

The Effects of Organoclay Systems with Different Functional Groups on Photopolymerization Kinetics and Properties.

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Introduction

Polymer-clay hybrid nanocomposites based on organically modified clays have attracted considerable research interest both industrially and academically. Organoclays dispersed on a nanoscale dimension into a polymer matrix affords increases in mechanical, thermal, barrier properties and other performance characteristics of polymer composites with relatively small amounts of loading compared to that of microscale fillers.¹⁻³ On the other hand, in-situ photopolymerization technique provides many benefits in the preparation of polymer-clay nanocomposites while avoiding disadvantages of conventional composite manufacturing processes involving thermal degradation or releasing large amounts of volatile organic compounds (VOC) during the process.³⁻⁶ Obtaining well-exfoliated clay dispersion is important to achieve advanced performance in clay nanocomposites. To this end the modification of clay surfaces by suitable surfactants to improve compatibility in polymer matrices is required.^{3,4,7-8} However, most widely used non-reactive quaternary ammonium surfactants⁹⁻¹¹ may act as impurities affecting the final performance because they inherently do not participate in the polymerization reaction.¹² To overcome this disadvantage, novel polymerizable organoclays possessing reactive functional groups on have recently been investigated through modification of clay surfaces using photopolymerizable surfactants that can react with monomers and incorporate into ultimate polymer matrices during the photopolymerization process.¹³⁻¹⁴ It has been demonstrated using (meth)acrylate systems that photopolymerizable organoclays facilitate the further exfoliation of clay platelets during the polymerization process, resulting in additional property enhancement due to increased interaction between clay surfaces and polymer networks, as well as increased polymerization rate.

Recently, thiol-ene photopolymerization has been widely studied to overcome the drawbacks of (meth)acrylate-based photopolymerization such as oxygen inhibition and significant shrinkage during photopolymerization.¹⁵⁻¹⁸ Thiol-ene systems photopolymerize via a step-growth reaction mechanism that produces more homogeneous network structures than acrylate homopolymerization. Additionally, thiol-enes significantly reduce shrinkage and oxygen inhibition during photopolymerization.^{17,19-21} Due to flexible thioether linkages, however, it is not easy to obtain hard and tough cured materials via thiol-ene photopolymerization.²¹⁻²³ The addition of suitable amount of organoclay may allow enhancement in mechanical properties and may present enhanced gas barrier properties by generating longer diffusion distances for gas molecules.^{3,4} In addition, due to the inherent characteristics of step-growth reaction mechanism for thiol-ene photopolymerization, the type of functional group on clay surfaces and monomer diffusivity into clay galleries could affect the stoichiometric balance at the clay surface, resulting in difference behavior during the photopolymerization process.¹⁸ Because properties of thiol-ene photopolymer nanocomposites depend largely on the degree of exfoliation as well as network

structure of ultimate nanocomposites, understanding the relationship between photopolymerization behavior and clay exfoliation is important to achieve desirable properties.²⁴⁻²⁵

This research studies the relationship between clay exfoliation and photopolymerization kinetics for thiol-ene compositions with the addition of polymerizable organoclays bearing acrylate or thiol reactive moieties in their structure. The degree of clay exfoliation is compared and correlated with the kinetic results of the system. Selected thiol-ene systems composed of acrylic and thiol monomers having different hydrophilicity and functionality are investigated to examine the effect of monomer structure on clay exfoliation.

Experimental

Materials

Considering that hydrophilicity, functionality, and molecular weight may all influence exfoliation, a the relatively hydrophobic 1, 6-hexanedioldiacrylate (HDDA) was compared with less hydrophobic tripropyleneglycol diacrylate (TrPGDA) from Sartomer Inc. (Exton, PA). 1,6-hexanedithiol (HDT, Aldrich) having a similar structure to HDDA was selected as the difunctional thiol and trimethylolpropane trimercaptopropionate (TMPTMP, Aldrich) was used as a trifunctional thiol monomer to induce higher crosslink density.

Cloisite Na (Southern Clay Products – Gonzalez, TX), a natural montmorillonite, was ion exchanged with acrylate or thiol modified quaternary ammonium surfactants as described previously.¹⁴ Hexadecyl-2-acryloyloxy(ethyl) dimethylammonium bromide (C16A) is an acrylated quaternary ammonium surfactant synthesized following methodologies described previously.²⁶ Organoclays possessing thiol functional group were synthesized by incorporating a multifunctional thiol monomer into acrylic modified organoclays via Michael addition reaction based on the procedures reported elsewhere.²⁵ Two types of nonreactive organoclays were used for comparison. Cloisite 93A (CL93A, Southern Clay Products), a montmorillonite clay modified with dihydrogenated tallow, was used to represent typical commercial nonreactive organoclays, and TTABorganoclay modified by trimethyl tetradecylammoniumbromide (TTAB, Aldrich) was synthesized in the lab.¹⁴ 2,2-dimethoxyphenyl acetophenone (DMPA, Ciba Specialty Chemicals) was used as the free radical photoinitiator. Figure 1 shows the chemical structures of materials used in this research. All chemicals were used as received.

Methods

Real time infrared spectroscopy (RTIR, Thermo Nicolet Nexus 670) was used for the kinetic study for thiol-ene photopolymerization.²⁷ Monomer mixtures were placed between two sodium chloride plates with 15 μm spacers. The polymerization was performed with a 365 nm light with an irradiation intensity of 3.0 W/cm². During irradiation RTIR absorption spectra were continuously collected with 6 scans per second and evaluated at 810 cm⁻¹ and 2575 cm⁻¹ for acrylate and thiol conversion respectively. Conversion profiles as a function of time were obtained by monitoring the decrease in the height of the absorbance peak from the initial height of the absorbance peak prior to polymerization. Small angle x-ray scattering (SAXS) studies were used to evaluate the exfoliation degree of organoclays. A Nonius FR590 X-ray apparatus equipped with a Cu K α radiation source ($\lambda = 1.54 \text{ \AA}$) at 40kV and 30mA intensity was utilized for SAXS experiments.²⁸ Dark curing experiments were performed by shuttering the light at a designed time to control the initial illuminating conversion and then continuously monitoring a change in functional group conversion without irradiation to compare the change in conversion in the dark.²⁹ Dynamic-thermomechanical experiments were conducted utilizing dynamic

mechanic analysis (DMA- Q800 DMA TA Instruments) To investigate the effect of organoclays on ultimate mechanical properties, rectangular samples with dimensions of 2 x 13 x 25mm were utilized. Specimens were tested under tensile mode at 1Hz frequency from -100C to 100C with a heating rate of 3°C/min.

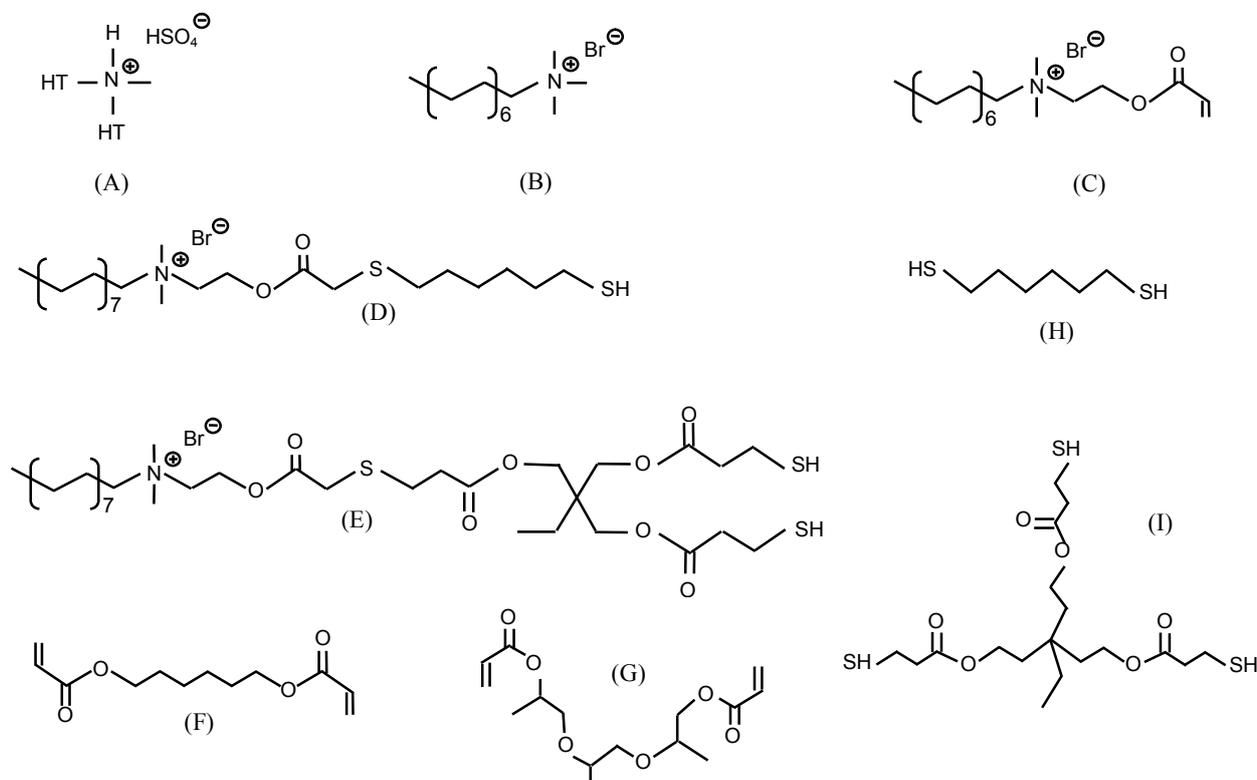


Figure 1. Chemical structures of A) methyl dihydrogenated tallow sulfonate, (Closite 93A) B) tetradecyl trimethylammonium bromide (TTAB), C) hexadecyl-2-acryloyloxy(ethyl) dimethylammonium bromide (C16A) D) tetradecyl 2-(1,6-mercaptohexyl mercaptane) acetoxy(ethyl) dimethylammonium bromide (C14AT; Monothiol) E) tetradecyl 2-(bis(3-mercaptopropionate) mercaptopropionyl trimethylolpropyl) acetoxy(ethyl) dimethylammonium bromide (PSH2; Dithiol), F) 1,6-hexanediol diacrylate (HDDA), G) tripropylene glycol diacrylate (TrPGDA), H) 1,6-hexanediol dithiol (HDT), and I) trimethylolpropane tris(3-mercaptopropionate) (TMPTMP).

Results and Discussion

Although the addition of fillers usually decreases the photopolymerization rate by both scattering and absorbing the incident light,³⁰ previous research based on (meth)acrylate monomers demonstrated that well exfoliated clay particles induce higher rates of photopolymerization with the addition of polymerizable organoclays.^{14,15,25} It is believed that both the template ordering effect³¹ of reactive monomers on the clay surface and decreases in termination rate by immobilization of propagating chain during the photopolymerization compensate for the light interference of clays inducing increases in overall polymerization rate.¹⁴

Due to the inherent step-growth reaction mechanism of thiol-ene photopolymerization, thiols can only react with ene groups resulting in photopolymerization kinetics that primarily depend upon the stoichiometric balance between thiol and ene functional groups. When polymerizable organoclays are

incorporated into thiol-ene photopolymerization systems, several factors could affect the local stoichiometric balance. For instance, the type of functional group on clay surfaces may affect the functional group ratio especially near the organoclay surfaces and could have greater influence than the overall (meth) acrylate compositions. Lee *et al.* demonstrated that thiol functionalized silica nanoparticles decreased the polymerization rate while there was less change induced by nonreactive particles because of stoichiometric imbalance at the spherical silica surface and immobilization of propagating thiyl-radicals.¹⁸ In addition, the difference in monomer diffusivity into clay particles based on the degree of compatibility between monomers and organoclays could potentially affect the stoichiometric balance in clay galleries. The organic modification of natural montmorillonite clays usually decreases the polarity of clays. For examples, C16A acrylated clay modified from Cloisite Na natural clay shows higher viscosity in tetrahydrofuran while it shows lower viscosity in polar ethanol/water mixture implying that the surface decreases in polarity by surfactant modification. With further modification from C16A acrylated clay to PSH2 thiolated clay, the same trend is observed. Among the three organoclays, PSH2 thiol clay shows the most hydrophobic characteristics as indicated by viscosity behavior. Due to this difference in hydrophobicity of organoclays, the chemical structure of monomers might be closely related with organoclay compatibility.

To demonstrate the effect of surface modification of clays on the compatibility with monomer systems comprised of different thiol-acrylate combinations, exfoliation behavior of three different types of organoclays was investigated, including non-polymerizable organoclays modified by TTAB and two polymerizable systems modified with C16A, and PSH surfactants, having acrylate and thiol functional groups respectively. Exfoliation behavior of these organoclays was examined via SAXS. Figure 2

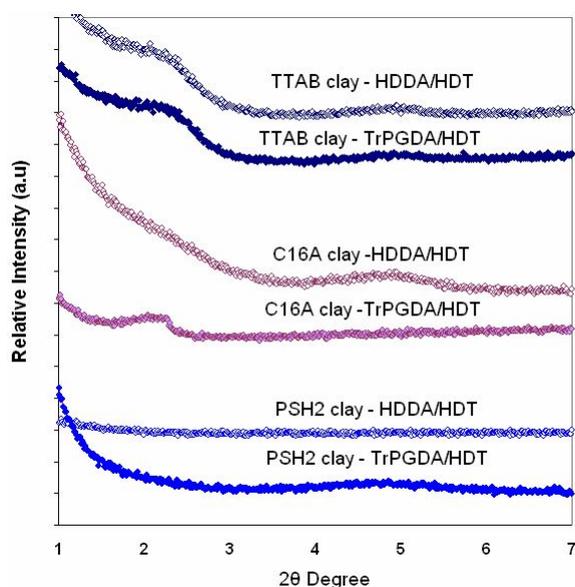


Figure 2. SAXS profiles of 3wt% TTAB-organoclay (●, ○), 3wt% C16A-organoclay (▼, ▽), and 3wt% PSH2-organoclay (■, □) for HDDA/HDT (unfilled symbols) and TrPGDA/1,6-HDT mixture (filled symbols) with 2:1 molar ratio based on functional groups. Photopolymerizations were initiated with 0.1 wt% DMPA using 365nm light at 3.0 mW/cm².

shows the scattering profiles of 3wt% organoclay in different monomer mixtures including hydrophobic HDDA/HDT and less hydrophobic TrPGDA/HDT. The profiles are offset for better comparison. In the SAXS profiles, a noticeable primary peak at approximately 2.3° and a small second peak around 5° of 2θ degree corresponding to d-spacing of 3.7 nm and 1.8 nm respectively indicate intercalated organoclay domains, whereas the small primary peak or absence of a peak suggests that the organoclays are significantly exfoliated. The strong primary peak in TTAB organoclay indicates the clay is mostly intercalated when using these non-polymerizable surfactants. Acrylated organoclays (C16A) are almost completely exfoliated in the TrPGDA/HDT system but not exfoliated in hydrophobic HDDA/HDT. In contrast, thiolated PSH2 organoclays are completely exfoliated in HDDA/HDT system having at least a 8.8 nm d-spacing which is the detection limit of the instrument and also show enhanced exfoliation in TrPGDA/HDT systems compared to that of HDDA/HDT. The exfoliation behavior discussed in Figure 2 implies acrylated organoclay has better compatibility with hydrophilic monomer systems

while the compatibility of thiolated organoclay decreases by increasing hydrophilicity of monomer systems.

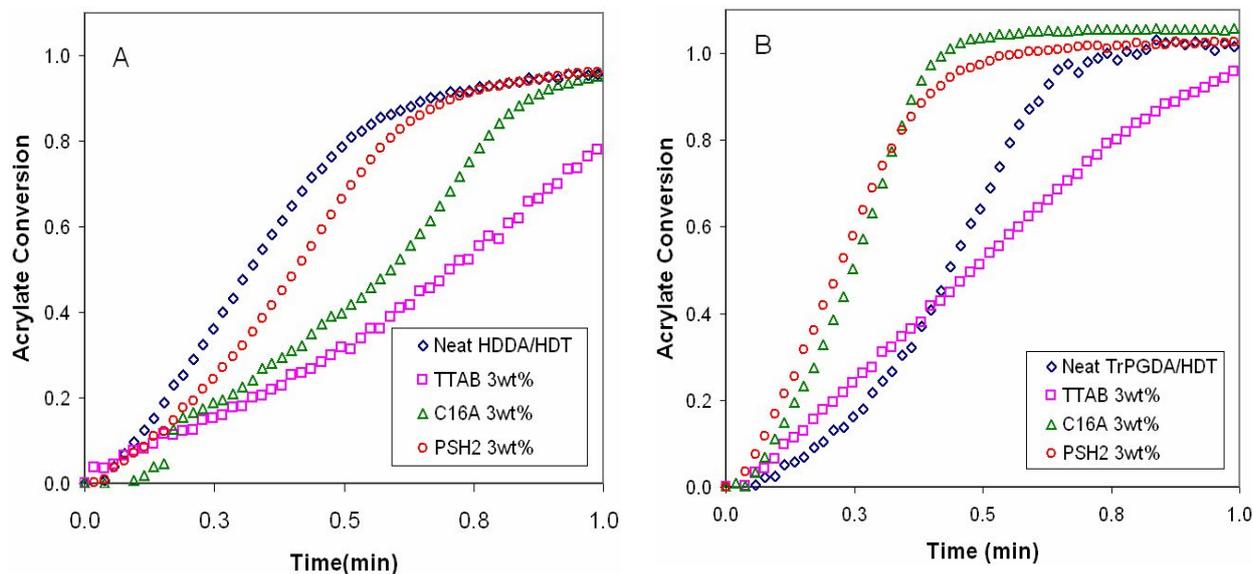


Figure 3. Acrylate double bond conversion profiles of thiol-acrylate mixture with 2:1 molar ratio (based on functional groups). Shown are (A) conversion profiles for HDDA/HDT and (B) for TrPGDA/HDT with 3 wt% organoclays. Photopolymerizations were initiated with 0.1 wt% DMPA using 365 nm light at 3.0 mW/cm².

To understand how the difference in degree of exfoliation in organoclays affects the photopolymerization behavior, RTIR was utilized to examine functional group conversion. For these studies, 3wt% organoclay was added to the two thiol-ene formulations having different hydrophilicity discussed previously. The rate of photopolymerization as a function of time for each thiol-acrylate mixture having 2 to 1 mole ratio is shown in Figure 3. Two types of polymerizable organoclay, C16A (acrylated) and PSH2 (thiolated) organoclays were compared with non-reactive TTAB organoclay. Neat thiol-acrylate mixtures without any organoclay were used as controls. As predicted, the rate of polymerization decreases significantly by adding non-reactive TTAB organoclay due to negative filler effects such as scattering and absorbing the incident light. When C16A organoclay was incorporated into HDDA/HDT systems, the rate of photopolymerization also significantly decreased by adding 3wt% of clays as shown in Figure 3 (A). This behavior again indicates the effect of light interference from clay particles is more dominant than effects that may increase the rate such as template ordering of monomers and immobilizing propagating radicals on the organoclay surface. The incorporation of thiolated organoclay into HDDA/HDT mixture, however, induced no significant decrease in photopolymerization rate. This implies that thiolated clays in HDDA/HDT mixture provide sufficient surface areas for inducing increases in polymerization rate even at levels as low as 3wt%. This different polymerization behavior is only possible when thiolated organoclays are more exfoliated than acrylated organoclays in the HDDA/HDT monomer composition. This expectation is consistent with the results in clay exfoliation discussed previously. Overall, the kinetic behavior suggests that thiolated organoclays are more compatible in relatively hydrophobic HDDA/HDT mixtures compared to acrylated organoclays.

In contrast to the trend of the HDDA/HDT system, the addition of organoclays to the TrPGDA/HDT system increases polymerization rate regardless of the type of polymerizable organoclay as shown in Figure 3(B). This result indicates monomers are well diffused into the clay galleries allowing significant monomer/clay interaction. Such behavior is also consistent with the exfoliation results of organoclays in TrPGDA/HDT as shown in Figure 2. In addition to the different effects on acrylate conversion behavior, the type of polymerizable organoclays induces the difference in the degree of thiol-ene step polymerization. Figure 4 shows the thiol conversion profiles of the same TrPGDA/HDT mixture to Figure 3(B). Interestingly, while the photopolymerization rates of the two polymerizable organoclay systems were not significantly different, overall thiol conversion with thiolated organoclay system is about 15% higher than that with acrylated organoclay. This implies thiolated organoclays enhance thiol-ene reaction. Overall, quite different polymerization behavior was observed between HDDA/HDT and TrPGDA/HDT systems with the addition of organoclays. Because thiol-ene photopolymerization occurs via a step-growth mechanism, that is, thiol can react with only acrylate double bond while acrylate can react with both thiol and acrylate, it is reasonable to assume that the affinity

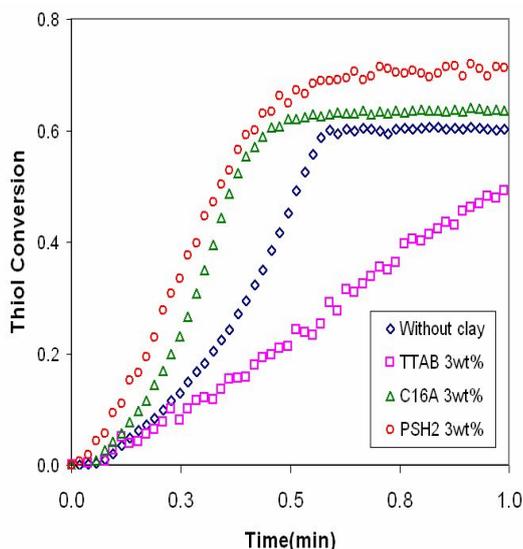


Figure 4. Thiol conversion profiles of 2:1 molar ratio TrPGDA/1,6-HDT mixtures with addition of 3wt% organoclays. Photopolymerizations were initiated with 0.1wt% DMPA using 365 nm light at 3.0mW/cm².

between thiol and acrylate species might be a critical factor to determine the degree of thiol-ene reaction during the photopolymerization process.

The previous results demonstrate that the type of functional group in organoclays significantly influences the photopolymerization behavior of thiol-ene systems. To further understand what

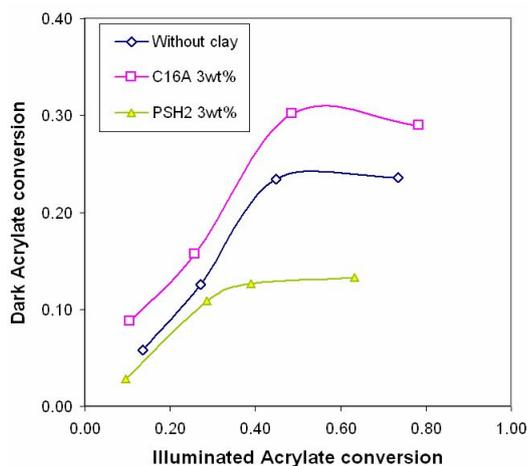


Figure 5. Dark acrylate conversions for equimolar TrPGDA/HDDA mixture at different initial illuminated conversions. Photopolymerizations were initiated using 365 nm light at 3.0mW/cm² with 0.1wt% of DMPA.

mechanism near the surface of organoclay causes the difference in photopolymerization behavior, dark curing experiments were performed to monitor the difference in further reaction after eliminating light from the system.²⁹ Once the light was blocked at certain points of time during photopolymerization, no new radicals can be generated. Any reaction after eliminating the light is induced by residual radicals in the system. By comparing the dark curing behavior of neat system without organoclay with that of the systems including polymerizable organoclays, the effects of organoclay functionality on photopolymerization mechanism can be further understood. Dark curing behavior for equimolar mixtures of TrPGDA/HDDA containing 3wt% C16A acrylated organoclays or PSH2 thiolated organoclays are shown in Figure 5 with various initial illuminated

conversions. A neat monomer mixture was also evaluated for comparison. In the figure, dark acrylate conversion as a function of illuminated conversion based on RTIR experiments is plotted. To control the initial illuminated conversion, light was shuttered after illumination for 6, 12, 18 and 24 seconds. Initially, regardless of the system, dark conversion increases as the illuminated conversion reaches about 0.5. This behavior is mainly because increased system viscosity at higher illuminated conversion decreases the rate of bimolecular termination due to diffusion limitations on radicals. In addition, although all experimental systems have different initial illuminated conversions, the systems with acrylated organoclays always show higher dark conversion while thiolated organoclay systems exhibit lower dark conversion than the neat system.

These differences may come from the different characteristics of two residual radicals on each organoclay surfaces. Acrylated organoclay systems exhibit higher dark conversion than the neat system perhaps due to the immobilization of propagating acrylate chain radicals that are on the organoclay surfaces, which results in reduction of bimolecular termination based on significantly lower mobility. Residual acrylate radicals that are on the acrylated organoclay surfaces are thus likely to have much longer radical lifetime than those in bulk regions. This immobilization of radicals makes the effective concentration of residual radicals in the systems with acrylated organoclay always higher than the neat system at any initial illuminated conversion. Because the residual radicals on the surfaces of acrylated organoclays essentially originate from acrylic double bonds and could rapidly react with other acrylate and/or thiol monomers, much higher dark acrylate conversion are induced. While the residual radicals on the surfaces of thiolated organoclays are also immobilized as in the systems with acrylated organoclays, the radical is the thiyl radical and can react only with double bonds of acrylated monomers, which result in slower reaction rate due to lower collision probability of the residual thiyl radical to acrylate monomer than to both acrylate and thiol monomers. In addition, the step-growth mechanism of thiol-ene reaction inevitably involves the chain transfer in each step, which makes its reaction rate slower than acrylate homopolymerization.³² The propagating secondary radical produced by the reaction between thiyl radical and acrylic double bond should be transferred to another thiol monomer for further reaction. Because the rate of radical termination is much faster than that of radical transfer in general, effective radical concentration on the surfaces of thiolated organoclay is rapidly decreased if there is no further radical initiation. All of these functions may contribute to lower dark conversion in the system with thiolated organoclays. This difference in dark curing behavior also confirms that thiolated organoclay accelerates the thiol-ene copolymerization by significant formation of thiyl radicals on the clay surfaces.

DMA results further support the proposed mechanism for the polymerization behavior between acrylated and thiolated organoclays. The storage modulus profiles as a function of temperature for TrPGDA/HDT systems with addition of 3 wt% organoclays are shown in Figure 6(A). For this relatively low cross-linked systems, when acrylated organoclay was incorporated, significant increases in modulus at the rubbery stage over glass transition temperature was observed due to dominant acrylate homopolymerization. The modulus of the system with thiolated organoclays was lower than the system with acrylated organoclays but was still slightly higher than the neat system. To the contrary, the diacrylate with trithiol showed a much higher increase in modulus when thiolated organoclay was added than those of neat and acrylated organoclay systems as shown in Figure 6(B). On the other hand, enhanced thiol-ene step growth reaction by addition of thiolated organoclays may make the polymer chain more flexible itself, but it is hypothesized that much more cross-linked networks are generated by trithiol, compensating for any enhancement in flexibility.

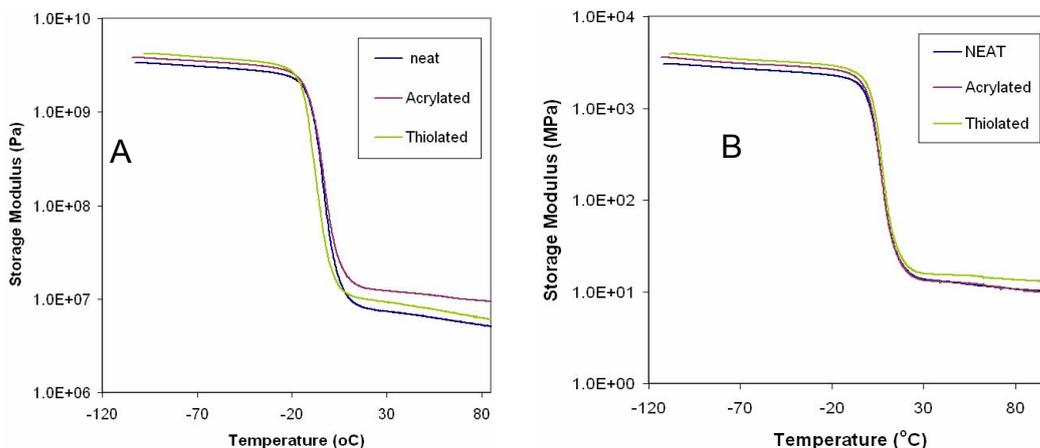


Figure 6. Storage modulus profiles of (A) diacrylate/dithiol (TrPGDA/HDT) (B) diacrylate/trithiol (TrPGDA/TMPTMP) with 3 wt% of organoclays. Acrylate/Thiol =2/1 mole ratio based on functional group.

Conclusions

The effects of the type of polymerizable organoclay on in-situ thiol-ene photopolymerization behavior have been investigated. The compatibility between organoclays and monomer systems affects the degree of clay exfoliation significantly. Both the incorporation of functional groups on organoclay surfaces and enhanced clay exfoliation increase overall photopolymerization rate of thiol-ene compositions while lower degrees of clay exfoliation decreases it. Comparing the results in polymerization behavior between non-reactive organoclays and polymerizable organoclays, the most important mechanism driving the increase in photopolymerization rate is the immobilization of propagating radicals during polymerization. In addition, the type of polymerizable organoclays determines the degree of thiol-ene step polymerization by primarily affecting stoichiometric balance between thiol and ene functional group at and near the clay surfaces. RTIR experimental and dark curing results support that thiolated organoclays enhance thiol-ene reaction compared to acrylated organoclays. Mechanical properties also thiol-ene networks in the cured thiol-ene networks by incorporating thiolated organoclays.

Acknowledgements

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