CURRENT PROBLEMS IN RESEARCH

Structural and Rheological Properties of Glass

Both thermal and technological factors are believed to influence the "past history" of glass

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A large variety of glasses are made today by using special batch mixtures and by varying the manufacturing process. The major classifications include soda-lime glass, borosilicate glass, lead glass, aluminosilicate glass, 96-percent silica glass, and fused silica. In addition, various specialty glasses are made, such as opal glass, radiation-absorbing glass, photosensitive glass, optical glass, and metal-coated glass.

Development of glass ceramics has largely depended on a precise understanding of the way in which crystals can be made to nucleate and grow in glass. In heterogeneous nucleation, such as occurs in the making of glass ceramics, the nucleating agent must possess several essential properties: (i) it should be readily soluble in the glass at high temperatures and insoluble at low temperatures; (ii) the interfacial tension between the foreign particle and the phase to be nucleated must be low; and (iii) the crystal structure and interatomic distances of the foreign particle and the phase to be nucleated must be fairly similar.

One of the extraordinary properties of glass is its enormous and continuous increase in viscosity as it cools from the molten state; as a consequence, equilibrium states occurring at high temperatures are frozen in as the glass cools. It is the extremely slow nucleation rate that prevents glass from crystallizing. When special nucleating agents are used to crystallize glass, it is presumed that each particle of nucleating agent initiates the growth of a single crystal; the number of crystals formed is then the same as the number of particles of nucleating agent. Usually, between 10^9 and 10^{15} particles of nucleating agent are precipitated per cubic millimeter of glass. The crystals formed range in diameter from 10,000 down to 100 angstroms.

The actual strength of glass is far less than its intrinsic strength (3 million pounds per square inch) because of surface imperfections. The maximum working strength of annealed glass is 1000 pounds per square inch, and that of tempered glass is 2000 to 4000 pounds. For practical purposes, glass can be considered a perfectly elastic material. At room temperature, it is elastic up to the point of fracture.

When a liquid melt is cooled, there is a process of aggregation of like atoms or atomic groups, caused by the same forces as those which lead to the formation of a crystal lattice. The ordering process during glassy solidification terminates at an intermediate stage between ideal disorder of the components in the liquid melt and ideal order in the crystalline state. Cellular aggregation of like ions, which is the initial stage and preliminary condition of crystallization, takes place in definite regions. Owing to the rapid cooling of the melt, these regions harden in glassy form, while because of the considerable energy differences between the regions of honeycomb order and their surroundings, they acquire surface boundaries and form drops. The structure of the droplike regions has a higher degree of order than that of the surrounding glassy phase, and the composition of the droplike glass phase approximates the composition of stable crystalline compounds.

Recent work on glass structure seems to indicate that not only the crystallite but also the molecular structure of glasses is much more diverse and complex, and depends more sharply on the thermal history of the glass, than the phase diagram of a given system would suggest. Ordered structural formations in glass change with temperature, becoming increasingly distinct with progressive cooling and, conversely, more amorphous with increasing temperature. Curves for x-ray scattering become gradually more complicated as a liquid passes from the critical-temperature regions into the undercooled state and its structure progressively approximates that of polycrystals.

All the experimental data and theoretical conjectures presently available indicate that the concept of the "history" of a glass should be extended beyond merely thermal effects; both thermal and technological factors are believed to influence the "past history" of the glass. When a glass is made, its structure and properties are influenced by such factors as batch composition, the melting schedule, and the temperature and duration of "fining."

Mechanical and Rheological Characteristics

It has been found in recent studies that, above the vitrification temperatures, glass specimens in the unloaded state undergo spontaneous deformation (torsion). This seems to indicate that frozen, high-elastic stresses and deformations exist in the glass specimens. Regardless of their chemical composition, inorganic glasses have two kinds of mechanically reversible deformations (elastic and high-elastic) and, correspondingly, two kinds of stresses.

If a small load is applied to a specimen which has been annealed to the point where frozen stresses have totally disappeared, then, above the vitrification temperature, deformation of the same type that occurs in spontaneous torsion begins to develop, and it reaches its maximum value over a certain temperature range, indicated by the plateau on curve 2 in Fig. 1; above the flow temperature T_f, the material flows. The extent of the high-elasticity region and its position on the temperature scale depend on the type of glass and the magnitude of the stress.

High elastic properties are found in

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glasses differing both in chemical composition and in the method of forming. The deformation curves for some glasses have two plateaus, probably owing to the microheterogeneity of these glasses. The occurrence of the first plateau is probably associated with transition of the high-melting component (the silica framework) from the glassy to the high-elastic state, and the occurrence of the second, with transition of a low-melting component (such as sodium borate in borosilicate glass) into the viscofluid state (Fig. 2).

Below the flow temperature, the high elastic deformations are reversible. After removal of the load the specimens gradually return to their initial form. The slowness of the restoration is due to the considerable internal friction of the material. Tests carried out under different loads on specimens previously annealed to remove completely the frozen internal stresses show the existence of a yield point at shear stresses of the order of 0.5 kilogram per square centimeter. The plateaus on the curves disappear at higher loads. Therefore, glasses above the vitrification temperature behave like viscous materials under high stresses and like high-elastic materials under low stresses. The low yield point is probably the consequence of the low strength of the spatial structure in inorganic glasses.

The rheological curve for glass resembles the curves characteristic of thixotropic systems. At stresses greater than 1 to 2 kilograms per square centimeter, glass behaves like a Newtonian liquid in the anomalous range (Fig. 3). Viscosity is usually determined at even higher stresses. This explains why high elasticity has not been detected in the anomalous range, and why inorganic glasses above the vitrification temperature were regarded as highly viscous Newtonian liquids.

Breakdown of glass structure under loads in excess of the yield value is detected from the decrease in the elasticity modulus in repeated tests on the same specimen. If such a specimen is then kept for a long time, the former structure is restored and the elasticity modulus increases.

The influence of thermal history on the structure of glass is manifested in the differences in behavior of rapidly cooled and of annealed specimens. Under the same experimental conditions high elastic deformation is much greater in chilled than in annealed specimens (Fig. 4). The explanation is that chilling freezes in a structure that occurred at

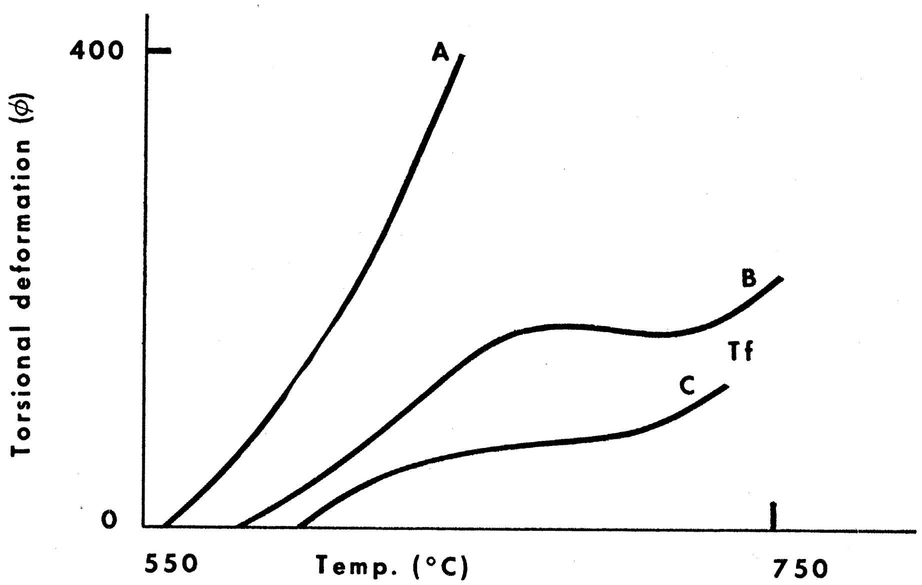


Fig. 1. Torsional deformation-temperature curves for specimens of rolled glass under various loads: (*A*) 93.4 g; (*B*) 13.2 g; (*C*) 11.7 g.

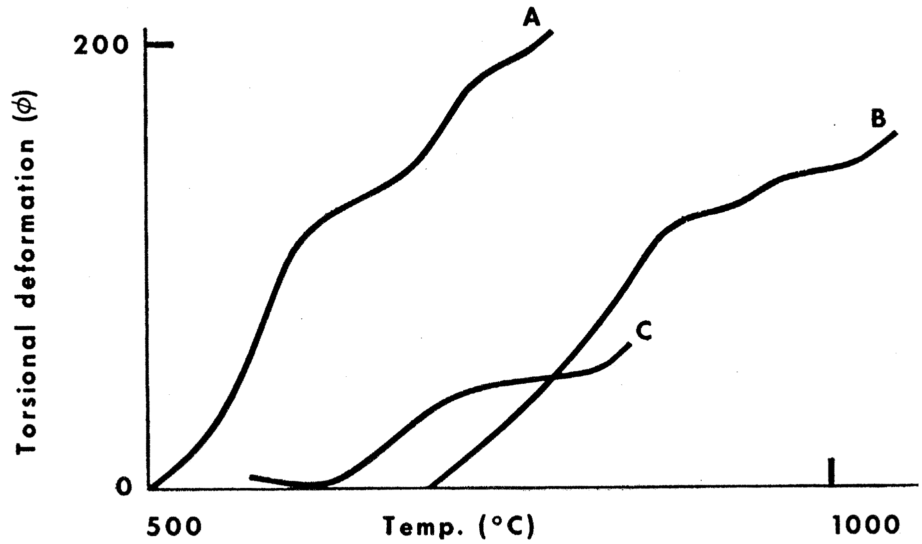


Fig. 2. Torsional deformation-temperature curves at constant torque for glasses of microheterogeneous structure. (*A*) Optical F-1 glass; (*B*) borosilicate glass; (*C*) high-zirconia T_s–18 glass.

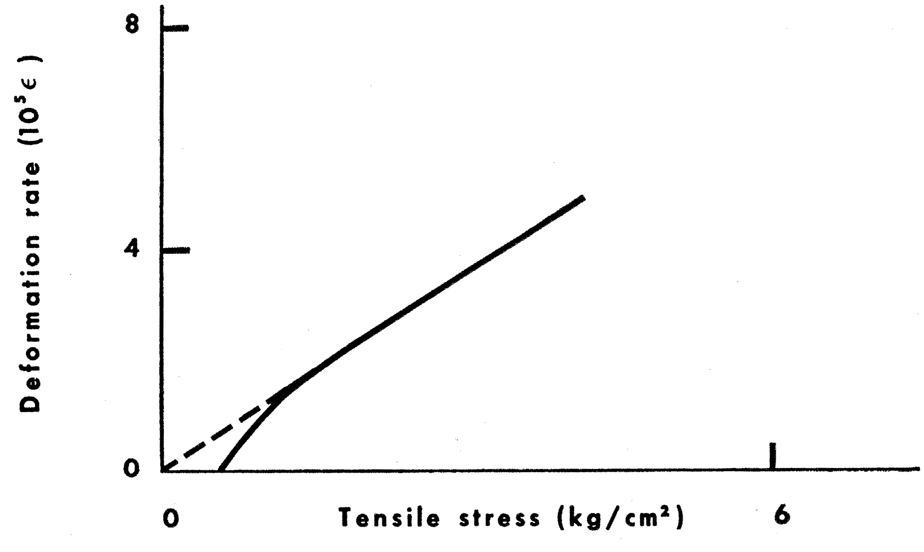


Fig. 3. Deformation rate plotted against tensile stress.

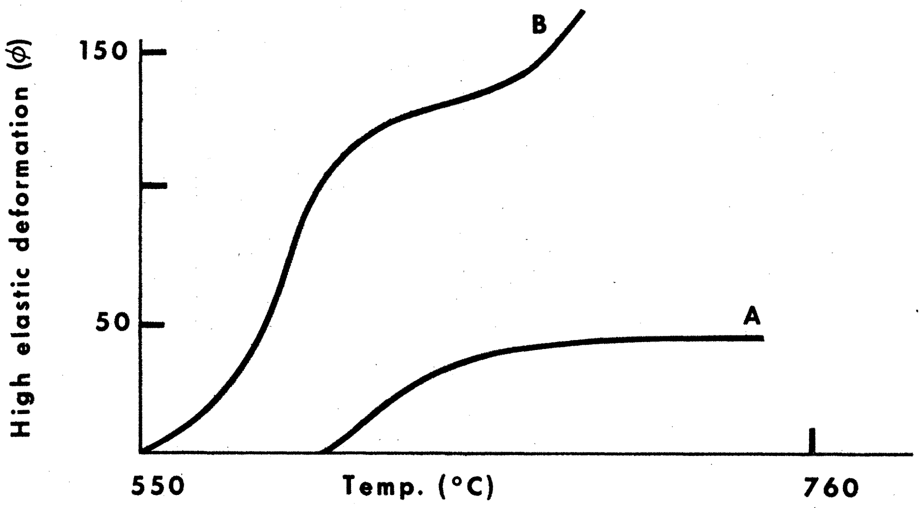


Fig. 4. Effect of heat treatment on high-elastic deformation of rolled glass. (*A*) Annealed specimen; (*B*) chilled specimen.

higher temperatures. Therefore, the spatial network is less dense in a chilled than in an annealed specimen, and the elasticity modulus is lower. The elasticity moduli, like the densities, of annealed and chilled glasses differ by a few percentage points, whereas the moduli of high elasticity differ severalfold; this indicates that high-elastic deformation is a structure-sensitive property of glass.

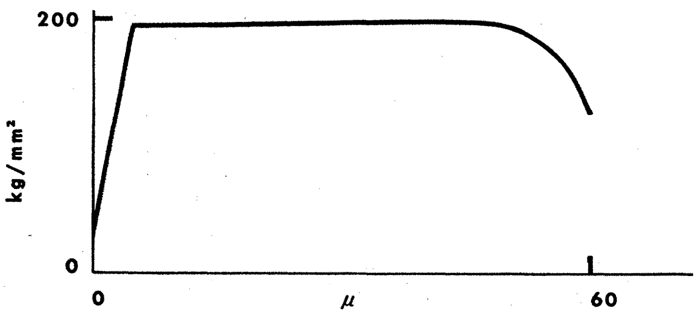
When glass is heated under static load, mechanical softening and structural softening take place simultaneously, and the anomalous range is shifted toward higher temperatures with increase in the heating rate. The observed behavior in the anomalous range, together with other known facts, leads to the conclusion that many inorganic glasses have chain structure. Such glasses are branched-network polymers of more complex and less regular structure than organic polymers. Their spatial structure is readily broken down under small loads and is partially restored after removal of the load.

The nature of the high strength of glass fibers is accounted for by two hypotheses: the statistical theory of the scale effect and the molecular orientation theory of reinforcement. From the statistical theory of the scale effect it follows that fiber diameter and fiber strength are inversely related, for where there is less volume or surface, there is less probability that the specimen contains dangerous defects which can cause failure. According to the other hypothesis, the greater strength of glass fibers as compared to bulk glass is due to molecular orientation resulting from drawing; as the result of orientation of stable bonds along the fiber axis, the defects become less dangerous, crack growth is retarded, and glass fibers therefore have greater strength than bulk glass. If the statistical theory fully accounted for the dependence of tensile strength on the diameter of glass fibers, the strenth would increase with decrease in diameter even after removal of the surface layer. However, this is not the case in practice. This means that the strength of the glass fibers depends mainly on some physical property other than changes in cross section as such. Such a factor—one which is not influenced by the surface etching of the glass fiber—is the magnitude of viscous deformation determined by the degree of drawing (Fig. 5).

The mechanism of strengthening in relation to viscous flow during drawing of glass fibers is still obscure. It is possible that strength increases because of decrease in the linear transverse dimensions of the defects as the result of irreversible viscous deformation. These dimensions decrease in proportion to $\alpha^{\frac{1}{2}}$, where α is the degree of drawing, and therefore the defects become less dangerous. It is also possible that drawing causes orientation of stable bonds along the fiber axis, and that the strength of the material in the direction of the fiber axis increases with the degree of drawing.

The important role of surface defects is confirmed by adsorption effects in the lowering of strength and elastic aftereffects in glass fibers. The strength of glass fibers, regardless of chemical composition, decreases in moist air, water, and solutions of surface-active substances. In an inactive medium elastic, aftereffects in glass fibers are very weak, but in the presence of a surface-active medium, a decrease in strength is accompanied by a considerable number of direct and reverse aftereffects (Fig. 6).

Figure 7 illustrates the dependence



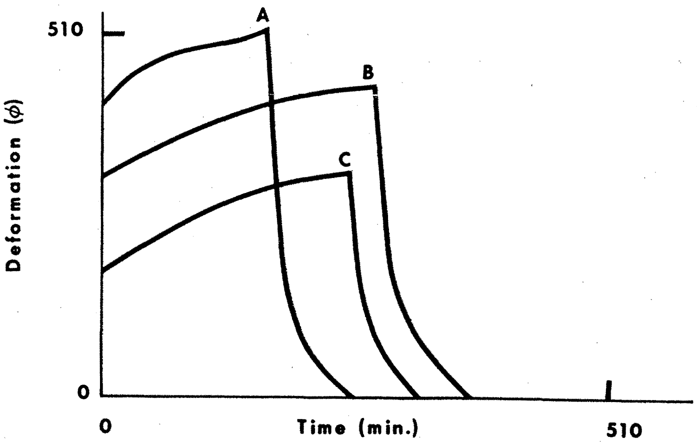
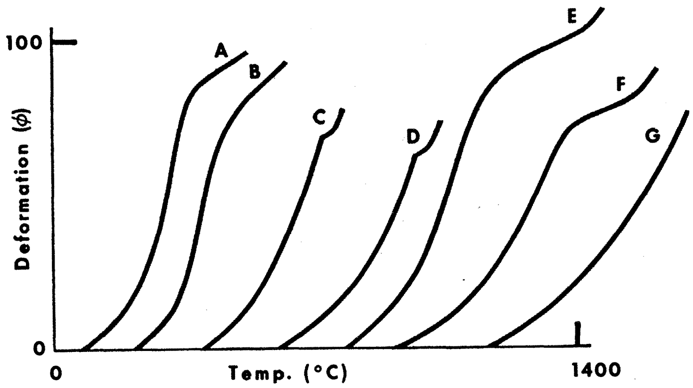


Fig. 5 (left). Effect of the thickness of the surface layer removed by etching on the strength of aluminochlorosilicate glass fibers (diameter, 63 μ). Fig. 6 (right). Deformation plotted against time. (*A*) Kerosene medium; (*B*) water medium; (*C*) potassium oleate solution.



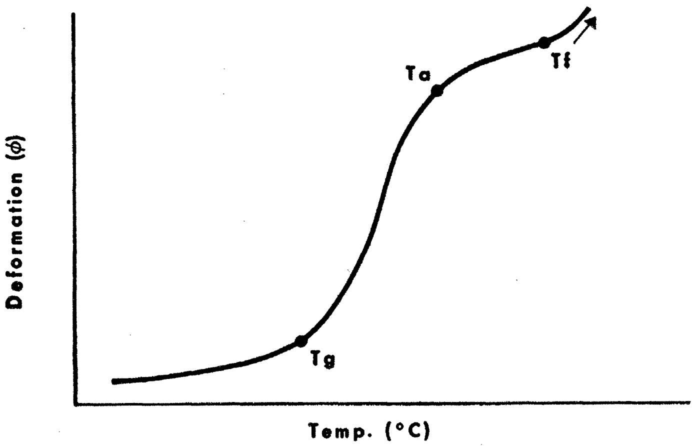


Fig. 7 (left). Deformation-temperature relationships for various glasses as follows: (*A*) TF—5; (*B*) TF–1; (*C*) window glass; (*D*) TK–10; (*E*) glaze; (*F*) glaze; (*G*) fused silica. Fig. 8 (right). Deformation plotted against temperature.

of the elastic properties of different glasses on temperature. The first appreciable increase of mobility in fused silica is observed at about 1100°C. Plastic deformation begins above this temperature. In view of the fact that x-ray structure data indicate that the structure of glass remains unchanged between 20° and 400°C and that the elastic properties of glass remain constant in this temperature range, it may be assumed that the structure of glass undergoes no appreciable changes up to glaze temperature (T_g). The glass remains in a nonequilibrium, thermodynamically unstable, "frozen" state. The relaxation time at these temperatures is so great that relaxation has no detectable influence on deformation. Glass passes into a different kinetic state and undergoes corresponding structural rearrangement, only above T_g. The energy of particle vibration then becomes high enough to weaken the bonds and even to break the weakest of them.

Figure 8 illustrates the basic deformation temperature relationship for glass. The endothermic effect in the T_g–T_a range indicates that the structural rearrangement is accompanied by absorption of heat. The specific heat of glass rises rapidly in this temperature range. However, regrouping of the structural elements cannot keep pace with the temperature changes, as the relaxation time is still very large in comparison to the rate of heating of the glass. Weakening of the bonds causes disintegration of the unit cells, weakening of the whole coordination network, and distortion of the framework under load; in this temperature range glass is much more easily deformed than at other temperatures.

In addition to instantaneous-elastic deformation, retarded-elastic and plastic deformations begin to occur. This is indicated by the greatly increased area of the hysteresis loop and the changed slope of the major axis of its ellipse, by the fact that the unloading branch of the loop does not return to zero, and by the "deformation-time" curves which reveal "flow" of the material. At temperature T_a the relaxation time becomes less than the time needed to introduce the corresponding quantity of heat, and a thermodynamically stable state is attained. The system becomes more rigid than it was during the preceding period of structural rearrangement in the T_g–T_a range and exhibits elastic behavior under small loads. The deformation curve forms a distinct plateau. The area of the hysteresis loop decreases, and the unloading branch slowly returns to the original position. The new and final state of equilibrium is reached at temperatures above T_f. Here the viscosity falls sharply and the glass becomes a liquid.

It appears that these characteristics of the elastic and plastic properties of glass, and especially the existence of the T_a–T_f plateau on the "deformation-temperature" curve when the flow which started at T_g temporarily ceases, are of considerable interest for further theoretical problems related to studies of silicate structure in the glassy state. It is likely that these observations can also be applied in the solution of practical problems in the heat treatment of glass, and in particular in the delicate heat treatment involved in the production of new constructional materials from glass.