The Effects of Polymerizable Organoclays on Photopolymerization Behavior and Ultimate Properties of Thiol-ene Nanocomposite Systems.

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Introduction

The incorporation of clays into a polymer matrix with well-exfoliated morphologies can significantly enhance many performance aspects such as mechanical and barrier properties, thermal stability, and chemical resistance, etc.[1-4] *In situ* preparation of polymer-clay nanocomposites based on photopolymerization, on the other hand, provides a simple way to get nano-scale dispersion of clay particles, avoiding several disadvantages of conventional processes.[5-9] The aim of this research is the development of advanced photopolymer-clay nanocomposites combining the advantages of photopolymerization and nanoscale dispersed clay particles. In this research, unique polymerizable surfactants have been developed to modify the clays. The incorporation of reactive groups on the clay surfaces can maximize the interaction between clay and organic phase during and after polymerization as well. Our previous results in this research have demonstrated that the addition of polymerizable organoclays induce significant improvement in both nanocomposite properties with enhanced clay exfoliation and photopolymerization rate as well compared to the system with conventional nonreactive organoclays. [10-12]

Due to its unique polymerization mechanism and properties, on the other hand, thiol-ene photopolymerization has been widely studied in recent decade. Thiol-ene photopolymers based on the step polymerization mechanism could overcome major drawbacks of free radical polymerization such as oxygen inhibition and polymerization shrinkage.[13-16] In recent years, clay-nanocomposites also has been investigated based on thiol-ene photopolymerization systems to understand the effects of polymerizable organoclays on polymerization behavior as well as ultimate nanocomposite properties.[12, 17-18] Different clay exfoliation and photopolymerization kinetics were observed by changing the monomer composition controlled in polarity and functionality. Incorporation of polymerizable organoclays with sufficient exfoliation increased photopolymerization rates significantly due to increases in the effective surface area inducing more surface immobilization of propagating radicals. Chemical compatibility between monomers and organoclay is of primary importance for achieving clay exfoliation and determining monomer composition in the clay gallery as well. Thiolated organoclays enhance thiol-ene reaction proportionally to added clay concentration up to 10 wt% while acrylated organoclays encourage acrylate homopolymerization. The addition of thiolated organoclays in moderately cross-linked thiol-ene systems usually decreases both modulus and glass transition temperatures of the systems due to enhanced thiol-ene reaction.

Based on these studies in the reaction mechanism and thermo-mechanical properties with polymerizable organoclays, this research has studied the effects of polymerizable organoclays on both oxygen inhibition and volume shrinkage. While non-reactive organoclay and acrylated organoclay do

not change volume shrinkage during thiol-acrylate photopolymerization, thiolated organoclays induce less shrinkage than a neat system. For oxygen inhibition of various thiol-acrylate systems comprised of oligomer-monomer mixtures, the use of thiolated organoclays is more beneficial to improve the reaction of thiol-acrylate mixtures under oxygen atmosphere than acrylate organoclays.

This research further investigated the overall effects of adding polymerizable organoclays on oxygen inhibition, shrinkage in thiol-acrylate polymerization, and ultimate performance of clay-photopolymer nanocomposites. For more practical information, oligomer-monomer systems based on the examples of industrial formulations have been utilized for the experiments. Mechanical properties based on tensile experiments and thermal properties have been examined and the influence of clays on nanocomposite on toughness has been studied. Based on the results in volume shrinkage behavior, the effect of organoclays on shrinkage stress, which could provide useful information for many real applications, has been further investigated. On the other hand, improving the gas barrier properties is one of the most anticipated characteristics of clay-photopolymer systems. Water vapor permeability has been examined based on an industrial ASTM standard by changing the monomers as well as organoclays to compare the gas barrier property.

Experimental
Materials
Considering that hydrophilicity, functionality, and molecular weight may all influence exfolation, 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.[19-20] 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 elswhere.[10] Two types of nonreactive organoclays were used for comparison. Closite 93A (CL93A, Southern Clay Products), a montmorillonite clay modified with dihydrogenated tallow, was used to represent typical commercial nonreactive organoclays. 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.[21-22] 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 3.0W/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.
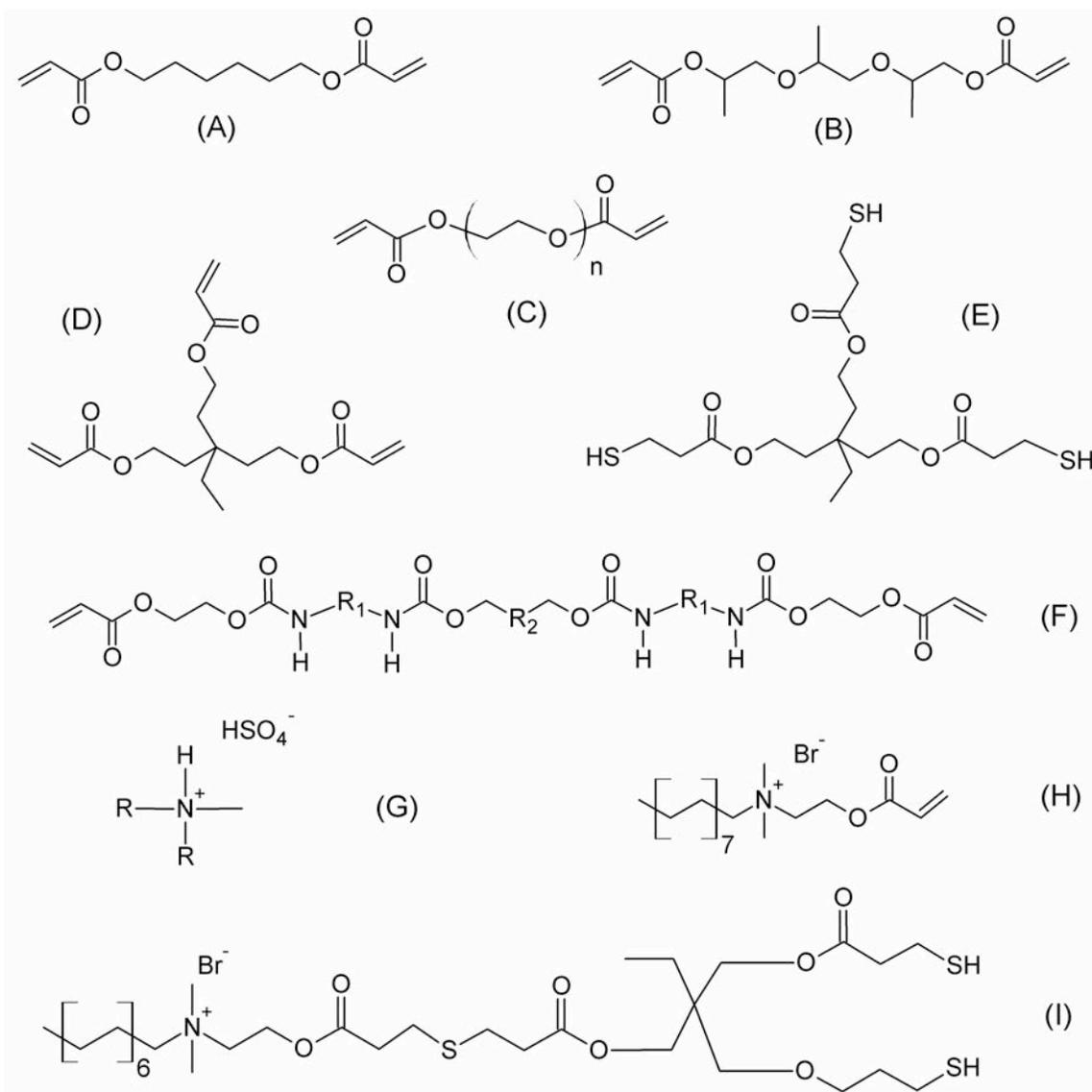
Figure 1. Chemical structures of monomers (A) 1,6-hexanediol diacrylate (HDDA), (B) tripropylene glycol diacrylate (TrPGDA), (C) polyethyleneglycol diacrylate (PEGDA, MW=742), (D) trimethylolpropane triacrylate (TMPTA), (E) trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), and (F) polyurethane diacrylate oligomer (CN9009). Additionally, the chemical structure of organoclay modifiers (G) methyl dihydrogenated tallow sulfonate (CL93A), (H) hexadecyl-2-acryloyloxy(ethyl) dimethylammonium bromide (C16A), and (I) tetradecyl 2-(bis(3-mercaptopropionate) mercaptopropionyl trimethylolpropyl) acetocy(ethyl) dimethylammonium bromide (PSH2) are shown.

Results and Discussion

To verify this functional group effect, RTIR experiments were performed for the two systems comprised of the TrPGDA/TMPTMP equimolar mixtures based on functional group with addition of different polymerizable organoclays. Figure 2 shows the thiol conversion profiles as a function of time with a gradual increase of the amount of thiolated organoclays. The unfilled TrPGDA/ TMPTMP system exhibits approximately 50% final thiol conversion. It appears that enhancement in final thiol conversion is related to greater clay concentration albeit to different degrees based on the type of organoclay. When 5 wt% thiolated organoclays were added, the final thiol conversion increased to 75% that corresponds to 50% enhancement from the ultimate conversion of the unfilled system. Further addition of organoclays up to 10 wt% does not enhance final thiol conversion much but increases the rate of photopolymerization. Even with this prominent enhancement in final thiol conversion, only slight decreases in final acrylate conversion were observed (not shown). The final acrylate conversion decreased from unity for the unfilled system to 0.94 by adding 10 wt% of thiolated organoclays. This behavior also indicates enhanced thiol-ene reaction. The use of trithiol increases cross-link density of the system with enhancement of thiol-ene reaction, resulting in faster gelation of the system before complete reaction of acrylate functional group. On the other hand, the addition of acrylated organoclays does not change final conversion or polymerization rate for both acrylate and thiol functional groups.

While acrylate photopolymers exhibit many advantages, several drawbacks could be improved to enhance photopolymer applications. One of major drawbacks is high volume shrinkage and shrinkage stress during photopolymerization. Low dimensional stability during polymerization often brings about significant problems in final performance of cured materials. For instance, high shrinkage stress deforms coated films and decreases peel-strength in many adhesive applications. Thiol-ene photopolymers polymerize via a step reaction mechanism with highly homogeneous cross-linked networks throughout the cured system.[23-24] This step polymerization mechanism thus can reduce polymerization shrinkage significantly compared to that of acrylate homopolymerization. In previous experiments, it has been demonstrated that adding polymerizable organoclays can either increase or decrease thiol-ene reaction according to the type of functional groups on the organoclay surface. If there is a significant difference in degree of thiol-ene reaction based on the organoclay type, the organoclay may also affect the amount
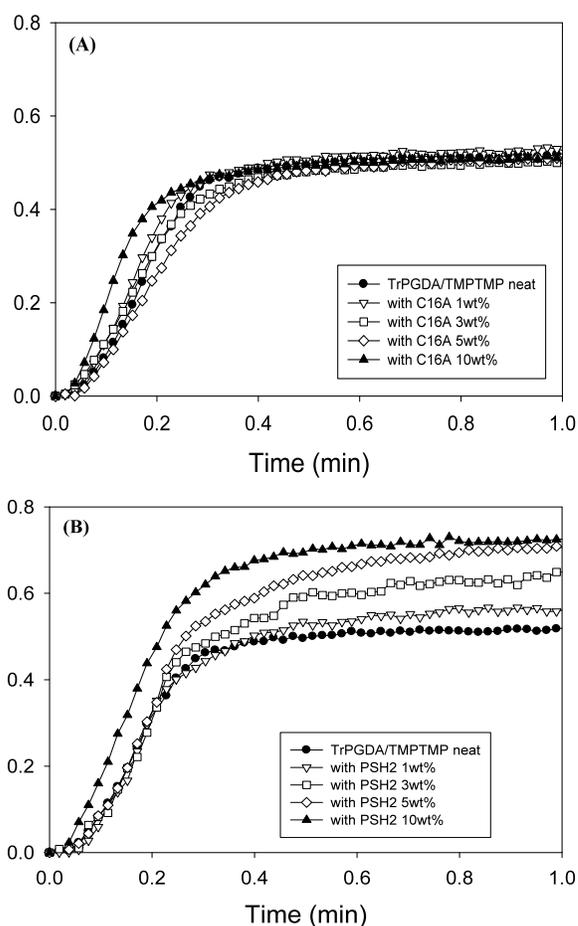
Figure 2. RTIR thiol conversion profiles with gradual increase in organoclay concentration for TrPGDA/TMPTMP equimolar mixture based on functional groups.

of polymerization shrinkage. In general, adding thiol monomers into acrylate photopolymer systems can reduce polymerization shrinkage, but also leads to significant decrease in thermo-mechanical properties such as modulus and glass transition temperature of cured products.[25-26] If incorporation of polymerizable organoclays can induce less polymerization shrinkage with increased thermo-mechanical properties, they could be beneficial for designing thiol-ene systems in many applications

A 1:1 weight mixture of PEGDA (Mw=742) and TrPGDA was used as an acrylate oligomer-monomer mixture having moderate polymerization shrinkage. Designated amounts of TMPTMP were added to control the thiol content in the systems. The addition of 5 mol% thiol functional groups significantly decreases the polymerization shrinkage and then continues to reduce the shrinkage up to addition of 20mol% thiol groups. Further addition of thiol groups does not reduce the polymerization shrinkage significantly. To demonstrate the organoclay effect on polymerization shrinkage, 3wt% of polymerizable organoclays were incorporated into acrylate system and thiol-ene system as shown in Figure 3. Even with thiol monomers in the system, incorporation of only 3wt% thiolated organoclays induces meaningful reduction in polymerization shrinkage. Adding acrylated organoclays shows either a small decrease or increase in polymerization shrinkage of the systems. It is believed that enhanced thiol-ene reaction by adding thiolated organoclays reduces polymerization shrinkage.
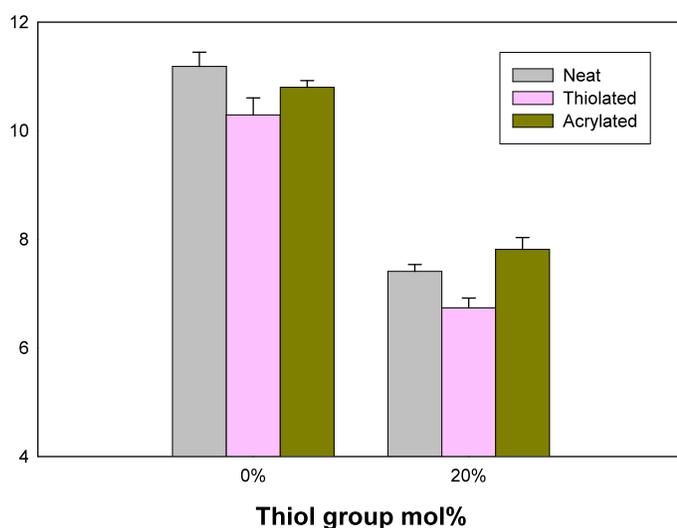
Figure 3. Polymerization induced shrinkage for PEGDA/TrPGDA systems with 3wt% organoclays for acrylate and thiol-acrylate formulations.

This decrease in volume shrinkage by adding thiolated organoclays could also be important in actual performance of nanocomposites because shrinkage stress is usually formed at the very end of polymerization stage. A few percent improvement in volume shrinkage may, thus, induces significant decrease in polymerization shrinkage stress that is more crucial in many real applications such as coating and packaging industries based on thin substrates. In order to investigate the effect of adding organoclays on shrinkage stress during photopolymerization, a modified ASTM method was used.[27-28] Fig. 4 shows the shrinkage stress profiles of (A) acrylate monomer-oligomer mixture and (B) trithiol-triacrylate mixture as a function of organoclay concentration. The natural clay system and nonreactive organoclay system were compared with the systems including acrylated or thiolated polymerizable organoclays. For the acrylate mixture, the addition of 5wt% acrylated organoclay decreases polymerization shrinkage stress by approximately 50% from the neat system while the same amount of thiolated organoclay or non-reactive organoclay only decreases the stress by about 30%. The addition of natural clays also decreases the stress to some degree but not nearly as much as the organoclays. In the

thiol-acrylate mixture both thiolated and acrylated organoclays greatly decrease the stress compared to that of neat system. An over 80% decrease in shrinkage stress is obtained by adding 5wt% organoclays while natural clay and nonreactive organoclays reduces the stress only 30% and 40%, respectively, with the same amounts of clay. The behavior from these different monomer mixtures by adding various clays imply that the improvement in shrinkage stress is due to not only the rearrangement of clay particles but also the different impact on the polymerization mechanisms of the systems by changing the type of reactive groups on the clay surfaces. Interestingly, based on the results of thiolated organoclays in acrylate mixture without thiol monomers, the thiolated organoclays act similarly to nonreactive organoclays as it was observed in our other studies demonstrating the effects of reactive groups on reaction mechanisms.
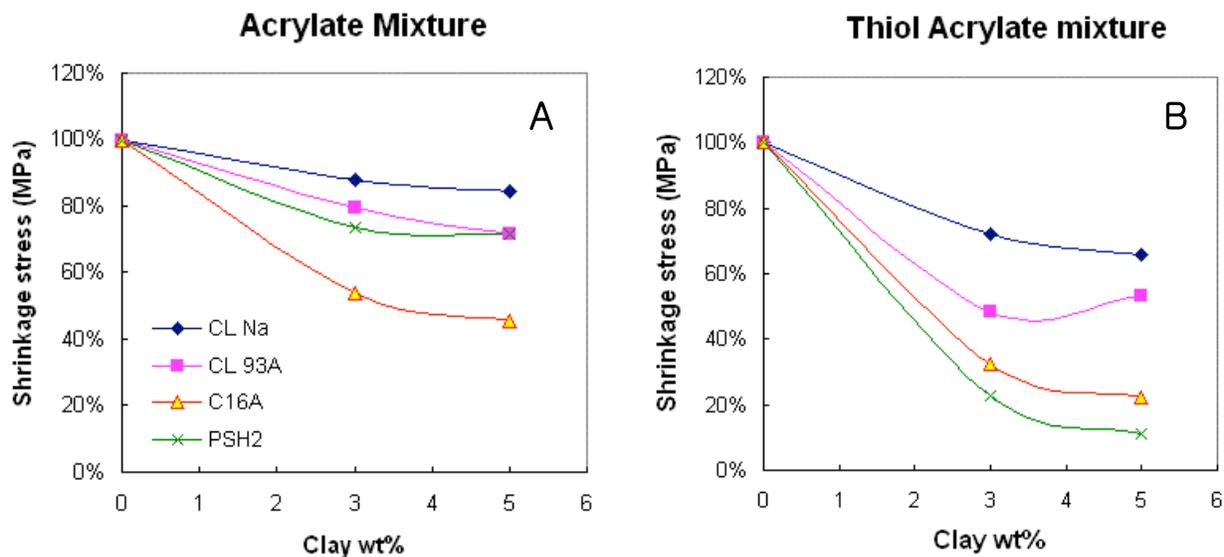
Figure 4. Shrinkage stress during photopolymerization of (A) acrylate mixture comprised of urethane diacrylate oligomer (CN9009)/TrPGDA/TMPTMA=30/30/40 wt% and (B) thiol-acrylate mixture comprised of TMPTA/TMPTMP=60/40 wt% with different types of clays. Where, CL Na is commercial natural clay (Closite Na), CL93A is nonreactive commercial organoclay (Closite 93A), and C16A and PSH2 are acrylate and thiolated polymerizable organoclays, respectively.

The other major advantage of thiol-ene photopolymerization is that it is less inhibited by oxygen than acrylate homopolymerization. This behavior is mainly due to inherent step growth reaction mechanism of thiol-ene polymerization based on chain transfer of secondary radical to other thiol monomers. This radical chain transfer to thiol monomers also works when the secondary radicals are peroxide radicals after reacting with oxygen dissolved in the systems as shown in the equations below, resulting in significantly lowered oxygen inhibition. [29-31]

Figure 5 shows how the addition of thiol monomers into acrylate systems reduces the oxygen inhibition. PEGDA/TrPGDA with different amount of TMPTMP was polymerized at 3mW/cm2 using 0.2 wt% DMPA. Shown polymerization profiles were obtained utilizing photo-DSC under air. Comparing the neat acrylate system, addition of only 5 mol% thiol monomers based on functional group ratio induces significantly faster profiles and continues to enhance the polymerization rate by increasing the amount of TMPTMP. When 30 mol% of thiol functional groups was added, the polymerization rate is similar to that observed under nitrogen atmosphere (not shown).

To investigate whether the incorporation of polymerizable organoclays could further reduce oxygen inhibition, 5wt% polymerizable organoclays having different functional groups were added. In Figure 6, reaction profiles on the left are for systems with addition of acrylated organoclays and those on the right are with thiolated organoclays. Without thiol monomers, both polymerizable organoclays show a longer induction time compared to the neat acrylate system. Interestingly, when thiolated organoclays are incorporated into the neat acrylate system, a much longer induction time is observed and the reaction is much slower than for the neat system. This implies that the peroxide radicals produced on thiolated organoclay surfaces by reaction with secondary radicals and oxygen have no reactivity in absence of thiol monomers and act as radical scavengers.
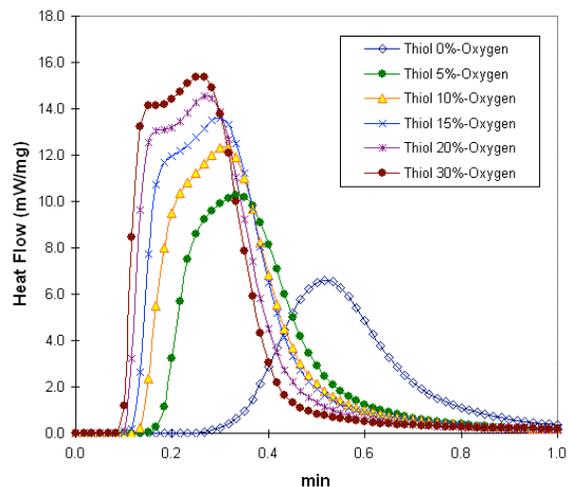
Figure 5. Photo-DSC polymerization profiles of PEGDA/TrPGDA systems with gradual increase of TMPTMP thiol monomers up to

For easy comparison, the polymerization profiles for 5 mol% thiol formulation with inclusion of different organoclays are plotted in Figure 6. Addition of nonreactive organoclay (CL93A) significantly decreases polymerization rate from that of a neat system under oxygen atmosphere. Two polymerizable organoclays, however, do not change induction time and overall polymerization rate significantly. Comparing the profiles of the system with acrylate organoclays to that of the system with thiolated organoclays, thiolated organoclays slightly enhance the polymerization rate and reduce initial induction time as well. The addition of thiolated organoclays makes the overall thiol mol% higher from the thiol groups on the clay surface.
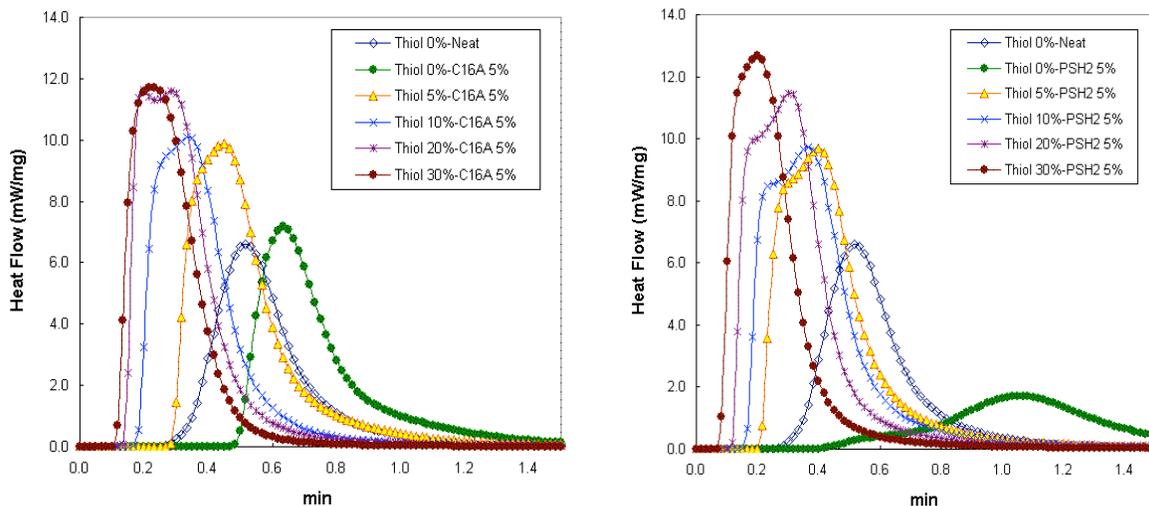
Figure 6. Photo-DSC polymerization profiles of PEGDA/TrPGDA systems with gradual increase of TMPTMP thiol monomers up to 30 mol% with addition of 5wt% polymerizable organoclays. Polymerized at 3mW/cm^2 using 0.2wt% DMPA under oxygen atmosphere.

In previous results based on DMA experiments, we demonstrated that the type of organoclays can either increase or decrease the modulus of clay-photopolymer systems by affecting the degree of thiol-ene reaction. The addition of thiolated organoclays into thiol-acrylate photopolymer systems usually decreases the modulus as well as the glass transition temperature due to increased thiol-ene reaction compared to those with acrylated organoclays.
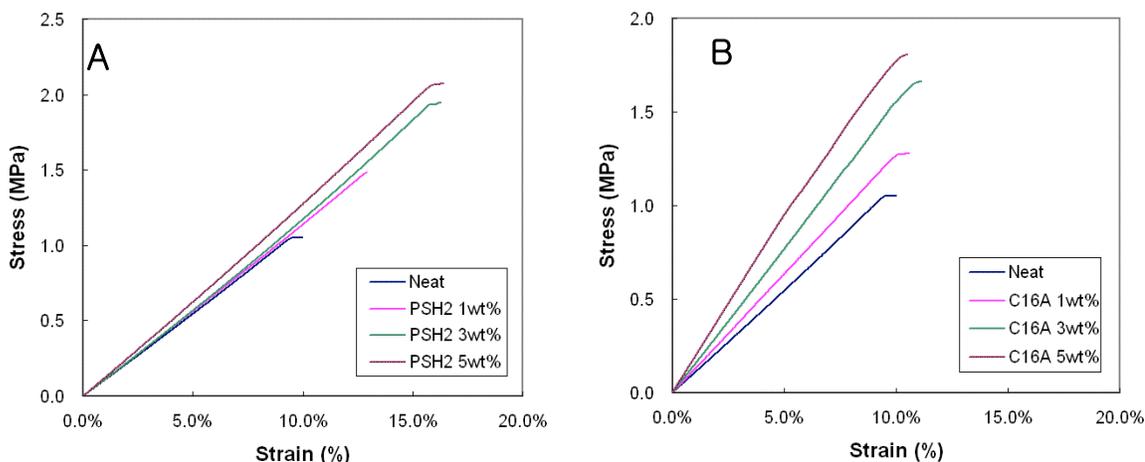
Figure 7. Tensile results for thiol-acrylate systems composed of 20mol% thiol functional groups. Shown are for samples with PSH2 thiolated clays (A) and with C16A acrylated clays (B).

Fig. 7 shows tensile elongation test results of thiol-acrylate formulation including 20 mol% of thiol groups. By adding thiolated organoclays, ultimate elongation has been remarkably enhanced while slopes corresponding to the stiffness (often called Young's modulus) of the materials are not changed to a great extent. The addition of up to 3wt% thiolated organoclays induces over 70% enhancement in ultimate elongation. Additional addition of organoclays does not change the elongation properties further. The addition of acrylated organoclays, on the contrary, significantly increases the stiffness of the materials while the overall elongation of materials is not changed significantly. By adding 1, 3, and 5wt% of acrylated organoclays, Young's moduli of nanocomposites increase 20, 65, and 80% from that of neat system without organoclays as the concentrations is increased. These different behaviors in both DMA thermal analysis and tensile experiments are mainly due to the different effects on polymerization mechanisms by the type of reactive groups in polymerizable organoclays as discussed in previous report. According to the RTIR and Photo-DSC experiments of the systems with different types of polymerizable organoclays, the existence of thiol functional groups on the clay surfaces induces much higher degree of thiol-ene step reaction than neat systems while the incorporation of acrylate functional groups on clay surfaces increases acrylate homo polymerization for many types of thiol-acrylate compositions. These different polymerization mechanisms are mainly due to the formation of propagating secondary radicals on clay surfaces by the reaction between thyl radicals and acrylic double bonds. These secondary radicals could only be transferred to other thiol monomers for further reaction because they cannot react with acrylic double bonds due to its relatively low reactivity, which results in accelerating the thiol-ene copolymerization through formation of thiyl radicals in the clay galleries.

Overall toughness of the material is a good indicator for evaluating the mechanical properties of materials that are used in coating and other engineering applications. According to the definition of

engineering terms, toughness of material is used to indicate overall energy to deform the materials and is calculated by multiplying stress and strain values at elongation break point, corresponding to the area of stress-strain curves in tensile experiments. Fig. 8 shows the relative toughness change from the neat system by adding 3wt% of organoclays. Toughness was calculated from elongation data. The addition of two polymerizable organoclays induces 30 to 40% increase in toughness of the acrylate mixture and a 60 to 80% increase in thiol-acrylate mixture compared to that of neat system while nonreactive Closite 93A decreases toughness about 10%. These results can provide good information in choosing the organoclay type to control the mechanical properties of nanocomposites. For instance, with significant enhancement in overall toughness of both polymerizable organoclay systems, the use of acrylated organoclay can make materials stiffer while the addition of thiolated organoclay produces more flexible nanocomposites than neat system.
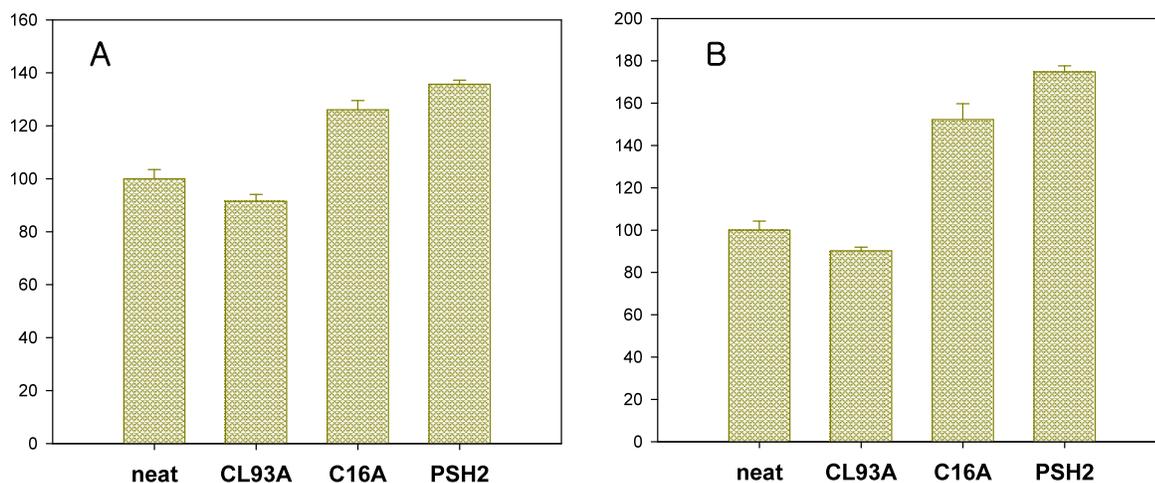
Figure 8. Comparison of the relative toughness for acrylate mixture (A) and for thiol-acrylate systems composed of 20mol% thiol functional groups (B) with different types of organoclays.

Conclusions

The effects of the type of polymerizable organoclay on *in situ* thiol-ene photopolymerization behavior have been investigated. Significant increases in thiol conversion are obtained with use of thiolated organoclays compared to diacrylate-dithiol systems. Incorporating acrylate organoclays does not change thiol conversion significantly. The addition of relatively small amount of thiol monomers reduces polymerization shrinkage and oxygen inhibition significantly. Incorporation of only 5 to 10 mol% of thiol functional groups into acrylate systems decreases shrinkage about 30 to 40%. When polymerizable organoclays were added into the acrylate and thiol-ene system, incorporation of only 3wt% thiolated organoclays induces a significant reduction in volume shrinkage in both systems while acrylated organoclay does not change it significantly. The addition of polymerizable organoclays significantly reduces the shrinkage stress and the impact is more significant than that simply from volume shrinkage. It is observed that only 3wt% polymerizable organoclays can decrease shrinkage stress of thiol-acrylate systems over 80%. Oxygen inhibition can be overcome by use of about 20 mol% thiol monomers. Upon addition of polymerizable organoclays into thiol-ene systems, similar polymerization rate and reaction induction time are observed under oxygen atmosphere while adding nonreactive organoclays induces much slower rate and longer induction time when compared to neat systems. The addition of relatively small amounts of polymerizable organoclays significantly changes

the mechanical properties based on tensile experiments utilizing DMA. Acrylate organoclay greatly increases the tensile modulus with no significant change in overall elongation and glass transition temperature of cured nanocomposites. Thiolated organoclays, on the other hand, make nanocomposites more flexible with decreased glass transition temperature. By increasing the amount of thiolated organoclays, ultimate elongation was significantly increased while Young's modulus was not changed significantly. Adding 5wt% thiolated organoclays into thiol-acrylate mixture induced 80% increase in elongation. Toughness of nanocomposites, compared by area of stress-strain curves in tensile experiments, is remarkably improved by adding polymerizable organoclays compared to the case of nonreactive organoclays. The addition of acrylated or thiolated polymerizable organoclays induces a 60 to 80% increase in toughness compared to that of neat system while nonreactive organoclay decreases it about 10%.

Acknowledgements

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