JOURNAL OF MATERIALS SCIENCE 26 (1991) 6685–6692

# Mechanical strength of particulate silica gels

E. M. RABINOVICH, C. R. KURKJIAN, N. A. KOPYLOV, D. A. FLEMING
*AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974, USA*

The wet and dry strengths of particulate (colloidal) silica gels have been studied. It is shown that these strengths are a function of particle size of the powders composing the sol, and the higher the surface area of the powders, the higher the strength values of the gels. Ageing the wet gels in moulds has no effect upon strength. The effects of binders and modes of preparation of the sols upon strength of the gels were also studied.

## 1. Introduction

Methods of preparation of particulate (colloidal) silica gel bodies have been developed at this laboratory previously [1–5]. Relatively large gel tubes and rods tend, however, to crack during drying, and thus consistent drying without fracture remains as the largest obstacle to manufacturing large glass bodies from gels. The purpose of the present study was to examine various factors affecting the mechanical strength of silica gels.

The procedure developed earlier [1, 2] includes dispersion of fumed silica in water. Some modification in the process has been done to provide for gelation of sols containing powders with relatively low surface area (near 50 $m^2 g^{-1}$). In our previous work [2] fumed silica with the area ~ 200 $m^2 g^{-1}$ or higher was used. There are important advantages in application of larger particles in the process: (1) these particles are packed in bodies with larger pores, and this facilitates drying; and (2) glasses produced from these bodies tend not to bubble on reheating even when no fluoride ion is added [5]. It is, however, more difficult to sinter gels with larger particles and pores into transparent glass.

Various factors affecting the strength are considered here, including several methods for addition of higher surface area powders and binders. The purpose was not only to study the final strength of dry gel bodies (this strength may be irrelevant because cracking and fracture occur in the process of drying) but to investigate wet strength and the change of strength during the drying process. Recently Pardenek *et al.* [6] studied the mechanical properties of wet silica gels and found both strength and modulus of elasticity to increase with ageing.

## 2. Experimental procedure

### 2.1. Materials

The following silicas were used in preparation of the mixtures.

1. Fumed silica Aerosil® of Degussa Corp. [7], grade OX-50, with the BET surface area (SA) near 50 $m^2 g^{-1}$.
2. Fumed silica Cab-O-Sil® of Cabot Corp. [8], grade M5, with the surface area near 200 $m^2 g^{-1}$.
3. Cab-O-Sperse which is a 50 $m^2 g^{-1}$ silica predispersed in water at the Cabot Corp.; this dispersion contains 46 wt % $SiO_2$.
4. Alkoxide-derived materials Nos. 40 (SA = 240 $m^2 g^{-1}$) and 405 (SA = 45 $m^2 g^{-1}$) prepared as previously described [1]. They were precipitated after hydrolysis of tetraethyl orthosilicate (TEOS) in ammoniated water (pH = 11) at the TEOS:Ethanol: $H_2O$–$NH_3$ molar ratio 1:0.5:37.5 for No. 40 and 1:2:4 for No. 405. The powders with parent solutions were aged in closed containers at 60 °C for 24 h and dried at 150 °C.
5. Alkoxide-derived fluorine-containing material 1F-16 prepared as described in [9].

Additional chemicals were used to provide for gelation of low surface area powders and accelerate gelation of all powders. A polyacrylamide type commercial binder was applied.

### 2.2. Preparation of specimens

Sols were prepared by mixing dry silica powder with water and chemicals except in case of Cab-O-Sperse when additional water was not required. The mixture was dispersed either by attrition with fused quartz cylinders in glass jars for 24 h as described in [10] or by mixing for 10 min in a high-speed mixer "Ultraturex" at 8000 r.p.m. When a binder was added, it was also added at this stage as an aqueous solution. The sols were cast into quartz tubes with an internal diameter of 1.1 to 1.25 cm and length of 40 cm which were then stoppered. The time of gelation was determined visually, and on gelation the gels were pushed from the moulds, cut into ~ 4 cm lengths and allowed to dry. If the wet strength was to be determined, the gelled rod was pushed out gradually, specimens of ~ 4 cm length were cut one by one and immediately tested while the rest of the sample continued to be protected from drying in the mould.

Many specimens were aged in the moulds for long periods of time – up to 1 week – before release to measure long-term wet strength or semi-dry and dry strength. To prevent drying during ageing, a small

0022-2461/91 $03.00 + .12 © *1991 Chapman & Hall*

quantity of water was poured on the top of the sample after gelation, in the space between the gel and the upper stopper.

Specimens released from moulds and lying on the table at room temperature at a relative humidity near 50% were arbitrarily described as "semi-dry" if they were tested less than 48 h after the release and as "dry" specimens after longer time periods. Some "dry" specimens were additionally held at 150 °C overnight.

## 2.3. Measurement of mechanical properties

All specimens – wet, semi-dry and dry – were tested using a TM model Instron and a bending device schematically shown in Fig. 1; the direction of bending was upside down and the cross-head speed was 0.51 cm min$^{-1}$. The results were calculated according to equations for bending strength, $\sigma$ in MPa

$$\sigma = \frac{16\,Pa}{\pi d^3} \tag{1}$$

where $P$ is a fracture load (in MN), $d$ the specimen's diameter (in m), $a$ is as defined in Fig. 1; $a = 0.713 \times 10^{-2}$ m.

Two problems arise in the testing of these bodies. The first is that it is desired to test as early in the forming process as possible. It has been shown [6] that these particulate gels have complicated viscoelastic properties, often showing non-linear behaviour. Thus it was decided to postpone a detailed study of their rheology and simply to test at a high enough strain rate ($\dot{\varepsilon}$) to induce fracture with a minimum of an elastic deformation. A satisfactory rate was found to be $0.51 \times 10^{-2}$ m min$^{-1}$. This strain rate was chosen after preliminary stress relaxation experiments, and after consideration of the relaxation time $\tau$ estimated as follows:

$$\tau \sim \mu/G$$

$$\mu \sim 10^{11}\ \text{Pa s}[6]$$

$$G \sim E/3 \sim 0.3\ \text{GPa} = 3 \times 10^5\ \text{N m}^{-2}$$

$$\tau \sim \frac{10^{11}}{3 \times 10^5} \sim 3 \times 10^5\ \text{s}$$

where $\mu$ is viscosity, $G$ shear modulus, and $E$ Young's modulus.

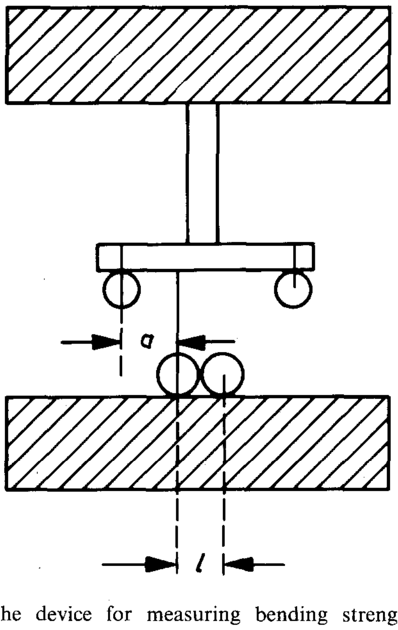

*Figure 1* The device for measuring bending strength of gels. The supports (above) and loading rods (on the bottom) are made of fused silica and glued to the metal supports with epoxy resin. $a = 0.713 \times 10^{-2}$ m, $l = 0.775 \times 10^{-2}$ m.

In addition, similar testing rates were found to be adequate for similar materials by Scherer *et al.* [11].

The second problem was to make meaningful strength measurements on the dried bodies. Since these bodies are brittle and will fail in tension, the condition of the surface will, in all probability, control the observed strength. In some sense that is desirable. The purpose of the study is to probe the mechanisms responsible for sample failure during processing, and thus surface strength and its control are important. On the other hand, it is also important to have a knowledge of the intrinsic bulk property, $K_{\text{IC}}$, the critical fracture toughness

$$K_{\text{IC}} = y\sigma C^{1/2} \tag{2}$$

where $y$ is a constant describing the geometry of a critical crack of length $C$. This value $K_{\text{IC}}$ is a material constant reflecting the intrinsic bond strength rather than a random flaw size, as is measured by the strength.

In the present investigation, $K_{\text{IC}}$ was measured using an empirical technique suggested by Chantikul *et al.* [12] because of the difficulty in measuring $C$. Vickers indents were made at loads ($L$) of 5 to 100 N using a standard Vickers diamond indenter. The failure stresses ($\sigma_{\text{m}}$) of the indented rods were measured to verify that $\sigma_{\text{m}}L^{1/3}$ was constant [12]. $K_{\text{IC}}$ was then evaluated according to

$$K_{\text{IC}} = \eta(E/H)^{1/8}\,(\sigma_{\text{m}}L^{1/3})^{3/4}\ \text{MPa}\cdot\text{m}^{1/2} \tag{3}$$

where $\eta$ is a geometrical constant, $E$ is Young's modulus and $H$ is the hardness; $L$ is in MN and $\sigma_{\text{m}}$ is in MPa [12].

Chantikul *et al.* [12] suggested that for most ceramics $\eta = 0.59$ and $(E/H)^{1/8} \geqslant 0.88$. Accepting the latter value of 0.88, we have $\eta(E/H)^{1/8} = 0.59 \times 0.88 = 0.5$, and Equation 3 can be presented as

$$K_{\text{IC}} = 0.5(\sigma_{\text{m}}L^{1/3})^{3/4} \tag{4}$$

In order to check the validity of Equation 4 in at least mimicking the trends of the "real" $K_{\text{IC}}$, two other measurements of $K_{\text{IC}}$ were made on a representative dry material. In the first case, the "real" $K_{\text{IC}}$ was calculated according to Equation 2 by measuring the crack size produced by the Vickers indent. In the second case, another approximate technique suggested by Anstis *et al.* [13] was employed. In this case a Vickers indent is made at a load $L$ and the crack size rather than the breaking stress is measured. Then

$$K_{\text{IC}} = 0.016\left(\frac{E}{H}\right)^{1/2}\left(\frac{L}{C^{3/2}}\right) \tag{5}$$

While Equation 2 leads to an "exact" value of $K_{IC}$, it clearly depends on the ability to measure $C$. As indicated, this is a difficult measurement in these materials because of poor crack definition, difficult optical microscopy due to intense light scattering from these materials and because of crushing and powdering around the indenter. Estimates of $C$ were made in the SEM. For use in Equation 5, $(E/H)$ is estimated according to the technique of Marshall *et al.* [14], which relies on a measurement of elastic recovery of a Knoop indentation. These three values of $K_{IC}$ for the representative material were

$$\begin{aligned} &\text{Equation 2} \quad K_{IC} = 3.5 \times 10^{-2}\,\text{MPa}\,\text{m}^{-1/2} \\ &\text{Equation 4} \quad K_{IC} = 2.2 \times 10^{-2}\,\text{MPa}\,\text{m}^{-1/2} \\ &\text{Equation 5} \quad K_{IC} = 3.4 \times 10^{-2}\,\text{MPa}\,\text{m}^{-1/2} \end{aligned}$$

The agreement found here is much better than expected since Anstis and Chantikul *et al.* [12, 13] claim no better than about 40% accuracy for their two approximations. In both of these techniques, the empirical constants were derived from measurements on ceramic materials having material properties in the following ranges:

$$\begin{aligned} H &\sim 1\text{–}70\,\text{GPa} \\ K &\sim 0.9\text{–}16\,\text{MPa}\,\text{m}^{-1/2} \\ E/H &\sim 10\text{–}50 \end{aligned}$$

while for these dried gels these values are quite different

$$\begin{aligned} H &\sim 0.01\text{–}0.06\,\text{GPa} \\ K &\sim 0.005\text{–}0.05\,\text{MPa}\,\text{m}^{-1/2} \\ E/H &\sim 5\text{–}100 \end{aligned}$$

The precision and accuracy of the techniques represented by Equations 4 and 5 are not expected to be high. The precision of measuring $C$ is not much better than this, suggesting to us that the experimentally much simpler technique of Equation 4 is justified.

Pore size distributions and bulk densities were determined on pieces dried at 150 °C using Autopore 9200 (Micromeretics).

## 3. Results

### 3.1. Strength of gels made of low surface area powders

The basic sol composition No. 6/7 consisted of OX-50 powder dispersed in water with additives. Table I shows the composition of several sols; all samples were prepared using 150 g of silica. When this quantity was not sufficient for all of the planned tests, a second or third batch was prepared and is indicated with a separate designation number in the table. Wet strengths of composition No. 7 are presented in Table II. As seen from this table, there is practically no increase in the wet strength of gels held up to 1 week (see also Fig. 2).

TABLE I OX-50 based compositions with additions of high-surface area powders (reduced to 100 g $SiO_2$)

| No. | Compositions (g) | | | | |
|---|---|---|---|---|---|
| | OX-50 | No. 40 | M5 | IF-16 | $H_2O$ |
| 6/7 | 100 | 0 | – | – | 164 |
| 5/9/11 | 50 | 40 | – | 10 | 164 |
| 10/12/13x | 50 | 50 | – | – | 164 |
| 14x | 75 | 25 | – | – | 164 |
| 15x | 75 | – | 25 | – | 164 |

The increase in strength of sample No. 7 during the drying process is shown in Fig. 3. It is seen that the deviation in strength increases drastically with increasing strength up to ~ 1 MPa. The preliminary hold of the specimen in the mould for 24 h had no effect on the strength after drying.

### 3.2. Effect of mixing of low- and high-surface area powders on the strength

Three series of gels composed of mixtures of low and high surface area powders were prepared. Two of them were based on OX-50 as a low-surface area powder. Table I shows the compositions of mixtures containing, in addition to OX-50, alkoxide-derived powder No. 40, fluorine-containing powder 1F-16 [9], or high-surface area Cab-O-Sil M5. All higher surface area silicas were added as dry constituents and dispersed together in a ball mill for 24 h. The second series contained three compositions with soluble silica binder (43.3 g for gel No. GO-51 and 86.7 g for gels Nos. GO-48 and 52 per 100 g OX-50). This binder was added to water (163.3 g plus 4.2 g glycerin per 100 g silica) used in preparation of OX-50 sols using the "Ultraturex" mixer. The third series listed in Table III represents ball-milled mixtures of alkoxide-derived powders Nos 405 and 40.

The results for wet strengths for the first two series are presented in Fig. 2. The following conclusions are seen from this figure.

1. Any addition of high-surface area powder significantly increases the wet strength of the gel, as is evident by sample No. 10 which contained 50% of high surface area alkoxide powder (No. 40) and had almost double the strength of conventional samples Nos. 6 and 7. The addition of fluoride-containing (1F-16) powder accelerated gelation but did not have any effect on the wet strength.

TABLE II Comparison of wet strengths of OX-50 specimens

| No. | Wet strength (MPa) after soaking in mould for designated time | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 h | 2 h | 4 h | 8 h | 24 h | 45 to 51 h | 168 h |
| 7 | 0.015 ± 0.001 | 0.018 ± 0.004 | 0.020 ± 0.009 | 0.023 ± 0.005 | 0.019 ± 0.003 | 0.022 ± 0.004 | 0.015 ± 0.004 |

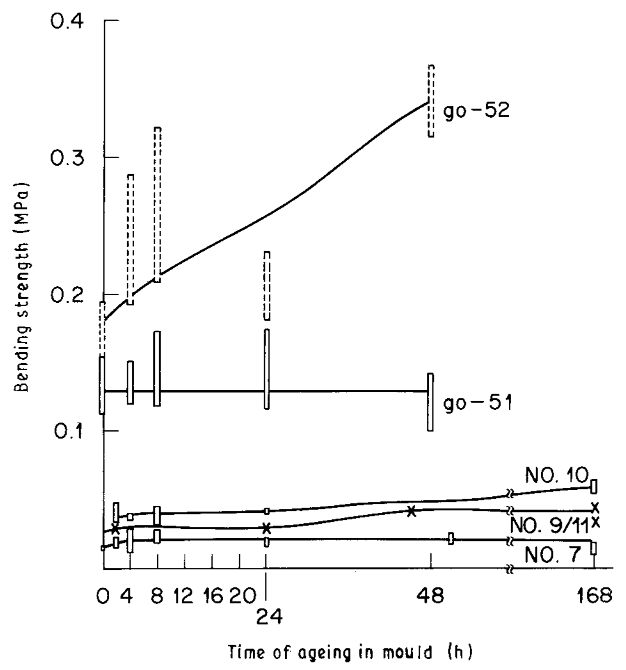

*Figure 2* Wet strength of gel specimens soaked in moulds (the compositions are given in Tables I and III).

2. Addition of even relatively small amount of soluble silica results in a dramatic increase (up to tenfold) in the wet strength. However, these specimens, especially GO-52, appeared very brittle immediately after release from the mould.

3. In most cases, ageing wet gels in moulds had no effect on the bending strength of wet gels with the exception of gel GO-52 where the strength almost doubled during the first 48 h.

The results for development of strength in the process of drying and for dry strength are given in Fig. 3 and in Tables III and IV. The results are typically in the same order as for the wet strength. As the samples dried, the strength increased, and the standard deviation of results increased.

Fig. 4 compares the development of strength in the process of drying for two identically prepared gels No. 7 and No. 6. The former gel first was pushed out of the mould immediately upon gelation, while the latter gel was aged in the moulds for 24 h before removal for drying. There is no significant difference between these gels, which confirms the previous finding that soaking gels in moulds does not noticeably affect the strength of gels in either the wet or dry state.

Table III allows comparison of the mechanical strength of samples to the bulk density and pore size distribution. It shows that sample No. 40 had the lowest bulk density but also the lowest average pore diameter and demonstrated the highest strength. Mixing 50% No. 40 with 50% No. 405 (low surface area) produces a significant increase in the strength compared with pure No. 405 in spite of the increase in the pore volume and the average-pore diameter. A lower water content in the sol (compare A4 and A5) also results in higher strengths of dry gel.

Table V shows the porosimetric data for gels Nos. 7 and 10 containing OX-50 silica. In this case, there is almost no difference in the bulk density, but No. 10 has a much smaller average pore diameter. All gels mixed of two powders show two peaks on the porosimetric curve (Tables III and V).

Heating gels in air at 150 °C for several hours after 2 to 3 days of drying on a table approximately doubles the bending strength.

Compositions 13x, 14x and 15x (Table I) show the effect of additions of dry powders No. 40 and M5 (both high surface area silicas) to OX-50. The wet strengths could be reliably compared after 2 h in the moulds, because gels aged for shorter time periods exhibited significant bending before fracture. As seen from Table IV, the strength of dry specimens does not

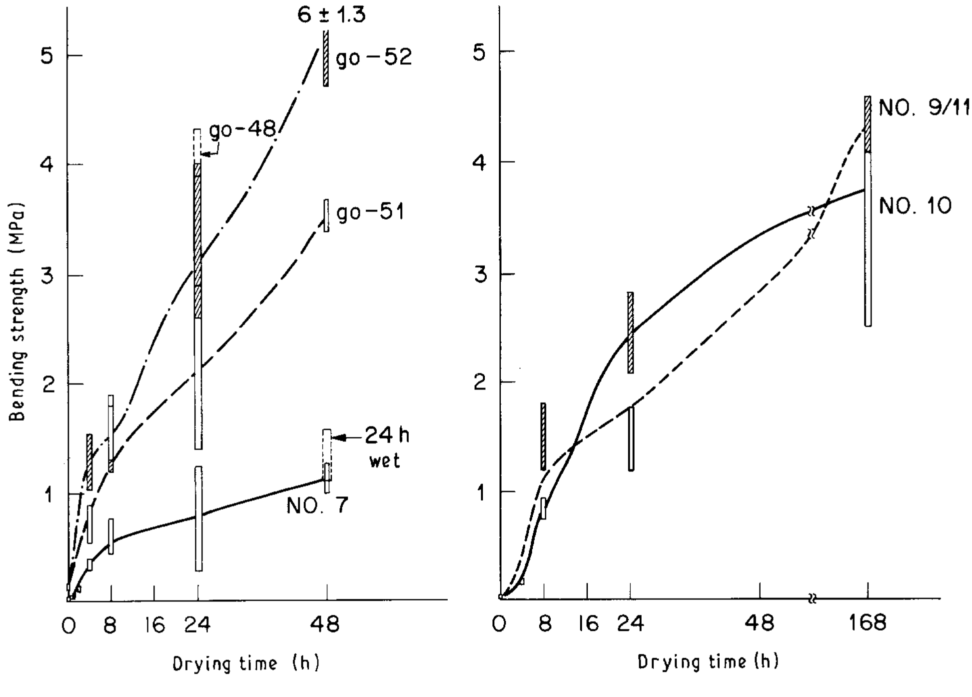

*Figure 3* Development of strength of gel specimens in the process of drying at room temperature (the compositions are given in Tables I and III). All specimens were released from the moulds immediately upon gelation except 1 set of No. 7 specimens held in the mould for 24 h.

TABLE III Dry strengths and porosimetric data of gels made of alkoxide-derived powders Nos. 405 and 40. The compositions are reduced to 100 g $SiO_2$

| No. | Compositions of sols (g) | | | Drying at 20 °C | | Drying at 150 °C | | Data for dried at 100 °C Specimens | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No. 405 | No. 40 | $H_2O$ | σ(MPa) | $K_{IC}$(MPa m$^{1/2}$) | σ(MPa) | $K_{IC}$(MPa m$^{1/2}$) | BET surface area, (m$^2$ g$^{-1}$) | Average bulk density, (g cm$^{-3}$) | Average pore size, (nm) | Amount of maxima of pores | Pore volume (cm$^3$ g$^{-1}$) |
| A1 | 100 | 0 | 126.7 | | | 1.1 ± 0.3 | 0.020 ± 0.002 | 40 | 0.83 | 64.3 | 1 | 0.69 |
| A2 | 100 | 0 | 176.7 | | 0.008 ± 0.001 | 1.7 ± 0.4 | 0.015 ± 0.002 | 45 | 0.83 | 67.3 | 1 | 0.70 |
| A3 | 80 | 20 | 126.7 | 1.5 ± 0.4 | 0.017 ± 0.002 | 3.1 ± 0.7 | 0.047 ± 0.005 | 98 | | | | |
| A4 | 50 | 50 | 126.7 | | 0.031 ± 0.003 | 4.9 ± 0.9 | 0.046 ± 0.004 | 160 | 0.85 | | | |
| A5 | 50 | 50 | 176.7 | 2.5 ± 0.7 | 0.026 ± 0.003 | 4.0 ± 0.8 | 0.036 ± 0.004 | 171 | 0.77 | 16.5 | 2 | 0.77 |
| A6 | 0 | 100 | 176.7 | 4.8 ± 1.2 | 0.045 ± 0.002 | 5.8 ± 1.0 | 0.042 ± 0.006 | 236 | 0.77 | 9.6 | 1 | 0.81 |
| A6a | 0 | 100 | 176.7 | 4.3 ± 0.9 | 0.040 ± 0.003 | 5.8 ± 0.9 | 0.055 ± 0.005 | 263 | 0.76 | 9.4 | 1 | 0.85 |

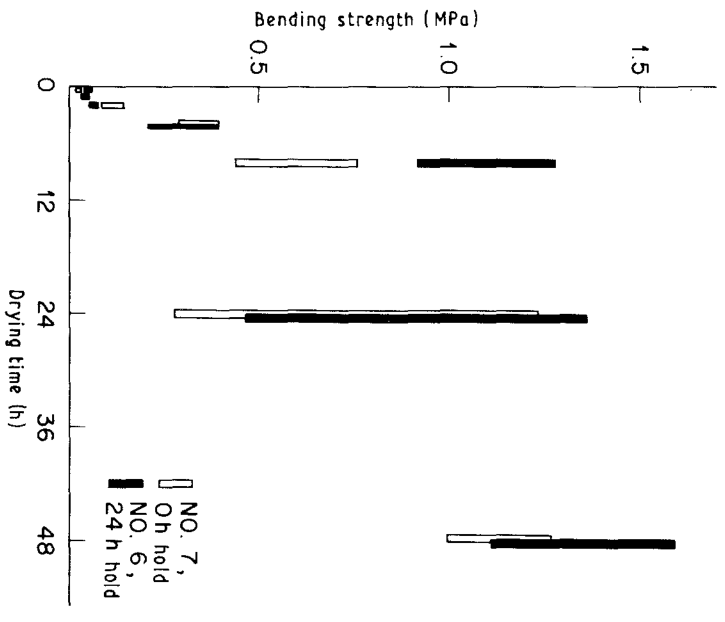

*Figure 4* Comparison of strength of gel specimens released from the mould immediately after gelation (No. 7) and held in the mould for 24 h. (No. 6).

increase appreciably after 48 h on a table (unless subsequent heating was applied). The dry strength of samples containing 25% No. 40 and samples containing 25% M5 are very similar. The dispersions of these strength values are so high that any possible difference is hidden. Samples containing 25% of high surface silica are weaker in the dry state then samples containing 50% of such $SiO_2$, however their immediate wet strength (i.e. strength during the first 2 h) is noticeably higher. The wet strengths of 13x and 14x (containing No. 40 powder) continue to grow up to 4 h, while the value for 15x (M5) peaks at 2 h.

Measurements of the fracture toughness $K_{IC}$ showed that its values have trends similar to the bending strength with several exceptions. Fig. 5 describes this tendency by plotting average values of $K_{IC}$ against average values of the bending strength σ, while it would be cumbersome to plot these values with their standard deviations which, as a rule, were significantly lower for the $K_{IC}$ values than for the σ values. As shown in Tables III and VI, the values for σ and $K_{IC}$ are 0.64 to 5.8 MPa and 0.005 to 0.055 MPa m$^{1/2}$, respectively. This results in a calculated value of 20 to 200 μm for *C*, the naturally occurring crack which controls the strength. On the other hand, some measured values of *C* resulting from the standard 500 g indentation is about 500 μm and thus is large enough to control the failure in these indentation tests.

## 3.3. Effect of binder

The polyacrylamide binder was introduced into fumed silica sols as an aqueous solution. The standard composition contained 100 g OX-50, 160 g $H_2O$ and additives; the binder concentration was varied using 0,

TABLE IV Wet and dry strengths of gels 13x, 14x and 15x

| Gel | Wet strength (MPa) | | | | | | Dry strength[a] (MPa) | |
|---|---|---|---|---|---|---|---|---|
| | 0 h[b] | 1 h | 2 h | 4 h | 24 h | 168 h | 48 h | 168 h |
| 13x (50% OX-50, 50% No. 40) | – | 0.035 ± 0.012 | 0.025 ± 0.005 | 0.039 ± 0.008 | 0.038 ± 0.009 | 0.040 ± 0.009 | 2.9 ± 0.6 | 3.5 ± 0.5 |
| 14x (75% OX-50, 25% No. 40) | – | 0.020 ± 0.002 | 0.026 ± 0.005 | 0.031 ± 0.005 | 0.031 ± 0.004 | 0.040 ± 0.003 | 2.4 ± 0.6 | 1.7 ± 0.9 |
| 15x (75% OX-50, 25% M5) | 0.026 ± 0.008 | – | 0.057 ± 0.005 | 0.048 ± 0.009 | 0.045 ± 0.005 | 0.028 ± 0.007 | – | 2.2 ± 0.5 |

[a] The specimens were released from the mould immediately upon gelation and dried on a table.

[b] The measurements were taken during the first 15 min after gelation.

TABLE V Mercury porosimetry data for dry gels Nos. 7 and 10

| Parameter | Gel No. 7 (OX-50) | Gel No. 10 (OX-50 + No. 40) |
|---|---|---|
| Total pore volume ($cm^3 g^{-1}$) | 0.95 | 0.89 |
| Pore area ($m^2 g^{-1}$) | 78 | 219 |
| Bulk density ($g cm^{-3}$) | 0.71 | 0.74 |
| Average pore diameter (nm) | 48.8 | 16.2 |
| Amount of peaks on the Hg porosimetry curve | 1 | 2 |
| The peaks are at pore diameter (nm) | 44.4 | 79.9 and 44.4 |

TABLE VI Effect of mode of dispersion on strength

| Condition of specimens | Bending strength $\sigma$(MPa) values in parentheses are $K_{IC}$(MPa $m^{1/2}$) | | |
|---|---|---|---|
| | M1 | M2 | M3 |
| Wet, held in mould for 2 h | 0.021 ± 0.002 | 0.025 ± 0.002 | 0.025 ± 0.003 |
| Wet, held in mould for 2 h at 60 °C | 0.013 ± 0.005 | 0.017 ± 0.005 | 0.032 ± 0.006 |
| Wet, held in mould for 49 to 50 h | 0.029 ± 0.003 | 0.015 ± 0.002 | 0.030 ± 0.004 |
| Wet, held in mould for 168 h | 0.018 ± 0.005 | 0.019 ± 0.006 | 0.025 ± 0.003 |
| Dried on table for 48 to 52 h | 0.95 ± 0.23 | 0.64 ± 0.35 | 0.32 ± 0.03 |
| Dried on table for 72 h | 0.92 ± 0.16<br>(0.0074 ± 0.0009) | 1.02 ± 0.43<br>(0.005 ± 0.001) | 0.62 ± 0.23<br>(0.008 ± 0.001) |
| Dried on table for 72 h + 24 h at 150 °C | 1.82 ± 0.37<br>(0.011 ± 0.001) | 1.62 ± 0.62<br>(0.012 ± 0.003) | 2.09 ± 0.26<br>(0.011 ± 0.002) |

1, 2, 3 and 4 g per 100 g of silica. Several similar compositions were also prepared using predispersed silica Cab-O-Sperse (46 wt % $SiO_2$ in water) rather than OX-50. Fig. 6 shows the strength results for the OX-50 mixtures. The relationship between strength and toughness is given in Fig. 5. As seen from Fig. 6, 1 or 2% of the binder slightly increased the strength of the material in the initial stages of drying, but the final dry strength of the gel did not increase and in some cases even decreased with these admixtures. Addition of 3% of binder increased the wet strength even more but the rate of gelation was too high, and the resulting sintered glass contained many bubbles. The general level of the "dry" strength of all these specimens was low.

Specimens made of Cab-O-Sperse had about the same wet strength as the OX-50 specimens but their level of strength upon drying was somewhat higher although not reproducibly. Additions of as little as 0.7 g polyacrylamide per 100 g $SiO_2$ increased the wet strength by 50% but had little effect on the dry strength.

Similar to the earlier specimens, heating these specimens at 150 °C significantly increased the strength. One experiment was, however, done only with Cab-O-Sperse specimens containing 1 g polyacrylamide per 100 g $SiO_2$. Several specimens were put in the cold drying oven, heated to 150 °C (~ 2 h) and kept at this temperature for 2 h (half of these specimens) or overnight (the other half). Yet another portion of the just released completely wet specimens was put in a preheated 150 °C oven and kept overnight. It was surprising to see that this thermal shock did not diminish the final result. The strength of the slowly heated, kept overnight, specimens was 2.3 ± 0.6 MPa as against 2.4 ± 0.6 MPa for the rapidly dried specimens. The slowly heated specimens kept only 2 h at 150 °C had the same strength as specimens dried on the table for 72 h: 1.0 ± 2 MPa.

## 3.4. Effect of the mode of dispersion

The effect of the method of dispersion was studied on gels containing polyethylene glycol (PEG) binder

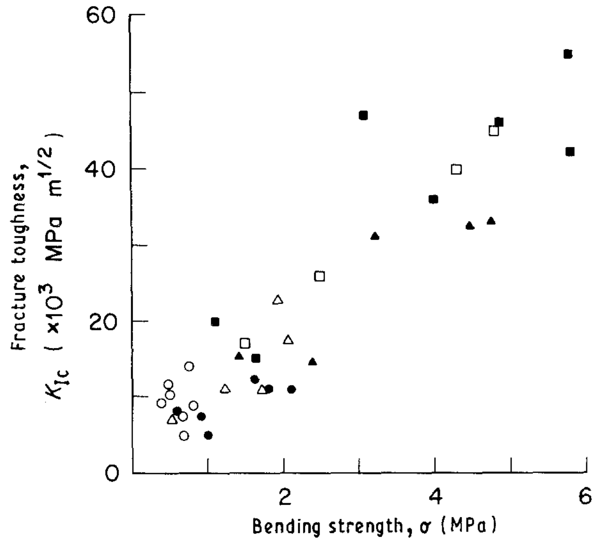

*Figure 5* Fracture toughness values ($K_{IC}$) for different dry gels plotted against their bending strengths (σ): triangles – OX-50 and its mixtures with M5 and No. 40; open circles – OX-50 with polyacrylamide binder; squares – mixtures of Nos 405 and 40; filled circles – OX-50 with PEG; open triangles and squares relate to specimens dried at 20 °C, blank – to those dried at 150 °C.

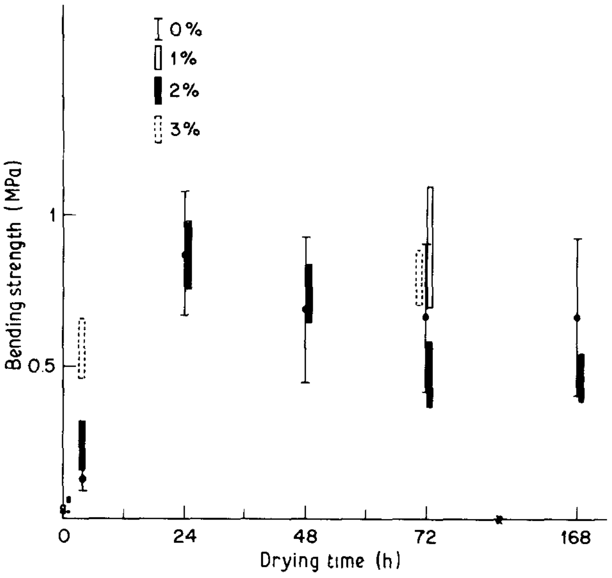

*Figure 6* Development of the strength of OX-50 gel containing 0, 1, 2 or 3% of polyacrylamide binder in the process of drying. To facilitate plotting, the symbols were slightly moved left or right of the exact time mark, these deviations do not mean real deviations in drying times.

having a molecular weight 3400. The composition contained 100 g $SiO_2$ introduced as Cab-O-Sperse, 121.4 g $H_2O$ (from Cab-O-Sperse and the PEG solution), 2 g of solid PEG introduced as a 33.3% aqueous solution, and gelation additives. The sol was prepared in a large batch containing 600 g $SiO_2$, mixed in a blender and divided into three equal parts:

1. M1 was cast immediately after the mixing in blender;
2. M2 was additionally mixed in the "Ultraturex" machine for 10 min and cast;
3. M3 was dispersed with fused silica cylinders in a glass jar (ball milling) for 24 h and cast.

The results of mechanical tests of these three batches are given in Table VI. As seen, all specimens show about the same "wet" and "dry" strength, although the strength at 48 h diminished with increase in the degree of dispersion. Apparently, more dispersed specimens are slower to dry, and they are not fully dried after 48 h under ambient conditions. Again, neither specimen showed any advantage in the wet strength if held in the moulds up to 1 week, and soaking in the mould at elevated temperature (60 °C) did not improve the strength. This absence of the difference was, however, found in the mixtures prepared of preliminary well dispersed silica of Cab-O-Sperse.

Versions M2a and M3a were prepared with addition of 25% of high-surface area powder M5, and they showed no advantage either in wet or dry strength; the dry strength of specimen M3a was even lower than that of M3.

## 4. Discussion

This study showed that the only way to significantly increase the wet and dry strengths of gels is to mix low-surface area powders with high-surface area powders without addition of binders. In fact, Table III shows that the strength and the toughness are simply functions of the surface area; the higher the surface area, the higher the strength.

The simplest explanation for this phenomenon is that the particles of different sizes provide better packing but this is not the case. The particles used in this experiment are not monosized and gels prepared from the lower surface area powder alone have the highest bulk density (Table III). Apparently, high surface area powders may dissolve and precipitate in the neck areas of contact between the larger particles forming strong bonds between these particles (Ostwald ripening).

On the other hand, molecules of binders apparently coat silica particles and do not encourage formation of strong necks, hence, their modest or zero effect on strength.

## 5. Conclusions

The conclusions are as follows.

1. Wet strength and dry strength of low-surface area silica powders can be significantly increased by mixing these powders with higher surface area powders.
2. Drying of gels at 150 °C significantly increases their strength in comparison with gels dried only at room temperature.
3. Additions of fluoride-containing powders to low surface area powders does not significantly increase the strength.
4. Additions of polyacrylamide binder increases wet strength but has no effect upon dry strength.
5. Soaking of wet gels in moulds before drying has no effect upon the wet and dry strength.
6. The drier the specimen, the higher its strength, but the dispersion of strength values also increases;

the fracture toughness measurements show lower deviation.

## Acknowledgements

The authors thank D. W. Johnson, Jr and J. B. MacChesney for helpful discussions.

## References

1. E. M. RABINOVICH, in "Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty Shapes", edited by L. C. Klein (Noyes, Park Ridge, NJ, 1988) pp. 260–294.
2. E. M. RABINOVICH, D. W. JOHNSON, Jr., J. B. MacCHESNEY and E. M. VOGEL, *J. Amer. Ceram. Soc.* **66** (1983) 683.
3. D. W. JOHNSON, Jr., E. M. RABINOVICH, J. B. MacCHESNEY and E. M. VOGEL, *ibid.* **66** (1983) 688.
4. E. M. RABINOVICH, J. B. MacCHESNEY and D. W. JOHNSON, Jr., in "Science of Ceramic Chemical Processing", edited by L. L. Hench and D. R. Ulrich (Wiley, New York, 1986) pp. 206–216.
5. E. M. RABINOVICH, D. L. WOOD, D. W. JOHNSON, Jr., D. A. FLEMING, S. M. VINCENT and J. B. MacCHESNEY, *J. Non-Cryst. Solids* **82** (1986) 42.
6. S. A. PARDENEK, J. W. FLEMING and L. C. KLEIN, in "Ultrastructure Processing of Advanced Ceramics", edited by J. P. Mackenzie and D. R. Ulrich (Wiley, New York, 1988) pp. 379–389.
7. R. BODE, H. FERCH and H. FRATZSCHER, Techn. Bull. Pigments, No. 11, Degussa, Frankfurt (Maine) (1978).
8. Cab-O-Sil Properties and Functions, Cabot Corp., Tuscola, IL (1983).
9. D. L. WOOD and E. M. RABINOVICH, *J. Non-Cryst. Solids* **82** (1986) 171.
10. D. W. JOHNSON, Jr., E. M. RABINOVICH, D. A. FLEMING and J. B. MacCHESNEY, *J. Mater. Sci.* **24** (1989) 2214.
11. G. W. SCHERER, S. A. PARDENEK and R. M. SWIATEK, *J. Non-Cryst. Solids* **107** (1988) 14.
12. P. CHANTIKUL, G. R. ANSTIS, B. R. LAWN and D. B. MARSHALL, *J. Amer. Ceram. Soc.* **64** (1981) 539.
13. G. R. ANSTIS, P. CHANTIKUL, B. R. LAWN and D. B. MARSHALL, *ibid.* **64** (1981) 533.
14. D. B. MARSHALL, T. NOMA and A. G. EVANS, *ibid.* **65** (1982) C-175.

*Received 12 March*
*and accepted 4 September 1990*