SAFER ADHESIVES VIA THIOL-ENE CHEMISTRY

The Toxics Use Reduction Institute
Academic Research Program

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Safer Adhesives Via Thiol-ene Chemistry

Smruti Patil
Biomedical Engineering and Biotechnology Program

Assoc. Prof. Daniel F. Schmidt
Department of Plastics Engineering

University of Massachusetts Lowell

Project Manager: Pam Eliason
Toxics Use Reduction Institute

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Academic Research Program

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1. INTRODUCTION

Adhesives are an integral part of our everyday life due to their convenience and their ability to offer broad range of applications from domestic to industrial use. A variety of adhesive formulations are available with varying strength and appearance depending on the source, reactivity/chemistry, and their application. Although there are many natural adhesives available, synthetic adhesives excel in performance, and are more versatile. These adhesives can be specifically formulated and easily modified to suit our needs. Most of synthetic adhesives available today are under scanner for their associated health and environmental concerns. Majority of high performance adhesive are based on toxic chemicals, and contain additives to enhance their performance or increase the product shelf life. Given their extensive usage, there is a constant need to develop a better product aiming towards higher occupational and consumer safety.

1.1. Project Background

A variety of adhesives available today are formulated using a host of different polymers to meet specific needs, and are classified based on their chemical type, bonding mechanism and their application. Some of the most effective adhesives commercially available contain compounds with significant associated hazards.

For example, epoxy adhesives – known for their strength, toughness, and their excellent environmental and chemical resistance, involve epoxy monomers based on bisphenols, primarily bisphenol A, and often contain aromatic amine hardeners. The endocrine disrupting potential of bisphenol A (BPA)[1] has been widely documented over the past few years, while aromatic amines are known to be toxic and skin sensitizers.

Likewise, reactive acrylic adhesives, classified as high performance structural adhesive are a two part system containing a resin and activator based on acrylate or methacrylate derivatives. In spite of all the advantages they offer (superior adhesion, flexible formulation and cure speeds), they are predominantly based on highly reactive low molecular weight reactive acrylate and methacrylate monomers and oligomers with added initiators and additives. Low molecular weight acrylate and methacrylate monomers are volatile and are skin sensitizers[2] known to cause dermatitis on acute and chronic exposure depending on the concentration levels.

Finally, polyurethane adhesives, widely used in industrial and household applications (e.g. Gorilla Glue[3]), known for their high strength and easy availability, are based on isocyanate chemistry[4]. Isocyanate based adhesives are also used in joining and finishing engineering wood products. Isocyanates are toxic and can produce contact sensitization and a range of subsequent allergic reactions on repeated exposure[5].

Having said that, not all synthetic adhesives available are toxic; however, it must be noted that monomers used to make them might be problematic as far as occupational health and safety is concerned. Cynoacrylate based adhesives (e.g. "superglue") are actually among the more benign adhesives, and were originally considered for use in surgical applications (i.e. for wound-closing[6]) due to their ability to bind skin and low toxicity, in spite of the impression the name of the monomer might otherwise give. Likewise, wood glues are typically water-based and consist of poly (vinyl alcohol) type adhesives, while many pressure-sensitive adhesives consist of lightly crosslinked silicone and acrylic polymers that are non-hazardous to end users. The aforementioned examples are only useful in very specific applications, however. Superglues are not gap-filling, wood glues do not work well with other materials, and pressure-sensitive adhesives require a substrate and are best used when joining stiff, clean, flat surfaces.

The objective of this work is to develop a new family of versatile, high-performance, solvent free adhesives based on safer components, using thiol-ene chemistry for network formation. All components used are readily available, aliphatic monomers (low toxicity) that are classified as no more than irritants, making it a practical, versatile, synthetic approach.

2. REACTION CHEMISTRY

Thiol-ene chemistry involves the reaction of thiol (-SH) groups with carbon-carbon double bonds (C=C), as shown in **Figure 1.**

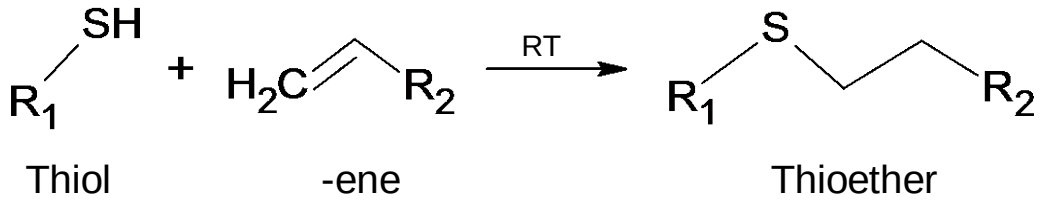


Figure 1: Schematic showing the thiol-ene reaction

Thiol-ene reaction is both specific and highly favorable, occurring rapidly via multiple reaction mechanisms[7]. In particular, network formation may proceed via a base-catalyzed Michael addition type mechanism, where the –SH group acts as a nucleophile and attacks the carbon-carbon double bond, or a free radical mechanism, where a source of free radicals breaks the S-H bond, activating the thiol and allowing it to attack the carbon-carbon double bond. Depending on conditions, both mechanisms may be active simultaneously. It has been reported that this type reaction can be performed in neutral aqueous media in matter of minutes, resulting in a well formed network[8], making it an attractive system given the detrimental effects of moisture on range of polymerization reaction. The low toxicity of aliphatic thiols coupled with the availability of wide range of –ene monomers makes them versatile and easy to prepare. Their

ability to be clear and colorless with increased refractive index due to the presence of sulfur acts as an added advantage for bonding transparent materials such as glass.

3. MATERIALS AND METHODS

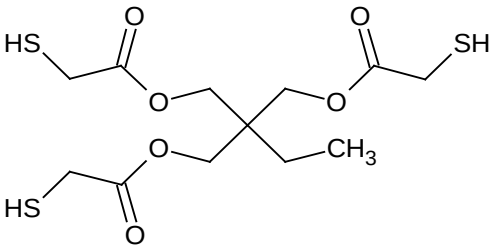
3.1 Materials

All materials chosen for the current work are based on criteria including, low toxicity (aliphatic monomers), high functionality (room temperature cure), high molecular weight to ensure convenient and safe handling especially in the case of the polythiols, and are classified as no more than irritants. All polythiols, -ene monomers, and catalysts selected are readily available commercially, emphasizing on immediate practical relevance, and were used as received unless otherwise specified.

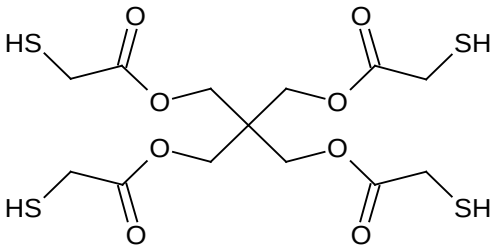
3.1.1 Polythiols

Four different aliphatic polythiols were identified based on above mentioned criteria and were donated by Evans Chemetics LP (USA). The chosen thiols are based on esters of trimethylolpropane (TMP) and pentaerythritol (PE) with either 2-mercaptoaceticacid or 3-mercaptopropionicacid [i,ii,iii,iv]. The names and structures of the commercial polythiols obtained from Evans Chemetics / Bruno Bock are shown in **Figure 2(a),** with their important properties listed in **Table 1**. In addition to these, tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate (TMEI)[v], purchased from Sigma Aldrich, and dipentaerythritol hexakis(3-mercaptopropionate) (DPHMP)[vi], purchased from Frontier Scientific, were also used to achieve improved network properties. The chemical structures of both are shown in **Figures 2(b)**.

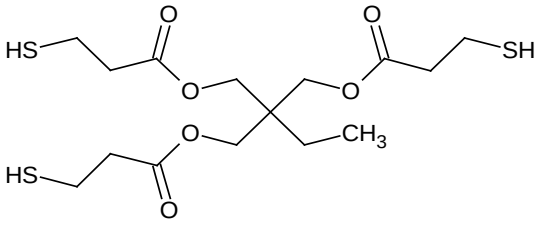
[i] http://www.evans-chemetics.com/%5CDokumente%5Cdown%5Cgeschuetzt%5CMSDS%5CMSDS_EC_TMPMA_120.pdf (viewed on 7/1/12)
[ii] http://www.evans-chemetics.com/%5CDokumente%5Cdown%5Cgeschuetzt%5CMSDS%5CMSDS_EC_PETMA_120.pdf (viewed on 7/1/12)
[iii] http://www.evans-chemetics.com/%5CDokumente%5Cdown%5Cgeschuetzt%5CMSDS%5CMSDS_EC_TMPMP_140.pdf (viewed on 7/1/12)
[iv] http://www.evans-chemetics.com/%5CDokumente%5Cdown%5Cgeschuetzt%5CMSDS%5CMSDS_EC_PETMP_510.pdf (viewed on 7/1/12)
[v] http://www.sigmaaldrich.com/catalog/product/ALDRICH/731250?lang=en&region=US (Viewed on 7/15/12)
[vi] (viewed on 7/19/12)



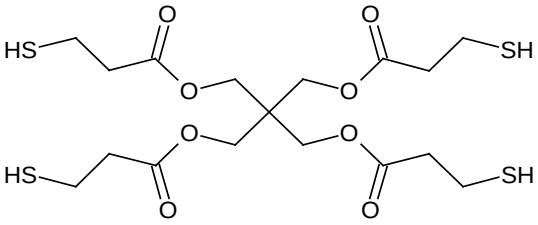
TMP tris(2-mercaptoacetate)i
(THIOCURE, TMPMA)



PE tetrakis(2-mercaptoacetate)ii
(THIOCURE, PETMA)

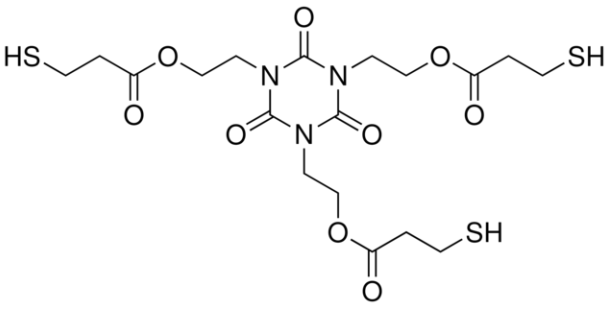


TMP tris(3-mercaptopropionate)iii
(THIOCURE, TMPMP)

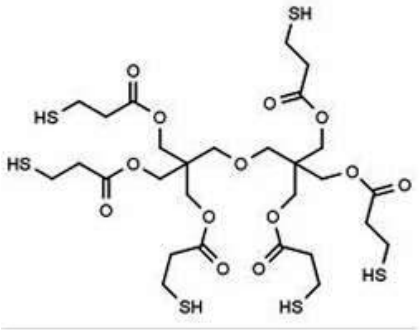


PE tetrakis(3-mercaptopropionate)iv
(THIOCURE, PETMP)

Figure 2(a): The structures of four chosen commercially available polythiols reagents used in network formation.



Tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate[v]



Dipentaerythritol hexakis(3-mercaptopropionate)[vi]

Figure 2 (b): Chemical structures of tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate (TMEI) and dipentaerythritol hexakis (3-mercaptopropionate) (DPHMP)

Table 1: Material properties according to suppliers of all polythiols used in the present work

Polythiols	Molecular Weight (g/mol)	% SH content (w/w %)	Specific gravity
PETMP	489	≈ 26	1.28
PETMA	432.5	≈ 29	1.38
TMPMP	398.6	≈ 24	1.21
TMPMA	356.5	≈ 26.5	1.28

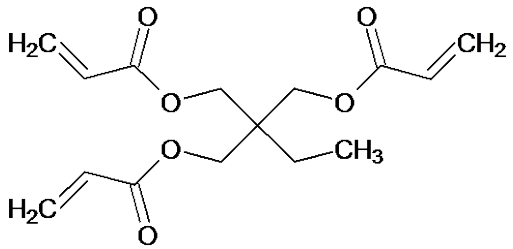
3.1.2 Poly ene-monomers

Based on the requirements, three different types of fully aliphatic poly-ene monomers where chosen for network formation – polyfunctional acrylates, allyl ethers of TMP and PE, and unsaturated vegetable oils.

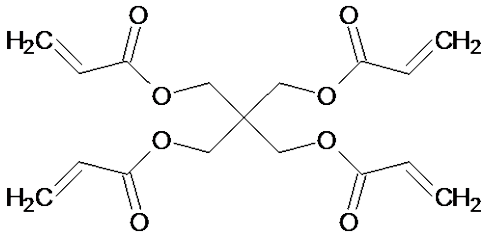
3.1.2.1 Acrylates

Low viscosity, high molecular weight polyfunctional acrylate monomers where chosen for the network formation, such that they undergo polymerization reaction with or without catalyst at room temperature. All acrylate monomers used in the present work are shown **Figure 3**, and were donated by Sartomer, USA.[vii,viii,ix,x] In addition to polyfunctional acrylates, acrylated linseed oil[xi] (CN160, Sartomer), and epoxidized soybean oil acrylate[xii] (CN111US, Sartomer) were also used in network formation with various polythiols and their representative structures are shown in **Figure 4**.

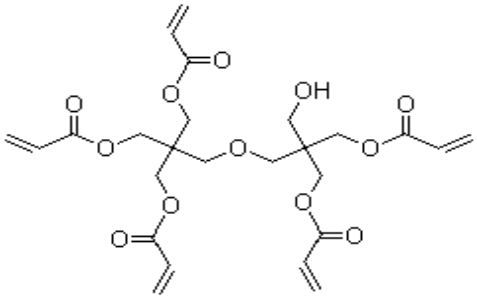
[vii] http://www.sartomer.com/wpapers/20551.pdf (viewed on 7/5/12)
[viii] http://www.sartomer.com/wpapers/2041.pdf (viewed on 7/5/12)
[ix] http://www.sartomer.com/wpapers/2060.pdf (viewed on 7/5/12)
[x] http://www.sartomer.com/wpapers/2057.pdf (viewed on 7/5/12)
[xi] http://www.sartomer.com/wpapers/2544.pdf (viewed on 7/5/12)
[xii] http://www.sartomer.com/wpapers/2472.pdf (viewed on 7/5/12)



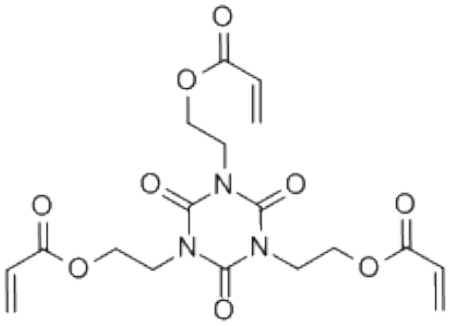
Sartomer 351-H[vii]
Trimethylolpropane Triacrylate (TMPTA)



Sartomer 295[viii]
Pentaerythritol Tetraacrylate (PETE)

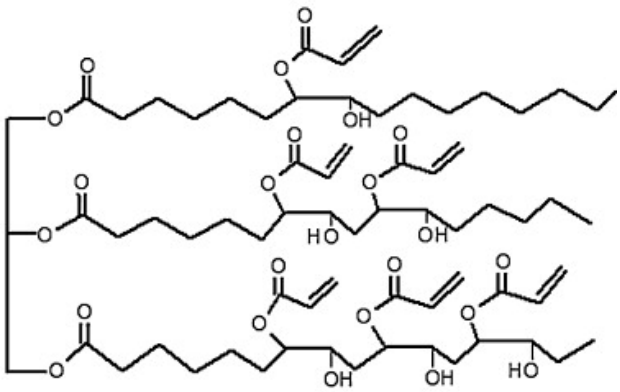


Sartomer 399[ix]
Dipentaerythritol Pentaacrylate (DPEPA)

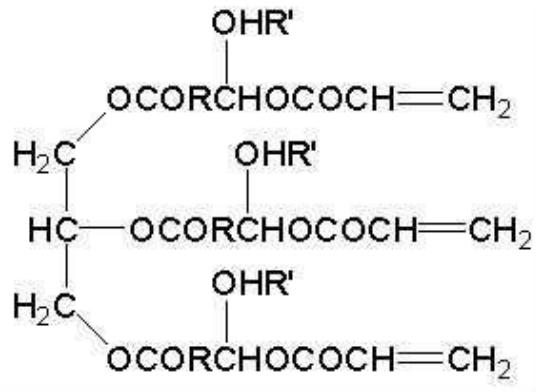


Sartomer 368[x]
Tris(2-hydroxy ethyl) isocyanurate triacrylate (THEIT)

Figure 3: Chemical structures of four different commercial available polyfunctional acrylic monomers chosen for thiol-ene network formation



CN 160[xi]
Acrylated linseed oil oligomer

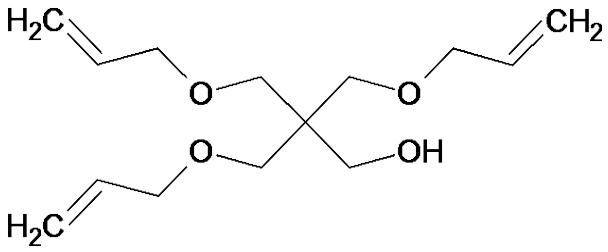


CN111 US[xii]
Epoxidized soybean oil acrylate oligomer

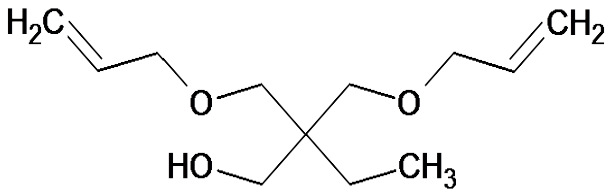
Figure 4: Representative chemical structures of organically modified vegetable oils used in thiol-ene network formation

3.1.2.2 Allyl Ethers

Polyfunctional ally ethers of pentaerythritol [xiii] and trimethylolpropane[xiv] were chosen based on the requirement and were purchased from Sigma Aldrich. The chemical structures of ally ether used are as shown in **Figure 5.**



Pentaerythritol tri(allyl ether)[xiii] (PETE)

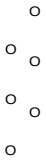


Trimethylolpropane di(allyl ether)[xiiv] (TMPDE)

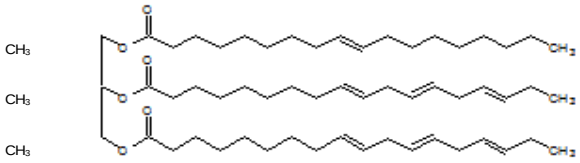
Figure 5: Chemical structure of polyfunctional allyl ether monomers chosen for thiol-ene network formation

3.1.2.3 Vegetable Oils

Two different vegetable oils, namely soybean[xv] and flaxseed[xvi] oil, were used as poly-ene monomers and were purchased from CIBARIA Int'l Inc. USA. Inherent unsaturation and the fact that they are naturally derived make them the most benign and sustainable among the selected poly –ene monomers. **Figure 6** shows their representative structures.



Soybean oil[xv]



Flaxseed oil[xvi]

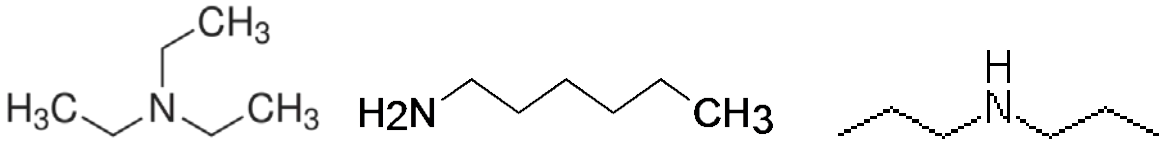
Figure 6: Representative chemical structures of vegetable derived oils used as poly-ene monomers in thiol-ene network formation

3.1.2.4 Catalysts

Three different catalysts were chosen to accelerate the cure speed and improve network formation. The catalysts used were triethylamine [xvii] (TEA), hexylamine [xviii] (HXA), and di-n-

[xiii] http://www.sigmaaldrich.com/catalog/product/aldrich/251720?lang=en&region=US (viewed on 7/6/12)
[xiv] http://www.sigmaaldrich.com/catalog/product/ALDRICH/416126?lang=en&region=US (viewed on 7/6/12)
[xv] http://cibariasoapsupply.com/Spec%20Sheets/Organic%20Soybean%20Oil.htm (viewed on 7/7/12)
[xvi] http://cibariasoapsupply.com/Spec%20Sheets/FLAXSEED,%20RBD%20EXPELLER.htm (viewed on 7/7/12)
[xvii] http://www.sigmaaldrich.com/catalog/product/sial/t0886?lang=en&region=US (viewed on 7/11/12)
[xviii] http://www.sigmaaldrich.com/catalog/product/aldrich/219703?lang=en&region=US (viewed on 7/11/12)

propylamine [xix] (DPA), all structural isomers of one another with the exact same chemical formula ($C_6H_{15}N$). All catalysts used shown in **Figure 7**, and were purchased from Sigma-Aldrich and used as received.



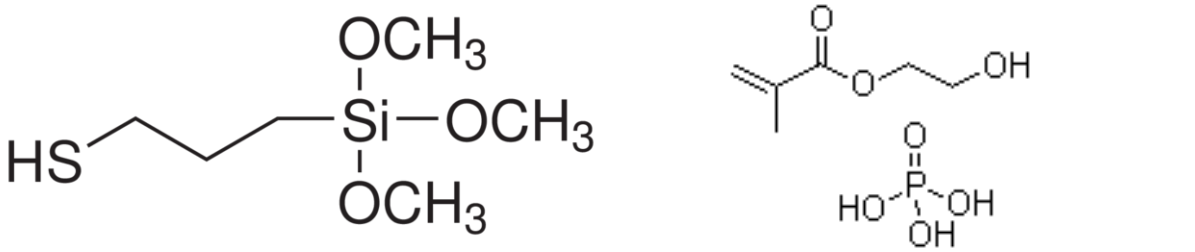
Triethylamine (TEA)[xvii] Hexylamine (HXA)[xviii] Di-n-propylamine (DPA)[xix]

Figure 7: Chemical structures of all catalyst used in Thiol-ene network formation

3.1.2.5 Adhesion promoters

Two different adhesion promoters were used to enhance the adhesion in thiol-acrylate formulations. A coupling agent such as, 3-mercaptopropyl trimetoxysilane [xx] (3-MPTMS) was purchased from Alfa Aesar was used as received.

A phosphate functionalized acrylic monomer was also used, namely phosphoric acid 2-hydroxyethyl methacrylate ester [xxi]. This compound, in stabilized form and containing 700-1000 ppm of 90 % monomethyl ether hydroquinone inhibitor according to the supplier, was purchased from Sigma-Aldrich. A ratio of 1:1 by weight of monomer to acetone (solvent) was used to dilute the monomer, and inhibitor was removed using prepacked ready to use disposable inhibitor removal column[9] (Al-154, Sigma Aldrich). The solvent in the monomer solvent mixture was evaporated first in the fume hood, and then by using vacuum for 24 hours. The purified monomer was collected in an air tight container and was stored in the refrigerator until use. The chemical structure of the adhesion promoters used are as shown in **Figures 8**.



3-Mercaptopropyl trimetoxysilane (3- MPTMS)[xx] Phosphoric acid 2-hydroxyethyl methacrylate ester[xxi]

Figure 8: Chemical structures of adhesion promoters used in thiol-acrylate systems

[xix] http://www.sigmaaldrich.com/catalog/product/aldrich/d214752?lang=en&region=US (viewed on 7/11/12)

[xx] http://www.alfa.com/en/gp100w.pgm?dsstk=B23726 (viewed on 7/11/12)

[xxi] http://www.sigmaaldrich.com/catalog/product/aldrich/695890?lang=en&region=US (viewed on 7/11/12)

3.2 METHODS

3.2.1 Sample Preparation

A stiochiometric ratio of 1:1 of thiol to –ene monomer was used to prepare all samples at 100 % (w/v) of total solids content and a total reaction volume of 10 mL. 20 mL polypropylene mixing container (Max 20, FlackTek) were used as reaction vessel and all reactions were carried at room temperature. An analytical balance (Sartorius, CP 324) was used to measure the amount of reactants added and disposable polypropylene transfer pipettes (SAMCO, 3mL bulb) were used to add reactants in mixing container. A 25 µL positive displacement micropipette (Drummond Digital Microdispenser) was used to add catalyst when required. The thiol and -ene monomer mixture was mixed using a speed mixer (FlackTek DAC-150FV, Speed Mixer) at 3540 rpm for 1 minute; this device ensures homogeneous mixing and degassing of the liquid mixture as well in a single step. All the samples were prepared following standard mixing order such that calculated amount of thiol was added to a known amount of –ene monomer present in the mixing container. When using additives such as catalysts, coupling agents or adhesion promoters, they were mixed with –ene monomer for 30 s in a speed mixer prior to the addition of thiol which was then mixed for 1 minute. **Figure 9** shows the sample preparation flow chart typically followed in this work.

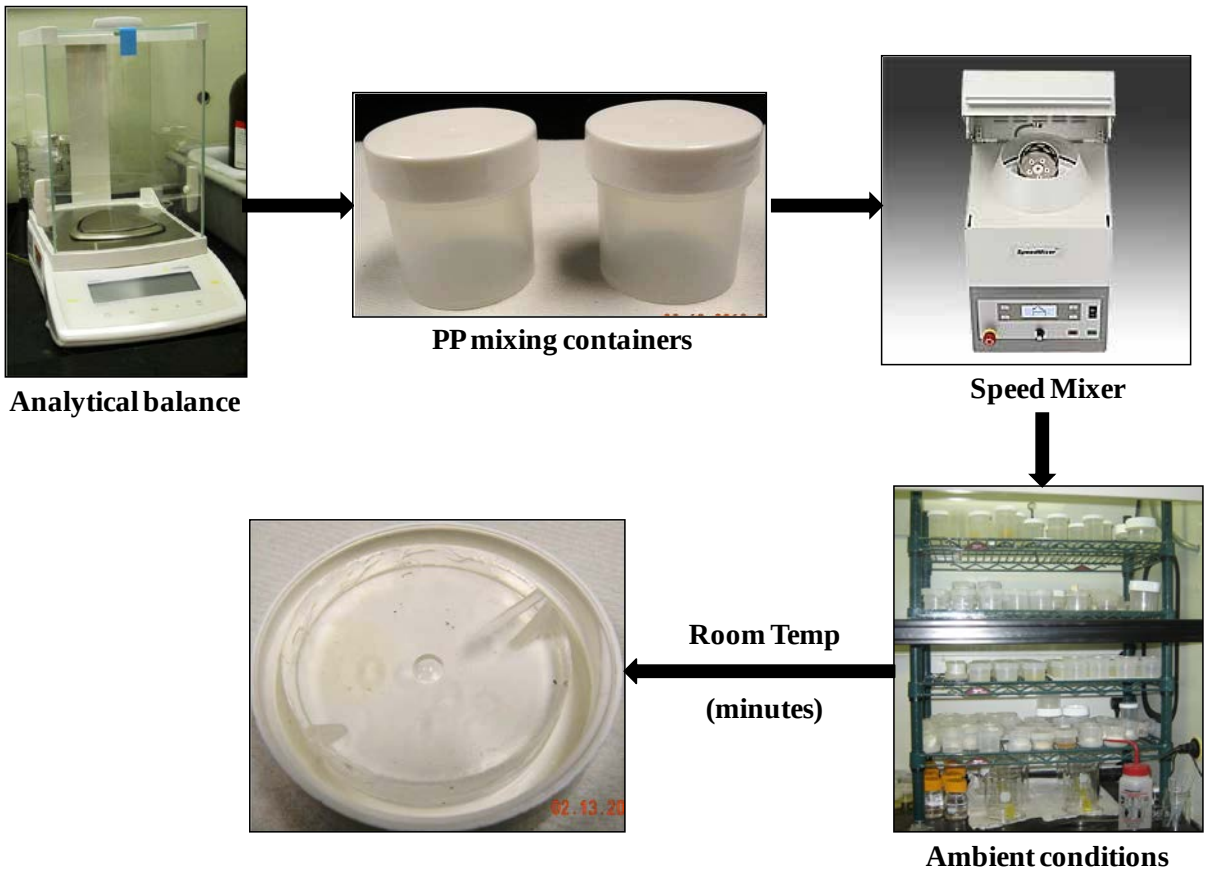


Figure 9: Sample preparation flow chart

3.2.2 Characterization Methods

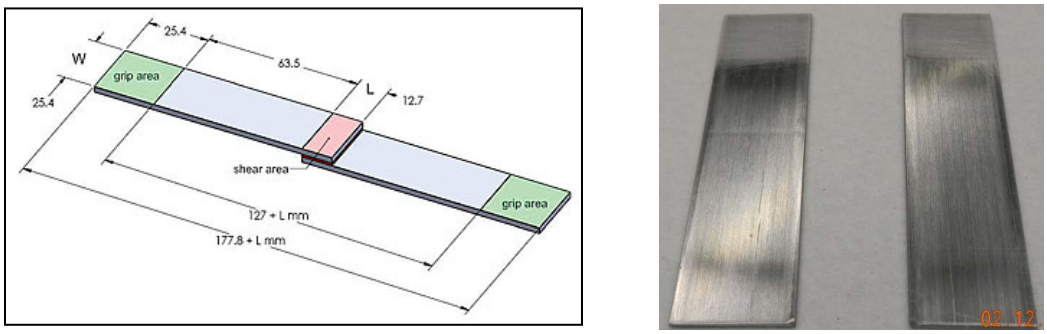
3.2.2.1 Hardness (Shore A)

Hardness values for cured samples were determined using a hand held Shore A Durometer (Shore Instruments, USA). Test specimens were prepared and the hardness value determined in accordance with ASTMD 2240-05 standard on a fully cured disk shaped samples. All test specimens were room temperature cured and were tested after 24 hours of network formation.

3.2.2.4 Single Joint Lap Shear Test

Adhesive bonded metal test specimens were subjected to testing in accordance with ASTM D1002-10 to determine the shear strength of different adhesives for bonding metals under tension. Low carbon steel (1008/1010) was used as substrate and was cut as per ASTM D 1002-10. The steel specimen used and their dimensions are shown in **Figure 10.** Prior to testing, steel samples were degreased with acetone and blast of air was used to remove all the surface dust. The surface for adhesive applications was prepared in accordance with ASTM D2651-01 using sand paper (NORTON, Grit 80-J), and air blast used to remove all traces of the abrasive.

Individual adhesive formulations were mixed and applied on one surface of one half of the cut steel specimen. The second half of the specimen was then bought in contact and pressure was applied to close the joint using a constant load. The adhesive was allowed to cure at room temperature and samples were subjected to testing after 24 hours of adhesive application. Each adhesive formulation was tested according to ASTM D1002-10 using a universal testing machine (Instron 4481) at crosshead speed of 0.05 inch/min (12.7 mm/min) using a 5000 N load cell. Test specimens were placed in the grips of the testing machine such that outer 25 mm of each end are in contact with the jaws and so that the long axis of the test specimen coincides with the direction of the applied pull through the center line of the grip assembly. A total of 5 samples were tested at room temperature for each formulation. Data obtained was recorded using Blue Hill software (version 2.6).



(a) Test specimen dimensions (b) Surface prepared test specimen

Figure 10: (a) Test specimen dimensions and (b) surface prepared steel test specimens ready for adhesive application.

4. RESULTS AND DISCUSSION

4.1 Material Synthesis

In scope of the present work, different thiol-ene formulations were tried using selected polythiols (section 3.1.1) in combination with different types of –ene monomers (section 3.1.2) with or without catalyst to achieve ideal thiol-ene network. An ideal thiol-ene network was characterized based on properties such as appearance (transparent vs. translucent to opaque, the latter indicating phase-separation), cure temperature and speed, network hardness, and mechanical stability. Only those formulations that resulted in a fast cured, robust, well formed homogeneous network at room temperature were further characterized to evaluate their adhesion strength (Section 3.2.2). All thiol-ene formulations were prepared at a 1:1 stiochiometric ratio of thiol to –ene monomer without any added additives unless otherwise stated.

4.1.1 Thiol-Acrylate formulations

In all systems thiol-acrylate polymerization was carried at room temperature using 1:1 stiochiometric ratio of thiol to acrylate (SH: C=C). All formulations tested are as shown in **Tables 2(a) to 2(e).**

Table 2(a): All Thiol-acrylate formulations based on Sartomer 351-H (-ene monomer) (Trimethylolpropane Triacrylate, TMPT)

Thiol reagent	Mixing time	Cure Time (Gelation time)	Cure Temperature	Appearance
PETMA	1 min	12-24 h	Room Temp	Partially cured
TMPMA	1 min	12 – 24 h	Room Temp	Partially cured
PETMP	**1 min**	**30 min**	**Room Temp**	**Transparent, soft, and elastic**
TMPMP	1 min	24 h	Room Temp	No network formation
TMEI	**30 sec**	**5 min**	**Room Temp**	**Transparent & rigid**
DPHMP	**30 sec**	**8 - 10 min**	**Room Temp**	**Transparent**

Table 2(b): All Thiol-acrylate formulations based on Sartomer 295 (-ene monomer) (Pentaerythritol tetraacrylate, PETA)

Thiol reagent	Mixing time	Cure Time (Gelation time)	Cure Temperature	Appearance
PETMA	1 min	24 h	Room Temp	Partially cured
TMPMA	1 min	24 h	Room Temp	Partially cured
PETMP	**1 min**	**30 min**	**Room Temp**	**Transparent, soft, & tacky surface**
TMPMP	1 min	24 h	Room Temp	No network formation
TMEI	**30 sec**	**5 min**	**Room Temp**	**Transparent & rigid**

Table 2(c): All Thiol-acrylate formulations based on Sartomer 399 (-ene monomer) (Dipentaerythritol pentaacrylate, DPEPA)

Thiol reagent	Mixing time	Cure Time (Gelation time)	Cure Temperature	Appearance
PETMA	30 sec	24 h	Room Temp	Partially cured
TMPMA	30 sec	24 h	Room Temp	Partially cured
PETMP	**30 sec**	**20 min**	**Room Temp**	**Transparent & elastic**
TMPMP	30 sec	24 h	Room Temp	Partially cured
TMEI	30 sec	24 h	Room Temp	No network formation

Table 2(d): All Thiol-acrylate formulations based on Sartomer 368 (-ene monomer) (Tris(2-hydroxy ethyl) isocyanurate triacrylate, THEIT)

Thiol reagent	Mixing time	Cure Time (Gelation time)	Cure Temperature	Appearance
PETMA	1 min	24 h	Room Temp	Immiscible
TMPMA	1 min	24 h	Room Temp	Immiscible
PETMP	1 min	20 min	Room Temp	Immiscible
TMPMP	1 min	24 h	Room Temp	Immiscible
TMEI	**30 sec**	**24 h**	**Room Temp**	**Transparent & elastic**
DPHMP	30 sec	< 24 h	Room Temp	No network formation

Table 2(e): All Thiol-acrylate formulations based on Sartomer CN160 and CN111US (Acrylated linseed oil oligomer, CN160 and Epoxidized soybean oil acrylate oligomer, CN111US)

Thiol reagent	-Ene monomer	Mixing time	Cure Time (Gelation time)	Cure Temperature	Appearance
PETMP	CN 160	1 min	48h	Room Temp	Partially cured & tacky
PETMP	CN 111US	1 min	24 h	Room Temp	Immiscible

The structure-property relations of the thiol-ene networks formed here largely depend upon the type of thiol and –ene monomers used. Based on the results, the rate of network formation increased with increase in the functional group concentration of acrylate monomers, as expected. However, not all thiols used were compatible with different acrylate monomers resulting in partial or no network formation and some phase separated on mixing resulting in translucent to opaque networks. PE tetrakis (3-mercaptopropinoate) (PETMP) showed good results with most of the acrylate monomers tried, both in terms of cure speed and network properties. Network formation occurred within 30 minutes of mixing of the thiol and –ene monomers at room temperature. This might be due to the fact that thiopropionates in thiol-acrylate polymerizations are reported to be less sensitive to inhibition due to the presence of oxygen[10]. Higher thiol concentrations coupled with high functionality further increases the rate of network formation.

TMEI (tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate) resulted in complete network formation with tri- and tetraacrylate monomers, with gelation occurring in 5 minutes at room temperature. The network formation occurred much faster and the network formed was much more rigid compared to other thiol-acrylate systems. This may be attributed to TMEI, being an isocyanurate derivative with a rigid, polar, highly interacting structure, enhancing physical crosslink density. DPHMP (dipentaerythritol hexakis(3-mercaptopropionate)) also resulted in a well formed transparent network when cured with a triacrylate as listed in table 2(a). In spite of good network formation, however, DPHMP, due to its relatively low purity (90% according to

the supplier) have a network with a strong sulfurous odor even after complete conversion. In contrast, the other materials formed tend to have little odor in the cured state.

In addition to polyfunctional acrylates, acrylated linseed oil (CN160) and epoxidized soybean oil acrylate (CN111US) were also used in network formation with various polythiols. These polymerizable, organically modified vegetable oils are more benign and less reactive in as compared to the polyfunctional acrylate monomers used in the present work and described above. Based on the results, as listed in Table 2(e), CN 160 resulted in slow network formation (about 48 hours) when tried with PETMP, demonstrating the chance of thio-ene network formation with added reaction accelerators. In contrast, CN 111US was immiscible with all selected polythiols, with further studies therefore discontinued.

Control of the mechanism of network formation was further explored by forcing crosslinking via Michael addition. Network formation through Michael addition of thiol to acrylate is well established and widely used[8,11,12]. The reaction is catalyzed in basic environments, where primary and secondary amines may act as nucleophilic catalysts thus eliminating the need of added initiator[7]. Apart from the thiol and acrylate involved, it has been reported that the type of amine catalyst used is also important, primary being more effective than secondary which is in turn more effective than tertiary and strongly affecting thiol-acrylate polymerization kinetics[13]. Only those formulations that resulted in slow network formation without catalyst were chosen from different thiol-acrylate formulations (Table 2a to 2e) and were catalyzed using different base catalysts (figure 7). All successful thiol-acrylate formulations with optimized catalyst content are as shown in **Table 3**.

Table 3: Base catalyzed thiol-acrylate formulations with optimized catalyst content. For all systems a 1:1 stiochiometric ration of thiol to acrylate was used at 100 % (w/v) total solids for total volume of 10 mL at room temperature and mixed for 1 min.

Thiol reagent	-ene monomer	Type of catalyst	Catalyst content (wt%)	Cure time (gelation time)	Appearance
PETMA	SR351-H	HXA	0.25	5 min	Transparent and elastic
PETMA	SR 295	HXA	0.25	5 min	Transparent and elastic
TMEI	SR 399	DPA	0.4	Less than 5 min	Transparent and rigid
PETMP	CN160	DPA	0.1	10 min	Transparent, yellow and elastic
TMPMA	CN 160	DPA	0.05	20 min	Transparent, yellow and elastic

Based on the results, different catalysts were chosen for different thiol-acrylate formulations, and the content required was optimized depending on cure speed and bulk properties. Among the three catalyst used, hexylamine (HXA) was the most effective when used

with tri- and tetraacrylate monomers. As little as 0.25 wt% of HXA resulted in complete network formation in about 5 min after mixing as compared to non-catalyzed systems which took 12 to 24 hours (Tables 2(a) and (b)) . Di-n-propylamine (DPA) was the next best choice, and was used for more reactive thiol-acrylate formulations. in spite of being less catalytic than HXA, DPA resulted in very fast network formation when used with TMEI and SR-399 (less than 5 minutes). At higher DPA contents, the accelerated curing coupled with exothermic reaction resulted in an inhomogeneous network, while lower catalyst contents delayed network formation. However, 0.4 wt% of DPA was deemed as ideal, giving transparent, homogeneous network. The isocyanurate core of TMEI further helped to enhance rigidity compared to the other polythiols used. DPA was also used to accelerate network formation in organically modified vegetable derived oils. CN 160 (acrylated linseed oil) when used with PETMP and TMPMA resulted in well formed, transparent networks with a yellow tinge, that were much more elastic, flexible, and had tacky surface on complete cure. This is logical given the inherent flexibility typically imparted by the long hydrocarbon chains present in vegetable oils.

To enhance the adhesion towards metal surface, two different adhesion promoters were used with different thiol-acrylate formulations. A silane coupling agent (3-mercaptopropyl trimethoxysilane, 3-MPTMS) was used in the range of 1 to 5 mol% for different formulations. Silane coupling agents are commonly used to enhance the bonding strength between two surfaces[14]. All successful formulations using silane coupling agent are listed in **Table 4**. Higher concentrations of MPTMS (5 mol%) significantly slowed network formation. For example, complete network formation with 5 mol% of 3-MPTMS in PETMA/SR-35 with HXA catalyst was observed in 4 hours, in contrast to 20 minutes when 1 mol% of 3-MPTMS was used. Similar effects on network formation were observed when used with CN160/PETMP with DPA catalyst as well. For these reasons the concentration of 3-MPTMS was kept at 1 mol% for both the formulations. Another adhesion promoter, phosphoric acid 2-hydroxyethyl methacrylate ester (PAHME), was also used to enhance the adhesion strength of already successful thiol-acrylate formulations. Phosphoric acid derivatives of this sort are reported to increase the adhesion strength to metal surface in thiol-ene networks[15]. However, PHAME was immiscible with all polythiols used in this work, resulting in translucent mixtures and delayed network formation; as such, additional work on this additive was discontinued.

Table 4: Thiol-acrylate formulations with 3- mercaptopropyl trimetoxysilane (3-MPTMS). For all systems a 1:1 stiochiometric ration of thiol to acrylate used at 100 % (w/v) total solids for total volume of 10mL at room temperature and mixed for 1 min.

Thiol reagent	-ene monomer	Type of catalyst	Catalyst content (wt%)	3-MPTMS (mol%)	Cure time	Appearance
PETMA	SR351-H	HXA	0.25	1	20 min	Transparent and elastic
PETMP	CN-160	DPA	0.1	1	5 min	Transparent and elastic

4.1.2 Thiol-Allyl ether formulations

Thiol-ene network were prepared using two polyfunctional allyl ethers based pentaerythritol (PE trial allyl ether, PETE) and trimethylolpropane diallyl ether (TMPDE) using all selected polythiols. All formulations were prepared at room temperature using 1:1 stiochiometric ratio of thiol to allyl (SH: allyl) at 100 % (w/v) total solids for total volume of 10 mL. Unfortunately, with the exception of the combination of TMPMA with either of the allyl ethers listed above, none of other thiol to allyl combinations resulted in network formation. The reduced reactivity of ally ether reduced the speed of network formation, which was observed to be much slower (24-48 hours) than those observed in the thiol-acrylate family of materials (minutes to hours), resulting in a transparent, flexible network with a tacky surface. The slow reaction speed coupled with poor network properties appears to be due to the lower reactivity of the allyl ethers in contrast to the acrylates, at least under the conditions used here. This highlights the need to explore other more highly functional –allyl ethers and / or different reaction chemistries. The addition of amine catalysts had no effect on cure speed or network properties.

4.1.3 Thiol-ene formulation using pure vegetable oil

Different combinations of polythiols with two selected biobased oils were prepared at a 1:1 stiochiometric ratio of thiol to allyl (SH: allyl) at 100 % (w/v) total solids for total volume of 10 mL. Unfortunately, both oils proved to be immiscible with all selected polythiols. A milky white reaction mixture was formed when thiol was added to the vegetable oil and there was no network formation observed over extended period at room temperature.

4.2 Material Characterizations

4.2.1 Hardness (Shore A)

Hardness testing is by far the most widely used, easy, non-destructive way to measure the bulk mechanical properties of an adhesive. In the present work, hardness values for individual adhesive formulations that resulted in high quality networks were obtained using a handheld Durometer (Shore A type). All test specimens were prepared and the hardness value determined in accordance with ASTM D2240-05 on a fully cured disk shaped sample. Test specimens used are as shown in **Figure 11**, while **Table 5** lists the hardness values for the successful formulations.

PETMP/SR-351H PETMP/SR-295

Figure 11: Fully cured test specimens used for Durometer hardness testing (Shore A).

Table 5: Hardness values (Shore A) measured for different adhesive formulations. All samples prepared using a 1:1 stiochiometric ratio of thiol to acrylate (SH : vinyl) with 100 % (w/v) total solids and a total reaction volume of 10 mL at room temperature

Thiol reagent	**-ene monomer**	**Catalyst type / content**	**Adhesion promoter / content**	**Shore A hardness (average ± SD)**
PETMP	SR-351-H	-	-	38 ± 1
PETMP	SR-295	-	-	55 ± 1
TMEI	SR-351-H	-	-	55
TMEI	SR-295	-	-	60
PETMA	SR-351-H	HXA-0.25 wt %	-	61 ± 1
PETMP	SR-351-H	HXA-0.25 wt %	3-MPTMS-1 mol%	63 ± 1
PETMP	CN-160	DPA-0.1 wt %	-	Elastomeric network,
PETMP	CN-160	DPA-0.1 wt %	3-MPTMS-1 mol%	tacky surface
TMEI	**SR-399**	**DPA-0.1 wt %**	**-**	**71**
Epoxy (Loctite)		-	-	80

From the results, it is clear that the hardness value increases with the increase in the functionality of –ene monomer which, consistent with what is expected during network formation. The hardness value for PETMP/SR-295 was as high as 55 (Shore A), compared to that of PETMP/SR-351-H which was around 38 (Shore A). The increase in crosslink density due to the higher functionality of SR-295 (f = 4) vs. SR-351-H (f = 3) increased the hardness value in the former case. Similarly, when combined with TMEI, the isocyanurate monomer with the rigid core, further increases in hardness values were observed for the two acrylates studied, resulting in more rigid networks. Finally, SR-399 (f = 5) in combination with TMEI with DPA catalyst produced the hardest network (71 Shore A) among all successful formulations tried.

4.2.2 Single Joint Lap Shear

Lap shear tests were conducted on different adhesive formulations chosen on a single type of metal (mild steel) substrate. Metal was chosen to minimize the substrate deformation during testing. Those formulations which resulted in complete, homogeneous, rigid networks, and exhibited good adhesion towards metal surface were subjected to lap shear testing in

accordance to ASTMD 1002-10. Lap shear samples prepared using a commercial available two part Heavy Duty Epoxy [xxii] (5 min, Loctite, Henkel Corporation) served as controls to validate the test method and sample preparation. **Table 6** lists all the results obtained from lap shear testing, with reference to the mode of failure for each test specimen.

Table 6: Lap shear test results for various adhesive formulations performed using steel substrates at room temperature under tension. All adhesive formulations were prepared using a 1:1 stiochiometric ratio of thiol to acrylate (SH: Vinyl) used at 100 % (w/v) total solids for total volume of 10mL at room temperature. Here, n = number of samples exhibiting type of failure.

Adhesive formulations (Thiol/-ene/additives)	**Break stress (MPa) average ± SD**	**Type of failure**
PETMP/SR-351H	2.2 ± 0.9	Cohesive and sample failed prior to test (n=2)
PETMA/SR-351H/HXA	2.4 ± 0.7	Adhesive (n = 4), cohesive (n= 1) and sample failed prior to test completion (n=3)
TMEI/SR295	-	Premature failure of test samples before testing
TMEI/SR399/DPA	4.6 ± 1.9	Adhesive (n = 4) and sample failed prior to test completion (n=1)
PETMA/SR-351-H/HXA/3-MPTMS	-	Premature failure of test samples before testing
PETMP/CN160/DPA	-	Premature failure of test samples before testing
PETMP/CN160/DPA/3-MPTMS	-	Premature failure of test samples before testing
Epoxy (Loctite) - Control	10.1 ± 2.7	Adhesive (n=4) & cohesive (n=1)

[xxii] http://www.loctiteproducts.com/tds/EPXY_HEAVY_tds.pdf (viewed on 7/21/12)

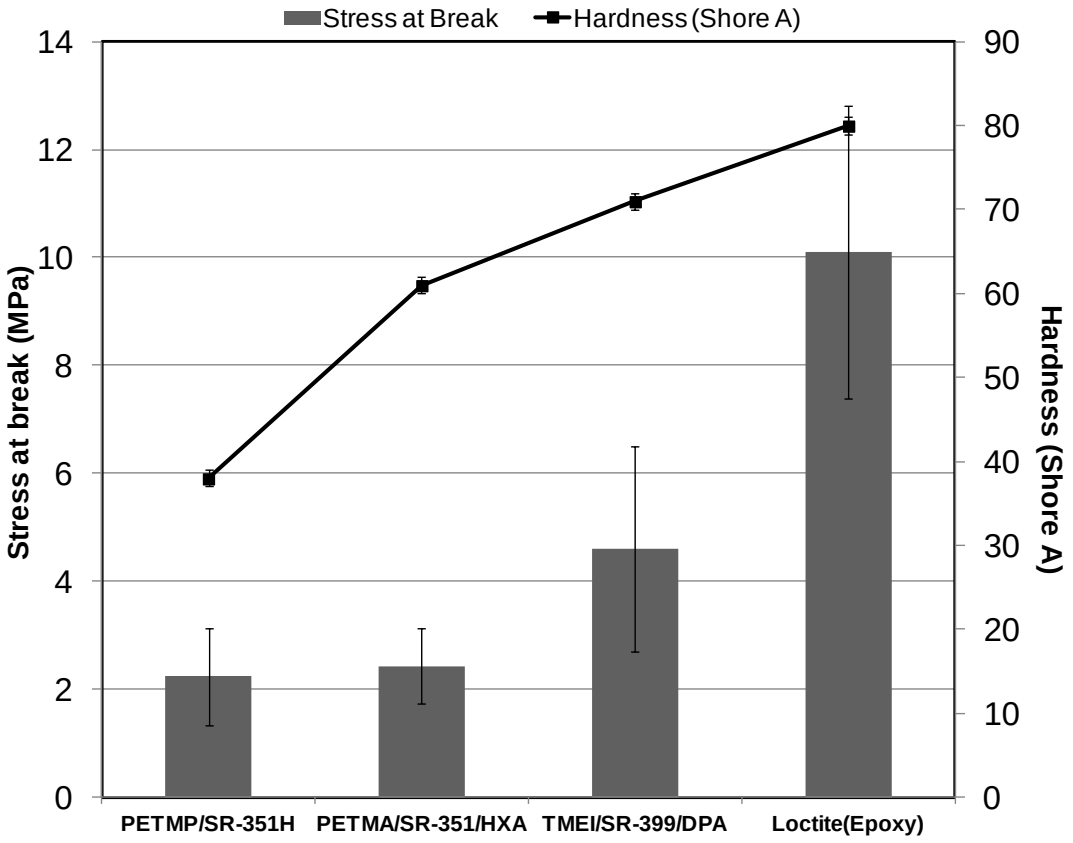


Figure 12: Hardness and stress at break of different adhesive formulations

Based on the test results, an overall trend of increase in break stress with increase in the hardness is observed consistent with the hardness values for different adhesive formulations as shown in **Figure 12**. Networks prepared from SR-351-H (with or without catalyst) showed similar results which can be correlated to the network properties. The elastic network formed on curing exhibited poor adhesion towards metal surface, and could be easily peeled. This caused test specimens to fail prematurely before testing. This effect was observed to become more pronounced with adhesives formulated using acrylated vegetable oils (CN160). In particular, all test samples prepared using CN160 in combination with PETMP and DPA catalyst failed before testing, demonstrating poor network formation and / or a lack of adhesion towards metal surfaces. Incorporation of adhesion promoters did not enhance adhesion, nor enhanced network properties in all formulations (shown in red in Table 6) and was discontinued. Adhesives prepared using TMEI with higher functionality acrylate monomers with DPA catalyst showed the best results among all of the adhesives tested. Samples prepared using TMEI/SR-399 with 0.4 wt % of DPA catalyst showed good results even without any adhesion promoters. For emphasis, it is noted that these test results depend not only on the adhesive chemistry but also on the substrate used[16]. These adhesives can and should therefore be tested on different substrates

such as plastic, rubber, wood etc. to further evaluate the bonding strength and the adhesive performance.

5. CONCLUSIONS AND RECOMMENDATIONS

Overall, different combinations of selected polythiols with -ene monomers resulted in successful network formation via thiol-ene chemistry at room temperature. The structure-property relations in these thiol-ene networks were observed to largely depends upon the type of thiol and –ene monomers used. Fine-tuning of network properties by adding additives (such as catalyst, adhesion promoters etc.,) and optimizing their concentrations is a must to achieve the goal. Based on the results, acrylate monomers proved to be most reactive and compatible with selected polythiols in contrast to other -ene monomers (allyl ethers and bio based vegetable oils). The network prepared via the combination of TMEI (tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate) with SR-399 (dipentaerythritol pentaacrylate) and 0.4 wt% DPA (di-n-propylamine) at a 1:1 stiochiometric ratio of thiol to acrylate showed the best results in terms of network properties and cure speed. Overall it was observed that network formation becomes faster with increased functional group concentration, but with the type and content of catalyst significantly affecting the polymerization rate as well.

Pure vegetable oils and allyl ethers used were not as reactive with the selected polythiols, resulting in delayed or no network formations with or without catalyst; some level of immiscibility was also seen in the context of the vegetable oils in particular. Incorporation of an adhesion promoter also decreased the cure speed and sometimes resulted in phase separation on mixing. The exploration of a greater variety of ally ethers and vegetable oils with more reactive functional groups is therefore recommended. Likewise, primary amines are confirmed to be more effective than secondary and tertiary amine in thiol-ene formation, opening the door for trials involving different base catalysts that could be used to further optimize network formation.

The inherent flexibility of thio-ether linkage reduced the overall hardness of the networks formed, directly affecting the adhesion strength when tested using single joint lap shear test on steel substrate. Most systems tested exhibited poor adhesion towards metal surface and could be easily peeled off resulting in poor bonding strength resulting in premature failure. The use of an isocyanurate derivative (TMEI) helped to increase the network hardness, and substantially improved adhesion to metal as well (though not to the level of the Loctite epoxy control). That said, additional success might be had using a different substrate such as wood, plastic, ceramic or glass, and could be useful in evaluating the adhesion strength and bonding efficiency. Network properties might be further altered by using higher molecular weight, highly polyfunctional prepolymers, while fumed silica could be incorporated to increase viscosity and impart shear thinning properties without sacrificing mechanical performance, so as to improve applicability of the adhesive. Likewise, the more elastomeric behavior observed in some of the present formulations might be useful for applications which require energy absorption, such as in

automobiles and other transportation applications, provided the adhesion strength is enhanced. Finally, photopolymerization of thiol-ene networks is shown to give good results in terms of network properties and cure speed, with or without added additives[10,17,18,19,20]. These experimental formulations may be subjected photopolymerization as well, which could result in a second means of applying the low toxicity adhesive materials described here.

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