

## EFFECT OF SHRINKAGE ON THE MODULUS OF SILICA GEL

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Received 17 November 1988

Revised manuscript received 10 February 1989

The shear modulus of alkoxide-derived silica gels was measured during aging and drying; base- and acid-catalyzed gels were examined, and gave qualitatively similar results. There is a continual increase in shear modulus ( $G$ ) during syneresis, which is most rapid for the first two weeks after gelation. If the gel is soaked in a liquid containing more water than the pore liquor, it shrinks and stiffens more rapidly; base-catalyzed gels exhibit phase separation (apparently from segregation of residual partially condensed TEOS). If evaporation is prevented,  $G$  only increases by a factor of  $\sim 2$  upon aging from 1 to 12 months. When the liquid is allowed to evaporate,  $G$  increases by about 3 orders of magnitude as the gel contracts by  $\sim 50\%$  linearly. There is an approximate exponential relation between  $G$  and the radial strain that applies about as well for samples aged in various solutions as for samples dried in air. The relation between  $G$  and strain (contraction) is nearly independent of drying rate when the linear strain exceeds  $\sim 10\%$ . The modulus of rupture rises by about 2.5 orders of magnitude during drying.

### 1. Introduction

It is difficult to make large bodies by the sol–gel process, because they tend to crack during drying. The drying stresses are generally attributed to large capillary forces generated in the very small ( $< 10$  nm) pores of the gel [1]. The magnitudes of the stresses can be calculated, given the permeability and viscoelastic properties of the gel network [2], but prediction of fracture requires knowledge of the strength of the material. The present work is a step toward acquiring the data necessary to evaluate theories of drying. The shear modulus and modulus of rupture have been measured for alkoxide-derived silica gels during aging and drying. A relatively simple relationship is found between the modulus and shrinkage of the drying gels. The permeability is much more difficult to measure; the meager data that have been obtained on these gels will be reported separately.

### 2. Experimental procedure

Silica gels were made according to two recipes. Gel A was an acid-catalyzed gel made by hydro-

lyzing distilled tetraethylorthosilicate (TEOS) using the molar ratios TEOS/H<sub>2</sub>O/C<sub>2</sub>H<sub>5</sub>OH/HCl = 1/16/4/0.01. The solution was refluxed under nitrogen for 2.5 h, then the solvent was stripped under reduced pressure until the density of the solution reached 1.100 g/cm<sup>3</sup>. The stripped solution was cast into plastic pipettes and allowed to gel at room temperature; gelation occurred in 8–14 h. This procedure was developed by Klein et al. [3]. It has been used in this laboratory for studies of structural evolution [4], viscoelastic behavior [5], and syneresis [6]. Gel B2 was made according to the two-step procedure described by Brinker et al. [7,8]. TEOS was first hydrolyzed during refluxing for 1.5 h in a solution (pH  $\approx$  0.3) with molar ratio TEOS/H<sub>2</sub>O/C<sub>2</sub>H<sub>5</sub>OH/HCl = 1/1/3.8/7.3  $\times 10^{-4}$ ; 20 ml of that solution was then mixed with 2 ml of 0.05 M NH<sub>4</sub>OH to produce a final ratio of water/TEOS = 3.7 and pH  $\approx$  7.9. These samples were also cast into pipettes and allowed to gel at room temperature; gelation occurred in  $\sim 2$  h. All of the samples used in this study were in the form of rods 6.0 mm in diameter.

The liquid in the pores of gel A is known [4] to be a 2/1 (by volume) solution of water/ethanol.

The gels were aged ( $\approx 10 \text{ cm}^3$  of gel in  $\sim 500 \text{ ml}$  solution) in this liquid, and in other water/ethanol solutions, including pure distilled water ( $\text{pH} \approx 6$ ) and water adjusted to  $\text{pH} = 2$  by addition of HCl. The later pH is close to the isoelectric point of silica gel, where the rate of syneresis is minimal [9]. Other samples (denoted "dried") were placed in a dish and covered with the pore liquid; the dish was loosely covered so that the liquid could evaporate. This method allowed the rods to dry in a matter of days without significant warping or cracking. The liquid in the pores of gel B2 immediately after gelation was determined by exposing the gel to vacuum ( $\sim 10 \text{ Pa}$ ) while heating at  $70^\circ \text{C}$  for 8 h, and capturing the vapor in a liquid nitrogen trap. The liquid was examined by gas chromatography (GC) and by density measurements (as in ref. [6]), and found to be a 1/9 (by volume) solution of water/ethanol. There may also have been unreacted TEOS, because gels aged in pure water exuded an oil that was found by GC to be heavier than TEOS; we believe it to be partially hydrolyzed and condensed TEOS. Samples of gel B2 were aged in the pore liquid and in other ethanol/water and ethanol/acetone solutions ( $\sim 10 \text{ cm}^3$  of gel in  $\sim 500 \text{ ml}$  solution); others were allowed to dry as described above.

It was explained in ref. [5] that the liquid does not have time to move out of the pores of the deformed gel during a beam-bending experiment, so there is no dilatation of the rod, only shape change. Therefore the measurement gives the shear modulus,  $G$ , rather than Young's modulus:

$$G = \frac{Lw^3}{144yI}, \quad (1)$$

where  $L$  is the load (force),  $w$  is the span of the fixture (5 cm, in this study),  $y$  is the deflection of the beam, and  $I$  is the moment of inertia, which for a solid circular cylinder of radius  $r$  is  $I = \pi r^4/4$ ; the samples had diameters of  $\sim 6 \text{ mm}$ , so the length-to-diameter ratio was  $> 8$ . The volume of the samples is not constant during bending for the fully dried gels, but the data presented here are not corrected for that fact. The difference would only be on the order of 25% [i.e., a factor of  $2(1 + \nu)/3$ , where  $\nu = \text{Poisson's ratio} \approx 0.2$ ], and

we do not know for certain to which samples the correction should be applied. The modulus of the wet gel was measured<sup>1</sup> while the sample was immersed in the same liquid in which it was aged; the apparatus and procedure are described in ref. [5]. Dried gels were immersed in their pore liquid prior to measurement, if their linear contraction was less than  $\sim 30\%$ ; gels dried beyond that point would crack if immersed or if exposed to the open atmosphere. This behavior is not fully understood, but it probably means that the ends of the rods are fully dried, so they crack when immersed, whereas the middle of the rod is still saturated, so it cracks if evaporation is too rapid. Such samples were quickly coated with a Teflon<sup>®</sup> spray and measured without immersion; no cracking occurred with this procedure. The diameter of each sample was determined before the modulus measurement using a gauge<sup>2</sup> accurate to 0.01 mm. The pressure applied to the sample by this device caused slight deformation if the gel was very compliant. For gels with moduli  $\leq 1 \text{ MPa}$ , the error in diameter,  $d$ , was  $\sim 0.09 \text{ mm}$ ; the resulting error in diametral strain, defined by

$$\epsilon_d \equiv 100[d(0) - d(t)]/d(0), \quad (2)$$

was  $\sim 1.5\%$  for the 6 mm rods used here. The error was much smaller for stiffer samples.

### 3. Results

As shown in ref. [5], the gels are viscoelastic, but the relaxation time is on the order of days, while the present experiments required a matter of seconds. Therefore, the samples showed no sensitivity to the rate of loading over the range of 1–100 mm/min; the data presented below were obtained at 10 mm/min. The load/displacement curves were linear up to the point of fracture, so the samples were linearly elastic. Figure 1 shows that there is a general increase in shear modulus with age for samples of gel A subjected to various treatments. However, other factors are obviously of importance. For example, the triangles repre-

<sup>1</sup> INSTRON Model 1122,200–200 g load cell.

<sup>2</sup> Starrett No. 1015MB-881 hand gauge.

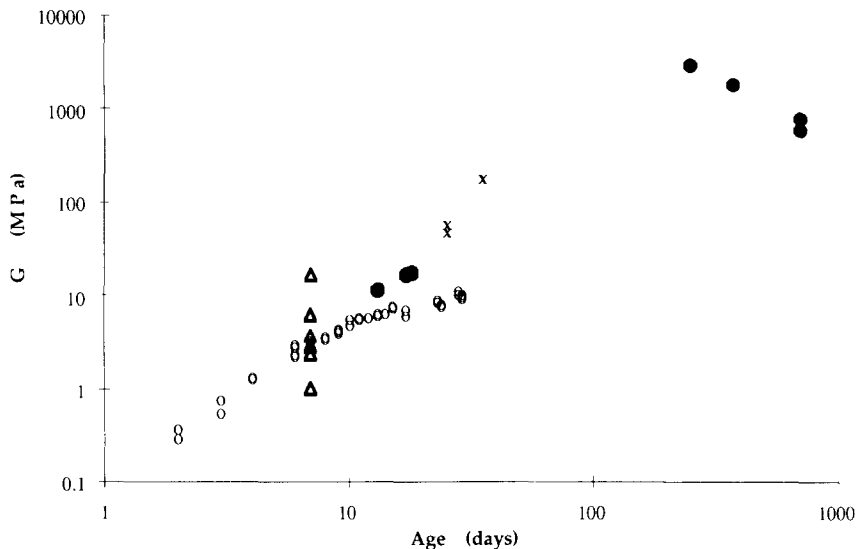


Fig. 1. Shear modulus (MPa) of gel A versus age (days) for: samples aged in (○) pore liquid (67 vol.% water/33% ethanol), (△) other water/alcohol solutions (data from ref. 10), or (x) water at pH 2, and (●) samples allowed to dry.

sent samples aged in various water/ethanol solutions for 7 days; it has been shown [10] that the modulus increases faster for gels aged in higher concentrations of water. As shown in fig. 2, there is a very clear correlation between the diametral strain and the modulus, regardless of the prior treatment. The samples aged in the pore liquid

(open circles) and in other solutions (triangles) fall on approximately the same curve. The steady increase in modulus with age is consistent with results from  $^{29}\text{Si}$  NMR [4] that show an increase in connectivity of the network produced by ongoing condensation reactions between silanol groups in the gel. When the gel is fully dried, the linear

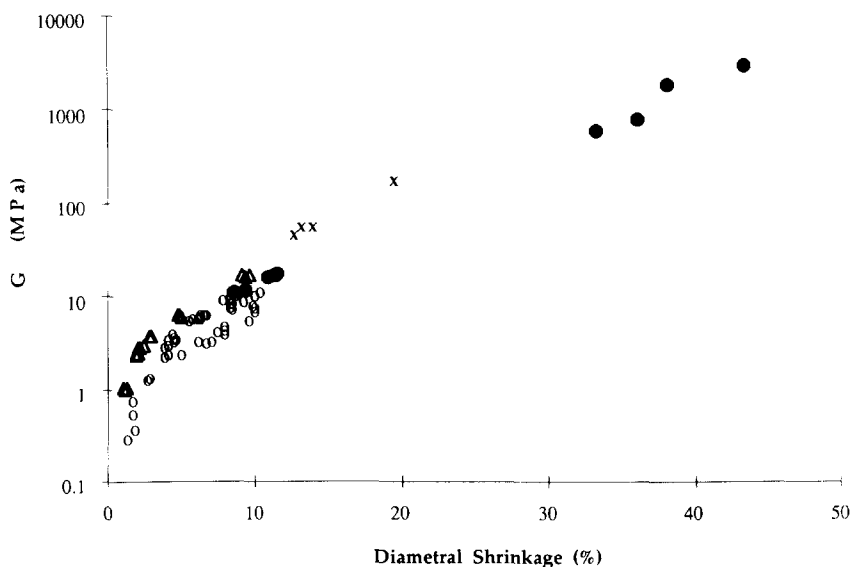


Fig. 2. Shear modulus (MPa) of gel A versus linear shrinkage (%) for same samples as in fig. 1.

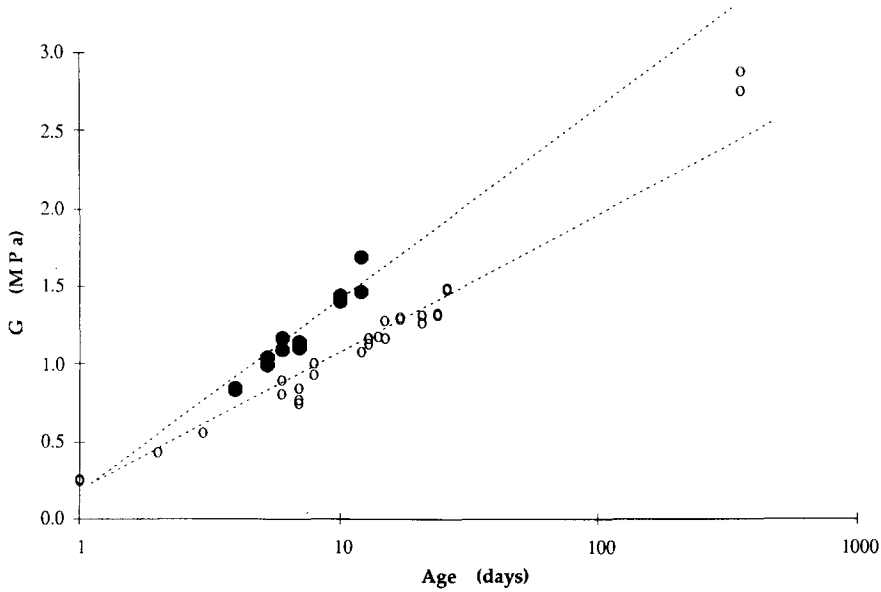


Fig. 3. Shear modulus (MPa) of gel B2 versus age (days) for samples aged in pore liquid (11 vol.% water/89% ethanol) at room temperature (○) or 35°C (●).

shrinkage exceeds 40% and  $G$  reaches  $\sim 3$  GPa. This is in good agreement with the value found by Murtagh et al. [11] for a similar gel.

Figure 3 shows that the modulus of B2 increases with age while soaking in the pore liquid; the increase is somewhat slower at room tempera-

ture (open circles) than at 35°C (shaded circles). Samples aged for 353 days (as a result of being forgotten on a shelf) at ambient temperatures fall between the extrapolations of the data from room temperature (in November) and 35°C. The rate of increase in  $G$  with time would be expected to

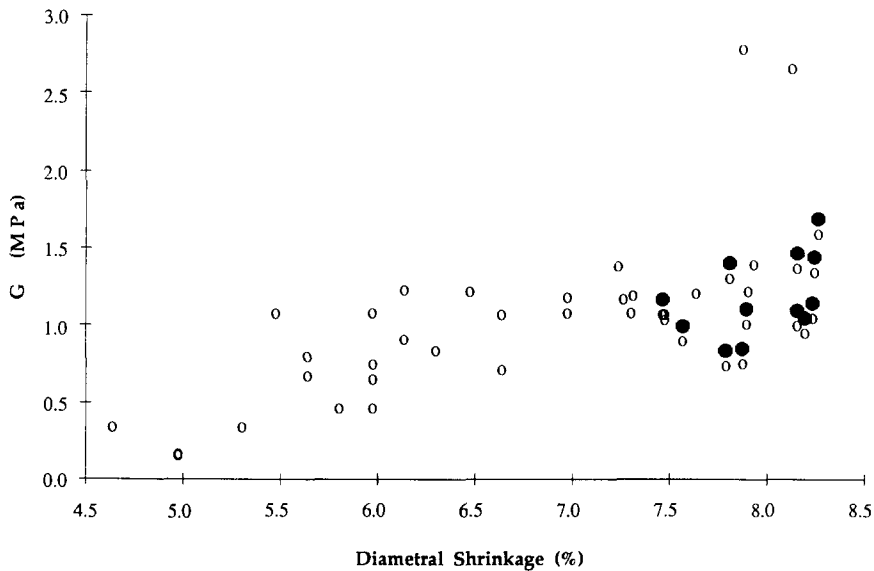


Fig. 4. Shear modulus (MPa) of gel B2 versus linear shrinkage (%) for samples shown in fig. 3.

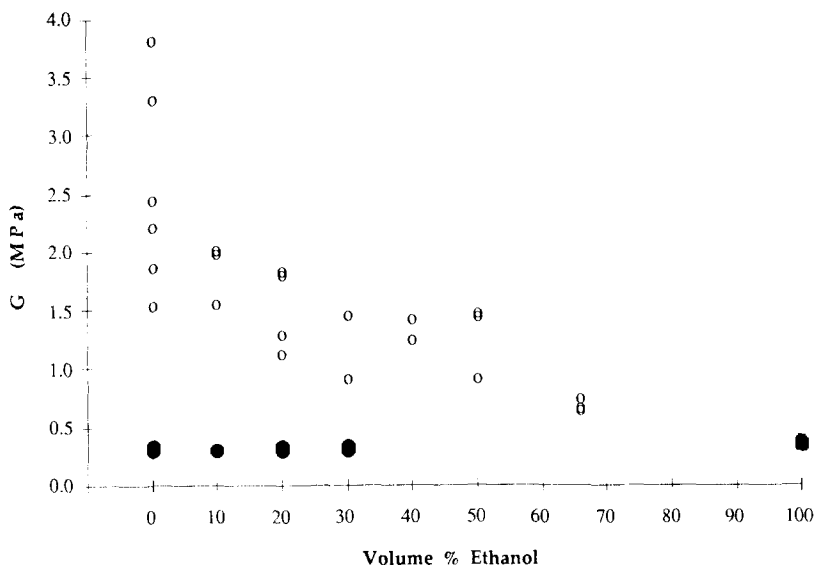


Fig. 5. Shear modulus (MPa) of gel B2 versus vol.% ethanol in soaking solution for samples aged 10–12 days in water/ethanol (O) or 9 days in acetone/ethanol (●).

decrease (as for open circles in fig. 1), rather than increase. The elevated temperatures of the appalling Delaware summer are probably responsible for the high modulus of the old (353 day) samples. The data for the two temperatures come together in fig. 4, where  $G$  is plotted against  $\epsilon_d$ . The scatter in this plot results principally from the error in measuring  $\epsilon_d$  on such soft gels<sup>3</sup>, but this cannot account for the deviation of the old samples (two points near  $G \approx 3$  MPa and  $\epsilon_d \approx 8\%$ ). It appears that there is not a one-to-one relationship between shrinkage and modulus: age can raise the modulus without producing commensurate shrinkage. More persuasive evidence for this idea is presented below.

Figure 5 shows the modulus of samples of B2 aged in ethanol/water (open circles) and ethanol/acetone (shaded circles) solutions. No change is observed in the latter after soaking for 9 days. The samples soaked 10–12 days in solutions containing water shrank and stiffened significantly; as for gel A, the aging rate is faster in solutions containing more water [10]. B2 gels soaked in  $\geq 80$  vol%

water exuded a colorless oil (apparently oligomers derived from TEOS) and the gels became white and opaque. In fact, Brinker et al. [8] detected unhydrolyzed TEOS in the B2 gel by NMR. Scanning electron micrographs shown in fig. 6 reveal circular inhomogeneities 3–5  $\mu\text{m}$  in diameter, which would be large enough to scatter light<sup>4</sup>. We speculate that these are fossils of regions into which the silicate oil separated during ageing. The development of phase separation may account for the greater scatter in moduli measured in distilled water.

The relation between modulus and shrinkage for the B2 gel is shown in fig. 7. The numbers show the age (in days) of the adjacent sample of dried gel (open circles). In some cases the samples were aged in the pore liquid for days or weeks before drying, and in others the drying rate was increased by loosening the cover over the sample. Evidently, the data for the dried samples fall very close to the line, which is given by

$$G(\text{MPa}) \approx 0.13 \exp(0.17\epsilon_d). \quad (3)$$

The crosses at  $\epsilon_d \approx 18\%$  represent samples aged in distilled water, and they also fall on the line. However, the samples aged in the pore liquid

<sup>3</sup> The abscissa of this plot is not much wider than the maximum error bound of  $\pm 1.5\%$ , so the uncertainty in a given datum could move it half way across the plot. The large number of measurements, however, clearly reveals the trend.

<sup>4</sup> See Note added in proof.

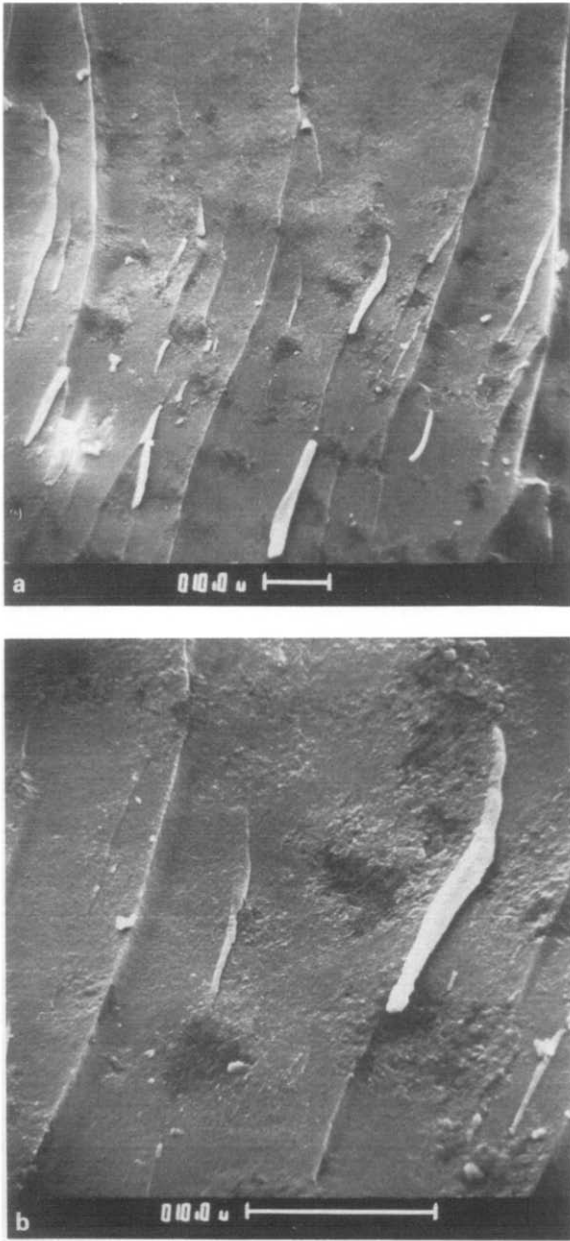


Fig. 6. Scanning electron micrographs of fracture surface of gel B2 after aging in pure water and drying. Opacity of the gel is attributed to the circular regions  $\sim 5 \mu\text{m}$  in diameter (bar =  $10 \mu\text{m}$ ).

(dots) show a stronger dependence of  $G$  on  $\epsilon_d$  than the dried samples; the 353-day-old samples are  $\sim 5$  times higher in modulus than dried samples with the same strain. We attribute this to

skeletal densification that stiffens the network, but causes relatively little shrinkage. Drying produces total shrinkage approaching 50% and a final modulus of 0.5–0.7 GPa. In spite of the shrinkage, the bulk density of the dried gel is only  $\sim 1 \text{ g/cm}^3$  [7], and this contributes to the low modulus.

The modulus of rupture (MOR), determined by the load at which the sample breaks during beam bending [5], shows a trend similar to that for the shear modulus (see fig. 8). There is more scatter, because the strength is influenced by random surface flaws. Assuming that the flaw distribution is roughly the same for all the samples, one may conclude that the structural changes that raise the modulus cause a corresponding (but smaller) increase in MOR.

#### 4. Discussion and conclusions

The chemical reactions that lead to gelation do not stop at the gel point, but continue to produce new siloxane bonds that stiffen the gel network. However, as shown in fig. 3,  $G$  only increases by a factor of two between one month and one year of aging in the pore liquid. This probably reflects the self-retarding nature of the process, as the stiffer network inhibits approach of labile silanol groups. It may be that aging produces reactions between silanol groups that are buried within the solid phase, as well as that fraction of silanols that are close to one another on the surfaces of pores; when those are consumed, shrinkage stops. If this gel is allowed to dry, the capillary forces produce contraction and the modulus of the gel rises by more than two orders of magnitude. Two factors could contribute to increase in modulus: reduction in the porosity and stiffening of the solid phase of the gel. The influence of porosity can be estimated from various models. For example, the Hashin–Shtrikman equation [12] for a porous body with a relative density of  $\rho$  is

$$G(\rho)/G(1) = \frac{\rho(7 - 5\nu)}{15(1 - \nu) - 2\rho(4 - 5\nu)},$$

$$\approx \rho/(2 - \rho), \quad (5a, b)$$

where eq. (5b) applies when Poisson's ratio for the

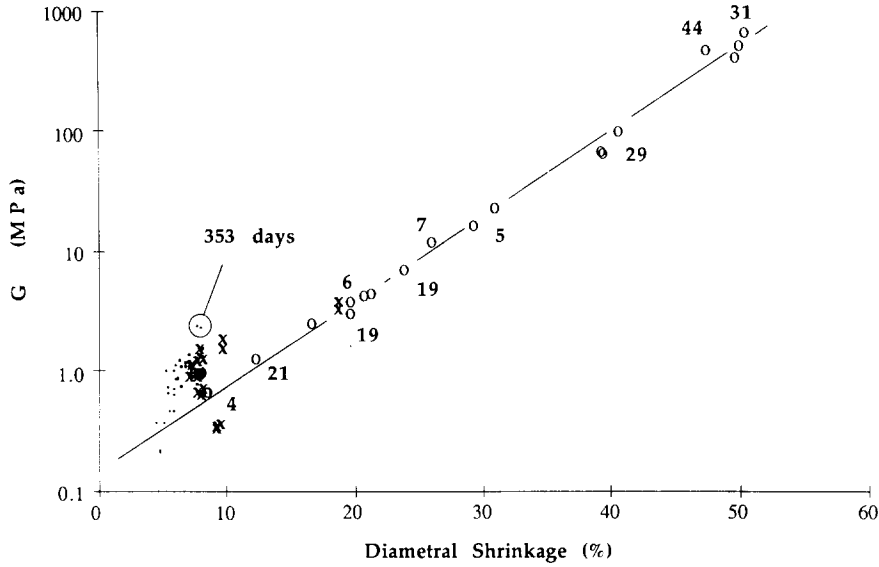


Fig. 7. Shear modulus (MPa) of gel B2 versus linear shrinkage (%) for samples aged in (•) pore liquid (11 vol.% water/89% ethanol), (x) other water/alcohol solutions, or (○) allowed to dry. Numbers indicate ages (in days) of adjacent dried samples, except for 353-day-old samples, which were aged in pore liquid.

solid phase is 0.2 (a typical value for silica and silica gel [11]). Gel A has  $\rho \approx 0.1$  at the gel point and  $\rho < 0.6$  after drying [5], and this model predicts  $G(0.6)/G(0.1) \approx 8$ . From the cylinder model

[13] the shear modulus can be approximated as [14]

$$G(\rho)/G(1) = \frac{3\rho}{6 - 4\rho + \sqrt{3\rho - 2\rho^2}} \quad (6)$$

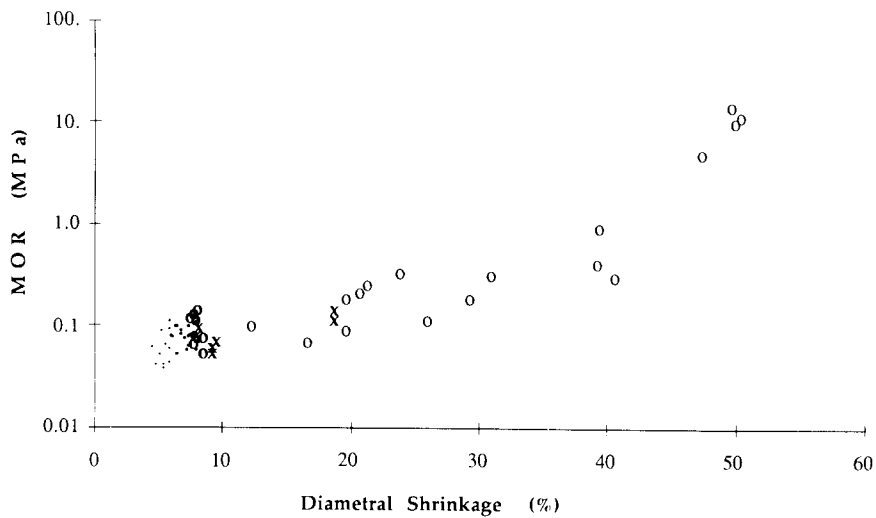


Fig. 8. Modulus of rupture of gel B2 versus linear shrinkage (%) for same samples as in fig. 7.

which leads to  $G(0.6)/G(0.1) \approx 14$ . Thus the models can account for only a small fraction of the increase in modulus during drying, presumably because they assume that the properties of the solid phase are constant as the porosity changes. The more rapid increase observed in  $G$  during drying is believed to result from new bonds formed as the contraction brings silanol groups close enough to condense.

The relationship between  $G$  and  $\epsilon_d$  is not simple, as indicated in fig. 7, because skeletal densification and decreasing porosity influence the modulus independently. During aging in the pore liquid,  $G$  increases with relative little shrinkage. This may be attributed to condensation of crowded silanols within the solid phase or on surfaces of pores, which produces stiff siloxane bonds but results in little volume change. In contrast, capillary stresses generated during drying cause huge shrinkage. The modulus increases because the porosity decreases (providing more load-bearing solid per unit area) and because more condensation is allowed as contraction brings silanols into proximity. Future work should include  $^{29}\text{Si}$  NMR analysis to relate mechanical properties directly to the extent of bonding.

I am indebted to Rose Swiatek for her help in carrying out these experiments, and to the Analytical Services Dept. of DuPont for GC analyses and SEM characterization of the gels.

*Note added in proof:* Recent work by P.J. Davis, C.J. Brinker and D.M. Smith shows that this gel does not become opaque when soaked in water if it is thoroughly washed first in ethanol; that treatment presumably removes the partially reacted TEOS.

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