3.2. Characterization of Vinyl Ester /Styrene Networks

3.2.1. Introduction

Although vinyl ester resins have been used in industry for more than thirty years, not much information is available in the literature on the formation-structure-property relationships in these networks.[1, 2, 3] These networks are becoming increasingly important in fiber reinforced composites because their cure characteristics are compatible with rapid composite processing operations such as pultrusion and resin transfer (or resin infusion) molding. The free radical cure mechanism allows for good stability at low temperatures, as well as rapid reaction at elevated temperatures. Therefore, it is of great scientific and technological interest to study and understand the structure and properties of vinyl ester networks.

Crosslink density is one of the most important structural parameters which control the properties of vinyl ester resins. This can be controlled by varying the styrene content in the resin, by controlling the final double bond conversion, and/or by changing the molecular weight of the vinyl ester oligomer. In this chapter, the crosslink densities of vinyl ester networks were determined from elastic moduli above the glass transition temperatures and via swelling experiments. The effect of crosslink density on network properties such as glass transition temperature are discussed. Characteristics of vinyl ester networks such as shrinkage and toughness have been measured at systematically varied levels of styrene monomer. The effect of styrene, molecular weight of vinyl ester oligomers and the cure temperature on properties of vinyl ester networks are discussed in this chapter.

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

[2] I. Yilgor, E. Yilgor, A. K. Banthia, G. L. Wilkes, J. E. McGrath, *Polym. Composites* 4, 120, 1983.

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

3.2.2.Crosslink Density of Cured Vinyl Ester Resins

Crosslink density, typically given as the average molecular weight between crosslinks(M_c), is an important factor governing the physical properties of cured thermoset resins. Vinyl ester oligomers have double bonds at each end that can be crosslinked. The crosslink density can be changed by adjusting the styrene content in the resins, adjusting the molecular weight of vinyl ester oligomers, altering the state (and also possibly the rate) of conversion, and control of the cure conditions, among others. In this study two series of vinyl ester (with two different number average molecular weights, 700 and 1000 g/mol) resins with varying styrene contents (from 20 wt % to 60 wt %) were studied.

There are several methods which can be used to determine the crosslink densities of highly crosslinked thermoset materials. Examples are swelling measurements and determination of the modulus at temperatures well above the glass transition temperature.[4-6] Solvent swelling data can give absolute values for crosslink density. However, the absolute crosslink density can only be obtained when accurate values of the Flory-Huggins polymer-solvent interaction parameter are available. For thermosets one frequently employed method is to calculate M_c by using the value of modulus in the rubbery plateau region.[7, 8]

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[4] A. R. Shultz in *Characterization of Macromolecular Structure*, D. McIntyre ed., Publication 1573, National Academy of Science, Washington, DC, 1968, p389.

[5] L. E. Nielsen, *J. Macromol. Sci, Revs. Macromol. Chem.*, C3(1), 69, 1969.

[6] *Encyclopedia of Polymer Science and Technology*, Vol 4, 350, N. M. Bikales, G. C. Overberger, and G. Menges, Eds., Wiley Publications, New York, 1988.

[7] *Encyclopedia of Polymer Science and Technology*, N. M. Bikales, G. C. Overberger, G. Menges, Eds., Wiley Publications, New York, 1988, Vol 3, p 306.

[8] L. W. Hill, *PMSE Preprints*, 387, Spring, 1997.

[9] L. W. Hill, *Paint and Coating Testing Manual*, J. V. Koleske Ed., Fourteenth Ed. Gardner-Sward Handbook, ASTM, Philadelphia, PA, 1995; Ch. 46, p. 534.

[10] L. E. Nielsen, *J. Macromol. Sci-Revs. Macromol. Chem.*, C3, 69, 1969.

According to the theory of rubber elasticity the equilibrium elastic modulus is given by [9-10]

$$\rho = G'/RT = E'/3RT \qquad (1)$$

where r is the crosslink density expressed in moles of elastically effective network chains per cubic centimeter of sample, *G'* is the shear storage modulus of the cured network at a temperature well above T_g, *R* is the gas constant and *T* is the absolute temperature at which the experimental modulus is determined. 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 affinely; (3) the internal energy of the system is independent of the conformations of the individual chains, and (4) the chains are treated as phantom networks (there is no excluded volume)[11]. For highly crosslinked systems the equation (1) will not hold any more. However, the elastic modulus is still independent of the chemical structure of the network and depends primarily on the tightness of the network structure. The elastic modulus at temperature above Tg is still a good empirical method of characterizing highly cross-linked materials. There have been numerous studies reported on application of theory of rubber elasticity for the rubbery region of highly crosslinked networks such as epoxy, [12-14] polyester, [15] and bismaleimide system. [16]

For highly crosslinked networks, chain entanglements are not present and, under small deformations, the relationship between crosslink density and the equilibrium elastic modulus

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[11] *Introduction to Polymer Viscoelasticity*, J. J. Aklonis and W. J. Macknight ed., Wiley-interscience, 2nd edition, 1983, p111.

[12] E. Urbaczewski-Espuche, J. Galy, J. Gerard, J. Pascault, and H. Sautereau, *Polym. Eng. Sci.*, 31, 1572, 1991.

[13] G. Levita, S. Petris, A. Marchetti, and A. Lazzeri, *J. Mater. Sci.*, 26, 2348, 1991.

[14] D. Katz and A. V. Tobolsky, *J. Polym. Sci*., 4, 417, 1963.

[15] T. M. Donnellan and D. Roylance, *Polym. Eng. Sci*., 32, 415, 1992.

[16] D. Katz and A. V. Tobolsky, *J. Polym. Sci., Part A*, 2, 1587, 1964.

can be expressed by using the kinetic theory of rubber elasticity (Equation (1)). Here G' = E'/3 is used, assuming that the samples do not undergo volume change with tensile strain (χ=0.5).

DMA was used to determine mechanical properties and glass transition temperatures of the vinyl ester networks. The curves of the storage and loss moduli and the loss tangents as a function of temperature were obtained. The temperatures of the maxima in the loss tangents are taken as the glass transition temperatures. The DMA instrument was a Perkin Elmer DMA-7e. The heating rate was 5 ^{o}C/min. and frequency was 1Hz under amplitude control. The strain amplitude was set at between 7-10 μm depending on the thickness of the samples so that the sample deformation was controlled at about 0.5%. The samples had sizes of 2.5-3 mm in thickness, 5.9-6.2 mm in width, and 18-20 mm in length.

The storage modulus above T_g was used to estimate the crosslink densities of the vinyl ester networks. The vinyl ester networks tested have well defined transition regions and rubbery plateau regions. In the rubbery plateau region, the storage modulus changes only slightly with temperature. To a first approximation, the modulus in the rubbery plateau were considered as constant up to the chemical degradation temperature. It is essential to keep the deformation small during modulus measurements for 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 rubbery plateau modulus and crosslink density.[8-10] The measurement of modulus is very sensitive to experimental conditions, Therefore, the calibration of the DMA instrument before testing is crucial in order to obtain accurate modulus data.

Two series of vinyl ester resins with varying styrene contents from 20 wt % - 60 wt % styrene were studied by DMA (Tables 3.2.1 and 3.2.2). All of these networks were cured at 140°C for one hour using 1.1 wt% benzoyl peroxide and 0.2 wt.% t-butylperoxybenzoate as the initiator. The densities above T_g were calculated from the densities at room temperature and the thermal expansion coefficients below and above T_g determined via thermomechanical analyses. For the series of resins with the vinyl ester oligomer Mn = 700 g/mol, Tables 3.2.1 and 3.2.2 show that the elastic moduli in the rubbery region decrease as styrene content in the networks is increased. The experimental crosslink densities calculated from these elastic storage moduli decrease linearly with increased styrene content (Figure 3.2.1). For the vinyl ester resins with M_n = 1000 g/mol, the crosslink densities calculated in the same manner also decrease as the styrene content in the network is increased from 20 wt % to 40 wt %, but to much less extent.

The vinyl ester-styrene resin cure reaction is a copolymerization of vinyl/divinyl monomers, in which the vinyl ester serves as the crosslinking reagent. Therefore, when the styrene content in the network increases, the percentage of vinyl ester (crosslinker) decreases, resulting in lower crosslink densities and lower elastic storage moduli. For vinyl ester resins containing the same weight percentage of styrene, increasing the molecular weight of the vinyl ester has two effects: increase of molecular weight between crosslinks and decrease of the mole fraction of terminal double bonds which serves as the crosslinker. Both of these effects result in lowering crosslink density and elastic storage modulus.

The average theoretical crosslink densities can be estimated from the compositions of the vinyl ester resins. Previous studies on the cure mechanism have shown that the conversion, as determined by FTIR and ^{13}C-NMR, was more than 95% for vinyl ester resins cured at 140°C using BPO and t-BPO initiators.[17] In this study, the conversion of vinyl ester

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[17] H. Li, A. C. Rosario, S. V. Davis, T. Glass, T. V. Holland, J. J. Lesko, and J. S. Riffle, *J. Adv. Mater., 28, 55*, 1997.

Table 3.2.1. Dynamic viscoelastic properties and crosslink densities of cured vinyl ester resins (cured at 140 ^{o}C). M_n = 688g/mol.

Wt% Styrene	20	25	30	35	40
T_g (Tanδ peak), ^{o}C	154.6	153.9	146.7	143.8	142.0
Tan δ Value (peak)	0.423	0.428	0.526	0.398	0.418
E' at Tg + 40^{o}C, GPa	0.0854	0.0809	0.07488	0.05792	0.4279
f_s, (mole fraction of styrene double bonds)	0.453	0.524	0.586	0.640	0.688
ρ, 10^{-3} mol/cm^3	8.0036.	7.5943	6.7678	5.5688	4.1319
Density at 25^{o}C, g/ml	1.189	1.1806	1.1765	1.1682	1.1547
Density at Tg+40^{o}C	1.053	1.042	1.0345	1.030	0.9952
M_c, g/mol	132	137	153	185	241
Theoretical M_c	286	306	328	353	382

Table 3.2.2. Dynamic viscoelastic properties and crosslink densities of cured vinyl ester resins (cured at 140 ^{o}C). M_n = 1000 g/mol.

Wt % Styrene	20	25	30	35	40
T_g (Tan δ), ^{o}C	131	126	128	124.9	125
Tan δ Value (peak)		0.623	0.584	0.70	0.68
E' at Tg + 40^{o}C, GPa	0.035	0.026	0.0349	0.028	0.022
f_s, (mole fraction of styrene double bonds)	0.546	0.616	0.673	0.721	0.762
ρ, 10^{-3} mol/cm^3	3.4717	2.611	3.487	2.8199	2.215
Density at 25^{o}C, g/ml	1.169	1.163	1.159	1.152	1.146
Density at Tg+40^{o}C	1.03	1.03	1.03	1.027	1.019
M_c, g/mol	297	394	295	354	460
Theoretical M_c	417	444	476	513	555

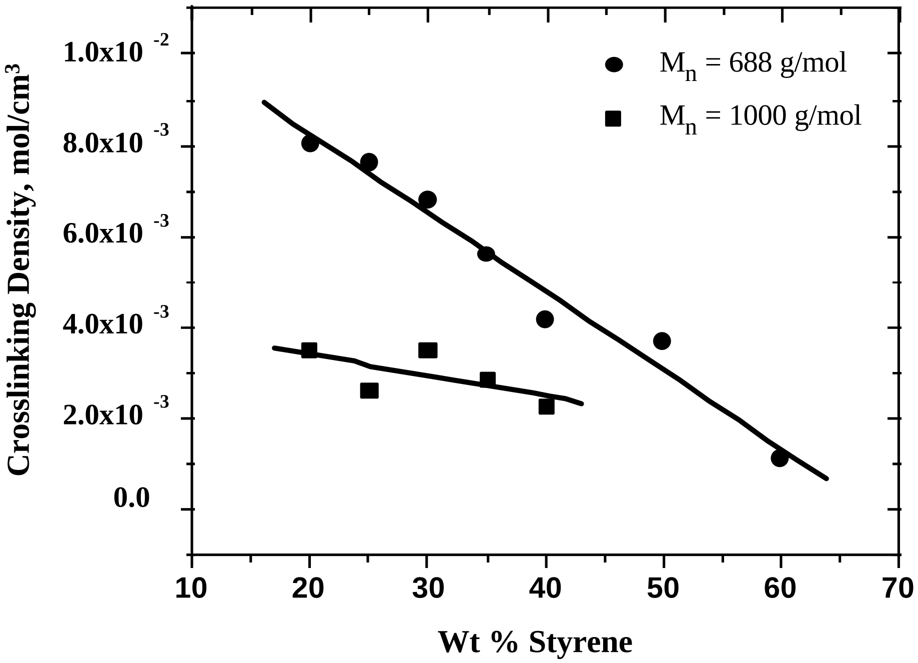

Figure 3.2.1. Crosslink densities vs. weight percentage of styrene in the cured vinyl ester resins.

resins with high molecular weight was confirmed again by FTIR and ^{13}C-NMR that the conversion is more than 95% (Figure 3.2.2). Thus, these networks can be considered close to fully cured.

The crosslink densities for the fully cured azeotropic vinyl ester-styrene samples were calculated as follows:

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

$$= \frac{(1-wt\%styrene)}{Mn} + 2\times\frac{(1-wt\%styrene)}{Mn} \qquad (2)$$

$$M_c = N^{-1}$$

The calculated M_c values are also listed in Tables 3.2.1 and 3.2.2. The M_c values determined by DMA are much lower than the theoretical M_C values, especially at low styrene contents for vinyl ester resins with M_n = 700 g/mol. This discrepancy may be due to the highly crosslinked nature of the system.[10,18] At modulus values greater than 0.01 GPa, the kinetic theory yields relatively lower M_c than theoretical M_c. The increase in modulus is much greater than the predicted value obtained from the kinetic theory of rubber. This discrepancy may be explained through entropic considerations. For highly-crosslinked networks, the number of possible conformations that the chain can achieve (i.e., lowers entropy) are greatly limited by the increased stiffness. In rubber elasticity theory, the rubbery modulus is related to the change in entropy. The increased stiffness in the network will therefore have the same effect as increasing the effective cross-link density (i.e., lowering M_c). Thus, equation (1) that based on rubber elasticity theory underestimates the changes in entropy, resulting in the underestimation of effective cross-link density. However, it is still a good empirical method of characterizing crosslinked materials. For longer vinyl ester chains, the M_c value determined by this technique was closer to the theoretical values. In light of the above discussion, this may be due to the

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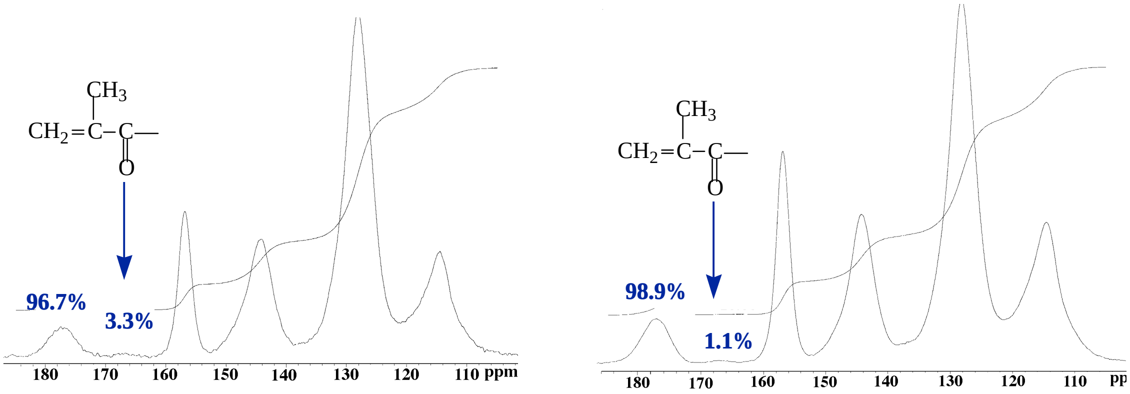
[18] D. Frich, K. Goranov, L. Schneggenburger, and J. Economy, *Macromolecules*, 29, 7734, 1996.

Conversion calculated from ^{13}C-NMR results of cured vinyl ester-styrene resins with Mn=1000 g/mol.

	20 wt% St.	**28 wt% St.**	**40 wt% St.**
Conversion of MMA	**97.2%**	**96.7%**	**98.9%**



28 wt% styrene

40 wt% styrene

conversions (calculated from FTIR) of vinyl ester-styrene resins cured at different temperatures

Cure condition	**Conv. of vinyl ester C=C**	**Conv. of styrene C=C**
100°C, 1Hr	**92**	**93**
120°C, 1Hr	**96-100**	**98**
140°C, 1Hr	**96-100**	**100**
(Derakane 441-400)		
100°C, 1Hr	**90**	**91**
140°C, 1Hr	**96-100**	**100**
(vinyl ester resin: 30wt% styrene, MW=1000g/mol)		

Figure 3.2.2. Conversions of cured vinyl ester-styrene resins calculated from both FTIR and ^{13}C-NMR.

crosslink densities of these vinyl ester networks being lower. Thus, the values obtained from DMA were more comparable to the theoretical values.

3.2.3. Glass Transition Temperatures of Cured Networks

The T_g's of vinyl ester/styrene networks were determined using both DSC and DMA. However, DSC could not be used to measure T_g's for the systems with highly crosslinked networks since there was only a very small measurable change in heat flow in the transition region. Therefore, DMA was the preferred technique for measuring the T_g's of at least the highly crosslinked networks.

DMA was run in the three-point bend mode in this study. Tables 3.2.1 and 3.2.2, which summarize the results of these analyses, show that as styrene content in the system increases, the T_g's of the networks decrease. The shifts in the glass transition temperatures can be attributed to two factors: the degree of crosslinking and the copolymer chemical composition. In vinyl ester resins, vinyl ester oligomers have double bonds at each end which serve as crosslinking sites. When the percentage of the vinyl ester is increased in the network (and the percentage of styrene is correspondingly decreased), the crosslink density increases. The data in Tables 3.2.1 and 3.2.2 clearly indicate the trend that both experimental and theoretical crosslink densities decrease as the styrene content increases. The increase in crosslink density always results in an increase in the T_g of the network. The changes in composition also affect T_g. The effect of composition on T_g is dependent on the nature of the two components and can be estimated according to the T_g of polystyrene and the T_g of phenoxy resins (which have the same backbone chemical structure as the vinyl ester oligomers). The effect of crosslinking on the glass transition follows equation (3):

$$T - T_{go} = \frac{K}{M_c}, \qquad K = 3.9 \times 10^4 \tag{3}$$

Here, T_{go} is the glass-transition temperature of the uncrosslinked resin. The T_{g0} value of the uncrosslinked copolymer can be estimated from Fox's equation. Here, the T_{go} value was calculated according to equation (4) for a random copolymer:

$$T_{go} = X_a T_{ga} + X_b T_{gb} \tag{4}$$

Where 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 T_g of polystyrene, and T_{gb} is the T_g of phenoxy resins which have the same backbone as the vinyl ester oligomer.

The calculated results are listed in Table 3.2.3. Since the T_g's of the two components are very close in this system, T_{go} increases only slightly as styrene content increases in the vinyl ester resins. Therefore, the major effect on the shift in T_g is due to crosslink density. Figures 3.2.3 and 3.2.4 show plots of the glass transition temperatures of the networks as a function of crosslink density. The results show that both T_g and T_g - T_{go} have linear relationships with crosslink density. However, for the vinyl ester oligomers with different molecular weights, the data points do not fall on the same line. The T_g's of vinyl ester resins were also measured by DSC. Under the experimental conditions used, the T_g's obtained by DSC were very close to those obtained by DMA.

Table 3.2.4 shows T_g (DSC) values of cured vinyl ester networks as a function of styrene content for the vinyl ester series with the oligomer M_n = 700 g/mol. The T_g values of vinyl ester networks cured at 140^oC are very close to the maximum T_g values obtainable when these resins were cured at higher temperatures and pressures (180^oC and 150 Pa). Since the cure temperature, 140^oC, is very close to the T_g of the vinyl ester resins, almost 100% conversion of the double bonds was achieved. The result is a decrease in T_g as the styrene content, and hence the molecular weight between crosslinks, increases. When the styrene content in the resins is increased from 28 wt % to 60 wt %, the T_g's change from 149°C to 134°C. The T_g becomes nearly constant at about 155°C when the styrene content is below 25 wt %. This is as a result of decreased conversion of methacrylate groups due to vitrification (82% for 25 wt. % styrene). It should be pointed out here that at low styrene contents the styrene conversion can reach almost 100% and it is primarily the methacrylate groups which remain unreacted, the explanation being that the styrene is used up prior to the vitrification.

Crosslink density also changes with different cure temperatures (Table 3.2.5). Figure 3.2.5 shows DMA results for the Derakane 441-400 vinyl ester/styrene resin (28 wt% styrene) cured at 100°C, 120°C and 140°C. As the cure temperature was increased, the peak of the loss modulus, tan δ, and the decrease in storage modulus were all shifted to higher temperatures. The DMA results suggest that the crosslink density increases from 3.1×10^{-3} mol/cm^3 to 6.1×10^{-3} mol/cm^3 when cure temperature was increased from 100°C to 140°C. Figure 3.2.5 shows that the Tan δ peak value also decreased with cure temperature due to the increase in storage modulus of the more highly crosslinked resins. These differences are undoubtedly a result of decreased double bond conversion at the lower cure temperatures.

The effect of temperature on the conversion of each type of double bond was examined by FTIR (Figure 3.2.6). The vinyl ester resin is Derakane 441-400 and the polymerization was initiated with 1.1 wt% BPO and 0.2 wt% t-BPT. One initiator is used which initiates the reaction at lower temperatures while the other is designed to initiates chains as the temperature increases. This is common for continuous processes. For this system inhibitors are not removed. This provides a desirable induction period, or working life, necessary for many applications. Vinyl ester network formation was extremely fast under these conditions. At 140°C, almost 100% conversion of the vinyl ester and 90% conversion of the styrene occurs within three minutes of the induction period, and the rate of reaction increases as the cure temperature increases. This system shows nearly 100% conversion at 120°C and 140°C, while at 100°C only about 90% conversion was achieved - even at reaction times of

Table 3.2.3. Calculated T_{go} of uncrosslinked vinyl ester/styrene copolymer.

Wt % Styrene	0	20	25	30	35	40	50	60	100
M_n = 688g/mol									
T_{go}	97	97.6	97.8	97.9	98.1	98.2	98.5	98.8	100
T_g	---	154.6	153.9	146.7	143.8	142.0	137.9	134.4	---
T_g - T_{go}	---	57.0	56.1	48.8	45.7	43.8	39.4	35.6	
ρ,10^{-3} mol/cm^3	---	8.00	7.59	6.77	5.57	4.13	3.68	1.08	---
M_n=1000g/mol									
T_{go}	97	97.6	97.8	97.9	98.1	98.2	---	---	100
T_g	---	131	126	128	124.9	125	---	---	---
T_g-T_{go}	---	33.4	28.2	30.1	26.8	26.8	---	---	---
ρ,10^{-3} mol/cm^3	---	3.47	2.61	3.49	2.82	2.22	---	---	---

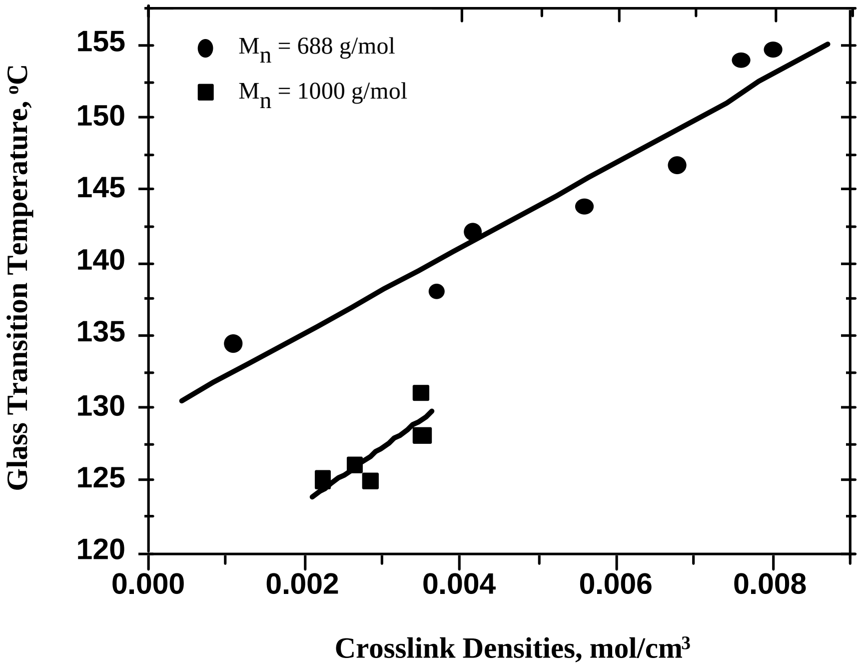


Figure 3.2.3. Glass transition temperature vs. crosslink density.

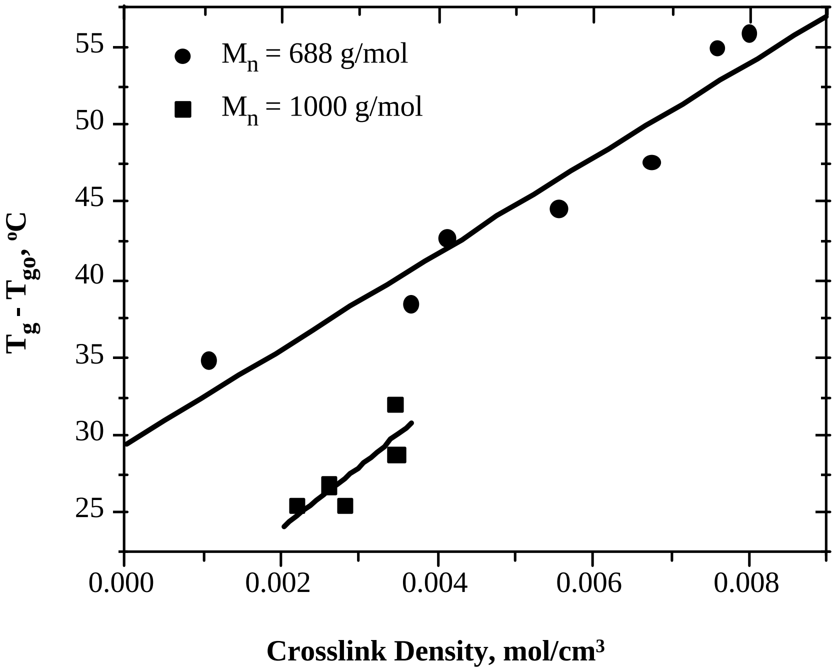


Figure 3.2.4. T_g-T_{go} vs. crosslink density.

Table 3.2.4. Glass Transition Temperatures of Cured Vinyl Ester/Styrene Networks (DSC), M_n = 690 g/mol.

Wt% Styrene	25	28 Derakane 441-400	30	35	40	50	60
T_g^1, ^oC cured at 140^{o}C	155	149	149	148	147	138	134
T_g^2, ^oC cured at 180^{o}C and 150Pa	156	151	150	149	148	140	135

Table 3.2.5. Properties of Derakane 411-400.

	Cured at 100^{o}C	Cured at 120^{o}C	Cured at 140^{o}C
T_g (Tanδ), _C	141.5	144.6	145.4
E' at 25^{o}C	2.03	2.83	3.20
E' at T_g + 40^{o}C	0.0318	0.0456	0.0637
ρ, mol/cm^3	0.00307	0.00437	0.00610
Density (g/ml)	1.1568	1.1590	1.1630
M_c, g/mol	376	265	191
Shrinkage (%)	6.8	7.0	7.3

greater than one hour. This is apparently due to vitrification since the T_g of the completely cured 28 wt% vinyl ester resin is 145°C. Cure temperatures lower than the T_g result in residual unsaturation.

3.2.4. Cure Shrinkage of Vinyl Ester Networks

The specific volumes of cured and uncured vinyl ester resins as a function of styrene contents were determined (Figure 3.2.7). It was found that the specific volume of both uncured resins with varying styrene concentrations and the corresponding fully cured networks follow a linear relationship. The specific volume of vinyl ester resins increases linearly with an increase in styrene concentration.

The effects of crosslinking on the specific volume of the cured network can be seen clearly by comparing two series of resins with different molecular weight oligomers. For the shorter vinyl ester resins with M_n = 700 g/mol, higher crosslink densities, as well as lower specific volumes can be expected. Longer chain vinyl ester networks with oligomer M_n = 1000 g/mol result in lower crosslink densities and higher specific volumes. The specific volumes were measured at 25 ^{o}C, which is below the glass transition temperature of the system. The structure of polymers is metastable below their glass transition temperatures and, therefore, the values of the specific volume obtained below glass transition temperature are higher than those which correspond to the thermodynamic equilibrium. The decrease of specific volume with increase in crosslink density suggests that the free volume in the resin system is reduced by cross-linking. For shorter chain vinyl ester networks, the molecular segments are tied up by cross-linking points more than longer chain systems, resulting in lower specific volume.[19 -20]

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[19] M. Cizmecioglu, A. Gupta, and R. F. Fedors, *J. Appl. Polym. Sci.,* 32, 6177, 1986.

[20] J. Stejny, *Polym. Bull.*, 36, 617, 1996.

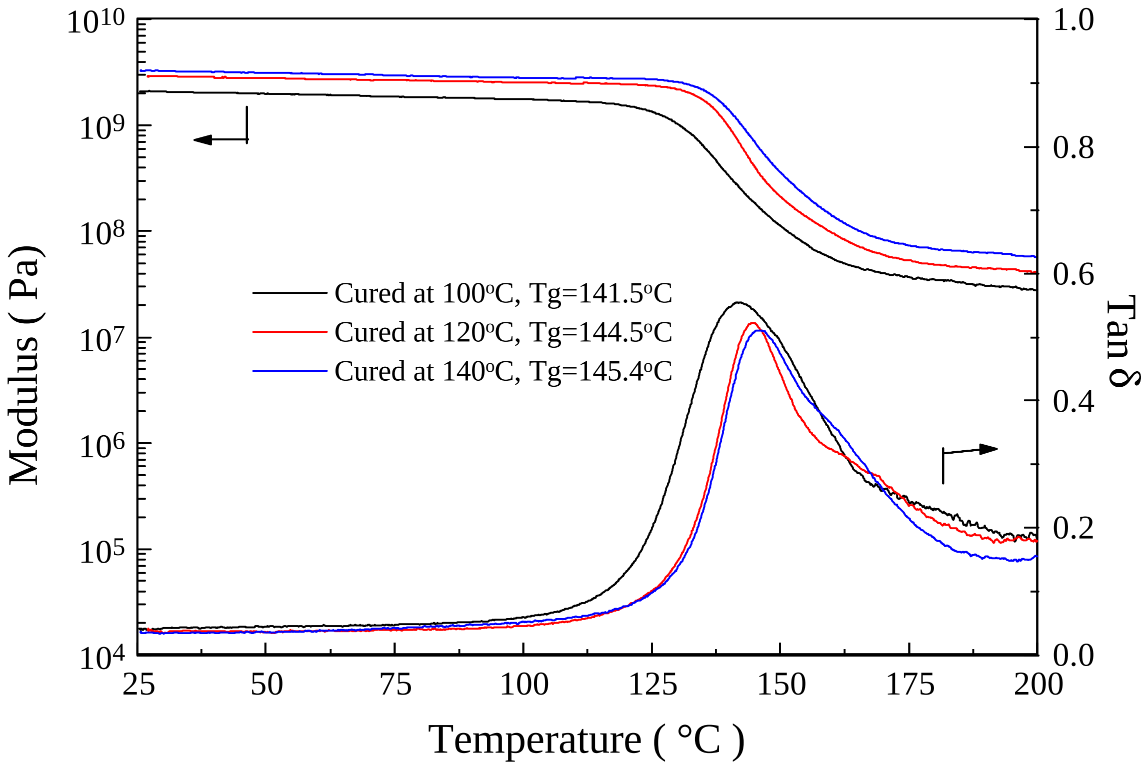

Figure 3.2.5. DMA results of Derakane 411-400.

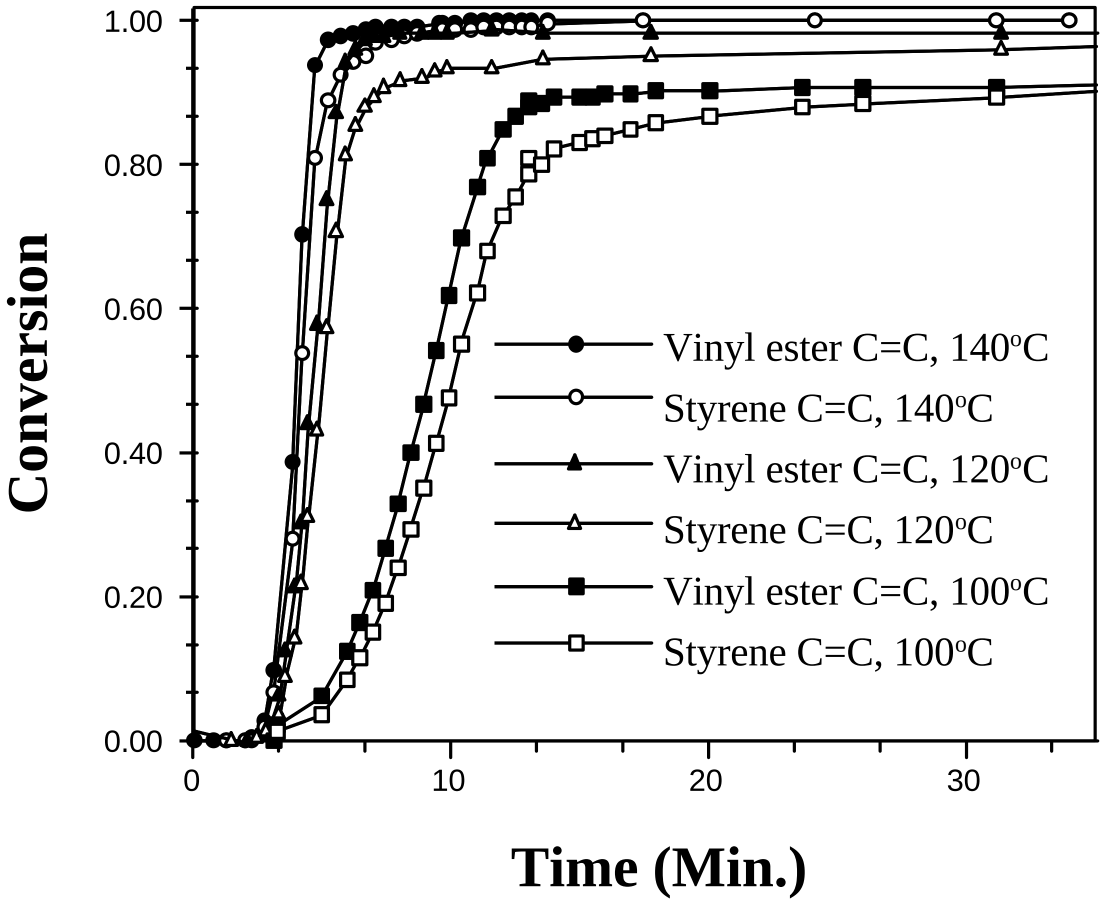

Figure 3.2.6. Reaction conversion at various cure temperatures.

The shrinkage was calculated based on density measurements. Figure 3.2.8 shows the cure shrinkage of two series of vinyl ester resins as a function of styrene concentration. As the graph suggests, the shrinkage of the vinyl ester resin with M_n = 700 g/mole increases from 2.1% to 9.1% as the small monomer styrene increases from 0 wt. % to 60 wt. %. The Derakane 441-400 undergoes between 6 and 7 volume percent shrinkage. Typically, most thermoset copolymers have minimal shrinkage (approximately 2-3%).[21] Vinyl ester/styrene resins undergo significant volume shrinkage upon cure which leads to residual stresses in the laminae.[22] These stresses may even exceed the strength of the matrix and lead to matrix cracking - even in the absence of shear. The results of Figure 3.2.8 show that resin shrinkage can be reduced by decreasing styrene content, although it is preferred to preserve the azeotropic styrene/methacrylate ratio of approximately 54 mol percent styrene(26wt% styrene) for M_n = 700g/mol. Another way to control volume shrinkage is to change the molecular weight of the vinyl ester oligomer. As suggested in Figure 3.2.8, higher molecular weight vinyl ester oligomer coupled with lower styrene content results in lower volume shrinkage.

3.2.5. Fracture Toughness Measurements

Because vinyl ester networks are used in structural composites, characterization of their toughness is very important. Toughness tests quantify the ability of a material to resist crack propagation under applied stress. Therefore, fracture toughness measurements of vinyl

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[21] H. Lee and K. Nevill, *Handbook of Epoxy Resins,* New York, McGraw-Hill, 1982.

[22] Y. J. Huang and C. M. Liang, *Polymer,* 37, 401, 1996.

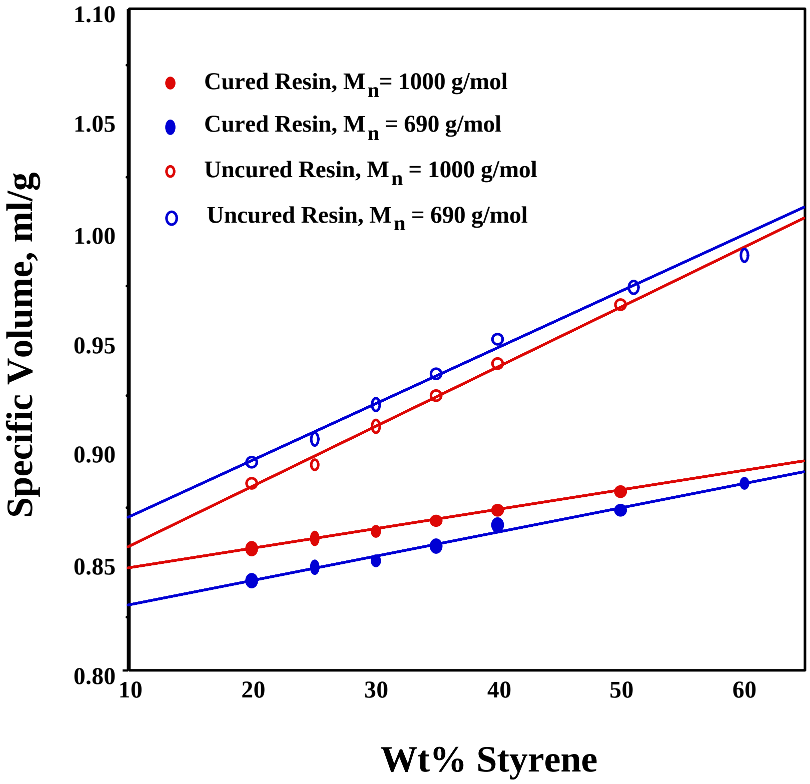

Figure 3.2.7. Specific volume of vinyl ester resin as function of styrene.

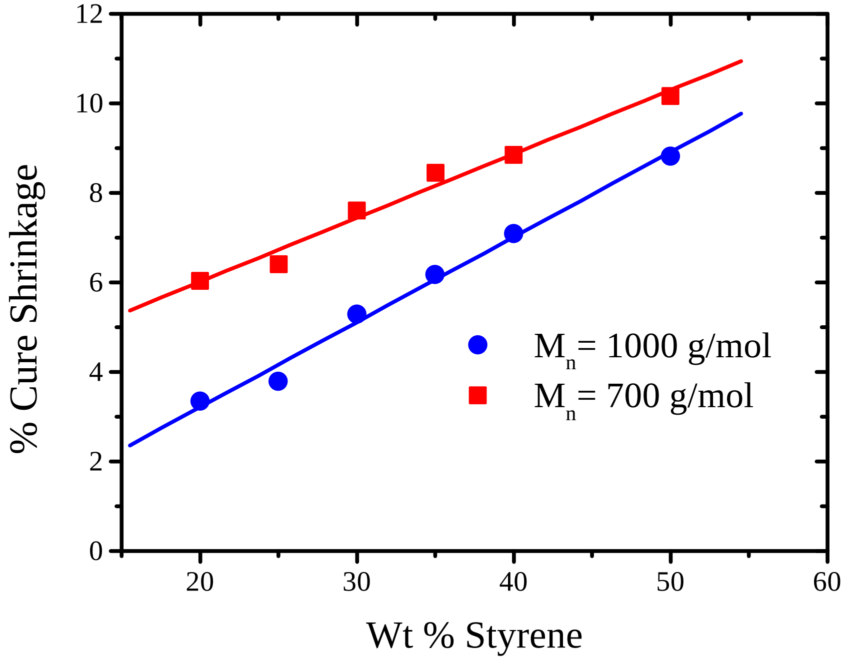

Figure 3.2.8. Cure shrinkage of vinyl ester resin as a function of styrene content.

ester networks were undertaken in collaboration with Ellen Burts, another graduate student in Dr. Riffle's group. Samples were tested with varying styrene content (from 20 wt% to 35 wt%). This is an allowable range to produce a reasonably homogeneous chemical network. A curve of load vs. displacement was developed for each sample. The K_{1c} values were calculated from the load obtained for each sample using an equation established on the basis of elastic stress analysis (Table 3.2.6).

$$K_{1c} = \frac{P}{BW^{3/2}} \; \frac{3(X)^{1/2}\,[1.99 - X(1-X)(2.15 - 3.93X + 2.7X^2}{2(1+2X)(1-X)^{3/2}} \tag{5}$$

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

Just like unmodified epoxy resins, vinyl ester resins also exhibit brittleness. For example, both commercial epoxy and vinyl ester Derakane 411 resins have similar K_{1c} values.[21, 23 -25] As the data in Table 3.2.6 indicated, both vinyl ester oligomer molecular weight and styrene content affect the toughness of the resulting cross-linked networks because of their influence on crosslink density. However, the effect of crosslinking on toughness is very complicated. A certain degree of crosslinking is required to obtain good network integrity and toughness; however, a very high degree of crosslinking results in a brittle material and decreases the toughness. Comparing the two series of vinyl ester resins shows that those with higher molecular weight oligomers have much higher K_{1c} values and are much tougher materials. For example, at 30 wt% styrene and the vinyl ester with M_n = 1000 g/mol, K_{1c} is 2.5 $MN/m^{3/2}$, compared to 0.75 for the corresponding styrene - vinyl ester resin with oligomer M_n

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

[24] V. Nigam, M. N. Saraf, and G. N. Mathur, *J. Thermal Analysis*, 49, 483, 1997.

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

= 700 g/mol. Lower crosslink density is the explanation for the much higher K_{1c} value for vinyl ester resins with these longer chain oligomers.

Table 3.2.6. Fracture toughness of vinyl ester resins.

Wt % Styrene	20	25	28	35	40
M_n = 690 g/mol:					
f_s	0.46	0.52	0.56	0.63	0.67
K_{1c} (MN/m$^{3/2}$)	0.87	0.77	0.72	0.63	0.91
Standard Deviation	0.07	0.12	0.11	0.11	0.4
M_n = 1000 g/mol:					
f_s	0.54	0.62	0.65	0.72	0.76
K_{1c} (MN/m$^{3/2}$)	2.13		2.03	1.24	1.11
Standard Deviation	0.043		0.04	0.3	0.1

However, for a given vinyl ester oligomer molecular weight, toughness decreases, yet the molecular weight between crosslinks increases, with an increase in the styrene concentration. The effect of styrene on the toughness is very complicated here and the copolymer effect may be a major factor. The styrene component yields a more brittle material compared to the vinyl ester component. In addition, higher styrene content increases the the shrinkage during cure, which also results in inferior properties in the cured networks. With higher styrene contents in the resins, the composition is far from the aezotropic point. As a result, in the latter stages of the cure reaction, only styrene remains, resulting in a heterogeneous chemical network structure. All these factors contribute to the poor toughness of vinyl ester resins at higher styrene concentrations. When the styrene content is higher than 50 wt%, the cured vinyl ester networks are so brittle that it is impossible to measure accurate K_{1c} values.

It has been proposed that toughness arises from a dynamic mechanical dissipation mechanism and should be proportional to the dynamic mechanical dissipation factor loss tangent. [26] Indeed, the dimethacrylate-styrene networks prepared with the 1000 g/mole oligomer did have higher tan δ values (Figure 3.2.9). Another interesting feature of dynamic mechanical analyses of these materials is that all of the networks exhibit a low temperature (ca. -66°C) secondary transition peak. It is unclear whether there is a correlation between the toughness K_{1c} values and the secondary transitions for these materials. Importantly, all of the materials prepared with the higher molecular weight vinyl ester were much tougher materials relative to those in the first series. Thus, the increase in M_c obtained by increasing the molecular weight of the vinyl ester component has a large positive effect on the resistance to crack propagation.

3.2.6. Swelling Experiments

The network structures of crosslinked vinyl ester networks were also studied by equilibrium swelling experiments. In this work, CH_2Cl_2, MEK, and water were used as solvents. Equilibrium swelling of crosslinked vinyl ester resins was achieved after swelling in these solvents for two weeks.

Tables 3.2.7 - 3.2.9 and Figure 3.2.10 show the swelling results. The procedure for swelling measurements and the definition for swelling index and gel fraction are given in section 2.7.12 of chapter 2. The data in these Tables shows that all of these systems exhibit low swelling in the solvents, indicating highly crosslinked systems. As styrene content was increased, the networks exhibited more swelling due to the decrease in crosslink densities for both series of resins with M_n = 700 g/mol and M_n = 1000 g/mol vinyl esters. The vinyl ester networks prepared with higher molecular weight vinyl ester oligomers (M_n = 1000 g/mol) show much higher swelling due to the longer chains between crosslinks. However, the swelling in

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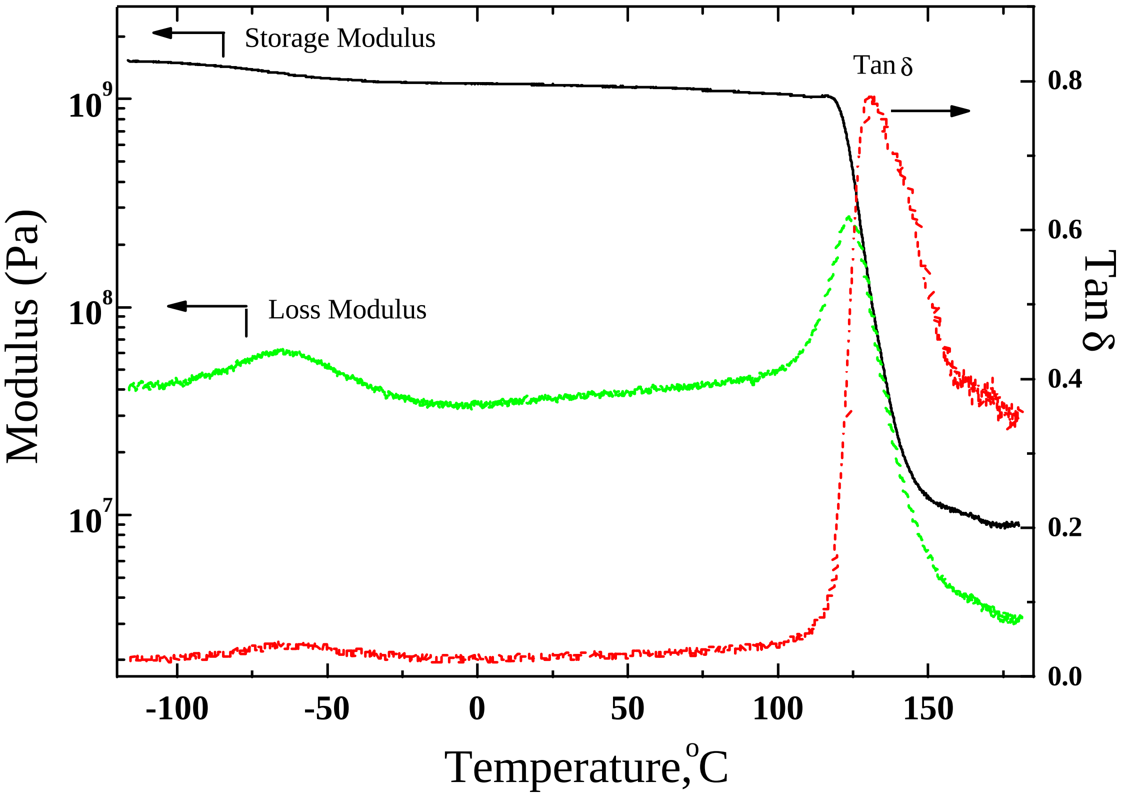
[26] E. Sacher, in Toughness and Brittleness of Plastics, R. D. Deanin and A. M. Crugnola, Eds., *Adv. Chem. Ser. 154,* ACS, Washington, D., 1976, p133.



	Secondary transition		Glass transition	
	Temp., °C	Peak Height	Temp., °C	Peak Height
28% St, Mn=700g/mol	-66.8	0.047	146	0.55
28% St, Mn=1000g/mol	-66.3	0.039	129	0.78

Figure 3.2.9. Typical dynamic properties of crosslinked vinyl ester-styrene resin (28 wt% styrene, Mn=1000 g/mol).

water showed a different trend. The swelling index decreased as the styrene content was increased, presumably due to the less hydrophilic character of polystyrene.

Solvent types also have a significant effect on the swelling behavior of the networks. Methylene chloride results in the highest swelling of the vinyl ester networks, possibly due to the fact that the solubility parameters of this solvent are very close to that of the networks. The solubility parameters of vinyl ester networks from 20 wt%-60 wt% styrene were calculated as 9.763 - 10.048 by group contribution methods using the MG&PC software.[26 -27] according to equation (6);

$$\delta = \rho \sum F_i / M \qquad (6)$$

Where Fi is the molar attraction constant of the group being considered, ρ is the density of the polymer, and M is the molar mass of the polymer. The summation was carried over all structural features in the molecule. The solubility parameter of CH_2Cl_2 is 9.7 while for MEK it is 9.3.

The crosslink densities of both series of vinyl ester - styrene networks were also determined from the swelling data.

$$\rho = \frac{-[\ln(1 - v_2) + v_2 + \chi_1 (v_2)^2] / V_1}{(v_2^{1/3} - \frac{v_2}{2})} \ , \qquad (7)$$

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[26] J. F. Graf, M. M. Coleman, and P. C. Painter, *The MG & PC Software, Miscibility Guide & Phase Calculator user manual*, V1.1.

[27] J. F. Graf, M. M. Coleman and P. C. Painter, *Miscibility Guide and Phase Calculator Software*, Technic Publishing Co., 1991.

Table 3.2.7. Swelling data of crosslinked vinyl ester/styrene networks (M_n = 690 g/mol).

Wt % of styrene	Swelling index in CH_2Cl_2	Swelling index in MEK	Swelling index in water	Gel fraction in CH_2Cl_2	Gel fraction in MEK
20	1.188	1.056	1.023	98.38	98.40
25	1.330	1.118	1.028	97.74	98.00
30	1.479	1.173	1.020	97.82	98.45
40	1.693	1.547	1.016	96.58	98.28
60	1.804	1.604	1.013	95.83	97.20
Derakane					
Cured at 140°C	1.566	1.441	1.035	97.52	98.00
Cured at 120°C	1.554	1.400	1.026	97.66	98.20
Cured at 100°C	1.536	1.463	1.020	97.73	97.88

* Swelling index = (volume of swollen gel)/(volume of dry gel)

Table 3.2.8. Swelling data of crosslinked vinyl ester/styrene networks (M_n = 1000 g/mol).

Wt % of styrene	Swelling index in CH_2Cl_2	Swelling index in MEK	Swelling index in H_2O	Gel fraction in CH_2Cl_2	Gel fraction in MEK
20	1.546	1.592	1.014	97.51	98.18
25	1.684	1.658	1.023	96.17	96.75
30	1.828	1.745	1.021	96.59	96.70
40	1.876	1.764	1.015	96.00	96.20

Table 3.2.9. δ and χ values and M_c determined by swelling measurements.

Wt% styrene	δ ($cal^{1/2}cm^{-3/2}$)	χ in CH_2Cl_2	M_c in CH_2Cl_2	χ in MEK	M_c in MEK
Mn = 690 g/mol					
20	10.05	0.353	53	0.425	34
25	9.98	0.348	91	0.410	53
30	9.92	0.345	139	0.398	71
40	9.90	0.344	220	0.394	244
60	9.70	0.340	265	0.364	260
Mn = 1000 g/mol					
20	10.04	0.352	164	0.423	292
25	9.98	0.348	219	0.410	328
30	9.94	0.346	285	0.402	385
40	9.86	0.343	305	0.387	385

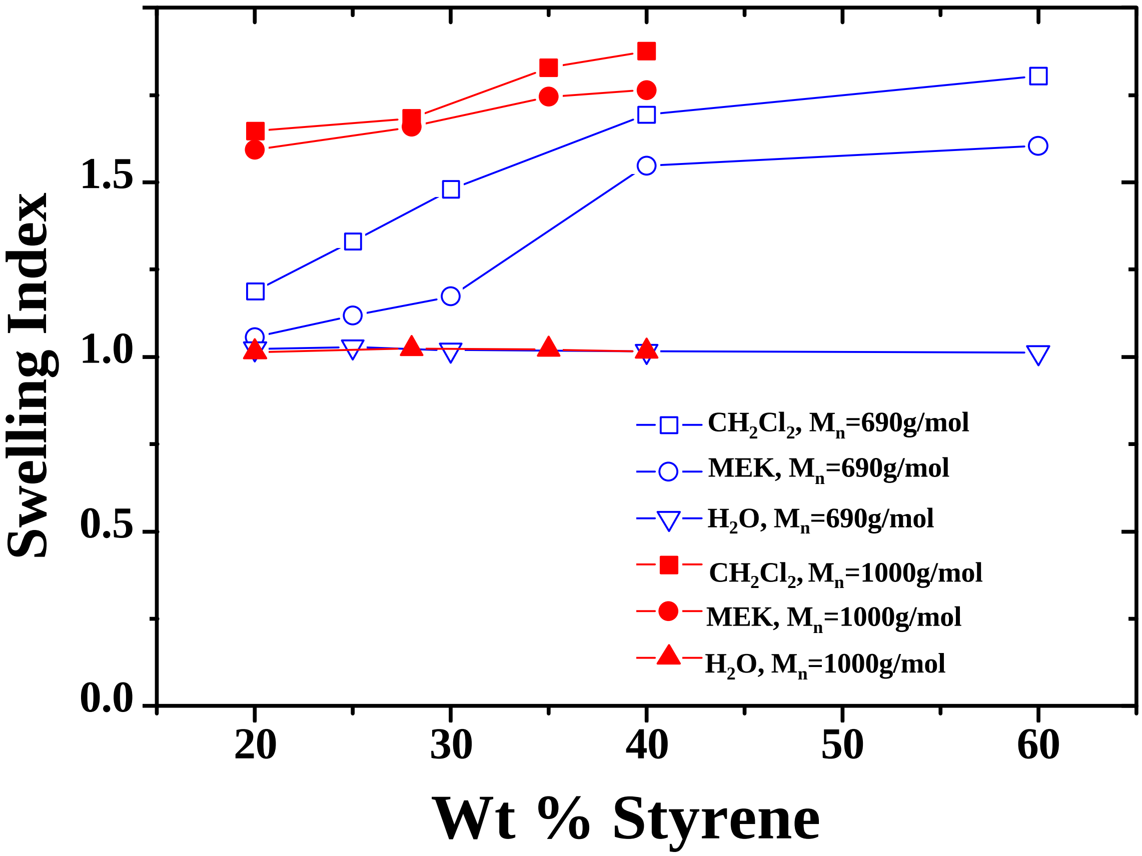

Figure 3.2.10. Swelling index as a function of styrene content.

where, V_2 is the volume fraction of polymer in the swollen gels, V_1 is the molar volume of solvent (64.10cm^3/mol for methylene chloride and 89.58cm^3/mol for methyl ethyl ketone), and χ_1 is the polymer-solvent interaction parameter which is estimated from values in the Polymer Handbook to be in the range of 0.34 - 0.35, according to equation (8):

$$\chi_1 = 0.34 + (\delta_1 - \delta_2)^2 V_1/RT \qquad (8)$$

The crosslink densities of the cured networks were calculated from equation (7) based on the swelling data obtained in methylene chloride. The low swelling of water and MEK makes it very difficult to obtain accurate crosslink density values. Table 3.2.10 lists the crosslink density values obtained from DMA and the swelling measurements. Although the values obtained by the two methods were not the same, they do reinforce the trend that higher styrene concentrations result in lower crosslink densities and that higher vinyl ester oligomer molecular weight results in lower crosslink densities.

Table 3.2.10. M_c (g/mol) values determined by different methods.

Wt % of styrene	Swelling		DMA	Calculated
M_n = 1000 g/mol	MEK	CH_2Cl_2		
20	164	292	337	417
28	219	328	445	444
35	285	385	332	476
40	305	385	408	513
M_n = 690 g/mol				
20	53	34	149	286
25	91	53	156	306
30	139	71	174	328
40	220	244	278	382
60	265	260	1049	573