

Organic—inorganic polymers hybrids

Takeo Saegusa

Kansai Research Institute, Kyoto Research Park, Shimogyo-ku, Kyoto, Japan 600
(Professor Emeritus, Kyoto University)

Abstract - A series of blends at molecular level dispersion between an organic polymer and metal oxide (mainly silica) are described. These blends are called "organic-inorganic polymers hybrids". The dimension of dispersion of "hybrids" is much smaller than that of the so-called "composites". The most suitable organic polymers for the formation of hybrids are those which consist of repeating unit containing N-alkyl and N, N-dialkyl carboxylamide groups "amide polymers".

Blending of various combinations between organic polymers and inorganic materials has been very useful for the exploration of new materials having unique properties and specific performances. They are called by a general term of "composites", which are usually heterogeneous materials. For example, an inorganic material such as silica in the form of particle is dispersed in a matrix of organic polymer.

This lecture is concerned with a new family of homogeneous transparent glass materials in which organic polymers and inorganic materials are blended with each other by mutual dispersion at molecular dimension (1).

They are termed "hybrids" in order to be differentiated from "composite". "Composites" and "hybrids" differ from each other in respect to the dimension of dispersion.

This lecture describes the following items about hybrids.

1. General Preparative Method
2. Structural Characteristics
3. Scope and Variations

1. General Preparative Method

Silica is representative of the inorganic components, whose structure is schematically expressed as a three-dimensional network consisting of a building unit of >Si—O—Si< linkage (Fig. 1). Thus, the wording of "inorganic polymer" has been adopted here. This concept may be generally applied to other metal oxides.

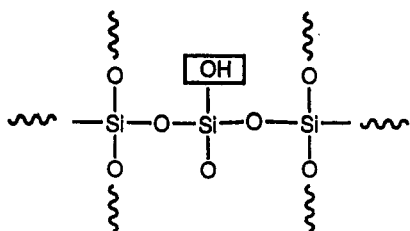
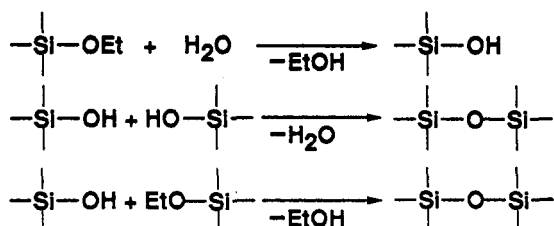


Fig. 1 Schematic expression of structure of silica

Hybrids are not prepared directly from metal oxide, e.g., silica. Instead, metal alkoxide is used as the precursor of metal oxide, which is dispersed at molecular dimension by dissolution in an organic solvent such as alcohol. Then, sol-gel process for the conversion of metal alkoxide to metal oxide, is performed in the presence of an organic polymer which is also being dissolved.

Elemental reactions of sol-gel process are shown below, where $\text{Si}(\text{OEt})_4$ is taken as a case.

Elemental Reactions of Sol-Gel Process



Species carrying silanol group assume a key role, which is generated by the hydrolysis of silicic ester group and, then, proceeds to the condensation reaction to form Si-O-Si linkage. Some of silanol groups remain after the completion of sol-gel process, which constitute the acidic sites of silica.

When the molecular level interaction between the intermediate species of sol-gel reaction of metal alkoxide and the organic polymer component is not strong enough, the so-called "phase separation" takes place to produce a translucent heterogeneous material or a mixture of metal oxide and organic polymer.

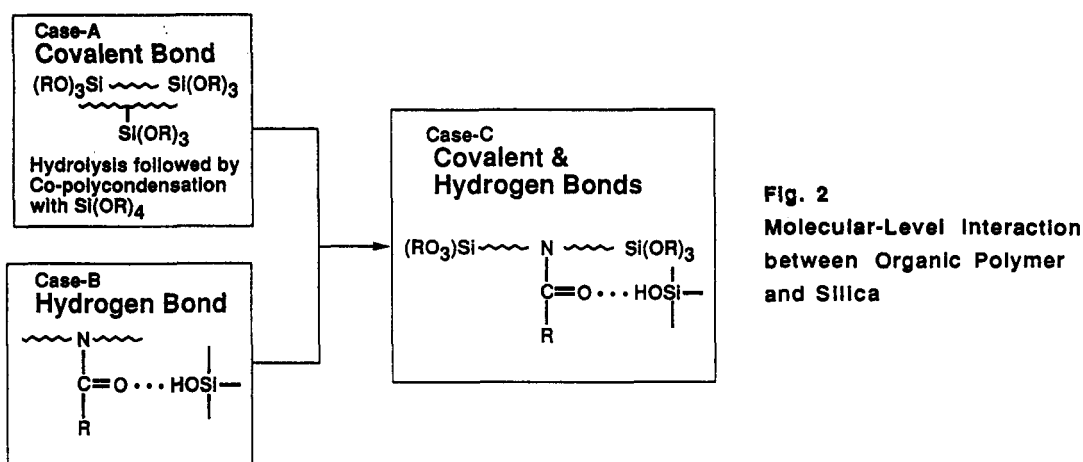


Fig. 2
Molecular-Level Interaction
between Organic Polymer
and Silica

Two types of interactions between organic polymer and silica have successfully been adopted in order to avoid the phase separation to produce homogeneous transparent material. The first one (Case A in Fig. 2) is due to the formation of covalent bond between organic polymer and silica (2). Organic polymers having $-\text{Si}(\text{OR})_3$ group at the end of polymer molecule or in the pendant groups are subjected to hydrolysis together with $\text{Si}(\text{OR})_4$ in homogeneous reaction system. Intermediate species having Si-OH (silanol) groups derived from $\text{Si}(\text{OR})_4$ and from $-\text{Si}(\text{OR})_3$ in polymer react with each other (co-polycondensation) to produce homogeneous materials consisting of chemically bound components. The second type interaction (Case B in Fig. 2) is due to the formation of hydrogen bond between silanol group of the intermediate species from $\text{Si}(\text{OR})_4$ and the basic group of the hydrogen acceptor function in organic polymer (1).

The third type (Case C in Fig. 2) is based on the combination of the above two types of interaction. Thus, an organic polymer having both $-\text{Si}(\text{OR})_3$ group and hydrogen acceptor group is subjected to hydrolysis together with $\text{Si}(\text{OR})_4$ and the subsequent co-polycondensation. The present lecture describes the method due to the second type interaction (Case B), i.e., hybrid materials on the basis of the hydrogen-bonding interaction.

Organic polymers having N-alkyl and N, N-dialkyl substituted carboxylic amide groups have been found most suitable for the preparation of hybrids with silica. Typical examples are shown below.

Amide Polymers

Polymers whose repeating units contain N-alkyl or N,N-dialkyl amide group

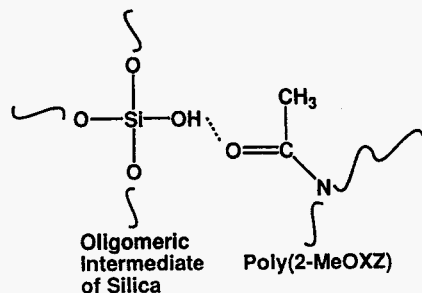
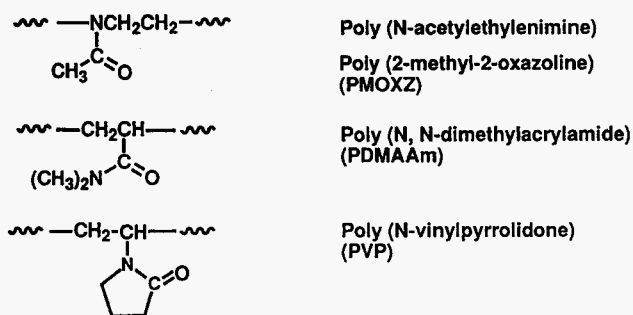


Fig. 3 Polymer molecule is pulled into the growing network of silica

In addition to the above polymers, oligomers of polyamide, polyurea and polyurethane perform well, which are characterized by a structural element of —NHC— , a strong hydrogen acceptor. In the present lecture, these polymers are called by a simplified term of "amide polymers".

Fig. 3 represents an imaginative mechanism for the incorporation of amide polymer molecule by being pulled into the growing intermediate network of silica by hydrogen bond.

2. Structural Characteristics

Fig. 4 shows a sketchy structure of PMOXZ-silica hybrid. PMOXZ, an amide polymer, is being dispersed into the framework of silica by means of hydrogen bond. The imaginative sketch has been found compatible with AFM picture of PVP-silica hybrid (Fig. 5), in which white parts are taken to represent silica (size 15-20 Å) and shaded parts correspond to the parts of PVP (15-30Å).

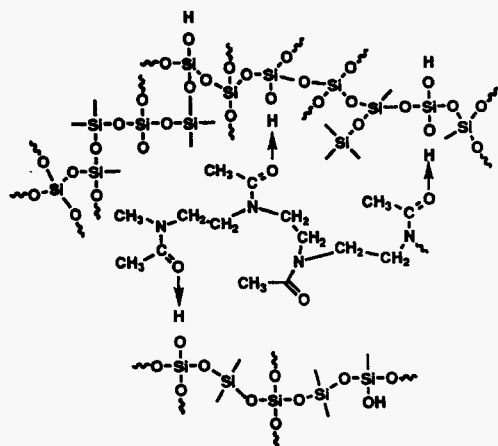


Fig. 4 sketching structure of PMOXZ-silica hybrid

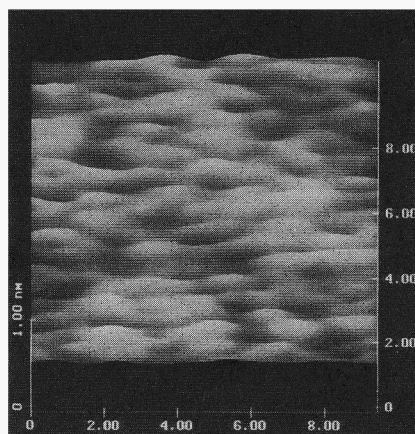


Fig.5 AFM Picture of PVP-silica hybrid (3)

Fig. 6 shows FT-IR spectra of three hybrid materials together with references of those of respective polymer components (1a,1b).

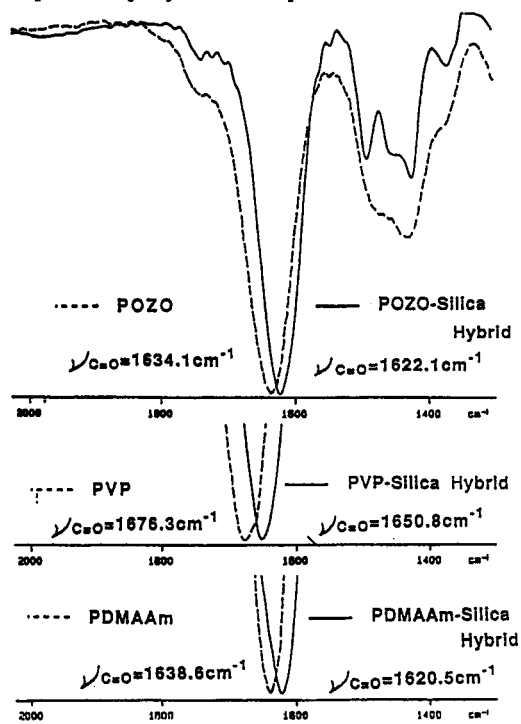


Fig. 6 FT-IR spectrum of organic polymers and hybrids (1a, 1b)

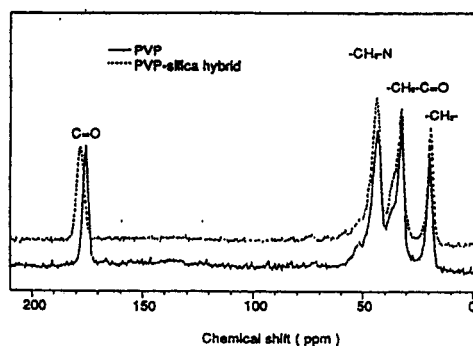


Fig. 7 CP MAS ^{13}C NMR spectra of PVP and PVP-Silica hybrid material (4)

Table 1. Surface area and pore volume (3)

	Surface Area m^2/g	Pore Vol. cm^3/g
Silica dry gel	859	0.6
PVP(67%) - silica hybrid	1.1	0.00

PVP: Poly(vinylpyrrolidone)

In each set of comparison, the shift of the absorption of amide carbonyl group ($1600 - 1650 \text{ cm}^{-1}$) to a longer wave length is observed, which affords a strong support to the formation of hydrogen bond in the hybrids.

Fig. 7 shows ^{13}C NMR (solid) spectrum of PVP-silica hybrid together with a reference of PVP. The shift of the peak due to carbonyl carbon atom at 177 ppm is clearly seen in the spectrum of the hybrid, which is taken to show an indication of the formation of hydrogen bond. No significant shift is observed with the peaks due to other carbon atoms (4).

Results of measurements of the surface area and the volume of inner pores present valuable information concerning the structure of hybrid (Fig. 8 and Table 1) (3).

In Table 1, surface area of inner pores and pore volume of the PVP-silica hybrid are compared respectively with the corresponding values of a reference sample of silica which has been prepared under the same conditions as those for the hybrid preparation (in the absence of PVP). Values of both measurements are very small for the hybrid in comparison with those for silica. These findings are explained by the assumption that the inner parts of silica are filled with polymer.

Fig. 8 shows the results of measurement of the pore size distribution of both PVP-silica hybrid and silica (3). In the range of all pore sizes, the hybrid shows very low values of pore volume (3). Thus, the results in Table 1 and Fig. 7 are compatible with each other, which are indicative of a filled-pore structure of the hybrid.

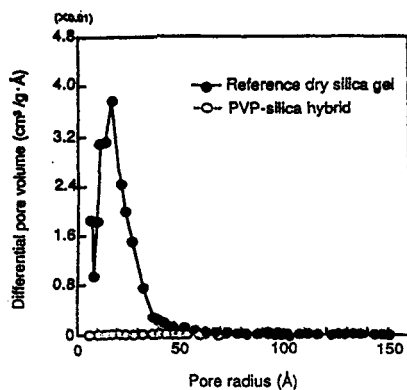


Fig. 8
Pore size distribution of PVP-silica hybrid
and reference of dry silica gel (3)

Fig. 9 represents the results of rheo-vibron measurement of the two samples of hybrid composed of copolyamide oligomer (soluble in EtOH) and silica. A reference (bottom) is a sample of the copolyamide. It is shown that the transition temperature of the copolyamide component becomes higher (12° to 17° to 28 °C) as the content of silica is increased from 0 to 20 to 40 weight percents. These results is understood in terms of the extent of confinement of the movement of copolyamide molecule by means of the hydrogen bond with silica. The rheo-vibron observation is taken to be an indirect support to the structure which has been assumed on the bases of IR and NMR spectrum analyses, pore volume and surface area measurements as well as pore-size distribution.

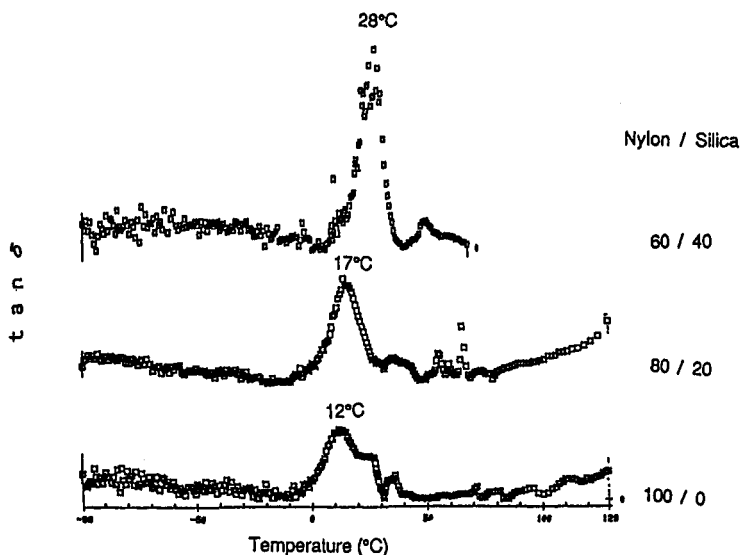


Fig. 9 Rheo-vibron Measurements of copolyamide-Silica and Silica (Copolyamide consisting of caprolactam, and the components of Nylon 6, 66, 610 and 612) (5, 6)

3. Scope and Variations

It has been described that organic polymers whose repeating units possess amide group are the most suitable for the formation of hybrid materials with silica. As the metal alkoxide precursor, $\text{Al}(\text{OR})_3$ (7) and binary mixtures of $\text{Al}(\text{OR})_3 / \text{Si}(\text{OR})_4$ (8) and $\text{Si}(\text{OR})_4 / \text{Ti}(\text{OR})_4$ (3) have successfully been employed to prepare the corresponding hybrids together with amide polymers such as PMOXZ and PVP. Transparent materials of hybrids of alumina, silica-alumina and silica-titania are of big interest.

One of interesting variations of hybrid is the incorporation of transition metal salts such as NiCl_2 , $\text{Cu}(\text{OH})_2$ and CuCl_2 at varying concentrations. Transparent hybrid materials of PMOXZ-SiO_2 having colors characteristic of metal ions have been prepared (7). Various applications on the basis of transition metal ions are conceived with these hybrids.

Another variation is the hybrid materials of ternary components of silica with two organic polymers, one being amide polymer and the other not amide polymer. For example, poly(vinyl chloride) (PVC) is not able to form a transparent homogeneous hybrid (binary component) with silica. However, PVC does form a transparent hybrid material with silica in the co-existence of PMOXZ. This finding is a kind of phenomenon of "compatibilization" of PVC in silica by means of PMOXZ. In fact, PVC and PMOXZ are highly compatible with each other (9). The amount of PVC compatibilized, however, is limited, i.e., up to about 20 wt% of PVC to PMOXZ is compatibilized. Elucidation of the mechanism of compatibilization of PVC in an inorganic material of silica needs further study.

Poly(methyl methacrylate) (PMMA) is compatibilized more readily with silica by PMOXZ. The highest amount of PMMA compatibilized is about 80% toward PMOXZ (10). The difference between PVC and PMMA concerning the limit of amount (wt% to PMOXZ) for compatibilization may be ascribed to the difference of the capability of hydrogen-bond formation (basic strength) between them.

References:

1. "Organic/Inorganic Polymers Hybrids" have been described in the following articles. References for individual papers are be found in these review articles.
 - a) T. Saegusa and Y. Chujo, *J. Macromol. Sci. Chem.*, **A27**, 1603 (1990);
 - b) T. Saegusa, *J. Macromol. Sci. Chem.*, **A28**, 817 (1991);
 - c) T. Saegusa and Y. Chujo, *Makromol. Chem., Macromol. Symp.* **51**, 2 (1991);
 - d) T. Saegusa and Y. Chujo, *Makromol. chem. Macromol. Symp.* **64**, 1 (1992);
 - e) T. Y. Chujo, and T. Saegusa, *Advances in Polymer Sci.*, **100**, 11 (1992);
2. For example, H. Schmidt et al, "Ultra-structure Processing of Advanced Ceramics" J.D. Mackenzie and D.R. Ulrich, Eds., John Wiley, 1988; H. Schmidt *J. Non-Cryst. Solids*, **112**, 419 (1889), G.L. Wilkes et al *Polymer Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, 26 (2), 300; *Macromolecules*, **1987**, 20, 1322; *Macromolecules* **1991**, 24, 3449
3. M. Toki, t.Y. Chow, T. Ohnaka, H. samura, and T. Saegusa, *Polymer Bull.* **29**, 653 (1992)
4. M. Toki Unpublished result
5. T. Y. Chow and H. Samura Unpublished result
6. A commercial sample of copolyamide, Toray Industries, Inc. Japan, CM8000, which consists of the components of Nylon 6, 66, 610 and 612.
7. H. Matsuki, S. Kure, Y. Chujo, and T. saegusa, *Polymer Preprints, Japan*, **41**, 3068 (1992)
8. H. Matsuki, Y. Chujo, and T. Saegusa, *Polymer Preprints, Japan*, **41**, 732 (1992)
9. S. Kobayashi, M. Kaku, and T. Saegusa, *Macromolecules*, **21**, 334 (1988)
10. Y. Chujo, H. Matsuki, and R. Tamaki, *Polymer Preprints*, **47**, 2970 (1993)