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# Effects of Gelation in the Glassy State

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Gelation and vitrification are the two fundamental events that are commonly encountered in the transformation of liquid thermosetting multifunctional monomers to glassy network polymers.[1] Gelation corresponds to the end of the processable fluid state of a polymeric system. Vitrification corresponds to the solidification when the glass transition temperature $T_g$ of the polymeric system precedes the experimental temperature $T$.

Two situations can be distinguished. First, the gelation precedes the vitrification during the polymerization. In this case, the system is in the molten state. The sol−gel transition is characterized by the divergence of the viscosity of the sol below the gelation point and by the abrupt increase of the modulus of the gel above it. Physically, the transition is analogous to the general critical phenomena in terms of scaling laws.[2−4] The second situation, which is of less concern, happens when the $T_g$ of a system rises relatively fast, and vitrification occurs before the gelation. In this case, the system is in its glassy state. Taking the epoxy polymerization as an example, the resin is simultaneously polymerizing and cross-linking. The resulting material can be either a thermoplastic glass or a thermosetting glass, depending on the stoichiometric ratio and the functionality of the reactants. Despite the technological importance of such glassy polymers, the physics associated with the gelation in the glassy state is poorly understood.

Recent studies show that for epoxy resins the isothermal density and modulus pass through a maximum in the glassy state with increasing chemical conversion.[5−7] Free volume measurement vs chemical conversion shows that the maximum in the isothermal density or modulus occurs approximately in the same location as the minimum found in the free volume.[8] The maximum found in density and modulus has a significant implication on all other physical properties, such as water absorption,[5] diffusion coefficient,[9] gas permeability,[9] thermal expansion coefficient,[10] and the physical aging rate.[11] Of most importance is that the same phenomenon has been observed in other systems, such as polycynurates[12,13] and phenolic resins.[14] This fact suggests that the glassy network polymers share a common physical nature in their glassy state.

To understand this nature of network polymers in the glassy state, systems of various gelation points are selected. Here we show from experimental data that the maximum in density is related to the gelation process, and the maximum usually occurs after the gelation point. In addition, we show that the maximum in density is not a kinetic phenomenon. The buildup of the network is responsible for the development of the maximum.

Four amine-cured epoxy resins were employed in this investigation. Three of them were thermosetting (or branched), and one was thermoplastic (or linear). In all cases, aromatic diamines were selectively used as the curing agents. The reason is that the basic chemistry of the curing reactions is clear, and unexpected side reactions in these reactants are negligible.[15] Also, using aromatic amines can provide materials that are of good thermal stability and high glass transition temperatures. The reactants used in this investigation are listed in Table 1.

In preparation, a stoichiometric amount of amine was dissolved into a liquid epoxy at around 80 °C. Complete dissolution took place within 30 min with vigorous stirring. Once the solution was clear, it was degassed under vacuum at 50 °C for 30 min. The degassed molten mixture was then used to fill a multicavity aluminum mold that was lined with aluminum foil. The cavities provided disk-shaped specimens of about 1 mm thickness. The disks were cured in the molten state (i.e., at $T_{cure} > T_g + 25$ °C) under nitrogen purging to different extents. Previous studies[1,5−7] showed that as long as $T_{cure} > T_g$ the effect of cure temperature was not important for the properties studied here. The disks were then inspected using a polarizing light microscope. All specimens used in this investigation were free from visible voids, bubbles, and cracks. Prior to density measurement, the specimen was further annealed at a temperature at least 15 °C above its $T_g$ and then cooled to room temperature at a constant rate of 5 °C/min. This procedure resulted in specimens with a well-defined and reproducible thermal history.

Thermal analysis was performed on a TA instrument modulated DSC 2920 using a nitrogen-purged cell at a flow rate of 80 mL/min. The heat capacity signal was calibrated using a sapphire at 5 °C/min heating rate, 40 s period, and 0.5 °C modulating amplitude. The same conditions were then applied for all test specimens. Chemical conversion of a partially cured specimen was calculated from the residual heat that appeared in the nonreversible heat flow vs temperature. This determination of the chemical conversion eliminated the effects that came from the change in heat capacity of the sample during increasing temperature. The values of $T_g$ were obtained from the reversible heat flow vs temperature. Usually, the thermal analysis was taken right after the annealing treatment.

The densities of specimens were measured at room temperature using a density gradient column. The device is particularly suitable for the present purpose because it can provide measurements with reasonably high sensitivity.[5,8] In this research, the density gradient column was prepared using two sodium bromide/water solutions. The temperature of the column was maintained at 23 ± 0.05 °C using a circulating water bath. The density gradient was calibrated with 4−6 specified density floats. The sensitivity of the gradient is about 0.0004 g per centimeter height. Usually two to three specimens of the same sample were dropped individually into the column. Readings were taken after about 30 min[16] when equilibrium was reached. The reproducibility of the measurement was about ±0.0001 g/cm$^3$.

For the systems investigated, the transformation from monomers to fully reacted polymers involves the glass transition temperature increasing from its initial value ($T_{g0}$) to its maximum value ($T_{g\infty}$). Figure 1 displays the change of glass transition temperature $T_g$ vs chemical

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**Table 1. Chemical Reactants**

| system examined | epoxy used | functionality of epoxy | aromatic amine used | functionality of amine | system | glass transition temp (K) |
|---|---|---|---|---|---|---|
| linear | diglycidyl ether of bis-phenol-A (from Dow Chemicals) | 2 | *N*,*N*′-dianilinoethane (from Aldrich) | 2 | DGEBA−DAE | $T_{g0} = 246$<br>$T_{g\infty} = 354$ |
| branch 1 | triglycidyl ether of *o*-cresylformaldehyde (from Aldrich) | 2.71 | *N*,*N*′-dianilinoethane (from Aldrich) | 2 | TGECF−DAE | $T_{g0} = 262$<br>$T_{g\infty} = 375$ |
| branch 2 | triglycidyl ether of *o*-cresylformaldehyde (from Aldrich) | 2.71 | 4′4′-methylenedianiline (from Aldrich) | 4 | TGECF−MDA | $T_{g0} = 277$<br>$T_{g\infty} = 433$ |
| branch 3 | diglycidyl ether of bis-phenol-A (from Dow Chemicals) | 2 | trimethylene glycol di-*p*-aminobenzoate (from Polariod Corp) | 4 | DGEBA−TMAB | $T_{g0} = 268$<br>$T_{g\infty} = 453$ |

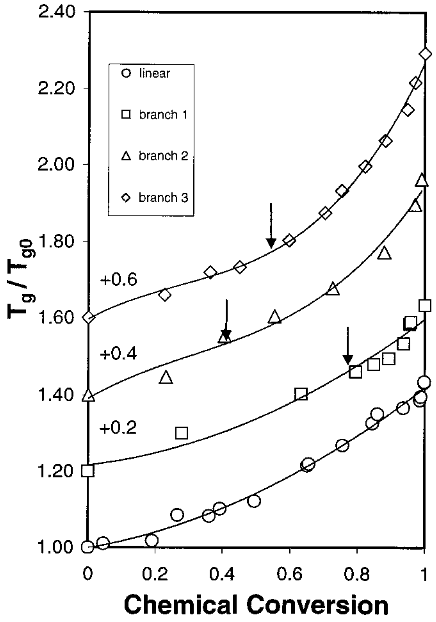

**Figure 1.** Nonlinear relationship between $T_g$ and chemical conversion for various systems. Arrows in the plot mark the locations of the gelation points for various systems.

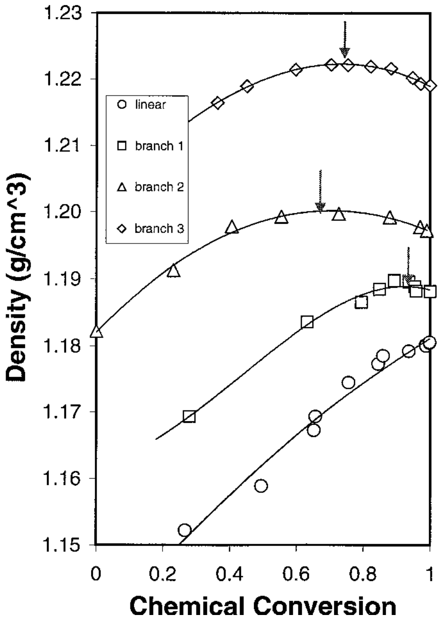

**Figure 2.** Isothermal density at 23 °C vs chemical conversion for various systems. The density passes through a maximum for cross-linking systems. For a linear system, the maximum is not observed. Arrows in the plot mark the locations of maxima.

conversion for various systems. The *y*-axis in this plot has been normalized with $T_{g0}$ for comparison. For the systems investigated, the glass transition temperature ($T_g$) is always a monotonic, smoothly increasing function of the chemical conversion. As for the $T_g$−conversion relationship, no significant difference can be seen between a thermosetting system (e.g., a branched system) and a thermoplastic system (e.g., a linear system) in this plot.

Figure 2 shows the change of isothermal density vs chemical conversion for various systems. For thermosetting systems, the density of the reactants initially increases with increasing the chemical conversion, reaching a maximum, and then decreases until the system is fully cured. A maximum is usually displayed in the density vs chemical conversion relationship for those systems. However, the same phenomenon is not observed for a thermoplastic (or a linear) system. As shown in Figure 2, the density in a linear system is a monotonically increasing function of the chemical conversion. This result suggests that the maximum in density is only associated with the glassy network polymers.

If comparing the gelation point in Figure 1 and the maximum in Figure 2, one may notice that the higher the conversion at the gelation point, the higher the conversion at the maximum. Clearly, the maximum in density is strongly related to the gelation point and thus verifies the previously suggested supposition.[5−7] However, the maximum in density does not occur at the gelation point. In general, the maximum in density occurs after the gelation point.

To understand further the phenomenon, we have systematically studied a resin at various cooling rates. In this study, all specimens were first annealed at a temperature at least 15 °C above the $T_g$ and were then cooled to room temperature at various cooling rates (e.g., 20, 5, or 0.5 °C/min). The density measurement and the thermal analysis were conducted right after the treatment. The test results are summarized in Figure 3. Under all test conditions, a maximum in density is always observed, and the phenomenon is independent of cooling rates. The widths and the heights of the density peaks, however, are affected by the cooling rates. As shown in Figure 3, the slower the cooling rate, the sharper the density peak. Those results demonstrate that the maximum in density is caused by a structure feature (i.e., the buildup of network structures) rather than a kinetic feature (i.e., cooling rate vs contraction rate). As is known, a kinetic phenomenon usually tends to diminish itself once the cooling rate is slowed down (e.g., the glass transition process). However, what we observed here is completely opposite. The maximum in density tends to intensify itself when the cooling rate is slowed down and is therefore not a kinetic phenomenon.

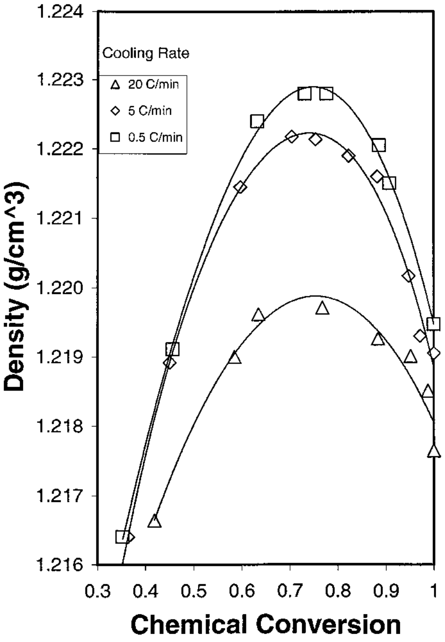

**Figure 3.** Isothermal density at 23 °C vs chemical conversion at various cooling rates for the DGEBA–TMAB system. The system is particularly suitable for this study due to its low reactivity.[5–7] A maximum in density is observed under all test conditions. The maximum tends to intensify itself when the cooling rate is slowed down.

In principle, an increased chemical conversion will result in an increase of the fraction of covalent bonds compared to van der Waals bonds. The volume is expected to decrease with increasing chemical conversion. This principle may hold true for linear polymers but is not applicable for network polymers in the glassy state. The results shown in Figures 2 and 3 suggest that the development of the maximum in density in the glassy state is due to loose packing of the molecular chains in a highly cross-linked network. To the best of our knowledge, this is the first time that experiments under well-defined conditions provide such clear evidence. We believe that the phenomenon is directly related to the nature of the glassy state. The mechanism in which the maximum in density may occur is important and is under investigation.

## References and Notes

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(16) Soaking a sample inside the density column for a long time is not recommended, because the epoxy resins may absorb water during a long time soaking.

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