Preparation and Application of Microparticles Prepared Via the Primary Amine-catalyzed Michael Addition of a Trithiol to a Triacrylate

Christopher O. Bounds,[1] Ronald Goetter,[2] John A. Pojman,[1] Max Vandersall[2]

[1]Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804
[2]Elantas PDG, Inc., 5200 North Second Street, St. Louis, Missouri 63147
Correspondence to: J. A. Pojman (E-mail: john@pojman.com)

Received 15 June 2011; accepted 29 September 2011; published online 14 October 2011
DOI: 10.1002/pola.25032

ABSTRACT: We report a novel approach to prepare microparticles via a dispersion polymerization using the amine-catalyzed addition of a trithiol to a triacrylate. Microparticles loaded with various core materials were produced and applied in various systems to improve the desired characteristics of the given system. We determined that this type of microparticle could be used as either a stimulated release or controlled release system for certain desired core materials. These microparticles were able to prevent the interaction between a Lewis acid initiator and fumed silica, improving the rheological properties of an epoxy system containing the initiator. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 409–422, 2012

KEYWORDS: Lewis-acid amine complex; microencapsulation; rheology; resins; thiol-ene

INTRODUCTION

Microencapsulation

Microencapsulation is a process in which a substance is enclosed in a material that affects its transfer to the surroundings.[1,2] Microencapsulation is used in many applications such as pesticides,[3,4] medications,[5] and scratch-n-sniff materials.[6,7] Some of the other common applications in which it is used include cosmetics,[8] as food preservatives,[9] and in carbonless copy paper, where ink contained in microcapsules is released when pressure is applied.[10]

Microencapsulation is often used to achieve the controlled release of a substance. This controlled release can be brought about in several different ways, depending on the type of microcapsules used and the application. For example, many prescription and nonprescription medications that are taken orally are described as "time-released." The medication does not release from the carrier until a certain time, usually when the carrier reaches the stomach.[5] In other cases, it is desirable to keep a constant concentration of drug in the system, which can be achieved with a biodegradable encapsulation material or by diffusion of the drug through an interfacial barrier.[11]

An example of a different controlled release mechanism is that of self-healing polymer composites, in which microcapsules are ruptured mechanically when the material cracks.[12–14] Dicyclopentadiene is normally the core material that is released when a crack reaches the capsules, and it polymerizes upon contact with Grubbs catalyst in the matrix, repairing the crack.

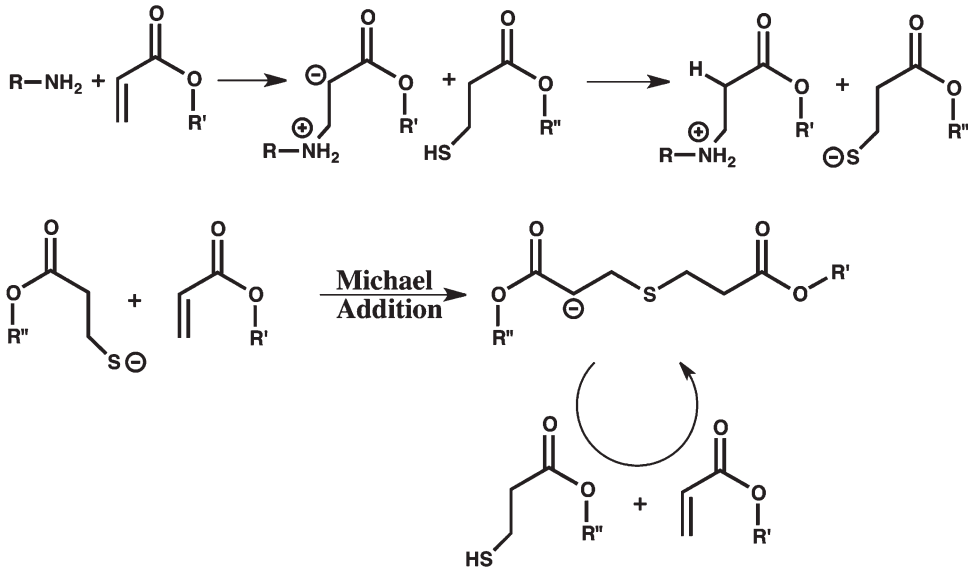
There are a multitude of encapsulation methods that use different polymer shell materials such as complex coacervation using gum arabic and gelatin,[10] interfacial polymerization using polyurea,[15–20] polyurethane,[21] polyurea-polyurethane dual shells,[22] and *in situ* polymerization producing poly (urea formaldehyde).[23] Porous methacrylate microparticles have been produced via the copolymerization of 2,3-epoxypropoxybenene and trimethylolpropane trimethacrylate.[24] Berkel and Hawker prepared composite polymer-metal nanoparticles via the miniemulsion polymerization of AIBN-initiated divinylbenzene. The surfaces of the resulting nanoparticles were post modified via thiol-ene chemistry facilitated by excess surface divynylbenzene.[25] Highly bioactive microparticles were produced by Gu et al. via AIBN-initiated free radical polymerization of a diacrylate followed by thiol-ene surface modification.[26] Costoyas et al. prepared core-shell hybrid silica/polystyrene composite nanoparticles via potassium persulfate initiated miniemulsion polymerization of styrene.[27] Each of these methods have disadvantages, including the need for a multitude of components, the necessity for elevated temperatures, nonambient conditions, and lengthy reaction times. We sought to produce the same quality microparticles with minimum complexities using a primary amine-catalyzed Michael addition of a thiol to an electron-deficient ene. The procedure used in this research only requires a small number of components, can be done in less than 1 h and proceeds at room temperature and ambient pressure.

Thiol-ene chemistry

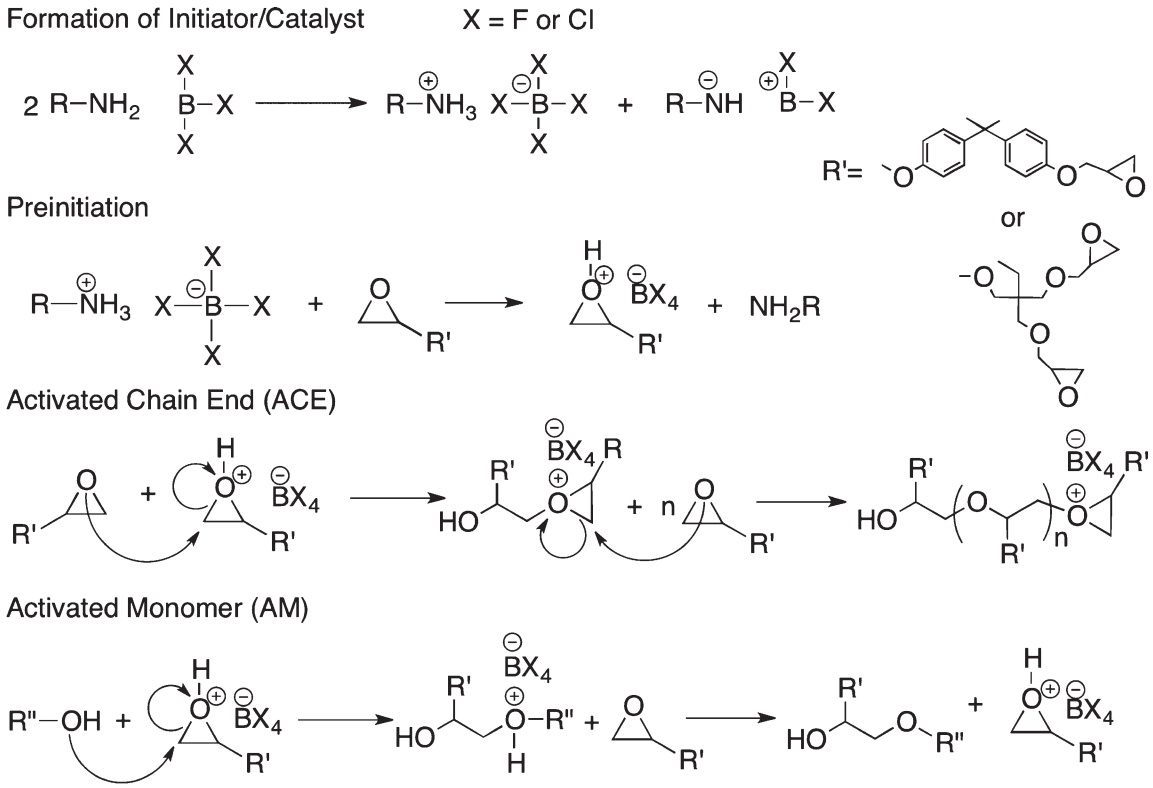
A resurgence of thiol-ene based chemistry has been observed in recent years, with the majority of the research being directed at the photopolymerization of such thiol-ene systems.[28–37] The photoinitiated polymerization of thiol-ene systems has been extensively studied, including the kinetics and the mechanical and physical properties.[29,30,36–39] The thiol-acrylate photopolymerization mechanism involves a dual process comprised of the thiol copolymerizing with the acrylate upon the hydrogen abstraction from the thiol followed by the addition of the thiyl across the double bond of the acrylate and the homopolymerization of the acrylate.[40] Cramer and Bowman[41] compared the glass transition of a homopolymerized diacrylate system with that of a diacrylate system to which tetrathiol had been added. It was observed that the addition of the tetrathiol caused a lower and narrower glass transition.[41] There is a great increase in the uniformity of the network produced when as little as 15 mol % of a multifunctional thiol is integrated into an acrylate network. This allows for the manipulation of both the physical and mechanical properties of a photopolymerized acrylate system by the addition of multifunctional thiols.[29] While preparing thiol-methacrylate dendrimer networks, Nilsson et al. demonstrated the use of excess thiol to obtain 100% conversion of methacrylate groups with residual thiol content available for further surface modification. This allowed for the production of highly functional dendrimer films with adjustable physical properties.[42] A collaborative study done by Koo et al. reported that radical thiol-ene chemistry is not a straightforward method for polymer–polymer conjugation. The two groups concluded that the propagation cycle of the radical thiol-ene process was interrupted by head-to-head coupling.[43]

A thiol-ene system can undergo an ionic polymerization mechanism utilizing a base catalyst, however this type of reaction is limited to electron-deficient unsaturated enes, such as acrylates.[28,30,44,45] Thiol-acrylate systems can be catalyzed using tertiary amines, which function as base catalysts that form thiolate anions that can add across acrylate double bonds. However, these tertiary amine catalysts are relatively inefficient in the formation of such thiolate anions.[28,46] Much more effective and efficient catalysts for the reaction between thiols and electron-deficeint enes include primary amines,[28,46] secondary amines,[46–52] or nucleophilic alkyl phoshine catalysts.[49,51] Lee et al. used a secondary amine to catalyze the Michael addition of thiols to acrylates to produce novel vinyl ester monomers for photopolymerization kinetic studies.[47] Matsushima and coworkers produced tunable hybrid thiol-isocyanate-acrylate systems via the amalgamation of thiol-isocyanate coupling, thiol-acrylate Michael addition, and acrylate homopolymerization using a phosphine catalyst system coupled with photolysis.[53] Chan et al. reported producing a 1:1 reaction of thiol and acrylate to >95% conversion in less than 3 min in the presence of <2% primary or secondary amine.[28] Akzo Nobel reported in a series of patents that a primary amine catalyzed the Michael addition of a thiol faster than did a tertiary amine.[54] Although attaching acrylate groups to a thiol-containing surface, Khire et al. determined that the thiol-acrylate reaction proceeds much faster when using ethylenediamine (almost instantaneously) compared with triethylamine (several hours) or diethylamine (a few minutes).[46] Chan et al. has recently examined the major properties and kinetics of the primary amine-catalyzed Michael reaction with various multifunctional thiols and acrylates.[28] Hu et al. used the formaldehyde-sulfite clock reaction to trigger the time-lapse Michael addition of a trithiol to a triacrylate.[55]

We report here a microencapsulation technique using a primary amine to catalyze the thiol-acrylate anionic chain reaction shown in Scheme 1. The reaction proceeds by the



SCHEME 1 General primary amine-catalyzed thiol-acrylate anionic mechanism. For visualization purposes, this scheme only illustrates a monoacrylate and a monothiol. The analogous acrylate used for this research was a triacrylate (TMTPA) and the thiol was a trithiol (TMPTMP).



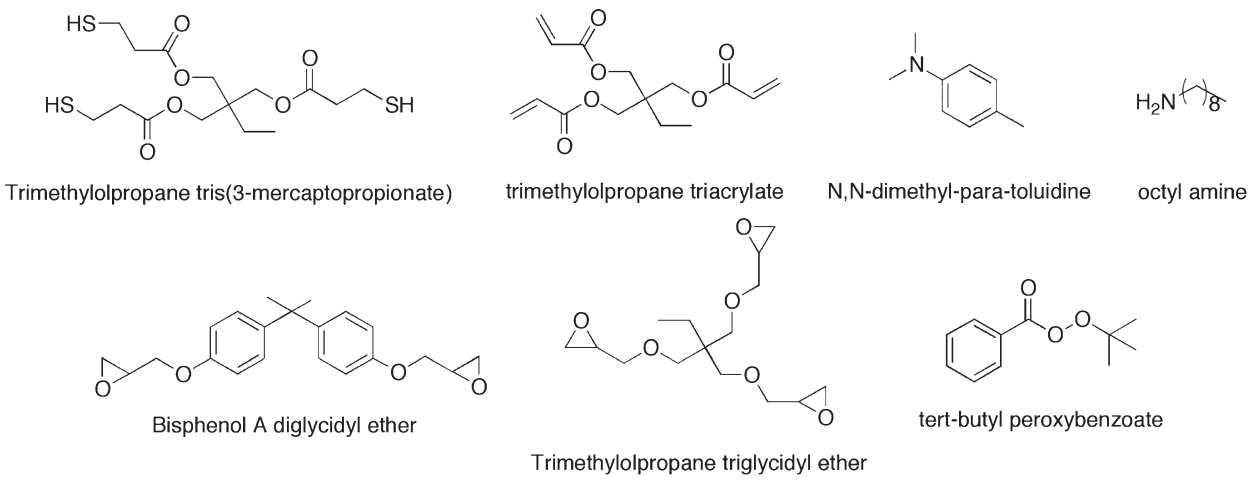
SCHEME 2 Basic Lewis acid initiated epoxy reaction scheme including the ACE and AM propagation mechanisms. X represents either Cl or F, boron trichloride or boron trifluoride, respectively; and R′ indicates the pendent group attached to the epoxy ring (Upper: BADGE and lower: TMPTGE).

addition of the catalyst to the electron-deficient ene and the successive abstraction of the thiol proton to form a thiolate anion allowing for the Michael addition across the acrylate double bond. Unlike the free-radical thiol-ene mechanism, once initiated, termination is not facilitated by the combination of two growing chains. Unlike tertiary amine base catalysts, the use of these nucleophilic catalysts produces systems that reach high conversion at room temperature in minutes or even in seconds.[30] This fast reaction time has been reported from multiple sources[28,30,46,54,56] and makes this process extremely useful as a microencapsulation technique.

Lewis Acid Initiators for Epoxy Resins

Epoxy resins can be cationically polymerized via Lewis acid initiators.[57,58] Lewis acids complex with amines allowing for low reactivity at room temperature but rapid curing at elevated temperatures because the acid–base complex dissociates at high temperatures.[59] Depending on the basicity of the associated amine, the reactivities of these complexes can vary.[60] At elevated temperatures, Lewis acid complexes dissociate into RNH_3^+ and BX_4^- (X being either Cl or F halogens), which activate an epoxy monomer by forming an oxonium ion. The propagation of this cationic polymerization proceeds by two competing mechanisms, the activated chain end (ACE) and the activated monomer (AM) mechanisms. The Lewis-acid-initiated epoxy initiation and propagation reaction scheme, including the ACE and AM mechanisms is shown in Scheme 2.[61] The ACE mechanism predominates at the beginning of the reaction until a sufficient number of polymer chains are formed, causing an increase in hydroxyl groups due to the polymer chain ends at which time the AM mechanism begins to become more favorable.[61]

We have found (both experimentally and from the producer's website, Leepoxy Plastics) that the use of some borontriflouride-amine Lewis acid initiators can cause the polymerization of epoxy resins in as little as 20 s at room temperature.[62] If it is highly reactive, Lewis acid initiator could be microencapsulated, separating it from the epoxy resin, then the result could be a highly reactive latent initiator for epoxy resins. This would be especially useful in a frontally-polymerizable system because high reactivity and heat release are necessary to sustain the front. In batch applications, a borontrichloride-amine (BCl_3-amine) Lewis acid initiator can be used to produce systems with a longer pot life at elevated temperatures, shorter full cure times, and a product that is much less brittle.[59] Also, BCl_3-amine complexes show much better hydrolytic stability.[59] However, in some applications, BCl_3-amine complexes interfere with the desirable thixotropy caused by fumed silica in epoxy resins. We sought to solve this problem by encapsulating the BCl_3-amines complex in a sphere or shell from which it could be released at the desired curing temperature of 170 °C.



SCHEME 3 Notable structures of shell forming monomers, core materials, and epoxy resins.

EXPERIMENTAL

Materials

All materials were used as received without further purification. BCl_3-amine was obtained from Huntsman under the name Accelerator DY9577. Borontrifluoride-amine (BF_3-amine) was obtained from Leepoxy Plastics under the name Leepoxy leecure B-612. *Tert*-butyl peroxybenzoate (TBP) was obtained from Ashland with 98% reported purity. Trimethylolpropane triacrylate (TMTPA) technical grade, trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), octylamine 99%, poly(vinyl alcohol) (PVA) 87–89% hydrolyzed, *N*,*N*-Dimethyl-*p*-toluidine 99%, Trimethylolpropane triglycidyl ether (TMPTGE), and Bisphenol A diglycidyl ether (BADGE) (epoxy equivalent weight of 172–176) were obtained from Sigma-Aldrich. Fumed silica $\geq$99.8 % was obtained from US composites under the name of Aerosil-Cabosil or Aerosil® 200 with a specific surface area of 200 $\pm$ 25 m^2/g and an average primary particle size of 12 nm.

Equipment

The agitation reactor used for dispersing the mobile phase consisted of an IKA RW 20 DS1 digital overhead stirrer equipped with a three-blade low shear propeller with a diameter of 54 cm. The sonicator used was a Branson Sonifier 450 with a maximum output of 400 Watts. All rheological measurements were obtained from a TA AR1000 equipped with parallel plates. All strength data were obtained using a three-point bending method with an INSTRON 5582 and Bluehill software. Optical microscopy was performed using a phase contrast Nikon ECLIPSE 50i microscope equipped with a Nikon Digital Sight DS-Fi1 camera. The optical microscopy measurements were made using calibrated NIS-Elements BR 3.0 software. The differential scanning calorimetry data were obtained using a TA Instruments. The thermal gravimetric analysis data were obtained using a TA instruments TGA 2950.

Generic Procedure

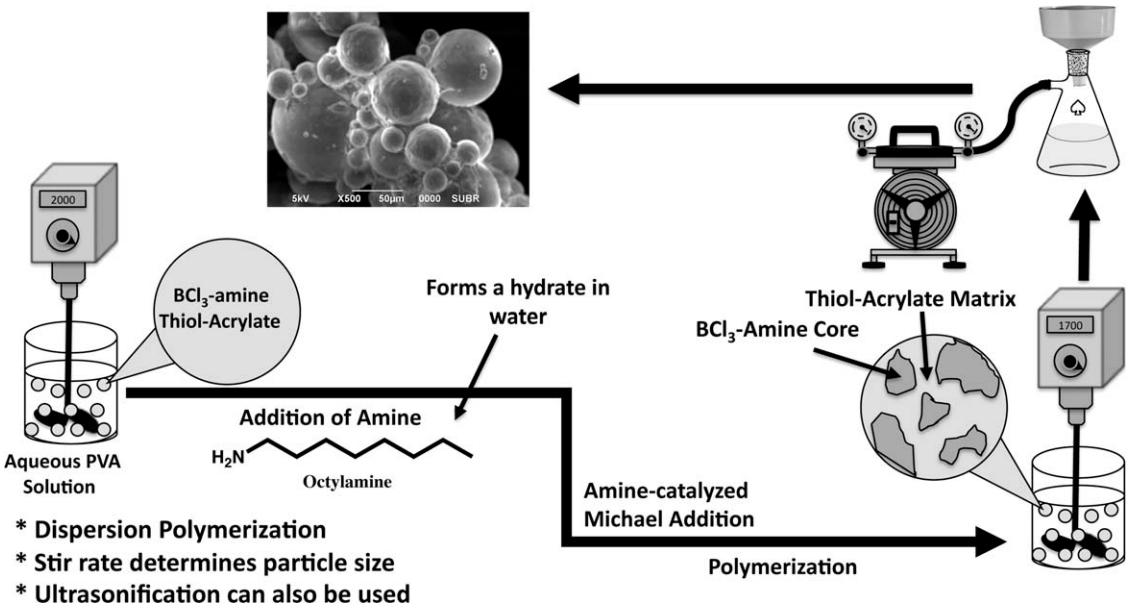
Scheme 4 illustrates a generic procedure used in the formation of the thiol-acrylate microparticles. The general procedure consisted of the dispersion of a solution containing some core material dissolved in a stoichiometrically equivalent solution of TMTPA and TMPTMP in a 1.28% PVA aqueous solution. This solution was dispersed using various amounts and sources of energy depending on the size of microparticles (or nanoparticles) desired. Once the droplet size was adequate, ~3% by volume of octyl amine was added to the dispersion to catalyze the thiol-acrylate reaction. The microparticles were harvested via vacuum filtration and dried overnight under ambient conditions. Depending on the contained core material, various solvents were used to wash the excess core material from the exterior of the microparticles before their testing and incorporation into a given system.

Microparticles containing DMpT

Microparticles containing dimethyl-*para*-toluidine (DMpT) as the core component were prepared with a matrix comprised of TMTPA and TMPTMP catalyzed by octylamine. A solution of stoichiometrically equivalent TMPTMP and TMPTA was prepared containing 15.94 and 11.85 g, respectively. The core DMpT (20 g) was dissolved in the trithiol/triacrylate solution. This solution was then emulsified in 500 mL of a 1.28% PVA aqueous solution with a stir motor equipped with a three-bladed propeller. The mixture was agitated for 30 min at 2100 rpm. Once the desired droplet size range was achieved, 3% by volume (~0.9 mL) of octylamine was added to the mixture to catalyze the polymerization, and the stir rate was decreased to 1,700 rpm. The mixture was allowed to react for 1 h at room temperature and ambient temperature with continuous mixing at 1,700 rpm. The microparticles were recovered by vacuum filtration and dried overnight. Any unencapsulated material was washed from the exterior of the shells using cyclohexane or hexane before the microparticles were used.

Microparticles containing BF_3-amine

Microparticles containing BF_3-amine (BF_3) complex as the core component were prepared with a matrix comprised of TMTPA and TMPTMP catalyzed by octyl amine. A solution of core material was prepared by dissolving 40 mL of a borontrifloride-amine complex in a stoichiometrically equivalent



SCHEME 4 Basic process for encapsulating a core material in a thiol-acrylate matrix. Small deviations from this process are needed in a few cases.

solution of TMTPA (11.85 g) and trimethylolpropane tris(3-mercaptoproionate) (15.94 g). Approximately 10% relative to the BF_3-amine complex of TBP was added to the core material as a rupturing component. The core solution was then emulsified using a stir motor equipped with a three-blade propeller in 500 mL of a 0.4% span in mineral oil solution contained in a water bath at 50 °C (heat necessary only to keep the viscosity of oil relatively low). The mixture was agitated for 10 min at 2000 rpm. Once the desired droplet size range was achieved, 2 mL of octylamine (~7% relative to the trithiol/triacrylate content) was added, and the stir rate was decreased to 1700 rpm. The mixture was allowed to react for 1 h at 50 °C with continuous mixing at 1700 rpm. After 1 h, the microcapsules were recovered by vacuum filtration. To remove the remaining viscous mineral oil from the system, the microcapsules were washed with cyclohexane.

Micro/Nanoparticles Containing Carbon Nanotubes

Microparticles containing 1% carbon nanotubes (CNTs) as the core component were prepared with a matrix comprised of TMTPA and TMPTMP (TT1) catalyzed by octyl amine. A solution of stoichiometrically equivalent TT1 and TMPTA was prepared containing 0.81 and 0.60 g, respectively. The core, CNTs (0.0140 g), was dispersed in the trithiol/triacrylate solution via a magnetic stirrer for 20 min. This solution was then emulsified in 25 mL of a 1.28% PVA aqueous solution in an ice bath (to keep the temperature low) with a Branson sonifier 450 at constant 45% output. The mixture was emulsified for 30 min with this constant sonification. Once the mixture was efficiently emulsified, ~3% by volume (0.05 mL) of octylamine was added to the mixture to catalyze the polymerization. The mixture was allowed to react for 1 h at room temperature with continuous sonication. The micro/nanoparticles were recovered by vacuum filtration and dried overnight.

Microparticles containing BCl_3-amine

Microparticles containing BCl_3-amine (BCl_3) complex as the core component were prepared with a matrix comprised of TMTPA andTMPTMP catalyzed by octyl amine. A solution of stoichiometrically equivalent TMPTMP and TMPTA was prepared containing 15.94 and 11.85 g, respectively. The core BCl_3-amine (60 g) was dissolved in the trithiol/triacrylate solution. This solution was then emulsified in 500 mL of a 1.28% PVA aqueous solution with a stir motor equipped with a three-bladed propeller. The mixture was agitated for 30 min at 2000 rpm. Once the desired droplet size range was achieved, 3% by volume (~0.9 mL) of octylamine was added to the mixture to catalyze the polymerization, and the stir rate was decreased to 1700 rpm. The mixture was allowed to react for 1 h at room temperature and ambient pressure with continuous mixing at 1700 rpm. The microparticles were recovered by vacuum filtration and dried overnight.

Preparation of TMPTGE samples for rheology testing

TMPTGE samples containing silica and dissolved BCl_3-amine, microencapsulated BCl_3-amine or no BCl_3-amine were prepared to examine the rheological benefit associated with separating the silica and BCl_3-amine via microencapsulation. Initially, 10 g of TMPTGE was placed in a vial and heated in a water bath at 50 °C for 20 min to decrease the viscosity. Next, 7.5 phr (parts per hundred resin) silica (Aerosil 200) was dispersed in the TMPTGE. The mixture was then returned to the water bath for an additional 10 min, periodically removing and stirring. The mixture was then removed and 10 phr BCl_3-amine was dissolved or dispersed (1 g dissolved or 1.54 g microparticles to compensate for matrix

material). The vials were then capped and stored for varying periods of time. Viscosity as a function of shear rate was determined at a constant temperature of 25 °C with the rheometer gap set at 500 μm.

Preparation of BADGE samples for rheology testing

BADGE samples containing Polygloss 90 (kaolin clay), silica and dissolved BCl_3-amine, microencapsulated BCl_3-amine or no BCl_3-amine were prepared to examine the rheological benefit associated with separating the silica and BCl_3-amine via microencapsulation. Initially, 10 g of BADGE was placed in a vial and heated in a water bath at 50 °C for 20 min to decrease the viscosity. Next, 1.5 phr silica (Aerosil 200) and 1.5 phr Polygloss 90 were dispersed in the BADGE. The mixture was then returned to the water bath for an additional 10 min, periodically removing and stirring. The mixture was then removed and 3 phr BCl_3-amine was dissolved or dispersed (0.3 g dissolved or 0.5 g microparticles to compensate for matrix material). The vials were then capped and stored for varying periods of time. Viscosity as a function shear rate was determined at a constant temperature of 25 °C with the rheometer gap set at 750 μm.

Preparation of TMPTGE Samples for Instron Testing

TMPTGE samples containing dissolved BCl_3-amine or microencapsulated BCl_3-amine were prepared to test the relative strength of the sample if BCl_3-amine microparticles were used instead of dissolved BCl_3-amine. The epoxy bars were 7.5 × 2.3 × 1.0 cm. Initially, 20 g of TMPTGE was placed in an 80-mL beaker and heated in a water bath at 50 °C for 20 min to decrease the viscosity. After the viscosity was acceptable, 2.5 phr (parts per hundred resin) fumed silica was dispersed in the TMPTGE. The mixture was then returned to the water bath for an additional 10 min, but periodically removed and stirred. The mixture was then removed, and 5 phr BCl_3-amine was dissolved or dispersed (1g dissolved or 1.54 g microparticles to compensate for shell material). The mixture was then placed under vacuum to remove the air introduced by stirring. Once the majority of the air had been removed, the mixture was poured into a poly(tetrafluoroethylene) mold and cured in an oven at 170 °C for 1 h. The epoxy bars were then subjected to Instron strength testing.

RESULTS AND DISCUSSION

There are many advantages to using nucleophilic primary amine-catalyzed thiol-acrylate chemistry as a microencapsulation method. First, the thiol-acrylate reaction is not affected by oxygen entrained into the system via mixing.[30] Second, because the primary-amine catalyzes the Michael addition of a thiol to an acrylate very rapidly,[46] this process has an advantage over many other types of microencapsulation techniques as it can be completed in less than 1 h, as opposed to many hours or even days. Third, this method can proceed at room temperature[30] as opposed to other microencapsulation techniques that require a reaction temperature of 50 °C or higher. Finally, as with other microencapsulation procedures and general dispersion polymerizations, the size of the droplets (mobile phase) can be easily manipulated by the surfactant concentration and/or agitation rate.

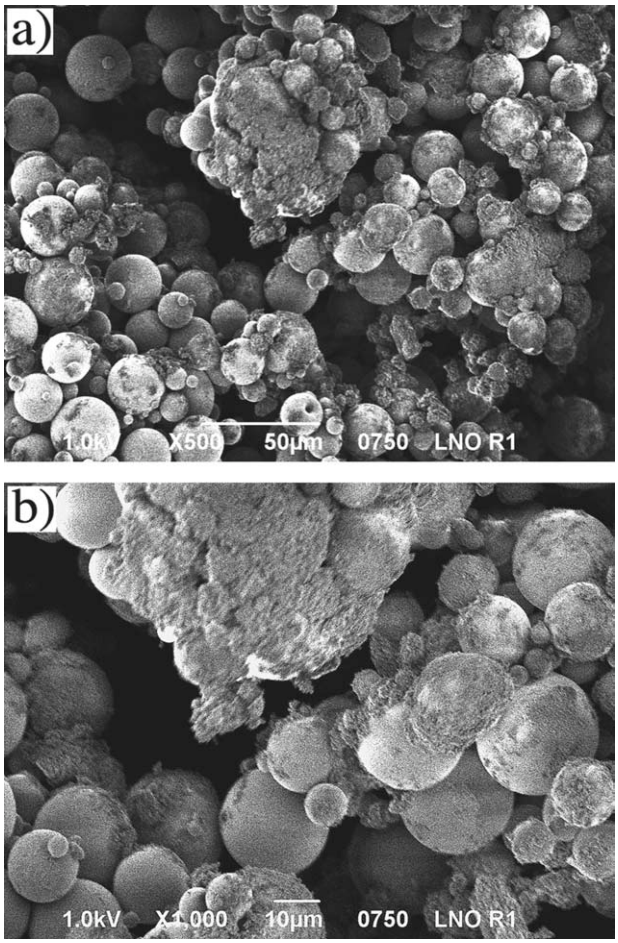


FIGURE 1 SEM images of microparticles containing DMpT. (a) ×500 magnification and (b) ×1000 magnification.

Incorporation of different core materials

Scanning electron microscopy (SEM) analysis was preformed on microparticles containing different core materials to determine the effectiveness of the microencapsulation technique relative to the core material. The SEM images can be observed in Figures 1–4.

Dimethyl-p-toluidine microparticles

DMpT, a tertiary aromatic amine that accelerats the decomposition of benzoyl peroxide at room temperature,[63] was microencapsulated using a thiol-acrylate matrix, and SEM images were obtained [Fig. 1(a,b)]. From these SEM images, it can be observed that most of these microparticles are uniform in shape and have diameters less than 50 μm. It can be noted that there was a significant amount of unencapsulated core DMpT remaining on the exterior of the microparticles. This unencapsulated core material caused the particles to agglomerate and be inefficient as a mechanism for separating the core material from its surroundings. This excess core material could be washed away using cyclohexane; however, the DMpT would eventually diffuse through the matrix material and again be present on the surface of the microparticles. Because of this leaching problem this was found to be an inefficient method for microencapsulating this particular

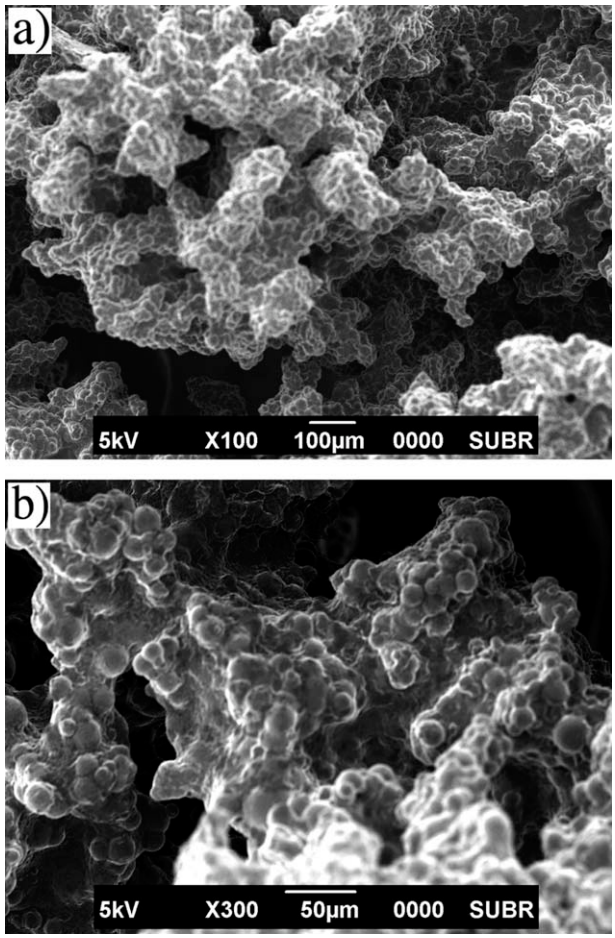


FIGURE 2 SEM images of microparticles containing boron trifluoride amine complex. (a) ×100 magnification and (b) ×300 magnification.

tertiary aromatic amine. However, this does open up new pathways for the use of thiol-acrylate microparticles as control release vessels, and these pathways will be explored in future work.

BF_3-amine microparticles

Boron trifluoride-amine 612 is a highly reactive Lewis acid-amine complex capable of initiating the polymerization of a bisphenol A epoxy resin in ~75 s at room temperature with only 8–12 phr of the initiator.[62] This Lewis acid initiator was microencapsulated using a thiol-acrylate matrix via an oil-in-oil dispersion polymerization, and SEM analysis was preformed on the resulting microparticles [Fig. 2(a,b)]. These microparticles had an overall agglomerated, sponge-like consistency that could be a result of multiple factors associated with the process. Figure 2(a) (low magnification) illustrates this overall agglomerated appearance; however, upon higher magnification [Fig. 2(b)], it can be observed that small particles can be distinguished from the agglomeration. They are simply fixed together by some material between each particle. Because these microparticles were prepared via an oil-in-oil dispersion as opposed to an oil-in-water dispersion, an adequate and a stable dispersion of the droplets could be more difficult as a result of the higher interfacial tension within the system, the more viscous continuous oil phase, and the large density difference between the continuous phase and mobile phase.

Another possible problem could be associated with the use of the thermal initiator, TBP, as a rupturing agent. The TMPTMP (trithiol) can act as an accelerator to decompose the TBP causing the homopolymerization of the TMPTA (triacrylate) via a free radical chain growth mechanism. This could leave excess, unreacted, viscous TMPTMP that could cause a high level of agglomeration. Future work and possible solutions to this agglomeration problem could include decreasing the viscosity of the continuous mineral oil phase by the addition of a less viscous oil such as cyclohexane, preparing the microparticles using an alternate rupturing agent or possibly no rupturing agent, and increasing the density of the continuous phase.

Another complication of the process is the miscibility of the amine catalyst in the mineral oil continuous phase. This forces the use of excess amine that could undergo an exchange reaction with the BF_3-amine complex, changing the associated amine thereby changing the reactivity of the

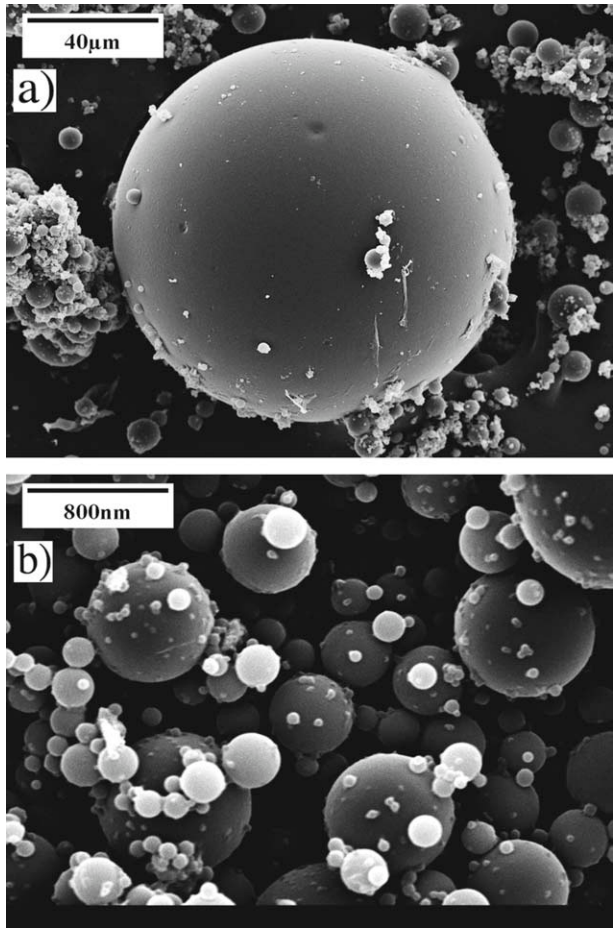


FIGURE 3 SEM images of microparticles containing CNTs. A fraction of the particles (a) were observed to be relatively large, however most (b) of the particles were observed to be <1 μm.

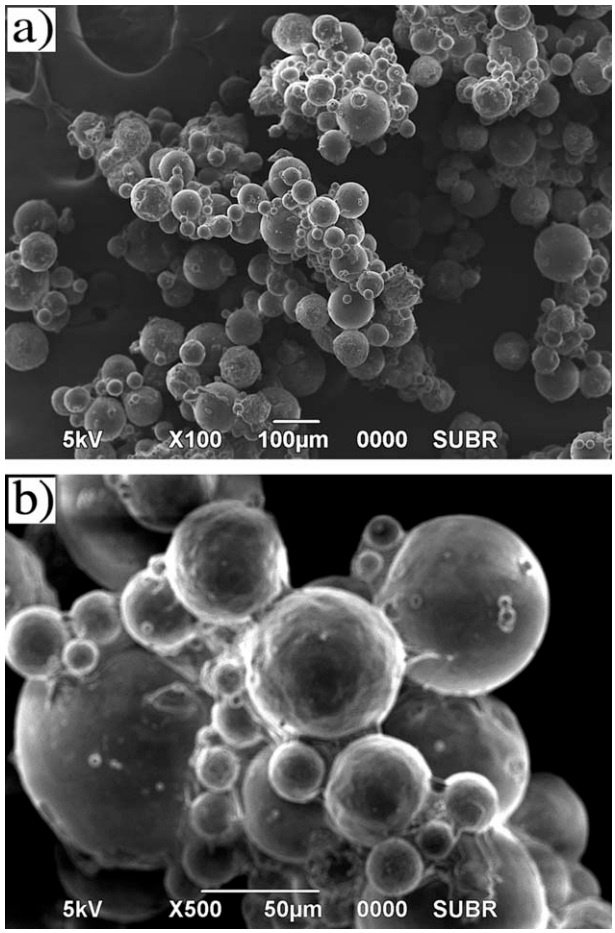


FIGURE 4 SEM images of BCl_3-amine microparticles. (a) ×100 magnification and (b) ×500 magnification.

initiator. One approach to preventing this problem and possibly achieving microparticles with different properties will include utilizing a true thiol-ene reaction instead of the thiol-acrylate reaction. A multifunctional electron-rich ene such as 2,4,6-triallyloxy-1,3,5-triazine or 1,3,5-triallyl-1,3,5-trazine-2,4,6-trione could be photopolymerized with the TMPTMP producing a copolymer composed of the simple ene rather that the acrylate.[30] Alternately, this reaction could also be initiated by the TBP as it can be decomposed at room temperature in the presence of a thiol, and the electron-rich ene cannot homopolymerize. This would produce microparticles with similar properties while reducing the problems associated with catalyst miscibility. The preliminary results associated with the application of these microparticles indicated limited and yet to be understood success. Because of the high agglomeration of the product, the BF_3-amine microparticles were very difficult to disperse in an epoxy system.

In some cases, the microparticles were observed to greatly increase the pot-life of the highly reactive BF_3-amine/epoxy system and still be somewhat reactive upon heating the system. The true cause of the increase in the pot-life of the system is still not completely understood. There is a possibility as mentioned above that the Lewis acid initiator underwent an exchange reaction with the amine catalyst used to produce the microparticles, thereby reducing the reactivity of the initiator and causing an increase in pot life. Future work will determine the effectiveness of these microparticles in extending the pot-life of a highly reactive epoxy system.

CNTs microparticles

Microparticles containing CNTs were prepared using the general thiol-acrylate microencapsulation procedure with a few small deviations, and SEM analysis was performed [Fig. 3(a,b)]. These particles were prepared with a smaller average particle size via the use of ultrasonication during the dispersion and polymerization process. The particles were observed to have a large particle size distribution ranging from 120 μm [Fig. 3(a)] to $<$75 nm [Fig. 3(b)]. These were the first thiol-acrylate microparticles (or nanoparticles) to be prepared using this method via ultrasonication. CNTs have the potential to improve many properties of composite materials including mechanical[64,65] and electronic[66–68] properties. A normal problem associated with the use of CNTs is that unmodified CNTs aggregate due to van der Waals interactions among the nanotubes.[69,70] This thiol-acrylate matrix could be useful in preventing CNTs from agglomerating when dispersed in a medium. Conductivity analysis and mechanical testing will be preformed to determine the validity of this method of improving composite materials via the use of well-dispersed CNTs.

BCl_3-amine microparticles

Another Lewis acid-amine complex, BCl_3-amine was microencapsulated using a thiol-acrylate matrix and SEM analysis was preformed on the resulting microparticles [Fig. 4(a,b)]. This BCl_3-amine complex is a latent, heat-activated initiator for epoxy systems that has a nearly infinite pot life.[59] The purpose for microencapsulating this initiator was unlike the other research performed here. We have found that there is some interaction that takes place between BCl_3-amine and fumed silica, which is normally added to epoxy systems as a thixotropic agent. This interaction causes an undesirable loss in the rheological properties of the monomer solution. By microencapsulating this initiator, the matrix material was observed to prevent this unwanted interaction by separating the initiator from the silica until heated, allowing the rheological properties to be preserved until the desired reaction took place. From the above SEM images [Fig. 4(a,b)], it can be observed that these microparticles were uniform in shape, free of agglomeration, did not contain any unencapsulated material around the exterior of the shells, and had a relatively narrow particle size distribution. For these and other reasons, these microparticles were the main focus of the research, and more extensive results were obtained regarding these microparticles relative to the other particles prepared here.

Particle Size Distribution

Microparticles containing no core material were prepared at different stir rates to determine the ease of manipulation of the microparticle size. The relative sizes of the microparticles

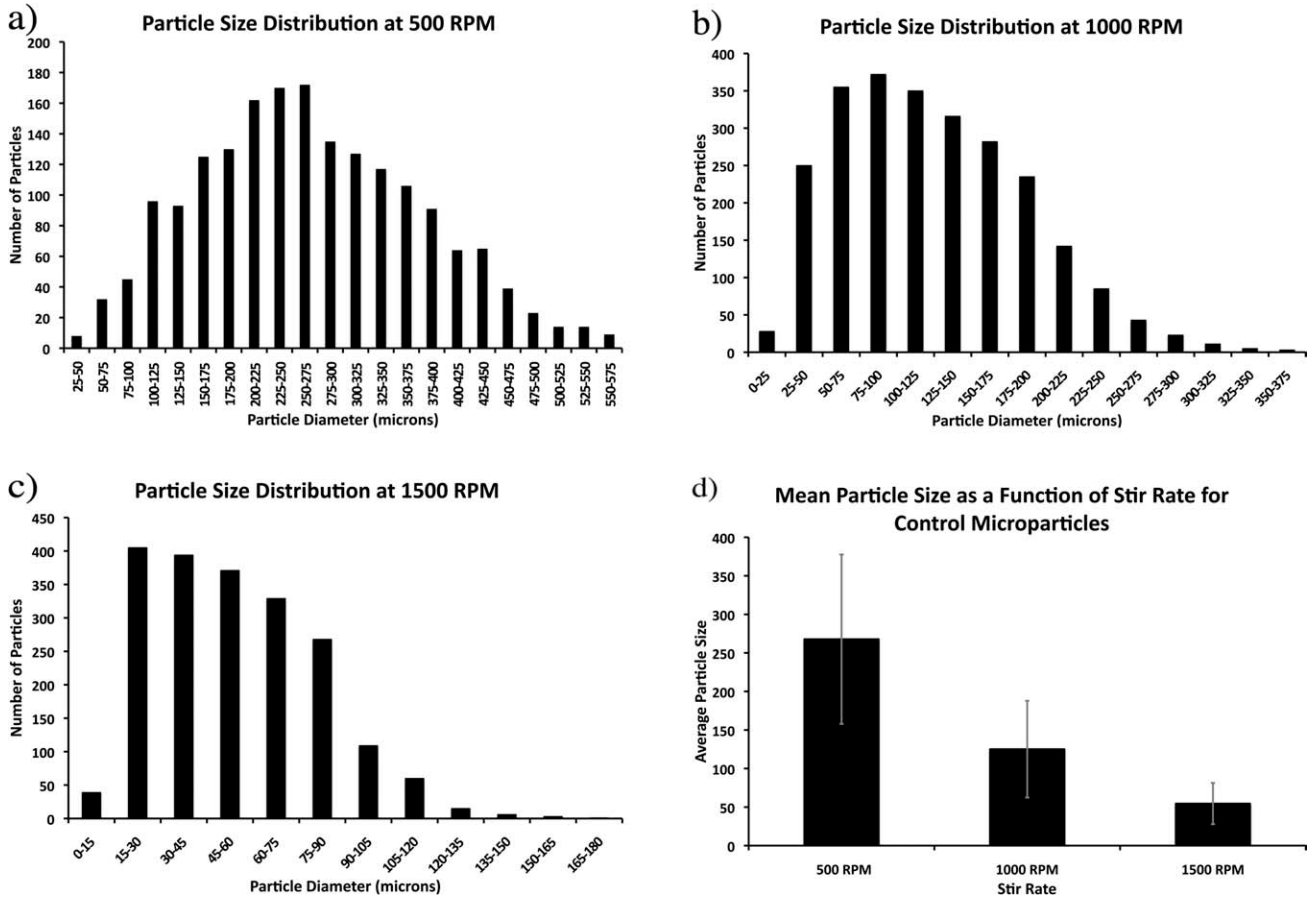


FIGURE 5 Particle size distribution data for solid control microparticles (no core component) at (a) 500, (b) 1000, and (c) 1500 rpm. (d) The distribution data were summarized (d). All data were collected via optical microscopy and particle size analysis software.

were determined via optical microscopy and size analysis software. The particle size distributions at different stir rates are illustrated in Figure 5(a–c). A summary of the statistics associated with these data is tabulated in Table 1.

As can be observed from the particles size distribution data, as the stir rate was increased from 500 rpm [Fig. 5(a)] to 1000 [Fig. 5(b)] to 1500 rpm [Fig. 5(c)], the mean particle diameter decreased. Also, as more energy was applied, the distribution became narrower, as was proven by the decrease in the values of standard deviation. Because these particles in Figure 5a–c were prepared with no core component, the exact size values cannot necessarily be used to forecast the average particle diameter of any given system. However, the trend can be applied to any system containing any core material.

BCl_3-amine microparticles were also prepared at different stir rates, and the particle size distributions were determined via optical microscopy and size analysis software. The particle size distributions at different stir rates are illustrated in Figure 6(a,b), and a summary of the statistics associated with these data is tabulated in Table 2.

As can be observed from the BCl_3-amine particles size distribution data, as the stir rate was increased from 900 rpm [Fig. 6(a)] to 2000 rpm [Fig. 6(b)], the mean particle diameter decreased, and the distribution became narrower. The average particle sizes for the BCl_3-amine microparticles do not fall into the size ranges indicated by the data for the empty microparticles as a function of stir rate. Higher stir rates were required to prepare BCl_3-amine microparticles with a comparable average particle size to that of the control particles. For example, empty control microparticles with an average particle size of 267.8 ± 109.9 could be obtained by agitating the system at 500 rpm while BCl_3-amine microparticles with a similar average particle size (268.3 ± 98.2) required an agitation rate of 900 rpm. Nonetheless, the same trends regarding the stir rate, mean diameter, and standard

TABLE 1 Control (Empty) Thiol-Acrylate Microparticles Statistics as a Function of Stir Rate

rpm	Mean Diameter (um)	Standard Deviation (um)	Maximum Diameter (um)	Minimum Diameter (um)
500	267.8	109.9	583.4	34.3
1,000	125.1	62.8	369.8	12.4
1,500	54.5	26.8	171.3	6.0

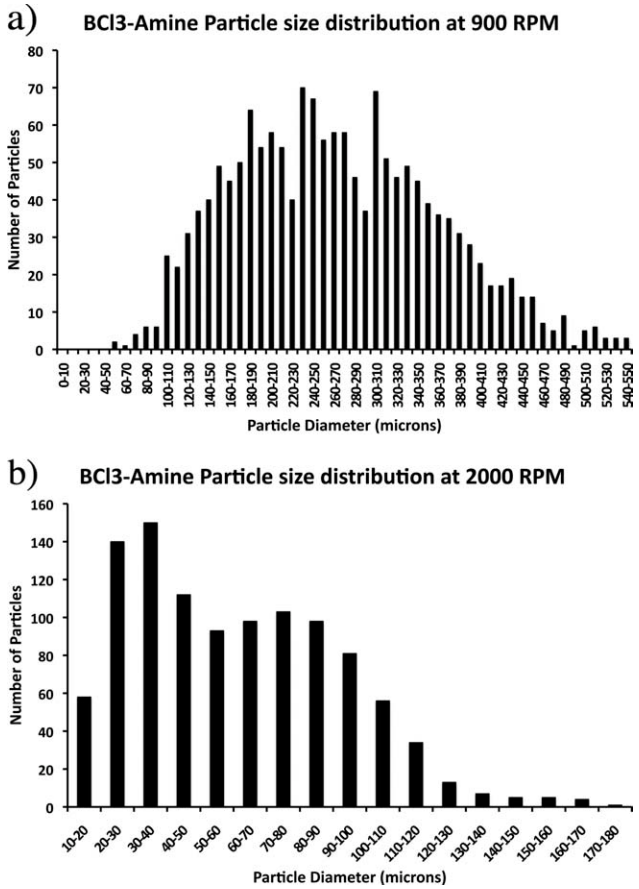


FIGURE 6 Particle size distribution for BCl_3-amine agitated at (a) 900 and (b) 2000 rpm. All data were collected via optical microscopy and particle size analysis software.

deviation were observed. Depending on the core component used, different amounts of applied energy will result in different average particle sizes and standard deviations due to the differences in the interfacial tensions between the continuous phase and the mobile phase of the given dispersion polymerization. However, regardless of the system in question, an increase in the stir rate resulted in a decrease in the average particle size and standard deviation.

Determination of Core Loading Percent for BCl_3-amine Microparticles

It was vital to know the percentage of core material contained within the microparticle matrix before a valid comparison to be made between systems containing the core in either the dissolved or microencapsulated form. The following formula was used to estimate the core loading percentage.

$$\text{Core Loading } \% = \frac{\text{Core}}{\text{Core} + \text{Monomer 1} + \text{Monomer 2}}$$

In this formula, for the BCl_3-amine system, the Core, Monomer 1, and Monomer 2 values corresponded to the amount of BCl_3-amine, TMPTMP, and TMPTA in grams, respectively. Using this equation, the core loading percent for the BCl_3-amine microparticles was calculated to be 68%. This formula was assumed to be reliable if all of the components used in the process were immiscible in the continuous aqueous phase because any excess materials, either unencapsulated core or unreacted monomer, would be easily observed due to the formation of a separate layer from the filtered aqueous phase in which they would be immiscible. The fact that the thiol-acrylate reaction is known to reach high conversion, as explained above, also adds confidence to this method of estimating the core loading percentage. However, because the above formula technically provides only the theoretical core loading if all of the components in the system were completely immiscible in water, thermal gravitational analysis was performed on microparticles containing BCl_3-amine (Fig. 7) to validate this method of estimating the core loading percent.

From the TGA data in Figure 7, the core loading percent appeared to be ~50%. This indicated that the theoretical equation was reasonably close to the experimental result. The lower core loading percent indicated by the TGA could be attributed to the slow release of the core component over time. Some of the core BCl_3-amine could have been trapped within the polymer matrix preventing its volatilization even at the elevated temperature. To confirm that the weight loss can be attributed only to the loss of the core material, the TGA data in Figure 7(b) illustrates both the pure and microencapsulated BCl_3-amine heated and held at both 120 and 170 °C for 1 h each. These temperatures were chosen to insure that the microparticles were free of water and because BCl_3-amine complex completely dissociates below 170 °C.[71] At the 170°C point, it can be observed that there was a steady loss of weight followed by relatively no weight loss until about 350 °C at which time the polymer matrix began to decompose. Both the data received from the TGA, and the theoretical equation was considered when determining the core loading percent, and from these data it was concluded that the core loading percent for the BCl_3-amine microparticles was ~60%.

Improvements in the Rheological Properties of an Epoxy System

Once the core loading percentage was determined, the BCl_3-amine microparticles were applied to two epoxy systems in an attempt to improve the rheological properties of the resulting systems prior to polymerization. The rheological data obtained can be observed in Figures 7 and 8. In can be deduced from these figures that the microencapsulation of the BCl_3-amine complex in a thiol-acrylate matrix was successful.

TABLE 2 BCl_3-amine Thiol-Acrylate Microparticles Statistics as a Function of Stir Rate

rpm	Mean Diameter (um)	Standard Deviation (um)	Maximum Diameter (um)	Minimum Diameter (um)
900	268.3	98.2	645.5	57.7
2,000	62.4	31.5	179.2	13.0

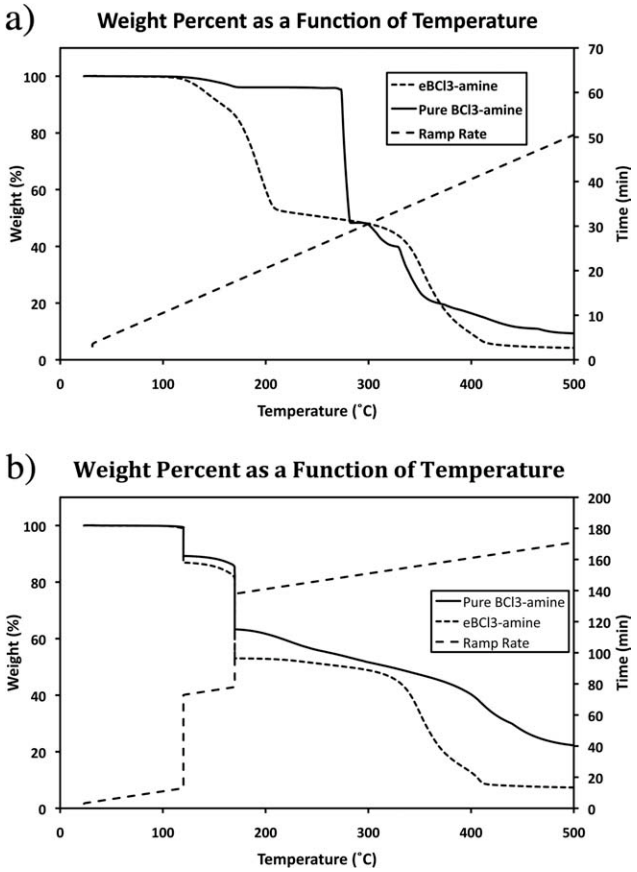


FIGURE 7 Thermal gravitational analysis data for BCl_3-amine thiol-acrylate microparticles. (a) Encapsulated BCl_3-amine ($eBCl_3$-amine) and pure BCl_3-amine heated at a rate of 10 °C/min with initial weights of 3.403 mg and 7.776 mg, respectively. (b) Encapsulated BCl_3-amine ($eBCl_3$-amine) and pure BCl_3-amine heated at a rate of 10 °C/min and held at 120 °C for 1 h and again at 170 °C for 1 h with initial weights of 7.497 and 7.595 mg, respectively. The heating rate is also added to show correlation between the heat and the weight loss.

TMPTGE rheological properties

Depending on the concentration of the fumed silica in a given system, different rheological properties (shear thickening, shear thinning, or even thixotropic) can be observed. High concentrations of fumed silica can cause shear thickening to occur.[72] In the case illustrated in Figure 8 where TMPTGE was the epoxy resin used, a higher concentration of fumed silica was used than would normally be incorporated into a commercial formulation. This was done to amplify the effect of the interaction between the BCl_3-amine and the fumed silica. The curves in Figure 8 therefore present a shear thickening effect.

It can be noted in Figure 8(a) that the curves corresponding to the system containing encapsulated BCl_3-amine were much more similar to the control system (no BCl_3-amine) than those corresponding to the systems containing the dissolved BCl_3-amine. As the rotational velocity was increased on the control systems (no BCl_3-amine), the viscosity was observed to display a shear thickening effect after ~3 rpm. The systems containing the microencapsulated BCl_3-amine followed a very similar shear thickening trend with a less intense increase in the viscosity after ~3 rpm of rotational velocity. The systems containing the dissolved BCl_3-amine were observed to act initially with a similar trend until ~3 rpm. At this point, instead of the shear thickening effect, the system stabilized with a constant viscosity well below that of the control or microparticle systems. The lack of the shear thickening effect of the system containing dissolved BCl_3-amine was caused by the interaction between the fumed silica and the BCl_3-amine. This interaction rendered the silica useless as an agent to improve the rheological properties of the system. The large difference in the rheological properties of the system containing the dissolved BCl_3-amine and the system containing the microencapsulated BCl_3-amine, as well as the similarities between the properties of the latter and the control system indicated that the polymeric matrix

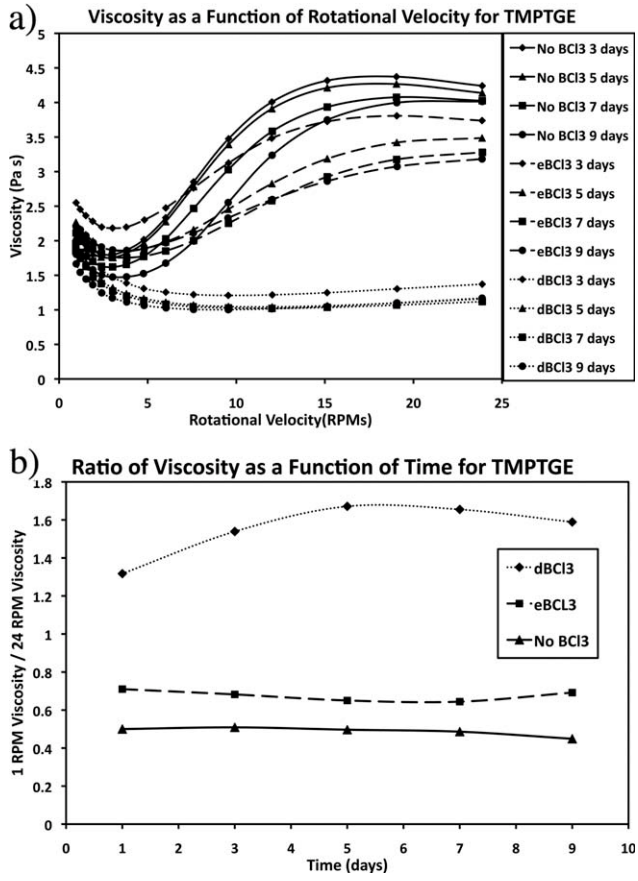


FIGURE 8 Rheology data for TMPTGE systems containing BCl_3-amine complex and fumed silica. Each TMPTGE sample contained 7.5 phr fumed silica and either no BCl_3-amine, 10 phr dissolved BCl_3-amine, or 10 phr microencapsulated BCl_3-amine (calculated based on core-loading). (a) raw rheometer data of viscosity (Pa s) was illustrated as a function of rotational velocity (converted to rpm) for different samples over a period of 9 days. (b) the ratio of low viscosity to high viscosity was illustrated as a function of time for three different types of samples.

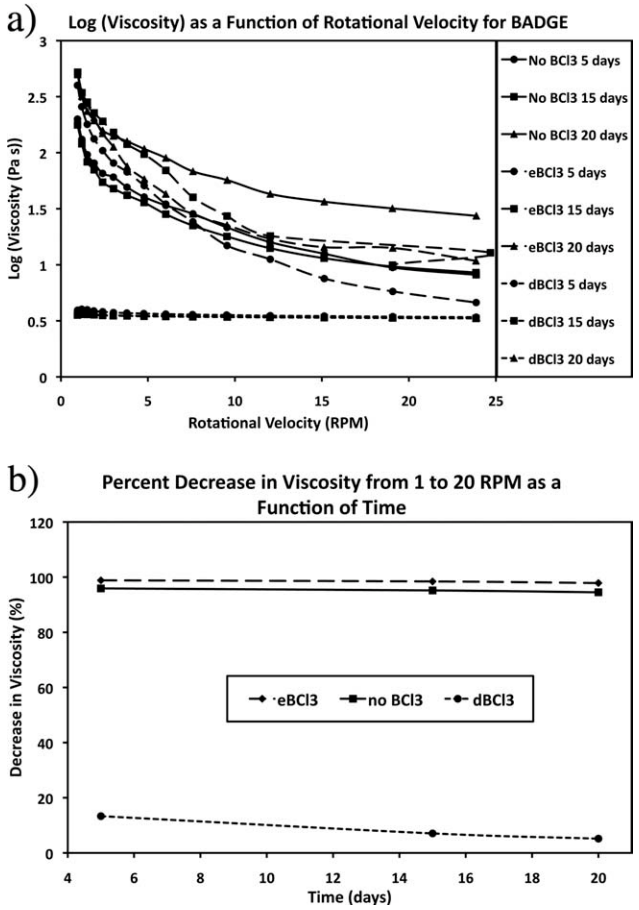


FIGURE 9 Rheology data for BADGE systems containing BCl_3-amine complex, fumed silica, and kayolin clay. Each BADGE sample contained 1.5 phr fumed silica, 1.5 phr polygloss 90. and either no BCl_3-amine, 10 phr dissolved BCl_3-amine, or 10 phr microencapsulated BCl_3-amine (calculated based on core-loading). (a) the raw rheometer data of viscosity (Pa s) was illustrated as a function of rotational velocity (converted to rpm) for different samples over a period of 20 days. (b) comparison of the decrease in viscosity from 1 to 20 rpm was illustrated as a function of time for the three different types of samples.

prevented the interaction of the BCl_3-amine complex with the fumed silica, allowing for the preservation of the rheological properties of the monomer solution.

BADGE rheological properties

In order to test the effectiveness of these microparticles in a real world setting, the rheology of a commercially useful BADGE system was studied. In this system, kaolin clay was also incorporated as additional filler, along with fumed silica (functioned mainly as a thixotropic agent). Figure 9 illustrates the results obtained from this study, and further proves the success of the microparticle systems.

As can be observed in Figure 9(a), both the control systems (no BCl_3-amine) and the systems containing the microencapsulated BCl_3-amine exhibit a shear thinning effect as a function of rotational velocity and follow almost identical trends. The systems containing the dissolved BCl_3-amine that was available to interact with the fumed silica displayed no signs of a shear thinning effect. Figure 9(b) further proves this point by illustrating the decrease in viscosity from 1 rpm to 20 rpm rotational velocity as a function of time. It can be noted from the curve corresponding to the dissolved BCl_3-amine system in Figure 9(b) that the interaction became more prominent with time from 5 to 20 days as the percent decrease approached zero. From these studies of the rheology of the two epoxy systems, it was concluded that the thiol-acrylate matrix was successful in separating the core BCl_3-amine from the fumed silica, preventing the undesirable loss in the rheological properties of the monomer systems.

Strength Testing of TMPTGE Systems

After determining that the rheological properties of an epoxy system could be maintained via microencapsulation, it was vital to determine if comparable strength data could be obtained using the microparticle systems. The strength of two TMPTGE systems differencing only in the method by

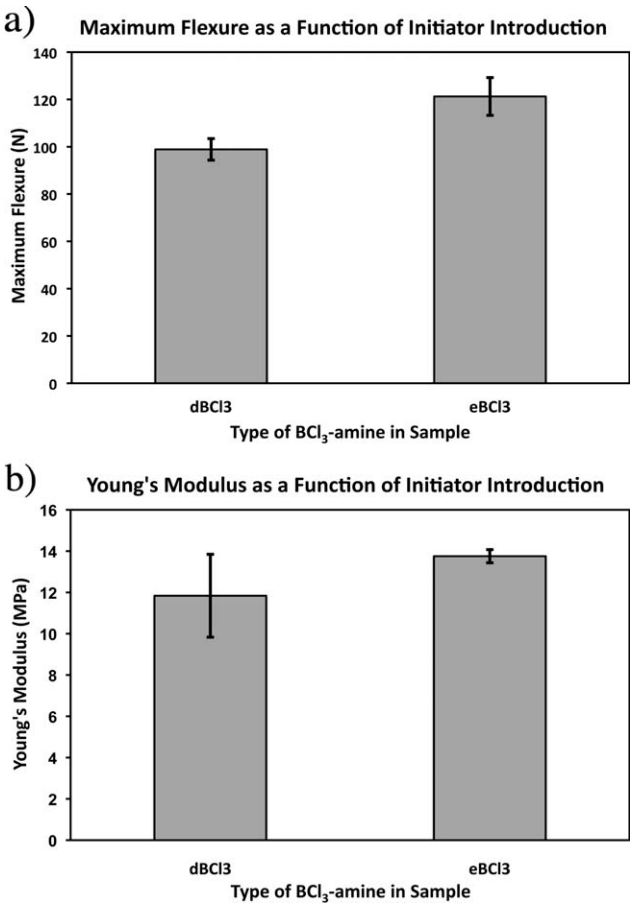


FIGURE 10 Strength data for TMPTGE systems containing BCl_3-amine complex and fumed silica. Each TMPTGE sample contained 2.5 phr fumed silica and 5 phr dissolved BCl_3-amine ($dBCl_3$), or 5 phr (calculated based on core-loading) microencapsulated BCl_3-amine ($eBCl_3$). The figures illustrate (a) the maximum flexure in Newtons and (b) the Young's modulus (MPa).

which the BCl_3-amine initiator was introduced into the system (ether microencapsulated or dissolved) were compared. Mechanical analysis was performed on epoxy block samples with the same dimensions utilizing the different types of introduction methods. The resulting data are plotted in Figure 10.

In both of the plots in Figure 10, the systems containing the microencapsulated BCl_3-amine complex on average demonstrated an increase in the respective measurement. The maximum flexure of the systems containing the microencapsulated BCl_3-amine was observed to increase by 23%, and the Young's modulus increased by 16%. The increase in the strength of the samples when BCl_3-amine microparticles were used as opposed to the sample containing the dissolved initiator could be due in part to the matrix material of the microparticles strengthening the material. To obtain a substantial increase in the strength of the material, a sufficiently strong interaction between the microparticles (filler material) and the epoxy matrix would needs to be present.[73] The free thiol groups present on the surface of the crosslinked polymer matrix due to steric hindrance preventing full conversion could explain this strong interaction. Thiols are known to react with epoxy resins via either a nucleophilic displacement or base-catalyzed addition reaction.[74] If this interaction is occurring, then the microparticles serve a dual purpose in separating the initiator from the monomer, thereby preventing undesirable rheological effects, and acting as a strengthening agent to produce a composite material with a thiol-acrylate matrix material as filler. From these data, it was determined that the strength of the epoxy polymer was not negatively affected by the incorporation of the BCl_3-amine in the microparticle form.

CONCLUSIONS

A novel approach to prepare microparticles via a dispersion polymerization using the primary amine-catalyzed addition of a trithiol to a triacrylate has been reported. Unlike most microcapsules having a thin shell containing a liquid core, these microparticles are composed of a solid matrix enveloping pockets of core material. This method of microencapsulation has multiple advantages over other methods of microencapsulation using various materials, as these microparticles can be prepared with a small number of components in less than 1 h at room temperature and at ambient pressure. The chemistry used to prepare these microparticles is very versatile in that a multitude of different monomers can be incorporated to prepare microparticles with varying properties. Also, the reaction used to prepare these microparticles can be initiated using various sources, which allows for variations if necessary.

The size of these microparticles can easily be manipulated depending on the amount of energy applied to the system. It was determined that this type of microparticles could be used as either a stimulated release (as with BCl_3-amine microparticles) or controlled release (as with DMpT microparticles) mechanism depending on core material. These thiol-acrylate microparticles have been prepared containing different initiators and activators including DMpT, a BF_3-amine complex, a BCl_3-amine complex, and CNTs. SEM analysis was preformed on the microparticles containing different core materials to determine the effectiveness of the microencapsulation technique relative to the core material. It was concluded that the DMPT microparticles were insufficient due to the leaching of the core material from the microparticle matrix. The BF_3-amine microparticles were observed to increase the stability of a highly reactive epoxy-Lewis acid system, however a high level of agglomeration prevented an even dispersion of the microparticles in an epoxy resin. The thiol-acrylate microparticles or nanoparticles containing CNTs require further investigation in order to determine the full benefit of using this method of encapsulation with this particular core. The preparation and application of microparticles containing one initiator in particular, a BCl_3-amine complex, was extensively studied. These microparticles were observed to prevent the interaction between the Lewis acid initiator and fumed silica by separating the two components, hence improving the rheological properties of an epoxy system containing the initiator while maintaining the strength of the resulting polymer product.

REFERENCES AND NOTES

1 Benita, S., Ed.; Microencapsulation: Methods and Industrial Applications; Marcel Dekker: New York, **1996.**

2 Yow, H. N.; Routh, A. F. *Soft Matter* **2006,** *2*, 940–949.

3 Yang, C. C.; Pan, I. H. (Industrial Technology Research Institute). U.S. Patent5,576,008, November 19, **1996.**

4 Hashemi, S. A.; Zandi, M. *Iranian Polym. J.* **2001,** *10*, 265–270.

5 Bodmeier, R.; Wang, J. *J. Pharm. Sci.* **1993,** *82*, 191–194.

6 Khopade, A. J.; Caruso, F. *Chem. Mater.* **2004,** *16*, 2107–2112.

7 Southwest Research Institute, The Art and Science of Microencapsulation. Available at http://www.swri.org/3pubs/ttoday/summer95/microeng.htm (accessed Jan 15, 2010).

8 Noda, A.; Yamaguchi, M.; Aizawa, M.; Kumano, Y. (Shiseido Company, LTD). U.S. Patent6,231,873, May 15, **2001.**

9 Lew, C. W. (Campbell Soup Company). U.S. Patent6,056,992, May 2, **2000.**

10 Jason, M. E.; Kalota, D. J. (Monsanto Company). U.S. Patent5,540,927, July 30, **1996.**

11 Washington, C. In Microencapsulation: Methods and Industrial Applications; Benita, S., Ed.; Marcel Dekker: New York, **1996; pp 155–181.**

12 White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. *Nature* **2001,** *409*, 794–797.

13 Kessler, M. R.; Sottos, N. R.; White, S. R. *Compos.: Part A: Appl. Sci. Manuf.* **2003,** *34*, 743–753.

14 Li, J.; Mazumder, M. A. J.; Stöver, H. D. H.; Hitchcock, A. P.; Shirley, I. M. *J. Polym. Sci. Part A: Polym. Chem.* **2011,** *49*, 3038–3047.

15 Zhuo, L.; Shuilin, C.; Shizhou, Z. *Int. J. Polym. Mater.* **2004,** *53*, 21–31.

16 McFarland, B. Investigations of free-radical polymerization systems using microencapsulated initiators. Ph.D. Thesis, The University of Southern Mississippi, Hattiesburg, MS, **2005.**

17 McFarland, B.; Popwell, S.; Pojman, J. A. *Macromolecules* **2004,** *37*, 6670–6672.

18 McFarland, B.; Popwell, S.; Pojman, J. A. *Macromolecules* **2006,** *39*, 53–63.

19 Yadav, S. K.; Suresh, A. K.; Khilar, K. C. *AIChE J.* **1990,** *36*, 431–438.

20 Li, G. Q.; Guo, J. B.; Wang, X.; Wei, J. *J. Polym. Sci. Part A: Polym. Chem.* **2009,** *47*, 3630–3639.

21 Shukla, P. G. S., S.; Rajagopalan, N. (Council of Scientific & Industrial Research) U.S. Patent5,962,003, October 5, **1999.**

22 Short, W. T. (General Motors Corp). U.S. Patent4,076,774, February, 28 **1978.**

23 Brow, E. N.; Kessler, M. R.; Sottos, N. R.; White, S. R. J. *Microencapsulation* **2003,** *20*, 719–730.

24 Grochowicz, M.; Bartnicki, A.; Gawdzik, B. *J. Polym. Sci. Part A: Polym. Chem.* **2008,** *46*, 6165–6174.

25 van Berkel, K. Y.; Hawker, C. J. *J. Polym. Sci. Part A: Polym. Chem.* **2010,** *48*, 1594–1606.

26 Gu, W. F.; Chen, G. J.; Stenzel, M. H. *J. Polym. Sci. Part A: Polym. Chem.* **2009,** *47*, 5550–5556.

27 Costoyas, A.; Ramos, J.; Forcada, J. *J. Polym. Sci. Part A: Polym. Chem.* **2009,** *47*, 935–948.

28 Chan, J. W.; Wei, H.; Zhou, H.; Hoyle, C. E. *Eur. Polym. J.* **2009,** *45*, 2717–2725.

29 Hoyle, C. E.; Lee, T. Y.; Roper, T. *J. Polym. Sci. Part A. Polym. Chem.* **2004,** *52*, 5301–5338.

30 Hoyle, C. E.; Bowman, C. N. *Angew. Chem. Int. Ed. Engl.* **2009,** *49*, 1540–1573.

31 Jacobine, A. F. In Radiation Curing in Polymer Science and Technology; Fouassier, J. P., Ed.; Elsevier: New York, **1993, pp 219–268.**

32 Cramer, N. B.; Scott, J. P.; Bowman, C. N. *Macromolecules* **2002,** *35*, 5361–5365.

33 Roper, T. M.; Kwee, T.; Lee, T.; Guymon, A. C.; Hoyle, C. E. *Polymer* **2004,** *45*, 2921.

34 Wei, H.; Senyurt, A. F.; Jonsson, S.; Hoyle, C. E. *J. Polym. Sci. Part A Polym. Chem.* **2007,** *45*, 822–829.

35 Cramer, N. B.; Davies, T.; O'Brein, A. K.; Bowman, C. N. *Macromolecules* **2003,** *35*, 5361–5365.

36 Cramer, N. B.; Reddy, S. K.; Cole, M.; Hoyle, C.; Bowman, C. N. *J. Polym. Sci. Part A. Polym. Chem.* **2004,** *42*, 5817–5826.

37 Kade, M. J.; Burke, D. J.; Hawker, C. J. *J. Polym. Sci. Part A: Polym. Chem.* **2010,** *48*, 743–750.

38 Hoyle, C. E.; Cole, M.; Bachemin, M.; Yoder, B.; Mguyen, C.; Jonsson, S. *Polym. Prepr.* **2001,** *42*, 697–698.

39 Hoyle, C. E.; Keel, M.; Kim, K. J. *Polymer* **1988,** *29*, 18–23.

40 Gush, D. P.; Ketley, A. D. *Mod. Paint. Coat.* **1978,** *68*, 58–66.

41 Cramer, N. B.; Bowman, C. N. *Polym. Prepr.* **2003,** *44*, 17–18.

42 Nilsson, C.; Malmstrom, E.; Johansson, M.; Trey, S. M. *J. Polym. Sci. Part A: Polym. Chem.* **2009,** *47*, 5815–5826.

43 Koo, S. P. S.; Stamenovic, M. M.; Prasath, R. A.; Inglis, A. J.; Du Prez, F. E.; Barner-Kowollik, C.; Van Camp, W.; Junkers, T. *J. Polym. Sci. Part A: Polym. Chem.* **2010,** *48*, 1699–1713.

44 Zienty, F. B.; Vineyard, B. D.; Schleppnik, A. A. *J. Org. Chem.* **1962,** *27*, 3140–3146.

45 Rim, C.; Lahey, L. J.; Patel, V. G.; Zhang, H. M.; Son, D. Y. *Tetrahedron Lett.* **2009,** *50*, 745–747.

46 Khire, V. S.; Lee, T. Y.; Bowman, C. N. *Macromolecules* **2007,** *40*, 5669–5677.

47 Lee, T.; Kaung, W.; Jönsson, S.; Lowery, K.; Guymon, C.; Hoyle, C. *J. Polym. Sci. Part A: Polym. Chem.* **2004,** *42*, 4424–4436.

48 Khire, V. S.; Kloxin, A. M.; Couch, C. L.; Anseth, K. S.; Bowman, C. N. *J. Polym. Sci. Part A: Polym. Chem.* **2008,** *46*, 6896–6906.

49 Clark, T.; Kwisnek, L.; Hoyle, C. E.; Nazarenko, S. *J. Polym. Sci. Part A: Polym. Chem.* **2009,** *47*, 14–24.

50 Sanui, K.; Ogata, N. *Bull. Chem. Soc. Jpn.* **1967,** *40*, 1727.

51 Shin, J.; Matsushima, H.; Chan, J. W.; Hoyle, C. E. *Macromolecules* **2009,** *42*, 3294–3301.

52 Chan, J. W.; Yu, B.; Hoyle, C. E.; Lowe, A. B. *Chem. Commun.* **2008,4959–4961.**

53 Matsushima, H.; Shin, J.; Bowman, C. N.; Hoyle, C. E. *J. Polym. Sci. Part A: Polym. Chem.* **2010,** *48*, 3255–3264.

54 Dijk, J. T. M. V. (Akzo Nobel N.V.) U.S. Patent6,639,046, October 28, **2003.**

55 Hu, G.; Bounds, C.; Pojman, J. A.; Taylor, A. F. *J. Polym. Sci. Part A: Polym. Chem.* **2010,** *48*, 2955–2959.

56 Leake, J. S. (Akzo Nobel N.V.). U.S. Patent6,521,716, February 18, **2003.**

57 Hamerton, I. Recent Develpments in Epoxy Resins; Rapra Technology Limited, Shawbury, United Kingdom, **1996.**

58 Chabanne, P.; Tighzert, L.; Pascault, J. P. *J. Appl. Polym. Sci.* **1994,** *53*, 769–785.

59 Pfann, J. R. P., Scotch; Kopacki, Adam F. and Westwood, N. J. (Stauffer Chemical Company). U.S. Patent3,395,121, July 30, **1968.**

60 Harris, J. J.; Temin, S. C. *J. Appl. Polym. Sci.* **1966,** *10*, 523.

61 Ghosh, N. N.; Palmese, G. R. *Bull. Mater. Sci.* **2005,** *28*, 603–607.

62 Leepoxy Plastics, Inc., available at: http://www.leepoxy.com/Docs/TB_Leecure_B.pdf (accessed March 14, 2010).

63 Vazquez, B.; Deb, S.; Bonfield, W. *J. Mater. Sci.-Mater. Med.* **1997,** *8*, 455–460.

64 Dalton, A. B.; Collins, S.; Munoz, E.; Razal, J. M.; Ebron, V. H.; Ferraris, J. P.; Coleman, J. N.; Kim, B. G.; Baughman, R. H. *Nature* **2003,** *423*, 703–703.

65 Yu, M. F.; Files, B. S.; Arepalli, S.; Ruoff, R. S. *Phys. Rev. Lett.* **2000,** *84*, 5552–5555.

66 Javey, A.; Guo, J.; Wang, Q.; Lundstrom, M.; Dai, H. J. *Nature* **2003,** *424*, 654–657.

67 Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. B* **1992,** *46*, 1804–1811.

68 Charlier, J. C.; Issi, J. P. *Appl Phys. A-Mater. Sci. Process.* **1998,** *67*, 79–87.

69 Ausman, K. D.; Piner, R.; Lourie, O.; Ruoff, R. S.; Korobov, M. *J. Phys. Chem. B* **2000,** *104*, 8911–8915.

70 Arnold, M. S.; Guler, M. O.; Hersam, M. C.; Stupp, S. I. *Langmuir* **2005,** *21*, 4705–4709.

71 The Hanson Group, LLC., available at: http://www.hanson-co.net/press-release-boron.pdf (accessed July 7, 2010).

72 Raghavan, S. R.; Khan, S. A. *J. Colloid Interface Sci.* **1997,** *185*, 57–67.

73 Bledzki, A. K.; Reihmane, S.; Gassan, J. *Polym.-Plast. Technol. Eng.* **1998,** *37*, 451–468.

74 Carioscia, J. A.; Stansbury, J. W.; Bowman, C. N. *Polymer* **2007,** *48*, 1526–1532.