Probing the dynamic and rehealing behavior of crosslinked polyester networks containing thermoreversible thiol-Michael bonds

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ABSTRACT

A thermoreversible thiol-Michael bond was incorporated into a series of covalently crosslinked polyester networks using base-catalyzed Michael addition polymerization. Variations in acrylate:acetoacetate ratio (crosslink density), thiol-Michael bond content and cure temperature were employed in order to gauge dynamic and rehealing properties. All of the networks investigated in this study were found to display rehealing behavior after being cut at 100 °C within 48 h. Increasing the curing temperature to 120 °C led to a decrease in time to reheal ($\leq$8 h), however the network which employed the highest thiol-Michael bond content, coupled with the lower acrylate:acetoacetate monomer ratio, did not recuperate the original crosslink density upon cooling as evidenced by strain recovery values in excess of 100% and a steady decrease in DSC T_g and TGA weight % as a functional of exposure time.

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1. Introduction

Polymeric architectures which incorporate dynamic covalent or other reversible bonds are attractive due to their ability to exhibit rehealing behavior [1–6]. Dynamic crosslinked polymers have become increasingly valuable since they demonstrate an ability to maintain their thermal and chemical stability after being reprocessed or recycled, unlike classical thermoset materials. To achieve these unique and attractive properties, a number of reversible covalent and/or non-covalent bonds (activated by an external stimulus such as heat, light or pH) have been employed. Common dynamic covalent bonds in polymeric materials have included Diels-Alder cycloadducts (furan-maleimide systems in particular) [7–11], aliphatic disulfide bond exchange [12,13], room-temperature aromatic disulfide metathesis [14,15] and boronic esters [16–18] while non-covalent systems have incorporated hydrogen bonding [6,11,19–21], π-π interactions [21,22] and host-guest interactions [23]. In some rare cases, doubly dynamic systems have been reported which utilize combinations of covalent and non-covalent interactions [11,24,25].

Many dynamic covalent bonds in polymeric materials have been directly taken from classic organic reactions which are efficient and high-yielding [5]. As dynamic covalent chemistry continues to

expand similar reactions are being explored for their potential reversibility. Thiol-based reactions such as the base-catalyzed thiol-Michael reaction [26,27] and the thiol-ene/yne 'click' photo-reactions [27–31] have seen extensive use in polymer chemistry due to their reaction efficiency and high compatibility with other functional groups. While small molecule studies have hinted at the dynamic behavior of the thiol-Michael bond, either at elevated temperatures [27,32,33] or pH levels [34,35], limited work has focused on incorporating dynamic thiol-Michael bonds into polymeric materials for the purposes of rehealing. Recently, Konkolewicz and coworkers demonstrated the utility of the thermoresponsive, dynamic thiol-Michael bond in a series of covalently crosslinked poly (hydroxyethyl acrylate) networks [36]. In these systems, a thiol-Michael diacrylate crosslinker (1.5–8 wt%) was polymerized with hydroxyethyl acrylate and the rehealing and malleability properties were measured. At just 1.5 wt% thiol-Michael crosslinker, the material was found to recover ~80% of the stress and strain at break, with the break point occurring away from the reseal juncture, after just 4 h at 90 °C (the minimum temperature required to achieve dynamic properties). All of the materials exhibited complete recovery of creep and the 1.5 wt% network could be molded into new shape, thus introducing a malleability component that is not seen with typical networks/thermosets.

Hager and coworkers have also observed thermoreversible behavior in covalently crosslinked networks which contained dynamic thiol-Michael bonds. Initial investigations involved the

crosslinking of a substituted bisacrylamide monomer with trimethyloylpropane tris(3-mercaptopropionate) [37]. Rehealing, as determined from scratch healing experiments, was observed starting at 60 °C. Higher curing temperatures, however, were found to result in loss of recovery of mechanical properties, as determined by rheological experiments and, ultimately, thermal degradation (loss of H_2S) as confirmed from thermogravimetric analysis (TGA) and chemical testing. Reversibility of the thiol-Michael bonds was observed by Raman spectroscopy. In an effort to improve upon the thermal stability of these thiol-Michael networks, a second set of networks were produced where 1,10-dodecanethiol or pentaerythritol tetra(3-mercaptoproprionate) and a copolymer of butyl methacrylate and a benzylcyanoacetamide monomer were polymerized in the presence of base (DBU) [38]. Once again, scratch healing experiments were conducted, requiring a minimum curing temperature of 100 °C and a time of 18—19 h for the systems which employed the dithiol crosslinker to completely heal. For the more crosslinked system (tetrathiol crosslinker), sufficient scratch healing was not observed until a cure temperature of 150 °C (18—19 h). Raman spectroscopy indicated that thermoreversiblity of the thiol-Michael bonds occurred starting at 100 °C for both systems with near complete recovery of crosslinking upon cooling.

As a result of these studies, it is apparent that a balance exists between curing temperature, dynamic bond concentration and degree of crosslinking. Inspired by this work, we wanted to probe the limits of these factors with respect to the dynamic thiol-Michael bond in polyester networks, thereby extending the work of Konkolewicz and Hager into a different network architecture. To prepare these networks, base-catalyzed carbon-Michael polymerization was chosen, a platform which has been used extensively in the preparation of network architectures with a variety of thermal, mechanical, and even conductive properties [26,39—43]. Carbon-Michael addition polymerization most commonly occurs between a Michael donor (enolizable functional group such as an acetoacetate) and a Michael acceptor (an activated alkene such as an acrylate). One can control the amount of crosslinking in the network by varying the acrylate:acetoacetate ratio since each acetoacetate group is difunctional (two enolizable protons). Carbon-Michael polymerization was specifically chosen for this study because, unlike conventional polyester network synthesis which often requires elevated temperatures to achieve high gel fraction, base-catalyzed Michael additions, given an active donor and acceptor, will proceed to high conversion under ambient conditions. This avoids a potential conflict between polymerization temperature and thermal activation of the targeted thiol-Michael bond.

In the present study, three variables were considered: crosslink density (acrylate:acetoacetate ratio), content of dynamic thiol-Michael bond and curing temperature (100 or 120 °C). Recovery of mechanical properties by tensile testing (dynamic mechanical analysis) was used to gauge re-healing and dynamic behavior. Thermal stability of the networks was also investigated by monitoring changes in DSC T_g and isothermal TGA weight % loss as a function of exposure time.

2. Experimental

2.1. General

All materials were purchased from commercial suppliers and used as received unless otherwise specified. Specifically, 1,4-butanediol diacrylate (>90%) was purchased from Sigma-Aldrich while 1,8-diazabicylco [5.4.0]undec-7-ene (DBU, 98%) was purchased from Acros Organics. TMADA ((2-((3-(2-acryloyloxy) ethoxy)-3-oxopropyl)thio)ethyl acrylate) was prepared following a published procedure [36]. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL 400 MHz spectrometer and chemical shift values (ppm) reported below were referenced to residual solvent signals (CDCl$_3$: [1]H, 7.26 ppm; ^{13}C, 77.16 ppm).

2.2. Synthesis of 1,4-butanediol diacetoacetate

To a 500 mL round-bottomed flask equipped with a cold-water condenser was charged 1,4-butanediol (10.0 g, 0.111 mol), *tert*-butylacetoacetate (52.7 g, 0.333 mol) and toluene (150 mL). The stirred solution was brought to reflux and held for 2 h. The cold-water condenser was replaced with a short-path distillation apparatus and the temperature was gradually increased from 120 to 140 °C over a 4hr period. The temperature was then lowered to 90 °C and a vacuum was gradually applied and held at < 0.01 mm Hg overnight to remove any volatile materials. The process resulted in a clear, light orange oil (26.9 g, 94%). ^{1}H NMR analysis indicated a 92:8 ratio of keto:enol tautomers. ^{1}H NMR (CDCl$_3$) δ 4.12 (m, 4H), 3.42 (s, 4H), 2.22 (s, 6H), 1.69 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 200.7, 167.2, 67.8, 50.1, 30.3, 25.13.

2.3. Michael addition polymerization

The example given here is for a 1.2:1.0 acrylate:acetoacetate ratio with 10 wt% TMADA (polymer 1.2:1.0—10%). Monomers 1,4-butanediol diacetoacetate (0.65 g, 2.52 mmol), 1,4-butanediol diacrylate (0.54 g, 2.72 mmol) and TMADA (91.3 mg, 0.302 mmol) were charged to a glass vial and mixed by hand until homogeneous. DBU (1,8-diazabicyclo [5.4.0]undec-7-ene) (16.8 μL, 2 mol %) was then added and mixing by hand continued for 2 min. The sample was then carefully syringed between two Rain-X® treated glass slides sandwiched around a 500 μm Teflon spacer to control the thickness of the resulting polymer film. The sample was allowed to set at RT for 24 h, then anneal in a convection oven at 60 °C for 24 h. Prior to any testing, the film was dried in a vacuum oven (50 °C, < 0.01 mm Hg) for 24 h.

2.4. Thermal analyses

A TA Instruments Q200 differential scanning calorimeter (DSC) was used to determine any thermal transitions of the resulting polymer networks. A 4—8 mg sample of polymer was placed inside of a hermetically sealed aluminum pan and scanned at 3 °C/min from −90 to 50 °C. Glass transition temperatures (T_g) were determined as the inflection point of the observed endothermic transition by the TA Instruments software. Reported values are from the second heating event for each experiment and represent an average of triplicate runs. Overlays of representative experimental DSC curves are presented as Figures A3 and A4. Variability in T_g was found to be less than ±0.8 °C across all samples. Thermal stability was determined using a TA Instruments Q500 Thermogravimetric Analyzer (TGA). A 4—8 mg sample was placed on a platinum pan and weight loss was monitored as a function of temperature at 10 °C/min from 30 to 800 °C. Reported values for $T_{d5\%}$, the temperature at which 5% of the material had decomposed, represent averages of duplicate experiments. Variation in $T_{d5\%}$ across all samples was found to be less than ±1.2 °C. Representative experimental TGA curves are presented as Figures A5 and A6. Isothermal TGA experiments (long-term thermal stability) were conducted by placing a 4—8 mg sample on a platinum pan and then monitoring weight loss as a function of time at either 100 or 120 °C over an 8 h time period.

2.5. Gel fraction and swelling properties

Gel fraction analysis was completed in duplicate for each sample via 24 h soxhlet extraction with tetrahydrofuran (THF) in order to assess the effectiveness of monomer incorporation into the networks. After the refluxing period, the swollen sample was weighted (m_{wet}) and then placed in a vacuum oven (50 °C, < 0.01 mm Hg) for 24 h in order to obtain the dry weight (m_{dry}). Gel fraction was determined as follows: gel fraction = (m_{dry}/m_{o})*100 where m_o represents the original weight of the sample prior to soxhlet extraction. Percent swelling was determined using the following equation: % swelling = (m_{wet}/m_{o})*100.

2.6. Mechanical analyses

A TA Instruments Q800 dynamic mechanical analyzer (DMA), in film tension mode at a heating rate of 5 °C/min with a single frequency of 1 Hz, was used to determine the mechanical properties (storage modulus E', tan δ max, crosslink density) of each polymer network. DMA T_g values were determined from the maximum of the tan δ curves (Figures A7 and A8). Crosslink density (ρ_x) of the networks was determined following rubbery elasticity theory using the following equation: $\rho_x = E'/3\,R\,T$ where E' is the storage modulus well above the T_g (100 °C in this study), R is the gas constant (8.314 J/mol-K) and T is the temperature [44]. Storage modulus experiments were completed in triplicate for each polymer sample.

2.7. Tensile testing

Polymer samples were subjected to tensile testing using the TA Instruments Q800 DMA. Rectangular samples were cut with a razor blade and placed into the film clamps. The extension was increased at a rate of 20 mm/min at 25 °C until each sample broke. Stress and strain at break measurements are reported and represent an average of three runs on each polymer sample.

2.8. Cutting and healing procedures

Rectangular films were cut with a razor blade completely through the polymer. The two cut ends were then overlapped by ~2 mm and were placed in gentle contact by finger pressure for several seconds. The materials were then placed in a convection oven at the desired temperature (100 or 120 °C) and removed at various time intervals for tensile testing in order to determine recovery of mechanical properties and rehealing potential (2, 4, 8 and 24 h; a 48 h reading was only taken if the sample had not re-healed after 24 h). Stress and strain at break for each sample are reported. A polymer is defined as "rehealable" in this study if a new break in the sample, away from the reseal point, was observed, along with at least 70% recovery of the stress and strain at break of the original (uncut) sample.

3. Results and discussion

3.1. Network synthesis

To probe the dynamic and rehealing properties of the thermoresponsive thiol-Michael bond in polyester networks, a series of Michael addition polymerizations was prepared utilizing 1,4-butanediol diacetoacetate (BDAcAc) as the Michael donor and a mixture of 1,4-butanediol diacrylate (BDAcr) and 2-(((3-(2-acryloyloxy)ethoxy)-3-oxopropyl)thio)ethyl acrylate (TMADA) as the Michael acceptors (Scheme 1). DBU (2 mol%) was used as the base to catalyze the polymerization. BDAcAc was prepared through

the transesterification of 1,4-butanediol with tert-butylacetoacetate while TMADA was prepared according to a previously published procedure and serves as the dynamic thiol-Michael crosslinker [36]. Once prepared, the homogeneous monomer/catalyst mixture was syringed between two glass slides, treated with Rain-X®, separated by a 500 μm Teflon™ spacer and held together by binder clips. The polymer was allowed to cure at RT for 24 h; then placed in an oven at 50 °C for 24 h. All of the samples were dried in a vacuum oven (50 °C, < 0.01 mm Hg) for 24 h prior to any analysis.
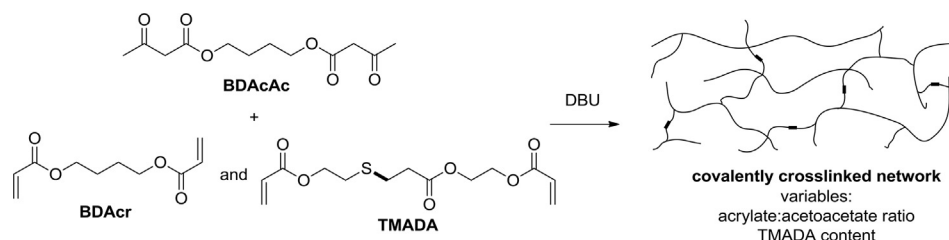
3.2. Thermal properties and gel fraction analysis

Initially, an acrylate:acetoacetate ratio of 1.2:1.0 was targeted in order to create polymer networks with high gel fraction (>90%) and relatively low crosslink density. Given this monomer ratio, the amount of TMADA was sequentially increased (0, 10, 20 and 30 wt% of total acrylate charge) to probe the effect that the concentration of the thermoreversible bond had on rehealing properties. Thermal properties and gel fraction analyses of this initial set of networks are provided in Table 1. The "Polymer ID" in Table 1 refers to the monomer ratio used (1.2:1.0 or 1.1:1.0) followed by the acrylate wt% of TMADA used. Due to the increased flexibility of the longer TMADA monomer, relative to 1,4-butanediol diacrylate, a gradual decrease in T_g was observed with increasing TMADA concentration. Swelling studies in THF provided further evidence in support of this hypothesis. Swelling was found to be the highest in the network containing 30 wt% TMADA where the amount of free volume would be the highest (it is assumed that the changes in THF solubility between network compositions is negligible). Thermal stability, as defined by $T_{d5\%}$, was observed to slightly decrease with increasing TMADA content (228–238 °C).

A second set of networks were then prepared where the acrylate:acetoacetate ratio was decreased to 1.1:1.0 in order to explore the effect of lower crosslinking on network properties. Once again, the wt% of TMADA used was varied (0, 10, 20, 30% of acrylate charge). With respect to the more crosslinked 1.2:1.0 networks, the T_g values of the 1.1:1.0 networks were generally lower by 2–10 °C and exhibited a higher % swelling with a lower gel fraction (80–84%). All of these observations can be directly attributed to the lower crosslink density of the 1.1:1.0 networks. Thermal stability of the 1.1:1.0 networks was found to be slightly lower than the 1.2:1.0 networks. Within the 1.1:1.0 networks, T_g and % swelling correlated with TMADA concentration in a similar fashion to what was observed with the more crosslinked 1.2:1.0 networks.

3.3. Mechanical properties and tensile testing

Dynamic mechanical analysis (DMA) was used to probe trends in the mechanical properties of the polymer networks (Table 2). The rubbery plateau modulus (E'; Figs. 1 and 2) and crosslink density (ρ_x) were generally higher for the 1.2:1.0 networks as expected since more of the acetoacetate groups would be participating in crosslinking. Within each series, increasing TMADA content led to a decrease in E' and ρ_x since the longer, more flexible TMADA linker effectively increases the molecular weight between crosslink points and decreases the crosslink density. DMA T_g values, as determined from the maximum of the tan delta curves (Figs. A7 and A8), were found to decrease with decreasing acrylate:acetoacetate ratio as expected due to a decrease in crosslink density. A general decrease in DMA T_g was observed, given a constant acrylate:acetoacetate ratio, with increasing TMADA content. This trend correlates well with the previously described DSC T_g data.

DMA tensile testing was also completed on each sample

Scheme 1. Preparation of Michael addition polyester networks containing TMADA monomer. The C-S bond highlighted in bold is the dynamic, thermoreversible bond.

Table 1
Thermal properties and gel fraction analysis of polyester networks.

Polymer ID	DSC T_g (°C)	TGA $T_{d5\%}$ (°C)	Gel fraction	% swelling
1.2:1.0−0%	−14.5	238	92.3 ± 0.8%	171 ± 4%
1.2:1.0−10%	−16.5	231	91.6 ± 0.7%	178 ± 2%
1.2:1.0−20%	−16.8	228	91.7 ± 0.4%	188 ± 5%
1.2:1.0−30%	−17.8	228	90.2 ± 0.2%	199 ± 2%
1.1:1.0−0%	−18.5	226	83.2 ± 0.6%	192 ± 4%
1.1:1.0−10%	−21.4	221	80.9 ± 0.6%	205 ± 7%
1.1:1.0−20%	−24.9	218	82.7 ± 0.5%	218 ± 5%
1.1:1.0−30%	−27.4	220	82.8 ± 0.7%	246 ± 3%

Fig. 1. DMA storage modulus overlay of polyester networks with an acrylate:acetoacetate ratio of 1.2:1.0.

(Table 2), in triplicate, to further probe the mechanical properties of these materials and to serve as a baseline set of measurements for the re-healing tests described later. In general, as the amount of TMADA was increased, the stress at break was found to decrease, regardless of monomer ratio (Fig. 3). The strain at break (% elongation) was generally found to increase, the exception being the 1.1:1.0−30% network.

3.4. Rehealing properties of the networks

Rehealing properties were probed by measuring the ability of the re-sealed (finger-pressed) materials to recover the original stress and strain at break at two different curing temperatures (100 and 120 °C). Rectangular strips from an original network sample were cut in half perpendicularly with a razor blade. The two cut ends were then overlapped by ~2 mm and finger pressed together for 1 min. The re-sealed samples were then placed in a convection oven at the desired temperature and removed at various time intervals for DMA tensile testing. In this report, a material is defined as "rehealable" if a new break in the sample, away from the reseal point, was observed, along with at least 70% recovery of the stress and strain at break of the original (uncut) sample (Fig. 4). All networks which incorporated the TMADA monomer were found to exhibit rehealing properties, regardless of temperature, within 48 h (most within 24 h). The networks that did not contain any TMADA did not exhibit the necessary "rehealable" properties; all of these samples broke cleanly at the re-seal point and never recovered
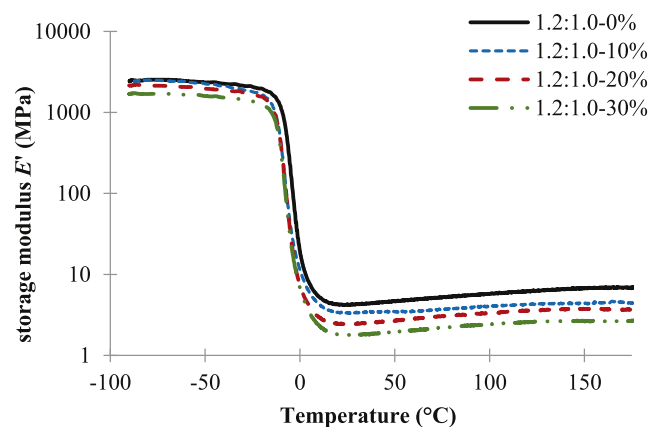

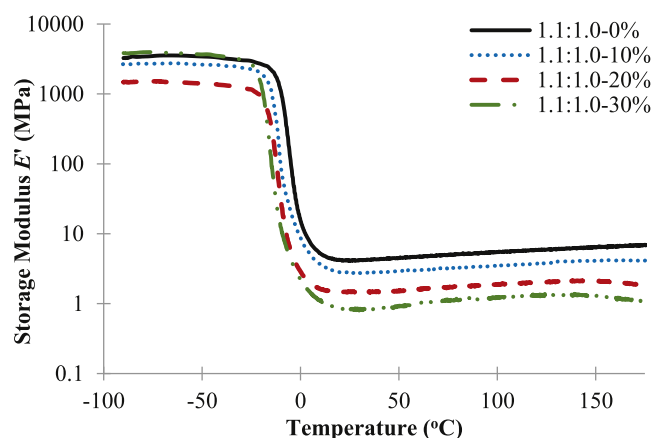**Fig. 2.** DMA storage modulus overlay of polyester networks with an acrylate:acetoacetate ratio of 1.1:1.0.

Table 2
Dynamic mechanical and tensile properties of polyester networks.

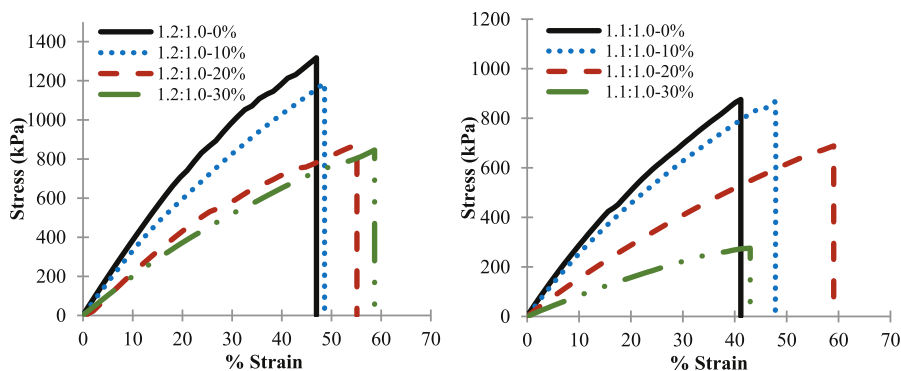| Polymer ID	E' (@ 100 °C)	ρ_x x 10^{-4} (g/cm³)	tan δ max (°C)	Tensile testing	
				Stress at break (kPa)	% Strain at break
1.2:1.0−0%	5.76 ± 0.31	6.19	4.8 ± 0.2	1349 ± 29	48.2 ± 5.5
1.2:1.0−10%	4.03 ± 0.21	4.33	−0.5 ± 0.3	1143 ± 50	49.2 ± 4.1
1.2:1.0−20%	3.33 ± 0.49	3.58	−4.3 ± 0.2	833 ± 47	54.4 ± 4.3
1.2:1.0−30%	2.41 ± 0.32	2.59	−8.0 ± 0.4	796 ± 43	56.4 ± 4.4
1.1:1.0−0%	5.46 ± 0.12	5.87	−3.1 ± 0.3	864 ± 45	41.8 ± 2.2
1.1:1.0−10%	3.54 ± 0.22	3.80	−9.5 ± 0.2	838 ± 60	44.6 ± 4.1
1.1:1.0−20%	1.88 ± 0.34	2.02	−9.4 ± 0.2	688 ± 33	58.1 ± 4.4
1.1:1.0−30%	1.21 ± 0.45	1.30	−12.1 ± 0.1	271 ± 11	40.7 ± 4.5

Fig. 3. Stress-strain curve comparison of 1.2:1.0 acrylate:acetoacetate ratio networks (left) and 1.1:1.0 acrylate:acetoacetate ratio networks (right) with variable TMADA content.
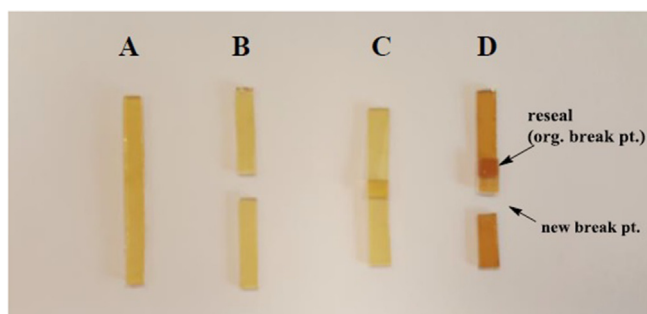

Fig. 4. Photograph of the 1.2:1.0–30% network showing the original uncut sample (A), the sample after the original stress-strain test (B), the finger pressed, re-sealed sample (C) and the re-healed sample (D) which shows a new break point from mechanical testing after 4 h at 120 °C.

more than 50% of the original stress and strain at break, even after 48 h at 120 °C. The small amount of recovery observed is believed to be due to weak dipole-dipole interactions between the broken polymer pieces, however the low T_g nature of the polymer networks could help in the formation of some entanglements between the pieces.

The rate of recovery and rehealing of the 1.2:1.0 acrylate:acetoacetate networks were found to be dependent upon both curing temperature and TMADA content (Fig. 5). All of the networks exhibited rehealing properties within 48 h at 100 °C; however, the time to re-heal decreased significantly (within 8 h) when the curing temperature was increased to 120 °C. Given a constant curing temperature, an increase in TMADA content generally was found to decrease the time to self-heal. For example, at 120 °C, the networks containing 10% TMADA was found to self-heal by the 24 h mark while the samples employing 20 and 30% TMADA were found to exhibit rehealing properties by the 8 h mark.

When crosslinking was decreased (acrylate:acetoacetate ratio of 1.1:1.0) similar trends were observed with regards to curing temperature and TMADA content and their influences on rehealing time (Fig. A9); however an interesting observation was made with regards to the 1.1:1.0–30% network (Fig. 6) at the higher curing temperature (120 °C). While the network was able to exhibit rapid rehealability (within 4 h), the result came with a noticeable increase in strain at break (>100% of the original sample). Such an observation is not a complete surprise. In previous work involving networks containing high concentrations of dynamic thiol-Michael bond, Hager et al. were able to show by Raman spectroscopy that dynamic thiol-Michael bonds can be significantly active above

100 °C and exhibit thermal instability (gradual elimination of H$_2$S from the free thiol) with at elevated temperature and/or prolonged heat exposure [37]. To provide evidence supporting the notion that H$_2$S is a probable decomposition product in these polyester networks, a stock solution of 2 mol % DBU and 1 wt % BHT inhibitor in TMADA was prepared. The solution was placed into a round-bottomed flask, sealed with a rubber stopper, and heated to 120 °C. The temperature was held for 24 h while a slight positive pressure of dry nitrogen was applied in order to force any gas produced from decomposition out of the flask and through a double-ended needle submerged into a glass vial containing 0.1 M silver nitrate solution (Figure A10). A black-grey precipitate gradually formed during the course of the experiment, confirming the generation of silver sulfide due to H$_2$S evolution. When the same experiment was completed at 100 °C no such precipitate was observed. As a result, we conclude that re-healing for this particular network (1.1:1.0–30%) is limited to a maximum of 100 °C. As an extension of the these experiments, the 1.1:1.0–30% network was examined for its dynamic behavior at 90 °C and rehealing properties were observed at the 16 h mark (Figure A11), thus indicating that thermal stability issues could be easily avoided by selecting a lower curing temperature. None of the other networks in this study were found to exhibit the required rehealing properties within 48 h at 90 °C.

In order to probe the thermal stability and the potential irreversible behavior of all of the networks examined in this study, a thermal history of each network was first conducted using DSC. If the networks are not re-establishing the original crosslink density, a decrease in the T_g should be observed with heating as a function of time. For example, over a 24 h period, ΔT_g ($\Delta T_g = T_{g,original} - T_{g,heated}$) of the 1.1:1.0–30% network was found to decrease by 4.4 °C (Fig. 7), indicating that a change in the network structure was occurring as a function of time. At a curing temperature of 100 °C however, ΔT_g was found to remain relatively small (0.6 °C) during the same 24 h time period. None of the remaining networks were found to exhibit a ΔT_g in excess of 0.8 °C over a 24 h time period at 120 °C.

The thermal instability of the networks was also probed using isothermal TGA. These experiments, albeit time consuming, provide a much more accurate depiction of long-term thermal stability versus standard TGA temperature ramp experiments. Fig. 8 shows a comparison of weight loss for the 1.1:1.0–30% network over an 8 h time period at 100 and 120 °C. Note that 1.65% of the original weight after 8 h at 100 °C is found to be lost, a value that increases to 3.05% over the same time period at 120 °C. Thus, while the thiol-Michael bond is clearly reversible and provides re-healing potential across all of the networks studied here, the systems are also prone
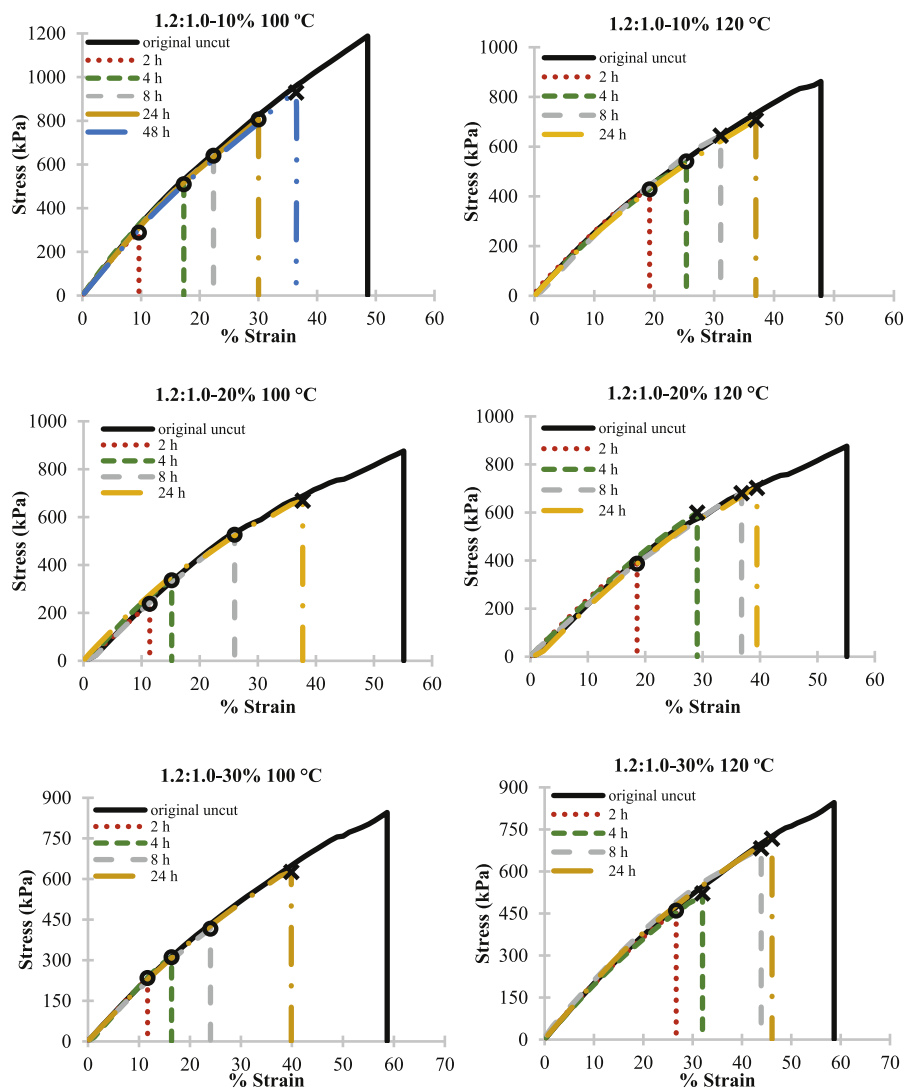
Fig. 5. Re-healing properties of networks employing a 1.2:1.0 acrylate:acetoacetate ratio after different times heated at 100 °C (left) or at 120 °C (right); (**O**) refers to a sample that broke at the original re-seal site after mechanical testing whereas (**X**) refers to a sample that exhibited a new break point after mechanical testing.
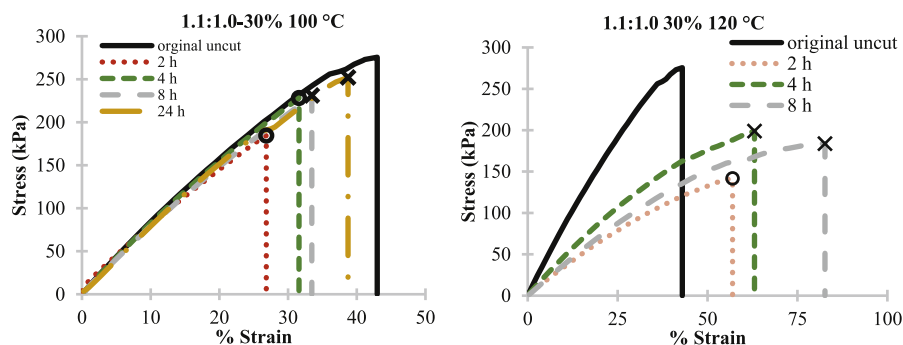

Fig. 6. Re-healing properties of the 1.1:1.0−30% network after different times heated at 100 °C (left) or at 120 °C (right); (**O**) refers to a sample that broke at the original re-seal site after mechanical testing whereas (**X**) refers to a sample that exhibited a new break point after mechanical testing.

to thermal degradation, especially at the higher curing temperature with higher TMADA content. Isothermal TGA studies across all of the networks (Table A2) indicated that thermal stability increased with increasing crosslink density, decreasing thiol-Michael monomer content as well as lower curing temperature. Networks that contained no thiol-Michael monomer exhibited little to no weight loss.
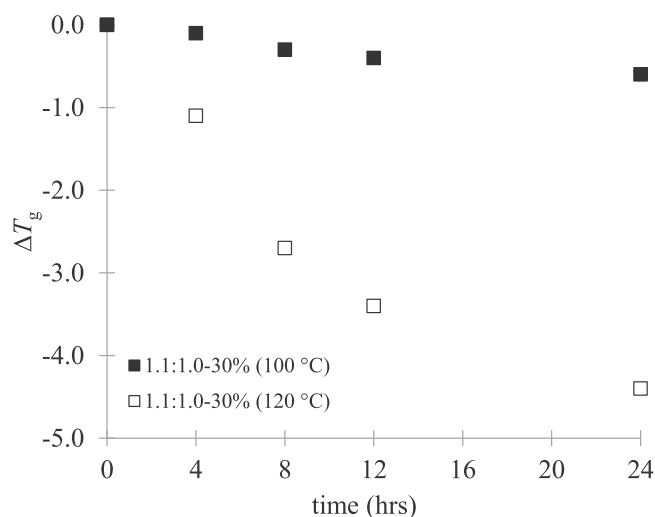
Fig. 7. An average of duplicate ΔT_g versus time plot, from DSC experiments, at curing temperatures of 100 and 120 °C for the 1.1:1.0−30% network over a 24 h time period.
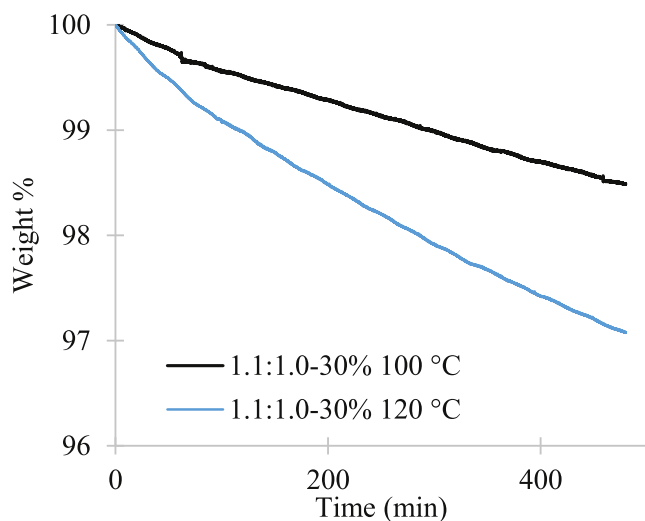

Fig. 8. Weight % as a function of time at curing temperatures of 100 and 120 °C for the 1.1:1.0−30% network.

4. Conclusion

A thermoreversible thiol-Michael bond was successfully incorporated into a series of covalently crosslinked polyester networks. The thermal and mechanical properties of the networks, as determined from DSC, TGA and DMA could be tuned primarily by an increase in the acrylate:acetoacetate ratio due to an increase in crosslinking. Since the monomer containing the thiol-Michael bond (TMADA) was more flexible than the non-dynamic 1,4-butanediol diacrylate monomer, an increase in thiol-Michael bond concentration led to a decrease in T_g and rubbery plateau modulus, coupled with an increase in % swelling. All of the networks exhibited rehealing properties, as determined from tensile testing, at a cure temperature of 100 °C within 48 h. Increasing the curing temperature to 120 °C decreased the time in which rehealing behavior was observed (≤ 8 h), however, for the network which employed the highest level of TMADA with the lower crosslink density (1.1:1.0−30%), the original crosslinking could not be

recovered upon cooling. Although not investigated, it is believed that a low crosslink density, along with relatively flexible monomers, must be employed in these systems to achieve a low enough T_g in order to promote rehealability between the broken pieces.

An investigation into the thermal history of this network by DSC and TGA revealed that the network was thermally unstable at the higher temperature. As a result of this work, although the dynamic thiol-Michael bond can be readily applied to a different polymer network architecture, care must be taken when pushing the boundaries of quick rehealing materials. While re-healing time can be decreased with an increase in temperature and/or dynamic covalent bond content and/or a decrease in crosslink density, there is clearly a limit where the network may not be able to re-establish its original crosslinked state.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.polymer.2018.05.009.

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