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Communications to the Editor

Physical and Mechanical Properties of Photopolymerized Thiol−Ene/Acrylates

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Photopolymerization is an efficient method for producing cross-linked materials with thicknesses ranging from a few microns to several millimeters. Traditional applications include protective films on floors and wood to coatings on compact disks and optical fibers.[1] A wide variety of monomers have been reported to undergo rapid polymerization when exposed to UV light in the presence of a photoinitiator. The large majority of industrial photopolymerization processes involve the free-radical chain growth polymerization of (meth)acrylates to produce cross-linked networks.[1] Early gelation in a multifunctional acrylate polymerization[2−6] leads to heterogeneous matrices with respect to cross-linking density, resulting in mechanical transition regions that can extend over a range of up to 200 °C. In contrast, photopolymerization of multifunctional thiols and enes occurs by a free-radical step-growth process that forms a highly uniform cross-linked network with a narrow DMA tan δ peaks.[7−10] Thiol−ene polymerizations are also known for proceeding with very little oxygen inhibition, with the oxygen incorporation into the matrix structure having a trivial effect on the final mechanical/physical properties.[7−10] On the basis of a consideration of the great differences in the matrix structures of photopolymerized acrylates and thiol−enes, we ask what type of matrix will be formed by the photopolymerization of mixtures of acrylates with thiol−enes and what will be the resultant impact on physical properties. Recently, Bowman et al. reported that the photopolymerization of ternary systems involving mixtures of a thiol, an ene that cannot inherently undergo homopolymerization, and an acrylate that can participate in both copolymerization (with the thiol) and homopolymerization leads to network formation by a complicated kinetic process.[11] From their kinetic analysis of a tetrathiol, a divinyl ether ene, and a monoacrylate, it can be speculated that a ternary system comprised of a trithiol and triene with a triacrylate will result in limited acrylate homopolymerization occurring simultaneously with thiol−ene and thiol−acrylate free-radical reactions. We are currently engaged in a comprehensive investigation of the physical and mechanical properties of networks formed by the photopolymerization of thiol−ene/acrylate mixtures that include several thiol−ene combinations with a range of acrylates. In this Communication, we report initial results for one system to illustrate the type of structural and mechanical property development that occurs for the polymerization of thiol−ene/acrylate systems. The results reported are indicative of the properties achievable with ternary thiol−ene/acrylates and suggest an opportunity for implementing a new strategy for fabricating photocurable materials for both thin film and thick cross-linked material applications.

This Communication focuses on the photopolymerization of ternary systems involving the three components in Figure 1: a trithiol (designated TriThiol), a triallyl ether (designated APE), and a propoxylated glycerol triacrylate (designated PGTA). Mixtures were prepared by blending TriThiol with APE based on equal molar functional groups and subsequently adding increasing molar concentrations of PGTA. Each mixture contained 1 wt % of the cleavage photoinitiator 2,2-dimethoxy-2-phenylacetophenone. Thick samples (4 mm) were radiated with low-intensity 254 nm low-pressure mercury lamps (0.1 mW/cm^2) in an air environment; we stress that extra cautions were taken to prevent the high-temperature rise during polymerization by exposing the sample for short intervals during the initial polymerization stage. Care was taken for the pure PGTA sample

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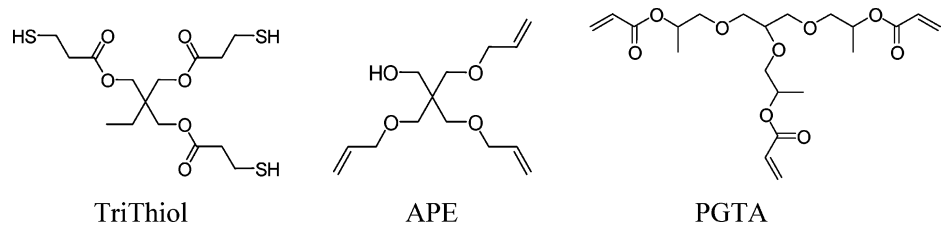

Figure 1. Monomer structures and acronyms.

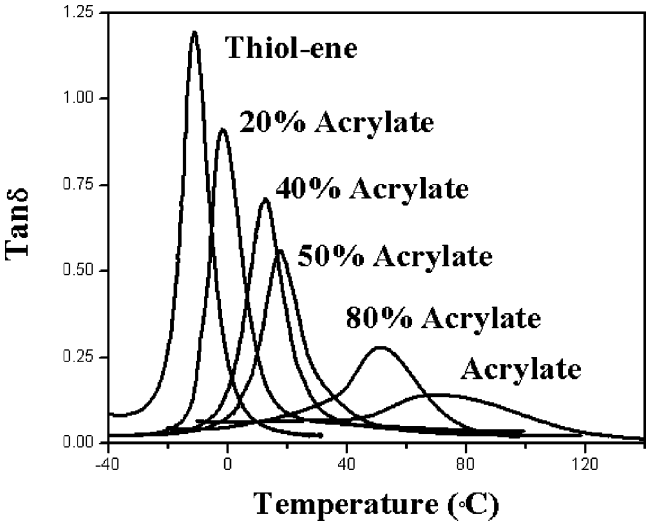

Figure 2. Tan δ vs temperature plots for 4 mm thick plates formed from pure TriThiol−APE and PTGA and mixtures of TriThiol−APE and PTGA with increasing mole percent concentrations of PTGA. DMA first scan plots obtained with scan rate 2 °C/min and frequency 1 Hz.

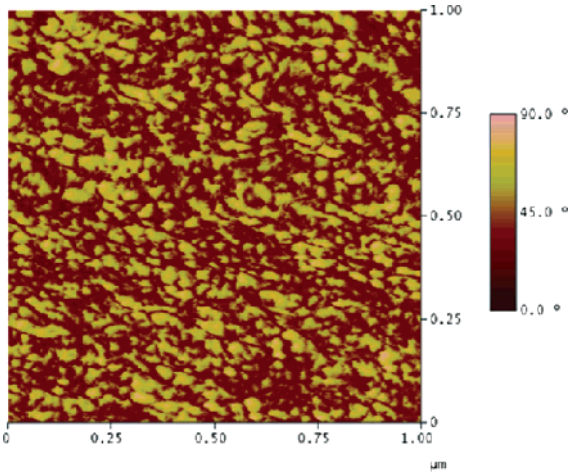

Figure 3. Phase image of Trithiol−APE/PTGA (50 mol % acrylate) film cross section.

in order to eliminate O_2 inhibition. Kinetic analyses were conducted with real-time FTIR in order to confirm high conversions of thiol−ene and acrylate monomers. The addition of the thiol−ene mixture to the triacrylate monomer results in acrylate conversion of ~100%. However, the thiol−ene monomer conversions are dependent on their initial concentrations. In the case of high thiol−ene concentrations (80% TriThiol−APE/ 20% PGTA), TriThiol and APE reach 90% conversions. On the other hand, in the samples with lower thiol−ene concentrated mixtures (30% TriThiol−APE/ 70% PGTA), 42% of the APE was converted while TriThiol and PGTA conversions reached 100%. For the sample containing 50% TriThiol−APE with 50% PGTA, acrylate and thiol groups were completely consumed during the polymerization, while APE reached 80% conversion.

Cured 4 mm thick plates were analyzed by dynamic mechanical analysis (DMA; 2 °C/min at 1 Hz) and differential scanning calorimetry (DSC; 10 °C/min scan rate) to determine mechanical/thermal transitions. DMA first scan results in Figure 2 clearly show that all of the plates formed by polymerizing samples with at least 20 mol % of the thiol−ene have symmetrical tan δ vs temperature plots that are substantially narrow compared to the sample formed by photopolymerization of pure PGTA. Pure PGTA has a broad tan δ plot with a main peak maximum around 80 °C and a very small peak around 20 °C. Hence, it can be readily concluded that, from a mechanical/thermal basis, the matrices become more uniform with increasing TriThiol−APE content. There is no indication of multiple peaks in the tan δ vs temperature plots for the films with TriThiol−APE present. To characterize thermal transitions, DSC scans (not shown) were recorded for the same samples. As in the case with the DMA plots, the DSC scans of samples with TriThiol−APE present were characterized by single, narrow thermal transition regions. Furthermore, neither DSC studies conducted at slower scan rates (1 °C/min) nor DMA studies with different strain rates revealed multiple transitions; i.e., only single mechanical or thermal transitions were observed for the cured samples based on thiol−ene/acrylate ternary systems.

While it is clear from the results in Figure 2 that films prepared by the photopolymerization of mixtures of the thiol−ene with the triacrylate are quite uniform on a scale that involves molecular motions affecting mechanical/thermal transitions, there is still some questions as to the presence of larger scale structure in the range between 10 and 100 nm. The atomic force microscopic (MultiMode AFM, RTESP with nominal resonance frequency of 275 kHz was used in the tapping mode) analysis of a cross section of freeze-fractured samples containing 50 mol % PGTA (with no surface treatment) clearly shows at room temperature a phase-separated morphology on the scale of 20−80 nm. Similar AFM analysis of the 4 mm thick plates formed by photopolymerization of pure TriThiol−APE and pure PTGA showed little variation in structure and certainly no indication of the phase-separated morphology shown in Figure 3 for the polymerized ternary thiol−ene/acrylate network.

In view of the observation in Figure 2 that thiol−ene/acrylate mixtures can be photopolymerized to give cross-linked films with relatively narrow transitions, whose peak maxima can be tuned to occur at a given temperature by the concentration of acrylate, an investigation of the impact resistances of the 4 mm thick samples were measured with a Tinius Olsen instrument modified to measure the energy absorbed by moderate impact (energy of 1.13 J) with a steel head. As shown in Figure 4, the photocured ternary samples containing 40 and 50 mol % PTGA are the most effective at dissipating impact energy at room temperature, as evidenced by the peak maximum of the energy absorbed vs the mole percent acrylate plot. The 40 and 50 mol % acrylate sample plates account for 84 and 86%, respectively, of the impact energy of the striking head being absorbed. The energy absorption depends on the tan δ value (at the frequency

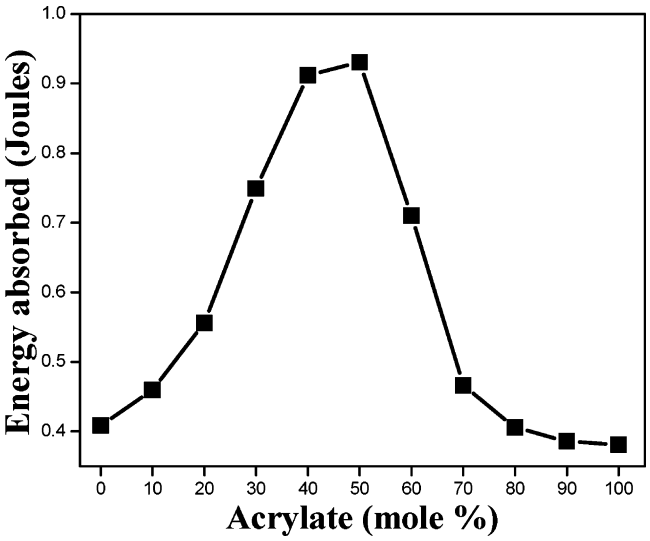

Figure 4. Energy absorption plot of thiol−ene/acrylate ternary systems as a function of acrylate mole percent concentration.

of the energy impact) at a given temperature. It is thus not surprising that the 40 and 50 mol % acrylate containing samples would be the most energy absorbing at room temperature where both have substantial tan δ values according to the 1 Hz DMA analysis in Figure 2. The nanophase structure in Figure 3 apparently does not interfere with energy absorption/dissipation. Finally, it is noted that the amount of energy absorbed is much greater than for traditional materials near room temperature; i.e., commercial ethylene vinyl acetate (EVA) based mouthguard elastomers absorb 40−50% of the 1.13 J impact energy.

Finally, we mention that photocured samples with low TriThiol−APE concentrations when heat aged at the temperatures well above their transition temperatures showed some changes in mechanical/physical properties and energy absorption upon impact. This heat treatment/postcure will be discussed in detail in a future publication.

In conclusion, analysis of photopolymerized thiol−ene/acrylate systems indicates narrow mechanical/thermal transition regions. The peak maxima in the tan δ can be readily changed by the concentration of acrylate to occur at essentially any temperature within the boundaries of the transition temperatures of the pure materials. This gives the flexibility to make materials with high energy absorbing properties tuned for maximum performance at a given temperature. Finally, the ternary systems are characterized by a phase-separated nanoscopic morphology.

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References and Notes

(1) Roffey, C. G. *Photogeneration of Reactive Species for UV Curing*; John Wiley and Sons: New York, 1997.
(2) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1−61.
(3) Kloosterboer, J. G.; Van de Hei, G. M.; Boots, H. M. *J. Polym. Commun.* **1984**, *25*, 354−357.
(4) Bowman, C. N.; Anseth, K. S. *Macromol. Symp.* **1995**, *93*, 269−276.
(5) Dusek, K. In *Developments in Polymerization*; Harvard, R. N., Ed.; Applied Science: London, 1982; Vol. 3, Chapter 4.
(6) Dusek, K.; Galina, H.; Mikes, J. *Polym. Bull. (Berlin)* **1980**, *3*, 19−25.
(7) Jacobine, A. F. In *Radiation Curing in Polymer Science and Technology III: Polymerization Mechanisms*; Fouassier, J. D., Rabek, J. F., Eds.; Elsevier: London, 1993; Chapter 7, pp 219−68.
(8) Hoyle, C. E.; Lee, T. Y.; Roper, T. *J. Polym. Sci.* **2004**, *42*, 5301−5338.
(9) Cramer, N. B.; Bowman, C. N. *Polym. Prepr.* **2003**, *44*, 17−18.
(10) Lu, H.; Stansbury, J. W.; Bowman, C. N. *Dent. Mater.* **2005**, *21*, 1129−1136.
(11) Bowman, C. N. *Conf. Proc. RadTech Eur.* **2005**, *II*, 9−14.

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