

Dynamic shear measurements of physical ageing and the memory effect in a polymer glass

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The real and imaginary parts of the dynamic shear modulus, G' and G'' , respectively, of 10% and 30% poly(2,6-dimethyl-1,4-phenylene oxide)-polystyrene (PPO-PS) blends were measured from 10^{-3} to 1 Hz during physical ageing up to 10^6 s. In the first experiment, isothermal ageing after cooling the samples from the rubbery to the glassy state, G' increased and G'' decreased monotonically with time at a rate that increased with decreasing frequency. In the second experiment, isothermal ageing of samples that had undergone densification during their previous ageing at a lower temperature, G' first decreased then increased and G'' first increased and then decreased, showing a minimum and maximum, respectively. The occurrence of minima and maxima is a reflection of the 'memory effect' observed earlier by others in the volume and refractive index studies of glasses. These results are analysed in terms of the change in shear relaxation time during ageing. A molecular picture of the memory effect is given. It takes into consideration the effect on physical ageing of the configurational states whose availability appears as both a secondary relaxation and an excess entropy below T_g . It is further suggested that dynamic shear measurements are a more sensitive and less tedious method for the study of the memory effect in glasses than are the volume and refractive index.

(Keywords: dynamic shear; ageing; polystyrene; blends; memory effect)

INTRODUCTION

A major characteristic of glassy materials is that their volume, enthalpy and entropy decrease on isothermal physical ageing at a rate that increases as the temperature approaches T_g . These changes affect the kinetic behaviour of a glass in different ways¹⁻⁶. The behaviour of a glass also depends significantly upon its thermal history below T_g . For example, an unusual effect on the volume of a glass during physical ageing was observed in poly(vinyl acetate) by Kovacs⁷. The effect was also known to occur in network glasses⁸⁻¹¹, e.g. B_2O_3 and GeO_2 , where it was referred to as the 'memory effect', and was originally found as a spontaneous expansion followed by contraction of an annealed poly(vinyl acetate) glass during isothermal measurements at a temperature T_1 when the temperature was suddenly raised from T_2 to T_1 both below T_g . A similar effect was also observed when the pressure of a B_2O_3 glass instead of the temperature was changed below the glass transition pressure¹⁰. Although Kovacs *et al.*¹² seem to have observed a consequence of the effect on both G' and $\tan \phi$ in a different (from the previous)⁷ sample of poly(vinyl acetate) at 307 K in one measurement during 'isothermal contraction' (Figures 12 and 13 in ref. 12), it is not certain whether the memory

effect has a pronounced mechanical consequence, and whether independent measurement of dynamic shear would exhibit it.

Because of the importance of the effect for our concepts of the structure of a glass, and for the technical applications of, in particular, polymer glasses, it is important to establish the changes in the dynamic shear modulus that can be characterized as a memory effect. We describe the changes in the shear modulus at very low frequencies of two polymer blends, 10% poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) in polystyrene (PS) and 30% PPO in PS, each of two different thermal histories, observed in two different experiments, namely (i) isothermal physical ageing at a temperature T_1 of a sample obtained by rapid cooling through T_g to T_1 and (ii) isothermal physical ageing at T_1 of a sample that was physically aged previously at a temperature below T_1 . We then propose a molecular picture of the memory effect in terms of entropy or volume associated with the secondary or β relaxation in a glass.

There has been no systematic study of the dynamic shear modulus of glasses, and the memory effect observed in the volume and refractive index studies is attributed to the non-exponential character of the relaxation and a set

of other parameters whose independent verification has not been possible. Therefore, we believe that the dynamic shear measurement and the discussion of memory effect given here will shed light on both the kinetics and the structure of the glassy state and hope that an incentive will be provided for the study of other glasses and use of other relaxational methods towards this aim.

EXPERIMENTAL

The polymer samples had an average molecular weight of 254 000 for polystyrene and 50 000 for PPO. Their blends were prepared by LeFebvre by a method described before¹³, and were used as such. The samples were cut to a dimension of about $2 \times 5 \times 35$ mm for measurement of the real and imaginary parts of the modulus with an inverted forced oscillation pendulum described earlier¹⁴. Several measurements were repeated for both the frequency and temperature variation and the results agreed within 1%. The temperature of the sample was kept constant to within ± 0.2 K, thus ensuring that the errors arising from temperature variations were minimal. The choice of polymer blends rather than of pure polymers was due to our current interest in the study of the detailed rheology of the molecular and polymer blends. The relative amplitude of deformation of the sample was about 5×10^{-5} .

The dilatometric/calorimetric glass transition temperature of the blends is 383 K for 10% PPO-PS and 403 K for 30% PPO-PS. The rheological behaviour of the blends that we observed complements the earlier conclusions reached by several workers^{13,15-18} that PPO and PS in the above-given composition are compatible polymers.

RESULTS

In the first experiment a sample of 10% PPO-PS blend was cooled from 400 K to 368 K at the rate of 0.2 K s^{-1} and after its temperature became constant at 368 K, in about 15 min, the real and imaginary parts of the complex modulus, G' and G'' , respectively, were measured at 10^{-3} , 10^{-2} , 10^{-1} and 1 Hz at frequent time intervals up to a period of about 5×10^5 s. These results are shown in *Figure 1*. At a constant frequency of measurement, G' increased but G'' decreased monotonically with elapsed time t at a rate that for G'' decreased with time at all frequencies, but for G' only below 0.01 Hz. It is also evident from *Figure 1* that, after a time t , the rate of change of G' and G'' with frequency ($\partial G'/\partial \log \omega$), and ($\partial G''/\partial \log \omega$), decrease with increasing frequency of the measurement.

In the second experiment, the sample was heated to 400 K and cooled through its T_g ($= 383 \text{ K}$) to 363 K at the rate of 0.2 K s^{-1} . It was then kept for 8 h at 363 K and then heated to 368 K. After the temperature became constant, at 368 K, in about 15 min, its G' and G'' were again measured at 10^{-3} , 10^{-2} , 10^{-1} and 1 Hz at frequent intervals up to a period of about 5×10^5 s. These results are also shown in *Figure 1*. In this experiment of physical ageing G' first decreased and then increased with elapsed time, thus exhibiting a minimum at about 10^4 s. The G'' first increased and then decreased with elapsed time with the maximum occurring after the same period of time as the minimum in G' . The positions of the minima and/or maxima shifted to longer times and the minimum became deeper and the maximum sharper as the measurement

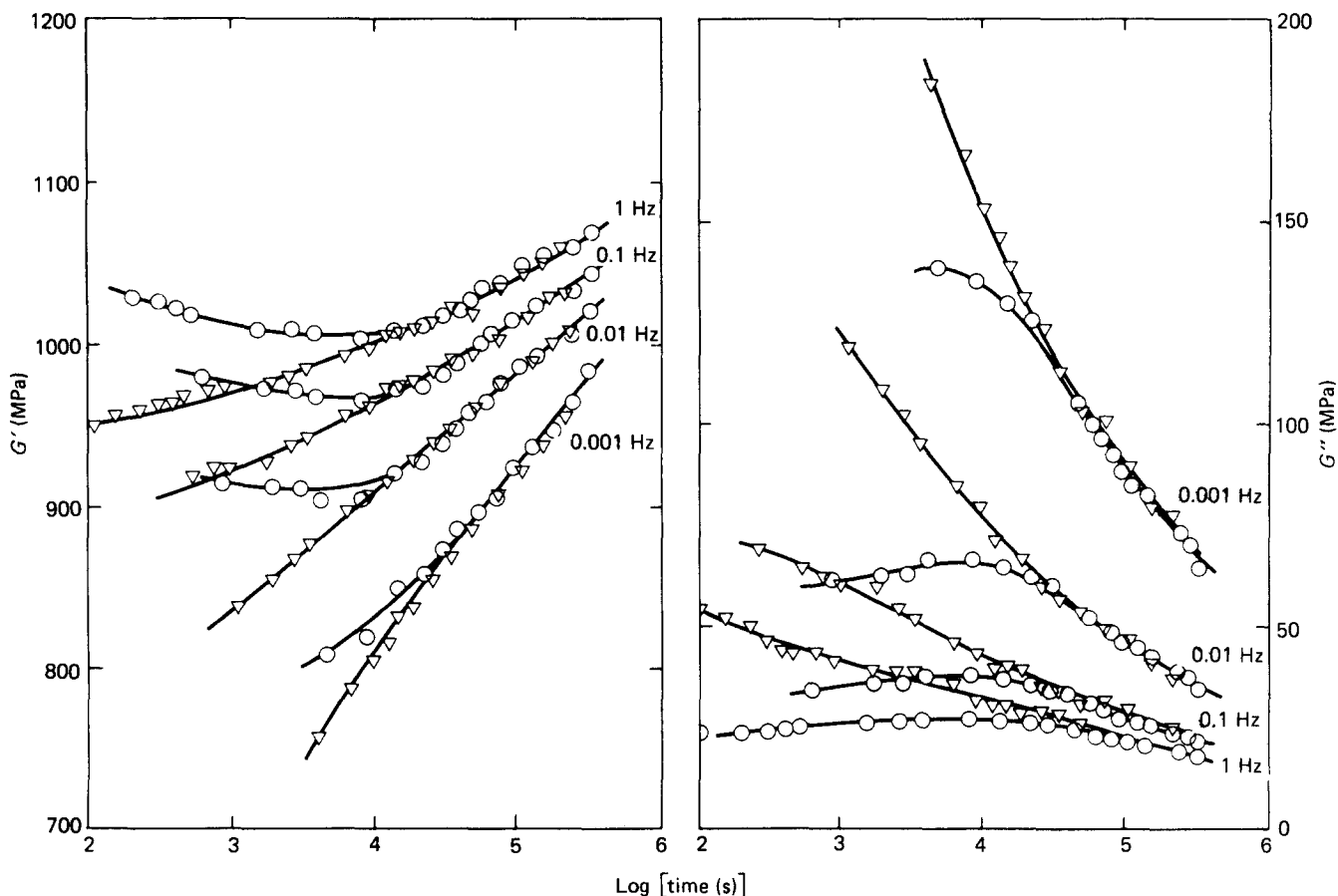


Figure 1 Changes in G' and G'' of a 10% glassy PPO-PS blend with time at several frequencies at 368 K. Triangles are the data for the glassy blend cooled from $T > T_g$ to 368 K and measured. Circles are the data for the glassy blend cooled from $T > T_g$ to 363 K, kept isothermally for 8 h and then heated to 368 K and measured. See text for details

frequency was increased from 10^{-3} to 1 Hz. In Figure 1, G' increases and G'' decreases with increasing frequency. This suggests that our measurements are at the high-frequency end of the isothermal dynamic-shear relaxation spectrum.

Similarly, a sample of 30% PPO-PS blend was cooled from 415 K to 388 K at the rate of 0.2 K s^{-1} and its G' and G'' were measured at 10^{-3} , 10^{-2} , 10^{-1} and 1 Hz at a constant temperature of 388 K at frequent intervals up to a period of about $1.5 \times 10^6 \text{ s}$. These results are plotted in Figure 2, and show a monotonic increase in G' and decrease in G'' with elapsed time in a manner qualitatively similar to that for 10% PPO-PS blend.

In the second experiment, the sample was heated to 415 K, cooled through its $T_g (= 403 \text{ K})$ to 383 K at the rate of 0.2 K s^{-1} , and kept at 383 K for 8 h. The sample was then heated to 388 K, and after its temperature became constant, its G' and G'' were again measured at 10^{-3} , 10^{-2} , 10^{-1} and 1 Hz at frequent intervals up to a period of about $1.5 \times 10^6 \text{ s}$. These results are also shown in Figure 2. During the physical ageing here, G' first decreased and then increased, but G'' first increased then decreased with elapsed time, in a manner qualitatively similar to the 10% PPO-PS blend. The positions of the respective minima and maxima were again in the range 10^3 – 10^4 s . They become sharper and their positions shifted to longer times as the measurement frequency was decreased from 1 Hz to 10^{-3} Hz .

In Figures 1 and 2, G' of the second experiment approaches G' of the first experiment from above and G'' of the second experiment approaches G'' of the first from

below. The values from the two experiments finally merge and then approach the limiting values of G' and G'' of the equilibrium state of the liquid. This suggests that the shortest time needed to reach a certain value of G' and G'' at a given temperature is by direct physical ageing as in the first experiment. Other thermal history may not allow a more rapid approach towards equilibrium, as noted also by Kovacs *et al.*¹.

DISCUSSION

The G'' curves in Figures 1 and 2 are remarkably similar to the corresponding curves of the change in volume of poly(vinyl acetate) obtained by Kovacs⁷. Since volume retardation is a primary effect in physical ageing, we consider that the isothermal changes in G' and G'' in Figures 1 and 2 are the dynamic shear analogue of the effects observed dilatometrically in poly(vinyl acetate) and of the effects observed in the refractive index measurements of B_2O_3 glass⁸ both during qualitatively similar thermal histories. Therefore, a discussion of results in terms of volume retardation and shear relaxation processes seems appropriate, where the spontaneous volume retardation affects the dynamic shear behaviour of the glass. A discussion in terms of entropy or enthalpy retardation is equally appropriate, but corresponding measurements of the two properties of glasses are not available and Petrie¹⁹ has already shown a qualitative similarity between the enthalpy and modulus relaxation during physical ageing of several polymers.

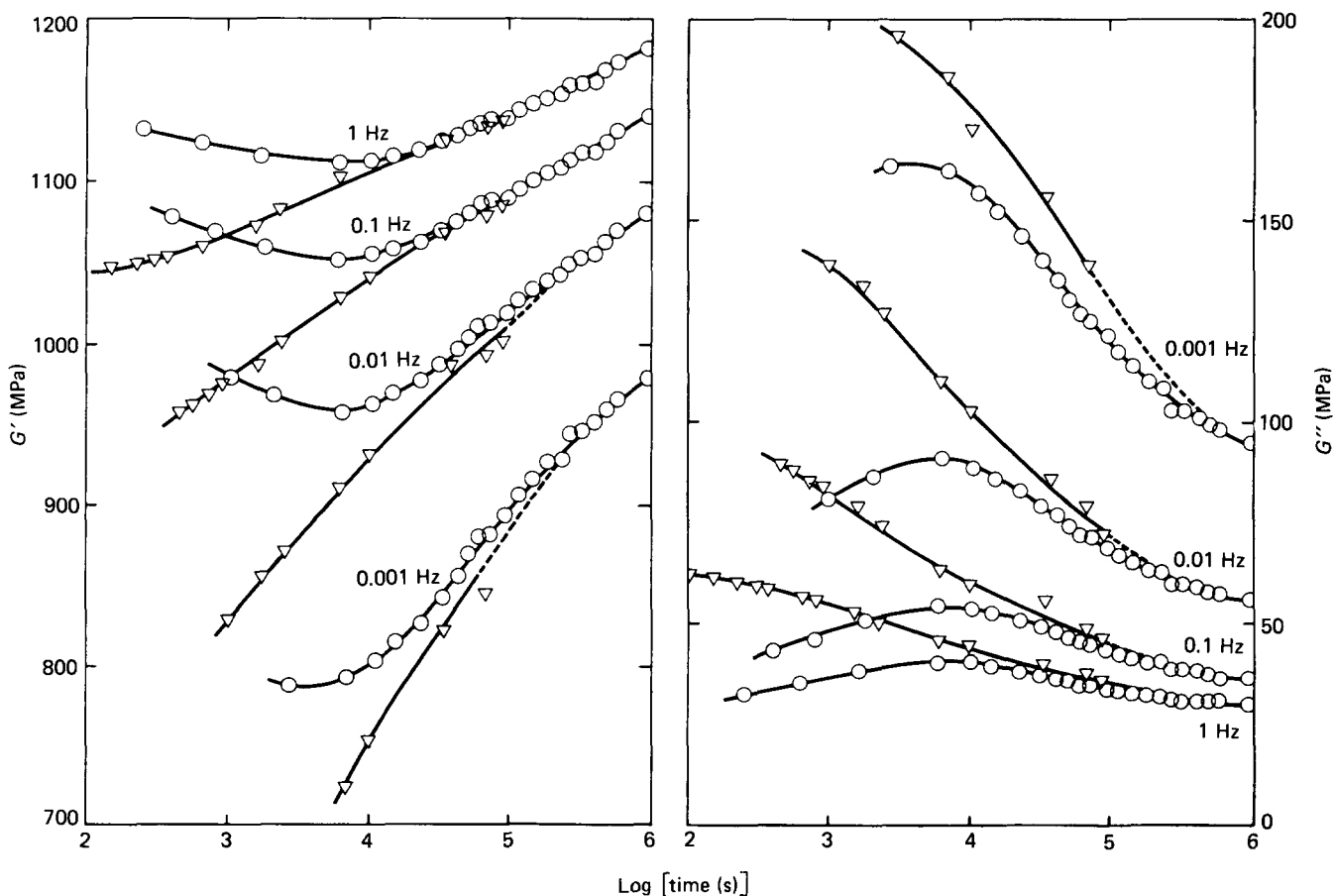


Figure 2 Changes in G' and G'' of a 30% glassy PPO-PS blend with time at several frequencies at 388 K. Triangles are data for the glassy blend cooled from $T > T_g$ to 388 K and measured. Circles are the data for the glassy blend cooled from $T > T_g$ to 383 K, kept isothermally for 8 h and then heated to 388 K. See text for details

We first discuss the secondary relaxations of a glass and its implications for the thermodynamics and physical ageing of a glass. Within these concepts we then discuss the two experiments separately as: (i) relaxation during isothermal annealing and (ii) memory effect.

Secondary relaxations and thermodynamics of a glass

The occurrence of localized molecular motions in the otherwise rigid matrix of a glass is now accepted as an intrinsic property of the disordered solids. Studies of polymer²⁰, molecular²¹, network²² and liquid-crystal²³ glasses and the glass-like state of orientationally disordered crystals²⁴ by dielectric²⁰⁻²⁴ and mechanical^{25,26} relaxations, n.m.r. spectroscopy²⁷, light scattering²⁸ and depolarization of phosphorescence²⁹ experiments have shown the existence of such molecular motions as secondary or β relaxations, which freeze out on the timescale of one's experiments at temperatures substantially below T_g . This alone shows that the configurational state of a glass does not remain unchanged on cooling between T_g and 0 K.

One expects that the localized configurational states available to a glass must also contribute to its volume, entropy and enthalpy and, therefore, this contribution must be considered in the theories of the effects of physical ageing on the thermodynamic and kinetic properties of glasses. Indeed several analyses³⁰⁻³³ of the thermodynamic properties of polymer, molecular, network and liquid-crystal glasses and of the glass-like state of orientationally disordered crystals have shown that molecular mobility that shows up as a secondary or β relaxation makes a substantial contribution to the expansivity³⁰, heat capacity and entropy³¹⁻³³ of a glass below T_g , and that this contribution at T_g is 40-70% of the total entropy loss that occurs on cooling to 0 K. Convincing evidence for a greater relative importance of secondary relaxation to the configurational entropy of a glass comes from the heat capacity data of a molecular glass³⁴, which shows a decrease in the excess heat capacity below T_g , and near the temperature³⁵ where the extrapolated time of secondary relaxation is about 10^4 s.

In view of the above-mentioned similarities in the kinetic and thermodynamic properties of a variety of different types of glasses, we believe that the physical ageing effects of polymer blends are best interpreted in a general way that transcends the details of molecular structure, specific models for motions or the state of molecular aggregation.

The enthalpy¹⁹ and entropy³¹ of a glass significantly decrease on annealing. This decrease is partly attributable to the decrease in the number of configurational states whose availability shows up as a secondary relaxation, and it is in addition to the decrease in the number of available configurations that involve very short times of the main relaxation and whose freezing out on the timescale of one's experiment causes the glass transition. The phenomenological theories of glass transition^{36,37} do not account for the occurrence of secondary relaxations, and therefore geometrical and structural models of the glassy state in general have been used to explain the origin of secondary relaxations. In such models of the glassy state, the secondary relaxations are envisaged either as hindered motions of relatively loosely packed molecules in the interstitial regions termed 'islands of mobility' dispersed between the well packed polyhedral cluster-like

structures in a glass³⁵ or as thermomechanical activation of certain defects which causes a local shear and this local shear is responsible for the internal friction^{25,26}.

Relaxation during isothermal annealing

It is now recognized that the decrease in volume, enthalpy and entropy during isothermal physical ageing of a glass affects both its dynamic shear and electrical properties in four different ways⁵, as follows:

(i) The relaxation time of the molecular process responsible for the viscous flow, or main relaxation, increases. The viscoelastic relaxation time is inversely related to the exponential of free volume³⁶ and configurational entropy³⁷, according to the free volume and entropy theories, and is consequently sensitive to a decrease in the volume and entropy on physical ageing. The values of G' and G'' therefore change according to the change in the relaxation time during annealing.

(ii) The mechanical modulus and the orientation polarization increase as a result of an increase in the density of a glass on annealing⁵. It is a relatively small effect and the resulting changes in G' and G'' are in the opposite sense of that in (i).

(iii) The number of molecules and molecular groups contributing to secondary relaxation decreases^{2,4,5,21}. The effect on G' and G'' is the same as in (i) but relatively small, particularly at low frequencies and low temperatures. Its relation with volume is not known.

(iv) The frequency-independent background loss over which the relaxation spectra are superposed decreases⁴. Since the changes in the vibrational frequencies during annealing are expected to be small, the effect on G' and G'' would be negligible.

It must be emphasized that, while all four processes occur during physical ageing of a glass, their relative importance in a given glass varies with the temperature of ageing.

Since the contraction of a glass during ageing itself reflects a decrease in free volume, one can calculate the time-dependent increase in the viscosity and viscoelastic or shear relaxation time from Doolittle's³⁸ or Cohen and Turnbull's³⁶ equations, from which one can in turn calculate the time-dependent change in G' and G'' of a glass. Now, if the calculated change is less than the observed change in G' and G'' , one would conclude that part of the decrease in volume does not affect the viscosity or shear relaxation time and that this part decrease in volume reflects the collapse of the loosely packed regions whose existence is associated with secondary relaxation. The rest of the decrease in volume affects viscoelastic relaxation time in the manner proposed by Doolittle³⁸ and Cohen and Turnbull³⁶. Since we did not measure the volume retardation of the PPO-PS blend, such an analysis for this polymer cannot be done. But the corresponding changes in volume, G' and G'' for poly(vinyl acetate) are given by Kovacs *et al.*¹², whose data we now use for such an analysis.

Kovacs *et al.*¹² concluded that '...about 20% of the total temperature dependence of relaxation times may be ascribed to an effect which is either independent of free volume or else associated with a small change in free volume with temperature which is achieved instantaneously, the same above and below T_g '. Of the several ways by which they reached this conclusion, the most direct one is based upon the relation between the

effect of temperature on G' , $\partial G'/\partial T$, which can be related to

$$\partial G'/\partial T = (\partial G'/\partial T)_f + (\partial G'/\partial f)_T (\partial f/\partial T) \quad (1)$$

where $(\partial G'/\partial T)_f$ is the rate of change of G' with T at a constant free volume, $(\partial G'/\partial f)_T$ is the rate of change of G' with free volume, or volume, during the course of isothermal physical ageing, and $(\partial f/\partial T)$ is the rate of change of free volume with temperature. They determined that $(\partial G'/\partial f)_T (\partial f/\partial T)$ is 80% of the measured $\partial G'/\partial T$ and, therefore, $(\partial G'/\partial T)_f$ is 20% of the total.

Their conclusion seems to imply a substantially large temperature dependence of G' on the occupied volume or on the anharmonicity of phonon modes. It seems unlikely that the anharmonicity of phonon modes in a glass can have a large effect on G' . We, therefore, suggest that the less-than-anticipated change in G' during physical ageing partly reflects the collapse of (configurationally) high-volume/high-entropy regions in the structure of a glass, which does not affect G' , viscosity or shear relaxation time, in the same way as does a decrease in free volume. The anharmonicity may still affect G' , but much less than 20%. In this sense the isothermal change in G' observed during the course of physical ageing cannot be related to the change in G' with temperature observed in the equilibrium liquid above T_g according to equation (1). It is also important to point out that, as shown earlier⁵, the densification of a glass on physical ageing affects its kinetic properties quite differently from densification on cooling or compression. Thus the changes in G' and G'' during isothermal physical ageing are partly due to a decrease in the amplitude of secondary relaxation and partly due to an increase in the shear viscosity and shear relaxation time according to either of the two phenomenological theories of viscosity^{36,37}.

Memory effect

The 2.5% initial decrease in G' at a constant temperature in the second experiment shown in Figures 1 and 2 suggests a decrease in the shear relaxation time due to a corresponding increase in free volume. This increase in volume would also lower $\Delta G (= G_R - G_U)$, which in turn may partially, though insignificantly, compensate for the change in G' and G'' due to a decrease in shear relaxation time.

The occurrence of a maximum for G'' and a minimum for G' seems, therefore, primarily a reflection of changes in the thermodynamic properties of a glass, i.e. that during isothermal physical ageing of our second experiment, V, H and S would first increase, reach a maximum value and then decrease nonlinearly with time. This has been observed in the volume⁷ of poly(vinyl acetate) and in the reciprocal of refractive index⁸ (which is related to volume by the Lorenz-Lorentz equation) of B_2O_3 , and is termed a memory effect.

Phenomenological descriptions of memory effect observed in the volume and refractive index studies have been offered^{1,11,39} in terms of (i) multiplicity of retardation mechanisms, and (ii) a slower-than-exponential decay function represented by an empirical function and a nonlinear dependence of relaxation time on time. The mathematical models for the effect are based on the assumption that the time and temperature dependences of a property are related by a superposition integral, and that only the main relaxation (which involves changes in viscosity) needs to be considered.

They overlook the observations that the configurational state of a glass changes on raising the temperature and that the expansivity, heat capacity and entropy of a glass are not entirely vibrational in origin but have a substantial contribution from these changing configurations³⁰⁻³³. For this reason the phenomenological treatments seem less adequate to us. Another reason that forces us to exclude these as satisfactory explanations is that time-temperature superposition cannot be assumed for the PPO-PS blends, as our attempts to reduce the isothermal spectrum of G' and G'' to a master curve by any procedure of shifting their isotherms did not succeed⁴⁰.

In several studies, the contribution to expansivity, heat capacity and entropy from secondary relaxations in a variety of glasses³⁰⁻³³ is shown to be substantially high near T_g . Also the amplitude of secondary relaxation in dynamic shear measurements is found to be proportional to the number of sites^{25,26} in a glass where molecular relaxation occurs, or as described in dielectric relaxation³³, to the number of 'islands of mobility', or, in general, to the number of localized configurational states, pictorially described by a corrugated bottom of the potential energy minima³⁵ in which the state of glass is trapped. We propose the following picture of memory effect in terms of secondary molecular relaxations.

The variation of V, H, S, G' and ϵ'' of the crystalline, liquid and glassy states of a material from $T > T_g$ to 0 K is illustrated in Figure 3a, and that of the excess calorimetric

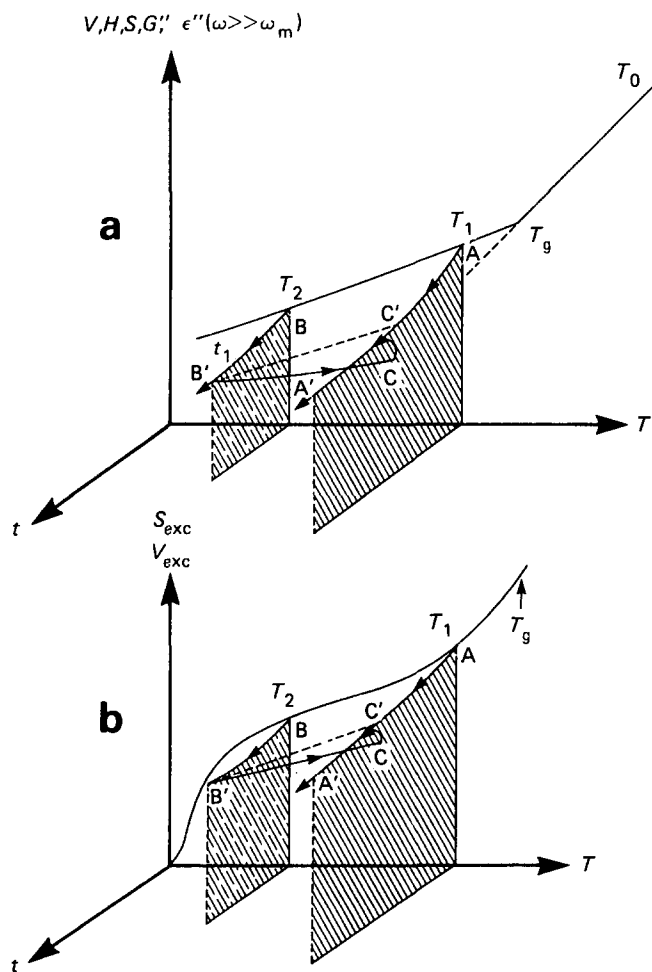


Figure 3 (a) An illustration of the changes in volume, enthalpy and entropy of a glass with temperature and time, showing the memory effect. (b) Similar illustration of the excess entropy and excess volume of a glass

entropy, S_{exc} , of a glass over that of the corresponding crystal in *Figure 3b*. In the calculation of S_{exc} , the residual entropy of the glassy and crystalline phases has been subtracted from the entropy of the phase, so that $S_{\text{exc}}=0$ at 0 K. Defined in a similar manner, $V_{\text{exc}}=0$ at 0 K. When a liquid is cooled from T_0 to a temperature T_1 or T_2 and the glass is held at either of these two temperatures, its V , H and S decrease monotonically from, say, point A towards point A'. Such effects are widely known and have been interpreted in terms of free-volume and/or configurational entropy theories, and we suggested in the previous subsection that the decrease in volume or entropy is partially due to a concurrent decrease in the number of high-volume and high-entropy configurational states in the structure of a glass, and that the changes in the dynamic shear properties on physical ageing also involve a decreasing contribution from secondary relaxations.

In our second experiment, when the glass is cooled from T_0 to T_2 , i.e. from point A to B in *Figure 3*, its V , H and S would decrease to a point B' in a manner similar to that at T_1 but at a rate less than at T_1 . If the time of ageing is sufficiently long, the decrease corresponds partially to the depletion of the mobile defects or islands of mobility, as discussed in the preceding subsection. If the glass is now heated to T_1 , i.e. from B' to C, in a short time, its V , H , S and S_{exc} increase because (i) the vibrational frequencies decrease with increase in temperature and (ii) those states whose relaxation time is less than the time taken in reaching from point B' to C (i.e. from T_2 to T_1) contribute to V , H and S . The relative importance of the two factors depends upon the time taken in raising the temperature. Now, when the glass is held at temperature T_1 at C the molecular motions responsible for its structural relaxation occur and allow the recovery of those high-volume high-entropy configurational states (defects or islands of mobility) which correspond to temperature T_1 towards C'. This may be compared with the attainment of a certain concentration of defects, in thermodynamic equilibrium, which are localized within the depleted zones, that is that molecular diffusion occurs only over short distances within the depleted zones in a way similar to that concluded by Quentrec⁴¹. Thus the values of V , H and S increase spontaneously. After the recovery of the initial concentration of defects, further physical ageing causes densification along the same path as the isothermal densification of the glass. Such changes in the concentration of defects on increasing the temperature have been observed to occur in ice⁴² and in crystalline aluminium⁴³, where the vacancy defects increase under isothermal conditions.

We emphasize that the recovery of the interstitial regions of loosely packed molecules, or islands of mobility, is not determined by the relaxation time of secondary relaxation, but rather by the rearrangement times of the majority of molecules inside the depleted zone, whose cooperative motions cause the structural change or increase in viscosity.

In the second experiment on the two polymer blends in *Figures 1* and *2*, therefore, the initial increase in G'' and decrease in G' are due to (i) the full recovery of high-entropy/high-volume states or of the configurational states that correspond to the secondary relaxation and (ii) a partial decrease in the shear relaxation time. As G' and G'' asymptotically approach their limiting values

spontaneously but at a relatively fast rate, a further increase in the shear relaxation time causes G' to increase and G'' to decrease and to merge with the curves obtained in the first experiment.

CONSEQUENCES OF THE PICTURE

According to the picture given above of the memory effect, for each nonequilibrium state point in *Figure 3*, the structure of a glass has an equilibrium configuration corresponding to the availability of localized configurational states, the latter showing up as the volume and entropy contribution and secondary relaxation. In an experiment, therefore, when the temperature of an annealed glass is raised too quickly to allow the recovery of the equilibrium configurational state, a memory effect would be observed. But, if the temperature was increased at an appropriately slow rate, the V , H , S and S_{exc} would follow a path B'C' rather than B'C, and a memory effect would not occur. Its dynamic shear consequence is that if G' and G'' were measured with slowly increasing temperature from point B' at T_2 to T_1 , such that the total time taken is equal to that in going from B' to C' via C in *Figure 3*, G'' would increase monotonically with temperature and would begin to decrease after reaching near point C'. The area under this curve when related to time, in for example a constant-heating-rate experiment, would be identical with the area under G'' -time curves in our second experiment in *Figures 1* and *2*. This is one testable consequence of the picture given above.

A second consequence is related to the possibility of obtaining a glass at temperatures far below T_g with the same volume but different relaxational properties. If two samples of a glass were allowed to age at T_1 and T_2 , and after an appropriate time in each case were cooled to a temperature far below T_g , such that their volumes at that temperature were the same, their kinetic properties would differ owing to the difference in the effect on secondary relaxations during ageing at T_1 and T_2 , and the freezing-in of the configurational states belonging to these relaxations. We realize that the assumptions of a non-exponential relaxation function and time-temperature superposition in the currently accepted mathematical descriptions^{1,11,39} would also suggest this consequence. But, as noted earlier, and shown elsewhere⁴⁰, the time-temperature superposition assumption is unsatisfactory for the dynamic shear measurements of the two polymer blends⁴⁰. It is also important to realize that the assumption of time-temperature superposition and the use of a shift parameter in describing the properties of glassy materials entails a violation of the Curie law, according to which the modulus and permittivity of a material must increase with decreasing temperature; the assumption of time-temperature superposition implies that modulus and permittivity of a material remain unchanged with decreasing temperature.

A third consequence is a corollary to the memory effect. Suppose a glass was physically aged at temperature T_1 in *Figure 3* to a certain point and then rapidly cooled to T_2 ; its volume, entropy and enthalpy would first decrease rapidly up to a certain period of time and thereafter decrease slowly at a rate corresponding to that of the isothermal physical ageing at T_2 . Its G'' would, therefore, change with time in the same manner as its volume; but its G' would first decrease slowly and then rapidly with time.

A fourth consequence of our molecular picture is that the larger the amplitude of secondary relaxation, i.e. ΔG (secondary relaxation), of a glass, the larger the magnitude of its memory effect. We suggest, therefore, that amorphous poly(methyl methacrylates) would show a larger memory effect than other polymers.

Finally, such effects in volume and refractive index have been referred to as a memory effect because the sample 'remembers that at a time t_2 as a result of its previous thermal history it does not possess a structure corresponding to the equilibrium properties at any temperature. Hence its properties evolve in a different fashion...'¹¹. In our explanation the glass at point C in Figure 3 remembers that in its structure all its localized configurational states have not been recovered, for the time allowed in changing the temperature from point B' to C was too short. Therefore, its properties change in a way such as to achieve that structure.

CONCLUSIONS

Dynamic shear measurements of two polymer blends show that physical ageing decreases G'' and increases G' at a rate that decreases with increasing frequency. When the temperature of a physically aged sample is raised, G'' shows a maximum and G' a minimum on physical ageing at that temperature. These are interpreted as the dynamic shear analogues of the effects observed in the thermodynamic properties of a glass, and have a striking resemblance to the memory effect observed by others. The dynamic shear measurements provide a more sensitive and informative and less tedious method for the study of such effects in glasses than do the volume or refractive index.

A significant fraction of volume decrease during physical ageing of a glass cannot be accounted for by the observed changes in G' and G'' . It is necessary to consider, therefore, that the collapse of high-entropy/high-volume configurational states in the otherwise rigid matrix of a glass contributes to a major decrease of its volume. This affects the magnitude of secondary relaxation and has only a minor effect on G' and G'' of a glass.

In an explanation of the memory effect, which recognizes the occurrence of secondary relaxation as an intrinsic property of a glass, and the effect of physical ageing on such relaxations, it is suggested that an equilibrium configurational state of secondary relaxations in the structure of a glass must be recovered on heating a previously annealed sample and that this recovery is determined by the timescale of the structural relaxation rather than the timescale of secondary relaxation. This explanation has four consequences, each of which can be experimentally tested.

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