

Photopolymer-clay Nanocomposite Performance Utilizing Different Polymerizable Organoclays

By Soon Ki Kim and
C. Allan Guymon

The effects of polymerizable organoclays on thermo-mechanical characteristics, gas barrier properties and thermal stability have been studied utilizing a thiol-acrylate mixture. Photopolymerization kinetic behavior shows that incorporation of thiolated organoclay into the thiol-acrylate composition induces a higher degree of step thiol-ene reaction than other organoclays. The addition of acrylated organoclay greatly increases tensile modulus with no significant change in either elongation or glass transition temperature of cured nanocomposites. On the other hand, the incorporation of thiolated organoclay decreases the glass transition temperature due to greater formation of flexible thio-ether linkages with higher thiol conversion.

This enhanced flexibility results in significant increases in maximum elongation of the nanocomposite, but interestingly no reduction in Young's modulus is observed. Significant increases of 60% to 80% in toughness, as determined by the area of stress-strain curves in tensile experiments have been observed by adding only 3 wt% acrylated or thiolated organoclays, while nonreactive organoclay actually decreases the toughness. Water vapor transmission rate (WVTR) of the photopolymer-clay nanocomposites has also been examined.

While adding 3 wt% natural clay reduces WVTR 16% compared to that of a neat system, polymerizable and nonreactive organoclays induce about a 30% decrease, indicating similar efficiency in reducing gas permeability through addition of organoclays when clays are modified with organic surfactants.

Introduction

The incorporation of clays into a polymer matrix with well exfoliated morphologies can significantly enhance many performance characteristics of polymer composites (such as mechanical and barrier properties, thermal stability and chemical resistance) with relatively small amounts of loading in comparison to systems based on microscale fillers.¹⁻³ *In-situ* preparation of polymer-clay nanocomposites based on photopolymerization, on the other hand, provides a simple way to produce nanoscale dispersion of clay particles, avoiding several disadvantages of conventional processes involving thermal degradation or releasing volatile organic compounds (VOC) during the process.³⁻⁶

To obtain the clay exfoliation necessary for achieving advanced performance in clay nanocomposites, modification of clay surfaces by suitable surfactants is required to improve

compatibility in polymer matrices.^{3,4,7,8} However, most widely used nonreactive quaternary ammonium surfactants⁹⁻¹¹ may act as impurities affecting the final performance because they inherently do not participate in the polymerization reaction.¹² In this research, unique polymerizable surfactants have been developed to overcome this disadvantage of nonreactive surfactants. The incorporation of reactive groups on the clay surfaces using photopolymerizable surfactants may also maximize the interaction between clay and organic phase during and after polymerization.

Previous results have demonstrated that the addition of polymerizable organoclays into various acrylate photopolymer systems induce significant improvement in both nanocomposite properties with enhanced clay exfoliation and photopolymerization rate compared to the system with conventional nonreactive organoclays.¹³⁻¹⁴ Increases of photopolymerization rate are also observed with incorporation of polymerizable organoclays, primarily due to greater immobilization of propagating radicals on the clay surface, subsequently resulting in a decrease of bimolecular termination of propagating radicals. Enhanced clay exfoliation facilitates this mechanism by increasing the effective surface area in the system.

Recent research has also focused on utilizing the potential of reactive clays in thiol-ene formulations. Due to its unique step polymerization mechanism and properties, thiol-ene photopolymerization has been widely studied in the past decade to help overcome major drawbacks of free-radical polymerization such as oxygen inhibition and polymerization shrinkage during photopolymerization.¹⁵⁻¹⁹ The effects of polymerizable organoclays on polymerization behavior as well as basic nanocomposite properties of the

thiol-acrylate-based photopolymers have been studied.²⁰⁻²² The incorporation of polymerizable organoclays increases both clay exfoliation and photopolymerization rates significantly as also observed in acrylate systems. Chemical compatibility between monomers and organoclay is of primary importance for achieving better clay exfoliation. Interestingly, the type of functional group on the clay surface significantly influences the polymerization behavior by affecting the stoichiometric balance between thiol and double bond in the clay gallery. Thiolated organoclays enhance thiol-ene reaction, while acrylated organoclays encourage chain acrylate homopolymerization.^{21,22}

Changes in polymerization behavior with different organoclays also induce significant differences in other aspects of the photopolymer system. For example, it was demonstrated that the addition of suitable polymerizable organoclays significantly reduces oxygen inhibition and polymerization shrinkage of acrylate and thiol-acrylate systems.^{23,24} Addition of only 5 wt% thiolated organoclays into thiol-acrylate copolymerization systems effectively eliminated oxygen inhibition during photopolymerization by reaching an almost identical conversion in air and nitrogen. This improvement is observed regardless of the basic acrylate composition in the thiol-acrylate formulations, whereas the addition of either nonreactive or acrylated organoclay typically decreases the conversion and polymerization rate in air. Incorporation of only 5 wt% polymerizable organoclays modified with acrylate or thiol functional groups induces up to a 90% decrease in the shrinkage stress while the reduction by the same amount of nonreactive clays is less than 20%. Real-time infrared spectroscopy (RTIR) and simultaneous near-infrared conversion analysis suggest that both changes in

the reaction mechanism and enhanced interaction between the polymerizable organoclays and monomer systems facilitate this reduction in shrinkage stress.

Likewise, differences in polymerization behavior for organoclay-containing materials may affect final performance of the nanocomposites based on the close relation of polymer properties with both polymerization mechanism and resulting network structure. Particularly in thiol-acrylate systems, the reaction competition between the thiol-ene step-growth mechanism and faster acrylate homopolymerization often results in lower thiol conversion than that of acrylate double bonds.^{25,26} This low thiol conversion further decreases the mechanical strength and barrier properties of thiol-acrylate photopolymers that already exhibit decreased glass transition temperatures from the more flexible thio-ether linkage.^{27,28} This shortcoming of thiol-acrylate systems may be significantly improved by incorporating well-dispersed organoclays that may not only increase the toughness of neat thiol-ene photopolymers, but also enhance gas barrier properties by generating longer path length for gas molecules.^{19,28-31}

The inherent control of reaction mechanism by incorporating polymerizable organoclays provides an intriguing means to control polymer properties. This research investigates the effects of polymerizable organoclays on the ultimate performance of photopolymer clay nanocomposites, including gas barrier properties and various thermo-mechanical properties such as glass transition temperature, storage modulus, ultimate elongation, Young's modulus and tensile strength in both acrylate and thiol-acrylate photopolymers. Additionally, reaction kinetics of systems with and without organoclays is investigated to provide

context for the nanocomposite behavior. Toughness of the material, determined by the area of stress-strain curves, was also compared as a parameter for discussing quantitative impact of organoclays on overall mechanical performance of nanocomposite materials. To study the effect of organoclays on improving gas barrier properties of photopolymer-clay systems, water vapor permeability was examined based on an industrial ASTM standard with different monomers as well as organoclay type. The results from this study provide an effective platform for design of advanced photopolymer-clay nanocomposites to overcome drawbacks in conventional acrylate photopolymer materials.

Experimental

Materials

Tripropyleneglycol diacrylate (TrPGDA), polyethyleneglycol (600) diacrylate (PEGDA, MW=742),

trimethylolpropane triacrylate (TMPTA), and polyester-based urethane-acrylate oligomer (CN9009, MW ~2,000) were supplied by Sartomer Inc. (Exton, Penn.). Trifunctional trimethylolpropane trimercaptopropionate (TMPTMP) was obtained from Aldrich. Cloisite Na (Southern Clay Products—Gonzalez, Texas) was used for natural montmorillonite clay. Cloisite 93A (CL93A, Southern Clay Products), montmorillonite clay modified with dihydrogenated tallow, was used as a typical nonreactive organoclay.

To produce polymerizable organoclays, sodium cations between silicate platelets of Cloisite Na were ion exchanged using acrylate or thiol-functionalized quaternary ammonium surfactants as described elsewhere.¹⁴ C16A acrylated organoclay-bearing, acrylate-functional groups on the clay surfaces were produced utilizing hexadecyl-2-acryloyloxy(ethyl)

dimethylammonium bromide (C16A surfactant) synthesized following methodologies described previously.^{14,15} PSH2 thiol-functionalized organoclays were synthesized via Michael addition reaction between thiol groups of trifunctional TMPTMP and the acrylate groups from C16A acrylated organoclay based on prior procedures.¹⁶ The chemical structures of monomers and surfactants used in this research are illustrated in Figure 1. Unless otherwise noted, 0.5 wt% 2,2-dimethoxyphenyl acetophenone (DMPA, Ciba Specialty Chemicals) was used as a free-radical photoinitiator in all experiments. All chemicals, including monomers and clays, were used as received.

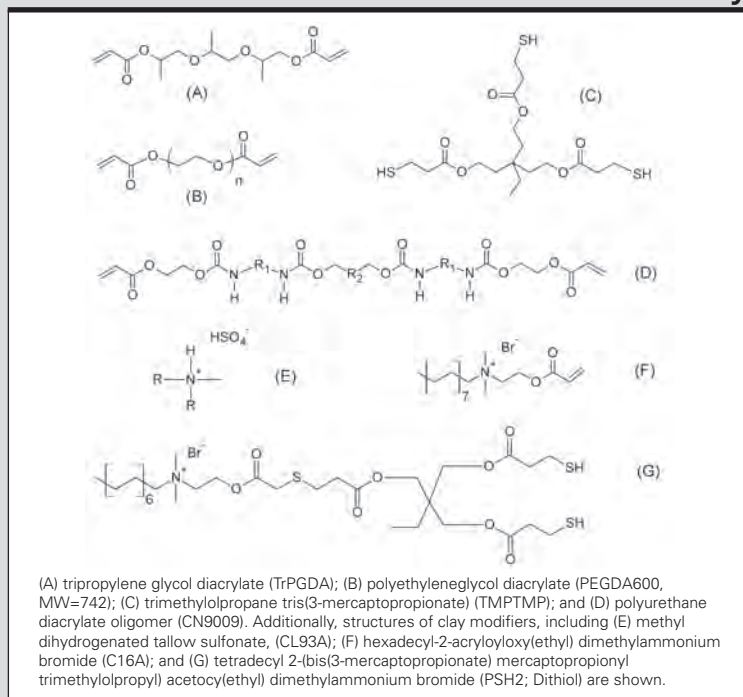
Methods

Thiol-ene photopolymerization kinetics was studied using RTIR (Thermo Nicolet Nexus 670). RTIR samples were prepared by sandwiching monomer mixtures between two sodium chloride plates. Measurements were performed at ambient temperature after purging the RTIR chamber for six minutes with dry nitrogen gas. UV light was provided by an optical fiber from a medium-pressure mercury lamp (EXFO Acticure). Functional group conversion was evaluated by monitoring the decrease in the height of the absorbance peak at 810 cm^{-1} for acrylate and at 2575 cm^{-1} for thiol.^{32,33} Photopolymerization reactions were initiated with a 365 nm light at 3.0 mW/cm^2 .

Dynamic mechanic analysis (DMA-Q800 DMA TA Instruments) was conducted to investigate the effect of organoclays on ultimate thermo-mechanical properties. To fabricate samples (2 mm x 13 mm x 25 mm) for testing, liquid monomer mixtures were injected between two microscope slides endcapped with 2 mm spacers. The sample was then irradiated for 10 minutes on each side using 365

FIGURE 1

Chemical structures of monomers used in this study



nm UV at 3.6 mW/cm² intensity under nitrogen atmosphere. To measure the modulus and glass transition temperature, samples were heated from -100°C to 100°C at 3°C/min. Measurements were made using the two-point bending mode at 1Hz frequency.

Tensile experiments were conducted based on DMA-controlled force tensile mode with 0.5N/min ramp rate at 30°C using rectangular samples (1mm x 5 mm x 20 mm), prepared using the same process described previously with 1 mm spacing glass molds. The most important factor for achieving reproducibility of the tensile experiments was the force ramp rate. Whereas 2N/min ramp rate generated high experimental errors as high as 20%, the error was reduced to about 5% for all nanocomposite compositions by utilizing a relatively low ramp rate of 0.5N/min. Young's modulus was calculated utilizing the slope of the stress-strain curve.

Water vapor transmission rate (WVTR) of photopolymer-clay nanocomposites including 3 wt% (organo)clay was examined based on an ASTM standard (ASTM E96³⁴) utilizing thin polymer films in comparison with neat systems. To fabricate the 100 μm composite films, controlled amounts of liquid monomer mixtures were placed between thick glass plates (150 mm x 150 mm x 20 mm). Glass plates were covered with 100 μm thick polyvinylidene difluoride film to allow easy release of the cured polymer films. On one of the glass plates, thin tape spacers were attached to control the cured film thickness. After placing the monomer mixtures on the bottom glass plate, bubbles were removed by applying a vacuum to prevent pinhole formation. Afterward, the upper plate was covered and the plates were clamped. The mold was then exposed to 250~450 nm UV light at 18 mW/cm² for five minutes on each side. Before covering the

glass WVTR vessel (12 cm diameter opening) with the prepared thin films, 100g of distilled water was charged into the vessel. The sealed vessels were placed in a convection hood controlled at 23°C and mass loss was measured. WVTR per unit area was calculated considering the thickness of composite films.

Results and Discussion

Many results for organic-inorganic composites have shown that the use of well-dispersed inorganic fillers improve properties of polymer systems.^{1,4} If inorganic fillers can chemically react with the organic phase, interactions between the filler surface and polymer matrix may increase to a greater degree than in systems with nonreactive fillers.²⁶ Interestingly, the incorporation of polymerizable organoclays into photopolymerization systems typically enhances the polymerization rate, whereas the rate usually decreases when nonreactive clays are added due to reduction in incident-light energy.^{13,14} In addition, the type of functional group (e.g., (meth)acrylate or thiol) on the clay surface significantly affects the polymerization kinetics and mechanism of thiol-acrylate systems.²⁰⁻²²

The type of functional group on the organoclay surfaces directs polymerization behavior by affecting the stoichiometric balance between thiol- and ene-functional groups in the clay galleries and by affecting the primary type of radicals on the clay surfaces, resulting in a different degree of thiol-ene reaction with different polymerizable organoclays. Such results indicate a great degree of interaction between the clay and polymers when reactive functional groups are incorporated on the clay surfaces. Therefore, it is reasonable to expect that greater improvement in the ultimate composite performance could be achieved with polymerizable

organoclays than with conventional nonreactive organoclays.

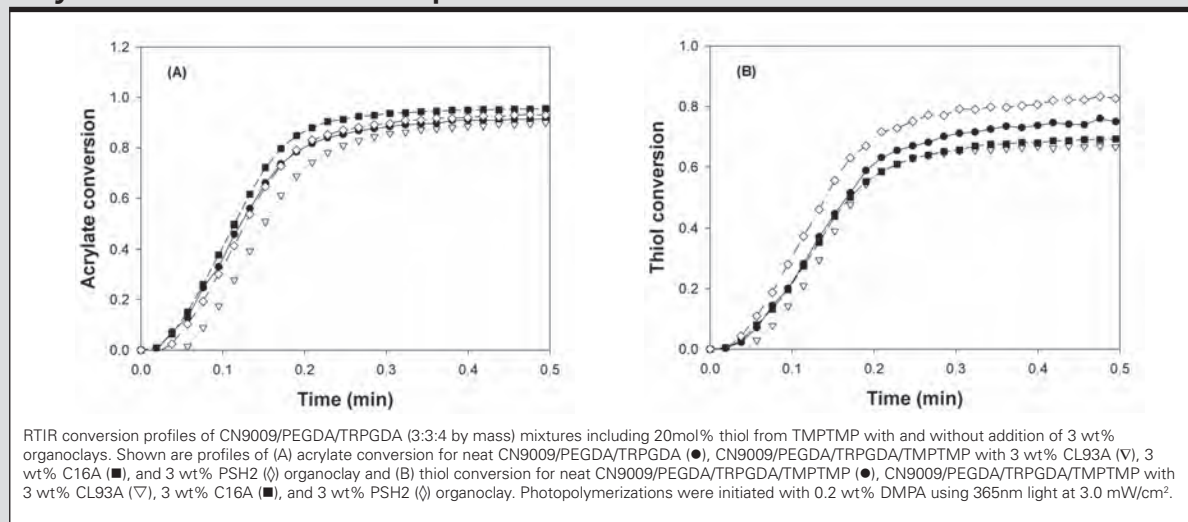
To verify this hypothesis, the effect of adding organoclays on thermo-mechanical property and polymerization behavior of thiol-ene photopolymer-clay systems was investigated with different reactive and nonreactive organoclays. In previous studies, low-molecular weight monomers were used for thiol-acrylate compositions as the high functional group concentration in these systems allowed good contrast in polymerization kinetics.^{21,22} For examination of the ultimate composite performance (such as mechanical and barrier properties), however, polymerized materials need sufficient toughness to make and handle thin films.

For instance, to conduct tensile tests using acrylate or thiol-acrylate formulations, use of suitable amounts of oligomers that increase the toughness of cured polymers is needed because simple monomeric compositions based on low-molecular weight multifunctional acrylate or thiol-acrylate mixtures are typically too brittle or weak for such experiments utilizing thin films. For this reason, mixtures of polyethyleneglycol diacrylate (PEGDA) and polyester-based urethane acrylate (CN9009) were used for the oligomer system.

Appropriate ratios were determined considering the flexibility and the strength of the cured films. Tripropyleneglycol diacrylate (TrPGDA) was also added to the oligomer mixture to adjust the viscosity of liquid reactant mixture. For the thiol-acrylate mixture, trithiol TMPTMP was added to the basic acrylate mixture with CN9009/PEGDA/TrPGDA using a 3:3:4 mass ratio. The amount of TMPTMP was controlled based on the overall mole ratio between acrylate and thiol functional groups in the system.

FIGURE 2

Acrylate and thiol conversion profiles



Based on the potential impact of polymerization behavior on network formation, understanding the relationship between polymerization kinetics and final properties may be crucial for improving basic thiol-acrylate materials. Therefore, the photopolymerization behavior was examined using RTIR kinetic experiments. The acrylate conversion and thiol conversion as a function of time for CN9009/PEGDA/TrPGDA systems, including 20 mol% thiol from TMPTMP, are shown in Figures 2 and 3 with and without 5 wt% organoclays. As shown in the reaction conversion profiles (Figure 2A), the incorporation of the different organoclays does not significantly change the acrylate conversion profiles. Ultimate acrylate conversion varies only from 0.90 for the system with nonreactive organoclay to 0.96 by adding acrylated polymerizable organoclay with the neat system showing a conversion of 0.93. The addition of nonreactive organoclay slightly decreases the polymerization rate but not nearly to the degree observed in previous research^{21,22} when

a nonreactive organoclay was added to low-molecular weight monomeric thiol-acrylate polymerization systems. This difference indicates that the increased system viscosity from incorporating oligomers reduces bimolecular

termination that is more dominant in low-viscosity monomer systems.

Thiol conversion profiles in Figure 2B, however, show much different behavior based on the type of organoclay. Incorporation of a

FIGURE 3

Storage modulus profiles as a function of temperature with addition of 5 wt% organoclays

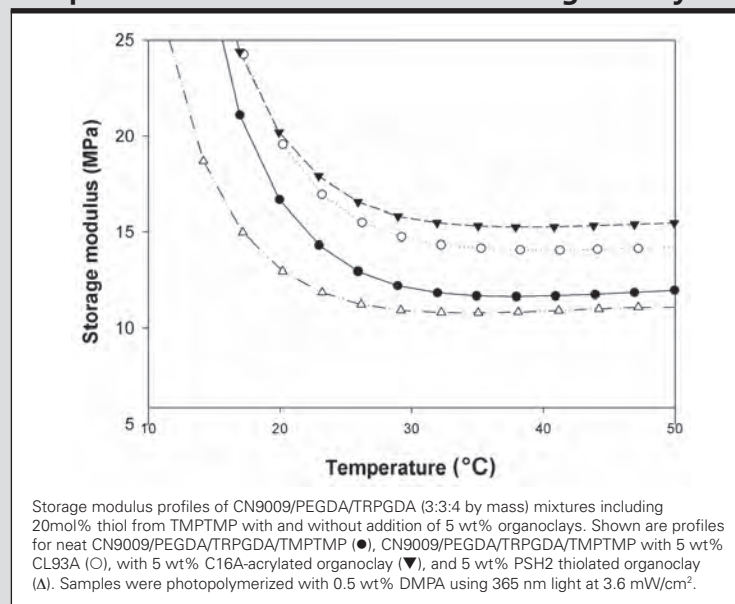
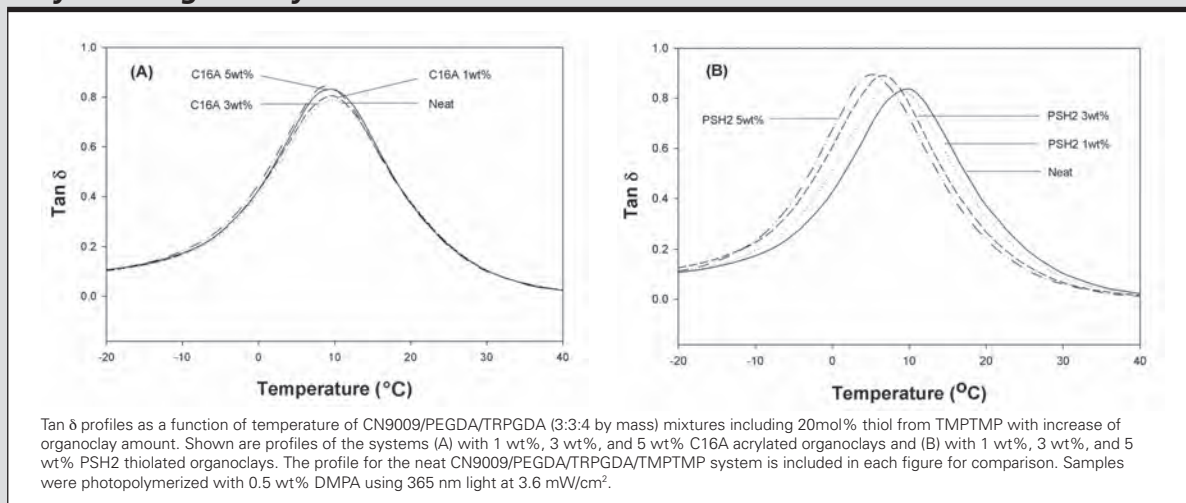


FIGURE 4

Acrylated organoclays



thiolated organoclay induces significant increases in photopolymerization rate and final thiol conversion. The incorporation of either nonreactive CL93A or acrylated C16A organoclay decreases ultimate thiol conversion to about 70% from 79% in the neat system, while the same amount of PSH2-thiolated organoclays increases thiol conversion to 87%, corresponding to a 10% enhancement. Even in this oligomer-monomer mixture that is similar to many practical formulations in industrial applications, it appears that ultimate thiol conversion can be varied over a 20% range simply with changing the organoclay type.

To determine whether these kinetic effects influence thermo-mechanical properties of thiol-ene photopolymer-clay systems, dynamic mechanical analysis (DMA) experiments were conducted for the same CN9009/PEGDA/TrPGDA/TMPTMP system, including 20 mol% thiol. The storage modulus profiles as a function of temperature with addition of 5 wt% organoclays are shown in Figure 3. The incorporation of either nonreactive CL93A- or C16A-acrylated organoclay

increases the rubbery storage modulus, whereas the modulus of the thiolated organoclay system is slightly less than that of the neat system. Based on similar or enhanced degrees of acrylate homopolymerization in CL93A and acrylated organoclay system, the inorganic filler generates a higher modulus than in the neat system. On the other hand, for the thiolated organoclay systems where the thiol conversion is much higher than that of the neat system, the storage modulus decreases due to formation of more flexible thio-ether linkages in the polymer network, which mitigates the strengthening effect from the inorganic filler. This modulus behavior confirms that increased acrylate homopolymerization through addition of acrylated organoclay forms harder domains in the nanocomposites, while thiolated organoclays induce a more flexible network due to enhanced thiol-ene step-growth reaction.

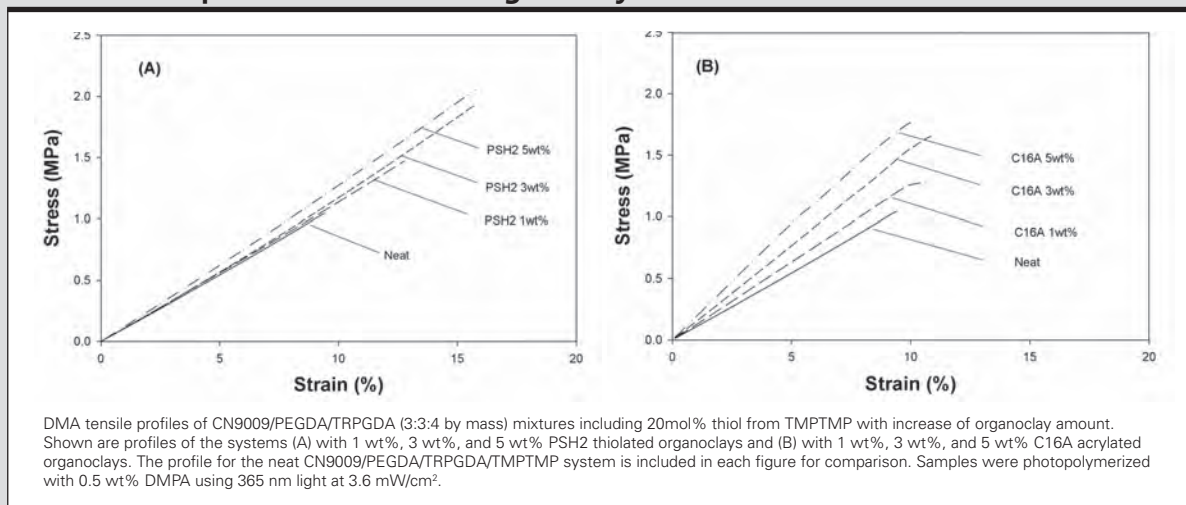
Further evidence of this effect is provided by the glass transition temperature behavior of these thiol-acrylate systems with addition of polymerizable organoclays into the

CN9009/PEGDA/TrPGDA/TMPTMP formulation. As shown in Figure 4A, no significant change in the glass transition temperature, as indicated by the tan δ peak of the system, is observed when increasing the amount of C16A-acrylated organoclay up to 5 wt%. The addition of PSH2 thiolated organoclays, however, decreases the glass-transition temperature (as shown in Figure 4A) due to the enhancement of thiol-ene reaction and greater flexibility in the network. The glass-transition temperature decreases about 3°C from that of the neat system by the addition of only 1 wt% thiolated organoclay and continues to decrease by increasing the clay amount up to 5 wt% with a substantial 6°C of substantial decrease.

In many applications, tensile properties such as toughness, overall elongation and Young's modulus are practical indicators regarding material performance. To investigate the organoclay effects on these mechanical properties of photopolymer clay composites, tensile elongation experiments were performed utilizing DMA for the 20 mol% thiol

FIGURE 5

Tensile stress profile of thiolated organoclays



CN9009/PEGDA/TrPGDA/TMPTMP composition. Figure 5 shows the tensile stress profiles as a function of strain until break of the cured films produced with increased amounts of thiolated or acrylated organoclays. The stress-strain profile for the neat system is also included in each figure for comparison. By adding thiolated organoclays (as shown in Figure 5A), ultimate elongation to break for the photopolymer clay composites are enhanced while the slope of the profiles, corresponding to the stiffness (or Young's modulus) of the materials, does not significantly change. The addition of only 3 wt% thiolated organoclay induces an enhancement of more than 70% in ultimate elongation. Interestingly, the addition of acrylated organoclays significantly increases the stiffness of the materials, while the overall elongation to break does not change significantly as shown in Figure 5B.

By adding 1, 3 and 5 wt% acrylated organoclay, the Young's moduli of photopolymer-clay composites increase 20% with 1 wt% organoclay to as much as 80% with 5 wt% organoclay

as compared to the neat system. These different results in tensile behavior are primarily due to the difference in polymerization mechanisms based on the type of reactive groups in polymerizable organoclays. Again, based on facilitated acrylate homopolymerization by incorporation of acrylated organoclays, crosslinking density is increased which induces greater stiffness in the composites. Thiolated organoclays, on the other hand, produce more flexible polymer networks that are able to withstand greater deformation by enhancing the thiol-ene reaction that allows more homogeneous polymerization with reduced crosslinking density based on the step-growth reaction. While one acrylate double bond acts as a difunctional group in chain-acrylate homopolymerization (which induce the polymer network), the same double bond in a thiol-ene step mechanism reacts with thiol only once and, thus, becoming monofunctional and resulting in lower crosslinking density.

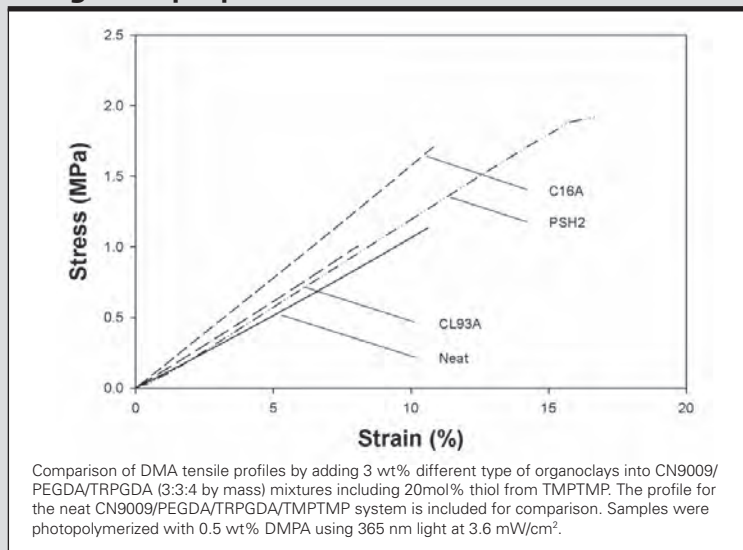
Figure 6 shows the overall comparison of organoclay effects in elongation properties by adding 3 wt%

of nonreactive, acrylated and thiolated organoclays into the thiol-acrylate mixture. This comparison clearly demonstrates how the organoclays structure induces different tensile properties in thiol-acrylate photopolymer clay composites. While adding nonreactive organoclay (CL93A) slightly increases the stiffness with some decrease in ultimate elongation, the addition of polymerizable organoclays improves either ultimate elongation (thiolated organoclay) or Young's modulus (acrylated organoclay). This behavior also indicates that the interaction between clay surfaces and polymer matrices are significantly improved by incorporating reactive groups on the clay surfaces,^{14,21} not only by inducing enhanced clay exfoliation but also by reacting with monomers and oligomers during the photopolymerization, forming strong covalent bonds between the filler surface and organic polymer networks.

In addition to tensile strength and elongation, the overall toughness of a material is an important parameter indicating energy absorptive capacity and durability of materials in many

FIGURE 6

Overall comparison of organoclay effects in elongation properties



engineering applications. The toughness of a material is typically defined as the overall energy needed to deform the materials to failure and is commonly found from the area under stress-strain curves in tensile experiments.³⁵ Figure 7A shows the toughness as calculated by the area under the stress-strain curve and

normalized to the toughness of the neat system. Toughness of composites with 3 wt% of organoclays into thiol-acrylate mixture, including 20 mol% thiol, are compared. The average toughness for each composition was obtained based on three independent tensile experiments. The addition of either C16A-acrylated or PSH2-thiolated

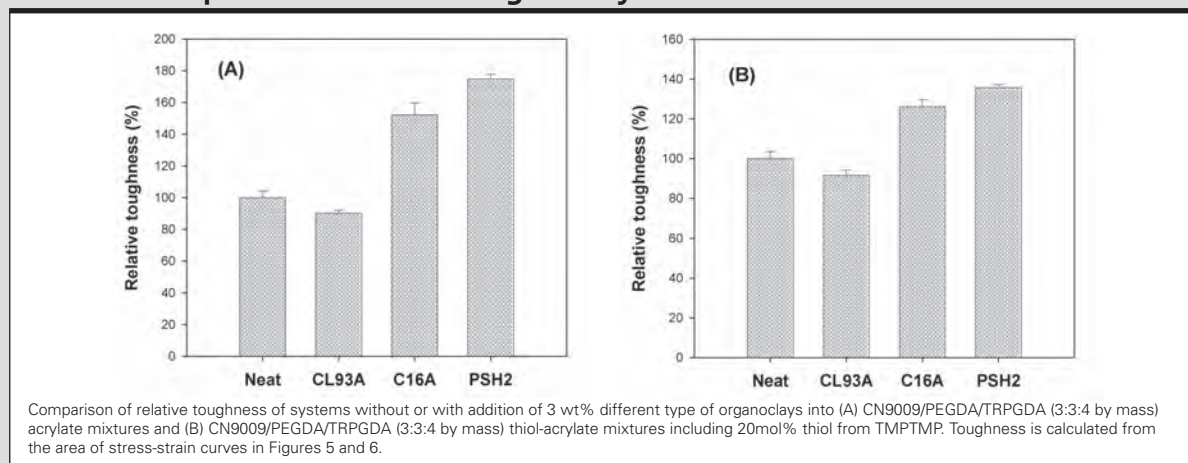
polymerizable organoclays induces 60 and 80% increases in toughness of the thiol-acrylate mixture compared to that of neat system, respectively, while nonreactive Cloisite 93A decreases the toughness about 10%.

To determine the impact of polymerizable organoclay in the acrylate photopolymerization system without thiol, tensile experiments were performed to evaluate the formulation utilizing the basic acrylate mixture as summarized in Figure 7B. Incorporation of nonreactive CL93A organoclay slightly reduces the toughness again. The addition of the two polymerizable organoclays induces a 30 to 40% increase in toughness of the acrylate mixture with thiolated organoclay producing the greatest toughness increase. This trend is similar to that observed in the thiol-acrylate mixtures but the degree of enhancement is significantly smaller in each organoclay system.

It is also important to note that the use of thiolated organoclay also increases the elongation of composite films significantly, whereas adding acrylated organoclay basically induces the highest Young's modulus.

FIGURE 7

Tensile stress profile of thiolated organoclays

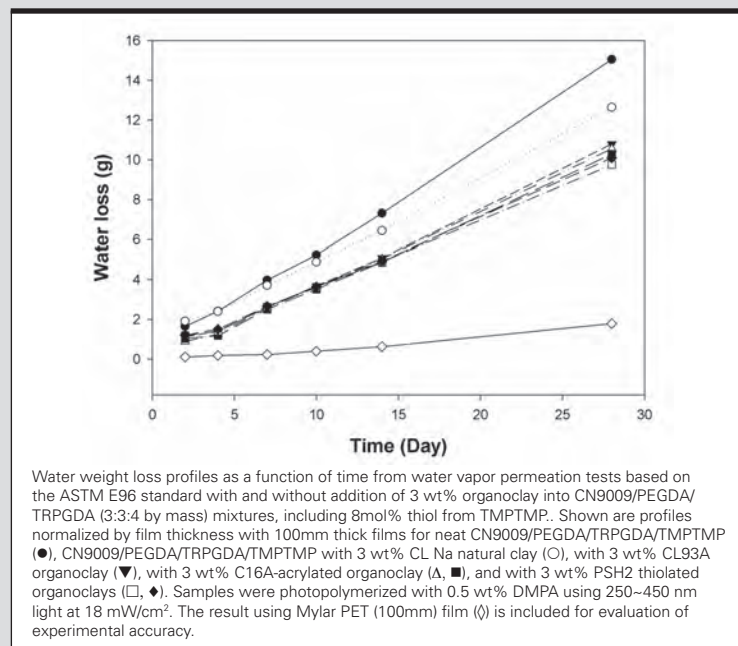


These results provide opportunity to control the mechanical properties of nanocomposites simply by choosing the organoclay type to control. For instance, with significant enhancement in overall toughness of both polymerizable organoclay systems, the use of acrylated organoclay can make materials stiffer while the addition of thiolated organoclay produces more flexible nanocomposites than the neat system.

Gas barrier properties for many gases (such as oxygen and water vapor) are often important characteristics in many photopolymer applications (i.e., as coating and film packaging). It is well-known that the addition of plate shape inorganic fillers such as silicates and micas can often improve the gas barrier properties by generating a longer diffusion path for gaseous materials.¹⁹ To demonstrate the impact of organoclay on barrier properties, the WVTR through photopolymer clay nanocomposite films, including organoclays, was compared. In studying the gas transfer rate, homogeneity in the thickness of the thin film and the absence of defects are critical to achieve good experimental results. The ultimate cured-film thickness was thus controlled to 100 microns with at most a 5% error. In addition, to make thin films that are not easily damaged during removal from the mold, the toughness of the cured film needed to be increased from that observed in the mechanical testing. To this end, the thiol concentration of the basic thiol-acrylate formulation was decreased to 8 mol%. The ratio of acrylic monomer composition was not changed. To compare the experimental reproducibility with an ASTM standard, 100 mm PET film (Mylar) was used as the control system. The measured WVTR value of the PET film was compared with the literature value obtained based on a similar methodology.³⁶

FIGURE 8

Water loss through the composite films as a function of time



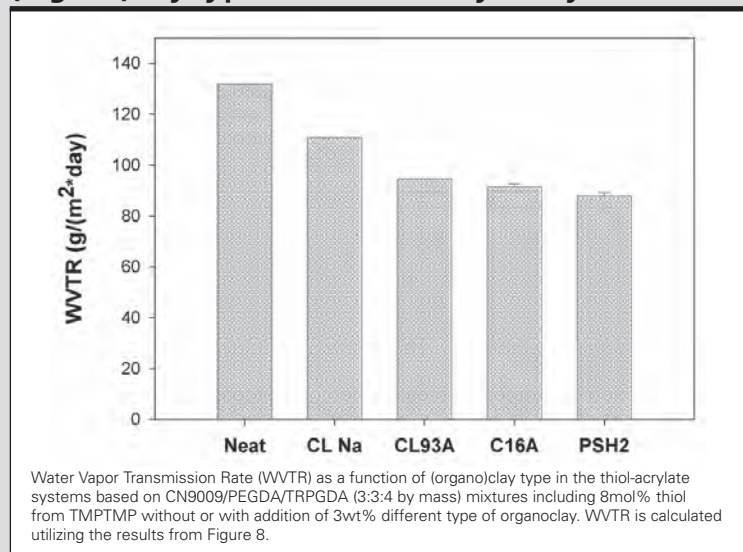
To investigate the organoclay effect on WVTR of photopolymer clay systems, 3 wt% of various organoclays were incorporated and compared with neat and natural clay systems. Figure 8 shows the water loss through the composite films as a function of time for the CN9009/PEGDA/TrPGDA mixture, including 8 mol% thiol from TMPTMP. The neat system is also evaluated for comparison with the result for Mylar PET film included to confirm experimental reproducibility. Measurements were performed for 28 days by recording the weight change of each experimental set. As shown in Figure 8, adding 3 wt% organoclays more significantly decreases the rate of water loss through the composite film than adding CL Na natural clay, but there appears to be no significant difference between organoclay systems. Even the system with nonreactive CL93A organoclay exhibits a similar trend in weight change as

compared to those of systems with polymerizable organoclays.

WVTR for each system is calculated from the overall water loss after 28 days. This data is summarized in Figure 9 after normalization for the film thickness. Each WVTR value is thus based on a 100 micron thickness. As shown in Figure 9, WVTR of a 100 micron Mylar film is 4.3 g/m²/day with literature value using similar experimental condition at 3.5 g/m²/day.³⁶ The experimental value is slightly higher than the reference values, but experimental accuracy appears reasonable. Addition of 3 wt% natural clay (CL Na) reduces WVTR about 16% from the value of the neat system. Further decrease in WVTR is observed when organoclays are incorporated into the thiol-acrylate mixture. Approximately 30% reduction in WVTR is achieved by adding 3 wt% CL93A or polymerizable organoclays, suggesting that the clay effect on water

FIGURE 9

Water vapor transmission rate as a function of (organo)clay type in the thiol-acrylate systems



permeability is within the experimental error when clay is organically modified and thereby dispersed with at least an intercalated morphology. The incorporation of thiolated organoclay induces decreases in glass transition temperature of the composites due to increased thiol-ene reaction as discussed previously, which may increase gas molecule passage through the composite layer. This WVTR behavior clearly shows that barrier properties are not detrimentally affected by incorporating thiolated organoclays into thiol-acrylate systems. The results are particularly interesting because a 30% decrease in WVTR is possible by adding only 3 wt% organoclay.

Conclusion

Incorporation of organoclay affects polymerization behavior and ultimate nanocomposite performance, including thermo-mechanical and gas barrier properties in photocurable thiol-acrylate systems. Incorporation of thiolated

organoclay induces higher thiol-ene reaction than other organoclays—which has a significant effect on nanocomposite characteristics. The addition of only 5 wt% acrylate organoclay (which enhances acrylate homopolymerization) increases the tensile modulus 80% with no significant changes in elongation and glass transition temperature. Thiolated organoclay, on the other hand, with greater thiol-ene polymerization induces greater flexibility in the nanocomposites with decreased glass transition temperature. Adding 3 wt% thiolated organoclays induces a 70% increase in elongation without significantly changing Young's modulus. The toughness of nanocomposites, as measured by the area under stress-strain curves, is substantially improved by adding polymerizable organoclays. The addition of 3 wt% acrylated or thiolated polymerizable organoclays induces 60% and 80% increases in toughness, respectively, while nonreactive organoclay actually decreases toughness. Additionally,

gas barrier properties of clay nanocomposites are also influenced by the addition of organoclays. Both polymerizable and nonreactive organoclays improve WVTR of the nanocomposites. While adding 3 wt% natural clay reduces WVTR 16% compared to that of neat system, polymerizable and nonreactive organoclays decrease it about 30%. ▀

Acknowledgements

The authors acknowledge financial support from the Industry & University Cooperative Research Program (I/UCRC) for Photopolymerization Fundamentals and Applications, and the National Science Foundation (CBET-0933450).

References

- Rodriguez F, Cohen C, Ober CK and Archer LA, *Principles of Polymer Systems*; Taylor & Francis, New York, Ch.9:pp 405-408 (2003).
- Vaia RA and Giannelis, EP, *Macromol* 30:7990-7999 (1997).
- Alexandre M and Dubois P, *Mater Sci Eng* 28:1-63 (2000).
- Ray SS and Okamoto M, *Prog Polym Sci* 28:1539-1641 (2003).
- Uhl FM, Davuluri SP, Wong SC and Webster DC, *Chem Mater* 16:1135-1142 (2004).
- Beck E, Lokai E and Nissler H, *RadTech Int North America*, Nashville, 160-161 (1996).
- LeBaron PC, Wang Z and Pinnavaia TJ, *Appl Clay Sci* 15, 11-29 (1999).
- Ogawa M and Kuroda K, *Bull. Chem Soc Jap* 70:2593-2618 (1997).
- Wang Z and Pinnavaia T J, *Chem Mater* 10:1820-1826 (1998).
- Decker C, Zahouily K, Keller L, Benfarhi S, Bendaikha T and Baron J, *J Mater Sci* 23:4831-4838 (2002).
- Uhl FM, Hinderliter BR and Davuluri SP, *Mater Res Soc* 16:203-208 (2004).
- Tan H, Nie J, *J Appl Polym Sci* 106:2656-2660 (2007).
- Owusu-Adom K and Guymon CA, *Polymer* 49:2636-2643 (2008).
- Owusu-Adom K and Guymon CA, *Macromol* 42:180-187 (2009).
- Decker C, *Polym Int* 45:133-141 (1998). *Polymer International*