Transition broadening and WLF relationship in polyurethane/poly(methyl methacrylate) interpenetrating polymer networks

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A range of simultaneous fully interpenetrating polymer networks (IPNs) based on polyurethane (PU) and poly(methyl methacrylate) (PMMA) were prepared and evaluated using dynamic mechanical analysis. The tests were conducted at resonance frequencies over a wide temperature range. The IPNs produced broad glass transitions, with a unique tan δ peak of rectangular waveform occurring at approximately 70/30 by weight PU/PMMA composition. Tan δ broadening was explained in terms of the patterns of behaviour of the dynamic loss and real moduli during the transition. The type of tan δ broadening was not experienced in PU by crosslinking variation alone. Multiplexed dynamic mechanical runs for the time–temperature superposition were conducted at various frequencies. The Williams–Landel–Ferry (WLF) equation fitted the experimental shift factors over the wide transition regions. The resultant WLF coefficients indicated the presence of larger-than-expected free volumes in the PU-dominated IPN compositions, which, in turn, precipitated glass transitions.

INTRODUCTION

Amorphous polymers and their random copolymers exhibit only one glass transition, while physical blends that are phase-separated possess multiple relatively sharp transitions, one for each phase. When the combination of polymers results in increased molecular mixing, then shifts, broadenings and even merging of the component glass transition temperatures (T_g) occur to a certain extent depending upon both the compatibility and the relative proportions of the constituent polymers[1-8]. The shifting/broadening of transitions thus becomes an indicator for the actual occurrence of interpenetration[9,10].

The present work examines the glass transition behaviour of interpenetrating polymer networks (IPNs) of polyurethane (PU) and poly(methyl methacrylate) (PMMA) using dynamic mechanical analysis and the Williams–Landel–Ferry (WLF) free-volume concept.

The time–temperature superposition principle enables prediction of the mechanical behaviour of polymers over long periods of time. In dynamic mechanical analysis, this is achieved by measuring the properties at different frequencies over a wide temperature range. An isothermal master curve may then be constructed by choosing a reference temperature and shifting the segments of curves at other temperatures along a horizontal logarithmic time scale until they all superimpose smoothly. Models exist to describe the magnitude of the shift at each temperature,

the most important of which relates to the WLF equation[11]:

$$\log a_T = -C_1(T - T_0)/(C_2 + T - T_0)$$

where C_1 and C_2 are constants, T_0 is a reference temperature and a_T is the shift factor. The equation describes accurately the time–temperature superposition in the glass transition region for all amorphous polymers. The time–temperature equivalence principle fails for multiphase blends[11,12] and its success for miscible polymer blends is not clear. The principle has been shown both to hold[13] and to break down[14] for poly(ethylene oxide)/poly(methyl methacrylate) blends. Shift factors based on the WLF equation hold approximately for a partially miscible graft copolymer of poly(ethyl acrylate) and PMMA[15]. However, a combination of shift factors based on the WLF equation and alternatives are required in the production of a master curve for styrene–butadiene–styrene (SBS) block copolymers[16]. This paper examines the extent of correlation that exists between the experimental and WLF shift factors for the IPNs under consideration.

EXPERIMENTAL

Table 1 lists the materials used in the production of the fully interpenetrating polymer networks (full IPNs) based on PU and PMMA. They are described as full IPNs, since both the components are crosslinked. A series of

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Table 1 Raw materials

Designation	Description
Urethane polyols	A mixture of 400 and 2000 molecular-weight poly(oxypropylene glycol) with OH values of 275 and 55, respectively
Urethane crosslinking agent	Trimethylolpropane
MDI	A semi-pure diphenylmethane diisocyanate of functionality 2.3 and NCO content 27.6%
Organomercury catalyst	Phenylmercuric ethanoate
MMA	Methyl methacrylate
EGDMA	Ethylene glycol dimethacrylate
AIBN	Azobisisobutyronitrile

Dynamic mechanical data were obtained using a Du Pont 983 Analyser in resonant frequency mode over a temperature range from -80 to $160°C$ at a heating rate of $4°C\,min^{-1}$. Multiplexed frequency scans for the time–temperature superposition were conducted at frequencies of 0.32, 0.5, 1, 3 and 5 Hz, and at temperature increments of $3°C$. The data were further analysed using Du Pont Superposition Software to generate time–temperature shift factors. Test-pieces were approximately 10 mm wide and the clamp separations were adjusted according to the stiffness of the specimens. Wider clamp settings are required for the stiffer and/or thicker specimens. The amplitude (peak-to-peak) of sinusoidal oscillations, mostly 0.3 to 0.6 mm, were also chosen according to the stiffness and thickness of the specimens.

RESULTS AND DISCUSSION

Dynamic mechanical properties in the transition region

Figures 1 to *3* show the dynamic mechanical properties of IPNs and the component polymers over a range of temperatures. The component polymers exhibited well defined changes in properties at the glass transition: sharp drops in E' and sharp peaks in E'' and $\tan \delta$ curves. In contrast, IPNs exhibited much more gradual changes, some of which occurred over a temperature range spanning the T_g values of the component polymers.
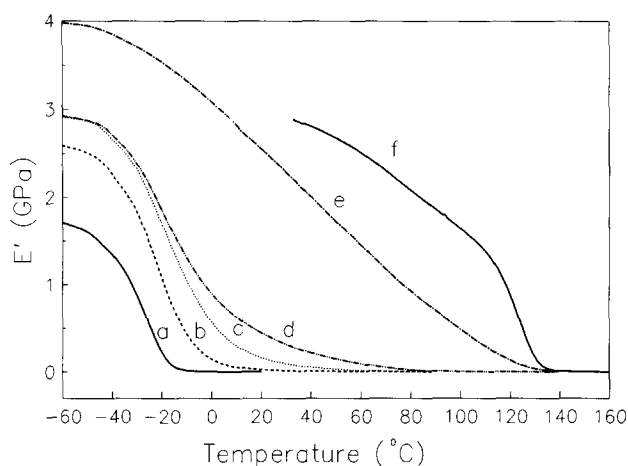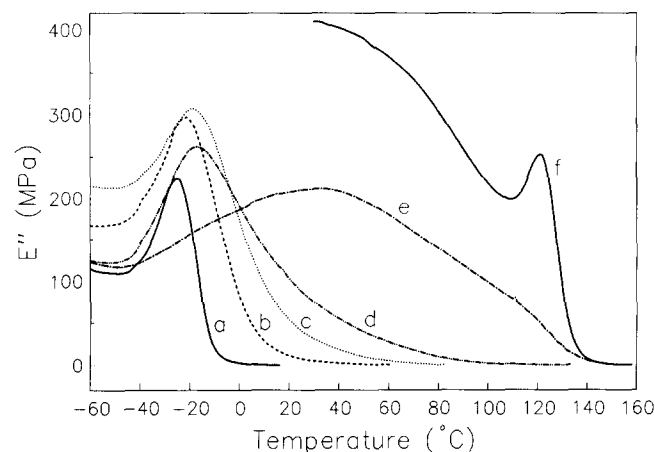

Figure 1 The E' *versus* temperature plots for IPNs with PU/PMMA compositions (wt%): a, 100/0; b, 80/20; c, 70/30; d, 50/50; e, 20/80; f, 0/100

IPNs were prepared using a simultaneous method. The procedure for the simultaneous IPNs is detailed elsewhere[17]. Briefly, it involved the mixing together of appropriate amounts of the urethane polyols with 0.7% by weight organomercury catalyst and the PMMA reagents (i.e. monomer MMA, 0.5% by weight initiator AIBN (azobisisobutyronitrile) and 0.3 mol% crosslinking agent EGDMA (ethylene glycol dimethacrylate)). The mixture of urethane polyols was at a ratio of 5 × (high-molecular-weight polyol) to 1 × (low-molecular-weight polyol). The reagents were well mixed and diphenylmethane diisocyanate (MDI) was added at a molar ratio of NCO/OH = 1.07/1. The final mixture was degassed and cast into moulds. The filled moulds were left at room temperature for 30 min, then heated to $60°C$ and held for 23 h, followed by 2.5 h at $80°C$ and 1 h at $100°C$ for MMA polymerization. The polymerized IPN sheets were allowed to cool down to room temperature prior to demoulding.

Polyurethanes with greater degree of crosslinking were produced by incorporating trimethylolpropane into the formulation.

Although the simultaneous IPN formation involved the synthesis of both polymers from their chemical constituents, the method is, more accurately, *in situ* sequential synthesis, since the networks do not gel simultaneously. There is effectively a two-step process, such that PU formation and gelation occur first followed by PMMA formation.

Figure 2 The E'' *versus* temperature plots for IPNs with PU/PMMA compositions as in *Figure 1*
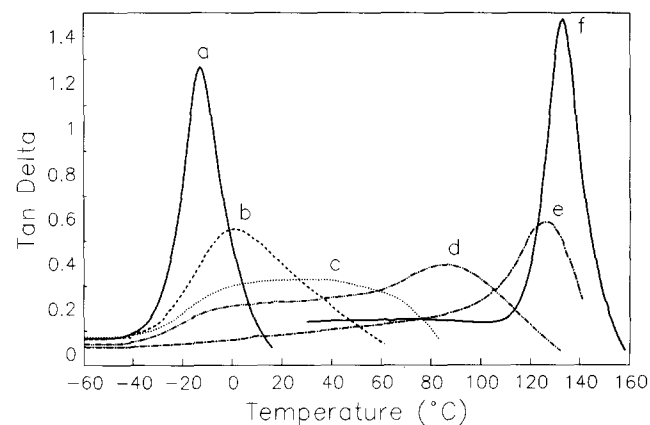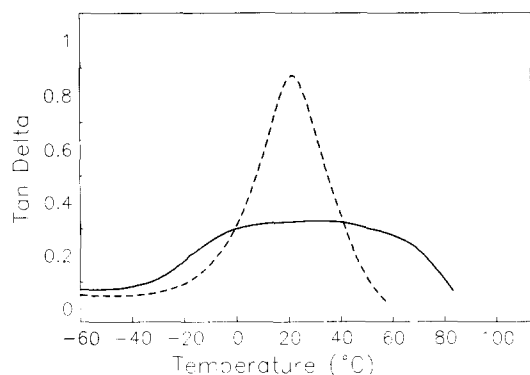

Figure 3 The $\tan \delta$ *versus* temperature plots for IPNs with PU/PMMA compositions as in *Figure 1*

Figure 4 The tan δ versus temperature plots for: (- - -) PU containing 10% crosslinker trimethylolpropane; (——) IPN with PU/PMMA composition (wt%) of 70/30

polymers are of the same order of magnitude as the estimations based on the universal value of the WLF constant ($C_1 = 17.4$). However, these are much greater for the IPNs, particularly at higher PU contents. This is to be expected since the relaxation of PU molecules requires less energy and such relaxations generate additional free volume and, in turn, precipitate transitions in the IPNs.

The exact pattern of behaviour for each property of the IPNs in the transition region can be identified: E'' curves produced peaks very close to the PU transition, followed by prolonged declines to the PMMA transition; similarly, E' curves exhibited sharp drops near the PU transition, followed by more gradual decreases approaching the rubbery region. This two-stage change in E' and E'', between the glassy and rubbery stages, was particularly evident in the IPNs with greater PU contents. At higher PMMA concentration the changes are of a uniform rate across the transition region. Tan δ peaks of the extreme IPN compositions occurred close to those of the respective component polymers. IPNs with intermediate compositions produced broader tan δ curves with flat tops spanning a considerable temperature interval between the component T_g values.

Glass transition broadening has been experienced[1,5,7,9,18,19] in IPNs composed of miscible polymers such as PU and PMMA. Explanations of the broadening include: microheterogeneity in the molecular mixing[20]; fine dispersion of the component domains[9,19]; smearing of phase transitions[11]; and, by the present authors[1], the concept of a compound transition generated by a spectrum of quasi-crosslink densities, which are a manifestation of the physical restriction imposed by the rigid polymer component on the molecular segmental mobility of the elastomer.
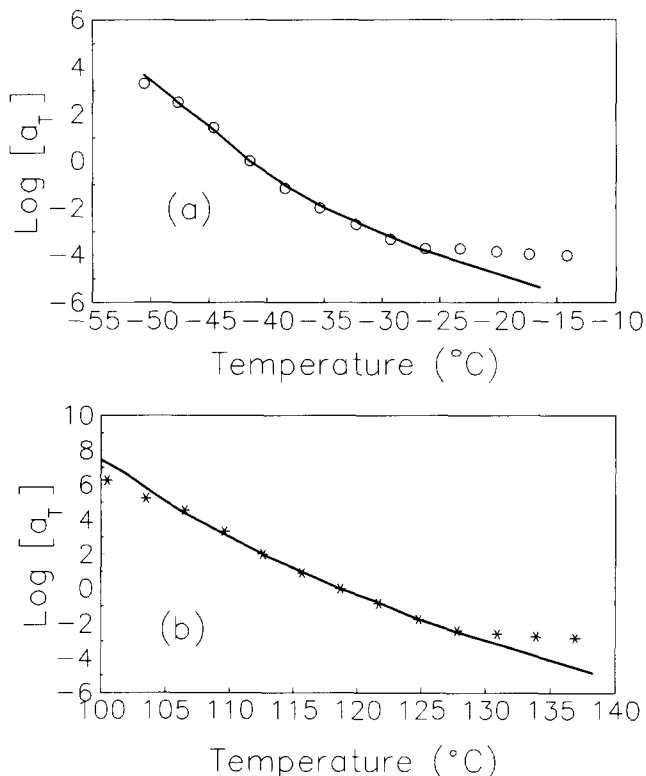
It must be clarified that the type of tan δ broadening experienced here cannot be engineered in an elastomer by just additional chemical crosslinking, since this will not result in a wide enough spectrum of crosslink densities. As demonstrated in Figure 4, the resultant tan δ peak will maintain the usual bell shape rather than the almost rectangular waveform exhibited by an IPN.

Figure 5 The $\log a_T$ versus temperature plots for (a) PU and (b) PMMA: (O, *) experimental; (——) WLF fit
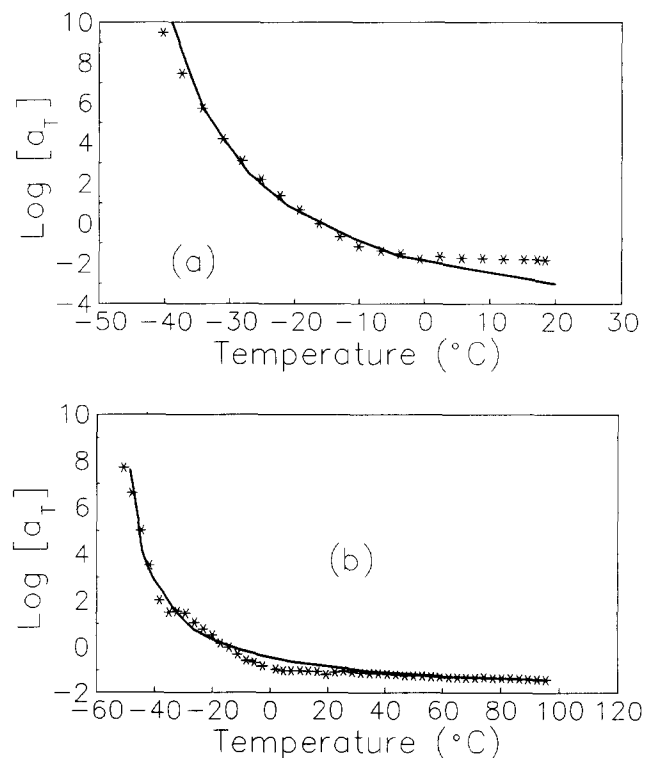
WLF relationships

WLF curves were fitted to the experimental shift factors generated for the time–temperature superposition of dynamic real moduli data. Figures 5–7 show the extent of agreement between the actual and the WLF shift factors for the component polymers and the IPNs. Further details of the WLF fit are presented in Table 2. The reference temperatures were chosen to provide best fits to the experimental shift factors. These were fairly close to the temperature of the E'' maximum, $(T_{E''})_{max}$. The WLF free-volume fractions (f_0) were calculated using the relationship $f_0/B = 1/2.303C_1$ and assuming $B \simeq 1$.

The fractional free-volume values for the component

Figure 6 The $\log a_T$ versus temperature plots for IPNs with PU/PMMA compositions (wt%) of (a) 80/20 and (b) 70/30: (*) experimental; (——) WLF fit
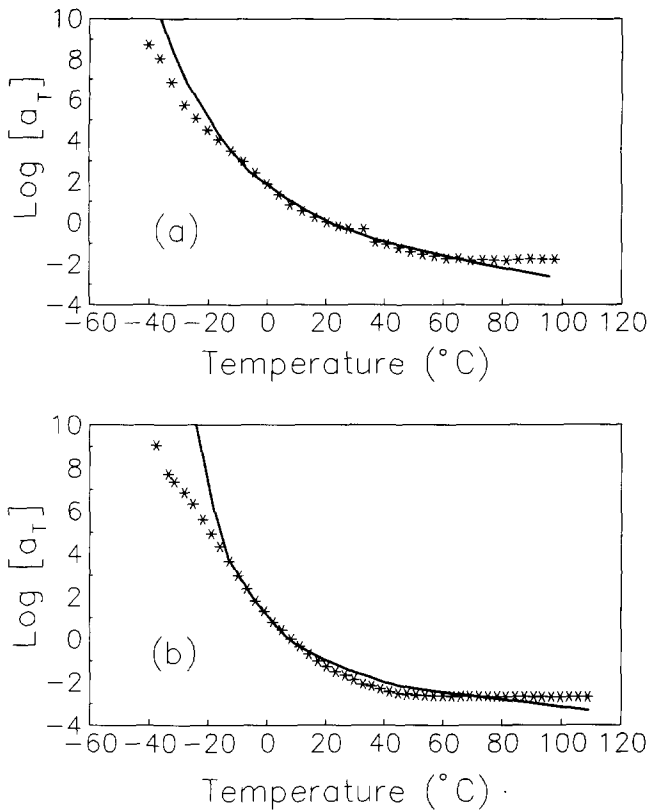
Figure 7 The log a_T versus temperature plots for IPNs with PU/PMMA compositions (wt%) of (a) 60/40 and (b) 50/50: (*) experimental; (——) WLF fit

Table 2 Details of the WLF fit to the experimental shift factors (where T_0 is the reference temperature, C_1 and C_2 are empirical WLF coefficients and f_0 is the fraction of free volume at T_0)

Composition PU/PMMA (by weight)	T_0 (°C)	$(T_{E''})_{max}$ (°C)	C_1	C_2	f_0	Range of fit (°C)
100/0	−41	−26	15.0	45.0	0.03	24
80/20	−16	−20	5.9	36.8	0.07	40
70/30	−14	−18	2.2	45.8	0.19	150
60/40	20	−12	5.5	85.2	0.08	90
50/50	8	−14	7.3	66.5	0.06	100
20/80	69	35	17.5	129.0	0.02	70
0/100	119	127	21.8	72.6	0.02	25

The WLF shift factors fitted the data reasonably well over the wide transition regions of the IPNs. The agreement is as experienced in homopolymers, but is in contrast to two-phase systems, where the degree of mixing does not extend to small enough volumes and the mixture exhibits separate transitions associated with the phases. The WLF shift factors have been shown[16] to hold only around each of the T_g values of polystyrene and polybutadiene in an SBS block copolymer.

Tan δ broadening

The IPNs exhibited various degrees of glass transition broadening depending on the composition. The resultant E'' curves maintained a bell-shape appearance throughout, whereas the tan δ curves assumed a near-rectangular shape at compositions with higher fractions of the elastomeric component. This was most obvious at approximately 70/30 ratio of PU/PMMA (see *Figure 3*),

where a constant tan δ value was maintained over a wide temperature range between the component T_g values.

The transitions of the PU-rich compositions exhibited three distinct regions. It is the combination of the tan δ contributions from these regions that generates the uniquely shaped broad tan δ curve, as illustrated in *Figure 8*. The E'' peak and E' inflection occurred at the start of the transition (region I), almost coinciding with the transition of PU, rather than at the usual position in the middle of a glass transition. The precipitated transitions in E' and E'' result from higher free-volume fractions indicated by WLF analysis. Consequently, E' and E'' values were found to be lower than expected in the middle of the transition (region II), where there is a gradual decrease in these values to the completion of the transition (region III).

It must be borne in mind that, in a normal glass transition, the tan δ peak occurs almost at the end of the transition[21], E' drops linearly rather than parabolically between glassy and rubbery states, and the E'' peak is symmetrical with a more straight trailing edge. These features are illustrated in *Figure 8*. Thus, a normal
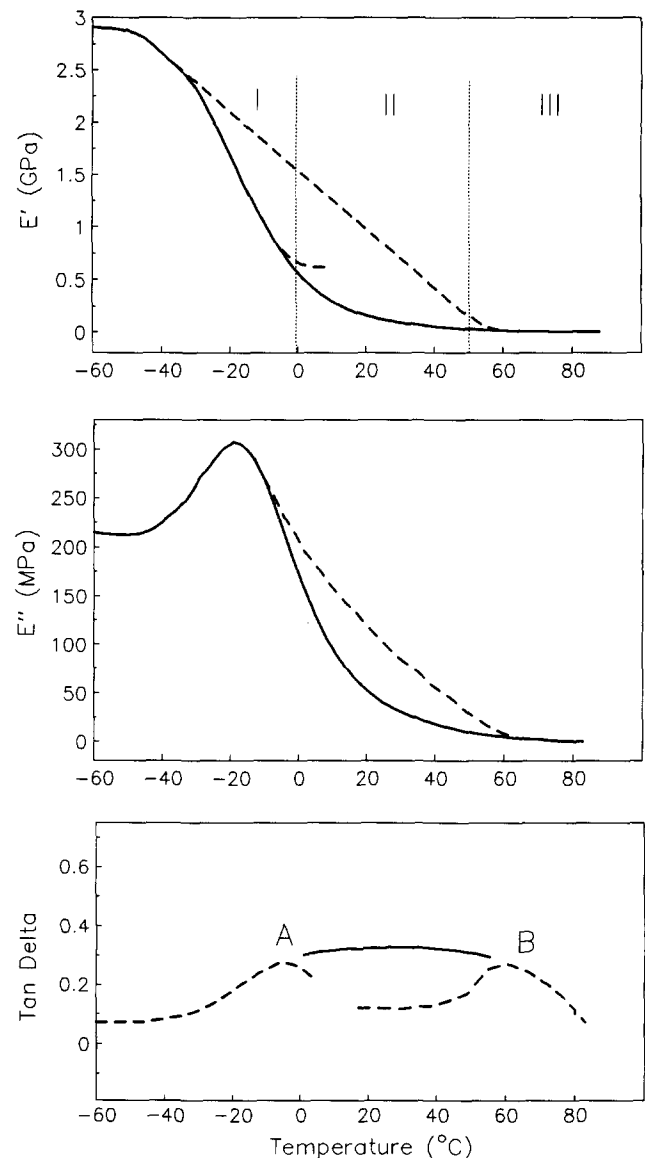

Figure 8 Generation of a broad tan δ peak from its components using E' and E'' data for the IPN with PU/PMMA composition (wt%) of 70/30: (——) experimental; (- - -) simulation of normal transitions

transition in region I alone produces tan δ peak A (see *Figure 8*). Similarly, tan δ peak B is produced when a normal transition is assumed across the full transition (covering all three regions). The peak tan δ values at A and B are linked together, by the high tan δ values obtained in region II, to produce the experimental rectangular shape of the tan δ curve. In region II, E' and E'' values are much reduced, and, since greater magnitudes of reductions are experienced in E', the peak value in tan δ ($=E''/E'$) is maintained.

CONCLUSIONS

Dynamic mechanical analysis of polyurethane/poly(methyl methacrylate) (PU/PMMA) interpenetrating polymer networks (IPNs) at higher PU concentrations indicates a two-stage change in the dynamic real modulus (E') and loss modulus (E'') over a wide transition region. The two stages consist of a sharp transition, as experienced in component polymers, and a subsequent more gradual transition, which is unique to IPNs and results in tan δ broadening. All the E'' curves exhibit a bell shape at transition, whereas the tan δ curve for the IPNs of approximately 70/30 PU/PMMA composition produces a broad peak of an almost rectangular waveform. Such a tan δ behaviour at transition, where a steady tan δ value is maintained over a wide temperature range, cannot be imparted into the elastomer component by the alternative route of additional chemical crosslinking.

A significant correlation exists between the experimental shift factors found in the time–temperature superposition of the real moduli of the IPNs and the WLF equation over wide transition regions. The WLF analysis indcates the presence of greater fractional free volume in the IPNs

with higher PU contents. The availability of extra free volume contributes to the glass transition broadening, starting it at lower temperatures.

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