Inter-Relationships Between Chemistry, Network Structure and Properties of Chain Growth Dimethacrylate Thermosets

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of Chain Growth Dimethacrylate Thermosets

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ABSTRACT

Dimethacrylate oligomers diluted with styrene reactive diluents (so-called vinyl ester resins) are becoming increasingly important for composites in applications such as transportation vehicles, printed wiring boards and civil infrastructure. This research has focused on the generation and comparative analysis of glassy dimethacrylate networks as a function of oligomer structure, the type of reactive diluent, composition and curing conditions. A novel cycloaliphatic dimethacrylate was synthesized (Figure 1) and its networks were compared to oligomeric structures containing dimethacrylates derived from epoxy terminated oligomers (from bisphenol-A and epichlorohydrin (Figure 2)). Both types of dimethacrylates co-cured with methyl methacrylate exhibited increases in M_c and fracture toughness as the concentration of methyl methacrylate was increased. By contrast, networks prepared with a styrene diluent displayed reduced toughness with increasing styrene and M_c.

Due to the need for long-term composite environmental durability, the effects of moisture and exposure to sunlight are important. Thus, these materials were exposed to

ultraviolet light on a rotating drum for 225 days and the exposure was carefully monitored. Initial results from this study suggest that both the networks comprising the aromatic dimethacrylate/styrene structures as well as the cycloaliphatic analogues cured with methyl methacrylate undergo reductions in rubbery moduli upon aging under these conditions. X-Ray photoelectron spectroscopy shows higher levels of oxidation on the bisphenol-A vinyl ester networks cured with styrene, especially those containing dimethylaniline and cobalt naphthenate as accelerators. Scanning electron microscopy indicates a smooth surface for the cycloaliphatic networks cured with methyl methacrylate and a pitted surface for the aromatic networks cured with styrene. Water absorption is also higher for the cycloaliphatic vinyl ester; however, curing with a longer alkyl chain methacrylate (butyl methacrylate) decreases the water absorption to levels comparable to those cured with styrene.
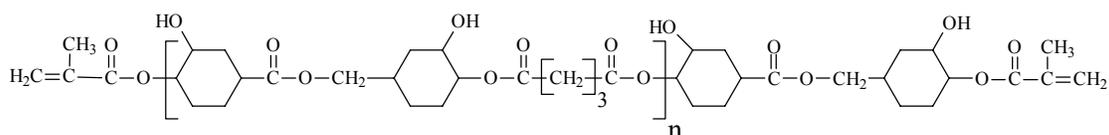

**Figure 1. Cycloaliphatic polyester oligomer with terminal methacrylate reactive groups**
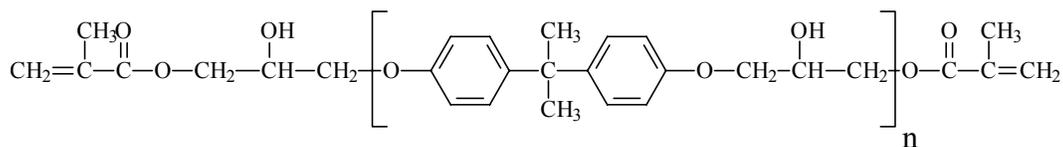
Figure 2. Aromatic dimethacrylate of a poly(hydroxyether) oligomer derived from bisphenol-A and epichlorohydrin

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Dedicated to my wife and family

for their support and encouragement.

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Chapter 1. Overview of the Dissertation

The research presented in this dissertation describes the design and synthesis of a novel aliphatic vinyl ester for improved UV resistance in composites and coatings. Polymer composites in civil structures are of interest where long service lives (50 or more years) are desirable due to their potential for improved corrosion resistance. Commercial dimethacrylate resins, the so-called "vinyl esters," are based on methacrylate terminated aromatic oligomers diluted with low molecular weight reactive monomers such as styrene. The oligomers generally have molecular weights between 700 and 2000 g/mole and the reactive diluent (styrene) is added to lower the viscosity below ≈ 2000 cps for preparing fiber reinforced composites in continuous processes such as pultrusion. The dimethacrylate oligomers and styrene are copolymerized to form void-free, hydrophobic, corrosion resistant networks via free radical chemistry. Aromatic compounds are inherently susceptible to UV absorption and degradation. The UV region of terrestrial sunlight ranges from 400-290 nm. Due to the high energy of radiation at these wavelengths, photo-oxidation can cause chemical and physical changes in polymers and their networks. This project involves the synthesis of a new class of "vinyl esters" with all aliphatic oligomers and methacrylate diluents to minimize UV absorption and degradation.

The second chapter is a review of unsaturated polyester technology of which dimethacrylates are considered a sub-class. This includes synthetic approaches and monomer selection when designing a particular unsaturated polyester resin. Also

discussed is the importance of reactive diluent selection and their contributions to network properties.

The third chapter is a collection of materials and methods used in the synthesis and characterization of the dimethacrylate oligomers and their corresponding networks. This includes monomer purification and synthetic approaches for the preparation of the aliphatic vinyl ester oligomer. It also contains comprehensive descriptions of the analytical techniques for fully characterizing the oligomer. Techniques employed for the evaluation of the network properties including environmental testing (UV accelerated aging and water absorption) is also discussed.

The fourth chapter presents the results and a thorough discussion of the author's research. This includes the synthetic approach and characterization of a novel cycloaliphatic vinyl ester. A thorough comparison and discussion is made between networks co-cured with styrene and/or methyl methacrylate. Systematically varied compositions of methyl methacrylate, and/or styrene, are co-cured with the bisphenol-A based vinyl ester and the cycloaliphatic vinyl ester for a comprehensive comparison of properties. The effects of reactive diluents on rubbery modulus, cross-link density, fracture toughness, microhardness, shrinkage, and water absorption, and accelerated UV aging are also described.

The fifth chapter provides an overview of the conclusions from the author's research described in chapter four. Based on the conclusions in the fifth chapter, the final chapter includes suggestions for future work in this area.

Chapter 2. Literature Review

2.1. Unsaturated Polyesters

2.1.1. Introduction

Unsaturated polyesters are step-growth polyesters that contain unsaturation along their backbones that can participate in a separate cross-linking process, Figure 3. Unsaturation usually comes from the use of maleic anhydride (MA) or fumaric acid as the unsaturated monomer. The unsaturated monomer, maleic anhydride, is reacted with a diol such as propylene glycol and a "saturated dibasic acid" such as phthalic anhydride. Dibasic acids, usually anhydrides, are incorporated since the reaction is driven by the removal of water. By incorporating an anhydride rather than a dicarboxylic acid there is one less water to be removed plus an anhydride is more reactive.
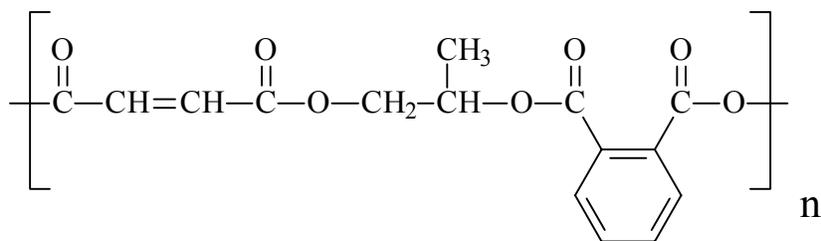
Figure 3. A typical structure of an unsaturated polyester.

The unsaturated polyester is then dissolved in a reactive diluent to lower the viscosity for processing and allow tailoring of properties. The reactive diluent is usually used between 20 and 50 weight percent of the total resin weight. Many reactive diluents

may be used that enhance mechanical properties; however, styrene is the most commonly used due to cost-performance criteria of the industry. The reactive diluent, usually styrene, contains a site of unsaturation to participate in the free radical curing process.

The degree of unsaturation in the polyester and the level of reactive diluent incorporated will influence the cross-link density of the resulting network. Higher levels of unsaturation incorporated into the polyester backbone increases the functionality of the polyester and increases the cross-link density of the network. However, increasing the amount of reactive diluent will lower the cross-link density by increasing the distance between network junction points.

The wide variety of condensation monomers and the number of possible reactive diluents make unsaturated polyester technology a real formulation science. The wide range of resulting properties allows its use for a wide range of applications. This review will focus on the effects of condensation monomers as well as the effects of reactive diluent on their corresponding network properties.

2.1.2. History

The first polyesters were made by the reaction of tartaric acid with glycol by Berzelius in 1847.[1,2] Vorlander in 1894 reacted ethylene glycol with succinic acid to form a polyester.[3] And in the 1920's Carothers made substantial progress in polyester synthesis and theories in condensation polymerizations. Carothers was the first to prepare well defined polyesters from ethylene glycol and several dibasic acids: phthalic anhydride, fumaric acid, and maleic anhydride.[4,5]

However it wasn't until the late thirties that Bradley, Kropa, and Johnston reported that unsaturated polyesters based on maleic anhydride become insoluble and infusible upon drying because of the unsaturation in the polyester chains.[6,7,8] Around the same time period Ellis reported that the cure rate of the unsaturated polyesters could be increased if unsaturated monomer such as styrene was present with benzoyl peroxide.[9] Subsequent improvements lead to the first commercial application of unsaturated polyesters in 1941.

With the beginning of the Second World War, unsaturated polyester technology increased dramatically. The United States Rubber Company in 1942 discovered the

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1   H. V. Boenig, *Unsaturated Polyesters: Structure and Properties*, Elsevier Publishing Co., New York, **1964**.
2   B. Parkyn, *Unsaturated Polyesters, Vol. 2*, American Elsevier Publishing, New York, **1967**.
3   D. Vorlander, *Ann. Chem.* **1894**, *280*, 167.
4   W. Carothers, *J. Am. Chem. Soc.* **1929**, *51*, 2548.
5   W. Carothers, *J. Am. Chem. Soc.* **1929**, *51*, 2560.
6   T. Bradley, *Ind. Eng. Chem.* **1937**, *29*, 440.
7   T. Bradley, *Ind. Eng. Chem.* **1937**, *29*, 579.
8   T. Bradley, E. Kropa, W. Johnston, *Ind. Eng. Chem.* **1937**, *29*, 1270.
9   C. Ellis, US 2,195,362, **1940**.

influence and importance that glass fibers have on the reinforcement of polyesters.[10] This technology became a large commercial endeavor. The first application of glass reinforced polyesters was in the radomes of aircraft. This provided physical protection over the aircrafts' radar equipment and minimum hindrance of radar transmission.

Resin manufacturers began to research new monomers and markets. Manufacturers began to investigate new dihydric alcohols, saturated and dibasic acids, and unsaturated reactive diluents. Processes such as castings and laminates provided the needed outlet for their products. By the late 1950's the unsaturated polyester technology had been well established with minor improvements to the present day. Unsaturated polyester commercialization started out with aircraft radomes and the technology has developed significantly to provide current day applications in electronics, house wares, appliances, furniture, transportation (from automobiles to farm equipment), tools, boats, bathroom stalls and tubs, skis, luggage, sporting goods, and the list is too long to even include all the applications in this review.

2.1.3. Synthesis of unsaturated polyesters

Unsaturated polyesters are synthesized generally from maleic anhydride (MA), propylene glycol (PG) and phthalic anhydride (PA), Figure 4. The maleic anhydride provides the sites for cross-linking, the saturated acid allows spacing of the unsaturated sites and the glycol provides the esterification to bring all the monomers together. The monomers are charged into a batch reactor with typical molar ratios of 1:1:2 (MA: PA: PG); depending on the level of unsaturation desired in the final oligomer these ratios may vary. The fact is stoichiometry is not used to control molecular weight. A one to one

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[10]   H. V. Boenig, *Unsaturated Polyesters: Structure and Properties*, Elsevier Publishing Co., New

molar ratio of diacid to diol is used and the reaction is carried out to low conversion in order to "control the molecular weight". In addition, the glycol is usually added in excess (5-20% excess) to compensate for the loss during the polymerization due to the inefficiency of the condenser while removing the by-product water.[11,12] The esterification is carried out under an inert atmosphere.[13,14] Esterification catalysts can be used such as dibutyl tin oxide, p-toluene sulfonic acid, and sulfuric acid; however, p-toluene sulfonic acid and sulfuric acid generally yield colored resins and need to be neutralized at the end of the reaction.[15,16] The temperature is brought up to 100°C to start the exothermic reaction in which the temperature may rise to 120°C.[17] Water is the by-product of the esterification process and is removed throughout the reaction by distillation in a dry process or by azeotroping with 10% xylene in an azeotropic process.[18] The azeotropic removal of water reduces polyesterification time by 30-50%.[19] For the dry process, the temperature is slowly brought up to 175°C, then once the acid number reaches $\approx$200 the reaction temperature is increased to 190°C.[20] The reaction is carried out until the desired acid number is reached which is usually between 38 and 50.

York, **1964**.

[11]   B. Parkyn, *Unsaturated Polyesters, Vol. 2*, American Elsevier Publishing, New York, **1967**.

[12]   in *Encyclopedia of polymer science and engineering, Vol. 12*, John Wiley and Sons, New York, **1988**, pp. 256.

[13]   D. Miles, J. Briston, *Polymer Technology*, Chemical Publishing Co., **1996**.

[14]   in *Encyclopedia of polymer science and engineering, Vol. 12*, John Wiley and Sons, New York, **1988**, pp. 256.

[15]   B. Parkyn, *Unsaturated Polyesters, Vol. 2*, American Elsevier Publishing, New York, **1967**.

[16]   W. Gum, W. Riese, H. Ulrich, *Reaction Polymers*, Hanser, New York, **1992**.

[17]   G. Gunduz, in *Polymeric Materials Encyclopedia, Vol. 11* (Ed.: J. Salamone), CRC, New York, **1996**, pp. 8469.

[18]   D. Miles, J. Briston, *Polymer Technology*, Chemical Publishing Co., **1996**.

[19]   G. Gunduz, in *Polymeric Materials Encyclopedia, Vol. 11* (Ed.: J. Salamone), CRC, New York, **1996**, pp. 8469.

[20]   B. Parkyn, *Unsaturated Polyesters, Vol. 2*, American Elsevier Publishing, New York, **1967**.

$$
\text{(maleic anhydride)} \qquad
\begin{array}{c}
CH_3-CH-CH_2 \\
\;\;\;\;\;\;\;\; | \;\;\;\; | \\
\;\;\;\;\;\;\;\; OH \;\; OH
\end{array}
\qquad \text{(phthalic anhydride)}
$$

$$
\Bigg[\; \overset{O}{\underset{\|}{C}}-CH=CH-\overset{O}{\underset{\|}{C}}-O-CH_2-\overset{CH_3}{\underset{|}{CH}}-O-\overset{O}{\underset{\|}{C}}\;\;\;\overset{O}{\underset{\|}{C}}-O\;\Bigg]_n
$$
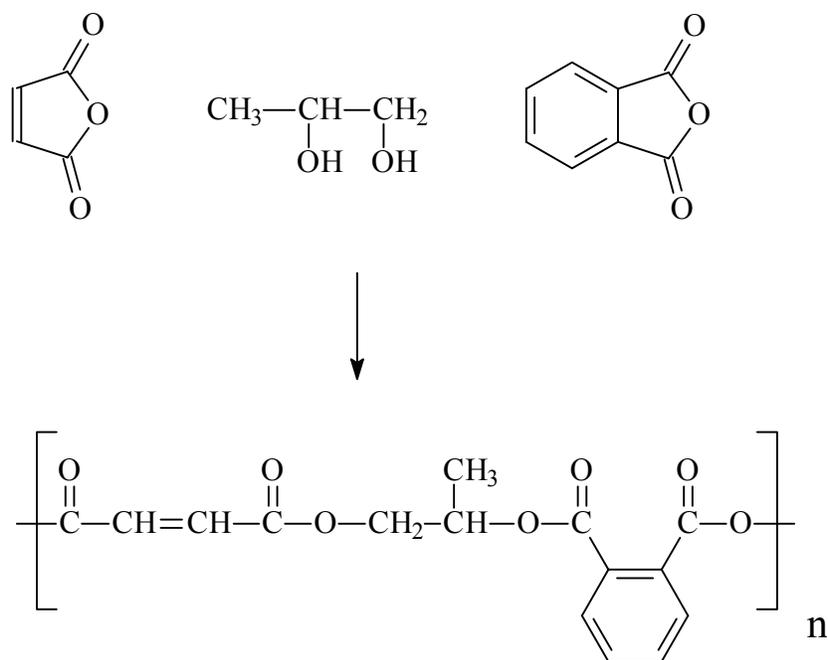
Figure 4. Synthesis of an unsaturated polyester.

Several factors are monitored during the reaction course such as the viscosity,
acid number and hydroxyl number. As the reaction proceeds the viscosity increases and
the acid number and hydroxyl number decrease. This is done by sampling the reaction as
a function of time and titrating it with .1 M alcoholic potassium hydroxide. The acid
number is expressed in milligrams of KOH needed to neutralize 1 gram of oligomer. The
molecular weight is related to the acid number by Equation 1.

Equation 1

$$Mw = 56100/\text{acid number}$$

Thus for an acid number of 50 the molecular weight would be 1122 g/mol. Essentially,
the purpose of titrating is to get the extent of reaction (p); which is the percent of acid
monomer reacted. Thus, the number average degree of polymerization (X_n) can be

calculated from Equation 2, where r =1.[21,22,23] This equation only works if r (the ratio of monomer A to monomer B) = 1; however, if excess glycol is used or glycol is lost during the reaction then r does not = 1 or is undefined. Again, Equation 1 only works if the oligomers contain one acid endgroup. A better method would be to consider both the hydroxyl number and the acid number when calculating the molecular weight. Other methods for molecular weight analysis such as vapor pressure osmometry or size exclusion chromatography are also employed, but these methods are not as common.

Equation 2

$$X_n = (1+r)/(1+r-2rp)$$

$$\text{Thus if } r = 1$$

$$X_n = 1/(1-p)$$

$$\text{Where } r = N_{monomer\ A}/\ N_{monomer\ B}$$

Even though the MA has a reactive double bond, during the polymerization the maleate ester does not homopolymerize. However, a side reaction of MA with glycols produces a resin with higher functionality with a decrease in the amount of unsaturation which can lead to gelation and poorer properties than if fumaric acid is used. Fumaric acid does not give side reactions and retains a high level of unsaturation in the polyester oligomer. Generally, resins containing fumaric acid have superior properties and higher reactivities with styrene, but suffer the disadvantage of the higher price of fumaric acid.

[21]   J. Cowie, *Polymers: Chemistry and Physics of Modern Materials*, Blackie Academic and Professional, New York, **1991**.
[22]   G. Odian, *Principles of Polymerization*, Third ed., John Wiley, New York, **1991**.
[23]   P. Painter, M. Coleman, *Fundamentals of Polymer Science*, 2 ed., Technomic Publishing Co., Lancaster, **1997**.

During the polymerization the maleate esters exist in the strained cis planer structure similar to the maleic anhydride structure below 160°C. Because the maleate esters have increased strain on the double bond, especially when propylene glycol is used, the maleate esters isomerize from the cis form to the trans-fumarate form. Long reaction times, bulky aromatic dibasic acids, secondary alcohols, and temperatures above 180°C allow higher conversion to the trans-fumarate.[24] A higher level of trans-fumarate isomerization is encouraged since it is more stable and is reactive with styrene.

Once the desired acid number is reached the reaction mixture is allowed to cool to ≈100°C. Styrene containing an inhibitor such as hydroquinone is then added to the unsaturated polyester oligomer. This mixture is then allowed to mix and cool to room temperature as soon as possible to prevent premature gelation. The resin is now ready to be sold or used in production.

2.1.4. Monomer composition effect

2.1.4.1. Unsaturated monomers

It is essential that unsaturated polyesters contain unsaturation in order to participate in the free radical curing process. In most commercial formulations maleic anhydride is usually incorporated into the backbone of the polyester for this reason. Maleic anhydride has a lower melting point than either maleic acid or fumaric acid. Maleic anhydride is also quite reactive when compared to a carboxylic acid moeity and there is loss of only one water molecule during the esterification process. In order to be effective during the crosslinking process the maleate ester must isomerize to the trans-

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[24]   in *Encyclopedia of polymer science and engineering, Vol. 12*, John Wiley and Sons, New York,

fumarate. The isomerization does not occur to 100% thus it is not uncommon for fumaric

acid to be used instead of maleic anhydride for improved mechanical properties,(Figure

5).
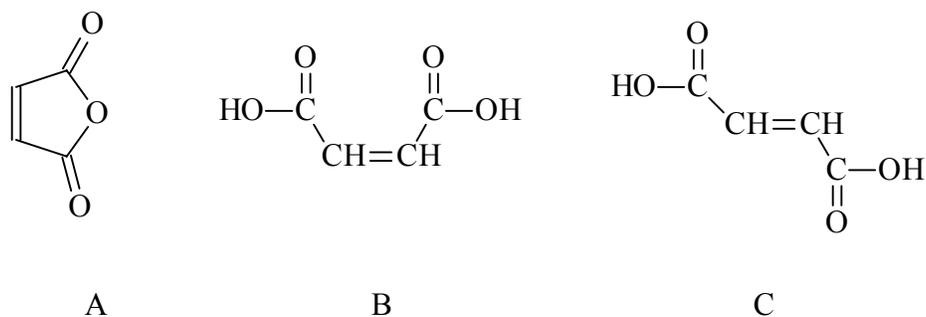
Figure 5. Unsaturated monomers: A, maleic anhydride; B, maleic acid; C, fumaric acid.

As described earlier, the ratio of trans-fumarate to maleate is very important. As

any level of maleate in the final oligomer is undesireable. The maleate ester reacts poorly

with styrene and thus is ineffective during the cross-linking step. Maleates can also

undergo a side reaction at high temperatures that fumarates usually do not. A glycol can

add to the site of unsaturation during the isomerism and cause branching, which is not

desired,(Figure 6).[25]
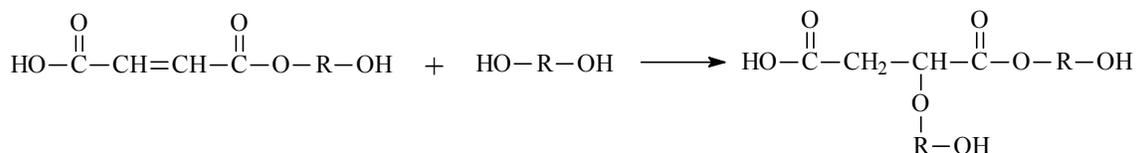
Figure 6. A side reaction between maleic anhydride (or maleate ester) and a glycol.

1988, pp. 256.

[25]   Y. Yang, J. Pascault, Modeling of unsaturated polyester prepolymer structures. 1. Chain branches and overall chain end numbers, *J. Appl. Polym. Sci.* **1997**, *64*, 133.

R   R
 \   /
  O O

O=C   C=O
  \   /
  CH=CH

$\longrightarrow$

O
||
RO$-$C
    \
     CH=CH
          C$-$OR
          ||
          O
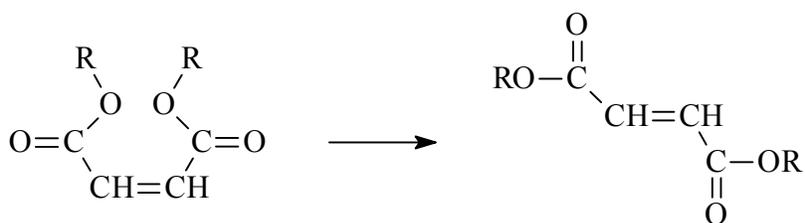
Figure 7. Isomerization from the maleate ester to the trans-fumarate ester.

During the initial stages of the reaction the maleate esters remain in their cis conformation,(Figure 7). But, as the reaction temperature is increased to greater than $\approx 180^{\circ}$C the maleate ester isomerizes to the more planar trans-fumarate, which reduces the amount of steric interactions. Typically, greater than 95% of the maleate will isomerize to the fumarate under typical reaction conditions of 15 hours at 190°C.[26] The trans-fumarate then can now participate in the curing process since the maleate ester will not react with styrene to any significant extent. Higher levels of trans-fumarate isomerization is encouraged since it has a reactivity with styrene 20 times greater than that of the maleate.[27] Mayo and Lewis has reported that in the presence of vinyl monomers diethyl fumarate is about forty times more reactive than diethyl maleate.[28] The decrease of maleate/styrene reactivity is associated with the anti-planar nature of the maleate, due to strain. The relative reactivity ratios (r_1 and r_2) in Table 1 are much closer for styrene-diethyl fumarate than for styrene-diethyl maleate. Thus, there will be very long segments of styrene in the network with little incorporation of the maleate ester for those resins with high concentrations of maleate esters.

[26]   M. Malik, V. Choudhary, I. Varma, Current Status of Unsaturated Polyester Resins, *J.M.S. Rev. Macromol. Chem. Phys.* **2000**, *40*, 139.

[27]   H. W. Melville, G. M. Burnett, *J. Polym. Sci.* **1954**, *13*, 417.

[28]   F. R. Mayo, F. M. Lewis, C. Walling, *J. Am. Chem. Soc.* **1948**, *70*, 1529.

M$_1$	M$_2$	r$_1$	r$_2$	r$_1$/r$_2$
Styrene	Diethyl fumarate	0.30	0.07	4.28
Styrene	Diethyl maleate	6.52	0.005	1304

Table 1. Reactivity ratios for styrene with two monomer pairs.[29]

Isomerism from the maleate ester to the trans-fumarate ester occurs at temperatures above 180°C and is aided by large bulky glycols, which cause higher maleate ester strains. For example, if ethylene glycol or diethylene glycol, a primary glycols, are used as the diol rather than propylene glycol, which is a secondary alcohol, then the resulting polyester will have a lower level of the trans-fumarate.[30] The added steric hinderence of the secondary alcohol provides more isomerization to the trans-fumarate under normal reaction conditions.

The isomerization of the maleate to the fumarate has been investigated by several researchers. The conversion of maleate to fumarate can be monitored by FTIR and ^{1}H NMR.[31, 32] H NMR can be also be used to monitor the isomerism from maleate to fumarate by the disappearance of the maleate vinyl hydrogen signal at 6.24 ppm and the appearance of the fumarate vinyl hydrogen at 6.82 ppm.[33,34] The rate of isomerization can

[29]   H. V. Boenig, *Unsaturated Polyesters: Structure and Properties*, Elsevier Publishing Co., New York, **1964**.

[30]   L. G. Curtice, a. co-workers, *Ind. Eng. Chem. Prod. Res. Dev.* **1964**, *3*, 218.

[31]   G. Gunduz, in *Polymeric Materials Encyclopedia, Vol. 11* (Ed.: J. Salamone), CRC, New York, **1996**, pp. 8469.

[32]   B. Parkyn, *Unsaturated Polyesters, Vol. 2*, American Elsevier Publishing, New York, **1967**.

[33]   M. Malik, V. Choudhary, I. Varma, Current Status of Unsaturated Polyester Resins, *J.M.S. Rev. Macromol. Chem. Phys.* **2000**, *40*, 139.

also be affected by the use of a catalyst. It has been shown that a cycloaliphatic amine,

morpholine, can promote isomerization at lower temperatures.[35] The isomerization from

maleates to fumarates has been known to be catalyzed by primary or secondary amines

by the following three steps: 1) reversible attack of the amine on the double bond, 2)

rotation of the intermediate formed, and 3) elimination of the amine used.[36]

Unsaturated monomers	Characteristics
Maleic anhydride	Lowest cost, moderate heat deflection temperature
Fumaric acid	Highest reactivity during cross-linking, higher heat deflection temperatures and more rigidity

Table 2. Unsaturated monomers incorporated into unsaturated polyesters and their corresponding properties.[37,38]

2.1.4.2.   Saturated Monomers

Saturated monomers, such as those in Table 3, are incorporated into the polyester

for several reasons. One reason is to provide spacing between sites of unsaturation due to

the maleic anhydride. Higher levels of saturated diester incorporation allow greater

34   V. Larez, J. Cristobal, G. Mendoza, Unsaturated Polyesters. V. Polyester from maleic anhydride and 1,6-hexanediol, *J. Appl. Polym. Sci.* **1993**, *47*, 121.
35   C. Shmidle, A. Schmucker, US 3,576,909, **1971**.
36   T. Otsu, O. Ito, N. Toyoda, Polymers from 1,2- disubstituted ethylenic monomers. V. Radical polymerization of dimethyl maleate in the presence or absence of isomerization catalyst., *J. Macromol. Sci.-Chem* **1983**, *A19*, 27.
37   I. Skeist, A polyester for every purpose, *Modern Plastics* **1964**, *41*, 80.
38   R. Burns, *Polyester Molding Compounds*, Marcel Dekker, New York, **1982**.

spacing of the double bonds and thereby ruduction of the cross-link density. Saturated

monomers also allow the tailoring of oligomeric and network properties such as

flexibility, dimensional stability, flame retardance, heat deflection temperatures, etc.

Nearly all formulations contain one of three saturated monomers, phthalic

anhydride, isophthalic acid, or terephthalic acid. In oligomers containing any of the three

monomers listed above, other saturated monomers may also be incorporated to improve

properties such as flexibility, flame retardance, dimensional stability and higher heat

deflection temperatures, etc. (Table 3).

Saturated monomers	Characteristics
Phthalic anhydride	Lowest cost, moderate heat deflection temperatures, and good mechanical strengths
Isophthalic acid	Better chemical and water resistance, improved mechanical properties, higher flexural and tensile strength
Terephthalic acid	Similar to isophthalic resins, improved chemical resistance
Adipic acid	Increased toughness and flexibility
Sebacic Acid	Similar affect as adipic acid but more expensive
Chlorendic anhydride (HET-acid)	Flame retardance
Nadic methyl anhydride	High Heat distortion temperature
Tetrachlorophthalic anhydride	Flame retardance

Table 3. Saturated monomers that are incorporated into unsaturated polyesters and their corresponding network characteristics.[39,40]

[39] I. Skeist, A polyester for every purpose, *Modern Plastics* **1964**, *41*, 80.
[40] R. Burns, *Polyester Molding Compounds*, Marcel Dekker, New York, **1982**.

2.1.4.2.1. Oligomers containing phthalic anhydride as the monomer

Phthalic anhydride is the lowest cost monomer typically utilized and provides good mechanical properties and moderate heat deflection temperatures. Phthalic anhydride has similar reactivity with a glycol as that of maleic anhydride and thus a one-stage melt reaction can be used for the synthesis of these resins.

In a one stage melt reaction process, all the monomers are typically charged into a reactor, usually in liquid form to facilitate heating, at the same time and allowed to react until the desired acid number is achieved. The temperature is slowly brought up to 190°C for about 15 hours depending on the desired acid number. While water is being removed to facilitate esterification some glycol is lost.[41,42] However, the loss of glycol can be overcome by using fractionating condensers or accommodated by using an excess of the stoichiometric required amount of glycol.

2.1.4.2.2. Oligomers containing isophthalate esters

Isophthalate ester resins cannot be produced by the one-stage melt process that is typically utilized for phthalate ester oligomers. Isophthalic acid reacts with glycols much slower than maleic anhydride or phthalic anhydride. In a one-stage process the saturated anhydrides or acids must compete with the unsaturated anhydrides for glycol. An additional problem is that isophthalic acid does not esterify below 190°C.[43] If a one-stage

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[41]   D. Miles, J. Briston, *Polymer Technology*, Chemical Publishing Co., **1996**.

[42]   in *Encyclopedia of polymer science and engineering, Vol. 12*, John Wiley and Sons, New York, **1988**, pp. 256.

[43]   in *Encyclopedia of polymer science and engineering, Vol. 12*, John Wiley and Sons, New York, **1988**, pp. 256.

fusion process was used all the maleic anhydride would react with the glycol and the isophthalic acid would be left unreacted. High temperatures above 240°C and long reaction times would be required to dissolve and react the isophthalic acid.[44] At these temperatures the unsaturation gives rise to side reactions. Upon cooling and the addition of styrene, any unreacted isophthalic anhydride would precipitate out and form a hazy resin. Thus, isophthalic resins are prepared from a two-stage melt process.

With a two-stage melt reaction process, the glycol and saturated dibasic acid are added all at once in the first step. The temperature is typically brought up to 190-220°C until a low acid value is achieved, ~8 hours, to completely esterify the saturated dibasic acid.[45] Modifications can also be made with this process where the first step is only taken to the half ester before the unsaturated monomer is added. The second step involves the addition of the unsaturated anhydride. The temperature is generally lowered to ≈150°C and the unsaturated anhydride is added. The temperature is then slowly raised to ≈190°C for the remaining time until the desired acid number is obtained. This process allows more flexibility and control of reactivity than achievable by the one-stage fusion process.

2.1.4.2.3.   Oligomers Containing Terephthalate Esters

Terephthalic resins are prepared in the same manner as the isophthalic resins. Terephthalic acid reacts very similarly to isophthalic acid and yields similar network properties with styrene. Resins containing terephthalic acid are less soluble in styrene

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[44]   in *Encyclopedia of polymer science and engineering, Vol. 12*, John Wiley and Sons, New York, **1988**, pp. 256.

[45]   in *Encyclopedia of polymer science and engineering, Vol. 12*, John Wiley and Sons, New York, **1988**, pp. 256.

than are the iso resins. If ethylene glycol is used, as with any resin, the solubility in styrene is reduced even further.

Terephthalic resins can also be prepared from the recycling of PET. Solid PET can be digested to the diester with glycols, i.g. : propylene glycol, via transesterification with excess diol.[46] The transesterification is typically carried out at 200°C with a catalyst such as tetraisopropyl titanate or dibutyl tin oxide.[47] However, most solid PET has enough transesterification catalyst in it from when it was synthesized. Once the propylene glycol esters are formed the temperature can be lowered and maleic anhydride added as in the second step in the reaction with isophthalic acid.

2.1.4.3. Glycols

Glycols, such as those in Table 4, are incorporated into the polyester to allow esterification and incorporation of the dibasic acid monomers. The glycol has a strong influence on the flexibility, water absorption, heat deflection temperature, and solubility in styrene. Propylene glycol is the diol of choice, although other diols are incorporated. Table 4 shows a small list of glycols and their use. There are many factors that contribute to the choice of monomers such as the desired properties, side reactions, and resin solubility. For example, ethylene glycol can limit the molecular weight of phthalic resins by forming cyclic esters with phthalic anhydride.[48] Also resins containing ethylene glycol have limited solubility in styrene.

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[46]   R. Calendine, M. Palmer, P. Bramer, *Modern Plastics* **1980**, *57*.
[47]   in *Encyclopedia of polymer science and engineering, Vol. 12*, John Wiley and Sons, New York, **1988**, pp. 256.
[48]   in *Encyclopedia of polymer science and engineering, Vol. 12*, John Wiley and Sons, New York, **1988**, pp. 256.

Glycol	Characteristics
Propylene glycol	Lowest cost, moderate heat deflection temperature, good flexibility, good water resistance, good compatibility with styrene
Dipropylene glycol	Toughness and flexibility, good compatibility with low profile additives
Ethylene glycol	Low cost, high heat distortion temperature, good mechanical strengths, less soluble in styrene
Diethylene glycol	Greater toughness, impact strength, flexibility, lower water resistance
Neopentyl glycol	Very good color, good wet strength retention and corrosion resistance.
Bisphenol-A	High heat distortion temperature, corrosion resistance, high flexural and tensile strength
Hydrogenated Bisphenol-A	High heat distortion temperature, corrosion resistance, high flexural and tensile strength

Table 4. Glycols incorporated in unsaturated polyester oligomers and their general network characteristics.[49,50]

Glycols can also cause branching in unsaturated polyester resins. In the reaction mixture, a glycol can react by a Michael addition with the unsaturation of a maleic diester. This addition usually occurs when the maleate ester undergoes isomerization to the trans fumarate. This particular side reaction is known as the Ordelt reaction, Figure 6. However, resins with fumaric acid rather than maleic acid do not undergo this side

[49] I. Skeist, A polyester for every purpose, *Modern Plastics* **1964**, *41*, 80.
[50] R. Burns, *Polyester Molding Compounds*, Marcel Dekker, New York, **1982**.

reaction with glycols, because it does not undergo isomerization. Thus, resins with fumaric acid generally yield higher performance resins.

2.1.5. Crosslinking mechanism

Unsaturated polyesters are diluted with a reactive diluent such as styrene to form a homogeneous resin with a low viscosity. Not only does the reactive diluent lower the viscosity, but it also copolymerizes with the unsaturated polyester to form a three dimensional network. The cross-linking process is a chain growth reaction between the trans-fumarate of the unsaturated polyester and the reactive diluent, Figure 8. The unsaturated polyester has a functionality greater than 2 and thus allows cross-linking. The reactive diluent has a functionality of 2 and thus it will only form linear segments connecting the higher functional unsaturated polyester. The cured network has a gel fraction and a sol fraction. There can be dangling ends, loops, entanglements, cross-links, and homopolymer in the final network.

In order to facilitate network formation a peroxide initiator must be used. When selecting a cure package or initiator, consideration must be given to the to the cure temperature and gel time for that particular resin. There are three broad processing temperature groups that exist: 1) room temperature cure (20-50°C) which includes contact molding, cold press molding, and resin injection; 2) intermediate temperature cure (50-100°C) which includes continuous laminating filament winding; 3) high temperature cure (100-160°C) which includes hot press molding, SMC and DMC.[51]

There are six classes of peroxides: diacyl peroxides, ketone peroxides, hydroperoxides, dialkyl and diaralkyl peroxides, peroxyesters, and perketals

(peroxyketals) and they are generally supplied as a powder, a liquid, or a paste. Table 5 shows a list of common peroxides, with their corresponding half-life temperatures, used in curing unsaturated polyesters. Peroxides are activated by heat, so depending on the cure conditions or the curing process, peroxides may be used in conjunction with accelerators. Free radicals are generally formed from the thermal decomposition of peroxides such as benzoyl peroxide (BPO), Figure 8. When BPO is thermally decomposed, two radicals are generated that each can independently initiate their own chain.

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51   R. Weatherhead, *FRP Technology*, Applied Science, London, **1980**.

Peroxide	10 hour half life (^{o}C)	Half life (h)		
		100 ^{o}C	120 ^{o}C	150 ^{o}C
t-butyl peroxypivalate	55			
lauryl peroxide	62	0.1		
2,5-dimethyl hexane-2,5-diperoxy-2-ethyl hexanoate	67			
t-butyl peroxy-2-ethyl hexanoate	72			
benzoyl peroxide	72	0.5		
t-butyl peroxyisobutyrate	78			
2,5-dimethyl hexane-2,5-diperoxy benzoate	100			
t-butyl perbenzoate	105	18	1.6	.05
ethyl-3,3-bis(t-butyl peroxy)butyrate	110			
dicumyl peroxide	115	45	6.8	0.2
di-t-butyl peroxide	126	210	20	0.8
methyl ethyl ketone peroxide		16.2	6.0	0.2
cyclohexanone peroxide		7.7	0.9	

Table 5. Commonly used free radical initiators and their corresponding half lives.[52,53]

[52]   R. Burns, *Polyester Molding Compounds*, Marcel Dekker, New York, **1982**.
[53]   R. Weatherhead, *FRP Technology*, Applied Science, London, **1980**.
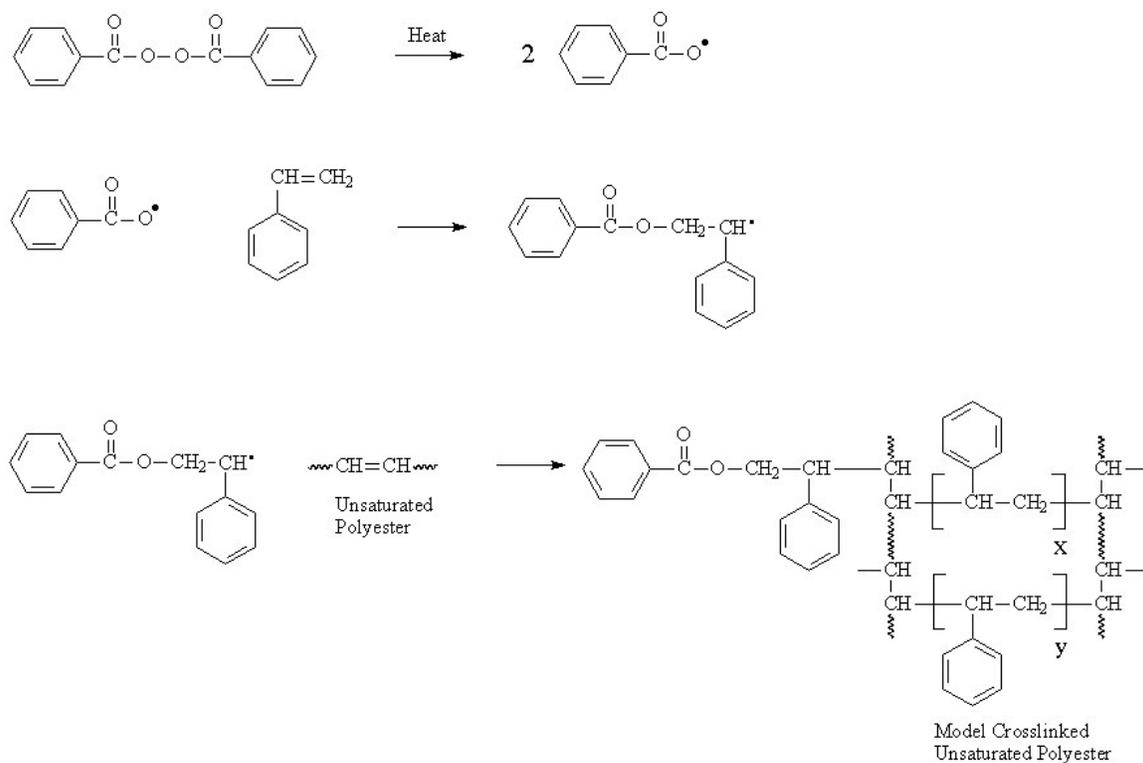
Figure 8. Thermal decomposition of benzoyl peroxide and network formation.

Peroxide/metal-salt redox initiator systems are effective at curing unsaturated polyesters at ambient temperatures with hydroperoxides such as MEKP. Peroxide/metal-salt redox initiator systems are effective with ketone peroxides, hydroperoxides, and peresters. However, they are ineffective with diacyl peroxides such as BPO. Metal-salt accelerators such as cobalt octoate or naphthenate catalyze the generation of free radicals at room temperature from hydroperoxides, Figure 9. Free radicals can be generated from hydroperoxides by either oxidation state of the cobalt.[54,55,56]

[54]   W. Brinkman, Accelerators for peroxide curing of polyesters, *Modern Plastics* **1968**, 167.

[55]   L. Ling, X. Sun, L. Lee, Low temperature of vinyl ester resins, *Polymer Engineering and Science* **1999**, *39*, 646.

[56]   W. Cook, G. Simon, P. Burchill, M. Lau, T. Fitch, Curing kinetics and thermal properties of vinyl ester resins, *J. Appl. Polym. Sci.* **1996**, *64*, 769.

$$ROOH + Co^{+2} \longrightarrow RO^{\cdot} + OH^{-} + Co^{+3}$$

$$ROOH + Co^{+3} \longrightarrow ROO^{\cdot} + H^{+} + Co^{+2}$$
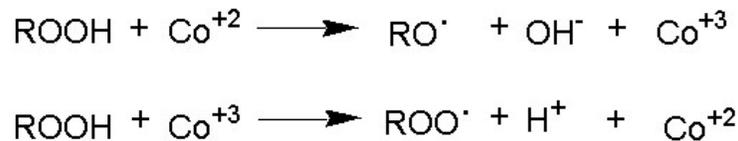
Figure 9. Redox initiation.

Dimethylaniline can be used with diperoxides such as BPO to cure unsaturated polyesters at ambient temperatures. Although the mechanism is unknown, the proposed mechanism of the decomposition of BPO by dimethylaniline is shown in Figure 10. This is an exothermic reaction in addition to any free radical curing reaction that may take place after decomposition and encourages thermal decomposition of BPO as well.[57]
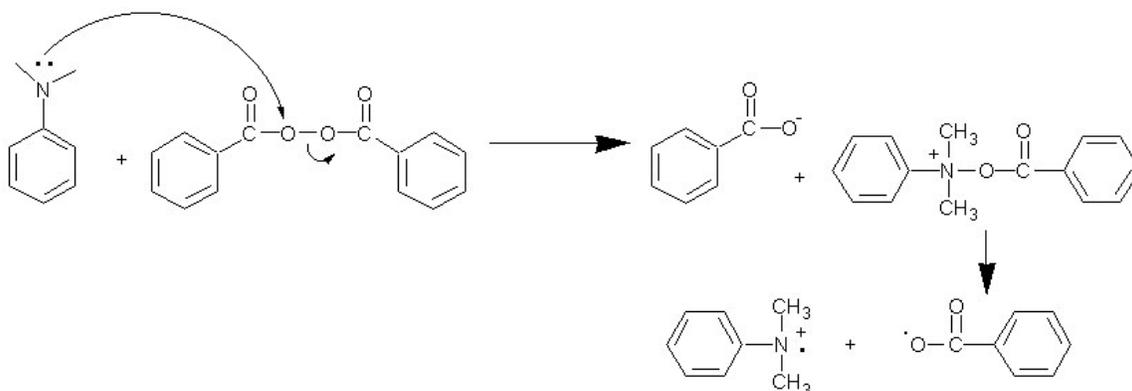
Figure 10. Proposed mechanism for the decomposition of BPO by DMA at ambient temperatures.

The level of unsaturation is another way to tailor the properties of the final network. Higher levels of unsaturation in the polyester tend to increase the cross-link density and the cure exotherm. Increasing the level of reactive diluent decreases the cross-link density but also increases the cure exotherm. The free radical cure is an exothermic reaction so any increase in the level of unsaturation is going to affect the peak

exotherm temperature. Cross-link density not only affects the mechanical properties but also the chemical resistance. Since the unsaturated polyester is polar and susceptible to hydrolysis, increasing the cross-link density will improve the chemical resistance.[58]

Upon curing the free volume decreases and thus the resulting network shrinks upon conversion of the double bond. For some applications a certain level of shrinkage is desirable; however, a high level of shrinkage can cause high levels of internal stress, warpage, and surface defects in composites. Table 6 shows the percent volume shrinkage of an unsaturated polyester co-cured with a wide range of reactive diluents. Shrinkage is generally reduced or controlled by the use of fillers and low profile additives.

Reactive diluent	Shrinkage (%)
Styrene	17
Vinyl toluene	12.6
Diallyl phthalate	11.8
Methyl methacrylate	21
Vinyl acetate	27
t- butylstyrene	7

Table 6. Volume shrinkage of unsaturated polyester co-cured with a wide range of reactive diluents.[59,60]

Reactive diluents may influence the final network in several ways. Reactive diluents may be chosen for high heat stability, fire retardance, refractive index, peak cure exotherm time or temperature, rigidity or flexibility, and chemical resistance. Many reactive diluents have also been investigated for tailoring the properties of the cured network such as those in Table 7. The reactive diluent must have several characteristics

[57]   B. Parkyn, *Unsaturated Polyesters, Vol. 2*, American Elsevier Publishing, New York, **1967**.
[58]   C. Papaspyrides, The influence of structural features on the chemical resistance of unsaturated polyesters, *J.M.S. Rev. Macromol. Chem. Phys.* **1984**, *24*, 325.
[59]   in *Encyclopedia of polymer science and engineering, Vol. 12*, John Wiley and Sons, New York, **1988**, pp. 256.

to be a "good reactive diluent". The reactive diluent must have a high boiling point (low

vapor pressure), low heat of reaction, low cost, and copolymerize with the polyester.

Styrene meets all these requirements, is the most economical choice, and thus is used in

most cases.

Other reactive diluents such as alpha methyl styrene and vinyl toluene are used to

help control the cure exotherm temperature or time. Alpha methyl styrene is used in

conjunction with styrene to lower peak cure exotherm and increase the cure exotherm

time.[61] The addition of alpha methyl styrene allows for thick parts to be manufactured

with reduced localized heat build up in the thick sections. Alpha methyl styrene also

provides more flexibility and less shrinkage.[62] Vinyl toluene on the other hand is

incorporated to increase the cure exotherm and decrease the cure time.[63] Vinyl toluene

also has a higher boiling point and flash point than styrene and permits higher molding

temperatures and faster cycles for polyester premix putties.

Methyl methacrylate has a lower refractive index than styrene and thus can be

used to reduce the refractive index of the matrix to more nearly match that of the glass

fiber reinforcement and thereby yield optimum clarity in fiberglass roofing panels.

Methyl methacrylate also lowers the viscosity more than does styrene and provides better

adhesion to the fiber reinforcement. Another benefit of resins cured with methyl

methacrylate is that they exhibit better weathering than resins cured with only styrene.

Resins cured with methyl acrylate have similar results as with methyl

methacrylate. Methyl acrylate also reduces the refractive index of the network and

[60]   I. Skeist, A polyester for every purpose, *Modern Plastics* **1964**, *41*, 80.
[61]   G. Padma, I. K. Varma, T. Sinha, D. Patel, Effect of alpha methyl styrene on properties of epoxy-novolac based vinyl ester resins, *Die Angewandte Makromolekulare Chemie* **1993**, *211*, 157.
[62]   R. Weatherhead, *FRP Technology*, Applied Science, London, **1980**.

allows for the fabrication of transparent fiberglass panels. The methyl acrylate networks generally have high flexural strengths and increased light stability over those polyester networks cured with styrene.[64]

Allyl cured networks usually have high heat deflection temperatures and the resins have high viscosities and low copolymerization rates. Diallyl phthalate is more costly than styrene; however, it offers a high boiling point and is excellent for rigid, resilient end products.[65] Triallyl cyanurate can also be incorporated in networks that need to be heat stable.[66,67]

[63]   R. Helmreich, Vinyl toluene for premix putties, *Modern Plastics* **1958**, 168.
[64]   M. Slone, Methyl acrylate as a monomer in glass reinforced polyester laminates, *SPE Journal* **1960**, *16*, 1123.
[65]   R. Helmreich, Vinyl toluene for premix putties, *Modern Plastics* **1958**, 168.
[66]   R. Roth, R. Church, Copolymerization with triallyl cyanurate, triallyl isocyanurate, and diallylmelamine, *Journal of Polymer Science* **1961**, *55*, 41.
[67]   P. Elliott, Heat resistant copolymer of triallyl cyanurate and maleic alkyd, *Modern Plastics* **1952**, *29*, 113.

Reactive diluent	Characteristics
Styrene	Lowest cost, high reactivity, good heat distortion temperature, good mechanical properties, good compatibility
Alpha methyl styrene	Lower cure exotherm and longer exotherm times
Vinyl toluene	Low volatility, more flexibility and toughness than styrene, high reactivity
Methyl methacrylate	Light stability, good weatherability, fairly high heat distortion temperatures, lower refractive index
Methyl acrylate	Lower refractive index, light stability, similar to methyl methacrylate
Diallyl phthalate	High heat distortion temperature, low volatility, good light stability, long shelf life
Triallyl cyanurate	Very high heat distortion temperature, high reactivity, high flexural strength and tensile strength, flame retardance, good light stability

Table 7. Reactive diluents incorporated in unsaturated polyester networks along with their general network characteristics.[68,69]

[68] I. Skeist, A polyester for every purpose, *Modern Plastics* **1964**, *41*, 80.
[69] R. Burns, *Polyester Molding Compounds*, Marcel Dekker, New York, **1982**.

2.1.6. Material properties

2.1.6.1. Effect of dibasic acid

Ortho-phthalic resins receive wide acceptance for most applications. However, phthalic resins are limited to some applications. Ortho-phthalic resins are limited in use by heat resistance, fire retardance, chemical resistance, and processability. By substitution with another dibasic acid new materials have evolved with improved properties.

By substituting isophthalic acid for phthalic anhydride resins, improved mechanical properties and chemical resistance are achievable. It has been shown that, for the same mole percent unsaturation, iso-resins have higher tensile strengths than phthalic resins. Table 8 shows the tensile strength of six phthalic resins and six iso-resins; each pair having the same level of unsaturation and all being co-cured with 40 % styrene. At low levels of unsaturation in the prepolymer, which corresponds with the highest level of unsaturated dibasic acid, there is a more dramatic increase of tensile strength in the iso-resins. However, for all percentages of unsaturation the iso resins exhibit higher tensile strengths. As the percent of dibasic acid decreases, and the mole percent of unsaturation increases, it is evident that the tensile strengths increase. Although the tensile strengths increase, they appear to show a maximum tensile strength at 60 mole percent of unsaturation for both phthalic acid moieties. In general, both rigid and flexible castings exhibit improved mechanical properties such as tensile and flexural strength with increasing percentages of unsaturation until a maximum is reached. After the maximum properties have been reached for a given system, increasing the level of unsaturation causes a decrease in mechanical properties.

Tensile strength (psi)						
Mole % unsaturation	20	40	50	60	80	100
Maleic-Phthalic	3700	8500	8900	9000	8000	4000
Maleic-Iso-phthalic	5200	9000	9200	9200	8700	4000

Table 8. Tensile strength of unsaturated polyesters containing phthalic or iso-phthalic dibasic acids at different mole percents of unsaturation. All resins were co-cured with 40 % styrene.[70]

The flexural strength of the isophthalic resins is usually larger than those synthesized from phthalic anhydride, Table 9. The flexural strength of the phthalic resins appear to max out with 67 mole % unsaturation in the oligomer, that is the 1:2 phthalic: maleic ratio. And as styrene is incorporated into the network the flexural strength decreases significantly. The isophthalic resins seem to reach a maximum flexural strength between 50 and 33 mole percent unsaturation. The isophthalic resins show little effect associated with increasing percentages of styrene. This is attractive to resin manufacturers because resins with higher styrene levels can be used without affecting the mechanical properties significantly.

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[70]   W. Gum, W. Riese, H. Ulrich, *Reaction Polymers*, Hanser, New York, **1992**.5012

Polyester composition	Styrene content %	Flexural Strength $*10^3$ (psi)
PA:MA		
1:2	30	13
	40	15
	50	15
	60	13
1:1	30	14
	40	12
	50	12
	60	11
2:1	30	14
	40	12
	50	14
	60	13
IPA:MA		
1:2	30	12
	40	13
	50	15
	60	14
1:1	30	15
	40	17
	50	18
	60	17
2:1	30	14
	40	17
	50	18
	60	17

Table 9. Flexural strength of phthalic and isophthalic castings with systematically varying amounts of oligomer unsaturation and styrene.[71]

The isophthalic resins also out perform the phthalic resins in impact strength. In Table 10, both networks exhibit an increase in impact strength with decreasing levels of maleic anhydride. Thus as the cross-link density decreases the impact strength increases. However the iso resins have higher impact strengths at all ratios of saturated dibasic acid.

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[71]   H. V. Boenig, *Unsaturated Polyesters: Structure and Properties*, Elsevier Publishing Co., New York, **1964**.

	Molar ratio PA:MA			Molar ratio IPA:MA		
	1:2	1:1	2:1	1:2	1:1	2:1
Izod impact strength (unnotched) ft. lb./in.	1.9	2.3	2.5	2.3	3.3	3.6

Table 10. Izod impact strength vs. degree of unsaturation in propylene glycol based phallic and isophthalic based unsaturated polyesters co-cured with 40 wt. % styrene.[72]

The effect of unsaturation and styrene content on heat distortion temperatures is shown in Table 11. Both the phthalic and isophthalic resins exhibit the highest HDT at high unsaturation levels of the polyester oligomer. This means those resins with higher incorporation of maleic anhydride have the highest HDT. Styrene also has an effect on the HDT. Increasing the levels of styrene into the network leads to higher HDT values. Again the isophthalic resins provided superior HDT's over the orthophthalic resins. Although the isophthalic resins provide higher HDT values, reactive diluent types also become significant in tailoring HDT as discussed in the section on reactive diluents.

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[72]   H. V. Boenig, *Unsaturated Polyesters: Structure and Properties*, Elsevier Publishing Co., New York, **1964**.

Acid molar ratio	Heat Distortion Temp. (^{o}C)	% Styrene content
PA:MA		
1:2	99	30
	120	40
	120	50
	109	60
1:1	82	30
	94	40
	94	50
	94	60
2:1	64	30
	69	40
	70	50
	75	60
IPA:MA		
1:2	111	30
	129	40
	130	50
	120	60
1:1	96	30
	102	40
	102	50
	99	60
2:1	70	30
	74	40
	79	50
	80	60

Table 11. Heat distortion temperatures of phthalic and isophthalic resins with systematicly varied percentages of styrene.[73]

In general, isophthalic resins are superior to phthallic resins when it comes to higher performance applications. However, phthalic resins have the economical advantage and acceptable properties for most general purpose applications. Isophthalic resins do not form cyclic byproducts during the synthesis, as does phthalic anhydride.

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[73]   H. V. Boenig, *Unsaturated Polyesters: Structure and Properties*, Elsevier Publishing Co., New York, **1964**.

Isophthalic resins also provide greater modulus in flexure, tensile strength, and resistance to water.[74]

Other dibasic acids are incorporated into unsaturated polyesters such as adipic acid to provide improved flexibility and impact strength. However, usually increasing the flexibility of the network decreases the hardness.

Dibasic acids such as chlorendic anhydride (HET), tetrachlorophthalic anhydride (TCPA) or tetrabromophthalic anhydride (TBPA) are incorporated into the backbone to provide flame retardance. During the burning process hydrogen bromide or hydrogen chloride is released. These gaseous products suppress the burning process by eliminating oxygen radicals thus suppressing the highly exothermic oxidation reaction.[75] It is noted that at least 12% bromine content in the final network is needed for self-extinguishing properties and 25% chlorine content is needed.[76,77] However, it must be taken into consideration whether calcium carbonate, used as a filler, reduces the amount of hydrogen halide evolution during the oxidative burning process.

Both antimony oxide and organo-phosphorous compounds have been used in conjuction with halogenated resins to suppress flame propagation. When resins have to be non-halogenated, for electrical purposes due to fact that halogens can attack copper contacts, hydrated fillers such as alumina hydrate can be used.[78] Antimony oxide in concentrations from 1-4 % is often added to aid in flame suppression. Antimony oxide

[74]   I. Skeist, A polyester for every purpose, *Modern Plastics* **1964**, *41*, 80.
[75]   J. Selley, in *Unsaturated Polyester Technology* (Ed.: P. Bruins), Gordon and Breach Science, New York, **1976**.
[76]   G. Gunduz, in *Polymeric Materials Encyclopedia, Vol. 11* (Ed.: J. Salamone), CRC, New York, **1996**, pp. 8469.
[77]   J. Selley, in *Unsaturated Polyester Technology* (Ed.: P. Bruins), Gordon and Breach Science, New York, **1976**.
[78]   H. Kramer, in *Ullmann's Encyclopedia of Industrial Chemistry, Vol. A21*, fifth ed. (Eds.: B. Elvers, S. Hawkins, G. Schulz), VCH, New York, **1992**, pp. 217.

reacts with the evolving bromine or chlorine to form antimony trihalides, which are much less volatile and have lower boiling points than either HBr or HCl. The antimony trihalides then suppresse flame propagation in the same manner by interfering with the oxidative step and arresting the OH radicals. Organo-phosphorus compounds are more supplementary than inter-reaction effect as with the antimony oxide. Generally for self-extinguishing resins up to 1.5 % phosphorous content enables a reduction of the chlorine level by 50%.[79] Selley believes that phosphoric acid collects in the pyrolysis zone on the surface and forms polyphosphoric acids thereby eliminating water and generating a charred surface that arrests the pyrolysis.

It has been shown by J. Agrawal that substituting phthalic anhydride with tetrachlorophthalic anhydride (TCPA) or tetrabromophthalic anhydride (TBPA) improved flame retardance, Table 12.[80] Typically bromo-polymers are more flame resistant than chloro-polymers because the C-Br bond is weaker than the C-Cl bond. This allows for more generation of Br radicals at lower temperatures during the burning process to interfere with the flame propagation. It was shown that the order of flame retardance was tetrabromophthalic anhydride > tetrachlorophthalic anhydride > phthalic anhydride. Not only was the flame retardance increased but the tensile strength was increased and the percent elongation decreased when the halo monomers were incorporated.

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[79]   J. Selley, in *Unsaturated Polyester Technology* (Ed.: P. Bruins), Gordon and Breach Science, New York, **1976**.

[80]   J. Agrawal, K. Kulkarni, Comparative study of unsaturated halo and nonhalo polyesters and inhibition of double-base rocket propellants, *Journal of Applied Polymer Science* **1993**, *50*, 1655.

Polyester Acid ratio 1:1	Tensile strength (Kg/cm^2)	Elongation %	Burning rate (mm/sec)
PA:MA	78	19	.61
TCPA:MA	123	15	.45
TBPA:MA	129	3	.38

Table 12. Properties of halogenated resins vs. phthalic resins synthesized with diethylene glycol and co-cured with 35 % styrene.

2.1.6.2. Effect of the glycol

The contribution of the glycol is very important. The glycol has similar effects as the saturated dibasic acids do. They have significant contributions to the physical and chemical properties of the network. Typically aromatic groups tend to provide rigidity such as bisphenol-A. Aliphatic ether linkages generally increase flexibility and water absorption. It is fortunate that propylene glycol is inexpensive and provides excellent properties for general purpose resins.

The flexural strengths and moduli of unsaturated polyesters are influenced by the glycol component of the polyester. The glycol component can allow a significant amount of flexibility to the polyester. Table 13 shows that by increasing the ether linkages there is a decrease in the flexural strength and flexural moduli. In this study a 1:1 molar ratio of phthalic anhydride to maleic anhydride was used along with the corresponding glycol in Table 13. The resulting unsaturated polyester was then cross-linked with 30 weight percent styrene. It was shown that flexibility in the network can be incorporated by increasing the number of ether linkages in the glycol.

	PG	DEG	EPG	TMG	EDEG
Flexural strength $*10^3$	18.7	17.3	14.7	13.3	12.1
Flexural modulus $*10^3$	6.1	5.0	5.9	3.6	3.1

Table 13. Flexural strength and modulus of unsaturated polyesters synthesized with various glycols and co-cured with 30 wt % styrene (PG propylene glycol, DEG diethylene glycol, EPG ethylene propylene glycol, TMG trimethylene glycol, EDEG ethylene diethylene glycol).[81]

Impact strength on the other hand increases with long unbranched glycols. Table 14 shows order of impact strength as a function of the glycol. A series of unsaturated polyesters were synthesized with 1:1 molar ratio of phthalic anhydride to maleic anhydride with the corresponding glycol. It can be seen that by decreasing the length of the glylcol (i.e. going from 1,5 pentane diol to 1,4 butane diol) the impact strength decreases significantly. Also, increasing the level of branching of the glycol has a significant influence on impact strength as in the case of 1,4 butane diol (3.7 ft. lb./in.) to 2,3 butane diol (1.9 ft. lb./in.).

Glycol	Unnotched impact strength (ft. lb./in.)
1,5 Pentane diol	11.2
1,4 Butane diol	3.7
Dipropylene glycol	3.7
Propylene glycol	2.4
2,3 Butane diol	1.9
1,3 Butane diol	1.5

Table 14. Impact strength of cured unsaturated polyesters synthesized with various glycols.[82]

[81]   H. V. Boenig, *Unsaturated Polyesters: Structure and Properties*, Elsevier Publishing Co., New York, **1964**.

[82]   H. V. Boenig, *Unsaturated Polyesters: Structure and Properties*, Elsevier Publishing Co., New York, **1964**.

As a general rule, flexible unsaturated polyesters have a lower HDT than those of the rigid type. Table 15 shows the HDT and the effect of chain branching, chain length and ether incorporation in the glycol component of the UP. Pendant methyl groups generally increase the HDT as shown by going from ethylene glycol with one pendant methyl group (PG) to ethylene glycol with two pendant methyl groups (2,3 butane diol). However increasing the length of the glycol by one methylene unit, decreases the HDT (i.e. PG to 1,3 butane. Increasing the number of ether linkages has an even more dramatic effect on lowering the HDT than does the incorporation of a methylene unit.

Glycol	Heat distortion Temperature (^{o}C)
2,3 Butane diol	81
Propylene glycol	73
1,3 Butane diol	62
1,4 Butane diol	59
Dipropylene glycol	Below room temperature
Diethylene glycol	Below room temperature

Table 15. Effect of glycol on the heat distortion temperature.

Unsaturated polyesters are polar in nature and are susceptible to attack by alkalis, acids and polar compounds. Oxygen links in the glycol not only decrease the HDT but also decrease the resin's chemical resistance. Flexibilizing the network also decreases chemical resistance. Thus, increasing the glycol length also decreases the chemical resistance, but not as significantly as does the number ether linkages. Table 16 shows the effect of glycol length and the number of ether linkages in the glycol on water absorption. It can be seen that water absorbance increases going from 1,4 butane diol (.35%) to 1,5 pentane diol (.8%) by only increasing the number of methylene groups by one. An even

more dramatic is produced by substituting an oxygen for a methylene group in 1,5

pentane diol (.8%) to give diethylene glycol (2.6%).

Glycol	Water Absorption (%)
Diethylene glycol	2.6
1,5 Pentane diol	0.8
1,4 Butane diol	0.35

Table 16. Effect of glycol structure on water absorption of unsaturated polyesters synthesized with various glycols and co-cured with 33wt % styrene.

Improved chemical resistance can be achieved by substitution of propylene glycol

by cyclic diols such as Bisphenol-A, hydrogenated bisphenol-A, cyclohexane diol,

neopentyl glycol, and the diether of propylene glycol and bisphenol A.[83] Aromatic rings

tend to decrease water absorption. Bulky diols such as neopentyl glycol have the added

advantage of imparting imparting a steric contribution that increases hydrolytic stability

of the ester linkage.

Another class of unsaturated polyesters is the bisphenol fumarates. They are

generated by the reaction of ethoxylated or propoxylated bisphenol-A reacted with only

fumaric acid, Figure 11. This type of resin exhibits improved hardness, rigidity, and

thermal properties.

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[83]   B. Parkyn, *Unsaturated Polyesters, Vol. 2*, American Elsevier Publishing, New York, **1967**.
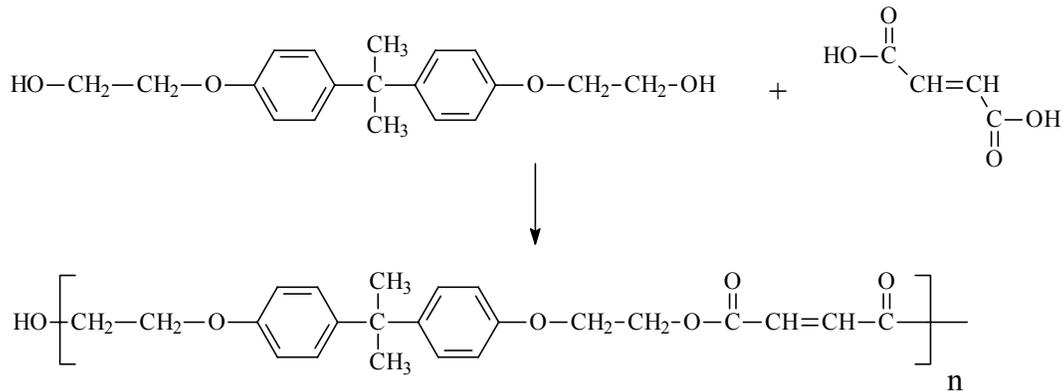
Figure 11. Ethoxy-based bisphenol-A fumarate

Recent work in the area of glycols has been the investigation of polyglycols in the synthesis of unsaturated polyesters. Tong and coworkers has shown the effect of polyethylene glycols on the network properties of unsaturated polyesters.[84] They synthesized a series of unsaturated polyesters from phthalic anhydride, maleic anhydride and one the following glycols: ethylene glycol, di(ethylene glycol), tri(ethylene glycol), and polyethylene glycols from 600 to 10,000 g/mol. It was found that increasing the molecular weight of the glycol resulted in increased flexibility, impact strength, and water absorption. However, other network properties such as hardness, heat distortion temperatures, tensile and flexural properties decreased.

Polyglycols have also recently been investigated in the synthesis of block copolymers with unsaturated polyesters in order to provide toughness. In order to toughen unsaturated polyesters Schulze and coworkers synthesized a block copolymer from an unsaturated polyester and polyethylene glycol. This was done by coupling an

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[84] S. Tong, Unsaturated polyester based on poly(ethylene glycol), *Polymer Engineering and Science* **1985**, *25*, 54.

acid terminated unsaturated polyester with polyethylene glycol mono-methyl ethers of

various molecular weights ranging from 350 to 2000 g/mol, Figure 12.[85]
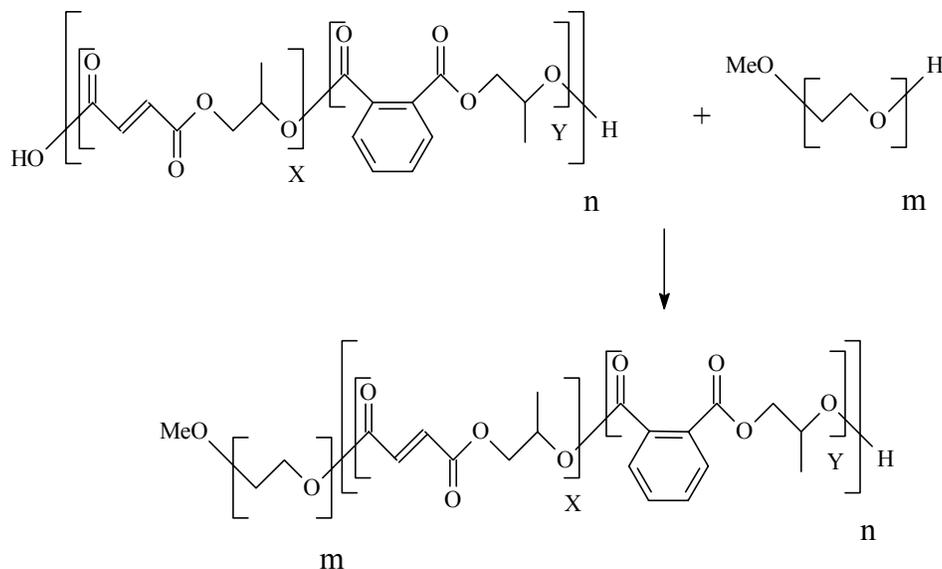
Figure 12. Synthesis of an unsaturated polyester and poly(ethylene glycol) block copolymer.

Traditional methods of toughening are by chemical or physical means. Typically

an elastomer such as butadiene-acrylonitrile is dispersed into the resin before curing.

This is an example of a physical method employing the formation of a heterogeneous

mixture. Chemical means of toughening can be achieved by incorporating long chain

diols or aliphatic dicarboxylic acids such as adipic acid into the unsaturated polyester

backbone. Although incorporating long chain glycols and aliphatic dicarboxylic acids

provides tougher networks, this usually comes at the expense of other properties.

Schulze and coworkers claim that modifying the unsaturated polyester with a

polyethylene glycol mono-methyl ether endgroup will have several advantages. By

conversion of the polar endgroups there should be reduced resin viscosity and improved

[85]   U. Schulze, M. Skrifvars, N. Reichelt, H. Schmidt, Modification of unsaturated polyesters by

flexibility due to the decrease in hydrogen bonding as well as a toughened network. Improved dispersion of polar fillers and their interfacial properties may also be improved by modifying the endgroup to a polyethylene glycol mono-methyl ether group.

2.1.7. Additives

There are several classifications or types of additives incorporated into unsaturated polyesters for a wide range of applications. Fillers are generally incorporated into the resin formulation to lower the cost and modify the properties of the network. Fillers can be used to modify or provide properties such as wear resistance, modulus, toughness, reinforcement, flame retardance, and environmental stability. Important factors of fillers are their modulus, particle size and distribution, surface treatment, surface area, and chemical composition. Table 17 displays the effects of fillers on the properties of the resin as well as the cured network; however, not all are applicable to each filler.

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poly(ethylene glycol) end groups, *J. Appl. Polym. Sci.* **1997**, *64*, 527.

The effect of filler on the liquid resin
Increases viscosity
Increases bulk
Produces thixotropy
Accelerates of retards cure
Abrasive fillers can cause wear on moulds during processing
The effect of filler on the cured network
Reduces cost
Renders opaque
Increases impact resistance
Decreases flexural strength
Increases rigidity
Reduces water absorption
Increases abrasion resistance
Modifies electrical and thermal properties
Reduces flammability
Raises heat deflection temperature
Abrasive fillers make machining difficult

Table 17. The effects of fillers on the resin and cured network properties.[86]

Several hundred fillers are available. A few common fillers include: calcium carbonate, quartz, clay, glass beads, talc, silica flours, and ground rubber. Other important fillers are those that improve flame retardance. Antimony trioxide is a dense white powder that is used in conjunction with brominated or chlorinated resins to improve flame retardance; however it produces an opaque resin. During the course of a fire the antimony trioxide reacts with the halogen to form antimony tribromide or trichloride, which blankets the fire and starves it of oxygen. Aluminium hydroxide (alumina trihydrate) also improves fire retardance by decomposing to alumina and water,

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[86]   R. Weatherhead, *FRP Technology*, Applied Science, London, **1980**.

which blankets the fire. This is important where non-halogenated resins must be used as in electronics.

Another important class of additives is low profile additives (LPA). Unsaturated polyester networks generally suffer from warpage, wavy surfaces, and voids due to shrinkage. Reactive diluents contribute significantly to the level of shrinkage in their corresponding networks. Table 6, in the above section on reactive diluents, shows the level of shrinkage for a wide range of reactive diluents. In order to combat this problem of shrinkage LPA's are added to reduce the level of shrinkage during network formation. A LPA is generally a thermoplastic that is added into the formulation at levels between 2 and 20 weight percent of the resin. Examples of thermoplastics that are used as LPAs are polyvinyl acetate, polycaprolactones, cellulose acetate butyrate, polyacrylates, polyethylene, polyvinyl acetate, polymethyl methacrylate, polyurethanes, and styrene-butadiene block copolymers.[87,88] However, the most commonly used LPAs are PVAc, PMMA, and PU based thermoplastics. The major uses of resins containing LPAs are, but not limited to, formulations for sheet and bulk molding compounds where low shrinkage is needed.

In a recent article, Huang and coworkers showed the effectiveness of four different LPAs and demonstrated that volume shrinkage decreases linearly with increasing percentages of the LPA.[89] In this study, the effectiveness of reducing volume shrinkage increased with increasing polarity of the LPA and the order of effectiveness was as follows: PU > PVAc > PMMA > PS.

[87]   R. Weatherhead, *FRP Technology*, Applied Science, London, **1980**.
[88]   M. Malik, V. Choudhary, I. Varma, Current Status of Unsaturated Polyester Resins, *J.M.S. Rev. Macromol. Chem. Phys.* **2000**, *40*, 139.

The mechanism by which LPAs reduce cure shrinkage is believed to involve phase separation during cure. During the cure cycle the thermoplastic becomes incompatible with the forming network and phase separates. As the temperature of the network increases during the curing process the thermoplastic LPA increases in volume thus compensating for the cure shrinkage. As the network cools the UP shrinks much less than the thermoplastic LPA thus creating micro voids in the LPA phase. However, the residual micro voids are the result of the shrinkage compensation due to the difference in thermal expansion. Another theory contributes the micro void formation to monomeric styrene diffusing out of the thermoplastic phase, during the cure, leaving micro voids. Although both mechanisms are possible, micro void formation is a necessary part or a by-product of the mechanism.

Liquid rubbers have also been incorporated into unsaturated polyester resins to impart toughness. Soluble liquid rubbers are dissolved in the resin prior to curing and upon curing phase separate and form a discontinuous phase. The discontinuous elastomeric particles are dependent on chemical composition of the rubber, molecular weight, terminal and pendent groups, UP resin composition, concentration, and molding conditions. Several materials have been investigated as liquid rubber modifiers such as poly(butadiene-acrylonitrile), polybutadiene, and poly(epichlorohydrin). The liquid rubbers are generally in the range of 2000-5000 g/mol and contain end groups with hydroxyl, carboxyl, amine and/or vinyl groups.

To overcome the limitations of solubility when blending liquid rubbers into the resin, recent developments of block copolymers of unsaturated polyesters and hydroxyl-

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[89]   Y. Huang, C. Liang, Volume shrinkage characteristics in the cure of low-shrink unsaturated polyester resins, *Polymer* **1996**, *37*, 401.

terminated polybutadiene have been investigated.[90] This was achieved by converting a

hydroxyl terminated polybutadiene (HTPB) to an isocyanate terminated rubber (ITBN)

and subsequently reacting it with the hydroxyl end groups of the UP prior to curing,

Figure 13. This forms a triblock copolymer of the type ABA (UP-ITPB-UP). The

incorporation of 10 weight percent ITPB into the network showed a marked increase in

fracture toughness and strain energy release rate at both high and low loading rates.

However, incorporating 10 weight percent of the HTPB showed little or no effect. This

suggests that there must be good adhesion (chemical or physical connection) between the

elastomer and the matrix.
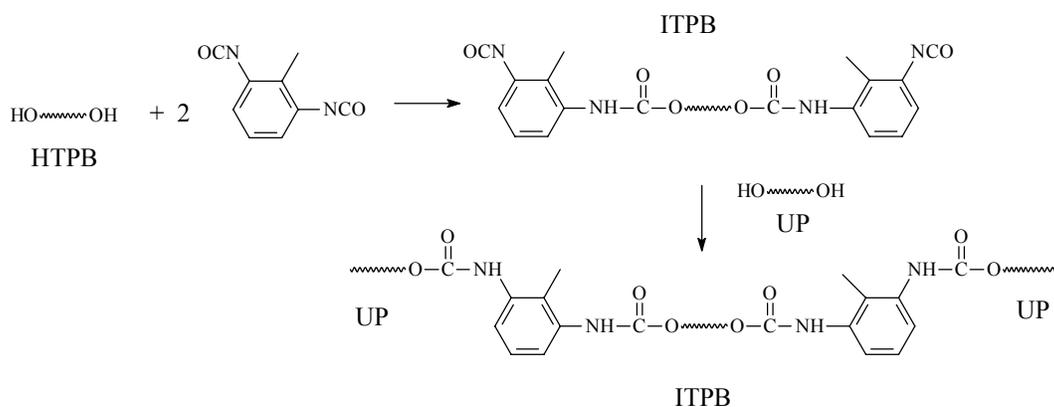
Figure 13. Synthesis of the triblock copolymer (unsaturated polyester-polybutadiene-unsaturated polyester) from an isocyanate terminated polybutadiene and a hydroxyl terminated unsaturated polyester.

Another approach taken by Ragosta and coworkers was to end-cap an amine

terminated butadiene acrylonitrile (ATBN) rubber with maleimide end groups.[91] Figure

14 shows the synthesis of the maleimido-terminated copolymer (ITBN). The advantage

[90]   E. Marticelli, P. Musto, G. Ragosta, G. Scarinzi, E. Bertotti, *J. Polym. Sci.* **1993**, *31*, 619.
[91]   M. Abbate, E. Matuscelli, P. Musto, G. Ragosta, M. Leonardi, A novel reactive liquid rubber with maleimide end groups for the toughening of unsaturated polyester resins, *Journal of Applied Polymer Science* **1996**, *62*, 2107.

of the ITBN is that it can chemically react with the forming network during the curing cycle.
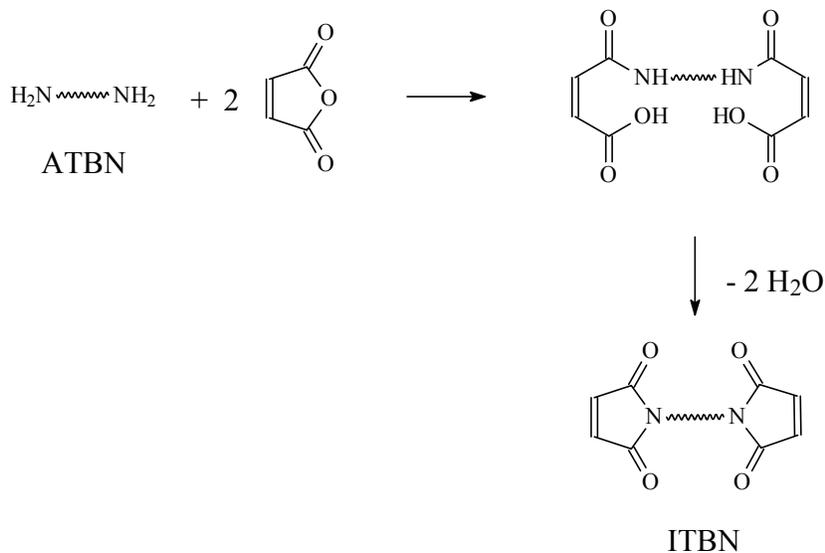
Figure 14. Synthesis of the maleimido terminated copolymer.

Ragosta and coworkers showed a substantial increase of toughness can be obtained when ITBN is used as a modifier as opposed to ATBN. Although, both the modulus and yield stress decreased slightly in both of these networks, it was less pronounced in the ITBN networks. ITBN is a more efficient toughener, and the increase in toughness can be attributed to the greater localized shear yielding in the matrix as a result of incorporating ITBN as the modifier. The primary source of energy dissipation shown by SEM and TEM was localized shear yielding of the matrix, which occurred to a greater extent in the ITBN modified networks.

Similarly, high molecular weight elastomers have been dispersed in UP resins to improve toughness of the cured network. Several of the solid rubbers dispersed in the UP resins include: polybutadiene, carboxylated diene rubbers, poly(vinyl chloride), natural rubber, styrene-butadiene copolymers, butadiene-acrylonitrile, halogenated butyl rubber,

and acrylate rubber. Like the liquid rubbers, they are generally designed to contain end groups with hydroxyl, carboxyl, amine, or vinyl groups to improve their properties by increasing their reactivity with the polyester matrix. However, there are some drawbacks to toughening with solid elastomers. Typically, there are incompatibilities between specific elastomers and the wide range of resin formulations, resulting in unstable dispersions. Another difficulty is the increased viscosity of the resin dispersion, which can cause difficulties in processing.

2.2. Vinyl Esters

2.2.1. Introduction

Typical dimethacrylate resins, the so-called "vinyl esters," are based on methacrylate terminated aromatic oligomers, Figure 15. These materials have also been referred to as "acrylic resins" and "epoxy acrylates." Dimethacrylates were first developed for composite applications in corrosive environments.[92] Dimethacrylate resins were first introduced by Shell Chemical Company in 1965 under the trade name Epocryl. Dow Chemical Company also provided a commercial dimethacrylate resin starting in 1966 under the tradename Derakane.
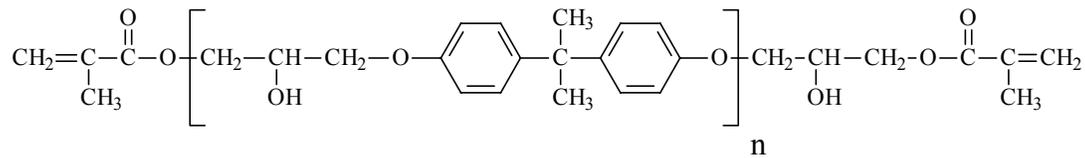
Figure 15. Bisphenol-A based poly(hydroxyether) endcapped with methacrylate groups. These are the so-called "Vinyl Esters."

Vinyl esters have several industrial niches and applications. Vinyl esters can be used for coatings, large-scale composites, and even dental resins. Vinyl Esters are a class of unsaturated polyesters that has superior mechanical properties and chemical resistance. They are diluted with a reactive diluent such as styrene and cured in the same manner as unsaturated polyesters to provide strong, tough networks. The oligomers generally have molecular weights between 700 and 2000 g/mole. The styrene lowers the viscosity and facilitates preform impregnation and fiber wetting during fabrication of fiber reinforced

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[92]   R. Weatherhead, *FRP Technology*, Applied Science, London, **1980**.

composites. The dimethacrylate oligomers and styrene are then free radically copolymerized to form void-free networks.

These types of dimethacrylates are generally synthesized by endcapping an epoxide oligomer with methacrylic acid. Dimethacrylates have similar properties to epoxide resins with the ease of processing as with the unsaturated polyesters. Vinyl esters have several important structural features such as: (1) aromatic rings that provide good heat resistance and mechanical properties, (2) the pendent hydroxyl groups on the backbone which can provide adhesion and hydrogen bonding as well as sites for further modification, (3) the ether linkages provide good chemical resistance, and (4) the terminal methacrylate groups allow for free radical crosslinking.[93]

Unlike the traditional unsaturated polyesters, vinyl esters contain unsaturation only at the ends of the oligomer. Unsaturated polyester oligomers contain trans fumarate units distributed randomly along the backbone to participate in the free radical curing process. Dimethacrylates on the other hand are endcapped with acrylates or methacrylates and thus have unsaturation on the terminal ends of the chain. Because of the terminal unsaturation there are no dangling ends and the mechanical properties are typically improved.[94] Another advantage of the vinyl ester is the reduced number of ester groups. Due to the reduction of ester linkages in the vinyl ester backbone there is much improvement in chemical resistance over that of the unsaturated polyesters, which contain ester linkages at every repeat unit.[95,96]

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[93]   R. Young, in *Unsaturated Polyester Technology* (Ed.: P. Bruins), Gordon and Breach Science, New York, **1976**.

[94]   E. Sacher, in *Toughness and Brittleness of Plastics, Vol. 154* (Ed.: R. Deanin), ACS, Washington, D.C., **1976**.

[95]   R. Meyer, *Handbook of polyester molding compounds and molding technology*, Chapman and Hall, New York, **1987**.

2.2.2.   **Synthesis**

As mentioned previously dimethacrylates as shown in Figure 14 are generally synthesized from low molecular weight diepoxides and methacrylic acid. It is well known that bisphenol-A / epichlorohydrin based diepoxides exhibit good mechanical properties. Typical epoxide resins of this type are made by reacting bisphenol A with epichlorohydrin under basic conditions, Figure 16. These epoxy resins are generally low molecular weight with epoxy equivalent weights of ≈264 g. However, higher molecular weight bisphenol-A terminated poly-hydroxyethers are made and used as a basis for sizings in fiber reinforced composites.[97]
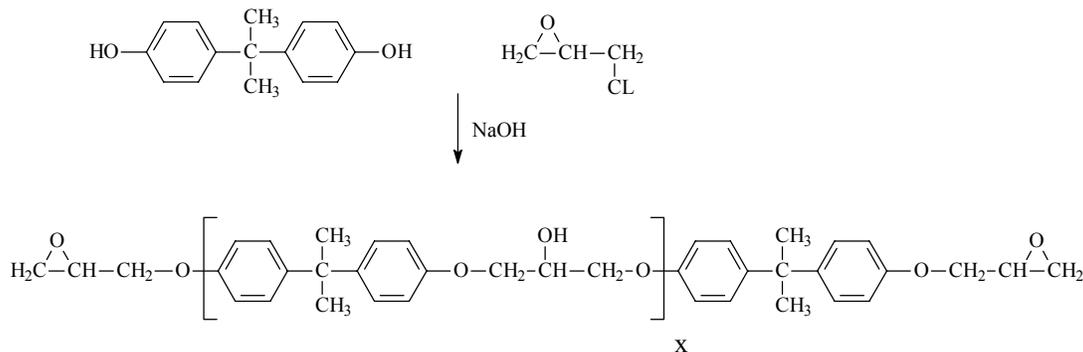
Figure 16. Synthesis of the bisphenol-A based diepoxide.

The low molecular weight epoxy resins can then be converted to dimethacrylates by the reaction with methacrylic acid. Figure 17 shows the synthesis of a dimethacrylate from the reaction of the bisphenol-A / epichlorohydrin diepoxide with methacrylic acid.

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[96]   R. Young, in *Unsaturated Polyester Technology* (Ed.: P. Bruins), Gordon and Breach Science, New York, **1976**.

[97]   M.A.F.Robertson, M.B.Bump, K.E.Verghese, S.R.McCartney, J. J. Lesko, J.S.Riffle, I.-C. Kim, T.-H. Yoon, Designed Interphase Regions in Carbon Fiber Reinforced Vinyl Ester Matrix Composites, *J. Adhesion* **1999**, *71*, 395.

Several catalysts have been used for the encapping step including: tertiary amines,

phosphines, alkali or -onium salts.[98]
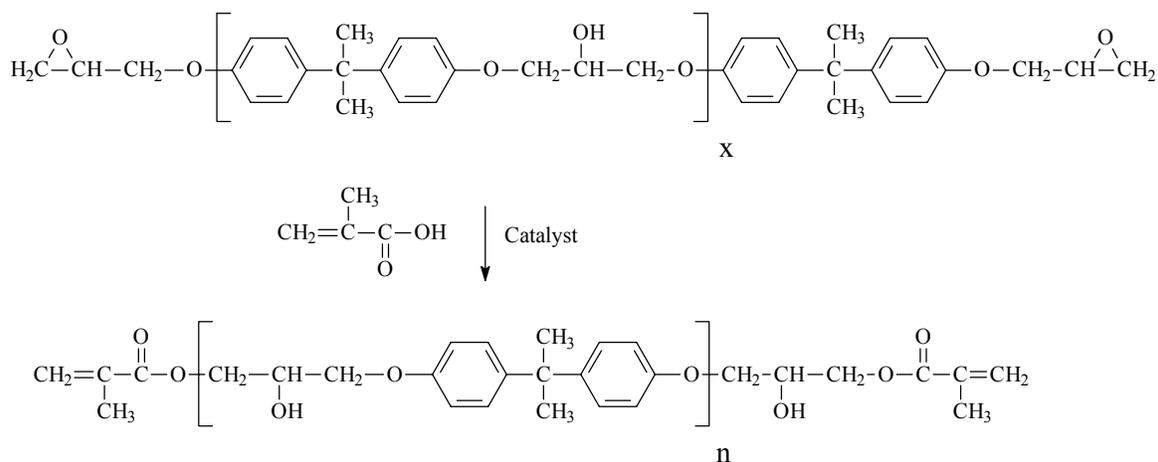
Figure 17. Synthesis of the bisphenol-A based dimethacrylate.

These are simple modifications of commercially available epoxy resins.

Although the majority of vinyl esters are synthesized from bisphenol-A/epichlorohydrin

resins, there is a long list of epoxy resins and thus there is a wide range of possible vinyl

esters. Not all dimethacrylates are made from epoxy resins. They can also be made from

dicarboxylic acids and glycidyl methacrylate, Figure 18.[99] However, these are not used

to a large extent.

[98]   R. Young, in *Unsaturated Polyester Technology* (Ed.: P. Bruins), Gordon and Breach Science, New York, **1976**.

[99]   F. Fekete, in *Unsaturated Polyester Technology* (Ed.: P. Bruins), Gordon and Breach Science, New York, **1976**.
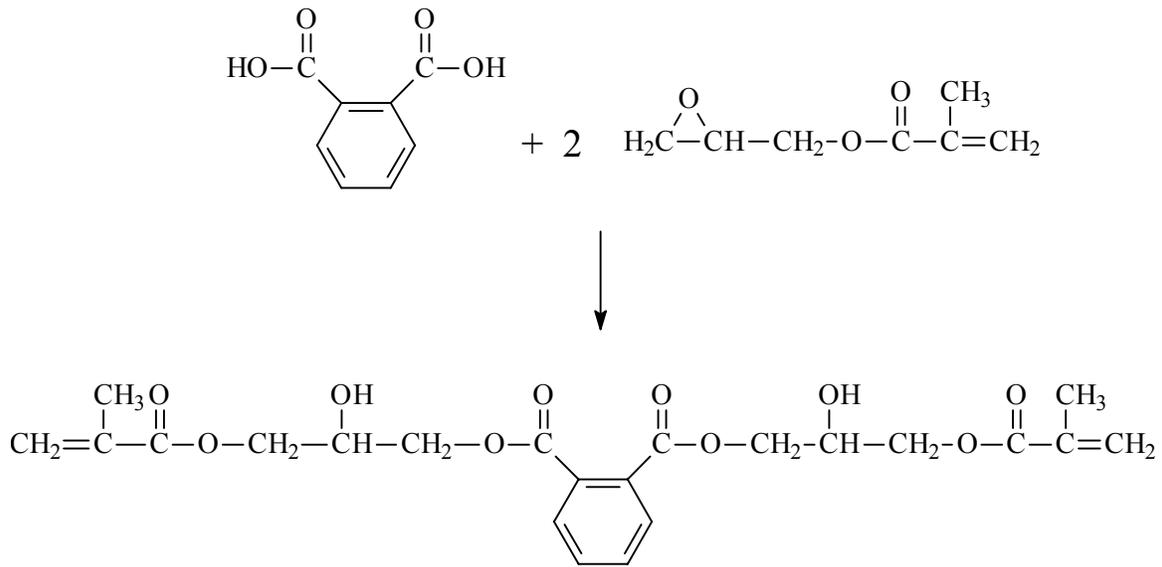
Figure 18. Synthesis of a dimethacrylate from a dicarboxylic acid (phthalic acid) and glycidyl methacrylate.

2.2.3. Crosslinking

Dimethacrylates cure in the same manner as unsaturated polyesters via a free radical addition copolymerization. Typically between 20 and 50 weight percent styrene is added to lower the viscosity for processing and manufacturing. Since vinyl esters are incorporated in highly corrosive applications styrene is generally the monomer of choice. However, all the monomers listed in the above section for unsaturated polyester may be used as well.

Many researchers have investigated the curing kinetics and reactivity ratios of the curing step in order to fully understand the network and how it goes together. Because styrene and the methyl methacrylate endgroups of the vinyl ester contain different unsaturation groups that participate in cross-linking, there are reactivity ratios involved

that dictate how the network forms. The reactivity ratios are the values that represent the rate of a monomer to add itself divided by the rate of it reacting with the other monomer, Figure 19. Thus, in chain growth polymerizations there are reactivity ratios for all pairs of co-monomers.

$$r_m = \frac{k_{mm}}{k_{ms}} \qquad r_s = \frac{k_{ss}}{k_{sm}}$$

Figure 19. The reactivity ratios for a given monomer pair (methacrylate-styrene), where r_m is for methacrylate and r_s is for styrene.

The reactivity ratios can be helpful in understanding the way in which a network is formed during the curing process. If for example r_m is much larger than r_s then initially all the methycrylate monomer will be incorporated into the network and at the latter stages of the network development there will be more styrene runs or styrene homopolymer formed. Thus, there can be a differentiating composition throughout the cure. However at the azeotropic composition the composition in the copolymer equals that in the feed.

H. Li and co-workers determined the reactivity ratios for the vinyl ester-styrene networks cured at 140°C. By using the Mayo-Lewis method and by monitoring the cure at 140°C by FTIR it was found that $r_s = 0.36$ and $r_m = 0.24$.[100] Monomer conversion was calculated individually at early conversions by monitoring the disappearance of the methacrylate double bond at 943cm^{-1} and the styrene double bond at 910cm^{-1}. For this

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[100]   H. Li, A. Rosario, S. Davis, T. Glass, T. Holland, R. Davis, J. J. Lesko, J. S. Riffle, Network formation of vinylester-styrene composite matrix resins, *J. of Advanced Materials* **1997**, *28*, 55.

particular system $r_s/r_m = 1.5$ which is higher than those values obtained for linear

copolymers of styrene ($r_s = 0.52$) and methyl methacrylate ($r_m = 0.46$) ($r_s/r_m = 1.1$)

measured at $60^{\circ}C$.[101] From Li's data it was also determined that the azeotropic

concentration is at 54 mole percent styrene which correlates to 26 weight percent styrene

(104 g/mol) and 74 weight percent vinyl ester (690 g/mol.). Thus, a network cured at the

azeotropic concentration should have the same monomer concentration in the copolymer

as in the feed.

2.2.4.   Recent trends

There are several novel dimethacrylates that have been investigated for use in

dental applications. Current trends have shown incorporation of fluorine into the

backbone of the vinyl ester reduces water absorption. Typically (2,2-bis-[4-(2-hydroxy-

3-methacrylooyloxypropoxy)phenyl}propane), bis-GMA, is used as the matrix resin in

dentistry. However, due to its high viscosity it is generally diluted with a lower viscosity

dimethacrylate such as tri-ethyleneglycol dimethacrylate (TEGDMA), which also allows

higher filler loads, Figure 20.[102,103] Generally these materials contain inorganic fillers and

are photopolymerized to yield high strength dental composites with low water absorption

and high wear resistance.

[101]   G. Odian, *Principles of Polymerization*, Third ed., John Wiley, New York, **1991**.
[102]   K. Davy, Novel aromatic dimethacrylate esters as dental resins, *Journal of Material Science: Materials in Medicine* **1994**, *5*, 350.
[103]   M. Sankarapandian, H. Shoba, S. Kalachandra, J. E. McGrath, D. Taylor, Characterization of some aromatic dimethacrylates for dental composite applications, *Journal of Material Science: Materials in Medicine* **1997**, *8*, 465.
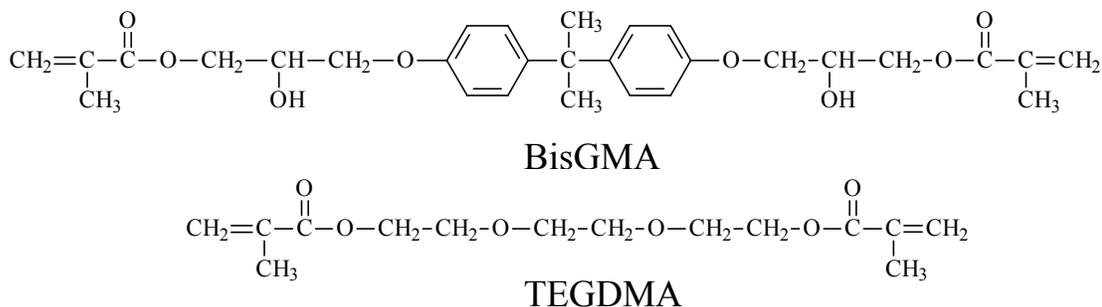
BisGMA

TEGDMA

Figure 20. The chemical structure of BisGMA and TEGDMA monomers used in dental resins.

Many researchers have been investigating the possibility of a new resin to minimize or eliminate the use of diluent monomers. Davy has investigated several aromatic dimethacrylates synthesized from glycidyl methacrylate and phthallic acid isomers and halogen substituted derivatives, Figure 21.[104] These monomers showed viscosities two orders of magnitude less than that of bis-GMA with comparable physical and mechanical properties. These materials can be used as direct replacements of bis-GMA or as diluent monomers. Incorporation of halogens provided opaqueness and X-ray opacity similar to tooth enamel. Thus the presence of the halogen reduces the need for heavy metal glasses to obtain X-ray opacity similar to tooth enamel.

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[104]   K. Davy, Novel aromatic dimethacrylate esters as dental resins, *Journal of Material Science: Materials in Medicine* **1994**, *5*, 350.
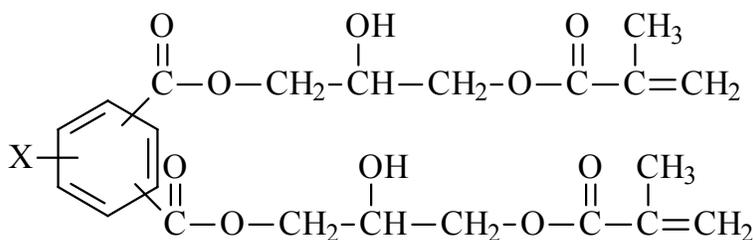
Figure 21. Novel dimethacrylates synthesized from glycidyl methacrylate with isomeric benzene dicarboxylic acids and their halogen derivatives.

Sankarapandian et al. have also investigated several dimethacrylates for improved dental resins with reduced bulk viscosities.[105] Twelve dimethacrylates have been investigated with four core units (bis-A, 6F, 3F, P) and three side chain possibilities (-OH, -H, -CH$_3$), Figure 22. It was shown that dimethacrylates with the fluorine containing core exhibit low levels of water absorption with increased surface hardness when compared to the bis-A control. The phosphine oxide core exhibits higher water absorption and lower hardness values than the control. As predicted, the hydroxyl containing side chain exhibits higher levels of water absorption when compared to the ethoxylated and propoxylated polymers. In general, by increasing the fluorine content a more hydrophobic network was prepared; however, by increasing the potential for hydrogen bonding the water absorption increased.

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[105] M. Sankarapandian, H. Shoba, S. Kalachandra, J. E. McGrath, D. Taylor, Characterization of some aromatic dimethacrylates for dental composite applications, *Journal of Material Science: Materials in Medicine* **1997**, *8*, 465.
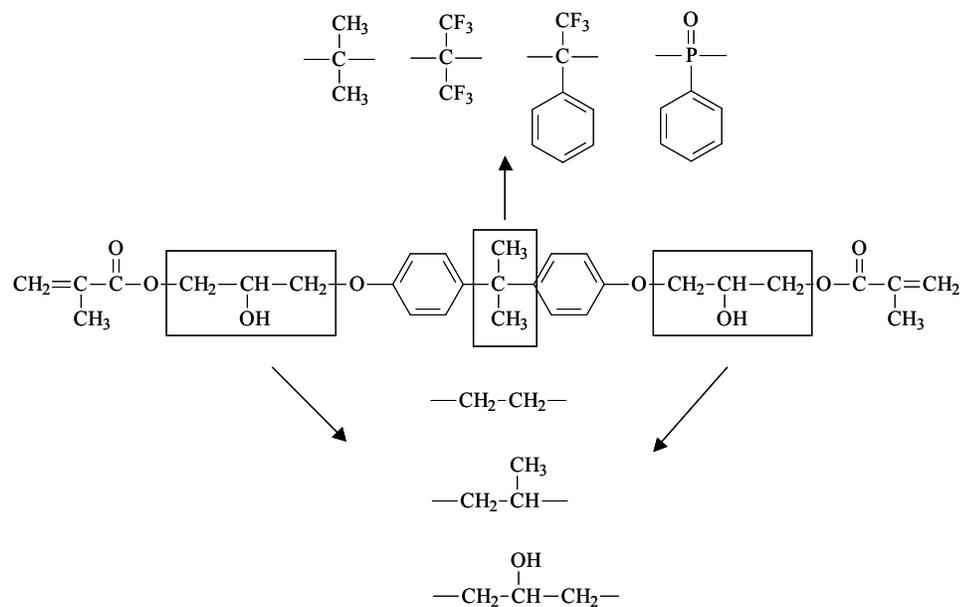
Figure 22. Twelve dimethacrylate structures with four different core units (bis-A, 6F, 3F, P) and three possible side chains (-OH, -H, -CH₃).

Another method to decrease water absorption in dental resins is by replacing

TEGDMA with fluorinated analogues. Wang et al. investigated the use of fluorinated

triethylene glycol dimethacrylate (FTEGDMA) as a replacement for TEGDMA as well as

the use of an ethoxylated bisphenol-A based dimethacrylate (bisEMA) rather than

bisGMA, Figure 23.[106] Introduction of the FTEGDMA exhibited significantly less water

absorption. This was improved farther by replacing bisGMA with bisEMA. Again this

emphasizes the importance to either increase the fluorine content or decrease the potential

for hydrogen bonding in order to decrease the level of water absorption in dental resins.

BisGMA

BisEMA

TEGDMA

FTEGDMA
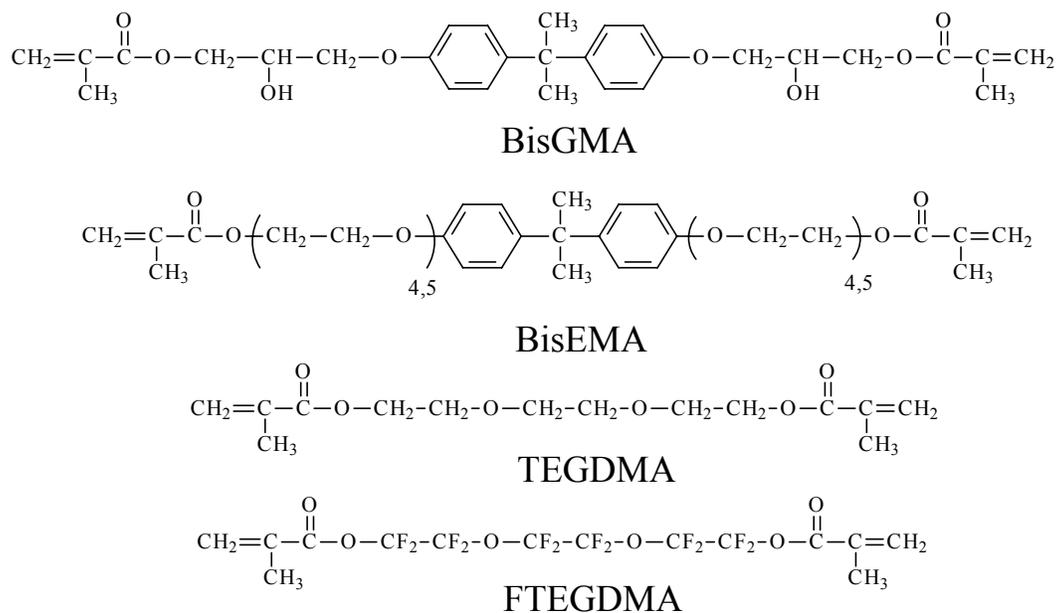
Figure 23. Structures of several fluorine and non-fluorine containing dental monomers (dimethacrylates).

Other recent trends have been to understand the mechanical properties and the effects of reactive diluent concentrations and/or cure conditions on their corresponding networks. Burts et al. have shown that by increasing the percent styrene, fracture toughness decreases even though the molecular weight between crosslinks increases.[107] This is quite unusual since increasing Mc should provide more flexibility in the network and provide a higher fracture toughness value with increasing percentages of styrene. Burts et. al. have also shown that curing vinyl ester networks at 25°C followed by a postcure at 115°C yields networks with improved mechanical properties (such as fracture toughness) over those cured with benzoyl peroxide at high temperatures (140°C). This

[106]   G. Wang, B. Culbertson, D. Xie, R. Seghi, Effect of fluorinated triethylene glycol dimethacrylate on the properties of unfilled, light cured dental resins, *J.M.S. Pure Appl. Chem.* **1999**, *36*, 237.

can be explained by the higher rubbery modulus values (thus higher cross-link densities) of the networks cured at 140°C. This shows that the curing process does matter and changes in temperature may affect the reactivity ratio and thus the way the network is formed. Unpublished data from our group (investigated by Astrid Rosario) shows that reactivity ratios do change with temperature for the styrene (r_s) and vinyl ester (r_m) monomer pair, shown in Table 18. The ratio of the reactivity ratios (r_m/r_s) decreases significantly with increasing temperature; which suggests that at ambient temperatures more styrene is being incorporated into the network and higher molecular weights between crosslinks are achievable with lower temperatures.

Temperature (^{o}C)	r_m (VE)	r_s (styrene)	r_m/r_s
25	0.35	0.19	1.84
60	0.55	0.15	3.67
140	0.88	0.17	5.18

Table 18. Reactivity ratios for the styrene(r_1)/bisphenol-A based dimethacrylate(r_2) monomer pair.

[107]   H. Li, E. Burts, K. Bears, Q. Ji, J. J. Lesko, D. A. Dillard, J. S. Riffle, Network Structure Properties of Dimethacrylate-Styrene Matrix Materials, *Journal of Composite Materials* **2000**, *34*, 1512.

2.3. Cycloaliphatic Epoxies

Epoxy resins are oligomers or prepolymers that contain on average two or more epoxide (epoxy, epoxide, oxirane, or ethoxyline) groups per molecule.
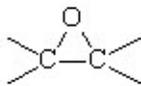
Figure 24. An epoxide group

Commercial epoxy resins contain either aliphatic, cycloaliphatic, or aromatic backbones. The epoxy group can react with a variety of substrates to form an insoluble infusible thermoset network upon curing. These resins may also contain additives such as fillers solvents, diluents, plasticizers, and accelerators to tailor processing or final network material properties. Epoxy networks exhibit high chemical and corrosion resistance, low shrinkage, good adhesion, electrical properties and can be processed in many ways.

The beginning of today's epoxy resin technology started in the 1930's. The first patent was issued to Schlack of I. G. Farben whose application date was 1934.[108] By 1946 Ciba A.G. demonstrated the use of an epoxy resin adhesive at the Swiss Industries

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[108]   W. Potter, *Epoxide Resins*, Springer-Verlag, New York, **1970**.

Fair.[109] In the United States a paint company Devoe and Raynolds had been working with Shell Chemical Company to develop epoxy resins suitable for the surface coatings industry. This lead to a series of new patents filed in the U.S.A. with the first patent filed on September 1943 by Greenlee and coworkers of Devoe and Raynolds. By the 1960's other resin types began to emerge: epoxidized novolaks, halogenated resins, resins with improved flexibility, and research teams of Union Carbide Corporation as well as CIBA investigated many cycloaliphatic epoxy resins.

The majority of the resins sold are of the diglycidyl ether of bisphenol A type.[110] The market dominance of this epoxy resin is because of its low cost and moderate to superior properties. These epoxy resins are synthesized from the reaction of Bisphenol A with epichlorohydrin under basic conditions, (Figure 25).[111] These epoxy resins are also the backbone of the commercial aromatic dimethacrylates; which are diglycidyl ethers of bisphenol A endcapped with methacrylic acid (Figure 17).

[109]   W. Potter, *Epoxide Resins*, Springer-Verlag, New York, **1970**.
[110]   J. Muskopf,, *Vol. A9* (Ed.: W. Gerhartz), VCH, Weinheim, **1987**, p. 548.
[111]   L. McAdams, J. Gannon, in *Encyclopedia of polymer science and engineering, Vol. 6*, John Wiley and Sons, New York, **1986**, pp. 322.
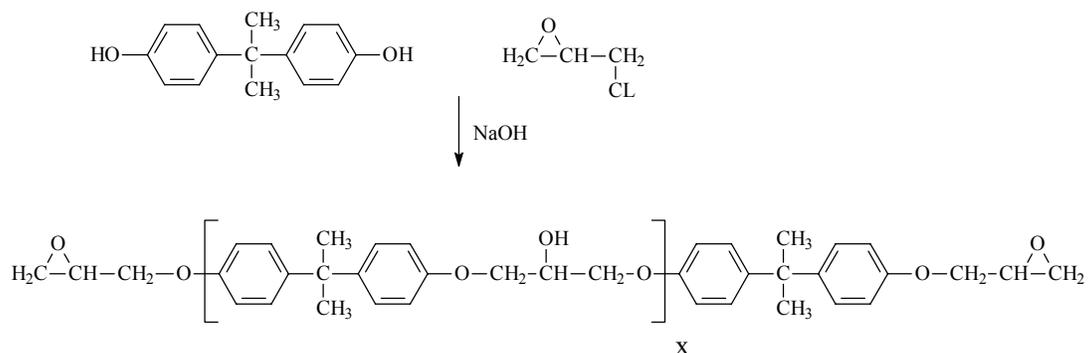
Figure 25. Synthesis of the diglycidyl ether of bisphenol A epoxide from epichlorohydrin and bisphenol A.

The cycloaliphatic epoxides were first introduced in 1957 in the USA by Union Carbide.[112] These aliphatic resins are typically used in applications where good weatherability and electrical properties (high HDT, arc and track resistance) are needed. These resins are based on diepoxides of cycloaliphatic dienes, (Figure 26).[113] The dienes are typically made from Diels-Alder reactions of 1,3- butadiene and acrylaldehyde. The ester can be readily obtained by the condensation of the tetrahydrobenzaldehyde in the presence of alcoholate catalysts by the Tishchenko reaction.[114,115] The cyclo-olefin is then epoxidized using peracetic acid to form the cycloaliphatic diepoxide (ERL-4221). Thus, the peroxidized resins contain no chlorine or ash (inorganic salts). This is particularly

[112] R. Dowd, in *Epoxy Resins Technology* (Ed.: P. Bruins), Interscience Publishers, New York, **1968**, pp. 1.

[113] B. Ellis, *Chemistry and Technoloy of Epoxy Resins*, Chapman and Hall, New York, **1993**.

[114] B. Ellis, *Chemistry and Technoloy of Epoxy Resins*, Chapman and Hall, New York, **1993**.

[115] M. Aslam, in *Encyclopedia of Chemical Technology, Vol. 9* (Ed.: Kirk-Othmer), John Wiley and Sons, New York, **1994**, p. 772.

important in electrical applications, as it will adversely affect the electrical properties as with the Bisphenol A based resins that contain approximately 1% chlorine.[116,117]
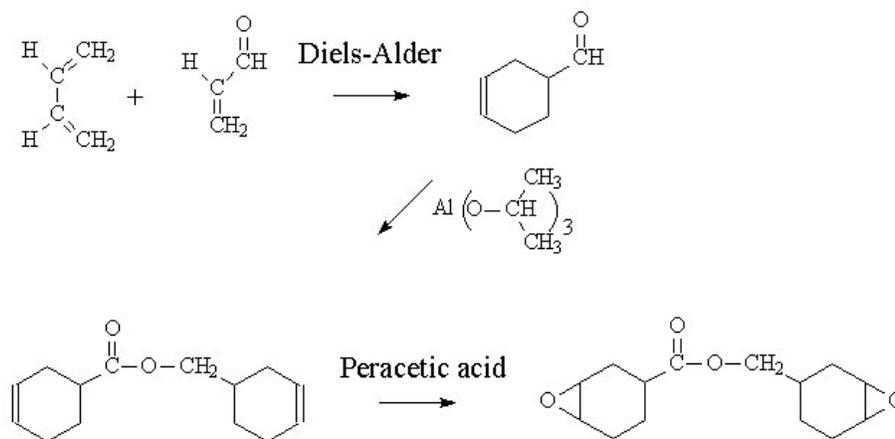
Figure 26. Synthesis of 3,4-epoxycyclohexylmethyl- 3,4-epoxycyclohexane carboxylate (Union Carbide: ERL-4221).[118]

The cycloaliphatic resins can be cured by several methods: acid/anhydrides, cationic, etc; however, they react sluggishly with amines. The best network properties are generally achieved with anhydrides such as hexahydrophthalic anhydride.[119] Curing reactions of acid anhydrides with epoxy resins can also be accelerated by the use of catalysts, e.g., tertiary amines or Lewis acids such as boron trifluoride.[120,121] The cyclohexane ring structure, short side chains and high cross-link densities of the

[116] B. Ellis, *Chemistry and Technoloy of Epoxy Resins*, Chapman and Hall, New York, **1993**.
[117] M. Xie, Z. Wang, Synthesis and Properties of a Novel Cycloaliphatic Epoxide, *Macromolecular Rapid Communications* **2001**, *22*, 620.
[118] B. Ellis, *Chemistry and Technoloy of Epoxy Resins*, Chapman and Hall, New York, **1993**.
[119] in *Encyclopedia of polymer science and engineering, Vol. 5*, John Wiley and Sons, New York, **1986**, p. 797.
[120] W. Potter, *Epoxide Resins*, Springer-Verlag, New York, **1970**.

cycloaliphatic epoxies allow for high heat deflection temperatures, but result in rather brittle materials.[122]

Radiation curing is another method for curing cycloaliphatic epoxies to produce coatings. This is a cationic reaction that involves the use of radiation to initiate the cure mechanism. Cationic salts such as the tri-arylsulphonium salts have been found by Crivello to be exceptionally efficient radiation cure photoinitiators.[123] Radiation is absorbed (250-275nm is most effective) by the photoinitiator generating an acid such as HPF_6 that will initiate the polymerization of epoxides, particularly the cycloaliphatic epoxides, (Figure 27 and Figure 28).[124] The cationic photoinitiators not only exhibit rapid initiation for cycloaliphatic epoxies, but also have a long life and the reactions can continue once the radiation is removed.[125] The particular metal associated with the salt is also very important. Antimony or phosphorus is typically used with antimony salts having a cure rate of about twice that of the phosphorus based salts.[126]

[121] H. Lee, *Handbook of Epoxy Resins*, McGraw-Hill Book Co., New York, **1967**.
[122] J. Gannon, in *Encyclopedia of Chemical Technology, Vol. 9* (Ed.: Kirk-Othmer), John Wiley and Sons, New York, **1994**, p. 736.
[123] B. Ellis, *Chemistry and Technoloy of Epoxy Resins*, Chapman and Hall, New York, **1993**.
[124] J. Koleske, A Radiation Cure Primer, *Journal of Coatings Technology* **1997**, *69*, 29.
[125] J. Koleske, Cationic, UV-Cure Cycloaliphatic Epoxy Systems Formulation Parameters and Curing Characteristics, *Polymers Paint Color Journal* **1986**, *176*, 546.
[126] J. Koleske, A Radiation Cure Primer, *Journal of Coatings Technology* **1997**, *69*, 29.

$$Ar_3S^+PF_6^- \xrightarrow{UV} Ar_2S^{\cdot+} + Ar^{\cdot} + PF_6^-$$

$$Ar_2S^{\cdot+} + R\text{--}H \longrightarrow Ar_2SH^+ + R^{\cdot}$$

$$Ar_2SH^+ + PF_6^- \rightleftharpoons Ar_2S + HFP_6$$
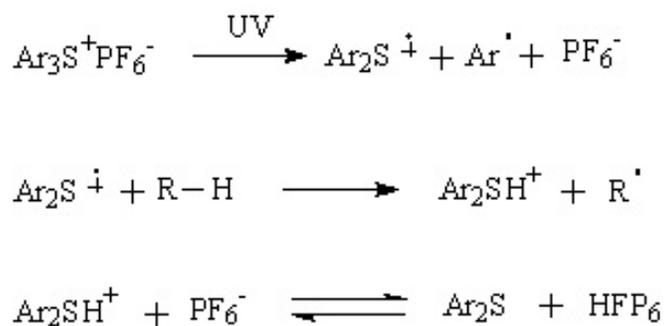
Figure 27. Generation of HFP$_6$ via UV radiation and triarylsulfonium salts.[127,128,129]

$$R\text{--}CH\!\!\overset{O}{\diagdown}\!\!CH_2 + H^+PF_6^- \rightleftharpoons R\text{--}CH\!\!\overset{\overset{H}{\underset{|}{O^+}}}{\diagdown}\!\!CH_2 + PF_6^-$$

$$R\text{--}CH\!\!\overset{\overset{H}{\underset{|}{O^+}}}{\diagdown}\!\!CH_2 + R\text{--}CH\!\!\overset{O}{\diagdown}\!\!CH_2 \longrightarrow HO\text{--}\underset{R}{CH}\text{--}CH_2\text{--}\overset{+}{O}\!\overset{CH_2}{\underset{R}{\diagup CH}}$$

$$HO\text{--}\underset{R}{CH}\text{--}CH_2\text{--}\overset{+}{O}\!\overset{CH_2}{\underset{R}{\diagup CH}} + R\text{--}CH\!\!\overset{O}{\diagdown}\!\!CH_2 \longrightarrow H\!\left(O\text{--}\underset{R}{CH}\text{--}CH_2\right)_n^{\!+}\!\overset{CH_2}{O}\!\underset{R}{\diagup CH}$$
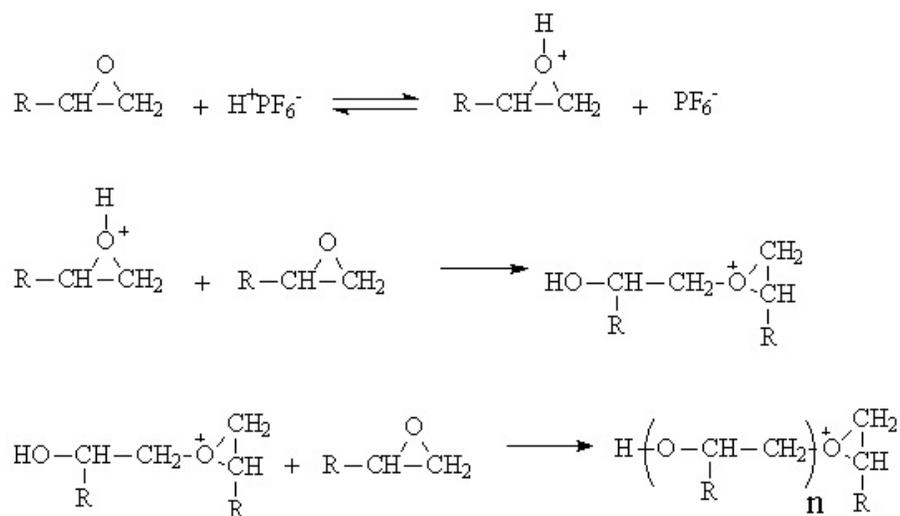
Figure 28. Curing epoxies via cationic initiation and propagation.[130]

127   B. Ellis, *Chemistry and Technoloy of Epoxy Resins*, Chapman and Hall, New York, **1993**.
128   L. McAdams, J. Gannon, in *Encyclopedia of polymer science and engineering, Vol. 6*, John Wiley and Sons, New York, **1986**, pp. 322.
129   J. Koleske, A Radiation Cure Primer, *Journal of Coatings Technology* **1997**, *69*, 29.
130   L. McAdams, J. Gannon, in *Encyclopedia of polymer science and engineering, Vol. 6*, John Wiley and Sons, New York, **1986**, pp. 322.

To over come the brittle nature of the cycloaliphatic epoxy networks much work has been done providing flexibility and toughness to the network. Toughness and elongation can be achieved by copolymerizing a polyol into the network. J. Koleske has evaluated the incorporation of caprolactone polyols and propylene oxide polyols into ultraviolet light cured cycloaliphatic epoxide resins, (Figure 29).[131] While both polyols contribute strength, toughness and flexibility, the particular polyol chosen for a given system will depend on the final desired coating characteristics. Typically, as the molecular weight of the polyol increases for the same weight percentage of polyol the mechanical properties decrease; although, improved flexibility is obtained.[132] However, the final hydroxyl content will have an effect on water resistance and adhesion; and the lower the molecular weight of the polyol the greater the final hydroxyl number. Thus it is necessary to optimize the final hydroxyl content to maximize adhesion and/or to minimize water absorption. It was suggested that the polycaprolactone containing network should have better ultraviolet light stability, oil and grease and high temperature stability over the polyether containing polyol (polypropylene oxide) network. However, the polypropylene oxide modified network should have improved hydrolytic stability over the polycaprolactone modified network.

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[131]   J. Koleske, Copolymerization and properties of cationic, ultraviolet light cured cycloaliphatic epoxide systems, *Polymers Paint Color Journal* **1989**, *179*, 796.
[132]   J. Koleske, Mechanical properties of cationic ultraviolet light cured cycloaliphatic epoxide systems, *Poymers Paint Colour Journal* **1988**, *178*, 501.
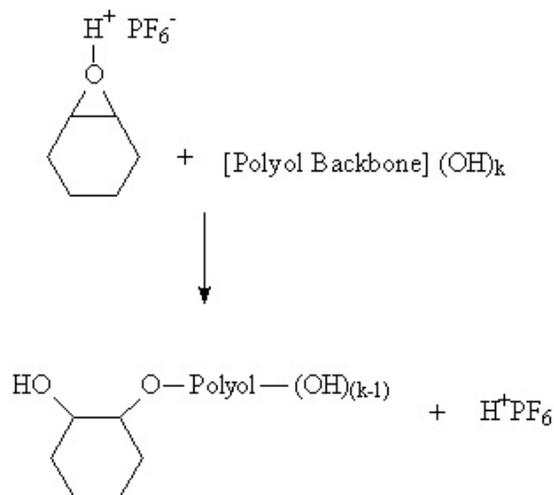
Figure 29. The incorporation of a polyol into a radiation cured cycloaliphatic network.[133]

Not only are the cycloaliphatic resins free of hydrolysable chlorine and ash they

do not contain aromatic compounds and hence are more stable to UV exposure. The

presence of aromatic rings in bisphenol A based resins increases the UV absorption,

discoloration and degradation.[134,135] Since they are free of aromatic rings they are not

carbonized by electrical arc either and exhibit outstanding arc and tracking

resistance.[136,137] Thus, applications for the cycloaliphatic epoxies include: coatings,

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[133]   J. Koleske, A Radiation Cure Primer, *Journal of Coatings Technology* **1997**, *69*, 29.

[134]   B. Ellis, *Chemistry and Technoloy of Epoxy Resins*, Chapman and Hall, New York, **1993**.

[135]   H. Batzer, Cycloaliphatic epoxides: Their synthesis and properties, *Chemistry and Industry* **1964**, *5*, 179.

[136]   H. Batzer, Cycloaliphatic epoxides: Their synthesis and properties, *Chemistry and Industry* **1964**, *5*, 179.

[137]   in *Encyclopedia of polymer science and engineering, Vol. 5*, John Wiley and Sons, New York, **1986**, p. 797.

molded articles, composites, coils, microelectronic packaging, insulators, transformers, bushings, motors and switchgear, etc.

Continued improvement in the area of vinyl esters is needed. The current vinyl esters are based on aromatic oligomers (derived from diglycidyl ether of bisphenol A epoxies) and aromatic reactive diluents such as styrene. These aromatic compounds are susceptible to UV absorption and degradation. For applications such as large scale composites for infrastructure and/or coatings that will be exposed to terrestrial sunlight will be susceptible to photo-degradation. The basis for the research I've conducted at Virginia Tech is in the design of a UV stable vinyl ester matrix material based on cycloaliphatic epoxy monomers with oligomer and network evaluation and characterization.

Chapter 3. Experimental

3.1. Materials

3.1.1.   ERL-4221

3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexylcarboxylate (ERL-4221), a cycloaliphatic diepoxide, was donated by Union Carbide Corp. It has a molecular weight of 252 g/mole and was purified by fractional distillation at 175°C/1 torr.
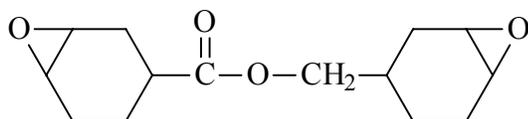
Figure 30. ERL-4221, diepoxide monomer

3.1.2.   Bisphenol-A based aromatic dimethacrylate

The methacrylate-terminated polyhydroxy ether oligomers were kindly supplied by Dow Chemical Co. These oligomers were of controlled molecular weight and polydispersity. The number average molecular weight was 690 g/mol. with a polydispersity index $M_w/M_n = 1.3$.
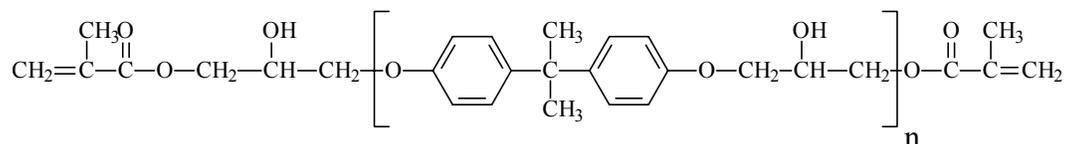
Figure 31. Bisphenol-A based vinyl ester.

3.1.3. **Aromatic epoxides**

The phosphine oxide, sulfonyl, and hexafluoroisopropylidene diepoxides were prepared in our lab by reacting epichlorohydrin with the corresponding bisphenol under basic conditions.[138]

3.1.4. **Triphenylphosphine**

Triphenylphosphine (TPP) was purchased from Aldrich: FW 262.29, mp 79-81°C, bp 377°C. Triphenylphosphine was used as a catalyst in the synthesis of the cycloaliphatic vinyl ester synthesis.
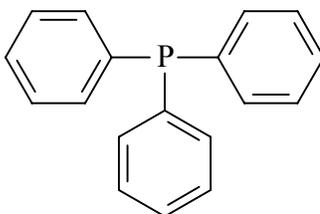
Figure 32. Triphenylphosphine, catalyst

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[138]   M. Bump, C. Tyberg, J. S. Riffle, *Proceedings of the 23rd Annual Meeting of the Adhesion Society* **2000**, 328.

3.1.5. Glutaric acid

Glutaric acid was purchased from Aldrich: FW 132.12, mp 95-98°C. Glutaric acid is a low melting dicarboxylic acid used in the synthesis of the cycloaliphatic dimethacrylate.

$$HO-\overset{\overset{\textstyle O}{\|}}{C}\!\!\left[CH_2\right]_3\!\!\overset{\overset{\textstyle O}{\|}}{C}-OH$$
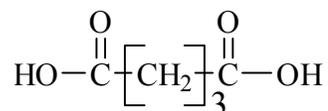
Figure 33. Glutaric acid, dicarboxylic acid monomer.

3.1.6. Methyl methacrylate

Methyl methacrylate was purchased from Aldrich: FW 100.12, mp –48°C, bp100^{o}C. Methyl methacrylate was used as a reactive diluent for improved UV stability. Both the aromatic bisphenol-A and CAVE were independently cured with methyl methacrylate and their mechanical properties have been compared. The aromatic bisphenol-A networks cured with methyl methacrylate have also been compared to those cured with styrene. One disadvantage is that methyl methacrylate does have a much lower boiling point and thus those networks containing methyl methacrylate were cured using the room temperature cure/post cure procedure listed under network formation.

$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-\underset{\underset{\displaystyle O}{||}}{C}-O-CH_3$$
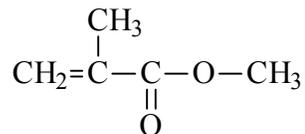
Figure 34. Methyl methacrylate, reactive diluent

3.1.7.   **Butyl methacrylate**

Butyl methacrylate was purchased from Aldrich: FW 142.20, bp 160-163°C.

Butyl methacrylate was used as a reactive diluent for a series of bisphenol-A vinyl esters

at 30, 40, 50 weight percentages. Butyl methacrylate has a much higher boiling point

than methyl methacrylate (100°C) and even higher than that of styrene (145-146°C) and

thus can be thermally cured with BPO as the initiator.

$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-\underset{\underset{\displaystyle O}{||}}{C}-O-CH_2-CH_2-CH_2-CH_3$$
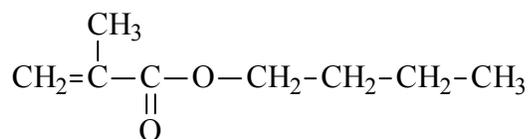
Figure 35. Butyl methacrylate, reactive diluent.

3.1.8.   **Styrene**

Styrene was purchased from Aldrich: FW 104.15, bp145-146°C. Styrene was

used as a reactive diluent for the bisphenol-A vinyl esters. These materials were both

thermally cured with BPO or by using the room temperature cure/ post cure procedure

listed in the network formation section. However, if styrene is used as a reactive diluent for the CAVE materials it phase separates above ~30 weight percent.

CH=CH$_2$
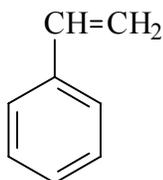
Figure 36. Styrene, reactive diluent.

3.1.9. Benzoyl peroxide (dibenzoyl peroxide) (BPO)

Benzoyl peroxide was purchased from Aldrich in a granular form: FW 242.23, mp105. Benzoyl peroxide was used as the initiator to free radically cure those networks cured at 140°C. Benzoyl peroxide was typically used at 1 weight percent with respect to the total resin weight containing the reactive diluent.
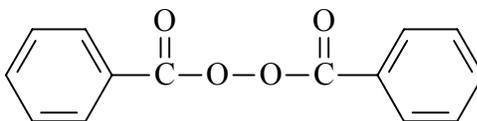
Figure 37. Benzoyl peroxide initiator.

3.1.10. Methyl ethyl ketone peroxide (2-Butanone peroxide)

Methyl ethyl ketone peroxide (MEKP) was purchased from Aldrich. It is supplied as a 32 weight percent solution in dimethyl phthalate. Commercial MEKP is a mixture of oligomers as shown in Figure 38; however, most is in the monomeric and

dimeric form.[139] It is generally made from methyl ethyl ketone and hydrogen peroxide. MEKP is used as the initiator in the room temperature cure/ post cure procedure. It was used in concentrations of 1.125 weight percent with respect to the total resin weight containing the reactive diluent.

$$R^1-\overset{\overset{\displaystyle O}{\|}}{C}-R^2 \quad + \quad H_2O_2 \quad \longrightarrow \quad R^1-\overset{\overset{\displaystyle OOH}{|}}{\underset{\underset{\displaystyle OOH}{|}}{C}}-R^2 \quad + \quad HOO-\overset{\overset{\displaystyle R^1}{|}}{\underset{\underset{\displaystyle R^2}{|}}{C}}-OO-\overset{\overset{\displaystyle R^1}{|}}{\underset{\underset{\displaystyle R^2}{|}}{C}}-OOH$$
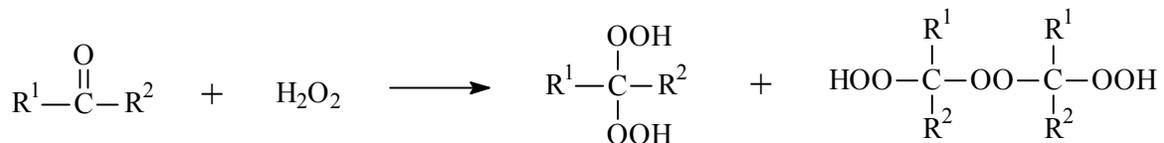
Figure 38. Formation of the MEKP oligomers.

3.1.11. N,N-Dimethyl aniline

N,N-Dimethyl aniline was purchased from Aldrich: FW 121.18, mp 1.5-2.5°C, bp193-194°C. Dimethyl aniline was used as an accelerator for the room temperature cure/post cure procedure listed in network formation. It was used in concentrations of 0.035 weight percent with respect to the total resin weight containing the reactive diluent.
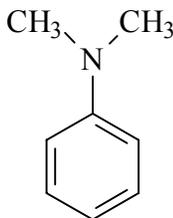
Figure 39. Dimethyl aniline.

[139]   D. Nwoko, T. Pettijohn, The Role of Monomeric and Dimeric Oligomers of Methyl Ethyl Ketone Peroxide in the Cure of Unsaturated Resin Formulations, *Proceedings of the 1999 International Composites Expo, Cincinnati, Ohio, May 10-12* **1999**.

3.1.12. Cobalt naphthenate (CoNap)

Cobalt naphthenate (53 wt % in mineral spirits (6 wt % Co)) was obtained from Alfa Aesar and used as received. CoNap was used as an accelerator to decompose the MEKP at ambient temperatures during the room temperature cure/post cure procedure. It was used in concentrations of 0.15 weight percent with respect to the total resin weight containing the reactive diluent.

3.1.13. d_6 -Dimethyl sulfoxide (d-DMSO)

Deuterated DMSO was purchased from Aldrich and used as a NMR solvent.

3.1.14. d-Acetone

Deuterated acetone was purchased from Aldrich and used as a NMR solvent.

3.1.15. d-Chloroform

Deuterated chloroform was purchased from Aldrich and used as a NMR solvent.

3.1.16. Dimethylacetamide

Dimethylacetamide was purchased from Aldrich: FW 87.12, mp-20°C, bp 164.5-166°C. Dimethylacetamide was used as a solvent for ^{13}C NMR in order to separate the ester carbonyl of the ERL-4221 and the glutaric acid carbonyl during the synthesis of the CAVE oligomer. These carbonyls overlapped in the ^{13}C NMR using d-dmso; however, in dimethylacetamide they can be resolved.

3.1.17. Ethanol

Spectrophotometric grade ethanol was purchased from Aldrich and used as received.   Ethanol was used as a solvent for solution UV measurements.

3.1.18. Acetonitrile

Spectrophotometric grade acetonitrile was purchased from Aldrich and used as received. Acetonitrile was used as a solvent for solution UV measurements.

3.1.19. Sodium Chloride Plates

The sodium chloride plates were purchased from Aldrich. The salt plates were used for studying the cure of the vinyl ester in situ by FTIR. After a vinyl ester has been cured between a set of salt plates, the salt plates became non removable. To recycle the plates after use, they were placed in a furnace at 400-450°C for 8 hours to burn out the crosslinked film. The plates once separated were then polished for reuse.

3.2. Synthesis

3.2.1. Cycloaliphatic vinyl ester (CAVE)

The aliphatic oligomers were prepared in melt, one-pot but 2-step synthetic sequences involving nucleophilic epoxy ring-opening with carboxylates. A synthesis example for a 1000 g/mole methacrylate terminated oligomer is provided. 3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexylcarboxylate (ERL-4221) (0.07143 moles, 18.0000 grams) was "pre-reacted" with methacrylic acid (0.05714 moles, 4.9142 grams) to form an endcapping reagent. 1.5 mole % triphenylphosphine (0.002143 moles, 0.5614 grams) with respect to the number of epoxy equivalents was used, and 500 ppm hydroquinone (0.0146 grams) was used as an inhibitor. The reaction was carried out in a 3 neck 100 ml round bottom flask at 90°C for one hour. The remaining epoxies were subsequently reacted with glutaric acid to yield controlled molecular weight, methacrylate terminated, all aliphatic oligomers (Figure 40). Glutaric acid (0.04286 moles, 5.6572 grams) was added to the flask and the temperature was increased up to 98°C to melt the acid, then lowered to 90°C and maintained for one hour. These reactions were conducted with air (atmospheric oxygen as an inhibitor) as the atmosphere to prevent gelation (due to polymerization of the methacrylate end groups).
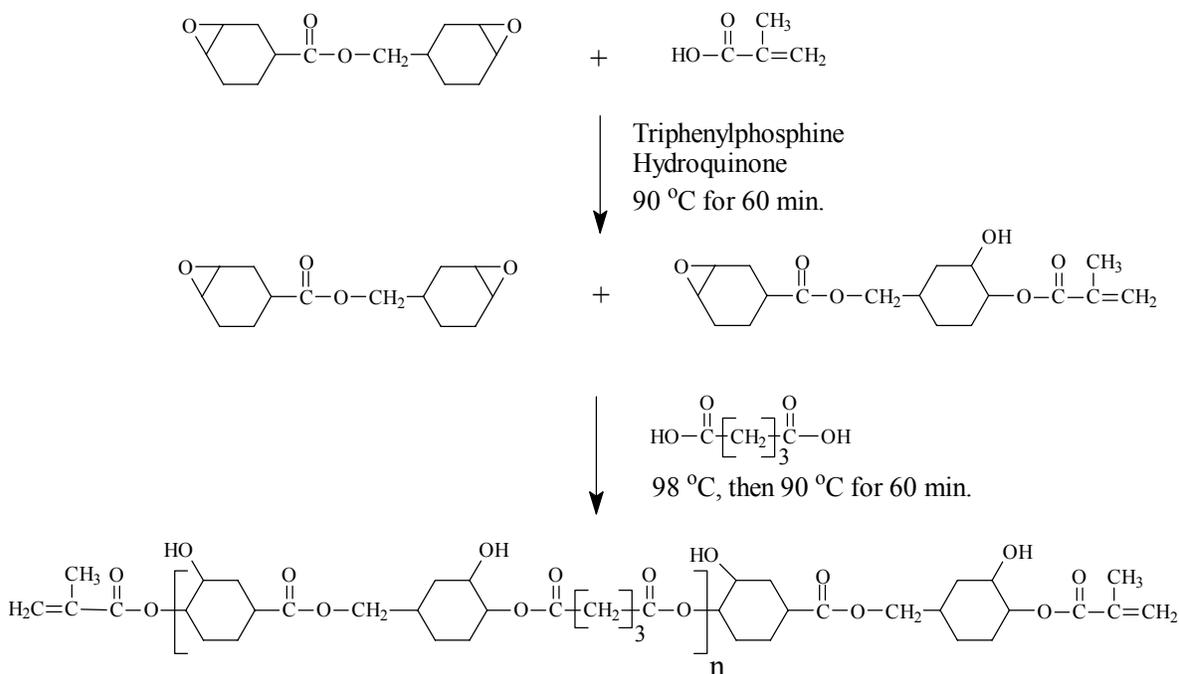
Figure 40. Synthesis of the cycloaliphatic dimethacrylate. A one pot reaction done in two steps.

3.3. Network Formation

3.3.1. Cycloaliphatic vinyl ester cured with methyl methacrylate

Systematically varied percentages of methyl methacrylate were added to the oligomer to prepare a series of resins for copolymerization studies. An example of a cure reaction is provided using a 1000 g/mole oligomer and methyl methacrylate. A resin containing 40 weight percent methyl methacrylate was prepared by charging a reaction vessel with 30.0000 g of a 1000 g/mole oligomer and 20.0000 g of methyl methacrylate. Accelerators and initiators were added in the following order and the mixtures were

stirred well between additions: 0.15 wt % cobalt naphthenate (0.0750 g) in mineral spirits, 0.035 wt % dimethylaniline (DMA) (0.0175 g), and 1.125 wt % methyl ethyl ketone peroxide (MEKP) (0.5625 g). This initiator and accelerator concentration allowed a working time of about 20 min at 25°C once the MEKP was added. The mixture was poured into a silicone mold and cured at 25°C for 24 hours, then postcured at 115°C for 2 hours.

3.3.2. **Aromatic vinyl ester network formation**

Systematically varied percentages of styrene were added to a bisphenol-A based dimethacrylate (vinyl ester) oligomer to prepare resins for the copolymerization studies. A 40 wt percent styrene resin was prepared by charging a stirred reaction vessel with 30.0000 g of the bisphenol-A based vinyl ester and 20.0000 g of styrene and co-dissolving them in the presence of air at 55°C for 2 hours. The mixture was cooled to room temperature, then accelerators and initiators were added in the following order and mixed well between additions: 0.15 wt % cobalt naphthenate (0.0750 g) in mineral spirits, 0.035 wt % DMA (0.0175 g), and 1.125 wt % MEKP (0.5625 g). This mixture was poured into a silicone mold and cured at 25°C for 24 hours, then postcured at 115°C for 2 hours. Networks cured with methyl methacrylate were prepared analogously and cured under the same conditions.

An alternative curing procedure was also investigated for comparison. Analogous mixtures as described above were charged to a reaction vessel and co-dissolved with 1.1 weight % benzoyl peroxide (0.5500 g). The resin mixture was degassed by mild vacuum at 25°C for about 1 minute, then cured in a silicone mold at 140°C for 1 hour.

3.4. Characterization

3.4.1. NMR

[1] H NMR and [13] H NMR were used to monitor the synthesis of the cycloaliphatic vinyl ester. [1] H NMR was collected on a Varian Unity 400 MHz instrument with a frequency of 399.954 MHz. A 22° pulse angle was used with an acquisition time of 3.7 seconds and a recycle delay of 1 second. ^{13}C NMR was obtained using the same instrument but with a frequency of 100.578 MHz. A 45° pulse angle was used with an acquisition time of 1.2 seconds and a recycle delay of 1 second. d_6-DMSO was normally used as the NMR solvent. However, the spectra in Figure 49 were recorded in DMAc to resolve the acid carbonyl from the ester carbonyl of the epoxy monomer.

3.4.2. Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography (GPC) was conducted to monitor the molecular weights and molecular weight distributions of the vinyl ester oligomers. Gel Permeation Chromatography was conducted using a Waters GPC 150C at 60°C. The flow rate was 1 ml/min of .02M P_2O_5 dissolved in N-methylpyrrolidone. A refractrive index and viscosity detector were used; however, the signal to noise ratio was too low to obtain an absolute molecular weight using a universal calibration.

3.4.3. DSC

Differential scanning calorimetry was used as a tool to measure the glass transition temperature of the dimethacrylate oligomers. Glass transition temperatures were measured using a Perkin Elmer Pyris 1 differential scanning calorimeter. Because these oligomers exhibit glass transition temperatures near room temperature, all DSC samples were run from –50 to 100°C at 10°C/min. Results are reported from the second heating scans.

3.4.4. Dynamic mechanical analysis (DMA)

Thermal analysis of the networks was investigated using a Perkin Elmer DMA7e Dynamic Mechanical Analyzer. The DMA was used to determine the glass transition temperature of the networks. A three point bend probe was used with a span of 10 mm. The sample height and width were 3 mm by 6 mm respectively. Glass transition temperatures were measured from the peak of the tan delta plot with a heating rate of 2°C/min.

3.4.5. Elastic modulus determination

Elastic moduli were determined according to ASTM D 5934-96. A three point bending attachment was used with a span of 15 mm. Thin uniform samples should be tested with a span to depth ratio of at least 10. Sample dimensions were 1.50 mm X 2.50 mm X 15.00 mm. A static force scan of 50 mN/min was done isothermally at Tg + 50°C to generate the slope of the load versus displacement data. It is also important to limit displacements to 10% of the sample depth. Molecular weights between crosslinks (M_c) were also calculated for the CAVE (cycloaliphatic vinyl ester) 808 and CAVE 1200

series. M_c was calculated from the rubbery modulus E' as shown in Equation 4 where: R is the gas constant (8.314 J/K*mol), T (Kelvin) is Tg+50°C, and ρ is the density at Tg + 50°C.[140] Densities at Tg + 50°C were estimated by using the room temperature density (measured with a Mettler-Toledo AG204 balance adapted with a Mettler-Toledo density kit) and the coefficients of thermal expansion (CTE) below and above Tg to estimate the new density at Tg + 50°C. The coefficient of thermal expansion (CTE) was measured above and below Tg using a quartz probe with a heating rate of 3°C/min.

Equation 3

$$E' = (P/\Delta)*g*(L^3 / 48I)$$

Equation 4

$$Mc = 3RT\rho/E'$$

P/Δ = slope of the load versus displacement plot

g = gravitational constant (9.81 m/s^2)

L = length between supports

$I = (1/12)wh^3$

w = width of sample

h = height of sample

[140]   I. M. Ward, D. W. Hadley, *An Introduction to the Mechanical Properties of Solid Polymers*, John Wiley and Sons, New York, **1993**.

3.4.6. Coefficients of thermal expansion

The coefficient of thermal expansion (CTE) was measured above and below Tg using a quartz probe on the TMA with a heating rate of 3°C/min.

3.4.7. Resin density measurements

Resin densities were measured in order to calculate the shrinkage of the network. Resin densities were measured for every oligomer with the corresponding percentage of reactive diluent. Measurements were made using a 10 ml specific gravity bottle obtained from Aldrich. The specific gravity bottle was first calibrated using distilled water. Each resin was weighed in the specific gravity bottle at 25°C using a Mettler-Toledo AG204 balance five to seven times to ensure accuracy and the average was taken to be the value. Care was taken not to handle the specific gravity bottle because heat from ones hand will cause an increase in the temperature of the specific gravity bottle and resin; thus, the density will not be accurate and lower than expected.

3.4.8. Network density measurements

Network densities of the cured samples were measured with a Mettler-Toledo AG204 balance adapted with a Mettler-Toledo density kit. The samples were first weighed in air (A) and then in distilled water (B) to the nearest 0.0001 gram. The density of the cured network (ρ) was calculated using the following formula (Equation 5) where ρ_o is the density of water.

Equation 5

$$\rho = A\rho_o/(A-B)$$

3.4.9. Cure shrinkage

Cure shrinkage was calculated from the liquid density of the resin and the corresponding cured network density. Percent cure shrinkage is the change in volume as the network cures and thus shrinks. It was calculated according to Equation 6, where $\rho_{uncured}$ is the density of the uncured resin and ρ_{cured} is the density of the cured network.

Equation 6

$$\% \text{ shrinkage} = 100 \text{ x } ((1/\rho_{uncured})-(1/\rho_{cured}\,)) \,/\, (1/(\rho_{uncured}))$$

3.4.10. UV-VIS

UV-VIS absorption spectra were recorded on the epoxy functional oligomers to compare the backbone absorptions of the vinyl esters. A Hewlett Packard spectrometer 8452A was used with ethanol as the solvent. Acetonitrile was used for obtaining the spectra of the sulfonyl diepoxide. All spectra were taken with .0328 mg of sample per ml of solvent in a 1 cm path quartz cell.

3.4.11. Infrared Spectroscopy (FTIR)

Network formation was monitored by FTIR using a Nicolet Impact 400 coupled with a thermostatically controlled IR cell (model HT-32 heated demountable cell, Figure 41). For the samples cured at 25°C the reaction was conducted over the 24 hour period in

a dessicator between salt plates between recordings of the IR spectra. The 2 hour post

cure was then monitored in situ in the FTIR instrument.
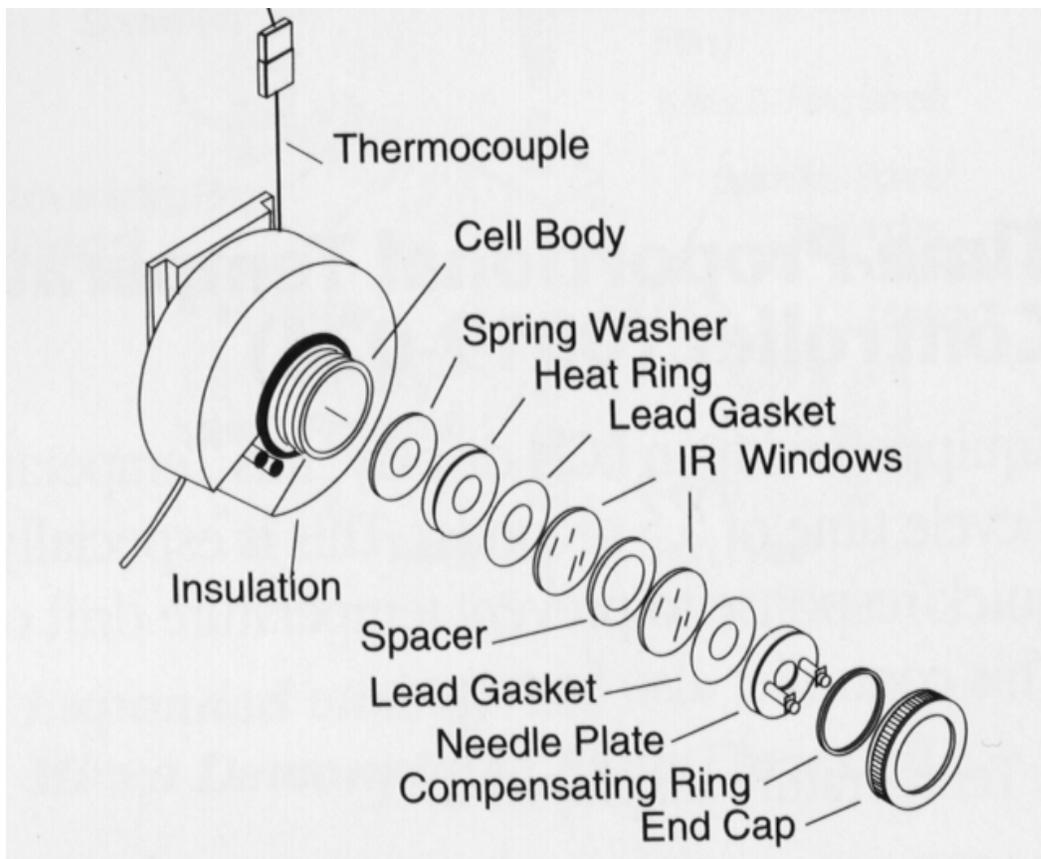
Figure 41. Heated demountable FTIR cell used for monitoring the network cure formation.

3.4.12. **Fracture toughness**

Fracture toughness measurements were conducted to characterize the toughness

of the vinyl ester networks according to ASTM D5045-91. An Instron model 4204 was

used with a crosshead speed of 1 mm/min, and a three point bend attachment set to a span

of 1 inch. All samples measured 0.250'' x 0.125'' x 1.50''. After machining and

polishing the samples a notch was placed in the center of the sample by sawing with a

mini-hacksaw. A natural crack was initiated in the notch by tapping a new razor blade

dipped in liquid nitrogen to generate a crack length of ~50 % of the depth. The samples

were then loaded individually in the Instron and tested with the notch down at 25°C,

Figure 42.

$$S = 4W$$
$$X = a/W$$

B

$$P_Q = \text{Load in kN}$$
$$B = \text{Thickness in cm}$$
$$S = \text{Span 2.54cm (1 inch)}$$
$$W = \text{Width (depth) in cm}$$
$$a = \text{Crack length in cm}$$
$$X = \text{Ratio of crack length}$$
$$\text{to the width (.45-.55)}$$

W

a

S
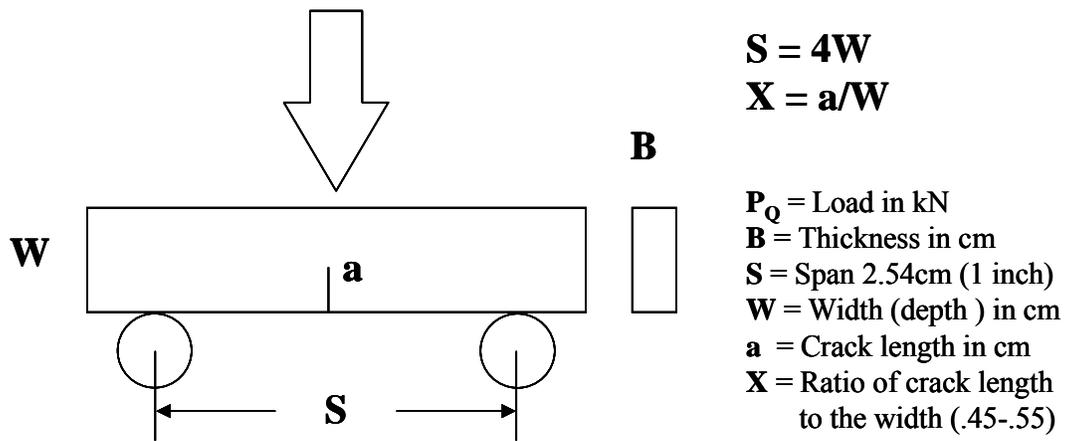
- $K_{1c} = \dfrac{(P_Q S)}{BW^{3/2}} * \dfrac{3X^{1/2}[1.99-X(1-X)(2.15-3.93X+2.7X^2)]}{2(1+2X)(1-X)^{3/2}}$

Figure 42. Fracture toughness test and specifications.

3.4.13. Vickers microhardness

Vickers microhardness was used to compare the hardness of the vinyl ester networks. Microhardness values were measured using a Tukon microhardness tester with a pendulum weight of 1100 grams and a repeatability value within 2 percent. The micro indentations were done with a pointed square-based pyramidal diamond that has face angles of 136°. The area of the indentation was then measured optically in mm^2. The Tukon microhardness tester calculated the microhardness by dividing the load in Kg by the area of the indentation measured optically.

3.5. *Environmental Aging*

3.5.1. **Water absorption**

Water absorption measurements were conducted with cured network samples that were 1 mm x 6 mm x 20 mm. Samples were generally made from broken fracture toughness bars. The samples were machined down to a thickness of 1mm and polished with (600 grit) sandpaper and each sample was measured with a micrometer. The samples were placed in a vacuum oven at 1/torr and 85°C overnight then weighed and placed in 15 ml of distilled water. The samples were then weighed at given intervals (every few hours the first day, every day followed by every other day, then every few weeks followed by every month). The data were normalized for thickness and plotted as percent water absorption vs. (hours$^{.5}$)/thickness(mm).

3.5.2. **Accelerated Ultraviolet Aging**

Networks were aged under a Xenon arc lamp for accelerated ultraviolet aging tests. The instrument was devised to have a rotating drum on which samples could be attached as shown in Figure 43. The light source (Oriel 1000 W xenon arc lamp model 6269) was focused down a metal tube and onto the drum with a beam width of three inches. The power supply was an Oriel 1000 W arc lamp power supply model 68820 and the intensity of the light was controlled by the Oriel light intensity controller; model 68850. The drum was 16 inches in diameter and was located 16 inches from the light source. The drum rotated at 3 rpm to allow intermittent exposure to all the samples and to

prevent over heating of the samples. Although not shown in the photograph, the drum

was covered in a glass matt as a backing for the samples.
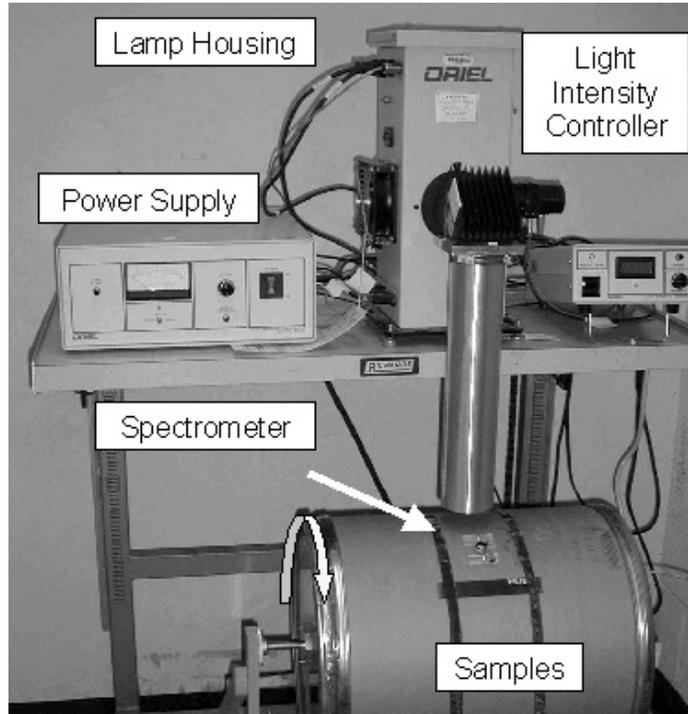
Figure 43. A photograph of the accelerated UV aging machine.

In the center of the drum we located a spectrophotometer lead with a UV

transmittable photo-optic cable (Ocean Optics P200-2-UV/VIS, 200-750 nm) so that UV

spectra could be taken at any time to monitor intensity and exposure of the samples. The

spectrophotometer (Ocean Optics s2000 spectrometer) was calibrated by NIST in order to

convert counts (the units of the spectrophotometer) to irradiance. Equation 7 was

generated from the calibration curve in Figure 44 and can be used to convert counts to

irradiance for each wavelength and integration time. Figure 45 shows the irradiance of

the xenon arc lamp as a function of wavelength. The irradiance is very linear in this region and can be integrated in order to calculate the amount of exposure per unit area (mW/m^2). Based on the diameter of the drum, exposure size, and drum rotation rate each sample is exposed to the light source 1.5 hours/day, Table 19. Thus the amount of exposure in MJ/m^2 per year can be calculated and compared to the level of exposure in Miami, FL and Phoenix, AZ as reported by Atlas Weathering Services Group, Table 20 and Table 21.

Equation 7

Irradiance = $(2.2946095220E\text{-}16x^6 - 7.5922590192E\text{-}13x^5$

$+1.0314018700E\text{-}09x^4 - 7.3610411037E\text{-}07x^3 + 2.9248500417E\text{-}04x^2$

$-6.2090682904E\text{-}02x + 5.6357885770E\text{+}00)$ *(counts/sec)

       X = Wavelength in nanometers

       Irradiance = $mW / (m^2 * nm)$

       Counts = Spectrophotometer units (measurement of intensity)

       Sec = Integration time in seconds (time in which the spectrum was obtained)

Samples were checked daily and spectra were taken three days a week to ensure consistency. The specifications of the test are as listed in Table 19. The sample temperatures were monitored for any increase in temperature by using an infrared digital camera. The room temperature was between 25 and 26^oC and the sample temperatures never reached above 28^oC as the drum rotated the samples in and out of the light.

Samples had dimensions of 1/4" x 1/8" x 3" and were placed on the drum with the 3" side parallel to the axis of the drum with the ¼" sides facing the drum and light source.

Part or Setting	Specification
Bulb	1000 W Xenon Arc
Power Supply Preset	1000 W
Light Intensity Controller Preset	51.2 (@90% of control limit)
Distance of Sample from Mirror	16 in.
Drum Size	16 in. diameter
Drum Rotational Speed	3 rpm
Exposure Size	3 in. diameter
Hours of Exposure per day	1.5 hrs./day
Light Spectrum Integration Time	10 ms

Table 19. A table of parts or settings for the accelerated UV testing with its corresponding specification.
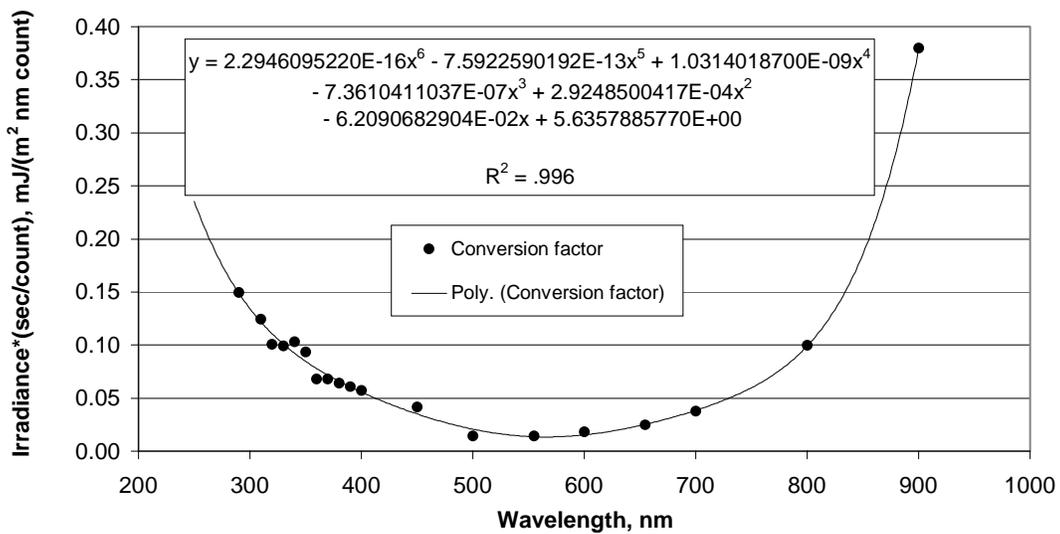
Figure 44. Calibration curve used to convert units of the spectrophotometer (counts/sec) to irradiance.
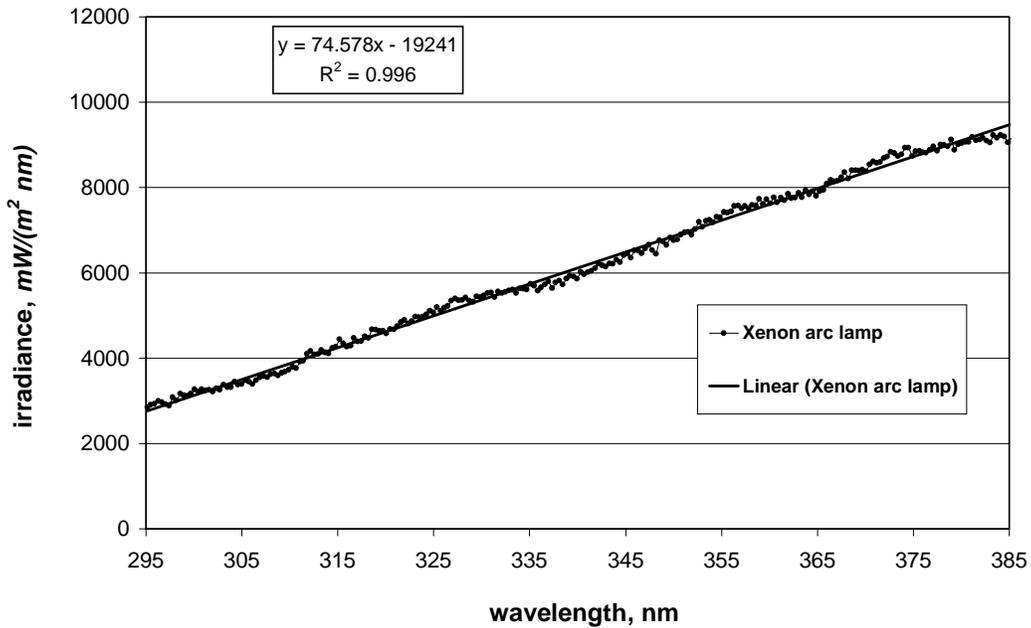
Figure 45. Irradiance of the xenon arc lamp from 295 to 385 nm and the linear regression line fit was integrated to calculate the total energy.

Light source or location	Exposure per year
Xenon Arc	1085 MJ/(m^2)
Miami, FL	280 MJ/(m^2)*
Phoenix, AZ	330 MJ/(m^2)*

Table 20. Exposure per year and yearly equivalence for Miami and Phoenix based on 225 days of xenon arc exposure. *As reported by Atlas Weathering Services Group.

Light source or location	Exposure Equivalence
Xenon Arc	225 days of aging
Miami, FL	2.4 years
Phoenix, AZ	2.0 years

Table 21. Exposure equivalence based on equivalent energy for 225 days of accelerated aging with the xenon arc lamp.

3.5.3. X-Ray Photoelectron Spectroscopy (XPS)

X-Ray photoelectron spectroscopy (XPS) is commonly used for surface composition and oxidation state analysis. XPS was implemented into the research to evaluate the oxidation and type of oxidation that has occurred from UV accelerated aging. XPS was conducted on specimens that have been aged for 225 days on the accelerated UV aging machine as well as on the control specimens that were not aged. XPS was conducted using a Perkin Elmer 5400. The XPS was run at 45° under the following conditions: pressure was 1×10^{-7} torr, the beam source was a Mg source at 1253.6 eV, the power was 14 KV and 300 watts, and a monochrometer was not used.

3.5.4. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is commonly used for surface morphology analysis. SEM was implemented into the research to evaluate surface defects that may have occurred from UV accelerated aging. SEM was conducted on specimens that had been aged for 225 days on the accelerated UV aging machine as well as on the control specimens that were not aged. SEM was conducted using an ISI SX40 at 5×10^{-5} torr with a beam of 20 KV. The samples were gold sputter coated with an Edward S 150 B at 1×10^{-2} torr.

3.5.5. **Digital Photographs**

A Nikon digital camera was used to take digital photographs of the control samples as well as those that were aged for 225 days under the UV light. These pictures were taken to capture the visual after effects of aging. This includes yellowing of the samples and the gloss that occurs on those samples cured with methyl methacrylate. Several pictures were taken with either a fluorescent light table or with a piece of white paper as the background, thus some pictures appear darker than others.

Chapter 4.   Results and discussion

4.1.   Introduction

Durable vinyl ester composites with long service lives, desirably over 50 years, are under investigation for use in civil infrastructure. This study involves the synthesis and structure property relationships of an aliphatic vinyl ester network and its comparison to aromatic dimethacrylate/styrene networks. It was reasoned that the aliphatic networks should have superior resistance to sunlight damage since they do not absorb radiation in the range where sunlight has the highest intensities (>290 nm). Moreover, it is well known that coatings containing cycloaliphatic epoxides exhibit excellent environmental resistance against sunlight relative to those containing aromatic glycidyl ethers.[141,142,143]

4.2.   Synthesis of a cycloaliphatic vinyl ester (CAVE)

The synthesis of the cycloaliphatic dimethacrylate terminated oligomer is a one-pot reaction done in two steps (Figure 46). Both steps in the synthesis are reactions of a carboxylic acid with an epoxide, catalyzed by triphenylphosphine (TPP).   It is hypothesized that TPP ringopens an epoxy group, forming an alkoxide anion which rapidly abstracts an acidic carboxylic acid proton. The resulting carboxylate then acts as the propagating nucleophilic species. The cycloaliphatic diepoxide starting material was prereacted with a minor amount of methacrylic acid to form an endcapping reagent. The

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[141]   J. Muskopf,, *Vol. A9* (Ed.: W. Gerhartz), VCH, Weinheim, **1987**, p. 548.

[142]   B. Ellis, *Chemistry and Technoloy of Epoxy Resins*, Chapman and Hall, New York, **1993**.

[143]   J. Brydson, *Plastic Materials*, Butterworths, Boston, **1989**.

amount of methacrylic acid used relative to the other monomers, calculated using the Carother's equation, determined the oligomer molecular weight.[144,145]
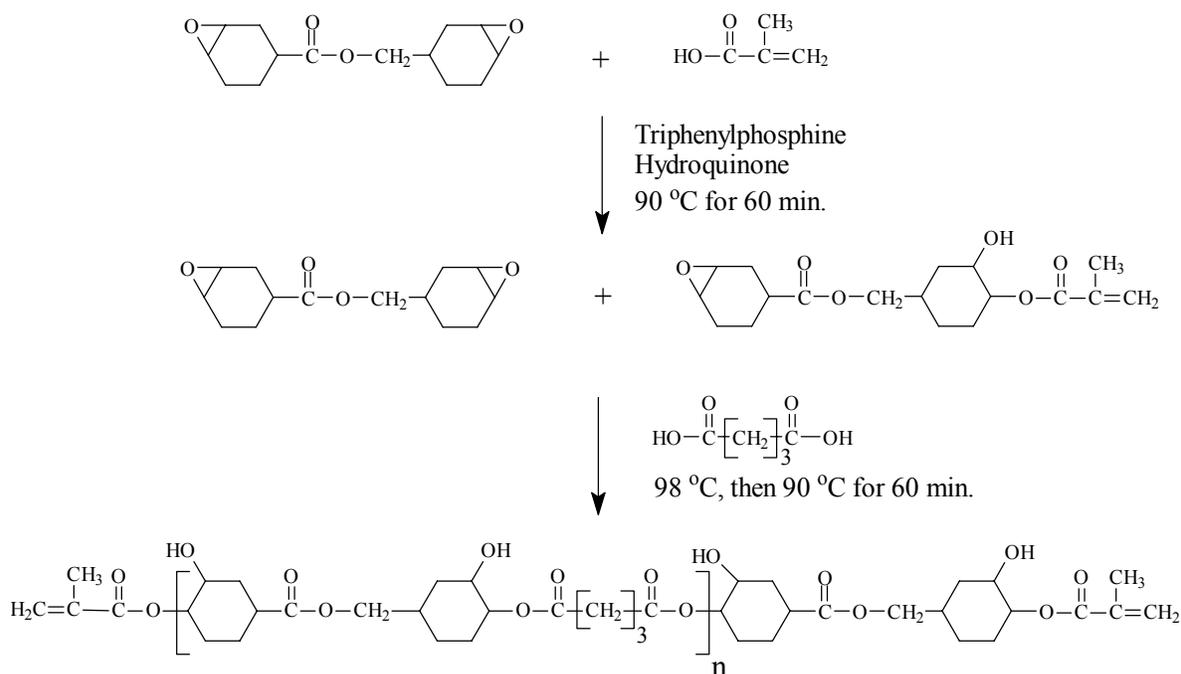
Figure 46. Synthesis of cycloaliphatic polyester oligomers terminated with methacrylate groups: A one-pot reaction conducted in two steps.

The progress of this first step was monitored by ^{1}H NMR and ^{13}C NMR (Figure 47 and Figure 48). The chemical shifts of the vinyl protons were monitored by ^{1}H NMR as the methacrylic acid was converted to an ester. The vinyl protons of methacrylic acid (I) have chemical shifts of 5.93 ppm and 5.54 ppm. As the methacrylic acid reacts and becomes an ester these peaks shift downfield to 6.01 ppm and 5.64 ppm respectively (II).

[144]   P. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithica, **1953**.
[145]   J. Cowie, *Polymers: Chemistry and Physics of Modern Materials*, Blackie Academic and Professional, New York, **1991**.

Full conversion was achieved after 60 minutes at 90°C. ^{13}C NMR is also useful to follow the synthesis of the first step, formation of the endcapping reagent. The acid carbonyl of methacrylic acid at 170.4 ppm shifts upfield to 166.0 ppm. As with ^{1}H NMR, ^{13}C NMR also shows complete conversion after 60 min at 90°C.
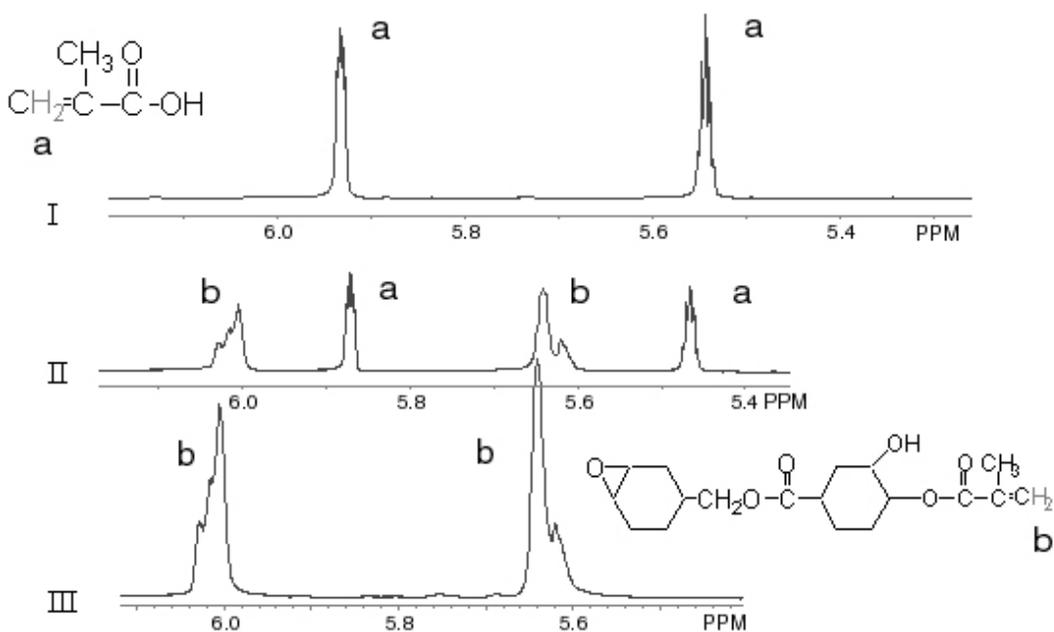
Figure 47. ^{1}**H NMR spectra showing the progression of endcapping reagent formation in the first synthetic step of the cycloaliphatic polyester oligomer synthesis. The reaction of methacrylic acid and ERL-4221 shows a downfield shift of the vinyl protons as methacrylic acid becomes an ester: (I), spectrum of methacrylic acid; (II), spectrum of the reaction mixture after 10 minutes; (III) spectrum of the reaction mixture after 60 minutes.**
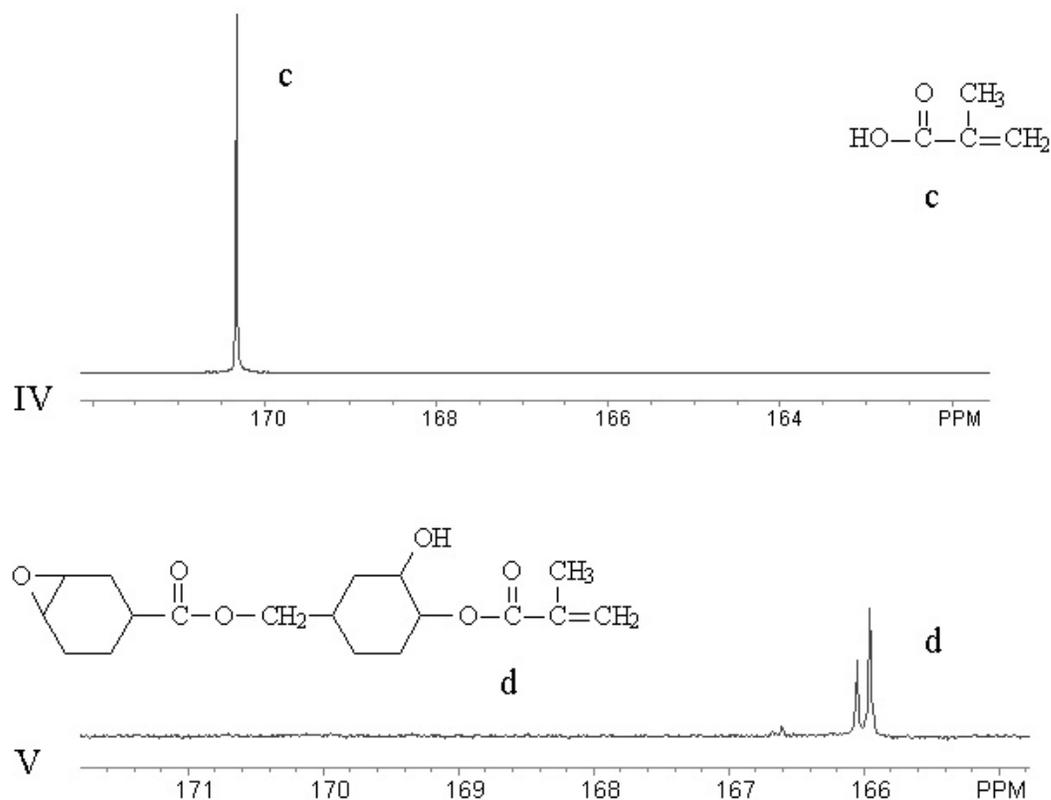
Figure 48. ^{13}**C NMR of the first synthetic step shows the appearance of the newly formed ester carbonyl with the complete disappearance of the methacrylic acid carbonyl: (IV), spectrum of methacrylic acid; (V), spectrum of the 60 minute reaction sample.**

The second step of the dimethacrylate oligomer synthesis involves chain extension of the oligomer with glutaric acid to form the corresponding dimethacrylate. Glutaric acid was chosen due to its relatively low melting point versus adipic acid. ^{13}C NMR peak overlap in d_6-DMSO of the reactants in the chain extension step made it necessary to use dimethylacetamide (DMAc) as a solvent for ^{13}C NMR to monitor this step (Figure 49). The glutaric acid carbonyl carbon resonance was resolved from the

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ester carbonyl of the epoxy monomer using DMAc versus d_6-DMSO as the solvent for ^{13}C NMR. The ^{13}C NMR spectrum confirms quantitative conversion to form the controlled molecular weight dimethacrylate oligomer.
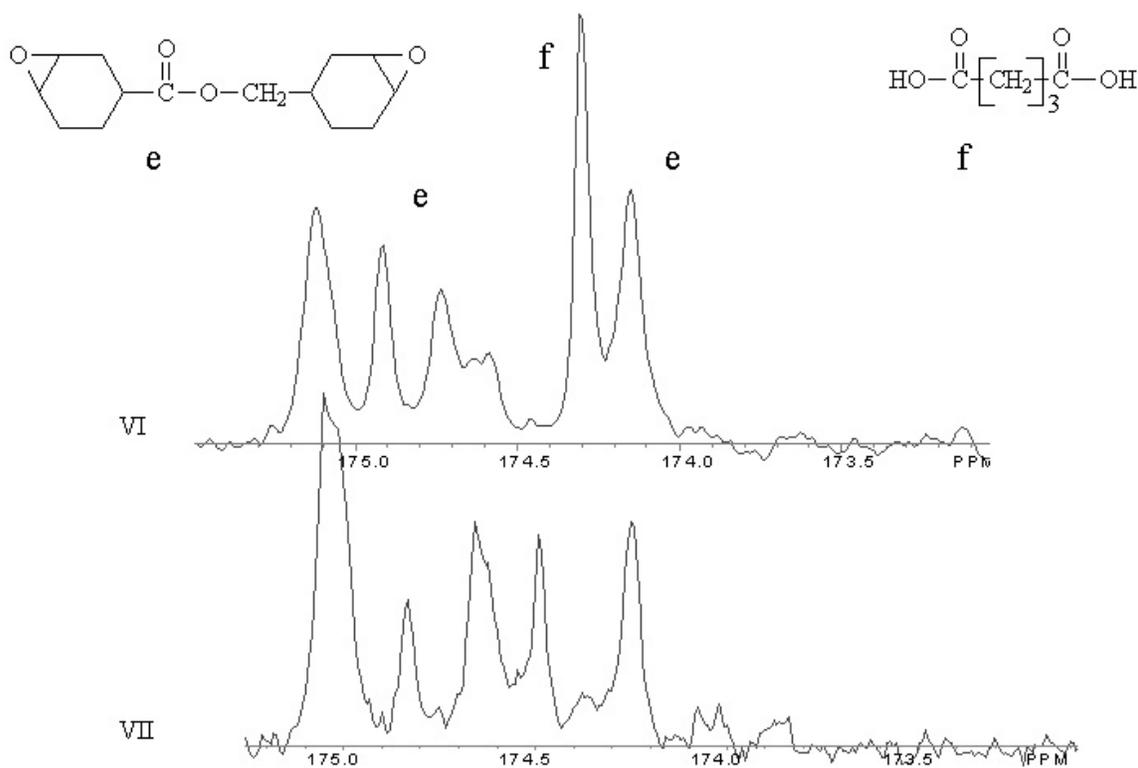
Figure 49. ^{13}C NMR shows the disappearance of the glutaric acid carbonyl (f) (174.3 ppm) as it becomes an ester.

4.3. Oligomer Characterization

The molecular weights of the dimethacrylate oligomers were qualitatively characterized by GPC in NMP using a refractive index detector and polystyrene standards (Figure 50). The molecular weight range of interest for these matrix materials was between about 700 and 2000 g/mole. These molecular weights provided reasonable resin viscosities and desirable network cross-link densities when diluted with reactive monomers. As expected, shifts to lower retention volumes with increasing target molecular weights were consistently observed. Several GPC detector types were tried to evaluate their utility for these measurements. Refractive index detection provided better sensitivity than either a viscosity or multi-angle light scattering method. Low signal to noise ratios with the latter types were encountered due to the low molecular weight range being investigated. Because these are low molecular weight oligomers we were not able to use the viscosity detector to obtain an absolute molecular weight with universal calibration curves.
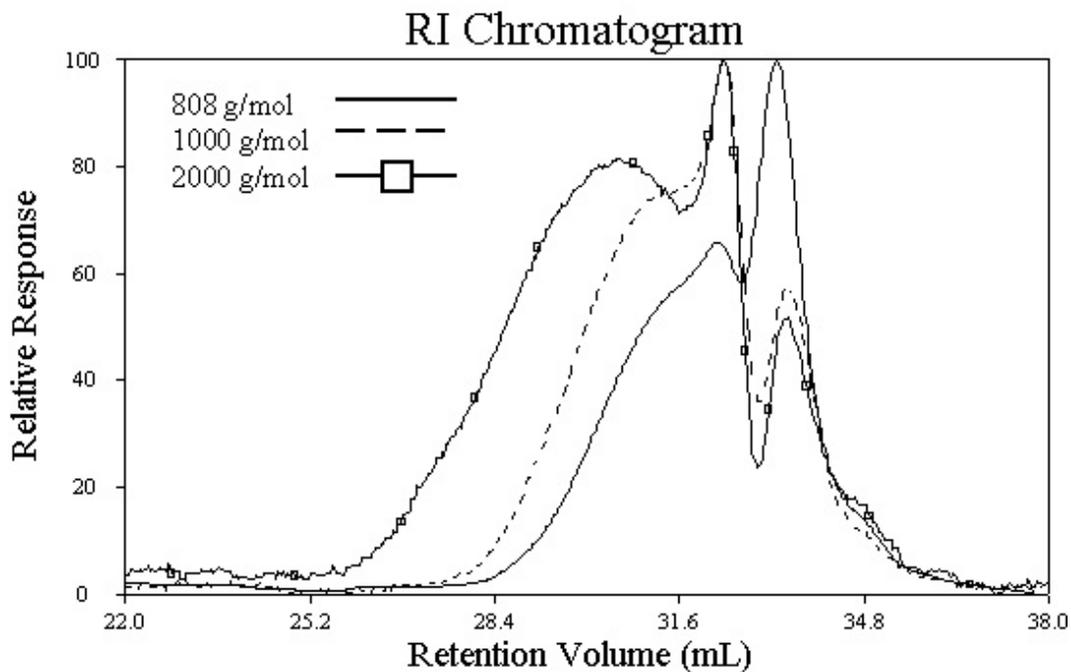
Figure 50. Gel permeation chromatography of 3 different molecular weight aliphatic dimethacrylate oligomers: (A), 2000 g/mol; (B), 1000 g/mol; (C), 808 g/mol.

Glass transition temperatures ranged from 29 to approximately 40°C for a series of molecular weights (Table 22). For a given molecular weight, the transition temperatures were similar to those observed for the analogous dimethacrylate series prepared from the bisphenol-A/epichlorohydrin based vinyl ester oligomers.

CAVE	Tg (°C)
808 g/mol	29
1000 g/mol	39
2000 g/mol	40
Bisphenol A Vinyl Ester	
700 g/mol	5

Table 22. Glass transition temperatures of the dimethacrylate oligomers.

UV absorption spectra of oligomers terminated with epoxy groups (i.e., not endcapped with methacrylates to avoid absorbance due to conjugated methacrylate bonds) were investigated at equivalent concentrations (Figure 51).   Ideally, their absorption would be minimal within the sunlight radiation range to reduce the probability of degradation. UV spectra for an acid terminated cycloaliphatic polyester (A in Figure 51) were compared to spectra for four aromatic epoxy oligomers containing isopropylidene, phosphine oxide, sulfonyl and hexafluoroisopropylidene groups (B, C, D, E in Figure 51). The cycloaliphatic polyester had minimal absorption in the wavelength range of terrestrial sunlight from 280-400 nm. The phosphine oxide diepoxide, although not as promising as the aliphatic structures, had the least absorption in this range of the aromatic oligomers. As expected, the bisphenol-A based diepoxide had a λ_{max} at 284 nm, which tailed off into the region of sunlight. This polymer, as well as the oligomers containing sulfonyl and hexafluoroisopropylidene groups, absorbed energy strongly in this region.
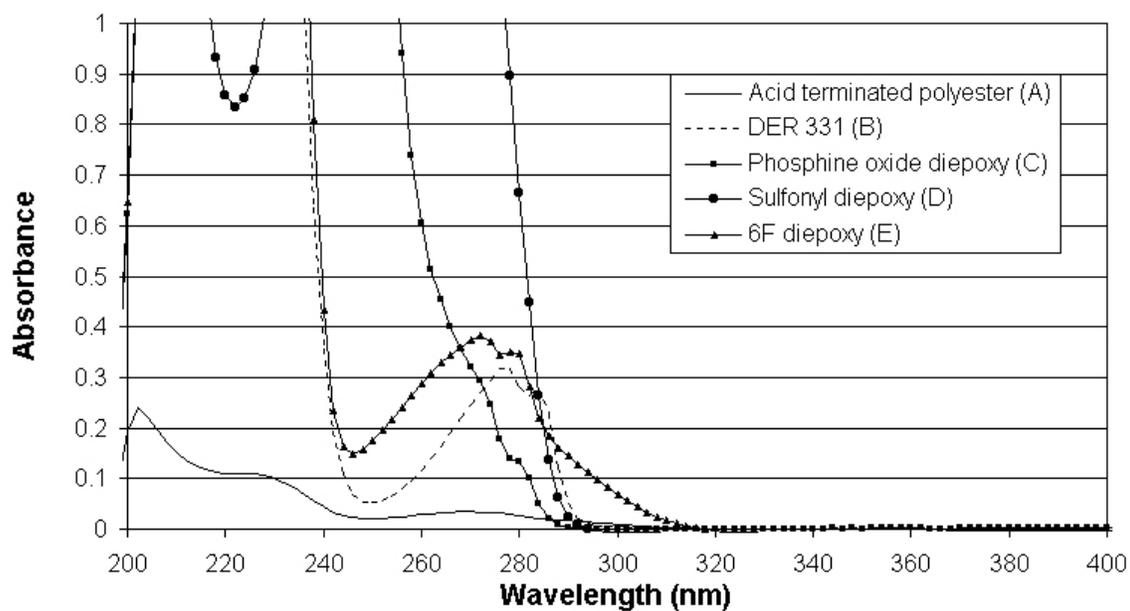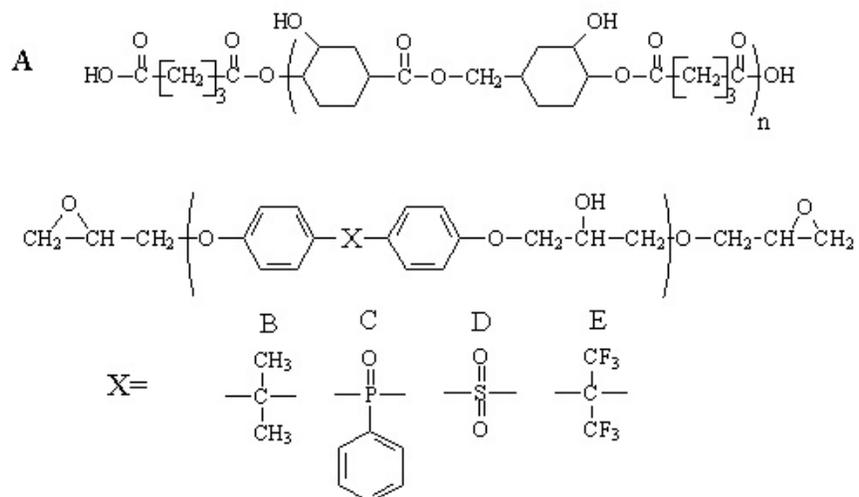
Figure 51. UV spectra of the acid terminated cycloaliphatic polyester (A), DER 331 (B), phosphine oxide diepoxide (C), sulfonyl diepoxide (D), hexafluoroisopropylidene diepoxide (E).

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4.4. Network Curing

The so-called vinyl ester and unsaturated polyester oligomers are diluted with reactive diluents to bring the glass transition temperatures of the resins down below room temperature for facilitating composite fabrication. This provides a sufficiently low viscosity for fiber wetting and preform impregnation under ambient conditions. The cycloaliphatic vinyl ester was diluted with methyl methacrylate due to its well-known resistance to UV degradation as compared to styrene. The cycloaliphatic resin diluted with methyl methacrylate was cured between salt plates in a heated cell and monitored by FTIR. The disappearance of the vinyl band at 1638 cm^{-1} was monitored to assess the extent of cure (Figure 52). The vinyl band corresponds to the methacrylate double bond of both the vinyl ester endgroup and the reactive diluent, methyl methacrylate. After the resin cures at room temperature, there is a small amount of unreacted methacrylate groups remaining that converts into the network upon post curing at 115°C for 2 hours. After post curing under these conditions all the methacrylate groups are reacted.
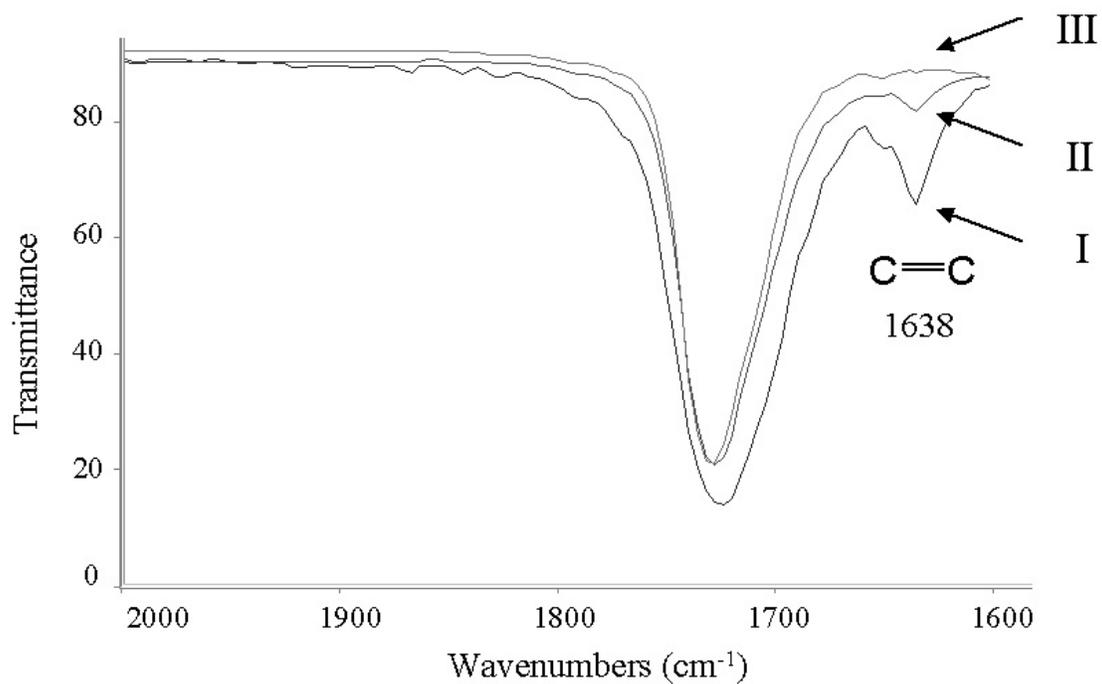
Figure 52. FTIR of the aliphatic vinyl ester cure reaction. Monitoring the disappearance of the carbon-carbon double bond (1638 cm^{-1}): after adding the initiators (I), after 24 hours at room temperature (II), after postcuring at 115°C for 2 hours (III).

4.5. Network Properties

A series of cycloaliphatic dimethacrylate networks prepared from systematically varied percentages of methyl methacrylate were compared to the bisphenol-A dimethacrylate-styrene networks. One advantage of using methyl methacrylate is that reactivity ratios for the methacrylate oligomer and diluent should be similar, whereas the dimethacrylate-styrene reactivity ratios are significantly different.[146]

4.5.1. Glass Transition Temperature of the Networks

The cycloaliphatic networks with varied percentages of methyl methacrylate exhibit network T_gs similar to those of the bisphenol-A based dimethacrylate/styrene network T_g of ~115°C.[147] As the molecular weight of the vinyl ester was increased, the T_gs of the networks decreased. This trend was expected since higher molecular weight oligomers produce networks with lower crosslink densities. However, the percent methyl methacrylate had little effect on the network T_gs (Figure 53).

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[146]   H. Li, A. Rosario, S. Davis, T. Glass, T. Holland, R. Davis, J. J. Lesko, J. S. Riffle, Network formation of vinylester-styrene composite matrix resins, *J. of Advanced Materials* **1997**, *28*, 55.

[147]   H. Li, E. Burts, K. Bears, Q. Ji, J. J. Lesko, D. A. Dillard, J. S. Riffle, Network Structure Properties of Dimethacrylate-Styrene Matrix Materials, *Journal of Composite Materials* **2000**, *34*, 1512.
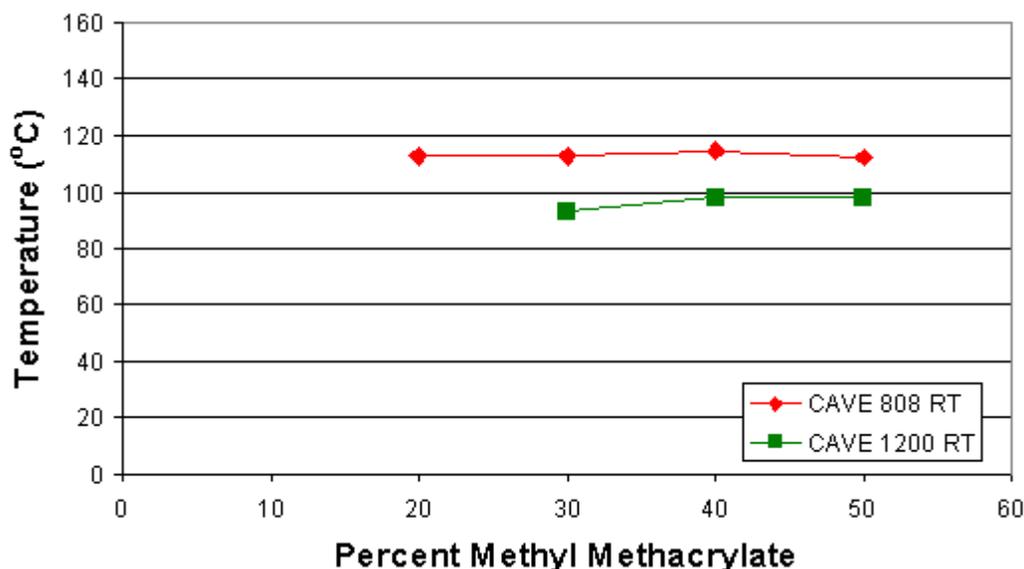
Figure 53. Network T$_g$s ofcycloaliphatic vinyl esters with two molecular weights as a function of the concentration of methyl methacrylate: A, 1200 g/mol; B, 808 g/mol.

4.5.2. **Molecular Weight Between Crosslinks**

According to the theory of rubber elasticity, the rubbery moduli of polymer networks should be proportional to the crosslink densities, Equation 8.[148] The molecular weights between crosslinks were calculated from the rubbery moduli determined from the slope of the force versus displacement curves in the rubbery region at Tg +50°C and the density at Tg +50°C. Equation 8 was derived to apply to active network chains only (not meant for chains with dangling ends or unconnected ends) and has four basic assumptions: (1) the chains obey gaussian statistics for their end to end distances, (2) the material deforms affinely, (3) the internal energy of the system is independent of the conformations of the individual chains, and (4) the chains are treated as phantom

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[148]   I. M. Ward, D. W. Hadley, *An Introduction to the Mechanical Properties of Solid Polymers*, John Wiley and Sons, New York, **1993**.

networks (no excluded volume).[149,150,151] The experimental trends in M_c followed the expected trend, Figure 54. As the molecular weight of the oligomer was increased from 808 g/mole to 1200 g/mole, M_c increased. In both cases, as the percent reactive diluent was increased, M_c increased. It is important to note that the measurements were made in bending and the moduli may be higher than those measurements made from uniaxial testing. Thus M_c would be artificially lower for the bending configuration.

Equation 8

$$M_c = 3RT\rho/E'$$
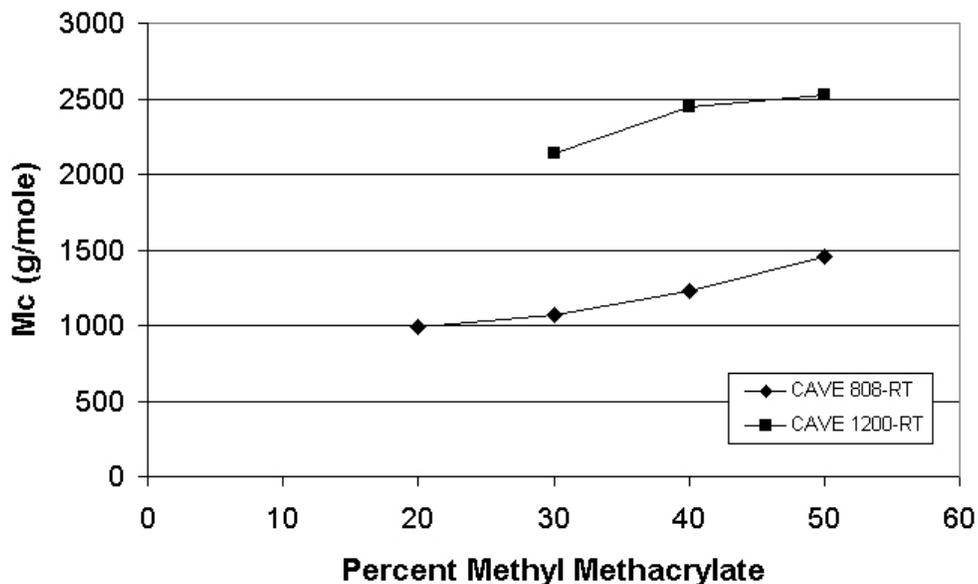
Figure 54. M_c versus percent methyl methacrylate.

[149]   I. M. Ward, D. W. Hadley, *An Introduction to the Mechanical Properties of Solid Polymers*, John Wiley and Sons, New York, **1993**.
[150]   H. Li, E. Burts, K. Bears, Q. Ji, J. J. Lesko, D. A. Dillard, J. S. Riffle, Network Structure Properties of Dimethacrylate-Styrene Matrix Materials, *Journal of Composite Materials* **2000**, *34*, 1512.
[151]   J. J. Aklonis, W. J. MacKnight, *Introduction to Polymer Viscoelasticity*, 2 ed., John Wiley and Sons, New York, **1983**.

4.5.3. **Fracture Toughness**

Fracture toughness of the cycloaliphatic vinyl ester networks was slightly lower than that of the aromatic materials derived from bisphenol-A for the oligomer molecular weights investigated (Figure 55). It should be noted that all the materials discussed thus far have been cured at room temperature then post cured at 115°C. Curve (D) in Figure 55 depicts fracture toughness for materials derived from bisphenol-A vinyl esters and styrene that were cured at 140°C. Interestingly this suggests that the properties are dependent on the cure path, and that care should be taken to compare networks cured under similar conditions.
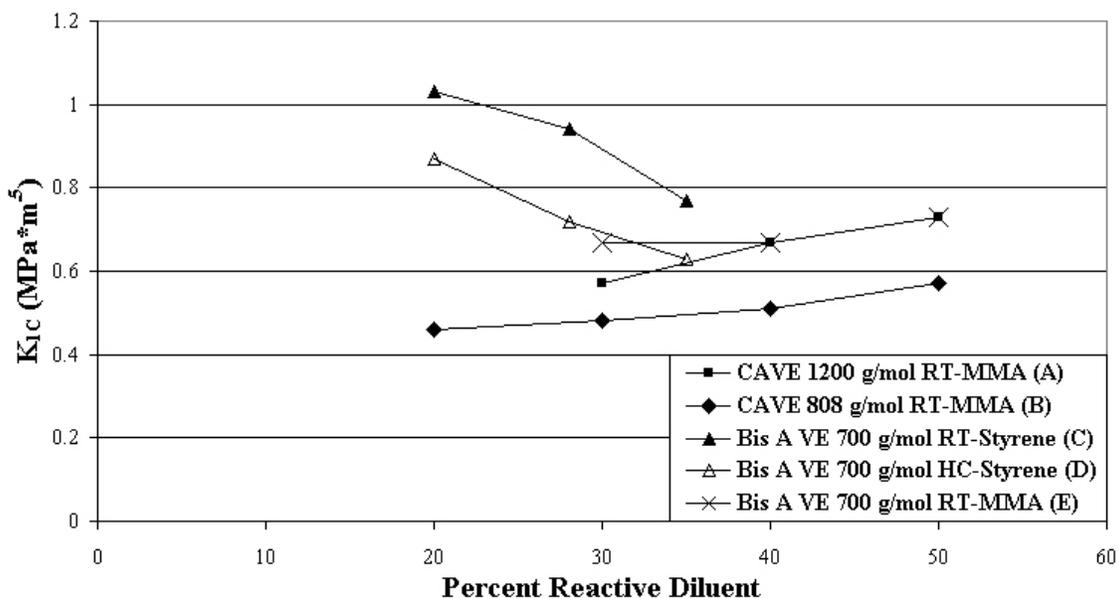
Figure 55. Fracture toughness (K_{1c} values) of the cycloaliphatic vinyl ester (CAVE)-methyl methacrylate networks (A and B, both cured at room temperature and postcured at 115°C), the bisphenol-A based vinyl ester (Bis A VE)-styrene networks (C cured the same as the aliphatic vinyl esters, and D is heat cured at 140 ^{o}C), and the bisphenol-A based vinyl ester-methyl methacrylate networks (E) cured under the same conditions as the CAVE networks.

The cycloaliphatic vinyl ester networks and the bisphenol-A networks increased in toughness as the weight percentage of the methyl methacrylate reactive diluent was increased. This was expected since the molecular weight between crosslinks should increase along this series.[152,153] By contrast, however, toughness of the bisphenol-A vinyl ester-styrene networks decreased as the weight percentage of styrene was increased. This was considered unusual since the molecular weight between crosslinks should also have increased along that series of materials. The decrease in toughness with increasing styrene could be attributed to a compositional effect as well as to a difference in reactivity ratios between the methacrylate endgroup and the reactive diluent styrene. A difference in reactivity ratios could lead to a variance in copolymer composition as a function of the extent of cure. It should also be noted that although the networks with the methacrylate diluent have somewhat lower toughness than those containing styrene at low diluent concentrations, the data suggests that there should be a crossover point at higher diluent concentrations. It is common practice in designing compositions for vinyl ester or polyester resins to include as much as 40 to even 50 weight percent of the diluent, so it may well be that networks containing methyl methacrylate would have better toughness than those with styrene at such concentrations.

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[152]   R. Morgan, in *Toughness and Brittleness of Plastics, Vol. 154* (Eds.: R. Deanin, A. Crugnola), ACS, Wachington D.C., **1976**.

[153]   W. Bradley, in *Toughened Plastics, Vol. 233* (Ed.: A. Kinloch), ACS, Wachington D.C., **1993**.

4.5.4. Vickers Microhardness

Vickers microhardness was also studied to compare these series of networks (Figure 56). The cycloaliphatic dimethacrylate networks were harder and the hardness decreased as the percent methyl methacrylate was increased. Thus, as the molecular weight between crosslinks increased, the hardness decreased. The bisphenol-A vinyl ester-styrene networks showed the opposite effect. Hardness values were lower, but increased as the percent styrene was increased. In all cases, decreases in hardness were associated with increases in K_{1c} fracture toughness.
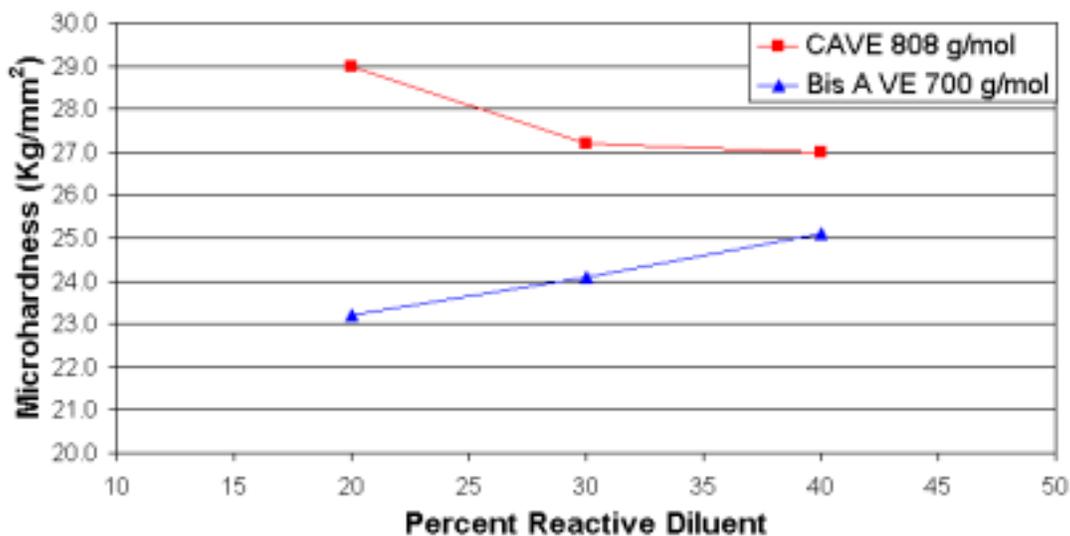
Figure 56. **Vickers microhardness of the cycloaliphatic vinyl ester (CAVE)-methyl methacrylate networks and the bisphenol-A vinyl ester (Bis A VE)-styrene networks cured at 140 C with benzoyl peroxide.**

4.5.5. Network Cure Shrinkage

Percent cure shrinkage was measured for both the CAVE networks and those networks containing the bisphenol-A based vinyl ester (Figure 57). The CAVE networks contained systematically varied percentages of methyl methacrylate as the reactive diluent and were cured with methyl ethyl ketone peroxide (MEKP) with accelerators at 25°C for 24 hours, then post cured at 115°C for 2 hours. In the case of the bisphenol-A based vinyl ester, two types of cure procedures and two types of reactive diluents were investigated. The bisphenol-A based vinyl esters co-cured with styrene were cured with benzoyl peroxide at 140°C or via MEKP with accelerators at 25°C for 24 hours followed by a post cure at 115°C for 2 hours. The bisphenol-A based vinyl ester containing systematically varied percentages of methyl methacrylate were cured using MEKP with accelerators at 25°C for 24 hours followed by a post cure at 115°C for 2 hours. These exhibited similar shrinkage values similar to those of the CAVE networks cured with methyl methacrylate.

Those networks containing systematically varied percentages of methyl methacrylate exhibited higher shrinkage than those containing styrene as the reactive diluent. Networks co-cured with methyl methacrylate exhibit higher levels of shrinkage because of the reactive diluent. Equation 9 shows the relationship between density, volume, and shrinkage. Methyl methacrylate shrinks more than styrene upon polymerization. Methyl methacrylate exhibits 21% shrinkage upon polymerization based on the density of methyl methacrylate (0.936 g/ml @ 25°C) and the density of PMMA

(1.188 g/ml @ 25°C) obtained from the Polymer Handbook.[154] Styrene only shrinks 13%

based on the density of styrene (0.909 g/ml @ 25°C) and the density of polystyrene

(1.047 g/ml @ 25°C) obtained from the Polymer Handbook.[155] It is also interesting to

note that for the two different oligomers cured under similar conditions with methyl

methacrylate, shrinkage is quite similar. This suggests that the diluent structure and

concentration is prime in controlling network shrinkage and that the differences in at least

these two oligomer structures do not result in differences in contraction upon cure.

Equation 9

$$(V_p - V_m)/V_m * 100\% = \text{Shrinkage}$$

$$V_p = \text{Volume of 1 gram of the polymer} (= 1/\rho * 1g)$$

$$V_m = \text{Volume of 1 gram of the monomer} (= 1/\rho * 1g)$$

Those networks cured with styrene at elevated temperatures (with BPO) have

higher cure shrinkage than those cured at room temperature followed by a post cure.

Even more interesting, those networks cured with either styrene or methyl methacrylate

via MEKP with accelerators at 25°C for 24 hours followed by a post cure at 115°C for 2

hours show no further densification of the network upon post curing even though there is

a significant amount of double bond conversion (Table 23). This suggests that the

physical dimensions of the network are fixed after the room temperature reaction step and

no further densification of the network occurs upon post curing. This too may help to

explain the improved mechanical properties for those networks cured via MEKP with

[154]   J. Brandrup, E. Immergut, *Polymer Handbook*, 3 ed., John Wiley and Sons, New York, **1989**.
[155]   J. Brandrup, E. Immergut, *Polymer Handbook*, 3 ed., John Wiley and Sons, New York, **1989**.

accelerators at 25°C for 24 hours followed by a post cure at 115°C for 2 hours over those cured with benzoyl peroxide at 140°C for 1 hour.
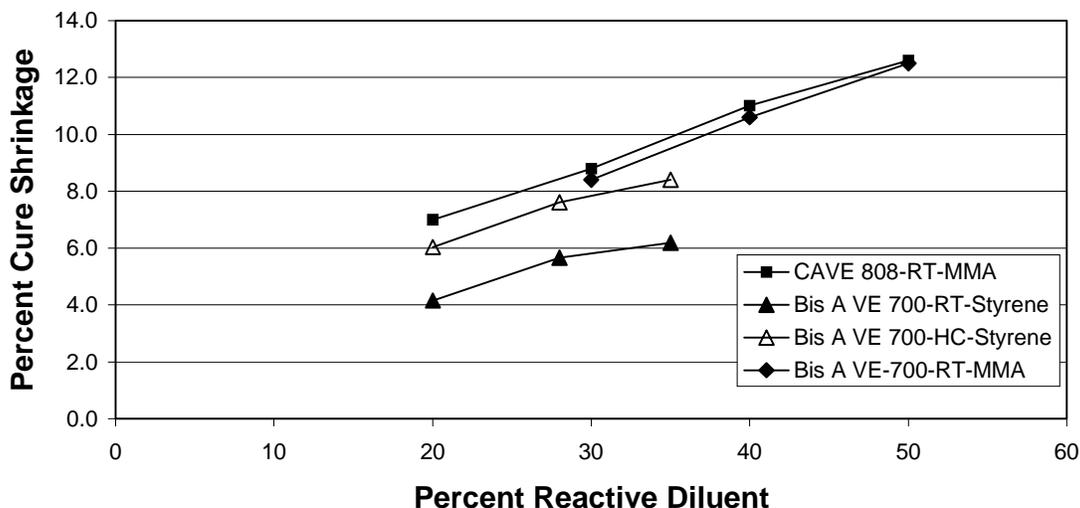
Figure 57. Percent cure shrinkage as a function of oligomer, reactive diluent, reactive diluent concentration, and cure procedure.

Vinyl Ester/ Reactive diluent	% Shrinkage before post cure	% Shrinkage after post cure	% Double bond conversion before post cure	% Double bond conversion after post cure
Bis-A VE (700g/mole)/ 28%styrene	5.1	5.5	70	91
CAVE (800 g/mole)/ 40% MMA	10.6	10.7	72	93

Table 23. Network cure shrinkage and double bond conversion before and after post-curing.

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4.6. Environmental Aging

4.6.1. Accelerated UV aging

Light and oxygen can induce chemical reactions in polymers that cause discoloration and unwanted changes in mechanical properties. Photo- and photothermal oxidative degradation cause chemical changes in the polymer structure with buildup of a variety of new functional groups such as carbonyls, acids, esters, alcohols and unsaturation. Furthermore, the mechanism often leads to chain scission and crosslinks.[156] Physical changes may take the form of discoloration, crazing, loss of gloss, erosion, cracking, tensile strength, and extensibility changes.[157]

The degradation of such polymers can be retarded with the use of UV stabilizers. There are many classes of UV stabilizers such as UV absorbers, quenchers, UV screeners, peroxide decomposers, and radical scavengers as described below.[158,159]

1.   UV absorbers: These are used to compete with the polymer for UV light and dissipate the absorbed energy in a harmless fashion. These materials such as the 2-hydroxybenzophenones have high extinction

[156]   A. Faucitano, A. Buttafava, G. Camino, L. Greci, Photo-oxidation and stabilization of Polymers, *TRIP* **1996**, *4*, 92.

[157]   N. Allen, Why Do Polymers Degrade in Sunlight, *TRIP* **1994**, *2*, 366.

[158]   A. Faucitano, A. Buttafava, G. Camino, L. Greci, Photo-oxidation and stabilization of Polymers, *TRIP* **1996**, *4*, 92.

coefficients in the 290-400 nm region.[160] This causes the UV intensity to drop more rapidly as it penetrates into the material. Thus, it would be more advantageous and economical if these absorbers could be preferentially located at the surface.[161]
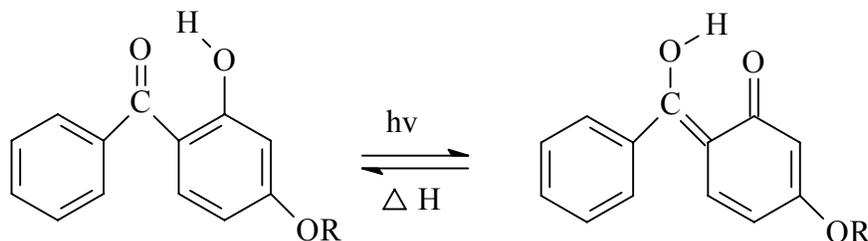
Figure 58. A strong intramolecular hydrogen bond allows the molecule (the 2-hydroxybenzophenones) to dissipate the absorbed energy by tautomerism.[162]

2.   Quenchers: These are light stabilizers (acceptor, A) that deactivate the excited molecule (or the excited chromophore, donor, D*) and release the energy in the form of emission or heat. These can be hydroxybenzophenones and hydroxybenzotriazoles, and more importantly nickel chelates. However, the nickel chelates have recently been shown to operate as hydroperoxide decomposers as well.[163]

159   S. Hamid, *Handbook of Polymer Degradation*, Marcel Dekker, New York, **1992**.
160   A. Padron, N. Allen,, (Ed.: S. Hamid), Marcel Dekker, New York, **1992**, pp. 261.
161   J. Salamone, *Polymeric Materials Encyclopedia, Vol. 3*, CRC, New York, **1996**.
162   A. Padron, N. Allen,, (Ed.: S. Hamid), Marcel Dekker, New York, **1992**, pp. 261.
163   S. Yachigo,, (Ed.: S. Hamid), Marcel Dekker, New York, **1992**, pp. 305.

$$D^* + A \longrightarrow D + A^*$$

$$A^* \longrightarrow A + \text{energy in the form of emission or heat}$$
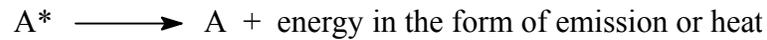
Figure 59. Exited states of chromophores deactivated to the ground state.[164]

3.   UV Screeners: These are pigments such as carbon black or titanium dioxide that make the polymers opaque to light. Thus, damage is confined to the surface due to the restricted penetration of the UV light.[165]

4.   Peroxide decomposers: This class of compounds (dialkyl dithiocarbamates, dialkyldithiophosphates, xanthates of Ni, Cu, Zn, and organic phosphates and sulfides) causes the decomposition of hydroperoxides to alcohols by radical and/or non-radical processes.

$$(RO)_3P + R'OOH \longrightarrow (RO)_3P=O + R'OH$$
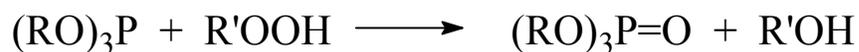
Figure 60. Decomposition of a hydroperoxide to an alcohol by a phosphite ester.[166]

[164]   J. Rabek, *Photostabilization of Polymers*, Elsevier Applied Science, New York, **1990**.
[165]   J. Salamone, *Polymeric Materials Encyclopedia, Vol. 3*, CRC, New York, **1996**.
[166]   B. Ranby, J. Rabek, *Photodegradation, Photo-oxidation and Photostabilization of Polymers*, John Wiley and Sons, New York, **1975**.

5.   Radical Scavengers: These stabilizers (such as Hindered Amine Light

Stabilizers, HALS, or the hindered phenols) act as chain breakers by

converting the propagating radical into relatively unreactive ones.
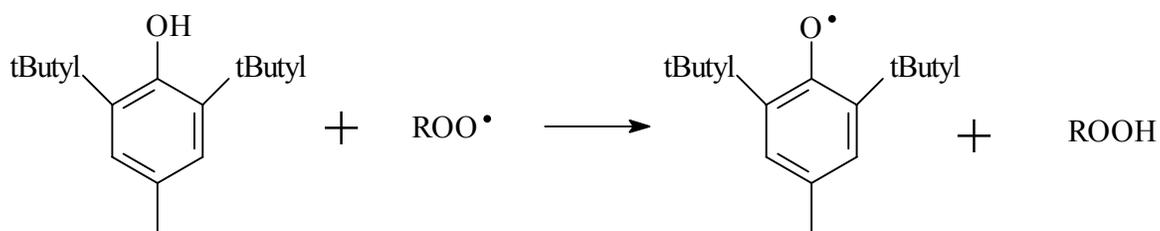


Figure 61. An antioxidant such as a hindered phenol (2,6-di-t-butyl-4-methylphenol) can react with a peroxy radical to form a highly stabilized radical.[167]

Depending on the degradation mechanism some types of UV stabilizers may be

used in combination, to stabilize a given polymeric material. In many applications the

longest lifetime can be achieved by the incorporation of a UV stabilizer (radical

scavenger) such as a Hindered Amine Light Stabilizer (HALS).[168] However in most

materials the HALS only last for a given induction period before constant degradation

occurs.[169]

Photostabilization of aromatic coatings is a major problem. Since aromatic

polymers absorb terrestrial sunlight it is not feasible to stabilize them directly with UV

absorbers even at high levels. Thus Breskman has investigated the use of quenchers (2-

hydroxybenzophenone derivatives) to efficiently deactivate the photo-excited state

[167]   B. Ranby, J. Rabek, *Photodegradation, Photo-oxidation and Photostabilization of Polymers*, John Wiley and Sons, New York, **1975**.
[168]   P. Gijsman, J. Hennekens, D. Tummers, The Mechanism of Action of Hindered Amine Light Stabilizers, *Polymer Degradation and Stability* **1993**, *39*, 225.

preventing photodegradation.[170] Quenchers require efficient resonance energy transfer

with the polymer and secondly the quencher must be capable of non-degradative

dissipation of the energy. Over time it is believed that the photo-degraded material

competes with the added quenchers resulting in degradation due to a more degradative

dissipation of energy. The 2-hydroxybenzophenones were efficient stabilizers for the

hydroxy terminated bisphenolA glycidyl ether polymers. However, the stabilization was

found to decrease substantially over time.

Little is known about structure-photostability relationships for epoxy networks.[171]

However, Mu-Shih Lin has shown that vinyl ester networks are more UV stable than

anhydride (hexahydrophthalic anhydride) cured diglycidyl ethers of bisphenol A

(DGEBA) networks.[172] It was also reported that DGEBA undergoes chain scission

leading to deteriorating mechanical properties. The chain scission was attributed to a

gradual decrease in C-O-C bonds as monitored by IR at 1265 cm^{-1}. However, the

DGEBA network cured via an anhydride exhibited remarkable increases in OH

absorptions (3500-3200 cm^{-1}) and C=O absorptions (1680-1800 cm^{-1}) over the

methacrylate terminated DGEBA network cured free radically. Thus it was concluded

that the methacryloyl moiety confers significant stabilization against photo-degradation.

Coatings and composites are typically exposed to two major aggressive

environmental factors; water and terrestrial sunlight. It is also becoming increasingly

evident that the combined effects of environmental factors are important, particularly in

[169]   P. Gijsman, J. Hennekens, D. Tummers, The Mechanism of Action of Hindered Amine Light Stabilizers, *Polymer Degradation and Stability* **1993**, *39*, 225.

[170]   E. Breskman, S. Pappas, Photostabilization of Coatings: Studies on Resonance Energy Transfer, *Journal of Coatings Technology* **1976**, *48*, 34.

[171]   V. Bellenger, J. Verdu, Structure-Photooxidative Stability Relationship of Amine Crosslinked Epoxies, *Polymer Photochemistry* **1984**, *5*, 295.

the presence of load.[173] In this present work, aliphatic dimethacrylate networks have been prepared and analyzed in efforts to better understand the issues controlling long-term environmental durability. For these studies an accelerated UV aging apparatus was developed to facilitate UV aging of the unstabilized networks.

Ideally, materials should be evaluated during and after aging in the actual service environment for which they were designed. However, due to time constraints, accelerated aging has become accepted as an alternative. In many cases, however, it is difficult to reproduce all the variables that may influence the degradative process and great care must be taken in interpreting data from such accelerated tests. Under the test conditions used in this work, the samples were exposed intermittently to a filtered xenon arc light source that contained wavelengths similar to those of terrestrial sunlight but at higher intensities. Due to the intermittent exposure of the samples at 25°C, the networks never exceeded 28°C as measured with a digital infrared camera.

Networks prepared by free radical copolymerization can be cured with several types of initiators, some of which contain so-called promoters or accelerators, and under different thermal conditions. In this research, one curing method was to first react the resin at room temperature using methyl ethyl ketone peroxide as the initiator promoted with a combination of dimethylaniline and cobalt naphthenate. It was assumed that this reaction would be retarded by vitrification at the point where the Tg of the thermoset reaction mixture approached room temperature. The materials were then post cured at 115°C to achieve sufficient mobility for conversion of additional double bonds. Those

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172   M. Lin, M. Wang, C. Lee, S. Shao, Accelerated ageing behavior of compatible IPNs based on epoxy and methacrylated epoxy resins, *Polymer Degradation and Stability* **1998**, *2-3*, 505.
173   J. White, N. Rapoport, Stress Effects on Polymer Durability in the Oxidative Environment, *TRIP* **1994**, *2*, 197.

networks cured from the onset at 100-140°C only required a peroxide initiator such as benzoyl peroxide that thermally breaks down to initiate the chain growth cross-linking polymerization. In this study it was important not only to study the different aliphatic and aromatic networks but also to evaluate any effects caused by the initiators or accelerators, or of the temperatures involved.

Cycloaliphatic networks containing 30 and 40 weight percent methyl methacrylate were aged along with the aromatic vinyl esters containing bisphenol-A, which were co-cured with 30 weight percent styrene. Cycloaliphatic networks containing 30 and 40 weight percent methyl methacrylate were prepared using the $25^{o}C/115^{o}C$ post cure procedure. One set of cycloaliphatic networks containing 30 weight percent methyl methacrylate was also prepared with benzoyl peroxide as the initiator. These materials were reacted at 80°C, which resulted in a cure exotherm above the boiling point of the methyl methacrylate comonomer diluent. Although this resulted in networks containing some voids due to methyl methacrylate evolution, it did allow for a qualitative comparison of properties.

The aromatic vinyl ester networks which contained bisphenol-A were co-cured with 30 weight percent styrene using two procedures. The first set of (bisphenol-A VE/styrene networks) samples was prepared by using methyl ethyl ketone peroxide, cobalt naphthenate, and dimethylaniline. They were cured at $25^{o}C$ for 24 hours, then postcured at $115^{o}C$ for 2 hours. The second set was prepared at $140^{o}C$ using benzoyl peroxide as the initiator.

Equation 10 was generated from the calibration curve in Figure 62 and was used to convert counts to irradiance for each wavelength and integration time. This calibration

was constructed in collaboration with workers at NIST with our spectrometer and a NIST standard xenon arc light source with a known irradiance profile. Figure 63 shows the irradiance of the xenon arc lamp (of the accelerated aging apparatus) as a function of wavelength. The irradiance is linear in this region and was integrated to calculate the amount of exposure per unit area (mW/m^2). Based on the diameter of the drum, exposure size, and drum rotation rate, it was calculated that each sample was exposed to the light source for a total of 1.5 hours/day, (Table 19). Thus the amount of exposure in MJ/m^2 per year was calculated and compared to the average level of exposure in Miami, FL and Phoenix, AZ as reported by the Atlas Weathering Services Group (Table 24 and Table 25). Based on total energy emitted, intermittent exposure for 225 days under the xenon arc lamp was calculated to be equivalent to 2.4 years in Miami, FL and 2.0 years in Phoenix, AZ.

Equation 10

Irradiance = (2.2946095220E-16x^6 -7.5922590192E-13x^5
+1.0314018700E-09x^4 -7.3610411037E-07x^3 +2.9248500417E-04x^2
-6.2090682904E-02x +5.6357885770E+00) *(counts/sec)

       x = Wavelength in nanometers

       Irradiance = mW / (m^2 * nm)

       Counts = Spectrophotometer units (measurement of intensity)

       Sec = Integration time in seconds (time over which the spectrum was obtained)

The equation on the chart reads:

$$y = 2.2946095220\text{E-16}x^6 - 7.5922590192\text{E-13}x^5 + 1.0314018700\text{E-09}x^4$$
$$- 7.3610411037\text{E-07}x^3 + 2.9248500417\text{E-04}x^2$$
$$- 6.2090682904\text{E-02}x + 5.6357885770\text{E+00}$$

$$R^2 = .996$$
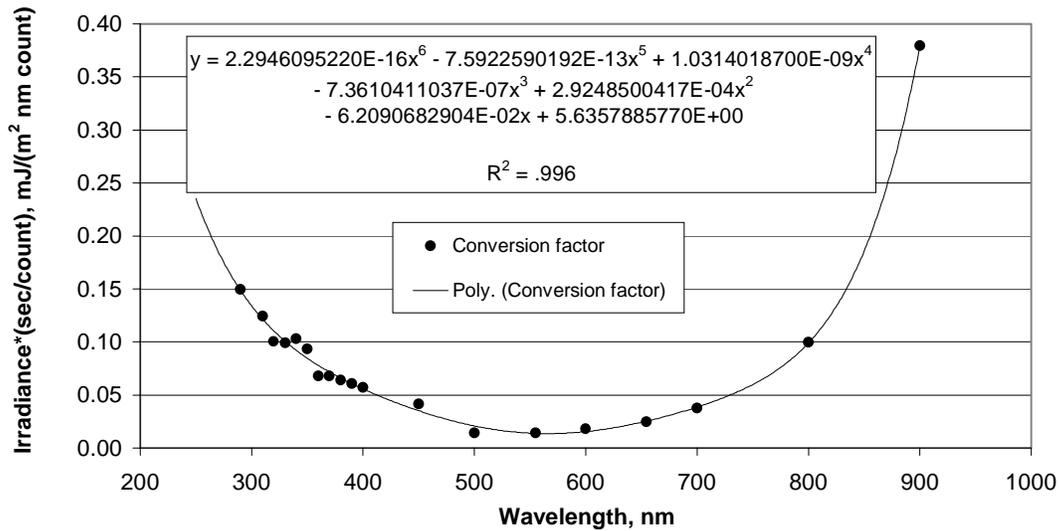
Figure 62. Calibration curve used to convert units of the spectrophotometer (counts/sec) to irradiance.

Light source or location	Exposure per year
Xenon Arc	1085 MJ/(m2)
Miami, FL	280 MJ/(m2)*
Phoenix, AZ	330 MJ/(m2)*

Table 24. Exposure per year and yearly equivalence for Miami and Phoenix based on 225 days of xenon arc exposure. *As reported by the Atlas Weathering Services Group.

Light source or location	Exposure Equivalence
Xenon Arc	225 days of aging
Miami, FL	2.4 years
Phoenix, AZ	2.0 years

Table 25. Exposure equivalence based on equivalent energy for 225 days of accelerated aging with the xenon arc lamp.
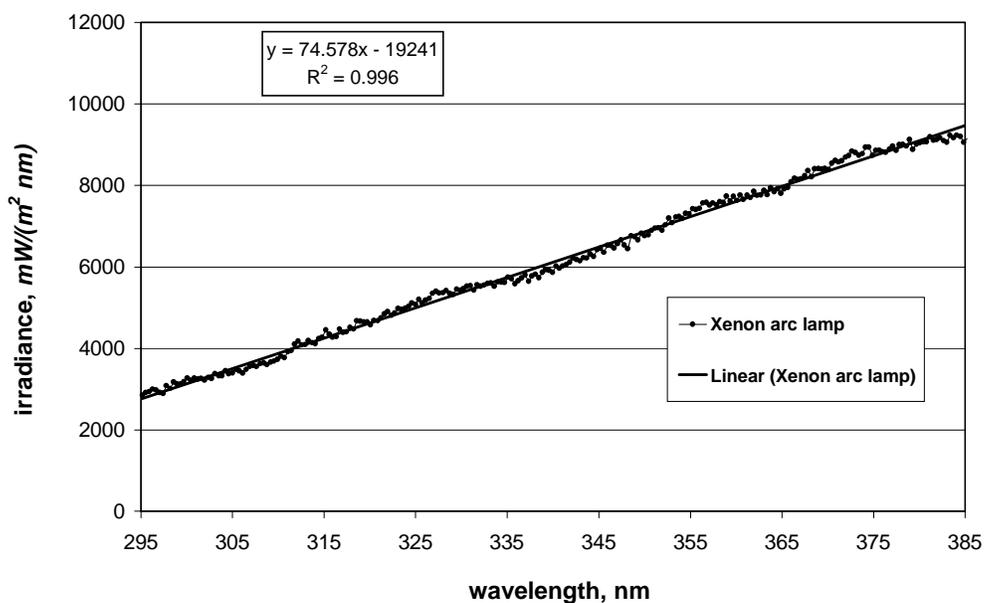
Figure 63. Irradiance of the xenon arc lamp from 295 to 385 nm. The area under the linear regression fit line was integrated to calculate the total energy.

4.6.1.1. Bulk Properties

Networks from both the aromatic vinyl ester containing bisphenol-A co-cured with 30 weight percent styrene, and the CAVE oligomer with 30 weight percent methyl methacrylate, showed a reduction in rubbery modulus upon aging. Both networks that were evaluated were cured using methyl ethyl ketone peroxide as the initiator with cobalt naphthenate and dimethylaniline as cure accelerators, for 24 hours at 25°C, then were postcured at 115°C for 2 hours. They were aged 225 days on the UV aging apparatus. The aromatic vinyl ester networks exhibited 7 ± 5 % reduction, while the CAVE networks exhibited 11 ± 5 % reduction in the rubbery moduli. These reductions in

rubbery moduli suggest that both of these materials have undergone some chain scission after 225 days of exposure.

Fracture toughness was conducted on the specimens aged under the xenon arc lamp, but no changes were observed (within experimental error). It was therefore reasoned that aging under the conditions specified may not affect bulk glassy properties. This may be a function of the time and intensity of aging. Thus these phenomena should be further evaluated with longer aging experiments.

4.6.1.2. Surface Properties

X-ray photoelectron spectroscopy and scanning electron microscopy (SEM) were used to examine any chemical or topographical changes on the aged surfaces after 225 days of aging on the accelerated UV aging apparatus.

Aged specimens that had been cured at room temperature for 24 hours, then postcured at 115°C for 2 hours with methyl ethyl ketone peroxide as the initiator accelerated by the addition of dimethylaniline and cobalt naphthenate, consistently exhibited a higher level of oxidation relative to those cured at an elevated temperature with benzoyl peroxide as the initiator. This was true for both the all-aliphatic and for the aromatic poly(hydroxyether)-styrene networks. Table 26 shows the atomic surface compositions for the aged specimens taken from XPS data. The aged surfaces of the cycloaliphatic networks co-cured with 30 wt. % methyl methacrylate and benzoyl peroxide as the initiator exhibited an oxygen to carbon ratio 1.2 times that of the control (which was not aged). The same CAVE oligomer cured with 30 wt. % methyl methacrylate (using methyl ethyl ketone peroxide, cobalt naphthenate and

dimethylaniline), at room temperature (24 hours) then post cured at 115°C (2 hours)) exhibited 2.5 times the ratio of surface oxygen to carbon relative to the control. However, by curing with 40 wt. % of the methyl methacrylate diluent using the same room temperature cure procedure, the level of oxidation was lowered to 1.2 times the control. This suggests that the accelerated oxidation may be due to the presence of dimethylaniline and/or cobalt naphthenate, but the reasons for this behavior are not clear.

The aromatic vinyl ester thermally cured (using benzoyl peroxide) with 30 wt. % styrene exhibited an increase of 2.1 times the ratio of oxygen to carbon of the control. However, the aromatic networks co-cured with 30 wt. % styrene (via methyl ethyl ketone peroxide, cobalt naphthenate and dimethylaniline, at room temperature (24 hours) then postcured at 115°C (2 hours)) exhibited an increase by 3.7 times the level of oxygen to carbon of the control. Thus, the reaction accelerators appear to lead to increased oxidation rates in both the aromatic and aliphatic networks.

Specimen	% Carbon unaged	% Oxygen unaged	Ratio (O/C) unaged	% Carbon aged 225 days	% Oxygen aged 225 days	Ratio (O/C) aged 225 days	(Ratio aged)/ (Ratio unaged)
CAVE-30 mma-RT	77	18	.23	60	35	.58	2.5
CAVE-30 mma-HC	66	27	.41	65	32	.49	1.2
CAVE-40 mma-RT	68	26	.38	65	30	.46	1.2
BisAVE-30st-RT	71	21	.30	38	41	1.1	3.7
BisAVE-30st-HC	74	19	.26	60	33	.55	2.1

Table 26. The atomic surface compositions (±1 percent) of aged and unaged specimens.

Even though the level of oxygen on the surface of the CAVE networks increased, there was no evidence of any new peaks in the binding energy spectra. However, it was interesting that increasing the concentration of methyl methacrylate resulted in a decrease in surface oxidation. It is well known that poly(methyl methacrylate) performs well in outdoor applications under intense sunlight for extended periods. It may be that the networks containing more methyl methacrylate have surfaces highly populated with methyl methacrylate. Unfortunately, it was not possible to detect this with the present experiments since the atomic compositions of the networks and poly(methyl methacrylate) are close. This aspect warrants further study since it may be that higher concentrations of methyl methacrylate would lead to a protective surface overlayer.

The C_{1s} peaks were deconvoluted to separate carbons next to oxygen relative to carbons adjacent to less electronegative elements (i.e., to C). Table 27 shows the results of deconvoluting the C_{1s} XPS peaks to obtain the relative percentages ($\approx\pm$ 1 %) of carbons not bound to oxygen (284.9 eV), carbons singly bound to oxygen (286.5 eV), and carbons doubly bound to oxygen (288.9 eV). The C_{1s} binding energy spectra for examples of these materials are provided in Figure 64 - Figure 69 since the curve shapes also qualitatively reveal significant differences in surface atomic compositions.

CAVE networks cured with 30 wt. % methyl methacrylate (independent of the curing procedure) showed a 5% increase in carbonyl carbons on the surface upon aging. The shoulder at 288.9 eV corresponding to carbonyl carbons in the aged sample (Figure 64 and Figure 68) is clearly more prominent than in the unaged material (Figure 65 and Figure 69). However, this increase may be explained by migration of methyl methacrylate or polymethyl methacrylate to the surface since it contains a higher

144

percentage of carbonyl carbons than the cycloaliphatic vinyl ester oligomer, (Table 27).

Figure 70 shows the C_{1s} binding energy sprectrum of polymethyl methacrylate as a

reference. The CAVE network cured with 40 wt. % methyl methacrylate showed no

change in carbon type or oxidation state when compared to the unaged control samples.

Observation of the C_{1s} spectra (Figure 66 and Figure 67) shapes do not reveal any

significant shape differences. This is consistent with the constant O/C ratios on those

surfaces, suggesting that these materials are highly resistant to sunlight.

Specimen		% Carbons not bound to Oxygen 284.9 eV	% Carbon (C-O) 286.5 eV	% Carbon (C=O) 288.9 eV
CAVE oligomer (808 g/mol)	Theoretical	61	24	15
Bis A VE oligomer (700 g/mol)	Theoretical	67	28	5
PMMA	Theoretical	60	20	20
Polystyrene	Theoretical	100	0	0
CAVE-30 mma-RT	Theoretical	61	23	16
	Control	64	24	12
	Aged 225 days	59	24	17
CAVE-30 mma-HC	Theoretical	61	23	16
	Control	64	24	12
	Aged 225 days	59	24	17
CAVE-40 mma-RT	Theoretical	60	23	17
	Control	64	24	12
	Aged 225 days	65	22	13
BisAVE-30st-RT	Theoretical	79	18	3
	Control	74	21	5
	Aged 225 days	68	20	12
BisAVE-30st-HC	Theoretical	79	18	3
	Control	77	19	4
	Aged 225 days	63	19	18

Table 27. The deconvoluted percentages of carbonyl, ether, and of carbons not bound to oxygen from the XPS binding energy spectra as compared to the theoretical compositions.
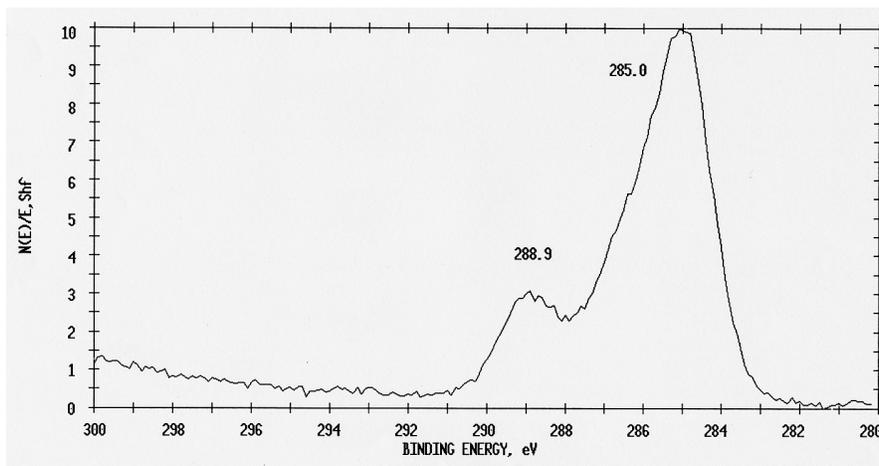
Figure 64. The C$_{1s}$ region of the XPS binding energy spectrum of an exposed CAVE network surface that was prepared with 30 wt. % methyl methacrylate and cured with methyl ethyl ketone peroxide, cobalt naphthenate and dimethylaniline.
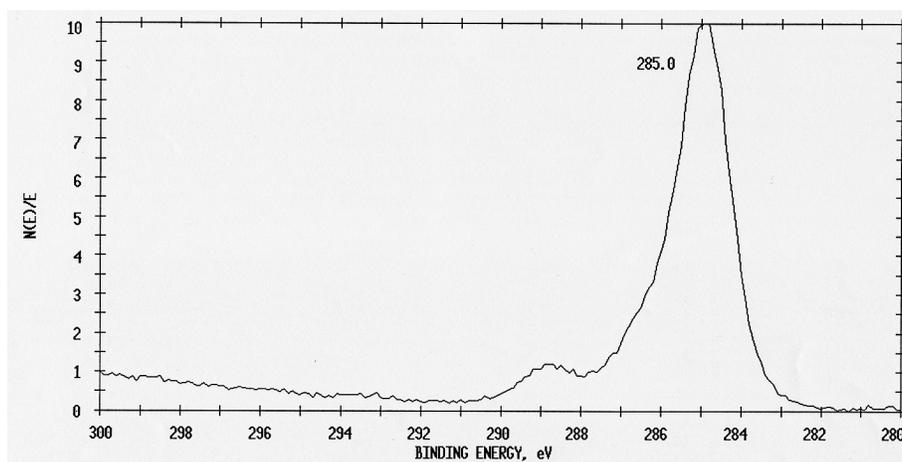

Figure 65. The C$_{1s}$ region of the XPS binding energy spectrum of the control (not aged) CAVE network surface that was prepared with 30 wt. % methyl methacrylate and cured with methyl ethyl ketone peroxide, cobalt naphthenate and dimethylaniline.
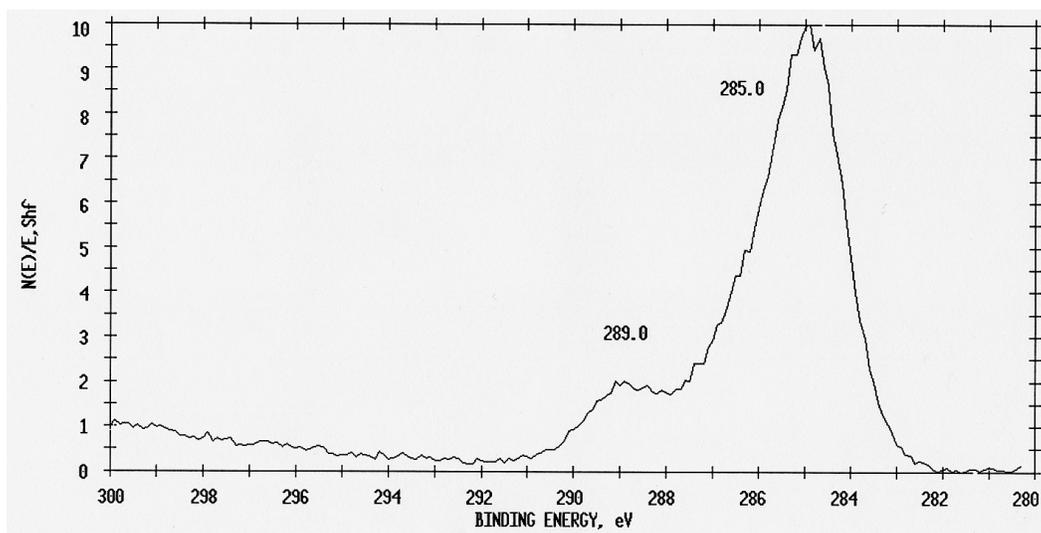
Figure 66. The C$_{1s}$ region of the XPS binding energy spectrum of the exposed CAVE network surface that was prepared with 40 wt. % methyl methacrylate and cured with methyl ethyl ketone peroxide, cobalt naphthenate and dimethylaniline.
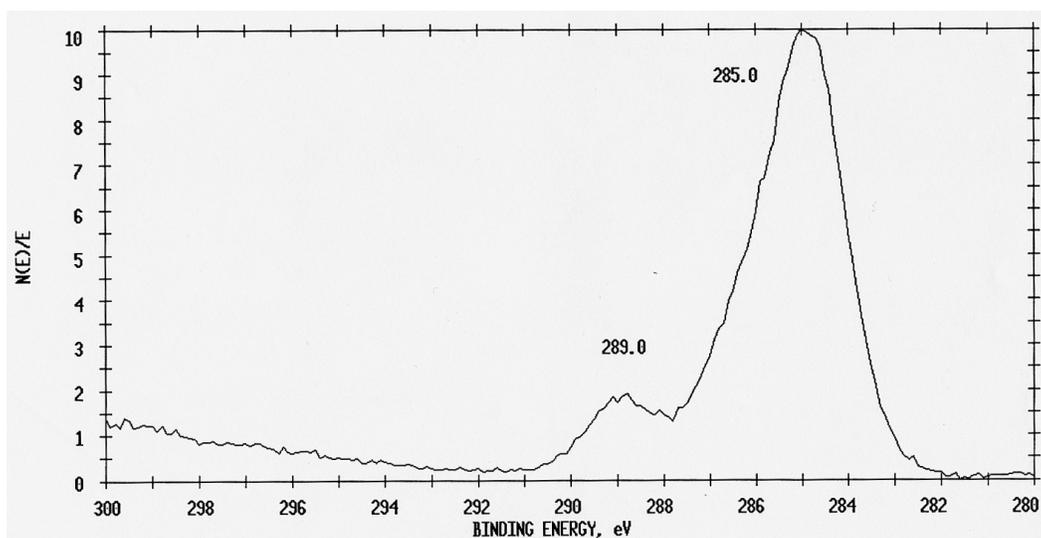
Figure 67. The C$_{1s}$ region of the XPS binding energy spectrum of the control (not aged) CAVE network surface that was prepared with 40 wt. % methyl methacrylate and cured with methyl ethyl ketone peroxide, cobalt naphthenate and dimethylaniline.
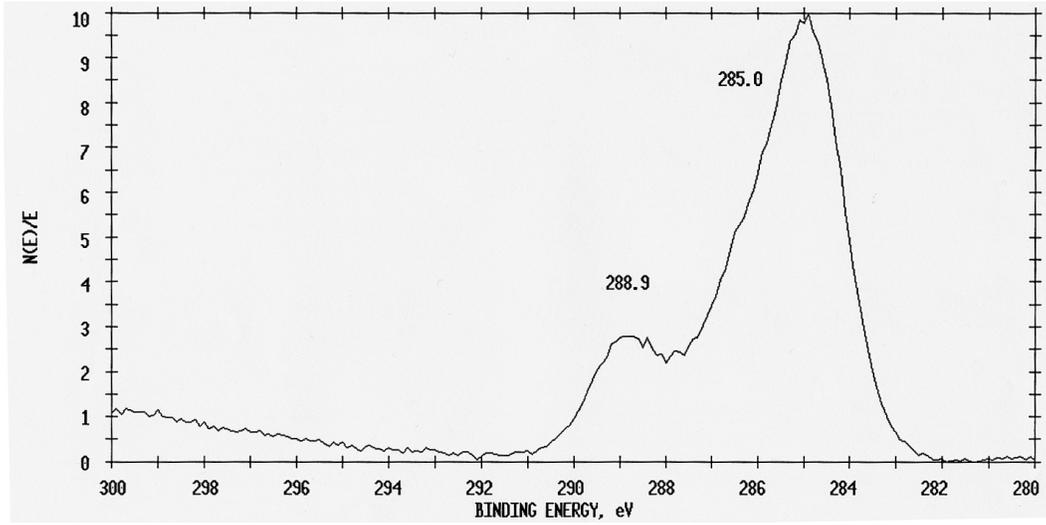
Figure 68. The C$_{1s}$ region of the XPS binding energy spectrum of the exposed CAVE network surface that was prepared with 30 wt. % methyl methacrylate and cured with benzoyl peroxide.
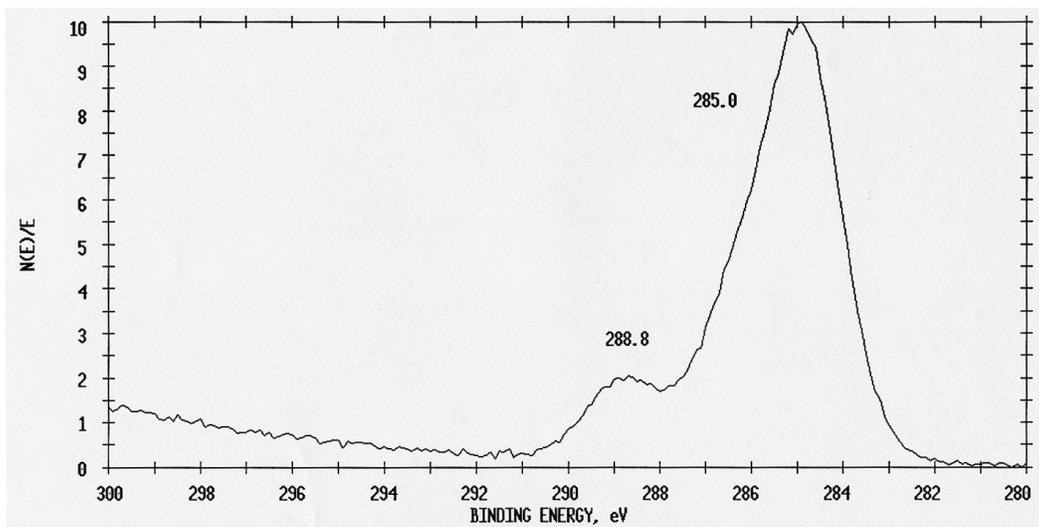

Figure 69. The C$_{1s}$ region of the XPS binding energy spectrum of the control (not aged) CAVE network surface that was prepared with 30 wt. % methyl methacrylate and cured with benzoyl peroxide.
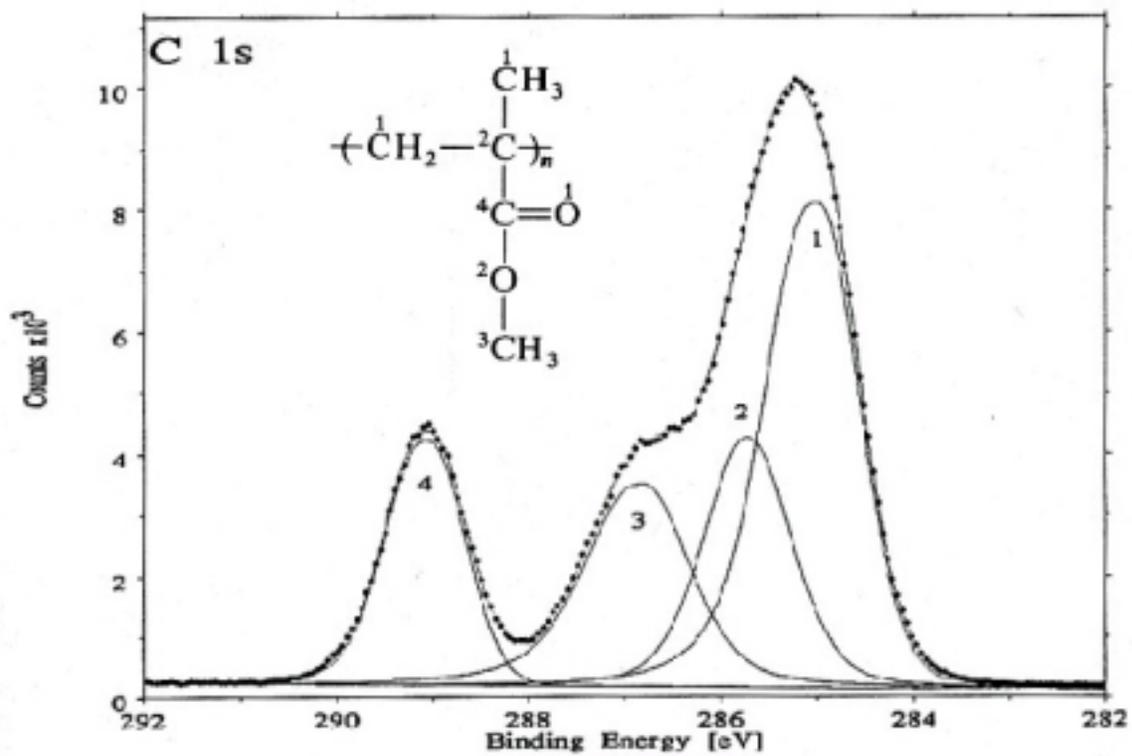
Figure 70. The C$_{1s}$ region of the XPS binding energy spectrum of polymethyl methacrylate (not aged).[174]

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[174]   G. Beamson, D. Briggs, *High Resolution XPS of Organic Polymers*, John Wiley and Sons, New York, **1992**.

There were significant differences in the binding energy spectra of the aged vs. unaged aromatic bisphenol-A containing vinyl ester networks cured with styrene,(Figure 71 - Figure 74). The C_{1s} peaks for these spectra were also deconvoluted to quantify the atomic concentrations of carbon next to oxygen (Table 27). Curve fitting the areas between 285 and 290 eV revealed a significant amount of oxidation in the aged materials. This was further supported by the qualitative shapes of the binding energy spectra (Figure 71 - Figure 74). A small amount ($\approx$1%) of potassium was also present on some of these surfaces (evident at 293 and 296 eV), which was attributed to surface preparation prior to aging (polishing).

The percentages of carbon singly bonded to oxygen remained constant upon aging, but there were significant increases in carbonyl concentration. The exposed aromatic vinyl ester networks cured with 30 wt. % styrene and benzoyl peroxide exhibited a 6 atomic % decrease of carbons not bound to oxygen with a concurrent 7 % increase in carbonyl carbons (note the prominence of the carbonyl peak at 288.8 eV in Figure 71 vs. its low intensity in Figure 72). The exposed aromatic vinyl ester networks cured with 30 wt. % styrene and methyl ethyl ketone peroxide, cobalt naphthenate and dimethylaniline exhibited a 14 % decrease of carbons not bonded to oxygen and a 14 % increase in carbonyl carbons. This is reflected by the strong shoulder at 288.8 eV in the spectra of the aged samples (Figure 73) vs. the absence of such a peak in the controls (Figure 74).
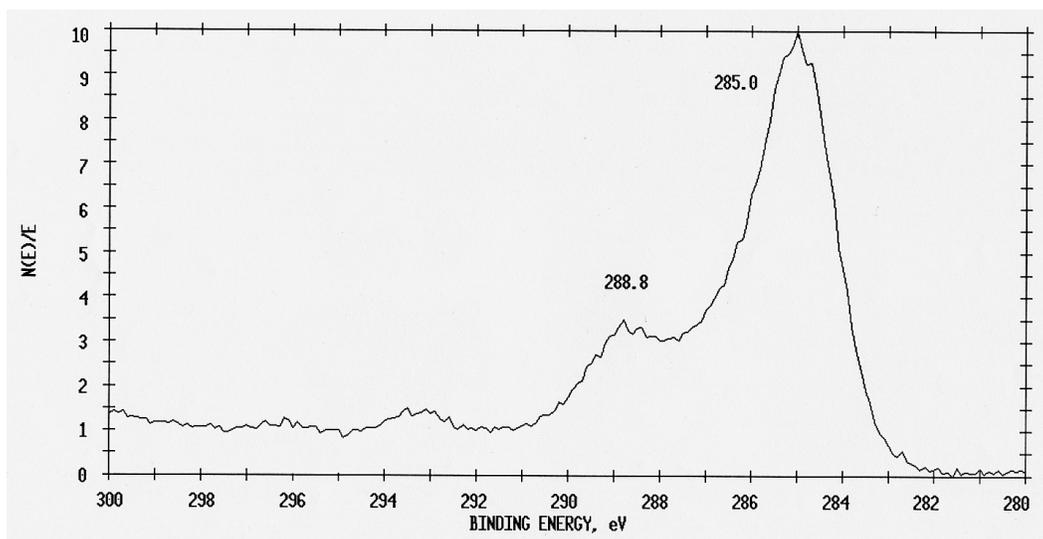
Figure 71. The C$_{1s}$ region of the XPS binding energy spectrum of the exposed aromatic vinyl ester network surface that was prepared with 30 wt. % styrene and cured with benzoyl peroxide.
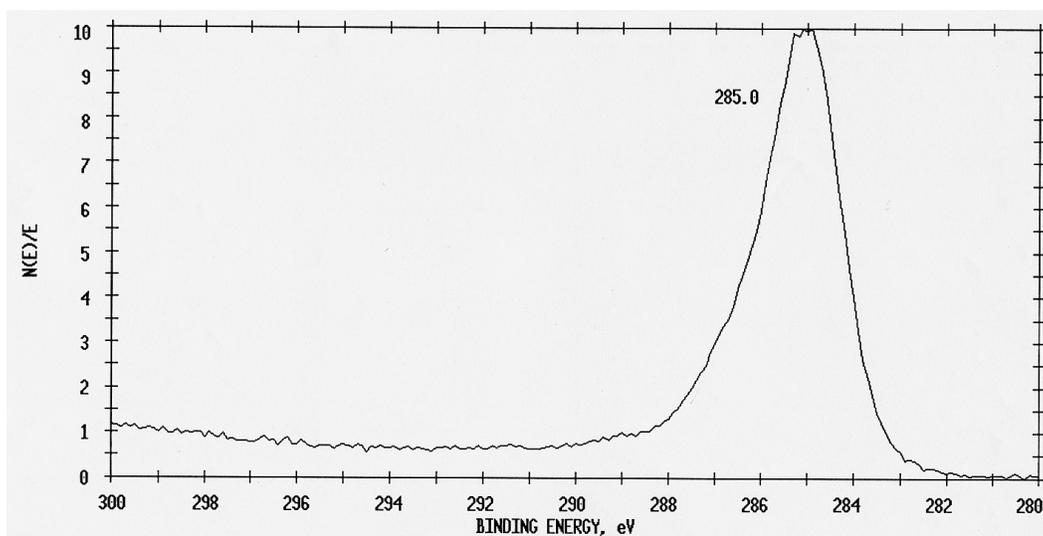

Figure 72. The C$_{1s}$ region of the XPS binding energy spectrum of the control (not aged) aromatic vinyl ester network surface, that was prepared with 30 wt. % styrene and cured with benzoyl peroxide.
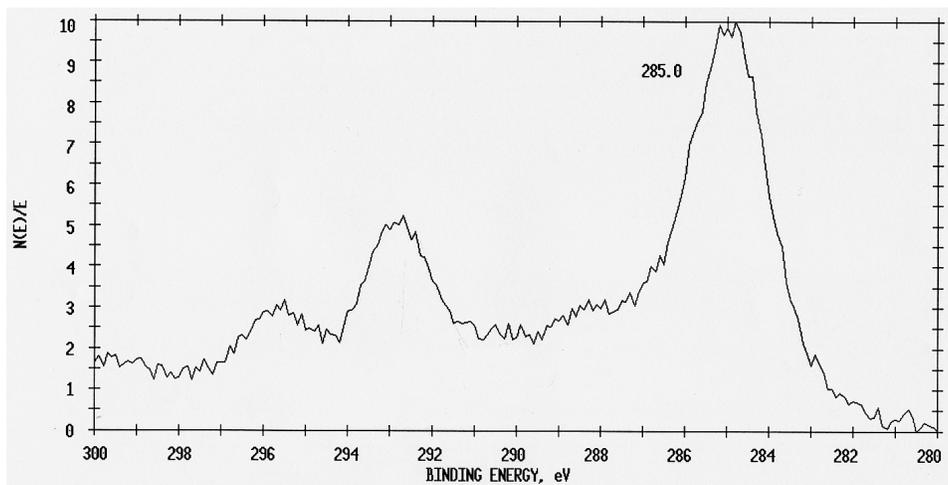
Figure 73. The C_{1s} region of the XPS binding energy spectrum of the exposed aromatic vinyl ester network surface that was prepared with 30 wt. % styrene and cured with methyl ethyl ketone peroxide, cobalt naphthenate and dimethylaniline.
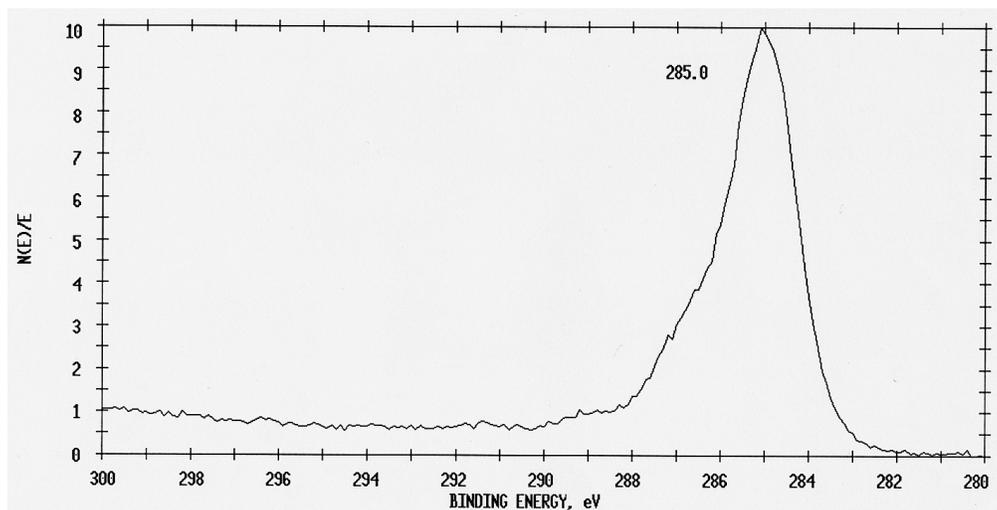

Figure 74. The C_{1s} region of the XPS binding energy spectrum of the control (not aged) aromatic vinyl ester network surface that was prepared with 30 wt. % styrene and cured with methyl ethyl ketone peroxide, cobalt naphthenate and dimethylaniline.

Another interesting point is that there was ≈2-5 % silicon on the surface of all the samples. This was probably from the silicone mold used for curing the networks. Initially all the silicon was bound to two oxygens with a binding energy of 102.5 eV (Figure 76). Upon aging the binding energy of 103.3 eV (Figure 75) was indicative of silicon in SiO_2. Due to the silicon contamination on the surface, it was reasoned that analyses of the carbon binding energy spectra might be more reliable for assessing surface oxidation.

In conclusion, the cycloaliphatic networks displayed good oxidation resistance to the accelerated UV aging protocols, and the different curing initiator/accelerators and conditions which were investigated had little effect on their behavior. It was also evident that the CAVE networks performed even better as the methyl methacrylate concentration was increased. The aromatic networks cured with methyl ethyl ketone peroxide, cobalt naphthenate, and dimethylaniline exhibit a higher level of oxidation than those cured with benzoyl peroxide.
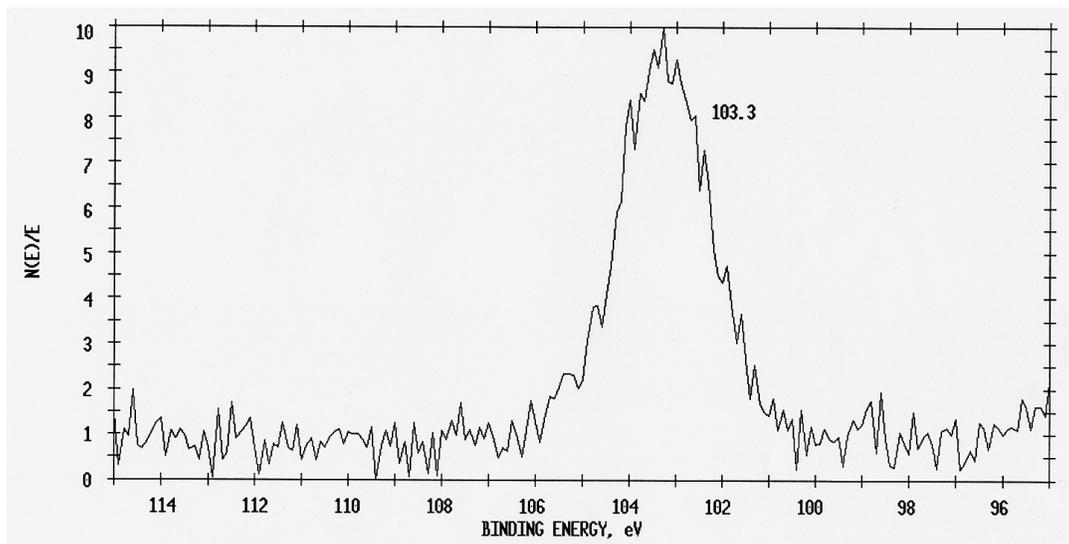
Figure 75. The XPS binding energy spectrum of the exposed aromatic vinyl ester network surface that was prepared with 30 percent styrene and cured with methyl ethyl ketone peroxide, CoNAP and DMA.
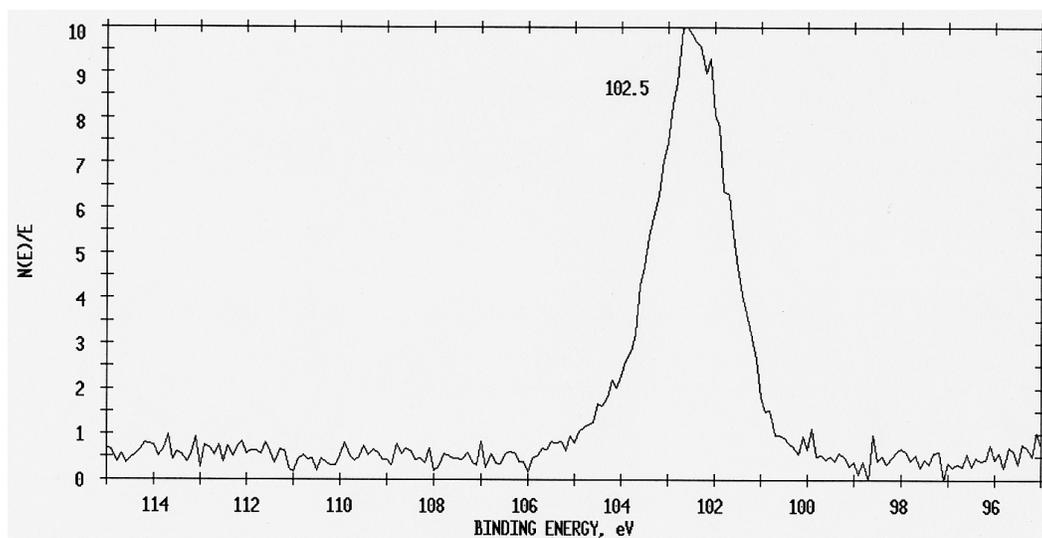

Figure 76. The XPS binding energy spectrum of the control (unaged) aromatic vinyl ester network surface that was prepared with 30 percent styrene and cured with methyl ethyl ketone peroxide, CoNAP and DMA.

Scanning electron microscopy (SEM) was conducted on all the networks that were aged for 225 days on the accelerated UV aging apparatus as well as the control networks that were not aged. During the accelerated UV aging process it was noticed that the cycloaliphatic vinyl ester/methyl methacrylate networks became glossy on the surface and the bisphenol-A networks became dull upon exposure. Scanning electron microscopy (SEM) also validates a smoother surface on the cycloaliphatic vinyl ester/methyl methacrylate networks and pitting on the surface of the aromatic bisphenol-A VE/styrene networks.

Surface scratches were evident on all samples due to the surface preparation. The SEM images of the control networks are shown in Figure 77 - Figure 81 and the aged networks are shown in Figure 82 - Figure 86. However, after 225 days of aging, the surface scratches have mostly disappeared on the cycloaliphatic networks cured with methyl methacrylate. The smoothed surface on the cycloaliphatic networks was not observed before 60 days of aging. It must have occurred gradually and was not evident until somewhere between 60 and 225 days of accelerated aging. Besides the disappearing surface scratches, macro surface cracking was apparent on all three cycloaliphatic networks. There was no evidence that the surface cracks were related to any particular reaction conditions during cure. Cracks approximately 5μ wide and 100 to 2000 μ long formed an inter-woven surface crack on all the networks cured with methyl methacrylate. The smoothing and surface crack formation may be due to migration of methacrylate, or poly(methyl methacrylate) to the surface; even though FTIR shows complete conversion after post-curing. If further curing accompanied the surface migration of monomer or

oligomer, sufficient tensile forces from cure shrinkage may have caused the surfaces to form cracks.

Surface scratches from sample preparation were also present on the bisphenol-A VE/styrene networks. However, these remained visible with SEM after aging even though the aged samples were severely pitted from UV exposure. Surface pitting was also apparently independent of the curing procedure (Figure 85 and Figure 86). This was to be expected since polystyrene has little resistance to damage from sunlight.
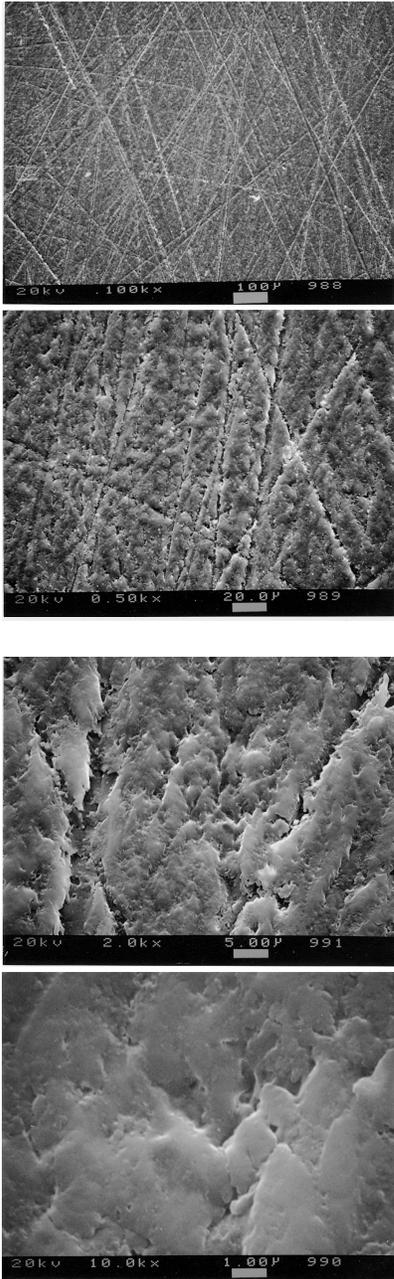
Figure 77. SEM of the unaged CAVE network cured at room temperature with 30 weight percent methyl methacrylate. The white scale bar is located in the lower black area beneath each of the SEM micrographs (and from top to bottom is 100, 20, 5, and 1 micron).
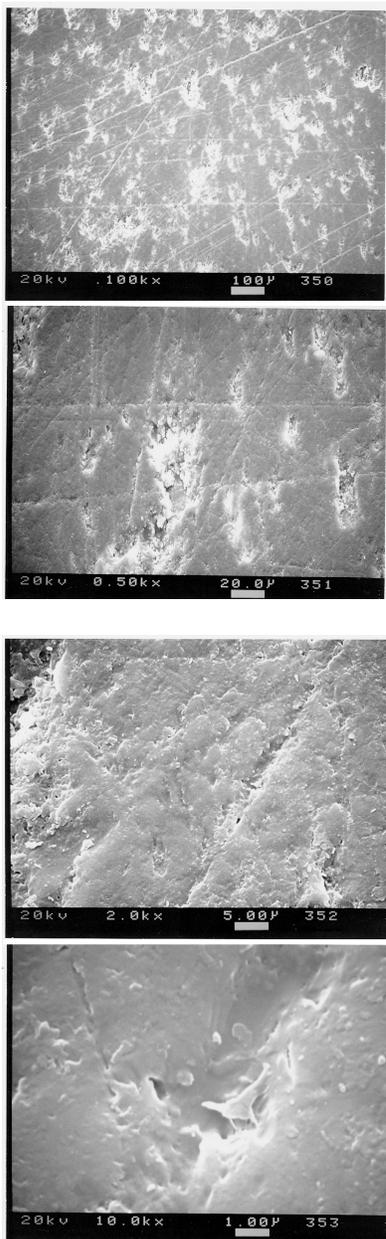
Figure 78. SEM of the unaged CAVE network cured at room temperature with 40 weight percent methyl methacrylate. The white scale bar is provided in the lower black area beneath each of the SEM (and from top to bottom is 100, 20, 5, and 1 micron).
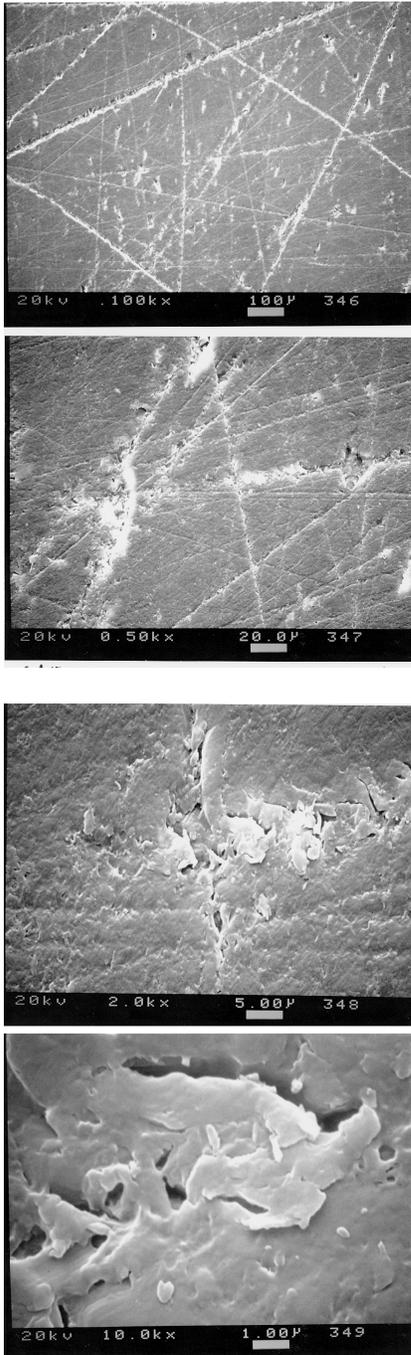
Figure 79. SEM of the unaged CAVE network cured with BPO and 30 weight percent methyl methacrylate. The white scale bar is located in the lower black area of each of the SEM (and from top to bottom is 100, 20, 5, and 1 micron).
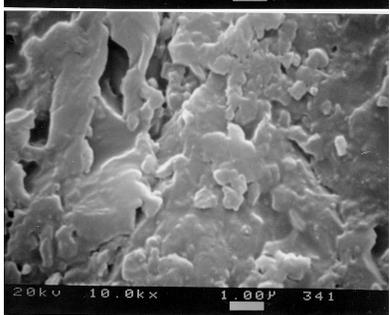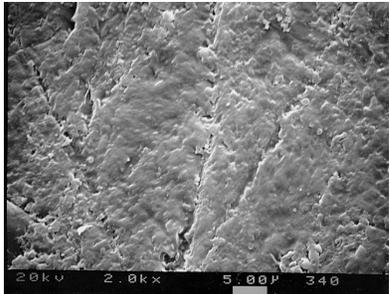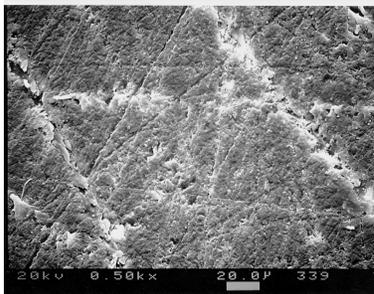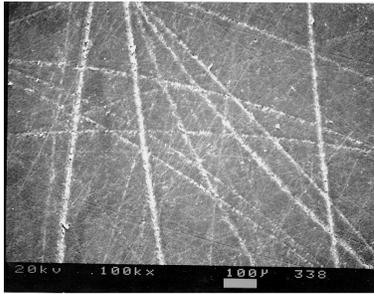
Figure 80. SEM of the unaged Bisphenol-A VE network cured at room temperature with 30 weight percent styrene. The white scale bar is located in the lower black area of each of the SEM (and from top to bottom is 100, 20, 5, and 1 micron).
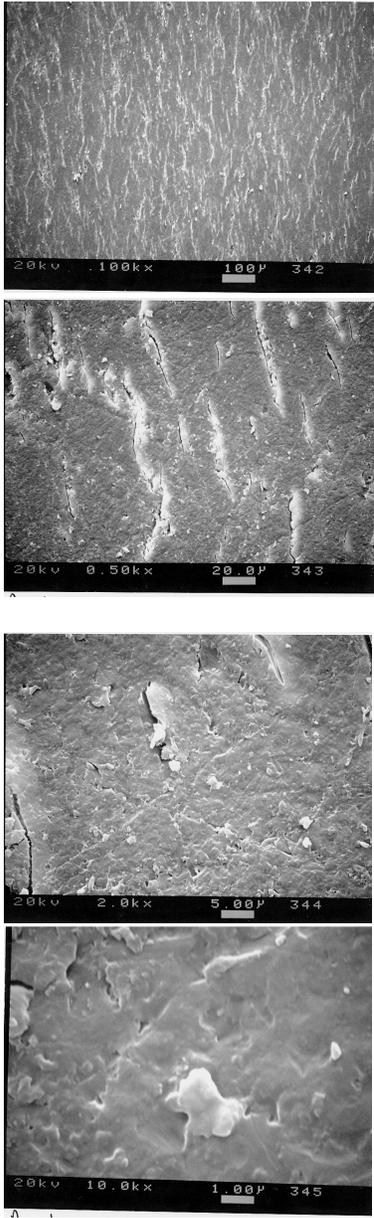
Figure 81. SEM of the unaged Bisphenol-A VE network cured with BPO and 30 weight percent styrene. The white scale bar is located in the lower black area of each of the SEM micrographs (and from top to bottom is 100, 20, 5, and 1 micron).
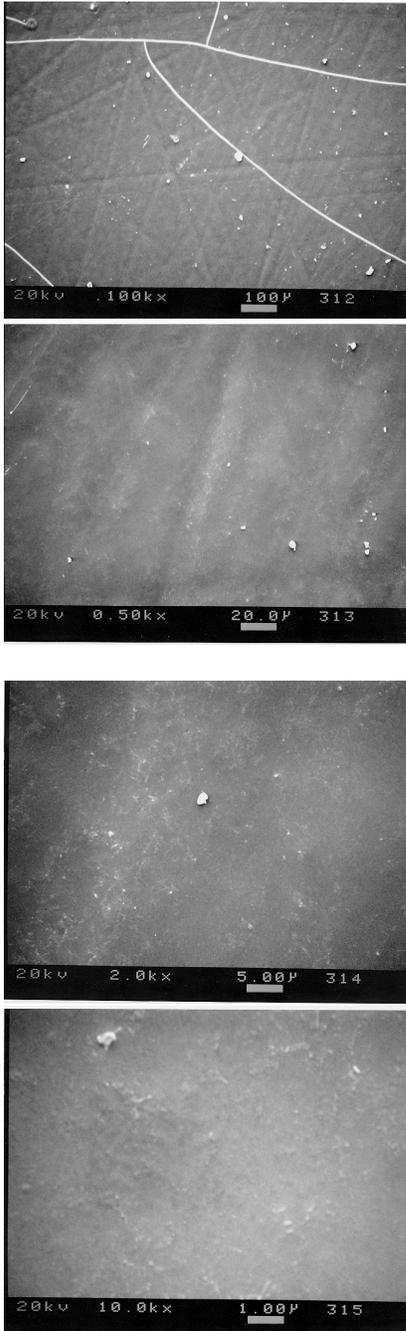
Figure 82. SEM of the exposed CAVE network surface (cured at room temperature with 30 weight percent methyl methacrylate). The white scale bar is located in the lower black area of each of the SEM (and from top to bottom is 100, 20, 5, and 1 micron).
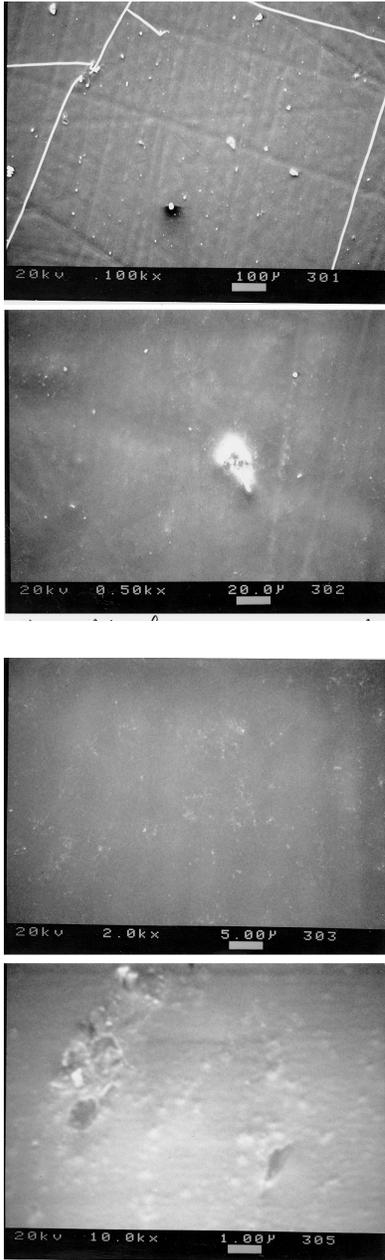
**Figure 83. SEM of the exposed CAVE network surface (cured at room temperature with 40 weight percent methyl methacrylate). The white scale bar is located in the lower black area of each of the SEM (and from top to bottom is 100, 20, 5, and 1 micron).**
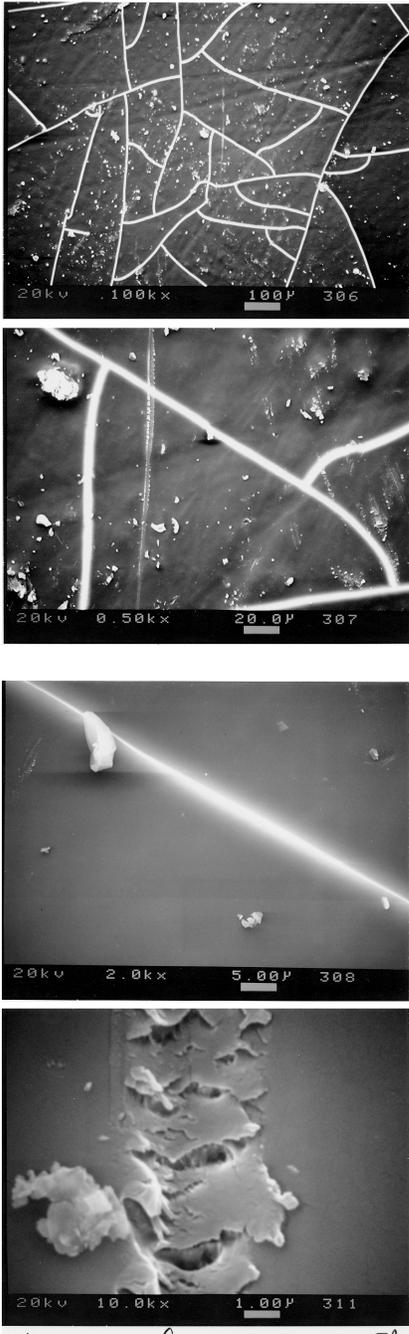
Figure 84. SEM of the exposed CAVE network surface (cured with BPO and 30 weight percent methyl methacrylate). The white scale bar is located in the lower black area of each of the SEM (and from top to bottom is 100, 20, 5, and 1 micron).
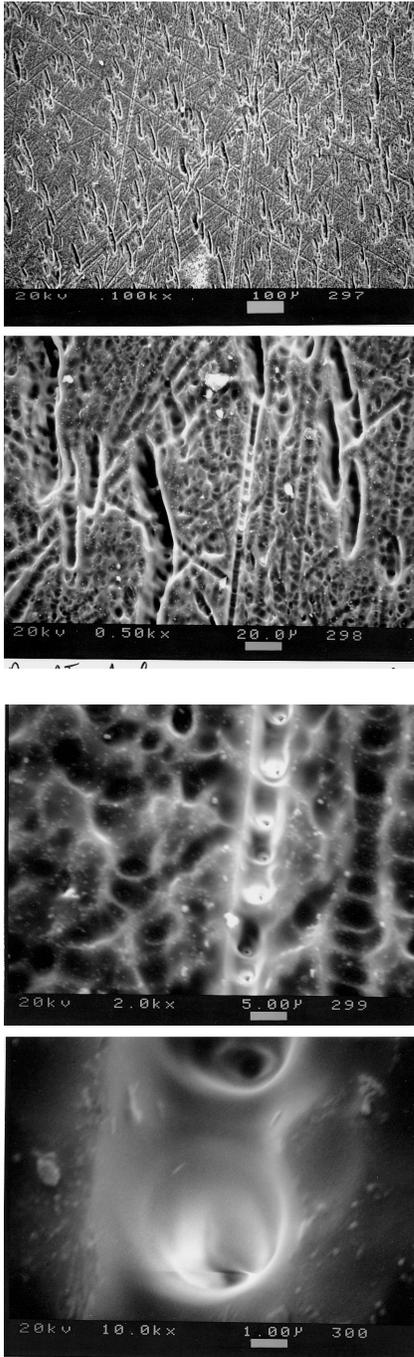
Figure 85. SEM of the exposed Bisphenol-A VE network surface (cured at room temperature with 30 weight percent styrene). The white scale bar is located in the lower black area of the SEM (and from top to bottom is 100, 20, 5, and 1 micron).
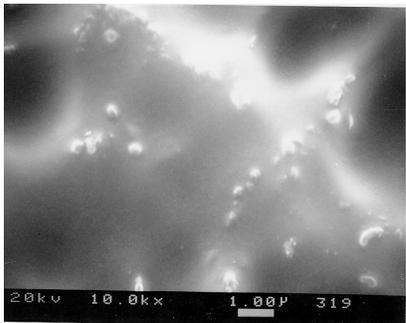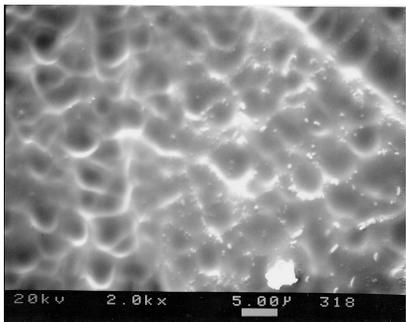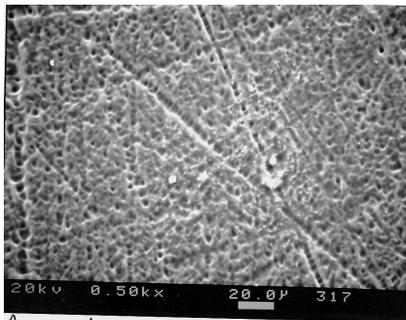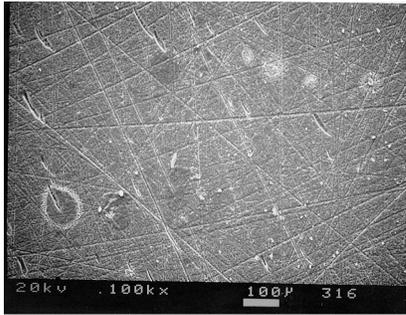
Figure 86. SEM of the exposed Bisphenol-A VE network surface (cured with BPO and 30 weight percent styrene). The white scale bar is located in the lower black area of the SEM (and from top to bottom is 100, 20, 5, and 1 micron).

### 4.6.1.3. Photographs of the Aged Specimens

Photographs were taken with a digital camera of both the aged and control specimens. Several pictures were taken with either a fluorescent light table or with a piece of white paper as the background, thus some pictures appear darker than others. The cycloaliphatic/methyl methacrylate networks cured with methyl ethyl ketone peroxide, cobalt naphthenate, and dimethylaniline exhibit no apparent yellowing; however, if cured with benzoyl peroxide (BPO) it is apparent, Figure 87 - Figure 89. This is not to say that the room temperature cured specimens don't yellow, but that it is not visually apparent due to the transparent tan color of these samples. It is also apparent that these materials become glossy from the photographs as well.

Upon aging, the surface of the aromatic vinyl ester networks cured with styrene yellow, Figure 90 - Figure 91. The visually apparent yellowing is also independent of the curing procedure and is present on both the BPO cured material and on those cured via methyl ethyl ketone peroxide, cobalt naphthenate, and dimethylaniline. Although it was not shown in the photographs these materials become dull after exposure to UV light.
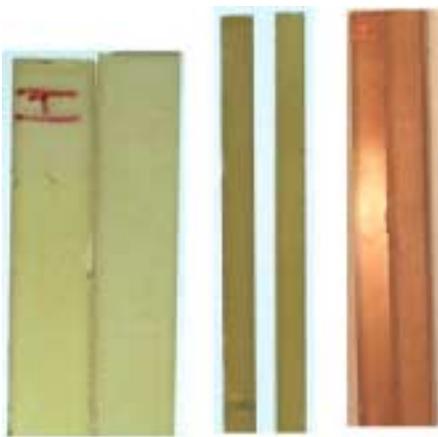
Figure 87. Digital photographs of the CAVE networks cured with 30 % methyl methacrylate via methyl ethyl ketone peroxide, cobalt naphthenate, and dimethylaniline. For each of the three pairs of samples the aged specimen is on the left and the control is on the right. The left and right pairs are top views (exposed side) and the center is a side view.
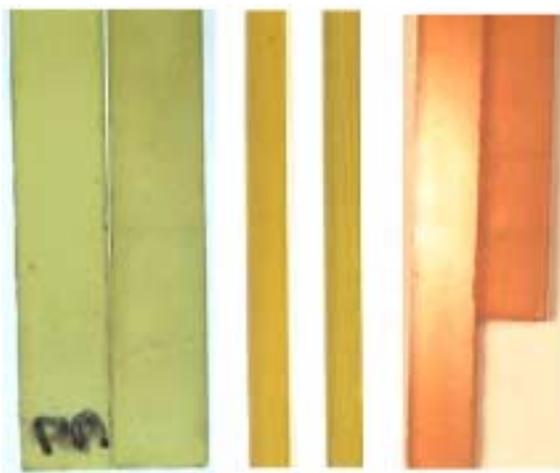
Figure 88. Digital photographs of the CAVE networks cured with 40 % methyl methacrylate via methyl ethyl ketone peroxide, cobalt naphthenate, and dimethylaniline. For each of the three pair of samples the aged is on the left and the control is on the right. The left and right pairs are top views (exposed side) and the center is a side view.

Figure 89. Digital photographs of the CAVE networks cured with 30 % methyl methacrylate and BPO (80°C for 1 hr, then 100°C for 1 hr). For each of the two pairs of samples, the aged is on the left and the control is on the right. The left pair is a top view (exposed side) and the right pair is a side view.
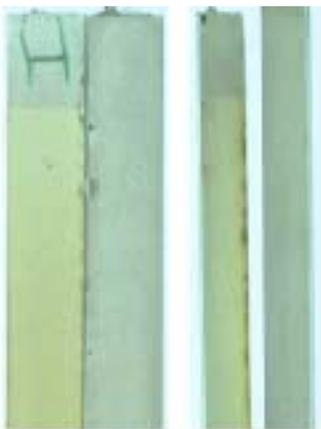
Figure 90. Digital photographs of the bisphenol-A vinyl ester networks cured with 30 % styrene via methyl ethyl ketone peroxide, cobalt naphthenate, and dimethylaniline. For each of the two pairs of samples, the aged is on the left and the control is on the right. The left pair is a top view (exposed side) and the right pair is a side view.
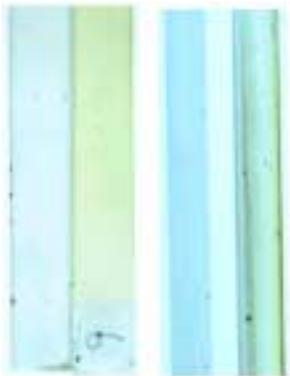
Figure 91. Digital photographs of the bisphenol-A vinyl ester networks cured with 30 % styrene and BPO. For each of the two pair of samples the aged is on the right and the control is on the left. The left pair is a top view (exposed side) and the right pair is a side view.

4.6.2. **Water absorption**

Low water absorption is important for long-term environmental durability. Water can cause hydrolysis of ester groups and promote degradation of the network. M. Ganem et al. have shown that hydrolysis has an autoaccelerated behavior because of the increased hydrophilicity of the network due to the products formed.[175] They have also shown that vinyl esters are at least one order of magnitude more stable than unsaturated polyester. Even though the vinyl ester is more stable than the unsaturated polyester, the presence of the hydroxyl group in the β position destabilizes the vinyl ester when compared to the vinyl ester analogue that does not contain the β hydroxyl group.

It is important to keep water absorption to a minimum in most applications for other reasons besides to reduce hydrolysis. Water absorption and desorption is very important as well. Evaporation of the water from a swollen or plasticized network can cause surface cracks, because the surface dries out first and the center of the material remains swollen.[176,177] Tensile stresses on the surface increase as the material begins to dry which can result in crack formation. This is further enhanced by repeated wet-dry cycles, which typically lead to further cracking.

K. Verghese et al. have shown that the vinyl ester network (Derakane 411-400) exhibits a maximum water content of 0.97% when submerged at 25°C.[178] They have also

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[175]   M. Ganem, B. Mortaigne, V. Bellenger, J. Verdu, Hydrolytic Ageing of Vinyl Ester Materials Part 1. Ageing of Prepolymers and Model Compounds, *Polym. Networks Blends* **1994**, *4*, 87.

[176]   J. Salamone, *Polymeric Materials Encyclopedia, Vol. 11*, CRC, New York, **1996**.

[177]   S. Hamid, *Handbook of Polymer Degradation*, Marcel Dekker, New York, **1992**.

[178]   K. Verghese, M. Hayes, K. Garcia, C. Carrier, J. Wood, J.S.Riffle, J. J. Lesko, Influence of Matrix Chemistry on the Short Term, Hydrothermal Aging of Vinyl Ester Matrix and Composites under Both Isothermal and Thermal Spiking Conditions, *Journal of Composite Materials* **1999**, *33*, 1919.

shown that by increasing the temperature, the material reaches saturation faster and equilibrates at an elevated level (1.60% at 84°C). In their report it was also shown that the water absorption of a vinyl ester analogue (the same structure as the above but without the hydroxyl group) to be .6 % at 66°C, whereas the Derakane 411-400 was 1.37% at 66°C. Thus removing the hydroxyl group results in a more hydrophobic network with decreasing levels of water absorption.

The levels of water absorption that K. Verghese reported are similar to those reported in this report. The bisphenol-A vinyl ester resins co-cured with styrene exhibit water absorption values of 0.9 percent and are independent of the cure procedure, (Figure 92). Water absorption was higher for the cycloaliphatic vinyl ester networks than it was for the bisphenol-A based networks co-cured with the same reactive diluent. The cycloaliphatic networks co-cured with methyl methacrylate showed water absorption values between 4 and 5 percent, figure 4.6.2-1. Whereas the bisphenol-A based vinyl ester showed water absorption values around 0.9 percent for the networks cured with styrene and about 2.2 percent for those cured with methyl methacrylate, (Figure 92 and Figure 93). Higher values of water absorption for the cycloaliphatic vinyl esters may be due to the higher polarity of the cycloaliphatic vinyl ester. Not only does the cycloaliphatic vinyl ester contain ester linkages every repeat unit but it also has pendent hydroxyl groups at every repeat unit. The pendent hydroxyl groups can hydrogen bond and thus increase the water uptake. It can be seen in Figure 92 and Figure 94 that increasing the percentage of methyl methacrylate in the CAVE networks from 30 to 50 percent, decreases the level of water absorption by 0.7 percent. The decrease in water

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absorption may be due to the fact that the number of hydroxyl groups per unit volume in the network is decreasing as the methacrylate diluent is increased.
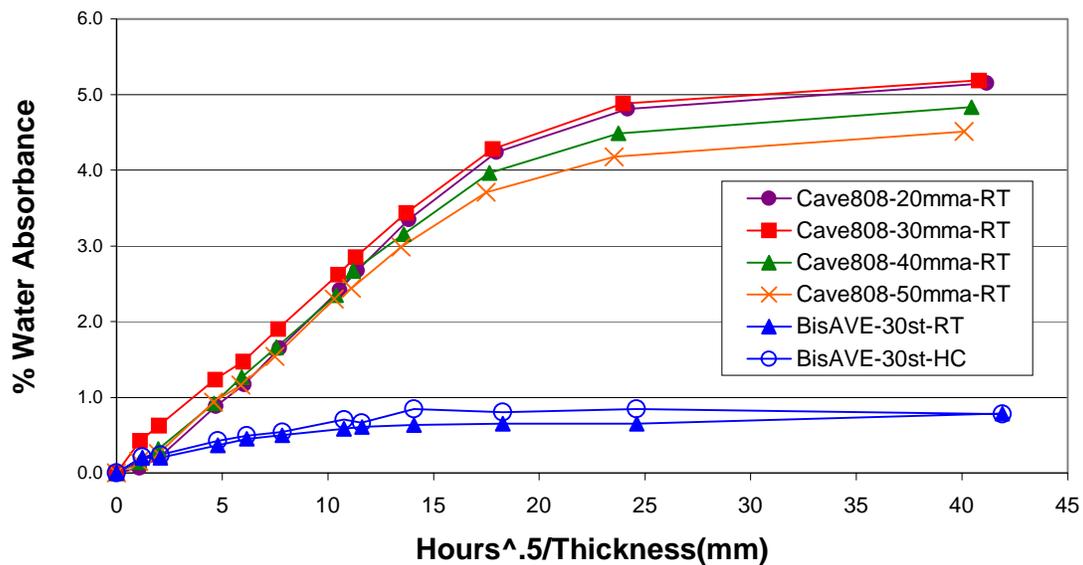
Figure 92. Water absorption of the 808 g/mole CAVE networks co-cured with 20, 30, 40, and 50 weight percent methyl methacrylate at room temperature (-RT) and postcured as well as the 700 g/mole bisphenol-A based vinyl ester networks co-cured with 30 weight percent styrene at 140°C (-HC) and those cured at room temperature then postcured (-RT).
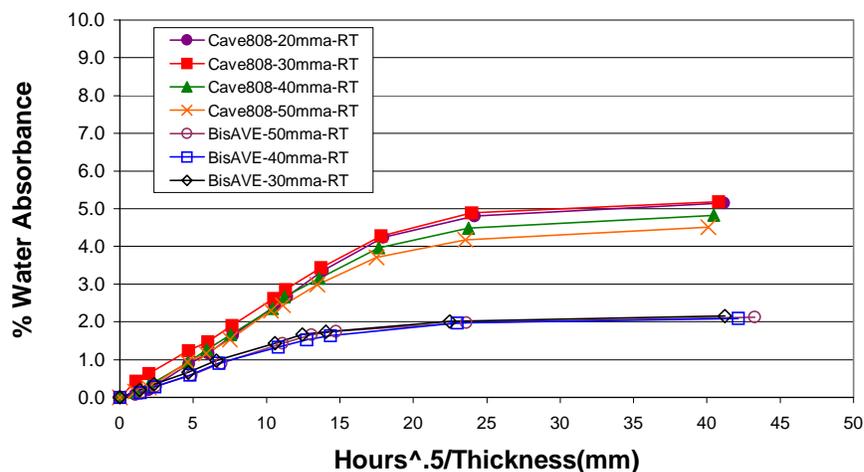
Figure 93. Water absorption of the 808 g/mole CAVE networks and the bisphenol-A vinyl ester networks co-cured with 20, 30, 40, and 50 weight percent methyl methacrylate at room temperature and postcured (-RT).

However, those networks cured with methyl methacrylate exhibit higher levels of water absorption than those co-cured with styrene, (Figure 92 and Figure 93). The bisphenol-A networks co-cured with styrene only show a 0.9 percent increase in water absorption where as the same oligomer co-cured with methyl methacrylate has about 2.2 percent increase in water absorption. Interestingly enough, by increasing the alkyl chain of the methacrylate to butyl (as with butyl methacrylate) the water absorption is low and comparable to those networks co-cured with styrene, (Figure 95).
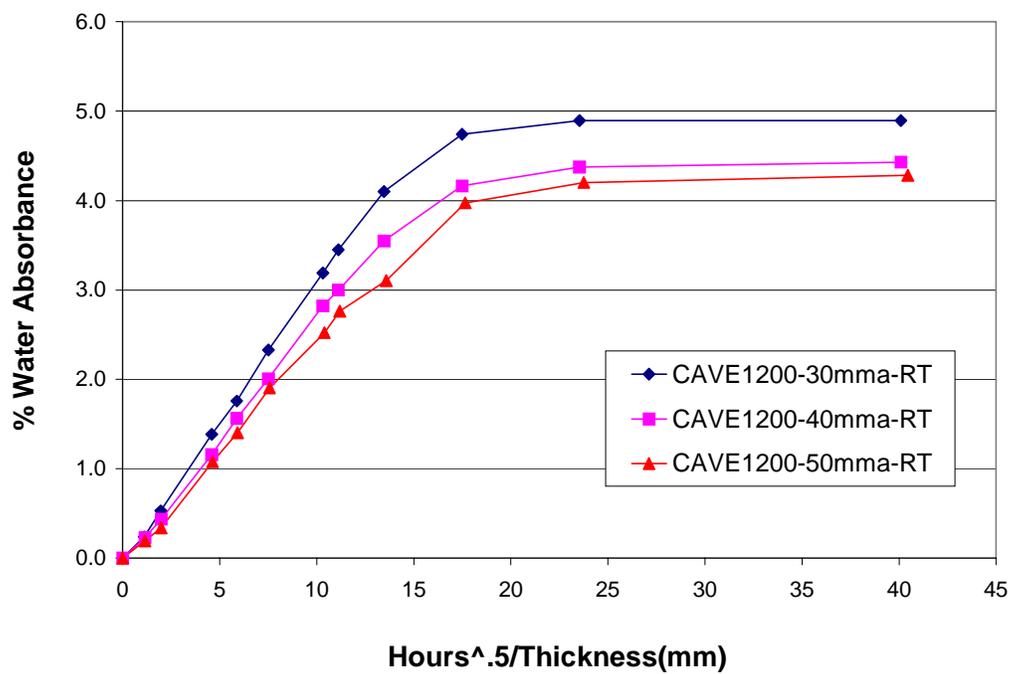
**Figure 94. Water absorption of the 1200 g/mol CAVE networks co-cured with 30, 40, and 50 weight percent methyl methacrylate at room temperature and postcured.**
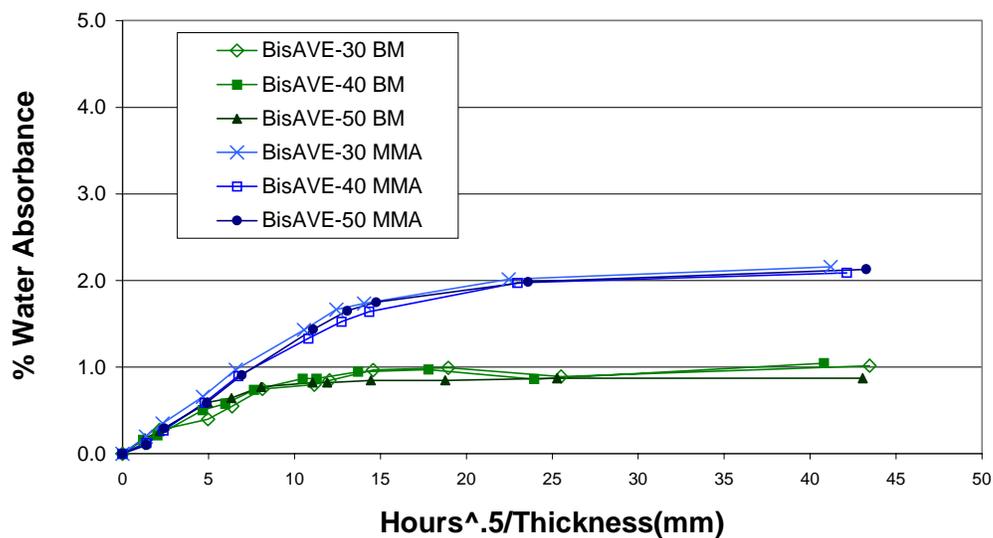
Figure 95. Water absorption of the 700 g/mole bisphenol-A based vinyl ester networks co-cured with 30, 40, and 50 weight percent butyl methacrylate at 140°C and those cured with 30, 40, and 50 weight percent methyl methacrylate at room temperature then postcured.

Chapter 5. Summary and Conclusions

Aliphatic dimethacrylate networks have been prepared using methyl methacrylate as the reactive diluent in a one pot melt reaction conducted in two steps.   The cycloaliphatic vinyl ester resins and the bisphenol-A resins co-cured with methacrylate diluents exhibited the expected trends in fracture toughness and microhardness.   The cycloaliphatic and bisphenol-A networks exhibited increased fracture toughness as the molecular weight between crosslinks increased due to the incorporation of the methacrylate diluent.   Microhardness also decreased under these conditions.   Increasing the molecular weight between crosslinks by increasing the molecular weight of the vinyl ester backbone also exhibited the expected trend.   The aromatic bisphenol-A vinyl esters cured with styrene displayed the reverse trend as styrene was increased.   This may be due in part to the difference in reactivity ratios.

Reactive diluents and curing procedures are very important factors when tailoring networks for specific properties.   Networks cured with methyl methacrylate exhibited higher levels of shrinkage than those networks cured with styrene.   Those networks containing styrene and cured at an elevated temperature with benzoyl peroxide also showed higher levels of cure shrinkage than those networks cured via the room temperature cure procedure (via methyl ethyl ketone peroxide, cobalt naphthenate, and dimethylaniline at 25°C for 24 hours and postcured at 115°C for 2 hours).   Interestingly enough, networks cured via methyl ethyl ketone peroxide, cobalt naphthenate, and dimethylaniline at 25°C for 24 hours with either methyl methacrylate or styrene exhibit

little or no farther densification of the network upon post-curing at 115°C for 2 hours even though there is significant level of curing taking place.

As expected the cycloaliphatic oligomer showed significantly reduced ultraviolet adsorption throughout the sunlight region of the spectrum. Thus, it is reasonable to expect improved durability in outdoor environments relative to aromatic analogues. Upon aging with the accelerated aging apparatus, the XPS results show low levels of oxidation for the cycloaliphatic networks cured with 30 percent methyl methacrylate and improved oxidative resistance when 40 percent methyl methacrylate is incorporated. However, the SEM indicates a smoothed surface where the surface scratches from sample preparation had nearly disappeared. The SEM also showed interwoven surface cracks, which may be due to extended curing on the surface. The enhanced surface gloss was also apparent by the naked eye, which may prove appealing for surface coatings. The cycloaliphatic networks cured with benzoyl peroxide exhibited some surface yellowing; however, yellowing was not apparent in the cycloaliphatic networks cured at room temperature and postcured. The surfaces may have yellowed but it was not apparent due to the initial transparent tan color of the network.

XPS results for the bisphenol-A vinyl ester reveal high levels of oxidation with increasing percentages of carboxyl and carbonyl functionality on the surface upon aging. SEM also indicates severe pitting on the surface of the aged aromatic bisphenol-A vinyl esters cured with styrene. Upon aging the surfaces became yellowed and dull to the naked eye, independent of the curing procedure.

Chapter 6. Suggestions for Future Work

It is extremely important to continue this research not only for obtaining an environmentally stable coating or matrix resin but also to further understand network formation and structure-property relationships. Exixting work, including this work, has shown the importance of reactive diluents and the importance of reactivity ratios with free radically cured networks. A better understanding of reactivity ratios and their impact on network formation is needed for several monomer pairs. Due to the wide range of reactive diluents, understanding the reactivity ratios may provide an understanding of network structure-property trends.

I believe other methacrylate diluents such as ethyl methacrylate should be investigated. This should provide resins with lower volatility than those containing methyl methacrylate. Ethyl methacrylate may provide a high enough boiling point to allow curing with benzoyl peroxide without forming voids due to the low vapor pressures of the reactive diluent and high cure exotherm temperatures. This would permit more thorough study of the curing procedure on the mechanical properties of the network.

The CAVE materials do show relatively high levels of water absorption; however, by curing with a longer alkyl chain methacrylate such as butyl methacrylate, the water absorption may be close to that of the bisphenol-A based dimethacrylates co-cured with styrene. It will also be advantageous to evaluate the effect of the methacrylate alkyl chain length on water absorption to a greater extent by the addition of ethyl methacrylate.

It is recommended to continue evaluating novel dimethacrylates for their use in environmental applications. The evaluation of a hydrogenated bisphenol-A vinyl ester should also be investigated. The hydrogenated bisphenol-A vinyl ester is an analogue to the current bisphenol-A vinyl ester where the bisphenol-A monomer is hydrogenated. This too would provide a non-aromatic dimethacrylate with improved hydrolytic stability when compared to the CAVE materials due to the reduced number of ester groups. Its solubility in several reactive diluents must also be investigated for potential comparisons to analogous materials. Measurements of fracture toughness, water absorption, and accelerated UV aging would also be deemed necessary for comparison.

In this particular study, the curing procedure showed little or no effect on aging properties of the aliphatic networks. Those materials cured via the room temperature curing procedure do contain DMA and CoNap. Even though higher surface oxidation of the aromatic networks was seen by XPS, samples should be spin coated before aging to eliminate the possibility of silicone on the surface when cast in a silicone mold (as in this study). This will eliminate farther oxygen content (contamination) on the surface. Understanding the effect of the cure package (initiators and accelerators) is important and thus it is also suggested that continued evaluation be done on the effect of the curing procedure.

Upon accelerated UV aging, the CAVE materials (independent of the curing procedure or methyl methacrylate content) become glossy. It is also important to fully understand the surface smoothing that has occurred with the CAVE networks. It is possible that these materials may provide coatings with superior gloss as well as the potential to reflect radiation. Bisphenol-A VE networks cured with methyl methacrylate

may aid in providing an explanation since the bisphenol-A VE/styrene networks become

dull and pitted upon aging. This will allow conformation that it is truly an effect of the

reactive diluent (methyl methacrylate). Although accelerated weathering is deemed

necessary there may be no substitute for the real thing.

LIST OF ABREVIATIONS

Instrumentation

DMA   Dynamic Mechanical Analyzer

TMA   Thermal Mechanical Analyzer

^{1}HNMR   Proton Nuclear Magnetic Resonance

^{13}CNMR   Carbon Nuclear Magnetic Resonance

DSC   Differential Scanning Calorimetry

FTIR   Fourier Transform Infrared Spectroscopy

XPS   X-Ray Photoelectron Spectroscopy

SEM   Scanning Electron Spectroscopy

Materials

BPO   Benzoyl peroxide

MEKP   Methyl ethyl ketone peroxide

DMA   Dimethylaniline

CoNAP   Cobalt naphthenate

CAVE   Cycloaliphatic vinyl ester

BisAVE   Bisphenol-A based vinyl ester

-RT   Room temperature cure procedure

-HC   Thermally cured network with benzoyl peroxide

Other abbreviations

K_{1c}	Stress intensity factor
CTE	Coefficient of thermal expansion
T_g	Glass transition temperature
M_n	Number average molecular weight
M_w	Weight average molecular weight
M_c	Average molecular weight between crosslinks
EEW	Epoxy equivalent molecular weight
PDI	Polydispersity index
MWD	Molecular weight distrobution

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VITA

Brian Craig Starr

The author is the eldest of two children born to Lois and Craig Starr of Chesterfield County, Virginia. After graduating from Manchester High School in Chesterfield County, Virginia in 1992, Brian began to attend Virginia Commonwealth University. While attending VCU, Brian coached a swim team and taught swim lessons at the local YMCA while conducting three semesters of undergraduate research in electrochemistry under the advisement of Dr. Fred Hawkridge. During the summer before his junior year at VCU, Brian received an internship at Ethyl Petroleum Additives where he developed a fundamental interest in polymer science. In 1996 he graduated Cum Laude with a Bachelor of Science Degree in Chemistry. Following his interest in polymer science he began his graduate work at Virginia Polytechnic Institute and State University under the advisement of Dr. Judy S. Riffle. While at Virginia Tech he presented papers at several national meetings and was an organic recitation instructor as well as a polymer and organic lab instructor. During his first two years he was a member of the Virginia Tech Clay Target Team and competed at collegiate nationals in San Antonio, TX; where he placed sixth at international skeet in 1997. In 1998 Brian married his high school sweetheart Angela Arthur Starr (daughter of Donald and Charlene Arthur) of Chester, Virginia. Brian obtained his Doctoral Degree in Organic/Polymer Chemistry in October of 2001. He will remain in Blacksburg, Virginia where he will be working at Acadia Polymers in the area of elastomers.