JOURNAL OF MATERIALS SCIENCE **31** (1996) 1335–1340

Formation of a compatible composite of silica/poly(vinyl alcohol) through the sol–gel process and a calcinated product of the composite

FUMIO SUZUKI, KOJI NAKANE, JIN-SHUN PIAO
Faculty of Engineering, Yamagata University, 4-Johnan Yonezawa, 992 Japan

A transparent composite film of poly(vinyl alcohol) (PVA) and silica was obtained through the sol–gel process using tetraethoxysilane (TEOS). By ESCA and X-ray diffraction measurements on the composite, it is confirmed that the PVA and silica were intimately mixed together. The Young's modulus increased with increasing silica content in the PVA, but the tensile strength decreased from 84 for pure PVA to 40 MPa (as the PVA content reaches 50 wt%). A maximum value of 145 MPa was observed for the 80% PVA composite. The composite could be drawn to 2 ~ 3 times its original length under saturated humidity conditions. The modulus and the tensile strength were increased by a factor of two by the drawing of the as-cast composite film. The residuals created by the removal of PVA from the composite films were transparent and showed a surface area of about 500 $m^2 g^{-1}$ (in the case of 80% PVA as the original material). The residuals showed permeability for gases. The gas permeability of the residuals rapidly increased with the PVA content in the original materials.

1. Introduction

In recent years, the appearance of the sol–gel process has radically altered glass making technology [1]. This process has stimulated the development of various kinds of functional glasses [2, 3], in particular, glass composites containing organic compounds including polymer substances. There are many reports for composites of glass with low molecular weight organic compounds, for example, silica doped with photochromic compounds (Qunizarin, Acridine, Rhodamine 6G), [4, 5] and also the photochemical hole burning reagent (1,4-dihydroxyanthraquinone) [6]. Moreover, by using copolymerization techniques, G.L. Wilkes *et al.* [7], H. Schmidt *et al.* [8] and Y. Imai *et al.* [9] have reported about hybrid glass/organic polymer materials that have interesting mechanical and/or optical properties. Simple blends of glass/organic polymers have been used in several kinds of composite. We have already reported on the formation of a compatible composite of alumina/PVA, which can be drawn to about 5 times its original size under saturated humidity, and also on its structure and some mechanical properties [10]. S. Ikoma *et al.* have reported the existence of a radical using ESR techniques [11] in the silica–sol mixed with PVA and warmed to 80 °C, but they were unable to discuss the structure or properties of the composite. In this paper we present a discussion on the formation of the composite between PVA and silica obtained by a sol–gel process. We will not only discuss the composite but also present data on the silica created after the PVA is burnt off from the composite. The properties were probed using ESCA, X-ray diffraction, adsorption and gas permeation techniques.

2. Experimental

2.1. Apparatus

The film properties were probed using a Shimadzu ESCA 1000. The X-ray diffraction, mechanical properties and the dynamic mechanical spectra were measured using a Rigaku Electric RAD-rA, a Toyo-Bowldwine Tensilon UMT-III500 and a Rheology DVE-V4 FT-Rheospectra, respectively.

2.2. Materials

The TEOS employed in the sol–gel process was obtained from Shin-Etsu Chemical Co. and used without further purification. The PVA was Kurare Co. Poval 124 (P = 2400 by viscometry). It was used after resaponification with an aqueous solution of NaOH and dialysed with a cellophane tube (Visking Tube) in flowing desalinated water. This dialysis was terminated when the electric conductivity of the solution was close to that of distilled water.

2.3. Synthesis

The prepared silica-sol:HCl (aq) solution was added slowly to the TEOS (aq) solution (H_2O:TEOS = 4:1 mol%) contained in a stirred ice bath. The ratio of

0022–2461 © 1996 Chapman & Hall

HCl the TEOS was 1 : 10 mol%. In the second preparation a fixed amount of silica-sol was dripped slowly into a 5 wt% PVA (aq) solution and the mixture was heated at 50 °C for 2 h in order to obtain a viscous sol. The mixed sol was cast on to a polystyrene dish with a flat bottom and placed on a mercury bath in a desiccator. The gelation was carried out over a period of 5 days. The resultant gel was dried in the atmosphere, and then was further dried *in vacuo*.

The preparation of the drawn samples was carried out under a saturated water vapour pressure at room temperature. The length of original specimens were 5 cm and they were drawn at about 5 cm h^{-1}.

3. Results and discussion

3.1. ESCA observations

The films of the composites containing PVA at concentrations above 50 wt% were transparent and flexible. However despite keeping their transparency, the composites below 50% PVA were brittle. In comparison to the composites of alumina/PVA [11], the composites of silica/PVA were isoluble in water. An ESCA spectrum on the 50% PVA composite was performed in order to investigate the C, O and Si content. Spectra were taken on the front (air side) and back (polystyrene dish side) sides of this specimen. In Fig. 1, the changes in the composition between the front (a) and the back (b) sides are shown as a function of the etching time. In the first 0.2 min, one molecular layer ($\times 10^{-1}$ nm) of specimen is etched. There were few differences in the composition between the surfaces and the bulk in this experimental range. The differences in the composition between the two surfaces were only −4, +2 and +2% for C, O and Si, respectively. These results show that the PVA and silica are well intermixed. The values of the composition for C, O and Si do not match the values expected from the amount of mixed silica and PVA, in particular with respect to the oxygen. We suggest that the above result is due to the existence of bonding between unreacted ethoxide groups and the silica. Such –Si–O–C bonding was observed in the IR spectrum. The considerably uniform dispersion was supported also by the ATR-IR spectra of the surfaces.

3.2. Observation by X-ray diffraction

In Fig. 2, the X-ray diffraction patterns of the PVA and the composites containing 80 and 50% PVA are shown. A strong diffraction peak is observed for the PVA at an angle of 19.5° in 2θ which reflects the diffraction of the [1 0 1] plane of the PVA crystal. A weaker diffraction peak was observed at the same angle for the 80% PVA composite. The diffraction peak for the 50% PVA composite was shifted to 21.3° in 2θ and further weakened and broadened compared to the 80% PVA composite. This shift was confirmed with a 50% PVA composite sample obtained in another preparation. These results show that the silica networks and the PVA chains considerably disperse but partially localize with each other. It is uncertain at the present stage of this experiment whether a co-crystal of silica and PVA exists or not in the 50% PVA sample.

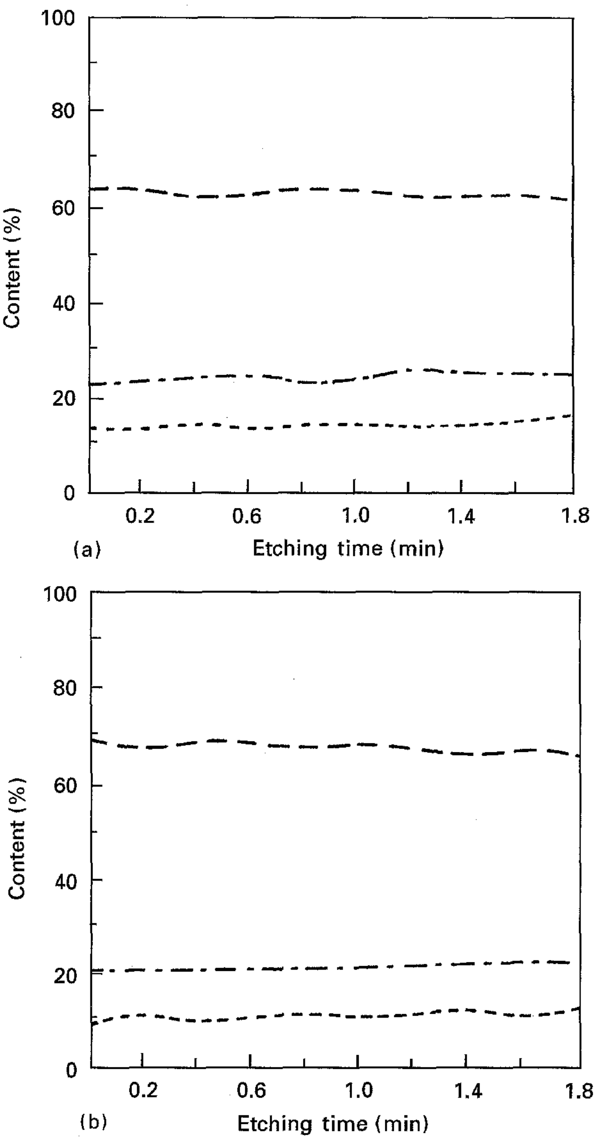

Figure 1 Distribution profiles of the elements from the front (a) and back (b) sides of composite film by ESCA measurement; —— : C(1s), — - —: O(1s), — — —: Si(2p).

The characteristics obtained from the X-ray diffraction experiments on as-cast and as-drawn (2 times) samples are listed in Table I. Moreover, the characteristics of the composites heat-set at 40 and 150 °C *in vacuo* are also listed in this table. The diffraction intensifies which correspond to the crystallinity of the PVA composites were corrected for the film thickness and the PVA composition. The diffraction intensity of the composites showed a larger value than that for the PVA, contrary to expectation. In a narrow space surrounded with the silica network, the PVA chains will be liable to produce many microcrystallines. The crystallinity of the composites was relatively unaffected by the heat treatment. The reason for the small changes caused by the heat treatment seems to be that the PVA chains are surrounded with the rigid silica networks and that therefore the mobility of the chains is decreased. Both the diffraction intensities of the composites and PVA were increased by drawing. For the as-drawn composite, there were major differences in

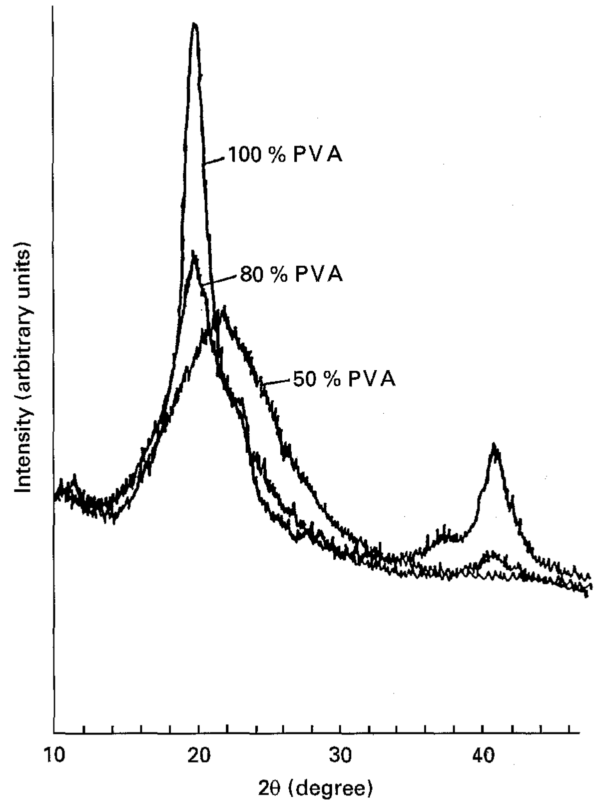

Figure 2 X-ray diffraction plots of PVA and the composites.

TABLE 1 Changes in the intensity of X-ray diffraction caused by heating and drawing of the composites

As-cast sample			
PVA (wt%)	100	80	50
40 (°C)	1.0*	1.2	1.4
150 (°C)	1.4	1.4	1.5
Sample after 3rd drawing			
40 (°C)	7.3	4.6	–
150 (°C)	12.3	4.9	–

* Reference datum 3.7 (CPS/l · PVA%), l = film thickness

the diffraction intensity between PVA and the composite. The diffraction intensity of PVA was increased by 7.3 (40 °C) and 8.8 (150 °C) times by drawing, but the corresponding increases in the composites is only a factor of about 3.5 times. Within the silica network, the molecular chains of PVA will find it difficult to produce a crystalline phase during the heating and drawing processes.

TABLE II Mechanical properties of the as-cast composites

PVA (wt%)	Modulus (GPa)	Strength (MPa)	Elongation (%)
100	3.2	84	110.0
80	4.4	137	36.0
70	6.0	147	11.6
60	6.3	45	8.5
50	7.4	40	0.5
80*	2.8	45	20
50*	2.2	23	3

* PVA dispersed silica powder

TABLE III Mechanical properties of the as-drawn composites

PVA (wt%)	Modulus (GPa)	Strength (MPa)	Elongation (%)
Sample drawn for a 2nd time			
100	5.7	132	90
80	7.4	183	19
70	7.5	190	8.5
60	9.6	230	5.2
Samples drawn for a 3rd time			
100	6.8	261	61.9
80	10.9	223	8.2
70	11.1	222	7.2

The composites containing 50% PVA could not be drawn for a 2nd time.

The composite containing 60% PVA could not be drawn for a 3rd time.

3.3. Mechanical properties

The mechanical properties of the as-cast and the as-drawn (2nd and 3rd times) composites are listed in Tables II and III, respectively. In order to compare them with the composites prepared by the sol–gel process, the samples dispersed silica powder in PVA are also listed. The Young's modulus of the composites increased with increasing silica content, with the tensile strength at break reaching a maximum value for the 70% PVA composite. The maximum strength was about 1.8 times that of the value for PVA. This result shows that the embrittlement increased in systems with less than 60% PVA content. The modulus of the 50% PVA composite is about 2.3 times that of the value of the PVA. The value for samples containing silica powder, however, is lower than that of PVA and also the composites. The samples containing less than 40% PVA were brittle and the values for their modulus is uncertain and thus we do not list these values in the table. The tensile strength of the powder containing samples decreased with the increase in silica powder. In addition the degree of elongation decreased with silica content.

From the above results, it is deduced that the composite is not a mechanical mixture of PVA and silica, but is formed from a compatible blend of the PVA chain and silica network. The facility of drawing in dry conditions decreased remarkably with silica content, because of the depression of the mobility of the PVA chains in the silica network. Therefore, the drawing of the composite must be carried out slowly under humid conditions.

As is shown in Table III, the drawn composites showed an increase of about 2 times in the modulus and 2 ~ 3 times in tensile strength as compared to the as-cast sample. The degree of elongation decreased with the mixing of silica. As is shown in Fig. 3, a linear relationship was obtained between the PVA content and the modulus. This result shows the additivity of the moduli of PVA and silica, and shows that a fairly compatible blend exists between them.

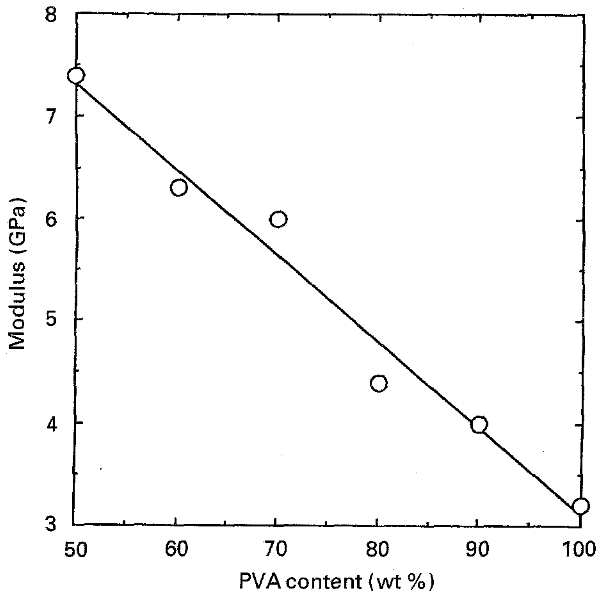

Figure 3 Relation between Young's modulus and the PVA content in the composites.

3.4. Dynamic mechanical spectra

In Fig. 4, the spectra of tan δ of PVA and the composites are shown. The peak corresponding to the PVA glass transition was shifted from 55.0 to 75.0 °C and the height of the peaks decreased upon complexing with silica. It seems that the molecular movements of the PVA chains in the composites are restricted by the silica networks. The values of the storage modulus (E') of the composites are shown in Fig. 5. The E' value of PVA (the 90% PVA composite shows nearly the same result) was constant with very small values above 100 °C with a further decline above 150 °C. The E' values of the 80% PVA and 50% PVA samples, however, displayed minimum values at about 120 °C and 90 °C, respectively. The value and the increasing slope of the E' for 50% PVA composite were somewhat larger than those for the 80% PVA composite. These phenomena are not general for thermoplastics. The increment of E' with temperature appeared to be the result of a cross linking reaction, which is caused either by the condensation of the $-OH$ group of PVA with any unreacted $-OC_2H_5$ groups or with any $-OH$ groups from the silica. To confirm this hypothesis, a 2nd heating cycle was performed on the 50% PVA sample and the result is shown on Fig. 5 by a black triangular symbol. The spectrum was entirely different from that observed from the 1st run. This result shows that the composite changes into the cross linked glassy state by condensation between PVA and silica. It seems that the reactivity between silica and PVA will be larger than that for between neighbouring PVA chains.

3.5. Pore structure of the "composite" after PVA removal

The specific surface area of the composites from which the PVA was removed by burning in air at 600 °C was measured by the BET method from nitrogen adsorption at −195 °C. The relation between the PVA (wt%) content in the composites and the specific surface area is shown in Fig. 6. Silica prepared by the sol–gel method without PVA had a surface area of about 15 $m^2 g^{-1}$. This small value is towards the measuring limits of our BET apparatus and there is some uncertainty in this value. The surface area of the silica prepared by removing the PVA in the composites was observed to increase with increasing PVA content in the as-cast composites. The n values, which correspond to an adsorbed layer of nitrogen, were of the order of 2.5 ~ 3.0. The silica calcined from the 80% PVA composite showed a surface area of about 500 $m^2 g^{-1}$. The residual silica was brittle, but transparent. The saturated amount of sorbed N_2 was 0.142 $cm^3 g^{-1}$ for the sample obtained from the 50% PVA composite. Its surface area was 220 $m^2 g^{-1}$. An average pore radius of 1.4 nm was obtained from the above two values by assuming a cylindrical shape for the pore. The structure of the composite 50% PVA was predicted as follows. It is well-known that PVA has crystallographic dimensions of $a = 0.78$ nm

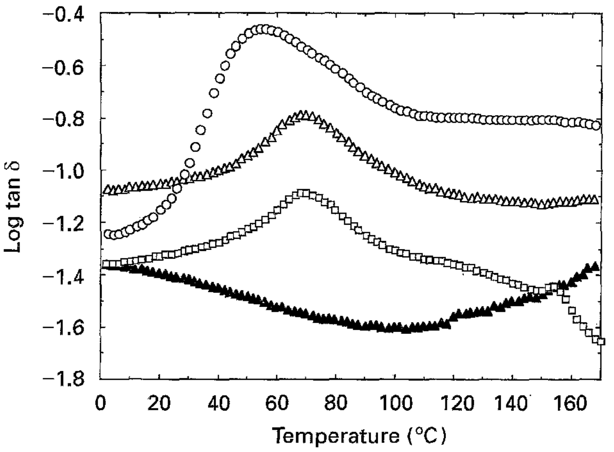

Figure 4 Dynamic mechanical spectra (tan δ) of PVA and the composites; ○: 100% PVA, □: 80% PVA, △: 50% PVA (1st run), ▲: 50% PVA (2nd run).

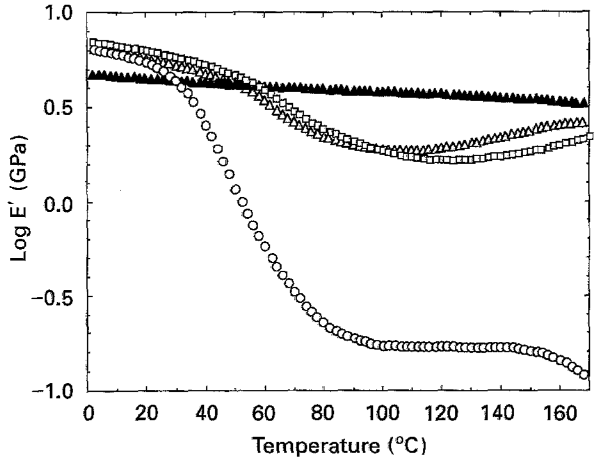

Figure 5 Dynamic mechanical spectra (E') of PVA and the composites; ○: 100% PVA, □: 80% PVA, △: 50% PVA (1st run), ▲: 50% PVA (2nd run).

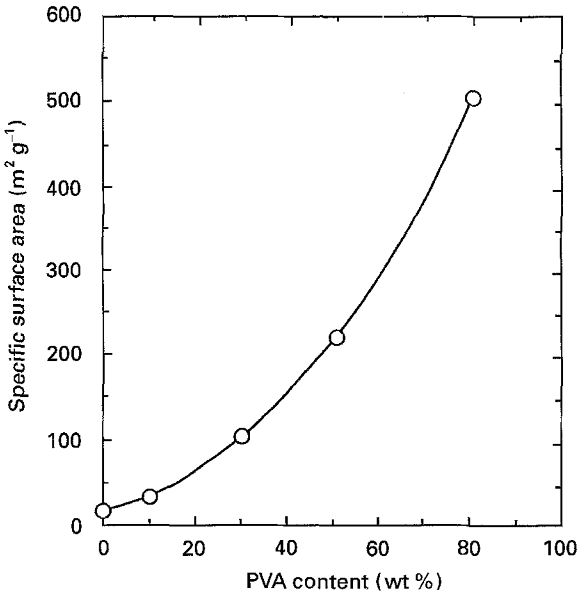

Figure 6 Relation between the specific surface area of the calcinated residues and the PVA content in the original composites.

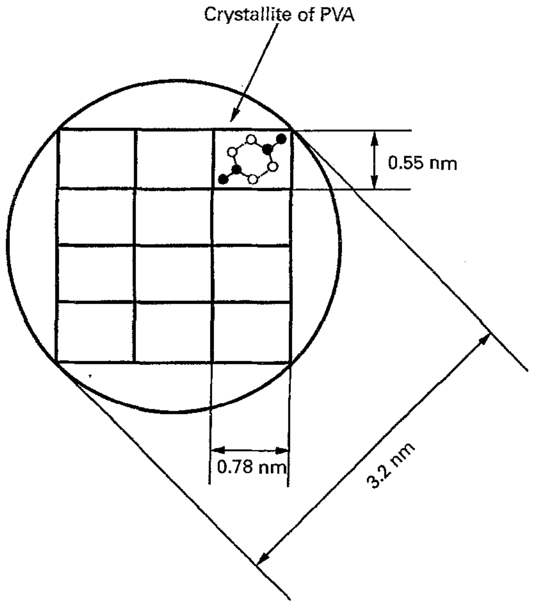

Figure 7 Simplified model suggested for the mixing state of the silica and PVA in the composite.

and $b = 0.55$ nm [12]. As is shown in Fig. 7, a pore diameter of 3.2 nm is able to arrange about 12 lattices of PVA crystallite. As 2 PVA chains are packed in each lattice, 20 ~ 30 chains ought to be able to be arranged in each pore like a bundle. The adsorbed cross sectional area (S) of a nitrogen molecule is known to be 0.17nm^2, and accordingly, about 36 N_2 molecules ($\pi \cdot 1.4^2/0.17$) can be arranged in this cross section of pore. As mentioned above, the adsorbed N_2 layer n was 2.5 ~ 3.0 and the diameter (d) of an adsorbed N_2 molecule, obtained from the occupied cross sectional area is about 0.44 nm [$d = ((S \cdot \sin 60)/3)^{1/2}$, $S = 0.17 \text{ nm}^2$]. Therefore, the average radius of the pore obtained from the BET n value is $0.45 \times (2.5 \sim 3.0) = (1.1 \sim 1.33 \text{ nm})$. From this result, the obtained pore radius of 1.4 nm is seen to be a reasonable value.

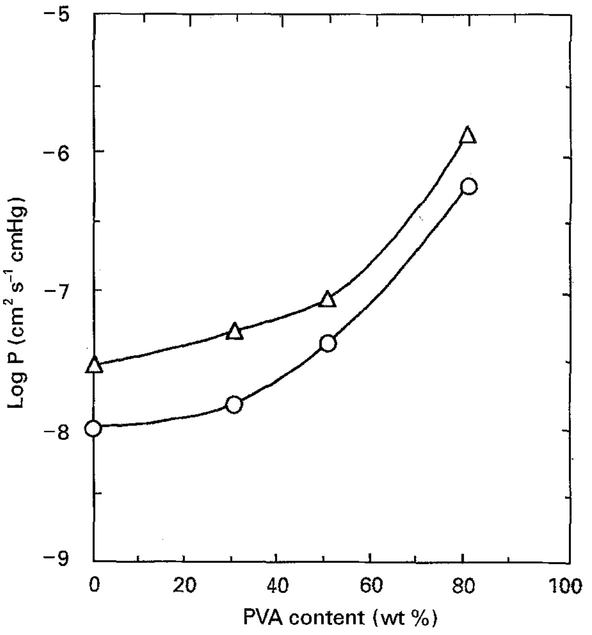

Figure 8 Relation between the gas permeability (P) of calcinated residues and the PVA content in the original composites: △ He, ○ H_2.

Moreover, the permeation of H_2 and He were measured in order to investigate the pore structure of the silica prepared from the composites by removing the PVA. The relations between the PVA content in the as-cast composites and the permeability of H_2 and He gases are shown in Fig. 8. Both the H_2 and He permeations increased remarkably with increasing PVA content in the as-cast composites. The increase in the permeabilities was especially remarkable in the silica obtained from the composites containing more than 50% PVA. The silica obtained from the 80% PVA composite showed a permeability value about 100 times greater than that of the silica prepared without PVA. By considering the gas permeability, it seems that the pore structure is not in a bottle shape with a bottom, but in a somewhat cylindrical shape through both surface sides. From these results, it was estimated that the structure of the composites would be a partially compatible mixture between PVA and silica, with the PVA existing in bundled chains.

Acknowledgement

The authors wish to thank Kenji Onozato and Miyoko Inoue for their helpful cooperation and to TOLI Co. Ltd. for partial financial support.

References

1. H. DISLICH, *J. Non-Cryst. Solids* **73** (1985) 599.
2. H. DISLICH and E. HUSSMANN, *Thin Solid Films* **77** (1981) 129.
3. S. SAKKA and T. KOKUBO, *J. Appl. Phys.* **22** (1983) 3.
4. D. AVNIR, D. LEVY and R. REISFELD, *ibid.* **88** (1984) 5956.
5. V. R. KAUFMAN, D. LEVY and D. AVENIR, *J. Non-Cryst. Solids* **82** (1986) 103.

6. T. TANI, H. NAMIKAWA and K. ARAI, *J. Appl. Phys.* **58** (1985) 3559.
7. R. H. GLASER and G. L. WILKES, *Polymer Bull.* **22** (1989) 527.
8. G. PHILIPP and H. SCHMIDT, *J. Non-Cryst. Solids* **63** (1984) 283.
9. A. MORIKAWA, Y. IYOKU, M. KAKIMOTO and Y. IMAI, *J. Mater. Chem.* **2** (1992) 679.
10. F. SUZUKI and K. ONOZATO, *J. Appl. Polym. Sci.* **39** (1990) 371.
11. S. IKOMA, E. NOMOTO and H. YOKOI, *Kobunshi Ronbunshu* **48** (1991) 53. Chem. Abs., **114** 63302t (1991).
12. C. W. BUNN, *Nature* **161** (1948) 929.

Received 5 October 1994
and accepted 8 September 1995