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Crosslinking induced volume expansion in the glass state

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Abstract

We have studied a very unusual phenomenon that occurs in the glassy state, that the isothermal density and modulus of a thermosetting polymeric material pass through a maximum in the glassy state with increasing chemical conversion. The maximum occurs approximately after gelation, and the specific volume of the material after gelation increases via further crosslinking. We show that this anomalous behavior is not a kinetic phenomenon, though the glass transition is a function of the experimental time-scale. In addition, we show that the anomalous behavior strongly depends on the overall crosslinking densities of the polymeric material, and tends to intensify itself as the overall crosslinking density increases. We interpret that the nature of this anomaly is related to the configuration entropy criterion required for forming a glass, as it can be explained by the packing efficiency falling off of the highly crosslinked networks.

Keywords: Density; Thermosetting; Glass state

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1. Introduction

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]. 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 crosslinking. The resulting material can be either a thermoplastic glass or a thermosetting glass, depending on the stoicheometric 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.

In principle, an increased chemical conversion in a polymeric material will result in an increase of the fraction of covalent bonds compared to the van der Waals bonds. The volume is expected to decrease with increasing conversion. This principle, however, may not be applicable for network polymers in the glassy state. 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]. Implications of the maximum have been found on all other physical properties, such as free volume [8], water absorption [5], diffusion coefficient [9], gas permeability [9], thermal expansion coefficient [10], and physical aging rate [11]. The 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 glassy network polymers share a common physical nature in their glassy state. To understand this nature, we have studied systems of various gelation points. We report our new observations based on this study and discuss the fundamentals of this very unexpected phenomenon.

2. Experimental

Table 1 lists the systems that are employed in this investigation. Five amine-cured epoxy resins were employed in this investigation. Four of them were thermosetting (or branched), and one was thermoplastic (or linear). In all cases, aromatic diamines were stoichiometrically used as the curing

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Table 1
Chemical reactants

System examined	Epoxy used	Functionality of epoxy	Aromatic amine used	Functionality of amine	System	Glass transition temperature (K)
Linear	Diglycidyl ether of bis-phenol-A (from Dow Chemicals)	2	*N*,*N*′-Dianilinoethane (from Aldrich)	2	DGEBA-DAE	$T_{g0}=246$; $T_{g\infty}=354$
Branched 1	Triglycidyl ether of *o*-cresyl-formaldehyde (from Aldrich)	2.7	*N*,*N*′-Dianilinoethane (from Aldrich)	2	TGECF-DAE	$T_{g0}=262$; $T_{g\infty}=375$
Branched 2	Triglycidyl ether of *o*-cresyl-formaldehyde (from Aldrich)	2.7	4′4′-Methylenedianiline (from Aldrich)	4	TGECF-MDA	$T_{g0}=277$; $T_{g\infty}=433$
Branched 3	Diglycidyl ether of bis-phenol-A (from Dow Chemicals)	2	Trimethylene glycol di-*p*-aminobenzoate (from Polariod Corp)	4	DGEBA-TMAB	$T_{g0}=268$; $T_{g\infty}=453$
Branched 4	Poly(bisphenol A co-epichlorohydrin), glycidyl end-capped (equiv wt = 865, from Aldrich)	2	Trimethylene glycol di-*p*-aminobenzoate (from Aldrich)	4	Poly(BAEP)-TMAB	$T_{g0}=337$; $T_{g\infty}=379$

agents. The reason is that the curing reaction is slow, and unexpected side reactions are negligible. All reactants were mixed and were degassed in vacuum prior to inject into a multi-cavity aluminum mold that was lined with aluminum foils. 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 extent. The disks were then inspected using a polarizing light microscope. All specimen used for this investigation were free from visible voids, bubbles and cracks. Prior to density measurement, the specimen was usually heated to 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. Variation of cooling rates was only conducted on a particular system, i.e. the DGEBA-TMAB in Table 1.

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/cm height. Usually, two to three specimens of the same sample were dropped individually into the column. Readings were taken after about 30 min [15] when equilibrium is reached. The error bar of the measurement was about ± 0.0002 g/cm^3 or less.

Isothermal modulus was determined using a dynamic mechanical analyzer (Rheometric ARES) at 1 Hz and 0.02% strain amplitude. The test specimen was a glass–fiber braid that was impregnated with a test resin. The specimen was about 30 mm in length and 2 mm in diameter. Reviews on the preparation of the composite specimens have been published elsewhere [6,7]. The specimen was initially heated to 25 °C above its T_g, and was then cooled through the glass transition to −20 °C at a constant rate of 5 °C/min. Modulus measurements were taken during the cooling. The specimen was then heated to above its T_g to permit further cure (i.e. at $T_{cure} > T_g + 25$ °C). By repeating the procedure many times, one specimen could be used for obtaining all of the modulus vs. extent of cure at different temperatures. This methodology facilitates a good comparison of small changes in modulus of the resin in the glassy state, though the modulus measured was that of resin-impregnated braid specimen, not the pure resin. Value of T_g was obtained from the peak in loss modulus. Chemical conversion of the specimen was found from the calorimetric T_g-conversion relationship. The difference between the dynamic T_g and the calorimetric T_g was usually about 3 °C or less. Such estimation of conversion was within the error bar in conversion measurement.

The T_g-conversion relationship of a partially cured material were measured on a TA instrument modulated DSC 2920 equipped with LNCA cooling system using a nitrogen-purged cell at 5 °C/min heating rate, 40 s period, and 0.5 °C modulating amplitude. The temperature and the heat flow signals were calibrated with indium. The heat capacity signal was calibrated with sapphire. Usually, about 10 mg sample was weighed into a DSC aluminum pan for the measurement. Chemical conversion of a partially cured specimen was calculated from the residual heat that appeared in the non-reversible heat flow vs. temperature. This determination of the chemical conversion eliminated the effects that came from the change of heat capacity of the sample during the increase of temperature. The values of T_g were obtained from the reversible heat flow vs. temperature. The error bar in T_g measurement was less than ±1 °C, and the error bar in conversion measurement was less than ±3%. Samples that were used for the density measurement and that had the same thermal history were used for the DSC measurement.

3. Results and discussion

Fig. 1 shows the change of isothermal density vs. chemical conversion. For thermosetting (or branched) systems, the density of the reactants initially increases with increasing the chemical conversion, reaching a maximum, then decreases until the system is fully cured. The maximum in density is not the same point where the gelation point locates. In general, the higher the conversion at the gelation point, the higher the

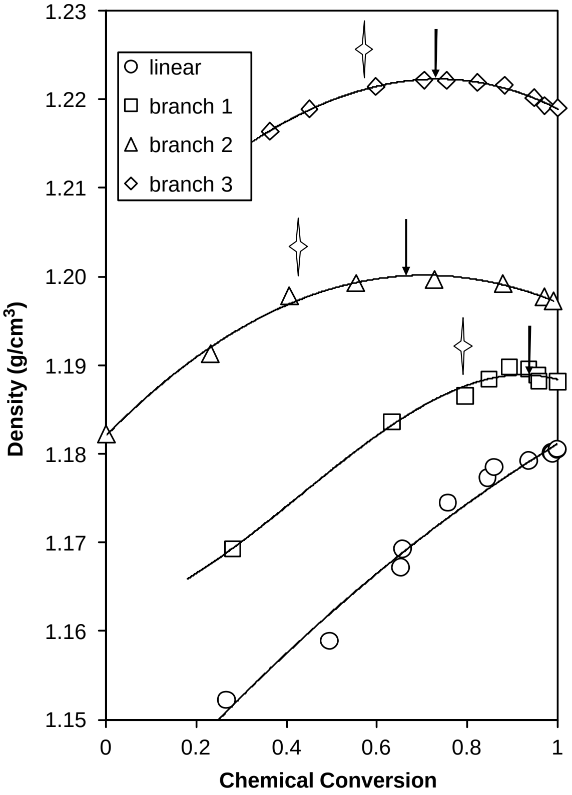

Fig. 1. Isothermal density at 23 °C vs. chemical conversion. Arrows in the plot mark the locations of maxima. Stars in the plot mark the locations of gelation. The maximum in density occurs after gelation point.

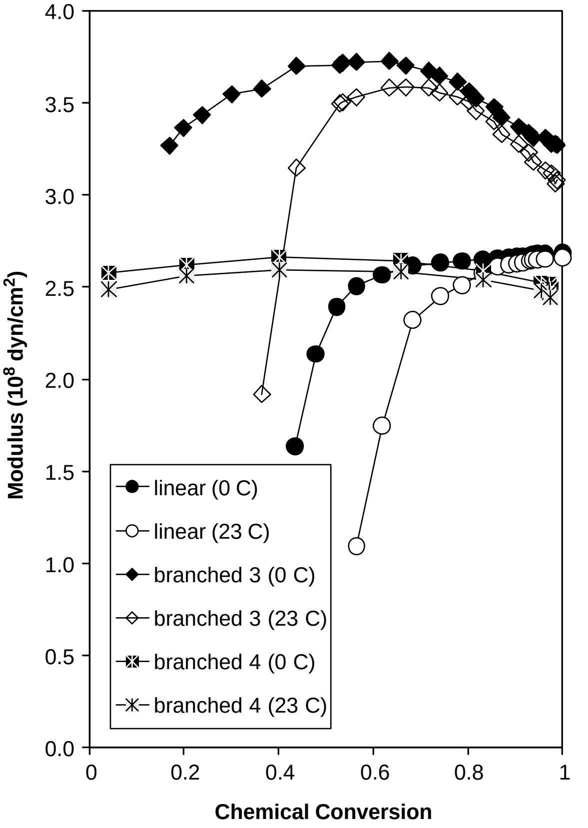

Fig. 2. Isothermal modulus in the glass state vs. chemical conversion. The maximum behavior intensifies itself as the overall crosslinking density increases. The overall crosslinking density of the system, branched 3, is about five times higher than the system, branched 4.

conversion at the maximum. The maximum in density occurs right after the gelation point. Interestingly, the same phenomenon is not observed in a thermoplastic (or linear) system. As shown in Fig. 1, the density in the linear system behaves as a monotonically increasing function with the chemical conversion. This result suggests that the maximum in density is only associated with the unique nature of thermosetting polymers in the glass state [15].

Fig. 2 shows the change of the isothermal modulus in the glass state vs. chemical conversion. For thermosetting systems, the modulus also passes through a maximum with increasing the chemical conversion. While, for a linear system the modulus is a monotonic increasing function of the conversion. The maximum in modulus occurs approximately in the same location as that found in the density for a given system. An important observation is that the maximum in modulus strongly depends on the overall crosslinking density of a system (i.e. that after fully cured), and the maximum behavior intensifies itself as the overall crosslinking density increases. This behavior is illustrated in Fig. 2, where the overall crosslinking density of the ‘branched 3’ system is about five times higher than the ‘branched 4’ system.

The maximum in density and its response to the gelation point and the crosslinking density are very interesting. Our first speculation of the reason could be due to the packing efficiency of molecules during cure. It is possible that the effect of crosslinking is to lead to material to a maximum in packing as a function of cure, which leads to a maximum in density. At high levels of crosslinking (i.e. above the gel point), the efficiency of packing branched molecules somehow falls off again, which then leads to a net expansion of the volume. However, there are two possible mechanisms that can lead the packing efficiency to fall off. One is kinetic, i.e. the density maximum is due to a faster rate of cooling (or a faster increase in the glass transition temperature) compared to a slower rate of decrease in volume for a crosslinked system. Another is thermodynamic, i.e. a branched molecule cannot pack tightly compared to a linear molecule even though in the equilibrium state. A decisive experiment that is needed to be done is to check how the maximum in density responds to the experimental cooling rate.

To understand the mechanism, we have systematically studied a resin (i.e. the DGEBA-TMAB in Table 1) at various cooling rates. The system is particularly suitable for this study due to its low reactivity [5–7]. In this study, all specimens were first heated to a temperature at least 25 °C above the T_g, and were then cooled to the room temperature at various cooling rates (e.g. 20, 5 or 0.5 °C/min). The density measurement at 23 °C and the calorimetric measurement were conducted right after the treatment. The test results are summarized in Fig. 3. Under all test conditions, a maximum in density is always observed, and the phenomenon is independent of cooling rates.

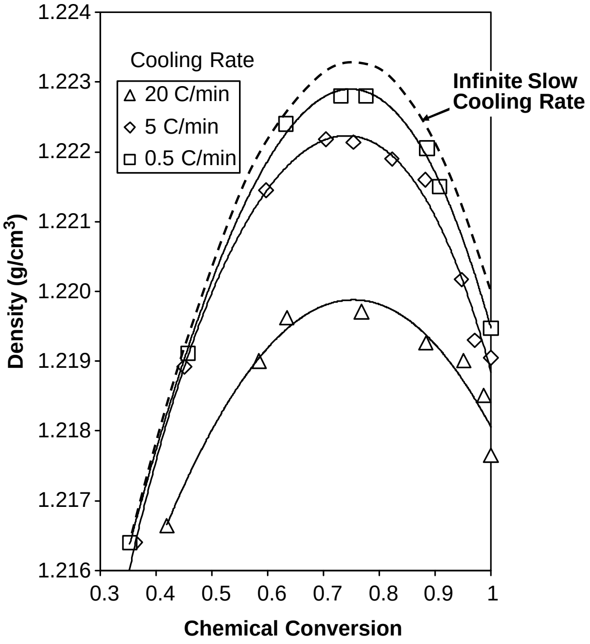

Fig. 3. Effects of cooling rates on the density peak for the DGEBA-TMAB system. The system is particularly suitable for this study due to its low reactivity. A maximum is observed under all test conditions. The maximum tends to intensify itself when the cooling rate is slowed down.

The widths and the heights of the density peaks, however, are affected by the cooling rates. The most stunning observation is that the slower the cooling rate, the sharper the density peak becomes.

As being known, a kinetic phenomenon usually tends to diminish itself once the cooling rate is slowed or when the system is closer to the equilibrium state. However, what we observed here is completely opposite. The maximum in density tends to intensify itself when the cooling rate is slowed down, and therefore is not a kinetic phenomenon. In addition, the characteristic time (τ) for volume recovery above nominal T_g can be generally described by the Vogel–Fulcher type of equations [16,17], e.g. $\ln\tau\sim 1/(T-T_2)$. The magnitude of τ depends on the distance $T-T_2$, where T_2 is approximately 50 °C below T_g. The competition between a constant cooling rate and volume recovery rate ($1/\tau$) certainly cannot intensify the maximum when the cooling rate is slowed down. Although a glass transition is a time-dependent event, the observed experimental results cannot be explained adequately by a kinetic argument.

The experimental facts thus suggest that the anomalous maximum in modulus and density may be related to an equilibrium event where the packing efficiency falls off for highly crosslinked molecules. To address this view, let us follow the entropy theory proposed by Gibbs and DiMarizio [18,19] for glassy polymers. For a crosslinking system, the entropy (S_c) can be expressed in terms of $S_c=S_c^{(0)}+S_c^{(1)}$; where $S_c^{(0)}>0$ is the configurational entropy for a linear system, and $S_c^{(1)}<0$ is the change in configurational entropy due to adding crosslinks [20]. According to the theory, the configuration entropy of a polymer system approaching to zero determines the formation of a glass. Thus, during a temperature cooling, the hole volume of the system must decreases in order to minimize the configuration entropy. However, a crosslinked system does not need to decrease its hole volume as much as what it needed in a linear system. The reason is that adding crosslinks into a system has decreased the total configurational entropy over what it would be in a linear system by reducing the conformation number of linear chains. If this effect is strong enough, a glassy network polymer will have higher hole volume fraction than that of linear polymers in the glassy state, and the isothermal volume of the system will show the expansion tendency via further crosslinking. As a consequence, the bulk density and modulus of thermosetting polymeric systems will display a maximum with increasing chemical conversion in the glassy state after the system passes its gelation point.

To discuss this in more detail, let us first take a look at the change in heat capacity, ΔC_p, due to the glass transition [18,20]

$$\frac{\Delta C_p}{R}=T\Delta\alpha\left\{-\frac{1}{v_p}\left[S_p+\ln\left(\frac{S_0^{z/2}}{v_0^{z/2-1}}\right)\right]+\frac{1}{v_0}\left[\left(\frac{z-2}{z}\right)\left(\frac{v_p-S_p}{v_p}\right)+\frac{S_0}{xn_r}\right]\right\}+\frac{xn_r-3}{xn_r}\left(\frac{\Delta\varepsilon}{kT}\right)^2 f(1-f)+\frac{3}{4}X_d\frac{\Delta\varepsilon}{kT}(1-f) \tag{1}$$

where $\Delta\alpha$ is the difference of expansion coefficients between a glass and a liquid and

$$\Delta\alpha=\frac{v_0\ln(v_0^{z/2-1}/S_0^{z/2})/T}{zS_p/2-2S_0\ln(v_0^{z/2-1}/S_0^{z/2})-(z-2)v_p/2} \tag{2}$$

k is the Boltzmann constant, R is gas constant, T is the absolute temperature, n_r is the number of rotatable groups per monomer, and x is the degree of polymerization. v_0 is the fraction of hole volume. $v_p=1-v_0$. $S_0=zv_0/\{[(z-2)xn_r+2]v_p/xn_r+zv_0\}$ and $S_p=1-S_0$. The parameter z is defined as that $z-1$ is the number of possible orientations of a rotatable group around a covalent bond. $\Delta\varepsilon$ is the 'flex energy'. f is the fraction of 'flexed bond' and is given by $f=[(z-2)\exp(-\Delta\varepsilon/kT)]/[1+(z-2)\exp(-\Delta\varepsilon/kT)]$. The parameter X_d is the crosslinking density in the system and is defined as the number of moles of crosslinks per mole of rotatable groups. The parameter f and v_0 is considered to be frozen at T_g and be independent of temperature for $T<T_g$. Now, let us define a new quantity

$$\Psi=\frac{\Delta C_p}{R}-\left(\frac{\Delta\varepsilon}{kT}\right)^2 f(1-f)-\frac{3}{4}X_d\frac{\Delta\varepsilon}{kT}(1-f) \tag{3}$$

Viewing that the change in heat capacity (ΔC_p) is approximately a constant or a weak decreasing function of conversion [21–23], and the flex energy ($\Delta\varepsilon$) is a constant at isothermal conditions, one may conclude from Eq. (3) that an increasing X_d will result in a decrease of the function Ψ. Mathematically, this gives $\partial\Psi/\partial X_d<0$. If taking the partial derivative of Eq. (3) with respect to X_d, while T and x to be constants, we obtain

(Appendix A)

$$\left(\frac{\partial v_0}{\partial X_\mathrm{d}}\right)_{T,x}=\left(\frac{1}{\Lambda}\right)\left(\frac{\partial \Psi}{\partial X_\mathrm{d}}\right)_{T,x} \tag{4}$$

where $\Lambda=(\partial\Psi/\partial v_0)_{T,x,X_\mathrm{d}}$is a function of v_0, x and z. The term $(\partial\Psi/\partial X_\mathrm{d})_{T,x,v_0}$ is virtually zero according to Eq. (1) and thus disappears in Eq. (4).

Depending on the sign of the parameter , there are two distinguishable situations. The first one occurs when $\Lambda>0$. In this case, $(\partial v_0/\partial X_\mathrm{d})_{T,x}<0$. Physically, this means that an increase of crosslinking density will result in a decrease of the fraction of the hole volume. A system in this situation will actually collapse via crosslinking. The second one, which is more interesting, happens when $\Lambda<0$. In this case, the derivative $(\partial v_0/\partial X_\mathrm{d})_{T,x}>0$. Accordingly, an increase of crosslinking density will result in an increase of the fraction of the hole volume, and crosslinking in the system will induce a net expansion in the specific volume in the glassy state.

The expression for the function Λ in general is very complex. However, if taking $xn_\mathrm{r}\gg 1$ and $v_0\ll v_\mathrm{p}\approx 1$, it can be simplified significantly (Appendix A). The result is

$$\Lambda=\lfloor(a+b+ab)+(a+b+2)\ln v_0+\ln^2 v_0\rfloor \tag{5}$$

where $a=(z/2)\ln[z/(z-2)]$ and $b=(1-2/z)+(z/2)\ln[z/(z-2)]$. Eq. (5) is a typical quadratic equation. The behavior of Λ as a function of v_0 is plotted in Fig. 4. The function Λ can be either positive or negative, depending on the value of v_0 and z. However, a physical meaningful value of v_0 at T_g of any linear polymers is restricted by about $v_{0\mathrm{c}}=0.025$, under this condition the parameter of Λ is mostly negative, which gives $(\partial v_0/\partial X_\mathrm{d})_{T,x}>0$ in most cases. Especially, when z is small (i.e. a system is composed of relatively stiff chains), this model suggest that the specific volume of the material will increase with increasing crosslinks and its density will decrease with increasing crosslinks after the gelation. The experimental results as discussed in Figs. 1–3, are possibly due to this mechanism. For system of very flexible chains, e.g. when the fraction of flexed bonds f is close to 1 and $z\geq 10$, and when crosslinking density is low, however, this model also suggest that the system will possibly approach a further dense packed state. The reason is that in this case few crosslinks in the system may not provide a sufficient reduction of the configuration entropy over what it would be for a linear system. We conclude that this model has taken into account of the specific features of thermosetting polymeric materials, and for the first time it has outlined the basis for this anomalous maximum in density and modulus in the glassy state.

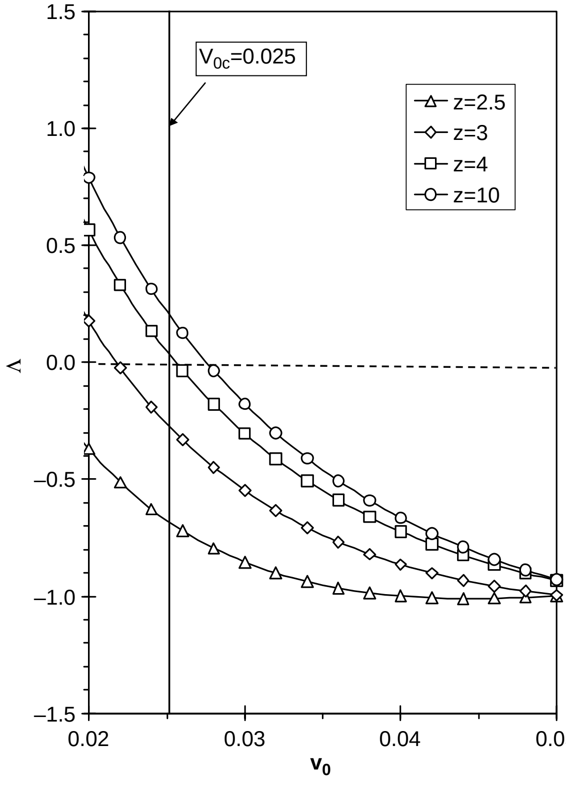

Fig. 4. Calculated Λ as a function of v_0. The horizontal dash line corresponds to $\Lambda=0$. The vertical bold line corresponds to the universal value of $v_{0\mathrm{c}}=0.025$ for any linear polymer.

4. Conclusion

In this study, it is shown that the isothermal density and modulus of a thermosetting polymeric material pass through a maximum in the glassy state with increasing chemical conversion. The anomalous maximum occurs approximately after gelation. The specific volume of the material after gelation increases via further reaction. This anomalous behavior is not a kinetic phenomenon, and tends to intensify as the overall crosslinking density increases. It is also shown that the anomaly stems from the configuration entropy criterion required for forming a glass, as it can be explained by the packing efficiency falling off of the highly crosslinked networks.

Appendix A

A.1. Derivation of Eq. (4) in the main text

At constant T and x, a small change of Ψ can be described as

$$\mathrm{d}\Psi=(\partial\Psi/\partial v_0)_{T,x,X_\mathrm{d}}\mathrm{d}v_0+(\partial\Psi/\partial X_\mathrm{d})_{T,x,v_0}\mathrm{d}X_\mathrm{d} \tag{A1}$$

Dividing Eq. (A1) by $\mathrm{d}X_\mathrm{d}$, while T and x to be constants, yields

$$(\partial\Psi/\partial X_\mathrm{d})_{T,x}=(\partial\Psi/\partial v_0)_{T,x,X_\mathrm{d}}(\partial v_0/\partial X_\mathrm{d})_{T,x}+(\partial\Psi/\partial X_\mathrm{d})_{T,x,v_0} \tag{A2}$$

The term $(\partial\Psi/\partial X_\mathrm{d})_{T,x,v_0}$ is virtually zero according to Eq. (1) and thus disappears.

The reason is that at constant T, x, and v_0, the function Ψ as defined in Eq. (3) is a constant.

Rearranging the derivatives in Eq. (A2), we thus obtain

$$(\partial v_0/\partial X_\mathrm{d})_{T,x}=(1/\Lambda)(\partial\Psi/\partial X_\mathrm{d})_{T,x} \tag{A3}$$

where $\Lambda=(\partial\Psi/\partial v_0)_{T,x,X_\mathrm{d}}$ is a function of v_0, x and z.

A.2. Derivation of Eq. (5) in the main text

First, let us define

$$A = v_0 \ln\left(\frac{v_0^{z/2-1}}{S_0^{z/2}}\right) \tag{A4}$$

$$B = -\frac{1}{v_{\rm p}}\left[S_{\rm p} + \ln\left(\frac{S_0^{z/2}}{v_0^{z/2-1}}\right)\right] + \frac{1}{v_0}\left[\left(\frac{z-2}{z}\right)\left(\frac{v_{\rm p}-S_{\rm p}}{v_{\rm p}}\right) + \frac{S_0}{xn_{\rm r}}\right] \tag{A5}$$

and

$$C = zS_{\rm p}/2 - 2S_0\ln(v_0^{z/2-1}/S_0^{z/2}) - (z-2)v_{\rm p}/2 \tag{A6}$$

Thus, the change in heat capacity, $\Delta C_{\rm p}$, due to the glass transition, of Eq. (1) can be written as

$$\frac{\Delta C_{\rm p}}{R} = \frac{AB}{C} + \frac{xn_{\rm r}-3}{xn_{\rm r}}\left(\frac{\Delta\varepsilon}{kT}\right)^2 f(1-f) + \frac{3}{4}X_{\rm d}\frac{\Delta\varepsilon}{kT}(1-f) \tag{A7}$$

and the difference of expansion coefficients between a glass and a liquid, $\Delta\alpha$, of Eq. (2) can be written as

$$\Delta\alpha = \frac{A/T}{C} \tag{A8}$$

Now, if the expression for $\Delta C_{\rm p}$ and $\Delta\alpha$ [i.e. Eqs. (A7) and (A8)] are used, one finds that the function Ψ is given by

$$\Psi = \frac{AB}{C} - \frac{3}{xn_{\rm r}}\left(\frac{\Delta\varepsilon}{kT}\right)^2 f(1-f) \tag{A9}$$

and the function Λ becomes

$$\Lambda = (\partial\Psi/\partial v_0)_{T,x,X_{\rm d}} = \frac{(\partial A/\partial v_0)B + A(\partial B/\partial v_0)}{C} - \frac{AB(\partial C/\partial v_0)}{C^2} \tag{A10}$$

where A, B and C has been defined previously.

Suppose that the system studied is in the post-gel state, the product of the degree of polymerization and the number of the rotatable groups per monomer is much larger than unity, i.e. $xn_{\rm r} \gg 1$. Thus

$$S_0 = \frac{zv_0}{[(z-2)xn_{\rm r}+2]v_{\rm p}/xn_{\rm r} + zv_0} = \frac{zv_0}{z-2v_{\rm p}} \tag{A11}$$

$$S_{\rm p} = 1 - S_0 = 1 - \frac{zv_0}{z-2v_{\rm p}} = \frac{(z-2)v_{\rm p}}{z-2v_{\rm p}} \tag{A12}$$

$$\ln\frac{S_0^{z/2}}{v_0^{z/2-1}} = \frac{z}{2}\ln\frac{S_0}{v_0} + \ln v_0 = \frac{z}{2}\ln\left(\frac{z}{z-2v_{\rm p}}\right) + \ln v_0 \tag{A13}$$

and

$$\frac{1}{v_0}\left[\left(\frac{z-2}{z}\right)\left(\frac{v_{\rm p}-S_{\rm p}}{v_{\rm p}}\right)\right] = \frac{1}{v_0}\left[\left(\frac{z-2}{z}\right)\left(1-\frac{z-2}{z-2v_{\rm p}}\right)\right] = \left(\frac{z-2}{z}\right)\left(\frac{2}{z-2v_{\rm p}}\right) \tag{A14}$$

Substituting expressions (A11)–(A14) into A, B, and C of Eqs. (A4)–(A6) yields

$$A = v_0\left[-\frac{z}{2}\ln\left(\frac{z}{z-2v_{\rm p}}\right) - \ln v_0\right] \tag{A15}$$

$$B = -\left[\frac{z-2}{z-2v_{\rm p}} + \frac{1}{v_{\rm p}}\frac{z}{2}\ln\left(\frac{z}{z-2v_{\rm p}}\right) + \frac{1}{v_{\rm p}}\ln v_0\right] + \left(\frac{z-2}{z}\right)\left(\frac{2}{z-2v_{\rm p}}\right) \tag{A16}$$

$$C = \frac{z}{2}\frac{z-2}{z-2v_{\rm p}}v_{\rm p} - \frac{2zv_0}{z-2v_{\rm p}}\left[-\frac{z}{2}\ln\left(\frac{z}{z-2v_{\rm p}}\right) - \ln v_0\right] - \frac{(z-2)v_{\rm p}}{2} \tag{A17}$$

Taking the derivations of function A, B, and C with respect to v_0 yields, respectively,

$$\frac{\partial A}{\partial v_0} = -\left[1 + \frac{z}{2}\ln\left(\frac{z}{z-2v_{\rm p}}\right) + \ln v_0\right] + \frac{zv_0}{z-2v_{\rm p}} \tag{A18}$$

$$\frac{\partial B}{\partial v_0} = \frac{2(z-2)^2}{z(z-2v_{\rm p})} + \frac{1}{v_{\rm p}^2}\left[\frac{z}{2}\ln\left(\frac{z-2v_{\rm p}}{z}\right)\right] + \frac{z}{v_{\rm p}(z-2v_{\rm p})} - \frac{1}{v_{\rm p}^2}\ln v_0 - \frac{1}{v_{\rm p}}\frac{1}{v_0} \tag{A19}$$

and

$$\frac{\partial C}{\partial v_0} = -\frac{z(z-2)}{2(z-2v_{\rm p})} - \frac{2(z-2)}{(z-2v_{\rm p})^2}v_{\rm p} - \frac{z}{z-2v_{\rm p}}\left[\frac{z}{2}\ln\left(\frac{z-2v_{\rm p}}{z}\right) - \ln v_0\right] - \frac{2zv_0}{z-2v_{\rm p}}\left(\frac{z}{z-2v_{\rm p}} - \frac{1}{v_0}\right) + \frac{z-2}{2} \tag{A20}$$

The expressions for A, B, C, $\partial A/\partial v_0$, $\partial B/\partial v_0$, and $\partial C/\partial v_0$ can be further simplified with using the condition of $v_0 \ll v_{\rm p} \approx 1$.

The results are

$$A = v_0\left[-\frac{z}{2}\ln\left(\frac{z}{z-2}\right) - \ln v_0\right] \tag{A21}$$

$$B = -\left[\left(1-\frac{2}{z}\right) + \frac{z}{2}\ln\left(\frac{z}{z-2}\right) + \ln v_0\right] \tag{A22}$$

$$C = 1 \tag{A23}$$

$$\frac{\partial A}{\partial v_0} = -\left[1 + \frac{z}{2}\ln\left(\frac{z}{z-2}\right) + \ln v_0\right] \tag{A24}$$

$$\frac{\partial B}{\partial v_0} = \frac{2(z-2)}{z} + \left[\frac{z}{2}\ln\left(\frac{z-2}{z}\right)\right] + \frac{z}{z-2} - \ln v_0 - \frac{1}{v_0} \tag{A25}$$

and

$$\frac{\partial C}{\partial v_0} = -1 + \frac{z}{z-2} - \frac{z}{z-2}\left[\frac{z}{2}\ln\left(\frac{z}{z-2}\right) + \ln v_0\right] \tag{A26}$$

Upon substituting equations of (A21)–(A26) into Eq. (A10), we finally obtain

$$\Lambda = (a+\ln v_0)(b+\ln v_0) + (b+\ln v_0) + (a+\ln v_0) + \mathrm{O}(v_0) \tag{A27}$$

where

$$a = \left(\frac{z}{2}\right)\ln\left(\frac{z}{z-2}\right) \tag{A28}$$

$$b = \left(1-\frac{2}{z}\right) + \left(\frac{z}{2}\right)\ln\left(\frac{z}{z-2}\right) \tag{A29}$$

If taking only the leading terms of Eq. (A27), the function Λ can be described by a rather simple quadratic equation

$$\Lambda = [(a+b+ab) + (a+b+2)\ln v_0 + \ln^2 v_0] \quad \text{when } v_0 \ll 1 \tag{A30}$$

Its roots for $\Lambda = 0$ provide the critical values for v_0, which define the boundary of the expanding region and the collapsing region. Explicitly, the critical values of v_0 is given by

$$v_{0c} = \exp\frac{-(a+b+2) - \sqrt{(a+b+2)^2 - 4(a+b+ab)}}{2} \tag{A31}$$

The solution with a positive sign in front of the square root has been rejected for physical meaningless. For a typical case when $z=4$, it can be estimated from Eq. (A31) that $v_{0c} = 0.0256$.

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