SYNTHESIS AND CHARACTERIZATION OF EPOXY-ACRYLATE VINYLESTER RESIN AND NETWORK STRUCTURE

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF EPOXY-ACRYLATE VINYLESTER RESIN AND NETWORK STRUCTURE

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Vinylesters are termosets resins that have reactive double bond at the chain ends. They are produced by the reaction of various epoxies and acrylic acids by step growth polymerization. Vinylester chains are oligomers with molecular weight from 600 to 1200 g/mol. The resin viscosity is very high; therefore, diluent is used for easy application. The generally used diluent is styrene with, reactive double bonds to form a crosslink between the chains. The diluted resin viscosities are between 200 – 2000 cps. Peroxide initiators are used for network formation. The mechanical properties of vinylester resin are enhanced with reinforcements such as glass fiber, carbon fiber, Kevlar or nanoparticules to make composites.

Various molecular weights of vinylester resins were synthesized and the samples were prepared with different styrene contents. The effects of the styrene content, temperature and molecular weight on the viscosity were measured and examined. The main effects were determined as styrene content and temperature, while the effect of molecular weight is negligible. The resins were characterized with IR and NMR spectroscopy. The molecular weights were determined by theoretical calculations, titration and H-NMR spectroscopy.

Peroxide initiators were used to cure the resins with the cobalt complex accelerator. The resins were post-cured at different temperatures. The completion of the curing was monitored by the disappearance of the carbon-carbon double bonds of methacrylate (943 cm^{-1}) and styrene (910 cm^{-1}), by FT-IR spectrum.

The effects of styrene content, post-cure conditions, and molecular weight on the mechanical properties were discussed. The glass transition temperatures were determined by DSC and DMA. The crosslink densities and rheological properties were determined by creep test. The important properties of vinylester resins, which are modulus, tensile and flexural strength, shrinkage, water absorption, glass transition temperature, HDT values and impact strength were investigated.

Keywords: vinylester, thermoset, network structure, composite, epoxy

ÖZ

EPOKSİ-AKRİLAT VİNİLESTER REÇİNE VE ÇAPRAZ BAĞLI AĞ YAPISININ SENTEZİ VE KARAKTERİZASYONU

ZEYTİN DERİN, Çiğdem

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Vinilester reçineler çapraz bağ yapabilen termoset reçinelerdir. Polimer zincirlerinin iki ucunda reaktif çift bağlar bulunur. Vinilester reçineler çeşitli epoksi ile akrilik asitlerin basamaklı polimerleşme reaksiyonu ile sentezlenir. Reçine zincirleri molekül ağırlığı 600 ile 1200 g/mol arası oligomerlerdir. Reçinenin viskozitesi çok yüksek olduğu için, çözücü katılarak kullanımı kolaylaştırılır. Genellikle, aktif çift bağ içeren ve zincirler arasında çapraz bağ oluşumuna katılan stiren çözeltisi kullanılır. Seyreltilmiş reçinenin viskozitesi 200 – 2000 cps arasındadır. Ağ oluşumunu başlatmak için peroksit başlatıcılar kullanılır. Vinilester reçinelerin mekanik özellikleri cam fiber, karbon fiber, Kevlar ya da nanoparçacıklar ile kompozit oluşturularak arttırılır.

Farklı molekül ağırlığında sentezlenen vinilester reçineler farklı miktarlarda stiren çözücü içinde çözünerek farklı numuneler hazırlandı. Stiren miktarı, sıcaklık ve molekül ağırlığının viskozite üzerindeki etkileri incelendi. Viskozite üzerindeki ana etkinin stiren miktarı ve sıcaklık olduğu, molekül ağırlığının etkisinin ise çok az olduğu tesbit edildi. Reçine IR ve NMR ile karakterize edildi. Molekül ağırlığı teorik hesaplama, uç grup titrasyonu ve H-NMR ile bulundu.

Peroksit başlatıcılar ve kobalt kompleks hızlandırıcılar reçineyi çapraz bağlamak için kullanıldı. Ayrıca reçineler farklı sıcaklıklarda post-kürlendi. Çapraz bağlanma reaksiyonu süresince metakrilat (943 cm^{-1}) ile stiren (910 cm^{-1}) çift bağlarının harcanımı FT-IR ile takip edildi.

Stiren miktarı, post-kür şartları ve molekül ağırlığının mekanik özelliklere etkisi detaylı incelendi. DSC ve DMA ile camsı geçiş sıcaklıkları tespit edildi. Çapraz bağ yoğunluğu ve kürlenmiş reçinenin reolojik özellikleri yük altında akma testi ile hesaplandı. Vinilester reçinelerin önemli özellikleri olan modulus, çekme ve eğilme dayanımları, çekme, su absorpsiyonu, camsı geçiş sıcaklığı, HDT değerleri ve darbe dayanımları incelendi.

Anahtar kelimeler: Vinilester, termoset, çapraz bağlı kürlenme, kompozit, epoksi

to the life….

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CHAPTER 1

1. LITERATURE REVIEW

1.1. Introduction

Vinylester resins were introduced commercially in the early 1960s. Today, they are one of the most important thermosetting materials which have been widely recognized as materials with excellent resistance to a wide variety of commonly encountered chemical environments. They are used to fabricate a variety of reinforced structures, including pipes, tanks, scrubbers and ducts. They are the 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, vinylesters are also being used in coatings, adhesives, molding compounds, structural laminates, electrical applications and military/aerospace applications [1,2,3,4,5]

Vinylester resins are step growth polymers of various epoxide resins and unsaturated monocarboxylic acids, most commonly methacrylic acid [6]. They have terminal reactive double bonds derived from the carboxylic acid used as shown in Figure 1.1.

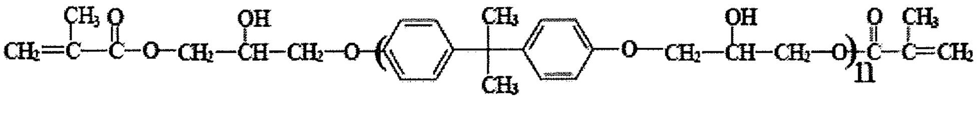


Figure 1.1 Structure of the methacrylate terminated polyhydroxyether oligomer, n is the number of repeating unit

These reactive groups can form a crosslinked network with or without the addition of a comonomer. It is common to dilute the vinylester 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. In many industrial products, vinylester resins contain 40-50 wt % styrene.

Although vinylester resins have been used in industry for more than 30 years, they are generally categorized together in the unsaturated polyester family [3]. There is less research cited in the literature on vinylester resins compared to the studies on unsaturated polyesters and epoxy resins, especially the studies on the synthesis, structure and properties of vinylester resins. Most of the information concerning the cure behavior and the morphology of free radical cured resins focus on unsaturated polyester resins. Developments and application of vinylester resins include the synthesis of new vinylester resins with new structural properties in an effort to improve toughness, reduce viscosity, decrease shrinkage etc. Understanding the mechanisms of the cure reaction, and gaining better control of the properties of these materials are also general interest.

Vinylester resins combine the best properties of epoxides 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 most polyester resins, especially hydrolytic stability, and at the same time offer greater control over the cure rate and the reaction conditions than epoxy resins. The unsaturated bonds on the terminal groups of the vinylester oligomers copolymerize with the comonomer to form a crosslinked network similar to the curing reactions of unsaturated polyesters.

However, the physical properties such as corrosion resistance of the vinylester networks are, in general, superior to the unsaturated polyesters. This can be at least partially attributed to the fact that the vinylesters 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 crosslink density can be better controlled in the vinylesters. 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 vinylesters, leaving the majority of the backbone of the molecule unaffected [7].

1.2. Preparation

Vinylester resins are step growth polymerization 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 [8]. The reaction to form the vinylester 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 when compared to other catalysts [9]. Typical reaction conditions are 120 ^{0}C for 4-5 hours, and hydroquinone is commonly used as the initiator. The conversion of the reaction is 90-95 %. The vinylester resins can also be prepared by the reaction of glycidyl methacrylate with a multifunctional phenol [10].

Figure 1.2 shows the reaction of a bisphenol-A glycidylether with methacrylic acid to prepare the bisphenol-A epoxy based vinylester resins which are the most widely used vinylester 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 chain 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 [11].

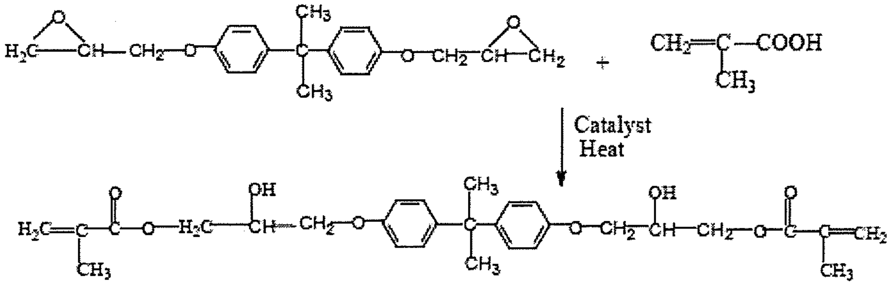
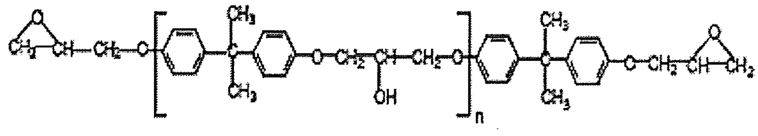


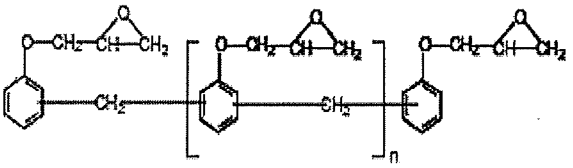
Figure 1.2 Synthesis of vinylester by the reaction of a bisphenol-A glycidylether with methacrylic acid

Vinylesters with considerable structural variations can be prepared by the combination of different epoxide resins with various unsaturated acids as shown in Figure 1.3. It is well known that bisphenol-A epoxy resins have very good mechanical properties and that cycloaliphatic epoxy resins are UV resistant. Vinylester resins produced from Novolac epoxy resins have high-temperature properties but are very brittle. Methacrylic acid is preferred for many applications. Methacrylate based vinylesters are more resistant to chemical attack than acrylate vinylester resins, because the methyl group of methacrylic acid can stabilize the polymer. Structural modifications of vinylester resins were also studied by many researchers to alter the properties in order to satisfy specific application requirements. For example, the viscosities of vinylester resins without diluents are typically in the range of about 1,000 to 8,000 poise and higher, which is too high for many applications. It is necessary to add lower viscosity reactive diluents. Many of these diluents are too volatile or toxic. The added diluent may act as comonomer and can make modified vinylester resins having improved toughness. The commercially toughened vinylester oligomers are Derakane 8084 (Dow Chemical Co.) and Hetron 1642 (Ashland Chemical Inc.), both of which contain a carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN). An excess of the selected epoxy resin reacts with a selected difunctional carboxyl-terminated reactive liquid polymer and an unsaturated monocarboxylic acid. The reaction is catalyzed by tertiary amines such as pyridine at 175 ^{0}C [12,13].

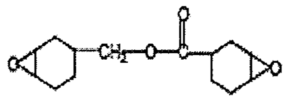
Epoxy Resins:



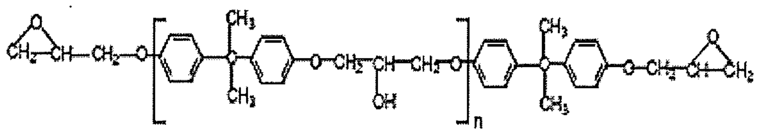
Diglycidyl Ether of Bisphenol A



Epoxy Novolac



Cycloaliphatic Epoxy

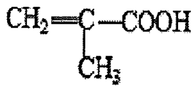


Diepoxidized Hydrogenated Bisphenol A

Unsaturated Acids

Acrylic acid: $CH_2{=}CH{-}COOH$

Methacrylic acid:



$CH_2{=}C(CH_3){-}COOH$

Crotonic acid: $CH_3{-}CH{=}CH{-}COOH$

Cinnamic acid:

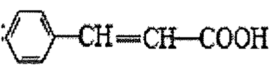


Figure 1.3 Various epoxy resins and acrylic acids, which are used for vinylester synthesis

1.3. Network Formation 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. The thermosets discussed in this dissertation are below their glass transition at room temperature. Usually, glassy thermosets are more brittle than thermoplastics [14].

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 as it is well known. 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 and tetrafunctional oligomeric components containing a double bond at each end of a linear chain. In this study, monomer is styrene and the oligomer is vinylester.

The accelerators most commonly employed are tertiary amines, such as dimethyl- or diethyl- aniline, and metallic soaps, such as cobalt or manganese octoate or naphthanate.

1.3.1. Crosslinking Reaction

The free radical polymerization of vinylester and unsaturated polyester resin systems is commonly initiated by the thermal or the chemical decomposition of various organic peroxides and organic hydroperoxides to produce free radical initiator. The various chemical types of peroxides include: the diacyl peroxides, ketone peroxides, hydroperoxides, dialkyl and diaralkyl peroxides, peroxyesters, and perketals (peroxyketals). Some common peroxides for room temperature are methyl ethyl ketone peroxide (MEK-P), cyclohexanone peroxide, and acetylacetone peroxide. 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.

Accelerators increase the rate at which peroxides break down into free radicals and 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 [15,16]. Metals salt are preferred in the industrial application because of its price and good handling properties.

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 has not been 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 [17].

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 polymerization with crosslinking have been pointed out in a few papers [18,19] such as the early onset of the Trommsdorff effect ("gel" effect) due to both the physical entanglement of polymer chains and the chemical crosslinking, incomplete conversion of pendant double bonds due to vitrification, and reactivity ratio changes with conversion [20,21]. Trapped radicals can also induce post-copolymerization with oxygen, cyclization, intramolecular crosslinking, microgelation [22].

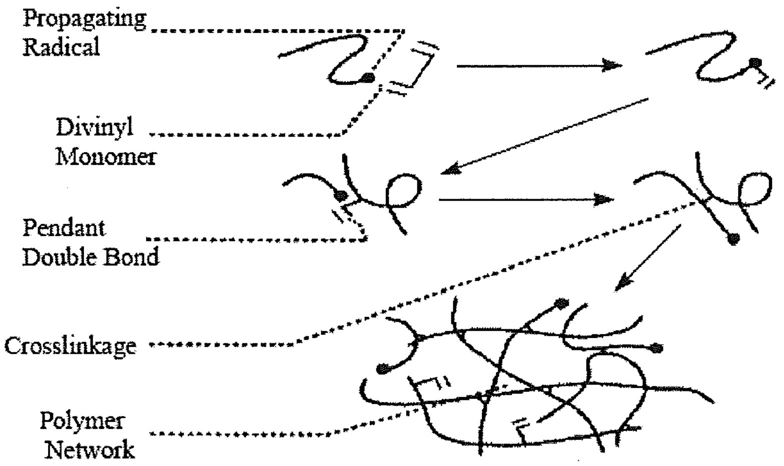


Figure 1.4 Free radical crosslinking mechanism [1]

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.

Vinylester resins usually contain 30-50 wt% styrene and 70-50 wt% vinylester 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 [23]. The methacrylate conversion is high relative to styrene, in the early stages of the reaction. Due to the very high concentration of divinyl monomers, gelation begins at very low conversions. For vinylester 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 the onset of the gel.

1.3.2. Kinetic Studies on Cure Reactions

Two methods have been employed to monitor the progress of the cure reactions of thermosetting materials [24]. Methods such as chemical analysis, IR and UV spectroscopy are based on monitoring the changes in the 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 mechanical 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 method to study the kinetics of cure reactions due to its simplicity and the capability of obtaining important thermal transition information without knowledge of detailed chemistry [22,25]. Other popular techniques found in the literature are spectroscopic analysis [26], rheological measurements [27], electromagnetic and dielectric techniques [28], and volumetric changes [29]. A variety of kinetic models has 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 interpretation of the cure reactions. Phenomenological models are usually preferred in studying the cure processes by DSC.

For the cure of vinylester resins, gelation and vitrification are important phenomena and have a great impact on the cure process. Vitrification is simply defined to occur at the point when the glass transition temperature (Tg) 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 and the gel cannot flow. The gel is insoluble, and swells in the presence of a solvent. Vitrification is known to have a great effect on the polymerization rates in thermosetting polymers. The diffusion rates of the monomers and the 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.

In order to account for the effect of vitrification on polymerization, it is necessary to determine the dependence of the glass transition temperature on the time of reaction and the conversion. Prediction of the gel point during the cure of a thermoset network is a problem. Many theories have aimed at determining the critical conversion at which gelation occurs.

Vitrification is the process by which a polymer passes into the glassy state from the liquid or rubbery state. Unlike gelation, vitrification can be avoided by raising the cure temperature of the polymer. However, vitrification can reoccur as the degree of cure increases. 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 is useful for identifying the onset of gelation and vitrification [30]. The TTT diagram plots the cure temperature of the polymer against the time of cure. Such diagrams allow for 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 (Figure 1.5) [31].

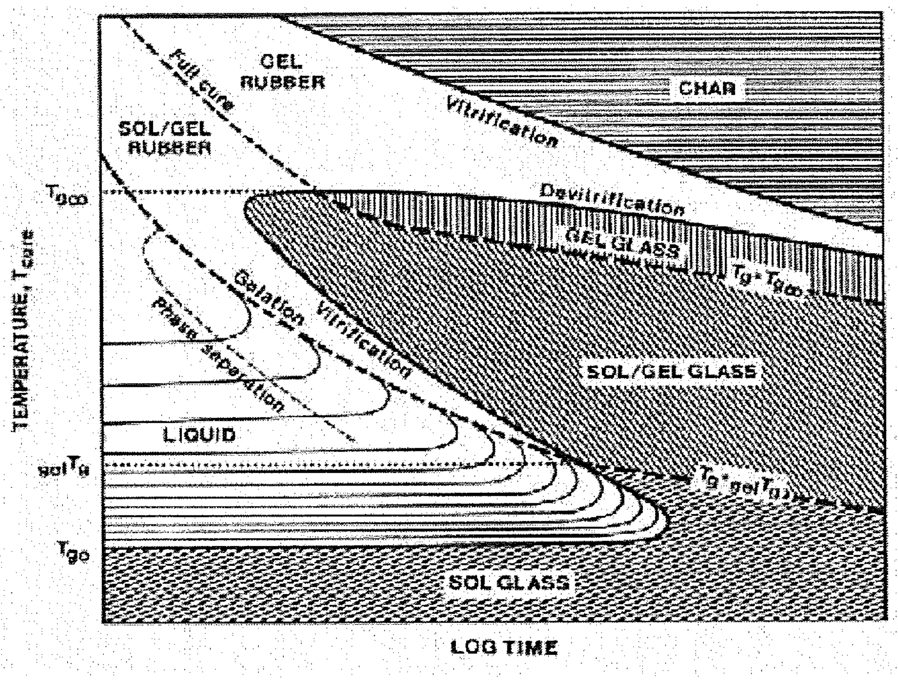


Figure 1.5 Generalized TTT cure diagram for thermosetting polymers [31].

For the kinetic studies of vinylester resins, several DSC results are reported [32]. 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 °C to 127.1 °C [35]. Benzoyl peroxide was used as the initiator. It was found in this study that the glass transition temperature increased linearly with the cure temperature [33]. In the completely cured state, the Tg is about 118 °C. 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 the glass transition temperature was considered as the gel point (15% conversion) [34,35].

A kinetic model was developed based on the cure behavior such as autocatalysis, gelation, and vitrification in another study [32]. The vinylester resin studied was prepared from epoxy resin (DGEBA) and methacrylic acid [33]. The molar ratio of vinylester to styrene was ½. Benzoyl peroxide (2 wt%) and N, N-dimethylaniline (1 wt%) were used as the initiator and the promoter.

A time-temperature-transformation cure diagram was plotted from the kinetic model. The gelation time and the vitrification time calculated from the kinetic model were in agreement with the experimental values. The addition of low profile additives slowed the cure rate of the vinylester resins. Vinylester resins with a compatible low profile additive (polyvinyl acetate (PVAC)) showed faster gelation, but slower vitrification than the vinylester resin with an incompatible low profile additive [38].

The isothermal cure kinetics and the rheological properties of an experimental "thickenable" vinylester resin (XD-7608.05) produced by the Dow Chemical Co. have been determined [39]. The peroxide/promoter was used as the initiator system. Both steady and oscillatory shear flow properties were determined by using a cone-and plate rheometer, and the curing kinetics were determined by using differential scanning calorimetry (DSC). Also determined were the rheological properties and the 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 (PV Ac) as a low profile additive.

The steady shear flow behavior observed with the vinylester resin was found to be very similar to that observed with a general purpose polyester resin, but significant differences in the oscillatory shear flow behavior were found between the two resins.

It was concluded in this study that dynamic measurements were much more sensitive to variations in resin chemistry than the steady shear flow measurements.

The Dow vinylester resin showed 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 Dow vinylester resins were determined, and it was found that the fully cured sample of the Dow vinylester resin had more than one relaxation transition (E"). DSC measurements can be used to determine the degree of cure as a function of cure time. By combining the rheological and the 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 vinylester resin was very similar to those found in the curing of the Ashland general-purpose unsaturated polyester resin. The degree of cure increased with the cure temperature. The ultimate heat generated by the Dow vinylester 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 was also much higher. Since this ratio may be used as a measurement 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 was more reactive than the Dow vinylester resin [40].

It is reported the curing kinetics and thermal properties of vinylester resins [41]. The bisphenol-A based resin used in this study had a molecular weight (Mn) of 1080 g/mol. The initiator was methyl ethyl ketone peroxide (MEKP) and the cocatalyst was cobalt octoate. The curing kinetics of vinylester resins were studied by scanning and isothermal calorimeter, gel time studies, and by DMTA. The rate of polymerization was increased 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 MEK-P and of destroying the primary and polymeric radicals.

The scanning calorimeter curves exhibited multiple peaks that 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 (Tg). For low and intermediate cure temperatures, the Tg 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 Tg 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 Tg was found to depend strongly on the degree of cure in the vinylester resin.

The kinetics of crosslinking reactions of vinylester resins can be studied by the copolymerization theory for linear systems. The kinetic studies of vinylester resins, by FTIR, have been reported in several papers [41]. The first detailed study on the copolymerization of vinylester resins by FTIR was on the system of bisphenol-A based vinylester resins (Mn=1100g/mol) containing variable initial styrene ratios from 25% to 60% by weight. The initiator system was comprised of methyl ethyl ether ketone peroxide (1%), dimethylaniline (0.06%) and cobalt octoate (0.018%). The curing 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 stage 1 to stage 2 was attributed to gelation. The second stage began when the conversion ratio reached about 20-30% [42]. 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 about the kinetics and the mechanisms of crosslinking reactions of vinylester resins. Vinylester systems with different MW were cured at different temperatures. The results of these studies indicated that the final conversion of the vinylester should be considered. It is very likely that room temperature cured systems have low conversion due to vitrification, although it is also believed that the conversion calculations from FTIR data need to be modified. The unreacted double bonds were determined at 910 cm^{-1} and 945 cm^{-1} for styrene and methacrylate endgroups. Accurate results could be obtained only after a small backbone peak was subtracted from the background at 945 $cm^{-1.}$ It was found that the copolymer composition equation could still be applied to the vinylester system at high cure temperature.

It was reported that, Dow Derakane 441-400 vinylester resin (33% styrene by weight) was mixed with styrene monomer to achieve the desired styrene/vinylester ratios of 41%, 50%, and 62%). An initiator (Witco USP 245 organic peroxide) was added at 1.75 wt.% [1]. FTIR was used to monitor the cure for vinylester-styrene systems at 70 °C, 80 °C, 90 °C, 100 °C and 110 °C. The concentration versus time data for each monomer were fit into an autocatalytic model, yielding kinetic parameters. It was found that in the reaction order, m, remained relatively constant at 0.85 for both the vinylester and the styrene monomers for all temperatures and resin compositions. The styrene monomer was found to react at a slower rate than the vinylester monomer. Generally, the styrene monomer did not react as rapidly in the early periods of cure as did the methacrylate groups associated with the vinylester. Microgel structures with a higher concentration of vinylester 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 vinylester while having little effect on the ultimate conversion of styrene. The effects 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.

The polymerization kinetics of polyurethane and vinylester resin interpenetrating polymer networks were studied using a Fourier transform infrared spectroscopy [43,44]. 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 the synthesis, the two pairs of reactants interfered with each other although they followed different polymerization mechanisms (the polymerization of polyurethane is step growth in nature, while the polymerization of vinylester resin follows free radical mechanism). This gave rise to depressed reaction rates. Increasing the reaction temperature was more effective than increasing the free radical initiator level concerning 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 the free-radical initiator for vinylester resin as well as adjusting the reaction temperature. Using vinylester resins containing pendant 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 [45].

Studies on the styrenated polyester resins indicated that use of α-methylstyrene did not adversely affect the physical properties of the cured products but prolonged the cure time required [1]. The cure behavior of a bismethacryloxy derivative of the diglycidyl ether of bisphenol A (vinylester 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 vinylester 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 vinylester 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 °C and then started losing weight above this temperature. Rapid decomposition was observed at 350 °C-450 °C and almost total volatilization of the sample occurred around 500 °C. In all the resin samples, an initial mass loss of about 3% to 8% was observed above 90 °C. This may be due to residual styrene or α-methylstyrene in these samples. This means that the cure was still not completed at 140 °C.

1.3.3. 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 vinylester networks has been reported [46]. In this study, the crosslink densities of vinylester networks with 30-45 wt.% styrene were determined using the rubbery elastic modulus. The samples were cured for three hours at ambient temperature and then post-cured for another four hours at 90 °C followed by four more hours at 140 °C. Based on their experimental results, the authors assumed that for these systems, the final structure was probably diphasic, with a first phase consisting of the vinylester network and a second phase rich in polystyrene. The structure of this vinylester network was also studied by using rubber elasticity theory. The crosslink densities were derived from rubbery elastic modulus. 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 the modulus variations. The authors tried to study this heterogeneity in the modulus predictions using a simple rule of mixture. 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 modulus 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 vinylester resins was investigated under many given common cure conditions. 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 [47]. Fracture toughness showed no change (styrene 40-60%) [48]. Based on the work described in this thesis, on the effect of styrene on the structure of vinylester resins (styrene 20-60%), the glass transition temperature decreased with increases in styrene content. The glass transition temperature was very sensitive to the network structure. Fracture toughness decreased when styrene content increased from 20%- 40%.

At low cure temperature, methacrylate immobilization through gelation and formation of styrene homopolymers caused polymer incompatibility problems, and evidence of a two-phase structure appeared [6,8,40]. Differential scanning calorimetry and dynamic mechanical thermal analysis (DMTA) of copolymers with styrene (45 wt.%) produced at room temperature also suggested a two-phase structure because two transitions were observed between 60 °C and 140 °C.

These transitions, however, were only seen on the initial temperature ramp. Further reaction as the temperature increased above the cure temperature drove the reaction to completion to give a highly crosslinked structure with a glass transition temperature of 118 °C. The final network structure was 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 the cure conditions, thickness, and 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 [49], numerous reports on microgel formation have been published on the homopolymerization of multivinyl compounds and their copolymerizations with monovinyl monomers [50,51].

1.4. Cured Networks and Properties

1.4.1. Mechanical Properties

Vinylester networks have excellent tensile and flexural properties, as well as high elongation compared to polyesters [52]. Vinylesters have very good thermal performance, excellent mechanical properties, and toughness, which is why they are "preferred" materials for structural composites. The mechanical properties changes with changing of molecular weight and degree of crosslinks. The mechanical properties of the vinylester can be increased by adding fiberglass filler. Vinylesters also have performance advantages over polyesters in fatigue studies. The advantage of the vinylesters was also shown at elevated temperatures [30]. At 105 °C, vinylester and 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 vinylester, compared to 12% for the isophthalate polyester [51].

1.5. Shrinkage Control During Cure

When compared to unsaturated polyesters, vinylester resins have better toughness, chemical resistance, and lower volumetric shrinkage [51]. However, vinylester resins have higher shrinkage (6-9%) than epoxy resins. It was found that the shrinkage of vinylester resins during the cure increased as the styrene concentration in the resins increased and decreased with the increase of the chain length of vinylester oligomers. The experimental results were discussed in Chapter 3.5.4. 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 shrinkage. The mechanism of volume shrinkage control by the use of a low profile additive has not been fully understood. It is generally agreed that the low profile additive and crosslinked polymer phase must separate first. Then microvoid and/or microcrack formations at the interface between the low profile additive and the 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. One example is a new thermoplastic polyester as a low profile additive for vinylester resins. The low profile additive is saturated polyester formed from a dibasic acid and a polyethyleneoxy/poylpropyleneoxy diol (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 [53]. Vinylester resins are often used in combination with fibrous reinforcements and inert fillers to manufacture composite structures called sheet molding compound or SMC.

1.5.1. Thermal and Oxidative Stability

Regardless of the polymer composition, at temperatures of around 300 °C, cured vinylester resins will undergo spontaneous decomposition. This is a characteristic of vinyl polymers, which is caused by their depolymerization to form monomeric species. The curing and the decomposition behavior of vinylester resins based on epoxy Novolacs and methacrylic acid were studied by DSC and TGA . These resins with varied acid values (11-48 mg KOH/g solid) were diluted by 40 wt.% styrene and benzoyl peroxide as the initiator. It was found that vinylester resins with lower acid values were more reactive during the crosslinking reactions than the resins with higher acid values. TGA data showed that temperatures for 5% weight loss at a 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 [54].

1.5.2. Chemical Resistance and Water Absorption

The organic or inorganic solvent resistance of vinylester resins was superior to all other polyesters tested. The vinylester resins are also acid and corrosive media resistant [6]. Vinylester resins show exceptionally good resistance to distilled water [55]. The cured vinylester oligomers without comonomers absorbed about 3% water at saturation. In contrast, copolymers with styrene (45 wt%) absorbed much less water, about 0.8 wt.% at room temperature, and the amount absorbed increased with temperature to about 1.2 wt.% at 90 °C [54]. The absorption obeys Fick's Law at 18 °C, but not at 90 °C. The polymer adsorbed 0.8 wt.% water and suffered a large decrease in elongation at break. This is probably due to 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 [31].

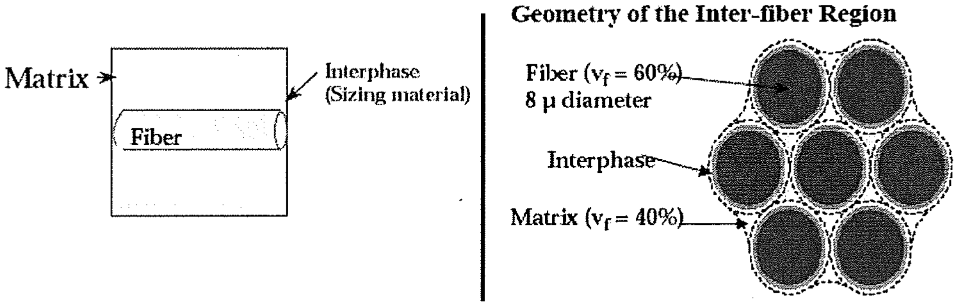
1.6. Applications

The vinylester resins combine the best properties of epoxides and polyesters. Although they are higher in cost than polyesters, vinylester resins have excellent chemical resistance and low water absorption in comparison with polyester resins. At the same time, vinylesters 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 were polyesters and epoxides are generally used.

Typical applications for vinylesters 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), vinylester resins provide greater toughness, heat distortion temperature, and corrosion resistance when compared to conventional unsaturated polyesters [56]. 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.

Novolac epoxy-based vinylester 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 vinylester resins is in the construction of waste incineration gas cleaning units [57]. Modified DGEBA resins are used where improved adhesion, wear resistance, and fracture toughness are required.

The applications for vinylester resins are related with fiber reinforced composites. Fiber reinforced polymer matrixcomposites for structural applications are comprised of long or continuous fibers embedded in a polymer matrix (usually a thermoset material). Such composites have high excellent corrosion resistance relative to steel. The function of the matrix is to protect the brittle reinforcing fibers and to transfer the load to the fibers (Figure 1.6). Other commonly employed polymer matrix materials include thermosets such as epoxides, unsaturated polyesters and selected thermoplastics such as, polyether ether ketone, polyethylene terephthalate, and polyphenylene sulfide. A third constituent of the composite, the "interphase", can drastically affect composite performance [58]. 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 used 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 [59]. 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, vinylesters are also being used in coatings, adhesives, molding compounds, structural laminate, electrical applications, and military/aerospace applications.



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 1.6 Composite components [30]

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 vinylester 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 "vinylester resins" coupled with the wide range of curing schedules obtainable make them desirable for such processes [60].

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 vinylester to replace resins such as bismaleimides (BMI), cyanate esters and other high performance polyimides and epoxides. 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. Typical applications include pipes, automotive accessories, and sporting goods. One important application in the electrical area includes printed circuit boards [61].

Generally, a halogenated epoxy is used to meet the flame retardancy requirement. Since vinylester resins have an excellent chemical resistance and lower water absorption, in comparison with polyester resins, they can also be used in applications ranging from electrorefining tanks to swimming pools [62].

1.7. Aim of the study

In this study, the aim was the synthesizing of the vinylester resins with different molecular weight based on the Bisphenol A epoxy resin. The shelf life of commercial resin, which is very short, does not allow enough time to import on demand. The shelf life is about 3-4 month. This time is not sufficient to export-import easily. Besides, these vinylester products can be found in 2-3 different determined molecular weights. It is not possible to supply the required molecular weight according to application needs. In addition, their water absorption values are comparably high which are reported as 0,7 – 0,8 % [54].

Therefore, in this study, the aim was to produce a vinylester with a longer shelf life, required tailor made molecular weight and lower absorption values. A new catalyst was synthesisd to complete the reaction. The two-step synthesis method was developed to obtain the required molecular weight of the resin. Then, an attempt was made to work this formulation and two-step methods on both a lab scale and an industrial scale. The trials were made by 2-liter glass balloon and in steel reactors, which have the capacities of 20 kg, 100 kg, 1000 kg.

Finally, a product was produced with a shelf life of 8-9 month. Very low water absorption values of around 0, 12 – 0, 15 % were obtained. Then, the vinylester with required molecular weights were obtained by two-step method.

CHAPTER 2

2. EXPERIMENTAL

2.1. Materials

Bisphenol A based Epoxy Resins

Huntsman Advanced Materials Company supplied epoxy resins with various epoxy equivalents, EEW. They were used for the synthesis of vinylester resin without any purification. Their EEW was confirmed by the epoxy end group titration method.

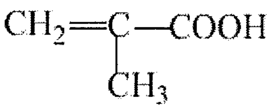
Novolac based Epoxy Resin

Novolac based epoxy resin was supplied by Huntsman Advanced Materials Company. It was used for the synthesis of vinylester resin without purification. Its EEW was confirmed by the epoxy end group titration method.

Methacrylic Acid, (MA)

Properties: b.p. 161 ^{0}C, m.p. 16 ^{0}C, FW 86

Methacrylic acid was kindly donated by POLİYA Poliester Company which was supplied by Richman Chemical Inc. It was used for the synthesis of all types of vinylester resin. It was kept in a plastic bottle to prevent corrosion.

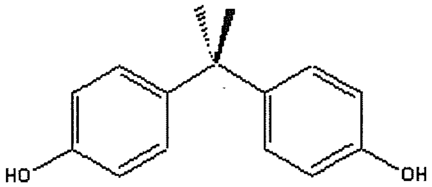


$$CH_2{=}C(CH_3){-}COOH$$

Bisphenol A

Properties: b.p. 220 ^{0}C, m.p.-150 ^{0}C, FW 228.28

POLİYA Poliester Company kindly donated Bisphenol A. It was used for the chain extension of epoxy resin.



Quaternary Ammonium Salt

A quaternary ammonium salt was used as a catalyst in the synthesis. It was kept in a closed bottle and in the dessicator. It was supplied by Aldrich.

$N^+ (R_4) X^-$

Triethylamine

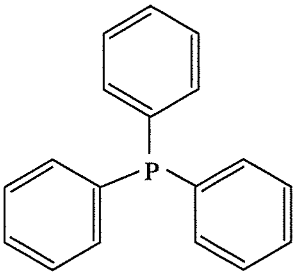
Properties: b.p. 88.8 ^{0}C, m.p.-115 ^{0}C, FW 101

Triethylamine was distilled from CaH_2 under nitrogen and was stored in a septum-sealed bottle until used. Triethylamine was used as a catalyst for the methacrylation reaction.

Triphenylphosphine

Properties: b.p. 377 ^{0}C, m.p.-80 ^{0}C, FW 262

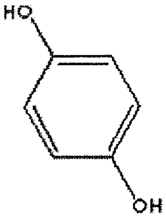
Triphenylphosphine was used as a catalyst for the methacrylation reaction. It was supplied by Aldrich.



Hydroquinone, HQ

Properties: b.p. 285 ^{0}C, m.p.175 ^{0}C, FW 101

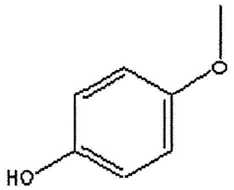
It was supplied by Aldrich. It was used as an inhibitor to prevent free radicalic reaction for the synthesis of vinylester resin.



Methyl Ether Hydroquinone, MEHQ

Properties: b.p. 243 ^{0}C, m.p.53 ^{0}C, FW 124

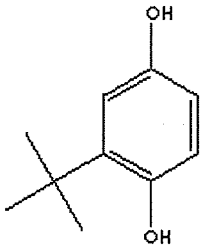
Aldrich supplied Methyl Ether Hydroquinone. It was used as an inhibitor to prevent free radicalic reaction during the synthesis of vinylester resin synthesis.



Tert-butylhydroquinone, TBHQ

Properties: b.p. 273 ^{0}C, m.p.127 ^{0}C, FW 166

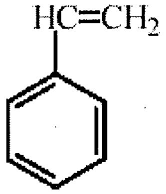
Aldrich supplied Tert-butylhydroquinone. It was used as an inhibitor to prevent free radicalic reaction during the synthesis of vinylester resin.



Styrene

Properties: m.p. -31 ^{0}C, b.p. 145-146 ^{0}C, FW 104.

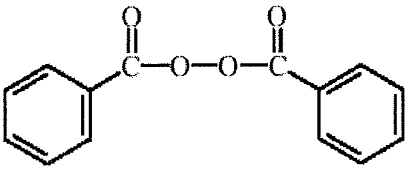
Styrene was kindly donated by POLİYA Poliester Company. It was used as a solvent and a reactive comonomer for the network formation of the vinylester resins.



Benzoyl peroxide

Properties: Aldrich, m.p. 104-106 ^{0}C, FW 242.23.

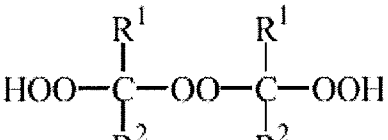
Benzoyl peroxide was used as a free-radical polymerization initiator for the vinyl ester oligomers and the styrene copolymerization.



Methly ethyl ketone peroxide (MEKP)

Properties: 32 wt % solution in dimethyl phthalate, b.p. 110 ^{0}C. MEKP was kindly donated by POLİYA Poliester Company. Commercially available MEKP was a mixture of several oligomers produced by the reaction of methyl ethyl ketone (2-

butanone) and hydrogen peroxide. The most readily synthesisd oligomers of MEKP exist in the monomeric and dimeric forms [63]. MEKP was used to initiate free radical copolymerization cures at ambient temperatures. MEKP was used as received.



$$\mathrm{HOO{-}\underset{R^2}{\overset{R^1}{C}}{-}OO{-}\underset{R^2}{\overset{R^1}{C}}{-}OOH}$$

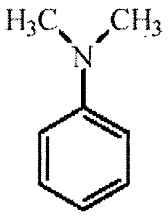
Cobalt (II) Napthanate solution (CoNaph)

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

N,N - Dimethylaniline (DMA)

Properties: Aldrich, b.p. 193-194 ^{0}C, m.p. 1.5-2.5 ^{0}C, FW 121

DMA is a tertiary amine and was used as an accelerator to promote the decomposition of peroxide at ambient temperatures during curing. DMA was used as received.



Acetic Acid, Glacial. CH_3COOH

Properties: JT.Baker, b.p. 117 ^{0}C, m.p. 16,7 ^{0}C, FW 60.5

Acetic acid was used as a solvent for the end group titration. It was used as received.

Hydrobromic Acid, HBr

Properties : Alfa Aesar, b.p. 126 ^{0}C, m.p. -86 ^{0}C, FW 81

Hydrobromic acid was dissolved in glacial acetic acid, in preparation of 0.1 N titrant for end group analysis

Crystal Violet

Properties: Aldrich

Crystal violet solution was prepared in glacial acetic acid (0.15 % w/v). The solution was used as an indicator in the end group analysis.

Sodium Hydroxide, NaOH

Properties: Aldrich, b.p. 1390 ^{0}C, m.p. 323 ^{0}C, FW 40

NaOH pellets were dissolved in ethanol to prepare 0.1 N titrate to determine the acid value.

Ethanol, C_2H_5OH

Properties: JT. Baker,

Ethanol was used as a solvent of acid group titration. It was purified by distillation before use.

Phenolphthaleine

Properties: Aldrich

Phenolphthaleine was the indicator of the acid group titration. Its 0.15 %(w/v) solution was prepared with ethanol before use.

2.2. Characterization

Viscosity Measurements

The viscosity of the vinylester-styrene solutions were measured by a Brookfield DV-3 viscometer at various temperatures. The number of the circular spindle was 5. The equipment was calibrated by standard silicon oil.

Density Measurements

The densities of the vinylester-styrene solutions were measured by a picnometer at 23 ^{0}C. The products in the picnometer were conditioned for 24 hours in an oven that was stable at 23 ^{0}C

Epoxy End Group Analysis

End group analysis of the epoxy groups were made by titration as explained in Appendices 1. The 0.1N KBr solution was placed in a burette. The resin was weighted in Erlenmeyer and dissolved with glacial acetic acid. Two drops of crystal violet solution were added to the resin solution. A magnetic stirrer mixed the solution, while the titrant was added drop by drop. The titration continued until the color turned from purple to light green. The EEW values were calculated.

Acid Value Determination by Titration

The reaction of resin synthesis was followed by titration as described in Appendices 2. The resin was weighted in an Erlenmeyer and dissolved in an ethanol solution. Two drops of phenolphthalein solution were added. A magnetic stirrer mixed the solution. A 0.1 N KOH solution was used as the titrate. The solution color turned from pink to yellow at the end point. The acid value was calculated as;

Acid Value = $V_{titrant}$ x Normalite of KOH / mass of sample

Determining Volume Shrinkage %

The volume shrinkage of the cured resin was determined by the following method:

% shrinkage= (100 × 1/ρ(uncured) – 1/ρ(cured)) / 1/ρ(uncured)

ρ: density

Determining Water Absorption %

The samples that had dimensions of 30 x 30 x 4 mm were prepared from the cured samples. The samples were weighted by a 5-digit balance (M1). They were placed into a distilled water tank by a very thin string. The samples did not touch each other or the tank walls. The temperature of the water was set to 23 ^{0}C. The samples were taken from the tank after 7 days. The water drops were wiped off gently then the samples were weighed again (M2). The water absorption % was calculated as:

Water absorption % = [(M2-M1) / M1] x100

Measuring Cure Exotherm

The cure exotherm was measured by a thermocouple. The required amount of peroxide and initiators were added to 100 g of the sample in a glass. The mixture was stirred with a stick to start a free radicalic cure reaction. The thermocouple was placed in the middle of the resin. The temperature rise was monitored on the display and plotted as a graph. The maximum temperature was determined as the peak temperature of the curing.

FT-IR

FT-IR spectra were collected using a Thermo Nicolet Nexus 670 ATR FT-IR spectrometer. The sampling surface was pressed into intimate optical contact with the top surface of the crystal such as ZnSe or Ge. In this study, the ZnSe crystal was used as a sample platform. The IR radiation from the spectrometer entered the crystal. It was then reflected through the crystal and penetrated "into" the sample. Each reflection along the top surface is called "evanescent" wave. At the output end of the crystal, the beam was directed out of the crystal and back into the normal beam path of the spectrometer [64]. Sixteen scans were collected per spectrum with resolution 8. The spectra were used to characterize the synthesisd extended epoxy and the vinylester resin. In addition, FT-IR was used to monitor the curing of the vinylester-styrene system.

1H-NMR

^{1}H NMR spectra were collected using a Varian Unity 400 instrument operating at 300 MHz. The proton NMR confirmed that the synthesis and the molecular weights of the vinylester oligomers were approximately 732, 932, 1100 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 also used to confirm the synthesis of novolac vinylester.

Determination of Elastic Modulus

Elastic modulus was determined using a Ceast HDT-VICAT 3P. The test specimens, with dimensions of height h (2.98 mm), width w (10.15 mm), and length l (10 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°C above Tg to measure the elastic modulus. Once the samples reached the set temperature, a small load (0.01 kg) was placed on the samples 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 loads vs. displacement curves were plotted. The slopes of these plots were calculated automatically by the computer and were used to determine the modulus according to the following equation.

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

P/Δ = slope of load versus displacement data
g = gravitational constant = 9.81 m/s^2
L = length between supports = 2.54 cm
$I = (1/12)wh^3$
w = width of sample
h = height of sample

HDT, Heat Distortion Temperature

Heat Distortion Temperatures were measured by Ceast HDT-VICAT 3P according to method ISO 75 [65]. The samples were prepared with a width of approximately 10 mm, height of 4 mm and length of 80 mm. The distance between the support points were 64 mm. The needle was placed in the middle of the support points. The applied loads were calculated by the equipment for each sample dimension and the samples were immersed in a silicon bath. The bath was heated until the needle penetrated into the determined deflection point. The temperatures were recorded to determine HDT at the deflection point.

Tensile Properties

The tensile properties of the cured vinylester matrix materials were measured according to ISO 527 [66]. Tensile tests were used to characterize the strength, modulus, and percent elongation of the vinylester networks at room temperature. The dogbone specimens had dimensions of type I as defined by the ISO standard. The samples were cured in a glass mould, and then they were cut by CNC. An Instron 4204, operating at a constant extension rate of 5mm/min, was used to obtain the tensile data. 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 with 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 of the grips. The modulus was determined from the slope of the initial linear portion of the stress-strain cure. The tensile strength at break was calculated by dividing the maximum load in Newton by the original cross-sectional area of the specimen in square mm.

Flexural Properties

The flexural properties of the cured vinylester materials were measured according to ISO 178 [67]. Flexural tests were used to characterize the strength, modulus, and percent elongation at break of the vinylester networks at room temperature. The specimens had dimensions of 4 mm x 10 mm x 80 mm according to ISO standard. The samples were cured in a glass mould, and then they were shaped by cutting with CNC. An Instron 4204 was operated with three-point bend equipment with a velocity of 1 mm/ s. The test was continued until breakage. The modulus, elongation and strength were determined.

Izod Impact Test, unnotched

The impact test was performed by the Ceast Resil 50 according to ISO 180 [68]. The samples were prepared by the same method. The dimensions of the samples were 3 x10 x80 mm. The samples were held at a 30 mm. Then a hammer with 3 kJ was released according to ISO 180 to break the samples. The computer in terms of kJ/m2 calculated the absorbed energy.

Hardness Measurement

Manuel Barcol 34 equipment was used to measure the hardness of the cured samples. The diameter of the needle was 0.8 mm.

2.3. Synthesis of Vinylester Resin

First Trials

The synthesis of the vinylester resin is not a basic polyaddition polymerization. Although the application areas of polyesters and vinylesters are similar, their synthesis procedures are quiet different. The synthesis reaction takes place between the methacrylic acid carboxyl group and the epoxy ring. Vinylester resins were synthesisd by the simple addition reaction to the epoxy ring. After the reaction, the epoxy ring was opened and the ester group was present along the chains [69].

At the beginning of this study, we used the known synthesis procedures of the polyester. A 2-liter glass balloon was placed in the heating mantle, equipped with the spiral condenser and mechanical stirrer. Then, 3 equivalents of epoxy, hydroquinone (inhibitor), 0.1 % triethanolamine catalyst and 3 equivalents of methacrylic acid were placed into the glass balloon. The reaction was carried out at 130 ^{0}C. However, the synthesis could not be achieved in this case. Gel was obtained in all the 17 trials. It was concluded that a new synthesis method has to be found to obtain vinylester resin. Firstly, we focused on the reasons for obtaining the gel. The reaction medium was acidic, therefore the basic catalyst promoted the addition reaction. However, methacrylic acid has a double bond, which could be destroyed during the reaction at 90 – 130 ^{0}C. The main problem in the vinylester synthesis was to prevent the free radical reaction of the vinyl groups in methacrylic acid. The double bonds would open at 110 ^{0}C, then cause to form free radicals to start crosslink reactions. In this manner, the gel formation would occur before the completion of the polycondensation reaction. This is undesirable, because the vinylester formation could not completed and insoluble gels were obtained. In order to prevent the addition reaction of vinyl group and the formation of a gel, inhibitors must be used. The inhibitors are free radical scavengers. They cap the free radicals of methacrylic acid and prevent cross-linking.

Trials in the Solvent

The reactions were carried out in the THF solutions at 130 ^{0}C. The distilled THF is used by 1/3 w/w. The aim was to dissipate the heat in the reaction medium, in order to prevent the high temperatures that polymerize methacrylic acid via vinyl groups. The gel formation was retarded however, not prevented. We decided to continue the studies with bulk polymerization.

Trials under N_2 gas

The synthesis of the polyesters does not require the N_2 atmosphere. However, the synthesis of the vinylesters could not be achieved without N_2. Then, the glass balloon systems were modified. N_2 inlet and outlet were added. The epoxy resins, methacrylic acids and the catalyst were put into the balloon. Then the condenser, mechanical stirrer and N_2 inlet-outlet were mounted to the balloon. The balloon was placed in the electrical heating mantle. The flowrate of the N_2 was adjusted to 0.01 bar. However, methacrylic acid vapors escaped from the reaction medium. Then, it was decided to stop purging N2 into the reaction medium. Thus, before starting of the reaction, the balloon was swept with N_2. Then, all of the outlets were sealed by silicone. Under these conditions, the reaction lasted longer. However, a gel was obtained after 12 hours; the reaction could not be completed successfully.

Trials under N_2 and with the Dropper

The glass dropper was added to the reaction system. The methacrylic acid was added dropwise for 4 hours. The aim was to keep the methacrylic acid concentration in the reaction medium under control. Also, the formation of the free radicals would be prevented. However, after 8 – 10 hours, gel formation was observed. This procedure was repeated 5 times with small modifications, but the reaction could not be completed successfully.

Trials with different inhibitors

After attempting different procedures unsuccessfully, the attention was focused on the chemical components like inhibitors, catalysts and other additives. According to the unsuccessful results of the experiments, it can be said that, uncontrolled free radicalic network formation starts in the reaction medium. There are three choices.

1. Decreasing the reaction temperature below 100 ^{0}C.
2. Capping the free radicals effectively
3. Increasing the rate of polycondensation reaction between epoxy and methacrylic acid by different catalyst.

Normally, we cannot decrease the temperature, because the epoxy ring opening reaction can be carried out at 110 ^{0}C – 130 ^{0}C [8]. However, at this temperature, the vinyl group of methacrylic acid were broken to produce free radical. Therefore, the efficiency of the inhibitors provides the realization of the polyaddition between the epoxy and methacrylic acid. Hydroquinone is the commonly used inhibitor [1,8]. Thus, 52 trials with hydroquinone were made under different conditions However, all of these trials were unsuccessful. The trials were performed at temperatures from 110 ^{0}C to 130 ^{0}C. Experimentally, the hydroquinone was not a suitable inhibitor for the vinylester synthesis. It is not sufficient to inactivate the methacrylic radicals. Inhibitors that are more suitable should be found. The solubility parameters of the Methyl Ether Hydroquinone MEHQ are higher than that of HQ. The methyl group is linked to O atoms increasing the efficiency of the radicals. Thus, MEHQ was tried instead of HQ. The reaction was carried out under the same conditions with 0.1 % MEHQ . The inhibitor was dissolved in methacrylic acid before starting the reaction. The acid numbers were controlled by the titration during the reaction. After 14 hours, the acid numbers decreased to 17. The reaction was continued for 18 hours, but the final acid value was measured as 15. After an additional two hours, gel formation was observed. Then, 0.2%, 0.3% and 0.4 % MEHQ were used in trials which were carried out at 130 ^{0}C and 110 ^{0}C, respectively. The acid value decreased to 13 when 0.4%

MEHQ was used. The resin was dissolved in the 35 % styrene. However, it was observed that the synthesisd resin could not be completely dissolved in the styrene. There were some small gel particles in the solvent. It was concluded that MEHQ showed better performance when compared to HQ, but it was not a suitable inhibitor for the vinylester synthesis.

At this stage, tert-butylhydroquinone (TBHQ) was tried as an inhibitor. It is soluble in water and organic solvents. TBHQ has a tertiary butyl group that provides more effective radical capping properties when compared to HQ and MEHQ. Tertiary butyl group provides the electron that stabilizes the free radicals. Then, the synthesis reaction was carried out with 0.1 % TBHQ at 130 ^{0}C. A gel was obtained after 20 hours. Then, the reaction temperature was reduced to 110 ^{0}C. The acid number was measured as 18 after 12 hours. The reaction was continued for 4 more hours and the acid value was 15. The acid value remained at 15 for the additional 5 hours. In order to obtain good physical and chemical properties, the maximum acid value of the vinylesters should be 9-11. The reaction did not turn to gel after 21 hours; however, the reaction was not completed either. The same experiment was repeated 3 times for 27 – 32 hours, obtaining similar results. However, this experiment gave very useful information. It was proved that, HQ and MEHQ are not suitable inhibitors for the vinylester reaction, while TBHQ performs very well, experimentally. No gel was obtained with TBHQ, over 32 hours. Now, the gelation problem was solved, but the acid number could not be reduced to the required values. The reaction between the methacrylic acid and the epoxy was not completed. As a result, the reaction rate should increase using a suitable catalyst.

Trials with the different catalysts

Triethanolamine was used as a catalyst during the determination of the inhibitors. Triethanolamine and triethlyamine are catalysts, which are efficient for the acidic polycondensation reaction, in the literature [1,8]. The reaction of the epoxy and methacrylic acid is the polyaddition reaction and the reaction medium is acidic. Therefore, we need a basic catalyst to promote the reaction. It is reported that the reaction would be completed in 5-7 hours [8]. However, a good progress could not be obtained with triethanolamine with concentrations of 0.1%, 0.2% and 0.3%. The trials with THBQ and triethanolamine did not turn to gel, but the acid numbers did not decrease to the required values. Other catalysts such as triethylamine were tried. The same formulation and reaction conditions were carried out with the triethylamine. The first trials resulted with 24 acid value after the 22 hours. The reaction did not turn to gel after 27 hours, however the acid number was measured as 23. Then, the the reaction temperature was changed from 110 ^{0}C to 115 ^{0}C and 120 ^{0}C. Eleven trials showed that triethanolamine and triethylamine were not effective catalyst for the vinylester synthesis. Another catalyst suggested for the acidic polyaddition reaction is the triphenylphosphine [8]. Due to the presence of aromatic rings, its basic character is stronger than that of triethylamine. Several trials were carried out with THBQ and at 110 ^{0}C. However, the required acid values could not be achieved. The reaction stopped after 18-20 hours at the level of 15-20 acids, and afterward there was no progress. A stronger basic catalyst had to be found. It was observed that quaternary ammonium salts are strongly basic. Quaternary ammonium salts are phase transfer catalysts which are used for the oxidation of thiophene [70]. Quaternary ammonium cations, also known as quats, are polyatomic ions of the structure $NR_4^+X^-$ with R representing the alkyl groups, and X is a halogens. Unlike the ammonium ion NH_4^+ itself and primary, secondary, or tertiary ammonium cations, the quaternary ammonium cations are permanently charged, independent of the pH of their solution. It was reported that, higher alkyl chain length and more nucleophilic counter anion showed a higher catalytic activity [71]. Thus, tert-butyl amine ions were used as a catalysts. The halogens, which are bound to the structure, are commercially confidential for POLİYA polyesters. The first reaction was realized with THBQ 0.15 % , Quats with 0.15 % and at 110 ^{0}C. The acid numbers decreased sharply to a value of 32 in the first 3 hours. No such large decrease in acid value could be obtained at the beginning of a reaction with the other catalysts. At the end of 6 hours, 28 acid value was measured. When, the reaction was continued for 17 hours, however acid value was 24. The following trials were carried out under similar conditions with Quats 0.2% , 0.3%, 0.4%. The same trends of acid number reductions were obtained. The acid value decreased sharply at the beginning, and then the reaction rate became slower. Therefore, it was thought that, the catalyst lost its activity during the reaction. There was no literature information about it, but the trials gave these results experimentally. Then, quats were added in two portions to the reaction medium. The 0.2 % quats were dissolved in the methacrylic acids and the solution was divided into two portions. The reaction was started under the same conditions, but with 0.1 % quats. After 3 hours, the acid value was measured as 34. Then, the second portion of quats was added to the reaction medium. After 3 hours, the acid value decreased to 15. The reaction was continued for 12 hours and the final acid value was obtained as 13. The same trials were repeated with 3 portions of 0.15%. After the addition of the third portion, the reaction was continued. Finally, the vinylester resin was obtained with 11 acid number without gelation. The trials were repeated for 3 times, the same successful results were achieved. The resin was dissolved in the styrene monomer easily without any small gel particles.

The trials were repeated with triethanolamine and triphenylphosphine by dividing them into 3 portions. However, the required progress of the reaction could not be obtained with these catalysts. Then, it was concluded that Quaternary ammonium salts is the suitable catalyst for the synthesis of vinylester resins.

The synthesis in the glass reactor;

After 82 trials, the best formulation and the reaction temperature were determined. The reaction was carried out in a four-neck 2L glass balloon with a nitrogen inlet and outlet, mechanical stirrer and spiral condenser. Joint points were closed with a silicon seal for every trial. The reaction was followed by the decrease in the acid value, which was measured by titration. Three equivalents of epoxy was placed into the glass balloon with the inhibitor TBHQ. They were mixed together and heated to 80 ^{0}C by heating mantle. Later, 0.1% of quatenary ammonium salts and catalysts were dissolved in 3 gr of methacrylic acid. Then, the catalyst was divided into three parts. The first part of the catalyst was added to 3 equivalents of methacrylic acid. Then, they were immediately added to the reaction medium under nitrogen gas. The nitrogen gas was passed through the glass balloon for 30 s. Then, the joint points were sealed with silicone to prevent the escape of methacrylic acid. Then, the temperature was set at the required value. The samples were taken from the reaction medium every 4 hours by a glass pipette to determine of the acid value. The reaction was monitored by titration. When the acid value reached 10 – 12, the heater was stopped and the content was cooled to 90 ^{0}C under nitrogen. Then the vinylester resin was completely dissolved in the styrene co-monomer. The styrene monomer was added to the reactor when the required acid value was obtained. The feeding of nitrogen gas and the stirring must be continued to dissolve the resin. Meanwhile, the solution must be cooled very quickly, in order to prevent of start the crosslinking reaction of the styrene. Styrene can form free radicalic polymerization at 90 ^{0}C, by the effect of the heat. Therefore, gelation can occur.

Finally, the reaction formulation to synthesis vinylester with molecular weight 550 g/mol was determined as;
1 eq Epoxy, (EEW ; epoxy equivalent weight ,185 g/eq)
1 eq Methacrylic acid
0.1 % Quaternary ammonium salt as a catalyst
0.15 % TBHQ as a inhibitors
T : 110 ^{0}C

The molecular weight of vinylester can be calculated by the following equation.

Epoxy EEW x 2 + FW of Methacrylic acid (172 g/mol)

The synthesis in the 20 kg vessel reactor;

The vessel reactor had a capacity of 20 kg. The reactor had two tanks, one for the reaction of the resin and the other for the dilution of the resin with styrene. The heating was done by hot oil circulation. The mechanical stirrer was automatic which can choose the speed according to the viscosity of the reaction media. A manometer was used to control the pressure inside the reactor. When the pressure increased, the valve was opened to the atmosphere. The temperature of the reactor was followed by the electrothermometer inside it. The condenser was cooled by water from the chiller.

The same formulation was fed into the reactor. When the acid value decreased to 10 – 12, the resin was transferred to the second tank that contained styrene and it was cooled. The transfer of the hot resin was done very slowly and carefully. The mixture was stirred slightly. The temperature of the styrene was always kept under 60 °C in order to prevent gelation of the styrene monomer.

2.3.1. Synthesis of the Different Molecular Weight Vinylester Resin

The molecular weight of the vinylester is calculated by the following equation:

Molecular Weight of Vinyl Ester = Epoxy EEW x 2 + 172 (Methacrylic acid)

2.3.1.1.One step reaction

Vinylester with different molecular weight show different mechanical properties. The aim of this study was to synthesis and compare vinylester resins with different MW. Epoxides that had different EEW were used for the synthesis of vinylester resins with different MW. The formulation trials were carried out with the epoxy that is 185 g/eq or 370 g/mol. According to the theoretical calculation, the MW of the synthesisd vinylester was 542 g/mol. This resin was a hard solid at the room temperature without the styrene solvent.

In order to obtain the higher molecular weight of vinylester resin, the experiments were done with different EEW of epoxides as shown in Table 2.1. The reactions were carried out under the conditions, which were determined by previous works.

There were many difficulties with the high EEW epoxides. With the increase of EEW in the epoxides, the epoxides went from being a fluid into solid, because of the increasing intermolecular forces between the long chains. The increase in the EEW raised the melting temperature of the epoxy resins. E3 and E4 did not melt at the reaction temperature. Their melting temperature was above 125 ^{0}C. The methacrylic acid vinyl bonds were opened above 125 ^{0}C. The free radicals caused gelation. Reaction medium viscosity was very high and diffusion was restricted. Therefore, the reaction rate decreased. The required acid value could not be achieved. When the reaction was slow, there was always a danger that gelation would occur. Therefore, high molecular weight vinylester resin could not be obtained by the one-step reaction. The one-step reaction served to synthesis only the vinylester resin with MW below 600 g/mol. In order to synthesis higher MW vinylester resins, modification in procedure had to be done.

Table 2-1 Trials for one-step synthesis with Bisphenol Epoxides with different EEW

No	Epoxy	EEW (g/functionality)	Molecular Weight Vinylester (g/mol)	Observations
1	E1	189	550	Reaction was completed and the resin dissolved in styrene easily
2	E2	250	672	Reaction was completed and the resin dissolved in styrene easily
3	E3	457	1086	Reaction was completed but very slowly, because some amounts of the epoxides did not melt during the reaction. The resin viscosity was very high. Mechanical stirrer stopped.
4	E4	685	1542	The reaction was not completed. The epoxy did not melt completely at the reaction temperature.

2.3.1.2.Two- Step Reaction

The two-step reaction method was developed due to the problems in synthesizing the high molecular weight vinylester by the one-step reaction method. Addition of the molecules were mentioned in the US patents, however there was no detailed information such as temperature, catalyst, calculations and the control of the reaction [56]. It was thought that addition of the Bisphenol A could be performed to extend the chain. All of these procedures were developed in this study through experimental research. The first step was the chain extension of epoxy to increase the molecular weight of epoxy to the required value. A 185 g/eq EEW epoxy resin was used as the base resin. In the first step, a certain amount of Bisphenol-A was added to the epoxy resin to extend its chain length. The amount of the Bisphenol-A was calculated according to Carother's Equation [72]. The amount of Bisphenol-A determined the final EEW of the chain extended epoxy resin. The required "n" could be obtained based on the Bisphenol-A amount used assuming complete reaction. The reaction was monitored by measuring the epoxy value with HBr titration of the epoxy groups. Epoxy value was measured to calculate the molecular weight of the extended epoxy chain; the methods are explained in Appendice A. The determined titration method was tested with the commercial epoxides with known EEW. The titration method worked very well to determine EEW values. During the chain extension reaction, epoxy value decreased, while EEW increased. EEW could be calculated at any time during the reaction. The representative chemical reaction is shown in Figure 2.2.

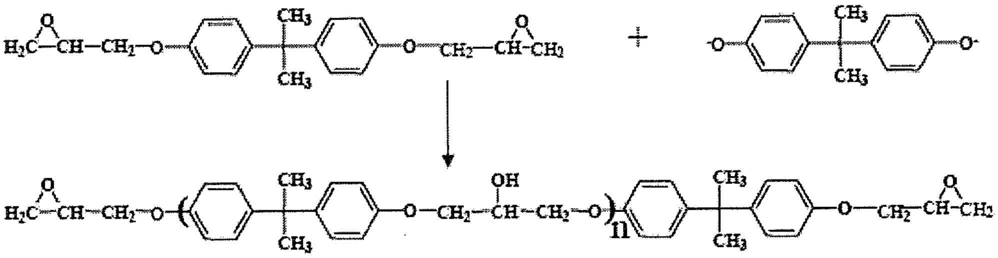


Figure 2.1 The chain extension of the epoxy resin MW, n is the number of repeating unit.

The first trials of the reaction between epoxy and Bisphenol-A were done without any catalyst and carried out at 110 ^{0}C. However, after 7 hours the reaction was stopped without reaching the required molecular weight. Triethylamine was added as a catalyst. The epoxy value decreased more quickly but the required value could not be obtained. Then it was decided to increase the reaction temperature systematically to 120 ^{0}C, 130 ^{0}C and 140 ^{0}C. The reaction, which was carried out at 140 ^{0}C, showed a different characteristic. When the temperature of the reaction medium reached 137 ^{0}C – 140 ^{0}C, the temperature started to increase immediately. The temperature increased to 153 ^{0}C in 2 minutes, although the heating mantle was turned off. After the peak, the temperature started to decrease. The samples from the reaction medium were then titrated. The epoxy value was measured as required. Experimentally, it was noted that the chain extension reaction was strongly exothermic. In order to start this exotherm, the reaction temperature should be around 140 ^{0}C. The exotherm temperature changed with the amount of the Bisphenol-A. In order to obtain a higher MW vinylester resin, a higher amount of Bisphenol-A was required. The exotherm peak reached to 176 ^{0}C, for the synthesis of vinylester resin with higher molecular weight. (>900 g/mol).

The EEW of the extended epoxy resin was calculated with HBr titration by the following equation. EV is the epoxy value, which was calculated from the results of titration. The detailed description was explained at Appendices A.

Chain extended epoxy EEW = 100 / EV

Initially, the epoxy (EEW 189 g/fonctional group) and the required amount of Bisphenol-A were placed into a glass balloon with %0.02 Triethylamine. The temperature was set to 140 ^{0}C while the mechanical stirrer was operating. The exotherm started at around 140 ^{0}C. The epoxy value was measured and the EEW was calculated every hour of the reaction. When the epoxy value decreased below 0.1 the heater was turned off and the reactants were cooled to 115 ^{0}C. The duration of the extension reaction, which changed between 2 and 4 hours, depended on the Bisphenol-A amount and the required EEW values.

When the required chain length of the epoxy was obtained, the addition reaction of the methacrylic acid was carried out as determined at the beginning of this study. The second step of the reaction was the same as the one-step reaction. The reaction medium was cooled to 115 ^{0}C. TBHQ (0.15 %, four portions) as inhibitor, quaternary amonium salt as catalyst and methacrylic acid were added to the balloon under nitrogen and mixed. The methacrylic acid amount was calculated according to chain extended epoxy EEW.

Eq. methacrylic acid = (2 x EEW initial epoxy + 2 x EEW Bisphenol A) / Chain extended EEW

The reaction was carried out until the acid value decreased to 10 -13 mg KOH / g polymer. The nitrogen gas was fed into the system when the required acid value was obtained. Then, the styrene monomer was added to the system by mechanical stirring and cooling. Finally, a dissolved homogenous solution of the vinylester resin in styrene was obtained. By using of the two-step method with different styrene content, 5 different molecular weights of vinylester resins were synthesisd. However, the vinylester resins, which have molecular weight higher than 1200 g/mol could not be used. They were very viscous, even if they were at high styrene content. Then three different molecular weights were chosen to examine in this study. The styrene content of the mixture are, as shown in Table 2.2.

Table 2-2 The synthesisd and prepared vinylester series samples with different molecular weight and styrene content.

Series of Resins	Molecular weight	Styrene Content %
VE 732/30	732	30
VE 732/38	732	38
VE 732/45	732	45
VE 932/30	932	30
VE 932/38	932	38
VE 932/45	932	45
VE 1100/30	1100	30
VE 1100/38	1100	38
VE 1100/45	1100	45

2.3.1.3.Synthesis of the Novolac Epoxy Based Vinylester Resin

The novolac based vinylester resin was synthesisd by the one-step method using the same procedure. Three equivalents of novolac based epoxy (EEW = 180 g/eq) was mixed with 1 equivalent methacrylic acid. The hydroquinone was added as an inhibitor (0.15 %). The quaternary ammonium salt was used as a catalyst. The reactor temperature was set to 115 ^{0}C under nitrogen atmosphere. A mechanical stirrer was used. The reaction was monitored by the titration method to determine the acid value. The styrene monomer was added to the balloon under nitrogen atmosphere when the acid value reached 12 -14 mg KOH / g. The mixture was stirred and cooled very quickly. Two samples are shown in Table 2.3.

Theoretical MW of the resin was calculated by the following equation;

$$\left\{(2 \text{ x EEW E1}) + (2 \text{ x EEW Novolac})\right\} / 2 \; + 172 \text{ (Methacrylic acid)}$$

Table 2-3 The synthesisd novolac vinylesters

Series Mn	**Styrene Content %**
732	28
732	38

CHAPTER 3

3. CHARACTERIZATION OF VINYLESTER RESIN AND NETWORK STRUCTURE

3.1. Introduction

Vinyl ester resins are synthesisd from various epoxy resins and unsaturated monocarboxylic acids, most commonly, methacrylic acid. The various types of the epoxides, acids, catalysts and inhibitors were mentioned in Chapter 1. The most common dimethacrylate terminated oligomers were formed by the reaction of methacrylic acid with epoxide resins from bisphenol-A and epichlorohydrin [73] as in Figure 3.1.

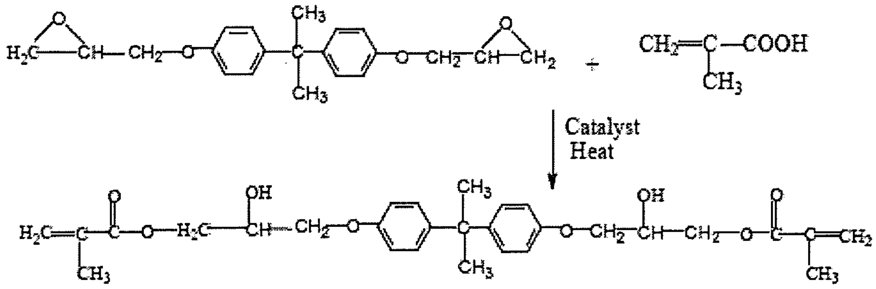


Figure 3.1 Synthesis of Vinylester resin

In order to obtain the required vinylester resin properties, different reactants were used and different reaction conditions were carried out during this study.

3.2. Characterization of Vinylester Resin

Vinyl ester resins were synthesisd by the addition reaction of extended epoxy resins and unsaturated methacrylic acid. The extension of the epoxy, catalysts and inhibitors were mentioned in Chapter 2. The chemical structure of synthesisd vinylester resins were investigated by IR and NMR techniques.

3.2.1. IR Analysis

Figure 3.2 shows the IR spectrum of the bisphenol A based epoxy, the extended epoxy and the vinylester, respectively. The epoxy ring observed at 915 cm^{-1} (Figure 3.2) in Bisphenol epoxy and extended epoxy FTIR spectra, disappeared in the vinylester spectrum. The extended epoxy gave hydroxyl groups' absorption bands at around 3500 cm^{-1}. Peaks in between 600 -1500 cm^{-1} (Figure 3.3) gave the characteristic peaks of the phenyl groups. The main evidence of the vinylester resin formation is the carbonyl peak at 1711 cm^{-1}. The epoxy resin did not contain carbonyl groups. However, after the addition reaction, the epoxy rings opened and reacted with methacrylic acid introducing a carbonyl group into the monomer (Figure 3.4). Other important evidence was the hydroxyl peak of the vinylester resin, which was at 3416 cm^{-1}. The epoxy did not have a hydroxyl group while the vinylester resins did. Also, vinyl groups at 3100, 1635 and 943 cm^{-1} in the vinylester spectrum (Figure 3.2 and 3.4) indicate an esterification reaction rather than a vinyl polymerization.

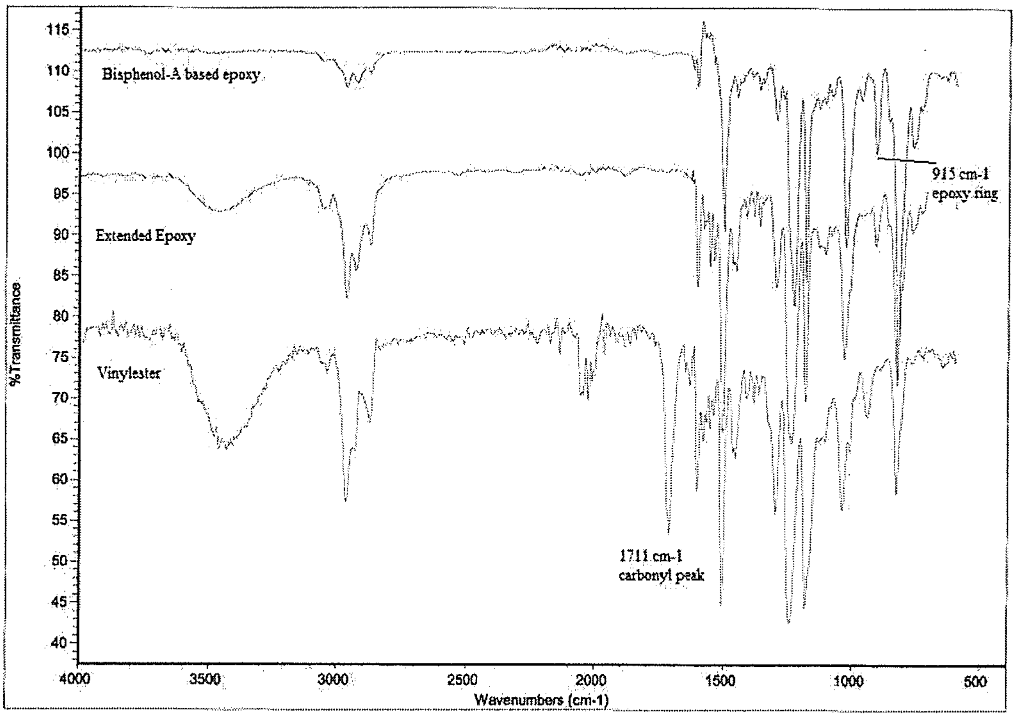


Figure 3.2 The IR spectrums of the bisphenol-A based epoxy, extended epoxy and vinylester resin with molecular weight 932 g/mol

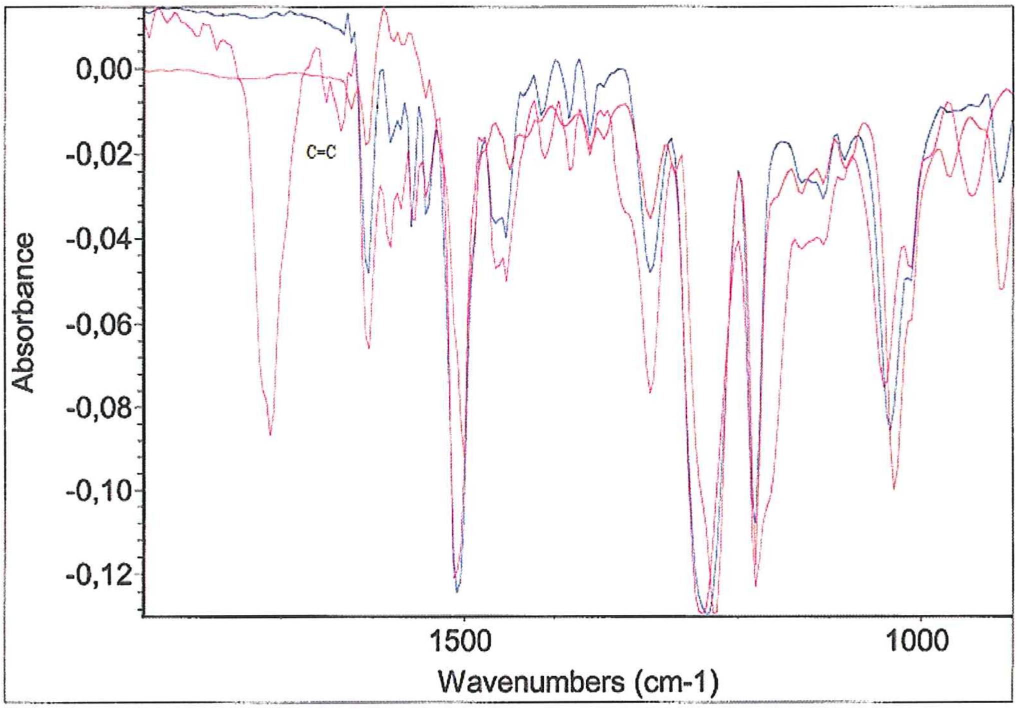


Figure 3.3 The extended fingerprint region

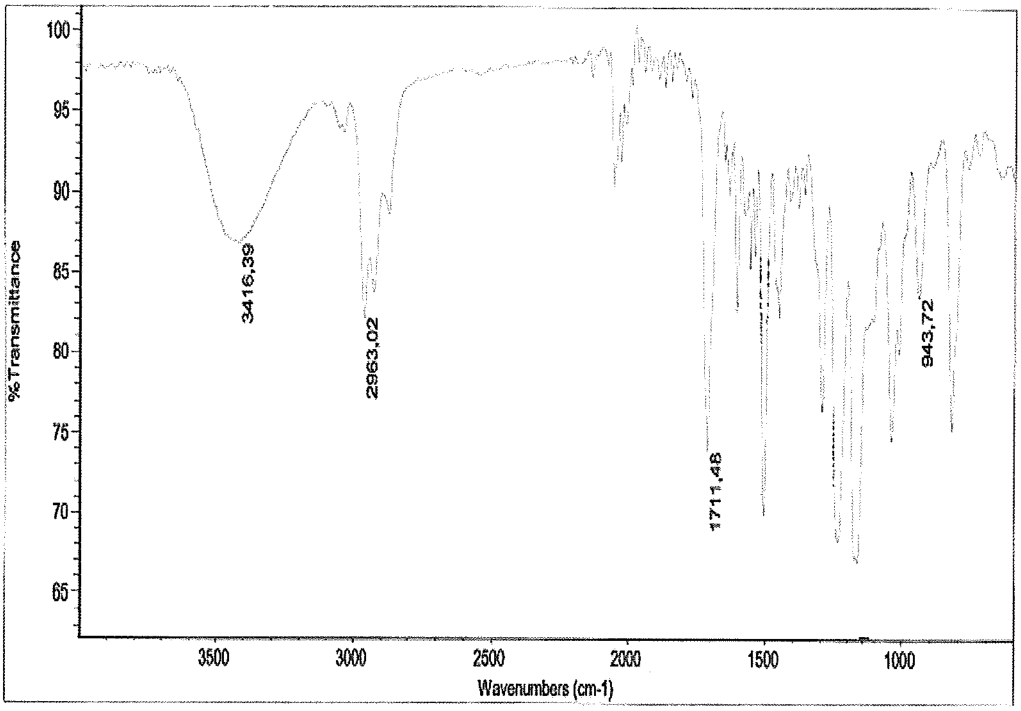


Figure 3.4 The IR spectrum of synthesisd bisphenol –A epoxy based vinylester resin with molecular weight 932 g/mol

3.2.2. ^{1}H-NMR Analysis

The epoxy resin of Bisphenol A and the synthesisd vinylester resins with three different molecular weight 732 g/mol, 932 g/mol and 1100 g/mol were investigated by ^{1}H-NMR. The protons of the methyl groups were observed for both of them at nearly the same place, for epoxy 1.73 ppm and for vinylester 1.74 ppm. The methyl protons on the methacrylate endgroups gave a peak at 2.0 ppm only for the vinylester resin. This was the first evidence of the conversion of epoxy to vinylester during the reaction. The vinylester resin had a broad peak at 3.11 ppm which was the hydroxyl proton. The hydrogen bonding interaction between the hydroxyl proton and the methyl protons on the methacrylate end groups caused broadening of the peak [74]. The hydroxyl peak of the epoxy at 3.00 ppm was not broad because of the absence of strong hydrogen bonding. Extended epoxy also contained hydroxyl proton as a sharp peak at 3.01 ppm. The peaks between 4.0 - 4.5 ppm belonged to the linear carbon protons. The second important proof of the reaction was peaks of the double bonded carbon protons at the end of the vinylester chain, which were observed at 5.71 ppm and 6.26 ppm. This separation of the peaks is characteristic of the double bonded carbon protons. These peaks could not be seen in the epoxy spectra due to the absence of the double bonded carbon on the epoxy chain. Finally, the peaks between 6.91 ppm and 7.35 ppm resulted from the phenyl protons, which existed, in both the epoxy and the vinylester chains. Therefore, the ^{1}H-NMR and the IR results proved that the polycondensation reaction successfully produced the vinylester resins. Figure 3.5 and Figure 3.6 show the ^{1}H-NMR spectra of the vinylester resin and the epoxy resin, respectively.

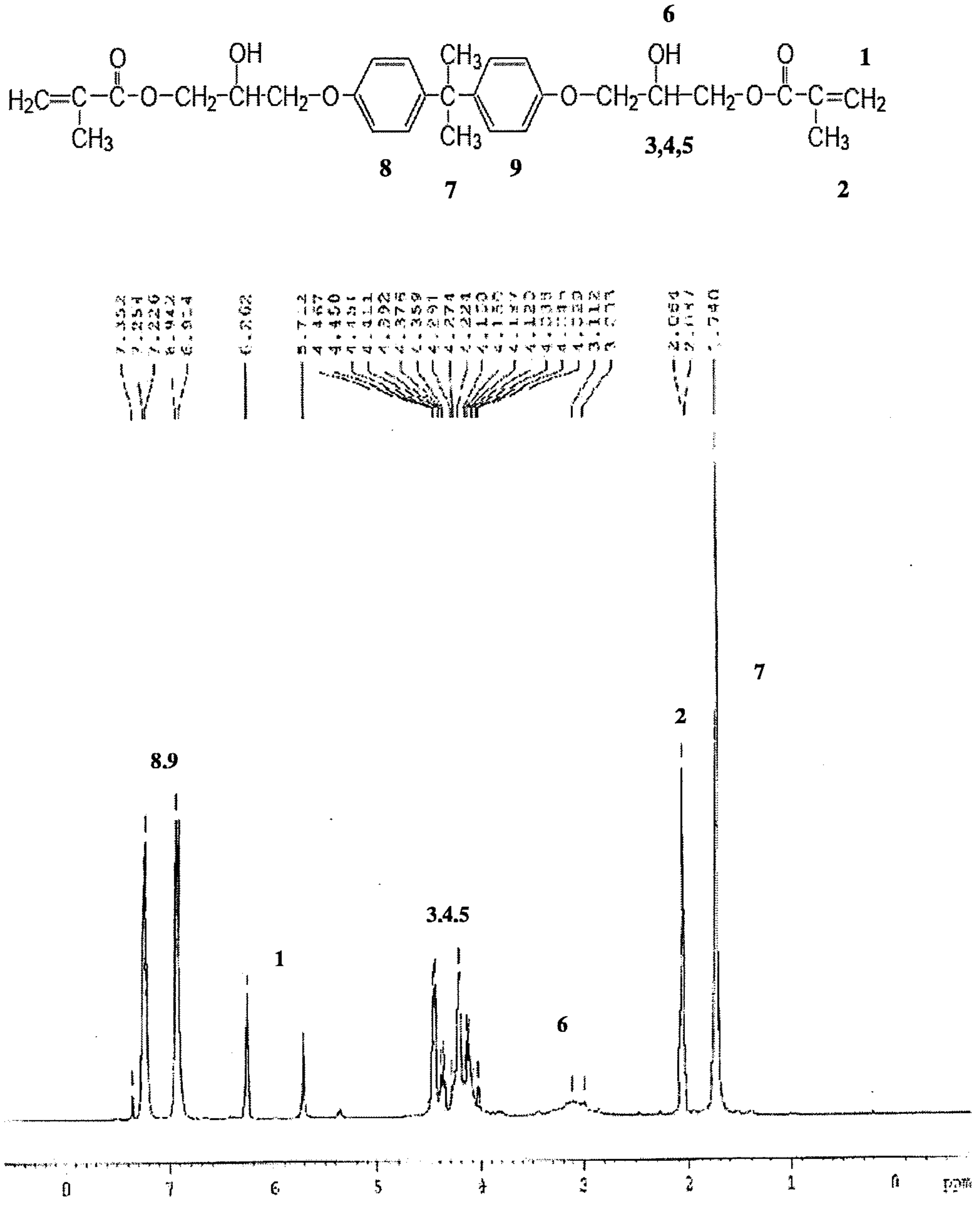


Figure 3.5 ^{1}H-NMR of vinylester resin, 932 g/mol.

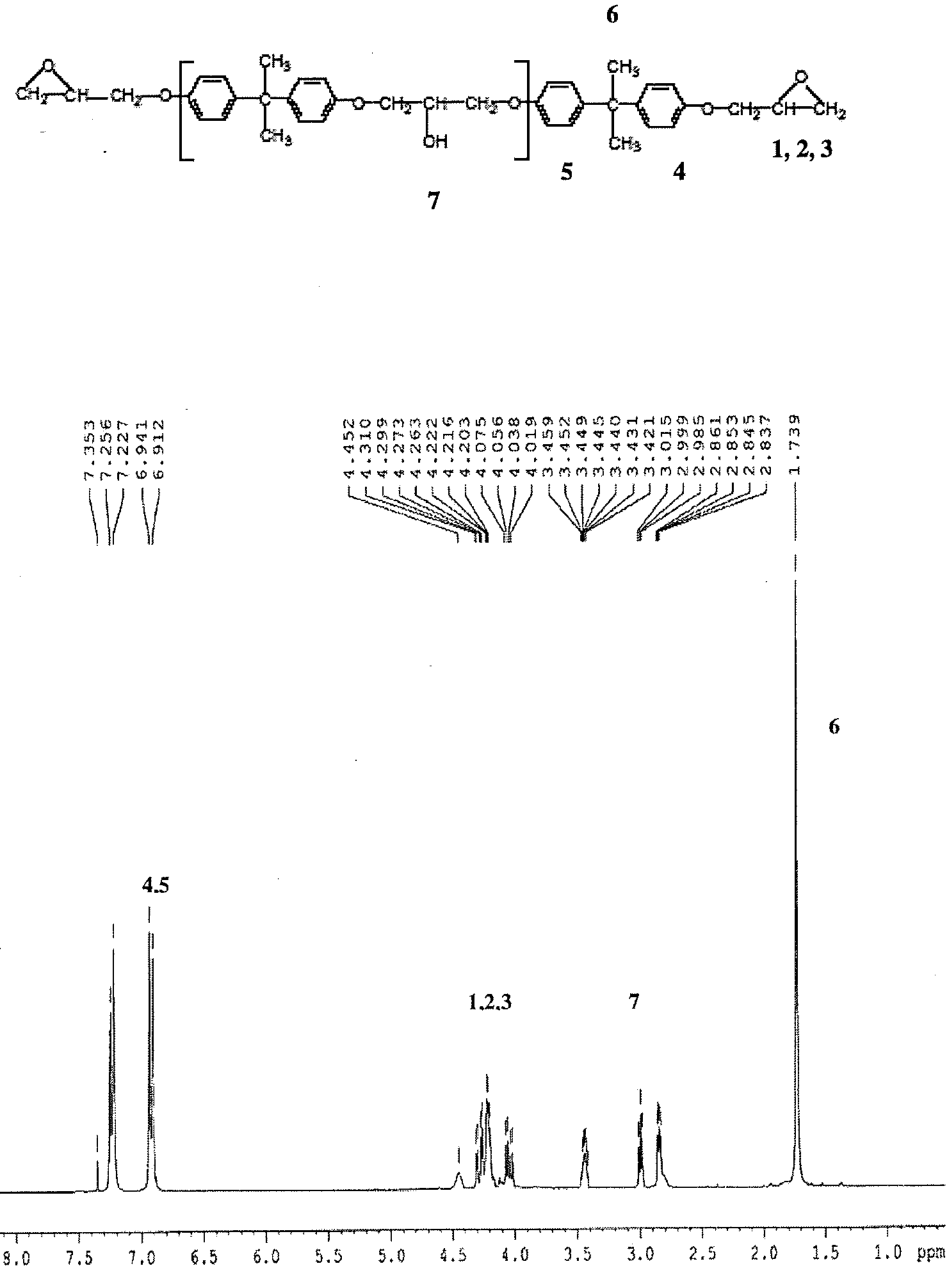


Figure 3.6 ^{1}H-NMR of extended Bisphenol-A epoxy precursor

3.2.3. Molecular Weight Determination

Three different series of the vinylesters were synthesisd in this study, with 3 different average number molecular weights, 732, 932 and 1100 g/mol. According to the two step reaction, the extended diglycidyl ether epoxy was synthesisd with base epoxy resin and bisphenol A. Epoxy resin was reported in its commercial technical sheet EEW = 189 g/mol was confirmed by epoxy end group titration. In the first step, bisphenol-A reacted with the epoxy resin to form a structure of the diglycidyl ether of bisphenol-A. The chain length or the degree of polymerization (n) in the oligomer series was controlled by reacting this diglycidyl ether with varying amounts of bisphenol-A. The amount of Bisphenol A was calculated according to the final required molecular weight of the vinylesters series that is explained in Chapter 3.1. When the desired molecular weight was achieved, the epoxide-terminated material reacted with methacrylic acid to produce controlled molecular weight vinylester with terminal reactive methacrylate groups.

Proton nuclear magnetic resonances ^{1}H-NMR and epoxy titration were used to characterize the average number molecular weights of the vinylester resin series.

The epoxy titration method was described in Appendices B, in detail. The epoxy terminated the precursor oligomer, obtained from the first step of the reaction. It was titrated with 0.1 N HBr acid in glacial acetic acid to determine the epoxy equivalent weight, EEW. EEW is the molecular weight per functional groups. Epoxy resins have two functional groups per chains. Therefore, EEW x 2 is equal to the molecular weight of the epoxy resin (g/mol). The atomic weight of methacrylate groups is 86 g/mol. Therefore, an additional 172 g/mole was added to calculate average number molecular weight derived from the methacrylic acid groups at the two ends of the chains, that are marked as A. (Figure 3.7). The approximate average deviation of the Mn values is +/- 15 according to literature [75].

Molecular Weight = ((EEW) X 2) + 172

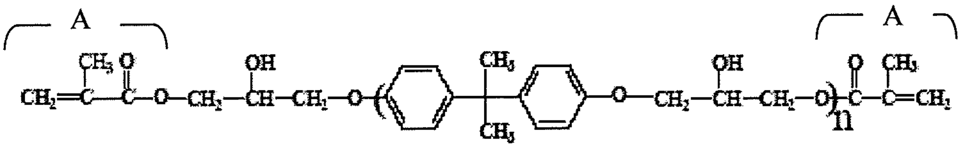


Figure 3.7 A groups which correspond to the methacrylate end groups of the vinylester resin, n is the number of repeating unit

Molecular weights obtained by ^{1}H-NMR were calculated from integral ratios of the repeat unit to the endgroup peaks as shown in Figure 3.7. The integral of the bisphenol-A methyl proton resonance at 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 at 2.0 ppm). For both the repeat unit and the endgroups, the number of protons each contained divided the integration number. Then, the endgroup value was doubled to account for both endgroups. The total molecular weight was obtained by adding on 138 g/mole to the endgroups marked as A. Therefore, 90 g/mole (B) is added to account for the remaining part of the structure, Figure 3.8.

$$\frac{[\text{Integration area of repeat unit / \# protons}] \text{ x Molecular Weight of Repeat Unit}}{[\text{Integration area for end groups / ((\# protons) x 2)}]} +138 +90$$

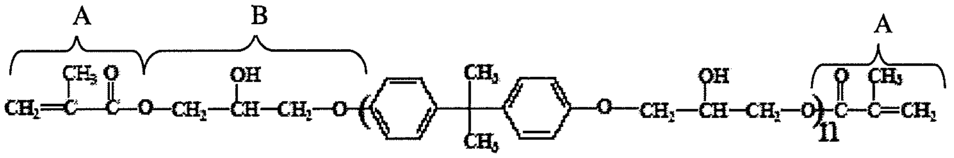


Figure 3.8 A and B regions corresponding to various parts of the structure and the equation used to calculate number average molecular weight, n is the repeating unit

The determined number average molecular weights are listed in Table 3.1. Molecular weight values were determined by the titration method and ^{1}H-NMR. Owing to the agreement of different methods, it can be easily said that, the reaction conditions were kept under control to obtain the required chain length of the vinylester resins.

Table 3-1 The measured molecular weight values for the synthesisd vinylester resins

VE Series	**EEW 1**	**Extended-EEW by Titration**	**Molecular Weight by Titration**	**Molecular Weight by ^{1}H-NMR**
g/mol	g/Eq	g/Eq	g/mol	g/mol
732	189	290	752	724
932	189	386	944	952
1100	189	470	1112	1190

3.3. Rheological Behaviour of the Vinylester Resin

Rheology deals with deformation and flow behaviors. Viscosity is one of the important responses of the rhelogical properties. Viscosity is the measurement of a fluid's resistance to flow. The viscosity of the resins is related to many fundamental properties of the resin. Besides, it is an important resin parameter which controls the processing of the vinylester. Vinylester resins need to have a low viscosity in order to diffuse and to get good wetting properties. The performance of the vinylester / fiber composites is directly dependent on the wetting of the fibers [76,77].

For a Newtonian liquid under shear, the rate of deformation, or shear rate, is proportional to the shear stress. Newton's law states that the ratio of the stress to the shear rate is a constant. That constant is viscosity. The common units for viscosity are poise (P), grams per centimeter second g/(cm.s), or dyne seconds per square centimeter (dyn.s)/cm^2). The centipoise (cP), one hundredth of a poise, is the most common unit. The SI units of viscosity is Pascal seconds (Pa.s)(1 mPa.s = 1cP) [78]. Vinylester resins need to have a low viscosity in order to flow into the fibers and to permit good wetting of the carbon-fibers. Styrene is used as a diluent to decrease the viscosity of the vinylester resins. Thus, the styrene concentration is an important factor that controls the viscosity of vinyl ester resins. Viscosity is highly sensitive to changes in temperature. Also the molecular weight of the vinyl ester oligomers affects viscosity significantly [6]. All of these factors need to be studied and understood so that the viscosity of the vinylester resins can be controlled.

Rheological behavior can be investigated by a variety of methods, including simple capillary viscometers, extrusion rheometers, and rotational viscometers [30]. In this study, the rheological behavior of vinyl ester resins was studied by using a Brookfield digital viscometer. The effects of temperature, styrene content and the molecular weight of the vinyl ester oligomers on the viscosities of the vinylester resins were examined. The relationship between viscosity, processing temperature and glass transition temperature is also discussed in this chapter.

3.3.1. Effects of Styrene Content on Viscosity

The styrene content affects the viscosity directly. It is known that typical vinylesters contain 35% -50% styrene monomer in many industrial applications. In order to determine the relationships, the viscosities were measured for a series of resins with various molecular weights and styrene contents that are shown in Table 3.2.

Vinylester resin is highly viscous; it is a solid at room temperature. The composite application was not possible for the vinylester resin. The styrene monomer diluted the vinylester. The viscosity of vinylester styrene mixtures decreased with increasing styrene content, as expected. The styrene content affects viscosity strongly up to 40 % styrene content. However, the decrease in the viscosity was lower above the 40 % styrene content.

Table 3-2 The vinylester series samples prepared with different molecular weights and the styrene contents

Molecular Weight (g/mol)	**Styrene Content (%)**		
VE 732 /30 /38 /45	30	38	45
VE 932 /30 /38 /45	30	38	45
VE 1100 /30 /38 /45	30	38	45

According to the measured values, the viscosity (η) decreased with increasing styrene content by a quadratic relationship. This equation was obtained from the curve in Figure 3.9.

$$\eta = 21312 - 919.5\ (\ \%\ \text{styrene}) + 10.07\ (\ \%\ \text{styrene})^2$$

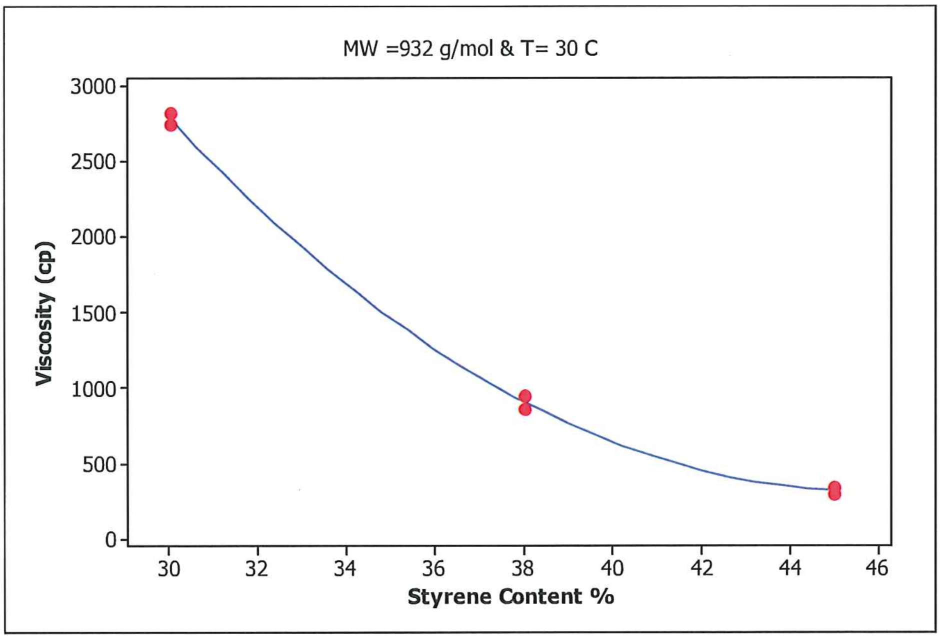


Figure 3.9 Effect of styrene content on the viscosity

3.3.2. Effects of Temperature on Viscosity

The viscosity generally decreases as temperature increases. Viscosities of the resin VE 932/38 were measured at different temperatures ; 20 °C, 25 °C, 30 °C, 35 °C, 40 °C, 50 °C. Plot of η versus T (°C) is shown Figure 3.10.

The equation of the plot was calculated:

$\eta = 7342 - 316.7\,T + 3.488\,T^2$

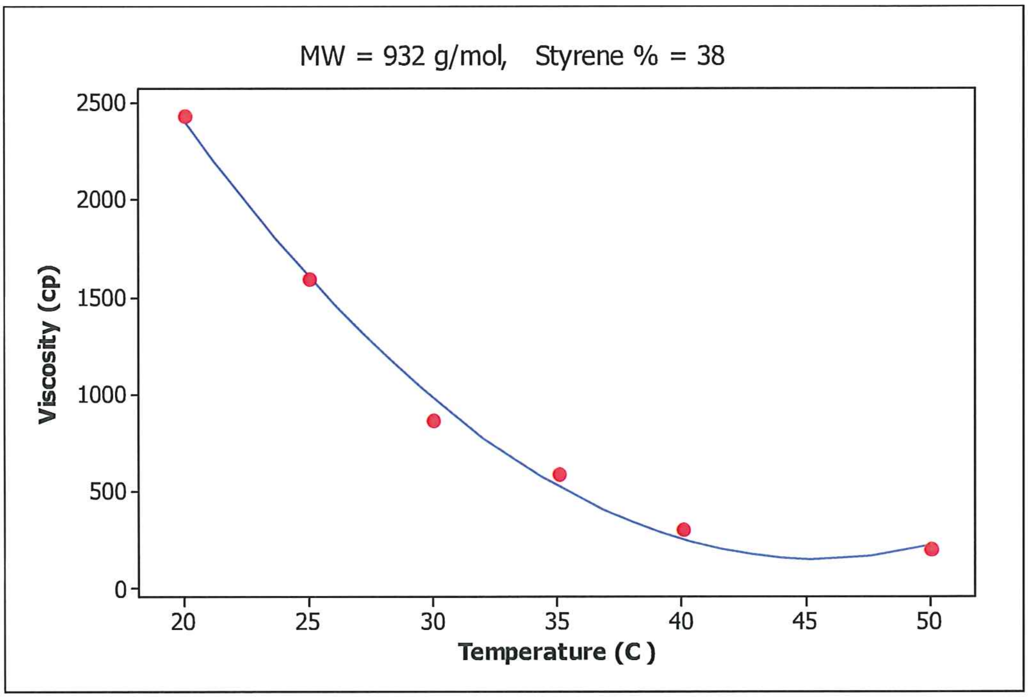


Figure 3.10 Effect of the temperature on the viscosity

Figure 3.11 show that the effects of temperature on the viscosity were higher at low styrene content. Larger viscosity changes were observed at lower temperatures. The temperature dependence of the viscosity changes decreased at high temperatures.

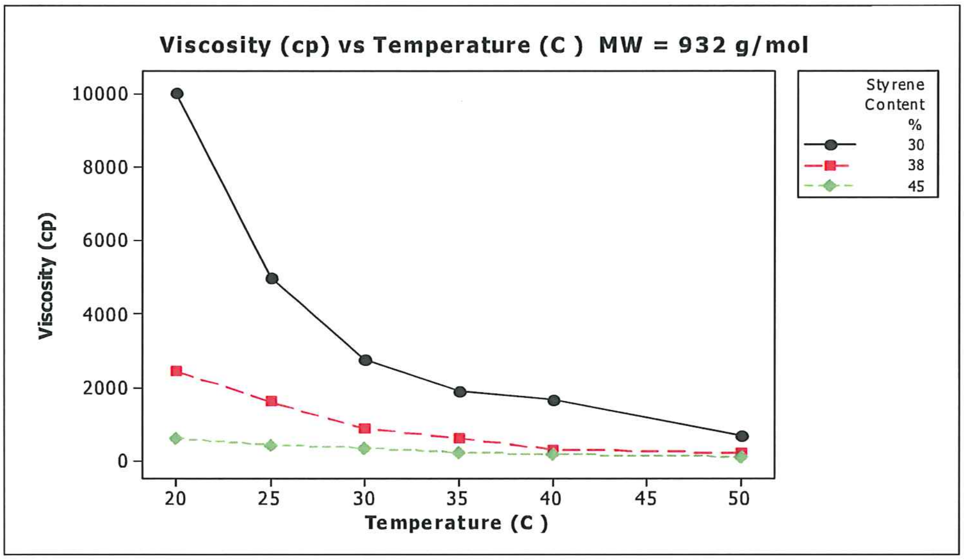


Figure 3.11 Effects of styrene content and temperature on the viscosity

3.3.3. Effect of Molecular Weight on The Solution Viscosity

Viscosity increased when the oligomer molecular weight increased or when the molecular weight decreased. The studies showed that the viscosity of the vinylester resins increased significantly when the molecular weight of the vinylester resin increased from 732 g/mol to 1100 g/mol. For example, at 30 % styrene at 23°C, the viscosity of the resin with molecular weight 732 g/mole oligomer was 291 cps, while that of the resin with the molecular weight 1100 g/mole oligomer was 3198 cps. The strong dependence of viscosity on molecular weight for vinyl ester resins in the oligomeric range (732-1100 g/mole) was due to intermolecular hydrogen bonding between hydroxyl groups in the vinyl ester molecules. The bulky groups increased the viscosity by increasing the intermolecular interactions [79]. The viscosity increased also with the styrene content. Oligomers with 932 g/mole had lower viscosities for the same temperature and the styrene content, than for the oligomers with 1100 g/mole. However, the effect of molecular weight became less at low viscosity [80] , in the mixture with 45 % styrene content as shown in Figure 3.12. The concentrated solutions showed high interaction between the chains. The entanglements of the chain play a very important role on the viscosity. The entanglements decreased at high styrene contents and the polymer chains reached to an unperturbed situation.

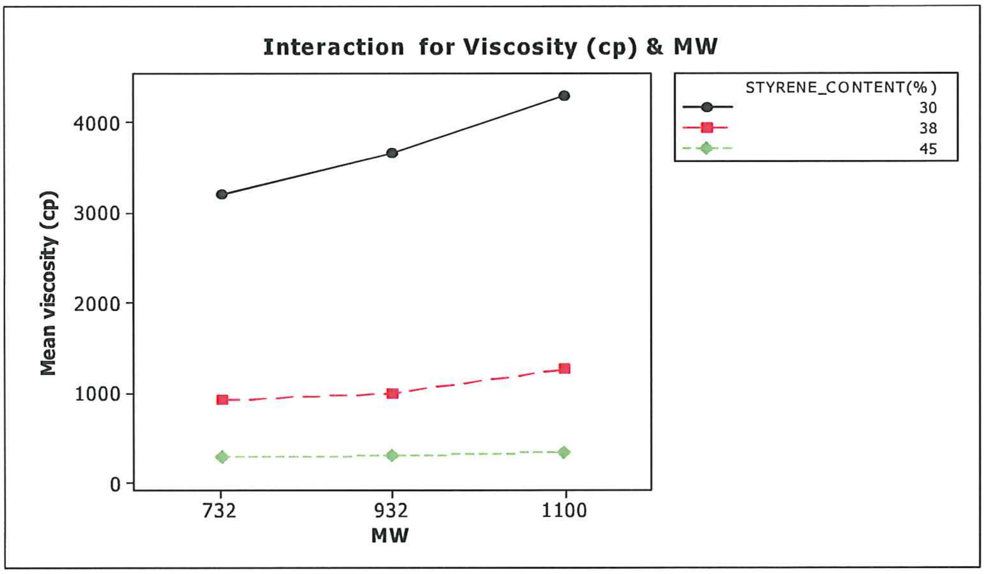


Figure 3.12 The effect of different molecular weight and styrene content of viscosity of vinylester resins, measured at 23 ^{0}C

3.3.4. The Main Effects on Viscosity

The measured viscosity values under different conditions were examined by a statistical operation to determine the main effects on the viscosity. The results are shown in Figure 3.13 et 3.14. The special statistical program which is called MINITAB was used to make these calculations and to plot the graphs. According to graph, the styrene content had the main effect on the viscosity changes of vinylester resin by 37.7 %. The temperature effect was lower than the styrene content. However, the effect of the styrene content and the temperature were higher than the molecular weight effect itself, 0.8 %. It can be said that, the effect of molecular weight was negligible when compared to the effects of styrene content and temperature.

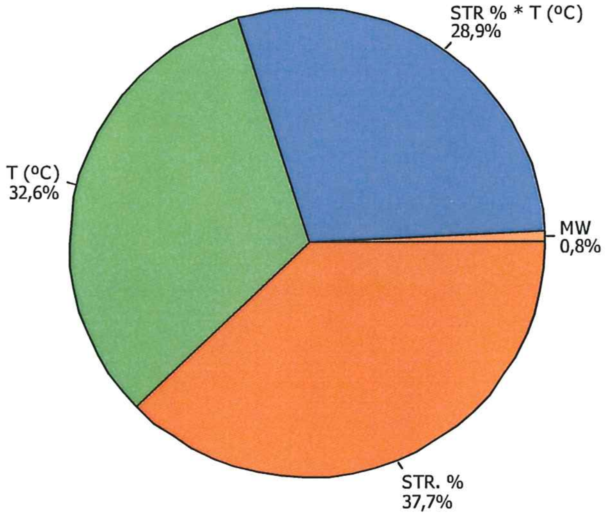


Figure 3.13 The main effects on the vinylester viscosity

The experimental values are plotted in 3-dimensions in Figure 3.14.

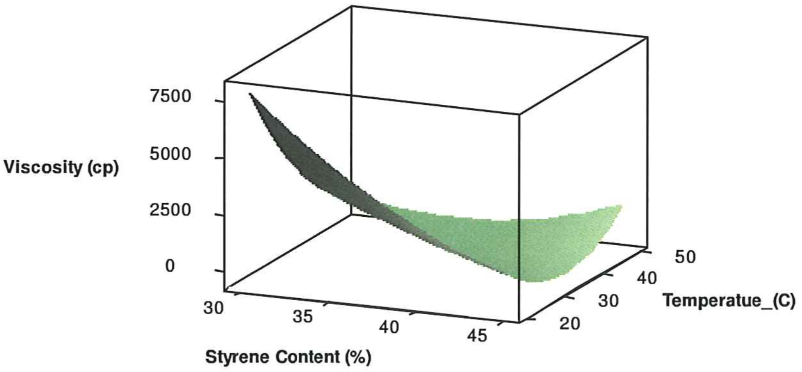


Figure 3.14 The dependence between viscosity on temperature (°C) and styrene content (%) of the vinylester resin.

3.4. Network Formation of Vinylester-Styrene System

Vinylester resin is a highly viscous fluid. Resin does not have as useful mechanical properties without crosslink. In order to enhance the mechanical properties, covalent bonded crosslinks are required. These bonds prevent the chains from sliding past one another, resulting in a higher modulus and improved creep resistance. Gelation occurs when a three-dimensional insoluble or an infinite molecular weight polymer is formed. The time to reach the gelation point at a particular temperature can be measured experimentally by using rheology or solubility experiments.

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 vinylester resins discussed in this work are crosslinked by free radical chain reaction copolymerization of methacrylate endgroups with styrene monomer. Styrene was used in the study as a co-monomer for 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. Owing to 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. The free radical polymerization of vinylester-styrene system is represented in Figure 3.15.

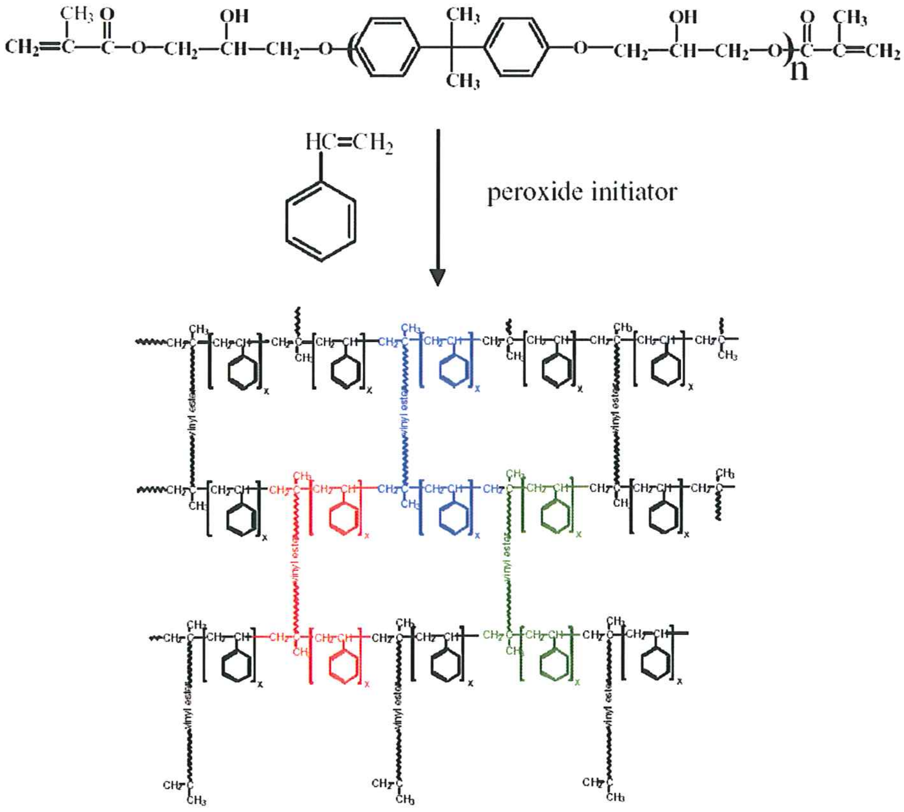


Figure 3.15 The general representation crosslinking between the vinylester chains with styrene [1]

Free-radical crosslinking polymerizations and copolymerizations of multi radicals systems are generally complex in nature. This complication arises from the mechanism and nature of a free-radical reaction. There might be incomplete conversion of pendant double bonds due to vitrification or immobility caused by other effects. The 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, and microgelation, etc [81].

The crosslinking reaction starts with the initiation step as a characteristic of free radical polymerization. In this study, benzoil peroxide was used as the initiator and cobalt naphtanate in acetone solutions was used as the accelerator. It provides the acceleration of peroxide initiator decomposition. The benzoil peroxide decomposes to free radicals, which attack the double bonds of the styrene monomers and the vinylester polymer chains. During crosslinking, the viscosity increase is not appreciable until the gel point. The point at which, the resin can not flow is called the gel point and the time to reach gel point is known as gel time. Gel time has very important properties for the application. The resin application must be completed within the gel time, because crosslinking is an irreversible process. The resin can not be reshaped after gel time. The concentration of the initiator and/or accelerators and the use of elevated temperatures can be adjusted to obtain the desired time required to reach the gel point. In order to obtain high gel time, a dilute hydroquinone solution was used in this work.

The crosslinking reaction is highly exothermic. The heat is generated from destroying the л double bonds on the chains in order to form the б bonds between the chains. Therefore, the heat released is directly related to the crosslink density of the resin. A large amount of heat is released when the crosslink density is high. The exotherm temperature was measured by a thermocouple with a plotter, then the peak temperature was determined and released heats were calculated.

3.4.1. Determining Accelerator/Initiator Combination for Elevated Temperature

Decomposition of the initiators is affected by heat. Then, accelerators or promoters cause rapid decomposition of the initiator at a given temperature. In this study, MEK-P and BPO were used with different accelerators/ promoters systems. The trials were carried out in order to determine suitable curing agent types and amounts. The gel time was adjusted between 20 minutes and 25 minutes. This gel time was sufficient to apply the resin. As seen in Table 3.3, different amounts of initiators and accelerators were used with different combinations to achieve this gel time. The room and the resin temperature were set to 23 °C before the experiments.

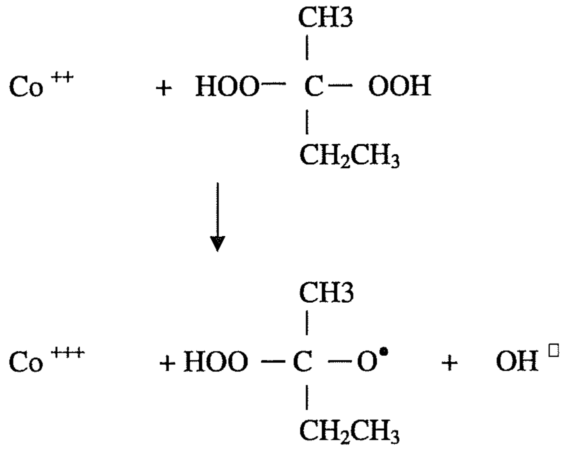
Table 3-3 The different catalyst systems used to adjust the gel time.

RESIN : VE 932/38					
Trials No	**CoNaph, 6% (mass %)**	**DMA (mass%)**	**BPO (mass%)**	**MEK-P (mass%)**	**Gel Time**
1	0.1	0	0	1	1h 30min 17s
2	0.1	0	0	2	1h 1min 35s
3	0.3	0	0	1	55min 2s
4	0.1	0	1	0	52min 43s
5	0.1	0	2	0	40min 15s
6	0.3	0	1	0	37min 13s
7	0.3	0.1	1	0	11min 07s
8	0.3	0.05	1	0	22min 15s
9	0.3	0.05	0	2	23min 28s

Figure 3.16 shows the mechanism of the MEK-P decomposition with the CoNap promoter to generate free radicals. The promoters transferred an electron to the hydroperoxide which activated its decomposition into free radicals and anions. The radicals reacted with the unsaturated bonds of the monomers to initiate copolymerization. During the decomposition of methyl ethyl ketone peroxide by cobalt, the purple cobalt II was transformed to green cobalt III. Cobalt III was reduced back to cobalt II since the trivalent form was not stable and because it could react with the peroxide [28].

$$\mathrm{ROOH} + \mathrm{Co}^{++} \longrightarrow \mathrm{RO}^{\bullet} + \mathrm{OH}^{\square} + \mathrm{Co}^{+++}$$

$$\mathrm{Co}^{+++} + \mathrm{ROOH} \longrightarrow \mathrm{ROO}^{\bullet} + \mathrm{H}^{+} + \mathrm{Co}^{++}$$



$$\mathrm{Co}^{++} + \mathrm{HOO}-\underset{\displaystyle \mathrm{CH_2CH_3}}{\overset{\displaystyle \mathrm{CH3}}{\mathrm{C}}}-\mathrm{OOH}$$

$$\downarrow$$

$$\mathrm{Co}^{+++} + \mathrm{HOO}-\underset{\displaystyle \mathrm{CH_2CH_3}}{\overset{\displaystyle \mathrm{CH3}}{\mathrm{C}}}-\mathrm{O}^{\bullet} + \mathrm{OH}^{\square}$$

Figure 3.16 Free radical formation from MEK-P with CoNaph promoter

Tertiary aromatic amines can also transfer an electron to a peroxide or hydroperoxide to activate decomposition of such compounds. Figure 3.17 illustrates the mechanism by which BPO in combination with DMA, initiated copolymerization at low temperatures in the present work.

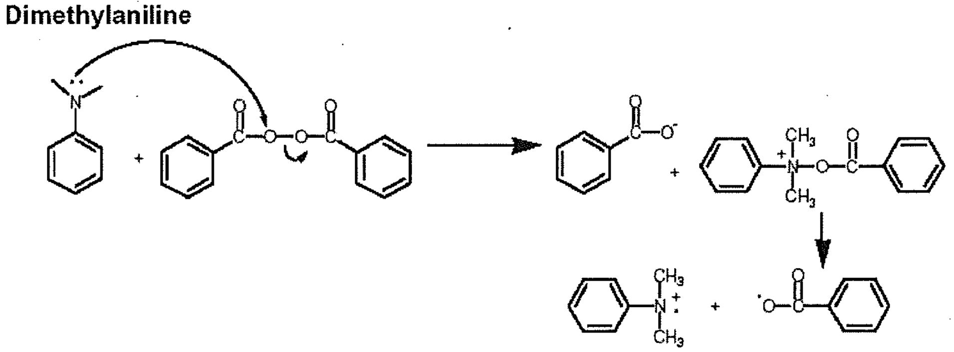


Figure 3.17 Free radical formation from BPO with DMA promoter

MEK-P was used as the initiator and a solution of CoNaph was used as an accelerator for the first 3 trials. Longer time for gel formation were measured even at high MEK-P amounts. Therefore, MEK-P was used in combination with both CoNaph and DMA to promote cures at room temperatures. BPO was used as an initiator with 6% CoNaph. The gel times were decreased at certain times, but the target could not be reached yet. Higher CoNaph and peroxide content led to a very rapid degradation of peroxide resulting the release of large amounts of heat in a short time. High heat destroys the vinylester chains it referred to as "burning of the resin". As a result, in order to obtain lower gel time, we could not increase the amount of CoNaph. Therefore, a co-catalyst was used to obtain lower gel time by controlling of heat released. For the last 3 trials, co-catalyst dimethlyaniline (DMA) was used without changing the content of the CoNaph and the peroxides. Finally, the required gel time was obtained by the following 2 combinations for 100 g of resin;

1. 0.3% CoNaph, 0.05% DMA, 1% BPO
2. 0.3% CoNaph, 0.05% DMA and 2% MEK-P

Two combinations of accelerators and initiator amounts were used for all the sample preparations that were investigated in this work. BPO is a white gel at room temperature, which needs the right temperature to mix easily. Therefore, MEK-P was preferred because of its easy handling and its ability to mix with the resin for a room temperature cure.

3.4.2. The Curing Reaction Temperature and Resin Reactivity Relationships

The curing reaction of vinylester resins is highly exothermic because of network formation. The heat release is proportional to both the amount of the broken chemical bonds and the formed chemical bonds during the reaction. The network formation capability of the resin without post-curing is called the reactivity. Post-cure is the application of high temperature to the resin after curing, to enhance the network formation. Under real application conditions, the resin users may not have the high temperature post-cure facility. Therefore, the resin has to complete the network formation by its own heat of curing reaction. The high network formation can be attributed to high reactivity. Reactivity of the resin affects all the mechanical properties of the resin without the post-cure. This is discussed in part 3.6.

In this study, the temperature rise during curing was followed by the thermocouples, which were connected, to a digital display and the time-temperature graphs were obtained for the various resin systems as shown in Figure 3.18. The temperature increased to a maximum point which is called the peak temperature. This peak temperature gave important information about the resin. Higher peak temperatures mean higher reactivity, which is important for the applications. Highly reactive resins are more stable towards strong acids and alkaline. It is assumed that the heat released was directly proportional to the peak temperature because the same amounts of resins were used under the same conditions for all measurements. Thus, the peak temperature will be evaluated in this chapter.

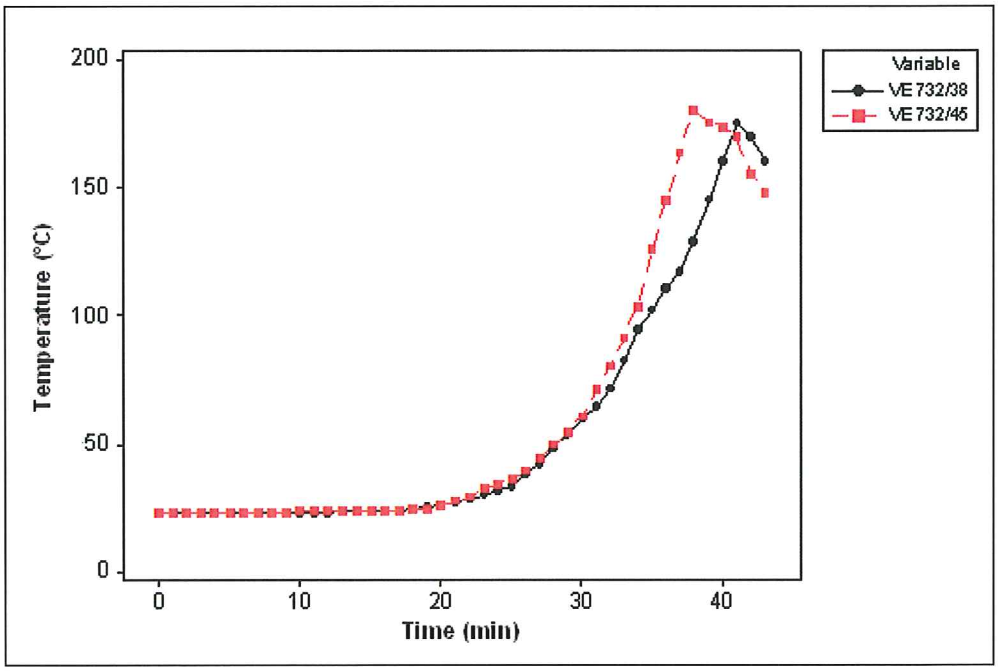


Figure 3.18 The time-temperature graph of the curing reaction for the resins VE 732/38 and VE 732/45

The experimental results showed that by increasing the molecular weight increases the gel time. The peroxide radicals cause formation of active radicals on the polymer chains and open the end group double bonds.

The crosslinking reactions started between the chains and the styrene resulted in the increase of the viscosity. The resin temperature increased very slowly up to the gel formation. After the gel point, the temperature increased rapidly and the resin became hard. The time for the obtaining of gel with 0.3% CoNaph, 0.05% DMA and 2% MEK-P was called natural gel time in this study. Natural gel times are high for higher molecular weight, because, the double bond concentration decreases by the increasing of chain length. Therefore, the network formation was retarded because of the long distance between the double bonds results with high gel time. As it is seen in Table 3.4, the sample VE 732 has shorter natural gel time in comparison to VE 932 and VE 1100.

The styrene amount also affected the natural gel time as seen in Table 3.4. The resins, which had higher styrene contents, showed shorter time to reach the gel point. The styrene monomers formed a bridge between the chains. The higher styrene content meant higher capability to cap the active radicals at the end of the polymer chains. The chains were linked to each other more easily by increasing the styrene content. According to the measurements, natural gel times were shorter at higher styrene contents for all molecular weights, under the same conditions.

Table 3-4 The cure peak temperature of the synthesisd vinylester resins at the same gel time

Samples	MW	% Styrene	Natural Gel Time	Adjusted Gel Time	Peak Temperature (°C)
VE 732/38	732	38	17min 38s	23min 07s	174.8
VE 732/45	732	45	14min 42s	22min 48s	180.1
VE 932/38	932	38	23min 28s	23min 28s	166.2
VE 932/45	932	45	20min 14s	20min 14s	170.1
VE 1100/38	1100	38	37min 15s	24min 34s	158.9
VE 1100/45	1100	45	33min 54s	23min 13s	160.3

Heat was generated from the crosslinking reaction between the chains. The peak temperature could give us information about the crosslink density of the resin. The peak temperature was dependent on the gel time. In order to compare the peak temperatures, the gel times must be nearly the same. In this study, the gel times were adjusted to 20 minutes and 25 minutes by using a retarder and an accelerator. Adjusted gel times are shown in Table 3.4. Therefore, we were sure that these chemicals would only affect the gel time, not the peak temperature. A well-known retarder hydroquinone was used to increase the gel time, when needed. DMA (Dimethyl Aniline) was used as an accelerator to decrease the gel time of the samples. The The peak temperature for vinylester resin with molecular weight of 732 g/mol was higher than for molecular weight 932 g/mol and molecular weight 1100 g/mol. These results proved that the decrease in the molecular weight caused large amounts of crosslinks between the chains. In other words, the low molecular weight resins were more reactive than the high molecular weight resins.

The results also showed that increasing the styrene content for the same molecular weight caused an increase in the peak temperature. The styrene amount did not affect the peak temperature after saturation. The saturation point was reached by consuming all probable double bonds on the chains. In order to determine the saturation points, the experiments were done and the results were plotted as shown in Figure 3.19. As it is seen, the peak temperatures of vinylester with molecular weights of 732 g/mol increased up to 45 % styrene content very sharply, and then the slope became smaller.

The polymer and the styrene double bonds reacted with each other easily by increasing styrene content. However, increasing styrene amounts caused dilution of the polymer solutions. Then, the opposite effect caused the double bonds to separate from each other. Therefore, the number of active free radicals and their efficiencies decreased. According to experiments; firstly, the peak temperatures increased sharply by increasing in the styrene amount, then slight increases were observed up to the maximum point of 50% styrene content for VE 732. The efficient styrene content is determined by the maximum peak temperatures were. For example, the maximum peak temperature was observed at the 55 % styrene content for VE 932. This is the saturation point of this resin. It is not efficient to add more styrene to this resin. After the saturation point, the peak temperature decreased very slightly. According to results on Figure 3.19, the styrene content effect on the peak temperature was higher for VE 932.

In conclusion, the reactivity of the vinylester resins increased with the addition of the styrene up to the saturation point. After the saturation point, the low viscosity reversely affected the reactivity. The effect of the styrene concentration on the reactivity was greater for resins with higher molecular weight.

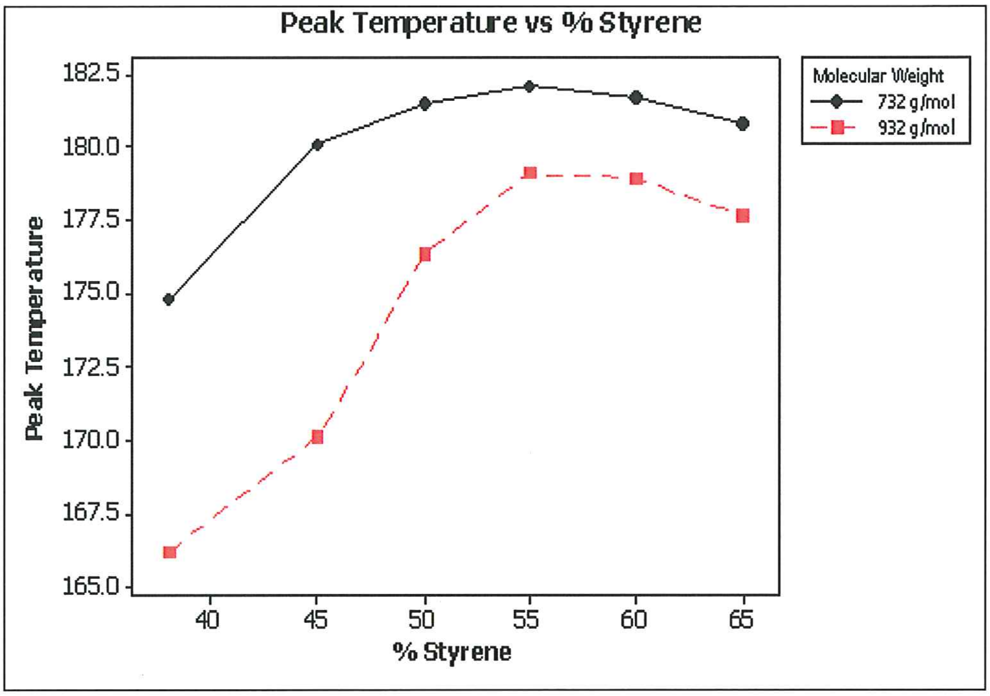


Figure 3.19 The effect of the styrene content and molecular weight on the peak temperature of VE 732 and VE 932

3.4.3. The Effects of Cure Conditions on the Vinylester Double Bond Conversion

The degree of the double bond of the vinylester resins was the major parameter affecting the bulk physical properties after curing. The aim of curing is that all of the double bonds on the chains should join the network. Generally, higher double bond conversion in the free radicalic network formation results in greater mechanical strength. The maximum mechanical properties could be obtained by 100% crosslinking. However, the room temperature cured systems were reported to have low double bond conversion due to vitrification [1]. During the curing reaction, the viscosity increases very quickly and results in the reduction of diffusivity and chain mobility. Under these circumstances, some of the double bonds are frozen in the networks without crosslinking.

Differential scanning calorimeter (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, it is very difficult to obtain the information on the curing mechanism by DSC. IR allows monitoring both unreacted and reacted monomer concentrations during very fast copolymerization.

In this study, FTIR - ATR spectroscopy was used to investigate the effects of post-cure temperature and reactant composition on curing kinetics of vinylester resin. The resins were cured by using 1.5% MEK-P in combination with 0.05% DMA and 0.3% CoNaph, which was discussed in the previous section of this chapter. The post-cure conditions given in Table 3.5 were applied in order to observe the effect of post-cure on the degree of vinyl group conversion,

Table 3-5 The cure conditions of vinylester resin, VE 932.

Sample No	Cure Temperature (°C)	Cure Time (hours)
1	23	7
2	50	1
3	90	1
4	150	1

The loss of the methacrylate vinyl peak at 943 cm^{-1} and that of the styrene double bonds at 910 cm^{-1} were monitored during copolymerization. Figure 3.20 shows the ATR FT-IR graphs of the double bonds region of the vinylester resin. The measurements were done with 1 g of vinylester sample. The sample was put on the crystal of the ATR FT-IR. After the first measurement, the same sample was cured at the required temperature. Then, the measurements were done on the same sample. According to ATR FT-IR data, conversion of styrene vinyl group was just 39.2% after 7 hours at room temperatures, while that of the methacrylate vinyl group was 50%. After room temperature curing, the resin was exposed to post-cure at 50 °C for 1 hour. The conversion for styrene increased to 51.8% and methacrylate to 63.6%. After 1 hour at 90 °C, the ATR FT-IR showed that the sample was not completely cured and it was decided to continue curing further at higher temperatures. Then, the final cure was performed at 150 °C for 1 hour. All of these measurements were done on the same sample. The results are shown in the Figure 3.20. The calculated styrene double bond conversion was 95.3 % and methacrylate conversion was 86.4 %. An additional 1 hour was carried out at 150 °C. However, no further conversion was obtained. Higher cure temperature was not performed to prevent chain scission. It was concluded that the maximum conversion could be obtained by the applied cure cycle that is shown in Table 3.5.

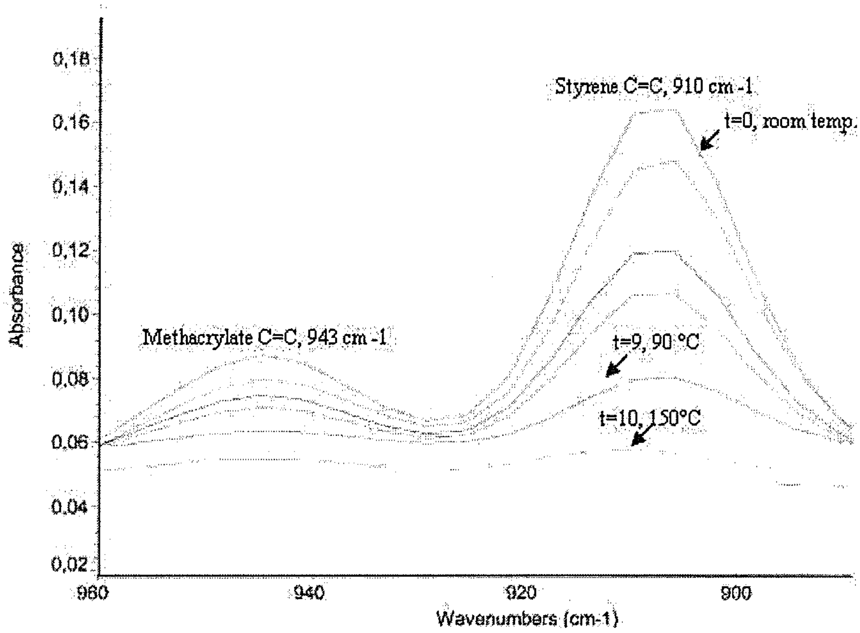


Figure 3.20 FT-IR spectra during cure of same sample, which was cured 8 h at room temperature, 1 h at 90 ^{0}C, 1 h at 150 ^{0}C

Figure 3.21 shows that the initial rate of conversion of the methacrylate was higher than that of the styrene double bonds. However, the styrene reached a noticeably higher conversion than the methacrylate at a higher temperature. Both the methacrylate and the styrene conversion rates were affected by the temperature to the same extent up to 150 °C. However, it was seen that the rate of the conversion reaction was higher for styrene above 150 °C. This means that the reactivity ratios of the monomers changed during the cure reaction. The styrene conversion was 95% at the end of the reaction while the methacrylate conversion remained at 86%. The curing reaction of the vinylester was diffusion controlled. Therefore, the mobility of the monomer was an important issue. Gelation occurring during the reaction resulted in the lack of mobility. After achieving the maximum reaction rate, the reduced mobility caused diffusion-controlled propagation and auto acceleration to occur.

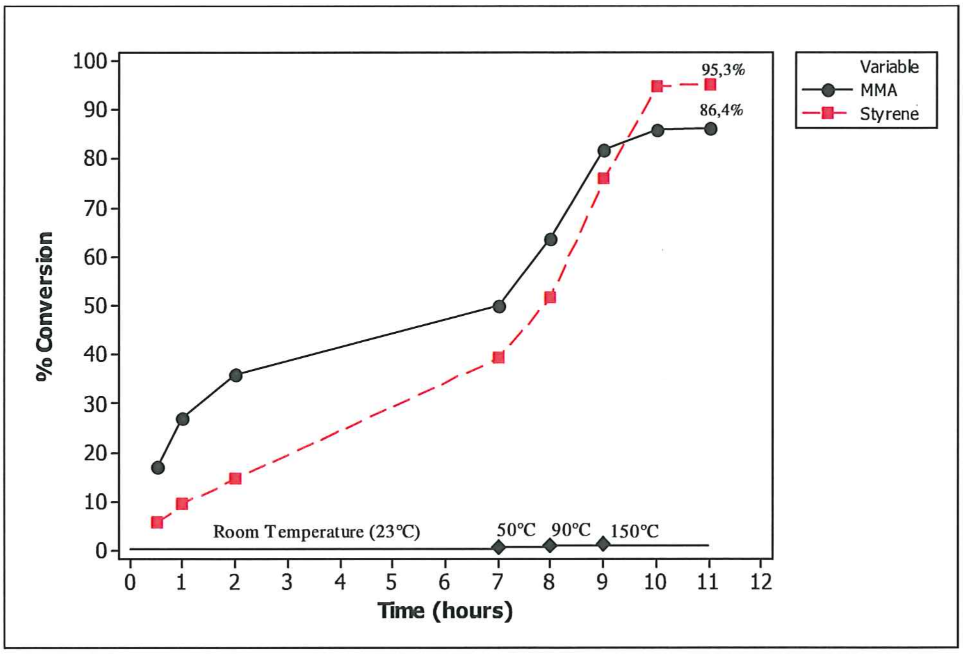


Figure 3.21 The calculated % double bond conversions of the vinylester resin VE 932/45

The vitrification suppressed the propagation stopping the cure reaction. The styrene molecules were more mobile due to their smaller size compared to vinylester molecules. It could reach conversion of 95 %, before vitrification. The essential homopolymerization of the styrene can also occur during the cure reaction. The mobility of the vinylester chain decreased more quickly than that of styrene. Therefore, the methacrylate conversion remained at 86 % at the end of the reaction.

The FT-IR results were supported by the following barcole hardness measurements during the cure reaction. The hardness of the network increased with the propagation of the crosslink density. In many industrials lines, the resin applicators use this technique practically, to follow the network formation, which was described in Chapter 2. Barcole 34 was used in this study and the results are shown in Figure 3.22. After 7 hours at room temperature, the hardness was measured as 20 shore and the value increased with time. The hardness was 29 shore, a significant increase was measured after 1 hour at 90 ^{0}C. However, the barcole hardness was determined as 36 shore even after an additional 1 hour cure at 150 ^{0}C. The barcole hardness did not change with additional time, and then the final value was determined as 36 shore. This means that, there was no opportunity to establish new crosslinks. In other words, the double bond conversion stopped and the final hardness was obtained. These results were in accordance with the FT-IR results for double bond conversion.

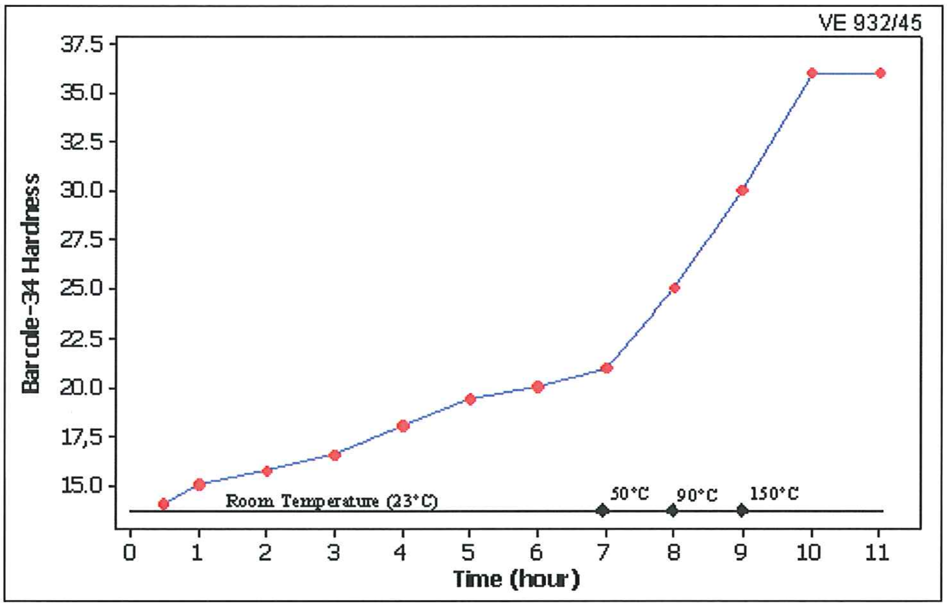


Figure 3.22 Barcole-34 hardness changes during the cure reaction for the vinylester VE 932/45

3.5. Physical Properties and Crosslinking Relation of Vinylester – Styrene Networks

Vinylester or dimethacrylate oligomers are divinyl oligomers which are used as crosslinking agents in free radical reactions. They cure free radically with other vinyl monomers, such as styrene, to produce crosslinked networks [82]. They form three-dimensional network after curing. The result is a higher modulus and improved creep resistance. Crosslink density is one of the most important structural parameters, which controls the physical properties of the vinylester resins. It provides a general means of characterizing the physical network structure and can be controlled by varying the styrene content in the resin. It has been successfully employed as a material structural parameter to understand the variations in small-strain and the ultimate mechanical properties of crosslinked rubbers. Other descriptive chemical and structural parameters may be the description of the detailed mechanical behavior as discussed in section 3.6. Therefore, this chapter describes an investigation of the relationships between the network structure and the physical properties. In this study, different molecular weights were studied with systematically varied styrene concentrations to determine effects of crosslinking on rubbery modulus, glass transition temperature, crosslink density, average molecular weight density and shrinkage.

3.5.1. Glass Transition Temperature (Tg)

In fact, the real glass transition temperature cannot be considered for the high crosslinked systems. However, the temperature at which phase transfer observed, is called representative glass transition temperature of vinylester resin. Tg is used to represent this phase transfer in this study.

In order to determine the Tg's of the vinylester networks, both DSC and DMA were used in this study. However, the sensitivity of DSC was not enough to measure this phase transition of highly crosslinked systems because of the very small changes in the heat flow in the glass transition. For the highly crosslinked series, Tg could not be determined by DSC. Therefore, DMA was more suitable to determine the Tg values of the crosslinked networks. Figure 3.23, 3.24 and 3.25 show the DMA thermograms for the resins of VE 932/30, VE 932/38, VE 932/45, respectively.

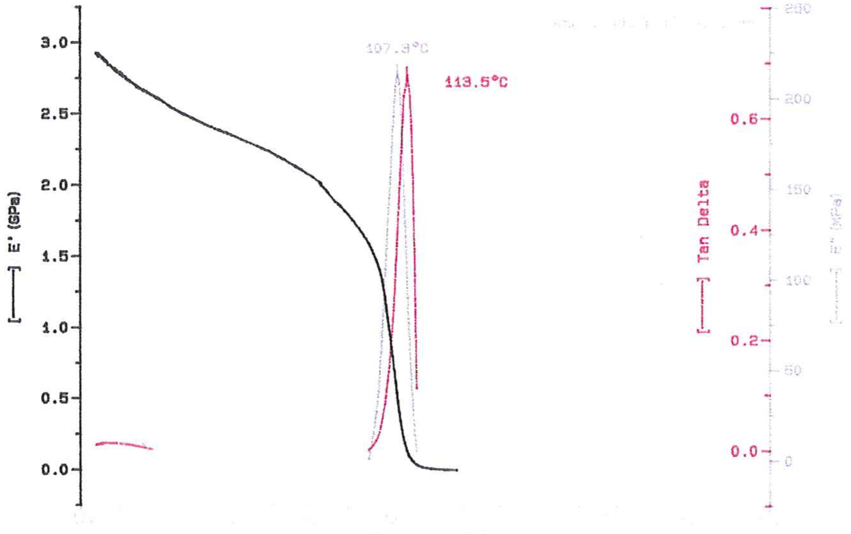


Figure 3.23 DMA thermogram of vinylester sample VE 932/30, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

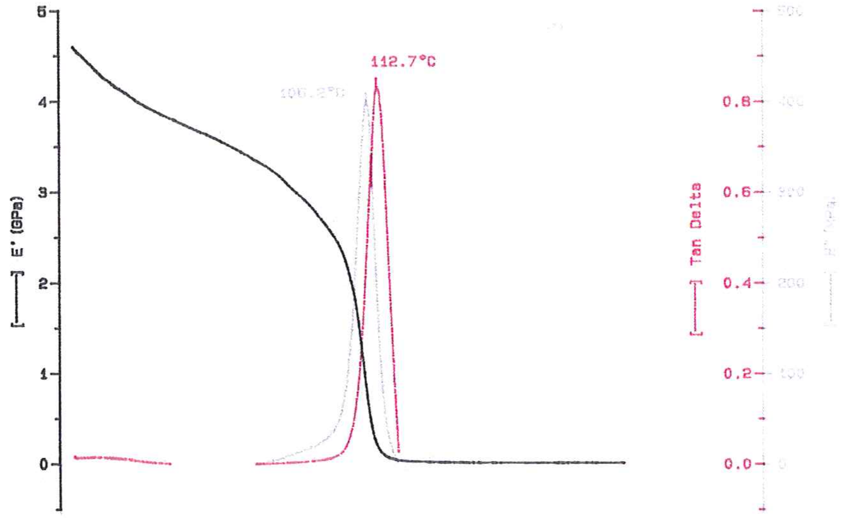


Figure 3.24 DMA thermogram of vinylester sample VE 932/38, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

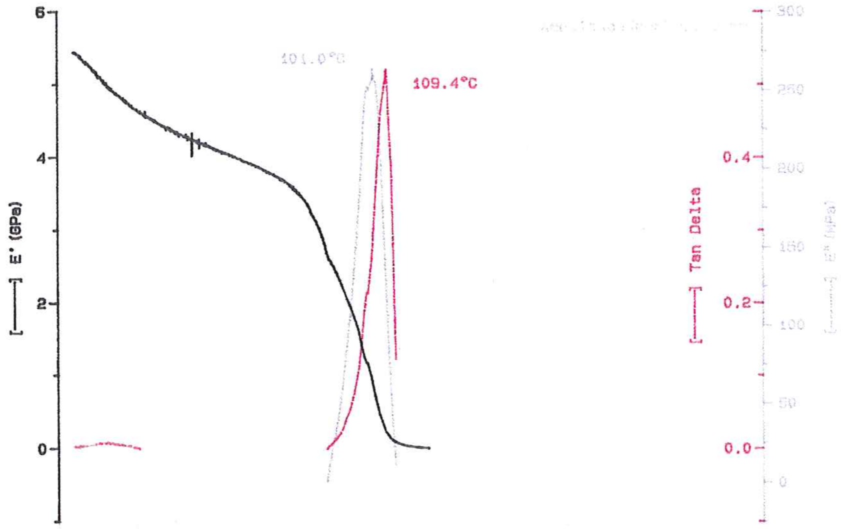


Figure 3.25 DMA thermogram of the vinylester sample VE 932/45, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

The tan (delta) peak was used to determine the glass transition temperature. The loss modulus relates to the amount of unrecoverable energy lost within a deformed material (dash-pot behavior). In a plot of tan delta versus temperature, the Tg was taken as the peak of the tan delta, as listed in Table 3.6.

Table 3-6 The glass transition temperatures by DMA ; vinylester resins with different molecular weight and different styrene content. Cure conditions: 1 h at 50 ^{0}C, 1 h at 90 ^{0}C, 1h at 150 ^{0}C

Molecular Weight	**% Styrene**	**Tg**
g/mol	**w/w**	**^{0}C**
732	30	118.4
732	38	115.8
732	45	113.9
932	30	113.5
932	38	112.7
932	45	109.4
1100	30	108.3
1100	38	108.3
1100	45	105.2

It is reported that the glass transition temperatures of crosslinked networks are strongly dependent on the degree of crosslinking [1]. There are two independent factors, affecting the Tg, the degree of crosslinking, and the copolymer chemical composition (copolymer effect). The degree of crosslink is directly related to the molecular weight of the dimethacrylate oligomer. The high molecular weight of the dimethacrylate oligomer provides high molecular weight between the crosslinks (Mc) resulting in low degree of crosslinks. In addition, Mc is directly changed by the chemical composition of vinylester, and by the dimethacrylate oligomer relative to styrene in the chemical structure. It is important to know which effect is greater. Figure 3.26 shows the results that with increase of the styrene content, the Tg of the networks decreases. In vinylester resins, vinylester oligomers have double bonds at each end that serve as crosslinking sites. When the percentage of the vinylester chains in the network increased, the percentage of styrene correspondingly decreases resulting in lower crosslink density. Generally, the experimental results showed that in lightly crosslinked networks, Tg is less dependence on the crosslink density. Theoretically, Mc can be quantitatively predicted based on the shift on Tg. However, for the networks in this study, it was difficult to make a direct correlation due to the change in chemical composition with changing Mc. The Tg of the networks were expected to be relatively insensitive to changes in Mc due to the chemical composition and the copolymer effect. This was shown in the literature in the estimation of the Tg of uncrosslinked vinylester copolymers using the Fox equation 3.1. [1]

$$T - T_{go} = K/Mc, \quad K = 3.9 \times 10^4$$ **Equation 3-1**

$$T_{go} = X_a T_{ga} + X_b T_{gb}$$

X_a and X_b are weight fractions of monomer units, A and B respectively. A is styrene, and B is the vinyl ester oligomer. T_{ga} is the Tg of polystyrene, and T_{gb} is the Tg of phenoxy resins which have the same backbone as the vinylester oligomer. According to experimental results (Table 3.6) the Tg only increased slightly as styrene content in the vinylester resins increased.

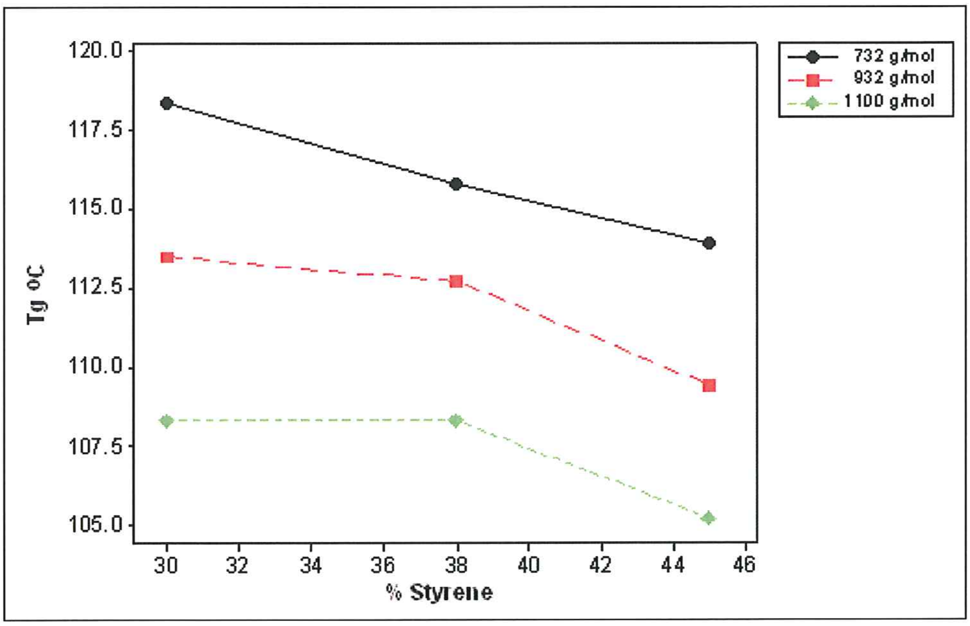


Figure 3.26 The effects of the styrene content and molecular weight on the glass transition temperature (Tg)

The change in the Tg may be due to two effects: the degree of cross-linking and the changes in composition. As discussed above, the copolymer effect is not large on the glass transition temperature. Overall, increasing the crosslink density always resulted in an increase of the Tg in the network. In other words, as the degree of crosslinking increased, the temperature must be higher in order to initiate the molecular mobility. According to Table 3.6, it was experimentally determined that when the styrene content in the system increased, the Tg of network decreased. For example, when the styrene content in the resins increased from 30 weight % to 45 weight %, the Tg changed from 118.4 °C to 113.9 °C for the 732 g/mole resin. Figure 3.26 shows that the same trends are valid for the vinylester resin with different molecular weight. As the molecular weight increased, the distance between crosslink junctions increased. An increase in Mc resulted in a decrease in the crosslink density of the network and the glass transition temperature. The difference in Mc was the greatest between these two systems. As it was shown in Figure 3.26, there was a great decrease in Tg when the oligomer molecular weight was increased from 732 g/mole to 1100 g/mole. The molecular weight affected Tg more strongly than the styrene content. Therefore, it is concluded that the major effect on the shift in Tg should be more dependent on changes in crosslink density and Mc due to oligomer molecular weight.

3.5.2. Crosslink Density and Rubbery Modulus Relations

The statistical theory of rubber elasticity was derived based on four basic assumptions;

1. An individual network chain obeys Gaussian statistics,
2. Upon deformation, crosslink junctions transform perfectly,
3. The internal energy of the system is independent of the conformations of the individual chains,
4. The chains are treated as phantom networks (there is no excluded volume) [91]

The elastic modulus at temperatures above Tg is still a good empirical method of characterizing highly cross-linked materials. The elastic modulus is independent of the chemical structure of the network. It depends primarily on the tightness of the network structure. There have been numerous studies reported on the application of the theory of rubber elasticity for the rubbery region of highly crosslinked networks such as epoxy [83] polyester [84], and bismaleimide systems [85].

In this work, a creep test in 3-point bending mode was used to calculate the rubbery modulus of the crosslinked vinylester resins. The rubbery modulus was determined at 40^0C above the glass transition temperature. Tg values were determined by DMA. The effects of the styrene content and the molecular weight on the rubbery modulus were evaluated. 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. 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 modulus according to the equation 3.2.

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

P/Δ= slope of load versus displacement data (kg/m)

g = gravitational constant = 9.81 m/s^2

L = length between supports = 0.0254 m

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

w = width of sample

h = height of sample **Equation 3-2**

Vinylesters vary widely in their mechanical behavior depending on the degree of crosslinking and the values of Tg [86]. Crosslinked polymers with high Tgs are usually characterized by high strength and low extensibility. Although strength is lost near the Tg for these materials. The crosslinked polymers retain a fair amount of strength beyond the Tg, known as the rubbery region. It can be clearly seen in Figure 3.27 spectrum how the modulus form a plateau in the rubbery region.

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 is observed. However, at higher temperatures, the uncoiling of the chains produces the response resulting in lower modulus values in this rubbery plateau region. This intermediate region, where the modulus drops from glassy to rubbery, is known as the leathery region from the leather-like feel of materials with moduli in this range [87].

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, and the uncoiling leads to a material that only responds by the straining of bond angles and lengths.

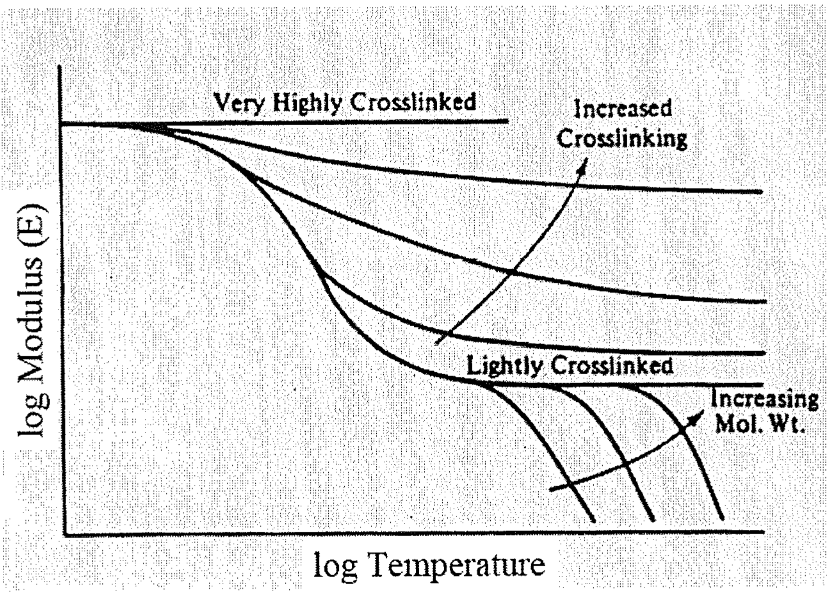


Figure 3.27 The general relations of the modulus, crosslinks and molecular weigths of the thermoset resin

Both copolymer composition and the degree of crosslinking affect the rubbery modulus of cured vinylester resin networks. The measured rubbery modulus values are in Table 3.7.

Table 3-7 The measured rubbery modulus of the synthesisd vinylester series

Molecular Weight	**Styrene %**	**Modulus (MPa)**
732	30	36.7
732	38	30.2
732	45	23.1
932	30	25.3
932	38	19.6
932	45	13.8
1100	30	15.4
1100	38	14.2
1100	45	12.7

According to data shown in Figure 3.28, the rubbery modulus increased 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 the oligomer molecular weight resulted in a looser network. The number of the crosslinked sites decreased resulting in less resistance to deformation above Tg, and in a lower rubbery modulus. For the vinyl ester resins with oligomer Mn=1100g/mole, the crosslink density decreased only slightly as the styrene content increased from 30 weight % to 45 weight % in the resins. The oligomer "crosslinks" were actually contributing to the network modulus as elastic chains. Therefore, the percent change in the average distance between the crosslinks when the styrene content increased is less than when the oligomer has a higher molecular weight. It should also be noted that the absolute number of crosslink junctions per cm^3 was less for the higher molecular weight dimethacrylates.

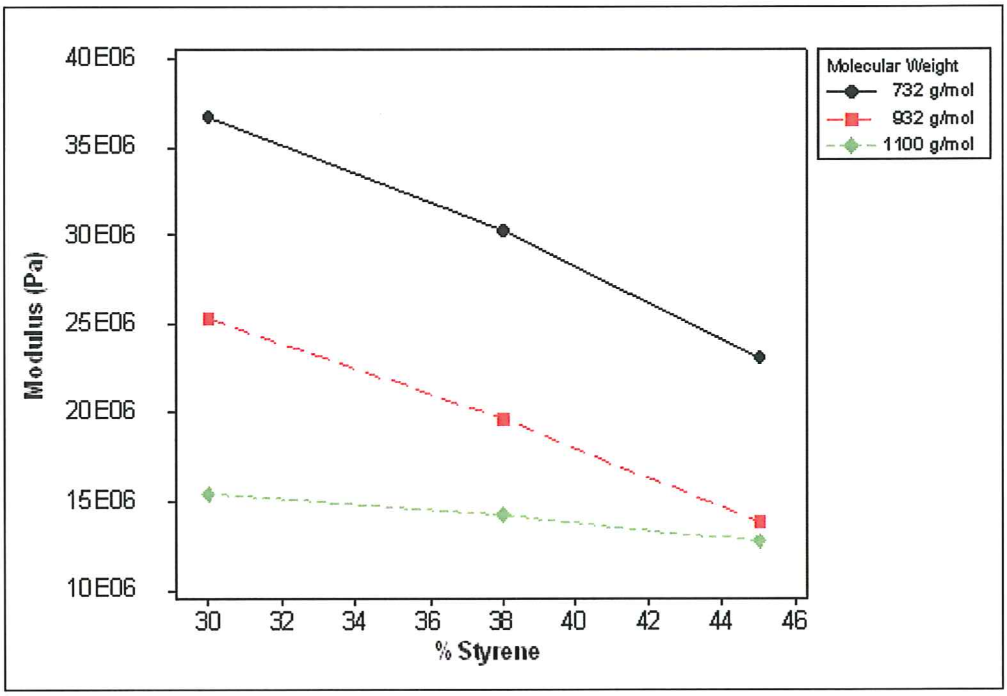


Figure 3.28 The effects of the styrene content and molecular weight on the rubbery modulus, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

The crosslink density is an important structural parameter which controls many physical properties of vinylester resins. The crosslink density can be controlled by varying the length of the vinyl ester precursor, the molecular weight distribution, the relative amount of styrene used during the crosslinking reaction, and by controlling the final double bond conversion. For a highly crosslinked network, chain entanglements were not present. The vinylester networks tested had well defined transition regions and rubbery plateau regions. In the rubbery plateau region, the storage modulus changed only slightly with temperature. The first approximation is that the modulus in the rubbery plateau was considered as constant up to the chemical degradation temperature. It was essential to keep the deformation small during modulus measurements for the highly crosslinked networks. Only under small deformation can the network chain respond to deformation by undergoing changes in conformation that require only rotations of bonds in the network chains. Large deformations complicate the relationship between the rubbery plateau modulus and the crosslink density [92].

Dynamic mechanical tests and/or creep tests are rapid and very sensitive techniques to determine the cross-linking density at temperatures above Tg. According to the theory of rubber elasticity, the equilibrium elastic modulus is given with the following equation;

$$\rho = G'/RT = E'/3RT$$ **Equation 3-3**

where ρ is the crosslink density expressed in moles of elastic effective network chains per cubic centimeter of sample. *G'* is the shear storage modulus of the cured network at a temperature above Tg. E' is the rubbery elastic modulus of the network at a temperature above Tg. *R* is the gas constant and *T* is the absolute temperature at which the experimental modulus is determined. Here G'=3E' is used assuming that the samples do not undergo volume change with strain [93].

The rubbery modulus were determined at 40 ^{0}C above the glass transition temperatures by creep tests. These modulus values were used to calculate crosslink density. The calculated crosslink densities are shown as in Table 3.8.

Table 3-8 The crosslink densities of the synthesized vinylester resins

Mn g/mol	**Styrene %**	**CrosslinkDensity (mol /cm^3)**
732	30	3.41E-03
732	38	2.83E-03
732	45	2.17E-03
932	30	2.38E-03
932	38	1.85E-03
932	45	1.31E-03
1100	30	1.47E-03
1100	38	1.35E-03
1100	45	1.22E-03

According to experimental results, the crosslink densities of the vinylester networks decreased linearly with an increase in the styrene content and the oligomer molecular weight. 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. When the molecular weight was increased, the effect of the styrene content on the crosslink density decreased. Molecular weight increased with an increase in the chain length of the precursor epoxy oligomer. When the oligomer was large, the unsaturated reactive double bonds were far away from each other. This resulted in the long distance between the linkages in the network. Therefore, crosslink densities decreased with molecular weight as shown in Figure 3.29.

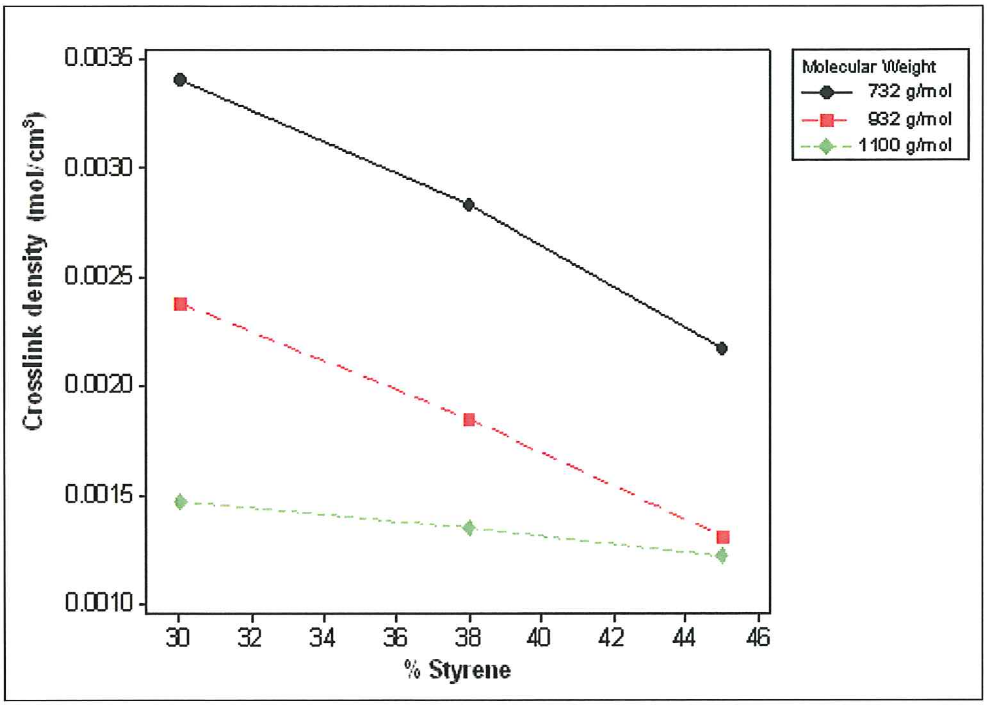


Figure 3.29 The effects of the styrene content and molecular weight on the crosslink densities of the cured vinylester resin, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

The data in Table 3.9 clearly indicate the trend that the crosslink density decreased as the styrene content increased. The increase in the crosslink density always resulted in an increase in the Tg of the network. The changes in composition also affected Tg. Since the glass transition temperature of high molecular weight polystyrene is similar to that of high molecular weight phenoxy, and both are near 100 ^{0}C. The effect of composition on Tg was dependent on the nature of the two components and could be estimated by the Tg of polystyrene and the Tg of phenoxy resins which had the same backbone chemical structure as the vinylester oligomers.

Table 3-9 The glass transition temperatures, crosslink densities and modulus of the synthesisd vinylester resins

Mn	**% Styrene**	**Tg**	**Crosslink density**	**Modulus**
g/mol	**w/w**	**^{0}C**	**mol/cm^3**	**MPa**
732	30	118.4	3.41E-03	36.7
732	38	115.8	2.83E-03	30.2
732	45	113.9	2.17E-03	23.1
932	30	113.5	2.38E-03	25.3
932	38	112.7	1.85E-03	19.6
932	45	109.4	1.31E-03	13.8
1100	30	108.3	1.47E-03	15.4
1100	38	108.3	1.35E-03	14.2
1100	45	105.2	1.22E-03	12.7

Figure 3.30 showed the relationship among Tg, crosslink density and the molecular weight of the vinylester resin at three different styrene contents. It was shown that higher molecular weight results in lower crosslink density and lower Tg. It was seen that, the changing the styrene content greatly affected the low molecular weight vinylester resin, largely. Therefore, the change in crosslink density was also great in low Mn vinylester resin at different styrene content. As a result, Tg was increased more in the high crosslink density resins.

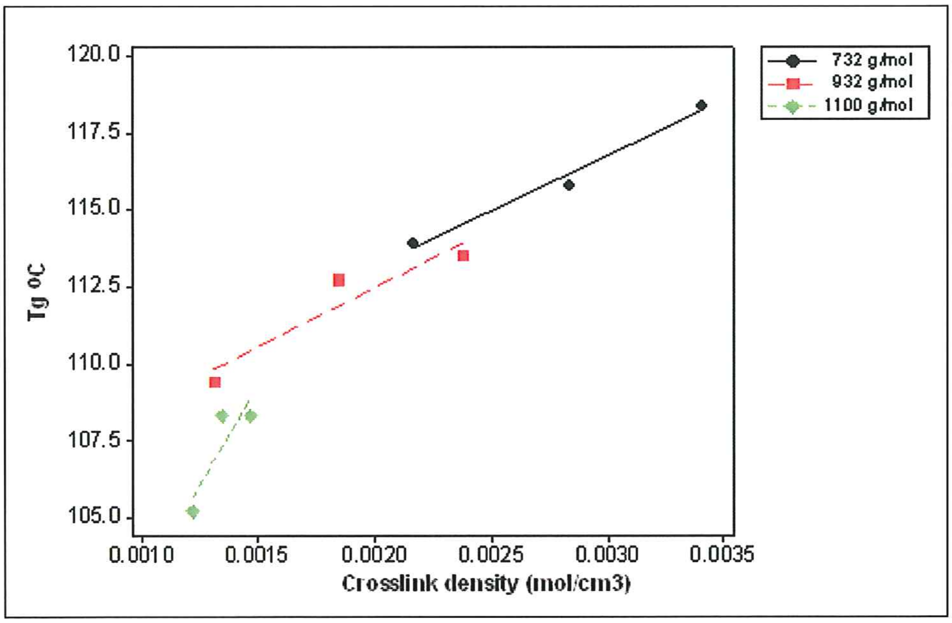


Figure 3.30 The relations between the Tg and crosslink density for the vinylester which have different molecular weight and styrene content, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

3.5.3. Average Molecular Weight (Mc) Between Crosslinks

The number average molecular weight between crosslinks was strongly dependent on the average molecular weight of the precursor epoxy oligomers, the amount of styrene present relative to epoxy oligomer, the extent of double bond conversion, and the molecular weight distribution of vinylester with styrene. In this study, the special chain extension method was applied to synthesis precursor dimethacrylate oligomers from the epoxy oligomers and bisphenol-A. This special method was explained in chapter 2. By this method, the molecular weight of the dimethacrylate oligomers was adjusted by the amount of the Bisphenol-A by controlling the distance between the reactive double bonds at the chain ends. The theoretical molecular weight and Mc were calculated using the reaction stochiometry. In this study, Mc was determined experimentally by using the densities at 40°C above Tg (Table 3.10) and the elastic moduli (determined from creep test measurements). The molecular weights between crosslinks (Mc) were calculated by equation 3.4.

$Mc = 3RTd/E$ **Equation 3-4**

E = the elastic modulus above the Tg (Pa)
Mc = the molecular weight between crosslinks (g/mole)
R = the gas constant (Pa.m^3/mol.K)
T = temperature 40^0 above Tg (K)
d = density at 40^0 above Tg (g/cm^3)

Relation with the crosslink density and Mc is obtained by reorganization of equations 3.3 and 3.4.

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

In order to calculate theoretical Mc, the system is assumed to be the fully cured vinyl ester-styrene samples, all chains were equal in length and no dangling ends existed [8,91]. Theoretical Mc was calculated as follows:

N = number of vinyl ester oligomers + number of polystyrene segments

N = (1- wt%styrene)/Mn+ 2 (1- wt%styrene)/Mn

$Mc = N^{-1}$ **Equation 3-5**

Theoretical calculation of the Mc was not sufficient to determine precisely the Mc value of the crosslinks because there are several assumptions. Therefore, it has to be determined experimentally. According to the rubber elasticity theory, the rubbery moduli of polymer networks should be proportional to the crosslink densities [94]. Equation 3.3 applies to elastically active network chains only. The assumptions of the elactic chains were listed in section 3.5.2.

The theoretically calculated and experimentally determined Mc values are listed in Table 3.10.

Table 3-10 The theoretical and experimental molecular weight between crosslinks (Mc) of vinylester resin, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

Mn	**Styrene**	**Density Tg+40**	**Therotical Mc**	**Experimental Mc**
g/mol	%	g/cm^3	(g/mol)	(g/mol)
732	30	1.205	349	353
732	38	1.118	394	396
732	45	1.113	444	513
932	30	1.211	444	509
932	38	1.115	501	604
932	45	1.109	565	847
1100	30	1.113	524	759
1100	38	1.104	591	817
1100	45	1.099	667	903

The experimental trends in Mc followed the expected increases as both the molecular weight of the dimethacrylate oligomer and the styrene concentration were increased. The results shown in Table 3.10 proved that average molecular weight between crosslinks (Mc) increased when the oligomer Mn or the styrene content increased. However, the results also showed that Mc strongly depends on the Mn of the dimethacrylate oligomer. It means that increasing the Mn of the oligomer from 732 to 1100 g/mole caused significant increases in Mc. For example, Mc was larger at 30-weight percent styrene for a 1100 g/mole oligomer than for 732 g/mole oligomer with as much as 45 weight percent styrene. Figure 3.31 shows the relationships among styrene content, molecular weight and Mc.

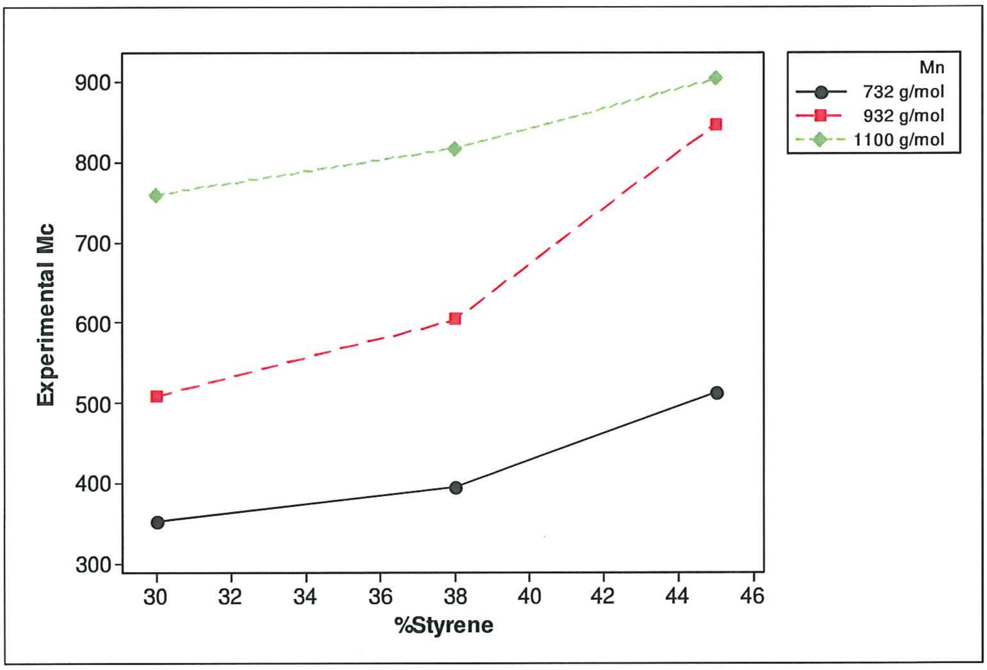


Figure 3.31 The effects of the styrene content and the molecular weight on the Mc, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

It is expected higher difference between experimental Mc and theoretical Mc for networks, which have greater number of dangling ends. The experimental values were uniformly higher than predicted from theoretical calculations. This difference may be partially attributed to "the dangling chain ends" which were elastically inactive segments. Therefore, they did not contribute effectively to the rubbery moduli. As a result, experimentally tested samples with dangling end had lower rubbery modulus values, which result in the higher Mc values that are shown in Table 3.11.

Table 3-11 The lists of the modulus, crosslink density and Mc for the synthesisd vinylester resin series

MW	**% Styrene**	**Modulus**	**Crosslink density**	**Experimental Mc**
g/mol		MPa	mol/cm^3	g/mol
732	30	36.7	3.41E-03	353
732	38	30.2	2.83E-03	396
732	45	23.1	2.17E-03	513
932	30	25.3	2.38E-03	509
932	38	19.6	1.85E-03	604
932	45	13.8	1.31E-03	847
1100	30	15.4	1.47E-03	759
1100	38	14.2	1.35E-03	817
1100	45	12.7	1.22E-03	903

According to the results indicated in Table 3.10, the differences between the theoretical and the experimental Mc become larger with increasing the molecular weight of the vinylester resin. This can be explained by the increase in the polydispersity of the chains with increasing the molecular weight of the dimethacrylate oligomer. In reality, two dimethacrylate oligomers could react with each other instead of with styrene. Therefore, long flexible parts could be present in the networks. For large precursor oligomers, the longest of the flexible parts increases elasticity because of this dublication. Thus, the elastic moduli decreased in the high molecular weight vinylester-styrene system in comparison to the low molecular weight systems; because, systems with high molecular weight have higher Mc, and enhance the flexibility. It can be said that the dangling effect becomes higher with the increasing molecular weight of the vinylester resin. Therefore, the difference between the theoretical and the experimental Mc is larger for the high molecular weight vinylester as seen in Figure 3.32.

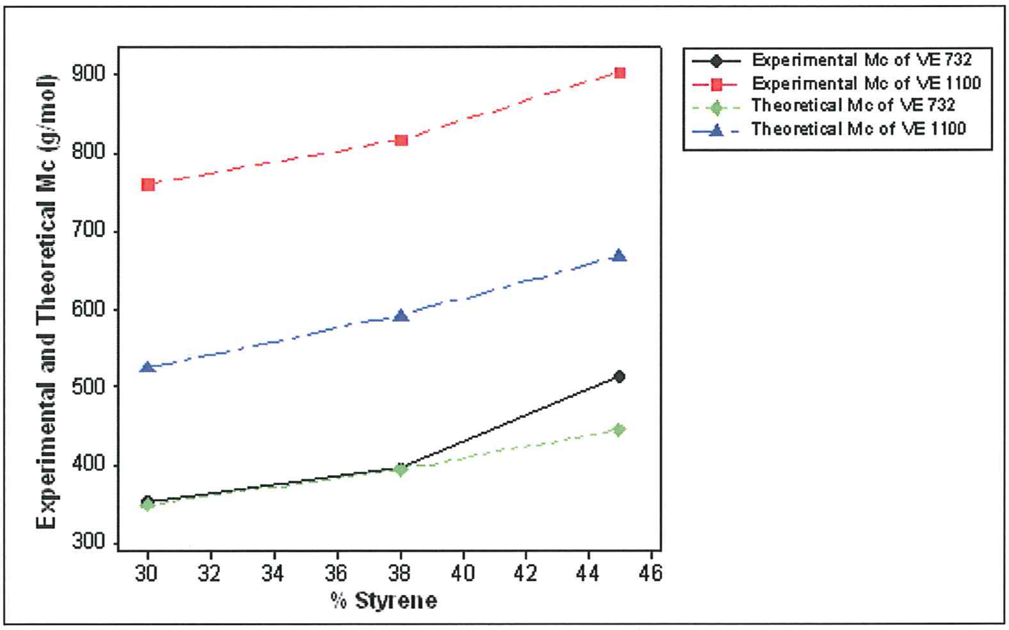


Figure 3.32 The changes of the experimental and the theoretical Mc with the styrene content and molecular weight of the vinylester resin, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

3.5.4. Cure Shrinkage of Vinylester Resin

During the curing reaction, networks were produced by the crosslinking reaction causing volume reduction. Typically, most thermoset copolymers have minimal shrinkage approximately 2-3% [91]. The specific volume (1/density) of uncured resins and fully cured networks was determined as a function of oligomer molecular weight and styrene content. Volume shrinkage upon cure was calculated as:

$$\% \text{ shrinkage} = (100 \times 1/\rho(\text{uncured}) - 1/\rho(\text{cured})) / 1/\rho(\text{uncured}) \qquad \textbf{Equation 3-6}$$

It was observed that, shrinkage was calculated based on density measurements. The cure shrinkage for the three series of vinyl ester resins as a function of styrene concentration was examined in this study. The cure shrinkage of the cured materials increased linearly with increased styrene concentration under different cure conditions. The cure shrinkage was determined according to the method explained briefly in Chapter 2. The results are listed in Table 3.12 and are shown in Figure 3.33. The shrinkage of the vinyl ester resin with Mn = 732 g/mole which contains no styrene was 2.4 %. The shrinkage increased from 7.6 % to 9.7 % as the % styrene increased from 30 wt. % to 45 wt. %. This could be explained by the reduction in density in going from monomeric styrene with a density of 1.09g/cm^3 to polystyrene with a density of 0.9 g/cm^3, corresponding to approximately 17 % volume shrinkage [21].

Table 3-12 The shrinkage % of the synthesisd of the vinylester resins

Molecular Weight	**Styrene**	**Shrinkage %**	
g/mol	%	cured 2h at 90 ^{0}C,	Cured 2h at 90 ^{0}C, postcured 1h at 150 ^{0}C
732	0	2.7	2.9
732	30	6.9	7.6
732	38	7.4	8.7
732	45	8.1	9.7
932	0	2.3	2.6
932	30	5.9	6.3
932	38	6.2	6.9
932	45	6.7	7.9
1100	0	2.1	2.3
1100	30	4.3	5.5
1100	38	5.1	6
1100	45	5.5	6.7

The results of Figure 3.33 show that resin shrinkage was reduced by decreasing the styrene content for all series of molecular weight. Another way to control volume shrinkage was to change the molecular weight of the vinylester oligomer. Figure 3.33 shows that the cure shrinkage decreased by increasing the molecular weight of the resin. It can be said that, the higher molecular weight vinylester oligomer coupled with the lower styrene content resulted in lower volume shrinkage. When the molecular weight was decreased, there were greater 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 the three series of resins with the different molecular weight oligomers. For short chain with VE 732, a higher crosslink density was found in section 3.5.2, and a lower specific volume could be expected. Long chain vinylester resins with Mn=1100 g/mole resulted in a lower crosslink density and a higher specific volume. As can be seen clearly in Figure 3.35, the decrease in the specific volume with crosslink density suggests that the free volume in the resins system was reduced by crosslinking. For the low molecular weight resins, the polymer chains were tied up by crosslink points more than the higher molecular weight systems. High cure shrinkage occurs resulting in low specific volume.

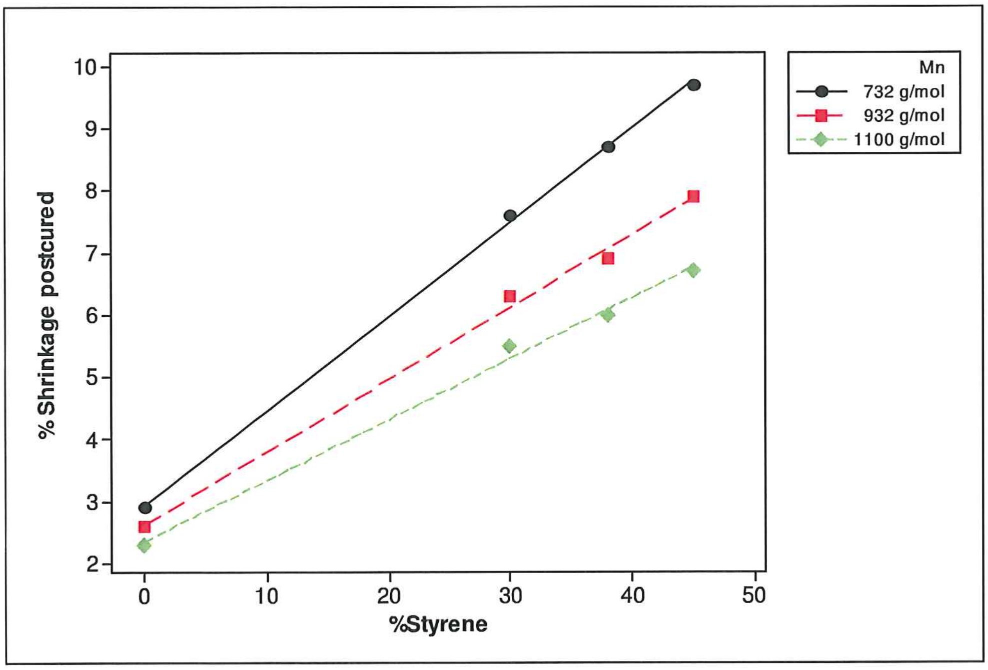


Figure 3.33 The effects of the styrene content and molecular weight on the cure shrinkage %, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

The cure conditions also affected the specific volume of the vinylester network. In order to investigate the effects of the cure conditions, two series of samples were cured at 90 ^{0}C for 1 hour at first, then for only one postcure at 150 ^{0}C for 1 hour. In chapter 3.5.2, the effect of the postcure on the crosslinking reaction completion was examined with the resin 932/45. For the post-cure resin, the styrene and methacrylate double bond conversion were found as 95% and 86 %, respectively. On the other hand, the resin, which was cured at 90 ^{0}C, had styrene conversion of 51.8% and the methacrylate as 63.6% (Table 3.13). According to these results, it is expected that the resin, which is post-cured, should have higher crosslink density resulting in higher cure shrinkage. In addition, during crosslinking some styrene produced some polystyrene. Polystyrene has higher density. Thus, when the styrene content increased, the observed density was increased. As a result calculated (Equation 3.6) shrinkage was higher. The experimental results in Table 3.13 showed that the post cured resins have higher shrinkage due to the higher crosslinking.

Table 3-13 The conversion and the shrinkage of the cured vinylester resin VE 932/45

Resin VE 932/45	**Methacrylate conversion** %	**Styrene Conversion** %	**Shrinkage** %
cured 90 ^{0}C, 1h	63.6	51.8	6.7
cured 90 ^{0}C, 2h postcured 150^{0}C, 1h	86	95	7.9

3.5.5. Water Absorption

Vinylester resins can be used in construction of ships, boat etc., which are in contact with water. Therefore, the water absorption properties are very important for vinylester materials. In order to produce good service, water absorption must be low. Absorbed water is trapped in the network and damages the network structure in time. The vinylester resins are reported to have water absorption values that are lower than those of polyesters [59]. This is one of the important advantages of the vinylester resins when compared to polyesters.

Synthesisd vinylester resins were cured by DMA and BPO at 90 ^{0}C, 2h and 140 ^{0}C, 1h postcure in the mould. The cured resins were cut by CNC into 1.5 cm X 1.5 cm samples. The samples were dried at 50 ^{0}C for 12 hours, then conditioned at 23 ^{0}C in desiccators. They were weighed (M1) .They were, then immersed in water bath at 23 ^{0}C. The samples were held by very thin wires to prevent their contact with each other and with the walls of the bath. The samples stayed in the bath for 7 days. After that, the samples were dried with a towel and they were reweighed (M2). The absorbed water values were calculated by the equation 3.7.

$$\% \text{ Water absorption} = ((M2-M1) / M1) \times 100 \qquad \textbf{Equation 3-7}$$

The results are listed in Table 3.14. It was seen that the water absorption generally decreased with an increase in the styrene content. This tendency was attributed to the relatively hydrophobic character of the styrene. Because of the hydrophilicity of the styrene, the capability of the hydrogen bonding of the system decreased resulting in lower water absorption values. Increasing the molecular weight of the resins affected the water absorption values. The crosslink density decreased with increasing molecular weight resulting in higher free volume of the network structure. Therefore, the network capacity to keep the water increased slightly with the increase in the molecular weight of the vinylester resin as seen in Figure 3.34.

Table 3-14 The water absorption values of the synthesisd vinylester series, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

Mn	**Styrene**	**Water Absorption**
g/mol	%	%
732	30	0.1237
732	38	0.1233
732	45	0.1229
932	30	0.1481
932	38	0.1476
932	45	0.1447
1100	30	0.1596
1100	38	0.1582
1100	45	0.146

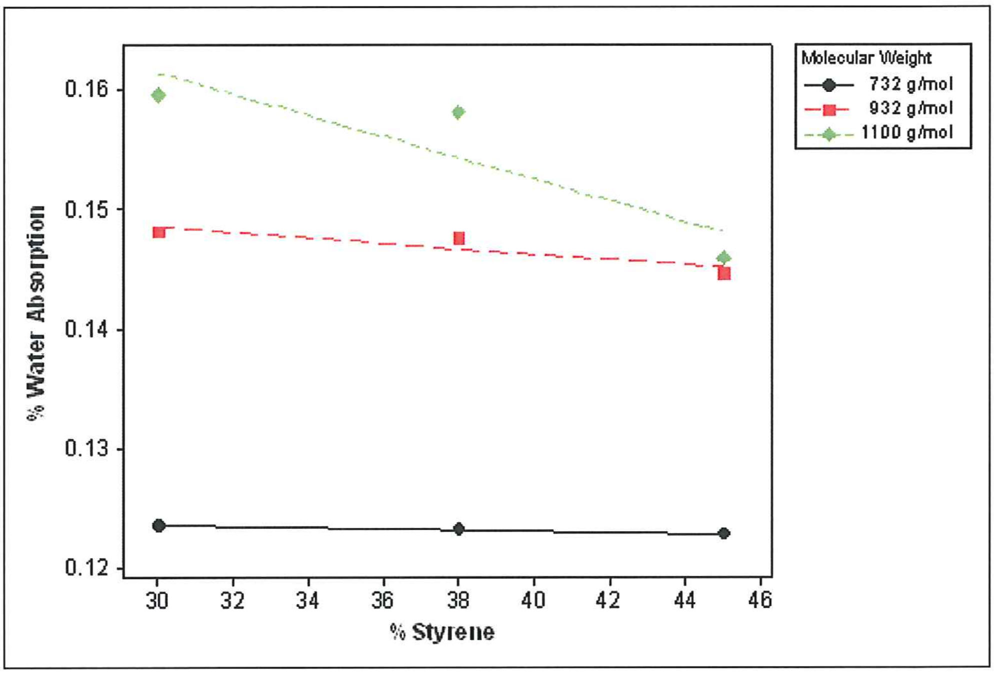


Figure 3.34 The effects of the styrene content and molecular weight on the water absorption properties of the vinylester resins, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

The effects of the cure conditions were studied and the results are shown in Figure 3.35. Different cure temperatures were applied for the same vinylester resin sample VE 732/38. The water absorption value was decreased by increasing the cure temperature. The crosslink density was enhanced with increasing cure temperature, and thus reducing the free volume in the network. Therefore, the capacity of water absorption was decreased by increasing the cure temperature.

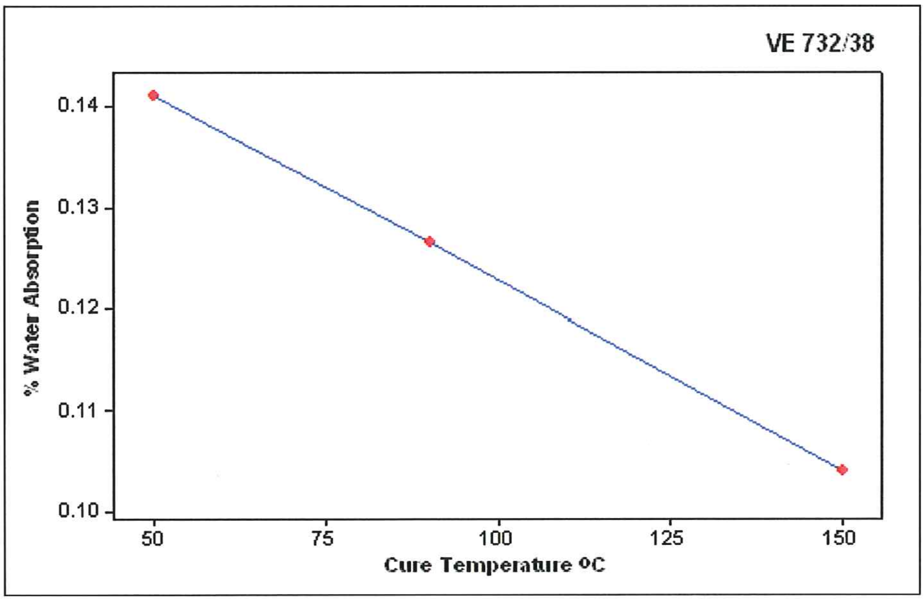


Figure 3.35 The effects of the different cure temperature on the water absorption of vinylester resin which has molecular weight 732/38. Three samples were prepared under the cure conditions: Sample 1, 1h at 50 ^{0}C; Sample 2, 1 h at 90 ^{0}C; Sample 3, 1 h at 150 ^{0}C

3.6. Mechanical Properties Relationships of Vinylester Resin Networks

The vinylesters are used in several applications because of their excellent mechanical properties and their easy process ability. The final mechanical properties of vinylester resins are determined by many parameters such as, molecular weight, styrene content, cure conditions, amount of curing agents, and cure temperatures etc. In order to obtain the desired mechanical characteristics, these parameters must be optimized. The incorporation of styrene have both positive and the negative effects on properties such as modulus, tensile strength, and hardness. Temperature affects mechanical properties due to its influence on intramolecular motion and intermolecular interaction. Mechanical properties are also affected by molecular weight. When the molecular weight is low, the applied mechanical stress causes molecules to slide 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. The mechanical properties of the network are directly related with the cure condition. It is reported that the crosslinking is not completed at low cure temperatures [93]. The effects of different cure temperatures are examined in this study. Another important factor, which affects mechanical properties in network systems, is the number of crosslinks per unit volume, which will be examined in this chapter. The crosslink density provides a general means of characterizing the physical network structure.

Crosslink density has been successfully employed as a material structural parameter to understand variations in small-strain and ultimate mechanical properties of crosslinked rubbers [90]. Copolymerization of vinylester resin with styrene monomer can affect both the physical and the mechanical properties. The incorporation of styrene will be shown to have both positive and negative effects on properties such as modulus, tensile strength and hardness. These topics will be discussed in this chapter. As it was examined in section 3.5.1, copolymerization with styrene decreased the glass transition temperature of these vinylester-styrene networks. Styrene was added to provide a workable viscosity for processing the uncured resin. Also, styrene affected the mechanical properties of pure resin.

3.6.1. Tensile Properties

Tensile data were obtained from load versus displacement curves using dogbone specimens pulled in tension according to ASTM D638 as shown Figure 3.36. This test is one of the most widely used and well known methods to determine stress-strain curves in tension for engineering plastics. Stress-strain curves were generated by continuously measuring the force that was developed as the samples were elongated at a constant rate of extension.

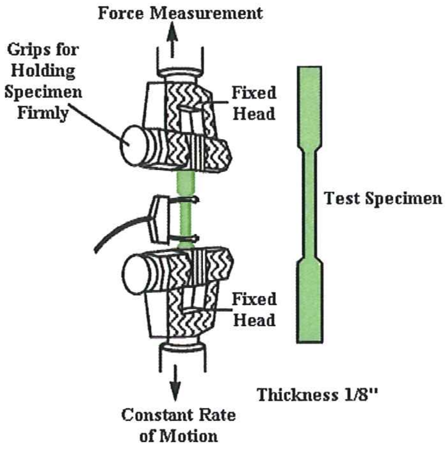


Figure 3.36 The tensile test equipment and the dog-bone specimen

These vinylester networks match with the class of materials known as rigid thermosets, which are categorized by their relatively moderate strengths and low extension due to the in crosslinked structure. These thermoset networks have relatively low elongation values at break when compared to typical flexible plastics and elastomers. However, they should show a greater elongation at break in comparison to 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 epoxides and unsaturated polyesters, these polymers are characterized as brittle. However, the elongation at break of the vinylester networks is higher than for the polyester networks. Polyester networks have crosslinking along the chain while vinylesters have it only at the end of the chain. That is why there is higher elongation in vinylester resins.

Table 3.15 shows the tensile strength and the tensile elongation at break changes with molecular weight and styrene content. According to experimental results, in the same molecular weight series, increasing the styrene content results in enhancing of both tensile strength and elongation at break. As investigated in section 3.5.2, increasing the styrene caused a decrease in crosslink density. Reduction of crosslinking caused increasing in chain mobility. Therefore, the ability to move under tensile stress increased. The elongation at break was reduced. It was shown that, a low degree of crosslinking increased the mechanical properties such as tensile strength and elongation at break. Very high degrees of crosslinking decreased the tensile strength.

Table 3-15 The tensile properties of the synthesisd vinylester series as shown Appendices C Cure conditions; 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at150 ^{0}C.

Mn	**Styrene**	**Tensile Strength**	**Tensile Elongation at break**
g/mol	%	MPa	%
732	30	53.2	1.84
732	38	63.1	2.32
732	45	70.1	2.87
932	30	65.0	2.55
932	38	70.3	2.79
932	45	78.2	3.44
1100	30	68.7	2.69
1100	38	71.1	2.97
1100	45	72.4	3.17

In addition, the elongation at break was reduced and the polymer became brittle with increasing crosslink density. This result can be attributed to very thin cracks that develop from internal stress resulting from the shrinkage during the cure, as well as decreased chain mobility at high crosslink density.

The tensile test plots obtained are shown in Figures 3.37, 3.38, 3.40.

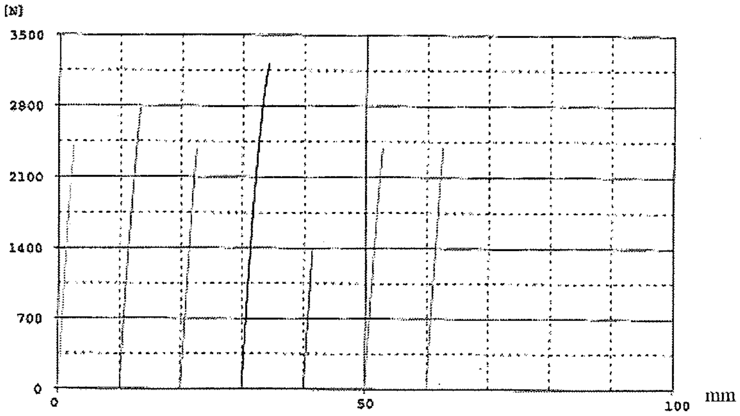


Figure 3.37 The tensile test graph of vinylester resin, VE 732/45, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

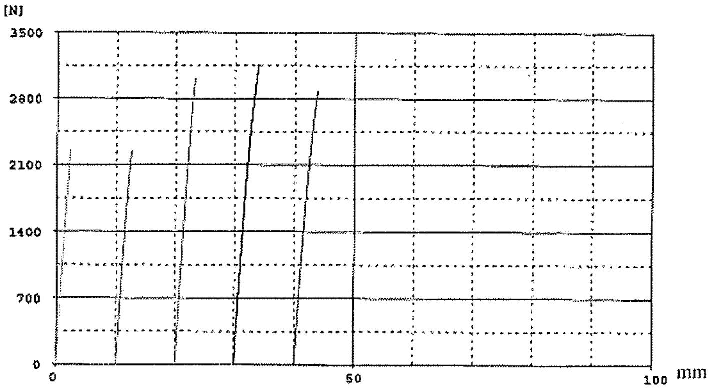


Figure 3.38 The tensile test graph of vinylester resin, VE 932/45, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

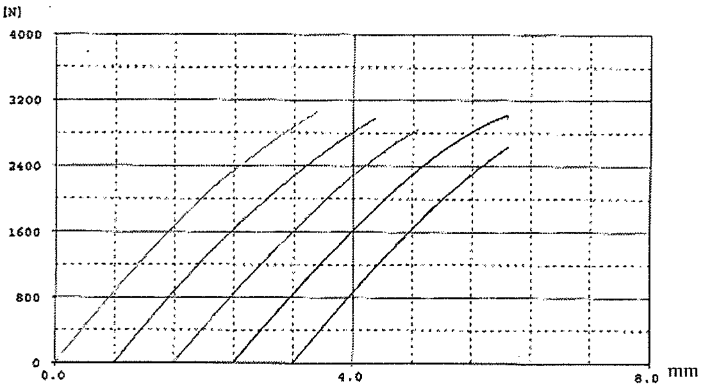


Figure 3.39 The tensile test graph of vinylester resin, VE 1100/45, Cure conditions: 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at 150 ^{0}C

The same increasing trends in tensile strength and elongation were observed for the increase in the molecular weight of the vinylester resin. The elongation is due to the arrangement of the chains between crosslinks. The elongation at break increases with increasing Mc, molecular weight between crosslinks. Figure 3.40 and 3.41 showed the effects of the molecular weight and styrene content on the tensile properties of vinylester resin.

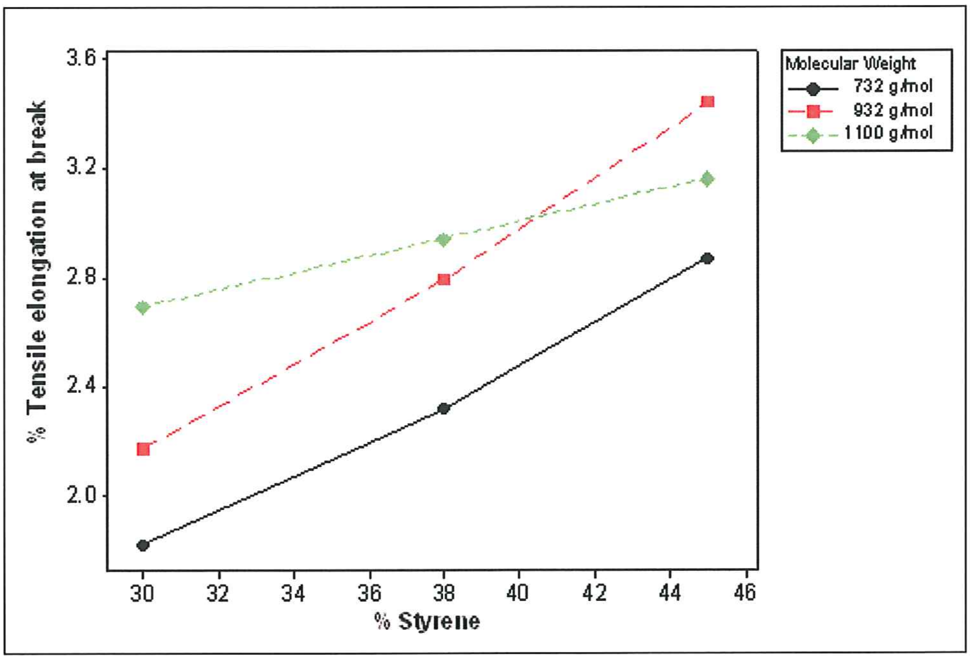


Figure 3.40 The effects of the styrene content and molecular weight on the tensile elongation at break of the vinylester resin, cure conditions; 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at150 ^{0}C.

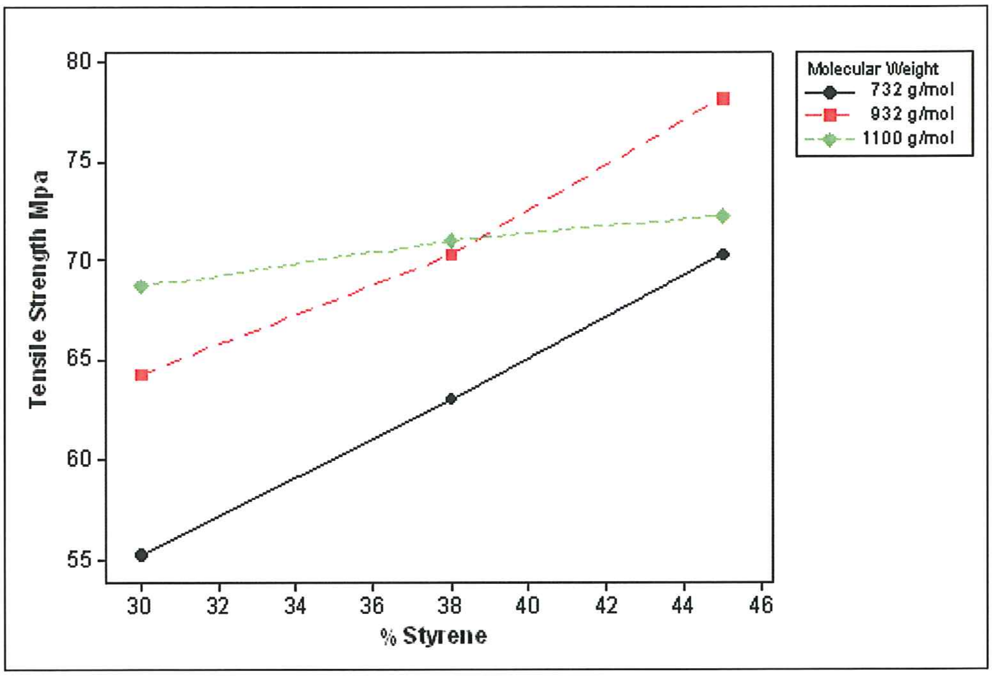


Figure 3.41 The effects of the styrene content and molecular weight on the tensile properties of the vinylester resin, cure conditions; 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1h at150 ^{0}C.

The cure conditions of the thermoset polymers affect the mechanical properties because there is a direct relationship between the degrees of the crosslinking and cure conditions. Figure 3.42 shows that at low cure temperature, the tensile strength were high. This resulted from the uncompleted network formation at low temperatures. Therefore, the chains were still mobile and elongation at break was high. Increasing the cure temperature forced the formation of a tightly network structure, resulting in enhanced tensile properties. However, at very high temperatures the tensile properties were lower. This can be attributed to the beginning of the chain scission at very high temperatures. Consequently, in order to obtain good mechanical properties, the cure conditions and the styrene content must be optimized for the given molecular weight vinylester resin.

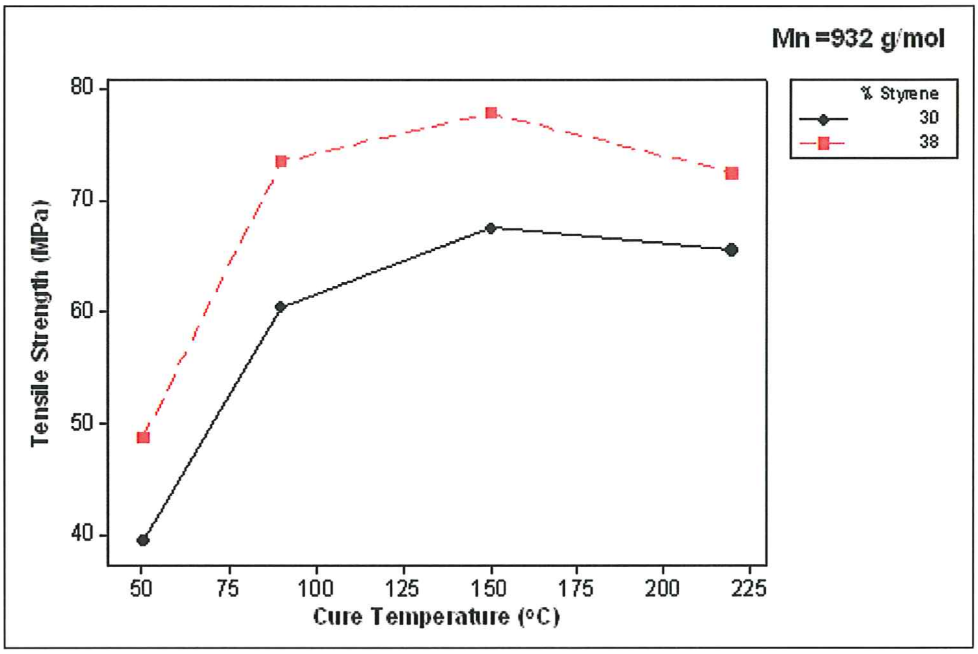


Figure 3.42 The effects of the cure temperature on the tensile strength of Mn=932 with styrene content 30% and 38%. The samples of each molecular weight were prepared under different cure conditions: Sample1, 1 h at 50 ^{0}C; Sample 2, 1 h at 90 ^{0}C, Sample 3, 1 h at 150 ^{0}C.

3.6.2. Flexural Testing of Plastics

The flexural strength of a material is defined as its ability to resist deformation under load. For materials that deform significantly but do not break, the load at yield, typically measured at 5% deformation/strain of the outer surface, is reported as the flexural strength or flexural yield strength. The test beam is under compressive stress at the concave surface and the tensile stress at the convex surface. Figure 3.43 shows the test geometry for ASTM D790. The analogous test to measure flexural strength in the ISO system is ISO 178. These test methods also give the procedure to measure a material's flexural modulus, which is the ratio of stress to strain in flexural deformation in the linear range. ISO 178 was used to measure flexural properties in this study.

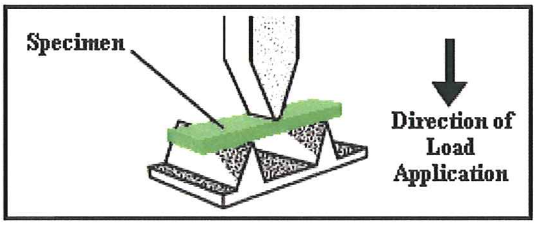


Figure 3.43 The flexural three points bend test equipment and the test sample

The flexural test was used to confirm the results of the tensile properties. The flexural elongation increased with increasing molecular weight. Enhancing the styrene content helped to increase the elongation, as expected. The flexural strengths were higher than the tensile strength because of the direction of the applied force. The results are listed in Table 3.16. All test results were shown in Appendices 3.

Table 3-16 The flexural properties of the vinylester resin series

Mn	**Styrene**	**Flexural Strength**	**Flexural Elongation**
g/mol	%	MPa	%
732	30	126.9	3.99
732	38	146.7	4.36
732	45	151.1	4.41
932	30	133.3	4.43
932	38	140.7	5.17
932	45	157.8	7.19
1100	30	147.8	5.54
1100	38	150.7	7.32
1100	45	159.3	6.53

The cure condition affects all mechanical properties. Different cure conditions were applied to the same polymer which has molecular weight 932 g/mol and a styrene content 45%. At a very low cure temperature, the double bonds could not be converted to crosslinks as monitored by IR in section 3.3.3. The elongation at the break of the resin, cured at 50 ^{0}C, 1h was 10.8 %. It was 7.2 at 90 ^{0}C, 1h as shown in Table 3.17. The decreasing of the cure temperature decreased the flexural modulus. The crosslink density was decreased resulting in flexibility in the networks at low temperatures. The uncompleted crosslinks provided the free movement of the vinylester chains, which formed flexible networks.

The flexural test results of VE 932/45 at different temperature are shown in Figure 3.44, 3.45, 3.46.

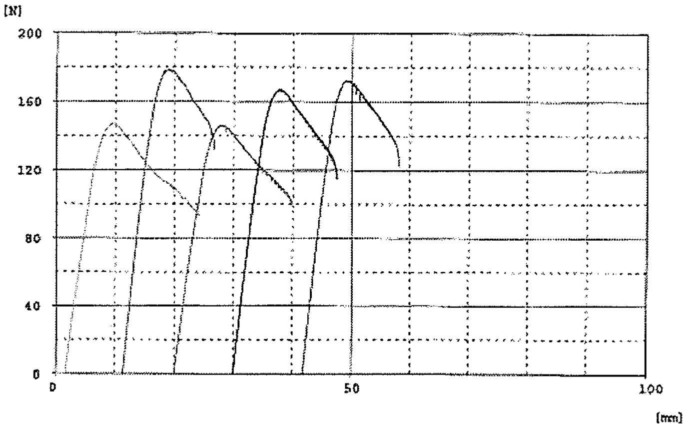


Figure 3.44 The flexural test graph of VE 932/45 which is cured at 50 ^{0}C, 1h

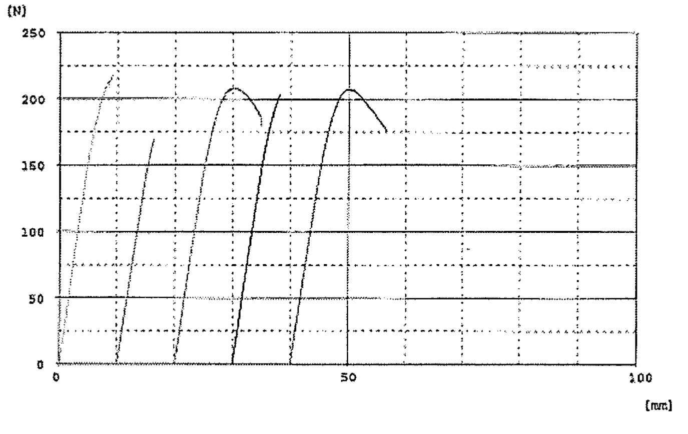


Figure 3.45 The flexural test graph of VE 932/45 which is cured at 90 ^{0}C, 1h

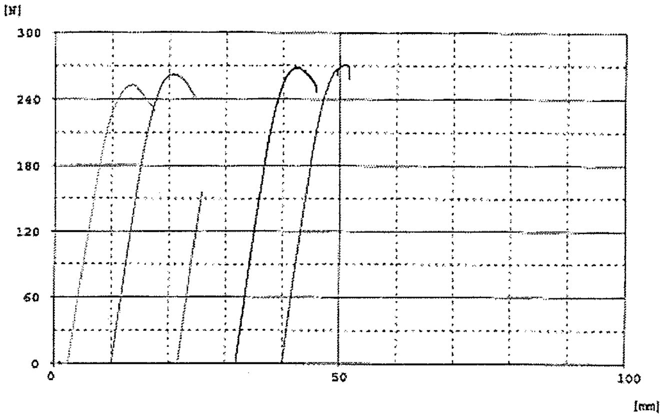


Figure 3.46 The flexural test graph of VE 932/45 which is cured at 150 ^{0}C, 1h

Table 3-17 The flexural properties depending on the cure temperatures

Sample	Temperature ^{0}C	Time h	Flexural Elongation %	Flexural Strength MPa
932/45	50	1	10.8	99.9
932/45	90	1	7.2	131.2
932/45	150	1	7	152.3

3.6.3. Heat Deflection Temperature, HDT

The deflection temperature is a measure of a polymer's resistance to distortion under a given load at elevated temperatures. The deflection temperature is also known as the deflection temperature under load, heat deflection temperature, or heat distortion temperature (HDT). The two common loads used are 0.46 MPa and 1.8 MPa. The common ASTM test is ASTM D 648, while the analogous ISO test is ISO 75. In this study, the test is performed under 1.8 MPa for ISO 75 Method A, by increasing temperature 2 °C/min until the specimen deflects 1 mm. Figure 3.47 shows the test equipment.

The deflection temperature test results are useful measurements of relative service temperature for a polymer when used in load-bearing parts. However, the deflection temperature test is a short-term test and should not be used alone for product design. All parameters such as the time of exposure to elevated temperature, the rate of temperature increase, and the part geometry affect the performance.

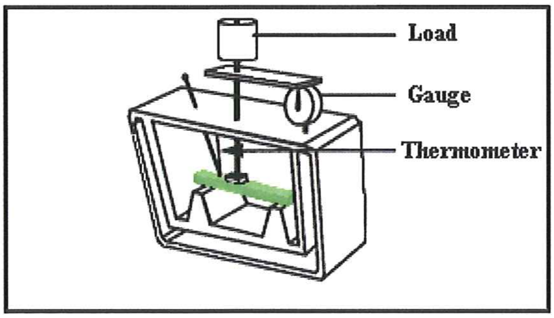


Figure 3.47 The HDT test equipment and the test sample

According to the results shown in Table 3.18, HDT values were directly affected by the styrene content and the molecular weight. Increasing the styrene content caused reduction in the HDT values. These results were due to the decrease in the crosslink density as the styrene content increased. High crosslinked density prevented the mobility of the chains under load. Therefore, 1 mm distortion required higher temperature. Figure 3.48 shows the relationships between the styrene content and the Mn on the HDT values. The increase of the crosslink density provides increase in the deflection temperature. A stiffer network could be obtained at high crosslink densities. The deflection of the temperature became higher. (Figure 3.49)

Table 3-18 The heat distortion temperatures (HDT) of the synthesisd vinylester resin series, Cure conditions; 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1 h at 150 ^{0}C

MW	% **Styrene**	**HDT**
g/mol	w/w	^{o}C
732	30	103.1
732	38	100.2
732	45	99.5
932	30	98.6
932	38	96.3
932	45	95.4
1100	30	93.7
1100	38	92.8
1100	45	92.1

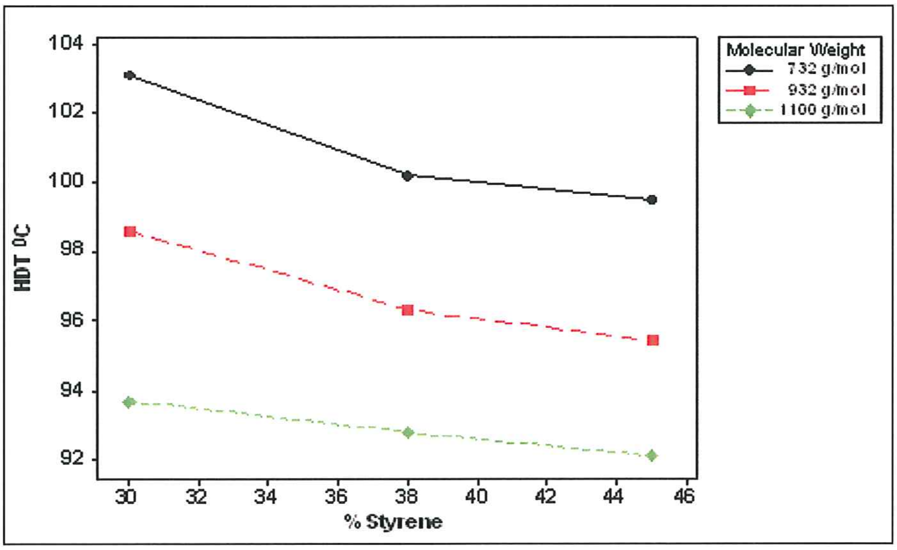


Figure 3.48 The relations between styrene content, molecular weight and HDT, Cure conditions; 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1 h at 150 ^{0}C

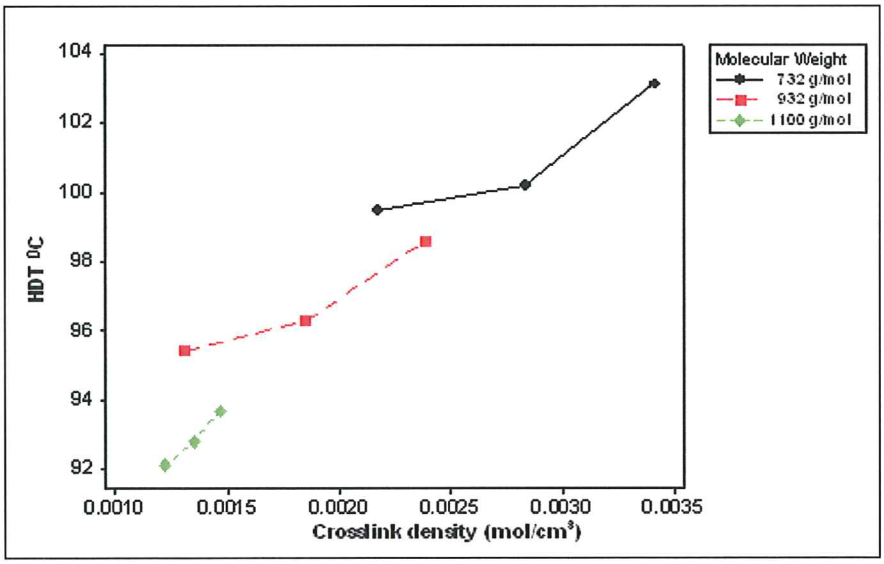


Figure 3.49 The relation between HDT values and crosslink densities for different molecular weight, Cure conditions; 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1 h at 150 ^{0}C

Cure condition was very important in determining the mechanical properties of the vinylester networks. Figure 3.50 shows the change in the HDT values for the samples which were cured at different temperatures. A low HDT value was obtained at low cure temperature because of the incompleteness of the crosslinking. At low cure temperatures, the chains were still mobile and could give a response to applied force easily. The increase in the cure temperature increased HDT values as expected. However, at very high temperatures when the crosslinking reactions were completed, the chain scission resulted in the loss of mechanical properties and in the reduction of HDT values.

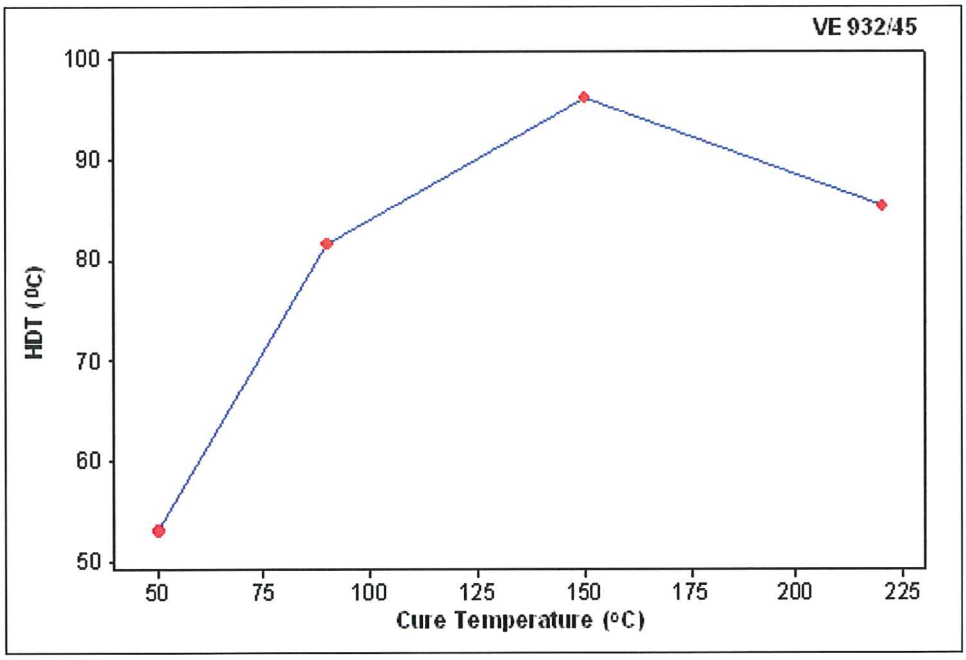


Figure 3.50 The effect of the cure temperature on the HDT values for the sample VE 932/45, The samples were prepared under different cure conditions: Sample1, 1 h at 50 ^{0}C; Sample 2, 1 h at 90 ^{0}C, Sample 3, 1 h at 150 ^{0}C and 1h at 215 ^{0}C

3.6.4. Izod Impact Strength Testing of Plastics

Several methods are used to measure the impact resistance of plastics - Izod, Charpy, Gardner, tensile impact, and many others. In this study, the un-notched Izod Impact test was used. This impact test allows designers to compare the relative impact resistance under controlled laboratory conditions and, consequently, is often used for material selection or quality control. However, these tests generally don't translate into explicit design parameters. Figure 3.51 shows the test apparatus of Izod impact strength. The result of the Izod test gives energy lost per unit of specimen thickness. The test methods generally utilized are ASTM D256 and ISO 180. In this study ISO 180 was used. The results may be reported as energy lost per unit cross-sectional area, kJ/m^2.

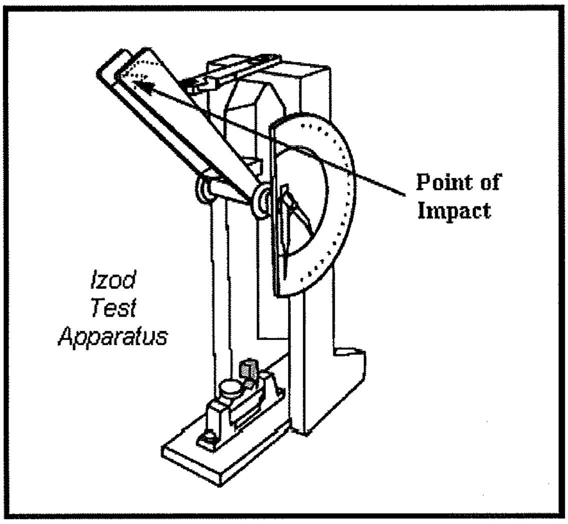


Figure 3.51 Izod Impact Test Equipment

A pendulum swings on its track and strikes the sample. The energy lost is measured for requiring the breaking the sample. The izod impact results are directly related to the toughness of the polymer samples. The results of the synthesisd vinylesters showed that, the impact resistance increased with the styrene content. The results could be explained by toughness. If the sample is tough, it can absorb more energy. Tough polymers have the ability to dissipate the energy internally. They have more free volume and more mobility. The energy can be dissipated without breaking of the chains. On the contrary, the networks that have a high crosslink density mean a decrease in toughness. The absorbed energy can not be distributed in these networks, because of the rigid structure. Therefore, the absorbed energy decreases with the increasing crosslink density. The degree of crosslinks increases the mechanical properties at a certain degree. But at high crosslink densities, the networks became rigid and some mechanical properties become lower. The effect of the molecular weight could be explained in the same way. The results showed that, the impact resistance increased by increasing the molecular weight of the precursor vinylester resin. Increase in the Mn means increasing the chain length, Mc, between crosslinks. Therefore, the resin became tougher and dissipated the absorbed energy. These relations are shown in Figure 3.52.

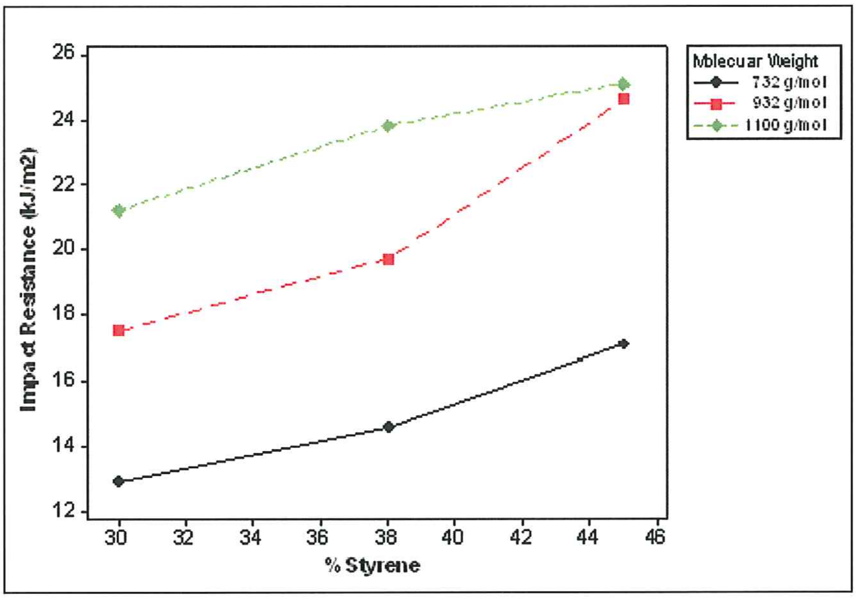


Figure 3.52 The effect of the styrene content and molecular weight on the impact resistance, Cure conditions; 1h at 50 ^{0}C, 1h at 90 ^{0}C, 1 h at 150 ^{0}C

Generally, cure conditions affected all the mechanical properties including impact resistance. The samples, which were cured at different temperature, were prepared for the impact test. The results of VE 932/45 are shown in Figure 3.53. At low cure temperatures, the impact resistance was low because of the low degree of the crosslink. Most of the vinylester resin chains remained without crosslinking resulting in the deterioration of the mechanical properties. When the cure temperature was increased, the networks became stronger and impact resistance increased. But the impact resistance may have decreased dramatically, because microcracks may have occured during the shrinkage at very high cure temperatures. This cause an increased deformation. In addition, it is known that chain scission that starts at high temperature results in lower mechanical properties.

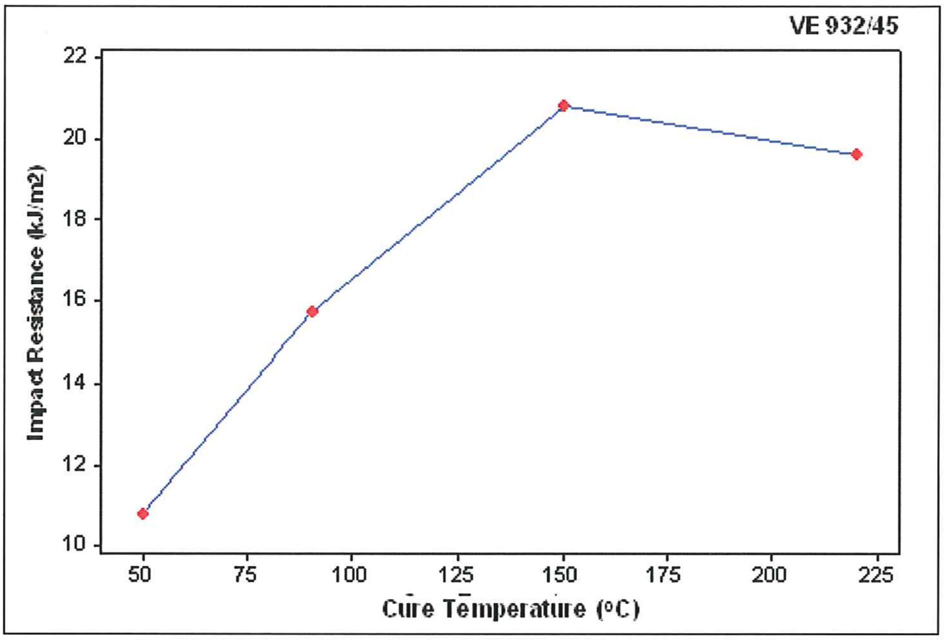


Figure 3.53 The effect of the cure temperature on the impact resistance for VE 932/45, The samples were prepared under different cure conditions: Sample1, 1 h at 50 ^{0}C; Sample 2, 1 h at 90 ^{0}C, Sample 3, 1 h at 150 ^{0}C and 1h at 215 ^{0}C

CHAPTER 4

4. CONCLUSIONS

The important results evaluated by this study can be summarized as follows:

1) The vinylester resin was synthesisd by a two-step method. The low molecular weight epoxy resin (EEW = 189 g/eq) was extended by the reaction with Bisphenol-A to obtain the required chain length. The consumption of the epoxy end group was followed by titration. Therefore, the EEW of the extended macromolecules could be estimated. The second polycondensation step between extented epoxy and methacrylic acid (MMA) was carried out at 110 ^{0}C. However, this step was not easy, because of the tendency of homopolymerization of MMA at 90 – 100 ^{0}C, caused gelation. This problem was overcome by using hydroquinone inhibitor to cap the radicals. The acid and epoxy ring consumptions during the reaction were followed by titration. Therefore, the esterification reaction between epoxy and MMA was carried out successfully.

2) Vinylester resins can not be used without diluting because of the very high viscosity. Therefore, all of the resins were dissolved in a styrene co-monomer. The styrene content directly affected the viscosity of the vinylester resin. The viscosity decreased as the styrene content increased, as expected. The viscosity of VE 932 with 30% styrene was 2700 cp, while with 38% styrene it was 1100 cp. Vinylesters with different molecular weight were synthesisd by

the two-step method. According to measurements, the vinylester with high Mn had higher viscosity. The viscosity of VE 732 with 30% styrene was 291 cp while the viscosity of VE 932 with 30% styrene was 910 cp. Longer chains had more entanglements resulting in higher viscosity. In addition, the intermolecular interactions were promoted with higher molecular weight. Therefore, the viscosity of the product could be adjusted by varying both the styrene content and the molecular weight of the resin to obtain the required application condition.

3) The network structure of the vinylester-styrene system was obtained by the free radical croslinking reaction. Benzoyl peroxide (BPO) and Methyl ethyl ketone peroxide (MEK-P) were used to produce the free radicals. CoNaph and Dimethylaniline (DMA) were the promoters used to initiate and to accelerate the decomposition of the peroxide. According to experimental results, BPO was more efficient compared to MEK-P. Two samples that had the same CoNaph and DMA content were crosslinked with BPO 1% and MEK-P 2%. Their gel points for the network formation were reached at the same time. BPO was semi-solid, while MEK-P was a low viscosity liquid. Therefore, MEK-P was preferred in this study, because of the easy handling properties.

4) The reactivity of the thermoset could give us a basic idea about the crosslinking ability, which is directly related with the mechanical and the rheological properties. This was a quick method and necessary to have information about the resin. The reactivity of the vinylester-styrene system was measured by the curing reaction temperature. The curing reaction was exothermic. The heat released during the crosslinking is related to both broken and the formed chemical bonds. The peak temperature was the maximum temperature measured by the thermocouple during the cure reaction. The gel times of the different samples were adjusted to the same time. Therefore, the

peak temperature could be compared for each 100 g of sample. The peak temperature of VE 732/38 was 174.8 ^{0}C, while for VE 932/38 was 166.2 ^{0}C and for VE 1100/38 it was 158.9 ^{0}C. It could be predicted that VE 1100/38 was lightly crosslinked. This means higher molecular weight results in low peak temperature. The high molecular weight resins had longer chains and the amount of the active end groups was lower to produce the crosslinks in the same amount of samples. According to measurements, the low molecular weight resins were more reactive than the high molecular weight resins in the same styrene content. However, the crosslinking mechanism was complex and it was investigated in more detail.

5) The cure condition was a very important factor used to obtain good mechanical properties. Four samples of VE 932/45 were cured at 23 ^{0}C for 7 h, 50 ^{0}C for 1h, 90 ^{0}C for 1h, 150 ^{0}C for 1h. The double bonds of methacrylate and styrene were monitored by FT-IR to observe the degree of double bond conversions to the network. The conversion of the styrene double bonds was 39.2% after curing at 23 ^{0}C, for 7 h. The conversion increased with higher cure temperatures; 51.8% at 50 ^{0}C, 1h and 95% at 150 ^{0}C,1h. However, the conversion could not be completed by applying additional 1 h at 150 ^{0}C because of the decrease in the mobility of the active end groups at the chain ends. Diffusion of the molecules decreased by the crosslinks, therefore the completion could not be realized. The initial rate of conversion of the MMA double bonds was higher than those of the styrene double bonds. However, the final conversion at 150 ^{0}C, 1 h was 86.4 % for MMA. The small styrene monomers were more mobile in comparison to MMA double bonds; therefore, styrene could continue to convert while conversion of MMA stopped.
6) The rubbery modulus of the samples was measured by the 3-point bending creep test. The test was applied to the samples at 40 ^{0}C above their Tg's. The

time-dependent deformation gave us important information about the rheological properties of the vinylester-styrene networks. The modulus was 36.7 MPa for the samples of VE 732/30, while it was 25.3 MPa and 15.4 MPa for VE 932/30 and VE 1100/30, respectively. Longer chains had more deformation under load owing to the higher mobility of the chains. The crosslink density decreased with increasing molecular weight of the resin. The crosslink densities were found to be 3.41E-3 mol/cm^{3,} 2.38E-3 mol/cm^3 and 1.47E-3 mol/cm^3 for VE 732/30, VE 932/30, VE 1100/30, respectively. The networks with low crosslink density resulted in large deformation during the creep test.

The styrene content affected the rubbery modulus of the vinylester networks. The rubbery modulus was 36.7 MPa for VE 732/30 while it was 30.2 MPa and 23.1 MPa for VE 732/38 and VE 732/45, respectively. The same trend was observed for all molecular weight series. This experimental result can be explained as follows; increase in the number of the styrene co-monomer molecules in the reaction medium resulted in loosing of network formation and obtaining lower crosslink densities. Therefore, lower modulus was measured in a high styrene content.

The effect of the styrene content was observed more strongly in samples with low molecular weight sample. The smaller polymer chains could be separated more easily from each other by the styrene. However, longer polymer chains had stronger intermolecular interactions and entanglements resulting in reduction of the styrene effect. Consequently, the rubbery modulus and crosslink densities decreased with increasing molecular weight and increasing styrene content.

7) The viscoelastic properties of the vinylester networks are defined by the Tg values. The Tg values were measured by DMA. The peaks of the tan delta were considered as Tg values. Tg values were measured as 118.4 ^{0}C, 113.5 ^{0}C, 108.3 ^{0}C for VE 732/30, VE 932/30 and VE 1100/30, respectively. Decreasing Tg was observed with increasing molecular weight. The micro segmental chain motions start at around the Tg. The low molecular weight vinylesters had short chain length between the crosslinks. The molecular weight between the crosslinks is called as Mc. The Mc values were calculated as 353 g/mol, 509 g/mol and 759 g/mol for VE 732/30, VE 932/30 and VE 1100/30. The segmental motions started at higher temperature in low molecular weight resins.

8) The vinylester resins shrink during the curing reaction as all the thermoset resins. The specific volume decreases owing to the crosslinks between the polymer chains. According to measurements, the shrinkage was enhanced with increasing styrene content. The shrinkage was measured 7.6 for VE 732/30 and 9.7 for VE 732/45. The effect of the molecular weight on the shrinkage of the vinylester resin was investigated. The shrinkage was measured as 6.9 %, 5.9 % and 4.3 % for VE 732/30, 932/30, 1100/30, respectively. The longer chains had high Mc that meant high volume between the chains. These results can be attributed to the higher specific volume caused by the low crosslink density in materials with for high molecular weight. The two samples of VE 932/45 were cured at two different cure conditions; 90 ^{0}C, 2h and 140 ^{0}C, 1h. The shrinkage of the low temperature cured resin was 7.4 %. However, the sample that was cured at 140 ^{0}C had 8.7 % shrinkage. When the resin was cured at high temperature, the crosslink densities were increased resulting in higher shrinkage.

9) Water absorption is one of the most important properties of the vinylester resins. According to experimental results, the water absorption values are directly related with the crosslink densities. When the crosslink densities decreased, the free volume in the network increased. This resulted in enhanced ability to keep the water in the network. VE 732/38 had higher crosslink density than VE 932/38. The water absorption was 0.1233 % and 0.1476 % for VE 732/38 and VE 932/38, respectively. At higher cure temperature, lower water absorption values were obtained, as expected.

10) The mechanical properties of the vinylester resin are strongly related with the network structure. The tensile extension at break was high for the resins, which had high styrene content and high molecular weight values. The chain mobility is higher at low crosslink densities. The tensile elongations at break were measured as 2.32 % and 2.79 % for VE 732/38 and VE 932/38, respectively. The toughness was increased by the molecular weight, and more flexible networks were obtained. The styrene content and the cure conditions also affected the tensile and the flexural properties. The samples were cured at 50 ^{0}C, 90 ^{0}C and 150 ^{0}C. The flexural elongations at break decreased with increasing temperature. High cure temperature means high double bond conversion to form a tightly network structure.

All mechanical properties were affected by the molecular weight of the vinylester resin, co-monomer styrene content and cure conditions. All of these effects were investigated and explained in this study.

11) The epoxy-acrylate based vinylester resin was synthesisd by the new 2 step method with new catalyst and inhibitor formulation which worked on both a lab scale and under industrial conditions. The new formulated vinylester called " Polives", as a trademark of Poliya Poliester. Many boat producers have used Polives instead of classical polyesters in Turkey since 2005.

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R. T. Dowd, et al., U. S. Patent 3, 634, 542; C. A. May, U. S. Patent 3, 637, 618;
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[66] ISO standart "Standard Test Method for Tensile Properties of Plastics"

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APPENDIX A

ACID VALUE DETERMINATION BY ACID END GROUP TITRATION

Phenolphthalein is used as a indicator.

0.1 N KOH solution in ethanol is used as a titrant.

Titration of resin

A - 0.9 – 1 g resin is weighted
B - The resin dissolved in ethanol
C – Three drops of phenolphthalein are added to solution
D – Resin solution is titrated by NaOH solution until end-point

Calculation

Acid value = V*N / M
V: Volume of consumed KOH solution (ml)
N : Normality of KOH solution (ml)
M: Weight of resin sample (g)

APPENDIX B

EPOXY VALUE DETERMINATION BY EPOXY END GROUP TITRATION

Indicator is prepared by dissolving of crystal violet in acetic acid. The solution is 1% of crystal violet.

0.5 N HBr is prepared by dissolving of HBr (47%) in glacial acetic acid.

Factor number of HBr is determined. Sodium Carbonate is weighted and dissolved in acetic acid. Three drops of crystal violet indicator is added to solution. Solution is titrated by HBr until observing of light green. Factor number of HBr solution is calculated by following equation:

$F = M*1000/ 26.5*V$

M: Weight of sodium carbonate

V : Volume of HBr (ml)

Titration of Solid Epoxy Resin:

A - 1.2 – 1.5 g of resin is weighted

B - 20 ml of chloroform is added and the resin dissolved in chloroform

C - 60 ml of acetic acid is added

D - Three drops of crystal violet solution in acetic acid are added as a indicator

E - The resin solution is titrated with 0.5N HBr solution until the color of resin solution turns from blue to green

Titration of Liquid Epoxy Resin

A – 0.6 – 0.7 g of resin is weighted

B – Resin is solved in 60 ml acetic acid

C - Three drops of chrystal violet solution in acetic acid are added as a indicator

D - The resin solution is titrated with 0.5N HBr solution until the color of resin solution turns from blue to green

Calculations

Epoxy Value, EV (mol epoxy/ 100g) = V*N*F / M*10

V: Volume of consumed HBr solution (ml)

N : Normality of HBr solution (ml)

F : Factor of HBr solution

M: Weight of resin sample (g)

EEW for solid epoxy resin (g/eq) = 1000 / EV

EEW for liquid epoxy resin (g/eq)= 100 / EV

APPENDIX C

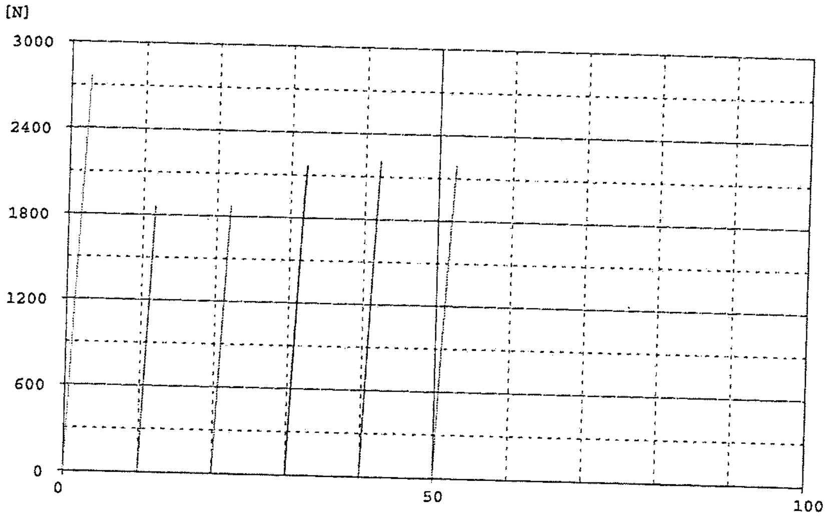
TENSILE TEST RESULTS OF VINYLESTER SERIES

The following graphics show tensile test results of vinylester samples with various molecular weight and styrene contents.

POLIYA ÇEKME TESTI ISO 527
SEFFAF

Tarih: 12.01.2005
Müsteri:
Num.Adi:
Sarj No: 732/30
Operatör:

Shape: Plate
Gauge Length: 105.00



Calc. CP1, CP2 CP Unit Pass-Fail Unit	Elastiklik Modülü 120.000, 1000.000 [N] -.--, -.-- [MPa]	Max-Yük -.--, -.-- [kgf]	Çekme Dayanimi -.--, -.-- [MPa]	Max-Yükteki Uzama -.--, -.-- [%]	Kopma Yükü -.--, -.-- [kgf]	Kopmadaki Uzama -.--, -.-- [%]	Width: -.--, -.-- [mm]	[mm] Thickness: -.--, -.-- [mm]
1	~~2500.87~~	~~208.135~~	~~67.1136~~	~~1.83429~~	~~202.022~~	~~2.88238~~	~~11.0000~~	~~5.00000~~
2	3468.00	224.974	48.8246	1.78238	209.974	1.77905	10.0000	3.85000
3	2990.10	191.000	50.9387	1.78476	197.499	1.78380	9.96000	3.77000
4	2907.49	273.626	57.5669	1.86524	272.499	1.86932	9.90000	4.00000
5	3925.19	272.519	57.1367	1.92190	224.524	1.92130	10.1000	3.71000
6	2997.30	276.000	51.7982	1.86324	271.000	1.86571	10.0000	3.86000
Mean	~~3131.35~~	242.182	~~55.5513~~	2.24497	241.040	~~2.01706~~	10.1616	4.03167
Std-D (N-1)	381.019	37.4992	11.3040	0.45519	36.6224	0.35246	0.57982	0.43737
~~Comment:~~								

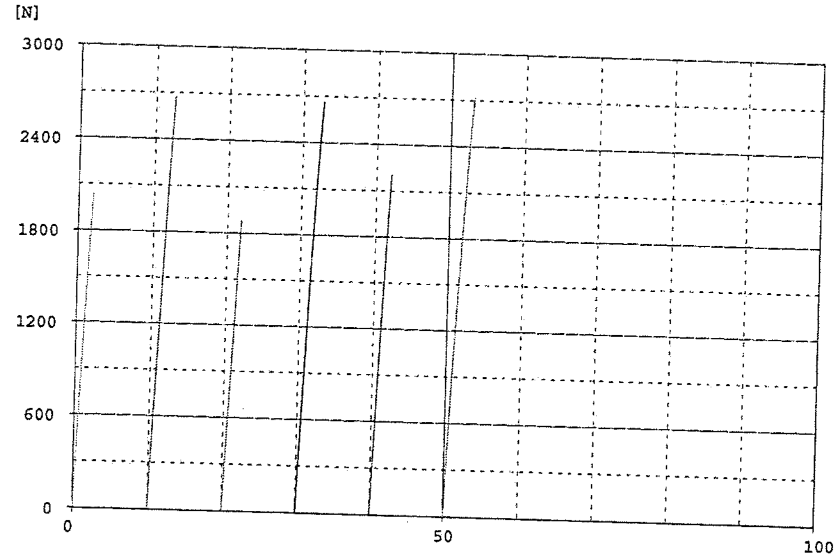
Figure C.1 Tensile test graph of VE732/30, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA ÇEKME TESTI ISO 527

SEFFAF

Tarih: 25.01.2005
Müsteri:
Num.Adi:
Sarj No: 732/ 38
Operatör:

Shape: Plate
Gauge Length: 105.00



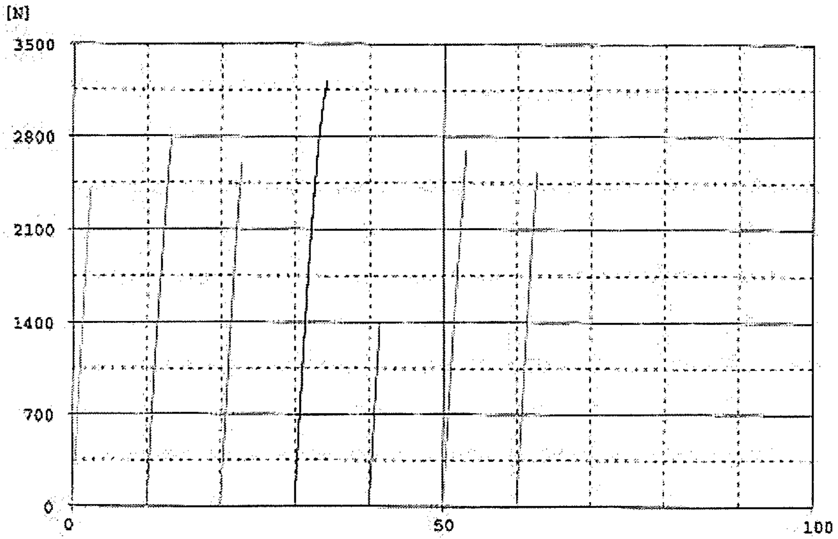
Calc. CP1, CP2 CP Unit Pass-Fail Unit	Elastiklik Modülü 120.000, 1000.000 [N] -.---, -.--- [MPa]	Max-Yük -.---, -.--- [kgf]	Çekme Dayanimi -.---, -.--- [MPa]	Max-Yükteki Uzama -.---, -.--- [%]	Kopma Yükü -.---, -.--- [kgf]	Kopmadaki Uzama -.---, -.--- [%]	Width: -.---, -.--- [mm]	[mm] Thickness: -.---, -.--- [mm]
1	~~2100.87~~	~~208.149~~	~~37.1136~~	~~1.83429~~	~~208.022~~	~~1.83238~~	~~11.0000~~	~~5.00000~~
2	3098.73	272.519	68.8646	2.48238	272.519	2.47905	10.0800	3.85000
3	2932.10	191.706	50.9284	1.78476	191.579	1.78381	9.95000	3.71000
4	2947.49	271.626	67.2664	2.57524	271.499	2.56952	9.90000	4.00000
5	3175.43	224.974	57.1567	1.92190	224.974	1.92190	10.0000	3.86000
6	2937.51	278.000	71.5983	2.86524	278.000	2.86571	10.1000	3.77000
Mean	~~2865.35~~	241.162	~~58.8213~~	2.24397	241.099	~~2.24206~~	10.1716	4.03167
Std-D (N-1)	387.673	37.5928	13.2040	0.45497	37.6281	0.45446	0.41282	0.48437
~~Comment :~~								

Figure C.2 Tensile test graph of VE732/38, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA ÇEKME TESTI ISO 527

SEFFAF

Tarih: 11.01.2005
Müsteri:
Num.Adi:
Sarj No: 732/45
Operatör:
Shape: Plate
Gauge Length: 105.00



Calc.	Elastik Modülü	Max-Yük	Çekme Dayanımı	Max-Yükteki Uzama	Kopma Yükü	Kopmadaki Uzama	Width:	Thickness:
CP1, CP2	120.020, 1020.660							
CP Unit	[N]							
Pass-Fail	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--
Unit	[MPa]	[kgf]	[MPa]	[%]	[kgf]	[%]	[mm]	[mm]
1	2116.11	246.643	~~-43.9772~~	2.24095	246.643	~~2.24095~~	11.0000	5.00000
2	2885.01	282.971	72.8012	3.06143	282.971	3.06095	9.65000	3.95000
3	2926.70	241.417	61.7486	2.31905	241.290	2.31810	10.1700	3.77000
4	2993.16	327.456	87.1859	4.04000	327.328	4.04000	9.42000	3.91000
5	2908.62	140.848	~~37.5011~~	1.30524	140.848	~~1.30286~~	9.42000	3.91000
6	2857.84	243.967	64.1206	2.56190	243.839	2.56190	9.95000	3.75000
7	3013.41	244.222	64.8796	2.38238	244.222	2.38190	9.95000	3.71000
Mean	2814.41	246.789	61.7449	2.55871	246.734	2.55810	9.93714	4.00000
S.D (N-1)	312.925	56.3962	16.7750	0.83742	56.3690	0.83803	0.54796	0.45059

Comment :

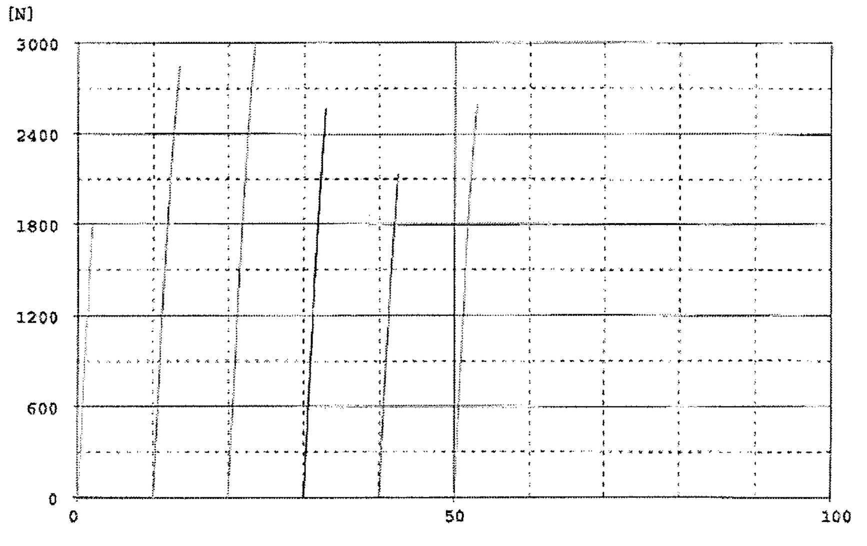
70.1 2.87

Figure C.3 Tensile test graph of VE732/45, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA ÇEKME TESTI ISO 527

SEFFAF

Tarih: 28.01.2005
Müsteri:
Num.Adi: 932/30
Sarj No:
Operatör:
Shape: Plate
Gauge Length: 105.00



Calc.	Elastiklik Modülü	Max-Yük	Çekme Dayanimi	Max-Yükteki Uzama	Kopma Yükü	Kopmadaki Uzama	Width:	Thickness:
CP1, CP2	0 20.000, 1000.000							
CP Unit	[N]							
Pass-Fail	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--
Unit	[MPa]	[kgf]	[MPa]	[%]	[kgf]	[%]	[mm]	[mm]
1	~~1916.31~~	182.146	~~32.4772~~	1.82476	182.019	~~1.81905~~	11.0000	5.00000
2	2976.11	289.217	71.9031	3.29667	289.217	2.94429	9.68000	3.81000
3	3097.02	315.347	70.5527	3.48429	315.347	2.80190	10.0500	3.82000
4	2894.43	261.557	63.9658	2.70571	261.557	2.20476	10.0500	3.99000
5	2789.52	217.709	56.3750	2.37667	217.709	2.37714	9.94000	3.81000
6	2879.04	264.488	64.9789	2.76714	264.488	2.46762	10.0800	3.96000
Mean	2758.57	255.077	60.5421	2.74254	255.056	2.43570	10.1333	4.06500
Std.D (N-1)	375.420	48.2571	17.2076	0.60587	48.2957	0.60654	0.44961	0.46496

Comment:

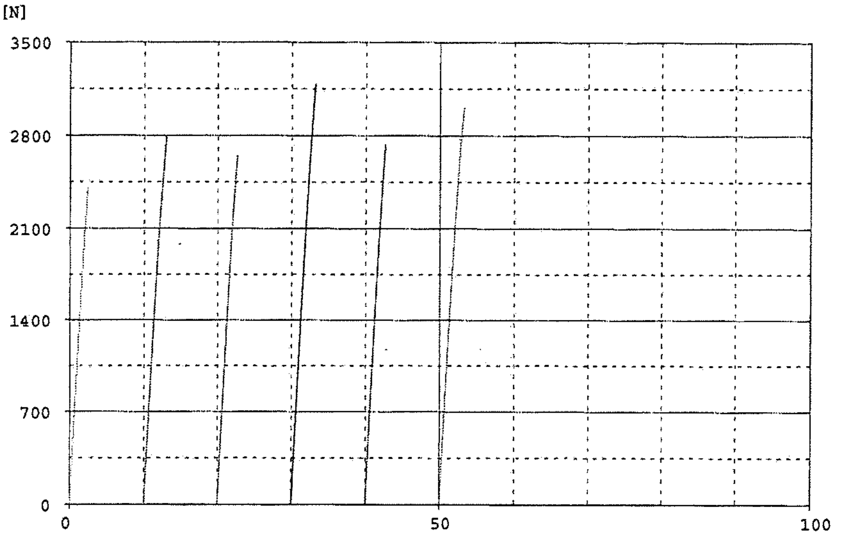
Figure C.4Tensile test graph of VE932/30, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA ÇEKME TESTI ISO 527

SEFFAF

Tarih: 26.01.2005
Müsteri:
Num.Adi: 932/38
Sarj No:
Operatör:

Shape: Plate
Gauge Length: 105.00



Calc.	Elastiklik Modülü	Max-Yük	Çekme Dayanimi	Max-Yükteki Uzama	Kopma Yükü	Kopmadaki Uzama	Width:	Thickness:
CP1, CP2	120.000, 1000.000							
CP Unit	[N]		✓			✓		
Pass-Fail	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--
Unit	[MPa]	[kgf]	[MPa]	[%]	[kgf]	[%]	[mm]	[mm]
1	~~2101.59~~	~~246.006~~	~~43.8636~~	~~2.24190~~	~~245.879~~	~~2.23524~~	~~11.0000~~	~~5.00000~~
2	2771.10	285.265	69.2094	2.85667	285.265	2.85524	10.0800	4.01000
3	2868.07	269.587	63.8855	2.51381	269.587	2.51143	10.0200	4.13000
4	2943.06	324.652	78.4538	3.04952	324.652	3.04571	10.1200	4.01000
5	2810.24	278.000	62.2786	2.47762	278.000	2.47810	10.3000	4.25000
6	2850.20	307.699	78.0714	3.06476	307.699	3.06476	9.45000	4.09000
Mean	~~2724.65~~	285.201	65.9604	2.70071	285.180	2.69841	10.1616	4.24833
Std-D (N-1)	323.236	27.9084	12.8019	0.33874	27.9443	0.33984	0.50137	0.37886

Comment:

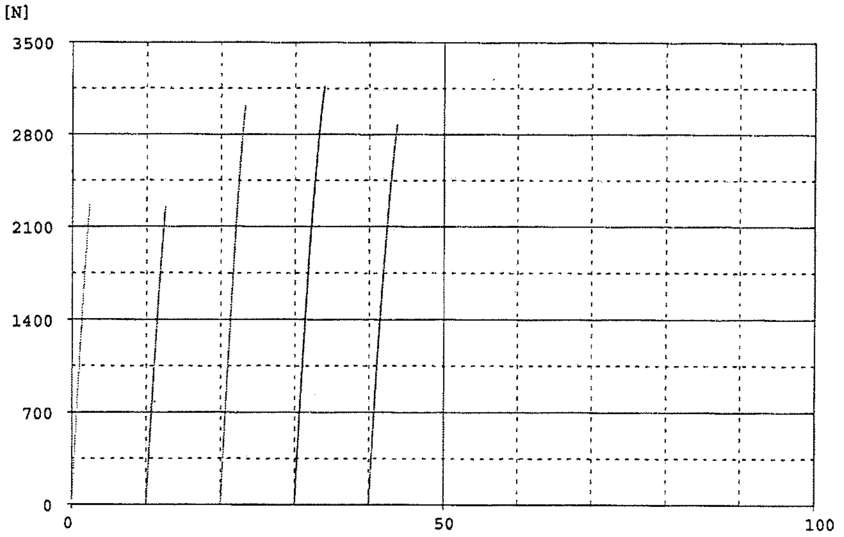
70,3 2,79

Figure C.5Tensile test graph of VE932/38, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA ÇEKME TESTI ISO 527
SEFFAF

Tarih: 22.01.2005
Müsteri:
Num.Adi: 932/45
Sarj No:
Operatör:

Shape: Plate
Gauge Length: 105.00



[mm]

Calc.	Elastiklik Modülü	Max-Yük	Çekme Dayanimi	Max-Yükteki Uzama	Kopma Yükü	Kopmadaki Uzama	Width:	Thickness:
CP1, CP2	120.000, 1000.000							
CP Unit	[N]		✓			✓		
Pass-Fail	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--
Unit	[MPa]	[kgf]	[MPa]	[%]	[kgf]	[%]	[mm]	[mm]
~~1~~	~~2097.75~~	~~230.710~~	~~41.1363~~	~~2.13714~~	~~230.710~~	~~2.13714~~	~~11.0000~~	~~5.00000~~
~~2~~	~~2687.34~~	~~228.926~~	~~57.3582~~	~~2.35333~~	~~228.926~~	~~2.35048~~	~~10.3000~~	~~3.80000~~
3	2883.14	307.444	78.0845	3.06667	307.317	3.06286	9.80000	3.94000
4	2729.82	322.485	81.1396	3.70857	322.357	3.70095	10.1500	3.84000
5	2691.23	293.423	75.2917	3.57095	293.423	3.56952	9.70000	3.94000
Mean	~~2617.86~~	276.598	66.6021	2.96733	276.547	2.96419	10.1900	4.10400
Std-D (N-1)	335.816	43.9273	16.9752	0.70521	43.8717	0.70350	0.51527	0.50466

Comment:

78.2 3.44

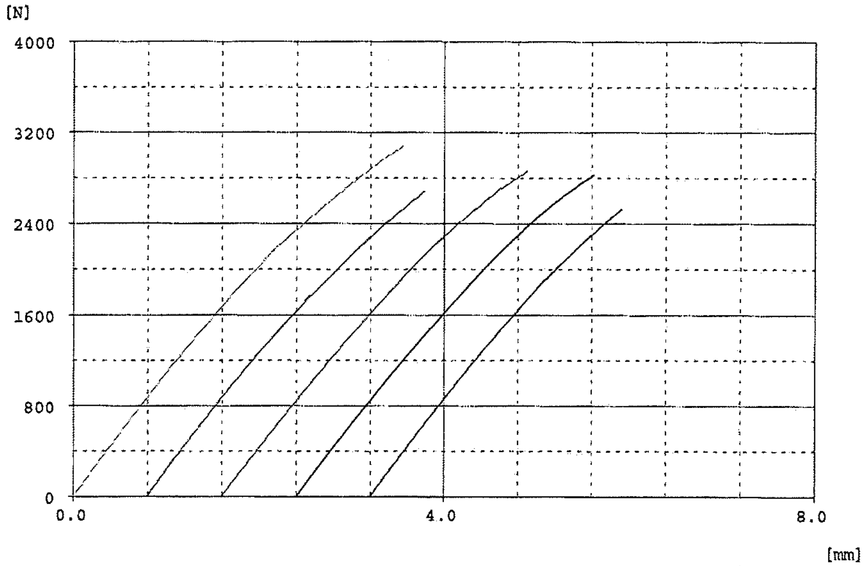
Figure C.6Tensile test graph of VE932/45, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA ÇEKME TESTI ISO 527

SEFFAF

Tarih: 12.02.2005
Müsteri:
Num.Adi: 1100/38
Sarj No:
Operatör:

Shape: Plate
Gauge Length: 105.00



Calc.	Elastiklik Modülü	Max-Yük	Çekme Dayanimi	Max-Yükteki Uzama	Kopma Yükü	Kopmadaki Uzama	Width:	Thickness:
CP1, CP2	120.000, 1000.000							
CP Unit	[N]							
Pass-Fail	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--
Unit	[MPa]	[kgf]	[MPa]	[%]	[kgf]	[%]	[mm]	[mm]
1	~~2178.50~~	~~321.395~~	~~59.7337~~	~~3.31714~~	~~341.291~~	~~3.37919~~	~~11.0000~~	~~5.00000~~
2	2663.51	303.238	73.9205	2.92100	308.336	2.92667	10.2000	4.01000
3	2701.13	289.344	72.0933	3.23429	283.344	3.23238	9.67000	4.02000
4	2889.75	308.336	73.2700	3.10423	303.238	3.10711	9.67000	4.03000
5	2730.36	267.675	65.0851	2.64905	275.634	2.64771	9.66000	4.05000
Mean	~~2632.76~~	295.998	~~68.7277~~	3.03695	295.972	~~3.05833~~	10.0800	4.21300
Std-D (N-1)	308.155	17.9456	6.39213	0.28100	17.1384	0.13258	0.58313	0.42067

Comment:

71.1 2.97

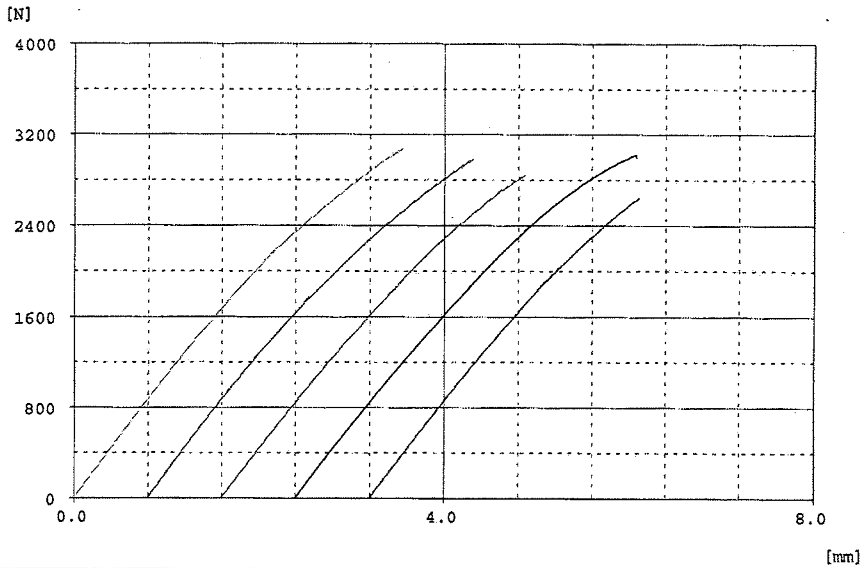
Figure C.7Tensile test graph of VE1100/38, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA ÇEKME TESTI ISO 527

SEFFAF

Tarih: 18.02.2005
Müsteri:
Num.Adi: 1100/45
Sarj No:
Operatör:

Shape: Plate
Gauge Length: 105.00



Calc.	Elastiklik Modülü	Max-Yük	Çekme Dayanimi	Max-Yükteki Uzama	Kopma Yükü	Kopmadaki Uzama	Width:	Thickness:
CP1, CP2	120.000, 1000.000							
CP Unit	[N]							
Pass-Fail	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--
Unit	[MPa]	[kgf]	[MPa]	[%]	[kgf]	[%]	[mm]	[mm]
1	~~2078.56~~	~~311.395~~	~~55.5227~~	~~3.33714~~	~~311.268~~	~~3.33619~~	~~11.0000~~	~~5.00000~~
2	2633.88	303.238	73.4241	3.33000	303.238	3.32667	10.1000	4.01000
3	2701.34	289.344	72.9933	3.11429	289.344	3.11238	9.67000	4.02000
4	2729.23	308.336	78.1734	3.50429	308.336	3.50571	9.67000	4.00000
5	2641.80	267.675	65.0751	2.74905	267.675	2.74571	9.96000	4.05000
Mean	~~2556.76~~	295.998	~~69.0377~~	3.20695	295.972	~~3.20533~~	10.0800	4.21600
Std-D (N-1)	319.815	17.9456	8.89813	0.29102	17.9184	0.29239	0.54713	0.43867

Comment:

72.4 3.17

Figure C.8Tensile test graph of VE1100/45, cured at 1h 50°C, 1 h 90°C, 1h 150°C

APPENDIX D

FLEXURAL TEST RESULTS OF VINYLESTER RESIN SERIES

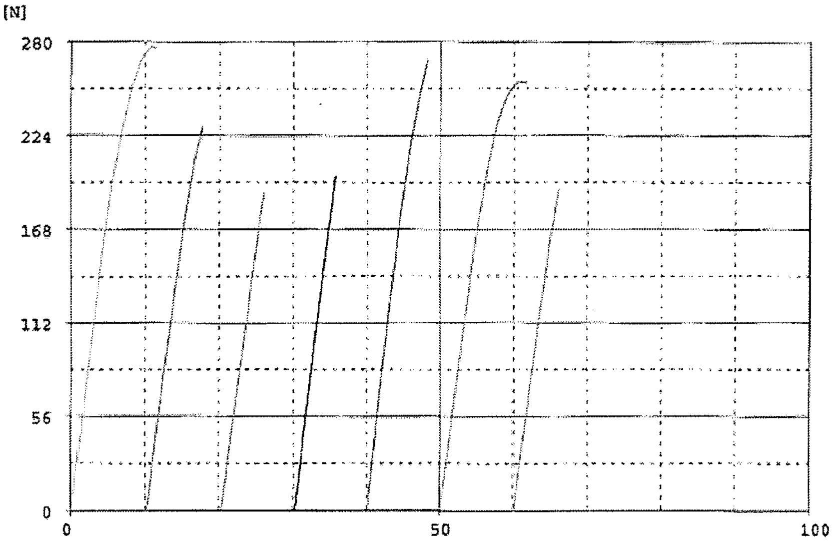
The following graphics show flextural test results of vinylester samples with various molecular weight and styrene contents.

POLIYA EGILME TESTI ISO 178

SEFFAF

Tarih: 12.01.2005
Müsteri:
Num.Adi: 732/30
Sarj No:
Operatör

Shape: Plate
Distance between supports: 64.00



Calc. CP1, CP2 CP Unit Pass-Fail Unit	Elastic 15.000, 80.000 [N] -.--, -.-- [MPa]	Max-yük -.--, -.-- [kgf]	Egilme dayanimi -.--, -.-- [MPa]	Max-yükteki uzama -.--, -.-- [%]	Kopma yükü -.--, -.-- [kgf]	Kopmadaki uzama -.--, -.-- [%]	Width: -.--, -.-- [mm]	[mm] Thickness: -.--, -.-- [mm]
1	~~3484.85~~	~~28.2971~~	~~155.696~~	~~6.65376~~	~~28.1824~~	~~6.90784~~	~~10.0800~~	~~4.12000~~
2	3581.41	23.3770	133.109	4.51778	23.3770	4.51896	10.1300	4.04000
3	3471.52	19.2675	120.139	3.55026	19.2624	3.54909	10.2700	4.01000
4	3967.49	20.3305	115.024	3.35391	20.3305	3.35449	10.4000	4.00000
5	3890.98	27.4303	146.296	4.98950	27.4303	4.98980	10.4000	4.11000
6	~~3631.42~~	~~26.0792~~	~~143.204~~	~~6.69911~~	~~26.0410~~	~~6.88124~~	~~10.3500~~	~~4.07000~~
7	3672.84	19.5913	120.327	3.54731	19.5913	3.54760	10.0700	3.98000
Mean	~~3672.93~~	23.4818	~~133.356~~	4.75880	23.4593	~~4.82129~~	10.2428	4.04714
Std-D (N-1)	169.619	3.83758	18.0630	1.43579	3.81036	1.53347	0.14762	0.05469
			126.9			3.99		

Comment:

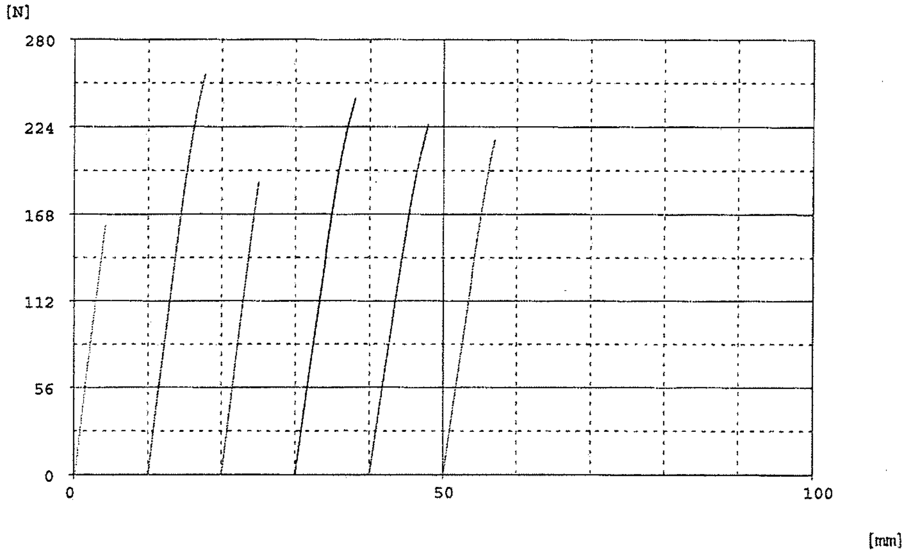
Figure D.1 Flexural test graph of VE732/30, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA EGILME TESTI ISO 178

SEFFAF

Tarih: 25.01.2005
Müsteri:
Num.Adi: 732/38
Sarj No:
Operatör

Shape: Plate
Distance between supports: 66.56



Calc.	Elastic	Max-yük	Egilme dayanimi	Max-yükteki uzama	Kopma yükü	Kopmadaki uzama	Width:	Thickness:
CP1, CP2	15 000, 80 000							
CP Unit	[N]							
Pass-Fail	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--
Unit	[MPa]	[kgf]	[MPa]	[%]	[kgf]	[%]	[mm]	[mm]
1	~~10361.8~~	~~17.6394~~	~~126.850~~	~~1.72440~~	~~17.6394~~	~~1.72419~~	9.88000	3.00000
2	3761.20	28.0676	146.433	4.70189	28.0676	4.70192	10.3000	4.10000
3	4525.48	~~19.1950~~	111.918	2.70520	19.1950	2.70520	9.95000	4.09000
4	4099.35	23.5658	140.456	4.35017	23.5658	4.35117	9.95000	4.17000
5	3719.66	23.7616	150.189	4.31897	23.7616	4.31897	9.90000	3.93000
6	3511.17	23.8978	148.437	4.08769	23.8978	4.08769	10.2500	3.92000
Mean	4996.68	22.6007	~~149.047~~	3.64447	22.6007	~~3.64818~~	10.0313	3.80677
Std-D (N-1)	2491.95	3.94335	20.6623	1.16017	3.94335	1.16189	0.19376	0.38293
			1467			4.36		

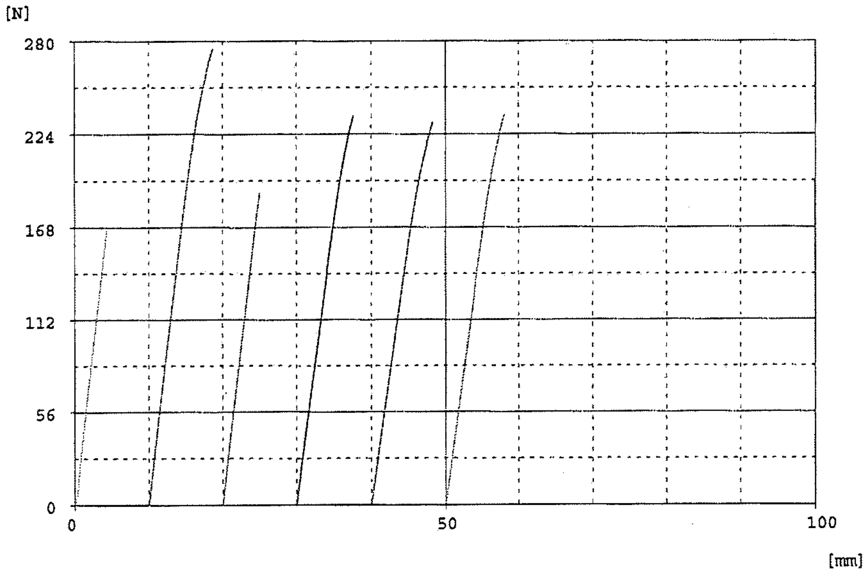
Comment:

Figure D.2 Flexural test graph of VE732/38, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA EGILME TESTI ISO 178
SEFFAF

Tarih: 11.01.2005
Müsteri:
Num.Adi: 732/45
Sarj No:
Operatör

Shape: Plate
Distance between supports: 66.56



Calc.	Elastic	Max-yük	Egilme dayanimi	Max-yükteki uzama	Kopma yükü	Kopmadaki uzama	Width:	Thickness:
CP1, CP2	15.000, 80.000							
CP Unit	[N]							
Pass-Fail	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--
Unit	[MPa]	[kgf]	[MPa]	[%]	[kgf]	[%]	[mm]	[mm]
1	~~10065.8~~	~~17.0394~~	~~176.850~~	~~1.82440~~	~~17.0394~~	~~1.82419~~	~~9.88000~~	~~3.09000~~
2	3853.20	28.0676	156.435	4.90189	28.0676	4.90442	10.2000	4.15000
3	~~4304.75~~	~~19.1961~~	~~112.919~~	~~2.75520~~	~~19.1961~~	~~2.75520~~	~~9.95000~~	~~4.09000~~
4	3889.12	23.9378	149.453	4.08817	23.9378	4.08897	9.95000	3.97000
5	3439.00	23.6446	150.190	4.41796	23.6446	4.41769	9.98000	3.93000
6	3417.44	23.9888	148.436	4.25117	23.9888	4.25117	10.3500	3.91000
Mean	4829.78	22.6457	~~149.047~~	3.70647	22.6457	~~3.70694~~	10.0516	3.85667
Std-D (N-1)	2351.76	3.92935	20.6623	1.16831	3.92935	1.16892	0.18236	0.38713

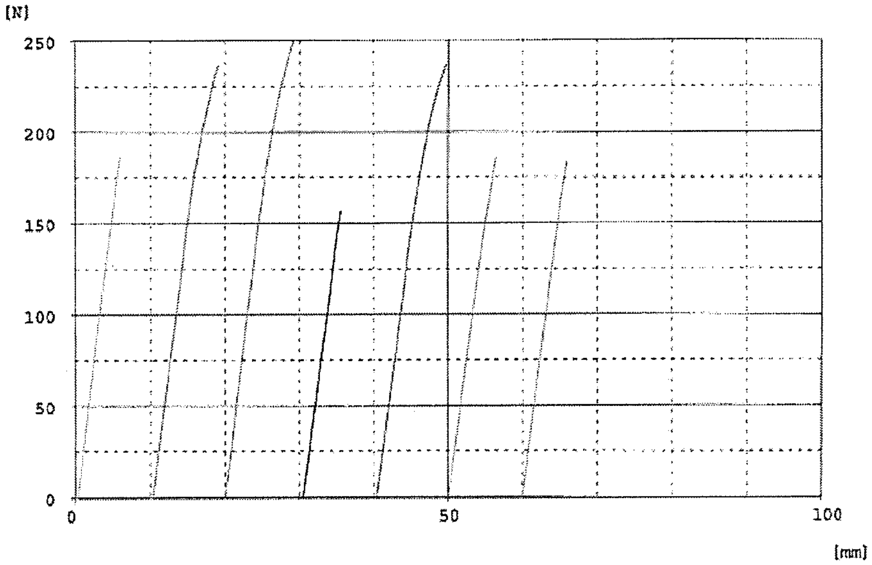
Comment:

Figure D.3 Flexural test graph of VE732/45, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA EGILME TESTI ISO 178
SEFFAF

Tarih: 28.01.2005
Müsteri:
Num.Adi: 932/30
Sarj No:
Operatör

Shape: Plate
Distance between supports: 64,00



Calc. CP1, CP2 CP Unit Pass-Fail Unit	Elastic 15.000, 80.000 [N] -.--, -.-- [MPa]	Max-yük -.--, -.-- [kgf]	Egilme dayanimi -.--, -.-- [MPa]	Max-yükteki uzama -.--, -.-- [%]	Kopma yükü -.--, -.-- [kgf]	Kopmadaki uzama -.--, -.-- [%]	Width: -.--, -.-- [mm]	Thickness: -.--, -.-- [mm]
1	3476.74	19.0534	130.911	3.50420	19.0534	3.70391	10.2000	4.00000
2	3651.12	24.0780	148.377	5.19230	24.0780	5.39201	9.86000	3.91000
3	3526.60	26.3214	150.877	5.83421	26.3086	5.83421	10.0500	3.99000
4	3521.66	15.9432	100.491	3.15332	15.9432	3.15304	9.72000	3.92000
5	3503.36	24.1290	144.721	5.56217	24.1035	5.58141	9.94000	3.92000
6	3455.90	18.9973	129.984	3.70343	18.9973	3.80285	9.75000	3.91000
7	3730.44	18.7372	128.959	3.38401	18.7321	3.58344	9.85000	3.88000
Mean	3552.26	21.0371	133.336	4.33338	21.0309	4.43584	9.91000	3.93286
Std.D (N-1)	100.412	3.78734	21.8889	1.14589	3.78143	1.14952	0.16951	0.04461

Comment:

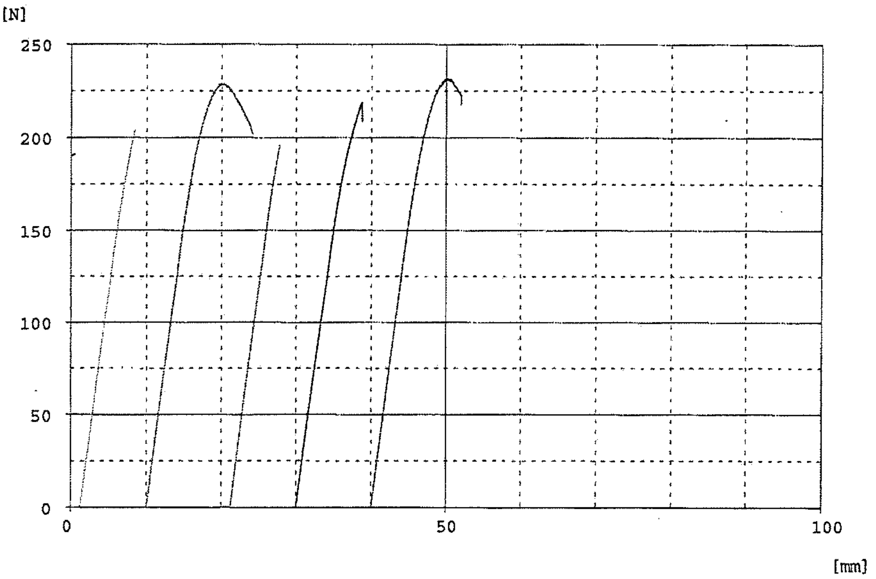
Figure D.4 Flexural test graph of VE932/30, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA EGILME TESTI ISO 178

SEFFAF

Tarih: 26.01.2005
Müsteri:
Num.Adi: 932/38
Sarj No:
Operatör

Shape: Plate
Distance between supports: 64.00



Calc.	Elastic	Max-yük	Egilme dayanimi	Max-yükteki uzama	Kopma yükü	Kopmadaki uzama	Width:	Thickness:
CP1, CP2	15.000, 80.000							
CP Unit	[N]							
Pass-Fail	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--
Unit	[MPa]	[kgf]	[MPa]	[%]	[kgf]	[%]	[mm]	[mm]
1	3215.36	20.8404	142.258	4.97520	20.8404	5.97637	10.0300	4.00000
2	3503.29	23.3387	143.916	5.70845	20.5727	7.93386	10.3000	3.85000
3	3535.87	19.9354	135.170	4.41092	19.9227	4.41035	10.1000	3.90000
4	3630.09	22.3190	144.071	4.86532	22.3190	4.86671	10.1000	3.80000
5	3189.16	23.6064	137.521	5.92518	22.7014	7.04756	10.0000	4.02000
Mean	3414.76	22.0080	140.787	5.17701	21.2712	6.04697	10.1060	3.91400
Std-D (N-1)	199.703	1.58755	11.0677	0.62589	1.18694	1.54752	0.11696	0.09476

Comment:

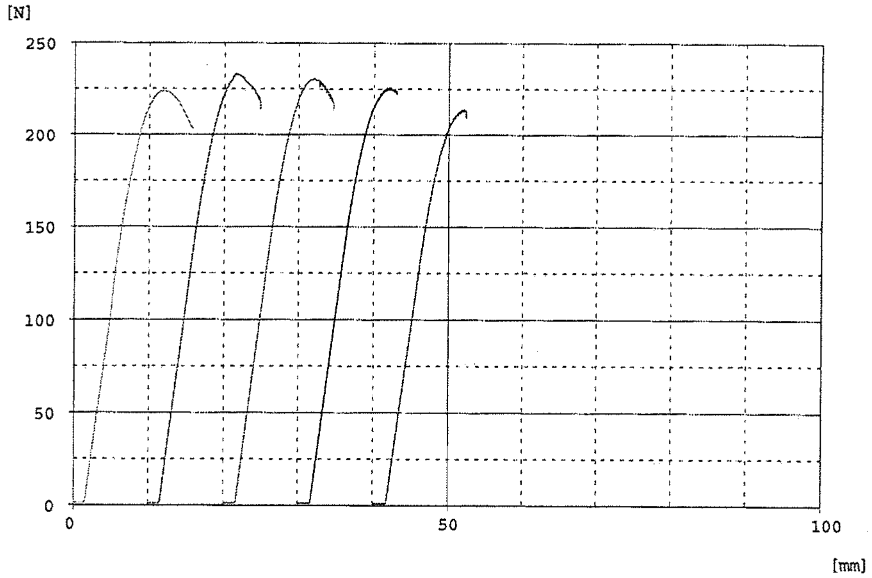
Figure D.5 Flexural test graph of VE932/38, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA EGILME TESTI ISO 178

SEFFAF

Tarih: 22.01.2005
Müsteri:
Num.Adi: 932/45
Sarj No:
Operatör

Shape: Plate
Distance between supports: 60.00



Calc.	Elastic	Max-yük	Egilme dayanimi	Max-yükteki uzama	Kopma yükü	Kopmadaki uzama	Width:	Thickness:
CP1, CP2	15.000, 80.000							
CP Unit	[N]							
Pass-Fail	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--
Unit	[MPa]	[kgf]	[MPa]	[%]	[kgf]	[%]	[mm]	[mm]
1	3075.65	22.8416	158.380	7.44656	20.7002	9.87500	10.1400	3.75000
2	3502.84	23.7976	156.405	6.99583	22.1405	9.00516	10.0800	3.65000
3	3387.14	23.5044	154.013	7.30395	22.0513	8.91878	10.3800	3.65000
4	3442.09	23.0073	155.892	7.14380	22.6886	7.92185	10.0900	3.64000
5	3546.88	21.8091	160.712	7.09860	21.7072	7.36020	9.60000	3.60000
Mean	3390.92	22.9920	157.880	7.19775	21.8576	8.61620	10.0580	3.65800
Std-D (N-1)	186.331	0.76380	5.85723	0.17797	0.73662	0.98578	0.28358	0.05541

Comment:

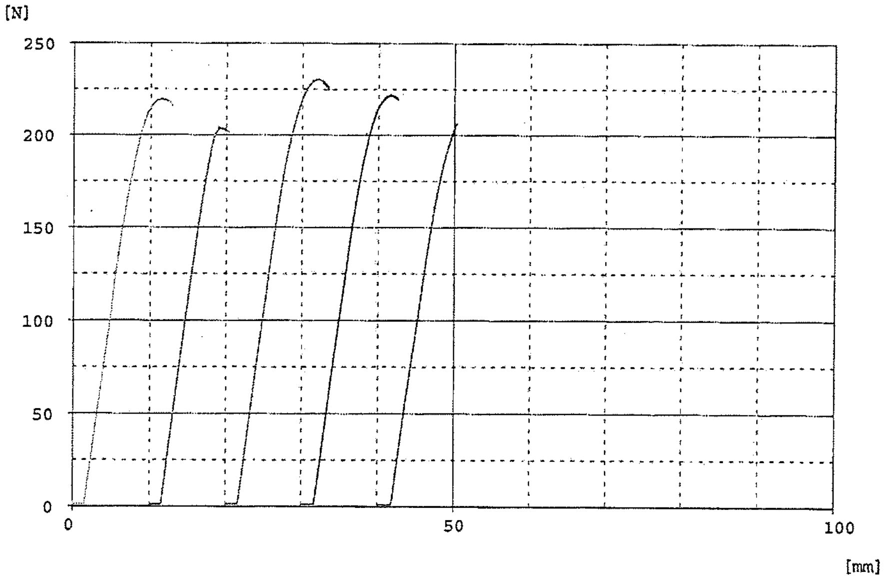
Figure D.6 Flexural test graph of VE932/45, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA EGILME TESTI ISO 178

SEFFAF

Tarih: 12.02.2005
Müsteri:
Num.Adi: 1100/38
Sarj No:
Operatör

Shape: Plate
Distance between supports: 60.00



Calc.	Elastic	Max-yük	Egilme dayanimi	Max-yükteki uzama	Kopma yükü	Kopmadaki uzama	Width:	Thickness:
CP1, CP2	15.000, 80.000							
CP Unit	[N]							
Pass-Fail	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--
Unit	[MPa]	[kgf]	[MPa]	[%]	[kgf]	[%]	[mm]	[mm]
1	3675.81	22.7016	141.500	7.43956	20.9762	7.47500	10.1500	3.75000
2	3392.02	23.1476	146.435	6.92583	22.1055	7.03516	10.0800	3.65000
3	3437.46	23.4054	157.163	7.87392	22.0572	8.11863	10.0800	3.65000
4	3592.14	23.7976	153.813	7.14516	22.5486	7.97805	10.0900	3.64000
5	3685.63	20.7002	154.912	7.25013	21.7083	7.25885	10.0900	3.65000
Mean	3556.92	22.7520	150.757	7.32692	21.8766	7.57620	10.0800	3.65000
Std-D (N-1)	146.353	0.80380	5.83843	0.13517	0.97662	0.99778	0.25558	0.05578

Comment:

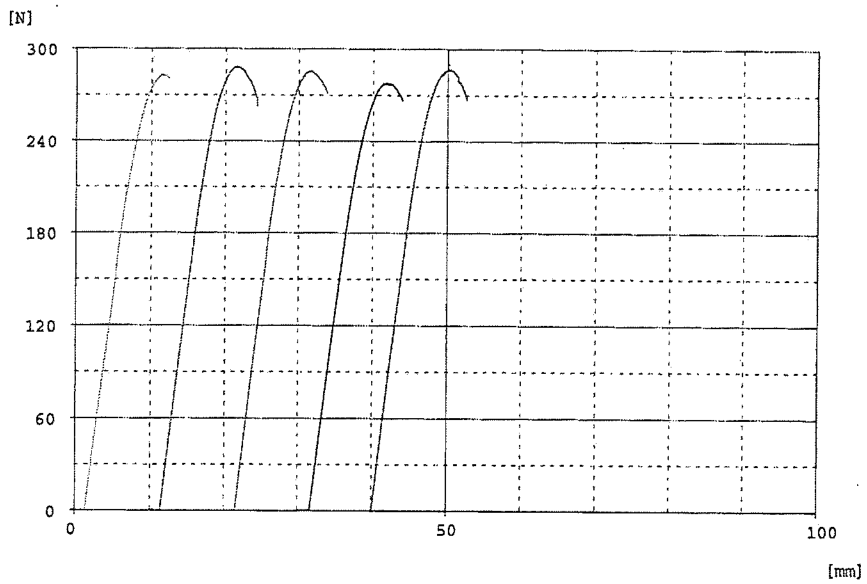
Figure D.7 Flexural test graph of VE1100/38, cured at 1h 50°C, 1 h 90°C, 1h 150°C

POLIYA EGILME TESTI ISO 178

SEFFAF

Tarih: 18.02.2005
Müsteri:
Num.Adi: 1100/45
Sarj No:
Operatör

Shape: Plate
Distance between supports: 66.10



Calc.	Elastic	Max-yük	Egilme dayanimi	Max-yükteki uzama	Kopma yükü	Kopmadaki uzama	Width:	Thickness:
CP1, CP2	15.000, 80.000							
CP Unit	[N]							
Pass-Fail	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--	-.--, -.--
Unit	[MPa]	[kgf]	[MPa]	[%]	[kgf]	[%]	[mm]	[mm]
1	3532.45	28.8707	158.710	6.56208	28.5902	7.00803	10.2700	4.15000
2	3620.21	29.3933	161.500	6.58246	27.2136	8.23901	10.0800	4.19000
3	3538.30	29.1383	160.195	6.69524	27.6980	8.07616	9.70000	4.27000
4	3229.06	28.3736	157.227	6.89775	27.2009	8.07021	9.90000	4.21000
5	3520.53	29.2786	158.959	5.94394	27.2264	7.22515	10.2500	4.18000
Mean	3487.86	29.0109	159.318	6.53630	27.5858	7.72371	10.0400	4.20000
Std-D (N-1)	64.8114	0.40619	1.61257	0.35693	0.59945	0.56360	0.24176	0.04472

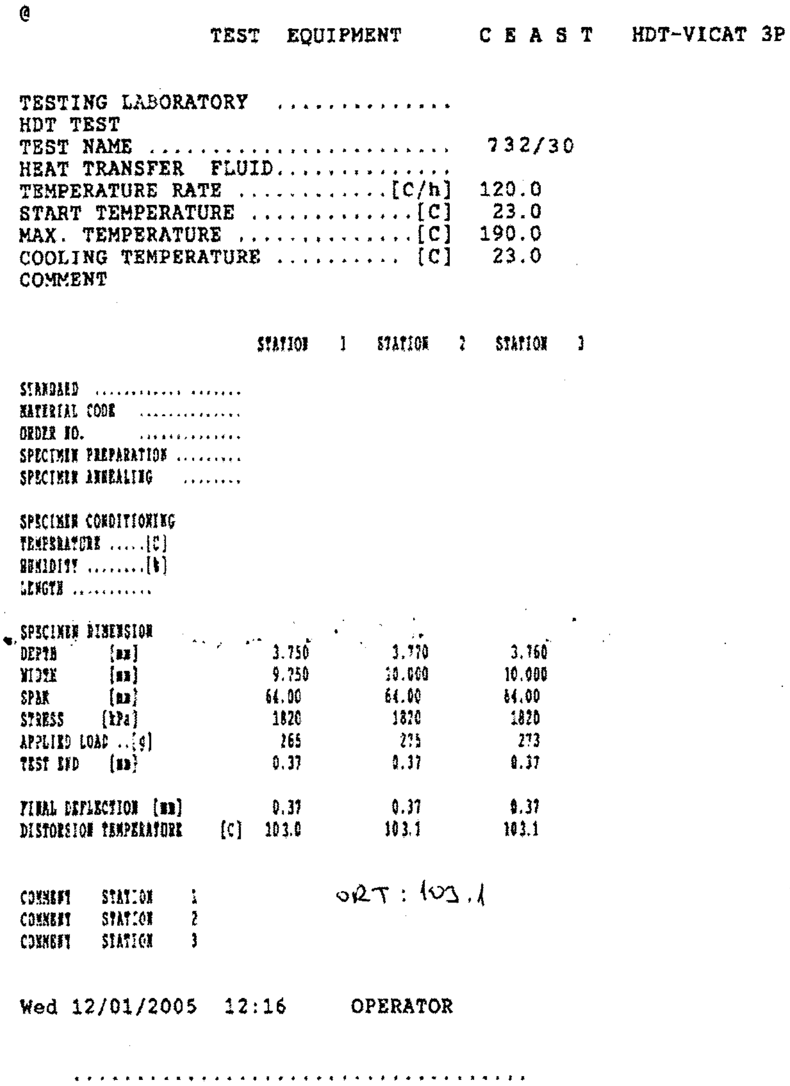
Comment:

Figure D.8 Flexural test graph of VE1100/45, cured at 1h 50°C, 1 h 90°C, 1h 150°C

APPENDIX E

HDT TEST RESULTS OF VINYLESTER SERIES

The following graphics show heat deflection temperature of vinylester samples with various molecular weight and styrene contents.



```
@
                TEST  EQUIPMENT      C E A S T   HDT-VICAT 3P

TESTING LABORATORY  ..............
HDT TEST
TEST NAME ........................   732/30
HEAT TRANSFER  FLUID..............
TEMPERATURE RATE ............[C/h]  120.0
START TEMPERATURE .............[C]   23.0
MAX. TEMPERATURE ..............[C]  190.0
COOLING TEMPERATURE .......... [C]   23.0
COMMENT


                          STATION   1   STATION   2   STATION   3

STANDARD ............ .......
MATERIAL CODE  .............
ORDER NO.      .............
SPECIMEN PREPARATION .........
SPECIMEN ANNEALING   ........

SPECIMEN CONDITIONING
TEMPERATURE .....[C]
HUMIDITY ........[%]
LENGTH ..........

SPECIMEN DIMENSION
DEPTH        [mm]              3.750        3.770        3.760
WIDTH        [mm]              9.750       10.000       10.000
SPAN         [mm]             64.00        64.00        64.00
STRESS      [kPa]              1820         1820         1820
APPLIED LOAD ..[g]              265          275          273
TEST END     [mm]              0.37         0.37         0.37

FINAL DEFLECTION  [mm]         0.37         0.37         0.37
DISTORSION TEMPERATURE   [C]  103.0        103.1        103.1


COMMENT    STATION    1              ORT : 103.1
COMMENT    STATION    2
COMMENT    STATION    3


Wed 12/01/2005  12:16      OPERATOR


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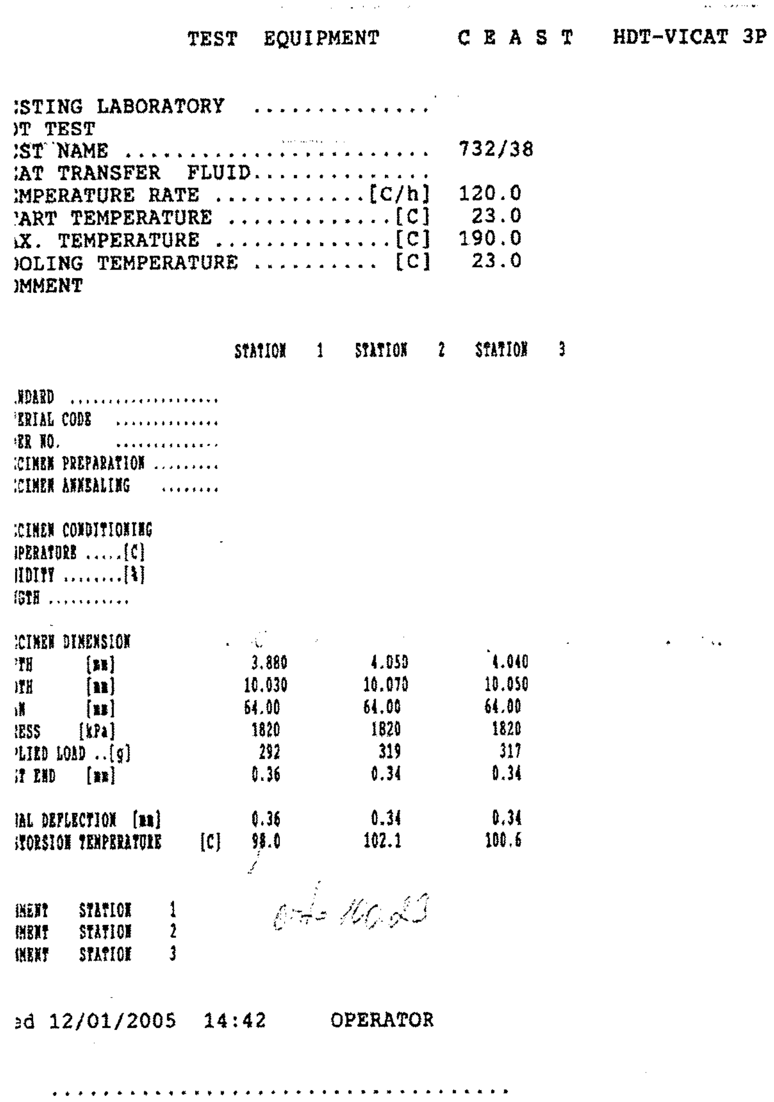
Figure E.1 HDT test result of VE732/30, cured at 1h 50°C, 1 h 90°C, 1h 150°C



```
                  TEST  EQUIPMENT      C E A S T   HDT-VICAT 3P

:STING LABORATORY  .............
)T TEST
:ST NAME .......................  732/38
:AT TRANSFER  FLUID.............
:MPERATURE RATE ...........[C/h]  120.0
'ART TEMPERATURE ............[C]   23.0
iX. TEMPERATURE .............[C]  190.0
)OLING TEMPERATURE .......... [C]   23.0
)MMENT

                       STATION   1   STATION   2   STATION   3

.NDARD ...................
'ERIAL CODE   .............
'ER NO.       .............
:CIMEN PREPARATION ........
:CIMEN ANNEALING    .......

:CIMEN CONDITIONING
IPERATURE .....[C]
IIDITY ........[%]
IGTH ..........

:CIMEN DIMENSION
'TH       [mm]             3.880        4.050        4.040
)TH       [mm]            10.030       10.070       10.050
iN        [mm]            64.00        64.00        64.00
IESS     [kPa]             1820         1820         1820
'LIED LOAD ..[g]            292          319          317
iT END    [mm]             0.36         0.34         0.34

IAL DEFLECTION  [mm]       0.36         0.34         0.34
iTORSION TEMPERATURE  [C]  98.0        102.1        100.6

IMENT   STATION   1          av= 100.23
IMENT   STATION   2
IMENT   STATION   3

ed 12/01/2005  14:42     OPERATOR

    ...................................
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Figure E.2 HDT test result of VE732/38, cured at 1h 50°C, 1 h 90°C, 1h 150°C

```
                    TEST  EQUIPMENT      C E A S T   HDT-VICAT 3P

TESTING LABORATORY  ..............
HDT TEST
TEST NAME ........................  732/45
HEAT TRANSFER  FLUID..............
TEMPERATURE RATE ............[C/h]  120.0
START TEMPERATURE .............[C]   23.0
MAX. TEMPERATURE ..............[C]  190.0
COOLING TEMPERATURE .......... [C]   23.0
COMMENT


                          STATION   1   STATION   2   STATION   3

STANDARD .....................
MATERIAL CODE  ..............
ORDER NO.      ..............
SPECIMEN PREPARATION .........
SPECIMEN ANNEALING   ........

SPECIMEN CONDITIONING
TEMPERATURE .....[C]
HUMIDITY ........[%]
LENGTH ...........

SPECIMEN DIMENSION
DEPTH       [mm]               3.980         3.980         4.040
WIDTH       [mm]              10.140        10.100        10.090
SPAN        [mm]              64.00         64.00         64.00
STRESS     [kPa]               1820          1820          1820
APPLIED LOAD ..[g]              311           309           318
TEST END    [mm]               0.35          0.35          0.34

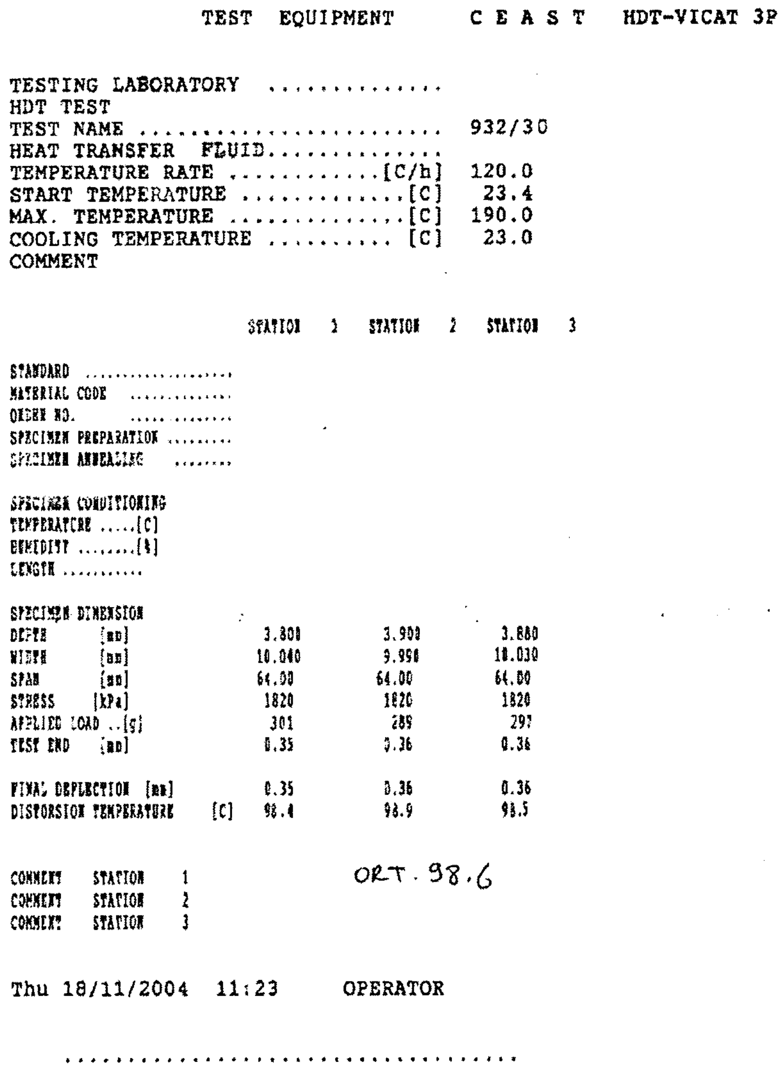
FINAL DEFLECTION  [mm]         0.35          0.35          0.34
DISTORSION TEMPERATURE   [C]   ~~97.1~~          98.0         100.9

                                                  ORT : 99.5
COMMENT   STATION    1
COMMENT   STATION    2
COMMENT   STATION    3


Wed 12/01/2005  17:02      OPERATOR    KURAL

      ..................................
```

Figure E.3 HDT test result of VE732/45, cured at 1h 50°C, 1 h 90°C, 1h 150°C



```
                 TEST  EQUIPMENT      C E A S T   HDT-VICAT 3P

TESTING LABORATORY  ..............
HDT TEST
TEST NAME ........................  932/30
HEAT TRANSFER  FLUID..............
TEMPERATURE RATE ............[C/h]  120.0
START TEMPERATURE .............[C]   23.4
MAX. TEMPERATURE ..............[C]  190.0
COOLING TEMPERATURE .......... [C]   23.0
COMMENT

                         STATION  1   STATION  2   STATION  3

STANDARD ....................
MATERIAL CODE  ..............
ORDER NO.      .... ........
SPECIMEN PREPARATION ........
SPECIMEN ANNEALING    ........

SPECIMEN CONDITIONING
TEMPERATURE .....[C]
HUMIDITY ........[%]
LENGTH ...........

SPECIMEN DIMENSION
DEPTH       [mm]              3.800        3.900        3.880
WIDTH       [mm]             10.040        9.990       10.030
SPAN        [mm]             64.00        64.00        64.00
STRESS     [kPa]              1820         1820         1820
APPLIED LOAD ..[g]             301          289          297
TEST END    [mm]              0.35         0.36         0.36

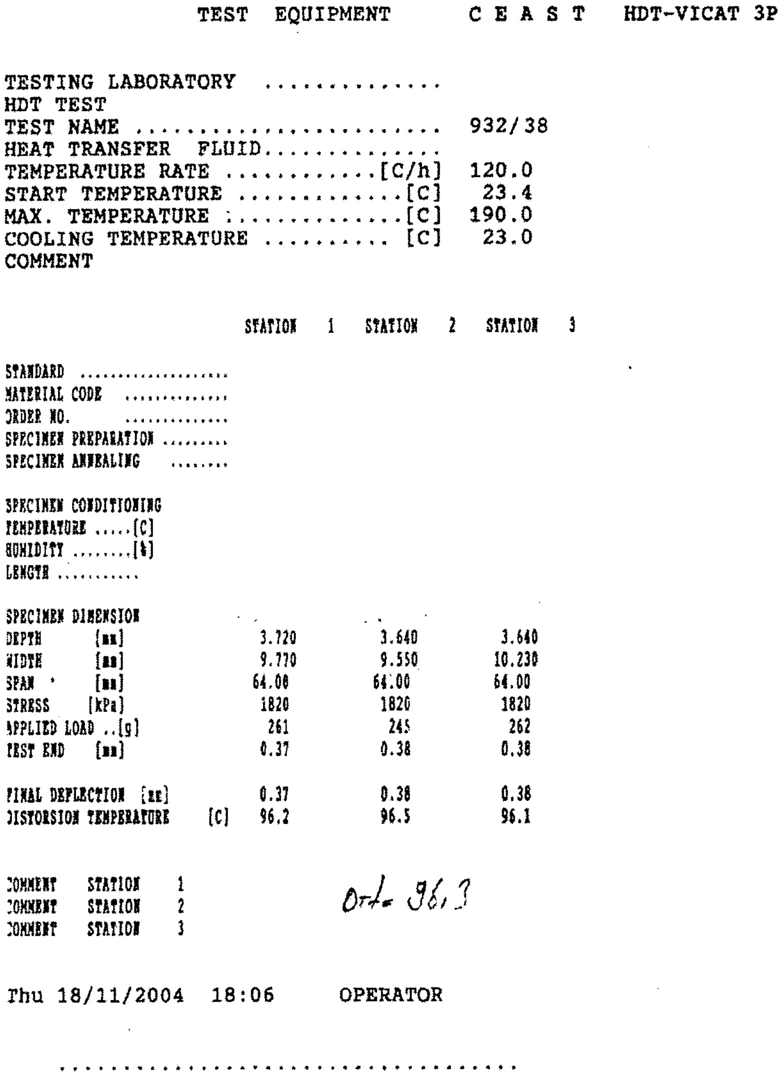
FINAL DEFLECTION  [mm]        0.35         0.36         0.36
DISTORSION TEMPERATURE   [C]  98.4         98.9         98.5


COMMENT   STATION   1                 ORT. 98.6
COMMENT   STATION   2
COMMENT   STATION   3

Thu 18/11/2004  11:23      OPERATOR

      ...................................
```

Figure E.4 HDT test result of VE932/30, cured at 1h 50°C, 1 h 90°C, 1h 150°C



```
                    TEST  EQUIPMENT      C E A S T   HDT-VICAT 3P

TESTING LABORATORY  ..............
HDT TEST
TEST NAME ........................  932/38
HEAT TRANSFER  FLUID..............
TEMPERATURE RATE ............[C/h]  120.0
START TEMPERATURE .............[C]   23.4
MAX. TEMPERATURE ..............[C]  190.0
COOLING TEMPERATURE .......... [C]   23.0
COMMENT

                                STATION  1   STATION  2   STATION  3

STANDARD ....................
MATERIAL CODE  ..............
ORDER NO.      ..............
SPECIMEN PREPARATION .........
SPECIMEN ANNEALING   ........

SPECIMEN CONDITIONING
TEMPERATURE .....[C]
HUMIDITY ........[%]
LENGTH ...........

SPECIMEN DIMENSION
DEPTH       [mm]                  3.720        3.640        3.640
WIDTH       [mm]                  9.770        9.550       10.230
SPAN  '     [mm]                 64.00        64.00        64.00
STRESS     [kPa]                 1820         1820         1820
APPLIED LOAD ..[g]                261          245          262
TEST END    [mm]                 0.37         0.38         0.38

FINAL DEFLECTION  [mm]           0.37         0.38         0.38
DISTORSION TEMPERATURE    [C]    96.2         96.5         96.1


COMMENT    STATION    1
COMMENT    STATION    2
COMMENT    STATION    3

Thu 18/11/2004  18:06      OPERATOR

     .................................
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Ort. 96,3

Figure E.5 HDT test result of VE932/38, cured at 1h 50°C, 1 h 90°C, 1h 150°C

```
                    TEST  EQUIPMENT      C E A S T   HDT-VICAT 3P

     TESTING LABORATORY  ..............
     HDT TEST
     TEST NAME ........................  932/45
     HEAT TRANSFER  FLUID..............
     TEMPERATURE RATE ............[C/h]  120.0
     START TEMPERATURE .............[C]   23.4
     MAX. TEMPERATURE ..............[C]  190.0
     COOLING TEMPERATURE .......... [C]   23.0
     COMMENT

                               STATION   1   STATION   2   STATION   3

     STANDARD ....................
     MATERIAL CODE  .............
     ORDER NO.      .............
     SPECIMEN PREPARATION .........
     SPECIMEN ANNEALING    ........

     SPECIMEN CONDITIONING
     TEMPERATURE .....[C]
     HUMIDITY ........[%]
     LENGTH ...........

     SPECIMEN DIMENSION
     DEPTH      [mm]            3.920         3.870         3.880
     WIDTH      [mm]           10.000         9.990         9.850
     SPAN       [mm]           64.00         64.00         64.00
     STRESS    [kPa]            1820          1820          1820
     APPLIED LOAD ..[g]          297           289           287
     TEST END   [mm]            0.35          0.36          0.36

     FINAL DEFLECTION  [mm]     0.35          0.36          0.36
     DISTORSION TEMPERATURE  [C] 95.4         95.6          95.3

     COMMENT   STATION   1
     COMMENT   STATION   2
     COMMENT   STATION   3

     Thu 18/11/2004  11:23      OPERATOR

        ...................................
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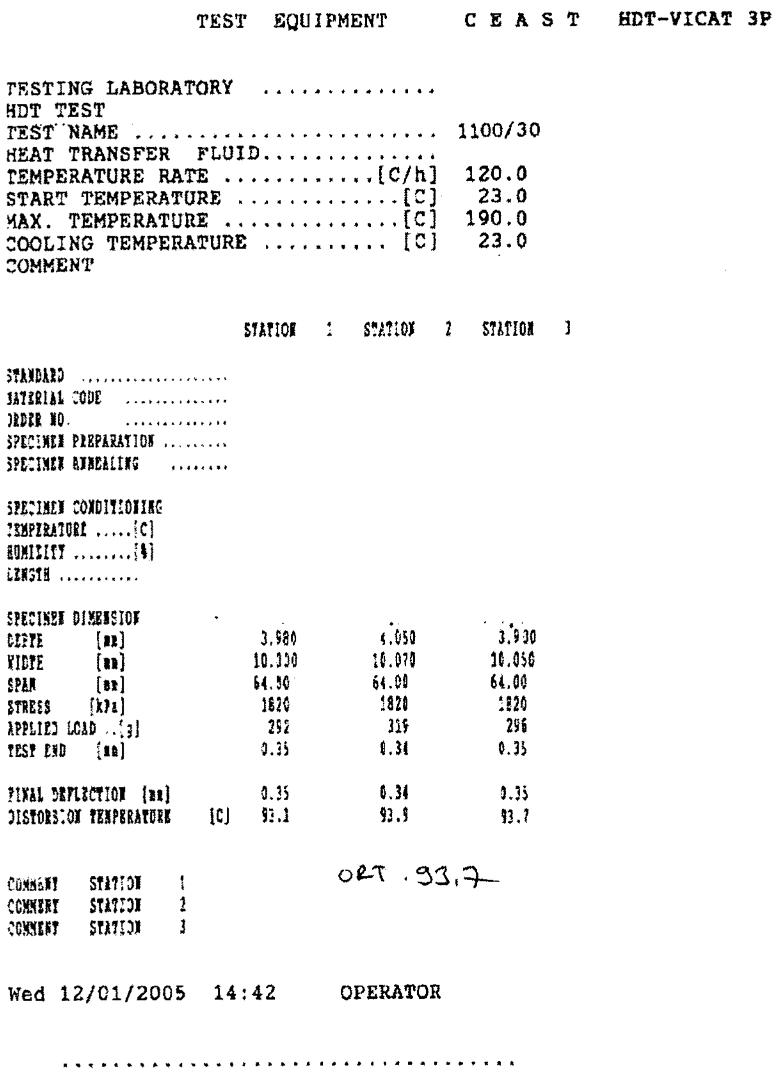
Figure E.6 HDT test result of VE932/45, cured at 1h 50°C, 1 h 90°C, 1h 150°C



```
                     TEST  EQUIPMENT       C E A S T   HDT-VICAT 3P

TESTING LABORATORY  ..............
HDT TEST
TEST NAME ........................ 1100/30
HEAT TRANSFER  FLUID..............
TEMPERATURE RATE ............[C/h]  120.0
START TEMPERATURE .............[C]   23.0
MAX. TEMPERATURE ..............[C]  190.0
COOLING TEMPERATURE .......... [C]   23.0
COMMENT


                          STATION  1   STATION  2   STATION  3

STANDARD ....................
MATERIAL CODE   .............
ORDER NO.       .............
SPECIMEN PREPARATION ........
SPECIMEN ANNEALING   ........

SPECIMEN CONDITIONING
TEMPERATURE .....[C]
HUMIDITY ........[%]
LENGTH ...........

SPECIMEN DIMENSION
DEPTH      [mm]             3.980        4.050        3.930
WIDTH      [mm]            10.330       10.070       10.050
SPAN       [mm]            64.50        64.00        64.00
STRESS     [kPa]           1820         1820         1820
APPLIED LOAD ..[g]          292          319          296
TEST END   [mm]            0.35         0.34         0.35

FINAL DEFLECTION  [mm]     0.35         0.34         0.35
DISTORSION TEMPERATURE [C] 93.1         93.9         93.7


COMMENT    STATION    1              ORT . 93,7
COMMENT    STATION    2
COMMENT    STATION    3

Wed 12/01/2005  14:42      OPERATOR

     ...................................
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Figure E.7 HDT test result of VE1100/30, cured at 1h 50°C, 1 h 90°C, 1h 150°C

```
                    TEST   EQUIPMENT      C E A S T   HDT-VICAT 3P

TESTING LABORATORY  ..............
HDT TEST
TEST NAME ........................  1100/38
HEAT TRANSFER  FLUID..............
TEMPERATURE RATE ............[C/h]  120.0
START TEMPERATURE .............[C]   23.4
MAX. TEMPERATURE ..............[C]  190.0
COOLING TEMPERATURE .......... [C]   23.0
COMMENT

                          STATION   1   STATION   2   STATION   3

STANDARD ....................
MATERIAL CODE  ..............
ORDER NO.      ..............
SPECIMEN PREPARATION .........
SPECIMEN ANNEALING   ........

SPECIMEN CONDITIONING
TEMPERATURE .....[C]
HUMIDITY ........[%]
LENGTH ...........

SPECIMEN DIMENSION
DEPTH       [mm]              3.960        4.080        3.900
WIDTH       [mm]             10.060        9.800       10.040
SPAN        [mm]              64.00        64.00        64.00
STRESS     [kPa]               1820         1820         1820
APPLIED LOAD ..[g]              305          315          295
TEST END    [mm]               0.35         0.34         0.35

FINAL DEFLECTION [mm]          0.35         0.34         0.35
DISTORSION TEMPERATURE   [C]   92.9         92.7         92.7

COMMENT   STATION    1
COMMENT   STATION    2
COMMENT   STATION    3

Thu 18/11/2004  13:35     OPERATOR    KURAL

     ...................................
```

ort 92.8

Figure E.8 HDT test result of VE1100/38, cured at 1h 50°C, 1 h 90°C, 1h 150°C

```
                    TEST   EQUIPMENT      C E A S T   HDT-VICAT 3P

TESTING LABORATORY  ..............
HDT TEST
TEST NAME ........................  1100/45
HEAT TRANSFER  FLUID..............
TEMPERATURE RATE ............[C/h]  120.0
START TEMPERATURE .............[C]   23.4
MAX. TEMPERATURE ..............[C]  190.0
COOLING TEMPERATURE .......... [C]   23.0
COMMENT

                              STATION   1   STATION   2   STATION   3

STANDARD ....................
MATERIAL CODE   .............
ORDER NO.       .............
SPECIMEN PREPARATION .........
SPECIMEN ANNEALING   ........

SPECIMEN CONDITIONING
TEMPERATURE .....[C]
HUMIDITY ........[%]
LENGTH ...........

SPECIMEN DIMENSION
DEPTH       [mm]                  3.740         3.850         3.770
WIDTH       [mm]                 10.040         9.920        10.040
SPAN        [mm]                 64.00         64.00         64.00
STRESS     [kPa]                  1820          1820          1820
APPLIED LOAD ..[g]                 271           284           276
TEST END    [mm]                  0.37          0.36          0.37

FINAL DEFLECTION  [mm]            0.37          0.36          0.37
DISTORSION TEMPERATURE    [C]     92.0          92.2          92.2


COMMENT   STATION    1                 Ort: 92.1
COMMENT   STATION    2
COMMENT   STATION    3

Thu 18/11/2004  15:07      OPERATOR     KURAL

    ...................................
```

Figure E.9 HDT test result of VE1100/45, cured at 1h 50°C, 1 h 90°C, 1h 150°C

APPENDIX F

LIST OF ABBREVIATIONS

EEW Epoxy equivalent weight, grams per each functional group on the chain.

VE 732/30 The vinylester resin sample with molecular weight 732 g/mol and 30% styrene content

VE 732/38 The vinylester resin sample with molecular weight 732 g/mol and 38% styrene content

VE 732/45 The vinylester resin sample with molecular weight 732 g/mol and 45% styrene content

VE 932/30 The vinylester resin sample with molecular weight 932 g/mol and 30% styrene content

VE 932/38 The vinylester resin sample with molecular weight 932 g/mol and 38% styrene content

VE 932/45 The vinylester resin sample with molecular weight 932 g/mol and 45% styrene content

VE 1100/30 The vinylester resin sample with molecular weight 1100 g/mol and 30% styrene content

VE 1100/38 The vinylester resin sample with molecular weight 1100 g/mol and 38% styrene content

VE 1100/45 The vinylester resin sample with molecular weight 1100 g/mol and 45% styrene content

MEK-P	Methyl Ethyl Ketone Peroxide, catalyst for network formation reaction
BPO	Benzoyl Peroxide, catalyst for network formation reaction
HDT	Heat Deflection Temperature
QUAT	Quaternary ammonium salts, catalyst for synthesize reaction
HQ	Hydroquinone, inhibitors
MEHQ	Methyl Ethyl Hydroquinone, inhibitors
TBHQ	Tert-Butyl Hydroquinone, inhibitor
MMA	Methacrylic Acid
CoNaph	Cobalt Naphthanate, accelerator of network formation reaction

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WORK EXPERIENCE

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Project Chief	OYAK-Renault, Bursa	Continuing
R&D Engineer	ORDA Automotive Plastic,Bursa	2006
R&D Responsible	POLIYA Poliester, Istanbul	2005
Raw Material Quality Engineer	AUNDE Teknik	2003