JOURNAL OF MATERIALS SCIENCE 15 (1980) 1194–1206

Physical and thermodynamic aspects of the glassy state, and intrinsic non-linear behaviour of creep and stress relaxation

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Rheology in the highly viscous liquid and the glassy state is reviewed and discussed. A distribution relaxation time due to the co-operative molecular motion is exhibited both in the highly viscous liquid and in the glassy states. However, only in the glassy state has the structure been frozen-in at some particular internal state resulting from the incomplete establishment of a thermodynamic equilibrium state. Therefore, the intrinsic non-linear rheological behaviour of the glassy state is explained from the physical and thermodynamic aspects in the glass transformation region. The volume relaxation of soda-lime–silica glass and the thermal history of glass during forming process have been studied. Finally, the role of rheology in thermal stress and fracture mechanics is also mentioned, which subsequently will allow us to re-evaluate the mechanisms of toughening and weakening of composite materials.

1. Introduction

Rheology is of fundamental importance in glass or polymer manufacturing processes, during which glass and polymer form a liquid state pass through its glass transformation temperature to enter a solid-like glassy state. Therefore, the physical and mechanical properties of glass vary with changes of temperature and cooling rate. To optimize the process, the rheological, physical and mechanical properties of the glass must be characterized. Unfortunately, from the liquid-like to the solid-like state, these properties of the glassy state are quite complex. Theoretical models and experimental results of rheological and physical properties of the glass will be reviewed in the present paper. A discussion regarding how to apply these properties to optimize the glass manufacturing or polymer processing will also be given.

Since the glassy state has been recognized as being in a non-equilibrium thermodynamic state, the phenomenon of the structural relaxation of the glassy state is a very important factor in predicting the physical and mechanical properties as well as for characterizing the internal structure of the glassy state. The behaviour of the dynamic physical properties, such as viscosity, thermal expansion coefficient, and modulus, which are governed by the phenomenon of structural relaxation are vitally important in the manufacture of glass and plastic as well as in composite materials fabrication. Therefore, the structural relaxation of the glassy state and the intrinsic non-linear behaviour of creep and stress relaxation will be explained from thermodynamic and kinetic aspects; and its application to the manufacturing process and predicting of the physical and mechanical properties of materials will also be mentioned. Since the thermodynamics are the same for the entire glassy state, the following discussion should be equally suitable for both glassy organic polymers or inorganic glasses.

2. Rheological behaviour of the glassy state

2.1. Glass transformation and viscosity theory

If a liquid can be super-cooled without crystallization to a temperature, T_g, where its viscosity is in the order of 10^{13} P, then the substance enters a

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0022–2461/80/051194–13$03.30/0

solid-like glassy state. Tammann [1] defined T_g as glass transformation temperature for any glass-forming substance. Davies and Jones [2] have pointed out that a "volume viscosity" instead of "shear viscosity" should be used as a determinant for the glass transformation, because ordinary viscosity refers to shearing motion while there is no need for shearing motion to occur during the stabilization of glass. However, the two quantities have been found to be roughly of the same order of magnitude so that in practice Tammann's criterion is a reasonable guide.

Kauzmann [3] has given an extensive analysis of dielectric relaxation in terms of rate theory, and has concluded that, for most glasses, T_g is roughly fixed for finding the temperature for which the Maxwell relaxation time, τ_R, is 30 min ($\tau_R = CV\eta_0/RT$; where C is a constant of the order of unity, V is the mole volume of the molecule, η_0 is the shear viscosity, and R is the gas constant). Therefore, the temperature at which the dielectric relaxation time is at the value of 30 min also has been defined as T_g. The other methods for determining T_g are by the measurement of physical properties such as heat capacity, thermal expansivity, volume, etc., during the super-cooling process. However, since glassy material is a non-equilibrium thermodynamic state, the physical properties depend on its thermal and mechanical history. As a result of different cooling rates, one would expect different values of T_g. This result also serves to explain why the glass transformation is not the second order phase transition of the Ehrenfest type [5] (for the glass transformation, the affinity does not equal to zero, i.e. $A \neq 0$). As a result Simon [6] claims that the glassy state is distinguished from the liquid state by the fact that an internal equilibrium state is not established.

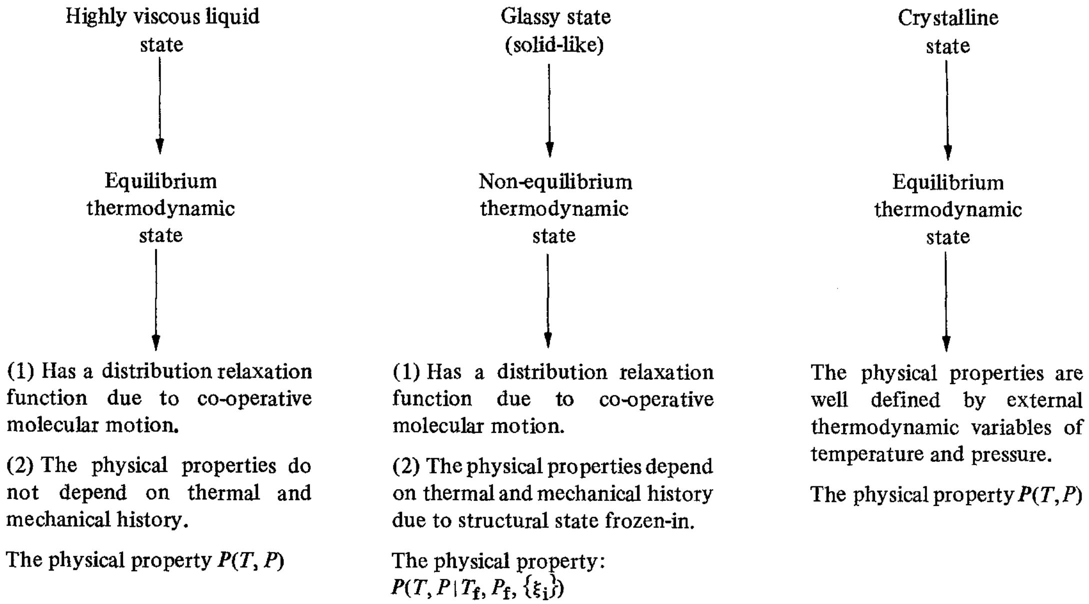
Litovitz, Macedo and their colleagues [7–11] did a systematic study on the viscoelastic relaxation of glass forming compositions. They concluded that a single relaxation time is exhibited in a high temperature Arrhenius region, in which the molecules are in "disassociated" state and, therefore, in a low activation energy state for viscous flow. Then the spectrum of relaxation times starts to broaden with decreasing temperature until the molecules are almost in a completely "associated" state. When the molecules are in this state, the spectrum of relaxation times no longer broadens with decreasing temperature and its viscosity is in a high activation energy Arrhenius region. Between the two Arrhenius regions of low and high activation energy, the activation energy of the viscous flow is a function of temperature due to the fact that the molecules are in a process to transform from the "disassociated" to "associated" state with decreasing temperature.

Litovitz *et al.* explained that the distribution of relaxation times is the phenomenon of "co-operative molecular motion" caused by the "associated" state of molecules. (Co-operative motion [12] is a phenomenon in which the energy needed to carry out an elementary process depends upon the state of the whole system.) They also found that the distribution of shear relaxation times was narrower than that of the longitudinal relaxation times, which implies that the distribution of volume relaxation should be broader than both the shear and the longitudinal. If this holds true for the glassy state, then one should wait until the volume (or structural relaxation) relaxation process is completed before taking high viscosity data, creep and stress relaxation, because the average volume relaxation time would be longer than the average shear relaxation time [9].

2.2. Frozen-in structure of the glassy state – the matter of the non-equilibrium thermodynamic state

As mentioned before, the solid-like glassy state is distinguished from the super-cooled liquid-like state by the fact that an internal equilibrium is not established. Therefore, the frozen-in structural state or the physical properties of the glass can be explained by a set of internal thermodynamic ordering parameters, $\{\xi_i\}$, i.e. $P = f(T, P, \{\xi_i\})$. The ordering parameters, $\{\xi_i\}$, have been frozen-in at some particular values depending on the thermal and mechanical history of the glass [13, 14]. Fig. 1 will help to distinguish the glassy state from other states of matter. The major difference between a highly viscous liquid and a glass is that a highly viscous liquid reaches its thermal equilibrium state on a time scale which is very short compared with the experimental observation time of the physical property measurement. The glassy state, on the other hand, has its internal structural state frozen-in at a particular thermal and mechanical history before it reaches thermal equilibrium.

Co-operative molecular motion or a distribution of relaxation times is exhibited both in the high viscous liquid and the solid-like glass [8, 9];



Highly viscous liquid state

Equilibrium thermodynamic state

(1) Has a distribution relaxation function due to co-operative molecular motion.

(2) The physical properties do not depend on thermal and mechanical history.

The physical property $P(T, P)$

Glassy state (solid-like)

Non-equilibrium thermodynamic state

(1) Has a distribution relaxation function due to co-operative molecular motion.

(2) The physical properties depend on thermal and mechanical history due to structural state frozen-in.

The physical property: $P(T, P \mid T_f, P_f, \{\xi_i\})$

Crystalline state

Equilibrium thermodynamic state

The physical properties are well defined by external thermodynamic variables of temperature and pressure.

The physical property $P(T, P)$

Figure 1 A comparison of the glassy state and other states.

therefore, one can conclude that a spectrum of relaxation times alone cannot completely account for the "memory effect" or "frozen-in structure" of the glassy state. For example, the viscosity of the glycerol at 12° C is only 24.6 P and its structural relaxation depends only upon temperature, not on thermal history. There is no frozen-in structure or memory effect for this liquid state of glycerol. Yet, glycerol at 12° C has a Davidson–Cole distribution in the dielectric relaxation measurement [15].

Simon [16] and Prigogine and Defay [12] both concluded that the relaxation process during stabilization of glass below its transition temperature, T_g, is a structural change towards a configuration in which only reduced rotational motions are possible. This, then, has an influence on the entropy. This fact is also demonstrated by Hsich [13, 14] in the study of the structural relaxation. The configurational (structural) part of the activation energy in glass has been frozen-in during the relaxation process. This explains why glass which is annealed at low temperature has a more significant contribution from the configurational art of the activation energy. In his non-linear structural relaxation model, Hsich has pointed out that two internal thermodynamic ordering parameters are needed for describing the structural relaxation as well as characterizing the structural state of the glass. Therefore, Toole's fictive temperature, T_f, along with the configurational part of activation energy, H_s, have been used as the two internal thermodynamic ordering parameters.

In the non-linear structural relaxation model, the physical property of the glass has been written as [13, 14]

$$\frac{P(T, t)-P_\infty}{P_0-P_\infty} = \psi_s(t) = \exp\left[-\left(\sum_i \frac{t_i - t_{i-1}}{\tau(T, t)}\right)^\beta\right] \tag{1}$$

$$\tau(T, t) = \tau_0 \exp\left(\frac{H_T}{RT} + \frac{H_S}{RT_f}\right) = \tau_0 \exp\left[\frac{(1-\xi)H}{RT} + \frac{\xi H}{RT_f}\right], \tag{2}$$

where P_0 and P_∞ are the initial and equilibrium physical properties of the frozen-in structure of the glass, R is the gas constant, τ_0 and β are the constants of the relaxational function; for a single relaxational function, $\beta = 1$. Therefore, $\beta = 1$ in the high-temperature melting-fining region. β decreases as the temperature is decreased, until the temperature has dropped well into the glass stabilization region, when β attains a constant value of about 0.4.

Fortunately, in the glass stabilization region, an Arrhenius behaviour (H = constant) is found, along with a distribution relaxation function which has the same shape (β = constant) regardless of the change of temperature. These behaviours allow us to simplify the study of structural relaxation and the prediction of the physical and mechanical properties of the glass. It should be noted that the internal thermodynamic state (or ordering parameters) can be frozen-in only if the relaxation process at that state is slower than the cooling rate. In general, when the temperature of glass is higher than the temperature of the stabilization region, the relaxation time is too fast to cause the glass to be frozen-in in that particular internal state. The thermal and mechanical history is taken into account only when the relaxation time of the glassy state is long enough to allow the structure to be frozen-in.

Other than the index of refraction, another good example of the consequences of the unique thermal-mechanical dependence of glass properties has recently been reported by Prod'homme [16]. He has shown that the viscosity of glass depends on its thermal history. For example, tempered samples which were rapidly cooled from the softening temperature had a viscosity lower than annealed samples which were stabilized by slow cooling in the temperature range below T_g. When the temperature was below 470° C, the viscosity of the tempered samples remained lower than the annealed samples, even when the tempered samples were heat-treated for 100h. This implies that the relaxation time of this soda-lime–silica glass is longer than 100h when the temperature is below 470° C. However, the viscosities of these two types of samples were always the same when the temperature was higher than 540° C. When the temperature was higher than 540° C, the relaxation time was very small. Therefore, the two types of samples reached the thermal equilibrium state before the data were taken.

2.3. The intrinsic non-linear behaviour of creep and stress relaxation

When glass is subjected to a mechanical or thermal stress, the stress–strain response can be written as

$$e(T, t) = \left[J_\infty + \frac{t}{\eta_0} + \psi(T, t\,|\,T_f, \xi)\right]\sigma, \quad (3)$$

where $J_\infty\sigma$ is the instantaneous strain due to glass compliance J_∞, η_0 is the Newtonian (steady state) viscosity, and $\psi(T, t|t_f, \xi)$ is the retardation function. As one can see from Fig. 2, the inverse of the slope of the strain response gives the dynamic (or non-equilibrium) viscosity if the creep and the structural relaxation processes are not complete. Thus the viscosity of the tempered samples of Prod'homme [16] was lower than the annealed samples, because the structural relaxation process of the tempered samples was not complete before the data were taken.

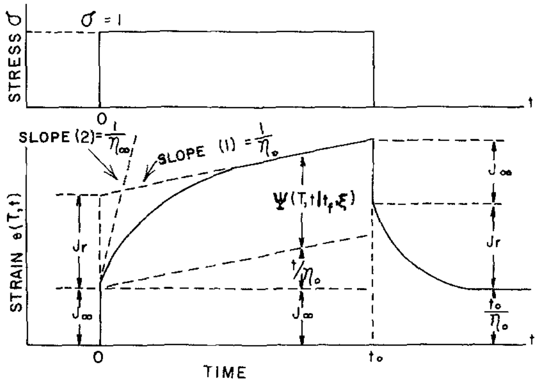


Figure 2 Stress–strain response of glass.

DeBast and Gilard [17] also studied the creep and stress relaxation of soda-lime–silica glass. They found that the unstabilized glass exhibiting a non-linear behaviour but the stabilized glass exhibiting a linear behaviour in which the Boltzmann superposition principle can be applied. Here the stabilized glass means that the glass is isothermally heat-treated until the structural relaxation process [13, 14] is almost complete. The stress relaxations for the stabilized and the unstabilized glasses are shown in Fig. 3. As one can see from Fig. 3, the unstabilized glass not only exhibits a stress relaxation, but also shows a structural relaxation which is prevailing from the high fictive temperature

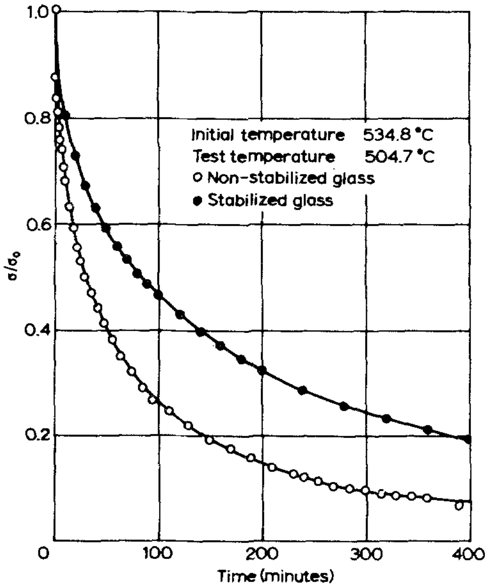


Figure 3 Comparison of relaxation curves for stabilized and unstabilized glasses (after DeBast and Gilard [17]).

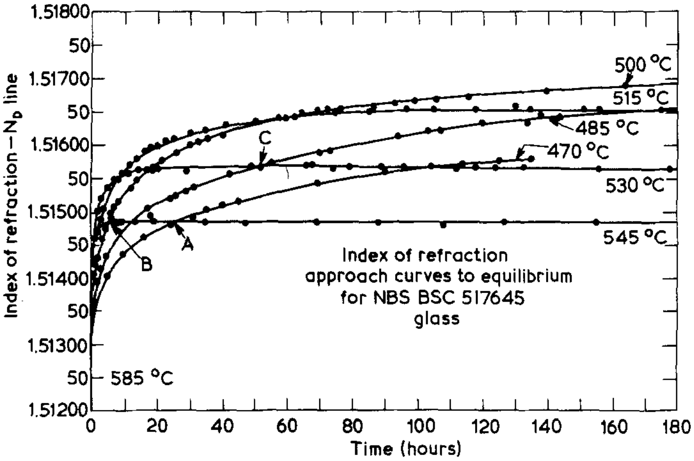


Figure 4 Index of diffraction approach curves to equilibrium for BSC glass (after Spinner and Napolitano [19]).

toward the low fictive temperature glassy state during the experiment. Therefore, in the study of creep and stress relaxation of the glassy state, one can separate the retardation and the relaxation functions into two parts, a linear and a non-linear (or structural relaxation). For a constant stress or strain, the stress–strain response can be rewritten as [18]:

(a) for constant stress:

$$e(T, t) = \left[J_\infty + \frac{t}{\eta_0} + \psi_l(T, t) + \psi_s(T, t|T_f, \xi)\right]\sigma \tag{3A}$$

or
$$\psi(T, t|T_f, \xi) = \psi_l(T, t) + \psi_s(T, t|T_f, \xi); \tag{3A}$$

(b) for constant strain:

$$\sigma(T, t) = [E_0 + \phi_l(T, t) + \phi_s(T, t|T_f, \xi)]\,e \tag{4}$$

or
$$\phi(T, t|T_f, \xi) = \phi_l(T, t) + \phi_s(T, t|T_f, \xi), \tag{4}$$

where E_0 is the static elastic modulus, ψ and ϕ are the retardation and relaxation functions respectively, and the subscripts l and s denote the linear and non-linear (or structural) part of function. The function $\psi_s(T, t|T_f, \xi)$ is the same function as in Equation 1 which is used by Hsich [13, 14] to explain the structural relaxation of the glassy state.

One of the best experimental methods for studying the structural relaxation of the glassy state was developed by Spinner and Napolitano [19]. In their study, glass was annealed with varied temperatures and times, before being quenched from the furnace temperature to room temperature. Therefore, the internal structure and physical properties of the glass were frozen-in at some particular state. The result of refractive index measurement was shown in Fig. 4. Since there was only thermal stress applied to the glass in Spinner and Napolitano's experimental method, there was no contribution from viscous flow in the stress–strain response. The contribution from the glass compliance, J_∞, is recovered immediately, once the thermal stress is released (quenched from the furnace temperature to room temperature). As a result, the data in Fig. 4 were completely caused by the phenomenon of structural relaxation of the glass or the retardation function, $\psi_s(T, t|T_f, \xi)$. That was the aspect of the structural relaxation of the glassy state by which Hsich [14] explained these data in his non-linear model. Spinner and Napolitano [19] demonstrated that glasses with different thermal and mechanical histories would exhibit different structural relaxation processes even though the same stress (mechanical or thermal) was applied to them. For example, at point C on Fig. 4 two glasses with different thermal histories had the same value of the refractive index (or fictive temperature); one was annealed at 485° C, the other was annealed at 530° C. However, when both glasses were continuously annealed at the temperature 530° C, the glass whose thermal history included being annealed at 485° C would exhibit a structural relaxation curve as shown in Fig. 5. This clearly demonstrated that one internal thermodynamic ordering parameter, T_f, alone could not characterize the structural state of glass [13, 14].

Davies and Jones [2] showed that a sudden isobaric change in temperature is more effective on the structural change of glass than a sudden pressure jump. The thermodynamic equivalence

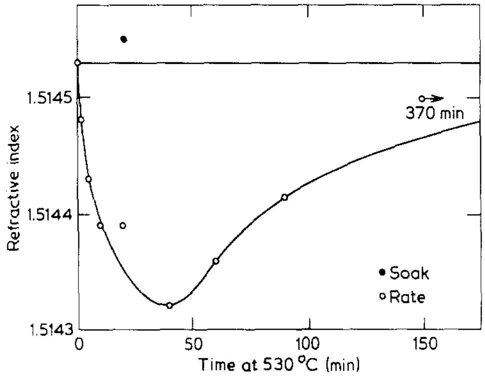


Figure 5 The cross-over curve of index of refraction (after Spinner and Napolitano [19]).

of the temperature jump and pressure jump can be written as

$$\delta P = -\left(\frac{\Delta C_\mathrm{p}}{T_\mathrm{g} V \Delta\alpha}\right)\delta T$$

where V is the mole volume. In Davies and Jones' calculation, $\delta P = 300\,\delta T$ atm for a reasonable glassy system. Therefore, they have concluded that one must apply a pressure of 3000 atm to have the same effect on the structure of glass as a sudden isobaric change in temperature of 10° C. In B_2O_3 glass, using data from Table I of Corsaro's paper [20], $\Delta C_\mathrm{p} = 0.14\,\mathrm{cal\,g^{-1}\,deg^{-1}}$, $T_\mathrm{g} = 548\,\mathrm{K}$, $V = 0.55\,\mathrm{cm^3\,g^{-1}}$, and $\Delta\alpha = 3.5 \times 10^{-4}\,\mathrm{deg^{-1}}$. Then,

$$\delta P = \left|\frac{\Delta C_\mathrm{p}}{T_\mathrm{g} V \Delta\alpha}\right| = 55\,\delta T\,\mathrm{atm} = 310\,\delta T\,\mathrm{psi}^*.$$

A temperature jump of 10° C would then be equivalent thermodynamically to a pressure jump of 8100 psi. The maximum pressure applied by Corsaro was only 400 psi. This pressure jump is equivalent to a temperature jump of only 5° C. In Corsaro's volume relaxation experiment, the temperature is about 500 K. Therefore this 5 K temperature jump is only 1% of the experimental temperature. As one can see from Equations 1 and 2, the difference between the actual temperature T, and the fictive temperature, T_f, is too small to detect the "non-linear" behaviour of volume relaxation in Corsaro's experiment. Consequently, he obtained linear behaviour in his volume relaxation study. However, Boesch *et al.* [21] have followed the same experimental method as Spinner and Napolitano [19] in B_2O_3 glass, and a "non-linear" behaviour [13] has been observed in their experimental result. The non-linear behaviour of the volume relaxation is also observed in glassy polymers. For example, when the temperature jump exceeded 1.8° C or the pressure jump exceeded 40 atm, non-linearity of the volume relaxation of atactic polystyrene has been observed [22, 24].

3. Role of rheology in material process

3.1. Structural relaxation of container glass

The experimental method of Spinner and Napolitano [19] was used for studying the structural (or volume) relaxation of container glass. The sample was prepared from the remelting of a commercially prepared container glass at 2650° F for 4 h. The composition of the glass was examined by X-ray fluorescence. The result is shown as follows:

Oxide	SiO_2	Na_2O	CaO	K_2O	Al_2O_3
%	71.8	13.5	10.2	0.22	1.25
Oxide	BaO	MgO	Fe_2O_3	TiO_2	SO_3
%	0.18	2.5	0.041	0.014	0.26

The results of the structural relaxation experiment are shown in Figs. 6 to 8. Fig. 6 is the equilibrium temperature–refractive index curve. Figs. 7 and 8 are the equilibrium approach curves starting from high and low fictive temperatures, respectively. The results of theoretical prediction from the non-linear structural relaxation model of Equations 1 and 2 are plotted in the smooth curves shown in Figs. 7 and 8. The activation energy, H, is the same activation energy of the viscous flow from the viscosity measurement. At a low temperature Arrhenius region, $H = 165\,\mathrm{K\,cal\,mol^{-1}}$. The other constants used in Equations 1 and 2 are: $\tau_0 = 9.54 \times 10^{-39}$ sec, $\beta = 0.45$. The second ordering parameter, ξ, in this study is shown in Fig. 9. It increased as annealing temperature decreased for the approach curves A. This is because at a low temperature, the more rotational molecular motion is reduced, the more activation energy has been frozen into the structural part of the activation energy. However, for the approach curves B, ξ has the same value for the different annealing temperature, since the frozen-in structure of glass is dominated by a low temperature thermal history as been explained before [13, 14].

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* $10^3\,\mathrm{psi} = 6.89\,\mathrm{N\,mm^{-2}}$.

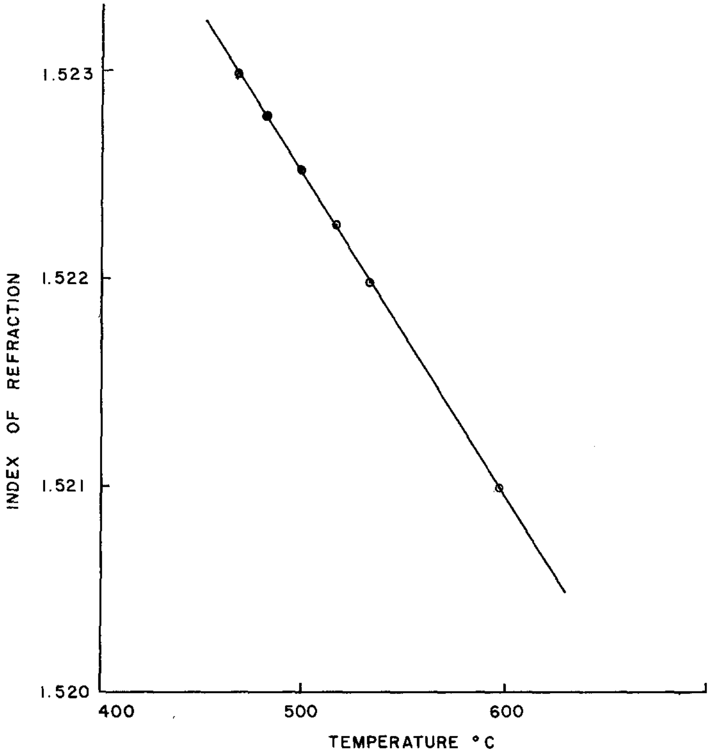

Figure 6 Equilibrium temperature–refractive index curve.

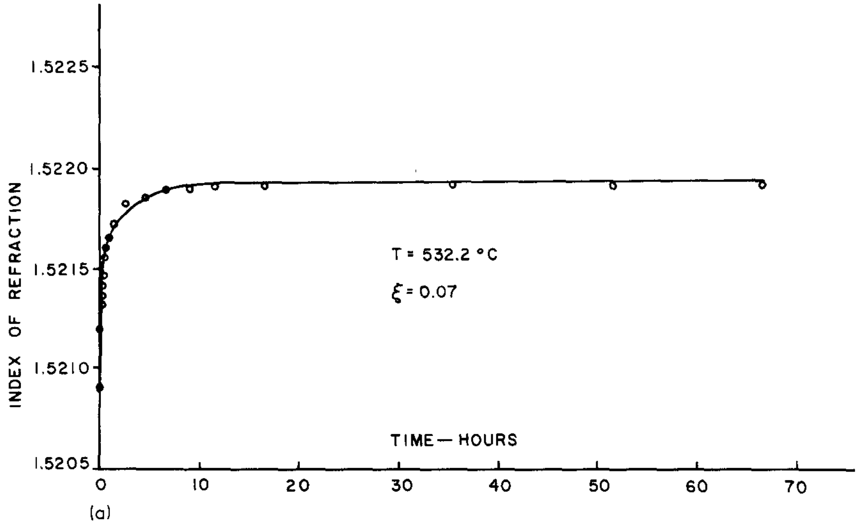

Figure 7 Approach curves A, starting from equilibrium temperature at 497.7° C.

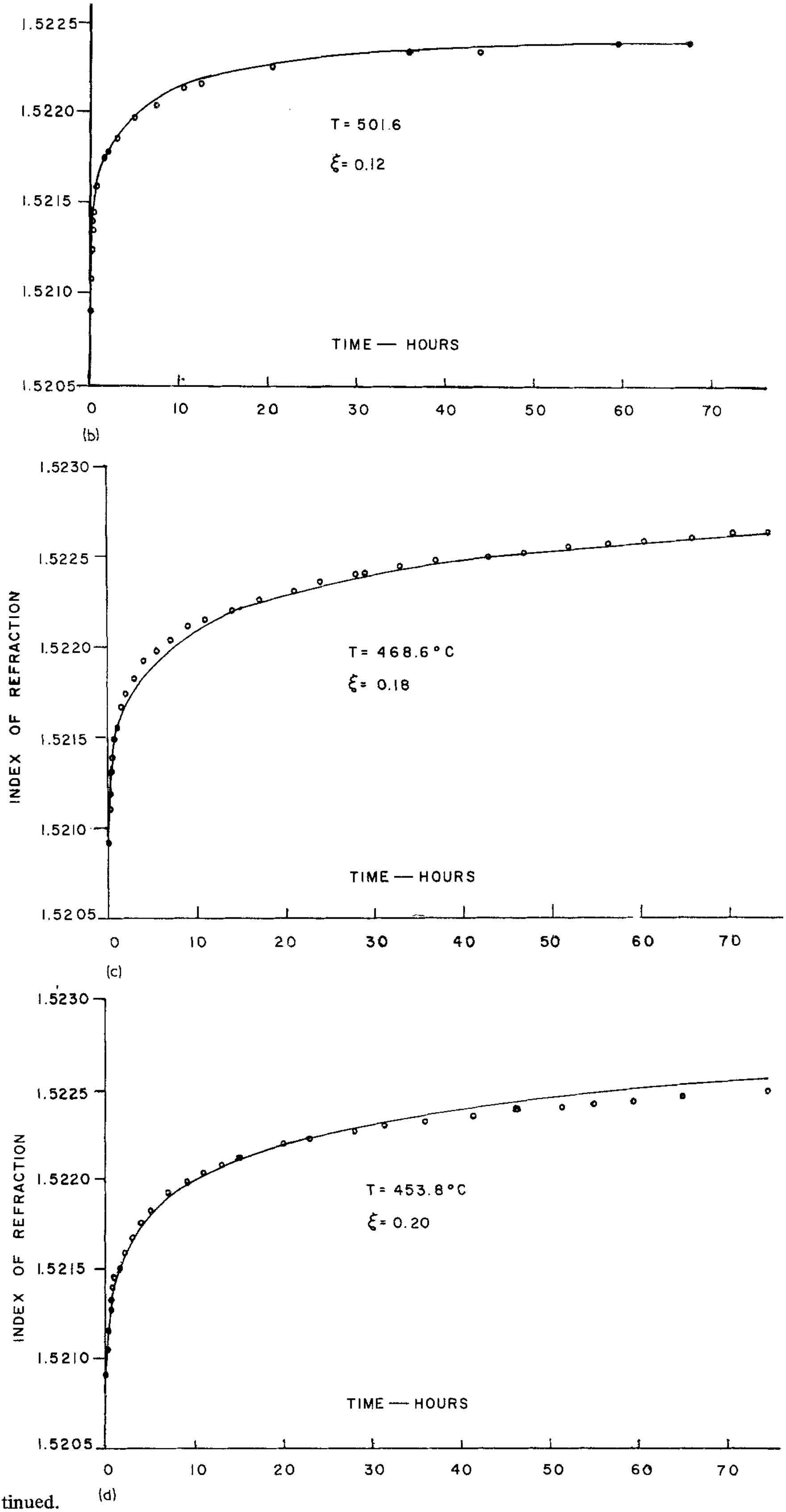

Figure 7 Continued.

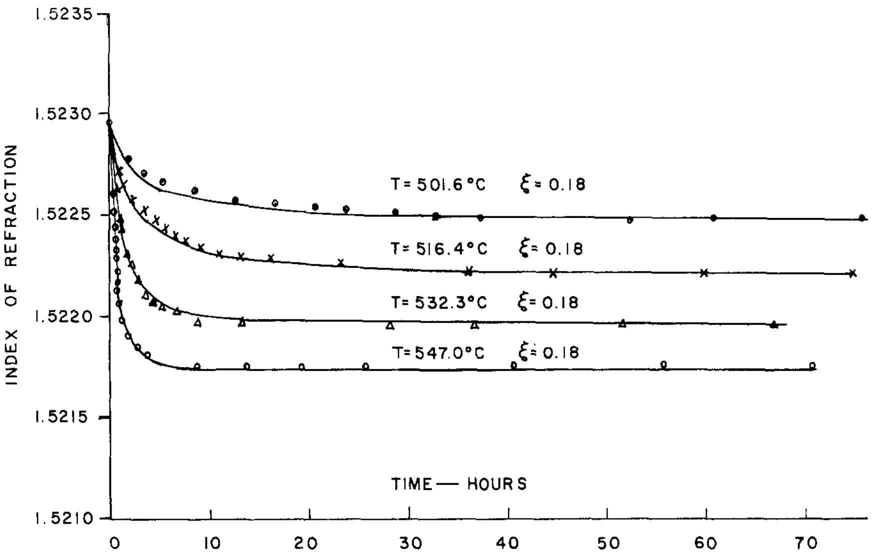

Figure 8 Approach curves B, starting from equilibrium temperature at 468.6° C.

3.2. Thermal history and homogeneity of container glass during forming

As is already known, the physical properties, such as refractive index, of container glass depend on thermal history. If two bottle glasses have the same composition and thermal history, their refractive index (or fictive temperature) should be the same. Therefore, glasses from four different stages of the manufacturing process, namely gob (glass melt delivered in blank mould from feeder), parison (the pre-formed bottle after first blow in the blow-and-blow process), hot end set-out (bottle before annealed), and after-lehr bottle (bottle after annealed) were chosen for measurement of their refractive indices after they were air-quenched to room temperature. Each bottle glass was cut into 10 samples of 1 cm × 1 cm, and the refractive index of each sample was measured at the four corners. The result of the measurements for 40 samples (160 points) at each stage is shown in Fig. 10. The annealed samples (from the cold end) exhibited a smaller thermal gradient and lower fictive temperature than the samples from the other stages. The fictive temperatures of the gob samples were a little lower than the samples from the parison or hot end. This result is not surprising because the glass temperatures at these three stages were higher than 620° C; therefore, the fictive

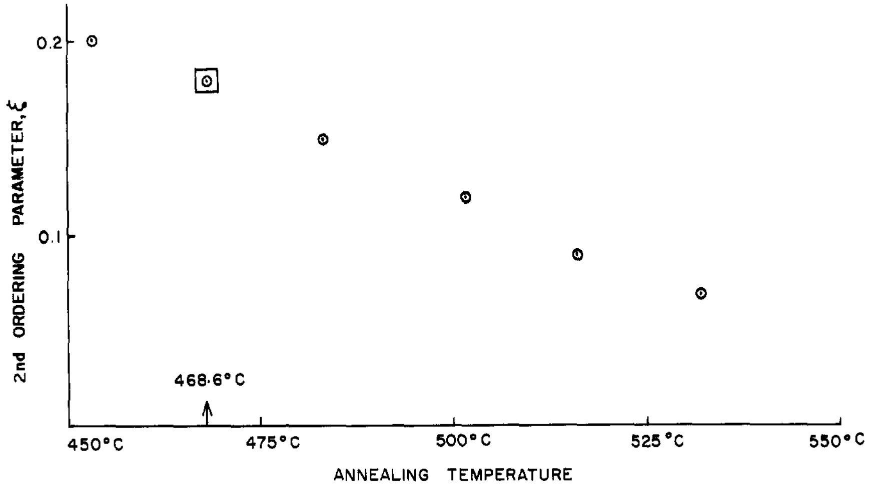

Figure 9 Second ordering parameter versus annealing temperature.

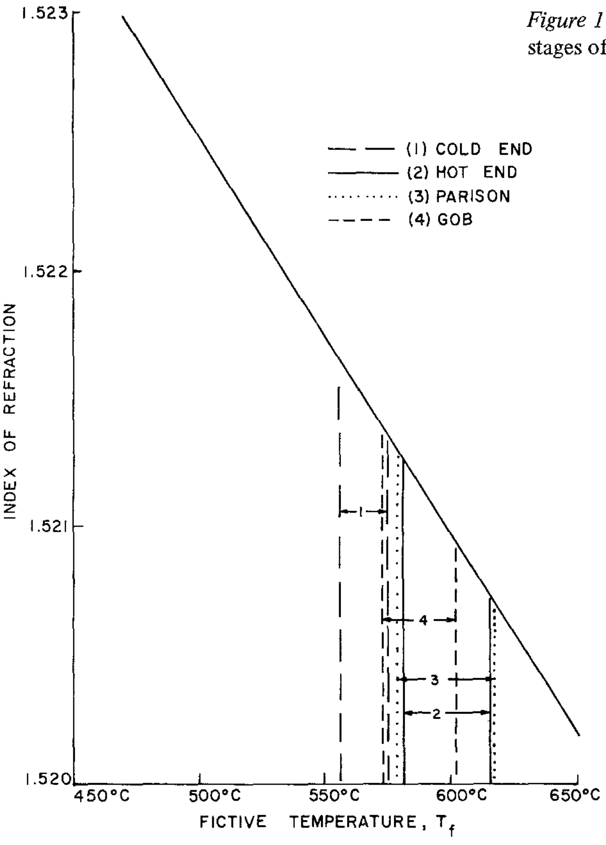

Figure 10 The fictive temperature of the glass at the various stages of glass formation.

temperature of the gob was dependent on how it was quenched to room temperature. As may be seen from Fig. 10, the fictive temperatures of all the samples were below 620° C. At 620° C, the relaxation time of this container glass was about 1 sec. [$\tau = \tau_0 \exp(H/RT)$] and, the relaxation time was too short for the glass structure to be frozen-in at a temperature higher than 620° C.

As has been mentioned, the physical properties and structural state of glass depend on its thermal and mechanical history. Since the thermal history of container glass during the forming process has been discussed above, we also would like to know whether the mechanical history or residual mechanical stress from operation at various stages has given any contribution to the internal state of the glass structure during the forming process. Usually during forming, all the mechanical stresses are applied to the glass at a viscosity less than 10^8 P or at a temperature higher than 720° C. The structural relaxation time is about 10^{-2} sec (i.e. $\tau \approx 10^{-2}$ sec) at 720° C. The average shear relaxation time, $\bar{\tau}_s$, is estimated to be about 10^{-2} sec for a viscosity of 10^8 P (using a reasonable value of instantaneous shear modulus, i.e. $G_\infty \approx 10^{10}$ dyn cm^{-2}, then $\bar{\tau}_s = \eta_0/G_\infty \approx 10^{-2}$ sec). When the relaxation time is less than 10^{-2} sec, the glass melt reaches its thermal equilibrium state before its structure is frozen-in; therefore, any thermal or mechanical history at this temperature will be wiped out by the relaxation process of molecules.

As shown in Fig. 10, the distribution of refractive indices or fictive temperatures of container glasses is due to the difference in the thermal histories and compositions of the glasses. The data show that annealed glasses are more homogeneous because the distribution and average value of the fictive temperatures are narrow and long, respectively, due to having a better thermal gradient. If all the glasses were annealed to have the same thermal history, then any differences of the refractive indices would be caused only by the composition gradient of the container glasses. Therefore, one can determine the homogeniety, thermal history and general quality of the glass by studying the refractive index.

3.3. Role of rheology in the mechanisms of thermal stress and fracture mechanics

We have mentioned that the glassy state always exhibits a process of structural relaxation because it is in a non-equilibrium thermodynamic state. When the time available for stress relaxation is small, the relaxation process becomes very important in determining thermal stress and fracture phenomena in glass. For example, Narayanaswamy and Gardon [25] have demonstrated the importance of the relaxation process in the calculation of residual thermal stresses, when glass is rapidly quenched from a temperature above its strain point. During the initial stage of quenching, the thermal contraction of the surface is greater than that of the midplane. In an elastic solid these stresses would actually appear, only to be cancelled by stresses of opposite sign during the later stage of quenching, in which the cooling rate of the midplane exceeds that of the surface. Because glass is not a true elastic material; it is in a relaxation state. At high temperature, the rate of relaxation is higher; therefore, stresses induced in glass at high temperatures have relaxed. Thus, most of the stresses induced initially, while the glass is still hot, relax, whereas most of the stresses induced in the later stage of cooling, when the glass is colder, remain. The result is that tempering leaves the surfaces of a glass plate in a state of permanent compression balanced by interior tension.

The relaxation process also affects the mechanisms of fracture. When a mechanical stress is applied to a glass or polymer melt, there is a competition between the processes of fracture and relaxation in molecules. If the relaxation effect predominates, the fracture process ceases to develop and the fractured molecules start to reheal through the relaxation process [26]. That is why the glass melt can sustain a fast cooling rate at a high temperature (say, $\eta_0 < 10^6$ P) without causing thermal shock; at this temperature range, the relaxation time is very small, therefore, before the structure of the glass is frozen-in, the relaxation process is complete and the fractured molecules are also rehealed. However, at a low temperature range, once the glass has been fractured by the thermal stress from too rapid a cooling rate, the structure of the glass might be frozen-in before the fractured molecules have been rehealed through the relaxation process, and consequently it causes a thermal shock in the glass.

During heat transfer in glass forming, there is a temperature distribution, $T(\chi, t)$, in the glass once the glass melt contacts with the blank or mould. Thus, there is a thermal stress built-up instantaneously in the glass due to the temperature distribution. If the glass is in the Y–Z plane with a thickness of $2C$ in the χ direction, then the equation of the instantaneous stress in the glass can be written as [27]

$$\sigma_y(t) = \sigma_z(t) = -\frac{\alpha TE}{1-\nu} + \frac{1}{2C(1-\nu)} \times \int_{-c}^{c} \alpha TE \, \mathrm{d}\chi + \frac{3\chi}{2C^3(1-\nu)} \int_{-c}^{c} \alpha TE\chi \, \mathrm{d}\chi. \quad (6)$$

However, the physical properties, α, E and ν (Poisson's ratio $0.5 \geqslant \nu \geqslant 0.22$) of the glass are a function of temperature and time, therefore they are also a function of χ. The dynamic value of the Young's modulus, $E(T, t)$, at a high temperature might be a couple of orders smaller than the value of Young's modulus of glass, E_∞, at the room temperature. Thus one must be very careful in using Equation 6 for the estimation of the instantaneous thermal stress in the glass or polymer melt. Gardon and Narayanaswamy [28] have modified Lee *et al.*'s [29] model for the calculation of residual thermal stress in visoelastic materials. The generalized equations for a glass plate are:

$$\sigma(\chi, t) = \frac{E_\infty}{1-\nu} \int_0^t \phi(t-t') \frac{\partial(e-e_{\mathrm{th}})}{\partial t'} \, \mathrm{d}t' \quad (7)$$

$$e_{\mathrm{th}}(\chi, t) = \alpha_{\mathrm{liq}}[T(\chi, t) - T_0] - (\alpha_{\mathrm{liq}} - \alpha_{\mathrm{g}}) \times \int_0^t \Psi(t-t') \frac{\partial T(\chi, t')}{\partial t'} \, \mathrm{d}t' \quad (8)$$

$$\int_0^l \sigma(\chi, t) \, \mathrm{d}\chi = 0, \quad (9)$$

where $\phi(t)$ is the relaxation function for Young's modulus, $\Psi(t)$ is the relaxation function due to the volume change in the structural relaxation process or the same function as used in Equation 1. e_{th} and e are the thermal and total strains respectively. T_0 is the initial temperature.

The importance of the rheology in determining thermal stress and fracture mechanics has been discussed; therefore, one should expect that these phenomena would also affect the fabrication of composite materials. Previously the mechanisms of toughening and weakening of composite materials have been considered only from the viewpoint of elastic behaviour [30–38]. For example Lange [31] has pointed out that there are three factors controlling the strength of materials. These are elasticity (or modulus), fracture energy, and cracks or pseudovoids formed during fabrication. The second phase in particulate composite material can toughen the materials by increasing the elasticity and fracture energy. Although large particle size dispersions result in the greatest increase of fracture energy, it might also cause large crack size. The design of ceramic microstructures of optimum mechanical integrity is based on high elasticity and fracture energy but small cracks in the composite materials. The expression for a critical sphere size below which crack extension will not occur is

$$D_c = 30 \frac{K_c^2}{\sigma_{\max}^2},$$

where K_c is the critical stress intensity factor, $\sigma_{\max}$ is the triaxial stress within the sphere given by

$$\sigma_{\max} = \frac{(\alpha_I - \alpha_m)\Delta T}{K} \tag{11}$$

$$K = \frac{1+\nu_m}{2E_m} + \frac{(1-2\nu_I)}{E_I}. \tag{12}$$

α, E, ν are the thermal expansion coefficient, modulus, and Poisson's ratio respectively. I and m denote the inclusion and matrix phases.

As may be seen from Equation 10, the mechanisms of toughening and weakening of composite materials are only dependent on the absolute value of the difference of thermal expansion coefficients between inclusion and matrix, i.e. $|\alpha_I - \alpha_m|$. However, it is always found when the thermal expansion coefficient of the inclusion is lower than the thermal expansion coefficient of the glass matrix, that the reduction of the strength is more pronounced [39]. In view of the foregoing discussion regarding the rheological behaviour of glass and polymers we should not be surprised by this finding, as during fabrication of the composite materials, not only are relaxation processes exhibited in the glass or polymer matrix, but the change of thermal expansion coefficient with the change of temperature of the matrix is much larger than the inclusion ($\alpha_{m,liq} > 2\alpha_{m,gl}$). One should expect that the stress concentration is larger in the case of $\alpha_m > \alpha_I$ than $\alpha_m < \alpha_I$, where α_m and α_I are the values measured at room temperature. Thus, it is important to consider the rheological behaviour in the design of composite materials.

4. Conclusions

Since the glassy state is considered to be one of the least understood states of matter, the rheological behaviour of the glassy state was reviewed and discussed for the purpose of shedding some light on the study of the dynamic mechanical and physical properties of glass or glassy polymer. The importance of the rheological behaviour in the thermal stress and fracture mechanics is also mentioned; consequently this will allow us to improve the material design.

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Received 24 May and accepted 28 August 1979.