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The Effect of Microstructure on the Physical Properties of Glasses in the Sodium Silicate System

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Samples of sodium silicate glasses heat-treated in the region of immiscibility were studied to characterise the physical properties and to determine the dependence of physical properties on microstructure. Independent measurements of the elastic moduli and thermal expansion characteristics were examined.

The magnitudes of elastic moduli and coefficients of thermal expansion were controlled by the total amount of soda present. The temperature dependence of the physical properties, however, was greatly influenced by the amount and distribution of the phases present. In general, glasses with two independently interconnected phases were more rigid than homogeneous materials having the same nominal composition. The properties of glasses with a second phase dispersed as particles in a continuous matrix phase were determined primarily by the properties of the continuous phase. The observed behaviour of the physical properties supports the conclusion of three-dimensional interconnectivity of phases developed in the unstable region of immiscibility for sodium silicate glasses.

1. Introduction

It has been demonstrated by many investigators that the behaviour of materials is greatly affected by microstructure. In fact, microstructural features may be the controlling factor with respect to physical properties such as strength and deformation in certain cases. The need for understanding the effect of microstructure on physical properties, and the behaviour of ceramic materials in particular, has become more evident in recent years.

In many glass systems there have been glass compositions observed which form two immiscible liquids at high temperature [1]. The result of this immiscibility is amorphous phase decomposition, or glass-in-glass separation. The mechanism of the decomposition will be determined by the initial state of the material which may be thermodynamically metastable or unstable. In the metastable region, decomposition occurs by classical nucleation and growth. Microstructures developed by this mechanism are characterised by discrete particles dispersed throughout a continuous matrix [2]. The particles will increase in number and in size until the compositional limits of the immiscibility gap are reached. In the unstable region, a different decomposition occurs and is characterised by diffuse boundaries. The phases formed during the decomposition grow by increasing the compositional contrast between the phases as predicted by Gibbs [3]. Microstructures developed by this mechanism are typified by irregular diffuse phase boundaries and both phases are independently interconnected. Amorphous phase decomposition may occur at temperatures higher or lower than the liquidus temperature.

Amorphous phase decomposition has generated a great deal of interest in the last few years [4]. In particular, the literature contains a significant amount of quantitative information on the region of immiscibility in the sodium silicate system [1(f), 5]. With the data contained in these references the immiscibility gap in the sodium silicate system was constructed. Fig. 1 illustrates that immiscibility gap and the metastable and unstable regions are indicated. Compositions within these two regions can be heat-treated to yield two radically different microstructures.

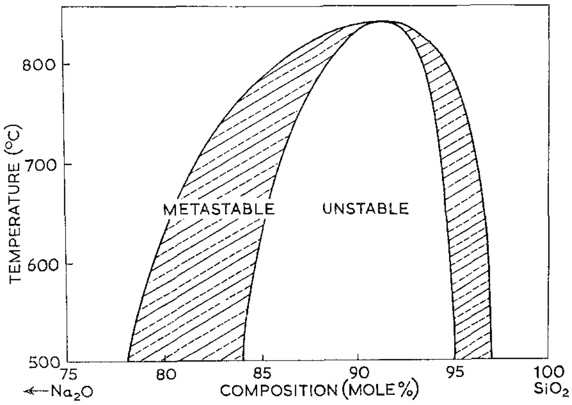


Figure 1 Immiscibility gap in the Na_2O/SiO_2 system.

The purpose of this study was to investigate the effect of microstructure on mechanical properties of some glass compositions in the immiscibility region of the sodium silicate system. The dependence of elastic moduli and expansion characteristics on microstructure are discussed in this paper.

2. Experimental Procedure

Six binary glasses in the sodium silicate system were studied. The composition and annealing history of these glasses are given in table I. The annealed glasses were further heat-treated at various times and temperatures to develop the desired microstructure. The samples were placed in silica boats in a tube furnace. After the requisite time, the boats were removed from the furnace and allowed to cool in air.

TABLE I Analysed compositions (mole %) and annealing histories of sodium silicate glasses

Composition number	Na_2O	SiO_2	Annealing history
1	18.4	81.6	525° C for 15 min
2	17.6	82.4	525° C for 15 min
3	14.8	85.2	480° C for 15 min
4	12.6	87.3	500° C for 15 min
5	10.3	89.7	505° C for 45 min
6	7.2	92.8	515° C for 15 min

The elastic moduli, Young's and shear, were measured on rectangular bars using Förster's method of suspension in the audible frequency range. From these moduli the bulk modulus and Poisson's ratio were calculated [6]. In most cases, only the relative Young's or shear moduli are reported. Precisely ground samples were used to obtain absolute values for some compositions.

Thermal expansion determinations were made with a horizontal dilatometer with an alumina measuring system. Expansion determinations were made from room temperature to the dilatometric softening point at a rate of 3.0° C/min on samples 5 cm in length. Duplicate samples for each heat-treatment were measured.

The dilatometric softening point is defined as the temperature at which viscous flow exactly counteracts thermal expansion during measurement; it is, therefore, the maximum point attained on the thermal expansion curve, and generally corresponds to a viscosity of 10^{11} to 10^{12} poises. The exact viscosity at which deformation will occur is dependent upon the measuring instrument and the load which it places on the sample. Since dilatometric softening point is influenced by the load on the sample, a constant sample cross-sectional area of 0.32 cm^2 was maintained. The dilatometric softening point was determined to the nearest 5° C.

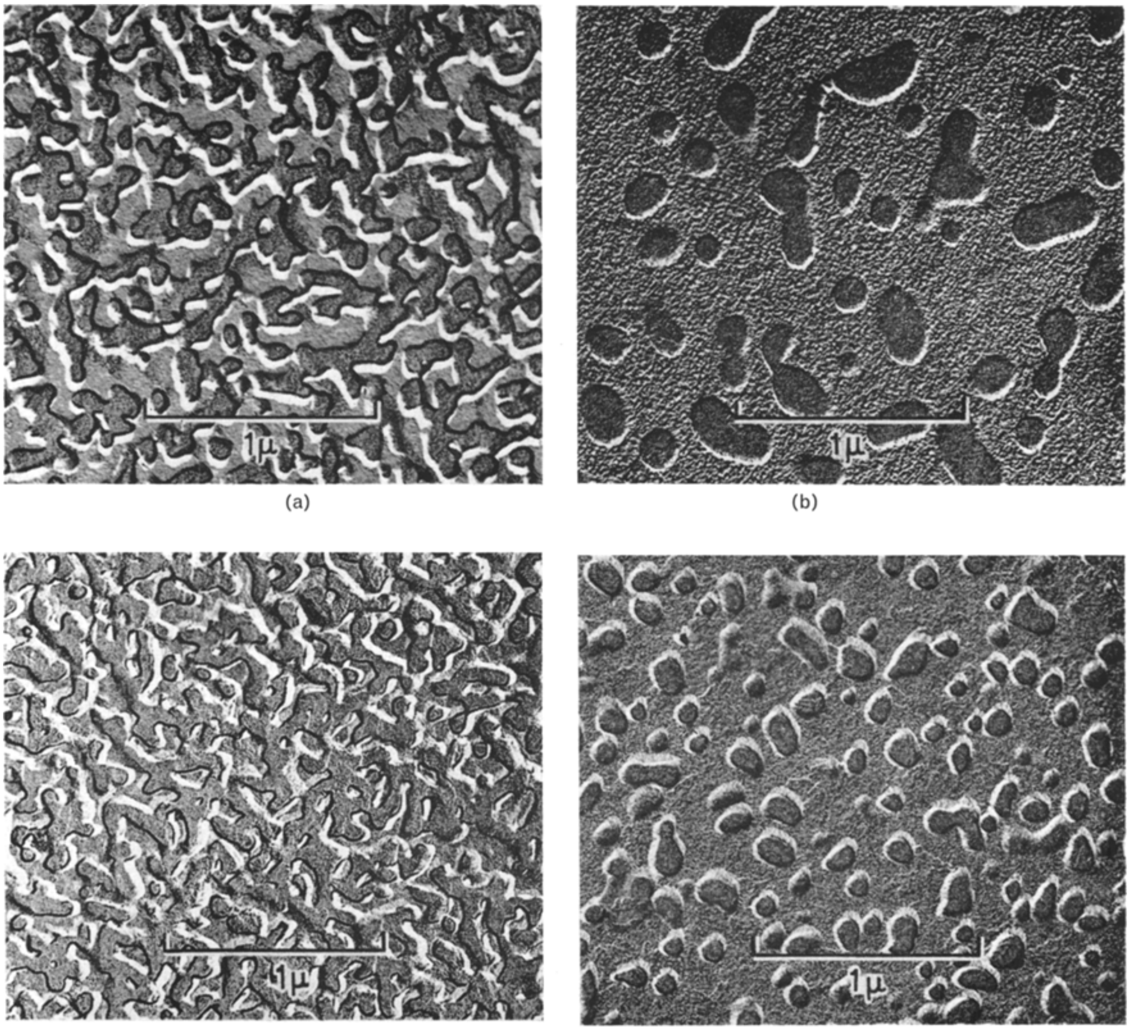
Electron micrographs of all the samples were made to characterise the microstructural features.

3. Results and Discussion

3.1. Microstructure

With proper heat-treatments it was possible to develop two distinct types of microstructure in the sodium silicate system. *Type 1* Two phases in which the second phase is dispersed as discrete particles in the continuous matrix phase. *Type 2* Two phases in which the two phases are independently interconnected.

Heat-treating of compositions in the metastable region resulted in classical nucleation and growth of particles. The microstructure obtained was that of particles of one phase dispersed in a continuous matrix of a second phase. Compositions heat-treated in the unstable region resulted in a microstructure consisting of two independently interconnected phases. These microstructures were typified by irregular diffuse phase-boundaries. These microstructures were consistent with past observations of the behaviour of amorphous phase decomposition occurring within the immiscibility region [2, 3, 4]. Micrographs exhibiting these types of microstructure for glass compositions containing 14.8 and 12.6 mole % Na_2O are shown in fig. 2. It should be noted that the micrographs and data presented in this investigation deal only with amorphous



(a) (b)

(c) (d)

Figure 2 Two basic types of microstructure observed in the sodium silicate system. (a) Interconnected phases, 12.6 mole % Na_2O, 8 h at 600° C; (b) dispersed particles, 12.6 mole % Na_2O, 1½ h at 770° C; (c) interconnected phases, 14.8 mole % Na_2O, 8 h at 600° C; (d) dispersed particles, 14.8 mole % Na_2O, 4 h at 680° C.

phases. No crystallisation has occurred in any of the samples.

3.2. Elastic Moduli

Table II lists the values of the elastic moduli of two samples each of glasses having 12.6 and 14.8 mole % Na_2O. The data are for two temperatures, room temperature and 400° C. Note that the moduli decrease with increasing soda content, and that Young's modulus, *E*, and the shear modulus, *G*, decrease with increasing temperature. The bulk modulus, *B*, and Poisson's ratio, μ, increase with increasing temperature. Also, notice that when glass with 14.8 mole % Na_2O developed the type 1 microstructure, a decrease in the magnitude of its elastic moduli resulted. The values in this table are estimated to be accurate to within 3 %.

Figs. 3 to 6 represent the behaviour of the relative elastic moduli of the sodium silicate glasses. The relative modulus is the ratio of the modulus at temperature, *T*, to that at room temperature, usually 24° C.

Fig. 3 illustrates the general behaviour of Young's modulus as a function of temperature for the three microstructures found in the sodium silicate system. The relative modulus of glass with 26.5 mole % Na_2O, a homogeneous, one-

TABLE II Absolute elastic moduli of two sodium silicate glasses

Composition of glass (mole %)	Heat-treatment	E(10^6 psi*) 24° C	400° C	G(10^6 psi) 24° C	400° C	B(10^6 psi) 24° C	400° C	μ 24° C	400° C	Structure type
Na_2O 12.6	× 600° C, 1 h	9.36	9.32	3.93	3.86	5.05	5.29	0.19	0.20	2
SiO_2 87.4	× 600° C, 8 h	8.38	9.36	3.93	3.87	5.10	5.35	0.19	0.20	2
Na_2O 14.8	× 600° C, 8 h	9.00	8.82	3.79	3.72	4.78	4.88	0.18	0.19	2
SiO_2 82.4	× 710° C, 4 h	8.97	8.77	3.77	3.65	4.79	4.88	0.18	0.20	1

*1.0 psi = 1.0 lb/in.^{2} = 7.0 × 10^{-2} kg/cm^2

phase glass, decreases sharply with temperature. The effect of the large numbers of mobile ions in the glass is seen as a dip in the modulus near 100° C. This relaxation is due to the large acoustic absorption occurring at that temperature. Glasses with a type 1 microstructure behave in much the same manner as homogeneous glasses. Finally, the type 2 microstructure can cause the modulus to increase with temperature. It will be shown below that this phenomenon is a result of, and dependent on, the volume fraction of the high silica phase present.

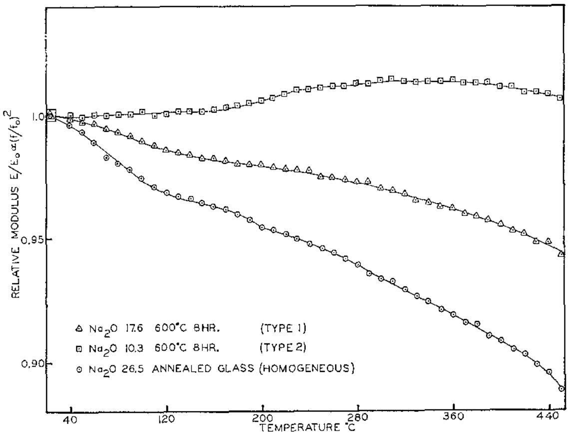


Figure 3 Behaviour of relative Young's modulus versus temperature for three different microstructures.

Fig. 4 shows the relative Young's modulus of some samples with 12.6 mole % Na_2O versus temperature. The modulus of samples heated at 600° C shows a definite increase in rigidity as the time at temperature increases. The 600° C samples all had type 2 microstructures. A sample heated at 770° C for 2½ h developed type 1 microstructure and the modulus/temperature relationship indicates that this configuration is much less rigid than the interconnected phase type. Fig. 5 is a plot of the relative Young's and shear modulus of the same composition heated at 600° C for 32 h. The rigidity of the structure has developed to the point where the moduli actually increase with temperature.

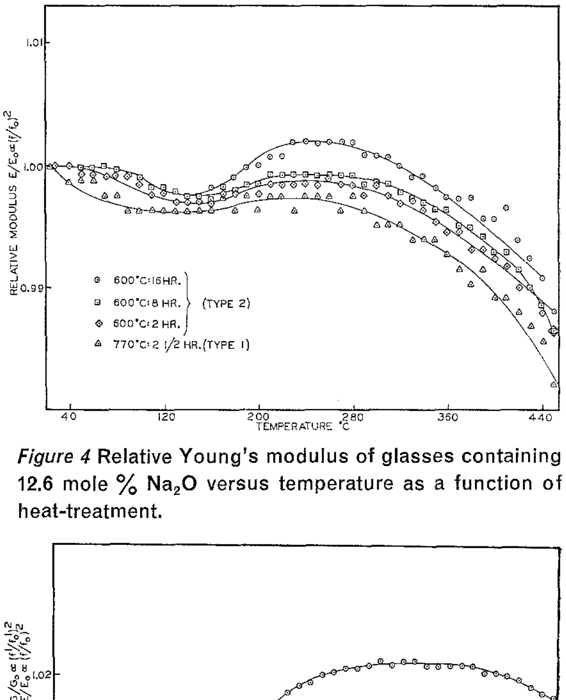


Figure 4 Relative Young's modulus of glasses containing 12.6 mole % Na_2O versus temperature as a function of heat-treatment.

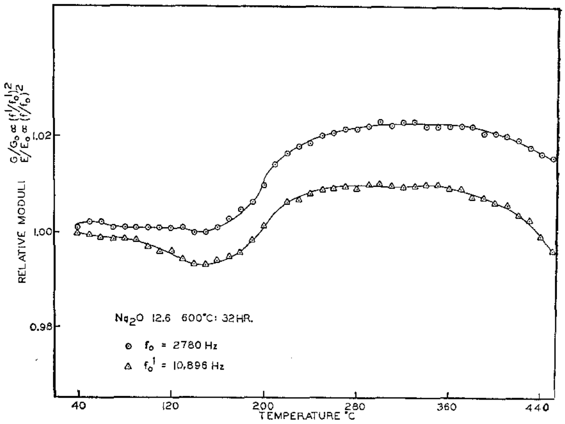


Figure 5 Relative moduli versus temperature of a glass containing 12.6 mole % Na_2O heat-treated 32 h at 600° C (type 2 microstructure).

Fig. 6 shows the relative Young's moduli of some samples with 7.2 mole % Na_2O versus temperature. All these samples had type 2 microstructures. The data show a sharp increase in Young's modulus with increasing temperature characteristic of fused silica. The composition of the high silica phase in this glass at equilibrium is approximately 3 to 5 mole % soda. Increases such as those observed are not, therefore, too surprising, if the glass is approaching its equilibrium composition.

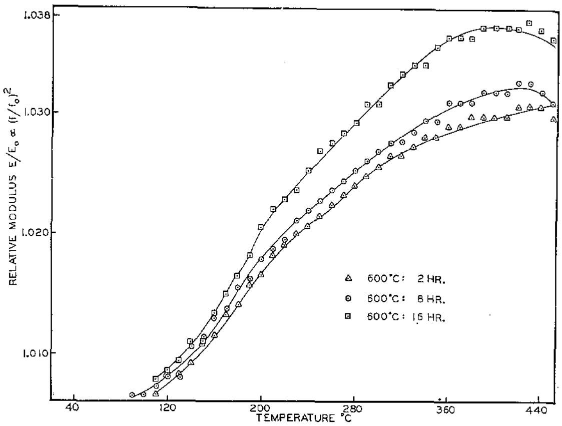


Figure 6 Relative Young's modulus of glasses containing 7.2 mole % Na_2O versus temperature after various heat-treatments.

Fig. 7 shows the bulk moduli versus temperature of some samples with 12.6 and 14.8 mole % Na_2O. The bulk modulus is the inverse of the adiabatic compressibility. These data show that the glasses are getting "softer" as the temperature decreases.

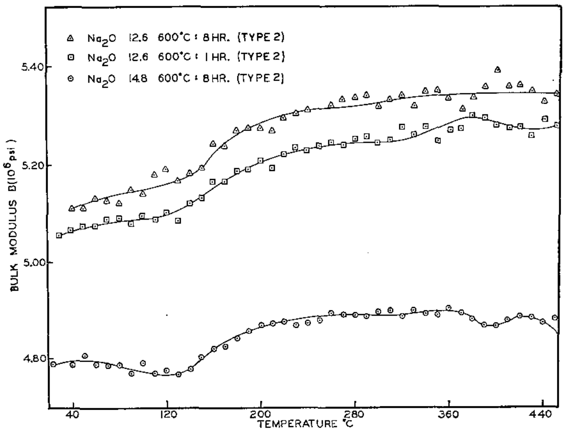


Figure 7 Bulk modulus versus temperature for two sodium silicate glasses.

With constant composition, the effect of long heating times on the moduli of the type 2 glasses should be to change only the distribution of phases. That is, if both phases are continuous, we can write that the observed modulus, M, is

$$M = f_L M_L + f_H M_H\,, \qquad (1)$$

where f_L, M_L are the volume fraction of the phase low in soda and its modulus, respectively. The quantities f_H, M_H refer to the soda-rich phase. Then

$$f_L + f_H = 1\,. \qquad (2)$$

And, in general,

$$M_L > M_H\,. \qquad (3)$$

Substituting, we obtain

$$M = f_L(M_L - M_H) + M_H\,. \qquad (4)$$

If we consider M_H and M_L as constants, characteristic of the end member compositions, we would interpret the behaviour shown in fig. 4 in terms of a changing volume fraction of the low soda phase. The volume fraction f_L does change, as shown in fig. 8*. Qualitatively, then, the behaviour of the moduli as a function of heat-treatment is understandable. Calculations based on equation 4 have shown, however, that the quantitative changes in the moduli can be explained only if the composition of the phases changes as well as the volume fraction.

The elastic moduli of homogeneous glasses usually decrease with increasing temperature.

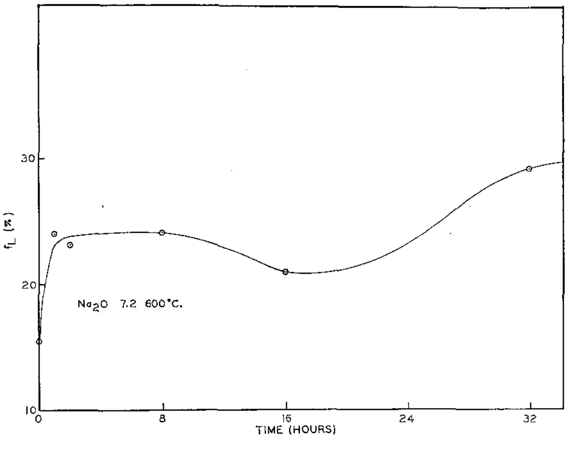


Figure 8 Volume fraction of the low soda phase of glass containing 7.2 mole % Na_2O as a function of heat-treatment time at 600° C. The data were determined by point count analysis of electron micrographs (courtesy of Dr M. A. Conrad).

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*Private communication from M. A. Conrad, Owens-Illinois Inc, Technical Center, Toledo, Ohio, USA (to be published).

This is the usual and expected behaviour of solids. As the glass receives more thermal energy, the atomic constituents spend more time farther away from their neighbours. As the elastic modulus is inversely proportional to the interatomic distance, the modulus decreases with increasing temperature [7].

Glasses with type 1 microstructure possess a matrix phase rich in soda. This matrix overrides any small effects exerted by the dispersed low soda phase, and the result is a decrease in the modulus as the temperature rises. That the rate of decrease is not as large as in homogeneous glasses may be due to the small extra rigidity offered by the dispersed low soda phase.

The behaviour of compositions with 12.6 and 14.8 mole % Na_2O indicates that (i) at least the low soda phase is continuous in samples with the type 2 morphology, and both phases are probably continuous, and (ii) the continuous phase in the type 1 microstructure is rich in soda. The rising moduli in the 32 h samples heat-treated at 600° C can be explained as follows. Differentiating equation 4 with respect to temperature, assuming f_{L} is constant, yields:

$$\frac{\mathrm{d}M}{\mathrm{d}T} = f_{\mathrm{L}}\left(\frac{\mathrm{d}M_{\mathrm{L}}}{\mathrm{d}T} - \frac{\mathrm{d}M_{\mathrm{H}}}{\mathrm{d}T}\right) + \frac{\mathrm{d}M_{\mathrm{H}}}{\mathrm{d}T} \tag{5}$$

Assuming that $\mathrm{d}M_L/\mathrm{d}T$ in samples with 12.6 mole % Na_2O is approximately that of Vycor (96% silica) glass, and using a value for $\mathrm{d}M_{\mathrm{H}}/\mathrm{d}T$ obtained from the new data on 26.5 mole % Na_2O presented here, it can be shown that $\mathrm{d}M/\mathrm{d}T$ is positive as long as $f_{\mathrm{L}} > 0.36$. The rising moduli of the 32 h sample containing 12.6 mole % Na_2O is explained by stating that the sample is near the end member equilibrium distribution and compositions. At the end members, the phase diagram predicts that $f_{\mathrm{L}} \simeq 0.47$ (fig. 1). The composition 14.8 mole % Na_2O, on the other hand, should have $f_{\mathrm{L}} < 0.36$ at the end member compositions (600° C) and would not be expected to show rising moduli with temperature. The data in table II show that neither Young's modulus nor the shear modulus of the 14.8 Na_2O samples heat-treated 8 h at 600° C increase in magnitude with temperature. Other data (not shown) on samples heated 32 h at 600° C show that these moduli always decrease with temperature. The bulk moduli of samples containing 14.8 mole % Na_2O do increase with temperature, however. Since the bulk modulus is calculated from the relation

$$B = \frac{E}{3(1-2\mu)} \tag{6}$$

and Poisson's ratio always increases with temperature in glass [8], whether or not B increases with temperature depends on the balance of the numerator and denominator of equation 6. Conceivably, except when $\mathrm{d}E/\mathrm{d}T > 0$, $\mathrm{d}B/\mathrm{d}T$ could be greater than, less than, or equal to zero. It should be noted that no quantitative explanation for the positive temperature coefficient of Poisson's ratio of glasses has been published to date. No such attempt will be made here either.

3.3. Thermal Expansion Properties

3.3.1. *Dilatometric Softening Point*

In some glasses, amorphous phase separation occurred spontaneously upon cooling from the liquid state. This made it impossible to obtain homogeneous glasses of every composition. Further phase separation occurred during the annealing heat-treatment. The arrangement of the two phases produced by the annealing heat-treatment was not sufficiently developed to the extent that the microstructure could be definitely classified as type 2. In such situations, the annealed glass was simply labelled "decomposed".

In general, the softening point of the annealed glasses was a function of the total Na_2O content. However, the fact that some of the annealed glasses were decomposed to different degrees also influenced the softening point, particularly in the case of the glass with 10.3 mole % Na_2O. The dilatometric softening points for the samples studied are listed in table III.

The dilatometric softening point was definitely influenced by the type of microstructure developed in the sample. The development of two independently interconnected phases resulted in increasing the softening temperature above that necessary to cause the annealed glasses to soften. For 14.8 mole % Na_2O, the increase in the dilatometric softening point was 135° C, while for 12.6 mole % Na_2O it was 20 to 35° C. It should be pointed out, however, that the glass containing 12.6 mole % Na_2O was not homogeneous, but was decomposed and would initially have a higher softening point if a silica-rich continuous phase were present. Therefore, less increase in softening point would be expected due to the interconnected phases becoming fully developed.

When these same compositions (14.8 and

TABLE III Expansion properties of heat-treated sodium silicate glasses

Composition (mole %) and heat-treatment			α_{RT-350} (10^7/° C)	Dilatometric softening point (° C)	Characteristic microstructure
Na_2O	18.4	Annealed glass	101.5	500	Homogeneous glass
SiO_2	81.6	600° C, 8 h	99.8	500	Type 1
Na_2O	17.6	Annealed glass	97.3	500	Homogeneous glass
SiO_2	82.4	600° C, 8 h	97.6	495	Type 1
Na_2O	14.8	Annealed glass	83.9	530	Homogeneous glass
SiO_2	85.2	600° C, 8 h	83.2	665	Type 2
		680° C, 4 h	83.6	510	Type 1
		710° C, 4 h	83.2	515	Type 1
Na_2O	12.6	Annealed glass	70.2	695	Decomposed
SiO_2	87.4	600° C, 8 h	74.8	715	Type 2
		650° C, 4 h	75.4	730	Type 2
		770° C, 1½ h	70.1	515	Type 1
Na_2O	10.3	Annealed glass	61.2	730	Decomposed
SiO_2	89.7	600° C, 8 h	64.0	740	Type 2
Na_2O	7.2	Annealed glass	47.0	720	Decomposed
SiO_2	92.8	600° C, 2 h	46.4	730	Type 2
		600° C, 8 h	48.1	735	Type 2

12.6 mole % Na_2O) were heat-treated to produce type 1 microstructure, the softening point was considerably lower than the softening point of the glass. In the case of 12.6 mole % Na_2O which had a microstructure of discrete particles dispersed in a continuous matrix, the softening point was 180° C less than that of the annealed glass, and for 14.8 mole % Na_2O, it was 15 to 20° C less. Again, the decomposed condition of the 12.6 mole % Na_2O glass should be considered to account for the large difference in magnitude of the softening point changes.

In the region of immiscibility, glass compositions decompose into two phases which approach the compositional limits of the immiscibility gap for a given temperature. It is impossible to determine the exact compositions of the two phases, but as the time of heat-treatment is increased, the phases approach closer to the compositions defined by the limits of miscibility. At 600° C, the compositional limits of the immiscibility region are approximately 4 and 19 mole % Na_2O. This means that the compositions of the two phases developed will differ greatly if the heat-treatment time were sufficient. From observations of the changes in physical properties and of changes in the microstructure, 8 h at 600° C was sufficient time to develop two phases of differing composition.

The development of two independently interconnected phases, one low in soda content and one high in soda content, accounts for the increase in dilatometric softening point. The low soda phase softened at a higher temperature, and that softening point was observed once the independent interconnectivity developed. The exact softening point was no doubt affected by the volume percentage of the high soda phase present, and probably the interfacial stress developed between the two phases.

When microstructures developed with one phase dispersed in a continuous matrix of the second phase, the softening point was less than the softening point of the annealed glass. For the compositions where it was possible to develop this dispersed type microstructure, the continuous phase was the high soda phase. The softening point in these samples was then characteristic of the continuous phase having a higher percentage of soda. The dispersed phase of low soda content had little effect on the softening point. As the difference in the composition of the annealed glass and the high soda phase increased, the difference in the softening points increased. For example, the differences between softening points for annealed glasses of 18.4, 17.6, 14.8, and 12.6 mole % Na_2O and the corresponding samples having a dispersed phase were 0, 5, 20, and 180° C.

3.3.2. Thermal Expansion Characteristics

The linear coefficients of thermal expansion determined over the temperature interval from room temperature to 350° C are listed in table III. These expansion coefficients were found to be a linear function of the total soda content. The slope of the straight line obtained from plotting the expansion coefficients versus the mole % soda for the annealed glasses was 4.9×10^{-7}/°C/mole % soda. The slope for the samples heat-treated for 8 h at 600° C versus total soda content was 4.6×10^{-7}/°C/mole % soda.

The presence of an isolated dispersed phase in a continuous second phase did not change the basic expansion characteristics. That is, a linear expansion region was observed followed by a transformation region, and then softening. The same type of curve was observed for annealed glasses having a single homogeneous phase (except that a transformation region was not observed). Curve A in fig. 9 is characteristic of these two types of microstructure.

However, the effect of the distribution of phases on the expansion characteristics was evident for samples having two independently interconnected phases. The expansion curves for samples in the unstable region are shown in fig. 9, curves B-D. These samples were heat-treated for 8 h at 600° C, and their microstructures exhibit well-developed interconnected phases. In these samples, a transformation region was observed around 425 to 475° C, and then increased expansion occurred until the dilatometric softening point was reached. This behaviour was characteristic of all samples heat-treated in the unstable region and the increased expansion continued until the softening temperature of the low soda phase was reached. The increased expansion was less in compositions of lower total soda content (fig. 9). The samples with lower total soda content are also the samples which would have less volume percentage of the high soda phase (application of phase rule to the immiscibility diagram).

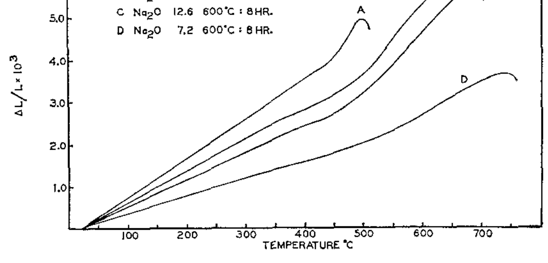

Figure 9 Expansion characteristics of heat-treated glasses.

The increased expansion after annealing is probably due to the fact that the dilatometric softening point of the high soda phase had been exceeded and expansion of this phase was increasing greatly. The low soda phase softening point had not been exceeded and the sample remained rigid and, therefore, the bulk expansion increased.

4. Summary and Conclusions

Independent measurements of elastic moduli and thermal expansion properties were made to characterise the mechanical behaviour of phase separated glasses in the sodium silicate system. Two general types of microstructures were observed throughout the region of immiscibility. Within the metastable region the microstructure was characterised by discrete particles of a second phase dispersed in a continuous matrix phase. Microstructures characteristic of the unstable region consisted of two independently interconnected phases. The behaviour of the physical properties studied was consistent with the observed microstructural distribution of the phases.

The following conclusions were made with respect to the mechanical behaviour of phase-separated sodium silicate glasses.

(i) The distribution and amount of phase separation affected the bulk physical properties. In some cases, the influence was large.

(ii) The mechanical properties of the interconnected phase morphology exhibited a nearly linear dependence on the amount and composition of the low-soda phase. Glasses with this morphology possessed a more rigid structure than homogeneous materials having the same nominal composition. The greatest influence of the phase separation was on the temperature dependence of the physical properties; the magnitudes of the physical properties were largely determined by the total amount of soda present. When this microstructure was present, positive temperature coefficients of elastic moduli were observed.

(iii) In the metastable region, the behaviour of the physical properties was controlled by the intrinsic properties of the continuous phase. The glass behaved in nearly all respects as a homogeneous material having the composition of the high-soda phase. The discrete particles of the second phase produced only small, second order effects on the mechanical properties.

One further point may be elaborated. Electron micrographs revealed two-dimensional representations of the distribution of phases. From the microstructural characteristics observed in the two-dimensional data, many investigators have maintained that the two phases are independently interconnected in three dimensions. Three-dimensional interconnectivity has not been proved, however, and some investigators are not convinced that the observed two-dimensional representations are sufficient evidence to declare the existence of three-dimensional interconnectivity. The observations made in this study lend support to the contention that the two phases are, indeed, independently interconnected in three dimensions. In fact, interpretation of the observed behaviour of the physical properties, particularly the temperature dependence, required the existence of interconnectivity.

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