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Ormosil coatings of high hardness

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Organically modified silicates (ormosils) of two systems were coated on polyethyleneterephthalate (PET) substrates. One was the tetraethoxysilane (TEOS)–vinyltriethoxysilane (VTES) system and the other was the TEOS–tetraisopropyltitanate (TIPT)–VTES system. The reactions among the alkoxides were examined by liquid state ^{29}Si nuclear magnetic resonance (NMR) spectroscopy. The chemical bonds between TEOS and VTES, between TEOS and TIPT, and between VTES and TIPT are shown in the spectra and the reaction schemes are proposed. Vickers hardnesses of the ormosil coatings were obtained by using the models developed by Jönsson and Hogmark, and the theoretical models developed by the authors were valuable to predict the hardness values. The ormosil coatings obtained in the present study were much harder than the hardest transparent plastics, and thus are very useful for hard or protective coatings on organic polymers.

1. Introduction

Organically modified silicates (ormosils) constitute an important new family of amorphous solids. Since the successful preparation of these new ormosils using the sol–gel method [1, 2], there has been increasing interest in making new organic–inorganic hybrid materials. These materials are synthesized by chemically incorporating organic polymers into inorganic networks, resulting in unique properties. One of the applications of these materials is to provide hard or protective coatings on organic polymers. Transparent synthetic polymers are used for many applications, but their scratch and chemical resistances are very poor. Ormosil coatings can improve the surface properties of organic polymers and protect them from deterioration. The organic parts of ormosil coatings react with polymer substrates to improve the adhesion between the coatings and the substrates, while the inorganic parts of ormosil coatings act to increase the hardness and chemical durability of the surfaces [3]. In this work, polyethyleneterephthalate (PET) was coated with ormosils. The ormosil solutions were prepared by the reaction of several alkoxides, and reactions among the alkoxides were examined by liquid state ^{29}Si NMR spectroscopy. Vickers hardnesses were measured for coatings of various thicknesses, and the hardnesses of the coatings were calculated from the models developed by Jönsson and Hogmark [4]. The theoretical models developed by the authors [5, 6] are considered for the hardness values, and also, the hardness values of the ormosil coatings are compared with those of the hardest transparent plastics and some glasses.

2. Experimental procedure

The substrates were Hostaphan polyester films (PET). Tetraethoxysilane (TEOS) and tetraisopropyltitanate (TIPT) were used as the inorganic components. Vinyltriethoxysilane (VTES) was used as the organic component. Ethanol and isopropanol were used as the solvents and hydrochloric acid (HCl, 38%) was used as the catalyst. In the NMR measurements, tetramethylsilane (TMS) was used as the reference, chloroform ($CDCl_3$) as the lock solvent and chromium acetylacetonate [Cr(acac)] as the non-polar paramagnetic relaxation agent.

The preparation procedure for the solutions of the TEOS–VTES system is as follows. First, two mixtures were prepared. One (A) was TEOS and VTES with 40% ethanol and the other (B) was water and HCl, with the balance ethanol. After pouring B into A, the resulting solution was intimately mixed using a magnetic stirrer for 30 min and the solution was kept at room temperature. The container of the solution was always closed. The molar ratios of H_2O–(TEOS + VTES), ethanol–(TEOS + VEOS) and HCl–(TEOS + VTES) were 4, 2 and 0.01, respectively.

The preparation procedure for the solutions of the TEOS–TIPT–VTES system is as follows. If TEOS and TIPT are hydrolysed at the same time, there is an obvious tendency to form large TiO_2 clusters because of the fast hydrolysis of TIPT [7]. Thus, TEOS was partially hydrolysed followed by addition of TIPT and further addition of water to complete hydrolysis. First, two mixtures were prepared. one (A′) was TEOS and VTES with 40% isopropanol and the other (B′) was 2 mol water mol^{-1} TEOS + 1.5 mol water mol^{-1} VTES and HCl with the balance isopropanol. After pouring B′ into A′, the resulting solution was intimately mixed using a magnetic stirrer. After 30 min stirring, TIPT was added into the solution and the solution was intimately mixed for 30 min again. After stirring, the solution was kept at room temperature. After one day, 2 mol water mol^{-1} TIPT was further added drop by drop to complete hydrolysis while stirring the solution intimately. The container of the solution was always closed. The molar ratios of isopropanol–(TEOS + TIPT + VTES) and HCl–(TEOS + TIPT + VTES) were 6 and 0.05, respectively.

PET substrates were coated by the dip-coating method with a withdrawal rate of 5 cm min^{-1}. The coated substrates were dried and cured in a microwave oven (750 W, 2.45 GHz) for 5 min. Thicker films were obtained by repeating the coating and drying several times.

Liquid state ^{29}Si NMR spectra were recorded on an AM 360 Bruker spectrometer with a pulse width of 10 μs and a relaxation delay of 6 s. Liquid sample solutions at various stages of the reaction were diluted to 50 vol % with ethanol or isopropanol, and quenched into liquid nitrogen to arrest the reaction until they were subjected to NMR spectroscopy. Four cubic centimeters of each diluted solution was thawed out just prior to the measurement, put into a 10 mm silica tube and mixed with 0.1 cm^3 of TMS and 0.9 cm^3 of a mixture of $CDCl_3$ and Cr(acac). $CDCl_3$ was used for internal field–frequency control (lock). Since ^{29}Si typically has a very long spin-lattice relaxation time and there exists the possibility of negative nuclear Overhauser enhancement (NOE), the non-polar paramagnetic relaxation agent, Cr(acac), was used at low concentration (~ 0.01 M) to relax ^{29}Si through the unpaired electron spin density of the metal ion, and hence shorten the time for data acquisition and eliminate NOE [8].

Vickers hardnesses were measured by using a Micromet II (Vickers) microhardness tester with a load of 10 g. The thicknesses of the coatings were measured by a Dektak II profilometer.

3. Results and discussion

3.1. Reactions among alkoxides

The reactions among alkoxides were investigated by liquid state ^{29}Si NMR spectroscopy. The ^{29}Si NMR spectrum of the solution of the TEOS–VTES with a molar composition of TEOS–VTES = 0.5:0.5 is shown in Fig. 1c and compared with the spectra of the solutions without TEOS (Fig. 1a) and without VTES (Fig. 1b). All of these spectra were taken after 24 h after mixing A and B. The peaks in both T (− 59 to − 82 p.p.m.) and Q regions (− 81 to − 110 p.p.m.) were observed in about 0.2 p.p.m. lower field regions in Fig. 1c than in Fig. 1a and b. These two field shifts are due to the chemical bonds between TEOS and VTES, and this trend is similar to the TEOS–methyltriethoxysilane (MTES) system [9]. The reaction schemes of the TEOS–VTES system are as follows. Immediately after mixing A and B, hydrolysis of TEOS, Equation 1, and VTES, Equation 2, occurred

$$\mathrm{Si(-OC_2H_5)_4 + mH_2O \rightarrow (C_2H_5O-)_{4-m}Si(-OH)_m + mC_2H_5OH} \qquad (1)$$

$$\mathrm{Si(CH = CH_2)(-OC_2H_5)_3 + \mathit{n}H_2O \rightarrow (C_2H_5O-)_{3-\mathit{n}}Si(CH = CH_2)(-OH)_{\mathit{n}} + \mathit{n}C_2H_5OH} \qquad (2)$$

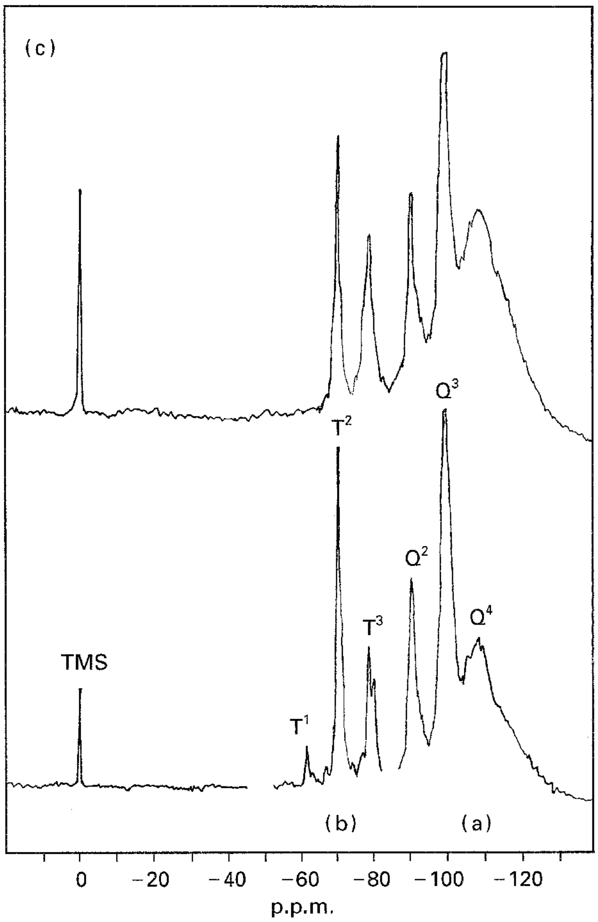

Figure 1 ^{29}Si NMR spectra of the solutions (after 24 h): (a) TEOS–VTES = 1:0, (b) TEOS–VTES = 0:1, (c) TEOS–VTES = 0.5:0.5.

Then the condensation Reactions 3 and 4 and the co-condensation Reaction 5 proceeded

$$\mathrm{(-O-)_3Si-OH + HO-Si(-O-)_3 \rightarrow (-O-)_3Si-O-Si(-O-)_3 + H_2O} \qquad (3)$$

$$\mathrm{(-O-)_2Si(CH = CH_2)(-OH) + HO-Si(CH = CH_2)(-O-)_2 \rightarrow (-O-)_2Si(CH = CH_2)-O-Si(CH = CH_2))(-O-)_2 + H_2O} \qquad (4)$$

$$\mathrm{(-O-)_3Si-OH + HO-Si(CH = CH_2)(-O-)_2 \rightarrow (-O-)_3Si-O-Si(CH = CH_2)(-O-)_2 + H_2O} \qquad (5)$$

The ^{29}Si NMR spectra of the solutions of the TEOS–TIPT–VTES system taken before (a) adding TIPT (30 min after mixing A′ and B′) and (b) after adding TIPT (30 min after adding TIPT) are shown in Fig. 2. The molar compositions were TEOS–VTES = 0.5:0.5 (Fig. 2a) and TEOS–TIPT–VTES = 0.35:0.3:0.35 (Fig. 2b). By the addition of TIPT, the peaks in the T and Q regions were further shifted to the lower field regions. The replacement of Si with Ti in the second co-ordination sphere of a given Si site causes a low field shift [10]. Thus, these low field shifts are due to the chemical bonds with TIPT. The chemical shifts affected by the TIPT additions are shown

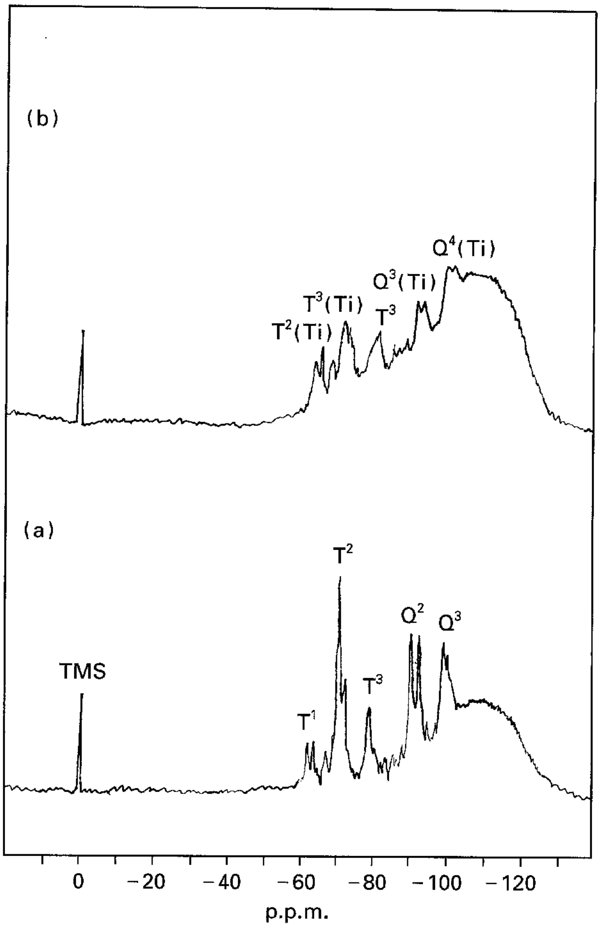

Figure 2 ^{29}Si NMR spectra of the solutions (a) before and (b) after adding TIPT: (a) TEOS–VTES = 0.5:0.5, (b) TEOS–TIPT–VTES = 0.35:0.3:0.35.

in Table I [6, 11]. By adding TIPT, $T^1 + T^2 + T^3$ become $T^2(Ti) + T^3(Ti) + T^3$ in the T region and $Q^2 + Q^3$ become $Q^3(Ti) + Q^4(Ti)$ in the Q region. The reaction schemes of the TEOS–TIPT–VTES are as follows. After mixing A′ and B′, Reactions 1–5 occurred. After adding TIPT, the co-condensation reactions between hydrolysed TEOS and TIPT, Reaction 6, and between hydrolysed VTES and TIPT, Reaction 7

$$(\text{-O-})_3\text{Si-OH} + \text{H}_9\text{C}_3\text{O-Ti(-O-)}_3 \rightarrow$$
$$(\text{-O-})_3\text{Si-O Ti(-O-)}_3 + \text{C}_3\text{H}_9\text{OH} \qquad (6)$$

$$(\text{-O-})_2\text{Si(CH} = \text{CH}_2\text{)(-OH)} + \text{H}_9\text{C}_3\text{O-Ti(-O-)}_3 \rightarrow$$
$$(\text{-O-})_2\text{Si(CH} = \text{CH}_2\text{)-O-Ti(-O-)}_3 + \text{C}_3\text{H}_9\text{OH} \qquad (7)$$

After further adding water, hydrolysis and polycondensation further proceeded without precipitation.

3.2. Vickers hardnesses of the ormosil coatings

Transparent coatings with various compositions were prepared. The molar compositions were TEOS–VTES = 0.3:0.7, 0.6:0.4, 0.9:0.1. In the microhardness measurements, when the ratio D/t of the indentation depth to the film thickness exceeds a critical value, the measured hardness is influenced by the substrate material and is no longer a characteristic of the coating. To obtain Vickers hardness values of the ormosil coatings, the models developed by Jönsson and Hogmark were used [4]. The equation derived from their models is

$$(H_m - H_s)/(H_c - H_s) = 2C(t/D) - C^2(t/D)^2 \qquad (8)$$

where H_m is the measured hardness, H_s is the hardness of the substrate, H_f is the hardness of the coating and $C = 2\sin^2 11°$. They showed that the experimental and calculated data from Equation 8 agreed well for $D/t > 1$.

For TEOS–VTES = 0.3:0.7, a sufficiently thick coating to measure directly the hardness of the coating was obtained. D/t should be less than 0.2 in order to measure the hardness of the coating directly [12]. For TEOS–VTES = 0.6:0.4 and 0.9:0.1, such thick coatings could not be obtained because of cracking. Thus, Vickers hardnesses were measured for various coatings with various thicknesses, and the hardnesses of the coatings were calculated by using Equation 8. The data for TEOS–VTES = 0.6:0.4 and TEOS–VTES = 0.9:0.1 are shown in Table II. The average values were chosen as the hardness values. The hardness of the PET substrate was 24 kg mm^{-2}.

The authors have developed theoretical models for the calculation of hardnesses of hard ormosils [5, 6]. The equation for Vickers hardness is given by

$$H_V = 337C'[1/(10.8V_t - 1)]^{1/2} V_t^2 \alpha^{1/2} G \qquad (9)$$

where H_V is Vickers hardness, C′ is a constant, V_t is the packing density, α is the relative bond strength (α = 1 for silica glass) and G is the dissociation energy per unit volume. In this equation, the units of H_V and G are given in kg mm^{-2} and kcal cm^{-3}, respectively. From Equation 9, the hardness increases with the increasing packing density and is proportional to $\alpha^{1/2}$ G. α is given by [13]

$$\alpha = \sum(f_i n_i \varepsilon_i)/\varepsilon_{Si}\sum(f_i n_i) \qquad (10)$$

where f_i is the number of cations, n_i is the co-ordination number, ε_i is the single bond strength of cation i to oxygen bond and ε_{Si} is the single bond strength of the Si–O bond. $\alpha^{1/2}$ G for various oxides were calculated and shown in Table III [14, 15]. From Table III,

TABLE I Effect of the TIPT addition on the ^{29}Si chemical shifts [6, 11]

	Silicate structure[a]	− δ (p.p.m.)	− δ (p.p.m.)
T^2	$\text{Si(CH}_2 = \text{CH)(-O}R\text{)(-O-Si} \equiv)_2$	67.0– 75.0 → T^2(Ti)	64.0–69.0
T^3	$\text{Si(CH}_2 = \text{CH)(-O-Si} \equiv)_3$	79.0– 83.0 → T^3(Ti)	70.0–76.0
Q^2	$\text{Si*(-O}R)_2\text{(-O-Si} \equiv)_2$	88.0– 94.0 → Q^2(Ti)	85.0–89.0
Q^3	$\text{Si*(-O}R\text{)(-O-Si} \equiv)_3$	96.0–104.0 → Q^3(Ti)	91.0–95.0
Q^4	$\text{Si*(-O-Si} \equiv)_4$	106.0–110.0 → Q^4(Ti)	99.0–103.0

[a] Each peak shows Si*. R = H or C_2H_5.

TABLE II Measured and calculated Vickers hardnesses of the TEOS–VTES system coatings

TEOS–VTES = 0.6:0.4					
Thickness (μm)	1.70	1.92	2.13	2.34	2.56
Measured hardness (kg mm^{-2})	28.70	31.10	32.20	32.70	33.00
Calculated hardness (kg mm^{-2})	94.00	115.00	119.00	112.00	108.00
TEOS–VTES = 0.9:0.1					
Thickness (μm)	0.89	1.07	1.25	1.42	1.60
Measured hardness (kg mm^{-2})	29.70	30.40	32.70	33.90	35.70
Calculated hardness (kg mm^{-2})	182.00	171.00	188.00	186.00	191.00

TABLE III $\alpha^{1/2}G$ for various oxides [14, 15]

Oxide	CN[a]	ε(kcal) [14]	α	G(kcal cm^{-3}) [15]	$\alpha^{1/2}G$
Al_2O_3	4	101.0	0.953	32.0	31.24
	6	67.0	0.632	32.0	25.44
ZrO_2	4	121.0	1.142	23.2	24.79
	6	80.8	0.762	23.2	20.25
	8	60.6	0.572	23.2	17.55
TiO_2	4	109.0	1.028	20.7	20.99
	6	72.5	0.684	20.7	17.12
SiO_2	4	106.0	1.000	15.4	15.40

[a] CN stands for co-ordination number.

TABLE IV Measured and calculated Vickers hardnesses of the TEOS–TIPT–VTES system coatings

TEOS–TIPT–VTES = 0.3:0.3:4					
Thickness (μm)	1.62	1.82	2.02	2.22	2.42
Measured hardness (kg mm^{-2})	29.70	31.70	33.60	33.90	34.20
Calculated hardness (kg mm^{-2})	112.00	126.00	136.00	129.00	123.00
TEOS–TIPT–VTES = 0.6:0.3:0.1					
Thickness (μm)	0.86	1.03	1.20	1.38	1.55
Measured hardness (kg mm^{-2})	30.60	31.40	33.60	34.40	37.60
Calculated hardness (kg mm^{-2})	211.00	197.00	211.00	198.00	219.00

Al_2O_3, ZrO_2 and TiO_2 substitution for SiO_2 is effective to increase the hardness.

Some 30 mol % TiO_2 containing ormosil coatings were prepared. The molar compositions were TEOS–TIPT–VTES 0:0.3:0.7, 0.3:0.3:0.4, 0.6:0.3:0.1. The porosity of the coatings are affected by the cluster size and the cluster size should be small to obtain dense coatings [16]. For the TEOS–VTES system, the solutions could be used for about one month to obtain dense transparent coatings, but for the TEOS–TIPT–VTES system, the solutions could be used only for several days, and after several days the coatings became porous and opaque. As in the case of the TEOS–VTES system, the hardnesses were measured directly for TEOS–TIPT–VTES = 0:0.3:0.7 and calculated by using Equation 8 for TEOS–TIPT–VTES = (a) 0.3:0.3:0.4 and (b) 0.6:0.3:0.1 (Table IV).

Vickers hardnesses of the coatings of the TEOS–VTES and TEOS–TIPT–VTES systems are plotted in Fig. 3. The packing densities decrease with increasing organic content since the organic sites do not participate in the network formation [5, 6]. If the VTES molar ratio is x and only chemical bonds are considered, $\alpha^{1/2}G$ for the TEOS–VTES and TEOS–TIPT–VTES systems are $15.4(1-4/x)^{2/3}$ and $15.4(1.008-x/4)^{1/2}(1.103-x/4)$, respectively [13–15]. The co-ordination number is kept at four below 400 °C in

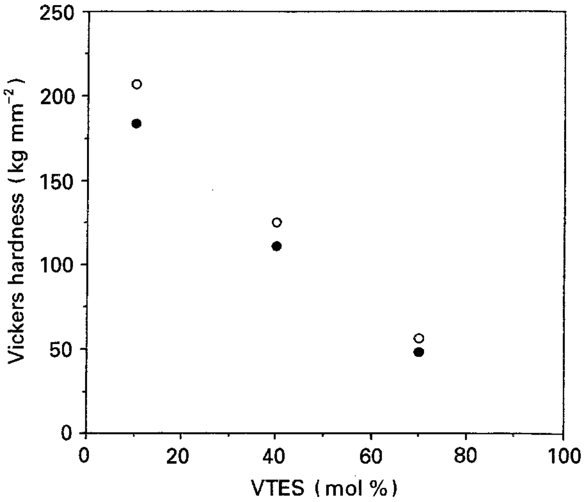

Figure 3 Vickers hardnesses of the ormosil coatings: (●) 0 mol % TiO_2, (○) 30 mol % TiO_2.

TABLE V Vickers hardnesses of the hardest transparent plastics and some glasses [12, 18, 19]

Material	Vickers hardness (kg/mm^2)
Polyethyleneterephthalate (PET) [12]	24
Polymethylmethacrylate (PMMA) [12]	19
Polycarbonate (PC) [12]	14–16
Borosilicate glass [18]	220–350
Window glass [19]	480–620

this preparation procedure [17]. $\alpha^{1/2}$ G also decreases with increasing x and is higher for the TEOS–TIPT–VTES system than for the TEOS– VTES system. These trends are consistent with experimental results. Even though Equation 9 was not applicable to ormosils with higher organic contents, because interactions between dangling organic sites must be considered [5, 6], Equation 9 is still valuable to predict the hardness values of ormosil coatings.

For comparison, Vickers hardnesses of the hardest transparent plastics and some glasses are shown in Table V [5, 6, 18, 19]. The ormosil coatings presented in this report are much harder than the hardest transparent plastics, and the hardest ormosil coatings have hardness values of soft glasses.

4. Conclusions

The chemical bonds between TEOS and VTES, between TEOS and TIPT, and between VTES and TIPT were proven by liquid state ^{29}Si NMR spectroscopy and the reaction schemes were proposed. Vickers hardnesses of the ormosil coatings were obtained by using the models developed by Jönsson and Hogmark, and the theoretical models developed by the authors were valuable to predict the hardness values. The authors' ormosil coatings were much harder than the hardest transparent plastics, and thus are very useful for hard or protective coatings on organic polymers.

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References

1. G. PHILIPP and H. SCHMIDT, *J. Non-Cryst. Solids* **63** (1984) 283.
2. G. L. WILKES, B. ORLER and H. HUANG, *Polym. Prepr.* **26** (1985) 300.
3. J. J. BIKERMAN (Ed.), in "The Science of Adhesive Joints" (Academic Press, New York, 1968).
4. B. JÖNSSON and S. HOGMARK, *Thin Solid Films* **114** (1984) 257.
5. T. IWAMOTO and J. D. MACKENZIE, in "Better Ceramics Through Chemistry VI", edited by A. K. Cheetham, C. J. Brinker, M. L. Mecartney and C. Sanchez (Elsevier, New York, 1994) p. 397.
6. *Idem, J. Sol-Gel Sci. Technol.* **4** (1995)
7. B. E. YOLDAS, *J. Non-Cryst. Solids* **38&39** (1980) 81.
8. G. C. LEVY and J. D. CARGIOLI, in "Nuclear Magnetic Resonance Spectroscopy of Nuclei Other Than Protons", edited by T. Axenrod and G. A. Webb (Wiley, New York, 1974) Ch. 17.
9. Y. SUGAHARA, Y. TANAKA, S. SAITO, K. KURODA and C. KATO, in "Better Ceramics Through Chemistry V", edited by M. J. Hampden-Smith, W. G. Klemperer and C. J. Brinker (Elsevier, New York, 1992) p. 231.
10. K. L. WALTHER, A. WOKAUN, B. E. HANDY and A. BAIKER, *J. Non-Cryst. Solids* **134** (1991) 47.
11. H. MARSMANN, in "NMR-17, Oxygen-17 and Silicon-29", edited by P. Diehl, E. Fluck and R. Kosfeld (Springer, Berlin, 1981) p. 65.
12. A. K. BHATTACHARYA and W. D. NIX, *Int. J. Solids Struct.* **24** (1988) 1287.
13. M. YAMANE and J. D. MACKENZIE, *J. Non-Cryst. Solids* **15** (1974) 153.
14. K. H. SUN, *J. Amer. Ceram. Soc.* **30** (1947) 277.
15. A. MAKISHIMA and J. D. MACKENZIE, *J. Non-Cryst. Solids* **12** (1973) 35.
16. C. J. BRINKER and G. W. SCHERER (Eds), in "Sol–Gel Science" (Academic Press, San Diego, 1990) p. 799.
17. H. MORIKAWA, T. OSUKA, F. MARUMO, A. YASUMORI, M. YAMANE and M. MOMURA, *J. Non-Cryst. Solids* **82** (1986) 97.
18. M. IMAOKA, H. HASEGAWA, Y. HAMAGUCHI and Y. KUROTAKI, *Yogyo Kyokaishi* **79** (1971) 164.
19. L. AINWORTH, *J. Soc. Glass Technol.* **38** (1954) 501.

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