

A Formation of Compatible Poly(vinyl Alcohol)/Alumina Gel Composite and Its Properties

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Synopsis

A formation of poly(vinyl alcohol) (PVA)/alumina gel composite was investigated with a viewpoint of compatibility of the composite. An alumina sol was prepared from aluminium iso-propoxide ($\text{Al}(\text{iPro})_3$). The alkoxide was hydrolyzed and the resultant hydrate was peptized to a clear sol with acetic acid. The composite were transparent in whole content of alumina. The effects of dispersed alumina on the sorption of water and mechanical properties of composite were examined. The composites containing PVA 40–50% are flexible. They are folded in various forms and can be drawn five times the initial length in humid state. The residues obtained by calcination to remove PVA at 600°C keep its original form and transparency.

INTRODUCTION

There are many investigations of the treatment of inorganic oxide particles or clay with organic polymer materials in heterogeneous systems.¹ In the systems, the sizes of particles treated are on the order of micrometers. The using particles are almost prepared by grinding. Finer particles must be dispersed into organic material with a view to obtaining a more homogeneous composite. The way to obtain a homogeneous composite would be the employment of alkoxide or sol.² Use of an alkoxide such as tetraethoxysilane has been investigated for the preparation of glass at low temperature.³ The composite is obtained by the hydrolysis of tetraethoxysilane in aqueous solution of PVA. Most of the alkoxides used in a sol-gel process are silicates. In a previous paper,⁴ we reported the gas permeabilities of the thin porous alumina membrane prepared from $\text{Al}(\text{iPro})_3$ in similar manner as Yoldas' method. However, few works have been reported on the composite of alumina sol/polymer. Therefore, it is the purpose of this study to investigate the formation of alumina sol/PVA composite and the properties of the resultant composite.

EXPERIMENTAL

Preparation of Alumina Sol

The sol can be obtained by two methods. One method is a utilization of alkoxide and another is that of an aqueous solution derived from inorganic

salt. Here, we adopted the former according to the procedure previously reported.⁵ The procedure comprises the steps of hydrolysis of alkoxide and peptization of the hydrolyzed product to a sol. In the latter step, hydrochloric acid, nitric acid, or acetic acid can be used as peptizer. We used acetic acid here because it gave easily a clear sol.

The transparent clear sol was prepared as follows. The mixture of $\text{Al}(\text{iPro})_3$ and water in the fixed ratio was heated for 3 h at 80–90°C under reflux. Then, acetic acid was added to the hydrolyzed precipitate formed in this way. It was heated for 48 h at 90°C until a clear sol was obtained. Next, the sol was dialyzed against pure water.

PVA was commercially obtained from Kurare Co. (Poval 124, $P = 2400$). An aqueous 3% PVA solution was prepared as a stock solution. It can be mixed as precursors for composite materials with alumina sol to yield the required composition before converting to gels. The gelation was carried out on polystyrene plate in a desiccator. Then, resultant gel was dried *in vacuo*.

Apparatus

A surface structure of composite membrane was examined by Shimadzu infrared spectrophotometer Model IR-435 and attenuated total reflection Model ATR-2.

X-ray diffraction was measured by model γ -RAD of the Rigaku Denki Co. The X-ray diffraction pattern was obtained by the following conditions: diameter of collimeter, 0.5 mm; distance between sample and film, 29.52 cm; irradiation period, 3h. The stress-strain curve was obtained by Toyo-Bowldwin Tensilon Model TMW-III-500. Sample sizes were 20 mm (length) \times 5 mm (width) \times 0.08–0.16 mm (thickness). The beam speed was 5 mm/min.

Water vapor sorption was equilibrated in desiccator saturated with a fixed vapor pressure of water generated from aqueous salt solution. The degree of sorption or swelling (D_s) was obtained from weight difference before and after water vapor sorption by using

$$D_s = \frac{W_s - W_0}{W_0} \quad (1)$$

where W_0 and W_s denote weights of pre and after sorption (swelling), respectively.

RESULTS AND DISCUSSION

Formation of Alumina Sol

Hydrolysis was done by pouring $\text{Al}(\text{iPro})_3$ into excess water at 80°C for 3 h under vigorous stirring. The weight ratio of water/ $\text{Al}(\text{iPro})_3$ was kept at around 15. The unhydrolyzed particles were removed by centrifuge. It is reported that the hydrolysis of the alkoxide produces alumina mono- or trihydroxides and only the monohydroxide thus formed can be peptized to a clear sol.^{6,7} In peptization, the type of acid plays a much more important role than the controlling pH of the solution. Here, two type acids (strong and

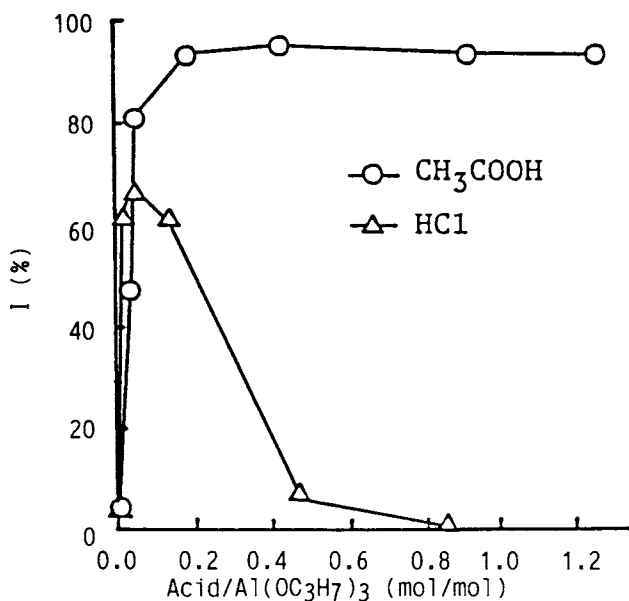


Fig. 1. Relation between ratio of acid/ $\text{Al}(\text{iPrO})_3$ and transparency (1%) of alumina sol.

weak) were employed as a peptizing agent. Various amounts of acids were added to the hydrolyzed precipitates. The samples added were heated at 90°C for 48 h. The transmittance of the prepared sol solution was measured by a spectrophotometric method using a wave length of 545 nm. Effects of acid concentration on transmittance are given in Figure 1. In the HCl system, a clear sol is obtained when about 0.06 mol per alkoxide is used and then its transmittance suddenly decreases with an increase of HCl as shown in the figure. In the weak organic acid such as acetic acid, the behavior is dissimilar to that in HCl system. The transparency increases with increasing ratio up to about 0.2 mol and then it gradually decreases. Acetic acid acts as a peptizer in wide range of its concentration. Hence, acetic acid was chosen in the system.

Formation of Composite

Alumina sol described above was mixed with PVA solution in various proportions. The resultant composite shows a homogeneous transparent property as shown in Figure 2. The transmittance as a measure of transparency at 490 nm are given in Table I for the composites. This fact shows that the particle size of alumina is at least less than 500 nm. They show values from 82.7 to 88.5%, averaged at about 85%. There are no differences in transmittances among composite, PVA, and alumina. The composites containing PVA below 20% are brittle and are difficult to be molded into membrane. On the other hand, the composites containing PVA above 70% are flexible and are easily molded. However, the residues obtained by calcination of the composites to remove PVA ($> 70\%$) at 600°C are fragile and lose their original forms. The composites containing 40–50% PVA are flexible and can be folded without difficulty. They can be drawn up to five times initial length in

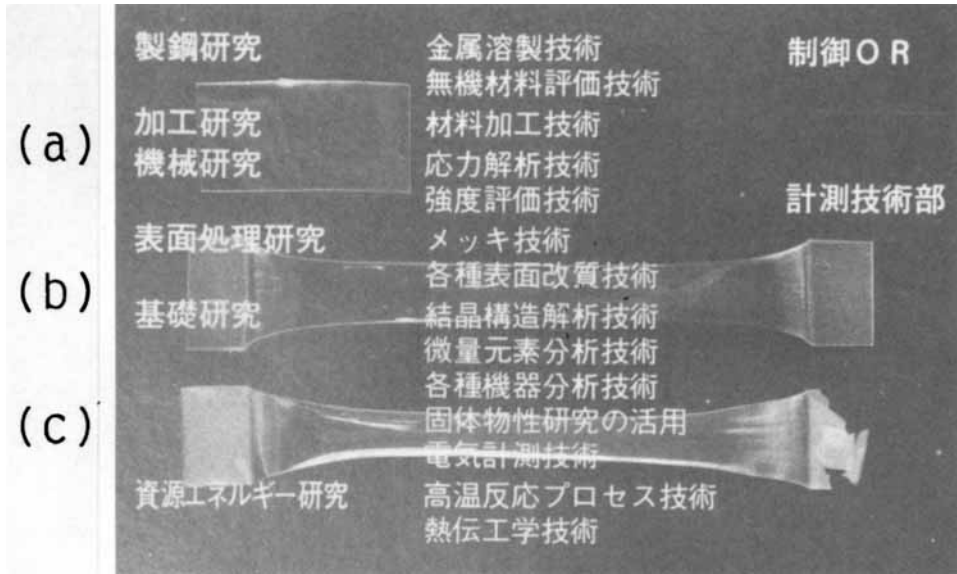


Fig. 2. Photographs of composite membranes: (a) as-cast membrane, (b) as-draw membrane, (c) calcination residue of as-draw membrane. PVA:alumina = 1 : 1.

TABLE I
Optical Transmittance of Composite^a

Wt ratio PVA : alumina	Thickness (mm)	Transmittance (%)
100 : 0	0.228	86.7
80 : 20	0.120	84.9
60 : 40	0.124	88.2
50 : 50	0.214	83.0
40 : 60	0.185	82.7
20 : 80	0.184	88.5
0 : 100	0.195	83.5

^aWavelength = 490 nm.

saturated vapor of water at 25°C. Moreover, the residues after calcination retain the original form.

X-Ray Diffraction of Composite

X-ray diffraction pattern of alumina obtained from $\text{Al}(\text{iPro})_3$ is shown in Figure 3. It indicates an existence of fine crystallites in alumina gel. The lattice calculated from this pattern is similar to that of boehmite reported by Paul et al.^{7,8} This may imply that insoluble bayerite and/or trihydrate which are produced frequently by a poorness in reaction condition are not present in the gel. The lattice distances of composite (PVA:alumina = 1 : 1) calculated from its pattern are given in Table II. The diffraction patterns are fairly consistent with those of PVA and boehmite as seen from the table. Therefore, it seems that there is no special reaction or an eutectic formation between

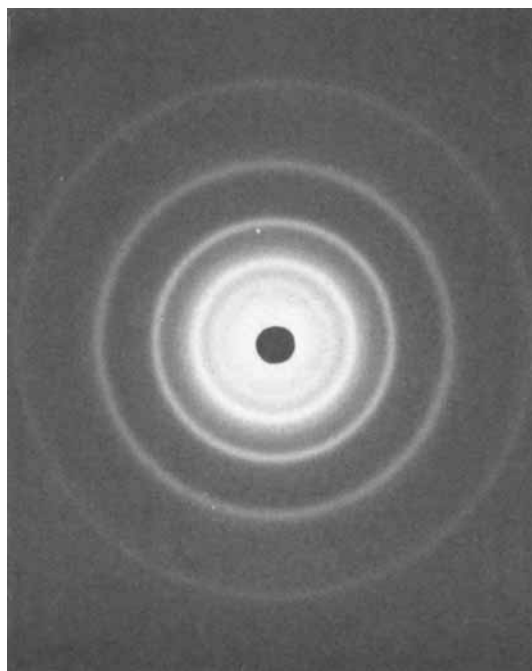


Fig. 3. X-ray diffraction pattern of as-cast composite membrane. PVA:alumina = 1 : 1.

TABLE II
X-Ray Diffraction of Composite Membrane (PVA : alumina = 1 : 1)

2θ	$d(\text{Å})$	(hkl)	Remark
11.209	7.894	(1 0 0)	PVA
14.437	6.135	(0 2 0)	Boehmite
19.795	4.485	(1 0 1)	PVA
22.785	3.903	(2 0 0)	PVA
27.855	3.203	(2 0 1)	PVA
		(0 2 1)	Boehmite
32.491	2.756	(0 0 2)	PVA
37.068	2.425	(1 1 0)	PVA
38.403	2.344	(1 3 0)	Boehmite
40.486	2.228	(2 0 2)	PVA
49.366	1.846	(0 0 2)	Boehmite

PVA and alumina. On the other hand, it is reported that the adsorption of PVA on silica occurs mainly at low pH where the hydroxyl groups of PVA form hydrogen bonding with uncharged silanol groups on the silica surface.⁹ A similar situation may presumably exist in this alumina-PVA system.

Spectroscopic Observation of Composite

As described above, it appears that the composite is a homogeneous mixture of two components. However, a question arises as to whether the components are disordered or ordered in double layer laminate which may be formed as

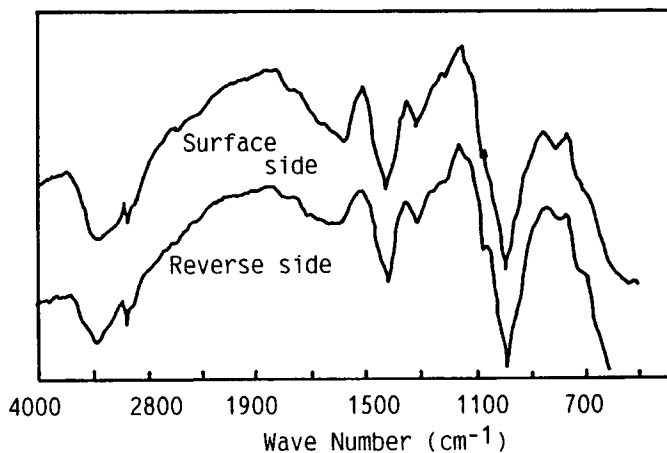


Fig. 4. IR-ATR spectra of surface and reverse sides of composite. PVA:alumina = 1:1.

the result of phase separation and difference of densities of PVA and boehmite. To confirm this question, both surfaces of the composite membrane were examined by a attenuated total reflection of infrared spectroscopy (IR-ATR). As shown in Figure 4, spectra are exactly like each other. A thickness of the composite membrane is about 200 μm . It is well known that a distance for instruction of IR ray into substance is nearly equal to the wavelength of IR, 2.5–25 μm . From these facts mentioned above, it is thought that the IR ray does not penetrate into reverse surface of the membrane. In addition, the spectra of the composite are in good agreement with those of PVA and alumina. Therefore, it is concluded that the composite membrane has no laminate structure.

Drawing of Composite

The composite membrane was conditioned at 25°C and 100% RH for 30 h before drawing. The membrane could be drawn in above conditions up to five times of initial length. The beam speed was 4 cm/h. A photograph of the drawn membrane is shown in Figure 2(b). As shown in the photograph, the membrane keeps the original transparency after drawing. The transmittance did not change from original one of 83%. The X-ray diffraction pattern of the membrane before drawing is shown in Figure 5. Both the pattern of PVA and that of boehmite changes from ringlike to arclike. This result indicates that the boehmite is orientated by drawing. Table III gives the intensity and half-band width of X-ray diffraction at 20.003° ([101] of PVA) for the as-drawn PVA and composite and the drawn ones treated at 180°C. The half-band width of the composite is larger than that of PVA. This fact should indicate that the crystallites of PVA in the composite are smaller than these in PVA alone; then the crystallites of PVA in the composite grow slightly by heat treatment. The number of counts as a measure of crystallite is 497×2 , taking into account PVA 50% in the composite. This value corresponds to 2/3

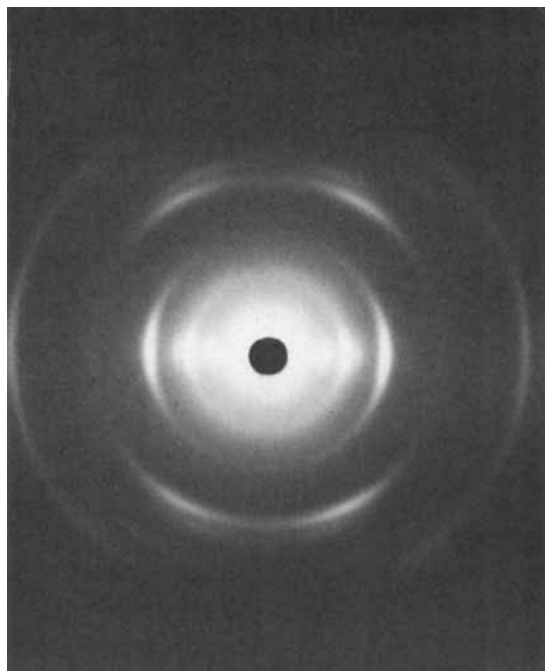


Fig. 5. X-ray diffraction pattern of as-draw composite membrane. PVA:alumina = 1 : 1.

of crystallites of PVA alone. The count value for PVA alone increases to 2.3 times of its original value by heat treatment. However, that of PVA in the composite increases slightly to 1.1 times by similar treatment. The recrystallization can probably not proceed in the composite since a movement of molecular chain of PVA should be restricted by the interaction with alumina. When this drawn membrane is treated in atmosphere at 600°C, it keeps its transparency but becomes brittle. In Figure 2(c), the sample appears partially white. However, it occurs because of some wrinkles and the influence of light scattering from them. The transmittance decreased slightly from 83 to 81%. The X-ray diffraction pattern of the treated product is shown in Figure 6. It shows clearly that the drawing results in the orientation of alumina.

TABLE III
Change of Intensity of X-Ray Diffraction by Heat Treatment

Sample	Heat set temp (°C)	Peak count	Count ratio
PVA	—	1487	2.3
PVA	180	3376	
Composite ^a	—	497	1.1
Composite ^a	180	553	

^aPVA : alumina = 1 : 1.

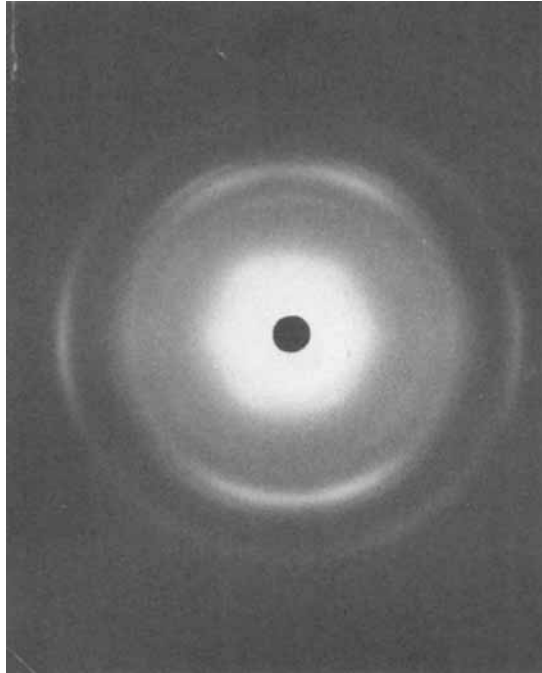


Fig. 6. X-ray diffraction pattern of calcination residue of as-draw composite membrane. PVA:alumina = 1:1.

Tensile Strength of Composite

The stress-strain curves were measured for the composites containing PVA ~ 40%. The results are shown in Figure 7. PVA alone shows a typical S-S curve which has a yield point and it is drawn up to two times its original

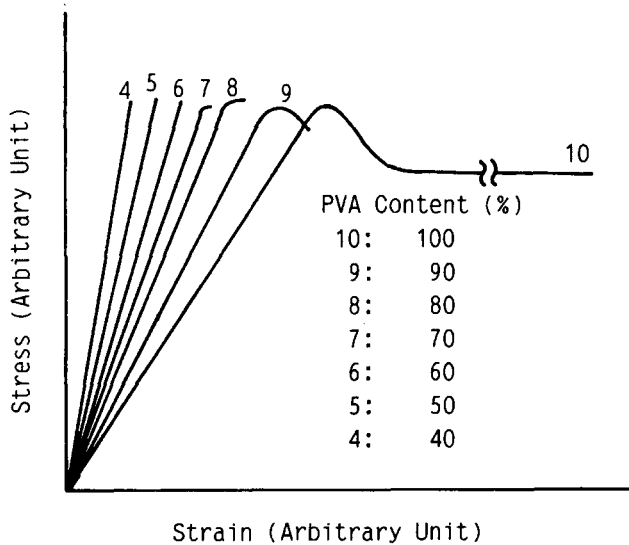


Fig. 7. Stress-strain curves of composite.

TABLE IV
Mechanical Properties of Composite

Wt ratio PVA : alumina	Maximum stress (kg/mm ²)	Maximum strain (%)	Young's modulus (kg/mm ²)
100 : 0	9.9	102.6	440
90 : 10	10.7	11.6	490
80 : 20	10.8	4.5	590
70 : 30	12.0	3.5	590
60 : 40	10.6	1.3	760
50 : 50	10.5	1.2	860
40 : 60	10.6	1.0	1250

length. The composites containing PVA below 40% are almost unable to be drawn at dry state and are cut off in the Hookian region without giving the yield point. From these curves the Young's modulus, maximum stress, and strain are obtained. They are given in Table IV. The maximum stress shows a maximum value at PVA 70% composite. However, the great difference between the composites cannot be observed. The maximum strain decreases from 100 to 1% by blending of alumina as given in the table. If alumina disperses in PVA like powder, the maximum elongation ought to decrease gradually with the mixing of alumina. Hence, these results show that alumina does not mix like powder but homogeneous phase as polymer with PVA. It is reported that the fine particles comparable to the size of the crystalline region have a prominent reinforcing effect in the orientated polymer matrix.¹⁰ A similar effect in this PVA/alumina system is predicted. However, more work is necessary to clarify that point.

Degree of Swelling and Sorption

The alumina obtained from the sol-gel method is dissolved in water, even though heat-treated at 180°C. PVA is also partially dissolved in water, even though heat-treated at 150°C. However, the PVA 50% composite is insoluble in water when heat-treated at 130°C.

Figure 8 shows a relation between PVA content in composite and degree of swelling as a function of swelling temperature. The composites containing PVA below 20% are dissolved in water except the temperature of 0.5°C. These curves have minimum values at the content of about 40% PVA. It is well known that when relation curve displays downward curvature, the interaction between different species is larger than that between the same species. Therefore, it appears that the interaction between PVA and alumina is very strong. To examine more quantitatively the interaction, the amount of humid sorption was measured at the humidity of 69.8 and 79.3%. The results are given in Table V. The amounts sorbed show minimum values both at PVA 50 and 60% contents in the composites. By use of an extended Flory-Huggins equation (2), the interaction parameters were calculated from an analysis of sorption data:

$$\ln a_w = \ln V_w + (1 - V_w) + (\chi_{wp} \cdot V_w + \chi_{wb} \cdot V_b) - \chi_{pb} \cdot V_p \cdot V_b \quad (2)$$

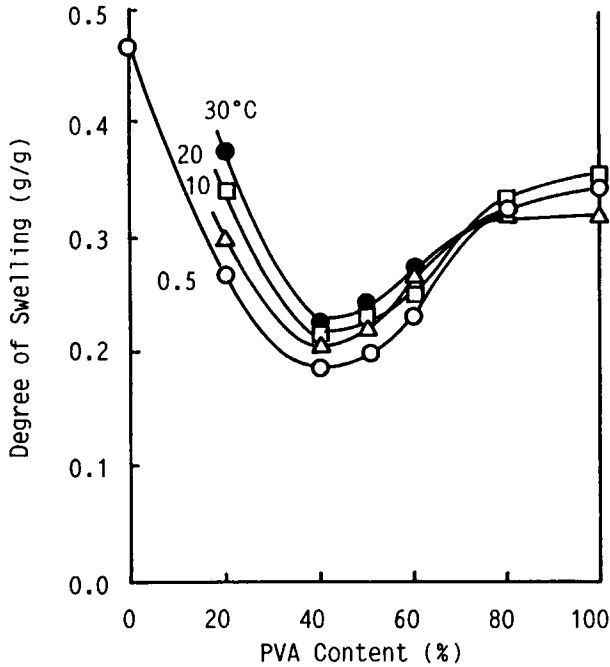


Fig. 8. Relation between PVA content in composite and degree of swelling in water. Numbers denote bath temperatures.

TABLE V
Change of Amount Sorbed Humid and Interaction
Parameter by PVA Content in Composite

Wt ratio PVA : alumina	Amount sorbed (g/g), relative humidity		Interaction parameter, relative humidity	
	69.8%	79.3%	69.8%	79.3%
100 : 0	0.060	0.100	—	—
80 : 20	0.043	0.067	-2.8	-2.7
60 : 40	0.035	0.058	-1.9	-1.1
40 : 60	0.052	0.066	-1.9	-1.4
20 : 80	0.068	0.082	-2.0	-1.1
0 : 100	0.089	0.125	—	—

where a , V and χ are the activity, volume fraction, and interaction parameter and the subscripts w , p , and b denote water, PVA, and alumina, respectively. The interaction parameters between PVA and alumina (χ_{pb}) shows some scatter, but they have negative values. These facts indicate that alumina mixes as a polymeric molecular state with PVA and that the interaction between PVA and alumina is very strong judging from the sorption and swelling.

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References

1. H. van Oelephen, *An Introduction to Clay Colloid Chemistry*, Wiley, New York, 1977;
- A. R. Greenberg and I. Kamel, *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 2137 (1977).
2. T. Hino, K. Mochida, and S. Okamura, *Kobunshi Ronbunshyu*, **40**, 225 (1983).
3. H. Scholze, *Proceedings of 2nd International Workshop on Glass and Glass Ceramics from Gels*, *J. Non-Cryst. Solids*, **63**(1/2), (1984).
4. F. Suzuki, K. Onozato, and Y. Kurokawa, *J. Non-Cryst. Solids*, **94**, 160 (1987).
5. F. Suzuki, K. Onozato, and Y. Kurokawa, *Kobunshi Ronbunshyu*, **43**, 767 (1986).
6. A. M. M. Leenaars, K. Keizer, and A. J. Burggraaf, *J. Mater. Sci.*, **19**, 1077 (1984).
7. B. E. Yoldas, *J. Appl. Chem. Biotechnol.*, **23**, 803 (1973).
8. P. R. Paul and W. J. Yost, *J. Chem. Phys.*, **14**, 495 (1946).
9. R. K. Iler, *J. Colloid Interface Sci.*, **51**, 388 (1975). Th. F. Tadros, *ibid.*, **64**, 36 (1978).
10. O. E. Otterstedt, J. -E. A. Otterstedt, J. Ekdaht, and J. Backmon, *J. Appl. Polym. Sci.*, **34**, 2575 (1987).

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