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THE EFFECT OF A SMALL FRACTION OF SPHERICAL
POROSITY ON THE ELASTIC MODULI OF GLASS

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During the preparation of a glass for other purposes, it was observed that glass specimens could be obtained containing perfectly spherical porosity. This note reports on the effect of these spherical pores on the overall elastic moduli of the glass.

The glass used was of the same composition as the "D-glass" (15% Na₂O, 15% B₂O₃, 70% SiO₂) employed in a previous investigation.¹ An intimate mix of sodium carbonate, boric acid, and silica was melted in a platinum crucible at 1300°C. The evolution of carbon dioxide and water vapor provided the gases for bubble formation. The relative amount of bubbles in the melt was an inverse function of the length of time the crucible was held at temperature. The melt was held at temperature from about 20 to 40 min, depending on the bubble content desired. Glass specimens (5 x 1/2 x 1/2 in.) were cast in suitable graphite molds preheated to 650°C.

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During forming, the bubbles retained their spherical shape under the influence of the surface tension. After forming, the molds were allowed to cool to room temperature after which the specimens were removed. In this manner a total of 22 specimens were prepared with a pore content ranging from approximately 0.5 to 2.5 volume percent. Because of the uncertainty in the zero-porosity glass density and elastic moduli, no attempt was made to obtain specimens containing no porosity. In addition, this would require retaining the melt at temperature for long periods of time, which conceivably might result in compositional changes in the glass. Figure 1 shows a micrograph of a specimen containing 1.62 volume percent porosity. The micrograph was made by focusing the microscope below the surface of the glass. Because of the relatively high depth of field more porosity is evident than on a volume fraction (or area) basis. Due to experimental difficulties, homogeneous specimens containing pore contents greater than about 2.5 volume percent could not be manufactured.

For the purpose of determining elastic properties the specimens were diamond-sawed and ground to measure approximately 4 in. long, 1/2 in. wide, and 1/4 in. thick. The dimensional accuracy of the length and width was 0.001 in., and for the thickness 0.0005 in. Young's modulus and the shear modulus were determined by a flexural and torsional resonance technique,² thereby yielding two values of Young's modulus and one value of shear modulus for each specimen. From the resonant frequencies, Young's modulus was calculated by means of tables compiled for this purpose.³ The shear modulus was calculated by means of the more precise expression for the shape-factor involved given by Spinner and Tefft.² The porosity was calculated from the true glass density and the bulk density of each specimen calculated from its weight and dimensions. The true glass density was

determined by crushing a number of pieces of glass of each batch and determining the density of the resulting powder by a pycnometer technique. Elastic properties were determined both before and after an annealing treatment. Since the elastic properties of the glass might depend on the thermal history of the specimen, a check was made on the consistency of the properties of the glass itself by means of index of refraction measurements carried out with an Abbé refractometer.*

In order to determine quantitatively the effect of porosity on elastic properties and also the zero-porosity elastic properties of the glass itself, the experimental results were fitted by a least square technique to an expression of the form:

$$\begin{aligned} E &= E_0 (1 - \alpha_E P) \\ G &= G_0 (1 - \alpha_G P) \end{aligned} \tag{1}$$

where E and G are the Young's modulus and the shear modulus, respectively of the porous specimens. E_0 and G_0 represent the Young's modulus and the shear modulus of the nonporous material, α is a constant, and P is the volume fraction porosity.

The theoretical value of α_E can be calculated from the solutions for the effect of spherical porosity on shear modulus and bulk modulus (K_0).^{4, 5, 6} This results in $\alpha_E = 3(9 + 5\nu_0)(1 - \nu_0)/2(7 - 5\nu_0)$, where ν_0 is Poisson's ratio of the nonporous material. The theoretical value of $\alpha_G = 15(1 - \nu_0)/(7 - 5\nu_0)$. The effect of porosity on the bulk modulus and Poisson's ratio can be computed directly from the effect of porosity

*Manufactured by the American Optical Company.

on the shear modulus and Young's modulus by means of the known relationships⁷ between these elastic properties. As a consequence no attempt was made to compute bulk modulus and Poisson's ratio independently for each specimen.

Figure 2 shows the experimental values of Young's modulus and the shear modulus before anneal. Included in Fig. 2 are the values of index of refraction (n). Since within the accuracy of measurement (± 0.0002) the index of refraction is independent of pore content, it appears reasonable to conclude that the changes in Young's modulus and the shear modulus can be attributed primarily to the presence of the pores. In Fig. 2, the lines marked "theoretical" were computed from the theoretical values of α_E and α_G and from the values of E_0 and G_0 determined from the experimental data by the least square technique. Good agreement between theory and experiment exists. The experimental values α_E and α_G are $2.06 \pm 0.06^*$ and $1.94 \pm 0.09^*$, respectively. These values compare favorably with the theoretical values of 2.00 and 2.00 for α_E and α_G , respectively.

The experimental results for the index of refraction and elastic moduli after an anneal appeared confusing. For the particular annealing treatment, identical for each specimen, the most porous specimens had indices of refraction as high as 1.5146, whereas the index of refraction of the most dense specimens remained unchanged. These results indicated that the glass was no longer uniform from specimen to specimen. As a consequence, the effect of anneal was not pursued any further. However, it was of interest to observe that the relative change in Young's modulus was approximately 23 times the relative change in index of refraction (i. e., $\Delta E/E = 23 \Delta n/n$). This is approximately the same relation found by

* Probable error.

Spinner and Napolitano,⁸ who observed $\Delta E/E = 21 \Delta n/n$ for a borosilicate glass. The difference in annealing treatment between specimens can possibly be attributed to the fact that these pores affect the thermal properties or overall viscosity of the glass.

Although the agreement found between theory and experiment over the range of porosity investigated strictly is valid only for the particular glass and technique of specimen preparation employed, it is suggested here that the results obtained can be extended to other materials and methods of preparation as well. It is postulated that the observed discrepancies between theoretical and experimental values of α_E and α_G obtained in previous investigations by various curve fitting techniques,⁹⁻¹² can be attributed primarily to the fact that the actual pore shape obtained deviated from the idealized spherical shape. A similar conclusion was reached by Spinner, Knudsen, and Stone.¹³

The range of porosity investigated presently was not sufficient to draw conclusions with regard to the applicability of Hashin's⁶ upper and lower bounds for higher volume fractions. Presumably some other specimen preparation technique should be employed.

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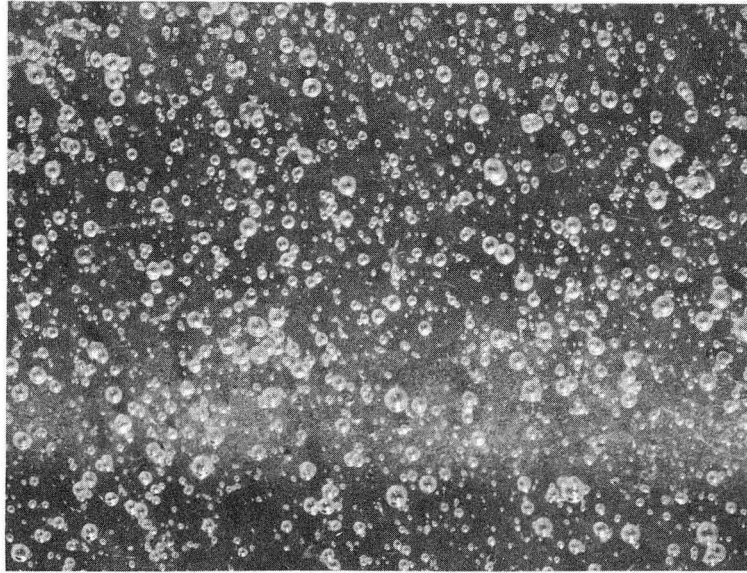
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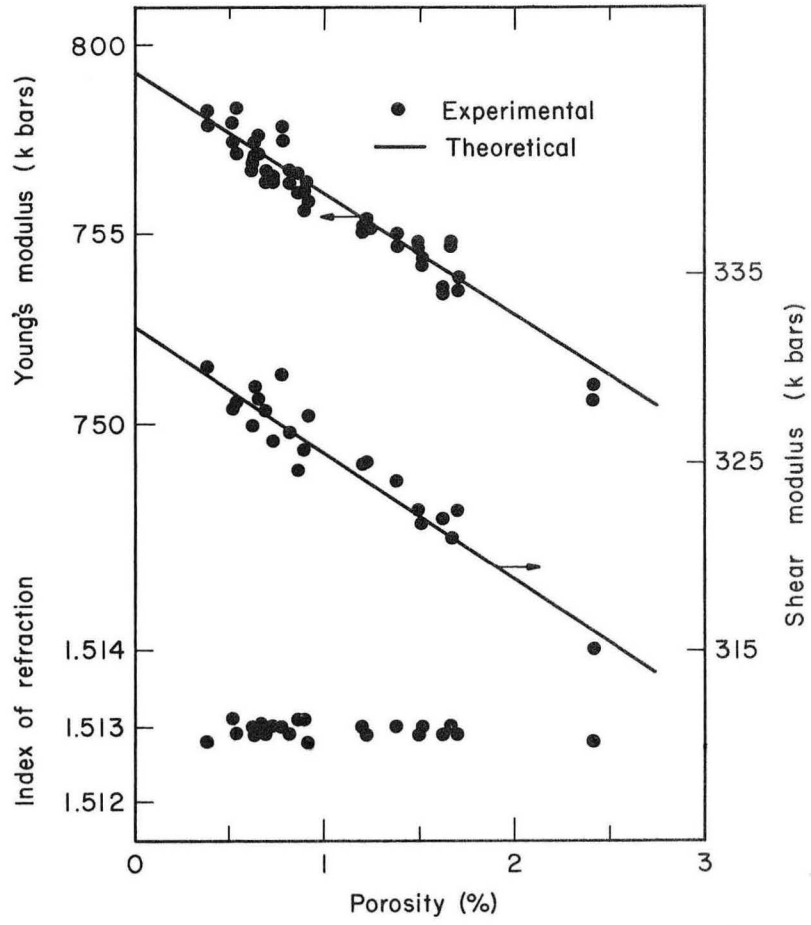
FIGURE LEGENDS

Figure 1. Photomicrograph of specimen containing 1.61 volume percent porosity (X 9).

Figure 2. Young's modulus, shear modulus, and index of refraction as a function of pore content.



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APPENDIX
Experimental Data

Table I. Young's modulus, shear modulus, index of refraction, glass density, and bulk density of glass specimens before anneal.

Specimen number	Young's modulus (kilobars)		Shear modulus (kilobars)	Index of refraction	Glass density (g/cc)	Bulk density of specimen (g/cc)
	E_{fw}	E_{ew}	G	n		
1	779.66	781.93	327.44	1.5128	2.480	2.4545
2	767.60	768.14	322.08	1.5129	2.478	2.4370
3	774.32	774.06	321.25	1.5130	2.476	2.4356
4	787.10	789.16	329.66	1.5130	2.481	2.458
5	787.24	789.93	327.76	1.5131	2.477	2.4644
6	753.33	755.09	315.19	1.5128	2.461	2.4170
7	771.19	771.85	321.79	1.5130	2.482	2.4395
8	776.00	775.94	324.95	1.5131	2.469	2.4473
9	787.11	785.18	329.08	1.5129	2.480	2.4616
10	778.01	781.74	325.72	1.5131	2.470	2.455
12	780.54	783.29	324.59	1.5131	2.471	2.4558
13	767.60	769.24	322.57	1.5129	2.464	2.435
14	773.53	774.08	322.52	1.5129	2.477	2.440
15	783.37	781.97	326.57	1.5129	2.460	2.4571
16	791.22	785.37	328.20	1.5129	2.472	2.4640
18	783.48	781.77	327.66	1.5129	2.469	2.460
19	777.09	776.14	324.99	1.5129	2.479	2.4473
20	784.54	784.28	326.97	1.5130	2.478	2.4617
21	782.16	782.69	326.14	1.5130	2.469	2.4591
22	775.37	773.50	324.05	1.5130	2.466	2.4428
23	791.30	789.35	330.16	1.5128	2.478	2.4677
24	788.28	785.73	328.38	1.5130	2.480	2.4610
					av. 2.477	

Table II. Young's modulus and index of refraction after anneal.

Specimen number	Young's modulus (E_{fw}) (kilobars)	Index of refraction
1	790.58	1.5131
2	--	1.5137
3	787.48	1.5136
4	799.69	1.5136
5	--	1.5140
6	771.41	--
7	--	1.5132
8	778.33	1.5132
9	797.34	--
10	787.35	1.5135
12	785.22	1.5134
13	780.65	1.5133
14	787.45	1.5146 (?)
15	798.25	1.5142
16	--	1.5138
18	788.18	1.5136
19	791.08	1.5136
20	797.61	1.5140
21	793.89	1.5141
22	786.23	1.5136
23	800.79	1.5131
24	796.16	--

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