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Enhanced Two-Stage Reactive Polymer Network Forming Systems

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Abstract

In this study, we develop thiol/acrylate two-stage reactive network forming polymer systems that exhibit two distinct and orthogonal stages of curing. Using a thiol-acrylate system with excess acrylate functional groups, a first stage polymer network is formed via a 1 to 1 stoichiometric thiol-acrylate Michael addition reaction (stage 1). At a later point in time, the excess acrylate functional groups are homopolymerized via a photoinitiated free radical polymerization to form a second stage polymer network (stage 2). By varying the monomers within the system as well as the stoichiometry of the thiol to acrylate functional groups, we demonstrate the ability of the two-stage polymer network forming systems to encompass a wide range of properties at the end of both the stage 1 and stage 2 polymerizations. Using urethane di- and hexa-acrylates within the formulations led to two-stage reactive polymeric systems with stage 1 T_g s that ranged from –12 to 30 °C. The systems were then photocured, upon which the T_g of the systems increases by up to 90 °C while also achieving a nearly 20 fold modulus increase.

1. Introduction

Click chemistry is a powerful tool for polymer modification, small molecule synthesis, and polymerizations [1–3]. Recently, the thiol-acrylate “click” Michael addition reaction has been utilized as a platform for biomaterial applications ranging from tissue scaffolds to drug delivery applications. [4–5] In addition to being insensitive to oxygen or water, and proceeding under relatively mild and solventless reaction conditions, the thiol-acrylate Michael addition reaction is also orthogonal to other common organic reactants[6–7].

Photopolymer networks afford the versatility and function of being able to perform as materials that vary from soft lithographic substrates to biomaterials such as dental restorative materials to high performance parts on aircrafts [8–10]. Photopolymerizations is an exciting and rapidly growing field due to the combination of rapid polymerizations, spatial and temporal control, solventless processing, and a wide range of achievable

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properties [11–14]. This work expands on the applicability of photopolymerizations by combining it with thiol/acrylate click chemistry to form a two-stage reactive polymer platform capable of achieving a wide range of properties and enabling two stages at which the system can be processed to increase functionality.

In a thiol-acrylate monomer system which has excess acrylates present, the initial stable network formed by a stoichiometric 1:1 thiol-acrylate Michael addition reaction leaves unreacted acrylate moieties attached to and throughout the polymer network. After this first stage reaction, intermediate polymer processing can be performed. The acrylates can then be induced to homopolymerize at a later point via photopolymerization, forming a highly crosslinked, high modulus polymeric network at the end of the reaction.

This generalized scheme is shown in Figure 1. We previously demonstrated that these systems enable the achievement of two distinct and largely independent sets of material properties at the end of the stage 1 Michael addition and later at the end of the stage 2 photopolymerization [15]. The stage 1 and stage 2 properties are varied dramatically by simple changes in the initial thiol to acrylate stoichiometry. The broad range of applications of the two stage reaction was demonstrated by utilizing simple changes in formulation and stoichiometry. Also, forming the intermediate polymer network at stage 1 in this manner ensures that the overwhelming fraction of the monomer will be bound into the network at the end of the stage 1 reaction. This covalent attachment is an advantage when the polymer is considered for applications such as biomedical devices in which the amount of extractables within the network can be detrimental to the material being considered as a potential device [16]. After photocuring, these networks exhibited stage 2 properties with glass transition temperatures and moduli as high as 195 °C and 200 MPa respectively. In this work, we explore the breadth of properties that can be achieved in the two-stage reactive systems by varying the stoichiometry, monomer structure, and monomer functionality. In doing so, we have shown that a wide range of stage 1 and stage 2 properties are achievable that may be suitable for an even broader range of applications than previously demonstrated.

2. Experimental

2.1 Materials

Pentaerythritol tetra(3-mercaptopropionate)(PETMP) was donated by Bruno Bock, tricyclodecane dimethanol diacrylate (TCDDA) was donated by Sartomer, and Ebecryls 220, 1290, 230, and 8402 were donated by Cytec. The photoinitiator Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone) was donated by Ciba Specialty Chemicals. The inhibitor aluminum N-nitrosophenylhydroxylamine (N-PAL) was donated by Albemarle. Triethyl amine (TEA) was purchased from Sigma-Aldrich. All samples contained 0.05 wt% inhibitor, 0.8 wt% triethyl amine as a catalyst for the first stage reaction, and 0.5 wt% Irgacure 651 to initiate the second reaction. Triethyl amine, Irgacure 651 and N-PAL were first added to the thiol and mixed thoroughly. The acrylates were then added to the thiol and mixed vigorously on a vortex mixer. For the stage 2 photopolymerization reactions, samples were cured with an irradiation intensity of 8 mW/cm² using a UV lamp (Black-Ray Model B100AP).

2.2 Dynamic Mechanical Analysis (DMA)

DMA experiments were performed using a TA Instruments Q800 DMA.

Glass transition temperature (T_g) was determined from polymer samples with dimensions of 10 x 3.5 x 1 mm. Sample temperature was ramped at 3 °C/min from -50 to 300 °C with a frequency of 1 Hz and a strain of 0.01 % in tension. The T_g was assigned as the temperature

at the $\tan \delta$ curve maximum. The rubbery modulus values were determined at a temperature 35 °C above the T_g for the stage 1 and 65 °C above the T_g for the stage 2 polymers.

2.3 Materials Testing System (MTS)

Compression test measurements were conducted on an Instron Universal Testing Machine (Insight 2.0) to ascertain the peak stress, strain at break and toughness measures of the system at the end of stage 1 and stage 2. Cylindrical samples of dimensions of 5 mm (diameter) $\times$ 6.5 mm (height) were used. A crosshead speed of 5 mm/min was applied.

2.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR experiments were performed using a Nicolet Magna 760. The acrylate peak absorbance was measured at 814 cm^{-1} and the thiol peak at 2575 cm^{-1} . Samples were prepared with TEA, mounted between salt crystals, and stored for 48 hours to allow substantial time for the first stage curing. After the first stage cure was complete, as observed by the total disappearance of the thiol peak, series runs were taken, and the peak areas for the acrylate were recorded, both before and after exposure to UV light for 15 minutes at 20 mW/ cm^2 . Acrylate conversion is given by $\alpha_{\text{acrylate}} = 1 - ((A_{\text{acrylate}})_{t=\text{final}} / (A_{\text{acrylate}})_{t=\text{initial}})$.

3. Results and discussion

The ability to achieve a range of properties at the end of stage 1 of the two-stage reactive system enables the polymer to be subjected to a variety of intermediate processing steps prior to when the final stage 2 modulus is attained. In this study, two-stage reactive thiol/acrylate systems were formulated and characterized with varying monomers and stoichiometric ratios to explore the range of properties that could be achieved at the various reactive stages. Previous work has characterized the mechanical and thermomechanical properties that could be attained by varying only the stoichiometric ratios of a single thiol-acrylate formulation [15]. The application potential of the two-stage reactive polymer systems was demonstrated with three examples: a shape memory polymer, a lithographic impression material, and an optical material with photo-patterned refractive index gradients. Here, a broad range of monomer formulations and differing stoichiometric ratios were used to control the material properties. A tetrathiol, PETMP, a diacrylate, TCDDA, and four different urethane acrylates were evaluated. The urethane acrylates in the study consisted of two urethane diacrylates and two urethane hexaacrylates. Ebecryl 230 is a high molecular weight diacrylate monomer that forms highly flexible materials while Ebecryl 8402 is a diacrylate monomer which forms polymers that are tough, in addition to being flexible. The aromatic urethane hexaacrylate (Ebecryl 220) and aliphatic urethane hexaacrylate (Ebecryl 1290) result in hard, abrasion resistant polymers.

Stoichiometric formulations with a 1:1 molar ratio of thiol to acrylate functional groups were first prepared to characterize the polymer properties that can be attained from these systems. The T_g and rubbery modulus of these systems are shown in Table 1. The 1:1 thiol-acrylate ratio results in the highest achievable crosslink density and hence the maximum attainable properties for these systems using a Michael addition reaction to form the polymer network; however, under these circumstances no acrylates remain to enable any additional evolution of the crosslinking or mechanical properties in stage 2.

Based on the data from Table 1, off-stoichiometric systems were formulated to achieve a range of glass transition temperatures and moduli at the end of the stage 1 and stage 2 polymerizations. The formulation compositions that contained the thiol, PETMP, the diacrylate, TCDDA, and the urethane acrylates are detailed in Table 2. Formulating materials with a range of stage 1 material properties considerably enhances the processing

capabilities of such two-stage reactive systems. The stage 1 F-230 system is soft and flexible at ambient temperature with a modulus of 1 MPa and a T_g of -12°C as shown in Figure 3. As this formulation goes from stage 1 to stage 2, the T_g increases to 12°C , and the final material is soft and retains considerable flexibility. This type of material would be ideal for applications where the stage 1 material can be molded into a particular geometry and then cured to achieve final stage 2 materials that retain considerable elasticity after the final cure. These types of properties may be useful for such applications as vibration dampeners and soft dental lining materials [17–19]. F-8402 has a final stage 2 modulus of 14 MPa, which is more than twice the stage 2 modulus of the F-230 formulation. The T_g of this system increased from -2 at stage 1 to 18°C at stage 2, resulting in a final polymer that is still rubbery and flexible at ambient temperature. The stage 1 and stage 2 thermomechanical properties of the F-8402 system make it suitable for applications such as bioimplants that have to function in a mechanically diverse environment [15, 20]. The F-220 material has a stage 2 T_g of 90°C and is highly crosslinked with a rubbery modulus of 125 MPa. Although both F-220 and F-8402 have stage 1 moduli that are similar, there is a 7-fold increase in the stage 2 modulus of F-220 in comparison with F-8402, thereby demonstrating the relative independence with which stage 1 and 2 properties can be controlled. The characteristics of a two-stage reactive system such as the F-220 with a stage 1 T_g of 18°C and modulus of 7 MPa, would be ideally suited for applications such as a holographic writing material which would have to be sufficiently rubbery at ambient conditions to allow index patterning and facile diffusion, followed by stage 2 curing resulting in a final material that is glassy and mechanically robust [15, 21, 22]. For applications that require high modulus materials for stage 2 properties, but also require a more mechanically robust stage 1 polymer network, the F-1290 system has a stage 1 modulus of 20 MPa and a T_g of 30°C . The F-1290 system has a stage 2 modulus of 77 MPa and a T_g of 82°C . Biomedical devices, such as orthopedic devices where high mechanical strength is often a prerequisite, could potentially benefit from these types of properties [15, 23].

The acrylate conversion as a function of time for the stage 2 reaction is shown in Figure 4.

The F-230 formulation exhibited close to 100% conversion of the remaining unreacted acrylate monomers during stage 2 curing within the first minute of being exposed to the UV light, whereas close to 80% of the remaining acrylate groups were polymerized by the end of stage 2 for the F-8402, comprising 5 minutes of irradiation. The high stage 2 T_g systems, F-220 and F-1290 had much lower stage 2 overall acrylate conversions, with 25% of the acrylate reacting for the F-220 system and 40% of the acrylates reacting for the F-1290 system. The low conversion in the hexa-acrylate systems is resultant from vitrification that arises from severe mobility restriction of the radicals and double bonds. As the polymerization proceeds, the decrease in free volume and the restricted mobility of radicals and their ability to reach the double bonds gives rise to the phenomenon of autodeceleration [24]. The reduced stage 2 conversion post-vitrification has also been observed in other polymerizing systems in which the cure temperature of the systems is far below the T_g of the polymer network. However, in spite of the relatively low stage 2 conversions, the urethane hexa-acrylate systems exhibit a significant increase in modulus, with the F-220 system showing an 18 fold increase in modulus and the F-1290 system showing a 4 fold increase in modulus, even with more than 50% of the remaining acrylate moieties remaining unreacted.

To characterize the mechanical properties of the polymer networks at the end of stage 1 and stage 2, compression tests were used to measure peak stress, strain at break and toughness. The presence of the urethane moieties within the polymer network is known generally to enhance the toughness of materials by providing extensive hydrogen bonding in these types of acrylic networks [25]. As shown in Figure 4, there were distinct differences in the peak stresses and strain to break that were attained at the end of each stage. The F-230

formulation did not exhibit a large increase in the peak stress and toughness values between stage 1 and stage 2. However, this system was able to achieve up to 70% strain at break even after stage 2 curing. Given that Ebecryl 230 is a high molecular weight di-acrylate, the high strain capacities at the end of each stage can be attributed to the considerably longer, flexible chains in the polymer network. The presence of the flexible chains extends mobility to the network and dominates the properties of this system. The F-8402, however, showed a 30% reduction in strain at break between stage 1 and stage 2 and stage 2 crosslinking of the polymer matrix also resulted in a 60% increase in toughness as it went from stage 1 to stage 2. Although F-230 and F-8402 systems are formulated from urethane di-acrylates and have similar stage 1 and stage 2 thermomechanical properties, it is of note that the F-8402 formulation can withstand 75% more stress in compression than the F-230 formulation. The variation in mechanical properties of the two urethane di-acrylate systems should factor in to application specific design considerations. The highly crosslinked F-220 stage 2 polymer system exhibited a dramatic 12-fold increase in toughness from stage 1. The compression test results for this system correlate with the thermomechanical data, which showed a highly crosslinked, high T_g polymer network with a rubbery modulus of 125 MPa. However, the strain measures for the F-220 system did not show considerable differences between stage 1 and stage 2 and remained at 30%. This behavior is resultant from only a modest crosslink density increase with 25% conversion of the remaining acrylates in stage 2. Interestingly, the urethane hexa-acrylate system, F-1290, had a stage 1 toughness that was 28 times that of F-220. This value is important as the mechanical measures at stage 1 determine the type of intermediate processing that the two-stage polymer networks can be subjected to. The F-1290 formulation though, showed a reduction in both strain to break and toughness measures following the second stage curing. Although the peak stress values remained within error near 100 MPa, a 33% reduction in strain to break and a 31% reduction in toughness were observed. Though a reduction in strain is expected after the second curing step due to the increased crosslinking of the hexa-acrylates within the polymer matrix, a reduction in toughness can be attributed to the formation of a more brittle, glassier material.

Overall, all systems showed that the strain at break, peak stress and toughness measures were a function of the amount of crosslinking within the polymer network and the specific nature of the monomers used within the formulations.

4. Conclusions

In this study, we have shown that with different monomer types having the same reactive functionality, it is possible to achieve a range of properties following both the initial and final curing steps. The F-8402 and F-220 systems demonstrated formulations with similar stage 1 properties and vastly different stage 2 properties. The F-230 formulation has similar mechanical properties as it went from stage 1 to stage 2, retaining a highly flexible polymer in spite of increased crosslinking. F-8402, with similar stage 1 properties to F-230, formed a tougher, stronger polymer after the final reactions, whereas the F-220 and F-1290 formulations had varied stage 1 properties, but displayed similar final material properties.

The four formulations thermomechanically and mechanically analyzed here exhibit a range of largely independent properties that can be achieved at each reaction stage in the two-stage reactive polymer approach. Given the range of possible stoichiometries and monomer types that is possible to use to formulate two-stage reactive networks, this study is representative of the possible systems that can be designed for a vast range of applications.

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Fig 1.

Non-stoichiometric molar mixtures of thiol and acrylate functional groups with excess acrylate groups present are reacted in an amine-mediated Michael Addition reaction (a). At the end of this reaction a stage 1 polymer is formed, which is now capable of undergoing additional, application specific processing. After processing, the excess acrylate functional groups are largely tethered within the network. At a later stage, the acrylates can be photopolymerized on command to result in the formation of a highly crosslinked, glassy network.

Fig 2.
Monomers, catalysts, and initiators used in this study.

Fig 3.

(a) The range of distinct glass transition temperatures and (b) rubbery moduli achieved at stage 1 and stage 2 for the two-stage reactive networks formed from the F-230, F-8402, F-220 and F-1290 formulations.

Fig 4.

Stage 2 acrylate conversion F-Eb230 (Δ), F-Eb8402 ($\bullet$), F-Eb220 ($\circ$), and F-Eb2190 ($\blacksquare$). The systems contained 0.8 wt% TEA and 0.5 wt% Irigacure 651 and were irradiated at 20 mW/cm². At the end of stage 1, 28.5% and 17% of the acrylates in the F-230 and F-1290 systems were unreacted, whereas the F-8402 and F-220, had 33% of the acrylates unreacted within the network.

Fig 5.

The peak stress that the polymer networks achieved at the end of each stage is contrasted in 2(a). 2(b) shows the reduction in strain as a result of the stage 2 cure and 2(c) is the calculated toughness at the end of each stage.

Table 1

T_g and rubbery modulus for the 1:1 thiol-acrylate systems. All formulations contained 0.8 wt% TEA and rubbery modulus was measured at T_g 35°C 35°C

Polymer System	Thiol:Acrylate Ratio	T_g (°C)	Rubbery Modulus (MPa)
PETMP/TCDDA	1:1	16 ± 2	7 ± 1
PETMP/Ebecryl 230	1:1	-33 ± 2	0.8 ± 0.2
PETMP/ Ebecryl 8402	1:1	-8 ± 2	3 ± 2
PETMP/ Ebecryl 220	1:1	33 ± 3	18 ± 8
PETMP/ Ebecryl 1290	1:1	41 ± 2	25 ± 1

Table 2

Thiol to diacrylate (TCDDA) and thiol to urethane acrylate molar ratios of functional groups.

Polymer System	PETMP:TCDDA Ratio	PETMP:Urethane Acrylate Ratio	Overall PETMP:diacrylate: urethane acrylate ratio
F-230 PETMP/TCDDA/Eb230	1:2.4	1:0.4	1:1.4
F-8402 PETMP/TCDDA/Eb8402	1:1.5	1:1.5	1:1.5
F-220 PETMP/TCDDA/Eb220	1:0.5	1:2.5	1:1.5
F-1290 PETMP/TCDDA/Eb1290	1:0.9	1:1.5	1:1.2