Influence of Vinyl Ester/Styrene Network Structure on Thermal and Mechanical Behavior

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ABSTRACT: The influence of vinyl ester/styrene network structure on thermal and mechanical properties was investigated. The crosslink density of the resins was altered by changing the molecular weight of the vinyl ester oligomer and by varying the amount of styrene used during the crosslinking reaction leading to variations in both the physical network structure and the chemical composition of the polymeric networks. The glass transition temperatures of the network polymers were found to increase systematically with increasing crosslink density without the additional influence of the chemical composition as determined from both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The breadth of the glass transition regions increased with crosslink density for the DSC data, but the breadth assessed from the DMA data did not vary significantly for the network materials. A secondary relaxation was observed for the materials using DMA, and this relaxation did not appear to be significantly affected by changes in either the crosslink density or the composition of the network. Cooperativity studies involving time–temperature scaling of dynamic mechanical data in the glass formation temperature region were also conducted. The degree of segmental cooperativity at T_g appeared to be primarily influenced by the chemical composition of the networks. These issues dealing with the structure of the networks provided insight into the associated fracture properties in the glassy state (ambient temperature). Specifically, an empirically based linear correlation was found between the fracture toughness of the networks and the cooperative domain size at the glass transition temperature normalized by the crosslink density. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 917–927, 2001

Key words: vinyl ester; styrene; polymer network; crosslink density; fracture toughness; cooperativity; glass transition

INTRODUCTION

The successful application of crosslinked polymer systems as adhesives and matrix materials for composites relies, in part, on their suitable mechanical performance characteristics in the glassy state. The crosslink density has been successfully employed as a material structural parameter to understand variations in small-strain and ultimate mechanical properties of crosslinked rubbers.[1] The crosslink density provides a general means of characterizing the physical network structure, but other descriptive chemical and struc-

tural parameters may additionally be needed to understand the mechanical behavior of more chemically complex thermosets that are used in the glassy state. One application property that is of particular relevance to the application of crosslinked polymers in the glassy state is fracture toughness. Brennan et al.[2] recently stated that a general expectation is that fracture toughness should exhibit a direct dependence on the molecular weight between crosslinks (M_c). According to these researchers, lower M_c values (higher crosslink densities) are associated with a higher network rigidity, which limits the development of the local plastic zone at the crack tip, thus reducing the degree of energy dissipation. Brennan and coworkers also illustrated via a review of the literature that the connection between fracture toughness and crosslink density is still ambiguous, despite the expected relationship. The influence of other important structural distinctions between polymer network systems besides crosslink density may be the cause for the undefined effect of M_c on fracture behavior.

Previous research concerned with the mechanical response of glassy polymeric networks has indicated that structural details other than the average crosslink density are often needed to understand the mechanical behavior. For example, crosslink functionality was observed to be a critical network characteristic by Crawford and Lesser,[3] and this parameter and crosslink density were quantitatively used in combination to explain fracture toughness variations for epoxy networks. Aside from purely architectural characteristics of crosslinked polymeric materials, the chemical makeup of the network is also of critical significance, because it can influence glassy density, secondary interactions, and chain stiffness, all of which can affect the mechanical response. Polymeric networks were prepared by Bos and Nusselder[4] from the reaction of a triisocyanate with poly(propylene glycol) polymeric diols of various molecular weights. It was suggested by these authors that the uncharacteristically strong decrease observed in fracture toughness with increasing crosslink density for the network materials was due to the additional influence of chemical composition, which varied with crosslink density. Networks were generated by Gupta et al.[5] from diglycidyl ether of bisphenol A (DGEBA) using a metaphenylene diamine crosslinking agent, and fracture toughness was found to be dependent upon the chemical structure and degree of intermolecular packing in addition to being influenced by crosslink density. Min and coworkers[6] noted that crosslink density was not the main determinant of glassy fracture toughness for epoxy materials composed of DGEBA crosslinked with diaminodiphenyl sulfone (DDS). Their conclusion was that molecular packing features and chain flexibility were more important than crosslink density in determining fracture toughness behavior. These studies, which assigned some responsibility of observed variations in fracture toughness characteristics to the chemical features of the polymeric networks, did so in a largely qualitative manner.

Structure–property studies of crosslinked polymers often involve varying the molecular weight between crosslinks by changing the density of crosslink junctions with different crosslinking agents or curing conditions without otherwise altering the chemical composition of the network chains. For the vinyl ester/styrene networks investigated herein, there are two methods of altering the molecular weight between crosslinks: (1) changing the molecular weight of the vinyl ester precursor; and (2) varying the relative amount of styrene used during the crosslinking reaction.[7] The crosslink density of the vinyl ester/styrene materials was systematically varied by using two different vinyl ester oligomer molecular weights and by employing two weight percentages of styrene. Probing the properties of networks that have crosslink density differences induced by the two distinct methods can help determine whether property changes are due solely to the general effect of the crosslink density variation or whether the chemical individuality of the components comprising the network also plays a role. The glass transition responses for these vinyl ester/styrene materials were studied using DSC and DMA to note changes in T_g and associated breadth. The dynamic mechanical testing also allowed the intermolecular cooperativity of the crosslinked materials to be probed in the glass transition temperature region, and enabled the study of secondary relaxations as a function of network structure. The influence of composition and crosslink density on fracture toughness behavior and on glassy density of the materials was additionally inspected. This communication will detail the results proceeding from this testing to discern whether crosslink density and composition both play important roles in determining the properties of the vinyl ester/styrene networks. An attempt will be made to relate crosslink density and intermolecular cooperativity characteristics
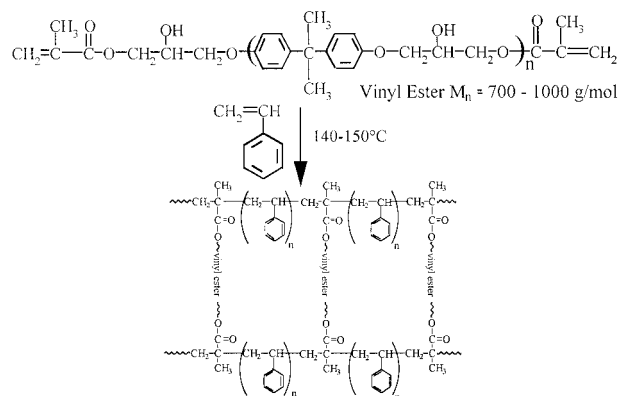
Figure 1 Diagram illustrating the network synthesis for the vinyl ester/styrene materials.

of the materials to the property of fracture toughness.

EXPERIMENTAL DETAILS

Material Preparation

The vinyl esters are a group of dimethacrylate resins from bisphenol A, epichlorohydrin, and methacrylic acid, and the general chemical structure of the vinyl ester/styrene neworks employed in this study is illustrated in Figure 1. Two different oligomer molecular weights of vinyl ester neat resins were supplied by the Dow Chemical Company. The number-average molecular weights for the oligomers were 1000 and 690 g/mol. Both of these resins were crosslinked with two different styrene contents, 20 and 35 wt %. The nomenclature that will be used to describe the materials is, for example, given by 1000–35%, where the first number represents the vinyl ester molecular weight in g/mol and the second number is the weight percent of styrene used during the crosslinking reaction. The network preparation involved mixing styrene monomer with the vinyl ester neat resin, having a molecular weight of either 1000 or 690 g/mol, in the ratio necessary to give the desired initial styrene content of 20 or 35 wt %. After the resin was dissolved by the styrene at 60°C, 1.1 wt % of benzoyl peroxide was added to serve as a reaction initiator. Constant stirring was carried out until a homogeneous mixture was formed. The mixture was then poured into silicone rubber molds and cured in an oven at 150°C for 1 h. The specifics of this reaction have been previously established.[8]

Characterization

The glass transition temperatures of the vinyl ester/styrene networks were measured by means of differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7. Sample weights of approximately 10 mg were used. The heating rate used during testing was 10°C/min, and two heating cycles from 30 to 200°C were applied, with an intermediate hold for 10 min at 200°C. Prior to the first heating scan, each sample was freshly quenched from 170°C into the glassy state at a cooling rate of 200°C/min. This quench rate of 200°C/min was also used between the first and second scans. The T_g was determined from the average midpoint value of the glass transition from the two DSC scans. The onset and end of each glass transition was determined using the analysis software provided with the instrument.

Thermal expansion behavior was determined for the networks below and above T_g via thermal mechanical analysis, and room temperature densities were also measured. Also, elastic moduli were assessed at 40°C above T_g. The procedural details of this testing are given elsewhere.[7] The molecular weight between crosslinks was evaluated from the experimentally determined values of the modulus and density at T_g + 40°C using basic rubber elasticity theory.[7,9]

Dynamic Mechanical Analysis

Dynamic mechanical testing of all samples was performed on a Seiko DMS 210 in tensile mode. Approximate sample dimensions were given by a thickness of 0.6 mm, a width of 3 mm, and a length suitable for a 10 mm grip separation to be used. The operating temperature range was from −150 to 220°C. The heating rate used was 2°C/min for the temperature range of −150 to 90°C, where the goal was to inspect secondary relaxation behavior. The heating rate was then changed to 0.2°C/min for temperatures of 90°C and above to acquire refined data in the glass transition temperature region to be used for cooperativity studies. The slow heating rate of 0.2°C/min essentially allowed isothermal data to be acquired as a function of frequency for temperatures in the glass formation region from approximately 15°C below to 40°C above the calorimetric glass transition temperature. The dynamic mechanical behavior was determined at 11 different frequencies, ranging from 0.05 to 20 Hz.

Fracture Toughness Testing

Fracture toughness properties of the resins were determined in terms of the critical-stress intensity factor K_{IC}. Following ASTM Standard D5045-91, three-point bend tests were performed at ambient conditions with the single-edge notch bending method. This testing procedure and the associated results for the vinyl ester/styrene materials have been previously detailed in the literature.[7]

RESULTS AND DISCUSSION

The results of this investigation will now be considered. Glass transition temperatures and breadths thereof were assessed using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), and the results for the vinyl ester/styrene materials will be detailed. A closer inspection of the glass formation process is afforded by time–temperature scaling of dynamic mechanical data in the glass formation temperature region, and interpretation of such an analysis will be made in terms of intermolecular cooperativity for each network studied. Finally, an examination of how the characteristics of crosslink density, secondary relaxations, glassy density features, and intermolecular cooperativity contribute to the noted differences in fracture toughness for the materials will be undertaken.

Glass Transition Behavior Observed by DSC and DMA

The location of the glass transition temperature region is an extremely important characteristic of polymers, and this was evaluated for the vinyl ester/styrene network materials. Differential scanning calorimetry was performed on the materials during heating at 10°C/min, and the responses that resulted from this DSC testing are shown in Figure 2. The upper and lower heating traces represent the first and second scans, respectively, for each network material. No significant amount of additional curing occurred during the first DSC heating scan nor the 10-min hold at 200°C. Evidence for this was provided from the essential equivalence of the results from the first and second heating scans for each network. Characteristics that describe this DSC data are detailed in Table I, along with the measured values of the average molecular weight between crosslinks
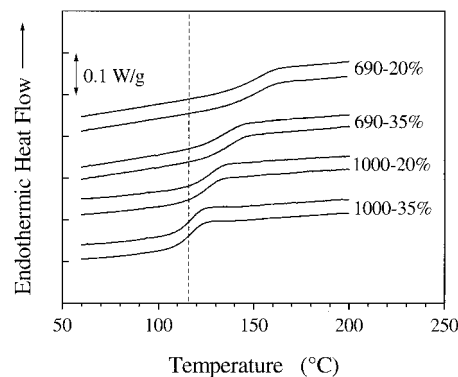

Figure 2 DSC glass transition responses for the network materials. For each material, the upper data curve represents the first heating scan and the second scan is given by the lower curve.

(M_c). The glass–rubber softening behavior of the materials was also investigated using dynamic mechanical analysis, and the tan δ peaks corresponding to the α-relaxations of the materials are plotted in Figure 3. The dependence of the glass transition temperature on $1/M_c$ is plotted in Figure 4. Although unusual departure from the typical[10] linear dependence of T_g on $1/M_c$ is observed from this plot, the glass transition temperature displays a smooth variation with respect to crosslink density for the vinyl ester/styrene materials. It should be mentioned that the use of predicted vs. measured M_c values for these networks results in a linear relationship between T_g and $1/M_c$. Despite the fact that the crosslink density was varied by the two distinct methods, a clear connection between glass transition temperature and $1/M_c$ was noted. This suggests that crosslink density was solely responsible for variations in the glass transition temperature for the vinyl ester/styrene materials, and styrene content was an unimportant factor except for its influence on M_c. It must be pointed out, however, that both polystyrene and a high molecular weight linear analog of the vinyl ester component have glass transition temperatures in the vicinity of 100°C. Therefore, the apparent lack of importance of chemical composition in determining the glass transition temperature may simply be due to this fact. It is worth noting that a systematic decrease in the degree of damping associated with the DMA glass transition region was also observed with respect to $1/M_c$ (see Fig. 5).

A closer examination of the glass transition responses can indicate whether the breadth of the glass transition temperature region was also in-

Table I   Characteristics of the Vinyl Ester/Styrene Networks

Vinyl Ester Oligomer M_n (g/mol)	Styrene Content (wt %)	Measured M_c (g/mol)	DSC T_g Onset (°C)	DSC T_g End (°C)	DSC T_g Midpoint (°C)	ΔC_p (J/g°C)
690	20	300	136	164	152	0.269
690	35	569	124	145	136	0.244
1000	20	812	115	133	125	0.322
1000	35	969	110	126	118	0.298

fluenced by the crosslink density. The breadth of the DSC glass transition was determined from the difference between the end and the onset of the transition (see Experimental Details). The breadth of each dynamic mechanical tan δ peak was assessed from the temperature range for which the value of tan δ was greater than 0.04. Networks with a greater crosslink density (lower M_c) possessed a broader glass transition according to the DSC results indicated in Figure 6, and this trend was independent of the method used to vary the degree of crosslinking. In contrast, the breadth inferred from the tan δ peak data was essentially constant with respect to $1/M_c$ (Fig. 6). The breadth of the mechanical glass transition response was either insensitive to the physical network structure represented by the crosslink density or there were other structural factors, which counteracted the influence of crosslink density. The width at half height was also evaluated from each tan δ peak, and was determined to be 24.2, 22.2, 19.8, and 21.4°C for the 700–20%, 700–35%, 1000–20%, 1000–35% materials, respectively. The fact that this parameter was also found to be roughly constant for the materials

strengthens the fact that the observed lack of dependence of the DMA glass transition breadth on crosslink density was real, and was not a consequence of an ill-defined method of breadth characterization. Further support for the lack of breadth variation observed by DMA will be given later when relaxation time function parameters are compared for the materials.

Intermolecular Cooperativity in the Glass Formation Region

Although chemical composition played an insignificant role in deciding variations in the glass transition temperature of the networks, it did have a notable impact on the glass formation process. The process of glass formation can be observed from the temperature and frequency (ω) dependence of dynamic mechanical data in the α-relaxation region. The behavior of an amorphous material during cooling toward the glass transition region can be interpreted in terms of cooperativity theory. The average relaxation time exhibits an increase as temperature is decreased
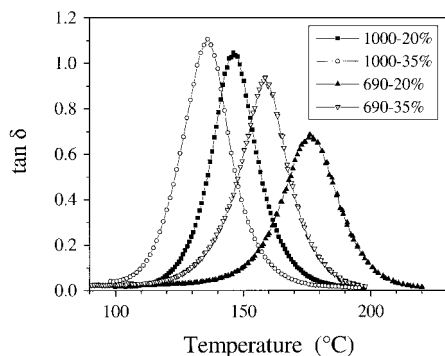

Figure 3   Dynamic mechanical tan δ data in the glass transition (α-relaxation) temperature region obtained during heating at 0.2°C/min using a testing frequency of 10 Hz.
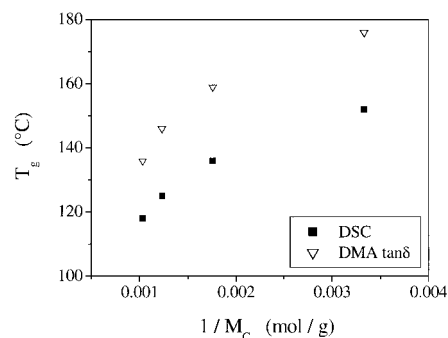

Figure 4   Glass transition temperature versus $1/M_C$. Indicated are T_g results obtained from DSC at 10°C/min and from the location of the tan δ maximum for DMA data obtained at a frequency of 10 Hz using a heating rate of 0.2°C/min.
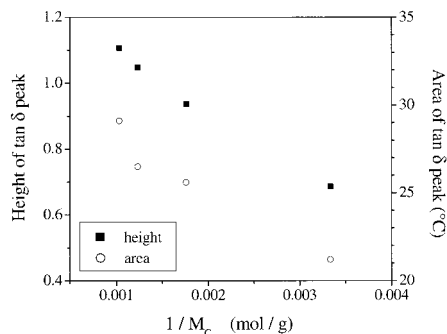
Figure 5 Glass transition damping characteristics for the networks as a function of $1/M_C$.

toward the T_g region. One reasonable explanation for this behavior is related to an increase in segmental cooperativity, which occurs as the free volume and configurational entropy decrease during the cooling process. If a glass forming material is envisaged to be composed of small relaxing segments, which could be polymer repeat units or even fragments thereof, then more and more of these segments must relax in concert as temperature is reduced due to geometric packing considerations or other restraints such as attractive chemical interactions.[11–13] Eventually the relaxation times become so large that a liquid-like state can no longer be maintained, and a glassy state is formed. The number of cooperative segments in a relaxing domain at the glass transition temperature where this departure into the glassy regime occurs is given by z_g. An in-depth explanation of this conceptual approach to understanding glass formation behavior, which was pioneered by Adam and Gibbs,[11] is given elsewhere.[14] Application of time–temperature superposition to dynamic mechanical data can provide a quantitative measure of this cooperativity, z_g,
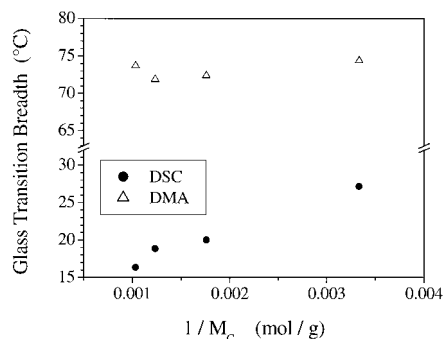

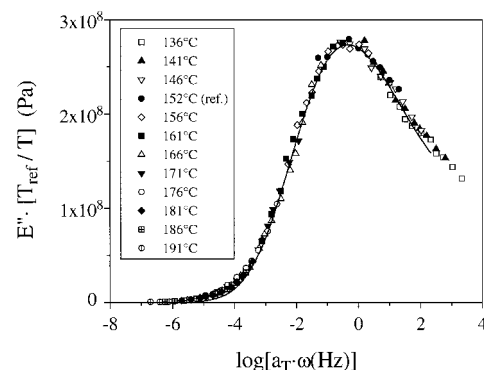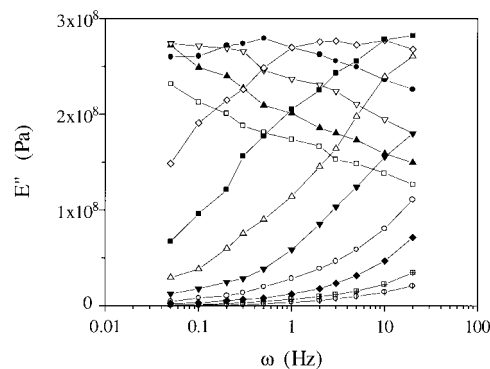**Figure 6** Glass transition breadth plotted as a function of $1/M_C$.

Figure 7 (a) Loss modulus data as a function of frequency at temperatures in the glass formation region for the 690–20% material; and (b) Master curve generated via time–temperature superposition (symbols) as well as the KWW fit (line). The caption given in (b) applies to both plots.

at the glass transition temperature that can help characterize the glassy state that is formed. The influence of crosslink density on cooperativity in the glass transition region has been investigated,[15–20] and a general understanding of how the degree of cooperativity depends on chemical structural features of linear polymer systems has been established to an extent by Roland, Ngai, and other researchers.[21–24] Both crosslink density and composition were varied in this study of the vinyl ester/styrene materials, and the following analysis will develop values of z_g, a parameter that can be used as another structural characteristic to help describe the polymer networks.

To thoroughly understand the dynamics of the glass formation region as influenced by the changes in the network structure, the temperature and frequency dependence of the dynamic mechanical spectra were determined for the materials. Typical loss modulus (E'') results are indicated in Figure 7(a), which presents the data for the 690–20% material. The frequency- and tem-

perature-dependent mechanical loss modulus data of each network were reduced into a master curve using the time–temperature superposition principle.[25,26] Horizontal superposition was performed on the log(frequency) scale, and the degree of shifting was quantified by a temperature shift factor, a_T, which is defined as:

$$a_T = \tau(T)/\tau(T_g) \qquad (1)$$

The parameter $\tau(T)$ is the relaxation time at temperature T and $\tau(T_g)$ is the relaxation time at the calorimetric glass transition temperature, T_g, which was appropriately selected as the reference temperature. Prior to the horizontal shifting that was performed, the loss moduli at each temperature were corrected vertically by multiplying by the ratio T_g/T. The final result of this superposition process was a master curve for each material, and the curve for the 690–20% network is shown in Figure 7(b). Decent master curves resulted from the data for all of the networks, and, hence, thermorheological simplicity, appeared to be at least approximately valid for the materials within the temperature and frequency ranges utilized.

Information about the glass formation kinetics of the crosslinked polymer systems was gleaned from the time–temperature scaling data. Shift factors were determined from the degree of horizontal shifting necessary to superimpose loss modulus data at one temperature with the data at the reference temperature which was T_g. This information indicated how relaxation times varied with temperature in the glass formation temperature region. The temperature dependence of viscoelastic relaxation times in the α-relaxation region of amorphous materials can be described well by the Williams-Landel-Ferry (WLF) equation[27]:

$$\log a_T = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \qquad (2)$$

where a_T is the temperature shift factor described above, and C_1 and C_2 are WLF constants. The dependence of the shift factor on T_g/T is plotted in Figure 8 for each vinyl ester/styrene network. The WLF fitting of each curve provided values of C_1 and C_2 for each network, and this information is listed in Table II. The relaxation time scaling data that was represented by the WLF function was subsequently used to determine the degree of segmental cooperativity at the glass transition

temperature. The cooperative domain size at the glass transition temperature can be expressed as[14]:

$$z_g = (T_g/C_2)^2 \qquad (3)$$

The values of z_g that resulted from this determination are given in Table II. Cooperativity was noticeably dependent upon chemical composition of the networks, but relatively unaffected by variations in crosslink density for a given styrene content. Although the location of the glass transition temperature was found to be independent of styrene content, the chemical makeup of the networks obviously influenced the glass formation process, which in turn, should affect the nature of the glassy state formed upon cooling through T_g. A larger z_g value implies that the motion of molecular segments is more interconnected, and hence, a general expectation is that more cooperative glasses are less mobile. Further discussion of the compositional dependence of z_g and its possible impact on mechanical response in the glassy regime will be undertaken later.

The shape of the loss modulus master curve also provided insight into relaxation time characteristics associated with the glass formation process. The relaxation of amorphous materials can often be described by the time-dependent stretched exponential decay function also known as the Kohlrausch-Williams-Watts (KWW) function[28,29]:

$$\phi(t) = \exp[-(t/\tau)^\beta] \qquad (4)$$

In the above expression, τ represents the most probable relaxation time at a given temperature. The β parameter is inversely related to the
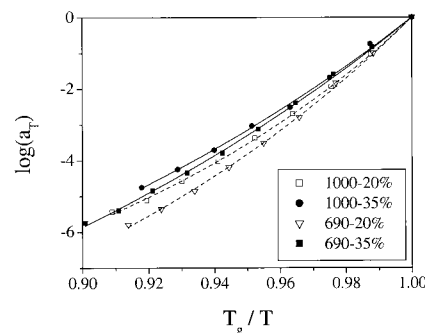

Figure 8 Cooperativity plots for the network materials (symbols). The sold lines represent the fits to the WLF equation.

Table II   Parameters Describing Dynamic Mechanical Data in the Glass Formation Region

Vinyl Ester Oligomer M_n (g/mol)	Styrene Content (%)	DSC T_g Midpoint (K)	Measured M_c (g/mol)	β	C_1	C_2 (K)	z_g
690	20	425	300	0.225	17.9	82.7	26
690	35	409	569	0.200	19.2	103.4	16
1000	20	398	812	0.225	17.1	74.2	29
1000	35	391	969	0.275	17.3	92.4	18

breadth of the relaxation response; when $\beta = 1$, then only a single relaxation time is necessary to describe relaxation, and the relaxation time function broadens as β is decreased from this value toward zero. The coupling model of Ngai and coworkers[30–32] relates the coupling parameter, n, to the β parameter according to $\beta = 1 - n$. Transforming the time-dependent KWW decay function to describe loss modulus data in the frequency (ω) domain can be accomplished using the following expression[33]:

$$\frac{E''(\omega)}{E_\infty - E_0} = \omega \int_0^\infty \phi(t)\cos(\omega t)\, dt \qquad (5)$$

where E_∞ and E_0 represent the moduli values in the respective limits as frequency approaches infinity and zero, and the quantity $E_\infty - E_0$ is, therefore, a measure of the relaxation strength. The KWW equation was numerically transformed[14] for selected values of the β parameter and comparison of the predictions with the shape of each loss modulus master curve enabled the determination of the β value that best described each curve. The results of this endeavor are summarized in Table II, and an illustrative fit is indicated by the solid curve plotted in Figure 7(b). Given the fitting error for β, which was approximately ± 0.0125, no significant variation in the relaxation time distribution was observed for the network materials. This is consistent with the lack of glass transition breadth variation observed from the tan δ peaks for the vinyl ester/styrene networks. Research has indicated[34] a general increase in β with decreasing fragility (which is closely related to the z_g parameter[14]) for a wide range of glassy materials. Such a correlation was not evident in this study, and this highlights the fact that these network structures are complex.

Influence of Network Structure on Fracture Toughness

The ultimate aim of this investigation was to develop an understanding of the factors leading to fracture toughness differences for the vinyl ester/styrene materials. In the Introduction, it was mentioned that M_c should influence the fracture toughness in the glassy state, and a natural question that was posed in this study was whether a correlation between K_{1C} and $1/M_c$ existed for the networks. Considering the results presented in Table II provides an answer to this question. At constant network composition, fracture toughness appeared to scale inversely with $1/M_c$. However, increasing the styrene content from 20 to 35 wt % served to significantly reduce the fracture toughness of the materials. Composition-dependent features were obviously active and of importance in dictating the fracture toughness properties.

The nature of secondary relaxations was investigated for the materials. As observed previously,[35,36] nearly all tough ductile glassy polymers with high impact strengths have prominent secondary relaxation peaks. Secondary relaxations should, therefore, play an important role in the mechanical behavior within the glassy state including fracture toughness response. The tan δ data, obtained at a frequency of 10 Hz, is shown in Figure 9 for the temperature range associated with the only secondary relaxation response noted for the materials. Polystyrene has a secondary relaxation in the temperature range of −140 to −100°C, but this relaxation is extremely weak.[37,38] Accordingly, the secondary relaxation for the network materials was likely associated with localized molecular motion of the vinyl ester component. It might be expected, therefore, that the relaxation intensity of the secondary relaxation of the vinyl ester/styrene networks should decrease with increasing styrene content. Al-
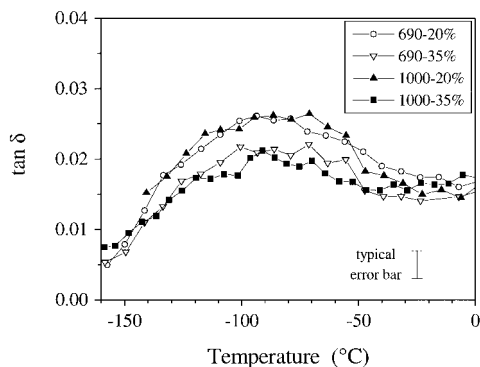
Figure 9 Dynamic mechanical tan δ data in the secondary relaxation temperature region obtained during heating at 2°C/min using a testing frequency of 10 Hz.

though the networks with 20 wt % styrene did display peaks that were slightly higher than those for the materials containing 35 wt % styrene, all of the secondary dispersions displayed relaxation strengths that were nearly the same within experimental error. Either the range of composition variation was too small to induce a noticeable change in the strength of the secondary relaxation, or other opposing structural operatives were present. The observed activation energies for the secondary relaxations of the various networks ranged from 66 to 78 kJ/mol, and it was concluded that no statistically significant variation in this parameter was present for the materials. Therefore, differences in secondary transition responses were relatively insignificant, and cannot be used to explain the marked reduction in fracture toughness associated with an increase in styrene content.

The macroscopic density in the glassy state was another structural variable that was compared for the crosslinked materials. The density at 25°C is plotted vs. $1/M_c$ in Figure 10. The density and the physical network structure were apparently closely linked for the materials, and styrene content did not appear to independently influence the state of packing in the glassy state. The densities at $T_g - 40$°C are also indicated in Figure 10 to illustrate that the observed trend at 25°C was not merely associated with the fact that the glass transition temperature varied with crosslink density, nor was it due to variations in thermal expansion behavior. Because of this apparent close tie between density and M_c, which is essentially independent of composition, density variations cannot offer any insight into the dependence of fracture toughness on styrene content.

The cooperativity, z_g, was the only structural characteristic in this study that appeared to be connected with the chemical makeup of the network. However, some interplay between the degree of cooperativity and the physical network structure must also have been present for the vinyl ester/styrene system. The value of z_g for neat linear polystyrene was observed to be 62 in another study.[14] One might intuitively expect that increasing the styrene content should result in a value of z_g, which is closer to that observed for pure polystyrene, but the opposite was found to be true. Another curious aspect is that the density of neat polystyrene at room temperature is 1.048 g/cc,[39] a value well below the range of densities observed for the vinyl ester/styrene networks. Angell[40] pointed out that the strong liquids with the lowest degree of fragility, or cooperativity, are expected to be the least closely packed upon quenching into the glassy state. The networks were noted to be much less cooperative than neat polystyrene, and yet were found to have higher densities in the glassy state compared to polystyrene. The complicated behavior of z_g and density, relative to each other, can be observed graphically by means of Figure 11. Although such details are not fully understood, it was clear from this study that z_g displayed a strong dependence on styrene content for the materials. The z_g parameter could not exclusively account for the fracture toughness properties, as is evident from Table II. However, the fracture toughness exhibited an interesting linear dependence on z_g divided by the crosslink density, N, where $N = \rho/M_c$ (see Fig. 12).

The convincing dependence of fracture toughness on the ratio z_g/N suggested that K_{1C} was directly and inversely related to z_g and crosslink
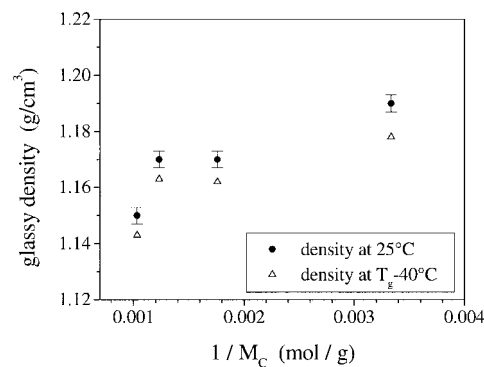

Figure 10 Glassy density as a function of $1/M_C$ for the vinyl ester/styrene networks.
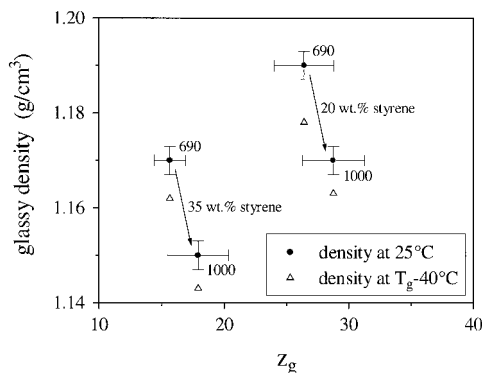
Figure 11 Glassy density vs. z_g. The arrows indicate increases in the molecular weight of the vinyl ester oligomer at constant styrene composition.

density, respectively. The inverse relationship between fracture toughness and crosslink density was an intuitive result, but the direct influence of z_g on K_{1C} was surprising. One possible explanation is that more cooperative glasses have a mechanism, by means of increased geometric connectivity, for enhancing the energy dissipation process. However, the general expectation is that more cooperative, or fragile, glass-forming materials are less mobile in the glassy state, which is in opposition to the observed direct correlation between K_{1C} and z_g. Glassy structures that have a heightened state of required cooperativity should provide more rigid responses, which should decrease properties such as fracture toughness. The z_g values were certainly decreased for the networks with 35 wt % styrene in comparison to the networks synthesized using a styrene content of 20 wt %. It is possible that the apparent direct relationship between fracture toughness and z_g is not a general result applicable to all networks, but rather was a coincidental consequence of the connection between z_g and styrene content for the specific network system investigated. Nevertheless, the empirically based K_{1C} vs. z_g/N relationship can be used quantitatively to represent the fracture behavior of the vinyl ester/styrene networks. It remains to test whether this relationship is valid for other crosslinked glassy materials.

CONCLUSIONS

The crosslink density of the vinyl ester networks was varied via two methods: by changing the precursor oligomer molecular weight, and by varying

the amount of styrene used during the network synthesis. The glass transition temperatures measured by both DSC and DMA systematically increased with increasing values of $1/M_c$ without the additional influence of chemical composition. A similar relationship was found between the breadth of the DSC glass transition and $1/M_c$, but the glass transition breadth observed by DMA was essentially invariant for the networks. From the dynamic mechanical spectra, it was found that the vinyl ester/styrene materials possess secondary relaxations that are largely indistinct from each other despite differences in the physical network structure and in the composition of the network chains. Glassy density varied with $1/M_c$ but appeared to be unaffected by changes in styrene content. The only structural parameter that displayed composition-dependent behavior was the glass transition cooperativity, z_g, which is a parameter that characterizes the degree of intersegmental cooperativity present in the glassy state formed via cooling through T_g. Fracture toughness in the glassy state was influenced by both crosslink density and styrene content. A linear relationship between fracture toughness and z_g normalized by the crosslink density, N, was noted for the system. Although this observed correlation between K_{1C} and z_g/N is intriguing and encouraging in terms of quantitatively understanding the fracture toughness performance of the vinyl ester/styrene networks, it should be reemphasized that this connection is empirical, and may be specific to this particular network system. Therefore, further critical examination of this correlation should be performed in the future using other network materials.
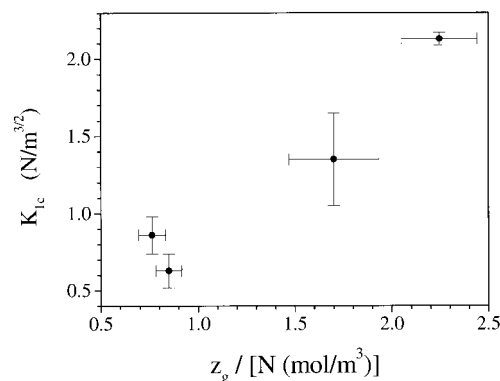

Figure 12 Apparent correlation between fracture toughness and the normalized cooperativity index. The N parameter is the crosslink density given by $N = \rho/M_C$.

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