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Responsive and Dynamic Cross-Linking Polymeric Binder/Liner Systems

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1.0 SUMMARY

The effect of glass transition temperature on the thermal decrosslinking of Diels-Alder (DA) crosslinked poly(n-alkyl methacrylate) networks was studied. A series of networks possessing a range of glass transition temperatures was prepared by copolymerizing two n-alkyl methacrylic monomers at various feed ratios, and the influence of the DA crosslinker was evaluated by comparison against triethylene glycol dimethacrylate-crosslinked thermosets and uncrosslinked thermoplastics using dynamic mechanical analysis (DMA). In general, it was found that rubbery networks decrosslinked more abruptly than glassier ones. However, from the storage moduli, the glassiest networks did not appear to decrosslink at all during the time scale of the experiment. Despite the inexplicable apparent lack of thermal response for these networks, preliminary examination of other DMA signals such as loss modulus and particularly tan delta suggests some degree of retro DA reaction is occurring, and current efforts to correlate the aforementioned mechanical property data with calorimetric data are underway.

2.0 INTRODUCTION

Most plastic-bonded explosives (PBX) and solid-state propellants utilize a polyurethane rubber binder to encapsulate the crystalline components of the explosive or propellant fill. Polyurethanes, while inexpensive and readily available, are thermoset materials produced by reacting a multifunctional isocyanate with a hydroxyl-terminated polymeric resin to render a highly crosslinked polymeric network incapable of melting or flowing once cured. Plasticizers are typically added to the polyurethane binder to reduce the explosive or propellant viscosity prior to cure, thereby allowing for additional solids loading and facilitating processing. Over time, the plasticizer molecules are prone to migrate out of the fill and into plasticizer deficient regions within the warhead, for example, into the asphaltic liner. Additionally, if any oxidizer is present or oxygen is able to interact with the explosive, the polyurethane binder can undergo oxidative crosslinking, resulting in deterioration of mechanical properties. The combination of plasticizer migration and oxidative crosslinking can result in embrittlement of the fill and an increase in shock sensitivity, thereby compromising survivability of the weapon during delivery or in response to insult from external stimuli.

In recent years, China Lake researchers examined a thermally reversible polyurethane system for propellants to improve the flow behavior of the fill under cook-off conditions. This approach utilized a curative with a DA moiety capable of undergoing a retro-cyclization in response to elevated temperatures, resulting in a loss of the structural crosslinks within the binder and thereby allowing the propellant fill to flow out of the case prior to the onset of catastrophic self-heating. While the approach was shown to be successful on the small scale, the chemistry was difficult to scale up and did not result in the desired flow characteristics needed to prevent cook-off.

While polyurethane resins afford a resilient binder, it would be advantageous to have a responsive binder system capable of undergoing intentional chemical changes in response to specific external inputs such as temperature, shock, etc. Responsive and dynamic crosslinks are an option to induce such behavior in binder or liner systems. A dynamic crosslink is one that is capable of reversible or continuous exchange, whereby chemical or physical bonds are continuously being broken and formed within the material. These materials still have desirable mechanical properties, due to a minimum number of crosslinks present in the material at any given

time and slow reversibility and exchange at non-catastrophic temperatures. An ideal binder or liner material would have enough crosslinks present to achieve the mechanical properties needed to survive weapon delivery conditions while being responsive to variable inputs or environmental signals, which trigger a chemical or physical change, designed to mitigate an undesirable violent response, thereby dramatically improving the insensitive munitions characteristic of the fill.

This effort sought to pursue the development of new binder and/or liner systems that incorporate reversible crosslinks and install responsive chemistries designed to induce responsive character to the binder/liner when subjected to various external input parameters, e.g. thermal, shock. The binder and/or liner systems were developed from monomers or resins which do not require plasticizers, eliminating aging and/or migration-induced sensitivity changes and elucidating the potential of non-urethane-based binder systems. The mechanical properties and dynamic response of the new binder/liner systems were tested to verify improvements in survivability and insensitive munitions response.

3.0 METHODS, ASSUMPTIONS, AND PROCEDURES

3.1 Materials

All chemicals were used as received unless otherwise noted. Furan ($\geq 99\%$), maleic anhydride ($\geq 99.0\%$), toluene (anhydrous, 99.8%), methanol (HPLC grade), ethanolamine ($\geq 98\%$), benzene ($\geq 99.0\%$), 4-(dimethylamino)pyridine (DMAP, $\geq 99\%$) methacrylic anhydride (94%, 2000 ppm topanol A), ethyl methacrylate (EMA, 99%, 15-20 ppm monomethyl ether hydroquinone), butyl methacrylate (BMA, 99%, 10 ppm monomethyl ether hydroquinone (MEHQ)), and hexyl methacrylate (HMA, 98%, 100 ppm MEHQ) were purchased from Sigma-Aldrich. Dichloromethane (DCM), sodium bicarbonate, ammonium chloride, and sodium chloride were purchased from Fisher Scientific, with the DCM dried through the use of an Innovative Technologies solvent purification system. Furfuryl alcohol (98%), triethylamine (TEA, 99%), and magnesium sulfate (anhydrous, $\geq 99.5\%$) were purchased from Alfa Aesar. Basic alumina (Brockmann I, 50-200 μm , 60 \AA) and methyl methacrylate (MMA, 99%, stabilized) were purchased from Acros Organics. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, $> 98.0\%$) and triethylene glycol dimethacrylate (TEGMA, $\geq 95\%$, MEHQ stabilized) were purchased from TCI America. Diethyl ether was purchased from EMD Millipore. The photopolymerization cuvettes were prepared by cutting 12" x 12" sheets of 2 mm thick 50A (medium) high temperature silicone rubber sheets (McMaster-Carr) with a razor blade to form a rectangular gasket fitting flush between two plain glass microscope slides (Fisherfinest™ Premium, Fisher Scientific), all of which were rinsed with DCM and acetone (Certified ACS, Fisher Scientific) and dried prior to assembly. After cleaning, the glass slides were coated once with Chem-Trend Zyvax® Sealer GP™ mold sealer and allowed to dry overnight. The apparatus was held together with 0.5" binder clips (Office Depot).

3.2 Methods

All polymerizations were performed in a UV nail gel curing lamp with four 9 W bulbs. These bulbs are available from ad hoc suppliers and emit UV light with a peak emission near 360 nm and a combined intensity of 7.0 mW/cm² as determined by a General UV513AB Digital UV AB Light Meter calibrated at 365 nm. Dynamic mechanical analyses were obtained with a TA

Instruments Q800 DMA in the "DMA Multi-Frequency - Strain" mode in air using a temperature ramp experiment from 0 °C to 200 °C at a rate of 3 °C/min, a frequency of 1 Hz, and the single cantilever clamp. DMA data were processed and plotted using TA Universal Analysis software.

3.3 Procedures

3.3.1 Synthesis of furan/maleic anhydride oxanorbornene. Furan (185 mL, 2.5 mol) and maleic anhydride (50 g, 0.51 mol) were taken up in toluene (500 mL) in a 1 L round-bottom flask equipped with a stir bar, and the reaction was stirred for 3 d at room temperature. The precipitated product was washed with toluene and dried under vacuum (82.4 g, 97%).

3.3.2 Synthesis of furan-protected N-(2-hydroxyethyl)maleimide. Furan/maleic anhydride oxanorbornene (81 g, 0.49 mol) was take up in methanol (180 mL) in a 500 mL round-bottom flask equipped with a stir bar and a reflux condenser. The reaction was cooled in an ice bath for 30 min. Ethanolamine (45 mL, 0.75 mol) was added dropwise while stirring. The resulting mixture was stirred in an ice bath for 1 h and was warmed to room temperature. The reaction was refluxed overnight. After cooling to room temperature, the product precipitated and was recovered by vacuum filtration. The filtrate was concentrated and stored in a freezer overnight to collect a second crop of product (72.1 g, 71%)

3.3.3 Synthesis of N-(2-hydroxyethyl)maleimide. Furan-protected N-(2-hydroxyethyl)maleimide (72 g, 0.34 mol) was added to a 1 L round-bottom flask equipped with a stir bar and a short reflux condenser. Toluene (430 mL) was added, and the reaction was refluxed overnight. After cooling to room temperature, the product precipitated after further cooling in an ice bath and was recovered by vacuum filtration. The filtrate was concentrated and stored in a freezer overnight to collect a second crop of product (36.7 g, 76%).

3.3.4 Synthesis of DA diol. N-(2-hydroxyethyl)maleimide (7.0 g, 49.6 mmol) was dissolved in benzene (75 mL) in a 250 mL round-bottom flask equipped with a stir bar and a reflux condenser. Freshly distilled furfuryl alcohol (4.86 g, 49.6 mmol) was added, and the solution was refluxed overnight. The product, which precipitated upon cooling, was washed with diethyl ether and dried under reduced pressure (7.4 g, 62%).

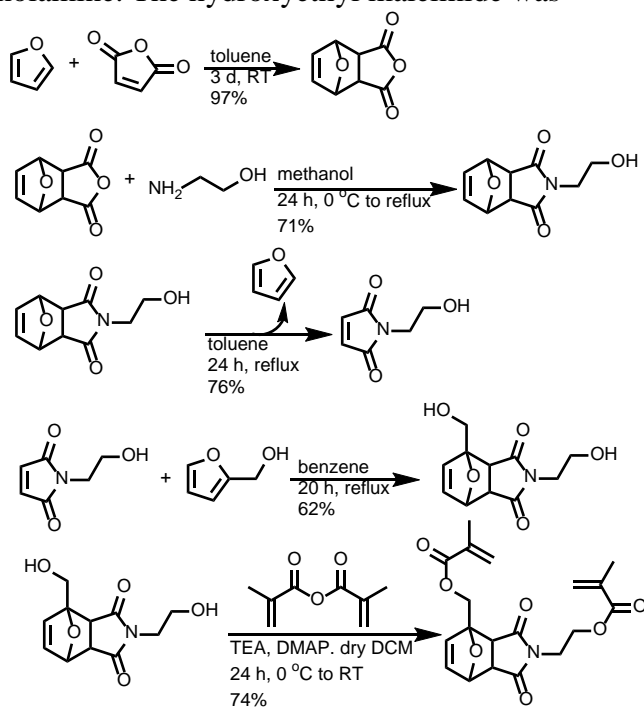
3.3.5 Synthesis of bismethacryloyl DA crosslinker. To a 100 mL round-bottom flask equipped with a magnetic stir bar and an addition funnel was added Diels-Alder diol (2.0 g, 8.4 mmol), TEA (7 mL), DMAP (407 mg), and dry DCM (40 mL). The reaction was cooled in an ice bath. The addition funnel was charged with methacrylic anhydride (5.0 mL, 33.5 mmol), which was added dropwise over a period of 30 min. The resulting mixture was stirred and allowed to warm to room temperature overnight. The solution was then diluted with DCM (40 mL) and washed with saturated sodium bicarbonate (80 mL), ammonium chloride (80 mL), and brine (80 mL). The organic layer was dried with magnesium sulfate and was passed through two plugs of basic alumina. The solvent was removed by rotary evaporation and reduced pressure, followed by bubbling through with argon (2.31 g, 74%).

3.3.6 Generalized photopolymerization procedure. Monomers were passed through a plug of basic alumina to remove inhibitor prior to use. DMPA (0.5 mol%) and crosslinker (DA, TEGMA,

or none) were weighed into a vial. Deinhibited monomer (2 mL total volume) was added, and the solution was shaken until homogenous. The solution was injected into the assembled cuvette, and the cuvette was irradiated in the UV lamp for 8 h.

4.0 RESULTS AND DISCUSSION

The investigation of non-urethane-based, temperature-responsive binders began with the synthesis of a divinyl crosslinker incorporating a thermally cleavable moiety. This would allow the preparation of polymeric thermosets capable of undergoing a transition to thermoplastic behavior dictated by the cleavage temperature of the reversible linkage, in this case, the DA adduct. Methacryloyl groups were selected for the divinyl functionality to aid copolymerization with methacrylic monomers, enabling the glass transition temperature (T_g) of the networks to be tuned both widely due to the broad T_g range of polymethacrylates and in a straightforward manner by simply changing the monomer(s) used. The synthetic pathway is shown in Scheme 1. After the forward DA reaction of furan and maleic anhydride, the resulting oxanorbornene was converted to the imide using ethanolamine. The hydroxyethyl maleimide was



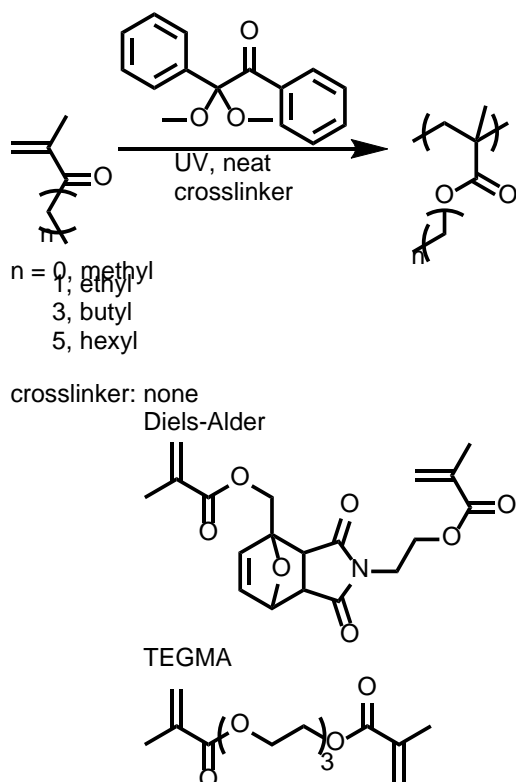
Scheme 1: Synthesis of a thermally reversible divinyl crosslinker incorporating Diels-Alder functionality

afforded by the retro Diels-Alder (rDA) reaction, liberating furan. This maleimide was then reacted with furfuryl alcohol to give the DA diol, which was converted to the dimethacrylate via methacryloyl anhydride. For the network synthesis, bulk conditions were chosen to aid in film preparation for mechanical characterization. A photopolymerization approach was taken to avoid potential risks associated with conventional thermal initiation, namely premature crosslinker cleavage at elevated cure temperatures and voids in the film due to the nitrogen byproduct of azo

initiator decomposition. The films were prepared in cuvettes consisting of glass microscope slides and silicone rubber sheets cut to form rectangular gaskets. This approach facilitated the preparation of uniformly thick films by injecting a solution consisting of initiator and crosslinker dissolved in monomer into the cuvettes and placing the cuvettes under an inexpensive commercial ultraviolet lamp.

It became apparent that the effect of T_g on the network decrosslinking behavior needed to be determined. Since a particularly attractive feature of this approach was the potential applicability of any methacrylic monomer, that assumption required verification. Towards this aim, two monomers that produced polymers of disparate T_g were copolymerized at various feed ratios to produce a set of networks possessing a broad T_g range. The monomers selected were n-alkyl methacrylates, particularly ones containing short alkyl chains ($n \leq 5$, Scheme 2), to eliminate mechanical property differences owing to structural variation. Because the purpose of incorporating the DA crosslinker was to explore the thermoset to thermoplastic transition upon thermal stimulation, two control crosslinking variations were explored: triethylene glycol dimethacrylate (TEGMA) to afford permanently crosslinked thermosets and no crosslinker to produce uncrosslinked thermoplastics (Scheme 2). Initially, MMA, T_g : 120 °C¹ and HMA, T_g : -5 °C¹ were selected, but the low T_g of HMA made mechanical characterization of uncrosslinked PHMA difficult. Therefore, BMA, T_g : 20 °C¹ was chosen as a replacement since it is the next lowest T_g commercially available n-alkyl methacrylate.

A series of 15 samples was prepared consisting of three crosslinking variations (DA, TEGMA, and uncrosslinked) and five monomer feed ratios (100:0, 75:25, 50:50, 25:75, and 0:100



Scheme 2: Generalized overview of network syntheses

BMA:MMA), and the series was characterized by DMA. An overlay of the storage moduli of the TEGMA crosslinked and uncrosslinked controls are shown in Figure 1, with the storage moduli

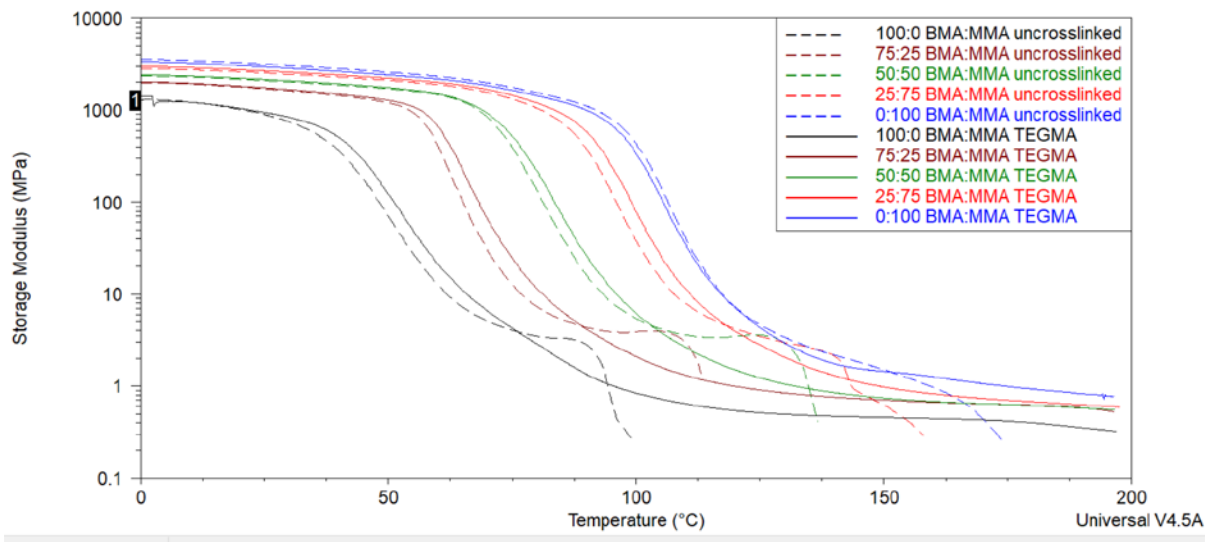


Figure 1: Overlay of storage moduli for uncrosslinked and 1 mol% TEGMA crosslinked controls

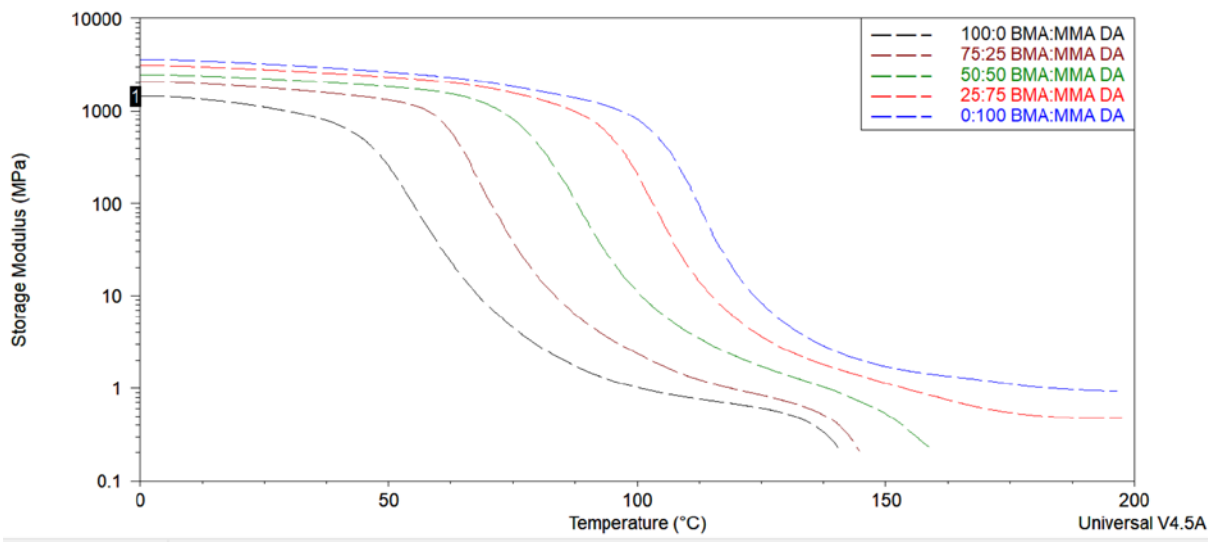


Figure 2: Overlay of storage moduli for 1 mol% DA-crosslinked films

of the DA crosslinked films in Figure 2. The storage moduli of the controls in Figure 1 display behavior typical of thermoplastics and thermosets.² All formulations start out at relatively high storage moduli which increase with the MMA loading. As the temperature increases, the samples undergo T_g , which also increases along with MMA concentration. After this, the TEGMA-crosslinked samples level off and enter the rubbery plateau regime, typical for thermosetting materials. The storage moduli then remain at approximately the same value until the end of the run, which again is largely dictated by the monomer feed. The uncrosslinked samples on the other

hand yield shortly after T_g , terminating the run. It was predicted that the DA-crosslinked films would exhibit behaviors intermediate to these two controls. Since the DA crosslinker can be treated as permanent before the temperature at which the rDA reaction dominates, prior to this temperature the films should resemble the TEGMA-crosslinked films. Above this temperature the films should begin to approximate the uncrosslinked films as decrosslinking takes place. As can be seen in Figure 2, these expectations were borne out to an extent. For the films containing 50% BMA and higher, the storage moduli yield at elevated temperatures. The existence of a second onset resembling T_g approximately between 125 and 150 °C denotes the rDA reaction. Before this transition, the films approximate the TEGMA permanently crosslinked films. After T_g the storage moduli enter the rubbery plateau, but shortly thereafter undergo the rDA reaction and yield as do the uncrosslinked films. Furthermore, the polymer backbone does appear to be playing a role in the rDA-induced decrosslinking, as the temperature for the transition associated with the rDA reaction seems to increase with T_g . However, while there does appear to be some small secondary transition in the 75% MMA film that does not result in material failure, there is little distinguishing the DA-crosslinked 100% MMA film from the TEGMA-crosslinked control.

Efforts were then directed at determining why the MMA-rich films did not yield. One working hypothesis was based on the reactivity ratios between MMA and furfuryl methacrylate (FMA; structurally related to the DA crosslinker). When copolymerized, both MMA- and FMA-derived radicals prefer to add to FMA.³ Since addition to FMA is preferred by both monomers, it is conceivable that blocks consisting of several units of crosslinker could occur in the MMA-rich films, resulting in regions of high local crosslinker concentration. Upon rDA, this arrangement would produce numerous reactive furan and maleimide functionalities in close proximity to one another, favoring the forward DA reaction and preventing or slowing decrosslinking. Up to this point, the amount of crosslinker used had been set at 1 mol%. This had been largely done because of the preciousness of the DA crosslinker and initial concerns about the solubility of the DA crosslinker in bulk monomer. However, to test this hypothesis, the crosslinker loading was varied.

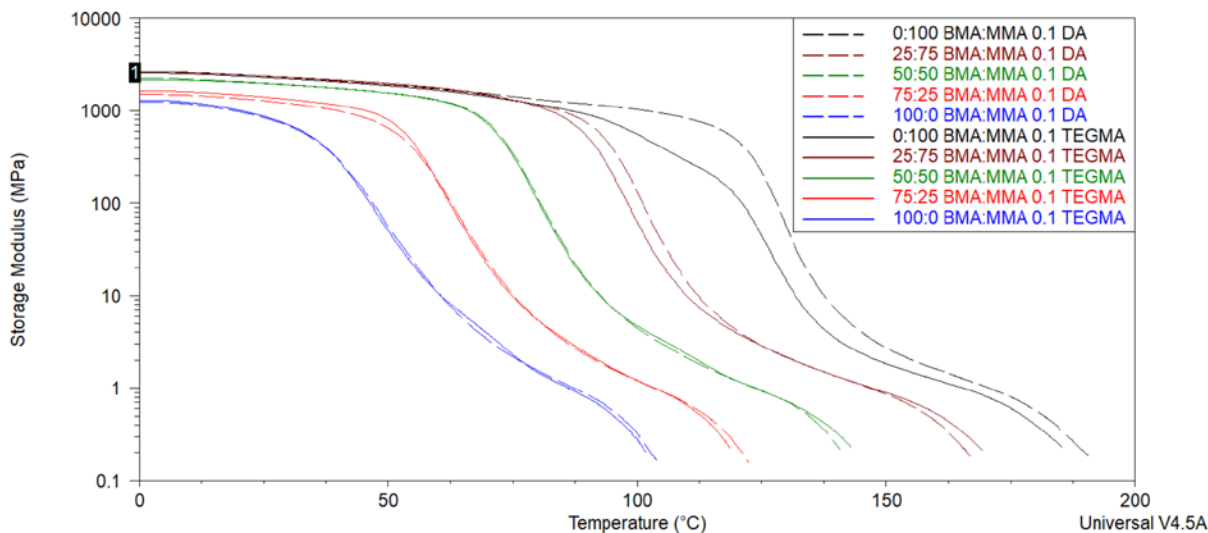


Figure 3: Overlay of storage moduli for 0.1 mol% DA- and TEGMA-crosslinked films

Decreasing the crosslinker content to 0.1 mol% initially looked promising, but when overlaid with the storage moduli from films crosslinked with 0.1 mol% TEGMA, it became clear from the TEGMA films yielding that the films simply were not crosslinked (Figure 3).

Increasing the crosslinker concentration to 0.5 mol% improved results somewhat, but the BMA-rich films were still insufficiently crosslinked (not shown). Raising the crosslinker content to 0.75 mol% essentially replicated the 1 mol% results (not shown). Other experiments were tried, including increasing the DA crosslinker content above 1 mol% to observe a greater change in mechanical properties during rDA, more rigorously purifying the MMA to remove any acidic impurities that could react with the DA crosslinker,⁴ and incorporating model DA linkages without methacrylate groups into the polymerizations to see if any reactions between the propagating radicals and the DA linkages were occurring. While none of these experiments conclusively proved why the DA-crosslinked MMA-rich films did not yield as the BMA-rich ones did, the current hypothesis is that rDA is still taking place in the MMA-rich films, just at a time scale slower than the DMA experiment (Figure 2). Since furans and maleimides are known to undergo side reactions at elevated temperatures, it could also be that permanent crosslinking is occurring before the rDA is completed. Isothermal DMA experiments and slower ramp rates are currently being investigated.

While working on another project, DA-crosslinked poly(ethyl methacrylate) (EMA, T_g : 65 °C¹) was prepared and characterized by DMA. While not possessing as high a T_g as MMA, EMA is next in the n-alkyl methacrylate series and was thermally reversible. Interestingly, when compared to DA-crosslinked poly(butyl methacrylate) (PBMA) (Figure 4), poly(ethyl methacrylate) (PEMA) appears to yield less abruptly. This observation confirmed what was seen in the BMA:MMA copolymers: that T_g affected the rDA behavior, with delayed and more gradual failure occurring with increasing T_g . With this

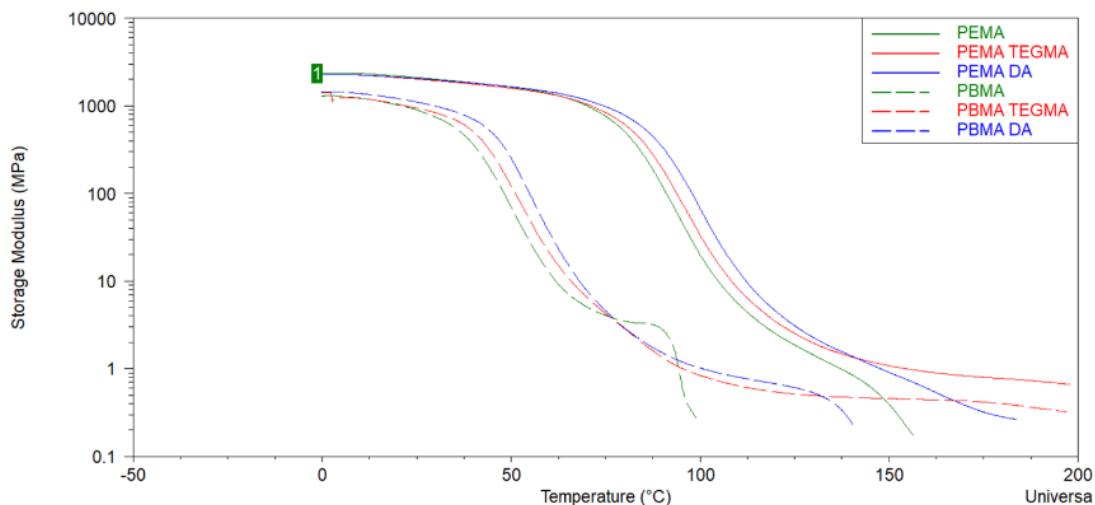


Figure 4: Storage moduli of preliminary PEMA DMA traces with BMA traces for comparison

information in hand, a similar series was prepared with the same 3 crosslinking variations and 5 feed ratios at the same mol% crosslinker as before. The control overlays are shown in Figure 5,

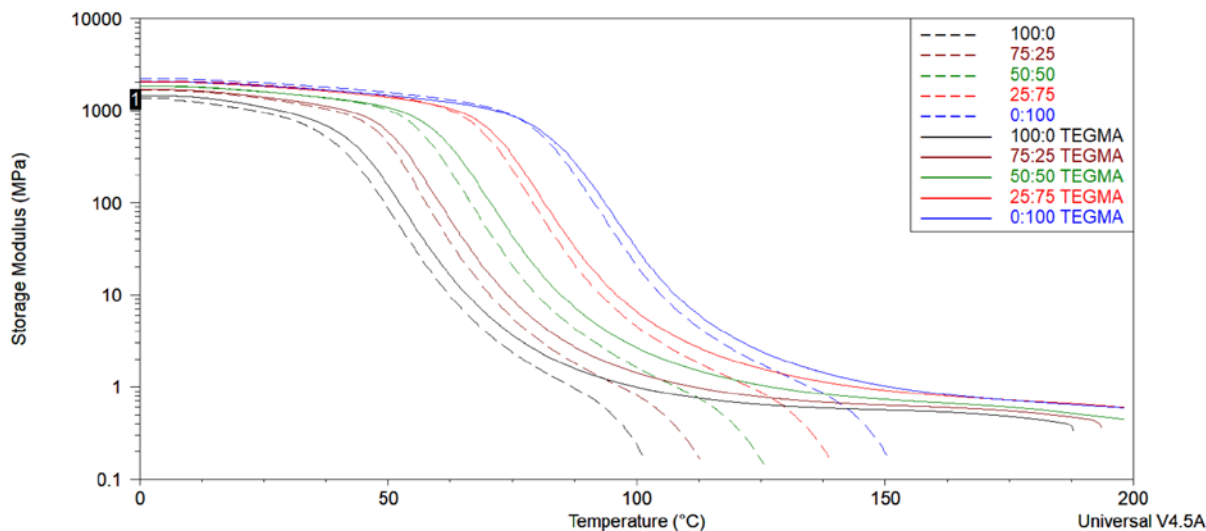


Figure 5: Overlay of storage moduli for uncrosslinked and 1 mol% TEGMA crosslinked controls incorporating EMA

and the DA traces in Figure 6. While the uncrosslinked films and the TEGMA-crosslinked films behaved as intended (with the exception of the TEGMA 100:0 and 75:25 films breaking near the end of the run), the DA-crosslinked films closely resembled the earlier MMA:BMA films with

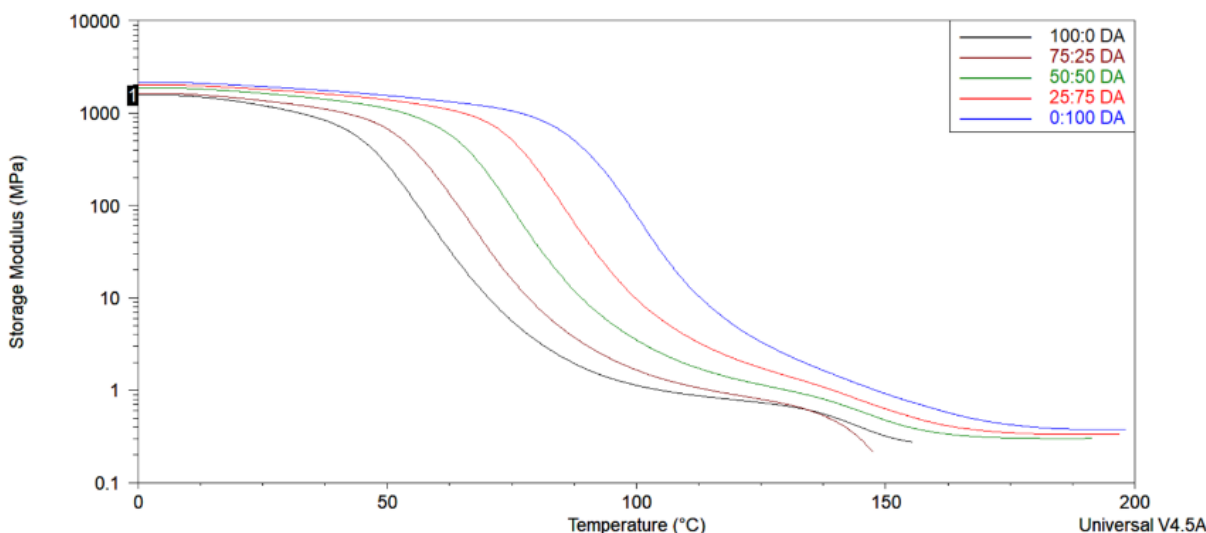


Figure 6: Overlay of storage moduli for 1 mol% DA-crosslinked films incorporating EMA

the only films that yielded as expected being the BMA-rich ones (100:0 and 75:25). Not even these films completely followed expectations, as the PBMA film yielded after the film containing 25% EMA. Therefore, efforts were directed at preparing DA-crosslinked PEMA films that would yield in the DMA by trying to imitate the original, successful films. Despite modifying several variables (glass slide mold release coatings, cure time, presence of radical inhibitor, UV light intensity, and others) the preliminary results were unable to be replicated. Currently, other DMA signals, including loss moduli and especially tan delta, are being studied. While the materials do not yield as expected, peaks in the loss moduli and tan delta do increase with T_g . Additionally, at higher DA crosslinker concentrations, endotherms corresponding to the rDA in differential scanning

calorimetry are visible. Efforts are ongoing to correlate these peaks with the DMA data to see if the calorimetry data follows the mechanical data.

5.0 CONCLUSIONS

A straightforward and scalable route to a dimethacryloyl DA crosslinker was demonstrated. Not only does the synthesis use inexpensive starting materials and simple purifications, but it involves an intermediate diol which can be incorporated into conventional polyurethane binder systems to potentially bestow thermal decrosslinking abilities. Networks with a range of T_g were fabricated through the copolymerization of two monomers at various feed ratios. Furthermore, a low-cost method for fabricating uniformly thick films for DMA testing was discussed. While thermally reversible DA-crosslinked PMMA and PEMA were unable to be prepared, despite promising initial results with PEMA, the general trend that the rubberier the network the more drastic the effect of rDA was borne out. Despite this setback, this finding is beneficial to PBX systems, as the typical desired T_g tends to be well below 0 °C. Therefore, formulations based on this methodology (with T_g well below that of PBMA) are predicted to flow at elevated temperatures. Future work is directed at developing these aforementioned binder systems as well as further characterizing the DA-crosslinked films for additional evidence of rDA.

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ACRONYMS

BMA	butyl methacrylate
DA	Diels-Alder
DCM	dichloromethane
DMA	dynamic mechanical analysis
DMAP	4-(dimethylamino) pyridine
DMPA	2,2-dimethoxy-2-phenylacetophenone
EMA	ethyl methacrylate
HMA	hexyl methacrylate
MEHQ	monomethyl ether hydroquinone
MMA	methyl methacrylate
PBMA	poly(butyl methacrylate)
PBX	plastic-bonded explosive
PEMA	poly(ethyl methacrylate)
PMMA	poly(methyl methacrylate)
rDA	retro Diels-Alder
TEA	trimethylamine
TEGMA	triethyl glycol dimethacrylate

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