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Mechanical Behavior of Porous Glasses Produced by Sintering of Spherical Particles

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Abstract

Young's modulus and biaxial flexure strength were measured for compacts of spherical glass particles sintered to various densities. The aim of the work was to relate the mechanical properties to the sintering process. In particular, changes in the interparticle neck sizes during the sintering process were measured from fracture surfaces. It had been postulated previously that the elastic moduli directly depend on the neck radius to particle radius ratio and such measurements allow the elastic behavior to be directly related to the sintering kinetics. The experimental results were consistent with both the mechanical and sintering models. There was also found to be a strong correlation between Young's modulus and strength of the porous glass bodies.

1 Introduction

One of the aims of the study of sintering science is the development of techniques that allow the experimentalist to characterize the geometric changes that occur in the powder compact as it undergoes sintering. A variety of characterization techniques, such as mercury porosimetry, surface area measurements, small angle neutron scattering etc., have been utilized. In other studies,[1,2] however, it was suggested that the elastic behavior of a porous body could be used to characterize the sintering process. For the case of partially sintered alumina, elastic moduli were measured for specimens that had been subjected to the initial stage of sintering. In this material, there was a rapid increase in the elastic moduli with minimal densification and it was suggested[1,2] that this behavior could be understood by the interparticle neck growth process, and particularly by surface diffusion. An attractive feature of utilizing the elastic behavior of a material to characterize the sintering process, is that the elastic constants can be measured to a high accuracy using nondestructive techniques, such as dynamic resonance or sound velocity measurements.

The aim of the current study was to determine the changes that occur in the mechanical properties of partially sintered glass and to relate these to the changes in the microstructure that occur during the sintering process. In order to simplify the compact geometry, a model system of spherical glass particles was utilized.

2 Background

There has been considerable scientific effort in predicting the elastic behavior of porous materials. In such analyses, the theoretical relationships for the elastic moduli are often expressed solely as functions of the fraction of porosity. In other cases, it has been suggested that pore geometry may play an important role and factors, such as pore shape, have been incorporated into some of the analyses. For materials with moderate or high fractions of porosity, it can be quite difficult to describe the complex nature of the pore structure, especially for materials produced by the sintering of powder compacts. As an alternative approach, Green *et al.*[1,2] have suggested it may be useful to consider the elastic behavior in terms of the interparticle neck growth process and the coordination of the particles. For example, for spherical particles subjected to the initial stage of sintering, it was suggested that[1]

$$\frac{B}{B_o} = \frac{3Nr(1-2\nu_o)}{8kR(1-\nu_o^2)} \tag{1}$$

where B is the bulk modulus of the porous compact, B_o and ν_o are the bulk modulus and Poisson's ratio of the particle, r is the neck radius, N the particle coordination number, R is the radius of the particle and k is an empirical geometric constant. For a given material, eqn (1) can be simplified to obtain

$$\frac{B}{B_0} = CN\left(\frac{r}{R}\right) \quad (2)$$

where C is an empirical constant that can be obtained by comparison with experimental data for a given material. Although the theoretical approach to obtain eqn (2) was considered to be only approximate, the dependence of the elastic constants on the particle coordination number and the ratio of the neck and particle radii is intuitively appealing. The idea of relating the interparticle neck size to the mechanical behavior of porous materials has also been put forward by other researchers[3,4] and in a related idea, Cytermann[5] has postulated that the Young's modulus is directly dependent on the contiguity of the porous solid.

As eqn (2) predicts a dependence of the bulk modulus on (r/R), this allows the sintering theories concerning neck growth in powder compacts to be directly related to the elastic behavior. For example, Frenkel[6] proposed that the sintering mechanism in glass is by viscous flow and derived an expression for the rate of neck growth for glass spheres, i.e.,

$$\left(\frac{r}{R}\right)^2 = \frac{3\gamma t}{R\eta} \quad (3)$$

where γ is the surface energy, η is the viscosity, r is the radius of the neck, R is the radius of the particle and t is the sintering time. Experimental studies by Kuczynski[7] and Kingery and Berg[8] on the sintering of glass beads were in agreement with Frenkel's analysis.

3 Experimental Procedure

Soda–lime–silica glass beads were obtained from a commercial source (Potters Industries Inc., Parsippany, NJ). The average particle size was determined to be 58·6 μm from microscopic observation (750–1000 particles).

3.1 Sample preparation

Twenty grams of the glass powder were mixed with 4 wt% polyethylene glycol (organic binder) which had been dissolved in 20 ml of ethanol at 50°C. The mixture was stirred and the ethanol was removed, by drying at the same temperature for about 6–8 h. The dried powder was crushed to obtain a free flowing glass powder, which was subsequently uniaxially pressed into pellets of 25·4 mm diameter, at a pressure of ~90 MPa. The theoretical density of the glass powder was determined with a helium pycnometer (Multivolume Pycnometer 1305, Micromeritics, Norcross, GA) and found to be 2420 kg m^{-3}.

The glass samples were sintered in two steps. The first step involved binder burnout at 300°C. In the second step, the samples were sintered at various temperatures, ranging, from 620 to 655°C for 2 h and at 625 and 645°C for various times, between 0·5 and 10 h. The density of the samples was calculated from their measured dimensions and weights.

3.2 Mechanical properties

The strength of the glass samples was measured by the biaxial flexure method[9] using a mechanical testing machine (Instron Corporation, Canton, MA). The strength was calculated assuming a constant value of 0·2 for the Poisson's ratio. A 10% error in the Poisson's ratio value gives rise to an error of 4% in the flexural strength value, and this was considered acceptable for the current study.

The Young's modulus of the samples was measured by determining the longitudinal sound velocity.[10] Ultrasonic transducers (2 MHz, Ultran Laboratories, Boalsburg, PA) were used to transmit and receive the signals and no liquid couplant was used between the transducers and the samples. The sound velocity was measured through the thickness of the glass samples and Young's modulus was calculated using[10]

$$E = \frac{V^2\rho(1-2\nu)(1+\nu)}{(1-\nu)} \quad (4)$$

where V is the longitudinal sound velocity, ρ is the density and ν is the Poisson's ratio. As mentioned earlier, a constant value of 0·2 was used for the Poisson's ratio. For typical values of ν, a 10% error will give a ~4% error in the Young's modulus value.

3.3 Microstructural analysis

Neck radius measurements were made on samples sintered in the range 625–645°C and at 625°C for 4, 6, 8 and 10 h. These measurements were accomplished by obtaining a series of micrographs (scanning electron microscope) of the fracture surfaces of four different samples for each of the chosen conditions. For these conditions, the materials fail primarily by the crack passing through the necks. The neck sizes were measured from the micrographs using an image analyzer (ZIDAS, Carl Zeiss, Inc., Thornwood, NY). About 100 necks were measured for each experimental condition and the values were arithmetically averaged to obtain the mean contact radii.

4 Results and Discussion

The average green density of the compacts was determined to be ~64% of the theoretical density.

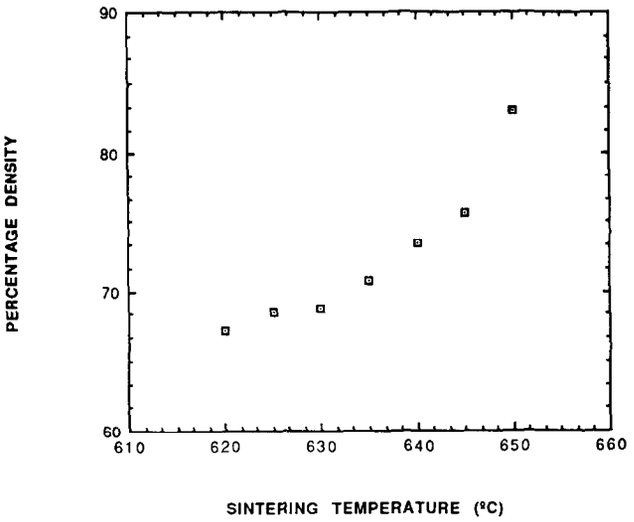

Fig. 1. Density of glass specimens after sintering at various temperatures for 2 h.

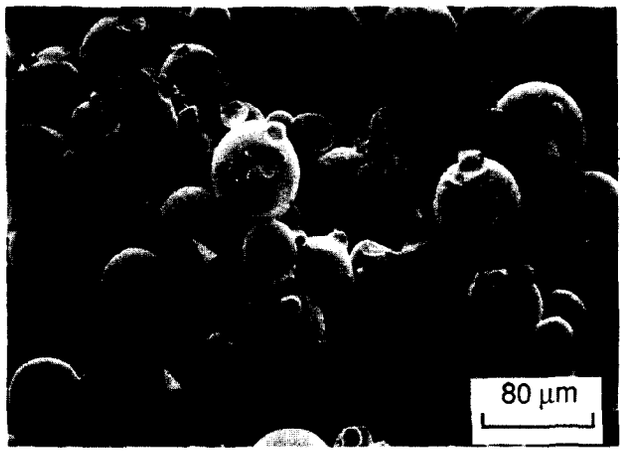

Fig. 3. Fracture surface for a specimen sintered at 620°C (4 h), showing the failed interparticle necks. Some of these necks are indicated by arrows.

The sample densities are shown in Fig. 1 as a function of the sintering temperature. The room temperature Young's modulus values obtained for these specimens are shown in Fig. 2 as a function of the % theoretical density. The Young's modulus values increase continuously with relative density, as expected. This behavior does, however, contrast strongly with the rapid increase in Young's modulus observed in partially sintered alumina.[1,2] For glasses, neck growth is expected to occur by viscous flow with densification, whereas for alumina, in which surface diffusion is prevalent at the lower sintering temperatures, the changes in the elastic moduli should occur without densification. If one considers the Young's modulus of dense soda lime silica glass is ~70 GPa, the data in Fig. 2 is also consistent with the recent analysis of Lam *et al.*,[11] in which the Young's modulus is predicted to be directly dependent on the degree of densification.

The fracture surfaces of the glass samples showed fractured necks which could be seen as small, almost perfect circles on the particles. Figure 3 shows the fracture surface for a glass sintered at 620°C for 4 h and the fractured necks, some of which are arrowed, are small but clearly visible. Transparticle fracture becomes more prevalent in samples sintered at higher temperatures or for longer times, making the neck size measurements more difficult. For example, Fig. 4 shows the fracture surface for a sample sintered at 620°C for 10 h. The ratio of the neck radius to the particle radius was calculated using the average particle size of the glass spheres. The presence of the transparticle failure complicated the current study, in that it may lead to a bias in the measured r/R values. For example, particles with the larger neck sizes may be obscured if the particles fail rather than the necks.

The model by Green *et al.*[1] predicts that the bulk modulus of a partially sintered sample is directly proportional to the product of the coordination of the compact and the radius ratio.

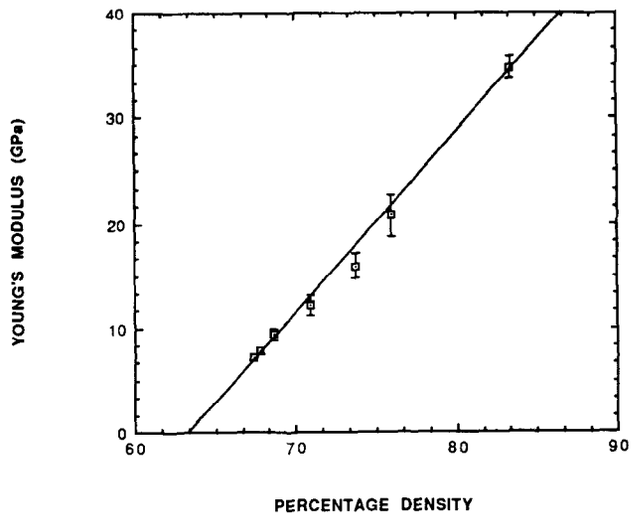

Fig. 2. Room temperature Young's modulus values for porous glass specimens after sintering to various temperatures. The error bars indicate the standard deviation in the data.

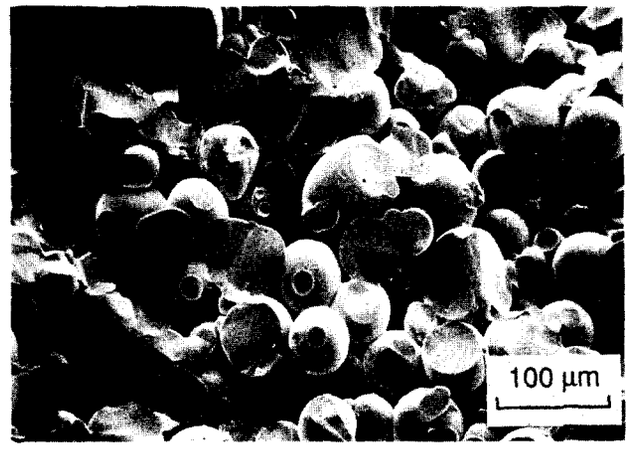

Fig. 4. Fracture surface for a specimen sintered at 620°C (10 h), showing the increase in transparticle failure for the longer sintering times.

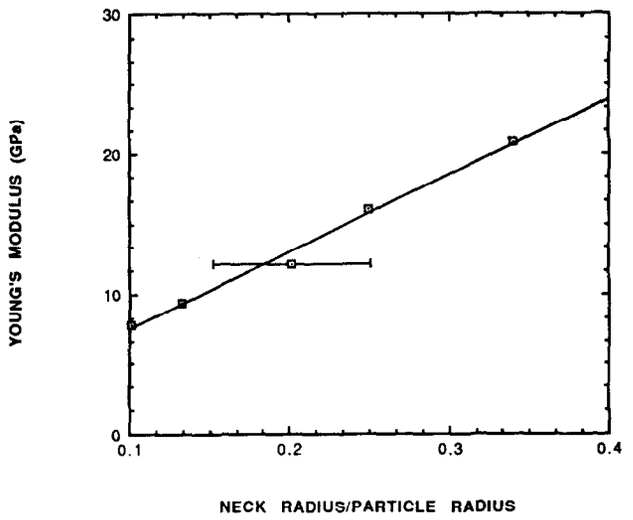

Fig. 5. Young's modulus values for porous glass specimens as a function of the neck to particle radius ratio. The error bar is a typical value of the standard deviation seen in the contact radius measurement.

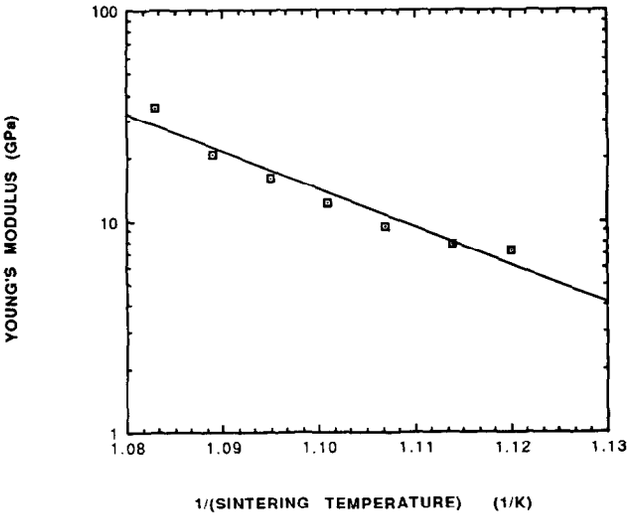

Fig. 6. Arrhenius plot for the (log) Young's modulus values for porous glass specimens as a function of the inverse sintering temperature.

In particular, eqn (2) predicts a linear relationship between the bulk modulus and r/R, assuming there is no change in particle coordination number. If one assumes that the value of Poisson's ratio for the porous glasses does not change significantly with densification, the same linear relationship will be obtained for the relative Young's modulus. To verify this prediction, the Young's modulus values of the porous glasses were plotted as a function of the radius ratio (r/R), as given in Fig. 5. Although the model was derived only for very small contact areas, a linear dependence on r/R is seen to not be unreasonable. From the data in Fig. 5 and eqn (2), if one assumes $(B/B_0) \approx (E/E_0)$ and $E_0 = 70$ GPa, one finds $CN \approx 1$.

In order to relate the elastic behavior to the sintering kinetics, one can combine eqns (2) and (3) to obtain,

$$\frac{E}{E_o} = CN\left(\frac{3\gamma t}{R\eta}\right)^{1/2} \tag{5}$$

where E and E_0 are the Young's moduli of the porous body and the spheres and η is the viscosity of glass at the sintering conditions. In addition, the viscosity is temperature dependent and can be written in the form of an Arrhenius equation near the glass transition temperature, i.e.

$$\frac{\eta}{\eta_o} = \exp\left(\frac{Q}{\mathrm{R}'T}\right) \tag{6}$$

where η_0 is a constant that depends on the glass composition, Q is the activation energy for viscous flow, R' is the universal gas constant and T is the absolute temperature. Substituting for η in Eqn (5), one obtains the following relationship between the Young's modulus and the sintering temperature

$$\frac{E}{E_o} = D\exp\left(-\frac{Q}{2\mathrm{R}'T}\right) \tag{7}$$

where $D = CN(3\gamma t/R\eta_0)^{1/2}$ The results of the analysis are shown in Fig. 6 and the activation energy for viscous flow was calculated from the slope and found to be 690 kJ mol^{-1}. This value is very close to 703 kJ mol^{-1}, which is the activation energy reported in literature[12] for soda lime silica glass in the temperature range 492–541°C.

The biaxial flexure strengths of the porous glasses are given in Fig. 7. The trend in the flexural strength data is very similar to that in the Young's modulus data, suggesting a similar dependence on the compact structure.

The densities of samples sintered at 625 and 645°C for various times are shown in Fig. 8. The density of samples sintered at 645°C increases more rapidly, reflecting the lower viscosity of the glass at this temperature. The Young's modulus and

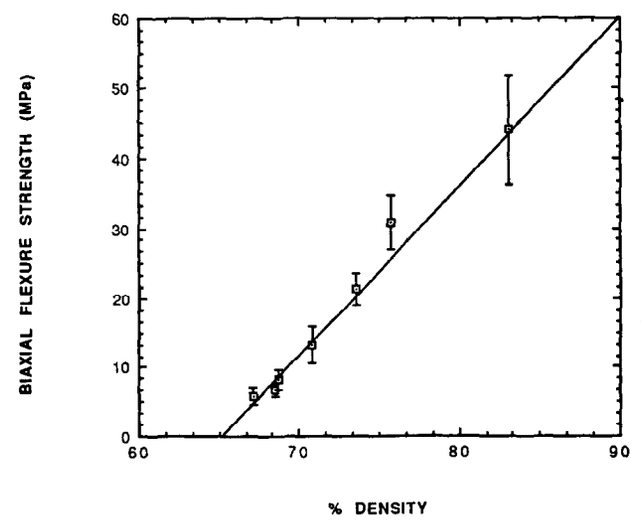

Fig. 7. Room temperature biaxial flexure strength values for porous glass specimens after sintering to various temperatures. The error bars indicate the standard deviation in the data.

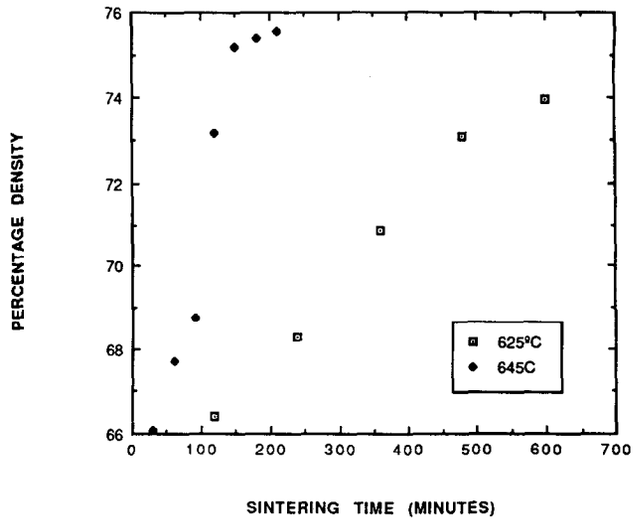

Fig. 8. Density of glass specimens after sintering at 625 and 645°C for various times.

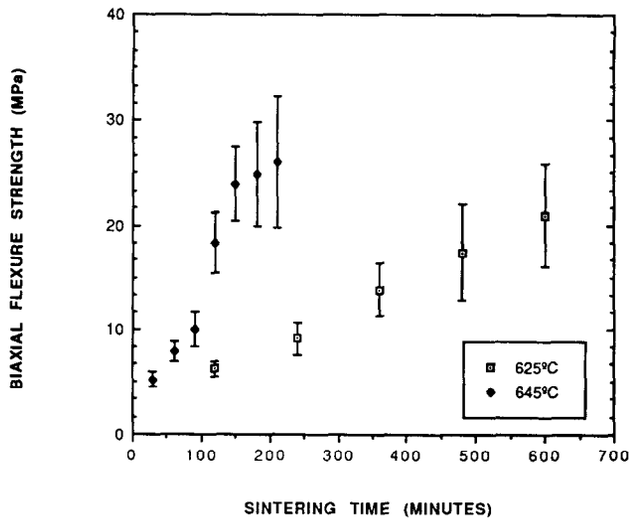

Fig. 10. Biaxial flexure strengths values for porous glass specimens after sintering at 625 and 645°C for various times.

flexure strength of these samples are presented in Figs 9 and 10, and in a similar fashion to the earlier data, show a strong correlation with each other.

From eqn (3), the neck/particle radius ratio is predicted to increase with sintering time with a time exponent of 0.5 and this can be tested using the measured r/R values. Figure 11 shows the data for the samples sintered at 625°C and although the data is rather scattered, a time exponent of 0·51 was obtained, in excellent agreement with the theory and with previous studies.[6,13,14] The data in Fig. 11 can also be used to estimate the glass viscosity at 625°C. From eqn (3), the square of the radius ratio can be plotted as a function of time and the viscosity can be obtained from a linear regression analysis. Using a value of 0·3 J m^{-2}, as suggested by Scherer,[15] the viscosity was calculated to be 10 GPa s. This value is in fair agreement with the value of 1·52 GPa s, reported by Hagy.[16]

The Young's modulus data on samples obtained from the isochronal and isothermal experiments have been combined in Fig. 12 to show the dependence on r/R. One would expect the two data sets to fit a single linear function, assuming there is no change in particle coordination. It appears, however, there is a significant difference between the two data sets. The reason for this difference could be that the particles undergo rearrangements during sintering, thus altering the coordination number and structure of the compact. The extent of these rearrangements may be different at the various sintering temperatures due to the differences in glass viscosity. Alternatively, it should be remembered that the model was only derived for small r/R values; therefore one would expect the agreement to be poor at large r/R values. Thus, although the model tested in this work seems be a reasonable first approximation, it is suspected that further refinements in the model are needed.

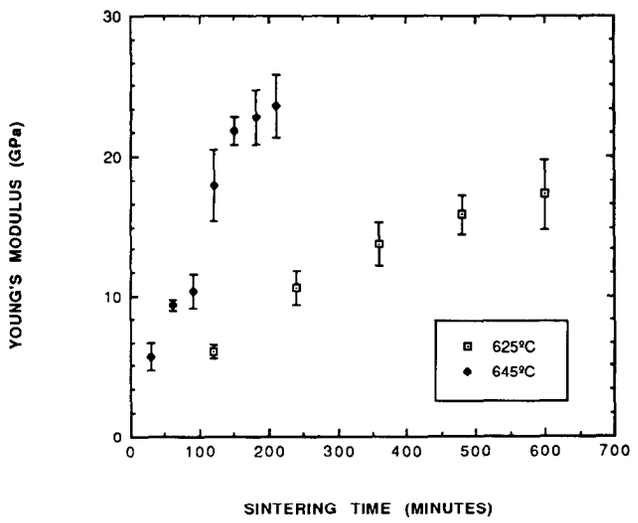

Fig. 9. Room temperature Young's modulus values for porous glass specimens after sintering at 625 and 645°C for various times.

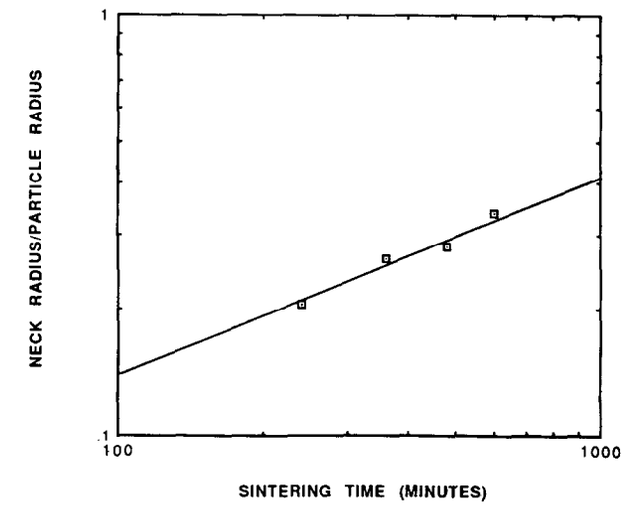

Fig. 11. The ratio of the neck to particle sizes as a function of the sintering time at 625°C. The log–log plot gives a time exponent of 0·51.

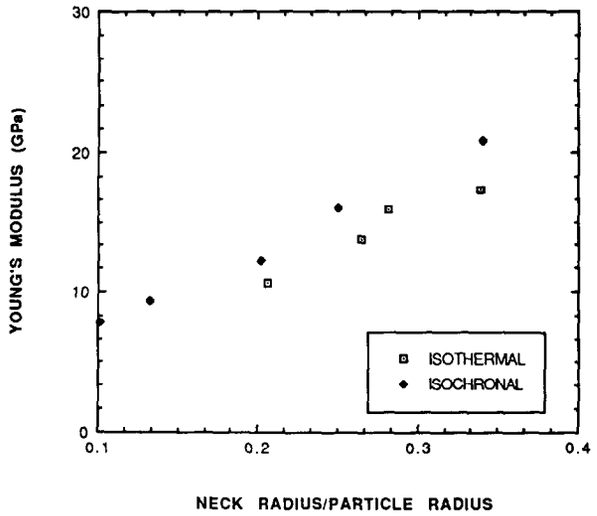

Fig. 12. Young's modulus values for porous glass specimens as a function of the neck to particle radius ratio for the isothermal and isochronal sintering experiments.

5 Conclusions

The Young's modulus and strength were determined for spherical glass particle compacts sintered under various conditions. These properties both increased with increasing density and the changes in the two properties were strongly correlated. The Young's modulus data were also analyzed in terms of the changes in the neck radius/particle radius ratio and an approximate linear relationship was confirmed, in agreement with earlier theoretical predictions. It was also possible to link the sintering kinetics to the elastic behavior and good agreement with the theory was found. Overall, it was found that elastic constant measurements are a very useful approach for characterizing porous ceramic bodies produced from powder compacts and gives insight into the sintering process.

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References

1. Green, D. J., Brezny, R. & Nader, C., The elastic behavior of partially-sintered ceramics. In *Adhesion in Solids*, MRS Symposium Proceedings, Vol 119, ed. by D. M. Mattox, J. E. E. Baglin, R. J. Gotschall and C. D. Batich. Materials Research Society, Pittsburgh, PA, 1988, pp. 43–48.
2. Green, D. J., Nader, C. & Brezny, R., The elastic behavior of partially-sintered alumina. In *Sintering of Advanced Ceramics*, ed. by C. A. Handwerker, J. E. Blendell and W. Kaysser. American Ceramic Society, Westerville, OH, 1990, pp. 347–56.
3. Woignier, T. & Philippou, J. Mechanical strength of silica aerogels. *J. Non-Cryst. Solids.*, **100** (1988) 404–8.
4. Kendall, K., Alford, N. McN. & Birchall, J. D., Elasticity of particle assemblies as a measure of the surface energy of solids. *Proc. R. Soc., Lond.*, **A412** (1987) 269–83.
5. Cytermann, R., A new way of investigating the dependence of elastic moduli on the microstructure of porous materials. *Powder Metall. Int.*, **19** (1989) 27–30.
6. Frenkel, J., Viscous flow of crystalline bodies under the action of surface tension. *J. Phys.*, **9** (1945) 385–91.
7. Kuczynski, G. C., Study of the sintering of glass. *J. Appl. Phys.*, **20** (1949) 1160–3.
8. Kingery, W. D. & Berg, M., Study of the initial stages of sintering by viscous flow, evaporation-condensation, and self-diffusion. *J. Appl. Phys.*, **26** (1955) 1205–12.
9. Wachtman, Jr., J. B., Capps, W. & Mandd, J., Biaxial flexure tests of ceramic substrates. *J. Materials*, **7** (1972) 188–94.
10. Schreiber, E., Anderson, O. L. & Soga, N., *Elastic Constants and their Measurements*. McGraw Hill, New York, 1973.
11. Lam, D. C. C., Lange, F. F. & Evans, A. G., Mechanical Properties of Partially Dense Alumina Produced from Powder Compacts. *J. Am. Ceram. Soc.*, **77** (1994) 2113–17.
12. Scherer, G. W., *Relaxation in Glass and Composites*. John Wiley and Sons, New York, 1986.
13. German, R. M., Simulation of diffusion controlled sphere–sphere sintering. In *Sintering-New Developments*, ed. M. M. Ristic. Elsevier Scientific Publishing Company, Amsterdam, 1979.
14. Scherer, G. W., Sintering of low-density glasses: I Theory. *J. Am Ceram. Soc.*, **60** (1977) 236–9.
15. Scherer, G. W., Viscous sintering of inorganic gels. *Surf. Colloid Sci.*, **14** (1987) 265–300.
16. Hagy, H. E., Experimental evaluation of beam-bending method of determining glass viscosities in the range of 10^8–10^{15} poises. *J. Am. Ceram. Soc.*, **46** (1963) 93–97.