STRUCTURE AND PROPERTIES OF
DIMETHACRYLATE-STYRENE RESINS AND NETWORKS

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Structure and Properties of Dimethacrylate-Styrene Resins and Networks

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ABSTRACT

One of the major classes of polymer matrix resins under consideration for structural composite applications in the infrastructure and construction industries is the dimethacrylate matrix resin. An investigation of the relationships between the chemical structures and properties of these dimethacrylate/styrene networks has been conducted. Oligomer number average molecular weights of the polyhydroxyether ranging from 700 to 1200g/mole were studied with systematically varied styrene concentrations to assess the effects of crosslink density and chemical composition on glass transition temperatures, toughness, tensile properties and matrix strain. Network densities have been estimated from measurements of the rubbery moduli at $T_g + 40^\circ C$. Within this rather small range in vinyl ester molecular weight, toughness of the resultant networks improved tremendously as the vinyl ester oligomer $M_n$ was increased from 700g/mole to 1200g/mole due to improvements in the resistance to crack propagation. As styrene concentration was increased along all series’ of materials, brittleness increased even though the molecular weight between crosslinks increased. This was attributed to the inherent relative brittleness of the polystyrene chemical structure relative to the polyhydroxyether component. This may also be related to the reactivity ratios dictating styrene and vinyl ester sequence length and warrants further investigation. As expected, the volume contraction upon cure also decreased significantly as styrene was decreased, and thus residual cure stresses may be reduced in fiber-reinforced composites. Vickers microhardness values decreased for each of the series when molecular weight increased and styrene content decreased.

Two different cure procedures were compared to assess the effects of conversion on the physical and mechanical properties. All mechanical properties investigated (i.e. fracture
toughness, tensile strength, and microhardness) were dependent on the cure procedure. Materials cured at 140°C were harder, more brittle, had lower elongations and higher rubbery moduli than those cured at 25°C followed by a 93°C postcure. A maximum in the degree of conversion occurred with increasing polymerization temperature and can be explained by the competition between the chemical reaction and molecular mobility. The overall shrinkage per moles of vinyl groups converted was the same when the materials were cured at 25°C or 140°C. However, in the room temperature cured samples, there was essentially no further densification of the network during postcure, regardless of the postcure temperature. A mono-methacrylate analogue of the dimethacrylate terminated poly(hydroxyether) oligomer was synthesized and copolymerized with styrene to study the effects of chain transfer during elevated temperature reactions.
Dedicated to my family for their support and encouragement

and

In memory of my mother, Gussie Ruth Palmer-Burts (1932-1993)
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CHAPTER 1. OVERVIEW OF THE DISSERTATION

The research presented in this dissertation evaluates relationships between the chemical structure and mechanical properties of dimethacrylate-styrene matrix resins and networks. Resins comprised of these types of oligomers (Figure 1-1) diluted with styrene are commonly termed “vinyl ester resins.” This term refers to a family of compositions in which the molecular weight and chemical structure of the methacrylate terminated multi-functional oligomer as well as the percentage of styrene can be varied. These resins are normally derived from epoxy terminated oligomeric precursors that have been post-reacted with methacrylic acid.

![Figure 1-1](https://via.placeholder.com/150)

Figure 1-1. The structure of the dimethacrylate terminated polyhydroxyether oligomer.

Dimethacrylate terminated reactive oligomers combined with styrene can be used to form resins which have excellent physical, mechanical and chemical properties and these have been used extensively as matrices for fiber reinforced composites. During the cure reaction, a highly crosslinked network is formed by free-radical copolymerization of the methacrylate functional groups with styrene. Thus, the object of this research was to study the copolymerization of such resins under typical conditions required for composite processing and to examine the mechanical properties of the cured networks. The overall goal of this research and for others working in this field has been to improve properties of these matrix resins and networks. However, a thorough understanding of the thermoset network is crucial to understanding how the mechanical properties will be affected. The correlation between chemical structure and mechanical properties has been studied as chemical composition, molecular weight, molecular weight distribution and cure reaction parameters were varied. Infrared spectroscopy was used to determine the extent of conversion of these networks cured at ambient and elevated temperatures.
A novel monofunctional methacrylate model monomer with a chemical structure similar to the dimethacrylate functional oligomer depicted in Figure 1-1 has also been synthesized and characterized. Since this model methacrylate monomer has only one reactive group, the functionality does not dictate that it should form a crosslinked network upon reaction with another monovinyl compound such as styrene. Therefore, it was synthesized in order to serve as a linear analogue to the network so that analytical techniques could be used that require a soluble material. The mono-methacrylate was copolymerized with styrene to study the possibility of side reactions such as chain transfer and catalytic chain transfer, which could prematurely terminate active chains and reduce molecular weight. Catalytic chain transfer is believed to occur in resins cured at room temperature when certain cobalt II compounds that are known to be catalytic chain transfer agents are used as accelerators.¹

The second chapter is a review of topics relevant to this dissertation that have already been published in the literature. It includes a review of synthetic routes, cure reactions, previous studies related to characterization and properties of dimethacrylate resins and networks and comparisons among other commonly used thermoset networks.

Chapter three contains a synopsis of each of the materials, their purification and synthesis. It also includes comprehensive descriptions of experimental methods and analytical techniques used to carry out the author’s research.

The fourth chapter presents the results of the research and includes a thorough discussion of the experimental data. In this chapter, the author addresses important structural features and their effects on the properties of networks. There is extensive discussion of the effect of crosslinking on the physical and mechanical properties of dimethacrylate networks. The rubbery moduli (obtained from creep tests) were used to calculate crosslink density, which is one of the most important structural parameters controlling the properties of vinyl ester networks. Some essential determinants of the crosslink density include styrene content in the resins, final double bond conversion, polydispersity, and the molecular weights of the precursor dimethacrylate oligomers.

A synopsis of the research is presented in the fifth chapter. In the final chapter, the author makes suggestions for future work in this area.
The schematic below shows an overview of the research described in this manuscript.

Figure 1-2. Overview of the research presented in the Results and Discussion chapter of this dissertation.
CHAPTER 2. LITERATURE REVIEW

2.1 Introduction

This chapter presents a review of developments in the field of free radical crosslinking polymerizations and of the networks formed therefrom. The focus is on the synthesis and reactions of difunctional methacrylate terminated polyhydroxyether oligomers and resin mixtures which include those oligomers. This chapter includes the discussions of the synthesis, characterization, network formation and applications of these resins and networks. This particular section introduces dimethacrylate functional materials and compares them to the more commonly used unsaturated polyester and epoxy resins.

Dimethacrylate terminated polyhydroxyether oligomers copolymerized with styrene have been important matrix resins for thermosetting materials. They were first introduced commercially in the early 1960s, primarily for solvent resistant networks to be used in industrial chemical plants. The oligomers, which have been derived from epoxies prepared with bisphenol-A and epichlorohydrin, can be combined with styrene and reacted to form strong, tough networks. The dimethacrylate/styrene resins are relatively easy to process due to their low viscosities at ambient temperature and the free radical copolymerization reaction used for their cure. Some of the excellent properties of these dimethacrylate/styrene resins can be attributed to the hybrid molecular structure of bisphenol-A/epichlorohydrin epoxies combined with the methacrylate functional groups. Some important structural features of these dimethacrylate oligomers include: (1) the aromatic rings which provide good mechanical properties and heat resistance, (2) the pendant hydroxyl groups on the backbone which can provide adhesion, hydrogen bonding sites and a reactive site for potential further modification, (3) the ether linkage which contributes to good moisture and chemical resistance, and (4) the methacrylate groups located at the ends of the polymer chains which allows for free radical polymerization mechanisms.

The epoxy terminated oligomer precursors are synthesized from bisphenol-A and an excess of epichlorohydrin in the presence of base. The diepoxide terminated diglycidyl ether can then be reacted with anions of bisphenol-A to produce a desired molecular weight. Once the desired molecular weight has been achieved, the diepoxide can be endcapped with various acids.
They are subsequently endcapped with methacrylic acid in the presence of a catalyst such as triphenylphosphine. The endgroups provide methacrylate sites for further reaction with the diluent styrene, which is generally used to reduce the room temperature viscosity of the resins.

Vinyl esters, unsaturated polyesters, epoxies, and phenolic resins are major classes of thermosetting matrix resins for both fiber reinforced and filler reinforced composites. Vinyl esters have many properties characteristic of epoxy resins, but with the processability of unsaturated polyester/styrene resins. Compared to unsaturated polyesters, vinyl ester resins have better toughness and chemical resistance (including hydrolytic resistance). They also generally undergo lower volumetric shrinkage during the free radical cure reactions, which can largely be attributed to the polyesters being diluted with more styrene. There is much less research cited in the literature on vinyl ester resins compared to the studies on unsaturated polyesters and epoxy resins, especially studies on structure-properties relationships of vinyl ester resins. Most of the information concerning the cure behavior and morphology of free radically cured resins focuses on unsaturated polyester resins.

Today, as vinyl ester resins are becoming more and more important in industry, the research on vinyl ester resins is expanding. Understanding the mechanisms of the cure reaction is essential in gaining better control of the properties of these materials. Therefore, the immediate objective of the current work has been to understand the structure-property relationships of dimethacrylate functional polyhydroxyether/styrene networks by varying chemical composition and cure procedure. The motivation behind the present research stems from both fundamental and commercial interest. A detailed understanding of vinyl ester resin crosslinking reactions is essential to the design and synthesis of novel resins with improved properties.
2.2 Synthesis of methacrylate functionalized oligomers derived from epoxy precursors.

Unsaturated polyester and vinyl ester resins are low molecular weight polymers with reactive double bonds either along the chains or at the chain ends, normally diluted with a reactive monomer such as styrene. Epoxy resins are also low molecular weight polymers with epoxy groups either along the chains or at the ends, normally reacted with curing agents in two part systems. More specifically, vinyl ester oligomers are addition products of various epoxide terminated resins and unsaturated monocarboxylic acids. The most common dimethacrylate terminated oligomers are formed by the reaction of methacrylic acid with epoxide resins from bisphenol-A and epichlorohydrin.\textsuperscript{2,5,6,7}

The diepoxide is formed by the reaction of bisphenol-A and epichlorohydrin. In addition to bisphenol A, bisphenol F (prepared with formaldehyde) can also be used as a starting monomer in the synthesis of epoxy precursors to vinyl ester resins (Figure 2-5). The bisphenol-A diglycidyl ether can be reacted with anions of bisphenol-A to produce a desired molecular weight. Generally, molecular weight can be controlled by ratioing the bisphenol-A anions to the diepoxide via the Carother’s equation. Usually an excess of the diepoxide is added to ensure that the precursor resin has terminal epoxy groups. Once the desired molecular weight has been achieved, the diepoxide can be endcapped with various acids. The most commonly used acid is methacrylic acid. However, acrylic acid has been used, but to a lesser extent. The synthetic scheme and chemical structure of the vinyl ester resin employed in this study is illustrated in Figure 2-1.

Many patents covering the syntheses and compositions of vinyl ester resins have been issued within the past 30 years.\textsuperscript{6} Tertiary amines, phosphines, and alkali or -onium salts are used to catalyze the reaction between the terminal epoxy and the acid functional group. Typical reaction conditions are 120°C for 4-5 hours, and hydroquinone is commonly used as the inhibitor. Conversions are typically 90-95%.

The addition of the methacrylate groups allows vinyl esters to be cured by free radical copolymerization similar to the curing of unsaturated polyester resins. Styrene or other reactive monomers allow low viscosities to be obtained at ambient temperature. Due to similar reaction
and processing methods, vinyl esters and unsaturated polyesters can quite often be used interchangeably with little or no process modification.

![Chemical structure](image)

Figure 2-1. Synthesis of a dimethacrylate (vinyl ester) oligomer.

Differences in structural variation can be achieved by the combination of different epoxide resins (Figure 2-2) with various unsaturated acids. It is well known that epoxy resins prepared from bisphenol-A and epichlorohydrin have good mechanical properties and cycloaliphatic epoxy resins are UV resistant, due to the absence of aromatic rings which absorb energy in the UV region.
Epoxies are generally prone to water absorption. The amount absorbed and the rate of absorption is dependent on the resin, the curing agent, and the type of cure. Environmental variables, such as temperature and relative humidity, are also factors. There have been numerous equilibrium water concentration values and diffusion coefficients quoted in the literature for an equally wide range of formulations and absorption conditions, ranging from .25 to 8%.\textsuperscript{8,9} This severely diminishes the mechanical properties, such as modulus and substantially reduces the $T_g$.

Several researchers have identified the molecular and structural features that need to be tailored to decrease the propensity for water absorption and to make the networks less sensitive to the effects of absorbed moisture.\textsuperscript{10} Epoxy networks cured with amines have a beta hydroxy amine linkage which typically leads to higher moisture sorption. By contrast, epoxy resins which are catalytically cured, often with imidazole catalysts, absorb less moisture. It has been
shown that incorporation of fluorine into the network structure of epoxy systems can considerably improve hydrophobicity. More specifically, fluorinated epoxy resins with the appropriate curing agents, developed by Griffith\textsuperscript{10}, can be used (Figure 2-3). Vinyl esters with decreased water absorption can also be synthesized from these fluorinated epoxy precursors.\textsuperscript{10}

\[
\begin{align*}
O & \quad CF_3 & \quad CF_3 & \quad O \\
CH_2-CH-CH_2-CH_2-CH-CH_2 & \quad C & \quad CH_2-CH_2-CH_2-CH-CH_2
\end{align*}
\]

\[
\begin{align*}
CH_3 & \quad CH_3 & \quad NH_2 & \quad (CH_2)_b \quad Si & \quad (CH_2)_b \quad NH_2 \\
O & \quad Si & \quad O & \quad Si
\end{align*}
\]

\[
\begin{align*}
O & \quad CF_3 & \quad CF_3 & \quad O \\
OH & \quad C & \quad C & \quad O
\end{align*}
\]

Figure 2-3. Fluorinated epoxy resins and curing agents used to synthesize hydrophobic vinyl ester resins.\textsuperscript{10}

Brominated derivatives are important for forming flame retardant vinyl esters. Commercial brominated resins are available with varied bromine contents. Brominated epoxies and vinyl esters may consist of resins prepared from only tetrabromobisphenol A or from blends with bisphenol A or bisphenol F resins (Figure 2-4 and Figure 2-5). These resins impart flame
retardance to composites and are most often used to manufacture fire retardant printed circuit boards.

![Chemical structure of tetrahydroxy bisphenol A](image1)

**Figure 2-4.** The diglycidyl ether of tetrabromobisphenol A.

![Chemical structure of bisphenol F](image2)

**Figure 2-5.** Bisphenol F used for the synthesis of epoxy resins.

Other structural variations in dimethacrylate resins have been investigated for applications in dentistry. Changing the monomer resin formulation can drastically alter the physical and mechanical properties of dimethacrylates for dental restoration. Bowman et al.\textsuperscript{11} studied network formation of dimethacrylate resins for potential use in restorative dentistry, comprising 2,2’-bis(4-(2-hydroxy-3-methacryloyloxyprop-1-oxy)phenyl)propane (BisGMA), triethylene glycol dimethacrylate (TEGDMA), ethoxylated BisGMA (BisEMA) and (TEGDMA) in varying compositions (Figure 2-6). BisGMA and TEGDMA are two common resin mixtures used in dentistry to produce crosslinked networks. Typically, the final conversion of double bonds in highly crosslinked systems is less than 100%. Due to toxicity issues and the potential harm that unreacted monomer may cause, it is essentially to increase the double bond conversion. Bowman found that increased double bond conversion could be achieved by increasing the TEGDMA component. For example, the conversion was increased from 42 to 55% by increasing TEGDMA from 25% to 50% in the TEGDMA/BisGMA system.
Generally, these dental materials are photopolymerized, which typically, with inorganic filler, produce materials with high strength, low solvent absorption and high wear resistance. However, it difficult to thoroughly examine the properties and structural heterogeneity of these materials due to the presence of trapped radicals. Bowman used living radical photopolymerization to avoid trapped radicals, employing p-xylene bis(N,N-diethyl dithiocarbamate) (XDT) as the living radical polymerization initiator. These systems were photocured using a high intensity light source at approximately 600m/W/cm².¹¹

Other novel aromatic dimethacrylates have been synthesized by Davy¹² by the reaction of glycidyl methacrylate with isomeric benzene dicarboxylic acids and their halogen substituted derivatives. These monomers were reported to have viscosities two orders of magnitude less than BisGMA, comparable mechanical properties to BisGMA, and X-ray opacity (similar to tooth enamel) due to the presence of halogens. Due to the opaqueness of the halogen-substituted esters, the need for heavy metal-glass fillers can be reduced in dental composites.

Other fluorinated dimethacrylates for use in dentistry were prepared by Culbertson et al.¹³ These fluorinated triethylene glycol dimethacrylate (FTEGDMA) resins (Figure 2-6) were designed to improve the properties over BisGMA and TEGDMA based networks. Water sorption and polymerization shrinkage decreased relative to networks prepared from BisGMA and TEGDMA. Introduction of the FTEGDMA reduced shrinkage 1.58 % relative to the BisGMA resin and 2.22 % relative to the TEGDMA resin. The networks made with the experimental fluorinated monomer absorbed approximately 10 micrograms/mm³ of water (after four weeks) compared to ~50 and ~15 for the BisGMA and TEGDMA networks, respectively. The water sorption determination was based on American Dental Association Specification No. 27 for resin based filling materials.
An oligomer investigated by McGrath et al.\textsuperscript{14,15} for use in dentistry was \([2,2’\text{-bis(4-(2-hydroxyprop-1-oxy)phenyl)propane dimethacrylate (BPAD). This material is also potentially interesting for composite matrix resins.\textsuperscript{16}}\) The \([2,2’\text{-bis(4-(2-hydroxyprop-1-oxy)phenyl)propane diol was synthesized from bisphenol-A and propylene oxide, then the endgroups were esterified with methacryloyl chloride (Figure 2-7). This synthetic route produced materials without hydrophilic hydroxyl groups pendant to the chain. Interestingly, these novel dimethacrylate resins exhibited lower initial viscosities compared to the poly(hydroxyether) materials derivatized with methacrylic acid. This is likely a result of less hydrogen bonding without the hydroxyl functional groups. The rheological data concerning this particular dimethacrylate is discussed further in section 2.3.\)
Another class of resins which are characterized by their high glass transition temperatures and excellent flame retardance is the epoxidized novolacs. Novolacs are prepared under acidic conditions by using an excess of phenol relative to formaldehyde. Typical number average molecular weights for these materials are between 500 and 1000 g/mole. Initially, phenol can be reacted with formaldehyde under acidic conditions through an electrophilic substitution on the phenol (Figure 2-8a). Reaction of the methylol-substituted phenol with additional phenol molecules produces the intermediate and dimer structures shown in Figure 2-8b and c. These novolac oligomers can then be reacted with epichlorohydrin to form epoxidized novolacs (Figure 2-9). Epoxidized novolacs can be cured with amines or other nucleophilic curing agents to produce materials with excellent strength, adhesion, dielectric properties and oxidation resistance.17,18
Figure 2-8. Novolac prepolymer formation.

Figure 2-9. Epoxidized novolacs.
2.3 Rheological Behavior of Dimethacrylate Resins

2.3.1 Introduction

This section examines the deformation and flow of dimethacrylate matrix resins. Viscosity (\(\eta\)) was measured as a direct method to study the resistance to flow of these resins. Some common methods used to study viscosity include the use of simple capillary viscometers, extrusion rheometers, and rotational viscometers. Viscosity is an important resin parameter that controls the processing of vinyl esters as they are incorporated into fiber-reinforced composites. The viscosities of vinyl ester resins need to be sufficiently low in order to infiltrate the fiber tows and permit good wetting of the fibers. The concentration of any diluent is an important factor that controls the viscosity of vinyl ester resins. Styrene is commonly used as both a reactive comonomer and diluent to decrease the viscosity. Viscosity is also highly sensitive to changes in temperature, molecular structure and oligomer molecular weight. This section will address the effects of temperature, diluent content and variations in molecular structure on the viscosity of vinyl ester oligomers.

2.3.2 Effect of styrene content on viscosity

Similar to unsaturated polyesters, it is common to dilute the vinyl ester oligomers with a low molecular weight comonomer. Reactive diluents such as styrene, vinyl toluene or methyl methacrylate can be used to reduce the room temperature viscosities of the mixtures and yield a solution with a typical viscosity in the range of 200 to 2000 cps at 25°C. In many industrial products, vinyl ester resins are comprised of 40-50 weight percent styrene. In dental applications triethylene glycol dimethacrylate is a common comonomer.

Viscosity was measured for a series of resins with a 700 g/mole vinyl ester oligomer prepared from bisphenol-A/epichlorohydrin/methacrylic acid and increasing styrene concentrations at room temperature.\(^{19}\) Figure 2-10 shows the effect of styrene concentration on viscosity. The viscosity decreased as the styrene content increased and viscosities below about 500 cps were obtained at 25°C with only 35 weight percent styrene. Thus, dimethacrylate terminated poly(hydroxyether) oligomers with varied added styrene concentrations provide resin mixtures with a wide range of low viscosities suitable for composite processing using various
methods such as pultrusion and vacuum assisted infiltration where the resin can be applied at ambient temperatures.

![Graph showing viscosity (cP) vs. styrene content (wt%)](image)

**Figure 2-10.** Viscosities of uncured vinyl ester resins at 25°C (M_n = 700 g/mole).^{19}

### 2.3.3 Effect of temperature on viscosity

Li’s study^{19} also showed that the logarithm of the viscosities decreased linearly with increased reciprocal absolute temperature (Arrhenius relation). The viscosities of resins containing a 700 g/mole M_n (LM) and a 1200 g/mole M_n (HM) oligomer were calculated and plotted versus 1/T. The temperatures used were 25, 35, 50 and 75°C, which are well above the glass transition temperatures of the resins. Figure 2-11 shows the results of these plots in terms of log η vs 1/T. For this temperature range, it was found that log η vs 1/T fell on a straight line for all tested resins. The resins containing the 700 g/mole oligomer was tested at 20, 25 and 30 weight percent styrene. The resin containing the 1200 g/mole oligomer, or relatively high molecular weight resin, was only tested at 30, 35 and 40 weight percent styrene since the range of viscosities for this material were considerably higher.
In a study of the rheological and thermal behavior of vinyl ester resins based on epoxy novolacs by Gaur and Pai, similar trends were noted.\textsuperscript{20} The zero shear viscosity decreased linearly with temperature. These vinyl ester/epoxy novolac resins contained methyl, ethyl and butyl acrylates as reactive diluents (40% w/w). It was also shown that the zero shear viscosity increased with the size of the alkyl substituent in the acrylate.

2.3.4 Effect of molecular structure on viscosity

Viscosity is also influenced by variations in molecular structure. As described earlier (section 2.2), a dimethacrylate terminated oligomer without pendent hydroxyl groups exhibited a lower viscosity than that of the polyhydroxyether dimethacrylate series’ of materials.\textsuperscript{16} The viscosity of the dimethacrylate prepared by adding one mole of propylene oxide onto each side of the bisphenol-A, then capping this material with methacryloyl chloride (Figure 2-7) at 25°C
is only 300 cps. Thus, it could be processed into fiber reinforced composites without dilution. Viscosities of the vinyl ester oligomers prepared from bisphenol-A and epichlorohydrin, then endcapped with methacrylic acid, without diluents, are typically in the range of about 1,000 to 8,000 poise and higher. Such viscosities are too high for processing in many applications. Figure 2-12 summarizes the structures and properties of these two dimethacrylate resins.

Although it is convenient to add reactive diluents to lower viscosity, many of these diluents are too volatile and/or toxic. For some applications such as coatings, there is a distinct need to design and prepare low viscosity oligomers to reduce the need for such reactive diluents.

![Molecular structure 1](image1.png)  \[T_g = -6^\circ C, \eta = 1,200,000 \text{ cps at } 25^\circ C\]

![Molecular structure 2](image2.png)  \[T_g = -27^\circ C, \eta = 300 \text{ cps at } 25^\circ C\]

Figure 2-12. Structural and viscosity comparison of two vinyl ester resins.¹⁶
2.4 Network Formation of Dimethacrylate Resins

2.4.1 Introduction to Thermosetting Reactions

Thermoset polymers have covalent bonds linking the polymer chains in three dimensions. These links prevent the chains from sliding past one another resulting in a higher modulus and improved creep resistance. Gelation occurs when a three-dimensional network or an infinite molecular weight polymer (insoluble gel) is formed. The time to reach the gelation point at a particular temperature can be measured experimentally by using rheology or solubility experiments. The thermosets discussed in this dissertation are below their glass transition at room temperature. Usually glassy thermosets are more brittle than thermoplastics. In 1994, more than $7.5 \times 10^9$ lb of thermosetting resins were manufactured in the United States. Phenolics accounted for almost one-half of the total production volume. Amino and unsaturated polyester resins were the next largest families, followed by epoxies.

Thermosets are often formed from polymeric chains, which are then covalently bonded to each other in a process known as crosslinking. Crosslinking can be initiated by heat, light, or the addition of other chemicals. It is generally not a reversible process, and therefore results in materials that cannot be recycled. The vinyl ester resins primarily discussed in this dissertation are crosslinked by free radical chain reaction copolymerization of methacrylate endgroups with styrene. Thus, these involve copolymerizations between a difunctional monomer with one double bond (usually styrene) and tetrafunctional oligomeric components containing a double bond at each end of a linear chain (the so-called vinyl ester). Figure 2-13 shows a schematic representation of a network formed by this type of free radical crosslinking reaction.

In the majority of free radical chain reaction polymerizations, a reaction mixture of monovinyl and divinyl monomers containing high molecular weight chains incorporated into the network and unpolymerized monomers are present at any given time. There may also be pendant chains containing unreacted groups. Because of the nature of chain polymerization, the sol fraction after the gel point consists primarily of monomers. These monomers may contain one or more reactive double bonds. After initiation, chains will continue to grow until recombination, chain transfer, or disproportionation reactions terminate the growth.

Free-radical crosslinking polymerization and copolymerization of multivinyl systems are generally complex in nature. This complication arises from effects during free-radical
polymerization such as the early onset of the Trommsdorff effect, incomplete conversion of pendant double bonds due to vitrification or immobility caused by other effects, and possible reactivity ratio changes with conversion. The rates of polymerization are very sensitive to chain transfer to the polymer, and trapped radicals may induce post-copolymerization with oxygen, cyclization, intramolecular crosslinking, microgelation, etc.\textsuperscript{22}

Figure 2-13. Schematic representation of the free radical crosslinking mechanism.\textsuperscript{51}

For vinyl ester resins, the onset of gelation occurs early in the conversion profile, usually right after the induction period, with little or no appreciable increase in viscosity prior to gelation. The rates of approach to the gelation point are dependent on the concentration of free radicals, the concentration of each reactive type of double bond, reactivity ratios and temperature. Increasing the concentration of the initiator and/or accelerators and the use of elevated temperatures will shorten the time required to reach the gel point.

Vitrification (discussed in more detail in section 2.4.3) is the process by which a polymer passes into the glassy state from the liquid or rubbery state. Unlike gelation, vitrification can be erased by raising the cure temperature of the polymer. However, vitrification can reoccur as the degree of cure increases. Gelation and vitrification are very important physical phenomena involved in the curing of a thermosetting polymer. In order to achieve the optimal cure, it is
crucial to know when these events will take place in a polymeric system. The isothermal time-temperature-transformation (TTT) cure diagram developed by Gillham\textsuperscript{23-24} is useful for identifying the onset of gelation and vitrification. The TTT diagram plots the cure temperature of the polymer against the time of cure. Such diagrams allow the identification of events like the curves of constant viscosity or conversion and the range of temperatures in which a polymer can actually be gelled or vitrified. Some significant values on the TTT cure diagram include the resin glass-transition temperature, the gel glass-transition temperature, which is the temperature at which gelation and vitrification occur simultaneously, and the glass-transition temperature of the fully cured polymer. The information supplied on a TTT diagram can be especially useful in designing desirable cure temperatures and times.

![Generalized TTT cure diagram for thermosetting polymers.\textsuperscript{24}](image)

Figure 2-14. Generalized TTT cure diagram for thermosetting polymers.\textsuperscript{24}
2.4.2 Free Radical Initiators

The free radical polymerization of vinyl ester and unsaturated polyester resin systems is commonly initiated by the thermal or chemical decomposition of various organic peroxides and organic hydroperoxides to produce a crosslinked network. The various chemical types of peroxides include: the diacyl peroxides, ketone peroxides, hydroperoxides, dialkyl and diaralkyl peroxides, peroxyesters, and perketals (peroxyketals). Peroxides, usually in the form of powders, pastes, or liquids, must be thoroughly dispersed throughout the resins for uniform curing. The cure of these systems can be achieved at both ambient and elevated temperature conditions depending on the initiators used. In both cases, the peroxide is cleaved into free radicals which then react with the unsaturated bonds of the polymers. The type of initiating system is determined by the type of vinyl ester resin, the method of fabrication, and the requirements of the application.

Initiators frequently used for elevated temperature cures are benzoyl peroxide, t-butyl perbenzoate, and cumene hydroperoxide. However, there are numerous peroxides available for specific applications and temperature ranges. Some common peroxides for room temperature are methyl ethyl ketone peroxide (MEKP), cyclohexanone peroxide, and acetylacetone peroxide.

Accelerators increase the rate at which peroxides break down into free radicals and also initiate dissociation of the peroxides into free radicals at room temperature. The latter function of accelerators makes the cure reaction possible without external heat. The accelerators most commonly employed for room temperature cures are tertiary amines such as dimethyl and diethyl aniline, and metal salts such as cobalt (cobalt II complexes) and manganese octoate or naphthenate. Benzoyl peroxide can also be accelerated with a tertiary amine to initiate cure without the addition of heat.

2.4.3 Cure Reactions of Monovinyl and Divinyl Free Radical Copolymerizations

The final conversion in vinyl polymerizations is determined to a large extent by the mobility of the reactive groups. When functional monomers such as methyl methacrylate are polymerized above their T_g, complete conversion can be achieved. However, at lower
temperatures, propagation becomes diffusion-limited and incomplete conversion results. Polyfunctional monomers have the additional limitation of final conversion due to the reactive groups becoming attached to the network early in the polymerization reaction. Additionally, when more than one type of chemical double bond is involved, reactivity ratios will affect the mobility of the network as it forms.

Infrared spectroscopy can provide detailed information concerning free radical copolymerizations, and these measurements can be conducted in situ so that thermosetting polymer mixtures can be monitored effectively. Rapid cure reactions can be monitored and different types of double bond conversion can be assessed independently and simultaneously.

The reaction kinetics of vinyl ester resins have been investigated previously using FTIR at room temperature and the results have been interpreted based on the copolymerization theory. The vinyl ester mixtures copolymerized at ambient temperatures were reported to have low conversions (~50%) due to vitrification. Vitrification occurs when the $T_g$ of the system reaches the cure temperature and the reaction stops due to lack of mobility (Figure 2-15). If the temperature is increased above the $T_g$, the chains will have the necessary mobility to continue propagating. The effect of vitrification is less pronounced at high cure temperatures.

![Figure 2-15](image-url)

Figure 2-15. The effect of the cure temperature and glass transition temperature on vitrification.
In a reaction kinetics study of a vinyl ester resin comprised of a 700 g/mole dimethacrylate terminated polyhydroxyether oligomer diluted with styrene conducted by Li et al., the Mayo-Lewis copolymerization equation (2-2) was used to analyze FTIR conversion data.\textsuperscript{31} The vinyl ester resin mixtures present an interesting case since they combine a low molecular weight difunctional monomer such as styrene with a higher molecular weight multifunctional monomer such as the vinyl ester oligomer. It is well known that multifunctional monomer polymerizations can exhibit a diffusion-controlled termination mechanism due to the limited mobility of macroradicals which form during cure.\textsuperscript{32,33} Shortly after the polymerization begins, this macroradical immobility leads to autoacceleration. At later a later stage, both termination and propagation are diffusion controlled. Polymerization stops when vitrification suppresses the propagation reaction.

Li showed that the effect of limited mobility in such a system only occurs at high conversions during a high temperature cure (above the $T_g$ of a completely converted reaction mixture). In this study, infrared absorbances of methacrylate (vinyl ester) and styrene double bond conversions were independently monitored at 943 and 910 cm$^{-1}$, respectively (Figure 2-16). The disappearance of the absorption peaks was used to quantitatively determine the percent conversion of each type of functional group.

Copolymerizations were studied at 140°C using a 700 g/mole vinyl ester oligomer diluted with systematically increasing amounts of styrene varying from 20 weight percent to 60 weight percent. The reaction was monitored for 10 minutes and quantitative conversion data showed that the resin was fully cured. Approximately 1.1 weight percent of the free radical initiator, benzyol peroxide was used. These results support one of the most desirable qualities about these resins; they can exhibit rapid reactions at elevated temperatures.

Li also studied the effect of styrene and temperature on conversion. It was shown that styrene reaches full conversion at 140°C regardless of the styrene content. However, the conversion of the methacrylate groups was inhibited due to lack of mobility at low styrene contents. When sufficient amounts of the more mobile comonomer styrene were present (>25 weight percent for a 700 g/mole $M_n$ resin), the methacrylate groups were sufficiently mobile to find radical chain ends and continue to propagate. The conversion of both styrene and methacrylate functional groups decreased as the cure temperature decreased. Nearly complete
conversion was approached between 120-140°C using a combined benzoyl peroxide and t-butyl peroxybenzoate initiator composition, while at 100°C only around 90% conversion was achieved even at reaction times of more than one hour.

Figure 2-16. Infrared spectra of a vinyl ester resin during cure (140°C).  

![Infrared spectra of a vinyl ester resin during cure (140°C).](image)

Similar to Li’s study, Scranton et al. also studied the effect of mobility on polymerization rate by varying the reactive diluent concentration. They evaluated thermal homopolymerizations of ethylene glycol dimethacrylate and copolymerizations with 2-hydroxyethyl methacrylate (HEMA). It was determined that as the solvent content was increased, both the initial polymerization rate and the magnitude of gel effects were reduced and the onset of the gel effect was delayed. Scranton also attributed these observations to the additional mobility of the polymer chains due to the increase in the amount of solvent.

Other researchers have studied effects of the mobility of the monomer structure on the free radical copolymerization system. Many complexities occur in multifunctional monomer polymerization systems, including autoacceleration, limited double bond conversion, physical
relaxation rate-dependent polymerization kinetics and diffusion-controlled termination. The
majority of this behavior has been attributed to the relative mobility of the reacting species.\textsuperscript{36} Many\textsuperscript{37,38,39,40,41,42} have studied the effects of increasing dimethacrylate concentration on the cure
behavior of methacrylate and dimethacrylate copolymerizing systems. In general, these
researchers have found that as the concentration of dimethacrylate monomer is increased,
macroscopic gelation occurs at lower conversions, and this severely limits translational and
segmental mobility of the polymer macroradicals. In Kopecek’s study\textsuperscript{37,38} of the effect of
mobility on the termination kinetics of a dimethacrylate resins system, it was found that
increasing the amount of the dimethacrylate concentration resulted in higher double bond
conversions at a given polymerization time.

In Hamielec’s study\textsuperscript{39,40,41} of the copolymerization of methyl methacrylate with ethylene
glycol dimethacrylate, there was a decrease in the conversion at which autoacceleration occurred
as the concentration of dimethacrylate increased. At higher conversions, a sudden decrease in
the conversion rate was noted. This was again related to the limited mobility of the monomer
molecules (diffusion-controlled propagation) and the initiator radicals (increased recombination
rate due to the cage effect). Hamielec also modeled the polymerization behavior and kinetics of
these copolymerization cross-linking reactions.\textsuperscript{43,44,45} Although many of the studies\textsuperscript{39,40,41}
conducted by Hamielec et al. were done in the low crosslinking regime (less than 5 weight
percent crosslinking reagent) the effect of gelation and crosslink density on mobility still holds.
In the homopolymerization of dimethacrylates (high crosslinking regime) autoacceleration is
apparent from the onset of the reaction since mobility is restricted upon the onset of gelation.\textsuperscript{36}
In many of the multifunctional monomer homopolymerizations in the previously mentioned
studies, gelation occurred at less than 1\% conversion of the vinyl groups. It was suggested that
the flexibility of the monomer should be increased in order to increase the mobility of the
reacting species.\textsuperscript{36}

Monomer reactivity ratios are useful in describing free radical copolymerization
reactions. They are defined as the ratios of the rate constant for a propagating species adding its
own type of monomer divided by the rate constant for its addition of the other monomer
(equation (2- 1)).\textsuperscript{32} Reactivity ratios are often calculated from the non-integrated form of the
copolymerization equation (equation (2- 2) and defined as $r_1$ and $r_2$. The copolymer
composition, $d[M_1]/d[M_2]$, is the molar ratio of the two monomer units entering the copolymer
and \([M_1]\) and \([M_2]\) are the concentrations of the two monomers in the feed. Reactivity \((r)\) values between zero and unity denote the tendency of two monomers to copolymerize. Values higher than one indicate the preference of one monomer adding to itself, whereas values less than one indicate one monomer preferentially adding the other monomer. A value close to zero suggests that a monomer is not capable of undergoing homopolymerization.

\[
\begin{align*}
    r_1 &= \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}}
    
\end{align*}
\]

Li\textsuperscript{31} used FT-IR data obtained at early conversions to calculate monomer reactivity ratios of the methacrylate and styrene at 140°C. The reactivity ratios of styrene with terminal methacrylates on vinyl ester oligomers was estimated to be \(r_s=0.36\) and \(r_m=0.24\) using the Mayo-Lewis approach.\textsuperscript{46} The reactivity ratios for the small monomer system, styrene and methyl methacrylate at 60°C, have been reported as 0.52 and 0.46, respectively.\textsuperscript{47} Although similar, the differences in reactivity ratios for the two sets of materials are partially due to the former set consisting of a monovinyl and divinyl system, whereas methyl methacrylate and styrene are both monovinyl systems. The difference may also be related to mobility of the reacting systems. The methyl methacrylate monomer is less bulky than the dimethacrylate oligomer, thus the reactivity of the methyl methacrylate is more closely related to that of the styrene.
Ganem also investigated the copolymerization kinetics of these vinyl ester/styrene networks using FT-IR.\textsuperscript{29} The vinyl ester oligomer (1100 g/mole) was diluted with concentrations of styrene ranging from 25 to 60 weight percent. The initiating system consisted of methyl ethyl ketone peroxide (1%), dimethylaniline (.06%) and cobalt octoate (.018%). Using the copolymerization theory, it was determined that there were three stages of crosslinking. Ganem was also able to obtain the monomer sequence distributions following each stage. The reactivity ratios for the first stage were calculated as $0.4 \pm 0.1$ and $1.2 \pm 0.5$ for styrene and methacrylate respectively. It was reasoned that the copolymerization kinetics in the first stage were due to the intrinsic reactivity of the styrene and methacrylate double bonds. The second stage was evident when approximately 20\% to 30\% conversion was reached, where the reactivity ratios were determined to be 0.8 and 0.7 for styrene and methacrylate respectively. Similar to Li’s study, Ganem attributed the decrease in the reactivity of methacrylate units with other methacrylate units and the increase of the styrene reactivity ratio was due to lack of methacrylate unit mobility caused by gelation. The styrene molecules were relatively unrestricted compared to immobilized methacrylate molecules which obviously have a higher molar volume. At the end of the second stage, no additional methacrylate conversion was observed. This was attributed to a decrease in the diffusivity of the reactive species with increasing crosslink density. Thus, only styrene monomer continued to react in the final stage (approximately 50\% to 60\% conversion). Ganem suggested that the final structure was likely two phases, with the first phase consisting of the vinyl ester network and the second phase consisting of essentially polystyrene.

Using similar curing systems with vinyl ester resins, others\textsuperscript{3,30,48} have also confirmed that styrene reacts to a much greater extent relative to methacrylate during later stages of the copolymerization reaction. The reactivity ratios were calculated for one of these systems\textsuperscript{30} using a 700 g/mole resin cured from 30\degree C to 50\degree C with styrene percentages ranging from 28 weight percent to 57 weight percent. The reactivity ratios for styrene and methacrylate were determined to be 0.1 and 0.05. In another system,\textsuperscript{48} the reactivity ratios for a vinyl ester ($M_n=908$ g/mole) with 45 weight percent styrene cured at 30\degree C were 0.45 and 1.54 for styrene and methacrylate, respectively. Additionally, reactivity ratios at 90\degree C were estimated to be 0.47 and .61 for styrene and methacrylate, respectively, suggesting that this increase in temperatures enhanced the reactivity of styrene into the network. The variability in these data makes interpretation difficult.
Li’s reactivity ratio data\textsuperscript{31} were also used to predict the azeotropic feed composition. This composition corresponds to the monomer feed ratio where the copolymer composition should remain constant throughout polymerization assuming that the reactivity ratios do not change during the course of the polymerization.\textsuperscript{31} The azeotropic point for the vinyl ester-styrene resin having a oligomer molecular weight of 690 g/mole was calculated to be approximately 26 weight percent styrene, indicating the essentially homogeneous network formation. The azeotropic point for these systems will differ in weight composition depending on the molecular weight of the oligomer. It may be important to make networks with compositions close to the azeotropic point to produce reasonably homogeneous network systems.

An analysis of the sol and gel can also be used to study the cure reaction of these dimethacrylate networks. Gelation occurs early in free radical reactions relative to networks such as epoxy resins which cure by step-growth mechanisms (Figure 2-17). As stated earlier, gelation occurs when an insoluble, but swellable polymer develops with infinite molecular weight and viscosity.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2-17.png}
\caption{A comparison of step versus chain polymerization.}
\end{figure}

Li et al.\textsuperscript{31} experimentally detected the first gel in a dimethacrylate/styrene resin system as early as 12\% double bond conversion using Derakane 441-400 (700 g/mole oligomer with ~30 weight percent styrene) at 140°C. Sols and gels isolated during a reaction with a feed composition very near the azeotropic point (700g/mole oligomer diluted with 26 wt. \% styrene)
suggested that the compositions of the gel remained nearly constant except at very early (less than 10% conversion) and very late stages of reaction.\textsuperscript{31}

Many workers, including Stockmayer\textsuperscript{53}, Matsumoto\textsuperscript{54}, Flory\textsuperscript{49} and Hamielec\textsuperscript{50,51} have theoretically predicted the gel point in free radical multivinyl polymerization systems. The models were based on probability theories with some of them including kinetic parameters. They all postulated a critical conversion at which gelation occurs.

A general approach was taken by Flory\textsuperscript{52} to determine the extent of the reaction in polycondensations required to produce a three dimensional network. Equation (2-3) describes the connection between the critical conversion at gelation ($\alpha_c$) and the weight-average functionality ($f_w$) of the initial system.

\begin{equation}
\alpha_c = \frac{1}{f_w - 1}
\end{equation}

For a vulcanization reaction where the initial polyfunctional material consists of chains of units each bearing a single functionality (e.g. polybutadiene), $f_w$ corresponds to the weight-average degree of polymerization, $P_w$, of the initial material. Therefore, equation (2-3) can be written as:

\begin{equation}
\alpha_c = \frac{1}{P_w - 1}
\end{equation}

Stockmayer\textsuperscript{53} modified equations (2-3) and (2-4) to describe free radical chain reactions (equation (2-5)) in order to predict the gel point of networks prepared from monovinyl and divinyl monomers. $P_w$ is the weight-average degree of polymerization of the primary chains

\begin{equation}
\alpha_c = \frac{1}{\rho} (P_w - 1)^{-1}
\end{equation}

which would result if all crosslinks in the network at the gel point were cut (Figure 2-18), and $\rho$ is the fraction of all double bonds residing on divinyl units in the initial system. Limitations of this equation include the assumptions that the double bonds of both monomers have the same
reactivity and no cyclization occurs. Although this was not the case for the dimethacrylate/styrene systems studied in this work, it represents a first approximation for networks being formed from free radical systems.

The length of the primary chain, $P_w$, can be thought of as an aggregation of chains which would remain if each of the doubly-reacted divinyl units in the polymer were cut in half. This was visually illustrated using the general representation of a vinyl-divinyl copolymerizing system (Figure 2-18). Each of the chains could be cut at X, and the weight average degree of polymerization of the resulting chains (with no vinyl groups attached) was described by $P_w$. It is difficult to theoretically predict $P_w$, since this depends on various kinetic parameters for the specific free radical polymerization. One method which has been pursued for experimentally approximating $P_w$ was by obtaining the degree of polymerization for a linear polymer prepared from a mono-unsaturated monomer, under conditions simulating the network forming reaction.

$$R-(CH_2CHY)_p-CH_2CH-(CH_2CHY)_q-R$$
$$\quad X$$
$$R-CH_2CH-(CH_2CHY)_r-CH_2CH-(CH_2CHY)_s-R$$
$$\quad X$$
$$R-(CH_2CHY)_t-CH_2CH-(CH_2CHY)_u-CH_2CH-(CH_2CHY)_v-R$$
$$\quad X$$
$$CH_2=CH$$

Figure 2-18. General schematic of vinyl-divinyl copolymer chains that can be used in the approximation of $P_w$ (the weight average degree of polymerization). $P_w$ of the primary chain was defined as the number of units in a chain which results after cutting the crosslinks (represented by the top two X’s).

Models can be used to theoretically predict gel point and many cases, have correlated well with experimental data. It is generally difficult to predict gel formation due to the complexities of free radical copolymerizations of multivinyl compounds. Large deviations of the gel point from theoretical calculations are usually due to four main factors: intramolecular
cyclization, reduced reactivity of pendant vinyl groups from the prepolymer, intramolecular crosslinking, and microgelation. These factors are not taken into account in ideal network formation, which is the basis for many of the earlier theoretical models. Beyond the gel point, the reactivity of the system changes toward copolymerization of the gel with unreacted monomer and polymerization proceeds heterogeneously in later stages of the reaction. These microheterogeneities present further challenges for researchers.

Walling obtained reasonable agreement with Stockmayer’s equation for the critical conversion at gelation for both methyl methacrylate-ethylene glycol dimethacrylate (MMA-EDMA) and vinyl acetate-divinyl adipate systems. $P_w$ was approximated from the degree of polymerization of methyl methacrylate and vinyl acetate homopolymers. Polymerizations were carried out under the same conditions as the gelation experiments in order to obtain accurate values of $P_w$. Agreement between experimental gelation points and theoretically predicted values were only obtained when less than 0.2 mole% of the divinyl monomer was used. At higher divinyl monomer concentrations, Walling experimentally measured gel points which were higher than those predicted by Stockmayer’s equation. Walling attributed inconsistencies at higher fractions of the divinyl monomer to discrete swollen polymer molecules whose rate of diffusion was slower than that of polymer chain growth and to cyclization.

Dotson et al. used the Stockmayer equation (equation 2-5) in their study of methyl methacrylate and ethylene glycol dimethacrylate networks. Gelation was predicted for copolymer mixtures ranging from 0.111 to 0.819 mole fractions of double bonds on the divinyl molecule. The degree of polymerization of the primary chain, in this case, was obtained by measuring weight average molecular weight vs. conversion in the pre-gel region and extrapolating that data to zero conversion. In all cases, the predicted values for the critical extent of reaction at gelation was one order of magnitude larger than the experimentally calculated value. For example, the gel point for a polymer with a divinyl double bond mole fraction of 0.111 was found to occur at approximately 2.27 ± 0.08% conversion whereas the Stockmayer equation predicted gelation would occur at 0.140 ± 0.016% conversion.

In an investigation of the structure of diallyl phthalate prepolymer by Simpson et al., it was demonstrated that cyclization was an important phenomenon which had a major effect on gelation. Based on Simpson’s work, Gordon extended the network theory to account for the
conversion at gelation for a polymerizing monomer which undergoes cyclization. Gordon’s modification of the Stockmayer equation is given by:

\[(2-6)\]

\[ (1-bc) = 1- ((r(2P_w-3)-1)/(r(2P_w-3)+1))^2 \]

where \((1-bc)\) is the conversion of the monomer at the gel point and \(r\) is the fraction of monomer units having pendant double bonds in the polymer. The definition for \(P_w\) is the same as described in equation (2-5).

Gordon applied this equation to Simpson’s diallyl phthalate data and obtained good correlation between experimental and predicted gel points. The reactivity of all double bonds were assumed to be uniform. Gordon also tested this equation using networks formed from maleated polyethylene and methyl methacrylate. The experimental data from these studies agreed with prediction made according to equation (2-6).

Naghash et al. compared experimental gel formation data to a kinetic model to predict the free-radical crosslinking copolymerizations of a methyl methacrylate/ethylene glycol dimethacrylate and styrene/p-divinyl benzene comonomer system.\(^60\) Polymer gels contained varying amounts of crosslinker and solvent and were prepared by solution free-radical copolymerization. The structural characteristics of the gels were determined experimentally using gel fraction measurements after equilibrium swelling in toluene. The equilibrium volume-swelling ratio of the gel was calculated from the crosslink density of the gel and the polymer-solvent interaction parameter using Flory’s swelling equation.\(^61\)

The kinetic model used by Naghash et al. was applicable to free radical copolymerizations involving monovinyl monomers (MVM) and divinyl monomers (DVM). The model was able to distinguish between three types of vinyl groups with different reactivities on: MVM \((M_1)\), DVM \((M_2)\) and polymer chains (pendant vinyls) \((M_3)\) (Figure 2-19).\(^60\) In general, MVM-DVM copolymerizations are complicated, in that they involve three kinetically distinguishable radicals, four initiation, nine propagation and twelve termination reactions. Instantaneous rate constants for propagation and termination reactions were defined in order to simplify the kinetic treatment of the system. Now, the copolymerization system can be viewed as consisting of three propagation reactions with instantaneous rate constants \(k_{pi}\), where \(i\) is the type of vinyl group \(M_i\) involved in the reaction. Cyclization is not accounted for in this model.
However, the authors state that these reactions can be included in their kinetic model by using cyclization constants for primary and secondary cyclization. Although these multiple crosslinking reactions are significant in free radical copolymerization reactions\textsuperscript{62}, Naghash et al. suggested that they could be neglected due to low DVM concentrations (.23 and .46 mol %). The model also assumed steady-state concentration for the radicals in the reaction system and the validity of the limitations from the Flory lattice theory (section 2.5.2) and the theory of rubbery elasticity (section 2.5.2)\textsuperscript{64}. Overall, the model correctly predicted the development of the gel properties in free-radical crosslinking copolymerization. For highly crosslinked systems, the effect of cyclization reactions and the conversion dependence of the elementary rate constants (termination and crosslinking reactions) must be taken into account.

\[ p_{gel}^2 = \frac{1}{(1-f)(g-1)} \]
where \( f \) and \( g \) are the functionality of the two monomers. BMI monomer is difunctional with respect to copolymerization with amines and tetra-functional with respect to homopolymerization. Drawbacks to this approach include the fact that primary and secondary amines are treated as identical, even though the secondary amine (DDM) is much less reactive than the primary amine. Therefore, estimation of the gel point was not highly accurate.

Another approach by Fasce and Williams\(^{63}\) involved the calculation of gelation at 60% conversion in an equimolar BMI/diamine formulation, which was close to Flory’s estimation of 58%. This was unexpected since ideally, Fasce’s system consisted of two difunctional monomers, unlike Flory’s difunctional/tetrafunctional system. The authors explain the unexpected gelation as the influence of the homopolymerization reaction (of the BMI) on the crosslinking.\(^{63}\) In these relatively complicated cases, both Flory and Fasce developed models that characterized the overall conversion without taking the stoichiometric ratios of the monomers into consideration.
2.5 Characterization of Dimethacrylate Networks

2.5.1 Introduction

Glassy thermosets can have excellent mechanical, thermal, electrical, and chemical resistance properties which enable them to be used in structural applications. They can be designed with significantly improved toughness relative to ceramics and their densities are much lower than metals. Thermosets are three-dimensional polymer networks that lead to improved machinability, low rates of gas permeability, low mold shrinkage, and improved high-temperature performance compared to linear materials. Resin precursors to thermoset networks can often be designed to have low initial viscosities that permit the incorporation of large amounts of fillers or fibers, and this feature has led to the development of many low-cost fabrication processes. Additionally, thermoset networks can also offer reduced creep and improved solvent/stress crack resistance over thermoplastics.

Vinyl esters, unsaturated polyesters, epoxies, and phenolic and urea resins are major classes of matrix resins used worldwide for the fabrication of relatively low-cost fiber reinforced composites and for preparing coatings and adhesives. Although there is a wide range of properties obtainable with thermosetting resins, there are some general characteristics common to each class. Unsaturated polyesters are versatile in their processing characteristics; unsaturated polyesters can be processed by a variety of fabrication techniques. They are also used in many high-performance composite applications. Epoxies generally have better mechanical properties than unsaturated polyesters. Although epoxies can sometimes be processed by similar types of fabrication methods as unsaturated polyesters, they are usually more expensive, and therefore, are limited in their applications. Phenolics offer a combination of high-temperature and chemical resistance and low cost. Urea-formaldehyde and melamine-formaldehyde resins are widely used in the coatings industry. Their highly crosslinked nature yields materials with high hardness; these materials can also be dyed well to obtain a wide variety of colors. Vinyl esters yield products that have properties similar to the epoxies but are processed in manners similar to the polyesters. Despite the fact that many thermosets can be designed to have cure times less than 1 min at elevated temperatures, molding cycles for thermoplastics can generally be faster and their properties are often less affected by slight changes in operating conditions.
2.5.2 Crosslink Density

The chemical crosslinking in a thermoset polymer corresponds to the physical nature of the polymer’s cure. The crosslink density, which is related to the degree of cure, is a quantitative measure of the number of crosslinks that exist in a given volume in a thermosetting polymer. The degree of cure does represent a certain level of chemical crosslinking in the thermoset, but the numerical value obtained is relative. In other words, the uncured and fully cured states of the material must be defined to determine the degree of cure. Once these limits have been characterized, the degree of cure and the crosslink density are directly related. Since the crosslink density of a polymeric network is an absolute quantity, the only means by which the relationship between crosslink density and the degree of cure can be defined is from direct measurement of the crosslink density of the polymer network.

Dimethacrylate terminated oligomers have methacrylate groups at each end which, when cured, serve as crosslink points. The number of these crosslink points per unit volume is defined as the crosslink density. In the current systems, the crosslink point is defined as the intersection of 3 or more segments. The crosslink density is one of the most important structural factors controlling the properties of the cured network. Crosslink density can be controlled in vinyl ester resins by varying the concentration of the reactive diluent, controlling the final double bond conversion, and by changing the molecular weight of the precursor oligomers. There are several methods for determining the crosslink density of highly crosslinked thermoset materials. These include chemical methods, measurements of swelling in solvents, measurements of elastic moduli above the glass transition temperature, creep tests (for rubbers), mechanical damping (for rubbers) and shifts in glass transition temperatures.\textsuperscript{64}

Two of the most common techniques are solvent induced swelling and determination of the modulus at temperatures well above the glass transition temperature. The two thermodynamic phenomena that are observed with these two techniques include an increase of entropy of the network-solvent system by the introduction of small molecules as diluents, and a decrease of entropy of the polymer chains by the isotropic dilation. The Flory-Huggins lattice theory describes the first effect, i.e. the mixing of the polymer and the solvent or diluent. Solvent induced swelling can provide absolute values for crosslink density using equation (2-8),
when accurate values of the Flory-Huggins polymer-solvent interaction parameter ($\chi$) are available. $^{49,82}$ This parameter characterizes the interaction between the solvent and the polymer. A negative value indicates a good solvent, 0.5 represents the theta condition and higher values correspond to poor solvents. $^{64}$ Using this method, one must assume a perfect network with no elastically inactive chains or dangling ends. This is a typical method used for calculating $M_c$ values for vulcanized rubbers with $M_c$ around 5000 g/mole. For highly crosslinked networks with lower $M_c$ values, this method is not quantitatively accurate. However, qualitatively, the general trend still holds (networks with higher $M_c$ values swell more). To account for elastically inactive chains, or dangling ends, $M_c$ must be divided by a correction factor (1-2$M_c/M_n$). Flory has derived modifications of this equation for highly crosslinked systems. $^{49}$

$$\[ \ln (1-\nu_2) + \nu_2 + \chi \nu_2 \] = \left( V_1 / \bar{v}M_c \right) (1- (2M_c / M_n)) \left( \nu_2^{1/3} - \nu_2 / 2 \right)$$

$v_2$ is the volume fraction of polymer in the swollen polymer in equilibrium with the pure solvent
$V_1$ is the molar volume of the solvent
$\bar{v}$ is the specific volume of the polymer
$M_n$ is the number-average molecular weight of the polymer before crosslinking
$M_c$ is the number-average molecular weight between crosslink junctions

Dynamic mechanical tests can provide a rapid and very sensitive technique for determining crosslink density at temperatures well above $T_g$. For highly crosslinked networks, chain entanglements are not present and under small deformations, the relationship between crosslink density and the equilibrium elastic modulus can be expressed by using the kinetic theory of rubber elasticity. $^{64}$ This theory relates the equilibrium elastic modulus at temperatures well above the glass transition temperature to the density of crosslinks by
\[ G = \frac{r^2}{r_0^2} (dRT/M_c) (1-2M_c/M_n) \]

where \( G \) is the shear modulus of elasticity, \( d \) is the density, \( T \) is the absolute temperature, \( R \) is the gas constant, \( M_n \) is the molecular weight of un-crosslinked polymer, and \( r^2/r_0^2 \) is the ratio of the mean-square distance between network junctions to the mean-square end-to-end distance of network chains in free space. The \( r^2/r_0^2 \) term is often neglected since this ratio is generally about 1.0.

Aklonis and MacKnight made four assumptions concerning the statistical theory of rubber elasticity:

1) The internal energy of the system is independent of the conformations of the individual chains
2) An individual network is freely jointed and volumeless, and obeys Gaussian statistics
3) Crosslink junctions in the network are fixed at their mean positions, and upon deformation, these junctions transform affinely (in the same ratio as the macroscopic deformation ratio of the rubber sample) and
4) The total number of conformations of an isotropic network of such Gaussian chains is the product of the number of conformations of the individual network chains.

However, Nielsen has shown that the elastic moduli at temperatures well into the rubbery region are a good empirical method for characterizing crosslinked materials even when the assumptions described above are not valid. Lemay et al. neglected these assumptions based on the fact that densely crosslinked epoxy networks contradicted the assumptions of Gaussian statistics and negligible internal energy changes.

The unsaturated bonds on the termini of the vinyl ester oligomers copolymerize with a comonomer to form a crosslinked network similar to the curing reactions of unsaturated polyesters. Vinyl ester resins are similar to unsaturated polyester resins in that both systems contain styrene monomer as the reactive diluent. However, the physical properties of the vinyl
ester networks are, in general, superior to those of the unsaturated polyesters. This can be at least partially attributed to the fact that the vinyl esters have reactive double bonds only at the ends of the chains, while the unsaturated polyester resins have the reactive double bonds distributed throughout the chains. Thus, the crosslink density can be better controlled in the vinyl esters (Figure 2-20).

Figure 2-20. A comparison of idealized chemical structures of a vinyl ester and an unsaturated polyester network.

Although the vinyl ester resins have been used in industry for over thirty years, very little information is available in the literature on formation-structure-properties relationships in these networks. These networks are becoming increasingly important for fiber reinforced composites because their cure characteristics are compatible with rapid composite processing operations such as pultrusion and resin transfer (or resin infusion) molding. Their free radical cure mechanisms allow for good stability at low temperatures, yet rapid reaction at elevated temperatures. It is therefore of great interest to study and understand the structure and properties
of vinyl ester networks. A detailed study on the effect of crosslink density on the physical and mechanical properties of vinyl ester networks will be presented in Chapter 4.

2.5.3 Cure Shrinkage

Cure shrinkage is directly related to the volumetric contraction caused by linking many small monomeric molecules together to form a polymeric species. In free radically cured thermoset network formation, shrinkage inevitably results from converting double to single bonds. Although some double bonds remain unreacted due to immobilization caused by gelation, vitrification or steric isolation, there is still some shrinkage resulting from double bond conversion, which may cause service failures. This reduction in density is quite obvious in the polymerization of styrene to form polystyrene. Monomeric styrene at room temperature has a density of 1.09 g/cm$^3$ compared to polystyrene with a density of 0.9 g/cm$^3$, which corresponds to approximately 17% volume shrinkage.

As vinyl ester resins cure, the network becomes tighter, and thus, there is an increase in the density. Density is inversely related to the specific volume. Vinyl ester resins generally have lower volumetric shrinkage than unsaturated polyesters due to higher styrene concentrations in the polyesters. However, vinyl ester resins typically undergo approximately 6-9% volume contraction upon cure compared to epoxies which have approximately 3-4% volume shrinkage. Cure shrinkage can often lead to problems such as surface distortion, internal cracks and voids in the matrix material. This shrinkage can lead to residual stresses in fiber-reinforced composites and cause cracking and delamination.

Shrinkage during cure can be decreased by the addition of low profile thermoplastic polymeric additives. The initial step in the mechanism of volume shrinkage compensation due to low-profile additives in unsaturated polyester systems involves the phase separation of the low profile additives and the crosslinked polyester during the cure process. Many researchers believe that subsequent microvoid and/or microcracks occur at the interface between the low profile additive and the unsaturated polyester which leads to volume shrinkage compensation. Commonly used low profile additives includes polyvinyl acetate, and polycaprolactone.

Lee et al. used density measurements to investigate thickeners in the control of volumetric shrinkage of unsaturated polyester resins. Magnesium oxide (MgO) and methylene diphenyl diisocyanate (MDI) were employed individually as the thickeners in this study.
Rheological measurements showed that by using magnesium oxide (MgO), there was a slow viscosity build-up during thickening and the viscosity continued to change during storage. Upon heating, there was a substantial decrease in viscosity, but the initial viscosity was never reached. Phase separation occurred during cure and was attributed to decreased ionic bonding between MgO and the carboxyl groups of the polyester at the elevated temperatures. The shrinkage control of MgO thickened materials showed improvement over MDI thickened compounds, but were still not as good as unthickened compounds. However, when diketo compounds were grafted on, the MDI-thickened material showed a faster increase in viscosity during thickening, a stable viscosity control during thickening, and good shrinkage control during curing.

A dilatometer, designed and built by Lee et al., was then used to study effects of low profile additive concentrations and cure temperatures of the previously mentioned systems. They found that the optimum low profile additive concentration shifted to a high concentration when the heating rate was increased. This was consistent with findings by Atkins, in an evaluation of industrial processes using sheet molding compounds (SMC) (high reaction rate and temperature requirements), where a low profile additive similar to MDI was added to unsaturated polyesters. This study showed that an increase in heating rate improved the polymerization shrinkage control, regardless of the low profile additive concentration. They were also able to show a correlation between shrinkage control and polymer morphology of low profile unsaturated polyester resins. They found that the optimum shrinkage control correlated with a more loosely packed structure. The optimal isothermal morphology showed an irregular shaped particle.

Linear shrinkage according to equation (2-10), density, and dilatometry (similar to Lee et al.) were used to study the volume shrinkage in the cure of four “low-shrink” unsaturated polyester resins (cured at 110°C). Y. Huang’s investigation found that the fractional volume shrinkage decreased linearly with increasing low profile additive concentration. Of the four low profile additives used, the order of shrinkage control was polyvinyl acetate, followed by polymethylmethacrylate and polystyrene. The shrinkage control behavior of a thermoplastic polyurethane was dependent on its concentration. The three techniques correlated well.
\[
\Delta V/V_o = (1 + \Delta l/l_o)^3 - 1
\]

1 is the length
V is the volume
\(\Delta l/l_o\) is the linear shrinkage
\(\Delta V/V_o\) is the volume shrinkage

\(l_o\) and \(V_o\) are the linear dimension and volume of the mold into which the samples were poured

2.5.4 Mechanical Properties

The properties of fiber reinforced engineering thermosetting matrix resins allow them to be used in many structural applications as alternatives to metallic or ceramic materials. Compared to ceramics, thermoset engineering plastics offer lighter weight, better toughness, and easier processing. One limitation of thermosets is their relatively poor impact resistance.

Vinyl esters are used in numerous structural composite applications due to their excellent mechanical properties. Some typical room temperature properties of a 700 g/mole vinyl ester oligomer with 28 weight percent styrene are listed Table 2-1.\textsuperscript{77} The first column lists properties of the neat matrix material. Generally, fabrication into a composite requires the addition of carbon or glass filaments or a hybrid or both. The second column gives the properties of the same vinyl ester matrix material filled with 40 weight percent glass filaments. The laminate described in column two is ¼ inch thick. Both columns one and two reflect the properties of the material cured at room temperature followed by a 93\(^0\)C postcure. It is instructive to note that these properties are dependent on the cure procedure. Chapter 4 of this manuscript discusses the effect of the cure procedure on the physical and mechanical properties of these matrices.
Table 2-1. Typical room temperature properties of vinyl ester resins and laminates.

<table>
<thead>
<tr>
<th>Property</th>
<th>Neat Resin</th>
<th>Laminate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, psi</td>
<td>13,000</td>
<td>21,500</td>
</tr>
<tr>
<td>Tensile modulus, units $10^5$ psi</td>
<td>5.2</td>
<td>13.4</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>7-8</td>
<td>--------</td>
</tr>
<tr>
<td>Flexural strength, psi</td>
<td>24,000</td>
<td>21,800</td>
</tr>
<tr>
<td>Flexural modulus, units $10^5$ psi</td>
<td>5.1</td>
<td>11.5</td>
</tr>
<tr>
<td>Heat Deflection Temperature, °F</td>
<td>245</td>
<td>--------</td>
</tr>
<tr>
<td>Barcol Hardness</td>
<td>35</td>
<td>--------</td>
</tr>
</tbody>
</table>

The degree of brittleness of glassy polymers is reflected by the amount of flow that occurs during the failure process, either microscopically or macroscopically. Flow occurs microscopically via crazing or shear banding and macroscopically via necking. This flow absorbs energy during failure and decreases the brittleness of the glassy polymer. The flow process involved in the failure mechanism is affected by the movement of polymeric chain segments past one another and the alignment of ordered regions. The amount of flow is also affected by:

1) chemical composition
2) molecular weight
3) degree of crosslinking
4) low molecular weight additives
5) the number, size and size distribution of microvoids
6) the presence of fillers
7) fabrication stresses and
8) types of stress fields applied to the polymer glass.\textsuperscript{78}
The toughness of thermoset materials such as epoxy networks, unsaturated polyesters and vinyl esters can be improved by incorporating elastomeric modifiers. The elastic modifiers are small rubbery domains of a definite average size which can be formed in situ during cure. Rubber particles toughen a glassy thermoset by easing the crack growth in the glassy regime. These elastomers must: 1) have reactive functional groups; 2) be miscible in the precursor resin before cure; and 3) precipitate and form a uniformly distributed elastomeric microphase (e.g., spheres of about 25 µm average diameter) in the thermosetting matrix. Carboxyl-terminated copolymers of butadiene and acrylonitrile (CTBN) are one group of rubber components that are widely used as reactive modifiers for thermosets. Alternatively, preformed rubbery particles with defined sizes can be dispersed in the precursor resin.

Both approaches serve to increase the impact and crack resistance. Small particles (<0.5 µm) normally lead to shear deformation as the dominant mode of failure. However, crazing is associated with microvoid development around the rubber particles when larger particles (1-5 µm) are used. Maximum toughness can often be obtained under conditions of combined shear and craze deformation. This condition is usually obtainable with a bimodal distribution of particle sizes.

Pham and Burchill used low molecular weight modified polybutadienes to toughen vinyl ester resins. Due to the incompatibility of the vinyl ester resin with hydroxyl-terminated polybutadiene, the polybutadiene was copolymerized with 17.5% acrylonitrile. By adding only 5% of the modified rubber to Derakane 411-45, there was a 2-3-fold increase in the stress intensity factor \( K_{1c} \) (0.72 MPa-m\(^{1/2} \)) and a 10-fold increase in the energy required for fracture \( G_{1c} \) (157 J/m\(^2 \)). However, there was a decrease in the glassy modulus and \( T_c \). Scanning electron micrographs were used in the analysis of the blends, and showed that appreciable amounts of styrene and a lesser amount of the methacrylate component react with the rubber to give a volume fraction of dispersed phase 2-3 times greater than the original addition of liquid rubber. The increase in toughness was attributed to the greater volume fraction of the dispersed phase (11%) and a reduction in the dispersed phase particle size (from 20.7 to 5.6 µm). The particles in this study were large and had a broad size distribution, however, optimum toughness was achieved for particles less than 5 µm.

Auad et al. conducted compression tests (at room temperature) with epoxy-based divinyl resins (a polyhydroxy ether of bisphenol A encapped with methacrylic acid) with styrene
concentrations varying from 3.4 to 80 weight %. The $M_n$ of the epoxy-based divinyl resin (measured by GPC using polystyrene calibration) was approximately 583g/mole. Increased amounts of styrene resulted in decreased crosslink density in the copolymers. It was found that as the concentration of styrene increased, inhomogeneous shear deformation changed from very localized to a more diffuse region, leading to brittle fracture. At very low styrene concentrations (<20 weight %) there was considerable plastic deformation before fracture took place. The yield stress also increased with increased crosslink density (decreased styrene concentration) of the material. This relationship between crosslink density and properties will be addressed in the following section.

2.5.5 Structure Property Relationships

This section will address the effect of crosslinking on various physical and mechanical properties such as toughness, modulus, density and creep. Due to the complexity of thermoset network systems, it is difficult to evaluate their properties. Networks are not perfect due to ineffective intramolecular crosslinks in the form of polymer loops or branches. These imperfections usually show up in mechanical tests in the form of reduced modulus and strength. For example, submicroscopic cracks due to internal stress can severely decrease the tensile strength of polymers.64

Incorporating crosslinks into a polymer can be achieved by various means. Crosslinking agents can be introduced and in some cases, a reactive comonomer can be used. Due to the numerous comonomers and crosslinking agents available, networks can often be complex and varied in nature. Another possible problem in thermosetting polymers is the fact that the chemical structure of the polymers changes simultaneously with the degree of crosslinking and it becomes difficult to decide the cause of the observed effects.

It is well known that the stress-strain behavior of polymers shows pronounced variation with crosslinking. There is usually a maximum in tensile strength and toughness as a function of crosslink density. A certain degree of crosslinking is necessary to achieve network integrity, but highly crosslinked systems become very brittle and the properties are diminished. In a study of polystyrene crosslinked by divinyl benzene, the tensile strength increased from 6700 ksi with no
crosslinking to 7400 ksi at 4% divinyl benzene. However, the tensile strength drastically decreased to 1000 ksi at 25% divinyl benzene.81

Crosslinking can be incorporated into polymeric systems to reduce creep (the elongation or deformation over time under an applied load). Crosslinking has a greater effect on creep over extended periods of time. At short times, entanglements can act as temporary crosslinks in rubbery materials and decrease the elongation. Creep is reduced in highly rigid systems at long times and temperatures much higher than the glass transition temperature. The creep rate also decreases as the amount of crosslinking increases. However, at temperatures well below the glass transition temperature, crosslinking has virtually no effect on creep in polymers. Due to “frozen molecular motions” in rigid brittle polymers, additional crosslinks are usually unnoticeable. In general, thermosets such as phenol-formaldehyde and melamine resins have high modulus values, low mechanical damping, and high glass transition temperatures which tend to reduce creep and creep rate. Some epoxy, polyester and vinyl ester resins may have increased creep due to low-temperature, secondary glass transitions, resulting in reduced shear modulus values.

Crosslinking also affects the specific volume of polymers. For both rubbers and rigid polymer, the specific volume decreases nearly linearly with increasing crosslink density:

\[ v = v_o - \kappa \rho \] (2-11)

where \( v \) is the specific volume of the crosslinked polymer, \( v_o \) is the specific volume of the uncrosslinked polymer, and \( \kappa \) is a constant and \( \rho \) is the number of moles of crosslinking agent per gram of crosslinked polymer.64

There is a similar equation for the coefficient of thermal expansion:

\[ \alpha = \alpha_o - \kappa' \rho \] (2-12)

where \( \alpha \) is the coefficient of thermal expansion for the crosslinked material, \( \alpha_o \) is the coefficient of thermal expansion for the uncrosslinked material and \( \kappa' \) is an empirical constant. It should be noted that there is a different set of \( \kappa \) and \( \kappa' \) values above and below \( T_g \) for both the coefficients of thermal expansion and specific volumes.84
Crosslinking simultaneously increases the $T_g$ and broadens the transition region making it less and less distinct as crosslinking progresses. Dynamic mechanical tests (damping) provide a sensitive yet rapid means of measuring the amount of crosslinking above $T_g$, whereby the data can be interpreted using the kinetic theory of rubbery elasticity. At low degrees of crosslinking, shifts in $T_g$ upon crosslinking are minimal, but at high degrees, the shift can be quite large and is sensitive to even small changes in $M_c$ ($\sim 1/$crosslink density). Below $T_g$ where the polymer is rigid, crosslinking has very little effect on the modulus (at temperatures well below the damping peak). When the temperature exceeds the damping peak, the modulus is strongly dependent upon the degree of crosslinking. One study that illustrates this point was done using phenol-formaldehyde networks. Moreover, it was found that this large increase in modulus was much more dependent on crosslinking than the kinetic theory of rubber elasticity predicted. Along with changes in modulus, there is also a shift to higher temperatures and a broadening in the damping peak. This broadening is not only due to crosslinking, but also to the heterogeneity in the crosslinked structure.

A thorough study by Ogata et al. described the effect of crosslink density on numerous physical properties of phenol-formaldehyde novolac cured epoxy resins. In summary, it was found that as the crosslink density increased, the $T_g$ increased and the relaxation time became longer. In the rubbery region, as the crosslink density increased, the coefficient of linear thermal expansion decreased and the elastic modulus increased. In the glassy region, the coefficient of linear thermal expansion, the specific volume, water absorption, diffusion coefficient, and permeability increased while the elastic modulus decreased.

Overall, crosslinks impart rigidity into a polymer system and provide added dimensional stability. However, excessively high degrees of crosslinking have an adverse effect. High levels of crosslinking can cause a polymer to become very brittle and the strength, toughness, and elongation are greatly reduced. Although thermally these materials are suitable for many high temperature applications due to a high $T_g$, brittle materials are still severely limited based on their mechanical properties.

In a study by Zawadzki and Sereda, the mechanical behavior of polymethylmethacrylate networks was evaluated based on varying degrees of crosslink density. In this work, methylmethacrylate was copolymerized with ethylene glycol dimethacrylate to assess the effect of crosslink density ($1/M_c$) on the flexural strength and impact resistance. It was shown
that both of these mechanical properties increased in value with decreased crosslink density. Flexural strength increased 22.2% and impact resistance increased 71.4% when $M_c$ increased from approximately 600 to 3000 g/mole.

Mechanical properties are also affected by varying the crosslink density through the cure procedure. This issue will be addressed in detail in this present study (Section 4.3). Ziaee and Palmese\textsuperscript{48} noted that isothermal cure temperature had a significant effect on physical and mechanical properties of vinyl ester/styrene resin systems. Properties were examined based on a vinyl ester/styrene resin system (Derakane 411-C-50) with $M_n=554$ g/mole with 45 weight percent styrene cured at 30°C and 90°C and postcured at 125°C. The initiating system included cobalt naphthenate (.43 weight %), a proprietary carboxylic ester (45 weight %), and cumyl hydroperoxide (45 weight %). A three-point bend flexural test, a tensile test, and a fracture toughness test were conducted based on ASTM standards. Their results, summarized in Table 2-2 and Table 2-3, confirm that the initial cure temperature affects the mechanical behavior of vinylester resins.

Table 2-2. Summary of tensile and flexural properties of cured vinyl ester resin 411-C-50.\textsuperscript{48}

<table>
<thead>
<tr>
<th>Curing Cycle</th>
<th>30°C Cure</th>
<th>30°C Cure; 125°C Postcure</th>
<th>90°C Cure</th>
<th>90°C Cure; 125°C Postcure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus (ksi)</td>
<td>453.6 ± 2.3</td>
<td>486.6 ± 10.2</td>
<td>497.1 ± 4.5</td>
<td>510.3 ± 7.0</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>0.407 ± 0.014</td>
<td>0.375 ± 0.009</td>
<td>0.353 ± 0.002</td>
<td>0.373 ± 0.011</td>
</tr>
<tr>
<td>Strength (psi)</td>
<td>7810 ± 190</td>
<td>8870 ± 470</td>
<td>7730 ± 500</td>
<td>6140 ± 410</td>
</tr>
<tr>
<td>Strain at break (%)</td>
<td>15.20 ± 1.23</td>
<td>5.26 ± 0.51</td>
<td>5.16 ± 0.41</td>
<td>3.36 ± 0.42</td>
</tr>
<tr>
<td>Flexural strength (Ksi)</td>
<td>14.8 ± 0.0</td>
<td>23.3 ± 0.6</td>
<td>19.2 ± 0.8</td>
<td>19.6 ± 0.6</td>
</tr>
<tr>
<td>Modulus of elasticity in Bending, $E_m$ (ksi)</td>
<td>448 ± 4</td>
<td>591 ± 18</td>
<td>433 ± 35</td>
<td>443 ± 27</td>
</tr>
</tbody>
</table>

Tests were conducted at room temperature at a crosshead speed of 0.05 in./min. The reported error for each value is one standard deviation.
Table 2-3. Results from three-point bending fracture toughness testing of cured vinyl ester resin 411-C-50.\(^{48}\)

<table>
<thead>
<tr>
<th>Cure Condition</th>
<th>Plane-Strain Fracture Toughness (MPa m(^{0.5}))</th>
<th>Critical Strain Energy Release Rate (J/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C Cured &amp; 125°C postcured</td>
<td>0.87 ± 0.11</td>
<td>116 ± 14</td>
</tr>
<tr>
<td>90°C Cured</td>
<td>1.07 ± 0.11</td>
<td>82 ± 2</td>
</tr>
<tr>
<td>90°C Cured &amp; 125°C postcured</td>
<td>0.91 ± 0.06</td>
<td>41 ± 6</td>
</tr>
</tbody>
</table>

The experiments were performed at room temperature at a crosshead speed of 0.05 in./min. The reported error for each value is one standard deviation.

2.5.6 Chemical Resistance and Water Absorption

Vinyl ester networks resist a range of chemicals, from strong acids to strong alkalis. Vinyl esters have better chemical resistance than unsaturated polyester resins, especially as it relates to water and most aqueous solutions. The greater degree of corrosion resistance in vinyl esters is attributed to the fact that their ester linkages are only at the ends of the chains, while the unsaturated polyester resins have ester linkages within the repeat units (Figure 2-20). These ester groups are the most vulnerable part of the resin since they are subject to hydrolysis. Therefore, the attack can occur only at these terminal sites for vinyl esters, leaving the backbone of the molecule unaffected. Thus, methacrylate vinyl esters are more resistant to chemical attack. Another basic factor that explains the excellent corrosion resistance of vinyl esters over unsaturated polyesters is that the vinyl groups are very reactive, and complete cure of the backbone is easily accomplished. The addition of styrene as a diluent and comonomer also decreases water absorption due to the hydrophobic nature of styrene.

Crosslinking can also serve to decrease the absorption and swelling of polymers in solvents which have some affinity for the polymer. A classic demonstration of this was done by H. P. Wohnsiedler et al. with melamine\(^{86}\) in water. The water absorption decreased with increasing extent of cure. Since the volume of the polymer will increase nearly equal to that of the volume of absorbed liquid,\(^{87}\) the degree of crosslinking must be high to suppress the swelling and prevent fracture into numerous pieces.
Vinyl esters are steadily finding uses in applications involving corrosive environments. Corrosion-resistant reinforced plastics based on vinyl esters and other resins are continuously being used to replace traditional materials such as glass, steel, concrete and brick in many applications. Bisphenol-A-fumarate based and chloroendic-acid based unsaturated polyester resins are being used in applications similar to vinyl esters. With the exception of filament-wound pipe, epoxy resins have not traditionally been used in this market due to high viscosity, long cure cycles and the toxicity of the crosslinking reagents. Vinyl esters prepared from epoxidized novolacs have often been used to improve solvent resistance due to their increased crosslink densities. As discussed in section 2.2, halogenated epoxy precursors, such as the fluorinated epoxies, also improve hydrophobicity in vinyl ester resins.

2.5.7 Thermal and Oxidative Stability

Vinyl esters have relatively good thermal performance compared to epoxy and polyester resins. However, due to the organic nature of vinyl ester resins, they will burn if placed under the right conditions of heat and oxygen. At temperatures of around 300°C, both unsaturated polyester and vinyl ester networks will undergo spontaneous decomposition. This is a characteristic of aliphatic polymers and can be related to the relatively low bond strength of the aliphatic C-H vs. aromatic C-H bonds. Additionally, some linear vinyl polymers can depolymerize to monomers and other oligomeric species at elevated temperatures due to the temperature exceeding the polymer’s ceiling temperature.

Epoxidized novolacs have been used as precursors to react with methacrylic acid and prepare vinyl ester oligomers with multiple methacrylate reactive sites along the chain. The utility of such resins has been to provide highly crosslinked materials to improve the heat and high-temperature corrosion resistance of vinyl esters. Due to increased aromatic content and more crosslink sites in pendant positions along the backbone, these materials have \( T_g \)s 30 to 50°C higher than conventional vinyl esters. Compared with bisphenol-A-epoxy-based vinyl ester resins, these epoxidized novolac-based vinyl esters are often classified as “higher-temperature networks.” Brominated epoxy precursors and bisphenol F based resins have
improved flame retardance over the bisphenol A based resins, as well. (see discussion in section 2.2).

2.6 Applications

Thermosetting resins can be used in numerous applications. However, the largest single market is construction, which consumes approximately half of the resin production. Other applications include adhesives for plywood and particle board, binders for insulation, coatings, matrix resins for laminates and molding compounds. Although engineering plastics have considerably good mechanical properties, they lack the strength and stiffness of metals. Therefore, nearly all thermoset-engineering plastics contain particulate or fibrous reinforcements.

The applications for vinyl ester resins vary widely; however, these dimethacrylate terminated oligomers diluted with styrene, the so-called “vinyl esters,” form one of the major classes of matrix resins used in fiber reinforced composites. Fiber reinforced polymer matrix composites for structural applications are comprised of long or continuous fibers embedded in a polymer matrix (usually a thermoset material). Such composites have high strength to weight ratios and excellent corrosion resistance relative to steel. The function of the matrix is to protect the brittle reinforcing fibers and to transfer load to the fibers (Figure 2-19). Other commonly employed polymer matrix materials include thermosets such as epoxies, unsaturated polyesters and selected thermoplastics such as polyether ether ketone, polyethylene terephthalate, and polyphenylene sulfide.

Carbon fibers, primarily derived from pyrolysis of poly(acrylonitrile), impart high stiffness to the composite with a density of 1.8 g/cm³. In many aerospace and civil applications, other fiber types include ceramic, E-glass, aramids (kevlar) and high molecular weight polyethylene (Spectra).

A third constituent of the composite, the “interphase”, can drastically affect composite performance. The interphase is a region of finite mass located at the fiber/matrix interface. This region promotes the adhesion of the fiber to the matrix and has gradients in physical properties that greatly influence the performance of the final composite. One method to modify and control the physical properties of this interphase region is by applying a coating (sizing)
material to the surface of the fibers prior to impregnation with the matrix material. Applications for the composites include boats, automotive components, fascia for buildings, ladders, etc. More recently, these resins are being introduced into structural components in bridges, off-shore oil platforms, and boxcars. In addition to these applications, vinyl esters are also finding use in coatings, adhesives, molding compounds, structural laminate, electrical applications, and military/aerospace applications.

The cure procedure generally dictates the type of application for which these materials would be suitable. Composites prepared with these resins can be processed in relatively rapid molding operations such as pultrusion or resin transfer molding. They can also be sprayed onto pre-forms for boats, and bath and shower components. When vinyl ester resins are cured at room temperature, they can be used for the fabrication of cylindrically shaped parts, such as pipes, tanks, and ducting, or they can be used for fabricating very large parts using slower processes such as vacuum assisted molding (e.g., the SCRIMP process). The low initial viscosities of the “vinyl ester resins” coupled with the wide range of curing schedules obtainable make them attractive for such processes.

![Geometry of the Inter-fiber Region](image)

**Role of Matrix**
- bonds and holds filaments in place
- protects filaments
- provides transverse strength
- provides interlaminar toughness
- provides durability

**Role of Fibers**
- carries in-plane loads
- provides stiffness and strength

Figure 2-21. Composite components and their functions.
A recent application of vinyl ester/styrene composites as reinforcement materials involves the rehabilitation of a vehicular bridge. The Tom’s Creek Bridge (Figure 2-22) is located in Blacksburg, Virginia and was rehabilitated in June of 1997. In the design for the new bridge, 12 steel stringers were replaced with 24 composite beams. The 2-for-1 replacement was necessary because the shorter composite beams have a significantly lower modulus than the deeper steel beams. It is important to note that this bridge design is not optimum, as the composite beams were not designed for this particular application. However, this project still represents a unique opportunity to implement composites in a vehicular bridge and to study the durability of these materials in a low risk situation.\(^{91}\)

The driving force for this work stemmed from the fact that there are between 550,000 to 600,000 U.S. bridges, and approximately one third of them have been labeled “structurally deficient” or “functionally obsolete.”\(^{91}\) However, this will prove to be a very costly nation-wide project since the estimated repair cost is approximately 50 billion dollars annually.\(^{91}\) For more information on the Tom’s Creek Bridge Project, visit Professor J. J. Lesko’s (Virginia Polytechnic Institute and State University) web site at the following address: http://www.vt.edu:10021/eng/esm/jlesko/tcb/tcb.html.

![Figure 2-22. Tom’s Creek Bridge (front and side view)](image-url)
As fiber reinforced polymer matrix composites find greater use in markets such as civil infrastructure and ground transportation, the expectations placed on these materials are ever increasing. The overall cost and reliability have allowed polymers such as polyester and vinyl ester to replace resins such as bismaleimides (BMI), cyanate esters and other high performance polyimides and epoxies.

Epoxy resins used in composite applications are classified as either high performance aerospace, general purpose, or electrical. High performance-aerospace applications use specialty epoxy resins and curing agents, and are designed to provide excellent elevated-temperature resistance and good mechanical properties. Often TGMDA epoxies resins are used in this capacity. DGEBA is the preferred material for use as a general-purpose composite. Aromatic and aliphatic amines or anhydrides can be used since they provide the best compromise between cost and performance. Typical applications include pipes, automotive accessories, and sporting goods. One important application in the electrical area includes printed circuit boards. Generally, a halogenated epoxy is used to meet the flame retardancy requirement.

Since vinyl ester resins have excellent chemical resistance and lower water absorption, compared with polyester resins, they can also be used in applications ranging from electro-refining tanks to swimming pools. Novolac epoxy-based resins with their higher glass transition temperatures, are used in chemical storage vessels and chemical reactors. Modified DGEBA resins are used where improved adhesion, wear resistance, and fracture toughness are required.
CHAPTER 3. EXPERIMENTAL

3.1 Materials

3.1.1 Dimethacrylate (Vinyl ester) Oligomers

The methacrylate-terminated polyhydroxyether oligomers were kindly supplied by the Dow Chemical Co. These oligomers with controlled molecular weights and molecular weight distributions, were the reaction products of epoxy-terminated polyhydroxyethers derived from bisphenol-A and epichlorohydrin endcapped with methacrylic acid (Figure 1-1).

3.1.2 Benzoyl peroxide

Benzoyl peroxide (BPO) (Aldrich): m.p. 104-106 °C, FW 242.23. Benzoyl peroxide was used as a free-radical polymerization initiator for the vinyl ester oligomers and styrene copolymerization. The one-hour half-life decomposition temperature of benzoyl peroxide is 92°C and the 1-min half-life temperature of benzoyl peroxide is 131°C.92 BPO was used as received (Figure 3-2).

![Benzoyl peroxide initiator](image)

Figure 3-1. Benzoyl peroxide initiator.

3.1.3 Styrene monomer

Styrene monomer (Aldrich): m.p. -31 °C, b.p. 145-146 °C, FW 104. Styrene was used as a solvent and reactive comonomer for network formation of the vinyl ester resins. It was passed through a neutral alumina column to remove inhibitors before mixing with the methacrylate-terminated polyhydroxyether oligomers (Figure 3-3).
3.1.4 Methyl ethyl ketone peroxide

Methyl ethyl ketone peroxide (2-Butanone peroxide) (MEKP) (Aldrich): 32 wt % solution in dimethyl phthalate, b.p. 110 °C. Commercially available MEKP is a mixture of several oligomers produced by the reaction of methyl ethyl ketone (2-butanone) and hydrogen peroxide (Figure 3-4). The most readily synthesized oligomers of MEKP exist in the monomeric and dimeric forms. MEKP was used to initiate free radical copolymerization cures at ambient temperatures. MEKP was used as received.

\[
\begin{align*}
\text{O} & \quad \text{R}^1 \quad \text{R}^2 \\
\text{C} & \quad \text{H}_2\text{O}_2 \\
\text{R}^1 \quad \text{C} & \quad \text{R}^2 \\
\text{OOH} & \quad \text{OOH} \\
\end{align*}
\]

Monomer

\[
\begin{align*}
\text{R}^1 & \quad \text{R}^1 \\
\text{HOO} & \quad \text{C} \quad \text{OO} \quad \text{O} \quad \text{OOH} \\
\text{R}^1 & \quad \text{R}^1 \\
\text{R}^2 & \quad \text{R}^2 \\
\end{align*}
\]

Dimer

Figure 3- 3. Formation of monomer and dimer species in the synthesis of methyl ethyl ketone peroxide.

3.1.5 N, N-Dimethylaniline

N, N-Dimethylaniline (DMA) (Aldrich): FW 121.18, b.p. 193-194 °C, m.p. 1.5-2.5 °C.

DMA is a tertiary amine and was used as an accelerator to promote the decomposition of the MEKP or BPO at ambient temperatures (Figure 3-5). DMA was used as received.
3.1.6 Cobalt Naphthenate

Cobalt Naphthenate (CoNap) (Alfa Aesar): approximately 53% in mineral spirits,
CoNap was used as an accelerator to promote the decomposition of MEKP at ambient
temperatures. The cobalt naphthenate solution was used as received.

3.1.7 Dichloromethane

Dichloromethane (methylene chloride) (CH$_2$Cl$_2$) (Burdick and Jackson--Allied Signal): b.p. 39.8-40°C, m.p.-97 °C, FW  84. Methylene chloride was used as a solvent in swelling
experiments and in the synthesis of the linear mono-methacrylate model monomer. Methylene
chloride was used as received.

3.1.8 Sodium Chloride Plates

Sodium Chloride Plates (NaCl) (International Crystal Laboratories).
NaCl crystal plates were used for studying the cure reactions of vinyl ester resins by Fourier
Transform Infrared Spectrometry. In order to recycle the NaCl crystals plates, they were placed
in an oven at 450°C for 4 hours to remove the crosslinked polymer films. Then the NaCl crystals
were washed with acetone, dried at 90°C and stored in a dessicator until used again.

3.1.9 Deuterated Chloroform

Deuterated Chloroform (CDCl$_3$), (Aldrich) Gold Label 99%, was used as an NMR
solvent as received.
3.1.10 Glycidyl Methacrylate

Glycidyl Methacrylate (Aldrich): FW 142.15, b.p. 189°C.

Glycidyl Methacrylate was used as received as a reactant in the synthesis of the linear mono-methacrylate model compound (Figure 3-6).

![Glycidyl Methacrylate](image)

Figure 3-5. Glycidyl Methacrylate.

3.1.11 4-Cumylphenol

4-Cumylphenol (Aldrich): FW 212.29, m.p. 74-76, b.p. 335

4-Cumylphenol was used as received, as a reactant in the synthesis of the linear mono-methacrylate model compound (Figure 3-7).

![4-Cumylphenol](image)

Figure 3-6. 4-Cumylphenol.

3.1.12 Benzyltrimethylammonium chloride

Benzyltrimethylammonium chloride, (Aldrich): FW 185.70, m.p. 239

Benzyltrimethylammonium chloride (.0245g, .000132 mole) was evaluated as a phase transfer catalyst in the synthesis of the linear mono-methacrylate model compound (Figure 3-8).

![Benzyltrimethylammonium chloride](image)

Figure 3-7 Benzyltrimethylammonium chloride
3.1.13 Sodium Hydroxide

Sodium Hydroxide (NaOH) (Mallinckrodt): FW 40

Sodium hydroxide was used as received in the pellet form as a base in the synthesis of the mono-methacrylate model compound.

3.1.14 Magnesium Sulfate

Magnesium Sulfate (MgSO₄) (Mallinckrodt): FW 120.37

Anhydrous Magnesium Sulfate was used as received in the powder form as a drying agent in the syntheses of the mono-methacrylate model compound.

3.2 Preparation and cure of dimethacrylate resins

The neat solid methacrylate terminated polyhydroxyether oligomers were diluted with systematically varied amounts of styrene ranging from 20 weight percent to 50 weight percent. The oligomer was dissolved in the styrene at 50°C, then was allowed to cool to room temperature. After the resin mixture reached room temperature, 1.1 wt. % of benzoyl peroxide was added to serve as a reaction initiator. Constant stirring was carried out until a homogeneous mixture was formed. After the benzoyl peroxide was dissolved in the resin mixture, oxygen was removed using a freeze-thaw technique, with the resin under vacuum. The mixture was then poured into a silicone rubber mold, covered with an aluminum plate and cured in an oven at 140°C for one hour.

For resins cured at room temperature, the following amounts of initiators and accelerators were added in the order listed: 0.15 weight percent of the cobalt naphthenate solution, 0.04 weight percent of dimethylaniline, and 1.13 weight percent of methyl ethyl ketone peroxide. After the addition of each reagent, the mixture was stirred by hand. The reader is cautioned to work rapidly in order to prevent premature reaction before the mixture is charged to the mold. Upon the addition of the final reagent, the resin was poured into a silicone rubber mold and allowed to react for approximately 10 hours at room temperature. The networks were then postcured at either 93°C or 140°C for 2 hours. For postcuring, the networks were placed in the oven at ambient temperature, then the temperature was ramped to the postcure temperature at approximately 5-7°C/minute.
3.3 **Synthesis of the mono-methacrylate model compound**

Cumylphenol (2.81g, .0132moles) and glycidyl methacrylate (1.876g, .0132moles) were added to a 1-neck round bottom flask with a magnetic stir bar and co-dissolved at 40°C using a controlled-temperature oil bath. Approximately 10 mole percent sodium hydroxide (.0528g, .00132mole) was dissolved in water (ml) (10% solution). The temperature of the reaction mixture was raised to 70°C, and the sodium hydroxide solution was added drop-wise over a period of one hour. The reaction mixture was left open to air (oxygen serves as an inhibitor against premature polymerization of the methacrylate group on the glycidyl methacrylate) and allowed to stir for 48 hours. The crude product was dissolved in methylene chloride and then washed twice with H₂O. The organic layer was separated, dried over magnesium sulfate and filtered. The solvent was removed by rotary evaporation. The yields were 93-95% (Figure 3-9).

![Figure 3- 8 Mono-methacrylate model compound](image)

3.4 **Polymerization of the mono-methacrylate model compound with styrene**

The mono-methacrylate model compound was diluted with 28 weight percent styrene at room temperature. Then, 1.1 wt. % of benzoyl peroxide was added to serve as a reaction initiator. Constant stirring was carried out until a homogeneous mixture was formed. The mono-methacrylate/styrene mixture was polymerized at 140°C up to 12 hours to monitor the percent double bond conversion.

3.5 **Characterization**

3.3.1 **Proton Nuclear Magnetic Resonance Spectroscopy (¹H NMR)**

¹H NMR spectra were collected using a Varian Unity 400 instrument operating at 400 MHz. Proton NMR confirmed that the molecular weights of the vinyl ester oligomers were approximately 700, 900, 1000 and 1200 g/mole. The integrals of the peaks corresponding to the methyl groups of bisphenol-A (1.65 ppm) and for the methacrylate methyl endgroups (2.0 ppm)
were used to calculate these molecular weights. $^1$H NMR was used to confirm the compositions of resin blends by ratioing the integrals for the peak resonances for styrene vinyl protons (5.62 and 5.10 ppm) to methacrylate vinyl protons (6.02 and 5.46 ppm). $^1$H NMR was also used to verify the synthesis of the linear methacrylate monomer.

3.3.2 Epoxy Titration

Internal epoxy titration measurements were used to determine the epoxy equivalent weight of the precursor oligomers. The measurements were based on ASTM D1652-90 Test Method B "Standard Method for Epoxy Content of Epoxy Resins." The titrations were conducted using a Brinkmann Titrator Model 702 Automatic titrator using a standard pH electrode. The reagents for the epoxy titration: 0.10 N perchloric acid in glacial acetic acid, 100 g of tetraethyl ammonium bromide in 400 ml glacial acetic acid and 0.1% w/w crystal violet in glacial acetic acid. The endpoint of the epoxy terminated oligomers was determined by the autotitrator. The titration measurements were done by Dow Chemical Company.

3.3.3 Gel Permeation Chromatography (GPC)

Gel permeation chromatography was used as a tool to study polymer number- and weight- average molecular weights and molecular weight distributions. Dimethacrylate resins were analyzed using a Waters R-401 gel permeation chromatograph equipped with a Waters microstyrigel HR column set (10$^3$ and 10$^4$ Å) in chloroform at 30°C using a differential refractometer detector. Chromatograms were analyzed using TriSEC GPC Software (version 3.0) by Viscotek Corporation. The mobile phase was THF with a flow rate of 1 ml/min and the injection volume was 20 µl.

3.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were collected using a Nicolet Impact Model 400 instrument equipped with a controlled temperature cell (Model HT-32 heated demountable cell (Figure 3-9) used with an Omega 9000-A temperature controller). The initiator was dissolved in the dimethacrylate oligomer-styrene mixtures and oxygen was removed using a freeze-thaw technique. One drop of the material was placed between two NaCl windows which were then placed in a preheated controlled temperature cell in the FTIR. Eight scans were collected per spectrum. The time
between collection of spectra varied from one minute to 12 hours depending on the type of cure. The heights of the infrared absorbencies at 943 cm\(^{-1}\) and 910 cm\(^{-1}\), corresponding to methacrylate and styrene double bonds respectively, were monitored quantitatively and used to calculate reaction conversions. A small background absorbance assigned to the vinyl ester backbone overlapped the absorbance at 943 cm\(^{-1}\) (about 20 percent of the initial absorbance at 943 cm\(^{-1}\)). Therefore all spectra were subtracted by a spectrum where the conversion of methacrylate double bonds and styrene was complete. Solid state \(^{13}\)C NMR measurements confirmed that the residual absorbance was indeed due to the network as opposed to residual methacrylate double bond.\(^{31}\) Corrections for any changes in sample thickness during polymerization were made by normalizing the spectra to the phenyl peak of styrene at 700 cm\(^{-1}\) absorbance. Reaction conversion was determined from the change of the normalized absorbances “a” in equation (3-1) after subtraction of the background where \(A_o\) and \(A_t\) are normalized absorbances before the reaction and at reaction time \(t\).

\[
a = 1 - \frac{A_t}{A_o}
\]
Figure 3-9. Heated FT-IR cell for monitoring cure reactions.

3.3.5 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) was used to determine glass transition temperatures of the vinyl ester networks. The curves of the storage and loss moduli and the loss tangents as functions of temperature were obtained. The temperature of the maximum in the loss tangent peak was taken as the glass transition temperature. The DMA instrument was a Perkin Elmer DMA-7e. The heating rate was 5°C/min. and the frequency was 1 Hz under amplitude control. The amplitude was set at 10 mm. The samples had a thickness of 3 mm, width of 6.2 mm, and length of 20 mm.
3.3.6 Thermomechanical Analysis (TMA)

The coefficients of linear thermal expansion (CTE) ($\alpha$) were measured using a Perkin Elmer thermomechanical analyzer in the TMA mode. The thermomechanical analyzer consists of a quartz parallel plate and probe. The low-expansion quartz material transmits changes in the height of the probe to the transducer. The transducer senses movement of the probe that results from changes in the height of the specimen when subjected to a constant heating rate. The flat circular probe (7 mm in diameter) is designed such that it does not cause indentation of the specimen when load is applied within the temperature range employed. The vinyl ester specimens, approximately 3 mm in height, were placed in the holder under the quartz probe and the probe was lowered to contact the specimen. The samples were then heated at a constant rate of 5°C/min from room temperature (25°C) to 40°C above its $T_g$. The temperature sensor was placed within 6 mm of the specimen and the specimen height was measured in the direction of the expansion at room temperature. All data were taken from second heating scans. The CTE was calculated from the change in height of the probe as a function of temperature. A graph of probe height vs. temperature was obtained for each run and the changes in probe height and temperature were read directly from the information recorded on the graph. The height increased as temperature increased and the abrupt change in slope of the height vs. temperature curve was noted as the $T_g$. Linear CTE values were calculated below (50-60°C) and above (170-180°C) $T_g$ from the height vs. temperature curve. The linear expansion coefficients were multiplied by 3 to convert to volume expansion coefficients. These were then used to calculate the densities at 40°C above $T_g$ according to the following equations:

\[
\rho_{\text{room temp.}} = 1/V_1
\]

\[
\Delta V_1 = \alpha_1 (V_1) (T_g - T_{\text{room}})
\]

\[
V_2 = V_1 + \Delta V_1
\]

\[
\Delta V_2 = \alpha_2 (V_2) (T - T_g)
\]

\[
V_f = V_2 + \Delta V_2
\]
\[ \rho_{T_g + 40 \, ^\circ\text{C}} = \frac{1}{V_f} \]

where \( \alpha_1 \) and \( \alpha_2 \) are the CTE values below and above \( T_g \), respectively.

### 3.3.7 Elastic Modulus Determination

Elastic moduli were determined using a Dynastat calibrated with digital calipers accurate to 0.01 mm. The test specimens, with dimensions of height \( h \) (3.18 mm), width \( w \) (6.35 mm), and length \( l \) (38.1 mm), were placed on two flat supports with a span of 2.54 cm, in the three point bend setup. The samples were heated to 40\(^\circ\)C above \( T_g \) to measure the elastic moduli. Once the sample reached the set temperature, a small load (0.01 kg) was placed on the sample and the displacement at equilibrium was measured. The load was increased by increments of 0.01 kg up to about 0.08 kg and at each load the equilibrium displacement was recorded. From these data the load vs. displacement curves were generated and linear regression analyses were performed to determine the slopes of the lines. These slopes were used to determine the moduli according to equation (3-3).

\[
E = \frac{P}{\Delta} \times g \times \frac{L^3}{48I}
\]

- \( P/\Delta \) = slope of load versus displacement data
- \( g \) = gravitational constant = 9.81 m/s\(^2\)
- \( L \) = length between supports = 2.54 cm
- \( I = \frac{1}{12}wh^3 \)
- \( w \) = width of sample
- \( h \) = height of sample
3.3.8 Viscosity Measurements

A Brookfield Digital Viscometer (model DV-2) was used to measure the viscosities of vinyl ester resins at 25, 35, 50 and 75 °C. The zero shear viscosity (η₀) was determined by extrapolation of low-shear data from the plot of viscosity vs. shear rate.

3.3.9 Density Measurements

Room temperature density measurements of the cured samples were performed using a Mettler-Toledo AG204 balance adapted with a Mettler-Toledo density determination kit for AT/AG and PG/PR balances. The weight of each sample was measured in air (A) and in water (B) to the nearest +/- .001g. The density was calculated as:

\[ \rho = \left( \frac{A}{A - B} \right) \rho_o \]

where \( \rho_o \) is the density of water at the measurement temperature. The densities of the uncured dimethacrylate resin compositions were measured using a 10ml pycnometer. The volume of the pycnometer was calibrated with water. The densities at 40°C above \( T_g \) were calculated using the coefficients of thermal expansion below \( T_g \) and above \( T_g \) measured by thermomechanical analysis.

3.3.10 Swelling Experiments

Swelling measurements were carried out in water and dichloromethane (CH₂Cl₂) at room temperature. The vinyl ester network specimens were small blocks (3 x 3 x 5 mm). They were immersed in each liquid for approximately two weeks. The swelling equilibria were determined when the weights of the swollen networks became constant. The specimens were weighed in the swollen state, and then the swollen specimens were dried under vacuum at 150°C for three days to a constant weight. The swelling index was defined as follows:
Swelling Index = Vol. of swollen network = \[1 + \frac{(W_{t_{sw}} - W_{t_{dry}}) \rho_{network}}{W_{t_{dry}} \rho_{solv}}\]
\[
\text{Vol. of dry network}
\]

where \(W_{t_{sw}}\) is the weight of the network in the swollen state, \(W_{t_{dry}}\) is the weight of the network in the dry state, \(\rho_{solv}\) is the density of the solvent, and \(\rho_{network}\) is the density of the network. The gel fraction (the part not able to be extracted by solvent) was determined by equation (3-6).

\[
(3-6)
\]

\[
\text{Gel fraction} = \frac{\text{weight of insoluble part}}{\text{initial weight}}
\]

### 3.3.11 Fracture Toughness Testing

Three point bend tests were utilized to characterize the toughness of the vinyl ester networks in terms of the critical-stress intensity factor \(K_{1c}\), according to ASTM Standard D 5045-91. The specimens had thickness \(B\) (3.12 mm), width \(W\) (6.28 mm), notch depth (2.2 mm) and notch width (0.8 mm). The single-edge notch bending (SENB) method was used. First, a sharp notch was prepared in the sample by sawing. A natural crack was initiated by inserting a fresh razor blade (cooled by immersion in liquid nitrogen) and tapping. The depth of the natural crack generated by tapping was approximately twice the width of the sawed-in notch. The pre-cracked notched specimen was loaded crack down into a three-point bend fixture and tested using an Instron model 4204. The crosshead speed was 5 mm/min, and the testing was done at room temperature.

### 3.3.12 Tensile Testing

The tensile properties of the cured vinyl ester matrix materials were measured according to ASTM standard D 638-90. Tensile tests were used to characterize the strength, modulus, and
percent elongation of the vinyl ester networks at room temperature. The dogbone specimens (cured in dogbone-shaped silicone rubber molds) had dimensions for type I as defined in the ASTM standard. An Instron 4204 operating at a constant extension rate of 5mm/min was used to obtain the tensile data. The Instron 4204 is designed with a fixed or essentially stationary member carrying one grip and a movable member carrying a second grip. The ends of the dogbone specimens were placed in grips so that the long axis of the test specimen coincided with the direction of the applied pull through the centerline of the grip assembly. Specimens were aligned in the self-aligning grips in the direction of the applied pull. The samples were held in the grips by double-sided abrasive paper to eliminate slippage and breakage in the grips. The drive mechanism imparted to the movable member had a uniform and controlled velocity with respect to the stationary member. An extension indicator (extensometer) was attached to the dogbone test specimen within the gage length of the test specimen. For modulus determination, the extensometer continuously recorded the distance the specimen was elongated within the gage length, as a function of the load through the initial (linear) portion of the load-elongation curve. The modulus was determined from the slope of the initial linear portion of the stress-strain curve. The tensile strength at break was calculated by dividing the maximum load in pounds-force by the original cross-sectional area of the specimen in square inches. Percent elongation at break of the specimen was calculated by reading the extension (change in gage length) at break multiplied by 100.

### 3.3.13 Vickers Microhardness Testing

A Tukon Microhardness Tester (Page-Wilson Corporation) was used to determine the microhardness of the cured vinyl ester material. Microindentation was done using a pointed square-based pyramidal diamond with face angles of $136^\circ$. The indenter was forced into the surface of the cured resin under various test loads. The diagonal of the indentation made by the indenter was measured optically. The Vickers hardness value (HV) was obtained by dividing the applied load in kg of force by the surface area of the indentation in square millimeters. The surface area was automatically computed by the Tukon Microhardness tester from the mean of the measured diagonals of the indentation. The specimen was supported in grips and the indenter was smoothly and gradually brought into contact with the specimen under a predetermined load. A measuring microscope on the microhardness tester was used to measure the indentation.
load was varied from 300kg to 1100kg. As the load increased, the hardness numbers decreased and eventually leveled off at approximately 900kg and the hardness was then calculated from the linear region.

3.3.14 Cure Shrinkage

The densities of uncured and cured vinyl ester/styrene resin compositions were used to calculate the cure shrinkage. The procedure for calculation of density was described in section 3.3.9 using equation (3-4). Volume shrinkage upon cure was calculated as follows:

\[
\% \text{ shrinkage} = 100 \times \frac{1}{\rho(\text{uncured})} - \frac{1}{\rho(\text{cured})} - \frac{1}{\rho(\text{uncured})}
\]

Three samples were measured for each resin composition.

3.3.15 High Performance Liquid Chromatograph (HPLC)

HPLC was run on a Beckman, computer controlled HPLC system with a UV/VIS 168 nm diode array detector. This analytical gradient system was equipped with a Gold Nouveau for Window Workstation Software. Approximately 1 mg of sample was dissolved in 10 mL of isopropyl alcohol (Burdick and Jackson—a subsidiary of Allied Signal) and 50 µL of sample was injected using a Hamilton flat tip syringe. Samples were run on a silica column. HPLC was used to verify the purity of the mono-methacrylate model compound.

3.3.16 Dilatometry Experiments

A dilatometer designed and built by Professor L. James Lee et al. in the Department of Chemical Engineering at Ohio State University was used to measure shrinkage during cure. Degased resin was placed in a circular sample pouch (9 cm in diameter) and the edges of the pouch were heat-sealed using a T-bar Plastic Sealer, Model T-7, Harwil Co. The sample pouch was prepared by cutting a double layer piece of the laminated plastic film (Dazey Micro-Seal Film, .0051 cm thick) 10 cm in diameter. The edges of the circle were sealed leaving two gaps.
(one for the thermocouple the other to fill the pouch with resin) approximately 1 cm in length. The tip of the thermocouple (28 gauge K type) was placed inside the sample pouch near the center to measure the sample temperature. The sample thickness depended on the volume of the resin. Approximately 8 to 10 grams of resins was used. The sample chamber consisted of a cavity between two copper discs. The sample pouch was placed in the lower half of the sample chamber. The lower half of the chamber was connected to a small hydraulic cylinder, where degassed silicone oil (Dow Corning 550 fluid) was used as the encapsulating fluid. The silicone oil was continuously pumped into the lower valve and out of the top valve, working the cylinder piston until all the air was removed from the system. A bellow pump (Gorman Rupp Co.) was used to provide a pulsating flow that removed oxygen from the system. The upper half of the hydraulic cylinder was connected to a constant pressure source and was used to pressurize the sample pouch. Since the lower half of the dilatometer was considered to be a closed system, any volumetric response during cure was due to the sample, and was registered by the movement of the hydraulic cylinder piston. A Linear variable differential transducer (LVDT) followed the cylinder rod position and the response of the oil and the sample was recorded. Four 150-watt cartridge heaters were used to heat the dilatometer. The dilatometer was run in isothermal mode (heated to a set point and controlled). When the cure was completed, the heating system was removed and the dilatometer was allowed to cool to its initial temperature and final position. The thermal response due to the encapsulating oil was subtracted by repeating the thermal cycle (heating and cooling) without disassembling the apparatus. The final position of the cure was used as the initial position of the second heating cycle (baseline). If the baseline returned to the initial position when cooled, this was an indication that there was a complete cure and there were no leaks in the system. The volume change as a function of time was obtained by subtracting the cure position curve from the baseline. Upon subtracting the cure curve from the baseline, the thermal expansion difference between the monomer and the polymer was incorporated in the volumetric response. Figure 3-10 shows a cutaway view of the dilatometer cell.

The data were imported into a Microsoft Excel™ spreadsheet program with columns consisting of time, temperature (cure), position (cure), temperature (baseline), and position (baseline). The cure and baseline curves were shifted, as necessary, (by constant addition or subtraction) so that the initial position data for both the cure and baseline was zero. The baseline
was subtracted from the cure data to get $\Delta L$, or the difference in position. The percent volume change was calculated from $\Delta L$ by using equation (3-8).

$$\text{Percent Volume Change} = \left( \frac{\Delta L \pi R^2}{V} \right) \times 100$$

(3-8)

where:

$R$ is the cylinder radius, and

$V$ is the sample volume calculated by dividing the sample weight by the sample density.
Figure 3- 10. Dilatometer cell used to monitor cure shrinkage.
3.3.17 Solid State $^{13}$C Nuclear Magnetic Resonance Spectroscopy

$^{13}$C Solid state NMR spectra were collected using a Bruker MSL 300 instrument in the magic angle spinning (MAS) mode operating at a $^{13}$C frequency of 75.47 MHz. Approximately 0.25 g of cured resin was packed in a 7 mm diameter cylindrical zirconia rotor and retained with a Kel-F cap. The rotor was spun at 6.26 kHz using a block decay method. A 900 pulse (4.5 msec) was followed by a 30-millisecond acquisition time. A relaxation delay of 30 s was used between scans. Approximately 1500 scans were collected for each acquisition.

3.3.18 Differential Scanning Calorimetry

The glass transition temperature of the mono-methacrylate polymerized with styrene was obtained via a Perkin-Elmer DSC-7 instrument. The DSC was calibrated with indium and zinc standards, and ice water was used as the coolant. Samples in aluminum pans were heated from 25°C to 250°C. The glass transition temperature was calculated as the midpoint of the specific heat increase in the transition region.
CHAPTER 4. RESULTS AND DISCUSSION

4.1 Dimethacrylate Matrix Resins

4.1.1 Introduction

The present research is focused on the determination of relationships between the chemical structure of dimethacrylate networks and their physical properties. A systematic series of materials has been investigated wherein the molecular weights of the oligomers, the polydispersities, and the styrene concentrations were systematically varied. The dimethacrylate oligomers discussed herein were synthesized from bisphenol-A, epichlorohydrin and methacrylic acid (Figure 2-1). These materials are one of the major classes of polymer matrix resins under consideration for structural composite applications in the infrastructure and construction industries. These reactive methacrylate functional oligomers can form a crosslinked network with or without the addition of a comonomer. For composite resins, it is common to dilute the materials with styrene to tailor the room temperature viscosities of the mixtures for specified processing requirements. Resins comprised of these types of oligomers diluted with styrene are commonly termed “vinyl ester resins.” This term refers to a family of compositions in which the molecular weight of the methacrylate functional oligomer as well as the percentage of styrene can be varied.

The methacrylate double bonds on the termini of the oligomers copolymerize with styrene via a free radical addition polymerization mechanism to form solvent resistant thermoset networks (Figure 4-1). Figure 4-1 depicts an idealized network structure where styrene has been statistically distributed throughout the network and no dangling ends are shown. The copolymerizations were conducted under different reaction conditions to compare properties of the networks as a function of how they were formed.

Thermal expansion behavior was determined for the networks below and above T_g via thermomechanical analysis. Room temperature densities were also measured for the crosslinked materials. Elastic moduli and density values were assessed at 40°C above T_g and used to determine the average molecular weight between crosslinks using the rubber elasticity theory. Values of the average molecular weight between crosslinks were also calculated from the
chemical compositions of the resins and the number average molecular weights of the oligomers. This calculation method has been widely applied for polymer systems cured at an elevated temperature (140°C) that are considered fully cured and reasonably homogeneous. However, this theoretical calculation of $M_c$ may not be applicable for samples with styrene contents outside of the azeotropic range or samples that are not fully cured.

![Diagram](image-url)

Figure 4-1. Free radical polymerization of a dimethacrylate oligomer and styrene to form a crosslinked network.
Structure-property studies on crosslinked polymers often involve varying the molecular weight between crosslinks by changing the density of crosslink junctions with different crosslinking agents or curing conditions without otherwise altering the chemical composition of the network chains. The reactivity ratios can also play an important part in determining the resulting network structure. The crosslink density of the vinyl ester/styrene materials was systematically varied by using different vinyl ester oligomer molecular weights, changing the cure procedure and initiators, and by employing different weight percentages of styrene.

It is typical for glass transition temperatures and hardness to decrease, and for toughness to increase as the distance between crosslinks increases. This behavior is related to increased mobility as the density of crosslink junctions decreases. Such structure-property relationships of the “vinyl ester” materials are, however, complicated by the fact that they are essentially segmented copolymers and network properties are strongly dependent on the chemical composition. Thus, compositional effects, sequence lengths, and crosslink density effects become superimposed as they relate to physical properties.

The mechanical properties of the vinyl ester networks are in general superior to those from “unsaturated polyesters” (commonly prepared from propylene glycol, isophthalic acid and maleic anhydride and also diluted with styrene). This can be at least partially attributed to the fact that the vinyl esters have reactive double bonds only at the ends of the chains, while the unsaturated polyester resins have the reactive double bonds distributed throughout the chains. Thus, crosslink density can be better controlled in the vinyl esters and this provides at least the potential for synthesizing tougher networks. Another advantage of the vinyl ester resins compared to the polyester resins is hydrolytic stability. The polyester resins are less hydrolytically stable due to ester linkages within the repeat unit, since the carbonyl group is susceptible to attack by water. Figure 2-20 compares the polyester and vinyl ester networks.

The resins discussed in this dissertation include a group of dimethacrylate oligomers, which can be cured into crosslinked networks due to the two methacrylate groups per oligomer. Since these cured networks are insoluble in common solvents, they are difficult to study analytically. Thus a model compound with a structure simulating the dimethacrylate polyhydroxyether oligomer, but containing only one methacrylate double bond was synthesized.
4.1.2 Molecular Weight Characterization of the Methacrylate Terminated Polyhydroxyether Oligomers

A series of methacrylate terminated polyhydroxyether oligomers having approximate number-average molecular weights of 700, 900, 1000 and 1200 g/mole were studied. These oligomers were kindly prepared at the Dow Chemical Company using the base catalyzed polyhydroxyether oligomerization reaction described in Section 2.2 (Figure 2-1). In the first step, bisphenol-A was reacted with an excess of epichlorohydrin under basic conditions to form a structure that was approximately the diglycidyl ether of bisphenol-A. The chain length or degree of polymerization (n) in the oligomer series was controlled by reacting this diglycidyl ether with varying amounts of anions of bisphenol-A. Once the desired molecular weight was achieved, the epoxide-terminated material was reacted with methacrylic acid to provide controlled molecular weight oligomers with terminal reactive methacrylate groups.

Three analytical techniques were used to characterize the oligomeric number average molecular weights: Proton nuclear magnetic resonance (¹H-NMR), epoxy titration and gel permeation chromatography (GPC).

Molecular weights obtained by ¹H-NMR (Figure 4-3) were calculated from integral ratios of the repeat unit to the endgroup peaks. Figure 4-2 contains color-coded regions corresponding to various parts of the structure and the equation used to calculate $M_n$. The integral of the bisphenol-A methyl proton resonance (1.65 ppm) within the repeat unit was multiplied by the repeat unit molecular weight. This value was divided by the integral corresponding to the methyl protons on the methacrylate endgroups (2.0 ppm). For both the repeat unit and the endgroups, the integration number was divided by the number of protons each contained. Then the endgroup value was multiplied by two to account for both endgroups. The total $M_n$ was obtained by adding on an additional 138 g/mole for the endgroups (pink in Figure 4-2) and 90 g/mole (blue in Figure 4-2) to account for the remaining part of the structure.
Figure 4-2. Calculation of $M_n$ from $^1$H-NMR for the methacrylate terminated polyhydroxyether oligomers.

$\left\{ \frac{\text{Integration area of repeat unit} \div \# \text{ protons}}{\times \text{Molecular Weight of Repeat Unit}} \right\} + 138 + 90$

$\left\{ \frac{\text{Integration area for end groups} \div ((\# \text{ protons}) \times 2)}{+90} \right\}$

Figure 4-3. $^1$H NMR of the methacrylate terminated polyhydroxyether oligomer.
Epoxy titrations (Dow Chemical Company) were also used to calculate $M_n$. Prior to the addition of methacrylic acid, the precursor oligomer was a bisphenol-A based epoxy as shown in step 2 of Figure 2-1. The epoxy terminated precursor oligomer was tritrated with 0.1 N perchloric acid in glacial acetic acid to determine the epoxy equivalent weight (EEW). To calculate the $M_n$, the EEW was multiplied by two to account for two equivalents per mole. The green highlighted regions of the structure in Figure 4-4 represent groups present after the addition of methacrylic acid to the epoxy, which were not accounted for in the calculation of the EEW. The atomic weight of these groups must be accounted for in the calculation of $M_n$ of the dimethacrylate terminated oligomer. Therefore, an additional 172 g/mole was added to the EEW for the endgroups (derived from methacrylic acid) plus two additional hydrogens. The approximate average deviation of the EEW values was +/- 15.

$$M_n = ((\text{EEW}) \times 2) + 172$$

![Figure 4-4](image)

Figure 4-4. Calculation of $M_n$ from epoxy titration data for the methacrylate terminated polyhydroxyether oligomers.

Gel permeation chromatography was used to characterize the hydrodynamic volumes of methacrylate terminated polyhydroxyether oligomers. It was possible to separate out the amount of monomer, dimer, trimer and tetramer present within each oligomer. Since these are relatively low molecular weight oligomers, universal calibration techniques relating viscosities were not
used to determine $M_n$. Calibration curves were constructed based on the polyhydroxyether structures investigated in this work. This will be discussed in more detail in section 4.1.3. Table 4-1 shows $M_n$ calculated by epoxy titration, NMR and GPC. The data derived from the three different techniques correlate well. The values in the first column represent the nomenclature for molecular weights used throughout the text to refer to each of the oligomers.

Table 4-1. Calculation of $M_n$ (g/mole) by various experimental methods.

<table>
<thead>
<tr>
<th>$M_n$</th>
<th>EEW / $M_n$</th>
<th>NMR</th>
<th>GPC</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(700)</td>
<td>300 / 772</td>
<td>733 +/- 8</td>
<td>700</td>
<td>1.30</td>
</tr>
<tr>
<td>(900)</td>
<td>364 / 900</td>
<td>890 +/- 29</td>
<td>860</td>
<td>1.28</td>
</tr>
<tr>
<td>(900)</td>
<td>353 / 878</td>
<td>868 +/- 18</td>
<td>850</td>
<td>1.47</td>
</tr>
<tr>
<td>(1000)</td>
<td>459 / 1090</td>
<td>1085 +/- 4</td>
<td>970</td>
<td>1.37</td>
</tr>
<tr>
<td>(1000)</td>
<td>445 / 1062</td>
<td>1046 +/- 5</td>
<td>960</td>
<td>1.49</td>
</tr>
<tr>
<td>(1200)</td>
<td>510 / 1192</td>
<td>1196 +/- 22</td>
<td>1210</td>
<td>1.07</td>
</tr>
</tbody>
</table>

4.1.3 Molecular Weight Distribution of the Methacrylate Terminated Polyhydroxyether Oligomers

In addition to knowing the number- and weight-average molecular weights of a polymer, it is also desirable and necessary to know the distribution of these molecular weights. The ratio of the weight-average to the number-average molecular weight is a useful measure of the breadth of the chain lengths in a given polymer. This ratio is defined as the polydispersity index (PDI) or molecular weight distribution (MWD). This value is unity for a perfectly monodisperse polymer and the ratio increases with increasing polydispersity. There is usually a molecular-weight range for which any given polymer property will be optimum for a particular application.93
The 700g/mole oligomer has an unusually large fraction of very small chains (corresponding to the n=1 peak in the chromatogram) when compared to the relatively higher 1200g/mole oligomer (Figure 4-5). The variable “n” refers to the average number of repeat units in the oligomer. Two sets of oligomers (M_n=900g/mole and M_n=1000g/mole) were analyzed where the number average molecular weights were similar and only the molecular weight distributions were changed. Although not as obvious in these cases (Figure 4-6 and Figure 4-7), one oligomer within each set had a larger fraction of small chains. These oligomers with the higher fraction of chains with n=1 repeat units had the highest polydispersity and a more bimodal distribution. In order to quantitatively describe the distributions, the polydispersity (M_w/M_n) was calculated for each of the different oligomers from GPC data.

Using GPC, it was also possible to resolve the amounts of monomer, dimer, trimer and tetramer (repeat units) in each oligomer. The weight percentage of an oligomer having n repeat units can be described by equation (4-1).

\[
\text{weight \% \ } n = \frac{w_n}{\sum_{n=1}^{\infty} w_n} \times 100
\]

To calculate the number- and weight-average molecular weights of the six polydisperse oligomeric dimethacrylates, polymer concentration in the effluent was monitored by a differential refractometer. By using a predetermined volume of solution, volume increments of effluent could be recorded by pulsing a recorder each time this volume was collected. The resultant chromatogram included the recorder trace of the differential refractive index vs. the elution volume. The traces for the polydisperse dimethacrylates consisted of a “continuum peak” at lower elution volumes (higher molecular weights) followed by four peaks which could be ascribed to low molecular weight oligomers with known structures and molecular weights (n=1, n=2, n=3 and n=4 in Figure 1-1).
Figure 4-5. Gel permeation chromatograms of a 700g/mole oligomer and a 1200g/mole oligomer.

Figure 4-6. Gel permeation chromatograms of two 900g/mole oligomers with different molecular weight distributions.
Figure 4-7. Gel permeation chromatograms of two 1000g/mole oligomers with different molecular weight distributions.

Calibration curves (similar to the one illustrated in Figure 4-8) relating log M to elution volume ($V_e$) were prepared from these peak positions of the four lowest molecular weight oligomers for each of the polydisperse oligomers. These four datapoints were fitted to the relation:

\[
\log M = A + B(V_e) + C(V_e^2)
\]

(4-2)

Calibration curves for each of the polydisperse oligomers had a high correlation coefficient (>0.99962). Equation (4-2) was extrapolated into the lower elution volume (higher molecular weight) region to include the total range of elution volumes that had measurable refractive index differences. A TriSec software program (TriSec Software, Inc.) was used to integrate the chromatograms to yield the number- and weight average molecular weights for the polydisperse oligomers. Integrations were based on digital data sets for the traces represented by “x,y” pairs ($w_{logM}$, log M).
Figure 4-8 A standard GPC calibration curve relating the molecular weight of a dimethacrylate oligomer to the retention volume.

We can define a “polydispersity index” (PDI) that gives a measure of the breadth of the molecular weight distribution as

\[
PDI = \frac{M_w}{M_n}
\]

where \( M_n \) and \( M_w \) are defined by:

\[
M_n = \left( \sum \frac{w_i}{M_i} \right)^{-1}
\]

\[
M_w = \sum M_i \cdot w_i
\]

The variable \( w_i \) is the weight fraction of polymeric chains having a molecular weight \( M_i \).
The last column in Table 4-1 contains the PDI values for each of the oligomers under evaluation. Each value represents an average of two different runs. For the same number average molecular weight (as is the case with the 900g/mole and 1000g/mole oligomers) the higher polydispersity was obtained for the oligomer with the bimodal distribution vs. the oligomer with the more gaussian-like distribution. Since only the distribution changed within a set, the effect of MWD on the physical and mechanical properties could be studied individually. More specifically, the effect of having an unusually large fraction of n=1 chains could be evaluated. Due to the relatively low number-average molecular weight of these oligomers, the polydispersity index will have a more pronounced effect on the physical and mechanical properties, as will be discussed in sections 4.3 and 4.4.

Although all of the PDI values were calculated in the same manner, the value for the 1200 g/mole resin seems to be unusually low for a material synthesized by step-growth polymerization. Generally, step growth polymerization usually yields materials with a PDI of approximately 1.5-2.0. Although the 1200g/mole resin had the most gaussian-like distribution, it is still unlikely that the PDI would be as low as 1.07. Possible causes could be due to the limitations of the algorithm used by the TriSec Software Program to calculate the weight- and number- average molecular weights. If this is indeed the case, it is not clear at this point why only the 1200g/mole oliogmer was affected.

4.1.4 Rheological Behavior

In this chapter, the viscosity behavior of vinyl ester resins was studied using a Brookfield Digital Viscometer. The zero shear viscosity was determined by direct extrapolation of low-shear data from the plot of viscosity versus shear rate. The effect of temperature, styrene content, molecular weight and molecular weight distribution on viscosities of vinyl ester resins was examined.

The measurement of a fluid’s resistance to flow, or viscosity, is an important parameter for on-line processing of fiber-reinforced dimethacrylate composites. Figure 4-9 illustrates a continuous pultrusion process commonly used to convert a resinous material into a composite.
Low viscosity is desirable in order for the resin to flow into the fibers and permit good wetting. Styrene was used as a diluent to decrease the room temperature viscosity of the vinyl ester resins and was therefore, an important factor in controlling the viscosity. Upon dilution of the methacrylate terminated polyhydroyether oligomers with styrene, the solid material then becomes a viscous liquid. Vinyl ester resins with varied styrene contents provide systems with wide ranges of low viscosities suitable for numerous applications. Viscosity is also highly sensitive to temperature. In addition, the molecular weight and molecular weight distribution of dimethacrylate oligomers also affect viscosity significantly. These factors can each be tailored to achieve the desired rheological properties for a particular application. Approximately 2000 cps is desirable in the initial resins to provide efficient flow into fiber preforms in continuous, relatively rapid processes. The molecular weight, molecular weight distribution, temperature and percent styrene have been altered to assess their effects on the rheological properties for all of the resins under evaluation.

During compounding, the resins are generally heated to obtain a workable viscosity. The temperature must be maintained under approximately 50°C during any compounding or processing operations prior to cure, to avoid any premature reaction. This is especially true once
the free radical initiator has been added so that the initiator does not decompose into radical species. When accelerators for hydroperoxide decomposition are added, radical species can be generated at ambient temperature. Unlike the resins that employ an initiator (BPO) that decomposes at higher temperatures, room temperature cured samples, cannot be heated to reduce viscosity.

Proton NMR was used to verify the concentration of styrene in the resins. The compositions of these resins were confirmed by ratioing the integrals for the peak resonances for styrene vinyl protons (5.82 + 5.20 ppm) to methacrylate vinyl protons (6.22 + 5.66 ppm). Figure 4-10 shows a $^1$H-NMR spectrum of a polyhydroxyether oligomer terminated with methacrylate endgroups diluted with approximately 33 weight percent styrene.

Figure 4-10. A $^1$H-NMR of a methacrylate terminated dimethacrylate oligomer diluted with 33 weight percent styrene.
The viscosities were measured for a series of resins with varied molecular weights, molecular weight distributions and styrene contents. As expected, the viscosity of vinyl ester-styrene mixtures decreased with increasing styrene content and temperature (Figure 4-11). This is true for each molecular weight oligomer under evaluation. In the case of the 1200 g/mole oligomer (Figure 4-12), due to the much higher viscosities, a 20% styrene content was not used. At 20% styrene, this resin is extremely difficult to process and therefore, 28, 35 and 40% styrene contents were used.

Viscosity also increased when the oligomer molecular weight increased or the MWD decreased. The effect of MWD was illustrated by comparing the 900g/mole oligomers and the 1000g/mole oligomers (Figure 4-13 and Figure 4-14). As discussed in section 4.1.3, the increases in polydispersity for a set of oligomers with a given \( M_n \) were due to a larger fraction of shorter chains. Since viscosity decreases with decreasing molecular weight, shorter chains do not make as large contribution to the viscosity.

The viscosity of vinyl ester resins increased significantly when the molecular weight of the vinyl ester oligomer was increased from 700 g/mole to 1200 g/mole. For example, at 35 weight percent styrene and 25°C, the viscosity of the resin containing the \( M_n=700 \) g/mole oligomer was 521cps, while that of the resin with the \( M_n=1200 \) g/mole oligomer was 10500 cps (Table 4-2 and Table 4-3). The high dependence of viscosity on molecular weight for vinyl ester resins in the oligomeric range (700-1200 g/mole) is due to intermolecular hydrogen bonding between hydroxyl groups in the vinyl ester molecules.

The same trend is noted for the increase in molecular weight in going from 900g/mole to 1000g/mole (Table 4-4 and Table 4-5). Again, higher molecular weights contribute to an increase in the viscosity due to larger molecular chains. Regardless of the distribution, the 900g/mole oligomers have lower viscosities for the same temperature and styrene content, than the 1000g/mole oligomers. For reasons stated earlier in this section, when the molecular weight is constant, we expect that the oligomer with the lower polydispersity to have the highest viscosity. For example, at 25°C and 35% styrene, a 900g/mole oligomer with a PDI=1.47 and a 900g/mole oligomer with a PDI=1.28 have viscosity values of 1295cps and 2100cps, respectively. At 25°C and 35% styrene, a 1000g/mole oligomer PDI=1.49 and a 1000g/mole oligomer PDI=1.37 has viscosity values of 4380cps and 10600cps, respectively.
700g/mol oligomer $M_w/M_n=1.30$

Figure 4-11. Rheological behavior of 700 g/mole vinyl ester resins at various temperatures and styrene contents.
**Figure 4-12.** Rheological behavior of 1200 g/mole vinyl ester resins at various temperatures and styrene contents.
Figure 4-13. Rheological behavior of 900 g/mole vinyl ester resins at various temperatures, styrene contents and molecular weight distributions.
Figure 4-14. Viscosity of uncured vinyl ester resins at varied temperatures, styrene contents and molecular weight distributions (Mn=1000g/mole).
Table 4-2. Viscosity of uncured vinyl ester resins at various temperatures, styrene contents and molecular weight distributions (Mn=700g/mole).

<table>
<thead>
<tr>
<th>% styrene</th>
<th>20%</th>
<th>28%</th>
<th>35%</th>
</tr>
</thead>
<tbody>
<tr>
<td>temp(°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>14400</td>
<td>1125</td>
<td>700</td>
</tr>
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<td>496</td>
<td>250</td>
</tr>
<tr>
<td>50</td>
<td>1235</td>
<td>213</td>
<td>118</td>
</tr>
</tbody>
</table>

Zero Shear Viscosity (cps)----700 g/mol, M_w/M_n =1.30

Table 4-3. Viscosity of uncured vinyl ester resins at various temperatures, styrene contents and molecular weight distributions (1200g/mole).

<table>
<thead>
<tr>
<th>% styrene</th>
<th>28%</th>
<th>35%</th>
<th>40%</th>
</tr>
</thead>
<tbody>
<tr>
<td>temp(°C)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>&gt;31,000</td>
<td>10800</td>
<td>1340</td>
</tr>
<tr>
<td>35</td>
<td>15300</td>
<td>4956</td>
<td>622</td>
</tr>
<tr>
<td>50</td>
<td>4164</td>
<td>1120</td>
<td>256</td>
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</table>
Table 4-4. Viscosity of uncured vinyl ester resins at various temperatures, styrene contents and molecular weight distributions (Mn=900g/mole).

<table>
<thead>
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<th>temp (°C)</th>
<th>%styrene</th>
<th>20%</th>
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<th>35%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>21900</td>
<td>5150</td>
</tr>
<tr>
<td>25</td>
<td>25</td>
<td>15200</td>
<td>1433</td>
<td>1196</td>
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<tr>
<td>30</td>
<td>30</td>
<td>6098</td>
<td>639</td>
<td>624</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>2760</td>
<td>422</td>
<td>419</td>
</tr>
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</table>

Zero Shear Viscosity (cPs)-- 900g/mol, $M_w/M_n = 1.47$

<table>
<thead>
<tr>
<th>temp (°C)</th>
<th>%styrene</th>
<th>20%</th>
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<th>35%</th>
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<tr>
<td></td>
<td></td>
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<td>3015</td>
<td>1332</td>
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<td>6160</td>
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<td>908</td>
</tr>
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<td>40</td>
<td>40</td>
<td>2890</td>
<td>890</td>
<td>443</td>
</tr>
</tbody>
</table>
Table 4- 5. Viscosity of uncured vinyl ester resins at various temperatures, styrene contents and molecular weight distributions (Mn=1000g/mole).

**Zero Shear Viscosity (cps)--1000g/mol, $\text{M}_w/\text{M}_n=1.49$**

<table>
<thead>
<tr>
<th>temp(°C)</th>
<th>% styrene</th>
<th>20%</th>
<th>28%</th>
<th>35%</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>&gt;31000</td>
<td>16700</td>
<td>4380</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>26500</td>
<td>10800</td>
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</tr>
<tr>
<td>35</td>
<td>15300</td>
<td>6343</td>
<td>2180</td>
<td></td>
</tr>
</tbody>
</table>

**Zero Shear Viscosity (cps)--1000g/mol, $\text{M}_w/\text{M}_n=1.37$**

<table>
<thead>
<tr>
<th>temp(°C)</th>
<th>% styrene</th>
<th>20%</th>
<th>28%</th>
<th>35%</th>
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</thead>
<tbody>
<tr>
<td>25</td>
<td>&gt;31000</td>
<td>27400</td>
<td>10600</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>&gt;31000</td>
<td>11400</td>
<td>7680</td>
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<tr>
<td>35</td>
<td>23900</td>
<td>7350</td>
<td>4850</td>
<td></td>
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</table>
4.2 Dimethacrylate Network Formation

4.2.1 Introduction

Vinyl ester resins comprised of methacrylate terminated epoxy oligomers diluted with styrene can be cured in free radical copolymerizations to form three dimensional crosslinked networks. Crosslinking was initiated by the addition of peroxide initiators, heat and accelerators. In some cases, elevated temperature was needed to initiate polymerization and in other cases, free radicals were generated at room temperature. Data in section 4.2.3 suggests that the cure procedure, type of initiator and the extent of cure affects network formation. The crosslinking in these systems was not a reversible process and the resulting materials could not be recycled. Figure 4-1 shows vinyl ester resins crosslinked by free radical copolymerization of methacrylate endgroups with styrene. This system represents copolymerization of both vinyl and divinyl monomers.

4.2.2 Elevated Temperature and Ambient Temperature Initiators

The crosslinking reactions of vinyl ester resins were initiated by free radicals. The free radicals were generated in this study by using either benzoyl peroxide or methyl ethyl ketone peroxide. Decomposition of these initiators was affected by heat or by the use of accelerators or promoters which caused a more rapid decomposition of the initiator at a given temperature. In this study, MEKP and BPO were each used in conjunction with accelerators/promoters to produce free radicals at room temperature. BPO was also used with heat in the thermal initiation of radicals. A summary of the properties for BPO and MEKP are presented in Figure 4-15, where TLV is the threshold limit value.

Promoters/accelerators which were used to help initiate cure at room temperature were cobalt naphthenate (CoNap) and dimethylaniline (DMA). Methyl ethyl ketone peroxide was used in combination both CoNap and DMA to promote cures at room temperature. Alternatively, BPO was used in combination with dimethylaniline to promote a room temperature cure. However, when BPO was used alone, the materials were cured by heating at 140°C for one hour. The amounts used in curing were: .04 weight % of DMA, 1.5 weight % of MEKP, .15 weight % CoNap, and 1.1 weight % BPO, regardless of the type of cure. The
weight percents of MEKP and BPO used were comparable on a “per mole” (of peroxy bonds) basis.

Figure 4- 15. Properties of a commonly used peroxide and hydroperoxide.

**Benzoyl peroxide**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>242.2</td>
</tr>
<tr>
<td>Active oxygen content</td>
<td>6.6%</td>
</tr>
<tr>
<td>TLV</td>
<td>5 mg/m³</td>
</tr>
<tr>
<td>Melting point</td>
<td>103–5°C</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>70°C</td>
</tr>
<tr>
<td>Maximum storage temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Half-life: Temperature (°C)</td>
<td>72 88 92 102 136</td>
</tr>
<tr>
<td>Time (h)</td>
<td>10 2 1 0.5 0.017</td>
</tr>
</tbody>
</table>

**Methyl ethyl ketone peroxide**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>176</td>
</tr>
<tr>
<td>Active oxygen content</td>
<td>18.2%</td>
</tr>
<tr>
<td>TLV</td>
<td>0.2 ppm (1.5 mg/m³)</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>Flash point</td>
<td>65–104°C</td>
</tr>
<tr>
<td>Maximum storage temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Half-life: Temperature (°C)</td>
<td>100 120 150</td>
</tr>
<tr>
<td>Time (h)</td>
<td>16.2 6.0 0.2</td>
</tr>
</tbody>
</table>

MEKP is formed from methyl ethyl ketone (2-butanone) and hydrogen peroxide and is generally a mixture of monomer and dimers (Figure 3- 3).\(^5\) Nwoko and Pettijohn,\(^5\) showed that variations in the monomer and dimer concentrations affect the overall cure performance of resin systems. According to the authors, MEKP dimer is very effective in curing vinyl esters, since both the dimer and the end groups on vinyl esters are hydrophobic. However, the monomeric form was not as effective in curing vinyl esters since MEKP monomer is hydrophilic. It is the authors’ theory that this “like attracting like” helps drive the cure in this resin system and similar
systems. The authors are not certain of the mechanism driving the selectivity of monomer versus dimer formation.

Figure 4-16 shows how cobalt II complexes such as CoNap can be used to generate free radicals from hydroperoxides such as MEKP. The promoters transfer an electron to the hydroperoxide which activates its decomposition into free radicals and anions. The radicals react with the unsaturated bonds of the monomers to initiate copolymerization. During the decomposition of methyl ethyl ketone peroxide by cobalt, the purple cobalt II is transformed to the green cobalt III. Cobalt III is reduced back to cobalt II since the trivalent form is not stable and because it can react with the peroxide.\(^{28}\)

\[
\begin{align*}
\text{ROOH} + \text{Co}^{++} & \rightarrow \text{RO}^- + \text{OH}^- + \text{Co}^{+++} \\
\text{Co}^{+++} + \text{ROOH} & \rightarrow \text{ROO}^- + \text{H}^+ + \text{Co}^{++}
\end{align*}
\]

Figure 4-16. Generation of free radicals at room temperature using CoNap and MEKP.\(^{96}\)

Tertiary aromatic amines can also transfer an electron to a peroxide or hydroperoxide to activate decomposition of such compounds. Figure 4-17 illustrates the mechanism by which BPO in combination with DMA initiates copolymerization at low temperatures in the present work.
4.2.3 Double Bond Conversion in Free Radically Cured Dimethacrylate Networks

The degree of conversion in resin systems is one of the major factors affecting their bulk physical properties. Generally, higher double bond conversion in free radically initiated systems results in greater mechanical strength and increased shrinkage. The properties, as a result of double bond conversion, will be addressed in the next section. However, this current section will focus on the extent of cure in these free radically cured systems.

Differential scanning calorimetry (DSC) and infrared (IR) spectroscopy are two common techniques used to study the cure kinetics of thermoset systems. Using DSC, kinetic and thermal data can be simultaneously generated. However, two conditions must be met: the specific heat must be constant for isothermal runs and must vary linearly with scanning temperatures, and the rate of heat generation must be proportional to the rate of the cure reaction. IR is able to monitor both unreacted and reacted monomer concentrations during polymerization. Others have also used IR to determine the sequence distribution of the copolymer at early stages of the reaction using the copolymerization theory.

In the current study, Fourier Transform Infrared (FTIR) spectroscopy was used to investigate the effects of reaction temperature and reactant composition on the curing kinetics of mixtures of dimethacrylate oligomers with styrene. Each system was monitored using a heated IR cell (see details in section 2.4.3) for ten hours at room temperature (25°C) and postcured at 93°C for two hours, using 1.13 weight % MEKP in combination with 0.04 weight % DMA and

Figure 4-17. Generation of free radicals at room temperature using DMA and BPO.
0.15 weight % CoNap. The loss of the methacrylate peak at 943 cm⁻¹ and the styrene peak at 910 cm⁻¹ were studied independently and simultaneously. Previous studies and work by the current author have shown that samples cured with BPO at 140°C reached essentially 100% conversion for both types of double bonds. Room temperature cured systems in this present study did not reach 100% conversion. In a study of network formation by chain crosslinking photopolymerization of dimethacrylates, Kloosterboer et al. also noted that low temperature cures resulted in incomplete conversion of the reactive groups. In addition, their study found that the final extent of reaction and crosslink density increased with increasing temperature.

FT-IR (Figure 4-18) showed there was approximately 78 percent conversion of the methacrylate double bonds after ten hours at room temperature and an additional 6 percent conversion after the two-hour postcure at 93°C. There was approximately 63% conversion of the styrene double bonds (910 cm⁻¹) peak during the ambient cure and an additional 33% during the postcure. Since IR showed that the sample (due to the methacrylate peak) was not fully cured, it was believed that upon further heating, the sample might continue to cure. For this reason, an additional two hour postcure at 200°C was conducted to assess whether or not further curing would take place at a higher temperature. IR indicated that there was no further conversion even after the sample was heated to 200°C for two additional hours. It should be noted that the 200°C curing step was only used to verify whether additional curing would take place, so that other thermal properties could be measured without changing conversion during testing. However, physical and mechanical properties were conducted on materials that only underwent the 93°C postcure.

DMA (Figure 4-19) verified the results obtained by IR. The T_g obtained during the first heating scan following the 93°C postcure was around 113°C, which was much lower than the T_g of a fully cured system (147°C) with the same concentration of styrene. Even after the second heating scan, the T_g only increased slightly (119°C), indicating that no additional cure took place.
Figure 4-18. Double bond conversion and IR spectra of a 700 g/mole dimethacrylate terminated oligomer with 28 weight % styrene cured with MEKP/DMA/CoNap at room temperature followed by a 93°C postcure.

It should also be noted in Figure 4-18 that the rate of conversion of styrene was initially less than that of the methacrylate groups. However, styrene continued to react even after the methacrylate conversion ceased. This suggests that the reactivity ratios change throughout the reaction, probably due to lack of mobility caused by gelation. Reactivity ratios are generally calculated during early conversion (<10%) where both monomers are mobile.
Figure 4-19. Dynamic mechanical analysis used to determine the glass transition temperature of a 700g/mole dimethacrylate terminated oligomer with varied cure procedures and initiators.

Although the methacrylate double bonds in the present work did not reach full conversion, 84% conversion is a considerable amount for free radically cured systems. Since this relatively high percent conversion is not reflected in the $T_g$, it is believed that a different type of network (from the ones formed at 140°C) formed. The high conversion, yet low $T_g$, probably represents a more open network. Both density measurements at 25°C and crosslink density measurements confirmed the openness of these networks (section 4.3). A possible cause for the formation of this more open network could be due to the reactivity ratios of the methacrylate and the styrene at 25°C. Although reactivity ratios were calculated for oligomers cured at 140°C, they have not been calculated for this system. In the case of the 140°C cured materials, the reactivity ratios were fairly close, with values of 0.36 and 0.24 for styrene and methacrylate, respectively. This indicated that these materials were essentially good matches for a copolymerization. In other words, the two monomers show nearly equal reactivities toward the
propagating species. Current work in the group is focusing on the calculation of reactivity ratios for ambient cured oligomers. Another possible explanation for a relatively low glass transition temperature could be due to decreased network density caused by having some dangling ends (due to immobility caused by the Tromsdorff effect) with unreacted double bonds.

In this work, the initial rate of conversion of the methacrylate was higher than for styrene due to the reactivities of the propagating species. An important issue is that the styrene reached a considerably higher percent conversion than the methacrylate after the 93°C postcure. At the end of the reaction, there was essentially homopolymerization of polystyrene. The styrene almost reached full conversion (96%), since it was used up before vitrification. This could possibly be due to a mobility issue. With styrene being a smaller monomer, it was more mobile than the bulkier “vinylester” component. Another possibility is that the vinyl ester could be tied into the network with one unreacted dangling end, thus reducing its mobility. This effect of increased mobility was also seen (by the current author) during the copolymerization of a small monomer system such as styrene and methacrylate. In both an elevated cure and a room temperature cure (25°C) followed by a 93°C postcure, FT-IR showed that essentially both groups reached full conversion at approximately the same rate.

Systems cured using BPO and DMA at 25°C had different conversion curves versus those cured at 25°C using MEKP/DMA/CoNap (Figure 4-20 and Figure 4-21). Not only did the BPO/DMA systems reach higher overall conversion (after the 200°C postcure), this system also reached its maximum conversion at 25°C in a much shorter time span. The BPO/DMA system reached its maximum conversion at 25°C around one hour, whereas the MEKP/DMA/CoNap system took approximately 8 hours. However, the maximum conversion at 25°C and for the 93°C postcure for the BPO/DMA system was less than the MEKP/DMA/CoNap system. After the 200°C postcure, the BPO/DMA system exhibited higher conversions: 94 and 91 percent for the styrene and methacrylate double bonds, respectively.

Unlike the MEKP/DMA/CoNap system, there was additional curing even after the 93°C postcure. Apparently, reactive BPO radicals were still around, and effective, at the higher temperature (200°C). One possible explanation for this lies in the decomposition temperatures for each of the peroxides (Figure 4-15). BPO decomposes more rapidly and has a wider range of decomposition temperatures, as reflected by the half-life data. Even though BPO can be used
in an “ambient” or “elevated temperature cure”, these studies show that BPO is much more effective (in curing dimethacylate/styrene resin systems) when used for elevated temperature cures (140°C for one hour) since conversion reaches 100 percent.

Figure 4-20. Double bond conversion data and IR Spectrum of a 700g/mole (28 weight %styrene) resin cured with BPO/DMA at room temperature followed by at 93°C postcure.
<table>
<thead>
<tr>
<th>Methacrylate (%)</th>
<th>Styrene (%)</th>
<th>Cure Temperature</th>
<th>Time</th>
<th>Initiator System</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>63</td>
<td>25C</td>
<td>10 hrs</td>
<td>MEKP / DMA / CoNap</td>
</tr>
<tr>
<td>84</td>
<td>96</td>
<td>93C (postcure)</td>
<td>2 hr</td>
<td></td>
</tr>
<tr>
<td>84</td>
<td>96</td>
<td>200C (additional curing)</td>
<td>2 hr</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>75</td>
<td>25C</td>
<td>10 hrs</td>
<td>BPO / DMA</td>
</tr>
<tr>
<td>80</td>
<td>92</td>
<td>93C (postcure)</td>
<td>2 hr</td>
<td></td>
</tr>
<tr>
<td>91</td>
<td>94</td>
<td>200C (additional curing)</td>
<td>2 hr</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4-21. Comparison of double bond conversion for a 700g/mole dimethacrylate terminated oligomer with 28 weight percent styrene with varied cure procedures and initiators/promoters.

Again, DMA (Figure 4-22) served as a useful tool to confirm the results from IR. The first heating revealed a low $T_g$ around 119°C while the second heating showed a substantial increase in the $T_g$ to 130°C. Although the $T_g$ in this system (BPO/DMA) is still much lower than a fully cured system, there is still more conversion than that in the MEKP/DMA/CoNap system, due to the higher extent of cure.

In both cases (MEKP and BPO cures), the samples reached fairly high conversions, as noted by IR. The lower $T_g$ values were most likely due to the lower postcure temperature. Therefore, it is believed that differences in $T_g$s and properties were due to the manner in which the network was formed (i.e. differences in crosslink density) and not the extent of conversion of the network. It should be noted here that physical (with the exception of swelling data) and mechanical properties of the room temperature cured systems were only conducted on systems that used MEKP as the peroxide initiator (section 4.3 and section 4.4).
Figure 4-22. Dynamic mechanical analysis used to determine the glass transition temperature of a 700g/mole resin (28 weight % styrene) with varied cure procedures using BPO as the initiating species.

Solid state $^{13}$C-NMR was also used to confirm the residual unsaturation in the networks cured with MEKP/DMA/CoNap at 25°C followed by a 93°C postcure. Thin films were used to study conversion by FT-IR, while all other characterization techniques employed bulk samples (3mm thick). Therefore, it was important to verify that the conversion determined by FT-IR was consistent with the conversion obtained in the bulk samples. It was reasoned that thicker samples (less efficient heat transfer) might have higher double bond conversions due to the build-up of heat in these samples during cure. Thin films (cured at 25°C followed by a 93°C postcure) were analyzed by FT-IR and $^{13}$C NMR to verify that these two techniques were comparable. FT-IR showed that the methacrylate component reached 84% conversion after the postcure compared to 84.4% conversion by $^{13}$C-NMR. Since similar results were obtained by the two techniques, it was concluded that $^{13}$C NMR could be used to study residual unsaturation in bulk samples, which could then be compared to IR data. Only the amount of residual
methacrylate double bonds could be confirmed by $^{13}$C NMR since the carbonyl groups adjacent to the methacrylate groups could be readily distinguished. It should be noted however, that styrene reached essentially full conversion in the MEKP/DMA/CoNap systems and therefore quantifying residual styrene double bonds was less important.

After the bulk samples were cured, they were crushed to a fine powder and analyzed by solid-state $^{13}$C-NMR. They were analyzed after the 25$^\circ$C cure step and after the postcure. Table 4- 6 shows 7% less unsaturation before the postcure step and 4% less unsaturation after the postcure step for the bulk samples compared to the thin film samples.

Table 4- 6. Determination of residual unsaturation in cured, bulk (3mm thick) network samples by solid state $^{13}$C NMR.

<table>
<thead>
<tr>
<th></th>
<th>Ambient Cure (no postcure)</th>
<th>Ambient Cure + (93 $^\circ$C Postcure)</th>
<th>140$^\circ$C Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR (thin Film)</td>
<td>22, 37</td>
<td>16, 4</td>
<td>0, 0</td>
</tr>
<tr>
<td>Solid State $^{13}$C (Bulk Sample)</td>
<td>15, N/A</td>
<td>12, N/A</td>
<td>0, N/A</td>
</tr>
</tbody>
</table>

A thermocouple was placed in the samples as they cured to measure the sample temperature directly during the ambient temperature (23$^\circ$C) cure (Figure 4- 23). There was an increase in temperature from 23$^\circ$C to 32$^\circ$C, verifying a slight exotherm. Therefore, it should be noted that bulk samples cured at room temperature have slightly higher conversions than obtained by FT-IR. Unlike the thin films cured by IR (which were in a controlled temperature cell), bulk samples were cured in an open mold and the ambient temperature was unable to be controlled at 25$^\circ$C.
Cure Exotherm of Bulk Sample
(thickness = 3.3mm; width = 6.1mm)

- Cobalt Naphthenate, Dimethyl Aniline and MEKP were added to the resin (700g/mol-28wt % styrene)
- A thermal couple was placed in the resin at room temp. (23C)
- After 17min, the temperature of the resin reached a maximum of 32C

Figure 4-23. Cure exotherm generated during a room temperature cure of a bulk sample.
4.3 Effect of Crosslinking on Physical Properties of Dimethacrylate Networks

4.3.1 Introduction

Vinyl ester or dimethacrylate oligomers are divinyl oligomers that serve as crosslinking agents in free radical reactions. They co-cure free radically with other vinyl monomers, such as styrene, to produce crosslinked networks. These thermosets consist of polymeric chains covalently bonded, linking the polymer chains in three dimensions. Since chains are not allowed to slip past one another, the result is a higher modulus and improved creep resistance. The crosslink density provides a general means of characterizing the physical network structure. It has been successfully employed as a material structural parameter to understand variations in small-strain and ultimate mechanical properties of crosslinked rubbers.\(^9\) When these networks are used in the glassy state, other descriptive chemical and structural parameters may additionally be needed to describe the mechanical behavior (section 4.4). Therefore, this current section describes an investigation of the relationships between the network structures and physical properties. Oligomer number average molecular weights were studied with systematically varied styrene concentrations and varied molecular weight distributions to assess effects of crosslinking on glass transition temperature, coefficient of thermal expansion, rubbery modulus, average molecular weight between crosslinks and crosslink density, density, shrinkage and chemical resistance.

4.3.2 Rubbery Modulus

The effect of styrene content, molecular weight and molecular weight distribution on the rubbery modulus was evaluated. The rubbery modulus \(40^\circ\text{C}\) above the glass transition temperature (3.3.7) was determined from creep tests (in 3-point bend mode) using a Dynastat. In general, creep tests measure the time-dependent deformation of a material while it is held under a constant applied load at a given temperature. Loads vs. displacement curves were generated and linear regression analyses were performed to determine the slopes of the lines. These slopes were used to determine the moduli according to Equation (4-6).
\[ E = \frac{P}{\Delta} \cdot g \cdot \left( \frac{L^3}{48I} \right) \]

\( \frac{P}{\Delta} \) = slope of load versus displacement data
\( g \) = gravitational constant = 9.81 m/s\(^2\)
\( L \) = length between supports = 2.54 cm
\( I = \frac{1}{12}bh^3 \)

Polymers vary widely in their mechanical behavior depending on the degree of crosslinking and values of \( T_g \). Crosslinked polymers with high \( T_g \)s are usually characterized by high strength and low extensibility. Although strength is lost near the \( T_g \) for these materials (drop in modulus in thermomechanical spectrum in Figure 4-24) crosslinked polymers retain a fair amount of strength beyond the \( T_g \), known as the rubbery region. Rubbery modulus values are usually four orders of magnitudes lower than glassy modulus values. It can be clearly seen in the following thermomechanical spectrum how the modulus plateaus off in the rubbery region even with an increase in temperature. Thermoset or crosslinked materials do not flow above the glass transition temperature. The sample will eventually degrade if the degradation temperature is reached.

This behavior can be explained in terms of a polymer’s viscoelastic behavior. At low temperatures, only bond angles and lengths can respond, and the typical glassy modulus of \( 10^9 \) to \( 10^{10} \) Pa is observed. However, at higher temperatures, the response is governed by the uncoiling of the chains and modulus values of \( 10^5 \) to \( 10^6 \) Pa is observed in this rubbery plateau region. This intermediate region, where the modulus drops from glassy to rubbery, is sometimes known as the leathery region from the leather-like feel of materials with moduli in this range. When even higher temperatures are reached, the modulus of thermoplastic materials drops from the rubbery plateau into the rubbery-flow region. The material is still elastic but has a significant flow component and then falls off rapidly as a result of molecular slippage in the viscous-flow region. However, in the limit of infinite molecular weight (crosslinking), flow is eliminated entirely, and the uncoiling leads to a material that only responds by straining of bond angles and lengths.
Both copolymer composition and the degree of crosslinking affect the rubbery modulus of cured vinyl ester resin networks. Data shown in Figure 4-25 through Figure 4-27 show that in all cases, the rubbery modulus increases with a decrease in the precursor oligomer molecular weight or a decrease in styrene content. This can be explained in terms of network density. An increase in either the styrene content or oligomer molecular weight results in a looser network, which has less resistance to deformation above $T_g$, resulting in a lower rubbery modulus. For the vinyl ester resins with oligomer $M_n=1200$g/mole, the crosslink density decreased only slightly as the styrene content increased from 20 weight % to 40 weight % in the resins. The oligomer “crosslinks” are actually contributing to the network modulus as elastic chains. Therefore, the percent change in the average distance between crosslinks when the styrene content is increased...
is less when the oligomer is of higher molecular weight. It should also be noted that the absolute number of crosslink junctions per cm$^3$ is less for the higher molecular weight dimethacrylates.

Figure 4-25 also shows a comparison between a 700g/mole oligomer with a large weight fraction of n=1 chains and a 1200g/mole oligomer with a more gaussian-like distribution (recall gel permeation chromatograms in Figure 4-5). However, since both the molecular weight and molecular weight distribution changes, it is difficult to distinguish the effect of $M_n$ or MWD. Therefore, Figure 4-27 better explains the effect of MWD, since the molecular weight remains nearly constant and only the MWD changes. Here, it can be seen with both the 900g/mole and 1000g/mole oligomers, a higher polydispersity results in a higher rubbery modulus. An increase in the number of short chains results in a tighter network, which increases the resistance to deformation in the rubbery region. Although the elastic modulus in the rubbery state increased as the crosslink density increased, in the glassy state, the effect of the crosslink density on the elastic modulus of vinyl ester resins is more complicated and will not be addressed in detail in this current manuscript. Table 4-7 provides a summary of the rubbery modulus values.

![Graph showing the effect of styrene content and oligomer average molecular weights and molecular weight distributions on the rubbery modulus for 700g/mole and 1200g/mole oligomers.](image)
900g/mol Oligomers

Figure 4-26. The effect of styrene content and molecular weight distribution on the rubbery modulus for 900g/mole oligomers.

1000g/mol Oligomers

Figure 4-27. The effect of styrene content and molecular weight distribution on the rubbery modulus for 1000g/mole oligomers.
Table 4-7. Rubbery modulus values of dimethacrylate/styrene networks.

<table>
<thead>
<tr>
<th>E (Pa)</th>
<th>700 g/mol, $M_w/M_n = 1.30$</th>
<th>900 g/mol, $M_w/M_n = 1.47$</th>
<th>900 g/mol, $M_w/M_n = 1.28$</th>
<th>1000 g/mol, $M_w/M_n = 1.49$</th>
<th>1000 g/mol, $M_w/M_n = 1.37$</th>
<th>1200 g/mol, $M_w/M_n = 1.07$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20% styrene</td>
<td>4.06E+07</td>
<td>20% styrene</td>
<td>2.95E+07</td>
<td>20% styrene</td>
<td>2.35E+07</td>
</tr>
<tr>
<td></td>
<td>28% styrene</td>
<td>2.77E+07</td>
<td>28% styrene</td>
<td>2.25E+07</td>
<td>28% styrene</td>
<td>1.95E+07</td>
</tr>
<tr>
<td></td>
<td>35% styrene</td>
<td>2.10E+07</td>
<td>35% styrene</td>
<td>1.88E+07</td>
<td>35% styrene</td>
<td>1.54E+07</td>
</tr>
</tbody>
</table>
4.3.3 Crosslink Density

Dimethacrylate endgroups provide unsaturated sites for reaction with the diluent, styrene. During the cure reaction, a highly crosslinked network is formed by free-radical copolymerization of the methacrylate groups and styrene. Crosslinking converts these materials from resinous fluids to solid networks. This network can be described in terms of the molecular weight between crosslinks and crosslink density. The crosslink density is an important structural parameter which controls many physical properties of vinyl ester resins. The crosslink density can be controlled by varying the length of the vinyl ester precursor, varying the molecular weight distribution, varying the relative amount of styrene used during the crosslinking reaction, and by controlling the final double bond conversion. More specifically, the crosslink density of the vinyl ester / styrene materials in this research was systematically varied by using four different vinyl ester oligomer average molecular weights (700, 900, 1000 and 1200 g/mole), and by employing three different weight percentages of styrene (20, 28 and 35%). There were two different molecular weight distributions for both the 900g/mole oligomer and the 1000g/mole oligomer.

The rubbery modulus 40°C above the glass transition temperature was used to determine the crosslink density of these highly crosslinked thermoset materials. Dynamic mechanical tests are a rapid and very sensitive technique to determine the cross-linking density at temperatures well above $T_g$. For a highly crosslinked network, chain entanglements are not present and under small deformations, the relationship between crosslink density and the equilibrium elastic modulus ($E'$) can be expressed by using the kinetic theory of rubber elasticity as follows:

$$\rho = \frac{G'}{RT} = \frac{E'}{3RT}$$

(4-7)

where $\rho$ is the crosslink density expressed in moles of elastically effective network chains per cubic centimeter of sample, $G'$ is the shear storage modulus of cured resin at a temperature well above $T_g$, R is the gas constant and T is the absolute temperature at which the experimental modulus is taken. Here $G'=3E'$ is used assuming that the samples do not undergo volume change with strain.
The calculated crosslink density (Table 4-8) values from the elastic storage modulus decreased linearly with an increase in styrene content and oligomer molecular weight. When the oligomer molecular weight distribution was broadened, the crosslink density also increased. As expected, these values follow the same trend as the rubbery modulus, since rubbery modulus and crosslink density have a direct relationship according to equation (4-7).

Table 4-8. Table of crosslink density values of dimethacrylate/styrene networks.

<table>
<thead>
<tr>
<th>Crosslink Density (mol/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700g/mol, Mw/Mn=1.30</td>
</tr>
<tr>
<td>20% styrene</td>
</tr>
<tr>
<td>3.48E-03</td>
</tr>
<tr>
<td>28% styrene</td>
</tr>
<tr>
<td>2.42E-03</td>
</tr>
<tr>
<td>35% styrene</td>
</tr>
<tr>
<td>1.85E-03</td>
</tr>
<tr>
<td>900g/mol, Mw/Mn=1.47</td>
</tr>
<tr>
<td>20% styrene</td>
</tr>
<tr>
<td>2.59E-03</td>
</tr>
<tr>
<td>28% styrene</td>
</tr>
<tr>
<td>2.03E-03</td>
</tr>
<tr>
<td>35% styrene</td>
</tr>
<tr>
<td>1.71E-03</td>
</tr>
<tr>
<td>900g/mol, Mw/Mn=1.28</td>
</tr>
<tr>
<td>20% styrene</td>
</tr>
<tr>
<td>2.06E-03</td>
</tr>
<tr>
<td>28% styrene</td>
</tr>
<tr>
<td>1.70E-03</td>
</tr>
<tr>
<td>35% styrene</td>
</tr>
<tr>
<td>1.35E-03</td>
</tr>
<tr>
<td>1000g/mol, Mw/Mn=1.49</td>
</tr>
<tr>
<td>20% styrene</td>
</tr>
<tr>
<td>2.03E-03</td>
</tr>
<tr>
<td>28% styrene</td>
</tr>
<tr>
<td>1.75E-03</td>
</tr>
<tr>
<td>35% styrene</td>
</tr>
<tr>
<td>1.60E-03</td>
</tr>
<tr>
<td>1000g/mol, Mw/Mn=1.37</td>
</tr>
<tr>
<td>20% styrene</td>
</tr>
<tr>
<td>1.37E-03</td>
</tr>
<tr>
<td>28% styrene</td>
</tr>
<tr>
<td>1.12E-03</td>
</tr>
<tr>
<td>35% styrene</td>
</tr>
<tr>
<td>1.04E-03</td>
</tr>
<tr>
<td>1200g/mol, Mw/Mn=1.07</td>
</tr>
<tr>
<td>20% styrene</td>
</tr>
<tr>
<td>1.28E-03</td>
</tr>
<tr>
<td>28% styrene</td>
</tr>
<tr>
<td>1.22E-03</td>
</tr>
<tr>
<td>35% styrene</td>
</tr>
<tr>
<td>1.05E-03</td>
</tr>
</tbody>
</table>
This same expected trend was also found in Grobelny’s study of the copolymerization and crosslinking effects of polyester/styrene networks. The unsaturated polyester networks were derived from maleic anhydride. Rubbery modulus values, used to determine crosslink density, were determined from static load tests with the sample specimen in tension. Copolymerization was investigated by solid-state $^{13}$C-NMR spectroscopy. Spin-lattice relaxation times (as a function of unsaturated polyester composition) were used to analyze the structural modifications accompanying crosslinking in these polyesters. As expected, they found that as the crosslinking effect was suppressed, the modulus of elasticity was decreased. Similar results were obtained in this study regardless of the fact that their measurements were made in tension and the measurements in this study were done in compression.

### 4.3.4 Average Molecular Weight Between Crosslinks (Experimental and Theoretical)

It was reasoned that the number average molecular weights between crosslinks should be dependent on the average molecular weights of the precursor dimethacrylate oligomers, the amount of styrene present relative to dimethacrylate oligomer, the extent of double bond conversion, and the molecular weight distribution of vinyl ester (methacrylate) with styrene. Using the densities 40°C above $T_g$ (Table 4-9) (calculated from coefficients of thermal expansion below and above $T_g$) and the elastic moduli (determined from compression test measurements) the molecular weights between crosslinks ($M_c$) were calculated by:

\[
M_c = \frac{3RTd}{E}
\]

\begin{align*}
E &= \text{the elastic modulus above the } T_g \text{ (Pa)} \\
M_c &= \text{the molecular weight between crosslinks (g/mole)} \\
R &= \text{the gas constant} \\
T &= \text{temperature } 40^0 \text{ above } T_g \\
d &= \text{density at } 40^0 \text{ above } T_g
\end{align*}
Equations (4-8) and (4-7) can be combined and rearranged to show the direct relationship between rubbery modulus and crosslink density and its inverse relationship to the molecular weight between crosslinks (equation (4-9)).

\[
\frac{d}{M_c} = \rho = \frac{E}{3RT}
\]

Table 4-9. Densities and coefficients of thermal expansion values of dimethacrylate/styrene networks.

<table>
<thead>
<tr>
<th>Density (room temp) (g/cm³)</th>
<th>CTE (below Tg) (/K)</th>
<th>CTE (above Tg) (/K)</th>
<th>Tg (°C)</th>
<th>Density (Tg + 40°C) (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700g/mol, M_w/M_n=1.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>1.189</td>
<td>3.15E-04</td>
<td>6.83E-04</td>
<td>155</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>1.177</td>
<td>2.58E-04</td>
<td>6.66E-04</td>
<td>147</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.168</td>
<td>3.35E-04</td>
<td>7.28E-04</td>
<td>144</td>
</tr>
<tr>
<td>900g/mol, M_w/M_n=1.47</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>1.160</td>
<td>4.21E-05</td>
<td>5.09E-04</td>
<td>144</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>1.140</td>
<td>5.92E-05</td>
<td>4.15E-04</td>
<td>132</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.120</td>
<td>4.42E-05</td>
<td>6.12E-04</td>
<td>126</td>
</tr>
<tr>
<td>900g/mol, M_w/M_n=1.28</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>1.140</td>
<td>2.03E-04</td>
<td>5.55E-04</td>
<td>144</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>1.120</td>
<td>1.41E-04</td>
<td>5.24E-04</td>
<td>146</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.100</td>
<td>1.86E-04</td>
<td>3.06E-04</td>
<td>144</td>
</tr>
<tr>
<td>1000g/mol, M_w/M_n=1.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>1.151</td>
<td>4.31E-04</td>
<td>7.47E-04</td>
<td>145</td>
</tr>
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<td>28 % styrene</td>
<td>1.145</td>
<td>3.20E-04</td>
<td>7.87E-04</td>
<td>140</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.139</td>
<td>3.30E-04</td>
<td>7.98E-04</td>
<td>142</td>
</tr>
<tr>
<td>1000g/mol, M_w/M_n=1.37</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>1.134</td>
<td>1.85E-04</td>
<td>6.17E-04</td>
<td>144</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>1.110</td>
<td>3.79E-04</td>
<td>9.57E-04</td>
<td>142</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.100</td>
<td>3.24E-04</td>
<td>7.72E-04</td>
<td>138</td>
</tr>
<tr>
<td>1200g/mol, M_w/M_n=1.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>1.169</td>
<td>3.11E-04</td>
<td>7.06E-04</td>
<td>131</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>1.159</td>
<td>2.55E-04</td>
<td>7.22E-04</td>
<td>128</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.152</td>
<td>3.16E-04</td>
<td>7.02E-04</td>
<td>125</td>
</tr>
</tbody>
</table>
Table 4-10 provides a summary of the rubbery modulus, crosslink density and $M_c$ values. The relationships among the three parameters, as shown in equation (4-9), hold for all of the networks under investigation.

Table 4-10. Rubbery modulus, crosslink density and experimental $M_c$ values of dimethacrylate/styrene networks.

<table>
<thead>
<tr>
<th></th>
<th>$E$ (Pa)</th>
<th>Crosslink Density (mol/cm$^3$)</th>
<th>$M_c$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>700g/mol, $M_w/M_n=1.30$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% styrene</td>
<td>4.06E+07</td>
<td>3.48E-03</td>
<td>320</td>
</tr>
<tr>
<td>28% styrene</td>
<td>2.77E+07</td>
<td>2.42E-03</td>
<td>477</td>
</tr>
<tr>
<td>35% styrene</td>
<td>2.10E+07</td>
<td>1.85E-03</td>
<td>618</td>
</tr>
<tr>
<td><strong>900g/mol, $M_w/M_n=1.47$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% styrene</td>
<td>2.95E+07</td>
<td>2.59E-03</td>
<td>437</td>
</tr>
<tr>
<td>28% styrene</td>
<td>2.25E+07</td>
<td>2.03E-03</td>
<td>558</td>
</tr>
<tr>
<td>35% styrene</td>
<td>1.88E+07</td>
<td>1.71E-03</td>
<td>647</td>
</tr>
<tr>
<td><strong>900g/mol, $M_w/M_n=1.28$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% styrene</td>
<td>2.35E+07</td>
<td>2.06E-03</td>
<td>528</td>
</tr>
<tr>
<td>28% styrene</td>
<td>1.95E+07</td>
<td>1.70E-03</td>
<td>650</td>
</tr>
<tr>
<td>35% styrene</td>
<td>1.54E+07</td>
<td>1.35E-03</td>
<td>807</td>
</tr>
<tr>
<td><strong>1000g/mol, $M_w/M_n=1.49$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% styrene</td>
<td>2.32E+07</td>
<td>2.03E-03</td>
<td>523</td>
</tr>
<tr>
<td>28% styrene</td>
<td>1.98E+07</td>
<td>1.75E-03</td>
<td>638</td>
</tr>
<tr>
<td>35% styrene</td>
<td>1.82E+07</td>
<td>1.60E-03</td>
<td>694</td>
</tr>
<tr>
<td><strong>1000g/mol, $M_w/M_n=1.37$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% styrene</td>
<td>1.56E+07</td>
<td>1.37E-03</td>
<td>813</td>
</tr>
<tr>
<td>28% styrene</td>
<td>1.27E+07</td>
<td>1.12E-03</td>
<td>962</td>
</tr>
<tr>
<td>35% styrene</td>
<td>1.17E+07</td>
<td>1.04E-03</td>
<td>1034</td>
</tr>
<tr>
<td><strong>1200g/mol, $M_w/M_n=1.07$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% styrene</td>
<td>1.42E+07</td>
<td>1.28E-03</td>
<td>893</td>
</tr>
<tr>
<td>28% styrene</td>
<td>1.34E+07</td>
<td>1.22E-03</td>
<td>930</td>
</tr>
<tr>
<td>35% styrene</td>
<td>1.15E+07</td>
<td>1.05E-03</td>
<td>1071</td>
</tr>
</tbody>
</table>
The average molecular weight between crosslinks ($M_c$) increased when the oligomer $M_n$ or styrene content increased. It is also instructive to note that increasing $M_n$ of the oligomer from 700 to 1200 g/mole led to significant predicted increases in $M_c$. For example, $M_c$ was larger at 20 weight percent styrene for a 1200 g/mole oligomer as compared to a 700 g/mole oligomer with as much as 35 weight percent styrene. Molecular weight distribution also affected $M_c$; oligomers with higher polydispersities had lower $M_c$ values even when the $M_n$ was the same. The oligomers with a higher $M_W/M_n$ value had a greater number of shorter chains ($n=1$) and therefore had shorter distances between crosslink points which resulted in lower $M_c$ values.

Theoretical number average molecular weights between crosslinks (Table 4-11) were predicted from the chemical compositions and the number average molecular weights of the oligomers assuming complete reactions. One assumption that was made in the calculation of the theoretical molecular weight between crosslinks was that all chains were equal in length. Therefore, the effect of molecular weight distribution was not considered. Two other assumptions made in the theoretical calculation of $M_c$ were that a segment consisted of any chain connected by two junction points and a junction point was defined as a point where at least three segments intersected. Each styrene segment and each vinyl ester oligomer segment was included in these calculations and averaged (assuming 2 styrene segments per vinyl ester oligomer and considering $M_c$ to equal the total weight of the 3 segments divided by 3). A divisor of 3 was used in order to calculate an average value, since three segments were involved. Using $M_c$ values calculated from the rubbery modulus data, an experimental value of $X$ was determined. The values in all cases were less than the value of 3 used in the theoretical $M_c$ calculations (Figure 4-28). This indicated that distances between junction points: 1) may not be long enough to actually be considered a segment 2) are not uniform throughout the network and 3) vary with molecular weight, molecular weight distribution and styrene content.
Table 4-11. Comparison of experimental and theoretical $M_c$ values (g/mole) of dimethacrylate/styrene networks.

<table>
<thead>
<tr>
<th></th>
<th>Experimental $M_c$ (g/mol)</th>
<th>Theoretical $M_c$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>700g/mol, $M_w/M_n=1.30$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>320</td>
<td>292</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>477</td>
<td>324</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>618</td>
<td>359</td>
</tr>
<tr>
<td><strong>900g/mol, $M_w/M_n=1.47$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>437</td>
<td>375</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>558</td>
<td>417</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>647</td>
<td>462</td>
</tr>
<tr>
<td><strong>900g/mol, $M_w/M_n=1.28$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>528</td>
<td>375</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>650</td>
<td>417</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>807</td>
<td>462</td>
</tr>
<tr>
<td><strong>1000g/mol, $M_w/M_n=1.49$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>523</td>
<td>417</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>638</td>
<td>463</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>694</td>
<td>513</td>
</tr>
<tr>
<td><strong>1000g/mol, $M_w/M_n=1.37$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>813</td>
<td>417</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>962</td>
<td>463</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1034</td>
<td>513</td>
</tr>
<tr>
<td><strong>1200g/mol, $M_w/M_n=1.07$</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>893</td>
<td>556</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>930</td>
<td>615</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1071</td>
<td>667</td>
</tr>
</tbody>
</table>

122
Since theoretical calculations were based solely on the chemical composition, the molecular weight distributions were not a factor. Therefore, within a given molecular weight (900 and 1000g/mole), the theoretical $M_c$ values were the same regardless of the MWD. However, the oligomer with the highest polydispersity (same $M_n$) had experimental values of $X$ closer to that of the theoretical value of 3 used for $X$. These higher experimental values of $X$ for the non-Gaussian distributed oligomers was indicative of their lower $M_c$ due to the incorporation of more “short chains.”

**Network Segments**  
(Theoretical vs. Experimental)

$$M_c = \frac{[M_n \text{ VE Segment} + (2 \times M_n \text{ Styrene Segment})]}{X}$$

<table>
<thead>
<tr>
<th>$M_n$ (g/mol)/MWD</th>
<th>20% styrene</th>
<th>28% styrene</th>
<th>35% styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>700/$M_c=1.30$</td>
<td>2.8</td>
<td>2.1</td>
<td>1.8</td>
</tr>
<tr>
<td>900/$M_c=1.47$</td>
<td>2.6</td>
<td>2.2</td>
<td>2.1</td>
</tr>
<tr>
<td>900/$M_c=1.28$</td>
<td>1.4</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>1000/$M_c=1.49$</td>
<td>2.4</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>1000/$M_c=1.37$</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>1200/$M_c=1.07$</td>
<td>1.8</td>
<td>1.9</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Figure 4-28. Theoretical vs. experimental network segments for dimethacrylate/styrene networks.
Although it is possible to predict the molecular weight between crosslinks, experimental methods are still necessary. Highly accurate predictions are based on the assumption that complete conversion was achieved, virtually no non-polymerization associated crosslinking occurred, and no dangling ends existed. Since this is not the case for most polymeric systems, experimental methods are essential to determine accurate molecular weights between crosslinks. According to rubber elasticity theory, the rubbery moduli of polymer networks should be proportional to the crosslink densities.\textsuperscript{64,101} Equation (4-9) applies to elastically active network chains only (and may not be accurate for materials with dangling ends or unconnected chains). The four basic assumptions that must be made are: (1) the chains have gaussian statistics, (2) the materials deform affinely, (3) the internal energy of the system is independent of the conformations of the individual chains and (3) the chains are treated as phantom networks (there is no excluded volume).\textsuperscript{64} Networks with a greater number of dangling ends would be expected to deviate the most from theoretical predictions.

The experimental trends in $M_c$ followed the expected increases as both the molecular weight of the dimethacrylate oligomer and the styrene concentration was increased. The experimental $M_c$ (Figure 4-29 through Figure 4-31 and Table 4-11) values, however, were uniformly higher than those predicted from stoichiometry (theoretically calculated) and the reasons for this are not totally clear at this point. This difference may be partially attributable to “dangling chain ends” which are elastically inactive segments. Therefore, they do not contribute effectively to the rubbery moduli. As a result, experimentally tested samples with dangling ends will have lower rubbery modulus values which result in higher $M_c$ values.

Martaigne et al. investigated the effect of dangling ends on styrene crosslinked polyesters.\textsuperscript{102} They investigated maleate/phthalate unsaturated polyesters crosslinked by approximately 40 weight percent styrene. The prepolymer $M_n$ values were between 1000 and 6000g/mole. $M_c$ values and the concentration of different types of dangling chains were estimated from a constituent repeat unit model (CRU) representative of the whole network structure and of the chain ends. In a comparison of these parameters with $T_g$ and the rubbery shear modulus, they found that the influence of dangling chains had a more pronounced effect on the shear modulus (determined by thermomechanical spectrometry) in the rubbery state than on the glass transition temperature. In this present study, since the concentration of dangling ends
was not calculated, it is difficult to quantitatively assess which parameter ($T_g$ or rubbery modulus) was most affected. However, both the glass transition temperature and the elastic modulus are highly dependent on the amount of crosslinking. Since dangling ends decrease the crosslink density, it is highly possible that values for $T_g$ and rubbery moduli were suppressed.

As shown in Figure 4-32, there was a decrease in the rubbery modulus and an increase in the average molecular weight between crosslinks when the oligomers were cured at room temperature followed by a 93°C postcure employing MEKP as the peroxide initiator. The IR data in section 4.2.3 showed lower conversion for the dimethacrylate vinyl groups in the room temperature cured samples, indicating a more open network. As shown in Section 4.3.2 and 4.3.5, the samples did not experience further cure and the $T_g$ did not increase significantly after the 93°C postcure step even when heated to 200°C. The rubbery modulus values could be calculated without postcuring the samples further. Later in this manuscript, the effect of this increase in $M_c$ on the physical and mechanical properties will be illustrated.

![Graph](image)

Figure 4-29. The effect of styrene content and molecular weight and on $M_c$ for 700g/mole and 1200g/mole dimethacrylate oligomers.
Figure 4-30. The effect of styrene content and molecular weight distribution on $M_c$ for 900g/mole dimethacrylate oligomers.

Figure 4-31. The effect of styrene content and molecular weight distribution on $M_c$ for 1000g/mole vinyl ester oligomers.
Figure 4-32. The effect of styrene content, oligomer molecular weight and cure procedure on rubbery modulus of 700 g/mole and 1200 g/mole oligomers.

4.3.5 Glass Transition Temperature

The loss modulus (tan delta peak) was measured by dynamic mechanical testing (in three-point bending mode) and was used to evaluate the viscoelastic properties of these networks, in terms of the glass transition temperature. The loss modulus relates to the amount of unrecoverable energy lost within a deformed material (fluidlike behavior). In a plot of tan delta versus temperature, the $T_g$ was taken as the peak of the tan delta cure. DSC was not used to measure the $T_g$ for the systems. In highly crosslinked networks, there are only very small measurable changes in heat flow and DSC is not as sensitive as DMA in detecting these changes.
It has been shown by Nielsen, that the glass transition temperatures of highly crosslinked networks are very dependent on the degree of crosslinking. However, for lightly crosslinked networks, there is less dependence of $T_g$ on the $M_c$. Generally, for highly crosslinked systems, very small changes in $M_c$ result in large changes in $T_g$. Theoretically, $M_c$ can be quantitatively predicted based on the shift in $T_g$. However, for the networks in this study, it is difficult to make a direct correlation due to the changing chemical composition with changing $M_c$. Since there are two independent factors affecting the $T_g$, when the network density is varied (degree of crosslinking and the copolymer effect), it is important to ascertain which effect is greater.

Glass transition temperatures and mechanical properties of the cured networks (in this current study) would be expected to be a function of (1) $M_c$ due to oligomeric $M_n$ and MWD and (2) $M_c$ due to the amount of the dimethacrylate oligomer relative to styrene in the chemical structure. Since the glass transition temperatures of high molecular weight polystyrene and also the analogous high molecular weight poly(hydroxyether)s (which have the same backbone as the vinyl ester oligomers) are both near 100°C, the $T_g$s of the networks were expected to be relatively insensitive to changes in $M_c$ due to chemical composition (copolymer effect). This was shown by Li in the estimation of the $T_g$ of uncrosslinked vinyl ester copolymers from the Fox equation. In this study, the $T_g$ only increased slightly as styrene contents increased in the vinyl ester resins. Therefore, it has been concluded that the major effect on the shift in $T_g$ in the present systems should be more dependent on changes in crosslink density and $M_c$ due to oligomer $M_n$ and MWD.

Due to the numerous variables encountered in highly crosslinking reactions, many have found it very difficult to correlate $T_g$ with the degree of crosslinking in network systems. Hale et al. modeled the dependence of the glass transition temperature on the extent of reaction for highly cross-linked thermosetting polymers. Although Hale et al. used a multifunctional epoxy-novolac system to obtain the $T_g$ and conversion data, their model is applicable to other thermosetting systems at low conversions using independently obtained data from monofunctional compounds. Their model assumes that the increase in $T_g$ is caused by 1) a decrease in chain-end concentration 2) the formation of effective crosslinks and 3) a further decrease in the configurational entropy due to departure from Gaussian chain statistics at high crosslink densities. The $T_g$ of the uncrosslinked polymer was allowed to vary with conversion in
order to account for the decrease in chain ends. Successful results were obtained when these assumptions were taken into account.

Figure 4-10 shows the $T_g$ values of vinyl ester resins cured at 140°C as a function of oligomer molecular weight, molecular weight distribution and styrene content. The $T_g$ values of vinyl ester resin cured at 140°C is very close to the maximum $T_g$ values cured at higher temperature and high pressure (180°C and 150 Pa). Since the cure temperature of 140°C is close to the $T_g$ of vinyl ester resins, it can be assumed that almost 100% conversion was achieved.

Table 4-12. Glass Transition Temperatures (°C) of vinyl ester/styrene networks cured at 140°C for 1 hour.

<table>
<thead>
<tr>
<th>Resin</th>
<th>20% styrene</th>
<th>28% styrene</th>
<th>35% styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>700g/mol, Mw/Mn=1.30</td>
<td>155</td>
<td>147</td>
<td>144</td>
</tr>
<tr>
<td>900g/mol, Mw/Mn=1.47</td>
<td>146</td>
<td>144</td>
<td>131</td>
</tr>
<tr>
<td>900g/mol, Mw/Mn=1.28</td>
<td>144</td>
<td>146</td>
<td>144</td>
</tr>
<tr>
<td>1000g/mol, Mw/Mn=1.49</td>
<td>145</td>
<td>140</td>
<td>142</td>
</tr>
<tr>
<td>1000g/mol, Mw/Mn=1.37</td>
<td>144</td>
<td>142</td>
<td>138</td>
</tr>
<tr>
<td>1200g/mol, Mw/Mn=1.07</td>
<td>138</td>
<td>132</td>
<td>132</td>
</tr>
</tbody>
</table>

The data show that the shifts in the glass transition temperature are indeed due to two effects: the degree of cross-linking ($M_n$ and MWD) and changes in composition (the copolymer effect). As stated earlier, the latter did not produce as large an effect on the glass transition temperature. Overall, increasing the crosslink density always results in an increase of the $T_g$ of the network. In other words, as the degree of crosslinking increases, the higher the temperature must be in order to initiate the onset of molecular mobility (Table 4-13). According to Table 4-12, it was found that when the styrene content in the system increased, the $T_g$ of network decreased. For example, when the styrene content in the resins increased from 28 weight % to 35 weight %, the $T_g$s changed from 147°C to 144°C for the 700g/mole resin. As the molecular weight increased, the distance between crosslink junctions increased. An increase in $M_c$ results in a decrease in the crosslink density of the network and the glass transition temperature. There was not much change in $T_g$ due to MWD, even though there were changes in $M_c$. Apparently this
increase was not large enough to significantly affect the $T_g$. However, there was a large decrease in $T_g$ when the oligomer molecular weight was increased from 700g/mole to 1200g/mole. The difference in $M_c$ was the greatest between these two systems.

As described in section 4.2.3, the glass transition temperature of the samples cured at room temperature (~24°C) followed by a 93°C postcure had significantly lower glass transition temperatures (Table 4-14). This was indeed due to a decrease in the crosslink density of these materials as a result of the cure procedure producing a more open network.

Table 4-13. Glass transition temperature vs. crosslink densities of dimethacrylate/styrene networks cured at 140°C for 1 hour.

<table>
<thead>
<tr>
<th>Crosslink Density</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mol/cm$^3$)</td>
<td>(°C)</td>
</tr>
<tr>
<td>700g/mol, $M_w/M_n=1.30$</td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>3.48E-03</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>2.42E-03</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.85E-03</td>
</tr>
<tr>
<td>900g/mol, $M_w/M_n=1.47$</td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>2.59E-03</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>2.03E-03</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.71E-03</td>
</tr>
<tr>
<td>900g/mol, $M_w/M_n=1.28$</td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>2.06E-03</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>1.70E-03</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.35E-03</td>
</tr>
<tr>
<td>1000g/mol, $M_w/M_n=1.49$</td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>2.03E-03</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>1.75E-03</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.60E-03</td>
</tr>
<tr>
<td>1000g/mol, $M_w/M_n=1.37$</td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>1.37E-03</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>1.12E-03</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.04E-03</td>
</tr>
<tr>
<td>1200g/mol, $M_w/M_n=1.07$</td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>1.28E-03</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>1.22E-03</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.05E-03</td>
</tr>
</tbody>
</table>
Table 4-14. Glass transition temperatures (°C) of dimethacrylate/styrene networks cured at room temperature (~25°C) for 10 hours and postcured at 93°C for 2 hours.

<table>
<thead>
<tr>
<th>Resin</th>
<th>20% styrene</th>
<th>28% styrene</th>
<th>35% styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>700g/mol, Mw/Mn=1.30</td>
<td>113</td>
<td>119</td>
<td>119</td>
</tr>
<tr>
<td>1200g/mol, Mw/Mn=1.07</td>
<td>118</td>
<td>116</td>
<td></td>
</tr>
</tbody>
</table>

4.3.6 Cure Shrinkage

Shrinkage is the reduction in volume or linear dimensions that occurs during cure. Shrinkage induces stresses, which can lead to early cracking under thermal cycling.\textsuperscript{107} The specific volume (1/density) of uncured resins and fully cured networks for each series of materials was determined as a function of oligomer molecular weight and styrene content. As the difference in specific volume when going from the uncured resin to the cured resin increased, the percent shrinkage increased. Volume shrinkage upon cure was calculated as follows:

\[
\text{% shrinkage} = 100 \times \frac{1}{\rho(\text{uncured})} - \frac{1}{\rho(\text{cured})} \frac{1}{\rho(\text{uncured})}
\]

(4-10)
Figure 4-33. Specific volumes and cure shrinkages of a 700 g/mole and 1200 g/mole dimethacrylate resin as functions of styrene content (cured at 140°C for 1 hour with BPO).

Figure 4-34. Specific volumes and cure shrinkages of a 900 g/mole dimethacrylate resin as functions of styrene content (cured at 140°C for 1 hour with BPO).
Figure 4-35. Specific volumes and cure shrinkages of a 1000 g/mole dimethacrylate resin as functions of styrene content (cured at 140°C for 1 hour with BPO).

Figure 4-36 shows the cure shrinkage for all of the resins cured at 140°C for 1 hour. The shrinkage in the vinyl ester resins ranged from 3.3% to 8.4% with varying molecular weight, MWD and styrene content. As the molecular weight decreased, there were larger differences in the specific volumes, resulting in higher shrinkage. The effects of crosslinking on the density of the cured network can be seen clearly by comparing two series of resins with different molecular weight oligomers. For short chain vinyl ester resins with $M_n=700$ g/mole, higher crosslink density, and lower specific volume can be expected. Long chain vinyl ester resins with $M_n=1200$ g/mole resulted in lower crosslink density and higher specific volume. The 900g/mole and 1000g/mole oligomers showed the same trend for percent shrinkage. The decrease in the in the specific volume with crosslink density suggests that the free volume in the resins system is reduced by crosslinking. For lower molecular weight resins or shorter chains, the molecular segments are tied up by crosslink points more than longer chain or higher molecular weight.
systems, resulting in lower specific volume. When the molecular weight is constant, the oligomer with higher polydispersity had the bigger difference in specific volume when going from the uncured to the cured state. The higher polydispersity, in each case, has a larger percentage of short chains, which shrink more when cured. Shrinkage is therefore higher in the case where the polydispersity is higher. Overall, the cure shrinkage increases with increases in the number of methacrylate double bonds per gram (lower dimethacrylate oligomer molecular weight or higher polydispersities for a given \( M_n \)) due to the decrease in number of molecules from polymerization.

![Graph](image)

Cured at 140°C for 1 hour

Figure 4-36. Cure shrinkage (%) as a function of styrene content, MW and MWD of dimethacrylate/styrene networks.

Figure 4-36 also shows the shrinkage of two series of vinyl ester resins as a function of styrene concentration. It was also found that the specific volume of the uncured resins with varied styrene concentrations and the corresponding fully cured networks follow the same linear relationship. The specific volume and the difference in specific volume of the uncured and cured materials increased linearly with increased styrene concentration.
As shown in Table 4-15, the shrinkage of the vinyl ester resin with Mn=700 g/mole, increased from 6.0% to 8.4% as the small monomer styrene increased from 20 weight % to 35 weight %. This was due to the reduction in density in going from monomeric styrene with a density of 1.09 g/cm³ to polystyrene with a density of 0.9 g/cm³, corresponding to approximately 17% volume shrinkage. Typically, most thermoset copolymers have minimal shrinkage (approximately 2-3%). The results of Figure 4-36 suggest that resin shrinkage can be reduced by decreasing styrene content, although it is preferred to preserve the azeotropic styrene/methacrylate ratio of approximately 52 mole percent styrene for a 700g/mol oligomer (28 weight percent).³¹

Table 4-15. Cure shrinkage values for crosslinked dimethacrylate/styrene networks.

<table>
<thead>
<tr>
<th>Resin</th>
<th>20% styrene</th>
<th>28% styrene</th>
<th>35% styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>700g/mol, M_w/M_n=1.30</td>
<td>6.03</td>
<td>7.61</td>
<td>8.4</td>
</tr>
<tr>
<td>900g/mol, MW/Mn=1.47</td>
<td>5.8</td>
<td>7.1</td>
<td>7.9</td>
</tr>
<tr>
<td>900g/mol, X=1.28</td>
<td>5.6</td>
<td>6.7</td>
<td>7.2</td>
</tr>
<tr>
<td>1000g/mol, MW/Mn=1.49</td>
<td>3.8</td>
<td>5.92</td>
<td>7.12</td>
</tr>
<tr>
<td>1000g/mol, X=1.37</td>
<td>3.5</td>
<td>5.6</td>
<td>6.83</td>
</tr>
<tr>
<td>1200g/mol, MW/Mn=1.07</td>
<td>3.3</td>
<td>5.3</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Although room temperature density measurements can be used to accurately calculate shrinkage, another method involves using dilatometry to determine the shrinkage as a function of cure. Due to the relatively large amounts of volume shrinkage for vinyl polymerization (23% for methylmethacrylate) dilatometry has long been a standard method for monitoring conversion during polymerization. The dilatometer used in this present study was built by Lee et al. In the present study, dilatometry measurements showed that the overall shrinkage or volume change was approximately 8% for a 700g/mole vinyl ester resin with 28% styrene. Figure 4-37 shows the volume change and the corresponding temperature profile as a function of time. In the percent volume change curve, there was an initial expansion corresponding to the onset of polymerization. Since percent volume change was calculated by subtraction of the polymer (baseline) and the reacting monomer, the initial expansion was caused by the differences in thermal expansion of the monomer and the polymer. When polymerization began, the difference
in the coefficients of thermal expansion between curing monomer and cured polymer lessened and polymerization shrinkage became the dominating factor.\textsuperscript{75}

Shrinkage measurements from room temperature densities (3.3.9) resulted in approximately 7.61% final shrinkage compared to 8.03% with dilatometer measurements. With dilatometry, the shrinkage could be followed throughout the reaction. Although not exact, there is a close correlation between the two techniques. This difference could be due to the curing procedure and the sample size. Samples employed in the dilatometry measurements had a circular geometry (approximately 8 cm in diameter) and were essentially thin film samples, whereas samples used in the simple density measurements were approximately 3 mm thick. The bulk samples were placed directly in a preheated oven at 140°C and held for 1 hour. Due to the nature of the dilatometry experiments, the sample chamber could not be preheated, therefore the samples were ramped up to 140°C and held for 1 hour. Benzoyl peroxide was used as the peroxide initiator in each case.

![Graph showing temperature and volume change](image)

**Figure 4-37.** Volume change and temperature profile of a 700g/mole resin with 28% cured at 140°C styrene from dilatometry measurements.
As shown in Figure 4-38, there was a decrease in the cure shrinkage when the oligomers were cured at room temperature followed by a 93°C postcure employing MEKP as the peroxide initiator. The cure shrinkage decreased from 7.6 to 5.5% for a 700g/mole oligomer with 28% styrene. There is usually more stress associated with systems cure at faster rates. This suggests that varying the extent of cure can reduce shrinkage, provided that the cure procedure is suitable for the intended application. However, cure shrinkage is also a function of vinyl group conversion. In other words, the more vinyl groups converted, the more shrinkage will occur in the system. The FT-IR data in section 4.2.3 showed lower conversion for the dimethacrylate vinyl groups in the room temperature cured samples. Therefore, we would expect lower shrinkage due to incomplete conversion of these double bonds. However, it is important to examine the data based on the moles of vinyl groups converted.

Figure 4-38. The effect of cure procedure on shrinkage of 700 and 1200g/mole oligomers.
Table 4-16 shows the shrinkage, total moles of vinyl groups converted and the shrinkage as a function of vinyl group conversion. There is very little difference between the samples cured at the elevated temperature of 140°C versus the samples cured at room temperature, both having approximately the same shrinkage based on the number of moles of vinyl groups converted. Although the room temperature samples are not completely cured, they have comparable shrinkage to the fully cured systems based on the amount of conversion in the system. This considerable amount of shrinkage is probably due to the high conversion of the styrene component (96%).

Table 4-16. Cure shrinkage of a 700g/mole resin with 28% styrene as a function of vinyl group conversion.

<table>
<thead>
<tr>
<th>Cure Procedure</th>
<th>Shrinkage (%)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT Cured</td>
<td>5.5</td>
<td>63 (styrene)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78 (Methacrylate)</td>
</tr>
<tr>
<td>93C Postcure</td>
<td>5.7</td>
<td>96 (styrene)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>84 (Methacrylate)</td>
</tr>
<tr>
<td>140C Postcure</td>
<td>6.3</td>
<td>98 (styrene)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>87 (Methacrylate)</td>
</tr>
</tbody>
</table>

It is interesting to note that the difference in shrinkage between the two cure procedures occurs in the postcure step of the room temperature cured samples. There is essentially no further densification of the network during the postcure. This occurrence is partly due to the build-up of relatively high conversion early on in these free radical reactions. FT-IR data in section 4.3.2 showed 63% and 78% for styrene and methacrylate, respectively. Apparently this conversion was large enough to lock the network in place. Figure 4-39 shows a schematic of the network before and after the 93°C postcure illustrating the fact that the overall size of the three
dimensional network does not decrease, however, additional conversion took place within the network. Additional ambient temperature cures were conducted with 115°C and 140°C postcures. There was still no significant increase in density even after the elevated temperature postcures.

Cure Shrinkage of a 700g/mol Resin with 28% Styrene Cured at Ambient Temperature, Followed by an Elevated Temperature Postcure

<table>
<thead>
<tr>
<th>After Ambient Cure</th>
<th>After 93°C Postcure</th>
</tr>
</thead>
<tbody>
<tr>
<td>22% Unreacted Methacrylate Vinyl Groups</td>
<td>16% Unreacted Methacrylate Vinyl Groups</td>
</tr>
<tr>
<td>37% Unreacted Styrene Vinyl Groups</td>
<td>4% Unreacted Styrene Vinyl Groups</td>
</tr>
</tbody>
</table>

Figure 4-39. Schematic of the ambient cured dimethacrylate network before and after the 93°C postcure.

Shrinkage is partially explained by the decrease in the van der Waals volume from the conversion of van der Waals bonds into covalent bonds. Some researchers feel that this explanation only accounts for a portion of the shrinkage behavior observed during polymerization, and underestimates the experimentally observed shrinkage. Other
researchers$^{36,97}$ have noted similar trends between volume relaxation, polymerization rate and conversion using photopolymerization of vinyl compounds.

In a study of the reaction kinetics and volume relaxation during polymerization of multiethylene glycol dimethacrylates by Anseth et al., it was found that at faster rates of polymerization, the macroscopic rate of volume shrinkage was much slower than the rate at which the double bonds were consumed.$^{36}$

Patel$^{109}$ characterized volume shrinkage for methacrylate vinyl groups and found that if the system relaxes much slower than the rate of polymerization, excess free volume is generated, which results in greater mobility of the reacting species. This was found to lead to a higher maximum functional group conversion and a shift in the peak maximum of the rate to higher conversion.

In Kloosterboer’s study of dimethacrylate networks$^{97}$, a delay of shrinkage was also found to occur with respect to conversion, proving that, volume shrinkage does not always occurs at the same rate as chemical conversion in crosslinking polymerizations. Since gelation occurs at very low conversion (Figure 2-17) in bulk crosslinking polymerization of divinyl compounds, the majority of the polymerization process proceeds in the gelled phase. Therefore, in order to convert the free volume generated by the chemical reaction into shrinkage, the entire gel must move cooperatively. Since this process is usually slower that the diffusional motion of free monomer molecules, shrinkage cannot keep up with conversion during polymerization.

Kloosterboer$^{110}$ also examined the effect of volume relaxation and thermal mobilization of trapped radicals on the final conversion of photopolymerized diacrylates such as tetra-ethyleneglycol diacrylate (TEGDA). In both the presence and absence of trapped radicals, there was a strong influence of thermal relaxation on the capability for further polymerization. Again, it was also shown that vinyl group conversion runs ahead of volume relaxation. Due to the formation of a network, the shrinkage process (driven by the chemical reaction) lagged behind the vinyl group conversion.

Kloosterboer$^{110}$ found that although chemical reaction drives the shrinkage process, a high extent of reaction reduces the rate of shrinkage. These results agreed with the current study, where shrinkage ceased (in the postcure step) after the build-up of a relatively high extent of conversion (in the room temperature cure step). Essentially all of the shrinkage occurred in the room temperature step, during the initial polymerization of the network (chemical reaction).
However, when the curing was done in one step, 140°C for one hour, the samples continued to shrink throughout the polymerization, thus confirming that shrinkage is chemically driven (Figure 4-37).

Alternatively, a high extent of shrinkage can also reduce the rate of chemical reaction. Kloosterboer noted that if partly polymerized samples were allowed to shrink, their capability for further photopolymerization at room temperature was greatly reduced. In this current study, samples cured at 140°C (continuous cure at an elevated temperature) reached full conversion for both the styrene and methacrylate vinyl groups. It was expected that room temperature-cured samples would show essentially full conversion when postcured at 140°C due to increased molecular mobility (over that of the 93°C postcure) with the higher postcure temperature. This was not the case, since the methacrylate double bonds only reached 84% conversion (although the styrene vinyl groups reached 96% conversion) even after a 140°C postcure. Regardless of the postcure, the same final (incomplete) conversion was achieved when the cure process was interrupted (non continuous-two stage cure). Therefore, it was concluded that in the current study, the final conversion was limited by the additional relaxation in the room temperature step. Kloosterboer\textsuperscript{110} also showed that an interruption of u. v. irradiation reduced the final conversion and attributes this behavior to the competition between chemical reaction and volume relaxation. This dependence of the rate of polymerization and the polymerization kinetics on the rate of volume relaxation was modeled by Bowman and Peppas.\textsuperscript{111}

As shown in this section, vinyl ester/styrene resins undergo significant volume shrinkage upon cure which leads to residual stresses in the laminae. It has been well established that these resins must be diluted to reduce the viscosity for processing. However, it has also been shown that large amounts of reactive diluents, such as styrene cause large shrinkages in the matrix materials. These shrinkages can facilitate processing by pulling away from the die walls during operations such as pultrusion molding. However, these strains can also exceed the strength of the matrix material, leading to residual stresses and matrix cracking. When the density changes take place in the liquid phase, no internal stresses can occur. However, stress is inevitable in the gelled or solid state especially if materials embedded in the resin have a different thermal expansion coefficient, which is the case with composites. When the matrix material is actually used in the fabrication of a composite (assuming that there is perfect adhesion between the matrix material and the fiber and that this bond remains intact) this shrinkage can cause the fiber
to be stressed in compression and the matrix to be stressed in tension (Figure 4-40). This generally results in residual stress in composites leading to visual flaws as well as microcracking. These defects make it impossible to gain accurate mechanical test results. During testing, the specimen will usually fail at the weakest point—the flaw. Lawerence et al. have used embedded optical fibers to examine stress in neat resins and residual stress in the corresponding composites.112-113

Figure 4-40. Matrix shrinkage at the micromechanics level.

4.3.7 Cooling Shrinkage

Dimethacrylate networks are expected to shrink upon cooling just as they expand upon heating. This expansion upon heating was evident from the values of the coefficients of thermal expansion in section 4.3.4. As expected, the cooling shrinkage was less for samples cured or postcured at lower temperatures. Cooling shrinkage was calculated using equation (4-11) which is similar to the calculation of cure shrinkage in section 4.3.7. The values for shrinkage upon cooling (Table 4-17) were between 1-4% for samples cured at 140°C for 1hour.
\[
\text{\% cooling shrinkage} = 100 \times \frac{1}{\rho_{140}} \frac{1}{1} - \frac{1}{\rho_{RT}}
\]

\(\rho_{140}\) is the density at 140°C and \(\rho_{RT}\) is the density at room temperature. The density at 140°C was calculated similar to the density calculated 40°C above \(T_g\) (equation (3- 2)). Cooling shrinkage values for room temperature cured samples postcured at 93°C were approximately 1% for both the 700g/mole and 1200g/mole precursor oligomers with 20-35% styrene.
Table 4-17. Cooling shrinkage for dimethacrylate networks cured at 140°C for 1hr.

<table>
<thead>
<tr>
<th></th>
<th>Cooling shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>700g/mol, M_w/M_n=1.30</strong></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>3.5</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>2.9</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>3.7</td>
</tr>
<tr>
<td><strong>900g/mol, M_w/M_n=1.47</strong></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>0.5</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>1.0</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>900g/mol, M_w/M_n=1.28</strong></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>2.3</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>1.6</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>2.1</td>
</tr>
<tr>
<td><strong>1000g/mol, M_w/M_n=1.49</strong></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>4.7</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>3.6</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>3.7</td>
</tr>
<tr>
<td><strong>1000g/mol, M_w/M_n=1.37</strong></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>2.1</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>4.2</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>3.7</td>
</tr>
<tr>
<td><strong>1200g/mol, M_w/M_n=1.07</strong></td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>3.8</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>3.4</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>4.1</td>
</tr>
</tbody>
</table>
4.3.8 Chemical Resistance and Water Absorption

The network structure of crosslinked vinyl ester resins was also studied by equilibrium swelling experiments. It has been determined that the extent of swelling is inversely proportional to the crosslink density of a network polymer. According to Nielsen, if an uncrosslinked polymer is soluble in a liquid, then the same polymer, when crosslinked, will swell in the liquid. The three types of data obtainable from swelling measurements are the amount of polymer that is not incorporated into the network structure (extractable fraction), the molecular weight of the sol fraction, and the amount of swelling of the gel fraction. Samples (3 mm thick) were immersed in two different solvents (dichloromethane and water) for ~2 weeks and dried under vacuum at 150°C for three days. Equilibrium swelling of crosslinked vinyl ester resins was achieved after swelling in these solvents for two weeks. In this work, dichloromethane (CH₂Cl₂), and water were used as solvents. Swelling indices (equation (4-12)) and gel fractions (equation (4-13)) were used to describe the chemical resistance of the networks. Swelling was studied as a function of molecular weight, solvent, cure rate and peroxide initiator.

\[
\text{Swelling Index} = q = \frac{\text{Volume of swollen gel}}{\text{Volume of unswollen gel}} = 1 + \frac{[(W_{sw} - W_d) (1/\rho_s)]}{[W_d (1/\rho_g)]}
\]

\(q = 1.00\) corresponds to no swelling

\(W_{sw}\) weight of gel in swollen state

\(W_d\) weight of gel in dry state

\(\rho_s\) density of solvent

\(\rho_g\) density of gel
Gel fraction = \frac{\text{weight of gel}}{\text{initial weight}}

When cured at 140°C (BPO), all of the networks exhibited low swelling in dichloromethane, indicating highly crosslinked systems (Figure 4-41). The vinyl ester-styrene network with a relatively high precursor molecular weight (1200 g/mole) had higher swelling indices than the vinyl ester-styrene networks with relatively low precursor molecular weight (700 g/mole) due to the longer chains between crosslinks in the former. When styrene contents increased, the networks exhibited higher swelling due to the decrease in crosslink density for both 700 g/mole and 1200 g/mole precursor vinyl ester resins. The gel fractions were calculated to be between 97-100% for all of the systems cured at 140°C for 1 hour. For samples cured at room temperature and postcured at 93°C (MEKP/DMA/CoNap), the gel fractions were between 94-95%. The swelling indices were also higher in room temperature cured samples followed by the 93°C postcure due to the decrease in network density as reflected by the increased M_c values (Figure 4-32).

Despite the amount of swell, these are insoluble, intractable networks with high gel fractions. Although these networks swell due to the decrease in network density and/or dangling ends, they are still insoluble in common solvents and there were no considerable extractable components, verified by FT-IR and ^1^H-NMR. If indeed there are dangling ends, and they are incorporated into the network by just one point, they are now a part of the network and cannot be extracted.
Swelling was also determined for room temperature cured samples using MEKP before the postcure to determine if there were any extractable components at that point. Bulk and crushed samples were utilized in this study. If there were extractable components, the larger surface area of the crushed samples would promote an enhanced rate of extraction. There was a higher percentage of the sol component and an increase in the swelling indices when the networks were immersed in solvent before they were postcured (Table 4- 18). Crushed samples represent the worst case scenario and exhibited the highest swelling indices and sol fractions. The sol fractions and the swelling indices decreased when the post cure was employed. These data are consistent with solid state $^{13}$C-NMR and FT-IR (section 4.2.3) data which showed an increase in the conversion after the postcure step. The fact that the crushed samples had lower swelling indices than the bulk samples after the postcure is likely due to experimental error (Figure 4- 42). However, the sol fraction did follow the correct trend (Table 4- 18).
Table 4-18. Sol fractions (%) of crushed and bulk samples cured at room temperature (before and after the postcure).

<table>
<thead>
<tr>
<th></th>
<th>3mm X 6mm X 20mm</th>
<th>crushed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient Cure (only)</td>
<td>18</td>
<td>31</td>
</tr>
<tr>
<td>Ambient Cure + 93°C Postcure</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>140°C</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 4-42. Swelling index as a function of sample size (3mm x 6mm x 20mm), cure rate, molecular weight and styrene content in dichloromethane.
FT-IR showed that there was considerable cure (63% and 78% for styrene and methacrylate, respectively before the postcure). However, there were also considerable sol fractions, around 31%, for the crushed samples. The solvent was examined after the samples were removed and no extractables were found by FT-IR or NMR for the bulk samples, despite the large percentage of sol fraction. This is possibly due to the fact that solutions were too dilute.

Solvent types also have a significant effect on the swelling behavior of networks. Methylene chloride (CH₂Cl₂) resulted in the highest swelling of the vinyl ester networks, possibly due to the fact that the solubility parameter of this solvent is very close to that of networks. The solubility parameters of vinyl ester networks from 20%-60% styrene were calculated as 9.8-10.0 by group contribution methods using the MG&PC software (Miscibility Guide & phase calculator)¹¹⁴,¹¹⁵. The solubility parameter of CH₂Cl₂ is 9.7.

In water, these networks exhibited almost no swell (average swelling indices approximately 1.02) (Figure 4-43). Therefore, the solvents chosen were ideal since they represent the extremes in chemical resistance for these networks. It was also shown by Verghese et al.¹¹⁶ that the equilibrium maximum water uptake of the vinyl esters is relatively low (1-2 wt. %). This is not only consistent with the current finding, but also comparable to or less than most epoxy networks.¹¹⁷ Within this range, the maximum water absorption generally decreases with an increase in styrene, presumably due to the relatively hydrophobic character of styrene and its lack of hydrogen bonding capability.

The peroxide initiator also has a significant effect on the swelling behavior of networks. As explained in section 4.2.3, BPO produced more conversion than did MEKP using the same room temperature cure schedule. Due to increased conversion, or a tighter network, ambient cures with BPO showed less swelling. Even though BPO can be used in an “ambient” or “elevated temperature cure”, BPO is much more effective when used to cure at elevated temperatures (140°C for one hour), resulting in the lowest swell index in Figure 4-44. The swelling index values are significant since there was only +/- .01 % error.
Figure 4-43. Swelling index as a function of cure rate, molecular weight and styrene content in water.
Figure 4-44. Swelling index as a function of cure rate and peroxide initiator.

700g/mol with 28% styrene
Solvent --- dichloromethane

Swelling Index

1.63
rm temp (MEKP)
1.59
rm temp (BPO)
1.56
140°C (BPO)

increasing conversion
4.4 Effect of Crosslinking on Mechanical Properties of Dimethacrylate Networks

4.4.1 Introduction

The mechanical behavior of polymers is time dependent, or viscoelastic, and design data based on short-term tests could be misleading in applications that involve long-term loading. The magnitude of the time dependence of polymers is very temperature dependent. Glassy or semicrystalline polymers are very weakly viscoelastic well below their glass transition temperatures and test data based on a time-independent analysis is adequate for these systems. Such is the case for the polymeric materials under investigation in this study, since they have relatively high glass transition temperatures (>100°C). Common factors affecting mechanical properties are temperature, molecular weight, molecular weight distribution and copolymerization. Each of these factors will be addressed in this chapter.

Temperature affects properties due to its influence on intramolecular motion and intermolecular interaction. This effect can be seen by examining the thermomechanical spectrum (Figure 4-24) where there is a four orders of magnitude drop in modulus going from below to above the T_g for these highly crosslinked systems.

Molecular weight also affects mechanical properties. When the molecular weight is low, the applied mechanical stress tends to slide molecules over each other and separate them. However, when the molecular weight is increased, the molecules become entangled and their mechanical strength increases. The sum of the entanglements and the intermolecular attractive forces exceed the strength of the individual covalent bonds in the backbone of the polymer chain. This is generally the case with very high molecular weight thermoplastics and crosslinked thermosets. Another important factor, which affects mechanical properties in network systems, is the number of crosslinks per unit volume, which will be addressed in detail in this chapter.

Copolymerization can affect both physical and mechanical properties. This effect can be both negative and positive, and is usually a trade off in designing polymeric systems. As shown in section 4.3.5, copolymerization with styrene decreases the glass transition temperature of these dimethacrylate networks (limiting their application), but provides a workable viscosity for processing the uncured resin as shown in section 4.1.4. Later in this chapter, the incorporation of
styrene will be shown to have both positive and negative effects on properties such as toughness, tensile strength and hardness.

Since dimethacrylate networks consist of thermoplastic polymer chains covalently bonded, the polymer is linked in three dimensions. The polymeric chains are not allowed to slip past one another; this results in good mechanical properties. This section will discuss the glassy state mechanical properties and describe the chemical and structural parameters which contribute positively to the mechanical behavior of these networks.

4.4.2 Fracture Toughness

Vinyl ester resins are generally considered brittle materials, therefore characterization of toughness of vinyl ester resins is very important. The degree of brittleness of a polymer glass is related to the amount of flow that occurs during the failure process. This flow absorbs energy during the failure and decreases the brittleness of the glassy material. Free volume, morphology, and small main-chain glassy state molecular motions all affect these flow processes. In order for a material to be structurally useful, it must be able to withstand a reasonable amount of flaws and stress before failing. Toughness tests quantify this ability of a material to resist crack propagation under an applied stress or load.

For each sample, a curve of load vs. displacement was obtained. The toughness values were obtained in terms of the plane strain critical stress intensity factor ($K_{1c}$) and were calculated from the load causing crack propagation in each sample using an equation established on the basis of elastic stress analysis (equation (4- 14)). The $K_{1c}$ values ranged from a very brittle .87 MPa-m$^{1/2}$ to a relatively tough 2.02 MPa-m$^{1/2}$ (Table 4- 19).

$$K_{1c} = \frac{P}{BW^{3/2}} \frac{3(X)^{1/2}}{2(1+2X)(1-X)^{3/2}} \left[ 1.99-X(1-X)(2.15-3.93X +2.7X^2) \right]$$

(4- 14)

P is the load, B is the specimen thickness, W is the specimen width, a is the crack length, and $X=a/W$. 

153
Table 4-19. Fracture toughness, K\textsubscript{1c} (MPa-m\textsuperscript{0.5}), values for fully cured dimethacrylate oligomer-styrene networks.

<table>
<thead>
<tr>
<th>Resin</th>
<th>20% styrene</th>
<th>28% styrene</th>
<th>35% styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 g/mol</td>
<td>0.87 ± 0.12</td>
<td>0.72 ± 0.11</td>
<td>0.63 ± 0.11</td>
</tr>
<tr>
<td>M\textsubscript{w}/M\textsubscript{n} = 1.30</td>
<td>0.94 ± 0.03</td>
<td>0.87 ± 0.09</td>
<td>0.76 ± 0.05</td>
</tr>
<tr>
<td>900 g/mol</td>
<td>0.97 ± 0.05</td>
<td>0.92 ± 0.03</td>
<td>0.79 ± 0.09</td>
</tr>
<tr>
<td>M\textsubscript{w}/M\textsubscript{n} = 1.47</td>
<td>1.03 ± 0.07</td>
<td>0.96 ± 0.12</td>
<td>0.82 ± 0.07</td>
</tr>
<tr>
<td>900 g/mol</td>
<td>1.51 ± 0.17</td>
<td>1.40 ± 0.12</td>
<td>1.24 ± 0.10</td>
</tr>
<tr>
<td>M\textsubscript{w}/M\textsubscript{n} = 1.37</td>
<td>2.02 ± 0.07</td>
<td>1.94 ± 0.02</td>
<td>1.52 ± 0.06</td>
</tr>
<tr>
<td>1000 g/mol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M\textsubscript{w}/M\textsubscript{n} = 1.49</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200 g/mol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M\textsubscript{w}/M\textsubscript{n} = 1.07</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Much of the success of crosslinked polymer systems as adhesives and matrix materials for composites is attributed to their glassy mechanical performance. One property that is of particular relevance to the application of crosslinked polymers in the glassy state is fracture toughness. Fracture toughness should exhibit a direct dependence on the molecular weight between crosslinks (M\textsubscript{c}).\textsuperscript{120} Increases in M\textsubscript{c} normally result in improved toughness and/or ductility in a network.\textsuperscript{79} In general, lower M\textsubscript{c} values (higher crosslink densities) are associated with a higher network rigidity, which limits the development of the local plastic zone at the crack tip, thus reducing the degree of energy dissipation.

All of the networks prepared with the higher molecular weight vinyl ester (1000-1200 g/mole) were much tougher materials than those prepared with the lower molecular weight vinyl esters (700-900 g/mole). Thus, the increase in M\textsubscript{c} obtained by increasing the molecular weight of the vinyl ester component has a large positive effect on the resistance to crack propagation. A certain degree of crosslinking increased the toughness. However, very high degrees of crosslinking resulted in brittle materials. Therefore, at very low M\textsubscript{c} values or high crosslink densities, the toughness decreased. Figure 4-45 shows a summary of the crosslinked resins at various molecular weights and styrene contents.
Similar to Brennan\textsuperscript{120}, Bos and Nusselder\textsuperscript{121} also found that the toughness in thermosets is directly proportional to the molecular weight between crosslinks. This trend (increasing toughness with increasing M\textsubscript{c}) is well known for crosslinked epoxy systems.\textsuperscript{21,96} In Espuche’s investigation of an epoxide terminated diglycidyl either of bisphenol A cured with 4,4’-diamino-3,3’dimethyldicyclohexylmethane, the crosslink density was varied by changing the amounts of a difunctional amine chain extender.\textsuperscript{121} M\textsubscript{c} values were calculated from rubbery moduli and showed the expected trend relative to toughness.

However, Brennan et al. also illustrated via a review of the literature, that the connection between fracture toughness and crosslink density is still ambiguous despite the expected relationship.\textsuperscript{120} Other important structural distinctions between polymer network systems besides crosslink density may be the cause for the undefined influence of M\textsubscript{c} on fracture behavior. The present study also varied the M\textsubscript{c} by varying the amount of the reactive comonomer. For each series, the plane strain critical stress intensity factors (K\textsubscript{1c}) consistently decreased as the styrene content was increased, despite the fact that M\textsubscript{c} also increased. This can be clearly seen in Figure 4- 46 (this figure also illustrates the 3-point bend method used to determine the k\textsubscript{1c} values). The effect of styrene on the toughness was very complicated here. The copolymer effect may be the major factor. It was reasoned that the decreases in toughness with increases in
styrene content could be the result of the vinyl ester backbone chemistry inherently providing a
tougher material (relative to having styrene segments included). In addition, higher styrene
content increased the shrinkage during cure, which could also contribute to poorer mechanical
properties of the cured networks. Additionally, with higher styrene contents in the resins the
composition is far from the azotropic copolymerization point. As a result, at the end stage of the
cure reaction, only styrene is left. This results in a heterogeneous structure. All these factors
likely contributed to the poor toughness of vinyl ester resins at high styrene contents. When the
styrene contents were higher than 50 weight percent, the cured materials were so brittle that it
was extremely difficult to obtain an accurate $K_{1c}$ value.

![Figure 4- 46. The effect of $M_c$ on fracture toughness when the precursor $M_n$ is varied (cured at 140°C).](image)

Decreasing the polydispersities of the oligomers (for a given $M_n$) also increased the
fracture toughness. It should be recognized that the 700g/mole dimethacrylate oligomer, with
the lowest toughness values, had an unusually large component of its molecular distribution

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skewed toward the low molecular weight fraction. When the molecular weight remained constant and only the distribution was changed, the skewed distributions had slightly lower toughness numbers (in both the 900g/mole and the 1000g/mole case). Since only the distribution changed within a set, this now allowed the effect of MWD to be studied independently. Again, the decrease in polydispersity of the oligomers (for a given $M_n$) increased the fracture toughness, due to an increase in $M_c$ (Figure 4-47). Although the difference in molecular weight distribution was not as obvious in these cases, it was, however, enough difference in chain length distribution to slightly alter the toughness.

Figure 4-47. The effect of $M_c$ on fracture toughness when $M_W/M_n$ is varied for 900g/mole and 1000g/mole precursor oligomers (cured at 140°C).

Cure procedure also had an effect on the toughness of these dimethacrylate networks. As shown in Figure 4-48, there was an increase in the fracture toughness when the oligomers were cured at room temperature (25°C) followed by a 93°C postcure employing MEKP as the peroxide initiator. Recalling the discussion in sections 4.3.4 and 4.3.5, the room temperature
cure produced networks with lower $T_g$s and higher $M_c$ values, which resulted in increased ductility in the network. The increase in fracture toughness was not as great as expected for the room temperature cured samples. This can be explained in terms of the way in which the network was formed. The FT-IR data in section 4.3.2 showed essentially homopolymerization of the inherently brittle component, polystyrene, in the postcure step.

![Graph showing the effect of styrene content, molecular weight, and cure procedure on fracture toughness.](image)

**Table 4-48.** The effect of styrene content, molecular weight, and cure procedure on fracture toughness.

<table>
<thead>
<tr>
<th>Resin</th>
<th>20% styrene $K_{lc}$ (MPa-m$^{0.5}$)</th>
<th>28% styrene $K_{lc}$ (MPa-m$^{0.5}$)</th>
<th>35% styrene $K_{lc}$ (MPa-m$^{0.5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700g/mol, RT Cure</td>
<td>1.03 +/- .04</td>
<td>.94 +/- .09</td>
<td>.77 +/- .05</td>
</tr>
<tr>
<td>700g/mol, 140C Cure</td>
<td>.87 +/- .12</td>
<td>0.72 +/- .11</td>
<td>.63 +/- .11</td>
</tr>
<tr>
<td>1200g/mol, RT Cure</td>
<td></td>
<td></td>
<td>2.20 +/- .20</td>
</tr>
<tr>
<td>1200g/mol, 140C Cure</td>
<td>2.02 +/- .07</td>
<td>1.94 +/- .02</td>
<td>1.52 +/- .06</td>
</tr>
</tbody>
</table>

(ASTM D5045-91)

Figure 4-48. The effect of styrene content, molecular weight, and cure procedure on fracture toughness.

As discussed in section 2.5.5, other researchers have also noted that a lower initial isothermal cure temperature of a vinyl ester/styrene resin system (Derakane 411-C-50) increased fracture toughness and tensile strength. This increase in tensile strength with decreasing cure temperature was also evaluated in the present study, and is discussed in the next section.
4.4.3 Tensile Testing

Tensile data were obtained from load versus displacement curves using dogbone specimens pulled in tension according to ASTM D638-90, as shown in Figure 4-49. This test is one of the most widely used methods to determine stress-strain curves (in tension) of engineering plastics. Stress-strain curves were generated by continuously measuring the force that developed as the samples were elongated at a constant rate of extension. A general stress-strain curve is illustrated in Figure 4-50. These dimethacrylate networks fall in the class of materials known as rigid thermosets, which are categorized by their relatively moderate strengths and low extension. Although the plot is generalized for the fiber, flexible plastic and the elastomer, the curve for the thermoset represents actual experimental data for a 700g/mole network cured with 28 weight percent styrene.

Figure 4-49. Schematic of dogbone specimen used in determining tensile data according to ASTM D638-90.
Tensile data were taken as a function of molecular weight, styrene content, and cure rate (Table 4-20 and Table 4-21). These data show an increase in tensile strength when the styrene content was increased. At higher styrene contents, more force was required to break the specimen in tension. The tensile strength was taken here to mean the point on the force-extension curve at which the specimen suffered a major disruption (resulting in fracture). Tensile strength was defined as the force at break divided by the original cross sectional area. It was acceptable to use the original cross sectional area since these are brittle materials and the strain is relatively small. For all practical purposes, the modulus values for all of the resins employed in this study did not show any appreciable difference regardless of the styrene content, molecular weight, or cure procedure.

It is important to note that the tensile properties were dependent on cure rate. Elongation percentages at break for each series remained low, (approximately 1% to 2%) until a slower cure procedure was used. These materials have relatively low elongation values at break when...
compared to typical flexible plastics and elastomers. However, they should show a greater elongation at break from that of a typical fiber. Since these materials are often used in fiber-reinforced composites, the elongation of the matrix should exceed that of the fibers for enhanced mechanical performance. Similar to highly crosslinked epoxies and unsaturated polyesters, these polymers are characterized as brittle. Brittle polymers have fracture at relatively low elongations in tension (2-4%). Others include polystyrene, poly(methyl methacrylate), and rigid (unplasticized) poly(vinyl chloride). Semicrystalline polymers such as polyethylene, poly(ethylene terephthalate) and nylons, and some amorphous polymers, such as polycarbonate exhibit considerable post-yield plastic deformation and are classified as ductile.

Tensile strength data for materials that undergo low extensions at break are affected by experimental error more than those for materials that undergo higher extensions. The primary sources of experimental error are poor alignment of the specimen/machine assembly, relative movement between specimen and clamp, inappropriate choice of specimen geometry, and poor specimen quality. The history of the sample has an influence on tensile properties, as well. A tensile bar prepared by injection molding with a high pressure tends to have higher tensile strength. The specimens in this study were prepared by pouring the precursor resins into a silicone mold and curing them. After cure, machining was used to adjust the specimens to the appropriate thickness. Although flaws were not visible, possible microscopic flaws and/or internal stress (leading to premature fracture) could have resulted from the machining.

When the samples were cured at room temperature followed by a 93°C postcure, the percent elongation increased considerably. This study also showed that strength decreased when samples were cured at a faster rate. There was an increase in tensile properties with a change in cure procedure for similar reasons described in 4.4.2 dealing with fracture toughness. This behavior is mainly due to the increased ductility in the network, which causes an improvement in mechanical properties.

Table 4-21 shows the effect of styrene content and cure procedure for a 1200g/mole resin. The same results regarding styrene content and cure procedure were not obtained as in the case of the 700g/mole oligomer (Table 4-20). When the slow, room temperature cure was used, the tensile strength decreased even though the oligomer molecular weight was increased from 700g/mole to 1200g/mole weight. The same reasoning applies here as in the proceeding chapter on toughness. An increase in the molecular weight between crosslinks resulted in a stronger
material, but very large values of $M_c$ resulted in reduced tensile strength. All tensile strengths had an average standard deviation of less than 2 percent.

Table 4- 20. Tensile data of a 700 g/mole precursor oligomer crosslinked using varied cure procedures.

<table>
<thead>
<tr>
<th>Strength (ksi)</th>
<th>Modulus (Msi)</th>
<th>%Elongation</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>700g/mol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 wt. % styrene</td>
<td>4.55</td>
<td>0.509</td>
<td>.97</td>
</tr>
<tr>
<td>28 wt. % styrene</td>
<td>5.50</td>
<td>0.442</td>
<td>1.31</td>
</tr>
<tr>
<td>35 wt. % styrene</td>
<td>6.67</td>
<td>0.515</td>
<td>1.67</td>
</tr>
<tr>
<td>20 wt. % styrene</td>
<td>6.61</td>
<td>0.515</td>
<td>1.4</td>
</tr>
<tr>
<td>28 wt. % styrene</td>
<td>8.02</td>
<td>0.499</td>
<td>1.9</td>
</tr>
<tr>
<td>35 wt. % styrene</td>
<td>9.33</td>
<td>0.513</td>
<td>2.5</td>
</tr>
<tr>
<td>40 wt. % styrene</td>
<td>7.98</td>
<td>0.538</td>
<td>2.1</td>
</tr>
<tr>
<td>28 wt. % styrene</td>
<td>13.29</td>
<td>0.516</td>
<td>5.23</td>
</tr>
<tr>
<td>28 wt. % styrene</td>
<td>12-13</td>
<td>0.52</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Table 4- 21. Tensile data of a 1200g/mole precursor oligomer crosslinked using varied cure procedures.

<table>
<thead>
<tr>
<th>Strength (ksi)</th>
<th>Modulus (Msi)</th>
<th>Elongation</th>
<th>Cure Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200g/mol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28 wt. % styrene</td>
<td>8.29</td>
<td>0.515</td>
<td>1.95</td>
</tr>
<tr>
<td>35 wt. % styrene</td>
<td>9.79</td>
<td>0.490</td>
<td>2.75</td>
</tr>
<tr>
<td>28 wt. % styrene</td>
<td>4.49 +/- .25</td>
<td>0.506 +/- .09</td>
<td>5.38 +/- .168</td>
</tr>
<tr>
<td>35 wt. % styrene</td>
<td>3.76 +/- .52</td>
<td>0.516 +/- .09</td>
<td>8.58 +/- 1.31</td>
</tr>
</tbody>
</table>
Figure 4-51 illustrates this maximum in tensile strength as the crosslink density is increased. Each data point represents an average of at least five samples. As shown earlier, two ways to increase $M_c$ is to decrease the cure rate or increase the number average molecular weight of the oligomer. Both of these techniques were employed, resulting in samples with the highest $M_c$ and the lowest tensile strength. There is apparently not enough network integrity at very high $M_c$ values to produce a reasonably strong network. This was confirmed by Nielsen, using a polystyrene crosslinked by divinyl benzene. It was shown that a small amount of crosslinking increased the tensile strength, but high degrees of crosslinking drastically decreased tensile strength and made the polymer very brittle. The decrease in tensile strength was attributed to submicroscopic cracks developing from internal stresses resulting from shrinkage and thermal changes after the mobility of molecular segments had been decreased by crosslinking.

\[
\frac{d}{M_c} = \rho = \frac{E}{3RT}
\]

Figure 4-51. Tensile strength versus crosslink density for a 700g/mole and 1200g/mole resin with varied cured procedures.
4.4.4  **Vickers Microhardness**

Microhardness is a measure quasi-static penetration of the specimen surface with a standard indenter at a given force and temperature. This resistance to penetration by an indentor was measured in force divided by the projected area of the indent. Macroscopic mechanical behavior can be related to the microscopic constituent phases by examining the hardness as a function of the rubbery modulus (3dRT/Mc). By decreasing the molecular weight of the oligomers or increasing the polydispersity (for a given Mn) the network became tighter due to a decrease in Mc, and the hardness increased (Table 4-22 and Figure 4-52). Also, as the styrene content was increased, the hardness increased. This is more difficult to explain but appears to correspond well to an increase in the more brittle component (styrene) and a decrease in the more plastic component (vinyl ester).

Table 4-22.  Vickers Microhardness Values (HV) (kg/mm²) for dimethacrylate networks cured at 140°C for 1 hour.

<table>
<thead>
<tr>
<th>Resin</th>
<th>20 % styrene</th>
<th>28% styrene</th>
<th>35% styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>700g/mol, Mw/Mn=1.30</td>
<td>23.2</td>
<td>24.1</td>
<td>25.1</td>
</tr>
<tr>
<td>900g/mol, Mw/Mn=1.47</td>
<td>22.1</td>
<td>23.6</td>
<td>24.3</td>
</tr>
<tr>
<td>900g/mol, Mw/Mn=1.28</td>
<td>21.7</td>
<td>22.1</td>
<td>23.4</td>
</tr>
<tr>
<td>1000g/mol, Mw/Mn=1.49</td>
<td>20.1</td>
<td>21.4</td>
<td>22.9</td>
</tr>
<tr>
<td>1000g/mol, Mw/Mn=1.37</td>
<td>19.9</td>
<td>20.6</td>
<td>21.6</td>
</tr>
<tr>
<td>1200g/mol, Mw/Mn=1.07</td>
<td>19.3</td>
<td>20.1</td>
<td>21.1</td>
</tr>
</tbody>
</table>
Figure 4- 52. Vickers Microhardness Values (kg/mm$^2$) as a function of styrene content, molecular weight and MWD for networks cured at 140°C for 1 hour.

Vicker microhardness values were also calculated for samples cured at room temperature followed by a 93°C postcure. The networks cured at room temperature exhibited less crosslinking (as calculated from rubbery modulus values) and did not resist quasi-static penetration as much as the networks cured at the elevated temperature. Since HV values decreased with increased oligomer $M_n$ and lower extent of cure, the resin containing the 1200g/mole oligomer cured at room temperature had the lowest HV values of all the oligomer resins under investigation. Table 4- 23 shows a comparison of microhardness values for the two cure procedures. All microhardness values had repeatability within 2 percent.
Table 4- 23. Vickers Microhardness Values (kg/mm$^2$) for dimethacrylate networks cured at room temperature followed by a 93°C postcure.

<table>
<thead>
<tr>
<th></th>
<th>HV (kg/mm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>140°C</td>
</tr>
<tr>
<td>700g/mol, M_w/M_n=1.30</td>
<td></td>
</tr>
<tr>
<td>20 % styrene</td>
<td>23.2</td>
</tr>
<tr>
<td>28 % styrene</td>
<td>24.1</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>25.1</td>
</tr>
<tr>
<td>1200g/mol, M_w/M_n=1.07</td>
<td></td>
</tr>
<tr>
<td>28 % styrene</td>
<td>20.1</td>
</tr>
<tr>
<td>35 % styrene</td>
<td>21.1</td>
</tr>
</tbody>
</table>

Figure 4- 53 shows a graphical representation of the HV values for the two cure procedures. The networks cured at room temperature also showed an increase in microhardness with an increase in styrene content.

Figure 4- 53. A Comparison of Vickers Microhardness Values (kg/mm$^2$) as a function of styrene content, oligomer molecular weight and cure procedure.
Balta-Calleja and Kilian studied the elastic and plastic properties of semicrystalline polyethylene. Similar to the present work (although vinyl esters are amorphous), they found a correlation between elastic modulus and hardness. It was shown that as the elastic modulus increased, the microhardness increased. Hardness of ductile materials is usually considered a measure of plastic yield properties and an indicator of irreversible plastic deformation. Since semicrystalline polymers can be thought of as materials with separate distinct hard and compliant elements, Balta-Calleja et al. have attributed the elastic deformation at small strains to the reversible behavior of the cluster-network. Also contrary to the mechanism of plastic deformation, they found an increase in hardness with an increase in the molar mass of the crystalline portion.

According to Tabor, the type of indentation formed depends on the nature of the solid. The deformation of ideal elastic solids is reversible and determined by classic elasticity. In real solids, plastic indentation is always accompanied by elastic strains, and when the indenter is removed, elastic stresses are partially released. However, in plastic-brittle solids, released elastic stresses may induce additional crack features and the materials may become compacted during indentation. Therefore, in brittle solids, the generation of cracks during or after indentation provides a measure of certain fracture properties.

There are many problems associated with indentation hardness measurements, including loading of the indenter, elastic recovery of the indentation in depth and diameter, and measurement of the effective area of the indentation. Other problems associated with the interpretation of hardness data concerns the flow of materials around the indentation. In both ductile and brittle solids, this involves the movement of dislocations. A problem arises when the dislocations are not concentrated immediately beneath the indenter. Due to a lack of understanding of the yield and failure properties of these complicated crosslinked networks, it is difficult to give a more extensive interpretation of these hardness measurements.

Hardness of a solid, as defined by Tabor, is the resistance to local deformation. Since hardness is defined as the load divided by the area of the indent, large indents will result in reduced hardness values. Sargent studied the indentation size effect on microhardness, but due to the complexity of this subject area, found that there were too many distinct effects for physically based models to be generally useful. Additional problems with the current system...
include the complexity of the copolymer effect, changing oligomer molecular weight distributions, and varying extent of cure.
4.5 A Mono-Methacrylate Model Compound

4.6.1 Introduction

A mono-methacrylate analogue of the dimethacrylate terminated poly(hydroxyether) oligomer has been synthesized to conduct model studies where the polymerization and copolymerization products might be soluble. Based on its difunctionality, this material should be incapable of producing a network-type structure, and thus copolymerization with a diluent such as styrene should produce a linear material (Figure 4-54). Although solvent resistant networks are advantageous for physical and mechanical performance, insolubility makes them difficult to study by many analytical techniques. The chemical structure of this new monomer has been characterized and confirmed by proton nuclear magnetic resonance (¹H NMR) and high performance liquid chromatography (HPLC).

Figure 4-54. Comparison of a dimethacrylate/styrene network and a mono-methacrylate/styrene copolymer.
4.6.2 Synthesis

The mono-methacrylate was synthesized by the reaction of cumylphenol and glycidyl methacrylate in a 1:1 mole ratio (Figure 4-55). Due to immiscibility of cumylphenol and glycidyl methacrylate at 25°C, they were co-dissolved at 40°C. Approximately 10 mole percent sodium hydroxide in water was used to catalyze the reaction by abstracting a proton from the cumylphenol. The interfacial reaction was carried out at 70°C and the sodium hydroxide solution was added drop-wise over a period of one hour. The cumylphenol anion opened the epoxide ring, producing an alkoxide pendant group. This alkoxide anion was then protonated by another cumylphenol, which thus regenerated the cumyl phenolate. The reaction mixture was left open to allow oxygen to serve as an inhibitor and prevent premature polymerization of the methacrylate. The recovered yields for this reaction were high, approximately 93-95%.

![Figure 4-55. Synthetic scheme of the model mono-methacrylate.](image)
It is well known that epoxy ring opening of a base catalyzed reaction proceeds by an $S_n2$ mechanism with attack at the least hindered position of the epoxide group. However, epoxide ring opening may also occur (to a lesser extent) at the more hindered position, producing the other isomeric form. Therefore, two forms of the mono-methacrylate were expected (Figure 4-56).

\[
\text{CH}_2\text{CH}_2\text{OH} \quad + \quad \text{H}_2\text{C} = \text{CH}-\text{CH}_2-\text{O}-\text{C} = \text{CH}_2
\]

\[\text{A} \quad \text{B}\]

Figure 4-56. Comparison of the two isomeric forms of the mono-methacrylate model compound.

The use of a phase transfer catalyst, benzyltrimethylammonium chloride, was evaluated to increase the reaction rate. Although benzyltrimethylammonium chloride is a water soluble salt, it has a large organic component which makes it soluble in organic phases. It was reasoned that due to counterion exchange reactions between sodium cumyl phenolate and this phase transfer catalyst (Figure 4-57), the phenolate could be efficiently transferred to the organic phase. Once the cumyl phenolate is transferred to the organic phase, it should be able to open the epoxide ring.

$^1$H NMR showed that there was no appreciable difference in the total conversion at various reaction temperatures ($40^\circ$C-70$^\circ$C) when the phase transfer catalyst was used. However, essentially complete conversion in each system was achieved at 70$^\circ$C after approximately 48 hours. It reasonable to believe that the phase transfer catalyst may increase the rate of conversion. However, this aspect was not further investigated. The overall recovered
yields were the same at all of the examined temperatures. Therefore, for simplification of the reaction, the phase transfer catalyst was not used.

\[
\text{CH}_2\text{N}^+\text{CH}_3\text{CH}_3\text{CH}_3^+ \text{Cl}^- \rightleftharpoons \text{CH}_2\text{N}^+\text{CH}_3\text{CH}_3\text{O}^-\text{CH}_3 + \text{NaCl}
\]

Figure 4-57 Equilibrium reaction between the phase transfer catalyst, benzyltrimethylammonium chloride, and sodium cumyl phenolate.

4.6.3 Characterization

The structure of the mono-methacrylate model compound was confirmed by \(^1\)H NMR and HPLC. The \(^1\)H NMR peak assignments for the protons in the mono-methacrylate monomer are shown in Figure 4-58. A closer examination of the spectra revealed the presence of very small side peaks between 3.6 ppm and 4.6 ppm, which did not correspond to the main product. These peaks were probably due the isomeric form from attack on the epoxide ring at the more sterically hindered position (Figure 4-56). Due to the structural similarities in the two isomeric forms, many of the peaks overlapped and could not be distinguished. However, the chemical shifts from 3.6 ppm to 4.6 ppm were slightly different since this region corresponds to the structural differences between the two isomeric forms.

HPLC showed two peaks with retention times of 2.74 (25%) min and 2.98 (75%) min for the mono-methacrylate. These data also confirmed that the second peak was not due to residual starting materials, since the retention times of the starting materials were 3.16 min and 2.76 min for glycidyl methacrylate and cumylphenol, respectively. Approximately 10 to 24% may be attributed to the isomer with the primary hydroxyl group. It is recommended that further analytical work be pursued to positively identify the isomers.
The mono-methacrylate was copolymerized with styrene (Figure 4-59) to study elevated temperature polymerizations. The copolymerizations were monitored by FT-IR, in a manner similar to that used for the networks. The mono-methacrylate model compound was diluted with 28 weight percent styrene at room temperature. Then, 1.1 wt. % of benzoyl peroxide was added to serve as a reaction initiator. Constant stirring was carried out until a homogeneous mixture was formed. The mono-methacrylate/styrene mixture was polymerized at 140°C up to 12 hours to monitor the percent double bond conversion.

Figure 4-60 shows the FT-IR spectra at several reaction times for the mono-methacrylate with 28% styrene cured at 140°C and 1.1 weight percent BPO. Also indicated in Figure 4-60 are the computed conversions of the methacrylate and styrene double bonds. The amounts of
styrene and BPO for the model compound were comparable, on a mole basis, with the network forming systems comprised of the 700 g/mole oligomer with 28 wt % styrene. After only 10 minutes, the conversions reached 84% and 88% for the styrene and methacrylate, respectively. However, after 480 minutes the conversion was only 91% and 90% for the styrene and methacrylate, respectively.

Figure 4-59. Polymerization of the mono-methacrylate model compound with styrene simulating the dimethacrylate/styrene network.
Figure 4- 60. FT-IR spectrum illustrating the double bond conversion of the mono-methacrylate with 28% styrene polymerized at 140°C with 1.1 wt% BPO.

DSC scans of the mono-methacrylate/styrene copolymer formed at 140°C showed a broad exotherm on the first heat beginning at 80°C, confirming that further reaction was taking place (Figure 4- 61). This exotherm during the first heat in the DSC probably accounts for additional polymerization and possibly also to side reactions (chain transfer). The glass transition temperature was determined on the second scan to be approximately 170°C.

Although both monomers in this copolymerization were difunctional, the product was insoluble in common solvents (dichloromethane, 1-methyl-2-pyrrolidinone, chloroform, tetrahydrofuran). It was reasoned that gelation must have occurred due to chain transfer. Under the elevated temperature reaction conditions, these chain transfer reactions could be partially responsible for the relatively brittle mechanical properties of the networks.
Figure 4-61. DSC (heating rate of 10°C/min) traces of the mono-methacrylate with 28 weight % styrene previously polymerized at 140°C with 1.1 wt% BPO for 1 hour.
CHAPTER 5. SUMMARY AND CONCLUSIONS

Network polymers have three-dimensional molecular linkages throughout the bulk polymer. The functionality of the monomer units and the degree of crosslinking are very important structural parameters. The functionality of the monomer units defines the microstructural characteristics of the network polymer and the crosslink density. The crosslink density ultimately defines the viscoelastic and mechanical properties of the polymer. The final conversion in vinyl polymerizations is largely determined by the mobility of the reactive groups; the mobility of reactive groups is determined by the degree of volume relaxation that has occurred. Due to the high degree of crosslinking, thermosets are infusible, insoluble, and dimensionally stable under loads. These properties make thermosets useful as adhesives, coatings, and matrices for composites. They can also be used in load-bearing applications. Thermoset classes include vinyl esters (dimethacrylates), epoxies, phenolics, polyesters, bismaleimides, and polyimides.

Dimethacrylates are unique in that they combine the best properties of two different thermosetting resin species into a single resin system. Similar to the unsaturated polyester resins, dimethacrylates can be cured free radically with or without the addition of other unsaturated monomers. On the other hand, their properties are comparable to highly crosslinked epoxy resin systems. Despite the fact that dimethacrylates or “vinyl ester” resins have been used in industry for over thirty years, there is still very little information available in the literature on structure-properties relationships of these networks. These networks are becoming increasingly important for fiber reinforced composites because their cure characteristics are compatible with rapid composite processing operations such as pultrusion and resin transfer (or resin infusion) molding. Their free radical cure mechanisms allow for good stability at low temperatures, yet rapid reaction at elevated temperatures. It is therefore of great interest to study and understand the structure and properties of vinyl ester networks.

This work involved a study of dimethacrylate thermoset networks; it addressed network formation in terms of crosslink density, and provided an assessment of its effect on properties. In order to provide a more thorough study, numerous factors such as diluent content, molecular weight, molecular weight distribution and extent of cure were systematically varied. Each of these variables was evaluated in terms of its individual effect on the network and properties.
Numerous graphs were also used to illustrate the collective effect of each of these factors functioning within a given system.

Dimethacrylate resins comprised of methacrylate terminated epoxy oligomers diluted with styrene were cured in free radical copolymerizations to form crosslinked networks. These epoxy oligomers functionally endcapped with methacrylate groups copolymerized with styrene form an important class of composite matrix resins commonly known as the “vinyl esters.” These epoxy based vinyl esters designed to provide superior toughness and high corrosion resistance. Structure-property studies on crosslinked polymers often involve varying the molecular weight between crosslinks by changing the density of crosslink junctions with different crosslinking agents or curing conditions without otherwise altering the chemical composition of the network chains. The crosslink density of the vinyl ester / styrene materials in this research was systematically varied by using four different vinyl ester oligomer molecular weights, (700g/mole, 900g/mole, 1000g/mole and 1200g/mole) and by employing three different weight percentages of styrene ranging from 20 to 35 weight percent. There were two different molecular weight distributions (MWD) for both the 900g/mole oligomer and the 1000g/mole oligomer. By keeping the oligomer molecular weight constant and changing the polydispersities in the MWD, it was shown that molecular weight distribution significantly affected mechanical properties. Higher MWD corresponded to the oligomer with the highest fraction of n=1 or “short chains”, as determined by GPC.

More specifically, the effects of crosslink density and chemical composition on glass transition temperatures, toughness, tensile properties, microhardness and shrinkage were reported. Within this rather small range in vinyl ester molecular weight, toughness of the resultant networks improved as the vinyl ester oligomer <M_n> was increased and polydispersity was decreased. Increases in M_c normally result in improved toughness and/or ductility in networks. However, for each series, the plane strain critical stress intensity factors (K_{ic}) consistently decreased as the styrene content was increased, despite the fact that M_c also increased. This was attributed to the inherent relative brittleness of the polystyrene chemical structure relative to the polyhydroxyether component. The plane strain critical stress intensity factors (K_{ic}) ranged from very brittle (.87 MPa-m^{0.5}) to relatively tough materials (2.02 MPa-m^{0.5}). Vickers microhardness (HV) decreased for each series with an increase in molecular weight and a decrease in polydispersity (for a given oligomer M_n) due to higher M_c values. However, with
an increase in styrene content, the HV values increased possibly due to the more rigid nature of styrene. Tensile properties and fracture toughness was also dependent on the cure procedure. Samples cured at the ambient temperature (25°C) followed by a 93°C postcure, exhibited decreased hardness and increased toughness and elongations compared to samples cured at 140°C.

Ambient temperature (25°C) cured samples did not reach 100% conversion and they had lower glass transition temperatures than samples cured at a higher temperature (140°C). It was concluded that this multifunctional monomer polymerization reaction exhibited a diffusion-controlled termination mechanism due to the limited mobility of the macroradicals. However, the conversion of the cure reaction of vinyl ester resin increased as cure temperature increased. Nearly complete conversion was approached at 140°C using BPO as the initiator and a more dense material was obtained at this higher cure temperature. The effect of temperature on the conversion of each type of double bond was examined by FTIR. At 140°C, almost 100% conversion of vinyl ester and styrene was achieved. Although essentially full conversion of the styrene peak was reached with a room temperature cure followed by a 93°C postcure, the methacrylate conversion was only around 84%. This residual unsaturation was likely due to vitrification and/or depletion of the initiator (MEKP). FT-IR of systems cured at room temperature showed virtually the same extent of conversion, regardless of the postcure (93°C or 140°C).

The viscosity of dimethacrylate-styrene mixtures was found to vary inversely with styrene contents and increasing temperature. It was shown that by altering the molecular weight distribution, temperature, and percent styrene, a desired low viscosity (2000 cps) for processing could be achieved for any of the resins under evaluation. Viscosity decreased when either the oligomer molecular weight decreased or the breadth of its MWD increased. As a result of decreasing viscosity, the amount of shrinkage also increased due to excess molecular mobility of the reacting system. The cure shrinkage increased from approximately 3.2 to 8.4 volume percent as the styrene content increased from 20 to 35 weight percent and the oligomer Mn decreased from 1200 to 700g/mole. It was concluded that shrinkage increases when a denser network is formed, regardless of how the density is increased. As the extent of cure decreased, i.e. going from to a 140°C cure to a room temperature cure, the shrinkage decreased. However, when shrinkage was determined based on the moles of vinyl groups converted, the overall shrinkage
was essentially the same for both systems. **It was interesting to note that postcuring (regardless of the postcure temperature), did not serve to further densify the networks after the room temperature cure.**

The dimethacrylate-styrene networks swelled more when the network density was decreased due to an increase in the oligomer molecular weight or lower extent of cure. Swelling extraction experiments showed that the gel fraction was approximately 98% for systems cured at 140°C and decreased when the room temperature initiator system (MEKP/DMA/CoNAP) was employed. Sol fractions were as high as 31% when crushed samples, which had only been cured at room temperature, were studied. The oligomers did swell more in CH$_2$Cl$_2$ than in water, due to a closer match of solubility parameters in the former. There was very little swelling in water regardless of the crosslink density.

A mono-methacrylate model compound was synthesized and its structure was confirmed by $^1$H-NMR and FTIR. This monomer has a structure similar to that of the dimethacrylate monomers in the vinyl ester resins and, as the name suggests, there is only one methacrylate endgroup. This material was polymerized with styrene to obtain a material that could possibly serve as a linear analogue to the dimethacrylate network. When polymerized with styrene, the resultant material was gelled. Since the functionality of the two monomers does not promote network formation, it was reasoned that at the high polymerization temperature (140°C), chain transfer might be a likely mechanism.
CHAPTER 6. SUGGESTIONS FOR FUTURE WORK

It is extremely important to continue this investigation of the structure/property relationships of dimethacrylate/styrene networks. There is still a great deal of information that needs to be ascertained in order to completely understand the network formation and its effect on thermal, chemical and mechanical properties. Previous work has shown that that for the cure of dimethacrylate matrix resins, gelation and vitrification are important phenomena and have a large impact on the cure process.\textsuperscript{19} Other studies of importance that need to be addressed include determination of the azeotropic monomer mixture compositions, and gel formation for networks cured at room temperature (25°C). The reactivity ratios should also be studied for this system. Another suggestion for future work includes a comparison between the kinetics of the cure reaction at 140°C and 25°C. Kinetic models could possibly be developed to relate the rate of the cure reactions of these thermosetting materials to temperature, amount of initiator, type of initiator and the extent of cure.

It is also recommended that a value for the primary chain length be determined in order to theoretically predict the gel point from the Stockmayer equation described in section 2.4.3. For the current systems, this could be calculated from the weight average molecular weight of styrene homopolymer. The homopolymerization reaction should be carried out under similar conditions (temperature and initiator concentration) as the gelation experiments described by Li,\textsuperscript{31} so that the predicted and experimental gel points are comparable. It is possible that the molecular weight of the mono-methacrylate copolymer may give more accurate values of the primary chain length since it represents both components of the network systems. However, the polymerization must be carried out under mild conditions (<140°C) such that a linear material is synthesized, since higher temperatures appear to promote chain transfer that results in gel formation. A possible draw-back is that this system will not represent the high temperature conditions of the network reaction, possibly resulting in discrepancies in gel point estimations. The linear copolymerization will also not mimic the high local viscosities and reduced methacrylate double bond accessibilities in the network polymerization.
The mobility of the reactive groups is a large determinant of the final conversion in vinyl polymerizations. Due to the complex features (autoacceleration, limiting double bond conversion, rate-dependent polymerization kinetics, and reaction diffusion-controlled termination) of multifunctional monomer polymerizations, it would be advantageous to do a more in-depth study of the effects of the mobility of the monomer structure on the polymerization system. This study will give insight into the polymerization behavior and underlying reaction mechanisms during cure. The mobility of reactive groups is affected by the degree of volume relaxation. Although the influence of volume relaxation on mechanical properties of thermoplastic matrices is well-established, thermosetting materials have not been as thoroughly investigated. Therefore, the influence of volume relaxation on the course of the polymerization process and the formation of the network should be investigated as it relates to the mechanical properties.

Embedded optical fibers could be used to determine the stresses in the cured matrix materials. This data could be used to calculate residual stresses in the composite. Sensors typically used in this type of study are coated with a polyimide for robustness. However, these fiber optic sensors could also be coated with sizing material (thermoplastic material between the fiber and the matrix) to determine stresses in the fiber-matrix interphase of the composite. This optional interphase material has been shown to enhance the mechanical properties of the composites. Additional experiments should also be conducted to better understand the effects of large cure shrinkages on mechanical properties.

The mono-methacrylate model compound (in this present study) polymerized with styrene at 140°C produced a material that gelled, possibly due to chain transfer. Steps should be taken to verify if this is indeed the reaction mechanism that is taking place. Reactivity ratios should also be calculated for this system, in order to determine their values relative to their values in the network systems.
**LIST OF ABBREVIATIONS**

**Instrumentation**
- **TMA**  Thermal Mechanical Analyzer
- **DMA**  Dynamic Mechanical Analyzer
- **$^1H$ NMR**  Proton Nuclear Magnetic Resonance
- **DSC**  Differential Scanning Calorimetry
- **HPLC**  High Performance Liquid Chromatography
- **FTIR**  Fourier Transform Infrared Spectrometry
- **$^{13}C$ NMR**  Carbon Nuclear Magnetic Resonance Spectroscopy

**Materials**
- **MEKP**  Methyl ethyl ketone peroxide
- **BPO**  Benzoyl peroxide
- **CoNap**  Cobalt naphthenate
- **DMA**  Dimethylaniline

**Other Terminology Used**
- **VER**  Vinyl Ester Resin
- **DR**  Dimethacrylate Resin
- **PD**  Polydispersity
- **$H_V$**  Vickers microhardness
- **$K_{IC}$**  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 Weight
- **PDI**  Polydispersity Index
- **MWD**  Molecular weight distribution
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One’s work may be finished some day, but one’s education never.

Alexandre Dumas, c. 1856
VITA

Ellen Burts

The author is the youngest of seven children born to Gussie R. Palmer and James Burts of Birmingham, Alabama. After graduating as class Valedictorian from West End High School in 1992, Ellen accepted a four year scholarship to attend Stillman College in Tuscaloosa, Alabama. During her matriculation at Stillman College, she worked for one summer as an intern in the Chemistry Department at the University of Alabama at Birmingham, and worked for two summers as a Technical Associate for Lucent Technologies-Bell Laboratories in Murray Hill, New Jersey. In 1996 she graduated Summa Cum Laude with a Bachelor of Science Degree in Chemistry. After graduation, she received fellowships from The David and Lucile Packard Foundation and Lucent Technologies-Bell Laboratories. Ellen entered Virginia Polytechnic Institute and State University in the fall of 1996 under the advisement of Professor Judy S. Riffle. While at Virginia Tech, she presented at numerous national meetings and served, for one semester, as an organic chemistry recitation instructor. In addition, she taught high school chemistry in the Upward Bound Program. She was the first student to serve on the Organic Faculty Search Committee and among the first to receive the Chemistry Department Advisory Council Graduate Research Award. In the spring of 2000, Ellen was featured in “Elements” (the Alumni Magazine of the Department of Chemistry of Virginia Tech). Ellen obtained her Doctoral degree in Organic/Polymer Chemistry in October 2000. She will reside in St. Paul, Minnesota, where she will work for the 3M Corporation in the Adhesives for Electronics Division.
REFERENCES

18 Mark; Bakales; Overberger; and Menges *Encyclopedia of Polymer Science and Engineering*, vol. 11, John Wiley and Sons, New York, 1988, Chapt. Phenolic Resins.
27 *Polymeric Materials Encyclopedia*, vol. 11, 8471 (1997)
36 K. S. Anseth, L. M. Kline, T. A. Walker, K. J. Anderson, and C. N. Bowman, 
NewYork (1953).


