Investigations Toward Tunability of Mechanical, Thermal, and Impact Properties of Thiol-ene Networks for Novel High Energy Absorbing Materials

Olivia Devon McNair

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INVESTIGATIONS TOWARD TUNABILITY OF MECHANICAL, THERMAL, AND IMPACT PROPERTIES OF THIOL-ENE NETWORKS FOR NOVEL HIGH ENERGY ABSORBING MATERIALS

by

Olivia Devon McNair

Abstract of a Dissertation
Submitted to the Graduate School of The University of Southern Mississippi in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

May 2013
ABSTRACT

INVESTIGATIONS TOWARD TUNABILITY OF MECHANICAL, THERMAL, AND IMPACT PROPERTIES OF THIOL-ENE NETWORKS FOR NOVEL HIGH ENERGY ABSORBING MATERIALS

by Olivia Devon McNair

May 2013

The UV polymerization of thiols with electron rich alkenes is a highly resourceful reaction that has been utilized by scientists within various disciplines to produce an even more versatile display of applications. This dissertation focuses on a newer application, thiol-ene network (TEN) materials for energy absorption devices. TEN networks display a host of positive polymer properties such as low stress, high optical clarity and uniformity, but they also suffer from unfavorable mechanical properties such as low toughness and elongation at break. The poor mechanical properties demonstrated by TENs prohibit them as choice materials for applications requiring thicker material forms, including energy damping devices. The chapters in this dissertation focus on enhancing the toughness of TENs via urethane or thiourethane incorporation wherein toughness is enhanced by either hydrogen bonding or underlying network morphologies. Impact behaviors of base systems were investigated and correlated to polymer glass transition temperature. The tunability of the temperature associated with viscoelastic relaxation was also investigated by developing hybrid networks containing two thiol components. The relevance of the works performed is highlighted by the major contributions realized by understanding structure-property relationships and network morphology on underlying principles of energy absorption.
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May 2013
DEDICATION

This work is dedicated to my family and friends. Thank you for continuously supporting my lifelong efforts. To my parents for being supportive of my “weird” demonstrations of a scientific mind in my youth. To the late Professor Charles E. Hoyle, who dedicated so much of his time on earth to his students and research. I am ever grateful. Finally, to my husband for his understanding throughout this entire process.
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CHAPTER I
INTRODUCTION

Polymers and Polymer Networks

Polymers play an important role in scientific advancements throughout a broad array of fields because of their wide display of attainable physical properties, the ability to tune thermal response, the capability to engineer other “smart” responsiveness, and the expanding catalog of methods by which to synthesize them. In fact, the role of polymers in our daily routines is vast and invaluable. For instance the shift from metal to composite-based aircraft, cars and ships translates to conservation of precious and limited natural fuel resources. Light weight and high toughness construction materials has allowed man to erect some of the shapeliest, intricately designed and safe buildings. For the first time in history scientists are able to design site specific drug delivery vehicles that will carry medicine solely to affected human cells, sparing the healthy cell population. The versatility of polymers originates from their bottom-up construction wherein careful monomer selection along with appropriate molecular architecture makes it possible to create materials specific to nearly any application. This newer class of materials have rightfully become an era all their own.

Polymer Networks

Polymers are normally synthesized through either step-growth polymerization, chain-growth polymerization or a combination of the two. Indifferent from the technique utilized to make the polymer material the result is the same; long chains of monomer repeat units. As mentioned before underlying network architecture profoundly affects final material properties. Two major classifications based on polymer architecture are
thermoplastic polymers and thermoset or network polymers. Thermoplastic polymers are linear polymers wherein some critical molecular weight, the entanglement molecular weight, must be reached in order to gain sufficient mechanical properties to make it useful for many applications. On the other hand, polymer networks typically gain their mechanical robustness by way of cross-linking reactions.

Polymer networks can be generally formed in one of two ways: 1) the connection of linear polymers during a postpolymerization reaction as in the cross-linking of natural rubber (vulcanization) or 2) the polymerization of multifunctional monomers upon which some critical conversion is required for network formation. In the former the only requirement to form a network is to have one link between each chain, while the latter is dependent on some critical conversion of functional groups and is slightly more complex. While scientists have developed methods, i.e “living polymerization”, to very precisely determine molecular weight, molecular weight distribution and end groups, the cross-linking reaction of multifunctional monomers proves much harder to control.

What typically occurs during cross-linking reactions, especially in UV polymerization reactions, is the formation of high molecular weight polymers at the beginning of the polymerization reactions. These regions of high molecular weight form microgels or small dense polymer regions. The microgels in turn limit collision events of the remaining polymerization reactions resulting in the formation of a network with very local differences. At some point, reactions are “frozen out” as the glass transition temperature of the network approaches the reaction temperature and vitrification essentially prevents further reactivity.
In the first instance, wherein chains are linked together in postpolymerization reactions, the consequence of chain linking is a gel point. Mathematically, the gel point is expressed as the probability that one chain participates in at least one cross-linking reaction. In the second instance involving the polymerization of multifunctional monomers, the critical point is described be a critical conversion of functional groups. Both the gel point and critical conversion can be expressed by the following equations\(^5\), where \(w\) is the critical conversion of cross-links for a chain of \(N\) repeat units and \(f\) is the critical extent of a reaction where the total number of functional groups is \(f\).

Although there are many similarities between linear polymers and polymer networks, there are a few mechanical effects by which they are different. First thermosets, unlike thermoplastics, do not exhibit melting points or flow because cross-linking essentially converts an aggregation of linear polymer chains or multi-functional monomers into one large molecule. As a result, thermoset polymers typically exhibit higher tensile moduli than their linear analogs, demonstrate decreased elongation at break, possess higher hardness, and in general are less flexible and impact resistance because of the “locked-in” conformation of polymer segments. In both cases, monomer structure plays a major role concerning material properties such as glass transition temperature, modulus and melting point if applicable but more importantly in networks the degree to which cross-linking occurred and the uniformity within the network structure are very important aspects which dictate important mechanical behaviors.
Polymer Viscoelasticity

Thermosets and thermoplastics have their differences, but they are both truly polymers in a traditional sense and both materials demonstrate typical polymer characteristics. One such description is polymer viscoelasticity. Viscoelasticity is used to describe the combination of solid and liquid-like traits demonstrated by these materials. In the simplest form, the solid component is modeled by a spring, wherein the spring constant, k, describes the stiffness factor of the spring and a dashpot, wherein the strain rate is directly proportional to force by way of viscosity, \( \eta \) as in the Maxwell and Voigt models.\(^5\)

The amount of solid character and liquid character are both temperature and time dependent and many complex theories have been generated to describe polymer behavior. More simply, at low temperatures and high frequencies polymers display more solid-like character and at high temperatures and low frequencies they display more “liquid-like” character. During the alpha transition period, or glass transition temperature, when polymers are at a cross-over regime between liquids and solids, polymers can be exploited for their unique ability to dissipate mechanical energy. This is termed viscoelastic damping or dissipation. For this reason polymers, regardless of their underlying architecture, are frequently utilized in applications which require energy or noise damping.

This region can be clearly visualized by rheometric experimentation such as a Dynamic Mechanical Analysis (DMA) experiment. During a DMA experiment, a sinusoidal stress or strain is applied to a polymer in order to separate the elastic and viscous components. In short during a DMA experiment, a set oscillatory strain is applied
to a sample while the sinusoidal stress response is measured. Although the stress will oscillate at the same frequency the response will be shifted by some phase, $\delta$. In a perfect solid, such a shift would not exist. Essentially by decomposing the stress wave into two waves, wherein one is in phase with the strain wave, the in phase and out of phase components can be quantified.\(^6\) The quantifiable components corresponding to the in phase and out of phase components of the complex modulus of the material, $E^*$, which are the elastic or storage modulus ($E'$) and the loss modulus ($E''$). The ratio of the loss modulus to the storage modulus, or $\tan \delta$, is what is often of interest to researchers seeking polymer damping materials. If $\tan \delta$ is high, mechanical energy can be converted to heat energy.\(^7\) The relationship between the complex modulus, storage modulus, loss modulus and $\tan \delta$ can be described by the following equations.

\[
E^* = E' + iE''
\]
\[
\tan \delta = \frac{E''}{E'}
\]

**UV Polymerization**

A popular method utilized to generate polymer networks is photopolymerization. During this type of polymerization technique, liquid monomer is exposed to UV light and converted to a solid polymer network. This is an attractive method because it is low cost (no waste and low energy consumption), efficient (high conversion) and fast (rapid kinetics).\(^8\) Historically vinyl monomers, which are highly subject to radical polymerization, have been photopolymerized for many years beginning in the 1940’s. These types of materials have found use in the electrical, optical, coating and automotive industries to name a few.\(^9\)
UV light is lower wavelength (higher energy) than visible light and is capable of breaking chemical bonds to form radicals in many monomer species and photoinitiators. Once a radical is formed and adds to the first monomer in the initiation step, propagation proceeds when this radical is added across another susceptible monomer, so on and so forth. Termination events of UV polymerizations include radical coupling events which form stable bonds and inhibit the polymerization process. Figure 1 illustrates the mechanism of a typical UV polymerization through vinyl-based monomers.

![Figure 1. General UV Polymerization Process.](image)

While there are many types of photoinitiators capable of producing a reactive radical species, thermally stable and fast cleavage-type photoinitiators are highly attractive for UV polymerization reactions. These types of photoinitiators are single molecules which rapidly separate into two radical species and will then add directly to a monomer, rearrange, or abstract protons from a monomer to generate a radical. The overall overlap of the absorbance of the photoinitiator and UV light should be matched for optimal radical production. For the research performed in this dissertation UV polymerizations were carried out with dimethoxy acetophenone or DMPA, a cleavage type photoinitiator. This photoinitiator is consistently used due to the high efficiency of
radical generation and the good overlap between the mercury bulb output and photoinitiator absorbance.

A dominant choice for UV polymerizations is acrylate monomers. Acrylates are electron poor vinyl-based monomers which come in a wide variety of functionalities and structures monomers. The R group substitution (Figure 1) of acrylates is attractive because it provides a synthetic handle to control final polymer properties. Acrylates are infamous for rapid kinetics and substitutability, but the rapid kinetics of acrylate UV polymerization leads to the aforementioned microgels which in turn lead to an inhomogeneous polymer product with local differences. This is denoted by the very broad tan delta curve obtained from a Dynamic Mechanical Analysis (DMA) experiment. Acrylate UV/radical polymerizations are also highly sensitive to oxygen inhibition. Oxygen is a natural radical scavenger and often retards radical polymerization reactions. Once reacted with radicals oxygen converts to peroxide radicals which will react with other radical species and impede propagation. Although acrylates are well understood species and heavily used in UV polymerizations, it is clear they may not be the optimal choice where a highly uniform network is required.

One attractive alternative polymer synthesized via UV polymerizations is thiol-ene reactions. These reactions have been performed on multifunctional thiols and alkenes to produce thin films, surface micropatterns and thick thermoset polymer materials measuring up to a meter thick. Although less is understood about thiol-ene photopolymerization reactions thiol-ene networks (TENs), they have demonstrated initial success on a variety of levels across a broad array of scientific research areas. These networks will be the basis of experimentation and discussion throughout this dissertation.
Thiol Chemistry and Thiol-Ene “Click” Chemistry

The character and chemical reactivity of thiols have been exploited throughout many years. They were once used to capture mercury, which is why they are also called mercaptans and because low molecular weight thiol molecules generally have pungent odors, they are used as additives in natural gas to give it a distinct smell, warning people of gas leaks. Thiols, the sulfur analog of alcohols, are known to react with a variety of compounds under a diverse set of conditions and through multiple mechanisms. They are inherently different from alcohols in that thiol atoms have a larger diameter than oxygen atoms, leading to different bond strengths. The chemical bond strength of sulfur and hydrogen is weaker than oxygen and hydrogen giving way to the observed difference between bond length and reactivity of each respective functional group. The oxygen-hydrogen bond length is about 0.96 Angstroms while the sulfur-hydrogen bond length is 1.3 Angstroms respectively\(^{12}\) and while electrons surrounding alcohols are close to the nucleus in oxygen they are significantly further away from the nucleus and more loosely bound in thiols. Therefore thiols are more reactive and readily susceptible to participate in a variety of chemical reactions with an impressive list of functional groups. In fact, thiols are known to react efficiently and predictably with a wide variety of compounds under mild conditions.

Thiols are less polar bonds than alcohols which make them inherently different from alcohols and to some extent advantageous in polymer synthesis. In 2001 Sharpless and coworkers described a new approach toward molecular synthesis which essentially demands scientists to streamline complex synthetic techniques by only using reactions that are simplistic in nature. Ideally these reactions would have been proven facile and
efficient throughout years of research by chemists and other scientists alike. This new set of requirements would meet certain standards be target to complete synthetic tasks.  

For example this battery of modular reactions should:

1. have high percent yields
2. few or no by-products
3. be regioselective and stereospecific
4. react under mild conditions
5. demonstrate oxygen/air insensitivity
6. proceed without solvent or with a benign solvent
7. have products that can be easily isolated
8. boast a diverse group of starting materials to select from

Thiol-based reactions generally involve converting thiols to thiolate anions or thyl radicals. The thiolate anion is generated by base catalysis. Heat or radiation is used to generate the thyl radical. These high energy intermediate species will react to an appropriate species to generate a lower energy product. The platforms of these well studied thiol-based reactions of thiols are shown in Figure 2. A variety of groups including epoxies, alkyl halides and unsaturated bonds are known to react both in a regioselective and orthogonal manner to thiols under mild conditions.
Figure 2. Thiol "Click" Reactions Based on Thiol Radical and Thiolate Anion Addition.

The robust, efficient, and orthogonal radical addition of thiols to select unsaturated compounds or alkenes meets the standards of such named “click” reactions. The thermodynamic driving force behind the thiol-ene “click” reaction is the conversion of π bonds into σ bonds which is also the driving force of many polymerization reactions involving vinyl monomers. The available toolbox of commercial and synthesized thiol and alkene monomers capable of undergoing “click” chemistry is certainly plentiful. Both primary and secondary thiols have high reactivity (when sterics are favorable) and vinyl monomers are certainly abundant. This hypothetical battery of monomers can be used to generate polymers with a variety of properties.

The radical addition of thiols to vinyl monomers was reported as early as 1938 and many years later in the 1960s through 1970s as the UV enhancement of thiol-ene reactions was widely investigated leading to commercial significance of this reaction.
By the mid 1970s commercial applicability of the radical addition of thiols across a double bond by light (UV) reactions was widely accepted throughout industry where thiol and vinyl monomers were used on a commercial scale in coatings and electronics. 18-22

Structure Effects

As mentioned before there is an exhaustive list of benefits concerning thiol-ene “click” reactions as tools for polymer synthesis but there are a few limitations. The pioneering work of C. R. Morgan and coworkers has had an immense impact concerning the UV polymerization of thiols with alkenes with respect to the effect of thiol structure on the rate of reaction with a vinyl monomer and vice versa.18 From that work some general inferences could be made about kinetics with respect to monomer structure. Electron donating substituents in close proximity to the reacting vinyl group increase reaction rates while electron withdrawing species decreased the rate of reaction (see Figure 3). Mercaptopropionate esters boast a higher reactivity that mercaproacetates which have higher reactivity than alkane thiols. Since then, other structural effects of thiols and enes have been investigated in a similar manner to produce a larger body of knowledge about the effects of monomer structure on the kinetics of a thiol-ene UV reaction. 23-25

**Figure 3.** Relative Reactivity of Vinyl Monomers with Respect to UV Polymerization with Thiols.
The position of the alkene reactive group has also been found to be important with respect to the kinetics of the reaction. Vinyl monomers having its reactive alkene group at the exterior positions are more reactive than those where the reactive species is internal. Furthermore, there is an evident difference between cis and trans monomers due to steric interactions, slowing the intermediate propagation step. Recently molecular modeling experiments confirm experimental observations. More specifically reaction kinetics has been related to reaction parameters such as $k_p$, $k_{-p}$ and $k_T$ with respect to the alkene moiety. The worst conditions for UV polymerization reactions with respect to the alkene moiety occur when the alkene is conjugated. Congugated dienes tend to react slower due to stability of the radical intermediate by resonance. This type of behavior tends to favor termination events through carbon radical coupling. In general, unless an alkene is internal, sterically hindered or stabilizing, reactions with thiols are typically fast and reach full conversion within a matter of seconds.

The thiol structure also plays a role regarding reaction kinetics and overall conversion thiol-ene photopolymerizations. Secondary thiols have been found to be relatively active unless bulky substituents are present. However, the presence of a terminal thiol one carbon removed from a carbonyl group, as in the mercaptopropionate type thiol, species, the reactions are significantly faster. Fortunately there are not many commercial thiols which hamper the radical addition process.

*Thiol-Ene Reaction Mechanism*

Since both acrylate and thiol-ene UV polymerizations proceed by the same techniques it stands to reason that the resulting difference in underlying polymer network structure stems from a different source. The mechanism of the thiol-ene “click” reaction
is not purely radical or chain growth it is a combination of chain and step polymerization processes. As it turns out this important detail is all the difference between homogeneous and inhomogeneous network formation.

Similar to other UV polymerizations, radical addition of thiols to vinyl groups is commonly enhanced by addition of a photoinitiator or photosensitizing species. Upon UV irradiation or heating, thiyl radicals are readily formed to give a reactive species that can add across a carbon carbon double bond. The resulting carbon centered radical can proceed to react further. With a photosensitizer, the radicals are generated by the photoinitiator first. These radicals then begin the reaction process. More specifically, photoinitiators are utilized to break apart the thiol hydrogen bond generating a thiyl radical which adds across a double bond to generate a carbon centered radical as in traditional chain growth polymerizations. However in the next step the radical abstracts a proton from a second thiol (as opposed to adding to another vinyl monomer) which is similar to step growth polymerizations lending the reaction mechanism a step-growth chain mechanism resulting in anti Markovnikov addition of a thiol across an unsaturated group yielding a thioether product (see Figure 4).\textsuperscript{9,18}

Termination events of thiol-ene photopolymerizations occur when any coupling events of radical species fails to generate a new radical capable of proton abstraction such as coupling of two carbon centered radials, two thiyl radicals or a thiyl radical with a carbon centered radical occurs. The small percent (0.1-1wt%) of photoinitiator serves to enhance the generation of radical species at the beginning of the polymerization thereby increasing the rate of the reaction and diminishing the need for specialized lasers or lamps.
Figure 4. Accepted Mechanism of the Addition of Thiols to Alkenes via UV Polymerization.

Though it is possible for the radical addition reaction to proceed upon UV light irradiation in the absence of a photoinitiator, developmental gains afforded in photoinitiators makes the UV radial polymerizations of thiols with alkenes an even more attractive synthetic technique. Past concerns with toxicity and photoactive by-products within the final network marked this process commercially impractical. Benzophenone, a once popular commercial photosensitizer for coatings formulations, in particular, is reputable for yellowing behavior, plastizer effects and photoactivity observed in films including thiol-ene films. Alternatively, dimethoxyphenyl acetophenone (DMPA), a cleavage-type photoinitiator is an excellent choice as a photosensitizer for initiation of thiol-ene polymerizations. Unlike benzophenone, a rearrangement of a carbon radical prevents residual photoactive species films.

Overall, the radical addition of a thiol to an alkene monomer is a two-step process which consists of a proton abstraction step and radical transfer step which proceeds under mild conditions with rapid kinetics, high yields and little to no byproducts. The battery
of thiol and vinyl monomers capable of reacting without solvent is certainly plentiful. Careful selection of monomers and incorporation of small amounts of photoinitiators can ensure reactions will proceed smoothly and rapidly, meeting “click” reaction standards.

**Thiol-Isocyanate “Click” Reaction**

Polymerization reactions involving thiols with isocyanates have been documented since the 1960s when Dyer and coworkers synthesized linear polymers from solution. In this instance tertiary amine catalysts were utilized to produce polymers with yields ranging between 10 and 87 percent. From this initial investigation, it was determined that melting points of thiolcarbamate polymer or thiourethanes were higher than polymers made from alcohols of similar structure, they were more insoluble and tended to yellow in the light and with hot solvents. More so, in recent times, this reaction has been utilized to synthesize polymer without solvent or catalyst. These advancements of this new and facile synthetic method have sparked interest to synthesize or manipulate material and have been exploited across a variety of fields.

More specifically, the orthagonality of thiol click reactions by site-specific catalyst has been reported in the literature. The thiol-isocyanate click reaction was allowed to proceed in an initial reaction to form thiol terminated pre polymers followed by the previously described UV polymerization of those thiols to alkenes. In other words, since the first reaction is base catalyzed (thiolate-based) and the other is a UV catalyzed (thiyl-based) then the thiol isocyanate addition reaction can proceed independently and separately from the thiol alkene reaction. The reaction of a thiol to an isocyanate is without a doubt a highly efficient and robust reaction commonly used in molecular
synthesis and specifically polymer synthesis due to rapid kinetics and predictability of the final compound and absence of side products.\textsuperscript{13}

As mentioned before the bond energy of a sulfur hydrogen bond is less than an oxygen hydrogen bond. The weaker bond strength translates to lower \( pK_a \) values (higher acid character) of thiols. Protons are then readily abstractable by base catalyst. The accepted reaction mechanism is shown below in Figure 5. Thiols are readily turned to activated nucleophiles by tertiary amine catalysts such as TEA or DABCO. The thiol nucleophile is regenerated in the last step when the negatively charged amine adjacent to the carbonyl group abstracts a proton from a second thiol molecule. This is similar to the two step radical addition reaction for thiol-ene click reaction. The nature of the thiol bond accounts for the fact that this reaction proceeds cleanly and rapidly even in the presence of other protic species such as water and alcohols.

![Proposed Mechanism for Tertiary Amine Catalyzed Thiol Isocyanate “Click” Reaction.](image)

One advantage regarding thiourethane linkages in polymer networks is the enhancement of thermal stability. As previously stated, thio-ene “click” reactions are responsible for networks containing thioether linkages predominately. Ether linkages are flexible while the thiocarbamate or thiourethane linkages are more rigid due to \( sp^2 \)
hybridization and hydrogen bonding. The interactions between these sp² hybridized regions generate increase intermolecular interactions can be beneficial if incorporated into TENs. In some instances monomers containing thiourethane linkages in the monomer backbone structure have been developed to enhance TENs.⁴¹,⁴² Thiourethanes have been incorporated into TENs by way of prepolymer, monomer and sequential synthesis methods to enhance the mechanical properties of what would have been highly flexible, brittle and low toughness networks.

Thiol-Ene Networks (TENs)

TENs are produced when the total number of functional groups of thiol and vinyl monomers in the system is greater than 4 (f > 4). These multifunctional thiol and alkene monomers generate a three dimensional polymer network. There is a toolbox of available commercial multifunctional thiol and alkene multifunctional monomers being used to develop a broad array of networks with an equally diverse set of thermal and mechanical properties (see Figure 6).

One of the major distinctions of TENs from other networks is the chain/step polymerization mechanism. Unlike other polymer networks, thiol-ene networks are produced from chemistries that can proceed to quantitative conversions within a matter of seconds to yield networks with very unique properties. TENs are ideal model systems that demonstrate unique network properties including; high uniform cross-link density, narrow glass transition temperatures and high tanδ values. TENs are low stress (low shrinkage) networks that can be synthesized in air (oxygen) with little to no effect on the reaction kinetics and final network properties. TENs are also optically superior (high refractive index) due to their high sulfur content.⁹,¹³,⁴³
Figure 6. Examples of Multifunctional Thiol and Alkene Monomers.

The high network uniformity of TENs originates in the unique reaction mechanism. The effects of the rate of molecular weight build-up during network formation during can be easily explained by some common examples. Matrix materials for aerospace composites are synthesized by reacting multifunctional epoxies with multifunctional amines monomers. Reactions between epoxies and amines are typically carried out in two steps instead of one. The second step involves both high temperature and pressure to drive the reaction to an appreciable conversion whereby matrix properties will be up to aerospace standards. This is a highly energy inefficient process. Another example is the radical polymerization of multifunctional acrylate monomers. The resulting glassy networks can have glass transition temperatures that can span over 100 degrees. The shear breadth of the glass transition region is an indication of the inhomogeneity of the network at the microscopic level. In fact most networks are not perfect. They exhibit flaws such as dangling ends, loops and even linear polymer that
managed to escape the cross-linking process called the sol fraction.\(^5\) In TENs the step-growth character of the reaction mechanism translates to delayed molecular weight build up.\(^4^4\) Because gelation is delayed, TENs are highly uniform and reach high conversions without extraneous post polymerization annealing processes.

Although a variety of commercial thiol and alkene monomers exist, their monomer functionalities are not typically greater than 4. Monomers are also limited with respect to functional group incorporation. For instance thiol monomers are typically of the mercaptoacetate, mercaptopropionate or alkane thiol type. Structural features known to add mechanical strength typically require scientists to synthesize a new monomer prior to polymerization. The same is true for alkene monomers although there are a few monomers containing ringed structures that are readily available such as that found in TATAT (Figure 6). The limitation of monomer availability is a real concern for scientists and new solutions to this problem are being developed at rapid rates.

Scientists are approaching this problem from a variety of ways. Some of the first approaches appear to be incorporating acrylates, urethanes and epoxies. In 1978 Ketley and coworkers noted that thiol ene monomers could be copolymerized with acrylate monomers to achieve synergistic materials with little effect on the polymerization kinetics.\(^4^5\) Additionally, Hoyle and coworkers further found that the broad glass transition region of acrylates became more narrow when thiol/alkene monomers were copolymerized with acrylates even though the acrylates homopolymerize and form acrylate rich sections within the networks.\(^3^0, 4^6, 4^7\) Cramer and coworkers have made strides toward using similar systems as dental restorative materials.\(^4^8, 4^9\) Other methods include the synthesis of novel monomers such as those based around norbornene and
benzoxazine,\textsuperscript{50, 51} while other researchers are utilizing a third component to generate hybrid networks wherein the third component generally contains some molecular feature reputable for creating tougher or higher Tg polymers.\textsuperscript{40, 50-52}

While acrylates and cyclic monomers help increase the glass transition temperature, they do not necessarily enhance the toughness of TENs. Polyurethanes are used in a multitude of applications that require robust materials. The combination of toughness and tunability of these types of materials are beneficial for a variety of reasons. Isocyanate components add a degree of rigidity and hydrogen bonding to the network while the polyol component contributes flexibility. This generates hard and soft segments within the polymer morphology which mimics elastomers in mechanical response. Urethanes or thiourethanes (product of thiol/isocyanate reaction) have been incorporated into TENs in efforts to enhance the toughness.\textsuperscript{42} Other efforts include simultaneous and sequential polymerization of thiol-ene-isocyanate mixtures and synthesis of thiol terminated thiourethane oligomers and sequential UV polymerization to achieve similar results.\textsuperscript{39, 41}

\textit{Impact Properties of Polymers and TENs}

Lastly, thick TENs have superior energy absorption capabilities compared to other network systems especially when the testing temperature overlaps the glass transition region, T\textsubscript{g}. Maximum viscoelastic damping behavior of polymer materials occurs at the polymer glass transition temperature or when the ratio of E” to E’ is maximal. The T\textsubscript{g}, which marks the onset of long range segmental motion and plays an important role in energy dissipation. The transfer of kinetic energy of an object to motions of polymer chains forms the foundation of energy dissipation in a bulk polymer
material. The kinetic energy from an impact is converted to heat energy during viscoelastic damping and therefore the energy which passes through a damping material should be minimal. Nondestructive energy absorb energy is highly ideal in many circumstances because using a new damping device with each impact event is economically unfavorable. TENs are great candidates for this type of material as it has been proven that thick TENs can be polymerized by simplistic under mild condition such as ambient condition having low energy requirements.\textsuperscript{11}

It has been proposed that TENs are an excellent candidate for mouthguards because of the simplistic synthesis and damping properties prospectively decreasing the incidence of injury to the orofacial complex. Because they are highly uniform networks that are essentially defect free, it is proposed that energy transfer throughout the material would be highly efficient.\textsuperscript{9} Additionally, these crosslinked networks are capable of deformations greater than other highly crosslinked networks meaning they can absorb unprecedented amounts of energy respectfully. To that regard some initial studies have been conducted to investigate the impact properties of modified TENs.

TENs formed from a series of thiourethane-based alkene monomers have been examined for their thermal, thermomechanical and most importantly, impact properties.\textsuperscript{42} Impact properties were measured using a modified ASTM setup for pendulum impact and 1.13J of energy. This setup was also utilized in this dissertation and will be discussed in greater detail in a later section. A reactive allyl ether diluent, diallyl ether (DAE) was used to both decrease viscosity of mixtures and tune the glass transition temperature to lower values. The energy absorption of some neat networks and those with reactive diluents were between 74\% and 91\%. As the glass transition temperatures were
decreased to values closer to room temperature there was a general increase in energy absorption. Between systems the impact properties were similar. The maximum energy absorption was around room temperature with maximum energy absorption being approximately 90% of 1.13 Joules.

In a separate study, Senyurt and coworkers investigated the impact properties of thiol/ene/acrylate systems. Acrylates, when copolymerized with thiol ene monomers, benefit from reaction parameters associated with thiol ene photopolymerizations. For instance, oxygen inhibition is reduced and networks become more but are not as uniform as pure TENs. Impact properties of several ternary thiol/ene/acrylate networks were investigated using the same pendulum impact test mentioned earlier. While some of the acrylates were capable of effectively tuning the glass transition temperature, others only changed it slightly. For those with glass transition temperatures near room temperature a significant improvement in energy absorption was absorbed. The maximum attainable impact value for systems reported in this study was 91% of 1.13J. For networks that did not have near room temperature or room temperature glass transition temperatures, the energy absorption was significantly less. Some of the networks reportedly shattered upon impact as well. In general the impact properties of thick thermoset thiol/enes have only been investigated to a small extent for systems containing a third component such as acrylates and urethanes. Investigations to gain a better understanding of this aspect of thick thiol-ene thermosets were undertaken in this dissertation.

Scope of Dissertation

Throughout the chapters in this dissertation, several aspects of TENs are explored including thermal, themomechanical response, physical characteristics of bulk material
and impact properties. In Chapter II we discuss an initial investigation of novel TENs based on acrylate and urethane based monomers with respect to their properties relative to common mouthguard material, ethylene vinyl acetate copolymer, EVA. In Chapter III we describe the synthesis of ternary TENs utilizing a one pot technique to make TENs with novel network architecture. Sequential curing of thiols with isocyanates and alkenes was conducted utilizing two catalysts in two separate steps. The focus was placed on the modifications of thermal and mechanical properties of TENs. In Chapter IV the focus is shifted toward gaining a better understanding of energy absorption and energy management by TENs. The TENs for this investigation were synthesized from commercial monomers. Energy absorption is explained by measured material properties such as T_g, monomer structure and molecular weight between cross-links. Also we have investigated the frequency dependence of T_g and calculated heat dissipation for one specific system at 38 °C at the different frequencies. In Chapter V we focus on the tunability of the glass transition temperature of TENs by way of a third thiol component. The significance of this investigation is to develop a simple and predictable method by which to tune peak impact performance. Chapter VI describes continuous and novel procedures to increase the glass transition temperate and toughness of TENs. Here we chose alcohol/isocyanate or thiol/isocyanate reactions to achieve the respective goal. Urethane or thiourethane linkages have been strategically placed along the side chains and the backbone of the polymer network. We discuss issues typical of such monomers as well in this section. Lastly, Chapter VII provides insight toward potential future investigations of thiol-ene networks taking into consideration the findings of the aforementioned studies.
Synthetic efficiency alongside ideal network properties make TENs highly ideal systems to investigate in a research setting. The UV polymerization of thiol monomers with electron rich terminal alkene groups is proven to be highly versatile and has been carried out under a variety of conditions throughout this dissertation. The thiol-ene and thiol-isocyanate “click” reactions have been utilized to create nearly perfect three dimensional networks which demonstrate high uniformity and the potential to absorb mechanical energy efficiently at temperatures corresponding to the glass transition temperature. Poor mechanical properties and common subzero glass transition temperatures are a few drawbacks of thiol ene polymerizations from commercial monomers and are addressed within the chapters of this dissertation. Additionally insight into impact behaviors is addressed for native TENs. Superior properties of TENs such few dangling chain ends and loops demand their utilization in future investigations toward novel materials.
CHAPTER II
CHARACTERIZATION OF MOUTHGUARD MATERIALS:
A COMPARISON OF A COMMERCIAL MATERIAL
TO A NOVEL THIOL-ENE FAMILY

Abstract

The goal of this study is to compare the thermal and mechanical properties of a commercial mouthguard material with a novel class of thermoset polymers based on thiol-ene ‘click’ chemistry. Thiol-ene systems UMTEN and AMTEN were synthesized and their properties compared with commercially available Polyshok™. Durometer hardness (ASTM D2240-05), water absorption (ASTM D570-98 (2005)), tear strength (ASTM D624-00), and impact attenuation (ASTM D6110-06f (modified)) were measured for physical property comparison. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used as a means to compare thermal properties. One-way ANOVA and independent t-tests were used to test for differences between Polyshok™, AMTEN and UMTEN samples. It was found that the novel thiol-ene networks exhibit higher impact attenuation at intraoral temperature compared with Polyshok™, although Polyshok™ demonstrates lower water absorption and hardness, as well as higher tear strength. With further modification, this family of thiol-ene materials may provide a platform for developing next-generation mouthguard materials.

Introduction

The use of mouthguards in sports has been shown to provide a protective effect against injury to the orofacial complex decreasing the likelihood of injury between 1.6 to 1.9 times in users compared to nonusers. Although this is a compelling statistic, the
majority of commercially available mouthguards are composed of some variation of ethylene vinyl acetate (EVA), a thermoplastic polymer known to have mechanical and thermal property limitations.\textsuperscript{68, 69} The most notable of these is an impact resistance that falls below the threshold set by the American National Standards Institute (ANSI) or Standards Australia International (SAI).\textsuperscript{68-71} In order to overcome limitations of commercially available EVA researchers have focused their efforts either on identification of possible improvements within existing materials systems by new design or the creation of novel systems that can alternatively meet safety standards such as those containing hard laminate inserts, air inclusions and even new material choices including photocurable materials.\textsuperscript{54, 72-78}

The current ASTM standard for mouthguards categorizes these devices by material type (Type I: thermoplastic; Type II: thermosetting) and by fabrication class (Class I: vacuum-formed; Class II: mouth-formed).\textsuperscript{79} Thermoplastic polymers can be highly deformable, which aids in energy absorption but over long periods of time these materials can become thinner. Pressure from teeth clenching and repetitive impacts will eventually compromise the protective ability of a mouth protector leading to inadequate levels of protection which is a common phenomena among many users.\textsuperscript{62, 80} Unlike thermoplastics, polymer chains of thermosets are interconnected by chemical bonds therefore generally shape is permanent and even if deformation occurs the material will return to its original shape in most instances. Cross-linked materials like butyl rubber (car tires), epoxies and foams are common thermosets that have resilient and highly variable properties which can be controlled by various factors such as starting material structure, molecular weight between cross-links, curing conditions and cross-link density lending
them to be highly elastic and pliable or rigid and stiff. To date, no known published research exists that investigates the potential thermosetting materials may have as a mouthguard material. Moreover, no commercially available thermosetting materials are known to be used in either the off-the-shelf or custom mouthguard markets. Due to published accounts of thermosets that suitably management impact energy\textsuperscript{42, 47, 81}, our intent is to explore novel synthesized thermosetting material systems manufactured via simple and efficient techniques.

One class of novel thermoset systems suitable for such an application is thiol-ene networks (TENs).\textsuperscript{9, 48} Thiol-ene networks are readily formed from a specified “click” reaction between a thiol functional group and an ene or vinyl functional group. This reaction is one among a minuscule list of reactions meeting the qualifications of “click” categorization based on high reaction efficiency, versatility and non-reactivity with atmospheric water and oxygen.\textsuperscript{13-15, 26, 29, 43, 82} Thiol-ene coupling reactions (TECRs) begin with UV irradiation to generate thiol radicals which subsequently add across vinyl groups producing carbon-centered radicals. In traditional chain polymerization, these carbon radicals would add across other vinyl groups, but in thiol-ene polymerization these radicals abstract hydrogen from other thiol groups, restarting the cycle again of a rather unique chain-transfer step-growth polymerization (Figure 7). The resulting bonds from such reactions are flexible anti-Markovnikov thioether linkages that are interconnected when choice starting materials are multifunctional.\textsuperscript{9, 13, 14} Amazingly this entire process approaches quantitative conversions within a matter of seconds to yield networks that are highly uniform, low-stress, optically advantageous, have minimal
chain-ends and most importantly high mechanical energy damping capabilities.\textsuperscript{9, 13, 14, 43, 83}

1. Initiation

\[ \text{Photoinitiator} \rightarrow \text{I}^* \]

\[ \text{R-S-H} \rightarrow \text{I.} \rightarrow \text{R-S}^* \]

2. Addition

\[ \text{R-S}^* \rightarrow \text{R-R'} \rightarrow \text{R-S}^* \rightarrow \text{R-R'} \]

3. Chain Transfer

\[ \text{R-S} \rightarrow \text{R-R'} \rightarrow \text{R-S} \rightarrow \text{R-H} \]

\textit{Figure 7.} Schematic Representation of a Typical Photoinitiator-Induced Thiol-Ene Polymerization.

In an effort to not only further abate dental injury but also broaden the scope of available end-use mouthguard materials which potentially improve upon the current functional capabilities of thermoformed EVA, we explore a thermoset type material that is known to possess high energy dampening capacities and glass transition temperature (temperature where maximum damping occurs) approaching intraoral temperatures (i.e., $37^\circ$C). As such, the purpose of this study was to synthesize two formulations of novel TENs and compare their physical, mechanical and thermal characterizations to a representative commercial, EVA-based, mouthguard material, Polyshok\textsuperscript{TM}.

**Materials and Methods**

*Commercial mouthguard material.* Polyshok\textsuperscript{TM} (Dentsply Raintree Essix, Sarasota, FL, USA) is a popular commercially available ethylene vinyl acetate (EVA)
thermoplastic material used for custom mouthguard fabrication. Polyshok™ has slightly superior properties compared with similar EVA commercial materials and thus best represents this family of materials as a comparison baseline for this study. All tests on this material were conducted on a single batch of material from the manufacturer.

Experimental mouthguard materials. Thiol-ene mouthguard materials were synthesized from several monomers listed below (Figure 8). Trimethylolpropane diallyl ether 90 (TMPDE90), isophorone diisocyanate (IPDI), dibutyltin dilaurate, allyl pentaerythritol (APE) and trimethylolpropane tris (3-mercaptopropionate) (Trithiol) were purchased from Sigma Aldrich. Dimethoxy-2-phenylacetophenone (DMPA) was received from Ciba Specialty Chemicals. Propoxylated glycerol tricarylate (PGTA) was obtained from Sartomer. All chemicals were used as received from the manufacturer.

Synthesis of urethane modified thiol-ene network (UMTEN). Synthesis and monomer characterization were performed according to previous published methods. UMTEN was synthesized in two parts. The first reaction was synthesis of a tetra-functional ene via the nucleophilic addition of an alcohol to an isocyanate, reacting a 2:1 mixture of TMPDE90 and IPDI. First 0.1 wt% (of the total weight) dibutyltin dilaurate was added to TMPDE90 under a nitrogen purge and mixing, While the temperature of the first mixture was lowered to 0 °C via ice bath, IPDI was added slowly from a second container, also under nitrogen purge, over a 30 minute period. The slow addition of IPDI prevents heat build-up and side reactions, however, after this period, the reaction temperature was slowly increased to 55 °C and continued stirring for 24 hours under inert atmosphere (N₂) to afford a tetrafunctional ene whereby urethane groups have been
incorporated into the backbone (Figure 8a). The reaction product was verified via nuclear magnetic resonance (NMR) technique.

In the second reaction, an efficient photo-initiated TECR proceeded between a trifunctional thiol and tetrafunctional urethane-modified ene (Figure 8a). UMTEN was then synthesized by reacting (A) with Trithiol in stoichiometrically equivalent amounts, based on functional groups of thiol and ene, utilizing a highly efficient photo initiated thiol-ene reaction. The photoinitiator, DMPA was initially dissolved in the thiol component, prior to mixing in the ene component (A). Thin (0.5 mm) and thick (4-6 mm) films were synthesized utilizing 1 wt % and 0.02 wt % of UV initiator DMPA. All samples were cured using a 9 mW/cm² (λ = 354 nm) light source for 30 minutes.

*Synthesis of acrylate modified thiol-ene network (AMTEN).* Methods similar to those previously published were used for making ternary thiol-ene/acrylate networks⁴⁷ Stoichiometrically equivalent ratios of Trithiol and APE were used while an additional 50 mol % (based on functional groups) of PGTA was added to the system. DMPA was first dissolved into Trithiol followed by addition of APE. The addition of the PGTA followed directly after blending the thiol-ene-catalyst system (Figure 8b). Complete mixing of all materials was achieved by mechanical stirring. Again, to make thin films (0.5 mm), 1 wt % of DMPA was utilized. A lower percentage (0.02 wt %) of DMPA was added to make thick (4-6 mm) thermoset samples. All samples were cured using a 9 mW/cm² (λ = 354 nm) light source for 30 minutes. Intermittent light was used for AMTEN network synthesis to minimize heat build-up from the highly exothermic acrylate reaction.
Figure 8. Schematic representation of chemical reactions leading to (a) UMTEN and (b) AMTEN. UMTEN is formed from an alkene monomer containing urethane groups and the network synthesized with this monomer consequently contains urethane linkages in the backbone. AMTEN is the acrylate-containing thiol-ene network. Total mole % of acrylate functional groups in AMTEN is 50%.

Thermal analysis of materials. The glass transition, melting, and crystallization temperatures were obtained using differential scanning calorimetry (DSC, TA Instruments Q200, New Castle, DE) calibrated against an indium standard using an N\textsubscript{2} purge (50 mL/min). Standard aluminum pans and specimens having mass of 8.0mg ± 1mg were used to create effective heat flow within the chamber and good contact with the pan bottom. Each specimen was initially cooled to -70°C and allowed to equilibrate for 10 minutes. Following initial cooling, the specimens were heated at a rate of 10°C/min to 150°C and annealed for 10 minutes to erase the thermal history. The specimens were then cooled at 10°C/min to -70°C and reheated to 150°C. Glass
transition values (taken via the inflection point method) were calculated from the second heating curve, while crystallization temperatures were taken from the cooling curve. This process was repeated on a total of 15 samples (3 materials x 5 replicates) and all relevant thermal values were averaged.

Storage modulus, loss modulus, and tan delta values were obtained by dynamic mechanical thermal analysis (DMA, Rheometric Scientific MK V, New Castle, DE). Instrument calibration was performed before testing as per the manufacturer’s instructions for both force and temperature. Measurements were conducted in the vertical tension mode on samples with dimensions of ca. 10 mm x 5 mm x 0.50 mm (L x W x T). The samples were cooled to -50°C and then heated at 5°C/min under a sinusoidal strain of frequency 1 Hz with 0.05% strain up to a final temperature of 150°C. This process was repeated on a total of 15 samples (3 materials x 5 replicates) and the glass transition, loss modulus, storage modulus, and tan δ values were averaged.

*Physical and mechanical analysis methods.* Shore A Hardness was used as the standardized test for comparison of novel thiol-ene materials to commercially available Polyshok™. The durometer hardness was measured according to ASTM guideline D2240-05 to measure the resistance toward indentation. The calibrated device is composed of a spring-based scale (0 to 100) on an indenter having a tip with dimensions (Tip = 0.031 ± 0.001mm; Taper = 35° ± 0.25° and Shaft=1.40 ± 0.005mm). All tested materials were at least 12mm in length, and 6mm thick. A thickness of 6mm was achieved by plying two 3mm sheets. Shore A hardness was measured at five locations per sample by carefully placing the indenter on the material without shock, followed by a firm press into the sample while on a solid, horizontal surface. The indenter was held for
one second and the highest reading was recorded at both room temperature 23 °C ± 2 °C (73.4 ± 3.6 °F) and intra-oral temperature 37±2 °C (98.6 ± 3.6 °F).

Water absorption was measured for all samples according to ASTM guideline D570-98. From this test, the percent mass increase due to absorption of water and rate of absorption can be determined. In previous water absorption studies of commercial materials, the 24 h procedure in combination with repeated 24 h immersion test (section 7.3) was utilized for a total of 9 hrs or 3 days. In this study, this same procedure was used for thiol-ene samples but for a significantly longer time period, approximately 20 days. This time allowed the desired test endpoint requirements to be achieved. Samples were molded into discs of diameter 50.8 mm and thickness 3.2 ± 0.3mm. The discs were conditioned for 24 hours in an oven and cooled in a desiccator prior to the first weighing. The samples were weighed to the nearest 0.001 gram to determine conditioned weight and placed upright in distilled water at the appropriate temperature. The TENs, AMTEN and UMTEN, were weighed every 24 hours until the weight increase remained unchanged (to 0.001 g) for two consecutive days. Five samples of each type were tested at room temperature 23°C ± 2 °C (73.4 ± 3.6 °F) and a separate set of five were tested at intra-oral temperature 37 ± 2 °C (98.6 ± 3.6 °F). Percent weight increase was calculated and reported according to equation 1 and reported to the nearest 0.01%.

\[
\text{% increase} = \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100\%
\]  

[1]

*Tear strength methods.* Failure of a mouthguard due to a tear is highly likely. Sharp edges of teeth may cause minor voids or imperfections to spread, progressing to a
larger area of material, eventually leading to equipment failure. ASTM test procedure D624-00 (die shape C) was used to determine tear strength, of novel thiol-ene materials. This ASTM test calls for measuring the tear strength of conventional vulcanized rubber and thermoplastic elastomers. While this test is appropriate for commercial EVA, thermoset materials are not a conventional material. This test, however, provides us with a method for direct comparison with previously published data on commercial materials. The tear strength is calculated by equation 2 where $F$ is the average maximum force required to propagate the tear, and $d$ is the sample thickness.

$$ T_s = \frac{F}{d} $$

Sample thickness was recorded as an average of three measurements, one taken directly and the notch and the others slightly left and right. A universal material testing machine (Model 3300 Instron, Norwood, MA, USA) was calibrated prior to the study and used to determine tear strength. Samples were placed consistently and deeply into the grip to lessen the chance of slippage. The test grips were separated at a rate of 500 ± 50 mm/min for five separate samples. Higher temperature 37°C ± 2 °C, was achieved by water bath equilibration.

Impact testing methods. The method used to measure impact absorption energy was a modified ASTM test for determination of impact resistance of notched specimens, ASTM D 6110. The full modification description is consistent with previously published literature, and readers are directed to reference 49 for a more thorough explanation. A pendulum style apparatus was used to measure impact absorption energy. A pendulum of known weight was set to a height corresponding to 1.13 J. Upon release, the pendulum swings and strikes the sample normal to the surface with a standard radius
Charpy style tup. Care was taken to ensure material energy dissipated by material flexion was negligible by layering two, 4 mm thick bars and mounting them to a steel plate. A total thickness of 8 mm further helps ensure minimal influence of the steel plate on the impact measurement.

**Statistical analysis.** Values from each sample set were analyzed using the Statistical Package for Social Sciences (SPSS) v. 16.0, SPSS Inc., Chicago, IL). Values in the tables are representative of the mean and the standard deviation. The independent variables for this study were temperature (23 °C and 37 °C) and material (Polyshok™, AMTEN, and UMTEN). The dependent variables of interest include mean Shore A hardness, water absorption, tear strength, and impact resistance values for the mechanical variables. For the DSC and DMA thermal measurements, the dependent variables include mean glass transition temperatures and tan δ at 37 °C (only for DMA). Several 2 (temperature) X 3 (material) factorial ANOVAs were conducted to test for differences between the materials on the mean mechanical and thermal properties of interest. In order to determine if the glass transition temperatures of the materials could be considered statistically different from intra-oral temperature, series one-sample t-tests were conducted. Due to the number of one-sample t-tests performed, the Bonferroni correction factor was applied to the type I error rate and set a priori at $p = 0.008 \ (0.05/6)$.  

**Results**

**DSC**

Figure 9 shows the thermograms from the first heating scan of the three tested materials. Heating from an initial temperature of -70 °C to 150 °C, glass transitions ($T_g$s) are present for all three systems. Polyshok™ has the lowest $T_g$ (-28 °C) of all systems.
The $T_g$s for UMTEN and AMTEM were comparable with one another (13 °C.) There was also evidence of trace post $T_g$ activity within all the samples. Three endothermic peaks are present in the Polyshok™ samples at approximately 44 °C, 73 °C and 95 °C, indicated melting of crystalline domains or similar processes. UMTEN and AMTEN also exhibited subtle post $T_g$ activity as evidenced by a very broad, low intensity, endothermic peak having a maximum around 100 °C.

Upon the second heating cycle it becomes apparent that the network morphology of UMTEN and AMTEN was affected by the first annealing step. The average glass transition temperature increased 6 °C for UMTEN, and 7 °C for AMTEN systems. In contrast, the $T_g$ of Polyshok™ was shifted lower, to -31 °C. The width of the glass transition region varied between samples. Qualitatively, the transition region for Polyshok™ samples was very broad. UMTEN had a very narrow transition region of about 9 °C, typical of a thiol-ene network. AMTEN had a broader transition region (ca. 20 °C) compared with UMTEN, but still much lower than Polyshok™. A statistical difference ($F_{2,12} = 10119.64, p < .05$) in mean glass transition temperature as measured by DSC was noted between the materials. A Tukey HSD post hoc test revealed two homogeneous subsets with Polyshok™ as sole membership in one group and AMTEN and UMTEN as members of the second group. The one-sample $t$-test revealed that the glass transition temperature of all of the samples tested were statistically different from intra-oral temperature ($p < 0.008$). Mean and standard deviations for DSC measurements of $T_g$ for all samples upon both first and second heating are presented in Table 1.
Figure 9. DSC first heating scans of commercial EVA (Polyshock), AMTEN, and UMTEN materials heated at a rate of 10°/min. Glass transition temperatures are indicated by the vertical black line and crystallization by an arrow.

**DMA**

Using DMA, several thermomechanical characteristics (i.e.: storage modulus (E’), loss modulus (E”)) and tan δ) were obtained as a function of temperature (Figure 10). At 37 °C (intraoral temperature) the storage moduli of UMTEN and AMTEN were on average 110 MPa and 213 MPa, respectively. In contrast, Polyshok™ had a significantly lower storage modulus (20 MPa) at the same temperature. A decrease in storage modulus observed for Polyshok™ around –40 °C indicates an earlier onset of the glass transition. UMTEN and AMTEN maintained high moduli until a much higher temperature (ca. 20 °C), corresponding to a later onset of T_g.

In a DMA experiment, the maximum value of the tan δ vs. temperature curve is indicative of T_g. Subsequently, as local segmental motion increases, there is a concomitant mechanical loss. In addition, when the tan δ value is highest, materials
exhibit maximum damping properties and the loss modulus vs. temperature curve will exhibit a peak corresponding to this transition. Upon heating AMTEN and UMTEN, the maximum in the tan δ vs. temperature occurred at approximately 38 °C for both samples. These values were confirmed by peaks in the E'' vs. temperature graphs for both materials. The value of tan δ at the maximum temperature for AMTEN and UMTEN were 0.53 and 1.0, respectively, indicative of a high mechanical loss and energy dissipation. In contrast, Polyshok™ samples showed only a maximum tanδ value of 0.31 at a much lower temperature (-9 °C) according to a previous study.68 The full width at half-max (FWHM) of the AMTEN and UMTEN tan δ vs. temperature curves coincide with DSC results for the width of the transition region mentioned above (Table 1).

A statistical difference (F_{2,12} = 3911.13, p < .05) in mean glass transition temperature as measured by DMA was noted between the materials. A Tukey HSD post hoc test revealed two homogeneous subsets with Polyshok™ as sole membership in one group and AMTEN and UMTEN as members of the second group. Another statistical difference between materials was noted for tan δ at 37 °C (F_{2,12} = 784.38, p < .05) with the same group membership previously noted. The one-sample t-test revealed that the glass transition temperature of the Polyshok™ sample was statistically different from intra-oral temperature (p < 0.008), but not the AMTEN and UMTEN samples. Mean and standard deviations for DMA measurements of T_g for all samples upon both first and second heating are presented in Table 1.
Figure 10. DMA scan plots from tests conducted at a 5°C/min heating rate at 1Hz with 0.05% strain. (a) the storage modulus ($E'$) plot of commercial Polyshok™, AMTEN and UMTEN, (b) loss modulus plot of each system and (c) Tan delta plots of three systems with peaks corresponding to glass transition temperatures.
### Table 1

*Thermal Analysis of Materials*

<table>
<thead>
<tr>
<th></th>
<th>$T_g^a$</th>
<th>$E'$ at 37 °C$^b$</th>
<th>$E''$ at 37 °C$^c$</th>
<th>DSC $T_g$ (1st Heating)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyshok™*</td>
<td>9.1 (1.91)</td>
<td>20 (4.02)</td>
<td>1.15 (0.07)</td>
<td>-28.4 (0.33)</td>
</tr>
<tr>
<td>UMTEN</td>
<td>38.07 (0.82)</td>
<td>110.0 (27.1)</td>
<td>111.0 (20.7)</td>
<td>12.8 (0.54)</td>
</tr>
<tr>
<td>AMTEN</td>
<td>37.84 (0.50)</td>
<td>213.2 (23.7)</td>
<td>110.0 (9.71)</td>
<td>13.1 (0.42)</td>
</tr>
<tr>
<td>Polyshok™*</td>
<td>-30.87 (0.83)</td>
<td>0.059 (0.004)</td>
<td>0.31 (0.006)</td>
<td>38.6 (0.85)</td>
</tr>
<tr>
<td>UMTEN</td>
<td>18.99 (0.55)</td>
<td>1.02 (0.066)</td>
<td>1.05 (0.035)</td>
<td>16.2 (0.866)</td>
</tr>
<tr>
<td>AMTEN</td>
<td>19.95 (0.52)</td>
<td>0.524 (0.009)</td>
<td>0.529 (0.008)</td>
<td>26.3 (0.609)</td>
</tr>
</tbody>
</table>

*a Temperature at tan δ maximum.
*b Storage modulus at 37 °C.
*c Loss modulus at 37 °C.
*d Tan δ value at 37 °C.
*e Maximum value of tan δ
*f Full width at half maximum of tan δ.
* Values reported from reference [17]

#### Hardness

Mean hardness values at room and intraoral temperatures are presented in Table 2. At room temperature AMTEN had a Shore A hardness of 80, slightly greater than the industry standard Polyshok™ which is reported to be about 77. UMTEN registered the highest room temperature hardness of the three systems at 85. The hardness for AMTEN and UMTEN declines to 68 and 70, respectively, at intraoral temperature. Polyshok™ follows the same trend, decreasing to approximately 68 (intraoral) from 77 (room temperature.) A statistical interaction ($F_{2,24} = 20.29, p < .05, f = 1.29$) between material and temperature indicated that mean hardness decreased at a greater rate for UMTEN than it did for either AMTEN or Polyshok™ at approximate intra-oral temperature. An additional implication of this interaction is that the three systems (while demonstrating...
statistically different mean room temperature hardness values) demonstrate equivalent mean hardness values at higher temperatures.

Water Absorption Studies

Mean water absorption values at room and intraoral temperatures are presented in Table 2. There was no visible warping, cracking, or change in physical appearance due to water immersion for any of the tested materials during the length of the test. Figure 11 shows percent water absorption vs. time for AMTEN and UMTEN at room and intraoral temperature. All thiol-ene-based systems appear to demonstrate identical behavior overall, characterized by rapid uptake of water within the first five days, a slower increase in mass, and finally reaching a terminal saturation. At room temperature 24 hours after immersion, the percent mass increase for AMTEN and UMTEN was 0.68% and 0.29% respectively. These water absorption values increased over the same time frame at 37 °C to 1.3% and 0.58%, respectively, approximately double the room temperature water uptake. The 96 hour values were 1.27% and 0.53% for AMTEN and UMTEN, respectively, at room temperature and 2.1% and 1.1% at 37 °C. Compared to Polyshok™, the percent water absorption was slightly higher for the modified TENs. At room temperature Polyshok™ has been reported to have water absorption of 0.37-0.46%. These values are higher at intraoral temperature, 0.56-0.58%. A statistical interaction ($F_{2,24} = 43.77$, $p < .05$, $f = 1.91$) between material and temperature indicated that the rate of uptake and maximum percent mass varied between the samples and was accelerated at intraoral temperature. Additionally, this analysis further indicates that the increased rate of water absorption between temperatures is equivocal for UMTEN and Polyshok™ and
higher for AMTEN. Note that none of the samples studied exhibited a significant mass increase (due to water uptake) under any testing conditions.

Figure 11. Water absorption graphs of thiol-ene networks AMTEN and UMTEN at room temperature and 38 °C. Each point is an average of five samples and standard deviations are represented by error bars.

Tear Strength Studies

Mean tear strength and % strain at room and intraoral temperatures are presented in Table 2. At room temperature, the average tensile modulus for AMTEN and UMTEN was 18.3 MPa and 24.4 MPa respectively. These values decreased appreciably at higher
temperatures to 10.7 MPa and 7.43 MPa, respectively, at intraoral temperatures. Tear strength, defined as the ratio of peak load to sample thickness, was 8.35 kN·m$^{-1}$ and 28.1 kN·m$^{-1}$ for AMTEN and UMTEN respectively. At 37 °C ± 2 °C, tear strength values decreased to 3.75 kN·m$^{-1}$ and 11.43 kN·m$^{-1}$ for AMTEN and UMTEN samples. Polyshok has a reported tear strength of 30.4 kN·m$^{-1}$ at room temperature and 21.5 kN·m$^{-1}$ at intraoral temperature. A statistical interaction ($F_{2,24} = 67.75$, $p < .05$, $f = 2.38$) between material and temperature indicated that the rate of mean tear strengths decreased at the elevated temperature for all samples. However, this analysis further indicates that the rate of decrease in tear strength was more profound for UMTEN than for AMTEN or Polyshok$^\text{TM}$. There were slight variations in strain % values for AMTEN at room temperature (4.18 %) compared to intraoral temperature (3.76 %) while UMTEN was essentially unaffected (18.1% vs. 18.5% respectively.) There was no statistical difference in the strain % for UMTEN at room and intraoral temperature.

**Impact Resistance Studies**

Impact resistance properties of these materials were measured by a modification of the ASTM D6110-06f method. Mean percent impact resistance at room and intraoral temperatures are presented in Table 2. At approximately 37°C, the percent impact resistance for AMTEN and UMTEN was 57% and 86% respectively. Polyshok$^\text{TM}$ has the smallest reported value, ca. 42% at 37 °C$^69$. To investigate energy absorption properties of these materials in more detail, percent impact resistance was measured as a function of temperature between 10 °C and 50 °C for UMTEN and between 10 °C to 35 °C for AMTEN for comparison with Polyshok$^\text{TM}$. Figure 12 shows percent impact vs. temperature for UMTEN, AMTEN and Polyshok$^\text{TM}$. In general, a plot of percent impact
versus temperature mimics a plot of tan $\delta$ versus temperature and is consistent with previous literature reports $^{69}$. A statistical interaction ($F_{2,24} = 113.65, p < .05, f = 3.07$) between material and temperature indicated that mean impact resistance increased for Polyshok$^{TM}$ and decreased for AMTEN and UMTEN materials at approximate intra-oral temperature. Additionally, this analysis further indicates that the rate of decrease in impact resistance was more profound for AMTEN than for UMTEN.
### Table 2

*Physical and Mechanical Properties*

<table>
<thead>
<tr>
<th>System</th>
<th>Shore A Hardness&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Water Absorption&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Impact Resistance&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water Absorption 24 hr</td>
<td>Water Absorption 96hr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>% Water Absorption</td>
<td>% Water Absorption</td>
</tr>
<tr>
<td>23 °C ± 2 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyshok&lt;sup&gt;TM&lt;/sup&gt;™</td>
<td>77.2 ± 4.2</td>
<td>0.37 ± 0.001</td>
<td>0.46 ± 0.041</td>
</tr>
<tr>
<td>UMTEN</td>
<td>85 ± 3.3</td>
<td>0.29 ± 0.030</td>
<td>0.53 ± 0.055</td>
</tr>
<tr>
<td>AMTEN</td>
<td>80 ± 1.6</td>
<td>0.68 ± 0.043</td>
<td>1.27 ± 0.067</td>
</tr>
<tr>
<td>37 °C ± 2 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyshok&lt;sup&gt;TM&lt;/sup&gt;™</td>
<td>67.6 ± 0.54</td>
<td>0.56 ± 0.004</td>
<td>0.58 ± 0.019</td>
</tr>
<tr>
<td>UMTEN</td>
<td>69.8 ± 1.5</td>
<td>0.58 ± 0.1</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td>AMTEN</td>
<td>68.2 ± 1.3</td>
<td>1.3 ± 0.2</td>
<td>2.1 ± 0.2</td>
</tr>
</tbody>
</table>

| Tear Strength<sup>c</sup> | Max tear (kN m<sup>-1</sup>) | Max Strain (% length) |                              |
|----------------------------|-------------------------------|-----------------------|                              |
| 23 °C ± 2 °C               |                               |                       |                              |
| Polyshok<sup>TM</sup>™    | 30.4 ± 1.06                   | 161.13 ± 18.85        | 60                            |
| UMTEN                      | 28.11 ± 1.61                  | 18.1 ± 2.3            | 92 ± 0.01                     |
| AMTEN                      | 8.35 ± 0.756                  | 4.18 ± 0.29           | 86 ± 0.004                    |
| 37 °C ± 2 °C               |                               |                       |                              |
| Polyshok<sup>TM</sup>™    | 21.5 ± 0.89                   | 161.43 ± 67.25        | 66                            |
| UMTEN                      | 11.4 ± 1.8                    | 18.5 ± 4.7            | 85 ± 4                        |
| AMTEN                      | 3.75 ± 0.40                   | 3.76 ± 0.92           | 57 ± 5                        |

<sup>a</sup> ASTM D2240-05 standard test method for rubbery property-durometer hardness.
<sup>b</sup> ASTM D570-98 (2005) standard test method for water absorption of plastics.
<sup>d</sup> Modified ASTM D6110-06 standard method for determining the charpy impact resistance of notched specimens of plastics.
<sup>*</sup> Values reported from reference [12]
Discussion

It is the intention of these studies to compare the physical and thermal properties of novel thiol-ene based thermosets with a commercial EVA-based material specific to end-use parameters associated with mouthguard materials. The materials tested in the current study represent two distinct classifications of polymers, thermoplastic (EVA, Polyshok™) and thermosets (AMTEN and UMTEN). Our findings demonstrated similarities and differences between the various classes of materials from a polymer perspective as well as industrial standards for the intended applications. The following discussion will focus on comparing properties of these materials specifically for mouthguard applications.

*Thermal characterization comparison.* DSC thermograms (Figure 9) revealed similarities in the thermal behavior of Polyshok™ to previous literature. In particular,
thermal analysis reveals a relatively low $T_g$ and several endothermic peaks corresponding to melting of crystalline domains, all of which melt below 100 °C. A large percentage of EVA-based mouthguards are formed to fit the mouth by heating in boiling water (i.e.: “boil and bite”); therefore melting of crystalline regions in EVA has proven beneficial with regards to ease of mouthguard fit. This process, however, leads to uncontrolled thinning in several regions, which may lead to less than ideal protection. Our novel TENs lack crystalline regions. During the first heating, there was a broad endothermic transition. This is a common phenomenon for thermoset materials that have not reached full cure. As molecular weight builds during polymerization, chain mobility decreases as viscosity rapidly increases. This can frustrate mobility of uncrosslinked chains causing vitrification. When the system is supplied with heat (as with a DSC experiment) unreacted monomers gain enough energy and mobility to complete the curing reaction. This endotherm is therefore not reversible and is only present upon the first heating; once the system becomes fully cured, there is no additional reaction. As a result, the $T_g$ of the second heating cycle is higher than the first. For all of the materials studied, $T_g$ was below intraoral temperature, although $T_g$ for AMTEN and UMTEN were much closer to 37 °C. As such the $T_g$s, or temperature where a polymer would absorb maximum energy, was measured to be closer to intraoral temperature for AMTEN and UMTEN compared to Polyshok™, which exhibited $T_g$s at subzero temperatures. A higher value of $T_g$ is clearly more ideal for a mouthguard material.

DMA (Figure 10) provides valuable information about the viscoelastic properties of polymer materials as a function of temperature and revealed important structural differences between the materials studied. Because EVA is a thermoplastic material,
polymer chains in Polyshok™ are not chemically bound to one another; rather the crystalline domains act as physical crosslinks and polymer chain entanglements, chain interactions and crystallinity are the dominant source of material properties. If sufficient thermal energy is provided (i.e.: $T > T_g$,) long-range segmental motions of the polymer chains are possible and chains can slip past adjacent chains lending the material deformable. For Polyshok™ this energy is minimal to overcome and is low enough that heat from ones mouth can cause the material to soften, rendering the mouthguard less protective due to thinning. In contrast, covalently cross-linked networks such as in AMTEN and UMTEN exhibit different behaviors because all chains are chemically bound forming one large, single network. The same segmental motions then require more energy and are constrained by chemical connections. Heating a thermoset does not cause chain slippage from local motions, and with further heating the entire network will remain intact until the system degrades.

Damping characteristics of the networks (quantified by tan $\delta$) demonstrated typical behavior for each class of material over a broad range of temperatures. Polyshok™ demonstrates only modest damping (quantified by the amplitude of the tan $\delta$ peak) over the entire temperature range, with a maximum at subzero temperatures. The stiffness ($E'$) decreased rapidly for Polyshok™ at temperatures approaching 0 °C from this tan $\delta$ maximum at -20 °C. This is detrimental for a mouthguard material given that stiffness possibly leads to bridging effects whereby energy concentrated in one area can spread throughout the entire dental bridge. This tan $\delta$ peak is broad and asymmetric, extending toward higher temperatures likely due to the presence of crystalline domains within the system. In contrast, AMTEN and UMTEN have maxima in tan $\delta$ at much
higher temperatures than Polyshok™, with UMTEN exhibiting superior damping properties compared with the other two materials. The former case AMTEN is chemically composed of three monomers; thiol, ene and acrylate. While the ene is only able to react with a thiol, the acrylate can react with thiol as well as with itself. The ability for both homo and cross polymerization means that at least two distinct domains are formed within the network, one soft (thiol-ene rich) and the other hard (acrylate rich.) This biphasic network exhibits one T\textsubscript{g}, potentially because the distinct domains are small (2-3 nm), but the damping capacity suffers due to a discontinuous system. In contrast, UMTEN exhibited superior properties compared with all other systems with regard to the temperature and amplitude of maximum damping. UMTEN is different from AMTEN in that urethane groups are built into the monomer, which may facilitate greater damping character. The sequential reaction of the urethane ene monomer with a thiol, is strictly between thiol and ene functional groups, leading to homogeneous networks with excellent damping character, typical of thiol-ene thermosets. Consistency of the networks leads to high tan \( \delta \)\textsubscript{max} values and consequently favorable damping behavior at intraoral temperatures. As mentioned previously, the temperature where the damping effects are greatest lie much closer to intraoral temperature for AMTEN and UMTEN (38 °C) compared with Polyshok™ (-9 °C), which is a significant property advantage for internal protective equipment.

Physical characterization comparison. The comfort level of the mouthguard material is important for the intended application, as these materials inevitably will contact soft tissues of the mouth such as the cheeks and gums. Shore A hardness of the materials at room and intraoral temperatures were measured and compared. The scale of
the Shore A Hardness ranges from 0 to 100, where 0 is the softest and 100 the hardest. The test is highly subjective and leaves room for significant error between testers. Nonetheless, it was determined that all of the materials tested fell within the range 77 to 85 at room temperature. At intraoral temperatures, the hardness was lower as expected, and the range was much smaller, only a 68 – 70, for all three materials. It was observed that UMTEN softened at a faster rate than AMTEN or Polyshok™. Interestingly, from a comfort standpoint at room temperature there might be a noticeable difference, but inside the mouth all three materials could very well feel the same.

The mouth is a very humid and moist environment, so water uptake is important for the intended application of these materials. ANSI and SAI guidelines call for the water absorption in mouthguard materials to be less than 0.5% by weight. Of the three materials studied, only Polyshok™ was compliant with this value. AMTEN had the highest equilibrium water absorption, measuring about four times the recommended amount (Figure 11). This may be explained chemically due to the fact that the acrylate component consists of ethylene oxide groups that modestly attract water. UMTEN exhibited slightly less water absorption compared with UMTEN, but still had values that are three times the guideline amount. Although at first these results may seem discouraging, two important factors should be considered: (1) The initial rate of water uptake was much slower for AMTEN and UMTEN compared to Polyshok™. For example, thiol-ene materials took ca. 3 days of constant submersion in water to reach 0.5% water absorption. Given that in typical use the mouthguard will not be in constant contact with water for more than a few hours at a time, the increase in equilibrium water absorption will not likely have an impact on end use. (2) Changes in the physical
properties under saturated conditions will likely be less dramatic for networks such as AMTEN and UMTEN compared with thermoplastics such as Polyshok™ and EVA.

Tear strength measurements are meant to mimic contact with the sharp points of teeth that could cause significant damage to the mouthguard over time. The tear strength of UMTEN and Polyshok™ at room temperature were similar, 28 kN·m⁻¹ and 30 kN·m⁻¹ respectively. At higher temperatures all systems show a decrease in tear strength; however the difference in tear strength between Polyshok™ and UMTEN widened to the point that UMTEN was only half as resistant to tear at intraoral temperatures. It is expected that at room temperature and intraoral temperature Polyshok™ is well beyond its Tₛ and is in an equilibrium state, while AMTEN and UMTEN are in a transition region. This means that small fluctuations in temperature can have large effects on tear strength.

Key differences in the tear behavior between thermoplastic vs. thermoset mouthguard materials are exemplified in the strain percent at tear. The strain percent at tear was 161% for Polyshok™ compared with 18% and 4.2% for UMTEN and AMTEN respectively. This result was not totally unexpected, as thermosets characteristically exhibit low strains and brittle failure. Tensile loading, as in a tear strength test of thermoplastics, causes chains to rearrange and align in pulling direction. In cross-linked networks, this rearrangement is not possible and the same load quickly breaks covalent bonds, leading to material failure. Surprisingly, the strain percent at tear for UMTEN is unchanged at higher temperatures. We speculate that the increased urethane content in UMTEN provides a mechanism for additional material reinforcement through hydrogen
bonding. For real applications, a high strain percent at tear is not necessary for mouthguard materials because strains are miniscule during use.

Arguably, the impact absorption energy of a mouthguard material is the most important physical property in terms of the potential end-use applications. Impact energy denotes the amount of energy the material is capable of managing, and it can be measured at various temperatures. Logically, any decrease in the amount of force transmitted through the mouthguard into the substrate (tooth/jaw/skull) is an important factor towards injury prevention. Our findings verify that the thermosets UMTEN and AMTEN absorb much more impact energy than the thermoplastic Polyshok™ material at intraoral temperatures (Figure 12). Ostensibly, greater than 90% of impact energy is absorbed for both TENs close to intraoral temperatures. This result is unmatched by any EVA-based commercial material and is perhaps the most advantageous property of the thiol-ene system.

Conclusions

Urethane-based TENs are highly promising as mouthguard material and have matched or exceeded values obtained by commercial EVA-based mouthguard materials in multiple facets of physical, mechanical, and thermal tests. Thermally, UMTEN demonstrates a $T_g$ around intraoral temperature and, although DSC shows post-curing effects, this is typical of networks and may be resolved by a simple annealing procedure. DMA confirms the findings of DSC and show that the monomer-up design approach leads to thiol-ene behaviors typical of other TENs (i.e., high $\tan \delta_{\text{max}}$ values and narrow glass transition regions).
From a physical testing sense, water absorption for EVA systems is lower than AMTEN and UMTEN networks, but the rate of water uptake is remarkably slowed for the thiol-ene networks and the effects of water on the mechanical behaviors of TENs remains a mystery. UMTEN, AMTEN and Polyshok™, have comparable tear strengths at room temperature, but at intraoral temperature, Polyshok™ excelled. It may be possible to increase the tear strength of such thiol-ene networks using a bottom-up approach consisting of careful monomer selection. In other studies, efforts have been made to incorporate urethane and thiourethane linkages into thiol-ene networks. This could offer tunability of T_g and increased tear strength at all temperatures. UMTEN exhibits excellent impact resistant properties at intraoral temperatures and may be the single system set apart from the others, as this factor has important implications for mouthguard applications. Having more than 90% absorption proximal to intraoral temperature, UMTEN excels in this regard.

Although these results were promising, it is important to continue efforts to optimize these systems. Along with other important thermal and mechanical properties yet to be measured (cyclic loading or hysteresis and in vivo), the fabrication of mouthguards out of thermoset materials necessitates an appropriate manufacturing technique. As 3-D printing technology evolves, an opportunity to meet this manufacturing need via deploying UV curable thermosets is promising. Ultimately, it is of great importance to continue making strides in novel material development and testing to offer the best protection possible. The material-human interface remains an important aspect of the sports world and this study represents only a small part of a very large challenge.
CHAPTER III
SEQUENTIAL THIOL CLICK REATIONS: FORMATION OF TERNARY
THIOURETHANE/THIOL-ENE NETWORKS WITH ENHANCED
THERMAL AND MECHANICAL PROPERTIES

Abstract

Thiol-ene networks (TENs) are becoming increasingly popular across a continuum of research investigations due to their ease of fabrication, i.e. photopolymerizable click reactions and ideal network properties such as high energy damping and network uniformity. Similar to other cross-linked networks, low maximum strain values translate to low toughness; therefore enhancing versatility of TENs means increasing toughness and temperature response of such systems. Ternary thiol-ene-isocyanate networks from glycol di(3-mercaptopropionate), triallyl-1,3,5,-triazine-2,4,6(1H, 3H, 5H)-trione and either HMDI, IPDI or H12MDI were synthesized via a sequential one pot curing technique using two catalysts. The first catalyst TEA was used to facilitate thiol/isocyanate chain extension reactions while the UV catalyst DMPA aided thiol-ene cross-linking photopolymerizations. Systems with formulations of mol percents: SH/C=C/NCO: 100/100/0, 100/90/10, 100/80/20, 100/70/30, 100/60/40, and 100/50/50 were synthesized and investigated using a variety of techniques. FTIR analysis demonstrated the thiol/isocyanate reaction proceeds prior to, and independently from the second thiol/ene photopolymerization reaction, with the sequential reactions yielding at least 90% thiol conversion in a matter of seconds. From DMA data, the rubbery plateau decreased as isocyanate content increased, suggesting decreased cross-link density with increasing isocyanate content. Tgs shifted to notably higher temperatures, especially for
systems with cyclic aliphatic isocyanate monomers, IPDI and H$_{12}$MDI. Despite decreases in cross-link density the Young’s modulus and $T_g$ increased with increasing NCO content for IPDI and H$_{12}$MDI networks. Young’s modulus increased from around 10 MPa in the native matrix to approximately 20 MPa, 600 MPa and 1300 MPa for systems containing 50 mol% HMDI, IPDI and H$_{12}$MDI respectively. Strain at break increased in systems with up to 40 mol% NCO but decreased at 50 mol %. Engineering toughness increased with increasing isocyanate content for IPDI and H$_{12}$MDI based systems, but no noticeable change in toughness was observed for HMDI-based networks. WAXD suggested that highly ordered domains were present in HMDI-based systems which affected mechanical properties. Adding a third component such as an isocyanate in traditional thiol-ene networks can increase Young’s modulus, $T_g$, and toughness without significantly compromising other properties of traditional thiol/ene networks such as rapid kinetics and network uniformity, by way of hydrogen bonding, monomer rigidity and structural effects.

Introduction

The copolymerization of multifunctional thiol and vinyl monomers by ultraviolet light has been accomplished since the 1970s for the creation of original coatings with excellent scratch resistant and high optical clarity. After only a few years in the coatings industry, the development and use of thiol-ene coatings declined, being displaced by less pungent and equally fast curing acrylate monomers. Until recently thiol-ene networks (TENs) have remained grossly understudied, but scientific endeavors for materials from facile and environmentally friendly synthesis has meant TENs are once again gaining prevalence into a wide variety of applications such as optics, biomedical,
surface modification, composites, dental restoratives and high performance protective gear. More specifically thick thermoset thiol-ene networks are being developed and investigated for their potentially high non-destructive energy absorption capabilities, but networks in their native forms are not very useful due to low toughness.

Thiol-ene networks are produced from a very unique polymerization mechanism which is a combination of both step growth and chain growth mechanisms. In the first step of this step-growth radical polymerization, UV irradiation generates thiyl radicals which add across carbon-carbon double bond generating a carbon centered radical as in radical polymerization. In the next step, however, the thiyl radical does not add across a second vinyl monomer, but instead it abstracts a proton from a second thiol monomer, forming anti Markovnikov thioether linkages and generating another thiyl radical. Though seemingly complex, the UV polymerizations of thiols with vinyl monomers are highly efficient and take place with or without catalyst under very mild conditions and in a predictable manner, i.e., orthogonal. In optimal conditions it is not uncommon to reach quantitative conversion within a matter of seconds. These and other specific properties of thiol-ene reactions prompted Sharpless and coworkers to classify the thiol-ene reaction into a category of “click reactions”, setting the stage for a new way of thinking about organic synthesis in that reactions should be selected based on efficiency, simplicity, and selectivity.

As a result of this unique and efficient polymerization mechanism, thiol-ene networks display exceptional physicomechanical properties such as low stress, uniform cross-link density, minimal chain-end presence, good adhesion to a variety of substrates, and high mechanical energy damping properties. For example a two-layer laminate
thiol-ene disc constructed to be a few centimeters thick captured bullets shot from a .22 and .38 caliber without shattering. This unique material behavior could be beneficial in many fields, especially the development of novel materials for personal protective equipment. Like countless other cross-like materials, they exhibit brittle mechanical failure and low toughness.

One essential criterion for the success of thick thiol-ene thermosets is to produce novel materials capable of withstanding larger mechanical stresses. TENs synthesized from off the shelf monomers typically exhibit low glass transition (T_g) temperatures, low strain at break, are brittle in nature, and have low toughness. For most applications, robust materials are highly desirable and high toughness is an attractive property. Researchers have attempted to modify thermal and mechanical properties of thiol/ene networks incorporating a third component such as acrylates or isocyanates. Acrylate networks are cured by UV polymerization, but are known to both homopolymerize and cross-polymerize with thiols in the presence of thiol and ene monomers. One drawback of this technique is that homopolymerization leads to phase separation of networks with some sections being acrylate rich. Nonetheless, the network uniformity is increased compared to the native acrylate network, but compared with the native thiol-ene matrices the glass transition region is broadened due to increased network inhomogeneity.

Other approaches to improve toughness in TEMs involve incorporation of urethane or thiourethane linkages, which have been found to only slightly increase network inhomogeneity, moderately increase T_g and increase toughness from intermolecular hydrogen bonding between donor and acceptor groups. Urethanes or
thiourethanes have been incorporated into thiol/ene networks in one of two ways: (1) synthesizing thiol or ene based monomers with reactive terminal ends followed by polymerization in a two-step process and (2) utilizing one-pot synthetic techniques in which two catalysts are used, one for thiol/isocyanate reaction and a second for UV polymerization reactions.\textsuperscript{39, 41, 42} The former method requires processing high viscosity monomers due to the hydrogen bonding between small molecules while the latter offers substantial synthetic and processing benefits.

The base-catalyzed reaction of thiols with isocyanate are also classified click reactions, and it has been proven that although all monomers are in one reaction vessel, thiol-isocyanate reactions can take place in the presence of and independently of thiol-ene reactions.\textsuperscript{39} Lower pKa values of thiols compared to alcohols increase reaction rates and serve to eliminate byproducts even in the presence of water. In 2010, Shin and coworkers synthesized ternary networks containing a difunctional thiol, trifunctional vinyl and trifunctional isocyanate monomers by sequential and simultaneous polymerization techniques yielding ternary TENs having \textit{T}_g\textit{s} dependent on isocyanate content, as well as increased pendulum hardness, Young’s modulus, peak stress and elongation at break.\textsuperscript{39} In the first step of a sequential polymerization technique the tertiary amine base catalyzed thiol-isocyante reaction (dark reaction) results in a network, and in the second step (light reaction) the difunctional thiol would further crosslink the network; thereby systems demonstrated a combination of either high peak stress and low strain at break values or vice versa essentially limiting the toughness of such systems. In this chapter we present the effects of isocyanate content in select TENs by sequential reactions using a one pot dual catalyst system, but instead using difunntional thiol
monomers and difunctional isocyanates in the initial reaction. This would theoretically mean linear thiol end-capped precursors for sequential thiol-ene UV polymerizations would be formed after the first step. While the isocyanate-thiol reaction proceeds at room temperature under ambient conditions, several minutes later, the second reaction, thiol-ene photopolymerization, was initiated by irradiation with a UV light (Figure 13).

Increased linearity within the TEN morphology, along with increased hydrogen bonding and increased monomer rigidity, could potentially increase toughness of TENs making them a more ideal material choice for a damping components and other applications yet to be recognized. Kinetic, thermal, thermomechanical and mechanical properties of the ternary networks were investigated. The results show that expected changes in material properties occur when linear rigid thiourethane regions are incorporated into TENs.

*Figure 13. Proposed Network Structure of Ternary Thiol, Ene, Isocyanate Networks.*
Experimental

Materials

Isocyanate and ene monomers, hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI), 4,4'-methylenebis(cyclohexyl isocyanate) (H_{12}MDI) and triallyl-1,3,5-triazine-2,4,6(1H, 3H, 5H)-trione (TATAT), were purchased from Sigma Aldrich Chemical Co. along with tertiary amine catalyst, triethylamine (TEA). The photoinitiator, 2, 2-dimethoxy-2-phenylacetophenone (DMPA) was obtained from Ciba Specialty Chemicals. Thiol monomer, glycol di(3-mercaptopropionate) (GDMP), was generously donated by Bruno Bock Thio-Chemicals-S. Structures of all monomers and catalyst are shown in Figure 14. All chemicals were used as received without purification.

![Molecular Structures](image)

*Figure 14. Molecular Structures of Thiol, Ene, Isocyanate, Photoinitiator and Tertiary Amine Catalyst.*

Sample Preparation. Formulations of ternary thiol/ene/isocyanate components in the range of 100/100/0, 100/90/10, 100/80/20, 100/70/30, 100/60/40, and 100/50/50 by mole percent of functional group were synthesized by a combination of two reactions in a
one pot synthesis. In the first step, a tertiary amine catalyst (TEA) facilitated thiol-isocyanate reactions followed by a traditional UV polymerization utilizing photocatalyst DMPA. In systems with only thiol and ene components, TEA catalyst was eliminated. In each series of formulations, the isocyanate component was changed to HMDI, IPDI or H_{12}MDI generating a total of 15 combinations of ternary TENs and a control.

DMPA photoinitiator, 1 wt% of total formulation weight was premixed and dissolved with GDMP (dithiol) by heating to 35 °C under sonication. After cooling, mixtures were covered to prevent premature curing before the vinyl curative TATAT was mixed in. The isocyanate component was added next with vigorous mechanical mixing to prevent inhomogeneous networks or gel formation from thiourethane-rich domains. In the final step, tertiary amine catalyst, TEA (1 μL), was dropped in, followed by rapid mechanical stirring.

Films were produced by adding small amounts of thiol/ene/isocyanate mixtures onto a glass plate containing a rectangular Teflon® mold of 0.5 mm thickness. A second plate was placed atop the first and affixed with clamps. Dogbones and tensile bars were formed by pipetting the mixture into preformed silicon molds with appropriate dimensions. Dogbone molds were in line with ASTM test D638M, while tensile bar molds measured 5.0 mm x 0.5 mm (width x thickness). The resulting films and bars were allowed to rest in ambient conditions for 30 minutes before irradiating with a low-pressure mercury UV lamp (intensity 20 mW/cm²) for 30 minutes. The 30 minute pre-UV time was necessary to permit thiol isocyanate reactions reach full conversion prior to initiating the second sequential UV polymerization reaction. Following UV treatment, all
samples were post-cured in an oven for 48 hours at 90 °C which is well above $T_g$ of any system.

Characterization

Kinetics

Kinetic analysis was investigated using stoichiometric mixtures of base monomers GDMP/TATAT along with 20 mol% of HMDI, IPDI or H$_{12}$MDI and 1 wt. % DMPA. A lower mol% NCO formulation was chosen due to the strong absorbance of isocyanate peaks. Conversion versus time plots were generated by real-time FTIR (RTIR) spectroscopy using a Nicolet 8700 FTIR spectrometer with a KBr beam splitter and a MCT/A detector along with a 320-500 nm filtered ultraviolet light source. An initial scan of the mixtures revealed the presence of characteristic thiol, isocyanate and ene peaks at 2551 cm$^{-1}$, 2250 cm$^{-1}$, and 3064 cm$^{-1}$ respectively. A second scan was run five minutes after TEA catalyst was added to measure isocyanate conversion. It should be noted material for the second scan was from the same batch however TEA was not added directly to the salt plates. Sample size for RTIR studies were relatively small, therefore minimal TEA was required. Constant volume of 1 μL TEA was added via micropipette for each 2 g sample. Although films and bars were allotted 30 minute reaction pre-UV periods, this length of time was inconvenient for kinetic runs. Additionally, at the time of the second scan, the peak height of the isocyanate peak was constant, indicating the reaction approached completion. Finally samples were irradiated with UV light, intensity 20 mW/cm$^2$, while real-time data was collected for a total of 200 seconds at a 1/sec scan rate of approximately 4 cm$^{-1}$. From real-time measurements, we determined the conversion of thiol and ene functional groups with respect to time.
Overall, using FT-IR and RTIR, effects of isocyanate structure on isocyanate conversion in the first step and UV network formation from thiol-ene kinetics were precisely monitored.

Thermomechanical and Mechanical Testing

Dynamic mechanical thermal analysis was performed with a TA Q800 DMA, TA Instruments, New Castle, DE. Bars 0.5 mm x 5.0 x 6.0 (width x thickness x length), were cooled and held isothermally, then heated at 5 °C/min to 100 °C while subjected to simultaneous oscillatory strain of 0.05% at an operating frequency of 1 Hz in tensile mode. Viscoelastic properties such as storage modulus (E’), loss modulus (E’’), and tan δ values were recorded as a function of temperature. Tg of the networks was recorded from peak values of the tan δ vs. temperature plot. Mechanical testing was performed using a MTS Insight™ material testing machine equipped with a 10 kN load cell and preset to collect 10 data points per second. Dogbone (ASTM D638M) samples with cross-sectional dimensions 13.0 mm ± 0.5 mm and 3.5 mm ± 0.5 mm (width x thickness) were carefully centered in clamps, then deformed in tensile mode at a strain rate of 0.2 in/min. Young’s modulus was calculated from the initial slope of the linear elastic region of the stress-strain curve. Peak load, peak stress, yield point and strain at break were also determined concurrently during the tensile tests.

Thermal Stability and Polymer Density

Thermogravimetric analysis (TGA) was performed using (ca. 8 mg) specimens in a standard platinum pan using a TA TGA Q500. After equilibrating the samples at 40 °C, they were heated 10 °C/min to a terminal temperature of 800 °C. Sample mass loss was measured as a function of temperature, and polymer degradation was determined as
the temperature corresponding to peak values of the derivative weight peak (%/°C) versus temperature curve. A simple, yet efficient method to determine polymer density is by Archimedes’ method. After allowing water to equilibrate to ambient conditions, moderately-sized rectangular samples were weighed in air then reweighed while immersed in water. The difference between the two masses was then used to determine the density of polymer samples. To assure accurate measurements, water bath temperature was measured occasionally between runs. Polymer density was calculated in g/cm³ for four samples of each formulation, and values shown in the following discussion represents an average value along with standard deviations.

WAXD

Wide angle x-ray diffraction (WAXD) was performed on polymer films containing 50 mol % isocyanate content (IPDI, HMDI, H₁₂MDI) along with the control sample. WAXD was conducted using a Rigaku Utima III diffractometer equipped with a Cu Kα radiation source where λ = 1.542 Å. The scan was taken from 2θ = 2 to 60 at a rate of 0.25 steps/min.

Results and Discussion

Kinetics of Dual Cure Thiol-Ene-Isocyanate Networks

In this study, we investigated thermal and mechanical properties of ternary thiol-ene-isocyanate networks to determine changes in material properties with respect to isocyanate structure, isocyanate content and network morphology. It is well accepted that both thiol-ene and thiol-isocyanate reactions are highly efficient, have rapid kinetics, reach high conversion, and can proceed independently. We investigated the reaction kinetics of the dual cure systems for each sample with respect to thiol-isocyanate reaction
(first reaction) and the UV polymerization of a thiol with an alkene in a second step. Individual peaks for each thiol ($\approx 2551 \text{ cm}^{-1}$) and isocyanate ($2250 \text{ cm}^{-1}$) functional groups were observed using FTIR analysis before, and five minutes after TEA catalyst addition. Isocyanate peak intensity decreased significantly in each case within the allowed five minute period. The initial thiol-isocyanate reaction was evident by disappearance of the isocyanate peak at $2250 \text{ cm}^{-1}$ and appearance of a peak around $3350 \text{ cm}^{-1}$ (Figure 15). The broad peak at $3350 \text{ cm}^{-1}$, which can assume a variety of shapes and intensities, relates to the N-H stretch of the newly formed secondary amide structures that are associated or involved with hydrogen bonding. Interestingly only one system, HMDI-GDMP-TATAT, appeared to reach full conversion based on complete disappearance of the isocyanate peak during the allotted time. This is likely due to an increased reactivity of the less sterically-hindered linear aliphatic HMDI monomer. Other systems likely reached near quantitative conversions, considering a significant portion of the reaction proceeded before the first data point was collected.

The second reaction, UV polymerization of the thiol-terminated oligomers and excess thiol, was investigated using Real-Time FTIR wherein peak intensity of thiol and ene peaks are measured with respect to time. Figure 16 confirms vinyl group conversion was greater than 90% for all systems thereby verifying thiol-ene photopolymerization indeed proceeded in the second step and not the first. This one pot synthetic method is a facile method to produce ternary networks with theoretical dual network morphologies. There was a slight inconsistency between thiol and ene conversion in some of the systems. For example, in Figure 16 we see that thiol conversion is lower than alkene conversion. Again this is likely an effect from some unreacted isocyanate from the first
reaction. The HMDI-based system however reacted in a more one-to-one fashion and was also the system that demonstrated the highest apparent isocyanate conversion in the first step.

![FTIR spectra of HMDI, IPDI and H12MDI mixtures with 20 mol% NCO content under N2 purge. The before images represent mixtures of DMPA, GDMP, TATAT, and their respective isocyanate. The after image represents the same sample five minutes after TEA catalyst addition prior to UV irradiation.](image)

Figure 15. FTIR spectra of HMDI, IPDI and H12MDI mixtures with 20 mol% NCO content under N2 purge. The before images represent mixtures of DMPA, GDMP, TATAT, and their respective isocyanate. The after image represents the same sample five minutes after TEA catalyst addition prior to UV irradiation.
Figure 16. RTIR conversion of Thiol (●) and Ene (■) functional groups for ternary systems composed of A) GDMP-TATAT-HMDI, B) GDMP-TATAT-IPDI and C) GDMP-TATAT-H12MDI. Mole percent of NCO in each compound was 20 mol%. Samples contained 1.0 wt% DMPA and were irradiated with a 320-500 filtered UV light source of 20 mW/cm² intensity for 200 seconds after a 10 s rest period.
Viscoelastic and Thermal Properties of Ternary Thiol-Ene-Isocyanate Networks via DMA

Dynamic mechanical analysis of polymer materials reveals an impressive amount of information about the viscoelastic properties polymer materials over a broad temperature range. In the following experiments, films of ternary networks were subjected to small oscillatory tensile strains from sub-ambient temperatures (-20 °C) through relatively high temperatures (100 °C) in order to resolve the storage modulus (E'), loss modulus (E'') and tan δ (the ratio of E'' to E'). With the exception of GDMP-TATAT-HMDI networks, Figure 17 (left) shows three major trends in DMA data with respect to the storage modulus, E': (1) E’ shifts slightly upward in the glassy regime with increased NCO content, (2) The glassy plateau is extended with increased NCO content, and (3) E’ in the rubbery plateau decreases with increasing NCO content. In the glassy regime, E’ ranges between 1400 and 2000 MPa for all the systems observed. The E’ in the glassy regime increases for all three systems as isocyanate content increases (Table 1.) This is likely due to network structure of the isocyanate additive, as this trend is more prominent for IPDI and H_{12}MDI systems which contain more rigid monomers. The extension of the glassy plateau is more pronounced in the IPDI and H_{12}MDI- containing systems compared to HMDI systems. Because all systems have equivalent NCO content, this observed difference could be attributed to structural differences of the isocyanate linker. Cyclic aliphatic groups are bulky and known to increase T_g of many networks, which in turn increases the temperature over which the glass modulus persists.

The storage modulus in the rubbery plateau regime varies between 6.1 and 2.8 (units?), and 6.1 and 4.0 for IPDI and H_{12}MDI containing networks, respectively, with moduli decreasing with increasing isocyanate content. The decrease in E’ plateau values
in the rubbery regime could be explained by the decrease in cross-link density with increasing isocyanate content; this is a direct result from chain extension of the difunctional thiol monomer, GDMP with the difunctional isocyanates. At the higher temperature, greater than 90 °C, effects from hydrogen-bonding would be irrelevant; therefore systems with high NCO content exhibit low values of E’. The HMDI-based systems demonstrated a different behavior. The storage modulus in the rubbery regime does not follow any particular trend. This observation will be explained in a later section of this discussion.

The breadth of the tan δ versus temperature curve directly relates to network uniformity, and the temperature corresponding to the peak of the curve is commonly reported as the glass transition temperature of a polymer system. Figure 17 (right) shows a noticeable broadening of the peaks and a shift in T_g toward higher temperatures for IPDI and H_{12}MDI systems as isocyanate content increases. Traditional thiol-ene networks exhibit very narrow tan delta vs. temperature curves as confirmation of high uniformity of the networks. Broadening of the curves indicates increased heterogeneity which could be explained by the presence of a second domain in the network morphology. Specifically, a second domain could cause the onset of a second, separate glass transition temperature. This subtle effect is evident in the 40-50 mol% NCO IPDI specimen. The shoulder on the left side of the tan δ curve could be attributed to a second, less rigid or linear amorphous domain with different thermal properties, but further experimental methods (such as small-angle scattering) would be necessary to prove the presence of multiple phases. Nonetheless, the broadening behavior of three component TENs is more exaggerated when the isocyanate content is higher.
The glass transition temperature shifts toward higher temperatures for all ternary systems as isocyanate content increases Figure 17 (left). Again this observation is more evident in the IPDI and H$_{12}$MDI systems. The shift in $T_g$ toward higher temperatures could be caused by a combination of structural effects along with hydrogen bonding. $T_g$ increased by 37 °C and 35 °C for IPDI and H$_{12}$MDI networks, respectively, but only 3 °C for HMDI-based networks. This is a significant observation because increases in isocyanate content would theoretically translate to increases in the length of the linear regions within the network, but $T_g$ increases by a similar range compared with networks made using 100 percent isocyanate and thiol monomers (ie. a fully hydrogen bonded system)$^{39}$. Therefore it is possible that hydrogen bonding is more effective in ternary thiol-ene network systems based on linear precursors which are reacted first, and this could allow for more efficient orientation of hydrogen within H-bonding regions. A complete description of the thermomechanical analysis of networks with between 0 and 50 mol% isocyanate content is listed in Table 3.

If difunctional thiols and difunctional isocyanates are utilized in sequential polymerizations, this would theoretically yield linear thiol-terminated prepolymers that would be embedded within a thiol-ene matrix upon completion of the thiol-ene reaction step. As such, we investigated the thermal degradation of these ternary networks for formulations with up to 50 mol% isocyanate content (Figure 18 left). We found that the onset of polymer degradation decreased with increased isocyanate content. A plot of the derivative of weight loss with respect to temperature shows an increase in an unresolved feature that has a lower degradation temperature (Figure 18 right). This finding is in good agreement with the theory of the presence of two domains, one linear system
composed of linear thiol-isocyanate regions and a second composed of the network system. In fact, the curve attributed to the native (around 340 °C), decreases as a second curve appears at a lower degradation temperature. This second feature is less thermally stable and does not appear until isocyanate content is around 20 mol%, thus we attribute this mass loss to the decomposition of isocyanate-containing linear regions within the network. These findings are consistent with a two-phase network morphology.

Table 3

*Summary of Thermomechanical Measurements of Sequentially Cured Thiol/Ene/Isocyanate Networks Obtained with a TA Q800 DMA Operating in Controlled Strain Rate Mode with 0.05% Strain Rate, 1Hz Frequency, and 5 °C/min Temperature Ramp Rate*

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<th>SH/NCO/C=C (molar ratio)</th>
<th>$T_g^a$ ($°C$)</th>
<th>$E'_{\text{glassy}}^b$ (MPa)</th>
<th>$E'_{\text{rubber}}^c$ (MPa)</th>
<th>$E''_{\text{max}}$ ($°C$)</th>
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</table>
Figure 17. Viscoelastic measurements of ternary thiol, ene, nco systems of A) GDMP-TATAT-HMDI, B) GDMP-TATAT-IPDI and C) GDMP-TATAT-H$_{12}$MDI from -20 °C – 100 °C at 5 °C/min, 0.05% strain and frequency of 1Hz. Isocyanate content was varied from 0-50 mol% in the following formulations: GDMP/TATAT/NCO - 100/100/0 (■), 100/90/10(●), 100/80/20(▲), 100/70/30(▼), 100/60/40(♦), and 100/50/50(◄). Samples were photopolymerized with 0.1 Wt% DMPA and a low-pressure mercury UV lamp, intensity 20 mW/cm$^2$, for 30 minutes followed by a 48 hour post-cure at 90 °C prior to testing.
Figure 18. Thermal Gravimetric Analysis of Ternary Thiol-Ene Networks with 0-50 mol% isocyanate content, A) HMDI B) IPDI and C) HMDI. Formulations containing either 0, 10, 20, 30, 40 or 50 mol% were heated from 40 °C and heated 10 °C/min to a terminal temperature of 800 °C. Content increases as the arrow on the left increased or as the right arrow decreases.
Improved Toughness of Thiol-Ene Networks

Stress-strain relationships of networks containing linear and cyclic aliphatic diisocyanates were measured using ASTM D638M standard dogbone samples and characteristic Instron tensile test methods. Samples were clamped in the grips and pulled using a 0.2 in/min strain rate while the resulting tensile (Young’s) modulus, strain at break, and peak load values were recorded in each case and compared to the native matrix. The neat matrix Young’s modulus value was 9.7 MPa, maximum strain at break was 25%, and peak stress of 2 MPa, which are typical for cross-linked thiol-ene network systems with proximal to room temperature T_g's. When comparing maximum strain at break and Young’s modulus values of the native matrix values to formulations involving linear aliphatic diisocyanate (HMDI), modulus values increased to 19 MPa, peak stress values increased to 3 MPa, while strain at break values increased to 32%. Greater effects were noticed when the isocyanate additive was cyclic aliphatic. For example, Table 4 shows comparative values for the native matrix, HMDI, IPDI and H_{12}MDI. The latter two demonstrated significant increases in the Young’s modulus, increasing from 9.7 MPa (native matrix) to 603 MPa and 1318 MPa for formulations containing 50 mol% isocyanate (IPDI and H12MDI, respectively) content. The increase in modulus can be contributed to hydrogen-bonding and increased T_g. Given the similarities of polymer densities and functionality of IPDI and H_{12}MDI formulations, differences in modulus for these formulations must be attributed somewhat to structural effects; theoretically, because of its larger size, H_{12}MDI monomer is more rigid. The graphs in Figure 19 are representative of the observed stress strain relationships.
One of the most desired combinations of polymer mechanical properties is high modulus along with high strain, and most systems synthesized for this investigation demonstrated that specific combination of properties. Unlike other polymer systems, a trade-off between modulus and elongation is not present. We feel this behavior is attributable to the unique underlying network morphology of these ternary systems. Usually, higher cross-linked systems demonstrate high Young’s moduli values but low elongation. Thiol-ene networks have lower moduli values and longer elongation due to the presence of flexible thioether groups within the polymer networks. When this is coupled with the bulkier isocyanate monomers in a linear amorphous region, the effects of hydrogen bonding and high $T_g$ exaggerate modulus and strain, making it possible to achieve both simultaneously.

As previously mentioned, the first reaction in the sequential process is a chain extension reaction which theoretically yields linear oligomers with thiol end groups. This would increase molecular weight between cross-links, thereby increasing expected elongation. Figure 20 shows that toughness is increased throughout all ranges of isocyanate incorporation for IPDI and $H_{12}$MDI networks, but there is essentially no increase in toughness for HMDI-based networks. This is likely due to the formation of ordered domains which dominate the mechanical response (vide infra). Figure 20 also demonstrates the relationship between strain at break and isocyanate content for formulations of all three sequentially cured thiol/ene/isocyanate networks. Strain at break increased for formulations containing up to 40 mol% isocyanate content followed by a slight decrease in strain at break for 50 mol% isocyanate content. Although values were highly skewed between linear and cyclic isocyanate systems, the trend in strain at break
was remarkably similar. A maximum in strain at break was observed at 40 mol% NCO for all systems, followed by a decrease in the 50 mol % NCO networks. This crossover behavior was observed in previous systems and is believed to result from a delicate balance which exists between structural effects and hydrogen bonding. The increase in strain at break along with a yield point for some systems with 50 mol% isocyanate content is further evidence that there is an increase in the size of linear domains within the ternary networks. A summary of mechanical testing for all formulations is listed in Table 4.

Table 4

*Summary of Mechanical Testing for 3.5 mm (thickness) Dogbone Samples of Thiol/Ene/Isocyanate Networks Cured in Sequential Order*

<table>
<thead>
<tr>
<th>SH/NCO/C=C (molar ratio)</th>
<th>Modulus (MPa)</th>
<th>Peak Load (N)</th>
<th>Peak Stress (MPa)</th>
<th>Strain at Break (%)</th>
</tr>
</thead>
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<tr>
<td>GDMP/HMDI/TTT</td>
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<td></td>
</tr>
<tr>
<td>100:0:100</td>
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<td>9.7</td>
<td>2.0</td>
<td>25</td>
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<tr>
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<td>8.8</td>
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<tr>
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<td>603</td>
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<tr>
<td>GDMP/H12MDI/TTT</td>
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<td>9.7</td>
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<td>7.3</td>
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<td>6.3</td>
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Table 4 (continued).

<table>
<thead>
<tr>
<th>SH/NCO/C= (molar ratio)</th>
<th>Modulus (MPa)</th>
<th>Peak Load (N)</th>
<th>Peak Stress (MPa)</th>
<th>Strain at Break (%)</th>
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</thead>
<tbody>
<tr>
<td><strong>GDMP/H12MDI/TTT</strong></td>
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<tr>
<td>100:50:50</td>
<td>1318</td>
<td>152</td>
<td>34</td>
<td>123</td>
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</tbody>
</table>
Figure 19. MTS data of sequential SH/ENE/NCO formulations as follows: (a) 00/100/0 (b) 100/90/10 (c) 100/80/20 (d) 100/70/30 (e) 100/60/40 and (f) 100/50/50. Mechanical testing was performed using a MTS Insight™ material testing machine equipped with a 10 kN load cell preset to collect 10 data points per second while samples were deformed in tensile mode 0.2 in/min.
Figure 20. Top – Toughness, calculated from integral beneath stress-strain curves from MTS tensile experiments and Bottom - Strain at break of ternary thiol-ene isocyanate networks containing between 0-50 mol% isocyanate content HMDI (■), IPDI (●), and H₁₂MDI (▲). The formulations represented are as follows: 100/100/0, 100/90/10, 100/80/20, 100/70/30, 100/60/40, and 100/50/50 of SH/ENE/NCO. Crosshead speed = 0.2 in/min.

Explanation of Anomalous Behavior of HMDI-Based Ternary Networks

For many of the experimental techniques performed, HMDI-based networks demonstrated little change in mechanical performance compared with the native matrix. Networks containing 50 mol% isocyanate (HMDI, IPDI and H₁₂MDI) along with a control was investigated by WAXD to probe for large ordered domains which might be present in one specific region of bulk materials. Films containing HMDI, were cloudy, which led us to believe there were crystalline domains within the network. Figure 21a
shows the WAXD patterns for the control, IPDI and H_{12}MDI systems, which generate diffraction patterns typical of amorphous polymers as the repetition of C-C connections along the backbone throughout essentially behave as long range ordering. In contrast, HMDI exhibits sharp peaks which can be associated with crystalline domains. The structures of GDMP and HMDI are such that linear regions can align in a way that crystalline formation is favorable (Figure 21b). The d spacing measurement for a 50 mol\% HMDI network was calculated from the 2θ peak as was found to be [GIVE NUMBER], similar to d spacing values of dominant crystalline forms of asymmetric nylons.\textsuperscript{102, 103} While these crystalline domains increase mechanical properties of linear polymer systems by way of hard segment/soft segment morphologies, the formation of these crystalline domains appears to be unfavorable for these network systems. The mechanical properties are dictated by the limiting softer thiol-ene network morphology which is why there is essentially no change in the network properties. The results from WAXD additionally strengthen the argument for a truly sequential reaction order, first thiol/isocyanate click reaction followed by thiol-ene click reaction.

Polymer density measurements were also in good agreement with the theory of a sequential reaction order and initial chain extension reaction. Figure 22 shows polymer density initially decreases linearly from 1.35 g/cm\textsuperscript{3} to 1.26 g/cm\textsuperscript{3} for IPDI and H_{12}MDI samples but approaches a plateau around 1.30 g/cm\textsuperscript{3} for formulations with 30 mol\% HMDI. Such a change in polymer network density would be evident by observed differences in the aforementioned E’ plateau values. The outlying system here again is the HMDI-based network system. If a crystalline domain is prominent in the network,
the close packing of this domain would cause the density to remain higher even though
the quantity of linear polymer segments is increasing.

![Figure 21. A) WAXD for ternary thiol-ene isocyanate networks containing a) 0 mol% NCO b) 50 mol% IPDI c) 50 mol% H_{12}MDI and d) 50 mol% HMDI and B) a representative diagram of the hydrogen bonding in Nylon 6,6 and the linear region of GDMP and HMDI.](image)
Figure 22. Polymer Densities, via Archimedes’ method, for various formulations of SH/ENE/NCO 100/100/0, 100/90/10, 100/80/20, 100/70/30, 100/60/40, and 100/50/50: HMDI (■), IPDI (●), and H₁₂MDI (▲). Error bars represent standard deviation measurements for an average of four measurements per sample.

Conclusions and Future Work

Ternary thiol-ene isocyanate networks were synthesized using a one-pot method using three diisocyanates: HMDI, IPDI and H₁₂MDI. Kinetic analysis demonstrated that the initial thiol-isocyanate reaction proceeds independently from the second thiol-ene photopolymerization. Analysis of the viscoelastic properties established that increasing the mol percent of cyclic aliphatic isocyanates increases the glassy modulus and extends the glassy plateau region. Rubbery modulus values demonstrated decreased with increasing isocyanate, consistent with a decrease in crosslink density. This is believed to be due to high linear polymer content from the thiol-isocyanate pre reaction. Glass transition temperatures increased for all systems, up to almost 40 °C in some cases. This is believed to be attributable to the more rigid monomers and in combination with hydrogen bonding. Tan delta versus temperature curves broadened slightly with increasing isocyanate content. Wider peaks correspond with a decrease in network uniformity, but were not as exaggerated as previously reported ternary thiol-ene network.
systems such as those with acrylates. There was evidence of possible phase separation noted by a second peak max for higher isocyanate content IPDI networks but a more conclusive technique should be performed for concrete evidence.

Mechanical properties of ternary networks were improved and mostly imparted a combination of increased Young’s modulus and strain at break. This was further evidence for the presence of increased linear regions within the networks. Strain at break values increased between 172% and 744% when compared to the native matrix. Young’s modulus was greatly improved, by nearly 3 orders of magnitude in some cases; however strain at break reached a maximum value in formulations containing 40 mol% isocyanates. Toughness was increased through the full range of NCO incorporation for IPDI and H_{12}MDI. WAXD patterns demonstrate higher range order for HDMI-containing networks, suggesting the presence of crystalline domains. These are believed to be partially responsible for the decreased mechanical properties of such systems. Polymer density decreased as the isocyanate content was increased due to a more linear system and bulkiness of monomers except for HMDI systems. The observed differences between HMDI and other isocyanate formulations containing IPDI and H_{12}MDI is attributed to structural differences of linear and cyclic aliphatic compounds. The onset of thermal degradation was also decreased as isocyanate content increased.

The viscoelastic properties and thermal response of networks containing linear thiourethanes are manipulated through simple sequential chemistries yielding novel network morphologies. For future investigations, the impact analysis and fracture toughness should be analyzed for their use as damping systems. Although peak height of tan δ is compromised, the peak is wider and still beyond the threshold for energy and
vibration damping by viscoelastic relaxation, i.e.: \( \tan \delta > 0.3 \). The temperature ranges of viscoelastic dissipation for these ternary systems are appropriate for a broad array of applications from intraoral mechanical energy damping devices to automotive sound damping devices.
CHAPTER IV

IMPACT PROPERTIES OF THIOL-ENE NETWORKS

Abstract

Thiol-ene networks are expected to demonstrate superior energy absorption properties, but only recently have information about impact properties of thick thiol-ene thermosets surfaced in literature. The ultimate goal in these materials would be to tune the glass transition temperature such that it aligns with temperature of an impact event. Modified thiol-ene network (TEN) systems have mainly used a third component as a molecular handle to gain control of the thermal response, while the impact properties of unmodified thiol-ene networks has yet to be established. In this study we synthesized a series of thiol-ene network films and discs having glass transition temperatures ranging between -30 and 60 °C utilizing several multifunctional thiols and two trifunctional alkenes with structural differences but similar molecular weight. We measured the viscoelastic properties and impact properties using Dynamic Mechanical Analysis, pendulum impact (1.13 Joules), and drop impact (4.4 Joules) testing protocols. Impact behavior was found to directly correlate to the glass transition temperature except when the temperature at which an impact event occurs overlaps with the temperature corresponding to the viscoelastic dissipation regime of the polymer, where then the impact properties are greatly improved due to viscoelastic dissipation. Network structure affects impact as well, such that networks from rigid monomer realize higher peak loads and vice versa. Additionally, we gained insight into the spacial limitations of energy dissipation for a thiol-ene network polymer. Overall we have gained considerable insight
into the impact behavior of highly uniform unmodified thiol-ene networks and established a platform for predictability for similar systems.

Introduction

Polymers are frequently used as energy dissipating materials owing to their viscoelastic character and the impressive range of properties attainable by way of adding fillers, manipulating underlying architectures, utilizing copolymers or by simply selecting appropriate monomers. Engineers take advantage of the viscoelastic nature of polymers and select damping polymers to absorb energy whether it is in the form of noise, vibrations or mechanical energy thereby protecting some underlying entity. One area where damping polymers are used extensively is in personal protective equipment (PPE). These materials aim to protect the human body from injuries by absorbing or redirecting kinetic energy from an impact event using a device such as foam padding, hard shells or even internal devices such as mouthguards. As researchers make advancements regarding core mechanisms which facilitate damage, both external and internal, it is likely that new standards will be established and that it will be increasingly important to develop a new material base capable of meeting new requirements.

The damping capabilities of polymers are dictated by a variety of factors but one important variable is viscoelastic relaxation. Viscoelastic properties of polymers are readily measured by dynamic mechanical analysis (DMA) which affords a great deal of information concerning individual components with respect to temperature and frequency. During a typical DMA experiment the stiffness of a material or modulus, \( E \), can be separated into two parts: the storage modulus, \( E' \) and the loss modulus, \( E'' \). The ratio of the loss modulus to the storage modulus or \( \tan \delta \) is simultaneously measured during such
experiment (Equation 3) and the temperature at which the ratio peaks is considered the glass transition temperature and is also the temperature at which viscoelastic damping is most favorable. Viscoelastic damping is caused by coordinated segmental motions, and for many damping applications a polymer material is selected to have a glass transition temperature similar to the use temperature.

— [3]

Polyethylene-co-vinylacetate (EVA), a semi-crystalline thermoplastic, is utilized in many damping applications for personal protective equipment, especially mouthguards. The glass transition temperature of EVA has been reported between -30 to around -10 °C depending on the method used to measure the value. Based on the fundamentals of damping and viscoelastic relaxation, this material in particular would not demonstrate optimal damping properties at temperatures appropriate for most application, especially when the temperature is intraoral temperature as is the case for mouthguards. Processing and crystallinity are additional absorption blocking mechanisms recognized in EVA. Despite these specific traits of EVA which are known to affect energy damping, EVA is a commonly used material for PPE and will serve as a benchmark for comparison in this investigation.

A new class of material with an established set of thermal and physical attributes which could be potentially beneficial for damping applications is based around thiol-ene networks. The viscous response of these amorphous thermoset materials is greater than most polymers within the glass transition region. Novel materials based on thiol-ene chemistry have already been suggested as a replacement material for EVA due to their easy fabrication and drop-in technology based on UV polymerization methods. The
radial – step growth reaction mechanism plays a key role in developing highly uniform, low-stress and flexible cross-linked networks (Scheme 1). 9, 13, 14, 44 These aforementioned attributes of TENs make them a rather unique class of materials which could be suitable for PPE applications and the next level of performance in polymer materials.

Thiol-ene networks (TENs) do offer several advantages over EVA regarding impact energy absorption. First, they are typically amorphous (optically clear) materials. 9 The lack of crystalline domains would mean the systems should be more static in nature such that crystalline domains are not growing and becoming more ordered over time. 9 Second, just as ether oxygen in poly-ether/polyurethane hybrid systems is believed to provide flexibility, sulfur atoms in thioethers afford more flexibility and further enhance mobility within the polymers, but the role of mobility in damping has not been thoroughly investigated for such systems at this point. 9 Third, networks would ideally afford systems with higher compressive and tensile properties due to reinforcement from junction points. Lastly, a span of TENs with $T_g$s from sub zero temperature to temperature significantly above room temperature are remarkably uniform as demonstrated by their typical narrow tan $\delta$ versus temperature curves. 9 The lack of network defects such as dangling ends and loops, along with increased flexibility, could surely affect the efficiency of energy dissipation via transfer of viscoelastic relaxation processes. 9 Despite the realized potential of TENs regarding mechanical energy damping neither energy dissipation nor energy management by pure TENs has been quantified or analyzed.

The focus concerning energy absorption properties of TENs has been somewhat studied in and is generally geared toward utilizing chemical methods to control the
location of the peak of the tan δ versus temperature curve in order to achieve optimal
glass transition conditions (tan δ\textsubscript{max} = temperature of testing). These conditions are used
to yield maximum energy dissipation or are determined as proof of concept that energy
dissipation trends with tan δ. In 2006, Senyurt and coworkers synthesized a series of
TENs of varying T\textsubscript{g}s by adding a third acrylate component\textsuperscript{46} and found that energy
absorption of the resulting networks directly correlated with mole percent acrylate which
in turn correlated with T\textsubscript{g}. The best performing systems in this study were among those
having T\textsubscript{g}s proximal to the testing temperature. Other acrylate-based three component
TEN systems have been investigated and also demonstrated energy absorption is highest
when the testing temperature is proximal to T\textsubscript{g}\textsuperscript{47, 91}, but network homogeneity is disrupted
when acrylate monomers are used which evident by broader tan δ curves. This is mainly
attributed to acrylate rich regions generated by acrylate homopolymerization which
occurs simultaneously with thiol-ene polymerizations. Additionally novel urethane-
based TENs were formulated via multifunctional allyl monomers wherein the glass
transition temperatures were controlled via reactive allyl ether diluent.\textsuperscript{42} Again the best
energy absorption properties were found when the T\textsubscript{g} was proximal to the temperature of
the experiment.

Energy absorption properties of TENs have been of great interest among
researchers, and although some data exist concerning energy absorption and modified
TENs, there is a considerable amount of critical information lacking in the literature
which is necessary to fully understand damping properties of TENs. In this study we
synthesized a battery of unmodified TENs from commercial monomers by common UV
polymerization techniques and measured the resulting viscoelastic properties and energy
absorption under ambient conditions via two methods. Underlying network architecture was varied by using monomers with two, three or four functional groups while network rigidity was manipulated using a rigid alkene monomer. Impact behavior was explained by polymer viscoelastic properties along with network architecture. The results of this study will implicate the anticipated impact behavior native TEN having a broad array of thermal and mechanical properties and provide a platform for future investigations of modified TENs.

Figure 23. Proposed Mechanism of Thiol –Ene Reaction Using Photoinitiator.

Materials and Methods

Materials

A variety of TENs were synthesized from commercially available multifunctional thiol and vinyl monomers. Commercial thiols, glycol di(3-mercaptopropionate) (GDMP) and ethoxylated trimethylolpropane tri(3-mercaptopropionate) (MW = 708) (ETTMP700)
were received from Bruno Bock Thio-Chemicals. Trimethylolpropane tris(3-mercaptopropionate) (TMPT) and pentaerythritol tetra(3-mercaptopropionate) (PETMP) were purchased from Sigma Aldrich Chemical Company. Commercial vinyl monomers, allyl pentaerythritol (APE) and 1,3,5,-triazine-2,4,6 (1H, 3H, 5H)-trione (TATAT) were received from Perstorp and Sigma Aldrich respectively. Photoinitiator 2, 2- dimethoxy-2-phenylacetophenone (DMPA) was purchased from Sigma Aldrich Chemical Company. All chemicals were used as received without further purification. EVA sheets (Sports Advantage Mouthguard Material, Thermal Forming Soft EVA), thickness = 4 mm, was obtained from Ortho Technology (Tampa, FL). Structures of all monomers and photoinitiator for thiol-ene network formulations are represented in Figure 24.

Figure 24. Molecular Structures of Monomers and Photoinitiator (DMPA).
**Synthetic Methods.** Thick thermoset plates suitable for impact and thin films for viscoelastic measurements were synthesized via UV polymerization of stoichiometrically balanced monomers mixture containing 0.1 wt% DMPA photoinitiator and a low pressure Hg lamp source. Thin films were synthesized using rectangular Teflon molds (Thickness = 0.4 mm) pressed between two glass plates while thicker samples were formed from silicon molds. Thicker samples were initially exposed to a lower intensity light to reduce heat buildup and material warping. The total curing time for all samples was 30 minutes. Following photopolymerization samples were removed from their respective molds and immediately placed in an oven at 90 °C for a period of one week to ensure thorough network curing. Samples were equilibrated at room temperature prior to testing.

**Techniques**

**Real Time FTIR.** Real time kinetics of monomer conversion was collected for each system with a Nicolet 8700 FTIR spectrometer equipped with a KBr beam splitter and MCT/A detector. An external light source, OmicCure Exfo 1000 Series, was guided to the sample via optic cable. Samples were irradiated with UV light (intensity = 25 mW/cm²) in the range of 320 nm - 500 nm while spectra were collected simultaneously at approximately 1Hz over a range of 650-4000 wavenumbers (cm⁻¹). Kinetic data of the synthesized thiol-ene systems can be viewed in the Supplemental Information section of this document.

**Shore A Hardness, Polymer Density and M₄ Measurements.** Shore A hardness of each plate was measured according to ASTM guideline D2240-05 which measures resistance to indentation. The spring-based device, scaled (0 to 100), contains an indenter tip (dimensions: Tip = 0.031 ± 0.001mm; Taper = 35° ± 0.25° and Shaft=1.40 ±
0.005mm) which was smoothly and firmly pressed into each 8 mm thick sample (two
layered 4mm samples). Measurements were taken from three separate regions of
material. Polymer density was determined using the Archimedes’ method on three
samples per formulation as well. Density combined with the $E'_\text{rubber}$ values from DMA
experiments allowed us to calculate average molecular weight between cross-links $M_c$,assuming $G' = E'/3$. Where $\rho$ is the polymer density, $R$ is the gas constant, $T$ is
temperature of $\tan \delta_{\text{max}} + 40 \, (T_g+40)$ and $G'$ is the shear modulus.

**Thermomechanical Testing.** Dynamic mechanical analysis was performed on
films using a Q800 DMA, TA Instruments (New Castle, DE) in tension mode. Sample
dimensions were 10 mm x 5 mm x 0.05 mm (length x width x thickness) respectively.
Data was collected after first cooling the specimen to -60 °C and annealing for 3 minutes.
Samples were strained at a rate of 1Hz and to a total 0.05% strain while heating 2°C/min
to a final temperature of 100 °C. This same experiment was repeated for ETTMP-
TATAT, GDMP-TATAT and TMPT-TATAT at 10 and 100 Hz. Glass transition
temperature, $T_g$, was taken as the peak of the $\tan \delta$ versus temperature curve and the
rubbery plateau modulus was recorded from the $E'$ (storage modulus) value at $T_g + 40$
°C.

**Impact Testing.** Impact testing was performed via two methods, a modified-
pendulum test and a linear drop test. Pendulum impact performance was measured via a
modified Tinus Olsen (Model 892, Horsham, PA, USA). The impact apparatus was
adapted by adding a Charpy dart in compliance for a modified ASTM D6110-06f test. The hardened steel dart (Taper = 45 ± 2°; radius = 3.17 ±0.12 mm) was raised to a height
corresponding to a standard testing energy of 1.13 J, and the difference in potential energy before and after impact was used to calculate absorbed energy. A more detailed description of this test setup can be found in the following reference. Impacted samples consisted of two stacked 4 mm thick plates (total sample thickness of 8 mm). Three samples (n=3) of each formulation were impacted (total of 24 impacts). An order effect was not expected and, therefore, the order of impacts was not randomized.

Impact performance was also measured via a linear drop test using an instrumented drop tower (Dynatup 9250HV, Instron, Norwood, MA). The drop mass assembly of 5.6 kg contained a piezoelectric 88kN (20,000 lb) load cell tup and a customized 63.5 mm (2.5 in) diameter flat cylindrical steel drop dart to eliminate shear forces during impact. The mass assembly was dropped from a height of 0.08 m resulting in an impact velocity of 1.25 m/sec (4.4 J). A total impact energy of 4.4 J was selected because it was previously used to test EVA and is reported as energy capable of damaging the orofacial complex. Samples were impacted under ambient conditions against a flat, hardened stainless steel anvil and impact velocities were confirmed using an optical velocity flag. Impacted samples were discs of 2 in diameter and 4 mm thick. Three discs of each formulation and three cut EVA discs is this EVA described elsewhere were impacted for a total of 27 impacts. An order effect was not expected and, therefore, the order of impacts was not randomized.

Force versus time data was collected simultaneously via Impulse Data Acquisition software (v. 3.2.30, Instron, Norwood, MA) at 327 kHz. The voltage signal output from the force sensor produced oscillations or “signal ringing” during impact testing and as a result, force data required smoothing. A Savitzky-Golay (SG) filter at 101 points of
window under a polynomial order of 2 with no boundary conditions was applied to load
versus time curves. Selection of a SG filter was utilized because the smoothing functions
better preserves features of the data such as peak height and width.

Results and Discussion

*Viscoelastic Properties of Thiol-Ene Networks from Dynamic Mechanical Analysis (DMA)*

One classic characteristic of UV polymerization of thiols and alkenes is the rapid
and quantitative kinetics giving way to low-stress uniform photo-cured films whereby
viscoelastic behaviors of the films can be measured by DMA which simultaneously
resolves the storage modulus (E’), loss modulus (E’’) and tan delta (E’’/E’) as a function
of temperature. The TENs demonstrated typical behaviors such that at low temperatures
E’ values were high and as the polymers passed through the glass transition region, E’
decreased approximately 2.5 decades before reaching the rubbery plateau regime at
higher temperatures. Between two systems synthesized with similar thiol monomer but
different alkene monomers the glassy moduli were higher for systems containing the
TATAT monomer (Figure 24) which suggests higher packing efficiency within these
polymer networks. This behavior is further evident by the observed differences between
density measurements which were 1.22 g/mL, 1.31 g/mL, 1.21 g/mL, 1.29 g/mL, 1.19
g/mL, 1.25 g/mL, 1.25 g/mL, and 1.30 g/mL for GDMP-APE, GDMP-TATAT, TMPT-
APE, TMPT-TATAT, ETTMP700-APE, ETTMP700-TATAT, PETMP-APE, and
PETMP-TATAT respectively. In each case between systems, the density of the TATAT-
based polymer network was higher. For instance if we compare GDMP-APE with
GDMP-TATAT, the latter would have a higher density. The most likely reason for this
observation is the more rigid TATAT monomer is relatively flat and potentially packs better, in addition to possible effects of $\pi-\pi$ interactions which would also facilitate in molecular stacking.

Figure 25. Storage modulus vsersus temperature for thiol-ene networks cured via UV polymerization with 1 wt.% DMPA photoinitiator. DMA was conducted from -60 to 120 at 2 C/min to 0.05% strain at a frequency of 1 Hz.

The rubbery plateau regime is a common phenomenon for network polymers due to constraints at junction points which prevent flow. The storage modulus in this regime is directly related to molecular weight between cross-links such that higher values translate to lower molecular weight between cross-links or higher dross-link densities. In this study we purposely selected alkene monomers with similar functionalities and molecular weight to compare across systems having different levels of rigidity but similar
cross-link densities. Considering Figure 25, for most systems the $E'_\text{rubber}$ values are similar (see Table 5) which mean systems synthesized using the same thiol have similar $M_c$ values. $M_c$ values were calculated using the polymer density, determined by Archimedes’ method, and the shear modulus, $G'$. It was assumed $G'$ is approximately one-third Young’s modulus, which was taken at $T = T_g + 40 \text{ K}$. As such, the $M_c$ values were 1473 g/mol and 1780 g/mol (GDMP-APE and GDMP-TATAT), 632 g/mol and 744 g/mol (TMPT-APE and TMPT-TATAT), 1120 g/mol and 1068 g/mol (ETTMP700-APE and ETTMP-TATAT) and 560 g/mol and 599 g/mol (PETMP-APE and PETMP-TATAT) (Table 6). Within experimental error it is evident that $M_c$ values correlate with beginning monomer molecular weights. The slight differences between some groups may be attributed mainly to packing differences between TATAT and APE monomers. Additionally APE contains a pendent hydroxyl group which can promote hydrogen bonding with surrounding hydroxyl groups especially for lower $T_g$ networks. This can give a $M_c$ value that is greater than may be expected.

The glass transition temperature is a very important measurement for damping of polymers. This value is often reported as peak temperature associated with the tan δ versus temperature curve. For the samples studied, at lower temperatures loss modulus values were low and they peaked at the onset of the glass transition regime. Network glass transition temperatures spanned across a broad range of temperatures. This behavior was expected and attributable to the range of monomer functionalities and rigidity that were chosen as part of this investigation. The measured glass transition temperatures by DMA were -27, 9, -5, 35, -30, -12, 5 and 53 °C for GDMP-APE, GDMP-TATAT, TMPT-APE, TMPT-TATAT, ETTMP700-APE, ETTMP700-TATAT, PETMP-APE, and
PETMP-TATAT respectively. Most \( T_g \)s were sub zero or relatively low, which is typical of TENs due to the flexible nature thioether linkages throughout the network. This effect is more pronounced when the flexible allyl ether monomer was used as a curing agent; however TATAT increased in glass transition temperatures (Figure 27). \( T_g \)s were between 18 and 50 degrees higher respectively when TATAT monomer was used.

Table 5

Summary of Thermomechanical Properties of Thiol-Ene Networks

<table>
<thead>
<tr>
<th>System</th>
<th>( T_g ) *  (°C)</th>
<th>( \tan \delta_{\text{Max}} )</th>
<th>( E''_{\text{max}} ) ** (°C)</th>
<th>FWHM ** (°C)</th>
<th>( E'_{\text{rubber}} ) *** (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDMP-APE</td>
<td>-27.2 ± 0.6</td>
<td>1.70 ± 0.03</td>
<td>-33.2 ± 0.7</td>
<td>10.3 ± 0.1</td>
<td>5.8 ± 0.2</td>
</tr>
<tr>
<td>GDMP-TATAT</td>
<td>8.60 ± 0.9</td>
<td>1.75 ± 0.05</td>
<td>1.25 ± 0.8</td>
<td>10.9 ± 0.6</td>
<td>5.9 ± 1</td>
</tr>
<tr>
<td>TMPT-APE</td>
<td>-5.01 ± 0.4</td>
<td>1.23 ± 0.08</td>
<td>-10.3 ± 0.8</td>
<td>8.9 ± 0.6</td>
<td>14.7 ± 2</td>
</tr>
<tr>
<td>TMPT-TATAT</td>
<td>35.4 ± 0.4</td>
<td>1.15 ± 0.02</td>
<td>27.9 ± 1</td>
<td>13.2 ± 0.2</td>
<td>15.1 ± 2</td>
</tr>
<tr>
<td>ETTMP700-</td>
<td>-29.6 ± 0.3</td>
<td>1.79 ± 0.05</td>
<td>-35.0 ± 0.7</td>
<td>9.2 ± 0.5</td>
<td>7.5 ± 2</td>
</tr>
<tr>
<td>APE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ETTMP700-</td>
<td>-11.7 ± 0.4</td>
<td>1.55 ± 0.01</td>
<td>-18.1 ± 0.7</td>
<td>10.0 ± 0.5</td>
<td>8.8 ± 0.8</td>
</tr>
<tr>
<td>TATAT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PETMP-APE</td>
<td>5.1 ± 0.5</td>
<td>0.941 ± 0.01</td>
<td>-1.2 ± 0.7</td>
<td>11.6 ± 0.04</td>
<td>17.7 ± 2</td>
</tr>
<tr>
<td>PETMP-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TATAT</td>
<td>53.2 ± 2</td>
<td>0.798 ± 0.03</td>
<td>42.5 ± 1</td>
<td>17.5 ± 0.2</td>
<td>19.8 ± 0.8</td>
</tr>
<tr>
<td>EVA 88</td>
<td>-3 - -10</td>
<td>0.31 ± 0.01</td>
<td>--</td>
<td>38.6 ± 1</td>
<td>--</td>
</tr>
</tbody>
</table>

* \( T_g \) is reported from the peak of the \( \tan \delta \) versus temperature curve
** FWHM is the distance across the \( \tan \delta \) versus temperature curve at a half maximum peak height.
*** \( E'_{\text{rubber}} \) is the storage modulus at \( T_g + 40 \) K
Tan δ curves of most systems were narrow (low FWHM) and possessed relatively high peak values. Since the tan δ is the ratio of $E''$ to $E'$, systems with high tan δ would demonstrate high energy dissipation at the temperature associated with the high values. The peak tan δ values and temperatures associated with unmodified monomers is shown in Figure 28. This significance here is that we demonstrate the capacity to probe systems that will absorb mechanical energy at specific temperature simply based on monomer choice, without complicating formulation with a third component. Because of poor mechanical properties of TENs, it is understandable why a third component is necessary, but until now a platform for base system performance was never available.

Table 6

*Summary of Physical Properties of Thiol-Ene Networks*

<table>
<thead>
<tr>
<th>System</th>
<th>Total $f$</th>
<th>Shore A Hardness</th>
<th>Density* (g/mL)</th>
<th>$M_c$** (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDMP-APE</td>
<td>5</td>
<td>24±4</td>
<td>1.22 ± 0.01</td>
<td>1473</td>
</tr>
<tr>
<td>GDMP-TATAT</td>
<td>5</td>
<td>51±3</td>
<td>1.31 ± 0.01</td>
<td>1780</td>
</tr>
<tr>
<td>TMPT-APE</td>
<td>6</td>
<td>76±2</td>
<td>1.21 ± 0.01</td>
<td>632</td>
</tr>
<tr>
<td>TMPT-TATAT</td>
<td>6</td>
<td>&gt; 100</td>
<td>1.29 ± 0.03</td>
<td>744</td>
</tr>
<tr>
<td>ETTMP700-APE</td>
<td>6</td>
<td>28±2</td>
<td>1.19 ± 0.01</td>
<td>1120</td>
</tr>
<tr>
<td>ETTMP700-TATAT</td>
<td>6</td>
<td>41±4</td>
<td>1.25 ± 0.01</td>
<td>1068</td>
</tr>
<tr>
<td>PETMP-APE</td>
<td>7</td>
<td>81±4</td>
<td>1.25 ± 0.01</td>
<td>560</td>
</tr>
<tr>
<td>PETMP-TATAT</td>
<td>7</td>
<td>84±1</td>
<td>1.30 ± 0.03</td>
<td>599</td>
</tr>
<tr>
<td>EVA</td>
<td>--</td>
<td>83 ± 1</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

*Measured using Archmedes’ method

**Calculated from on $E''_{	ext{rubber}}$ at $T_g + 40$, $\rho$, and $G$ assuming $G = E/3$
It is not uncommon for glass transition temperatures of polymer networks to span over a wide range. Microgel formation and vitrification lead to less than quantitative conversion; however TENs are in some ways well-known for their unique network homogeneity or narrow glass transition regions. Specifically we quantify this parameter by FWHM (full width half max) of the transition region, which is the width across at half the peak height of the tanδ versus temperature curve. In this study most systems demonstrated narrow tan δ curves (FWHM < 15 °C) (Table 5). The FWHM values are lowest for systems with low Tgs which can be attributed to less complex curing mechanics from low viscosity and low functionality monomers. A slightly different behavior is observed for those networks that have greater than room temperature Tgs such as TMPT-TATAT and PETMP-TATAT. It is expected higher functionalities and greater monomer rigidity lead to earlier gelation which decreases collision events and network homogeneity. As the chains become vitrified, the lack of mobility affects reactivity. The kinetic profiles suggest this behavior as lower overall thiol and alkene conversions were realized for these systems (Figure 26).
Figure 26. Real Time FTIR for photopolymerized Thiol-Ene Networks, using 1 wt. % DMPA photoinitiator, light intensity = 25 mW/cm$^2$ and 320 nm - 500 nm range, and scanning frequency = 1/s.
Figure 27. Glass transition temperatures of thiol-ene networks from thiols polymerized (UV) with APE and TTT alkene monomers. Glass transition temperatures are reported from the peak of tan delta curves from DMA experiments (-60 °C - 100 °C at 2°C/min, $f = 1$Hz, strain = 0.05%).

Figure 28. Tan delta versus temperature curves for thiol-ene networks from UV polymerization of the following formulations: (a) ETTMP700/APE (b) GDMP/APE (c) ETTMP700/TATAT (d) TMPT/APE (e) PETMP/APE (f) GDMP/TATAT (g) TMPT/TATAT (h) PETMP/TATAT. Experimental parameters - (-60 °C - 100 °C at 2°C/min, $f = 1$Hz, strain = 0.05%).
**Pendulum Impact Test of TENs**

Until now, impact behavior of unmodified TENs has not been investigated in such a way as to provide quantitative information regarding transmitted forces. To compare, across the board, a more qualitative pendulum impact test was performed on UV polymerized test specimens. This specific pendulum impact test has been used in previous investigations to measure percent of energy absorption for thiol-ene networks modified with acrylates and urethanes, but not unmodified TENs. During this investigation, many samples failed from this type of impact event, specifically those containing APE monomer. The lower $T_g$s, combined with lower packing efficiency, was insufficient for the more concentrated energies of the pendulum impact event. The tup is rounded and touches a relatively small surface area, theoretically leading to high localized pressures. Nonetheless, we are able to draw a few conclusions from this experiment.

Three of five thiol-ene samples studied absorb between 40 and 50% of energy from a 1.13J pendulum impact event Table 7. Systems which demonstrated this type of behavior had subzero $T_g$s, which in turn means that under ambient conditions such as room temperature, polymer networks are rubbery and elastic, beyond the range of effective viscoelastic relaxation (i.e. glass transition temperature range where $\tan \delta > 0.3$). Two systems which demonstrated superior pendulum impact properties were GDMP-TATAT and PETME-APE, which absorbed 89% and 74% of 1.13 Joules. Both of these systems had higher impact energy absorption compared with EVA, which under similar test conditions absorbs about 60% of the impact energy. This behavior was expected for GDMP-TATAT due to the temperature range where viscoelastic dissipation
is effectively overlapping with the testing temperature, having an upper limit of 22 °C (Table 8). The behavior of PETMP-APE was not so obvious. One way to possibly explain the observed behavior is to consider the high elastic modulus of PETMP-APE in the rubbery regime in combination with a glass transition region, which spans across the testing temperature. Therefore it is plausible that some viscoelastic dissipation is possible under the testing conditions of this experiment. We believe this effect is diminished when the amount of energy applied is higher and the method of impact is varied, as will be discussed below.

Table 7

*Summary of Impact Properties of Thiol-Ene Networks*

<table>
<thead>
<tr>
<th>System</th>
<th>DynaTup Peak Load (N)</th>
<th>Time to Peak Load (ms)</th>
<th>Pendulum Energy Absorption (% of 1.13 Joules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDMP-APE</td>
<td>4883±151</td>
<td>1.64 ± 0.06</td>
<td>shattered</td>
</tr>
<tr>
<td>GDMP-TATAT</td>
<td>5326±557</td>
<td>1.04 ± 0.4</td>
<td>89</td>
</tr>
<tr>
<td>TMPT-APE</td>
<td>6981±204</td>
<td>0.86 ± 0.07</td>
<td>49</td>
</tr>
<tr>
<td>TMPT-TATAT</td>
<td>8129±1112</td>
<td>0.80 ± 0.02</td>
<td>49</td>
</tr>
<tr>
<td>ETTMP700-APE</td>
<td>5564±821</td>
<td>1.46 ± 0.1</td>
<td>shattered</td>
</tr>
<tr>
<td>ETTMP700-TATAT</td>
<td>5985±364</td>
<td>1.15 ± 0.2</td>
<td>40</td>
</tr>
<tr>
<td>PETMP-APE</td>
<td>7613±205</td>
<td>0.62 ± 0.06</td>
<td>74</td>
</tr>
<tr>
<td>PETMP-TATAT</td>
<td>8712±904</td>
<td>0.60 ± 0.06</td>
<td>shattered</td>
</tr>
<tr>
<td>EVA</td>
<td>7686±111</td>
<td>0.75 ± 0.006</td>
<td>60</td>
</tr>
</tbody>
</table>
Table 8

*Effective Viscoelastic Region of Photopolymerized Thiol-Ene Networks*

<table>
<thead>
<tr>
<th>System</th>
<th>Effective Viscoelastic Relaxation Region(^{°C})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset</td>
</tr>
<tr>
<td>GDMP-APE</td>
<td>-34</td>
</tr>
<tr>
<td>GDMP-TATAT</td>
<td>0</td>
</tr>
<tr>
<td>TMPT-APE</td>
<td>-12</td>
</tr>
<tr>
<td>TMPT-TATAT</td>
<td>26</td>
</tr>
<tr>
<td>ETTMP700-APE</td>
<td>-36</td>
</tr>
<tr>
<td>ETTMP700-TATAT</td>
<td>-19</td>
</tr>
<tr>
<td>PETMP-APE</td>
<td>-3</td>
</tr>
<tr>
<td>PETMP-TATAT</td>
<td>42</td>
</tr>
</tbody>
</table>

* The effective viscoelastic region is defined as the temperature range where tan δ ≥ 0.3.

*Correlation of DynaTup Impact Properties to Glass Transition Temperature*

While the pendulum impact test allows us to compare these systems to other systems in the literature, it is qualitative and a mere snapshot of an impact event solely at the beginning and end. A more detailed analysis is realized using a drop system such as the DynaTup. From this test we obtained not only the energy absorbed, but we also gained insight into how the energy from an impact event is managed by each polymer system while controlling variables such as weight, impact velocity, tup shape and size and energy. Because there are often dimensional limitations on damping materials we
utilized 4mm thick slabs and 4.4 Joules of impact energy because this is the most appropriate thickness for a mouthguard and this energy was previously used to test impact properties of 4mm thick EVA. Load responses were plotted against time constructing impulse curves for TENs and an EVA standard. The values recorded for EVA were in line with previously published data\textsuperscript{77} and we were confident about measured values for our TEN systems.

Peak force recorded for TEN formulations were 4974, 5441, 7075, 8791, 5613, 6276, 8201, 10580, and 7957 N for GDMP-APE, GDMP-TATAT, TMPT-APE, TMPT-TATAT, ETTMP700-APE, ETTMP700-TATAT, PETMP-APE, PETMP-TATAT, respectively. To determine the effect of $T_g$ on impact performance we plotted peak load versus $T_g$ for all thiol-ene systems. Impact performance of the materials was directly related to $T_g$ such that systems with low $T_g$s demonstrated low peak performance values and those with high $T_g$s had higher peak loads. The two variables were correlated in an apparent linear fashion initially with minor discrepancy at the two extremes of $T_g$ (Figure 29). It stands to reason that the location of the glass transition temperature would indeed affect impact performance due to the large span of temperature dependent relaxations in polymer systems. For glassy networks, modes of dissipation are frozen out while systems with lower $T_g$s have more molecular mobility. The ability or inability for polymer segments to move and dissipate energy is the difference between energy being absorbed and mechanical failure.

GDMP-TATAT demonstrated anomalous behavior compared to the other TENs. We may consider this network formulation a special case because of the temperature associated with the effective viscoelastic relaxation region (given by the tan $\delta$ peak in
DMA), which is approximately between 0 °C – 22 °C (Table 8). This behavior is similar to what was observed in pendulum impact results and is again attributable to extra modes of energy dissipation via viscoelastic dissipation (Figure 29). Again we reiterate GDMP-TATAT performs optimally at ambient temperatures due to the fact that the testing temperature falls within the network glass transition region where tan δ is greater than 0.3. When compared to EVA, TENs with relatively similar T_g's demonstrate lower peak load values or better impact performance for this test type. We believe the higher peak load values of EVA material originate in its underlying network morphology. The crystalline domains of EVA are rigid with respect to its amorphous domain and the physical cross-links prohibit motion. EVA is represented on Figure 29 as point A and GDMP-TATAT is represented as point B.
Figure 29. Peak load versus $T_g$ for TENs. Peak load was measured using a DynaTup (Instron, Norwood, MA) a d = 2.5” steel drop dart and 88kN load cell. Samples were discs d = 2”, thick = 4 mm placed atop a hardened steel plate, where impact mass = 5.6 kg, drop height = 0.08 m, impact energy = 4.4 Joules and impact velocity = 1.25 m/s. Point A is representative of an EVA mouthguard material and point B is GDMP-TATAT.

The dependence of Impact Performance on $M_c$ and Monomer Rigidity

To further investigate the crowded region on Figure 29 at lower glass transition temperatures, a plot of peak load versus $M_c$ was constructed (Figure 30). $M_c$, which is related to $T_g$, is related to a length scale with respect to damping processes. Tighter networks have more junction points per unit volume and less linear chains between junction points for dissipating events to propagate between these junction points. Based on the resulting curve we observe two behaviors: (1) Systems synthesized with the more rigid TATAT monomer have higher peak loads in general and (2) regardless of the systems, at some critical $M_c$ value impact behavior becomes independent of $M_c$. 
The first behavior is likely due to polymer density, which is in turn related to the packing efficiency of the monomers. Upon the impact event, waves of energy propagate through the material, and if chain segments are mobile, this energy is absorbed by way of molecular motions. In contrast, more rigid systems would tend to restrict motions decreasing damping processes. The second observation that a threshold exists whereby impact performance becomes independent of $T_g$ can be explained by a length scale phenomena. In the spirit of the Rouse model, an applied force at the end of the chain will dissipate as it propagates down the chain. In a network, if the linear region between junction points is long enough, the energy will dissipate before reaching the next junction point. Under this condition, the relaxation becomes effectively like a thermoplastic, and the number of elastically effective chains would vanish. This is described by the following equation wherein $\Delta$ describes the natural logarithmic damping behavior of a material where the beginning amplitude is $A_n$ and the sequential amplitude is $A_{n+1}$. This function is also related to $\tan\delta$ so that when $\tan\delta$ is high, $\Delta$ increases. To this extent when $\tan\delta$ is highest, at the glass transition temperature, polymer damping is maximal.

--- [5]

[6]

We believe that the effect at high $M_c$ is similar to this analogy; that by increasing $M_c$ values, the effects of the junction points within the networks become less evident. Lower peak load values associated with GDMP-TATAT could be explained by a synergistic effect of high $M_c$ and viscoelastic dissipation. It should also be noted that systems with high $M_c$ might appear to be excellent choices for damping materials based on peak load, but the lack of mechanical robustness or structural integrity of many
loosely cross-linked TENs in this region is not sufficient for realistic application without some improvement in toughness first.

![Graph showing peak load versus M_c](image)

**Figure 30.** Peak load versus M_c. Peak load was measured using a DynaTup (Instron, Norwood, MA) a d = 2.5'' steel drop dart and 88kN load cell. Samples were discs d = 2'', thick =4 mm placed atop a hardened steel plate, where impact mass = 5.6 kg, drop height = 0.08 m, impact energy = 4.4 Joules and impact velocity =1.25 m/s. The line is a guide to the eye.

**Frequency Dependence and Damping Effects of TEN’s**

It is well known that the glass transition temperature is frequency dependent such that at higher frequency, T_g shifts to higher values. This could significantly impact damping as the damping is going to occur at a specific temperature. If we know how the glass transition temperature shifts with increasing frequency, it would provide a better idea about the actual use conditions of the material. A simple plot of the natural log of the frequency versus inverse T_g would reveal the activation energy of the glass transition, Equation 7. Furthermore, the dissipated heat, Q, can be directly measured from DMA analysis at one specific temperature utilizing stress, strain and delta for one cycle. Here
we measured the heat dissipation of TMPT-TATAT at 38 °C, or intraoral temperature. Notice that this equation is solely dependent on the loss modulus, $E''$, due to the sin component. To compare the values to experimental data, we have shown the $E''$ vs temperature plot of TMPT-TATAT at four frequencies: 0.1, 1, 10 and 100 Hz.

Figure 31 demonstrates a shift toward higher temperatures at higher frequencies. The change in temperature for most systems was about 7 degrees higher with each chance in decade with respect to frequency. The $E_a$ of the glass transition temperature was determined from the slope of the $\ln f$ versus $1/T_g$ plot. The systems demonstrated $E_a$ values between 200 and 300 kJ/mol. These are typical $E_a$ values for the glass transition temperature. There was no apparent correlation between network cross-link density and $E_a$. Additionally the heat dissipated during an impact event or DMA experiment can be calculated knowing the stress, strain and phase shift, $\delta$, at any one period of a DMA experiment. Here we calculated heat dissipated at 38 °C (intraoral) temperature for TMPT-TATAT. We specifically chose this system due to the overlap of viscoelastic dissipation and the temperature of interest. We found that there is a direct correlation of heat dissipated and $E'$. As the frequency increases, $E''$ at 38 °C increases, consequently $Q$ increases (Figure 32). However at much higher frequencies, the $E''$ peak would lie outside the range of 38 °C and damping would trend down to zero. This is a highly relevant tool for finding optimal conditions for a damping system.
Figure 31. (left) Tan δ versus temperature for thiol-ene networks, ETTMP700-TATAT, GDMP-TATAT and TMPT-TATAT at 0.1 (ETTMP700-TATAT only), 1, 10 and 100 Hz. (right) natural log of frequency versus tan δ max.
Figure 32. (top) $E''$ versus temperature for TMPT-TATAT at 1, 10 and 100 Hz. (bottom) heat dissipation ($Q$) at 38 °C for TMPT-TATAT at 1, 10 and 100 Hz.

Energy Management of Thiol-Ene Networks: Glassy, Rubbery and Transition Systems

The time dependence of an impact event is important for damping material. Ideally when an impact spans over a longer period of time, the peak force values are lower and the material absorbs more energy. To compare characteristic impulse
properties to a commercial damping material we first measured the impulse properties of EVA (Figure 33). The average peak load value of EVA was 7686 N which was similar to literature values reported for the same energy and similar impact surface (4.4 Joules).\textsuperscript{77} Time to peak force for EVA was 0.75 seconds on average which was higher than any of the TENs having a subzero glass transition temperatures. The semicrystalline morphology of EVA is most likely responsible for the shorter time response and high peak load values. In fact, the Shore A hardness values of EVA is more comparable to TENs with higher $T_g$ values such as PETMP-APE or PETMP-TATAT which have $T_g$s of 5 °C and 53 °C. Therefore even though the $T_g$ of EVA is below zero, the crystalline domains effectively harden the material, which proves to have a negative effect on impact behavior and stress management.

The impulse curves of TENs demonstrated clear trends in terms of time to peak load and total impact time. Systems having subzero glass transition temperatures, GDMP-APE, ETTMP700-APE and ETTMP700-TATAT, demonstrate the highest times to peak force, 1.64, 1.46 and 1.15 ms respectively (Figure 34). This is likely due to deformation of the material under compression. Other systems that have glass transition temperatures approaching and greater than room temperature had time to peak force values approximately one millisecond or less. The correlation between time to peak force and glass transition temperature is not unexpected. Higher $T_g$ systems would be more glassy and display less physical deformation upon an impact event whereas lower $T_g$ systems would respond more elastically. The elastic nature of the rubbery systems would translate to an extension of the time response under compression, or higher strains during
an impact event. The peak forces trend directly, whereby lower peak forces correlated to longer times and vice versa.

**Figure 3.** Load versus time curve for ethylene-co-vinylacetate (EVA), (Ortho Technology, Tampa, FL) Shore A Hardness = 85 Peak load was measured using a DynaTup (Instron, Norwood, MA) a d = 2.5” steel drop dart and 88kN load cell. Samples were discs (d = 2”, thick =4 mm), impact mass = 5.6 kg, drop height = 0.08 m, impact energy = 4.4 Joules and impact velocity =1.25 m/s.

Between systems (excluding GDMP systems for previously described reasons), we notice total time of the impact event is on average shorter for TATAT-based networks. This is likely an effect of higher T_g values realized from the rigid TATAT monomer considering M_c values are similar between systems This effect is not as evident for PETMP-based systems, but the higher T_g system (PETMP-TATAT) has slightly higher average peak load values. As suggested from Figure 29, the relationship between peak load and T_g at higher temperatures seem to deviate from linearity. The deformation and energy absorption of many TENs appear to be multimodal, becoming more prominent in higher T_g systems (Figure 34). The reason for this behavior is unknown and beyond the scope of this research; however what is observed is that TENs with T_g values comparable to
EVA have lower peak forces such as 5564 N, and 6981 N for ETTMP700-TATAT and TMPT-APE as compared to 7686N for EVA. The lack of crystalline domains and cross-linked nature of TENs give them a significant advantage over thermoplastic EVA and these appear to be ideal systems for future investigations for damping polymers.
Figure 34. Load versus time curve for UV polymerized TENs. Peak load was measured using a DynaTup (Instron, Norwood, MA) a d = 2.5” steel drop dart and 88kN load cell. Samples were discs (d = 2”, thick =4 mm), impact mass = 5.6 kg, drop height = 0.08 m, impact energy = 4.4 Joules and impact velocity =1.25 m/s.
Conclusions and Future Work

In this research study we investigated the impact properties of unmodified thiol-ene networks with similar $M_c$ values and differing monomer rigidity. In turn, we demonstrated a broad range of $T_g$s achievable via the UV photopolymerization of commercial thiol and alkene monomers. We correlated the effect of the rigid monomers with respect to $T_g$ and impact properties. Most importantly, we were able to demonstrate the relationship between $T_g$ and peak load of an impact event. The effects of junction points and impact performance were also explored and a critical length scale of dissipation was determined based on peak load values with respect to $M_c$. Time to peak load was lower for higher $T_g$ systems while networks with $T_g$s comparable to EVA demonstrated much lower peak load values. The higher peak load values of EVA is likely an effect of the rigid crystalline domains of the semi-crystalline polymer which. Impact properties of TENs appear to be fairly predictable unless the testing temperature overlaps the temperature range wherein viscoelastic dissipation is effective.

Until now, a platform for impact properties for TENs has not been established. Research from this investigation can be utilized in future studies to determine specific systems for damping applications at various temperatures. Additionally, we have gained a better understanding of the expected impact performance for a network outside its viscoelastic relaxation region and the effective length scale of damping. Although damping by viscoelastic relaxation is clearly evident, not a lot is known about maximal impact performance and $\tan \delta$ values. In this study maximum energy absorption via pendulum impact test was 89%. Other systems have higher reported values, but these systems were tested at the peak of $\tan \delta$. Whether a correlation between the peak value of
tan δ and peak load and energy absorption is exists is not known. Additionally, the amount of energy absorption attributable to viscoelastic relaxations, effects of network thickness and temperature departure from $T_g$ has not been determined for these systems, but these systems seem ideal to study for these purposes.
CHAPTER V
HIGHLY TUNABLE THIOL-ENE NETWORKS VIA DUAL THIOL ADDITION

Abstract

Throughout the past decade investigations of thick thermoset thiol-ene networks (TENs) have become increasingly prominent in literature due to facile, quantitative synthesis giving way to unique network characteristics, specifically high mechanical energy damping. Network glass transition temperature is highly indicative of the mechanical damping behavior of these systems. This relationship between glass transition temperature and damping has lead several researchers in the direction of gaining tunability of the glass transition temperature without affecting bulk properties or synthetic ease. Various methods such as acrylate and urethane incorporation into TENs have been investigated; however new matrix characteristics were inherently different compared to native matrices. For example, changes in the breadth and height of the tan δ vs. temperature curve were observed. Resolving a method that will achieve tunability of the glass transition temperature (T_g) without sacrificing other desirable properties (such as breadth of the transition region) is a key component to utilizing bulk TEN’s over a wide array of applications. In this study, a base TEN system was modified with a second thiol component. Ternary TENs containing two thiols, one difunctional and one trifunctional, of varying stoichiometric ratios (0/100, 20/80, 40/60, 60/40, 80/20 and 100/0) were synthesized by UV polymerization reacting the thiols with a trifunctional vinyl monomer (TATAT) in hopes of achieving networks with varying but predictable T_g's. The second thiol components (all difunctional), GDMP, PPGMP800, or PPGMP220 were expected to decrease the cross-link density and therefore decrease T_g of such
networks. Kinetics, thermal, and thermomechanical properties were investigated by RTFTIR, DSC, TGA, and DMA. The \( T_g \) values investigated using DMA showed that network glass transition temperatures could achieve a range of temperatures between -23 \(^\circ\)C and 59 \(^\circ\)C while DSC results demonstrated similar results show an obtainable range between -41 \(^\circ\)C and 35 \(^\circ\)C. The relationship between \( T_g \) and thiol composition appears to follow the Fox equation. Other thermomechanical analysis proves increasing thiol monomer molecular weight of the second component decreased network cross-link density. Polymer degradation temperatures varied between 343 \(^\circ\)C and 369 \(^\circ\)C and were related to cross-link density. As the dual thiol ratio approached 1:1 the full width at half-maximum slightly broadened for systems containing both PPGMP800 and PPGMP2200. RTFTIR analysis shows that all networks reach near quantitative yields, even with the presence of a second thiol component. Finally, we have shown that the glass transition temperature can be controlled by way of a second thiol component. This approach has high potential as simplistic tool for scientists and researchers in other fields to tune \( T_g \)s for select systems without detrimentally affecting fundamental thiol-ene polymerization expectations.

**Introduction**

Thiol-ene networks (TENs) are developed from facile photo-polymerization synthesis and demonstrate impeccable energy damping characteristics at the glass transition temperature due to their uniquely uniform crosslink densities. Synthesized via a “click” reaction between thiol and ene functionalities, TENs are the end product of a unique series of mechanism steps which proceed following initiation of monomers. More specifically, thiols readily react with pendent vinyl groups or enes via a radical-
step-growth reaction mechanism.\textsuperscript{13, 14} Upon UV irradiation of a photoinitiator, radicals are formed and abstract labile thiol protons, generating thyl radicals which sequentially add across a carbon-carbon double bond producing carbon-centered radicals. The carbon-centered radicals abstract protons from a second thiol resulting in anti-Markovnikov addition across a vinyl group and a newly formed thioether linkage. The nature of this rather less popular mechanism is the foundation of very unique system properties.\textsuperscript{26, 30} For example, contrary to other radical polymerization processes, significant molecular weight growth and gelation are delayed until the end of the polymerization process, yielding low-stress and highly uniform networks.\textsuperscript{9, 44} The networks are formed quickly, often within seconds and are often highly cross-linked, but like other cross-linked networks, they are plagued with low elongation and brittle nature.

Traditional and commercial applications for UV cured TENs are well established throughout coatings industries; nonetheless thick thermoset thiol-ene networks are still in developmental stages and are investigated for a vast number of nontraditional applications such as in biomedical devices, composites and dental restoratives.\textsuperscript{18, 45, 99, 112-115} In addition to aforementioned uses, the role of TENs in high performance sports protective equipment is rapidly gaining attention because of their unique network properties having led to proven performance in energy damping applications such as pendulum tests and even bullet proof testing.\textsuperscript{43, 48, 74, 90, 116} It was demonstrated by Gould and coworkers that mechanical energy damping of TENs relate directly to the respective glass transition temperature ($T_g$) (determined by tan $\delta$ versus temperature curves from Dynamic Mechanical Analysis) with maximum benefits occurring when the temperature of testing was equivalent to the $T_g$.\textsuperscript{68, 69} This phenomena was also observed for TENs by
McNair and coworkers (in preparation) when novel TENs were impacted and absorbed energy measured and plotted versus temperature. The networks proved capable of up to > 90% mechanical energy absorption at the maximum of the tan δ versus temperature curve.

\( T_g \) is a critical polymer property for scientist and engineers. This temperature range, which denotes the onset of long range segmental motion within a polymer system, often determines applications a polymer is suitable for. This value is typically narrow for TENs indicating the highly uniform nature of the network. From previous studies, \( T_g \) and other measured thermal and thermomechanical properties were investigated with respect to monomer structure of both thiol and ene components and cross-link density and as expected, higher monomer functionality leads higher \( T_g \) networks and vice versa.\(^{24}\) As aforementioned this is an important factor for protective equipment due to the correlation between \( T_g \) and damping behavior and therefore it is highly desirable and critical nonetheless to gain a synthetic handle to control both the breadth and maximum value of this region without sacrificing the integrity of the network.

A common approach to manipulate thiol-ene network properties is incorporating a third component such as acrylates and urethanes. Three-component or ternary TENs were synthesized in order to enhance polymer versatility but maintain the desirable properties of thiol-ene components. These three-part systems demonstrated hybrid network properties.\(^{41, 46, 101, 117-121}\) For example, networks with acrylate monomers had broader \( T_g \)s and were brittle, and those with added isocyanates were tougher. Acrylates are commonly polymerized via a UV initiated polymerization reaction marked by an inhibition period, early onset of gelation and high shrinkage. The copolymerization of
acrylates with alkenes yields networks with increased homogeneity, reduced oxygen inhibition, reduced shrinkage and lower stress systems. One drawback of this approach is incomplete network formation which occurs due to additional cross-polymerization of enes (intended to reach with thiols) and acrylate monomers and also homopolymerization of acrylates. In other words, acrylate monomers react with thiol monomers and with themselves consequently leading to incomplete network formation and phase separated networks. To develop a system having stoichiometric balance with acrylates would therefore seem nearly impossible. Nonetheless there was a clear association between acrylate content and $T_g$ with $T_g$, increasing from -10 °C and 70 °C as acrylate content increased but breadth of the $T_g$ region and maximum tanδ values were greatly compromised. 

Urethanes as a third component has been achieved both by (1) synthesis of novel urethane-based monomers and (2) one pot dual and simultaneous curing reactions. The former method is somewhat challenging due to mixing issues with high viscosity urethane monomers, while the latter is still under investigation.

Thiourethane or urethane linkages are desirable for enhancing mechanical properties of TENs. $T_g$ also ranges greatly with respect to isocyanate content represented by a 40 °C range in investigated systems. However, these methods complicate what could be a simple UV polymerization with highly desirable properties.

A ternary system whereby the third component is a second thiol to our knowledge has not been studied. In this paper we will explore network properties of TENs composed of two thiol monomers reacted simultaneously with a vinyl monomer via traditional UV photopolymerization. Specifically we will study how the structure of the second thiol component will alter the glass transition temperature, its range, maximum tan δ values in
addition to other thermomechanical properties such storage modulus, loss modulus, and cross-link density respectively. Ideally, the glass transition temperature would show predictable behavior and the breadth of the $T_g$ would increase without affecting the kinetics nor excellent properties of the thiol-ene networks. Additionally, the relationship between copolymer composition and $T_g$ will be sought after and retrofit to the Fox equation.

Experimental

Materials. Glycol di(3-mercapto propionate) (GDMP) and propylene glycol (3-mercapto-propionate) of two molecular weights, approximately 800 g/mol and 2200 g/mol (PPGMP800 and PPGMP 2200, respectively,) were graciously donated by Bruno Bock Thio-Chemicals-S. The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) was purchased from Sigma Aldrich. Trifunctional vinyl and thiol compounds, 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATAT), and trimethylolpropane tris(3-mercaptopropionate) (TMPT), were also purchased from Sigma Aldrich. All thiols, enes, photoinitiator, and catalysts were used without further purification. Structures for all materials used in this study are shown in Figure 35.

Sample Preparation. Dual thiol networks were synthesized by dissolving 0.5 wt. % DMPA (of total weight) in thiol or thiol mixtures, followed by addition of TATAT (the ene component) and mechanical mixing. Caution was taken to protect the mixtures from any sources of light during mixing. The stoichiometry of functional groups for total thiol (-SH) and ene (-C=C) was 1:1 for all mixtures. The mixtures were poured into silicon molds and passed under a UV Fusion line EPIQ 6000 fit with a D bulb and energy output
of 453 mJ/cm² and belt speed of 19 ft/min a total of 10 times. Following UV irradiation, samples were thermally post-cured at 90 °C for 24 hours to ensure fully cured networks.

**Figure 35.** Molecular structures of (a) Glycol di(3-mercaptopropionate) (b) Trimethylolpropane tris(3-mercaptopropionate) (c) Propylene glycol (3-Mercapto-propionate) (MW ≈ 800 g/mol) (d) Propylene glycol (3-Mercapto-propionate) (MW ≈ 2200 g/mol) (e) 1,3,5-Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione and (f) 2,2-Dimethoxy-2-phenylacetophenone.

**Kinetic Analysis.** Representative kinetic analyses were conducted using real-time FTIR (RT-FTIR) spectroscopy for binary formulations of thiol/ene (50/50 mol %) and ternary formulations of thiol/thiol/ene (25/25/50 mol % of functional groups,
stiochiometrically balanced with respect to total thiol and ene functional groups). Studies were carried out using a Nicolet 8700 FTIR spectrometer having a KBr beam splitter and MCT/A detector. An OmicCure Exfo 1000 Series external light source provided filtered UV light in the range of 320-500 by way of a guided optical cable. Spectra were collected at an approximate rate of 1 s\(^{-1}\) over a range of 650-4000 wavenumbers (cm\(^{-1}\)). Following a ten second rest period, the sample was irradiated with a UV light with intensity of 25 mW/cm\(^2\) while conversion of both thiol and ene functional groups was monitored. The peak corresponding to the S-H stretch was found to shift slightly with each different formulation (TMPT-TATAT, 2572 cm\(^{-1}\), GDMP-TATAT, 2573 cm\(^{-1}\), PPGMP800-TATAT, 2569 cm\(^{-1}\), TMPT-PPGMP2200-TATAT, 2575 cm\(^{-1}\)). The C=C stretch from the ene component remained nearly unchanged at 3084 cm\(^{-1}\). The total time of experiments was 320 s and all experiments were carried out under N\(_2\) at ambient temperature.

**Thermal and Mechanical Testing.** Thermomechanical properties were measured via dynamic mechanical analysis (DMA) using a TA Instruments Q800 DMA. Rectangular specimens with dimensions (ca. 6 mm ± 0.5 mm × 5 ± 0.05 mm × 0.5 mm ± 0.05mm) (length × width × thickness) were deformed in tension mode at a frequency of 1 Hz in air. The thermal history consisted of cooling to -40 °C followed by a two minute isothermal step, then heating to 100 °C at 5 °C/min while a strain of 0.05% was applied. Storage modulus, loss modulus and tan δ, were measured concurrently as a function of increasing temperature.

Thermal properties were determined via differential scanning calorimetry (DSC) using a TA Instruments Q2000 DSC. Thermal transitions were measured using samples
(6 mg ± 1 mg) placed into standard aluminum pans against a blank aluminum pan under nitrogen gas with a 50 mL/min flow rate. The samples were initially heated at 10 °C/min to 100 °C, remaining there 5 minutes to erase thermal history. The samples were then cooled to -70 °C at 10 °C/min, held and heated at the same rate to a final temperature of 140 °C. The glass transition temperature was measured from the second heating cycle.

Thermogravametric analysis (TGA) was performed with a TA Instruments Q500 TGA. Samples with mass 10 mg ± 1 mg were placed in a platinum pan and equilibrated at 40 °C, then heated at a rate of 10 °C/ min to 800 °C. The polymer degradation temperature was recorded as the peak value in the first derivative of weight loss vs. temperature curve. All samples were tested under a nitrogen purge with a flow rate of 40 mL/min. All instruments for thermal and thermomechanical analysis were calibrated prior to conducting tests on samples.

Results and Discussion

The ultimate goal of this research was to develop TENs that with tunable $T_g$s by way of a third thiol component without compromising desirable TEN characteristics. In order to fully understand the systems, kinetic analysis was performed followed by various thermal and thermomechanical testing. Herein we report our findings from our initial set of experiments. Figures36 and Figure 37 show kinetic conversion of functional groups via real time FTIR. Figures 38-39 focus on the tunability of the networks by measuring the $T_g$ using DSC and DMA. Figure 40 is representative of the relationships between $T_g$ and weight % of additive addition and ultimately represents the degree of control associated with this method. Figure 6 and Table 1 describe various measured variables while figures 7 and 8 display unexpected findings.
Comparison of kinetics. Real-time FTIR (RT-FTIR) was used to monitor the kinetics and conversion of thiol and ene moieties in the formation of TENs. Figure 36 shows the conversion as a function of time for binary systems of TATAT and the four thiols used in these studies. In general, the conversion of thiol and ene groups were consistent. In all cases there was negligible conversion until the sample was illuminated with UV radiation, upon which all samples reached maximum conversion after ca. 120 sec. It should be noted the thiol peak for PPGMP2200/TATAT formulation had very low intensity due to the low –SH concentration; therefore kinetic analysis was performed based solely on the ene conversion. Overall, conversion for the neat binary networks based on TMPT, GDMP, PPGMP800, or PPGMP2200 (reacting 1:1 stoichiometrically with TATAT) were 86%, 98%, 100% and 98%, respectively. For most systems, near quantitative conversions were achieved with the exception of the TMPT-TATAT native matrix. Both TMPT and TATAT are trifunctional, forming higher cross-linked, dense networks. It is not uncommon for higher functional group containing networks to fail to reach complete network cure due to proximity of reacting groups. 24

For ternary dual-thiol TENs, thiol content was manipulated by gradually decreasing TMPT content and increasing a second, difunctional thiol content, while maintaining stoichiometrically balanced systems. Kinetic profiles of ternary TENs are shown in Figure 37, where the observation of a single –SH peak represents the sum of the two distinct thiols. For each system, half of total thiol content was from TMPT, while the other half was GDMP, PPGMP800, or PPGMP2200. An equimolar amount of ene functional groups from TATAT was added to make stoichiometrically balanced systems. It is observed that the rate of the thiol-ene reaction is still remarkably fast; however all of
the conversions drop for the ternary TENs. The largest change in conversion (98 to 91%) occurred for the GDMP/TMPT/TATAT system, and the other two ternary TENs only showed small changes in conversion. Presumably the lower conversion observed in the TMPT/TATAT binary TENs above mean that the incorporation of TMPT and the corresponding increased crosslink density result in a slightly lower overall conversion in ternary networks. Nonetheless, the formation of ternary TENs yields high conversion with rapid kinetics upon illumination.

Figure 36. RTIR thiol and ene conversion for unmodified, stoichiometrically balanced, 1:1, formulations consisting of (a) TMPT-TATAT, (b) GDMP–TATAT (c) PPGMP800-TATAT and (d) PPGMP2200-TATAT in N₂ and 0.5 wt. % DMPA (Light intensity = 25 mW/cm²). Note: Thiol absorbance was miniscule for PPGMP2200-TATAT formulation, therefore only ene (–C=C) conversion of TATAT monomer is shown for that system.
Figure 37. RTIR thiol and ene conversion for networks from stoichiometrically balanced mixtures of thiols and ene formulations consisting of (a) TMPT-GDMP-TATAT, 25:25:50, (b) TMPT-PPGMP800–TATAT, 25:25:50 (c) TMPT-PPGMP2200-TATAT, 25:25:50 in N2 and 0.5 wt. % DMPA. (Light intensity = 25 mW/cm²).

Highly Predictable Glass Transitions Temperature of Ternary TENs

One of the key advantages of TENs is their high mechanical energy damping (characterized by a high mechanical loss, i.e.: tan δ) over a narrow temperature range (characterized in terms of the width of the glass transition region) due to high network uniformity. The challenge has been to design formulations whereby the glass transition temperature can be tuned while retaining the high mechanical loss.
Figure 3 presents tan δ results from DMA for stoichiometrically-balanced ternary systems containing (a) GDMP/TMPT/TATAT - (b) PPGMP800/TMPT/TATAT as a function of temperature at varying thiol composition. The composition in this case corresponds to the mol % of thiol groups coming from GDMP or PPGMP800, respectively, in the ternary formulation. The concentration of thiol groups from TMPT is then adjusted to maintain stoichiometric balance with TATAT ene groups. In both cases, the tan δ\textsubscript{max} shifts to decreasing temperatures with decreasing TMPT content. For example, the binary network containing TMPT/TATAT has a tan δ\textsubscript{max} at 59 °C. As the TMPT component is replaced with GDMP, the tan δ\textsubscript{max} steadily decreases to 23 °C, observed for the binary system of GDMP/TATAT. Similarly, replacing the TMPT with PPGMP800 steadily decreases the tan δ\textsubscript{max} to -23 °C, consistent with the PPGMP800/TATAT binary system. TENs containing PPGMP2200 exhibited phase separation, as we discuss later.

The same formulations tested by DMA were also investigated by DSC. After a brief annealing of the systems to erase thermal history, a second temperature ramp was conducted to investigate the T\textsubscript{g}. As expected, results similar to DMA were found from DSC scans. Figure 39 presents DSC thermograms for stoichiometrically-balanced ternary systems containing (a) GDMP/TMPT/TATAT and (b) PPGMP800/TMPT/TATAT as a function of temperature at varying thiol composition. The native TMPT/TATAT binary matrix exhibits a T\textsubscript{g} of 35 °C, and the incorporation of the second thiol (GDMP or PPGMP800) decreases the T\textsubscript{g} to 5 °C or -41 °C, respectively. PPGMP 2200 DSC data is not included due to the very low glass transition temperatures of ternary systems that lie outside the range of the DSC instrument used.
In ternary thiol/thiol/ene networks, the highest \( T_g \)s are observed in the networks with the highest crosslink density (TMPT/TATAT) as expected. Replacing the ternary thiol TMPT with a dual thiol (GDMP or PPGMP800) reduces the \( T_g \) in concert with the average crosslink density. To a first approximation, using thiol mixtures in the TENs is effectively like incorporating a statistical copolymer into the network. The relationship between the glass transition temperature and the composition of a second additive has been investigated for many systems including miscible polymer blends and statistical copolymers, and has been found to follow the Fox equation.\(^5,122\)

\[
\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}
\]

Where \( T_g, T_{g,1} \) and \( T_{g,2} \) correspond to the blend, component 1 and component 2, respectively, and \( w_1 \) and \( w_2 \) are the weight fractions of each component. In this treatment, we are assuming that the thiol/thiol/ene mixture produces a statistically-random network.

As mentioned before, the Fox equation generally applies to polymer blends and statistical copolymers which we clearly do not have here in either case, however, neglecting the cross-links, the resulting systems are very similar to a statistical copolymer system. Similar monomer reactivity and fast kinetics are two reasons we determined the system could be treated as a statistical copolymer system. The fit of the data to the Fox equation for ternary GDMP and PPGMP800 systems can be seen in Figure 40. Although Figure 40 shows a respectable correlation, a linear fit of the data shows a remarkable
parallel, especially for ternary TENs containing PPGMP800. Because of the promising findings it would be interesting to determine how other networks behave in this respect.

Typical TENs possess narrow $T_g$s due to uniform networks from a series of unique reaction mechanisms. The full width half max (FWHM) of the native matrix PPGMP800-TATAT is 12 °C and increases to 24 °C at 40 mol% PPGMP800. In both cases, adding a second thiol component increased the FWHM for the networks but this effect was less pronounced for TMPT-GDMP-TATAT TEN only increasing the FWHM by 5 degrees (See Table 9); Briefly, similar behavior was observed with TMPT-PPGMP2200-TATAT however data was only available over a limited range. This effect leads us to believe network uniformity is sacrificed with larger fractions of a second thiol component, even if the second thiol component has a similar reactivity. The uniformity must be dependent on the structure and similarity of monomers. Additionally, mechanical energy damping capabilities of any material is said to increase with increasing peak tan $\delta$ values above some critical point, however additional experiments are required to provide concrete evidence for this statement for these systems in particular. What remains true is that energy dissipation, regardless of its value, is maximum at the temperature corresponding to the peak of the tan $\delta$ versus temperature curve.
Figure 38. Tanδ vs temperature curves for stoichiometrically balanced ternary thiol ene networks consisting of a base thiol (TMPT) and a second thiol additive A (GDMP) and B (PPGMP800). Symbols represent mol % of each additive as follows: (■ - 0%, ● – 20 mol%, ▲ - 40 mol%, ▼ - 60 mol%, ◆ - 80 mol% and □ - 100 mol%).
Figure 39. DSC thermograms for ternary TENs containing stoichiometric mixtures of thiols (TMPT+ additive) where additives were A) GDMP and B) PPGMP800. The mol\% of thiol additive was varied as such: (a) 0 mol\%  (b) 20 mol\%  (c) 40 mol\%  (d) 60 mol\%  (e) 80 mol\% and (f) 100 mol\%. The glass transition temperature was measured from the second heating scan at 10 °C/min.
Figure 40. Glass transition temperatures with respect to increasing weight % of either GDMP or PPGMP800. Graph (A) represents experimental data fit to a line while graph (B) represents the same data fit to the Fox equation. Points represent experimental data and lines represent models.

**Thermomechanical Properties of Ternary TENs**

Other thermal and thermomechanical analysis reveals important features of the networks. The rubbery modulus, taken from the post $\alpha$ transition storage modulus, $E'$, value is directly related to the cross-link density of the networks such that the higher the modulus, the lower the molecular weight between cross-links and consequently the higher the cross-link density. For all the systems the crosslink density decreased with
increased mol% of the second thiol additive as expected when incorporating a network component with lower functionality. This observation is greatly influenced by the higher molecular weight additives, PPGMP800 and PPGMP2200. For example, adding 40 mol% GDMP, PPGMP800 and PPGMP2200 leads to plateau E’ values of 11, 7, and 1 MPa respectively. Loss modulus, or E’’, of the system theoretically correlates with the tan δ max value. As the elastic character (E’) decreases, the viscous component (E’’) becomes dominant. For all systems, a peak in the E’’ occurs as E’ decreases; therefore we can conclude E’’ correlates with tan δ and is representative of a true α transition, or Tg. A summary of all thermal and thermomechanical analysis is listed in Table 9.
Table 9

Summary of Thermal and Thermomechanical Properties of Dual Thiol Networks

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$T_g, \tan\delta$ (°C)</th>
<th>$T_g, DSC$ (°C)</th>
<th>Fwhm (°C)</th>
<th>$E'_{rubber}^*$ (MPa)</th>
<th>$E''_{max}$ (°C)</th>
<th>$T_{deg}$ (°C)</th>
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<tr>
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<td>14</td>
<td>12</td>
<td>41</td>
<td>369</td>
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<td>13</td>
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* Rubbery storage modulus measured at 60 °C, 50 °C and 40 °C for systems containing GDMP, PPGMP800 and PPGMP2200.

Thermal Stability Reduce with Decreasing Cross-link Density

Polymer degradation temperature directly relates to thermal stability of the networks. Thermogravimetric analysis provides insight to the effects of monomer structure and polymer composition on the ultimate material decomposition. Figure 41 shows how thermal stability decreases with increasing mol % of thiol additives GDMP, PPGMP800 and PPGMP 2200. While GDMP decreases in a somewhat linear fashion, PPGMP800 and PPGMP2200 ternary systems appear to decrease in thermal stability.
exponentially. This is likely due to the decreased crosslink density of these networks in conjunction with the high volume fraction of the higher molecular weight fraction when compared to GDMP. The native TMPT-TATAT network has a degradation temperature of 366 °C and other neat matrices, GDMP-TATAT, PPGMP800-TATAT and PPGMP2200-TATAT, show much lower T_{deg} values of 362, 347 and 343 °C. To ensure residual monomer or depolmerization was not the cause for the extreme differences, thermal stability of pure, non-reacted, monomers was measured. The degradation temperatures of GDMP, PPGMP800, PPGMP2200 and TATAT were 216 °C, 333 °C, 341°C and 195 °C all lower than any network. This suggests the cross-link density, and monomer composition greatly affects thermal stability as longer chain monomers have a greater affluence on thermal stability of the networks, composing a large volume fraction of networks overall at higher values.
Figure 41. Polymer degradation temperature with respect to mol% of GDMP (■), PPGMP800(●) and PPGMP2200(▲). The degradation temperature is measured from peak of the derivative curve of weight loss % vs. temperature. Samples were heated 10 °C/ min to 800 °C under a N₂ purge.

Evidence of Phase Separation in Ternary TENs with High MW Addend

Although we intended to solely investigate thermal properties of ternary networks, we carefully selected monomers with similar functionalities to eliminate complexities from demixing interaction. Nonetheless, upon UV irradiation, phase separation was immediately evident within ternary TENs containing PGMP2200 (Figure 42). This system contains a relatively similar volume fraction of each thiol component and could truly exhibit some degree of phase separation. It is well known that phase separated systems should exhibit two distinct glass transition temperatures. Lower temperature scans on a DMA analyzer indeed contributes proof for such a theory.
Investigation of TMPT:PPGMP2200:TATAT systems with ratios, 50:0:50, 40:10:50, 30:20:50 and 20:30:50 clearly shows a peak associated with pure PPGMP2200 matrix and second peak for pure TMPT for mixed networks, Figure 43. In light of these findings, we will further investigate phase separation of ternary TEN in the near future.

*Figure 42.* Image of stoichiometrically balanced, UV cured, dual TENs with vary mol% of PPGMP2200 (a) 0 mol%, (b) 20 mol% and (c) 40 mol%. PPGMP2200 was added to TMPT and cured with TATAT using 0.5 wt. % DMPA photoinitiator.
Figure 43. Tanδ as a function of temperature for select dual thiol networks containing PPGMP2200 and TMPT with TATAT mixed 1:1, of -SH to (-C=C) functional groups with 0.5 wt. % DMPA in the following ratios (TMPT:PPGMP2200:TTT): (a) 50:0:50, (b) 40:10:50, (c) 30:20:50 and (d) 20:30:50.

Conclusions

In conclusion, we have investigated thermal and thermomechanical properties of novel ternary TENs wherein the third component is a second reactive thiol component. We found the Tgs are highly tunable in and in a predictable manner based on the weight fraction of the second thiol component. However, high molecular weight monomers have negative impacts on the polymer degradation temperature and FWHM of tan δ versus temperature curves. Despite these drawbacks, results are promising for the aforementioned goal of fine-tuning the Tg with simple synthetic efforts. Kinetic profiles are relatively unaffected by addition of this third component for most systems, which
increases promise of utilizing a second thiol component in the many new applications of thick thermoset TENs. In the future we plan to investigate other systems with higher glass transitions temperatures as they will likely have more applicability in real world applications.
CHAPTER VI
TOWARD HIGH TG AND TOUGH THIOL-ENE NETWORKS

Introduction
The goal of much of the research presented in this dissertation has focused on fine tuning thermal, mechanical and thermomechanical properties such that novel damping devices from thiol-ene chemistries can be realized. The spotlight has been dominantly placed on the incorporation of either urethane or thiourethane groups in the backbone of the polymer chain. We lean more toward additives of this nature because of the drastic increases in toughness which is achievable mainly by hydrogen bonding. Additionally we notice enhancements in the glass transition temperature if we choose monomers that are rigid which is also beneficial.

In the first part of this section we will discuss a class of novel bulky alkene monomers which have been synthesized and incorporated into thiol-ene networks. The initial finds concerning network properties and impact performance will be discussed. In the second section we will highlight a novel material base which can be used to enhance both toughness and thermal properties but suffers from high viscosity. The emphasis here will be placed on novel curing profiles which could be utilized to synthesize novel thiol-ene networks.

Bulky Alkene Networks

Materials and Methods

Materials. Monofunctional isocyanates phenyl isocyanate (BZ), cyclohexyl isocyanate (CHX), and 1-napthyl isocyanate (NP) were purchased from Sigma Aldrich and used as received. Photoinitiator and thiol curative 2, 2- dimethoxy-2-
phenylacetophenone (DMPA), dibutyl tin dilaurate (DBTDL) and pentaerythritol tetra(3-mercaptopropionate (PETMP) were also purchased from Sigma Aldrich and used without further purification. Vinyl monomer Trimethylolpropane diallyl ether (TMPDE90) was donated by Perstorp and used as received.

*Monomer Synthesis and Sample Preparation.* Bulky divinyl monomers were synthesized by addition of monofunctional isocyanates to the pendent alcohol group on TMPDE90. 1 wt% DBTDL was dissolved in TMPDE90 in a round bottom flask over ice and purged with N₂ gas. BZ, CHX or NP was slowly added to the flask over a 30 minute period from a N₂ filled holding chamber. Following complete isocyanate addition, the temperature was ramped to 55 °C over an one hour period where the mixture remained stirring overnight for a total of 24 hours. Bulky monomers were synthesized in no greater than 10 gram batches for this study. An overview of monomers and monomer synthesis can be seen in Figure 44. FTIR of monomers can be found in the supporting information section of this paper (Figure 45).
Figure 44. Synthesis of bulky pendent group divinyl monomers and tetrafunctional thiol curative.

**Kinetic Analysis**

Real-time FTIR was performed on stochiometrically balanced mixtures of thiols and alkenes. The peaks corresponding to thiol (2600 cm\(^{-1}\)) and alkene (2064 cm\(^{-1}\)) moieties were monitored with respect to time using a Nicolet 8700 FTIR spectrometer with a KBr beam splitter and a MCT/A detector along with a 320-500 nm filtered ultraviolet light source. The lamp, intensity approximately 20 mW/cm\(^2\), was turned on at approximately 10 seconds wherein marked the beginning of the UV reaction. Real-time
data was collected for a total of 60 seconds at a 1/sec scan rate of approximately and 4 cm\(^{-1}\). It should be noted that the alkene peak could not be monitored for benzene based mixtures (TMPDE90BZ/PETMP) due to the presence of strong alkene peaks associated with benzene therefore the kinetic plot for that system only contains data for thiol conversion. Kinetic analysis was not performed for NP-based systems.

_Thermal and Thermomechanical Analysis_

_**DMA.**_ Dynamic mechanical analysis was performed on rectangular shaped samples were prepared via UV-curing in silicon molds followed by careful removal of samples (TA Q800 DMA, TA Instruments, New Castle, DE). Sample dimensions were kept consistent as length x width x thickness measured approximately (6 mm x 5 mm x 0.4 mm) for all samples. Beginning from a one minute isothermal at -50 °C, samples were deformed in tensile mode to a 0.05 % strain rate at 1Hz frequency while being heated 2 °C/ min to a terminal temperature of 150 °C. Glass transition temperature was recorded as the maximum temperature associated with the tan δ vs temperature curve while glassy storage modulus (\(E'_\text{glass}\)) and rubbery storage modulus (\(E'_\text{rubber}\)) values were recorded from temperatures from \(T_g - 40\) and \(T_g + 40\) respectively. Peak loss modulus values (\(E''_{\text{max}}\)) is represented by the temperature corresponding to the peak maximum.

_**DSC.**_ Differential scanning calorimetry was also performed using a TA Q2000, TA Instruments, New Castle, DE. Approximately 7 mg samples were placed into standard Al pans and heated to 100 °C to erase thermal history, quenched to -40 °C then reheated at 10 °C/min to 50 °C. The glass transition temperature was recorded from the second heating.
**MTS Analysis**

For mechanical analysis, dog-bone shaped standards with cross-sectional dimensions width x thickness (13.0 mm ± 0.5 mm, 3.5 mm ± 0.5 mm) were prepared by UV-curing materials into preformed silicone molds. The samples were equilibrated 24 hours in the testing room at 24 °C prior to experimentation to ensure consistency between runs. An Instron brand MTS instrument equipped with a 1kN load cell was used to deform the samples in tensile mode at a rate of 0.2 in/min while data was collected at a rate of 10 Hz. The resulting modulus, peak stress and strain at break were determined using the instrument computer program. Data was collected from 5 samples of each PETMP-TMPDE90 and PETMP-TMPDE90CHX and four samples of PETMP-TMPDE90BZ. Reported values in tables represent an average of the results with standard deviations included. MTS analysis was not performed for NP-based systems.
Figure 45. A) FTIR of Starting Reagents a) TMPDE90 b) CHX c) BZ and d) NP and B) FTIR of Ending Products a) TMPDE90CHX b) TMPDE90BZ and TMPDE90NP.

SEM Imaging. Fracture surfaces from tensile tests were examined by Scanning Electron Microscopy. A small slice of the fractures surface perpendicular to force direction was removed and sputter coated with high purity gold using a standard technique. Samples were charged under Argon gas and 25 mAmps for three minutes.
resulting in a gold coating of approximately 10 nm. SEM images were taken using SEM Quanta FEI 200 at 100X magnification.

*Impact Analysis.* Material response upon impact was measured using a Dynatup 9250 HV equipped with a 88 kN load cell. Thiol-ene and EVA discs measuring 2” in diameter and 4 mm thickness were impacted using a steel drop dart and impact energy of 4.4 J. The corresponding impact specifications were impact velocity = 1.25 m/s, drop height = 0.08 m, and drop mass = 5.6 kg. The samples were centered on top a hardened steel anvil to prevent flexion and a pneumatic brake was applied automatically following impact to prevent a second incidence of impact. Atmospheric conditions at the time of testing were 23 °C and 42% relative humidity. The impact conditions were selected based on Austrailian Standard 1544, 1989, where 4.4J is energy required of a cricket ball travelling 27 mph to damage the orofacial complex. Impact analysis was not performed for NP-based systems

*Results*

*Kinetic Profiles.* The kinetic profile for the systems containing novel alkene monomers were similar to typical thiol-ene kinetic profiles for UV polymerization reactions. The of a native matrix, PETMP-TMPDE90, was performed as a control system and demonstrated quantitative conversion for both thiol and alkene functional groups within a matter of seconds (Figure 46). The kinetic plot of PETMP-TMPDE90CHX was similar to the kinetic plot of the control (Figure 47). It can be shown the bulky group has little to no effect on monomer reactivity.
Figure 46. Kinetic Profile of PETMP-TMPDE90.

Figure 47. Kinetic Profile of PETMP-TMPDE90CHX.

The benzene based system was more difficult to observe with respect to reaction kinetics due to the presence of double bonds associated with the benzene ring. However the kinetics of the thiol functional group was still capable of being monitored. Assuming
the thiol conversion mirrors alkene conversion we see from Figure 48 that the kinetics for PETMP-PETMP90BZ was different from the other systems. Overall conversion was lower for the thiol species, approaching approximately 90% at the completion of 60 seconds. This discrepancy is likely due to off stoichiometry of alkene groups with excess alkene being attributed to the benzene ring.

![Kinetic Profile](image)

*Figure 48.* Kinetic Profile of PETMP-TMPDE90NBZ (alkene excluded).

**Thermal and Viscoelastic Properties.** Thermal and viscoelastic properties of select network films were measured by Dynamic Mechanical Analysis and DSC. The relevance of the findings is that it is capable of determining temperatures associated with viscoelastic relaxation. The glass transition temperature was measured for the control system PETMP-TMPDE90 as well as the novel networks containing novel bulky alkene monomers. The glass transition temperatures were -21, 7, 10 and 12 °C for PETMP-TMPDE90, PETMP-TMPDE90CHX, PETMP-TMPDE90BZ and PETMP-TMPDE90NP respectively (Figure 49). The glass transition temperatures of the networks from bulky-based alkene monomers were considerably higher than the control system. The presence
of bulky side groups along the backbone of the polymer chain is known to shift glass transition temperatures to higher values. Additionally, hydrogen bonding between pendant urethane groups is likely to cause the same effect so that the overall glass transition temperature is higher.

![DSC Curves](image)

*Figure 49.* DSC Curves for Novel Thiol-Ene Networks Synthesized from Novel Bulky Alkene Monomers.

The viscoelastic properties of the network systems were also measured via DMA. The viscoelastic properties provide significant insight about the expected damping properties of the materials, cross-link density and other fundamental aspects of polymer networks. Figure 50A shows how the storage modulus (E’) trends with respect to temperature for the network systems. The glass plateau both extends to upward and to the right. Compared to the control higher values in the glass modulus is associated with a stiffer material in the glassy state. The shift outward means the material would remain in the glassy state over a longer range (higher in this case) of temperatures. As expected the storage modulus decreases approximately two orders of magnitude as it passes through the alpha relaxation regime (glass transition temperature) and reaches a second plateau at
higher temperatures. The value of the plateau is relative to molecular weight between cross-links such that higher plateau values correspond to lower molecular weight between cross-links and vice versa. The control system demonstrates the highest rubbery plateau modulus between all systems and is the most tightly cross-linked systems. The decrease in the plateau modulus for other systems demonstrates that the materials with bulky side groups have a lower packing efficiency in the rubbery state. This is an effect of the bulky side group which gains considerable mobility at higher temperatures.
Figure 50. Viscoelastic Properties of Novel Thiol-Ene Networks from Novel Bulky Alkene Monomers.

The glass transition temperature, or the temperature associated with optimal damping condition from a thermal standpoint is determined from the peak of the tan δ versus temperature curve. Figure 50C shows the peak is shifted to higher temperatures and corresponds to the aforementioned DSC results. The loss modulus (E’’), Figure 50B, correspond to the tan delta values as well demonstrating peak values just before the peak
of the tan δ curves. The full width half max (FWHM) values, where the FWHM is the distance across the tan δ versus temperature curve at one-half its maximum value, are narrow (Figure 50 C). This is a typical phenomenon associated with UV polymerized thiol-ene networks which stems from the combination chain and step growth kinetics of the reaction. The nature of this narrow curve also demonstrates the network homogeneity and it appears here that this desirable property is not compromised from a new monomer structure. In fact the peak height is increased which could imply damping is enhanced for modified networks. Glass transition temperatures from DSC and DMA (tan δ peaks) agree appropriately.

*Mechanical Enhancements of TENs.* The tensile behaviors were improved in systems with bulky pendent groups. The tensile modulus, peak load and strain at break values were determined for three samples of each formulation (excluding PETMP-TMPDE90NP) in order to visual the effects of bulky side groups and hydrogen bonding. We saw a considerable increase in the strain at break for the modified systems PETMP-TMPDE90CHX and PETMP-TMPDE90BZ (Figure 51). Strain at break was 5 to 6 times higher, on average, compared to the native matrix material. This enhancement is likely due to side chain interactions, hydrogen bonding; at room temperature hydrogen bonds would play a considerable in overall material properties. Also at the testing temperature, the materials would likely be in the glass transition region for the modified systems which should separate out factors concerning monomer rigidity. The increase in strain at break was however compromised by lower modulus values. The nature of this observation lies in the fact monomers with bulky groups led to network systems with a
lower cross-link density. The relationship between strain at break and modulus is pictured in Figure 52 and a summary of MTS tensile properties are listed in Table 10.

**Figure 51.** MTS Tensile Curves of Novel Thiol-Ene Networks from Bulky Alkene Monomers.

**Figure 52.** Left) Strain at Break and Right) Modulus Values of Novel Thiol-Ene Networks from Bulky Alkene Monomers.
Table 10

*MTS Tensile Properties of Novel Thiol-Ene Networks Based on Bulky Alkene Monomers*

<table>
<thead>
<tr>
<th>System</th>
<th>Peak Load (N)</th>
<th>Peak Stress (MPa)</th>
<th>Strain at Break (%)</th>
<th>Young’s Modulus (MPa)</th>
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<tr>
<td>PETMP-TMPDE90</td>
<td>7.7 ± 1</td>
<td>1.1 ± 0.3</td>
<td>9.7 ± 3</td>
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<td>PETMP-TMPDE90CHX</td>
<td>17 ± 3</td>
<td>3.6 ± 0.5</td>
<td>50 ± 6</td>
<td>8.3 ± 0.2</td>
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<tr>
<td>PETMP-TMPDE90BZ</td>
<td>25 ± 1</td>
<td>5.2 ± 0.3</td>
<td>63 ± 2</td>
<td>8.7 ± 0.1</td>
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</table>

Optical imaging of fracture surface revealed considerable differences between the systems. Figure 53a demonstrates the brittle nature of the failure associated with the native network materials. This corresponds to higher modulus values and lower strain at break. The final two systems in the same image demonstrate a much smoother fracture surface, wherein higher elongation at break and lower modulus values are associated with this type of failure.
Figure 53. SEM Imaging of Thiol-Ene Networks from Novel Bulky Alkene Monomers; a) PETMP-TMPDE90 b) PETMP-TMPDE90CHX and c) PETMP-TMPDE90BZ.

**Impact Properties of Novel Networks**

Viscoelastic measurements showed that modified networks would have optimal damping properties at or near room temperature therefore we measured the impact properties via a drop tower testing system wherein impact energy is relevant for a mouthguard application. We compare the results of the modified networks to both a
control system and EVA, a common material used in commercial mouthguards. The important factors are peak load values (the highest force realized upon an impact event), time to peak load, overall time of an impact event and curve shape. All tested thiol-ene materials performed better than EVA with respect to peak load values. The peak load values on average were 7,815, 6693, 6999, and 5,681 N for EVA, PETMP-TMPDE90CHX, PETMP-TMPDE90BZ and PETMP-TMPDE90 respectively (Figure 54). The same figure shows that time to peak force may be slightly lower for thiol-ene based systems modified with bulky-groups. These materials have higher glass transition temperatures and would likely have a faster time response because the materials are stiffer at the tested temperatures. The control system however shows a longer time response and a characteristic trapezoidal shaped curve. The longer time response is because of the lower glass transition temperature associated with the network and more elastic deformation likely.

Surprisingly the systems with glass transition temperatures around the testing temperature were lower performing than the control. The nature of impact properties of thiol-ene networks is currently being investigated to further understand this result. Although the reported glass transition temperature of EVA is between -10 and 30 °C the impact behavior is significantly different from a thiol-ene network with a similar T_g. Impact performance of the thiol-ene network is better respectively. This is likely due to the increased rigidity of EVA due to crystalline regions.
Figure 54. Impact Curves of Thiol-Ene Networks from Novel Bulky Alkene Monomers. Each curve contains 5 curves of a different sample of material for a total of 20 samples.

Conclusions

Herein we have investigated a novel set of thiol-ene networks from novel alkene monomers having bulky pendant groups attached by urethane linkages. We have demonstrated that thermal properties are increased for modified networks compared to the native systems. Mechanical properties were also enhanced with respect to strain at break however this was compromised by lower realize modulus values. The impact properties were measured using a drop test system and energy relevant for a mouthguard material. The results demonstrates that thiol-ene networks outperform EVA mouthguard material regarding peak load values however time to peak load was comparable. The
control systems demonstrated the best impact properties even though it was not expected to, but thermal and mechanical properties of this system are insufficient for realistic applications. The nature of this observation is currently under investigation.

**Multifunctional Urethane-Based Alkene Networks**

*Synthesis of Urethane-Based Multifunctional Alkene Monomers*

Multifunctional monomers synthesized from diisocyanates and dienes were synthesized from alcohol/isocyanate reactions. The idea being to develop monomers which can be utilized in sequential thiol-ene UV polymerizations. The high molecular weight monomers will be utilized ideally to increase glass transition temperatures to a specific value or as a mechanism to increase robustness of a network. Figure 55 shows a schematic of monomer synthesis wherein any diisocyanate can be utilized in place of the one shown. So far we have synthesized the monomers in Figure 56. Due to the competitive nature of the reaction of alcohol and water in the presence of a catalyst, the reactions must be carried out under nitrogen. Additionally the reaction should be conducted at lower temperatures initially (i.e. 0 °C) until the isocyanate component is added. This prevents temperature spikes, which can lead to unwanted side products. The reactions were carried out as follows:

1. A round bottom flask is charged with allyl ether (APE or TMPDE90) and 0.1 wt% (of the total weight) dibutyltin dilaurate (DBTDL) catalyst and a stir magnet then purged with N₂.

2. A stoichiometric amount of isocyanate (1:1, OH:NCO) is measured out and added to an addition funnel (also under N₂ purge) and slowly added drowise over the period of one hour. Slow addition prevents temperature spikes.
3. The reaction was allowed to react for about one hour, at 0°C, and then the temperature was slowly allowed to increase to room temperature before using an external heating source to continue heating slowly to 55 °C.

4. The total time of the reaction is 24 hours from beginning to end, being careful not to let the reaction exceed 60 °C and the product should be viscous upon cooling.

Figure 55. Schematic of the Synthesis of A multifunctional Alkene Monomer via Alcohol/Isocyanate Chemistry.
Figure 5. Multifunctional Alkene Monomers TAE1 (Tetra Allyl Ether 1), TAE2 (Tetra Allyl Ether 2), HAE1 (Hexa Allyl Ether 1) and HAE2 (Hexa Allyl Ether 2).

**NMR Analysis of Monomers**

Monomer synthesis is readily verified by \(^{13}\text{C}\) Nuclear Magnetic Resonance (NMR) based on disappearance of peaks associated with isocyanate carbonyls and the presence of isocyanate carbonyl peaks. The NMR analysis of the synthesized monomers is shown in Figure 57 for a deuterated chloroform solution. Monomers based on IPDI have two carbonyl peaks. This is due to the facts that the isocyanates on IPDI are not similarly placed on the ring and this is an asymmetrical molecule.
Curing the Novel Monomers with Thiols

Because the monomers are both high molecular weight and strongly hydrogen bonded species, these monomers in particular prove difficult to mix and cure using conventional methods. The high viscosities are a real issue, but we noticed heating the monomers was a great help with mixing. We monitored the viscosity as a function of temperature in order to determine an ideal mixing temperature for such monomers. We determined 60 °C was an appropriate temperature. Based on Figure 58, 60°C is the temperature wherein the viscosity reached a plateau (H_{12}MDI/APE (HAE2) demonstrated
the same behavior). The formulations of thiols and alkenes were mixed at elevated temperatures. Photoinitiator was added to thiol first but the alkene was measured into a separate scintillation vial from a heated state. The thiol/initiator mixture was then added to this vial and then the monomers were mixed by mechanical stirring.

![Figure 58. A Typical Viscosity Profile for Urethane Based Multifunctional Alkene Monomer.](image)

**Preliminary DMA Investigations**

It is ideal that the viscoelastic properties demonstrate tan delta values that are high temperature and high damping. To investigate the nature of the tan $\delta$ versus temperature profiles of networks containing the new monomers, we performed Dynamic Mechanical Analysis in a manner similar to other networks mentioned in previous chapters. Since we expected vitrification would be a deterrent to high $T_g$ networks, we investigated the viscoelastic properties before and after a post cure analysis. Figure 59 shows that films from HAE2 monomer and trifunctional thiol TMPT have glass transition temperatures similar to what is achievable using commercial thiol and ene monomers that have not been modified such as PETMP-TATAT. However, the network is much more
inhomogeneous than conventional systems. After a post cure process, the glass transition temperature shifted about 30 degrees higher. However a decrease in the maximum tan delta value was also observed. The FWHM also increased which means the network is furthermore inhomogeneous at this point. A similar observation is observed when the thiol curative was switched to the four-functional PETMP monomer (Figure 60). One significant difference is that the beginning network seems to be more homogeneous in this case. This behavior was not expected as TMPT and PETMP are structurally similar.

![Figure 59. DMA Analysis of HAE2-TMPT Pre and Post Curing.](image)
Figure 60. DMA Analysis of HAE2-PETMP Pre and Post Curing.

We will continue to investigate systems from these monomers. This will include determining optimal curing conditions and formulations. To this point, mechanical properties of films or bars made from these monomers have not been determined but we expect that they will be significantly better than traditional thiol-ene networks. We have attempted to measure kinetics of reactions with these novel monomers and several thiols at elevated temperatures, but there is great discrepancy between thiol and alkene conversion. Nonetheless, the initial finds are promising. A simple post curing profile leads to glass transition temperatures unachievable by commercial thiol and alkene monomers.
CHAPTER VII

CONCLUSIONS AND FUTURE WORK

In conclusion, thiol-ene networks express predictable behaviors with respect to thermal, mechanical and viscoelastic properties. Networks were readily synthesized in their native form or in the presence of other chemical moieties such as acrylates and urethane with little to no effect on reaction kinetics. Networks mainly demonstrated narrow full width half max values and are in turn homogeneous systems. The damping properties of such systems were found to mimic the tan $\delta$ versus temperature curves. We initially sought to investigate this class of materials as a novel platform for damping devices by way of mouthguards and in the end gained much more insight. Despite our gained knowledge, much remains to be determined concerning network architecture, structure-property relationships, limitation of glass transition temperature and energy absorption of thiol-ene networks.

To this point we have demonstrated that thiol-ene chemistry is highly versatile and that mechanical and thermal properties can be readily changed to suit many individualized applications. In the first investigation (Chapter II) we sought to enhance mechanical robustness of a thiol-ene network and compare the new materials to commercial EVA, a common material used for mouthguards. We found that compared to EVA, thiol-ene networks were only significantly advantageous in one tested area, energy absorption. To address the other issues, high water absorption and low tear strength we turned to more chemical modifications. Since the urethane modified thiol-ene network performed best with respect to tear strength our research focus shifted toward incorporating more urethane or thiourethane groups with the goal being that hydrogen...
bonding would enhance network properties. This idea motivated the second significant research investigation.

In the second research investigation (Chapter III) we utilized thiourethane groups in a thiol-ene network while utilizing a second effort to enhance toughness, novel network morphology. Utilizing difunctional cyclic aliphatic diisocyanates we were able to enhance both thermal and mechanical properties of thiol-ene networks significantly. The chain extension reaction which took place during the first reaction step generated thiol-terminated prepolymers. In the same reaction vessel, we were able to cross-link those thiol-terminated oligomers together with addition thiol and a trifunctional alkene using traditional UV polymerization catalysts and techniques. The enhancement of both Young’s modulus and strain at break was impressive for this material set. The significance of this research investigation is that we have found a way to enhance the mechanical properties without using synthetic monomers but instead, react all components in one pot using sequential curing techniques. We have also avoided the problem of high monomer viscosity and mixing problems associated with urethane/thiourethane based monomers.

We have yet to determine the impact properties of these types of networks. I would speculate the impact properties of these systems would be enhanced due to the similarities between these materials and TPU’s (thermoplastic polyurethanes). It is still important to target maximum tan δ values which are proximal to the testing temperatures. The systems with significant enhancement in tensile properties (at least 40mol% NCO content) in the second research investigations had higher than desirable tan δ max values and therefore were not tested. To decrease the temperature associated with peak tan δ
max it would be reasonable to add a second thiol component with a flexible backbone and difunctionality. One suggested monomer would be PPGMP800 in addition to the GDMP which was used. This could lead to hardsegment/softsegment morphology inside the linear region of the hybrid system. If this is achievable, even greater mechanical enhancements could be realized.

The third research investigation (Chapter IV) the impact behavior of thiol-ene networks was investigated for the first time using a drop tower system. This allowed energy management of a thiol-ene network system to be visualized by way of force/time or impulse curves. We were able to develop network systems with a wide array of differences and similarities. For instance, glass transition temperatures ranged from around -30 through 53 °C. We were also able to compare systems with similar cross-link densities but structural differences by incorporating a flexible ally ether monomer and a rigid alkene monomer with similar functionalities and molecular weights. We found that impact behavior was directly correlated to the glass transition temperature such that systems with low glass transition temperatures demonstrated better impact properties (low peak load and long impact times) and vice versa. We were also able to separate structural effects concerning impact performance. Lastly, for the first time the benefit of utilizing a thiol-ene network capable of dissipating energy via viscoelastic relaxation with respect to impact performance. We essentially developed a platform for expected impact performance and thiol-ene networks of known glass transition temperatures.

Finally, we desired a method to tune the tan δ max values because the temperature associated with this peak value predicts impact performance. In Chapter V we have
demonstrated that a two thiol-based system allows us to decrease glass transition
temperatures systematically such that we could fit the data to the Fox equation. This find
is significant because now it we know two glass transition temperatures of systems that
have at least one component in common (either same thiol or same alkene) we are
confident that the glass transition temperature can be predicted before bulk material is
synthesized.

We have undoubtedly gained considerable insight about thiol-ene networks
concerning thermal, mechanical and viscoelastic properties but there are many questions
which arose during the course of these investigations. These are:

1. How does the monomer structure effect impact properties during the
viscoelastic dissipation regime? If we compared impact properties of
systems with similar glass transition temperatures at the glass transition
temperature, would there be a noticeable difference in energy absorption?

2. How does two phase morphologies, such as those produced in Chapter III,
affect impact behavior of a thiol-ene network?

3. What are the dimensional (thick) limitations for energy absorption in thiol-
enet networks? For instance is there any benefit of a 6 mm thick material
compared to a 4 mm material or a 3 mm material. For EVA this threshold
has been determined.

4. Can we find a method to cure highly viscous monomers which combines
heat and light without premature thiol-ene polymerization? The advantage
here would potentially be higher conversion which would in turn lead to
higher glass transition materials. This is a real concern for thiol-ene networks.

The investigations in this dissertation represent only a small aspect of the potential in thiol-ene networks. My hope is that the research continues and the material would once again be commercially viable.
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