Discussion

A comparison of gel pore volumes obtained by three methods

In a recent paper Brinker and Mukherjee (BM) [1] report their investigation of the conversion of monolithic silicate gels to glasses at elevated temperatures. They show that to convert gels to dense, organic-free glasses at temperatures near the glass transition temperature, it is necessary to hydrolyse the alkoxide precursors with excess water (Process I); incomplete hydrolysis leads to glasses which cannot be fully densified. This Discussion comments on the densification behaviour of Process I gels. Gel specific pore volumes as a function of treatment temperature are calculated from the authors' data using three independent methods.

1. Bulk pore volume. To determine the bulk pore volume, PV_B, we imagine that the gel is a porous glass consisting of two components: pores or voids of zero density, and a polymer or glass backbone of the same density as the fully densified glass, $2.27\,\mathrm{g\,cm^{-3}}$. This is not quite correct, however: it neglects the water and organics trapped in the gel (important at low temperature); it does not take into account the density change of the polymer backbone with temperature (more important at high temperature); and it assumes that the backbone structure, and hence density, is the same in the gel and the bulk glass (see later discussion of the fictive temperature of the backbone). Nevertheless we will use this model to calculate the bulk pore volume:

$$PV_B = \rho_{\text{gel}}^{-1} - \rho_{\text{glass}}^{-1}. \qquad (1)$$

Bulk pore volumes for Process I gels as a function of temperature are reported in Table I and in Fig. 1, using the density data of BM. BM report in colume 5 of Table I the volume fraction of pores, obtained by multiplying the pore volume by the gel density. Their numbers thus tend to understate the effect of temperature on the bulk pore volume.

2. BET pore volume. The pore volume may be determined from BET analyses of nitrogen adsorption–desorption isotherms, with the caveats discussed by BM. Using their surface area, *SA*, and mode pore radius, *MPR*, data, and assuming that the latter quantity remains constant above 500° C (a worst case – the pores must collapse eventually), we have

$$PV_{\text{BET}} = \frac{SA \cdot MPR}{2}. \qquad (2)$$

BET pore volumes are reported in Table I and Fig. 1; they agree with those calculated by BM.

3. Oil-immersion pore volume. In a second paper [2], Brinker and Mukherjee (BM2) exploit an elegant idea. They corroborate their BET pore volume determinations with refractive index measurements taken in two modes: on gels immersed in index-matching oils, which presumably could permeate the (continuous) pores, thereby measuring the refractive index of the polymer backbone; and on a prism of a gel monolith using the minimum deviation method, thus measuring the average refractive index of the bulk gel. We propose, however, to push BM2's idea further by reversing their formula [5]. Thus the two refractive index measurements may be used to calculate the volume fraction of pores, *P* and the pore volume PV_{RI}:

$$\rho_{\text{gel}} \cdot PV_{\text{RI}} = P = 1 - \frac{f(n_{\text{md}})}{f(n_{\text{oil}})}. \qquad (3)$$

BM2 use $f(n) = n^2 - 1$ to relate refractive index to pore volume. However, assuming that the gel structure may be represented by a polymer backbone and voids, the proper scaling relation is

TABLE I Specific pore volumes ($\mathrm{cm^3\,g^{-1}}$) for Process I gels

Treatment temperature (° C)	Method		
	Bulk density	BET surface area	Refractive index
100	0.63		
150	0.63	0.39	
200	0.63		0.28
250	0.62	0.40	
300	0.58		0.28
350	0.56		
400	0.51	0.34	0.28
450	0.49		0.28
500	0.44	0.32	0.27
550	0.33	0.20	0.16
575	0.23		0.03
600	0.13	0	0
625	0.03		

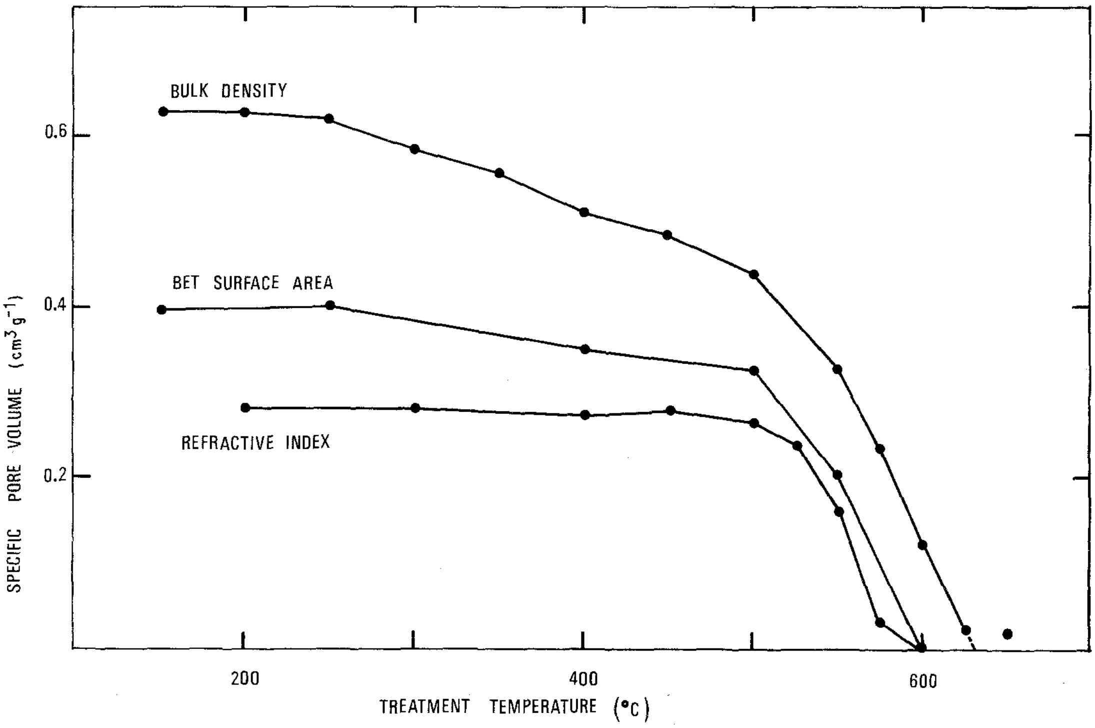

Figure 1 A comparison of gel pore volumes obtained by three methods.

$$f(n) = \frac{n^2-1}{n^2+2}.$$

This is based on the Clausius–Mossotti relation [3], and the fact that the electronic polarizability average per unit volume for a backbone/void model gel is simply the backbone polarizability diluted by the amount of void present. The defects of this model discussed earlier in the density section apply equally here (since density and refractive index behave similarly), but we will nevertheless use this model and the Clausius–Mossotti relation to derive a relationship between the specific pore volume and the two refractive index measurements:

$$PV_{\mathrm{RI}}\rho_{\mathrm{gel}} = 1 - \frac{n_{\mathrm{m}}^2-1}{n_0^2-1}\,\frac{n_0^2+2}{n_{\mathrm{m}}^2+2}. \qquad (4)$$

The results of pore volume calculations using this method are presented in Table I and Fig. 1.

Pore volumes determined by the three methods all show similar dependence on the treatment temperature – rather constant at low temperatures, and decreasing more or less abruptly to zero near 600° C as conversion from gel to glass occurs.

The three methods, however, yield different values for the pore volume. This is understandable if we assume that some pores are not part of the continuous pore network shown to exist by helium permeability measurements. In this case the isolated pores are not accessible to either nitrogen gas or an index oil, so the BET and refractive index techniques sample only the continuous pores. Of the two methods the BET data are less straightforward to interpret (see the caveat and discussion in [1]), so we will use the refractive index data as a measure of the accessible pore volume. We may then divide the accessible pore volume by the bulk pore volume to obtain the fraction of continuous pores. This is shown in Fig. 2 as a function of treatment temperature. At low temperatures roughly half the pores are part of the continuous network, and half are isolated. This analysis supports and quantifies BM2's suggestion that the gel contains isolated micropores.

This interpretation is more satisfying than BM2's alternative explanation that the discrepancy in pore volume determinations could arise from assumptions about the polymer backbone structure, and not from the presence of isolated pores. They speculate that the backbone structure might be similar to that of a glass with a high fictive temperature, so that the backbone density would be lower than the density of the annealed glass. If all

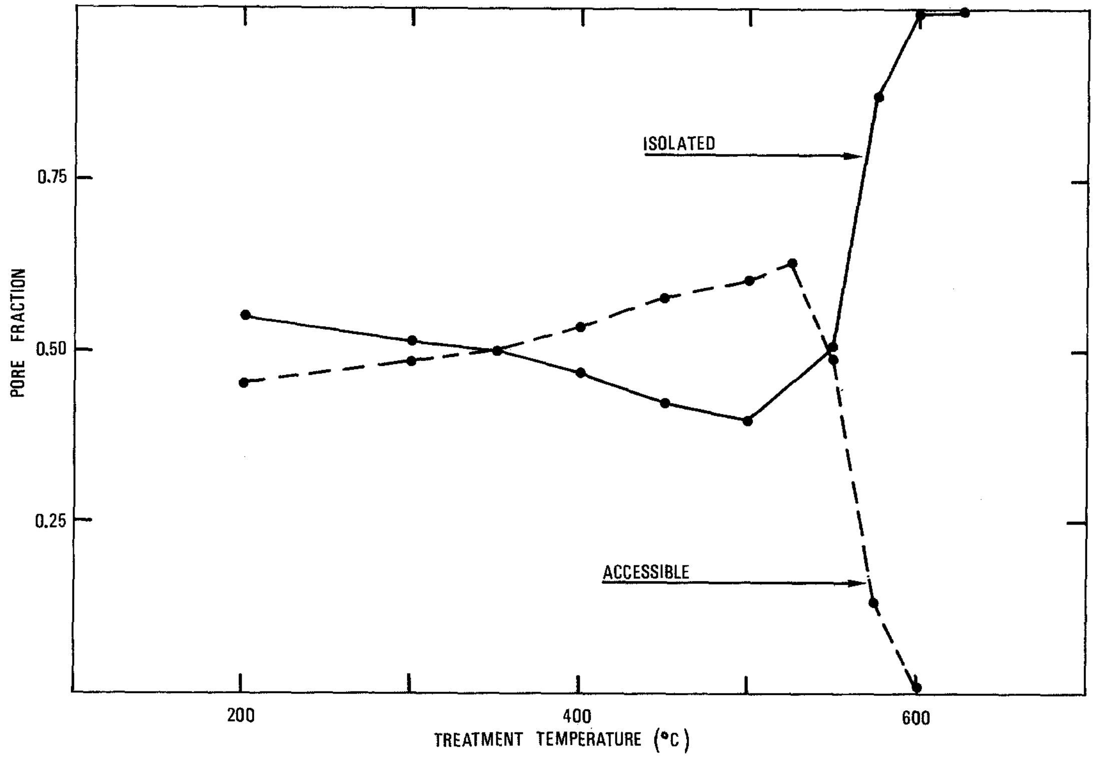

Figure 2 Fraction of continuous and isolated pores in a gel after heat treatment.

pores are accessible, Equation 1 may be inverted to determine the polymer backbone density. At 500° C this yields densities of 1.63 and 1.80 g cm^{-3}, using pore volumes determined by refractive index and BET methods, respectively. Both values are far too low to be physically reasonable. In addition, the difference in annealed glass (1.480) and Becke-line (1.442) refractive indices is much larger than normally associated with differences in fictive temperatures of otherwise identical glasses [4]. Thus, even though a high fictive temperature of the polymer backbone cannot be ruled out, it cannot account for the discrepancy in pore volume determinations.

In the gel-to-glass transition region at 525 to 625° C the refractive index and BET pore volumes parallel each other and go to zero at the same temperature, thus giving support to the idea that they are sampling the same accessible pore volume. In addition, the accessible pore volume vanishes at a lower temperature than the total pore volume as determined from density measurements. This analysis predicts that only isolated pores exist over a small temperature interval in the transition region.

In conclusion, we have combined bulk density determination on Process I gels as a function of treatment temperature with refractive index measurements with and without an immersion oil to estimate the amount of continuous pore structure in a gel monolith. At low temperature about half the pore volume is isolated, whereas in the gel-to-glass transition region all the pores become isolated before collapse to the dense glass finally occurs. It would be worthwhile to verify this with more detailed time–temperature measurements of the refractive index, or with helium permeability measurements in the transition region.

References

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