher silicate volume fractions. High clay volume fractions may hinder adequate polymer/clay dispersion, diminishing the reinforcing nature of the clay fillers on the nanoscale.

Figure 4 displays a representative example of the differences observed in the loss factor (tan δ) of the coatings containing MTEtOH compared to the nanocomposite films. The tan δ of each film was broad and bimodal, indicating that multiple dampening mechanisms are present within all the films. The tan δ plot for the nanocomposite film NC1_30B_*in situ* was less pronounced and had peaks shifted to higher temperatures than the control and Q1_MTEtOH_*in situ* films. The less pronounced loss factor peaks may be a result of the restricted mobility from the incorporation of the rigid organomodified montmorillonite clay.[45] In contrast, the tan δ plot of Q1_MTEtOH_*in situ* had loss factor peaks that were shifted to lower temperatures and were much more pronounced, an indication of possible plasticization of the MTEtOH organic modifier on the polyester film.

The difference in the behavior of the two organic modifiers plus the effect of the different processing methods is interesting and indicates that the nanocomposite preparation may not be as straightforward as many studies indicate. Both the organic modifiers are quaternary ammonium salts with one of the alkyl groups being an aliphatic hydrocarbon. In the case of MTEtOH,
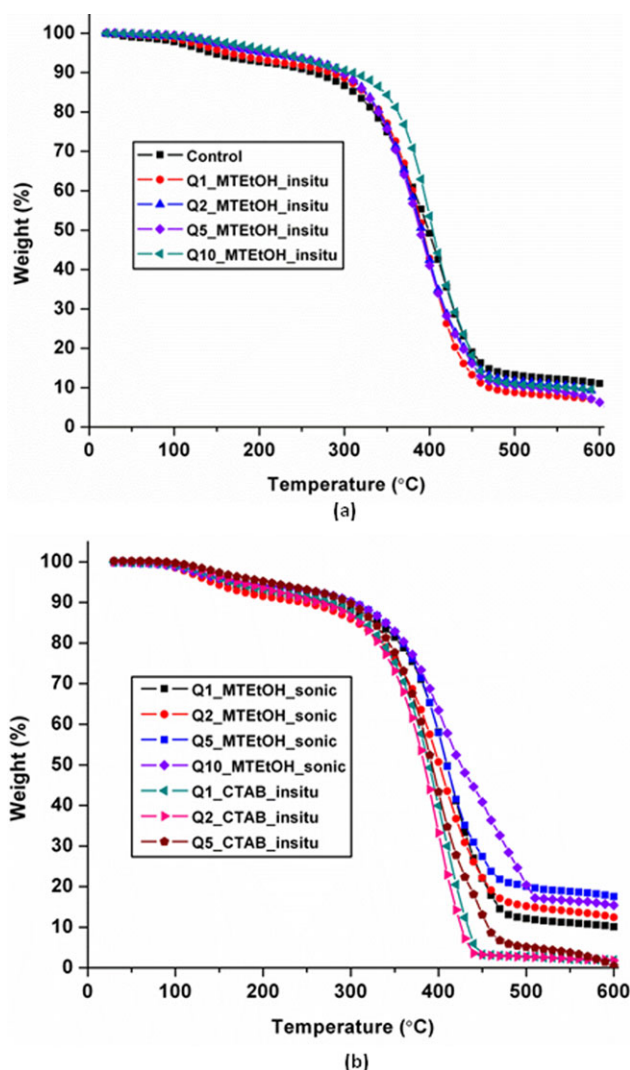
Figure 5. TGA degradation curves for (a) *in situ* preparation MTEtOH-containing coatings and (b) sonication MTEtOH-containing coatings and *in situ* preparation CTAB-containing coatings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the aliphatic group is derived from tallow and is a mixture of C_{16} and C_{18} hydrocarbons. In contrast, the aliphatic group in the CTAB organic modifier is a cetyl group, which is a C_{16} hydrocarbon. The CTAB organic modifier consists of a single species while the MTEtOH consists of a mixture of molecules with differing hydrocarbon chain lengths. In addition, the MTEtOH has two hydroxyethyl groups as substituents while the CTAB has only methyl groups as substituents. Thus, the MTEtOH has a more polar and hydrophilic character than CTAB. Furthermore, the MTEtOH is able to become incorporated into the polyester backbone during the *in situ* synthesis process. Thus, with the *in situ* process, the MTEtOH is able to very effectively plasticize the polymer, because it is chemically incorporated into the polymer and the network. When blended into the polymer through sonication, due to the polar nature of the MTEtOH as well as the polar nature of the polyester, it is expected that good interaction between the MTEtOH and

polymer can take place, resulting in a similar level of plasticization. For the CTAB organic modifier, the fact that plasticization is not observed tends to indicate that perhaps it is not as well dispersed into the polymer matrix as is the MTEtOH organic modifier and thus is not as effective in plasticizing the polymer.

Thermal Stability and Optical Clarity

The MTEtOH and CTAB organic modifiers did not influence the thermal stability of the coatings systems to the same extent as the mechanical properties. The TGA degradation curves are displayed in Figure 5, and the temperature at 10% weight loss ($T_{10}\%$) is reported in Table III. Each MTEtOH-containing and CTAB-containing coating had a $T_{10}\%$ at $\sim 300°C$, except for Q5_MTEtOH_sonic and Q10_MTEtOH_sonic. These two coatings had noticeable decreases in $T_{10}\%$, up to 50°C. Again, once the higher concentrations of MTEtOH were incorporated into the coating, diminishing thermal stability was observed. Comparisons of the nanocomposite degradation temperature to the organic modifier-containing coating of equivalent organic modifier concentration did not demonstrate any significant decreases in thermal stability. From this thermogravimetric analysis, the organic modifier does not appear to greatly impact the thermal stability of these coatings systems.

Coating optical clarity was not affected by incorporating the MTEtOH and CTAB organic modifiers into polyester resins (Table III). With the clay-containing nanocomposites, significant decreases in the transmittance were observed with 5–10 wt % clay loading, a trend not repeated with the organic modifier-containing coatings. The transmittance values of the organic modifier-containing coatings ranged from 93 to 99%. Neither the MTEtOH nor CTAB organic modifier decreased the optical clarity of these coatings. Therefore, the decreases in the optical clarity observed with the nanocomposite samples may be a direct result of the distribution of nanoclays within the coating, where less dispersed silicates diminished the transmittance of the nanocomposite films.

CONCLUSIONS

The structure and concentration of layered silicate alkylammonium organic modifiers MTEtOH and CTAB had a significant impact on both polyester resin and coating properties. MTEtOH-containing polyester molecular weight, viscosity, and T_g were all lower than their Cloisite® 30B clay-containing polyester counterpart regardless of organic modifier dispersion technique. These low-viscosity systems directly influenced the overall conversion of the UV-curable coatings systems, where the final conversion was approximately equivalent to the control coating. The higher viscosity CTAB-containing polyesters produced higher conversions. Coatings prepared from the MTEtOH-containing polyesters incorporated by either *in situ* synthesis or sonication demonstrated profound decreases in the mechanical performance, particularly storage moduli and crosslink density at high-organic-modifier concentrations (5–10 wt %). In the case of incorporation by sonication, these results paralleled those obtained with the corresponding nanocomposites made with Cloisite® 30B clay. In contrast, while the MTEtOH incorporated into the UV-curable materials using the *in situ* method

indicated that the organomodifier plasticized the materials, the corresponding nanocomposites showed a consistent increase in modulus values, indicating better interfacial interaction between the polymer matrix and the silicate reinforcement. Although coating mechanical properties were greatly affected by the organic modifiers, thermal stability and optical clarity of the coatings were relatively unaffected. This study demonstrates the impact of the organic modifier, without silicate filler, on the properties of polymer and coatings systems in which they are incorporated.

REFERENCES

1. Okada, A.; Kawasumi, M.; Kurauchi, T.; Kamigaito, O. *Polym. Prepr.* **1987**, *28*, 447.

2. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.* **1998**, *8*, 1179.

3. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J. Polym. Sci. Part A: Polym. Chem. 31*, 1755 **1993**.

4. Urresti, O.; González, A.; Fernández-Berridi, M. J.; Iruin, J. J.; Irusta, L. *J. Membr. Sci.* **2011**, *373*, 173.

5. Herrera-Alonso, J. M.; Marand, E.; Little, J. C.; Cox, S. S. *J. Membr. Sci.* **2009**, *337*, 208.

6. Gorrasi, G.; Tortora, M.; Vittoria, V.; Pollet, E.; Lepoittevin, B.; Alexandre, M.; Dubois, P. *Polymer* **2003**, *44*, 2271.

7. Lee, S.-R.; Park, H.-M.; Lim, H.; Kang, T.; Li, X.; Cho, W.-J.; Ha, C.-S. *Polymer* **2002**, *43*, 2495.

8. Ray, S. S.; Yamada, K.; Okamoto, M.; Ueda, K. *Polymer* **2003**, *44*, 857.

9. Ray, S. S.; Okamoto, M. *Prog. Polym. Sci.* **2003**, *28*, 1539.

10. Zhao, Q.; Samulski, E. T. *Macromolecules* **2005**, *38*, 7967.

11. Chang, J. H.; Jang, T. G.; Ihn, K. J.; Lee, W. K.; Sur, G. S. *J. Appl. Polym. Sci.* **2003**, *90*, 3208.

12. Zhou, C. H. *Appl. Clay Sci.* **2011**, *53*, 87.

13. Xidas, P. I.; Triantafyllidis, K. S. *Eur. Polym. J.* **2010**, *46*, 404.

14. Fornes, T. D.; Hunter, D. L.; Paul, D. R. *Macromolecules* **2004**, *37*, 1793.

15. Kim, Y.; White, J. L. *J. Appl. Polym. Sci.* **2005**, *96*, 1888.

16. Fan, X.; Xia, C.; Fulghum, T.; Park, M.-K.; Locklin, J.; Advincula, R. C. *Langmuir* **2002**, *19*, 916.

17. Fan, X.; Xia, C.; Advincula, R. C. *Langmuir* **2003**, *19*, 4381.

18. Mansoori, Y.; Atghia, S.; Zamanloo, M.; Gh, I.; Sirousazar, M. *Eur. Polym. J.* **2010**, *46*, 1844.

19. Nese, A.; Sen, S.; Tasdelen, M. A.; Nugay, N.; Yagci, Y. *Macromol. Chem. Phys.* **2006**, *207*, 820.

20. Qin, X.; Wu, Y.; Wang, K.; Tan, H.; Nie, J. *Appl. Clay Sci.* **2009**, *45*, 133.

21. Tan, H.; Nie, J. *J. Appl. Polym. Sci.* **2007**, *106*, 2656.

22. Tan, H.; Yang, D.; Han, J.; Xiao, M.; Nie, J. *Appl. Clay Sci.* **2008**, *42*, 25.

23. Zhao, H.; Farrell, B. P.; Shipp, D. A. *Polymer* **2004**, *45*, 4473.

24. Yang, Y.; Wu, D.; Li, C.; Liu, L.; Cheng, X.; Zhao, H. *Polymer* **2006**, *47*, 7374.

25. Bharathwaj, R.; Natarajan, U.; Dhamodharan, R. *Appl. Clay Sci.* **2010**, *48*, 300.

26. Djouani, F.; Herbst, F.; Chehimi, M. M.; Benzarti, K. *Constr. Build. Mater.* **2011**, *25*, 424.

27. Weimer, M. W.; Chen, H.; Giannelis, E. P.; Sogah, D. Y. *J. Am. Chem. Soc.* **1999**, *121*, 1615.

28. Ghannam, L.; Parvole, J.; Laruelle, G.; Francois, J.; Billon, L. *Polym. Int.* **2006**, *55*, 1199.

29. Konn, C.; Morel, F.; Beyou, E.; Chaumont, P.; Bourgeat-Lami, E. *Macromolecules* **2007**, *40*, 7464.

30. Salem, N.; Shipp, D. A. *Polymer* **2005**, *46*, 8573.

31. Samakande, A.; Sanderson, R. D.; Hartmann, P. C. *Eur. Polym. J.* **2009**, *45*, 649.

32. Samakande, A.; Juodaityte, J. J.; Sanderson, R. D.; Hartmann, P. C. *Macromol. Mater. Eng.* **2008**, *293*, 428.

33. Samakande, A.; Sanderson, R. D.; Hartmann, P. C. *Polymer* **2009**, *50*, 42.

34. Miyagawa, H.; Rich, M. J.; Drzal, L. T. *Polym. Compos.* **2005**, *26*, 42.

35. Shah, R. K.; Paul, D. R. *Polymer* **2006**, *47*, 4075.

36. Cervantes-Uc, J. M.; Cauich-Rodriguez, J. V.; Vazquez-Torres, H.; Cargias-Mesias, L. F.; Paul, D. R. *Thermochimica Acta* **2007**, *457*, 92.

37. Pluta, M.; Jeszka, J.; Boiteux, G. *Eur. Polym. J.* **2007**, *43*, 2819.

38. Fu, X.; Qutubuddin, S. *Polymer* **2001**, *42*, 807.

39. Kim, H. J.; Hwang, S. H.; Kim, J.; Huh, W.; Lee, S. W. *J. Kor. Indus. Eng. Chem.* **2004**, *15*, 533.

40. Pavlacky, E.; Ravindran, N.; Webster, D. C. *J. Appl. Polym. Sci.* **2012**, *125*, 3836.

41. Chen, Z.; Yang, G.; Zhang, Z. *Synth. Commun.* **2003**, *33*, 729.

42. Curtis, L.; Edwards, D.; Simons, R.; Trent, P.; Von Bramer, P. *Indus. Eng. Chem. Product Res. Dev.* **1964**, *3*, 218.

43. Carothers, W. H.; Arvin, J. A. *J. Am. Chem. Soc.* **1929**, *51*, 2560.

44. Yang, Y. S.; Pascault, J. P. *J. Appl. Polym. Sci.* **1997**, *64*, 133.

45. Liu, M.; Guo, B.; Du, M.; Lei, Y.; Jia, D. *J. Polym. Res.* **2008**, *15*, 205.