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Processing and Properties of Inorganic/Organic Hybrid Materials

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Abstract:

Nippon Steel has investigated the incorporation of organics into inorganic oxide networks at a molecular level to synthesize inorganic/organic hybrid materials which not only have both the properties of inorganic and organic materials but also the possibility of providing novel properties (synergistic properties) unknown in conventional materials. Monolithic and homogeneous inorganic/organic hybrids including various inorganic components were synthesized by sol-gel processing, which provides an inorganic oxide network at low temperatures through chemical reactions of alkoxide precursors. The incorporation of various inorganic components into the hybrids was realized by the chemical modification of metal alkoxides. The hybrids are transparent and flexible. The inorganic component derived from metal alkoxides was found to affect the mechanical properties of the hybrids.

1. Introduction

One of the study approaches long adopted for developing materials having novel properties is a method for combining materials completely different from one another in properties and thereby making the best use of their combined merits. More specifically, materials obtained by such combining are composite materials, and numerous examples are found in all fields including ceramics, metals, plastics and so on. Considering the field of materials, which are largely divided into inorganic and organic materials, as one example of such composite materials, organic coatings having dispersed inorganic pigments such as jeweller's rouge (Fe_2O_3) or titania (TiO_2) have long been used. Organic binders (thermally decomposed during burning) used during ceramic manufacturing play an important role for molding ceramics. Also, in this case, the combined properties of inorganic and organic materials are utilized.

Such property improvements by combining inorganic and organic materials have long been carried. But the sizes of the composite phases exceeded millimeters or microns in the initial stage. Following the shifting of studies to the developments of highly functional/high performance materials with higher added values, however, the sizes of the composite phases were gradually reduced to reach a nano-level (nano-composite) or even smaller. Under these circumstances, the concept of inorganic/organic hybrid materials emerged. When the sizes of the composite phases reach the nano-meter or smaller to approach the molecular level, combining based on simple mechanical mixing becomes impossible.

Sol-gel processing[1,2] known as a novel method of synthesizing ceramics or glass can form inorganic networks composed by metal-oxygen bonding (···M-O-M···) at low temperatures. Accordingly, organic materials can be incorporated into the inorganic networks at the molecular level. Inorganic/organic hybrids synthesized by sol-gel processing are called ORMOSILs (organically modified silicate)[3] or ceramers[4], and their studies started from around 1985. But it is only recently that inorganic/organic hybrid materials started to attract attention and active research started.

Nippon Steel has studied on inorganic/organic hybrid materials as well as ceramic materials through sol-gel processing for several years. From 1994, Nippon Steel has participated in a "Synergy-Ceramic" Project begun under MITI's Industrial Science & Technology Frontier Program and has made efforts to develop technology for incorporating organic components into inorganic oxide networks by controlling the molecular level to the microlevel. The purpose is to discover novel materials which have both properties of inorganic and organic materials or a synergistic effect of both properties[5,6].

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2. National Project "Synergy-Ceramics Research and Development"[5,6]

This project is designed to develop control technology for various material structures in a comprehensive manner from the point of view of "hyper-organized structure control". The objective is the development of a new type of advanced ceramic materials "synergy-ceramics" which will harmonize several trade-off functions and provide a synergistic propertices that would be difficult in conventional materials.

Considering the conventional material developments from the point of view of structure control, properties and functions were provided by mainly controlling the atomic level in the case of functional materials and the microlevel in the case of structural materials. Between these cases, hierarchies to be controlled differ. Generally speaking, however, both may be considered to be single hierarchy control. Such single hierarchy control can probably increase the levels of particular properties and functions. But there may be a limit to its ability to allow opposing properties to coexist at a high level and simultaneously provide multiple functions. Structural elements constituting a material are not limited to one hierarchy but exist over multiple hierarchy levels. In addition, hierarchy levels are not always identical to those where properties and functions are provided.

Considering the above, for allowing opposing properties to coexist and providing a synergistic effect, materials to be incorporated into respective hierarchies must be selected and the sizes and shapes of structural elements must be simultaneously controlled across multiple hierarchies. Such structure control is "hyper-organized structure control". "Synergy-ceramics" is ceramics which can allow various properties/functions to coexist at a high level and provide a synergistic effect between functions that would be difficult in conventional materials as a result of performing hyper-organized structure control.

Based on the above concept, Nippon Steel has presented a new idea for utilizing organic materials in ceramic structure control. Ceramics have many advantages that differ from those of metal and organic materials. But the range of use is limited because of its weakness. If a hybrid material can be formed by combining organic materials such as plastics with inorganic materials such as ceramics at the molecular level, then a novel material system having the strong points of both can be expected. For example, if the flexibility of organic materials can be incorporated into the inorganic networks of basically hard ceramics, there is a possibility that flexibility, conventionally non-existent in ceramics, may be provided. Moreover, since material designing is carried out at the molecular level, novel functions (synergistic properties) can probably be provided by functional fusion and a synergistic effect. Accordingly, the purpose of Nippon Steel's studies is to develop process technology for realizing, by controlling the molecular level to the microlevel, inorganic/organic hybrid structures where organic components are incorporated into inorganic networks.

3. Synthesis of Inorganic/Organic Hybrid

3.1 Low-temperature synthesis of ceramics by sol-gel processing

Studies on sol-gel processing as a new chemical synthesizing method have been carried out since around the 1970s. In sol-gel processing, metal organic compounds, especially metal alkoxides $M(OR)_n$ (M = metal, R = organic group) among them are used as starting raw materials (precursors). Metal alkoxides are easily hydrolyzed (1) and form inorganic networks of M-O-M bonding by dehydrated condensation reaction (2).

$$\text{M-OR} + H_2O \rightarrow \text{M-OH} + \text{ROH} \quad (1)$$
$$\text{M-OH} + \text{HO-M} \rightarrow \text{M-O-M} + H_2O \quad (2)$$

The above reaction formulas are only formal. In practice, reactions are more complex. Sol-gel processing has several excellent characteristics. Noteworthy among them is the formation of most parts of inorganic networks when the above reactions progress at a temperature near room temperature. Accordingly, glass is obtained with M = Si if heat-treatment is carried out at a temperature lower than normal. Oxides are obtained if M is other than Si, such as transition metal. Further, if hydrolysis and condensation reaction of the metal alkoxides are precisely controlled, crystalline oxides are produced even at a temperature near room temperature. For example, it has been reported that oxides such as simple TiO_2[7,8] and complex oxides including $BaTiO_3$[9], complex perovskite oxides[10,11] and so on are directly produced as crystalline fine particles.

Thus, since sol-gel processing provides a possibility of making ceramics and glass at an extremely low temperatures, efforts have been focused on making of inorganic materials by controlling hydrolysis and condensation reactions and completely eliminating residual organic compounds.

3.2 Application of sol-gel processing for inorganic/organic hybrid synthesis

For hybridizing inorganic and organic components, an inorganic network must be synthesized at a low temperature so as to prevent the loss of organic component properties. Thus, for formation of the inorganic network of inorganic/organic hybrid materials, the chemical reactions of the above metal alkoxides as the precursors of sol-gel processing are utilized instead of a conventional ceramic process.

Synthesis of inorganic/organic hybrids started from the incorporation of organic materials into a siloxane network (···Si-O-Si···) formed at a low temperature through hydrolysis/condensation reactions of tetraethoxysilane ($Si(OC_2H_5)_4$: TEOS). In this case, as the precursor of organic components, organoalkoxysilane ($SiR'_n(OR)_{4-n}$) or silanol-terminated polydimethyl siloxane ($HO(Si(CH_3)_2O)_nH$: PDMS) was used. Inorganic/organic hybrids synthesized from TEOS and PDMS are especially noted for good flexibility under composition and synthesis conditions[12,13]. Concerning the inorganic components of the inorganic/organic hybrids, most of the inorganic components of hybrids synthesized thus far have been derived from TEOS or the like.

Nippon Steel has investigated the synthesis of inorganic/organic hybrids containing various inorganic components through the reactions of metal alkoxides and PDMS[14,15], expecting that if inorganic/organic hybrids containing inorganic components other than siloxane can be synthesized, more diversified properties may be provided by an inorganic element intrinsic coordination and an electronic structure. As described above, in the case of metal alkoxides, hydrolysis/condensation reactions like those shown in the reaction formulas (1) and (2) easily occur and inorganic networks are formed at low temperature. In practice, however, alkoxide reactions differ depending on the kinds of metal. Silicon alkoxides such as TEOS are easy to handle because reactions are slow. But alkoxides other than Si, such as transition metals, have high reactivity and, if they are directly used, the alkoxides are converted into oxide or hydroxide particles and precipitated before reacting to PDMS (see **Fig. 1**).

Thus, for controlling the reactivity of the metal alkoxides during hybrid synthesizing, concerning alkoxides such as Al, Ti or Ta, the chemical modification effect of a chelate ligand mainly of ethyl acetoacetate (EAcAc) was systematically investigated. For the investigation, the molecular structure and the hydrolysis behavior of the chemically modified alkoxides were analyzed by using Raman spectrometry, infrared spectrometry or a nuclear magnetic resonance spectrometry. **Fig. 2** shows an example of titanium ethoxides reaction. Chemical modification by EAcAc prevents precipitation like that shown in Fig. 1 even if water is dropped. In other words, the hydrolysis/condensation reactions of the metal alkoxides are suppressed. As shown in Fig. 2, since EAcAc replaces an alkoxide group and is chelate-coordinated, hydrolysis is difficult and a three-dimensional network formed by condensation reaction does not grow so large.

Fig. 3 is a typical reaction of inorganic/organic hybrid synthesis utilizing alkoxides chemically modified by EAcAc and shows the process. In this manner, Nippon Steel succeeded in synthesizing various inorganic/organic hybrids containing inorganic components other than Si by dehydrated condensation with PDMS without precipitating any oxide or hydroxide particles. **Fig. 4** shows its typical sample picture. Alkoxides of Al, Ti and Ta were used as precursors of inorganic components. This example shows three kinds of inorganic/organic hybrids (Al-O-PDMS, Ti-O-PDMS and Ta-O-PDMS) made of different inorganic components.

4. Properties of Inorganic/Organic Hybrids

Nippon Steel investigated various properties of synthesized inorganic/organic hybrids made of different inorganic components and tried to clarify the effects of the inorganic components. As shown in

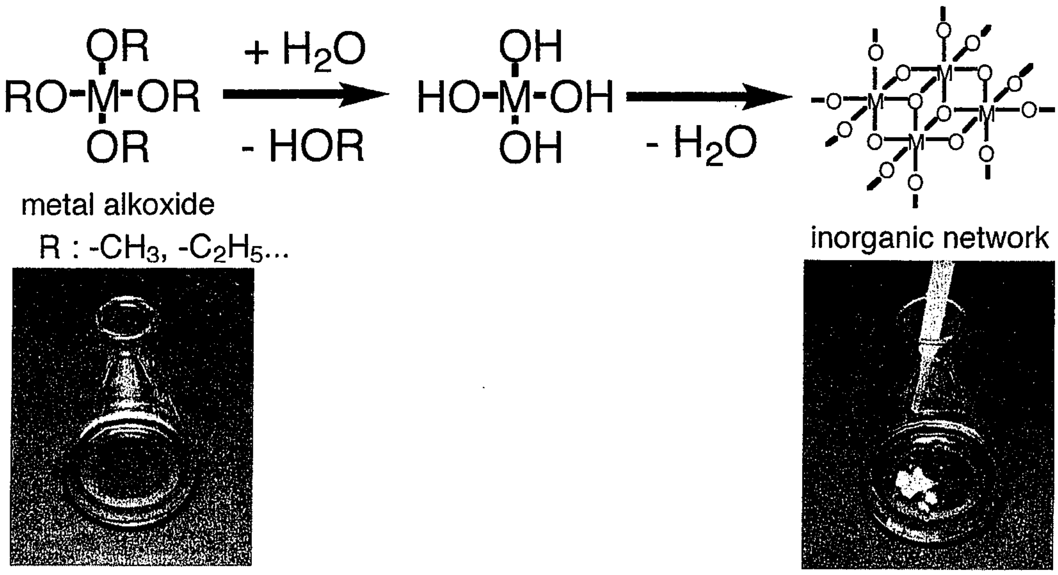


Fig. 1 Hydrolysis/condensation reaction of metal alkoxides

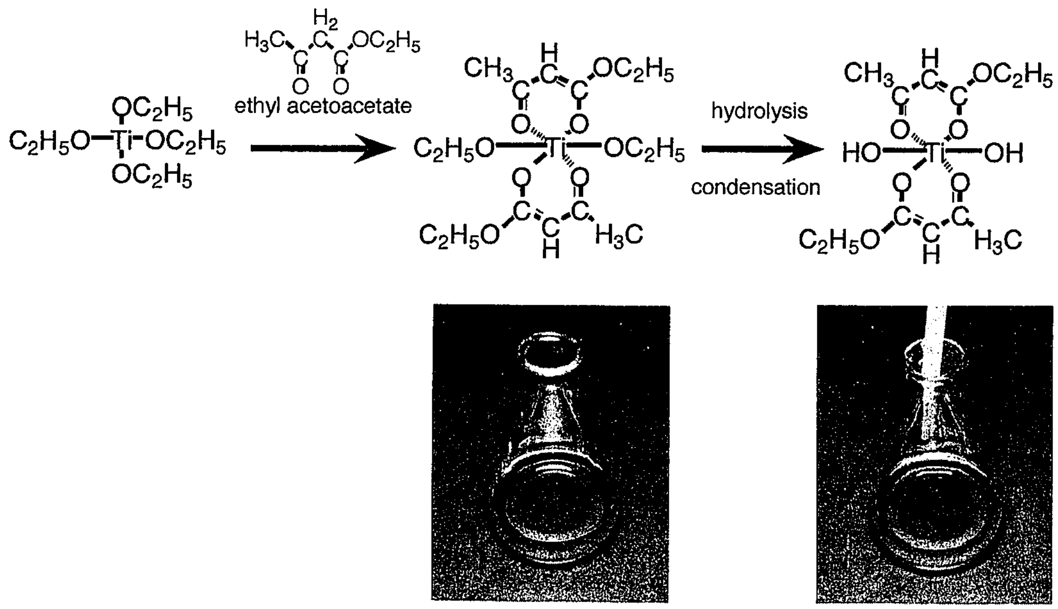


Fig. 2 Chemical modification of metal alkoxides

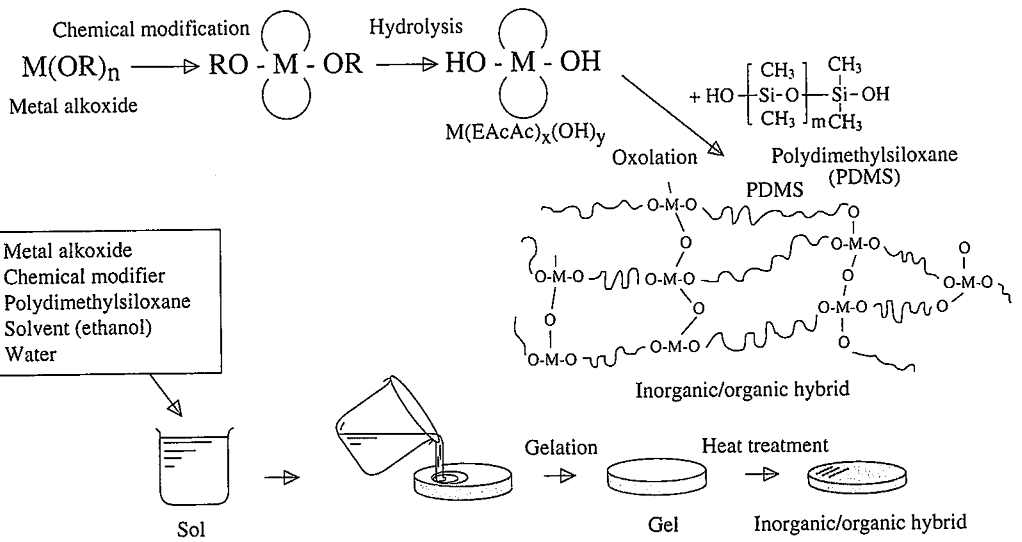
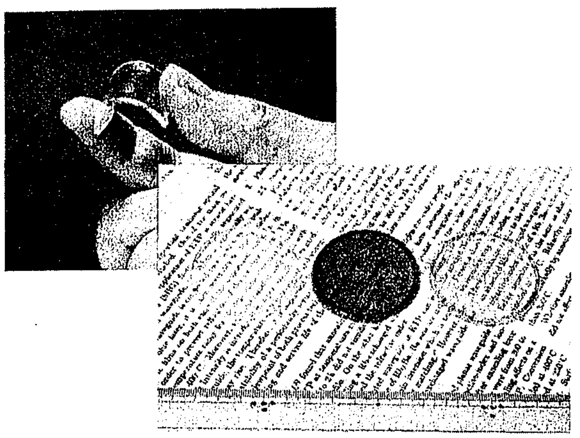


Fig. 3 Conceptual drawing and process of synthesizing PDMS inorganic/organic hybrids



derived from Al, Ti, and Ta alkoxides from left to right

Fig. 4 Photographs of synthesized PDMS inorganic/organic hybrids

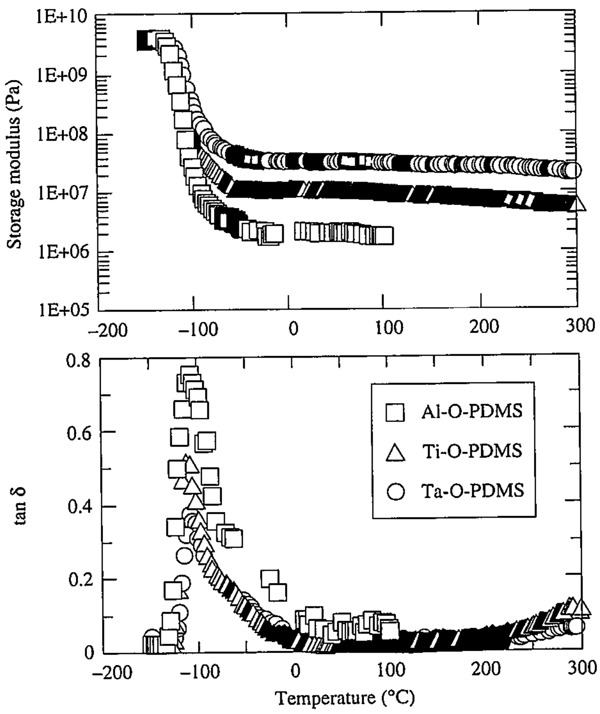


Fig. 5 Temperature dependency of storage modulus and tan δ in PDMS inorganic/organic hybrids (composition M/PDMS = 4)

Fig. 4, all the synthesized hybrids are transparent and homogeneous. Any of the hybrids are flexible, capable of being bent by fingers. For investigating the effects of the inorganic components by quantitatively evaluating the flexibility, first, dynamic elasticity measuring and a tensile test were carried out.

Fig. 5 shows temperature dependency of a storage modulus and tan δ (elasticity loss factor) in the case of a hybrid of composition M/PDMS = 4. At a temperature lower than −120°C, a high elastic modulus of about 10^{10} Pa is shown and, in this temperature region, hybrids are in hard glass states. Elastic modulus declines from −120°C to −80°C and, at this time, tan δ peaks. This indicates that glass transition of the hybrids has occurred. In a temperature region higher than around −80°C, there is a rubbery region and hybrids become soft like rubber. Effects of the difference in inorganic components are especially conspicuous in the rubbery region, and elastic moduli are higher in the order Al-O-PDMS, Ti-O-PDMS and Ta-O-PDMS. The peak height of tan δ around −100°C depends on inorganic components, and heights are lower in the order Al-O-PDMS, Ti-O-PDMS and Ta-O-PDMS. This result corresponds to an energy loss following glass transition and is attributed to friction between PDMS chains which constitute a network structure. As the constituting elements of inorganic components for connecting PDMS chains together weigh more in the order Al, Ti and Ta, the effects of suppressing the motion of PDMS chains is larger. Consequently, energy loss is reduced.

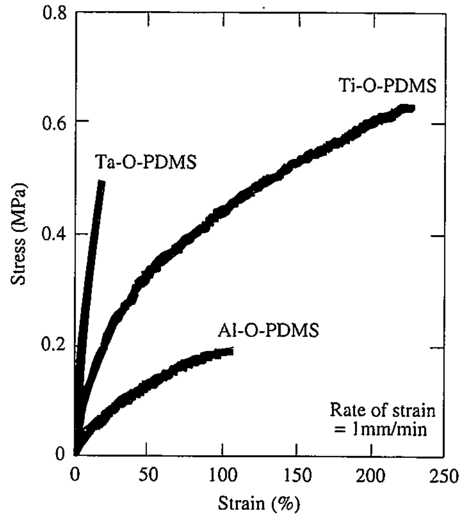


Fig. 6 Example of stress-strain curves of PDMS inorganic/organic hybrids (composition M/PDMS = 1)

Fig. 6 shows an example of stress-strain curves of hybrids (M/PDMS = 1). The inclinations of the curves are larger in the order Al-O-PDMS, Ti-O-PDMS and Ta-O-PDMS. This means that Young's moduli are larger in this order. On the other hand, elongations of the hybrids are larger in the order Ta-O-PDMS, Al-O-PDMS and Ti-O-PDMS, and Ti-O-PDMS shows elongation exceeding 200%. Considering that elongations are caused by loosening of the hybrid networks, the Al-O-PDMS hybrid having low Young's and storage moduli must show the greatest elongation. However, the Ti-O-PDMS hybrid shows the greatest elongation. Considering that fracture in the elongated point is caused by the strength of a hybrid network made of inorganic components and PDMS chains, elongation may be decided by both the growing degree of a three-dimensional network and the strength of interaction between the inorganic components and PDMS chains. Accordingly, it can be understood that the Ti-O-PDMS hybrid has two such factors in good balance and show the greatest elongation.

This paper describes the influence of inorganic components on mechanical properties based on comparisons of the dynamic elasticity of hybrids made of different inorganic components and stress-strain curves and also clarifies the effects thereof.

5. Conclusion

Nippon Steel succeeded in synthesizing various inorganic/organic hybrids made of different inorganic components by executing chemical modification of metal alkoxides and controlling the reactivity thereof. it was discovered that as indicated by dynamic elasticity and stress-strain curves, the properties of the hybrids can be changed by inorganic components. Needless to say, the properties can also be changed by organic components. For example, the organic components of the synthesized hybrids were methyl groups, but investigations revealed that hybrids containing phenyl groups have high heat resistance[16]. Thus, for the inorganic/organic hybrids, the degree of freedom for combining components, compositions, structures and so on is large, and various properties including an elastic modulus can be controlled in a wide range. Further, in the inorganic/organic hybrids, inorganic and organic components are mixed at molecular/atom levels, and it is expected that another interaction may be produced to provide novel functions. At present, efforts are being made to produce materials having novel functions by paying attention to not only dynamic properties but also optical[17], electromagnetic and chemical properties.

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