

# Organic–Inorganic Hybrid Materials. II. Preparation and Properties of Higher Silica Containing Polycarbonate–Silica Hybrid Materials

Motoomi Arakawa,<sup>1</sup> Kazuaki Sukata,<sup>1</sup> Masayuki Shimada,<sup>2</sup> Yasuyuki Agari<sup>2</sup>

<sup>1</sup>*Orient Chemical Industry, Limited, 8-1, Sanra-higashi-machi, Neyagawa, Osaka 572-8581, Japan*

<sup>2</sup>*Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536-8553, Japan*

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**ABSTRACT:** The sol–gel reaction of a polycarbonate (PC) oligomer having triethoxysilyl groups at both ends of the PC chain (PCS) with a tetraethoxysilane or tetramethoxysilane oligomer provided transparent or semitransparent films of higher silica containing organic–inorganic hybrid materials (HSPC-HMs). The films were superior to those from PC and from PCS in terms of the morphological homogeneity, heat

resistance, and surface hardness. The HSPC-HM films had minimum oxygen permeability at a PCS/tetraethoxysilane ratio of 3/7. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4273–4279, 2006

**Key words:** hybrid materials; polycarbonates; silicas; sol-gel reactions

## INTRODUCTION

Since the first organic–inorganic hybrid material was reported about 2 decades ago,<sup>1</sup> many reports have been published on hybrid materials with various conventional organic polymers, including vinyl polymers such as polystyrene<sup>2</sup> and poly(methyl methacrylate),<sup>3</sup> hydrophilic polymers such as poly(ethylene oxide)<sup>4</sup> and polyoxazoline,<sup>5</sup> and thermosetting resins such as phenolic<sup>6</sup> and epoxide types.<sup>7</sup> On the other hand, several organic–inorganic hybrid materials with engineering plastics, which are expected to be higher in function and in performance than those with conventional polymers, have also been investigated.<sup>8</sup>

Chujo and coworkers reported that the sol–gel reaction of tetraethoxysilane (TEOS) and phenyltriethoxysilane in the presence of polycarbonate (PC), well known as a high-performance engineering plastic, produced organic–inorganic hybrid materials, in which the hydrogen bonding between the silica–hydroxy and PC–carbonyl groups<sup>9</sup> and the  $\pi$ – $\pi$  interaction between the silica–phenyl and PC–phenylene  $\pi$  electrons played an important role in affinity with the organic and inorganic components,<sup>10</sup> respectively. On the other hand, we considered that the covalent bond between the organic and inorganic components should increase the interfacial interaction between the two components more than hydrogen bonding and

$\pi$ – $\pi$  interaction, producing materials with various superior properties. Based on this idea, our previous article<sup>11</sup> reported that the sol–gel reaction of a PC oligomer having triethoxysilyl groups at both ends of the PC chain (PCS) provided covalently bound polycarbonate–silica hybrid materials (PCS-HMs), which were superior to PC in heat resistance, mechanical strength, and surface hardness.

Because an increase in the silica content of PCS-HM was expected to make PCS-HM with improved performance, higher silica containing polycarbonate–silica hybrid materials (HSPC-HMs) were prepared by the sol–gel reaction of PCS with alkoxy silanes. This article describes the preparation and results of the evaluation of the heat resistance, surface hardness, oxygen permeability, and internal structure of HSPC-HMs.

## EXPERIMENTAL

### Materials

PC (Iupilon E2000 grade, Mitsubishi Engineering Plastics Co., Tokyo, Japan) was dried at 120°C for 5 h before use. Tetramethoxysilane oligomer [MKC Silicate MS56 grade (MS56), Mitsubishi Chemicals, Tokyo, Japan] was used as received. TEOS (Nacalai Tesque Co., Kyoto, Japan) and tetrahydrofuran (THF; Nacalai Tesque Co.) were used as received.

### Preparation of the hybrid materials

PCS [number-average molecular weight ( $M_n$ ) = 4400, 7500, or 9000] was prepared by the same method described in our previous article.<sup>11</sup> HSPC-HM was pre-

Correspondence to: K. Sukata (k\_sukata@orientchemical.com).

pared as follows. To 10 wt % THF solutions of PCS and TEOS (PCS+TEOS) or PCS and MS56 (PCS+MS56) of various weight ratios was added aqueous HCl (1 mol/L) equivalent to the number of alkoxy groups. The resulting solutions were stirred at a room temperature for 1 h, and this produced clear sol solutions.

#### Cast films

A sol solution was cast onto a stainless steel dish coated with Teflon, and then the volatile portion was slowly removed at room temperature over several days to produce a clear film. This method provided clear HSPC-HM films (cast films) having thicknesses of 81–216  $\mu\text{m}$  and various PCS/TEOS or PCS/MS56 weight ratios (10/0–0/10).

#### Film-coated glass

Sol solutions with various PCS/TEOS or PCS/MS56 weight ratios were spin-coated onto glass plates to produce HSPC-HM-coated glass plates. The thicknesses of the coating films were 2–20  $\mu\text{m}$ .

#### Film-coated low-density corona-charged polyethylene (LDPE)

LDPE (30  $\mu\text{m}$  thickness) was coated with sol solutions to produce LDPE coated with HSPC-HM. The thicknesses of the coating films were 4–33  $\mu\text{m}$ .

As a control, the cast films, film-coated glass, and film-coated LDPE with PC and TEOS (PC+TEOS) or PC and MS56 (PC+MS56) were prepared by the same method described previously.

#### Scanning electron microscopy (SEM) analysis

After a cast film was immersed in liquid nitrogen, the film was cracked. The cross section of the broken film was observed with a JSM-5800LVM (JEOL Co., Tokyo, Japan; 10–20 kV; magnification = 3000–10,000 $\times$ ).

#### Dynamic mechanical analysis (DMA)

Because the brittleness of the HSPC-HM films increased with an increasing TEOS or MS56 ratio, the measurement was performed only on films with a small ratio of TEOS or MS56. The measured sample was obtained as follows. After a cast film was heated at 150°C for 6 h, the film was cut to a typical size (25  $\times$  10  $\times$  0.1 mm<sup>3</sup>) for the measurement. DMA was performed with an SDM-5600 (Seiko Instruments, Inc., Chiba, Japan; tensile mode; 2.0°C/min rate from 25 to 300°C; 1 Hz).

#### Surface hardness evaluation

The measured sample was obtained as follows. Film-coated glass was heated at 80°C for 6 h and allowed to stand at 23°C in air with 50% relative humidity for 48 h. According to JIS K 5400, the surface hardness of the resulting film-coated glass was evaluated with a Heidon-14 [Heidon Co., Tokyo, Japan; sliding speed of sample table = 30 mm/min; loading = 1 kg; pencil = UNI (Mitsubishi Pencil Co., Tokyo, Japan)].

#### Oxygen permeability

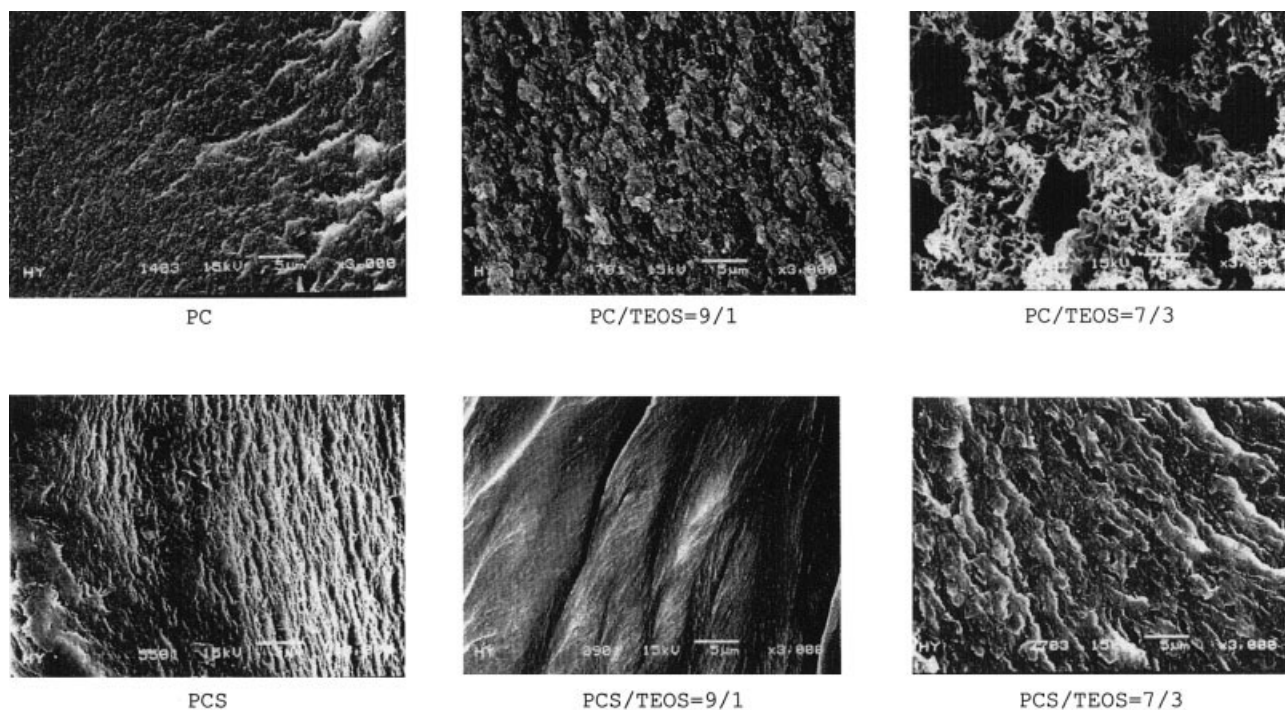
The sample to be measured was obtained as follows. Film-coated LDPE was heated at 60°C for 6 h and dried at room temperature for 15 h in vacuo. According to JIS K 7126, the oxygen permeability of the resulting film-coated LDPE was evaluated with an M-C3 [Toyo Seiki Co.; gas permeability coefficient = 300–580,000 or 300–60,000 cm<sup>3</sup>/(m<sup>2</sup>  $\times$  24 h  $\times$  atm); cell constant = 55,712].

## RESULTS AND DISCUSSION

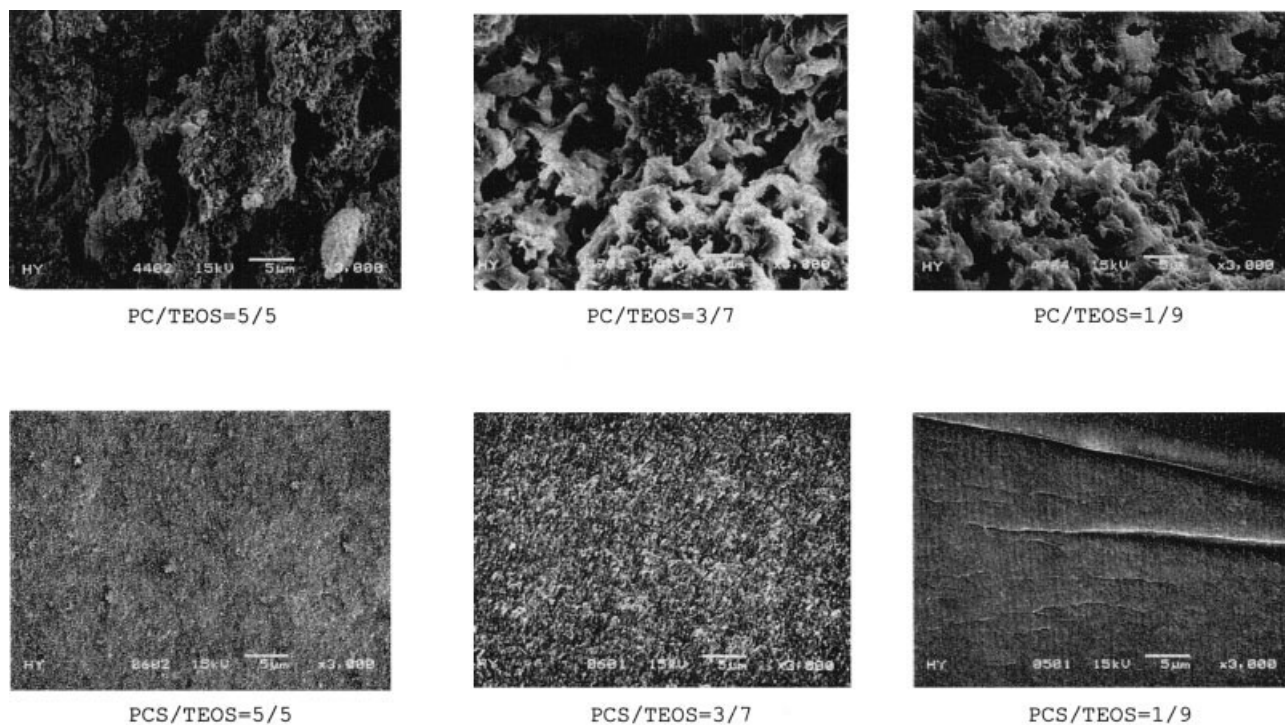
In general, the obtained HSPC-HM films were transparent or semitransparent, and their elasticity increased with an increase in the PCS content. On the other hand, the hardness and brittleness increased with the increasing silica content. When PC was used in place of PCS, the obtained film had many cracks and a large change in shape, being opaque and very brittle.

#### Morphology of HSPC-HM

The morphology of HSPC-HM obtained from PCS+TEOS was compared with that of the material obtained from PC+TEOS by SEM. SEM photographs of the cross section of the film obtained from PCS ( $M_n$  = 4400)/TEOS (9/1–1/9 ratios) and from PC ( $M_n$  = 36,100)/TEOS (9/1–1/9 ratios) are shown in Photographs 1–3. In all the films made from PC+TEOS, a large number of pores and grooves about 1–10  $\mu\text{m}$  in size were observed (3000 $\times$  for Photographs 1 and 2). The cross section is in an extremely rough state with numerous rugged spots. The roughness appears to increase with an increase in the TEOS content. Because PC having no triethoxysilyl groups and silica cannot link together and they are incompatible, they must easily gather themselves to produce the macrophase separation between the PC and silica phases in the film preparation. The pore is considered to be generated by falling off the large silica particles. On the other hand, the morphologies of all HSPC-HM films made from PCS+TEOS were much more homogeneous than those of the films made from PC+TEOS (3000 $\times$  for Photographs 1 and 2). This result indicates that no macrophase separation occurs for films made from PCS+TEOS. In PCS+TEOS, it is expected that



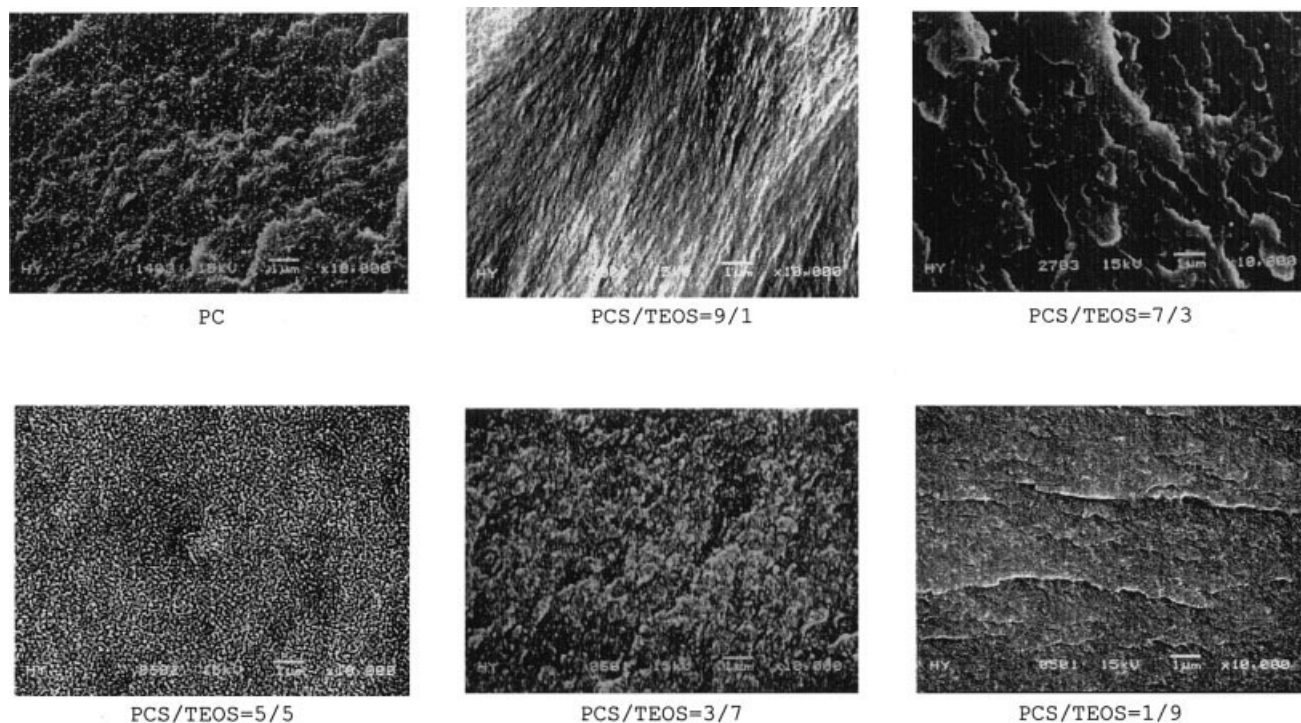
**Photograph 1** SEM photographs of typical HSPC-HM and PC/silica films ( $M_n$  for PCS = 4400;  $M_n$  for PC = 36,100; magnification = 3000 $\times$ ).



**Photograph 2** SEM photographs of typical HSPC-HM and PC/silica films ( $M_n$  for PCS = 4400;  $M_n$  for PC = 36,100; magnification = 3000 $\times$ ).

the ends of the PC chain will be covalently bound with silica during the sol-gel reaction to suppress the macrophase separation, that is, to provide a homogeneous morphology.

With 10/0 and 9/1 PCS/TEOS, a large number of stripes parallel to one another, which were strikingly similar to the morphology of PC, were observed (10,000 $\times$  for Photograph 3). With 7/3 PCS/TEOS, al-



**Photograph 3** SEM photographs of typical HSPC-HM films ( $M_n$  for PCS = 4400; magnification = 10,000 $\times$ ).

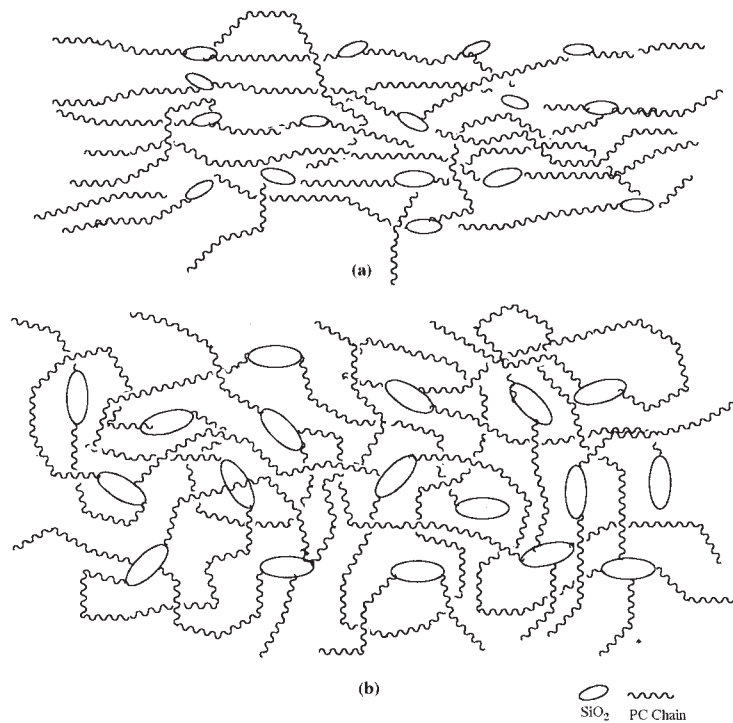
though this striped pattern was observed, a number of granular materials were also observed in the stripes. Over 5/5 PCS/TEOS, no striped pattern was observed. Although for 5/5 and 3/7 PCS/TEOS, granular materials less than  $1/10 \mu\text{m}$  in size appear to be homogeneously distributed, the morphology for 5/5 PCS/TEOS is more minute than that for 3/7 PCS/TEOS. The morphology for 1/9 PCS/TEOS appears to be much smoother than that for 5/5 and 3/7 PCS/TEOS. These characteristic features lead us to speculate that there are two types of morphologies. When the ratio of TEOS is relatively small, such as 10/0–7/3 PCS/TEOS, the crosslinking reaction between alkoxy groups is expected to be slow, and the crosslinking density is small because PCS has only two triethoxysilyl groups at both ends of the PC long chain. In the cast-film preparation, consequently, the polymer chains are thought to arrange in a certain order, namely, parallel to one another [Fig. 1(a)]. On the other hand, over 7/3 PCS/TEOS, the rate and density of the crosslinking reaction are so high that the polymer chains must complicatedly entangle with one another [Fig. 1(b)]. The morphology for 7/3 PCS/TEOS indicates a boundary between the two types. When more trialkoxysilyl groups are introduced into the PC chain, only the latter type of morphology is expected to be observed.

#### Heat resistance of HSPC-HM

The heat resistance of HSPC-HM was compared to that of PC ( $M_n = 36,100$ ) by DMA. Figures 2–5 show

the relation of the elastic modulus and  $\tan \delta$  with the temperature for HSPC-HM made from PCS ( $M_n = 4400$  or 7500) and MS56. For HSPC-HM, the drop in the elastic modulus with increasing temperature was much smaller than that for PCS-HM made from only PCS, and it decreased with an increase in the silica content. The start of the drop in the elastic modulus shifted to a higher temperature as the silica content increased. These results indicate that HSPC-HM maintains a substantial elasticity even over its glass-transition temperature ( $T_g$ ). Consequently, with few exceptions, the shape of the sample remained up to approximately  $300^\circ\text{C}$ . These results indicate that HSPC-HM has a higher heat resistance than PCS-HM, which is superior to PC.

$T_g$  of HSPC-HM was higher than that of PCS-HM and increased with an increase in the silica content. In addition,  $\tan \delta$  broadened and rapidly decreased with increasing silica content. The increase in  $T_g$  and the broadness and decrease in  $\tan \delta$  with an increase in the silica content can be explained as follows. The increasing silica content must increase the crosslinking density and the silica particle size of the crosslinking point, thus suppressing the molecular motion of the PC segment. This suppression of the molecular motion should increase  $T_g$  and reduce  $\tan \delta$ . On the other hand, it can be concluded that the wide distribution in the difference of the crosslinking structure broadens the  $\tan \delta$  peak.



**Figure 1** Model of the HSPC-HM polymer chain: (a) PCS/TEOS less than approximately 7/3 and (b) PCS/TEOS greater than approximately 7/3.

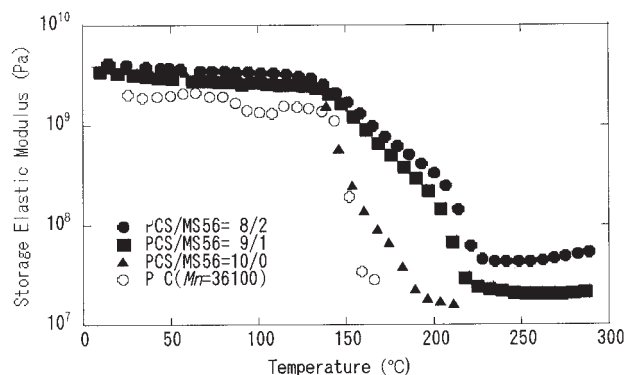
**Surface hardness of HSPC-HM**

The surface hardness of HSPC-HM in film-coated glass was measured (Table I). For the PCS/TEOS ratios of 7/3 and 5/5, the hardness was similar to that of PCS-HM, whereas it was superior to that of PCS-HM as the TEOS content increased. It can be concluded that this result was caused by an increase in the crosslinking density and in the silica particle size of the crosslinking point with increasing silica content. When PC having many more alkoxy groups was used in place of PCS, the crosslinking density was

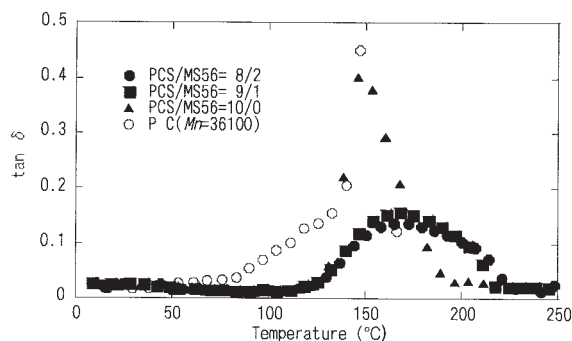
expected to increase, further increasing the surface hardness.

**Oxygen permeability of HSPC-HM**

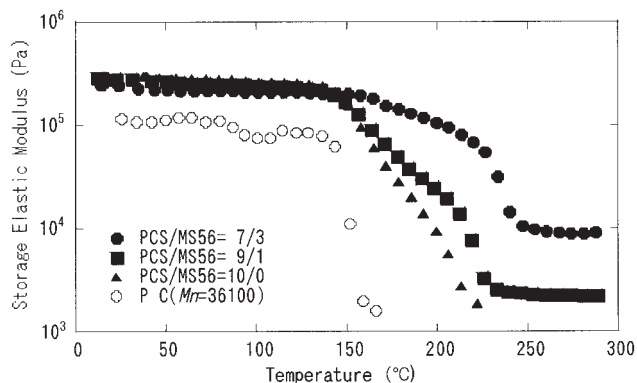
Figure 6 shows the relation of the oxygen permeability coefficient with the TEOS content. Although for 10/0–7/3 PCS/TEOS the oxygen permeability was strikingly similar to that of PC, for 5/5–3/7 PCS/TEOS, the oxygen permeability rapidly decreased with an increase in the TEOS content, and the oxygen permeability for 4/6–3/7 PCS/TEOS decreased by approximately one-fifth compared with the PCS/TEOS ratio



**Figure 2** Storage elastic modulus of HSPC-HM prepared from PCS ( $M_n = 4400$ ) and MS56 [tensile mode; frequency = 1 Hz; heat treatment = 150°C (for PC, 120°C)].



**Figure 3** Tan  $\delta$  of HSPC-HM prepared from PCS ( $M_n = 4400$ ) and MS56 [tensile mode; frequency = 1 Hz; heat treatment = 150°C (for PC, 120°C)].

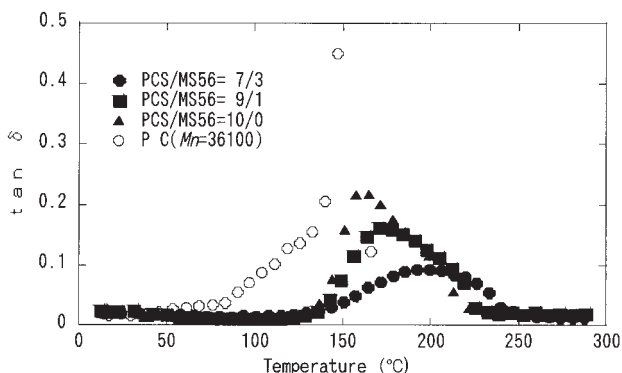


**Figure 4** Storage elastic modulus of HSPC-HM prepared from PCS ( $M_n = 7500$ ) and MS56 [tensile mode; frequency = 1 Hz; heat treatment = 150°C (for PC, 120°C)].

of 10/0. For 2/8 and 1/9 PCS/TEOS, the oxygen permeability increased again with an increase in the TEOS content. That is, the minimum oxygen permeability was observed for 4/6–3/7 PCS/TEOS.

For the permeation of an oxygen molecule through the PC film, the oxygen molecule must pass through the reticular structure consisting of the PC chains, which overlap and complicatedly entangle with one another. The permeation of an oxygen molecule, therefore, should decrease with a decrease in the mobility of the PC chain. In HSPC-HM, it is expected that increases in the crosslinking density and in the silica particle size of the crosslinking point will suppress the molecular mobility of the PC segment and reduce the oxygen permeability.

As shown in the Morphology of HSPC-HM section, for 10/0–7/3 PCS/TEOS, because their cross sections resemble that of PC in morphology and their crosslinking densities are low, the PC segments should have a mobility similar to that of PC. Consequently, their oxygen permeability would be similar to that of PC. On the other hand, over 7/3 PCS/TEOS,



**Figure 5** Tan  $\delta$  of HSPC-HM prepared from PCS ( $M_n = 7500$ ) and MS56 [tensile mode; frequency = 1 Hz; heat treatment = 150°C (for PC, 120°C)].

**TABLE I**  
Surface Hardness of HSPC-HM in Film-Coated Glass

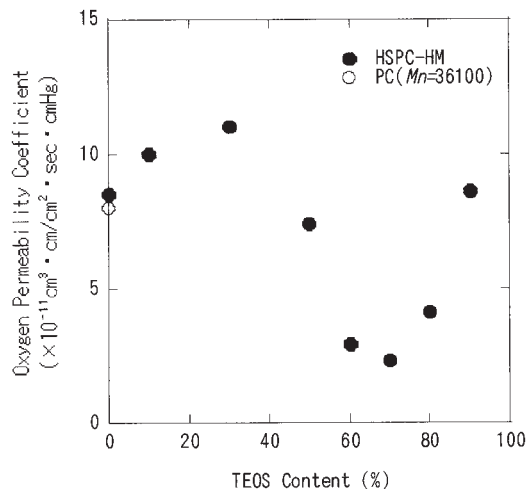
Sample <sup>a</sup>	$M_n$ <sup>b</sup>	Thickness ( $\mu\text{m}$ )	Pencil hardness
PC	36,100	8	HB
PCS/TEOS = 10/0	9,000	10	4H
7/3		6	3H
5/5		3	3H
3/7		6	5H
1/9		3	9H
PCS/TEOS = 10/0	7,500	18	4H
7/3		11	3H
5/5		3	4H
3/7		2	5H
1/9		2	9H
PCS/TEOS = 10/0	4,400	20	3H
7/3		3	3H
5/5		2	5H
3/7		2	8H
1/9		2	9H
PCS/TEOS = 0/10	—	1	9H

<sup>a</sup> Heat treated at 80°C.

<sup>b</sup> For starting PC and PCS.

the PC segments should be hard to move in comparison with those with 10/0–7/3 PCS/TEOS because the polymer chains complicatedly entangle with one another and the crosslinking density is greater. Therefore, an oxygen molecule is expected to be difficult to permeate through the film with an increase in the TEOS content.

The oxygen permeability was consistent with this expectation only for 10/0–3/7 PCS/TEOS. For 2/8 and 1/9 PCS/TEOS, however, the oxygen permeability increased with an increase in the TEOS content. This minimum region (PCS/TEOS = 4/6–3/7) appears to correspond to 5/5 PCS/TEOS, in which the morphology is most minute for 7/3–3/7 PCS/TEOS



**Figure 6** Oxygen permeability coefficient of HSPC-HM prepared from PCS ( $M_n = 4400$ ) and MS56.

films made for morphology observation. If the difference in the minuteness of the morphology is why the oxygen permeability increased with an increase in the TEOS content over 2/8 PCS/TEOS, it cannot be understood that the oxygen permeability for 1/9 PCS/TEOS, which has a more minute morphology than 3/7 PCS/TEOS, is greater than that for 3/7 PCS/TEOS. This result, therefore, should be explained as follows. When the silica particle size is too large, the generation of porous silica cannot be avoided. Over 3/7 PCS/TEOS, the oxygen molecule is considered to mainly permeate through this pore of the large silica particle generated by the sol-gel reaction in the higher silica content. The increases in the crosslinking density and in the silica particle size of the crosslinking point suppress the oxygen permeability, whereas over a certain PCS/TEOS ratio, the oxygen permeation through the sol-gel silica pore increases. It can be expected that the oxygen permeability will further decrease when the crosslinking density is increased and the size of the crosslinking point is decreased with the PC having many more alkoxy-silyl groups.

### CONCLUSIONS

The sol-gel reaction of PCS with silicon alkoxides provided transparent or semitransparent films of higher silica containing organic-inorganic hybrid materials (HSPC-HM). The films had a much more homogeneous morphology than those made from PC and silicon alkoxides. This fact demonstrates the usefulness of the alkoxy-silyl group at both ends of the PC chain. Furthermore, the films were superior to those

from PC and from PCS in heat resistance and in surface hardness. This result shows the importance of the silica crosslinking points. In addition, the HSPC-HM films had a minimum oxygen permeability at the PCS/TEOS ratio of 3/7.

This result indicates that not only the covalent linkage between the organic and inorganic components but also the density and size of the crosslinking point play an important role in the material performance, leading to the expectation that the use of PC having many more alkoxy-silyl groups will produce higher performing organic-inorganic hybrid materials.

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