Chapter 1. Literature Review

1.1. Introduction

Vinyl ester resins are addition products of various epoxide resins and unsaturated monocarboxylic acids, most commonly methacrylic acid.[1] They have terminal reactive double bonds derived from the carboxylic acid used. These reactive groups can form a crosslinked network with or without the addition of a comonomer. In many industrial products, vinyl ester resins are comprised of 40-50 wt.% styrene. In dental applications triethylene glycol dimethacrylate is the comonomer. It is common to dilute the vinyl ester oligomers with a low molecular weight comonomer, such as styrene, vinyltoluene or methyl methacrylate, to reduce the room temperature viscosity of the mixture and yield a solution with a typical viscosity in the range of 200 to 2000 cps.

Vinyl ester resins combine the best properties of epoxies and unsaturated polyesters. They can be easily handled at room temperature and have mechanical properties similar to epoxy resins. They have better chemical resistance than cheaper polyester resins, especially hydrolytic stability, and at the same time offer greater control over cure rate and reaction conditions than epoxy resins. The unsaturated bonds on the termini of the vinyl ester oligomers copolymerize with the 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 a reactive diluent and that both unsaturated polyester and vinyl esters provide crosslink sites. However, the physical properties of the vinyl ester networks are, in general, superior to the unsaturated polyesters, particularly corrosion resistance. This can be at least partially attributed to the fact that the vinyl esters have reactive double bonds at the ends of the chains only, while the unsaturated polyester resins have the reactive double bonds distributed throughout the chains. Thus, the

[1] R. E. Young, in *Unsaturated Polyester Technology*, P. E. Bruins, Ed., Gordon and Breach. New York, 1976, p.315.

crosslink density can be better controlled in the vinyl esters. The terminal location of the ester groups also contributes to the superior chemical resistance of these products. These ester groups are the most vulnerable part of the resin since they are subject to hydrolysis. Therefore, attack can occur only at these terminal sites for vinyl esters, leaving the majority of the backbone of the molecule unaffected.

Vinyl ester resins were first introduced commercially in the early 1960s.[2] Today, they are one of the most important thermosetting materials. Vinyl ester resins have been widely recognized as materials with excellent resistance to a wide variety of commonly encountered chemical environments. Vinyl ester resins are used to fabricate a variety of reinforced structures,[3-10] including pipes, tanks, scrubbers and ducts. They are prime candidates for use in composites for transportation and/or infrastructure. Such applications include fabrication of parts for automobiles and other surface transportation vehicles, fascia for buildings, reinforcements for bridges, etc. In addition to these applications, vinyl esters are also being used in coatings, adhesives, molding compounds, structural laminates, electrical applications and military/aerospace applications.

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[2] C. A. May, R. E. Burge, S. H. Christie, *Soc. Plastics Engrs. J.* , 1965, 21(9), 1106.

[3] M. E. Kelly, *in Unsaturated Polyester Technology*, P. E. Bruins Ed., Gordon and Breach, New York, 1976, P. 343.

[4] H. Y. Yeh, S. C. Yang, *J. Reinf. Plast. Compos*. 16(5), 414, 1997.

[5] S. S. Sonti, E. J. Barbero, *J. Reinf. Plast. Compos*. 15(7), 701, 1996.

[6] N. Hag and P. Harrison, *Corrosion Preventing & Control*, 43, 162, 1996.

[7] B. P. Singh, R. C. Jain, I. S. Bhardwaj, J. *Polym. Sci*, 2, 941, 1994.

[8] K. Liao, R. I. Altkorn, S. M. Mikovich, S. M. Milkovich, J. M. Fildes, J. Gomez, C. R. Schultheisz, D. L. Hunston, L. C. Brinson, *J. Adv. Mater*., 28(3), 54, 1997.

[9] J. R. Brown, Z. Mathys, *Composites*, 28A(7), 675, 1997.

[10] U. Sorathia, T. Dapp, *Int. Sample Symp. Exhib*., 42, 1020, 1997.

Although vinyl ester resins have been used in industry for more than 30 years, they are generally categorized together with the unsaturated polyester family. There is much less research cited in the literature on vinyl ester resins compared to the studies on unsaturated polyesters and epoxy resins, especially the studies on the formation-structure-properties of vinyl ester resins. Most of the information concerning the cure behavior and morphology of free radical cured resins focus 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. Developments and application of vinyl ester resins include the synthesis of new vinyl ester resins with new structural properties in an effort to improve toughness, to reduce viscosity, to decrease shrinkage, and so on. Understanding the mechanisms of the cure reaction, and gaining better control of the properties of these materials are also an interest of many researchers. This chapter is designed to review recent developments in the field of vinyl ester resins, including the preparation, crosslinking mechanism, toughening, properties and applications of these materials.

1.2. Preparation

Vinyl ester resins are addition products of various epoxide resins and ethylenically unsaturated monocarboxylic acids. Many patents for the preparation of these products have been issued within the past 30 years.[11] The reaction to form the vinyl ester oligomers is usually catalyzed by tertiary amines, phosphines, and alkalis or -onium salts. Research shows that triphenylphosphine is a more effective catalyst for this reaction as compared to other catalysts.[12] Typical reaction conditions are 120^{o}C for 4-5 hours, and hydroquinone is

[11] F. Fekete, et al., U. S. Patent 3,256,226; T. E. Doyle et al., U. S. Patent 3, 317, 465; C. A. May, U. S. Patent 3, 345, 401; C. A. May, U. S. Patent 3, 373,221; H. A. Newey, et al., U. S. Patent 3, 377, 406; C. A. May, U. S. Patent 3, 432, 478; J. W. Jernigan, U. S. Patent 3, 548, 030; D. H. Swisher, et al, U. S. Patent 3, 564, 074; R. T. Dowd, et al., U. S. Patent 3, 634, 542; C. A. May, U. S. Patent 3, 637, 618;

[12] B. Sandner, R. Schreiber, *Makromol. Chem*., 193, 2763, 1992.

[13] R. A. Bowen, U. S. Patent 3,179,623, 1965.

commonly used as the initiator. The conversion of the reaction is 90-95 %. The vinyl ester resins can also be prepared by the reaction of glycidyl methacrylate with a multifunctional phenol.[13]

Figure 1.1 Shows the reaction of a bisphenol-A glycidylether with methacrylic acid to prepare the bisphenol-A epoxy based vinyl ester resins which are the most widely used vinyl ester products. Bisphenol-A can also be used as a co-reactant to decrease viscosity and increase ductility of the cured resins. The pendant hydroxyl groups on the backbone can provide adhesion and a reactive site for further modification. For example, they can be reacted with anhydrides or isocyanates. It was reported that maleic anhydride reacted with the hydroxyl groups and improved the chemical resistance of the product.

Vinyl esters with considerable structural variations can be prepared by the combination of different epoxide resins with various unsaturated acids as shown in Figure 1.2. It is well known that bisphenol-A epoxy resins have very good mechanical properties and cycloaliphatic epoxy resins are UV resistant. Vinyl ester resins produced from Novolac epoxy resins have better high-temperature properties but are very brittle. Methacrylic acid is preferred for many applications. Methacrylate based vinyl esters are more resistant to chemical attack than acrylate vinyl ester resins since the methyl group of methacrylic acid can stabilize the ester group toward hydrolysis.

Structural modifications of vinyl ester resins were also studied by many researchers to alter properties in order to satisfy specific application requirements. For example, the viscosities of vinyl ester resins without diluents are typically in the range of about 1,000 to 8,000 poise and higher, too high for many applications. It is necessary to add lower viscosity reactive diluents. Many of these diluents are too volatile or are toxic. For some applications such as coatings, there is a distinct need to prepare low viscosity vinyl ester resins to reduce the need for such reactive diluents. It was found that low viscosity (43-193 poise) vinyl ester resins can be simply prepared by esterifying greater than 95% of the pendant hydroxyl groups of a vinyl

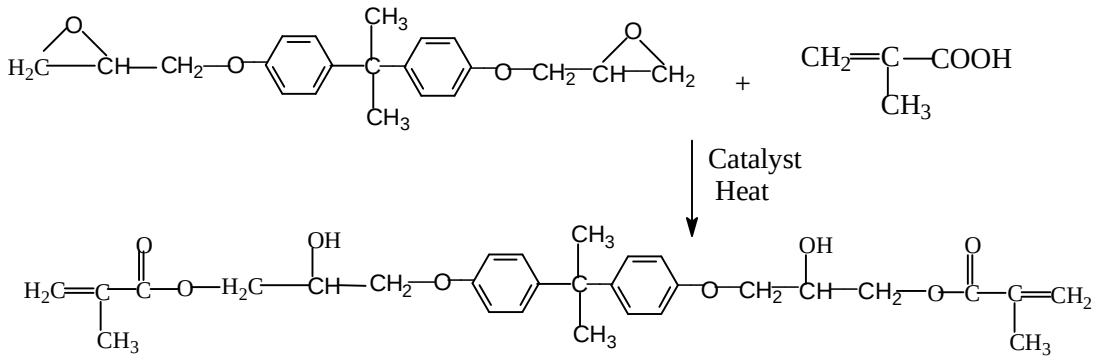
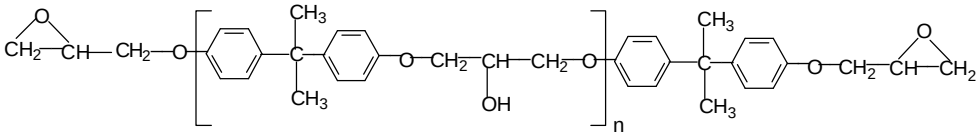
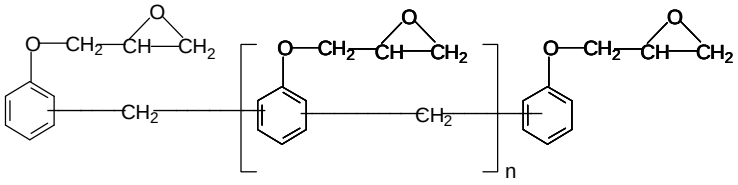


Figure 1.1. Synthesis of vinyl ester by the reaction of a bisphenol-A glycidylether with methacrylic acid.

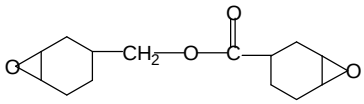
Epoxy Resins:



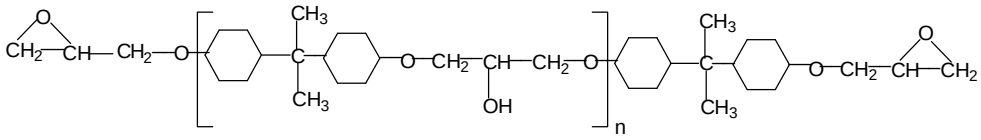
Diglycidyl Ether of Bisphenol A



Epoxy Novolac



Cycloaliphatic Epoxy



Diepoxidized Hydrogenated Bisphenol A

Unsaturated Acids

Acrylic acid: $CH_2=CH—COOH$

Methacrylic acid: $CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}—COOH$

Crotonic acid: $CH_3-CH=CH—COOH$

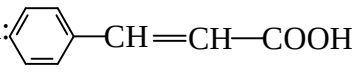
Cinnamic acid: 

Figure 1.2. Examples of components of vinyl esters

ester with a fatty acid or rosin oil acid.[14] The method for the preparation of low viscosity vinyl ester resins is to mix the vinyl ester resin with a fatty acid with phosphoric acid as catalyst and toluene as solvent. The reaction mixture was heated to 149 ^{o}C and allowed to proceed until no further water was collected. Subsequently vacuum was applied at 177^{o}C to remove the toluene.

Modified vinyl ester resins having improved toughness can be made by reacting reactive liquid polymers into their backbones. The commercial toughened vinyl ester oligomers[15-16] are Derakane 8084 (Dow Chemical Co.) and Hetron 1642 (Ashland Chemical Inc.), both of which contain a carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN). Figure 1.3 shows the reactions for the preparation of toughened vinyl ester oligomers. An excess of the selected epoxy resin reacts with a selected difunctional carboxyl-terminated reactive liquid polymers and an unsaturated monocarboxylic acid. The reaction is catalyzed by tertiary amines such as pyridine at 175^{o}C.

1.3. Crosslinking Reactions

1.3.1. Initiators [1]

The crosslinking reactions of vinyl ester resins are initiated by free radicals. Free radicals are generated in several ways, including thermal or photochemical decomposition of peroxides and hydroperoxides or azo and diazo compounds. The use of initiator systems are determined by the type of vinyl ester resins, the method of fabrication and the requirements of the application. The initiators most commonly used for vinyl ester resin cure reactions are methyl ethyl ketone peroxide, benzoyl peroxide and cumene hydroperoxide. Decomposition

[14] J. A. Lopez, C. W. Uzelmeier, U. S. Patent 4,357,456, 1982 .

[15] D. J. Najvar, U. S. Patent 3,892,819 (1975); W. D. Waters, U.S. Patent 3, 928,491 (1975).

[16] A. R. Siebert, U. S. Patent, 5,198,510 (1993).

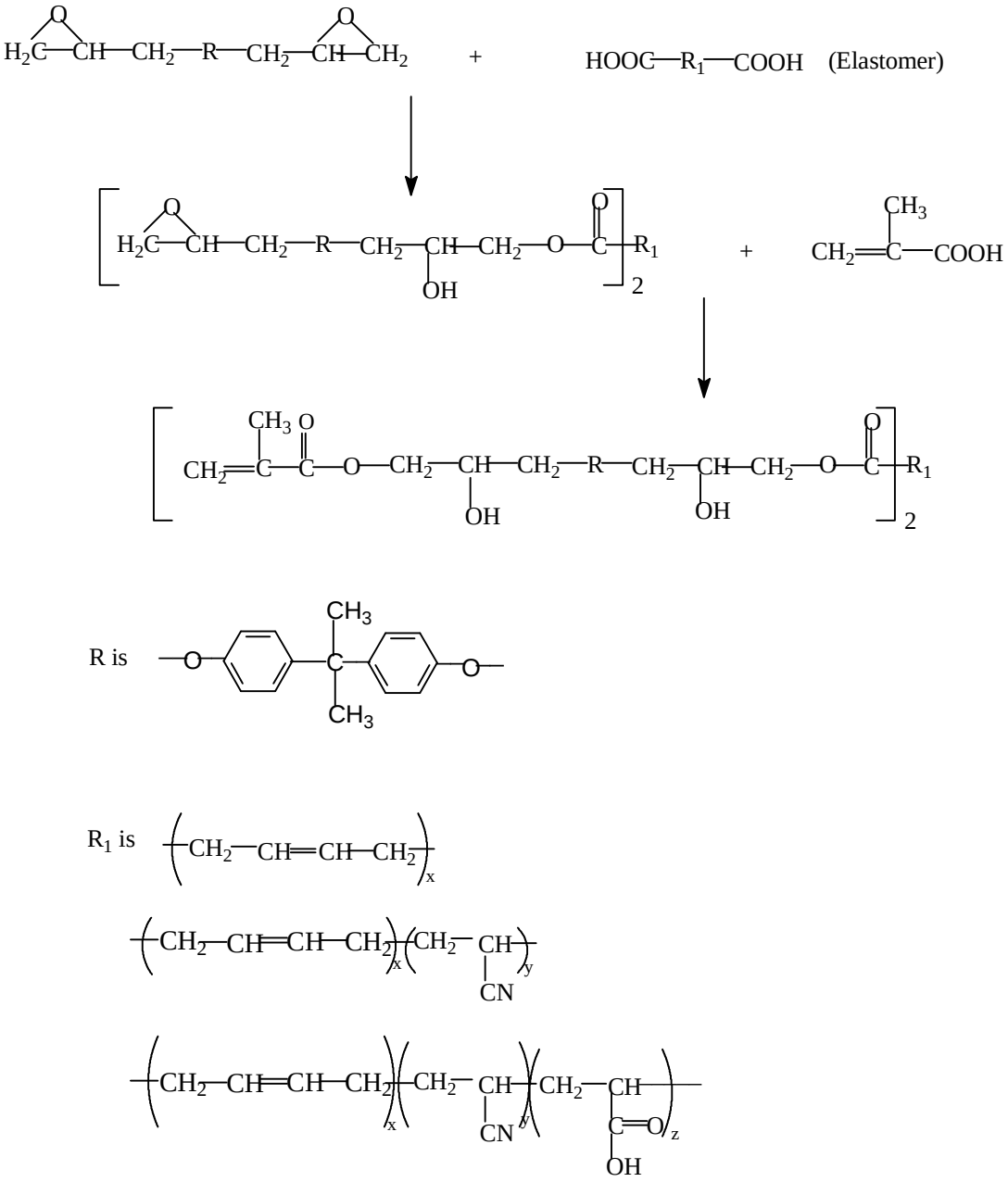


Figure 1.3. Preparation of toughened vinyl ester resins.

of these initiators can be effected by heat or by the use of accelerators or promoters which can cause a more rapid decomposition of the initiator at a given temperature. The accelerators most commonly employed are tertiary amines, such as dimethyl- or diethyl- aniline, and metallic soaps, such as cobalt or manganese octoate or naphthenate.

Vinyl ester resins can also be crosslinked via ionizing radiation - either actinic or high energy. Electron radiation has such a high quantum energy that the free radicals required for polymerization are formed directly from the vinyl ester resin. On the other hand, UV radiation has considerably lower quantum energy and requires the use of photo-initiators which decompose in resonance with UV light to generate free radicals. Formulation of radiation-curable coating systems from vinyl ester resins offers a practical approach to reducing air pollution since such formulations would be solvent-free.

1.3.2. Crosslinking Reaction

Vinyl ester resins are crosslinked by free radical copolymerization of methacrylate end groups with styrene. It is a system of copolymerization of vinyl/divinyl monomers. Figure 1.4 shows a schematic representation of the network formed by the free radical crosslinking reaction. Gelation occurs when a three-dimensional network or an infinite molecular weight polymer (gel) is formed. A gel molecule cannot be dissolved in any solvent. Experimentally, gel times (the time to reach the onset of gelation at a particular temperature) are measured using rheology or solubility experiments.

Free-radical crosslinking polymerization and copolymerization of multivinyl systems are very complicated and theoretical work in this field is not well established, although many papers have been published. Due to the overlap and entanglement of polymer chains, free-radical polymerizations are often diffusion-controlled even with linear chains. Crosslinking certainly confounds the diffusion-controlled reactions. However, there is no existing diffusion theory which is generally applicable to this type of system. Some special problems during free-radical

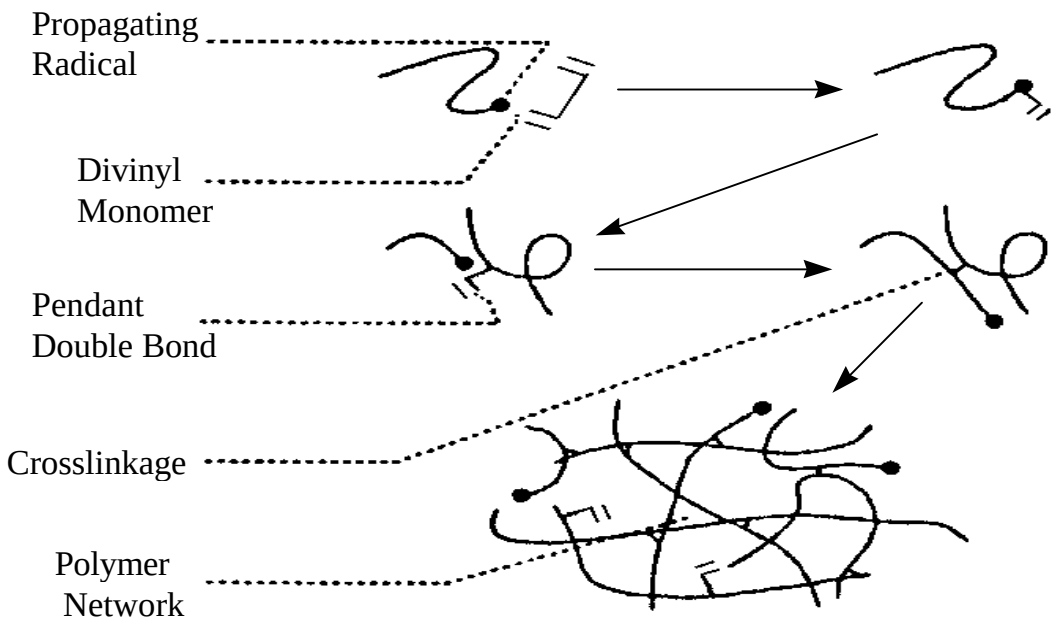


Figure 1.4. Schematic representation of free-radical crosslinking mechanism.

polymerization with crosslinking have been pointed out in a few papers,[17-20] such as the early onset of the Trommsdorff effect ("gel" effect) due to both physical entanglement of polymer chains and chemical crosslinking, incomplete conversion of pendant double bonds due to vitrification, and reactivity ratio changes with conversion. Trapped radicals can also induce post-copolymerization with oxygen, cyclization, intramolecular crosslinking, microgelation, etc.[21]

As is the case in all chain-reaction polymerizations, a reaction mixture of monovinyl and divinyl monomers contains primarily fully formed polymer chains and unpolymerized monomers at any given time. The sol fraction after the gel point consists only of monomers because of the nature of chain polymerization, where after initiation a chain continues to grow until the growth is terminated by recombination, chain transfer, or disproportionation reactions.

Vinyl ester resins usually contain 30-50 wt% styrene and 70-50 wt% vinyl ester oligomers. Early work on the model phenylglycidylether methacrylate showed that it reacted more rapidly than styrene in bulk or in solution because of hydrogen bonding between the polymer radical and the methacrylate monomer.[22] Reactivity ratios for this copolymerization with styrene show that, at least in the early stages of the reaction, the methacrylate content is high relative to styrene and methacrylate's copolymerization. Due to the very high concentration of divinyl monomers, gelation begins at very low conversions. For vinyl ester

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[17] A. Matsumoto, *Adv. in Polym. Sci.*, 123, 43, 1995.

[18] S. Zhu, A. E. Hamielec, *Markromol. Chem., Mmacromol Symp.*, 69, 247, 1993

[19] N. A. Dotson, T. Diekmann, C. W. Macosko, M. Tirrell, *Macromolecules*, 25, 4490, 1992.

[20] Y. Y. Chiu, L. J. Lee, *J. Polym. Sci.: Part A: Polym. Chem.*, 33, 257, 1995.

[21] S. Zhu, A. E. Hamielec, *Makromol. Chem. Macromol. Symp*., 63, 135, 1992.

[22] D. Ades and M. Fontanille, *J. Appl. Polym. Sci*., 23, 11, 1979.

[23] A. Yousefi and P. G. Lafleure, R. Gauvin, *Polymer Composites*, 18, 157, 1997.

resins, the onset of gelation is usually rapid (depends on reaction conditions) - right after the induction period with little or no appreciable increase in viscosity prior to gelation. The time to the onset of gelation is dependent on the concentration of free radicals. Increasing the concentration of the initiator and/or accelerators and the use of elevated temperatures will shorten the time to onset of the gel.

1.3.3. Kinetic Studies on Cure Reactions

Two types of methods have been employed to monitor the progress of cure reactions of thermosetting materials.[23] Methods such as chemical analysis, IR and UV spectroscopy are based on monitoring the changes in concentration of reactive functional groups consumed or produced during the cure reaction. The other methods are based on the effect of network formation on the physicomechanical properties of the sample. Of these methods, thermal analysis by differential scanning calorimeter (DSC) which monitors reaction heat release rate is the most commonly used to study the kinetics of cure reactions due to its simplicity and the capability of obtaining important thermal transition information without the knowledge of detailed chemistry.[23] Other popular techniques found in the literature are spectroscopic analysis,[24] rheological measurements,[25] electromagnetic and dielectric techniques,[26] and volumetric changes.[27]

A variety of kinetic models have been used to relate the rate of the cure reactions of thermosetting materials to the time, temperature, and the extent of cure. The kinetic models may be phenomenological models or mechanistic models. A phenomenological model is generally expressed by a relatively simple rate equation and is developed ignoring the details of how reactive species take part in the reaction. Mechanistic models are obtained from balances of reactive species involved in the reaction and give a better prediction and

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[24] R. Fountain and T. W. Haas, *J. Appl. Polym. Sci*., 19, 1767, 1975.

[25] F. G. Mussatti and C. W. Macosko, *Polym. Eng. Sci*., 13, 236, 1973.

[26] D. R. Day, *J. Reinf, Plast. Compos*., 13, 918, 1994.

[27] R. R. Hill, Jr., S. V. Muzumdar, and L. J. Lee, *Polym. Eng. Sci*., 35, 852, 1995.

interpretation of the cure reactions. Phenomenological models are usually preferred in studying the cure processes by DSC.

For the cure of vinyl ester resins, gelation and vitrification are important phenomena and have a large impact on the cure process. Vitrification is simply defined to occur at the point when the glass transition temperature (T_g) of the thermoset network equals the cure temperature. It represents the transition from a liquid or rubbery phase to a glassy state. Onset of gelation is defined as the moment when an infinite molecular weight polymer is formed. At gelation the viscosity of the gel becomes infinite as a gel cannot flow. In addition a gel is completely insoluble, it will instead swell in the presence of solvent. Vitrification is known to have a large effect on polymerization rates in thermosetting polymers. The diffusion rates of monomers and reactive chain ends decrease with increasing conversion. At some point the rate of diffusion will be the limiting factor in the rate of reaction and the reaction will be diffusion controlled. The effect of gelation and vitrification on cure is the main interest of much research. To take into account the effect of vitrification on polymerization, it is necessary to determine the dependence of glass transition temperature on the time of reaction and the conversion. Prediction of the gel point during cure of a thermoset network is a problem that has received substantial attention in the literature. Much theory has been aimed at determining a critical conversion at which gelation occurs.

For the kinetic studies of vinyl ester resins, several groups have reported their results obtained by DSC.[28-31] The cure reaction of Derakane 411-45 (45% styrene) obtained from the Dow Chemical Co. was studied by DSC from temperatures ranging from 86.1 ^{o}C to 127.1^{o}C.[32] Benzoyl peroxide was used as the initiator. It was found in this study that the glass transition

[28] C. D. Han and K. W. Lem, *J. Appl. Polym. Sci*., 28, 3155, 1983.

[29] C. D. Han and K. W. Lem, *J. Appl. Polym. Sci*., 28, 763, 1983.

[30] R. Mohan and T. H. Brentzer, *J. Reinf. Plast. Comp*., 14, 72, 1995.

[31] D. S. Lee and C. D. Han, *Polym. Eng. Sci*., 27, 955, 1987.

[32] J. H. Lee and J. W. Lee, *Polymer Engineering and Science*, 34(9), 742, 1994.

temperature increased linearly with the cure temperature. In the completely cured state, the T_g is about 118 ^oC. A phenomenological kinetic model with an autocatalytic reaction was used to describe the cure of this system. The kinetic parameters before and after gelation were evaluated by using the relationship between the glass transition temperature and the degree of cure. The inflection point of glass transition temperature was considered as the gel point (15% conversion).

A kinetic model was developed based on cure behavior such as autocatalysis, gelation, and vitrification in another study.[33] The vinyl ester resin studied was prepared from epoxy resin (DGEBA) and methacrylic acid.[33] The molar ratio of vinyl ester to styrene was ½. Benzoyl peroxide (2 wt%) and N, N-dimethylaniline (1 wt%) were used as the initiator and promoter. A time-temperature-transformation cure diagram was plotted from the kinetic model. The gelation time and vitrification time calculated from the kinetic model showed good agreement with experimental values. The addition of low profile additives slowed the cure rate of the vinyl ester resins. Vinyl ester resins with a compatible low profile additive (polyvinyl acetate (PVAC)) showed faster gelation but slower vitrification than the vinyl ester resin with an incompatible low profile additive.

The isothermal cure kinetics and rheological properties of an experimental "thickenable" vinyl ester resin (XD-7608.05) produced by the Dow Chemical Co. have been determined.[34] The peroxide/promoter was used as the initiator system**.** Both steady and oscillatory shear flow properties were determined using a cone-and plate rheometer, and the curing kinetics were determined using differential scanning calorimetry (DSC). Also determined were the rheological properties and curing kinetics of the resin when it had been thickened using magnesium oxide in the presence of calcium carbonate as a filler, and polyvinyl acetate (PVAc) as a low profile additive. The steady shear flow behavior observed with the vinyl ester resin was found to be very similar to that observed with a general purpose polyester

[33] M. S. Hong and I. J. Chung, *Polymer Journal*, 23(6), 747, 1991.

[34] C. D. Han and K. W. Lem, *J. Applied Polymer Science*, 29, 1879, 1984.

resin, but significant differences in the oscillatory shear flow behavior were found between the two resins. It was concluded in this study that dynamic measurement is much more sensitive to variations in resin chemistry than steady shear flow measurements. The Dow vinyl ester resin shows two peaks in loss modulus G' at high angular frequencies and a single peak in G' at low frequencies. Dynamic mechanical properties of fully cured samples of both an Ashland polyester and a Dow vinyl ester resins were determined and it was found that the fully cured sample of the Dow vinyl ester resin has more than one relaxation transitions (E"). DSC measurements can be used to determine the degree of cure as a function of cure time. By combining the rheological and DSC measurements, the authors in this study constructed plots describing how the viscosity increases with the degree of cure at various isothermal curing temperatures. It was found that Dow vinyl ester resin is very similar to those found in the curing of the Ashland general-purpose unsaturated polyester resin. The degree of cure increases with the cure temperature. The ultimate heat generated by the Dow vinyl ester resin (Q=345 J/g) was greater than that generated by the Ashland polyester resin (Q=275 J/g) and the ratio of the residual heat to the ultimate heat is also much higher. Since this ratio may be used as a measure of the amount of unreacted functional groups present in the resin upon completion of an isothermal cure, the author concluded that the Ashland polyester resin is more reactive than the Dow vinyl ester resin.

A very recent paper reported the curing kinetics and thermal properties of vinyl ester resins.[35] The bisphenol-A based resin used in this study had a molecular weight (M_n) of 1080 g/mol. The initiator was methyl ethyl ketone peroxide (MEKP) and the cocatalyst was cobalt octoate. The curing kinetics of vinyl ester resins were studied by scanning and isothermal calorimetry, gel time studies, and by DMTA. The rate of polymerization was raised by increasing the MEKP concentration. The cobalt octoate retarded the reaction rate, except at very low concentrations. The gel time was reduced for all increases in either peroxide or cobalt concentration. This contradictory behavior was explained by a kinetic scheme in which the cobalt species played a dual role - of catalyzing the formation of radicals from MEKP and of

[35] W. D. Cook, G. P. Simon, P. J. Burchill, M. Lau and T. J. Fitch, *J. Applied. Polymer Science*, 64, 769, 1997.

destroying the primary and polymeric radicals. The scanning calorimetry curves exhibited multiple peaks which were attributed to the individual influence of temperature on each of the fundamental reaction steps in the free radical polymerization. Physical aging appeared to occur during the isothermal polymerization of samples cured below the "fully cured" glass transition temperature (T_g). For low and intermediate cure temperatures, the T_g was found to be 11°C above the cure temperature due to the influence of diffusion on the polymerization rate. At higher cure temperatures, the T_g approached an upper limit as a result of nearly complete cure. For the sample cured at room temperature, two apparent glass transition regions were exhibited in the DMTA trace but only one transition was observed for the "fully" cured sample. The T_g was found to strongly depend on the degree of cure in the vinyl ester resin.

The kinetics of crosslinking reactions of vinyl ester resins can be studied by copolymerization theory for linear systems. Kinetics of vinyl ester resins studied by FTIR have been reported in several papers.[36 -38] The first detailed study[36] on copolymerization of vinyl ester resins by FTIR was on the system of bisphenol-A based vinyl ester resins (M_n=1100g/mol) containing variable initial styrene ratios from 25% to 60% by weight. The dimethacrylate vinyl ester prepolymer under study was supplied by Dow Chemical. The initiator system was comprised of methyl ethyl ether ketone peroxide (1%), dimethylaniline (0.06%) and cobalt octoate (0.018%). The cure was monitored at ambient temperature. It was proposed in this work that this system had three stages of copolymerization. The first stage was homogeneous copolymerization where methacrylate was more reactive than styrene. The change of the kinetic regime from

[36] M. Ganem, B. Mortaigne, V. Bellenger, and J. Veerdu, *J. Macromolecular Sci., Pure and Appl. Chem.*, A30(11), 828, 1993.

[37] R. P. Brill, R. L. McCullough and G. R. Palmese, *Advances in Polymers and Fibers*, 576, 1995.

[38] H. Li, A. C. Rosario, S. V. Davis, T. E. Glass, J. J. Lesko, and J. S. Riffle, *Polymer Preprint*, 38(2), 489, 1997.

stage 1 to stage 2 was attributed to gelation. The second stage began when the conversion ratio reached about 20-30%. The third stage was characterized by an interruption of the methacrylate copolymerization and continued styrene consumption. It began at a conversion of about 50-60%. This work provided some excellent explanations of the kinetics and mechanisms of crosslinking reactions of vinyl ester resins. However, only room temperature cured vinyl ester systems were investigated in this work. The results of these studies indicated that the final conversion of the vinyl ester was relatively low. It is very likely that room temperature cured systems have low conversion due to vitrification, although it is also believed that the conversion calculation from FTIR data needs to be modified. This question is addressed further in Chapter 3 of this dissertation. The unreacted double bonds were determined at 910 cm^{-1} and 945 cm^{-1} for styrene and methacrylate endgroups. As discussed in Chapter 3, accurate results can be obtained only after a small backbone peak is subtracted from the background at 945 cm^{-1}. It was found that the copolymer composition equation can still be applied to the vinyl ester system at high temperature cure.

In other work,[37] Dow Derakane 441-400 vinyl ester resin (33% styrene by weight) was mixed with styrene monomer to achieve the desired styrene/vinyl ester ratios of 41%, 50%, and 62%). An initiator (Witco USP 245 organic peroxide) was added at 1.75 wt.%. FTIR was used to monitor the cure for vinyl ester-styrene systems at 70 ^{o}C, 80 ^{o}C, 90 ^{o}C, 100 ^{o}C and 110 ^{o}C. The concentration versus time data for each monomer was fit to an autocatalytic model, yielding kinetic parameters. It was found that the reaction order, m, remained relatively constant at 0.85 for both vinyl ester and styrene monomers for all temperatures and resin compositions. The styrene monomer was found to react at a slower rate than the vinyl ester monomer. Generally, the styrene monomer did not react as rapidly in the early periods of cure as did the methacrylate groups associated with the vinyl ester. Microgel structures with a higher concentration of vinyl ester than the initial bulk were formed. The final extent of the reaction increased with increasing cure temperature over the range of temperatures studied. Increasing styrene concentration resulted in an increase in the ultimate conversion of vinyl ester while having little effect on the ultimate conversion of styrene. The effect of

temperature and styrene on the cure reaction were studied by this work. However, only the phenomenological model was used to analyze data obtained by FTIR. Here again the conversion calculation from FTIR data needs to be modified based on our own results to be discussed later in this thesis.

Polymerization kinetics of polyurethane and vinyl ester resin interpenetrating polymer networks were studied using Fourier transform infrared spectroscopy.[39-41] In this work, the pendant hydroxyl groups were capped with acetyl groups to minimize the possibility of chemical bonding between the two pairs of reactants. During the course of synthesis the two pairs of reactants interfere with each other although they follow different polymerization mechanisms (the polymerization of polyurethane is step growth in nature while the polymerization of vinyl ester resin is free radical mechanism). This gave rise to depressed reaction rates. Increasing the reaction temperature was more effective than increasing the free radical initiator level with regard to the final conversions of both components. The reaction sequence could be varied through adjusting the amount of the step-growth polymerization catalyst for polyurethane and free-radical initiator for vinyl ester resin as well as adjusting the reaction temperature. Using vinyl ester resins containing pendent hydroxyl groups could strongly affect the reaction kinetics of such interpenetrating polymer networks and lead to hybrid structures. The quick formation of one network would always depress the conversion of the other network in all interpenetrating polymer networks studied.

Studies on the styrenated polyester resins [42] indicated that use of α-methylstyrene does not adversely affect the physical properties of the cured products but prolongs the cure time required. The cure behavior of a bismethacryloxy derivative of the diglycidyl ether of

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[39] L. H. Fan, C. P. Hu, Z. P. Zhang, and S. K. Ying, *J. Applied polymer Science*, 59,1417, 1996.

[40] L. H. Fan, C. P. Hu, and S. K. Ying, *Polymer*, 37(6), 975, 1996.

[41] L. H. Fan, C. P. Hu, Z. Q. Pan, Z. P. Zhang, and S. K. Ying, *Polymer*, 38(14), 3609, 1997.

[42] R. Bhatnagar and I. K. Varma, *J. Thermal Analysis*, 35, 1241, 1989.

bisphenol A (vinyl ester resin) containing styrene as the reactive diluent (40% wt/wt) was studied using a gel point determination method and DSC. Partial replacement of styrene by α-methylstyrene may be helpful in the vinyl ester resin formulation because α-methylstyrene is an effective 'exotherm depressant". For example, the studies on systems of styrene/α-methylstyrene with ratios 40:0, 35:5, 30:10, 25:15, 20:20, 15:25 and 0:40 clearly indicated delayed curing in systems containing increasing proportions of α-methylstyrene. The energy of activation decreased from 869 kJ/mol to 333 kJ/mol as the concentration of α-methylstyrene increased in the formulations. However, no difference in thermal stability was observed by replacement of styrene with α-methylstyrene. It was concluded that in vinyl ester resins, 10-15% α-methylstyrene and 30-25% styrene could be used as reactive diluents. Resins containing styrene and α-methylstyrene were stable up to 300^{o}C and then started losing weight above this temperature. Rapid decomposition was observed at 350^{o}C-450^{o}C and almost total volatilization of the sample occurred around 500^{o}C. In all the resin samples an initial mass loss of about 3% to 8% was observed above 90^{o}C. This may be due to residual styrene or α-methylstyrene in these samples. This was an indication that the cure was still not complete at 140^{o}C.

1.3.4. Characterization of Cured Networks

Crosslink density is one of the most important structural factors controlling the properties of the cured networks. A detailed study on crosslink densities of vinyl ester networks has been reported.[43] In this study, the crosslink densities of vinyl ester networks with 35-55 wt.% styrene were determined from the rubbery elastic moduli. The shear modulus of cured vinyl ester networks well above T_g (T_g + 30K) were experimentally determined by using a Brabender torsion pendulum in the free oscillation mode with a starting angular deformation of 1^{o}. The samples were cured for three hours at ambient temperature and then post-cured for another four hours at 90^{o}C followed by four more hours at 120^{o}C. Based on their experimental results, the authors assumed that for these systems, the final structure is probably

[43] M. Ganem, E. Lafontaine, and B. Mortaigne, *J. Macromol. Sci. Phys*., B33(2), 155(1994).

diphasic, with a first phase consisting of the vinyl ester network and a second phase rich in polystyrene. The structure of this vinyl ester network was also studied by using rubber elasticity theory. The crosslink densities were derived from rubbery elastic moduli. Network models were based on a purely statistical approach. By taking into account the incomplete cure conversion, it was possible to predict the trends of modulus variations. A structural model for modulus predictions was also constructed assuming that the vinyl ester network was diphasic, one phase being composed of the vinyl ester network and the other of pure polystyrene. The authors tried to take this heterogeneity into account in modulus predictions using a simple mixture rule. However, this method failed for the systems with high styrene contents (>45%) for which the experimental modulus value was about 50% higher than the predicted one. Based on these results, the authors concluded that morphological change for a critical styrene weight fraction between 40% and 45% had occurred. Rubbery elastic moduli measurements showed that the maximum crosslink density coincided with the maximum conversion ratio as predicted from a network model (ignoring any possible morphological heterogeneity. The final conversion of styrene determined by styrene extraction was found to be 100%. The final conversion of methacrylate determined by ^{13}C-NMR ranged from 0.79 to 0.93.

The effect of styrene on the properties of vinyl ester resins under many given common cure conditions was investigated.[38] Mechanical properties of Derakane 411-45 copolymers showed small decreases in moduli and glass transition temperatures and increases in elongation at break as the styrene contents increased (Table 1.1).[44] Fracture toughness shows no change (styrene 40-60%).[45] Based on the work described in this thesis on the effect of styrene on the structure of vinyl ester resins (styrene 20-60%), the glass transition temperature decreases with increases in styrene content. The glass transition temperature is very sensitive to the

[44] I. K. Varma, B. S. Rao, M. S. Choudhary, V. Choudhary, and D. S. Varma, *Die Angewandte Makromolekulare Chemie*, 130, 191, 1985.

[45] P. Burchill and P. J. Pearce in *Polymeric Materials Encyclopedia*, J. C. Salamone ed., CRC Press, 1996, p2204.

network structure. Fracture toughness decreases when styrene contents increase from 20%-40%.

At low cure temperature, methacrylate immobilization through gelation and formation of styrene homopolymers causes polymer incompatibility problems, and evidence of a two-phase structure appears.[3, 36] Differential scanning calorimetry and dynamic mechanical thermal analysis (DMTA) of copolymers with styrene (45 wt.%) produced at room temperature also suggest a two-phase structure because two transitions are observed between 60°C and 140°C. These transitions, however, are only seen on the initial temperature ramp. Further reaction as the temperature increases above the cure temperature drives the reaction to completion to give a highly crosslinked structure with a glass transition temperature of 118°C. A comparable study of DGEBA diacrylate with butyl methacrylate as the diluent also showed the existence of a two-phase structure based on viscosity measurements during cure, dielectric properties, and preferential staining, with either methyl ethyl ketone peroxide, benzoyl peroxide or cumene hydroperoxide catalyst systems. The final network structure is influenced by the reaction exotherm and possibly by the reactivity of the initiating radicals. Ambient temperature cures may result in about 85-95% polymerization and a glass transition temperature of 50-100°C, depending on cure conditions, thickness, and the reaction exotherm. A post cure temperature of 120°C was required to give properties of the fully cured resins.

Since the formation of styrene-divinyl benzene microgels were first reported in 1935,[46-47] numerous reports on microgel formation have been published on the homopolymerization of multivinyl compounds and their copolymerizations with monovinyl monomers.[48-52]

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[46] V. Bellenger, J. Verdu, M. Ganem, et al., *Polym. Polym. Comp*., 2, 9, 1994.

[47] H. Staudinger, E. Husemann, *Chem. Ber. 68*: 1618, 1935.

[48] K. Horie, A. Otagawa, M. Muraoka, I. Mita, *J. Polym. Sci. Polym. Chem. Ed*., 13, 445, 1975.

Table 1.1. Mechanical properties of vinyl ester resin castings.[44]

Property	Styrene content (wt%)				
	20	30	40	50	60
Tensile strength ($psi \times 10^3$)	6.38	10.28	10.84	10.73	8.64
Tensile modulus ($psi \times 10^5$)	2.62	2.1	1.93	1.74	1.82
Elongation (%)	2.39	4.78	6.02	6.15	4.90
Flexural strength ($psi \times 10^3$)	13.37	15.41	13.40	14.78	14.67
Modulus of elasticity ($psi \times 10^6$)	9.12	9.16	6.75	7.06	6.20

The microgel is formed by an intramolecular crosslinking reaction. For unsaturated polyester resins, microgels which possess a higher density of crosslinks than the surrounding materials are found.[53] Some researchers believe that microgel forms at low conversions of vinyl esters and are linked to phase separation.[36, 54] It has been reported that closely packed microgels on the order of 100 nm in diameter were observed in the AFM (Atomic Force Microscopy) image of a cured vinyl ester prepared by etching with acetone which dissolves non-crosslinked material and exposes the crosslinked structures. However, our study found that the image of the completely cured vinyl ester networks showed a homogeneous one phase structure.

1.4. Toughening the Vinyl Ester Resins

It is well known that elastomeric modifiers can be used to improve the toughness of thermosetting materials such as epoxy resins and unsaturated polyesters. The same methods can also be applied for vinyl ester resins. These elastomers will ideally have reactive

functional groups, be miscible with the thermosetting components of the materials before cure and precipitate and form a uniformly distributed elastomeric microphase in the thermosetting matrix. The microphase has a small particle size, generally smaller than 15 μm,[55] and high interfacial bond strength between the microphase and the matrix. CTBN polymers (carboxyl-terminated copolymers of butadiene and acrylonitrile) are widely used reactive modifiers for thermosets. However, reactive liquid polymer additives such as vinyl terminated butadiene acrylonitrile copolymers, which are miscible with DGEBA epoxy resins, are immiscible with DGEBA-based vinyl ester resins.[45] The liquid resins' solubility parameters are 10.12 and 10.05 $(cal/cm^3)^{1/2}$ for DGEBA epoxy and vinyl ester resin (45 wt.%).[45] The commercial butadiene acrylonitrile copolymers have values between 9.1 and 10.8 $(cal/cm^3)^{1/2}$. Toughness can be improved for vinyl ester resins by incorporating a carboxy terminated reactive liquid polymer in the synthesis.[45] It was found that modified vinyl ester resins can be easily toughened by adding reactive liquid polymer.[45] The CTBN modified vinyl ester oligomers act as compatibilizers for blending additional butadiene copolymer.[45] Therefore, the toughness of modified vinyl ester resins can be further improved by mixing with more reactive liquid polymer.[56] Similar behavior was found for Novolac-based epoxy acrylate resins to achieve greater toughness as the data in Table 1.2 indicated.[57]

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[49] J. Spevacek, K. Dusek, *J. Polym. Sci. Polym. Phys. Ed*., 18, 2027, 1980.

[50] H. Galina, K. Dusek, Z. Tuzar, M. Bohdanecky, J. Sokr, *Eur. Polym. J.*, 16, 1043, 1980.

[51] A. C Shah, I. W Parsons, R. N Haward, *Polymer*, 21, 825, 1980.

[52] R. Leicht, J. Fuhrmann, Polym. Bull., 4, 141, 1981.

[53] E. Pezron, Y. S. Yang, and L. Suspene, *J. Reinforced Plastics and Composites*, 13, 314, 1994.

[54] Y. S. Yang and L. J. Lee, *Polymer*, 29, 1793, 1988.

[55] J. S. Ullett and R. P. Chartoff, *Polym. Eng. Sci*., 35, 1086, 1995.

[56] S. Pham and P. J. Burchill, *Polymer*, 36(17), 3279, 1995.

[57] C. D. Dudgeon, *Polyester Resins*, P96-99, *Properties of Constituent Materials.*

[58] J. Pearce, A. R. Siebert, D. R. Egan, C. D. Guiley and R. S. Drake, *J. Adhesion*, 49, 245, 1995.

[59] S. H. Yu, U. S. Patent 5, 506, 320 (1996).

Adhesive properties of elastomer-modified vinyl ester resins (Derakane 8084) which are further modified with an epoxy-terminated liquid nitrile rubber or a methacrylated-vinyl terminated liquid nitrile rubber are greatly enhanced.[58] Around 5% addition of reactive liquid polymer produced a three-fold increase in bond strength for aluminum and steel joints. At that addition level, lap shear tests showed a 30% improvement in strength of adhesion in an aluminum joint.

CTBN polymers are known to be inherently susceptible to ultraviolet light and thermo-oxidative degradation due to the presence of double bonds in the butadiene repeating units.

Table 1.2. Fracture toughness K_{1c} and Fracture energy G_{1c} values of several polymeric materials.[45]

Material	K_{1c} ($MN/m^{3/2}$)	G_{1c} (J/m^2)
a. Derakane 411-45(45 wt % styrene)	0.72	157
b. a+ modified polybutadiene	2.22	1948
c. Derakane 8084	1.15	432
d. c+ modified polybutadiene	1.71	1234
e. c+caprolactone modified PLP	2.97	2940
f. Novolac epoxy acrylate-styrene	0.54	63
g. f+caprolactone modified RLP	1.79	1628

Recently, saturated elastomeric comb copolymers were also reported as reactive liquid polymer to improve toughness or flexibility for thermosetting resins including epoxy resins and vinyl ester resins.[59] The comb copolymers have a backbone of polyacrylate with a carboxyl group at each end and pendent chains derived from a macromer of polycaprolactone. Due to the absence of double bonds in these comb copolymers, the resistance to ultraviolet

light and thermo-oxidative degradation can be greatly improved. The comb copolymer modified vinyl ester resins can be prepared in a manner analogous to that of CTBN (Figure 1.3).

1.5. Cured Networks and Properties

1.5.1. Mechanical Properties

Vinyl ester networks have excellent tensile and flexural properties, as well as high elongation as the data in Table 1.3 shows.[60] Vinyl esters have very good thermal performance, excellent mechanical properties, and toughness which is why they are "preferred" materials for structural composites. Vinyl esters also have performance advantages over isophthalate polyesters in fatigue studies.[61] The advantage of the vinyl esters was also shown at elevated temperatures.[62] At 105^{o}C, vinyl ester and isophthalic polyester composites (60% glass) were cycled to a stress level of 60-70 MPa. After 200,000 cycles, the drop in flexural modulus was only 5% for the vinyl ester, compared to 12% for the isophthalate polyester.[60]

1.5.2. Shrinkage Control During Cure

Compared to unsaturated polyesters, vinyl ester resins have better toughness, chemical resistance, and lower volumetric shrinkage.[60] However, vinyl ester resins have higher shrinkage (6-9%) than epoxy resins. It was found that the shrinkage of vinyl ester resins during cure increased as the styrene concentration in the resins increased and decreased with the increase of chain length of vinyl ester oligomers. Shrinkage during cure leads to problems such as surface distortion, internal cracks and voids. Low profile additives, which are usually specific thermoplastic polymers, are usually used during cure to decrease the

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[60] C. D. Dudgeon in *Handbook of Composites*, W. Watt and B. V. Perov Ed., Elsevier Sci. Publications, New York, 1985.

[61] B. Das, H. S. Loveless, and S. J. Morris, *36th Annual Conference of the Reinforced Plastics/Composites Institute*, The Society of the plastics Industry, Inc., 1981.

[62] P. K. Mallick, *37th Annual Technical Conference* , Society of Plastics Engineers, Inc., 1979, p589.

Table 1.3. Typical mechanical properties of vinyl ester resins.[60]

	Vinyl ester	40 wt.% fiberglass-vinyl ester
Barcol hardness	35	160
Tensile strength, MPa	80	160
Tensile modulus, Pa	3590	11000
Elongation, %	4.0	----
Flexural strength, MPa	140	220
Flexural modulus, Pa	372	9000
Heat deflection temperature, ^{o}C	100	----

shrinkage. Although the mechanism of volume shrinkage control by the use of low profile additive has not been fully understood, it is now generally agreed that the low profile additive and crosslinked polymer phase must phase separate first. Then microvoid and/or microcrack formation at the interface between the low profile additive and crosslinked polymer phases as well as inside the low profile additive due to the microstress cracking initiated at the interface take place and could lead to volume shrinkage compensation. Vinyl ester resins are often used in combination with fibrous reinforcement and inert fillers to manufacture composite structures called sheet molding compound or SMC. An improvement in the process is chemical thickening of the liquid resin with a Group 2 metal oxide or hydroxide and water to form a high viscosity gel after the resin has been mixed with all other ingredients in the molding compound. Low profile additives provide effective shrinkage control during cure and provide exceptionally smooth surfaces in SMC. One example is a new thermoplastic polyester low profile additive for vinyl ester resins. The low profile additive is a saturated polyester formed from a dibasic acid and a polyethyleneoxy/poylpropyleneoxy diols (EO/PO) block

copolymer. It was reported that good physical properties and zero shrinkage were achieved by the use of the new low profile additive.[63]

1.5.3. Thermal and Oxidative Stability

Regardless of the polymer composition, at temperatures of around 300°C, cured vinyl ester resins will undergo spontaneous decomposition. This is a characteristic of vinyl polymers which is caused by their depolymerization to form monomeric species. Curing and decomposition behavior of vinyl ester resins based on epoxy Novolacs and methacrylic acid were studied by DSC and TGA. These resins with varied acid values (11-48mg KOH g^{-1} solid) were diluted by 40 wt.% styrene and benzoyl peroxide as the initiator. It was found that vinyl ester resins with lower acid values were more reactive during the crosslinking reactions than the resins with higher acid values. TGA data show that temperatures for 5% weight loss at programmed heating rate of 10°C/min were 603 to 634 °C under a static atmosphere. The cured product with the lowest precursor acid value was found to be the most thermally stable and had an estimated lifetime of 16.58 years at 400°C.[64]

1.5.4. Chemical Resistance and Water Absorption

The organic chemical and solvent resistance of vinyl ester resins are superior to all other polyesters tested.[1] In acidic environments, vinyl ester resins have been found to be the most resistant of the resins tested in terms of greatest retention of properties in the largest variety of corrosive media.[1] Vinyl ester resins show exceptionally good resistance to distilled water.[1, 65]

The cured pure vinyl ester oligomers without comonomers absorb about 3% water at saturation, and copolymerization with other acrylates results in a much higher affinity for water, with contents from 3-6 wt.%.[65] In contrast, copolymers with styrene (45 wt%) absorb

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[63] J. Pearce, A. R. Siebert, D. R. Egan, C. D. Guiley and R. S. Drake, *J. Adhesion*, 49, 245, 1995.

[64] S. H. Yu, U. S. Patent 5, 506, 320, April 9, 1996.

[65] S. B. Lee and T. J. Rockett, *Polymer*, 33(17), 3691, 1992.

much less water, about 0.8 wt.% at room temperature, and the amount absorbed increases with temperature to about 1.2 wt.% at 90°C. The absorption obeys Fick's Law at 18°C but not at 90°C. The polymer adsorbs 0.8 wt.% water and suffers a large decrease in elongation at break. This is probably because of surface flaws, since the water has no plasticizing effect on the elastic modulus. Immersion in 20 wt.% sulfuric acid at 65°C did not produce as great a change in mechanical properties. Any chemical attack on the polymer is at the crosslink point, and the molecular weight of the backbone polymer is unaffected, unlike the behavior of polyester resins. In addition, the polymer's polarity renders it resistant to swelling and degradation by small-molecule organic liquids.

1.6. Applications

As mentioned in the previous section, vinyl ester resins combine the best properties of epoxies and polyesters. Although they are higher in cost than polyesters, vinyl ester resins have excellent chemical resistance and low water absorption compared with polyester resins. At the same time vinyl esters offer greater control over cure rate and reaction conditions than epoxy resins. They can be easily handled at room temperature and have properties close to epoxy resins. Therefore, they are used in applications in many of the same areas that typically use polyesters and epoxies as materials. Typical applications for vinyl esters include structural materials, coatings, adhesives, molding compounds, electrical applications, dental materials, and military/aerospace applications.

Because of their excellent thermal performance and mechanical properties, they are the prime candidates for composites in transportation or infrastructure with applications in construction of parts for automobiles and other surface transportation vehicles, fascia for buildings, reinforcements for bridges, etc. For example, as the materials for sheet molding compounds (SMC), vinyl ester resins provide greater toughness, heat distortion temperature, and corrosion resistance compared to conventional unsaturated polyesters.[66] Novolac epoxy-based

[66] J. Selley in *Encyclopedia of Polymer Science & Technology*, N. M. Bikales, eds., Wiley-Interscience, New York, 1987, Vol 12, p256.

vinyl ester resins with their higher glass transition temperatures are used for high temperature formulations such as chemical storage vessels and chemical reactors. Another application for Novolac epoxy-based vinyl ester resins is in the construction of waste incineration gas cleaning units.[67] Modified DGEBA resins are used where improved adhesion, wear resistance, and fracture toughness are required. Vinyl esters can also be used in applications ranging from electro-refining tanks to swimming pools.

Vinyl esters also find a variety of applications in optical fiber coatings, topcoats for metal containers, UV curing inks, as well as in printed circuit boards because of their ability to constitute photocrosslinkable systems.[68] For example, Actocryl-400, an aromatic epoxy-diacrylate resin based on DGEBA from Ancomer, Manchester, UK, can be photo-crosslinked with photo initiator dimethoxyphenylacetophenone (Irgacure 651 from Ciba Geigy), and used as a photo-crosslinkable coating materials.

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[67] D. H. Kelley and J. F. Perey, *Polymer Composites*, 18, 34, 1997.

[68] S. Radhakrishnan and R. A. Pethrick, *J. Appl. Polym. Sci*., 51, 863, 1994.