Coloration Behavior of Polydimethylsiloxane-Based Inorganic/Organic Hybrids Containing Various Inorganic Components Derived from Metal Alkoxides

Noriko YAMADA, Ikuko YOSHINAGA, Yoshio SUGIYAMA and Shingo KATAYAMA

Advanced Technology Research Laboratories, Nippon Steel Corporation, 3-35-1, Ida, Nakahara-ku, Kawasaki-shi 211-0035

金属アルコキシドから誘導された無機成分を含む PDMS 系無機・有機ハイブリッドの着色挙動

山田紀子・吉永郁子・杉山義雄・片山真吾

新日本製鐵(株)先端技術研究所, 211-0035 川崎市中原区井田 3-35-1

The coloration behavior of the inorganic/organic hybrids prepared from polydimethylsiloxane (PDMS) and chemically modified metal alkoxides was investigated by ultraviolet-visible (UV-VIS), X-ray photoelectron (XPS) and electron spin resonance (ESR) spectroscopies. Although the hybrids were transparent in the visible region, a broad absorption was observed from the visible to UV regions, leading to a color from yellow to wine-red. The color and the absorption edge of the hybrids depend on the inorganic components derived from metal alkoxides. XPS study showed the presence of a specific chemical state of metallic ions in the inorganic components derived from metal alkoxides. The XPS study revealed that a certain amount of metallic ions in the inorganic components derived from metal alkoxides is present in a specific chemical state that is distinct from a simple oxide. The ESR study showed the presence of localized electrons in the inorganic components derived from metal alkoxides or in an organic compound produced by decomposition of ethyl acetoacetate (EAcAc). The localized electrons may be relevant to the coloration of the hybrids.

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1. Introduction

The combination of inorganics and organics at a molecular level is attracting attention because of the possibility of providing not only properties of both inorganic and organic materials but also novel properties unknown in the conventional materials. The sol-gel process has made possible the combination of inorganics and organics at a molecular level and then provided inorganic/organic hybrids, which promise to have numerous applications in the optical, mechanical, chemical, electrical and biological fields. Especially, transparent hybrids are expected to be applicable as new optical materials such as filters, waveguides and hosts for photoactive species like organic dyes, semiconductor quantum dots and metal clusters. The transparent hybrids have a potential for combining both inorganic and organic optical materials and controlling optical properties in the wide material range from inorganic compounds to organic compounds.

There are reports on the preparation of inorganic/organic hybrids using tetraethoxysilane (TEOS) and silanol-terminated polydimethylsiloxane (PDMS) precursors.¹⁾⁻⁵⁾ These hybrids have been intensively studied, resulting in it being determined that they have unique mechanical properties. It has become clear that the mechanical properties and structure of the hybrids are strongly influenced by the reaction conditions such as acid concentration, TEOS content and molecular weight of PDMS.^{3),5)} The PDMS-based hybrids have the TEOS-derived siloxane network as the only inorganic component. The use of various metal alkoxides instead of TEOS is anticipated to alter the structure and properties of PDMS-based hybrids, reflecting the difference in molecular weight, valence and coordination number among silicon and other metallic elements.

The authors have examined metal alkoxides other than Si alkoxides as inorganic sources in the PDMS-based hybrids.

Transparent and monolithic PDMS-based hybrids including various inorganic components have been successfully synthesized from silanol-terminated PDMS and metal alkoxides chemically modified with ethyl acetoacetate.⁶⁾⁻⁹⁾ The effects of the inorganic components on optical properties⁹⁾ as well as mechanical properties^{7),8)} have been investigated. Although the hybrids were transparent in the visible region, especially in the long-wavelength region, they showed absorption bands at wavelengths shorter than 500-650 nm, leading to the yellow to wine-red color. The clarification of the coloration in the hybrids is necessary to be able to apply them to optical materials in the wavelength region correlated with the coloration, and also is of interest from the viewpoint of the possibility of determining new coloration phenomenon. Thus, the final goal of our study is to find out the origin of the coloration of the PDMS-based hybrids.

In the present work, the coloration behavior of the PDMS-based hybrids containing various inorganic components derived from Al, Ti and Ta alkoxides was investigated by ultraviolet-visible (UV-VIS), X-ray photoelectron (XPS) and electron spin resonance (ESR) spectroscopies.

2. Experimental

The metal alkoxides used as inorganic sources were aluminum *s*-butoxide ($\text{Al}(\text{O}-s\text{-C}_4\text{H}_9)_3$), titanium ethoxide ($\text{Ti}(\text{OC}_2\text{H}_5)_4$) and tantalum ethoxide ($\text{Ta}(\text{OC}_2\text{H}_5)_5$), which were commercially available. Liquid silanol-terminated PDMS with an average molecular weight of 3000 was purchased from Shin-Etsu Chemical Co., Ltd. Ethanol was dried and used as solvent. Ethyl acetoacetate (EAcAc) was used as a chemical modifier of metal alkoxides in order to prevent the formation of precipitates in the hydrolysis of the metal alkoxides. Metal alkoxide and EAcAc were mixed in a $\text{M}(\text{OR})_n : \text{EAcAc}$ molar ratio of 1 : 2, followed by ad-

dition of ethanol and PDMS. A mixture of water and ethanol was added to the ethanol solution of metal alkoxide and PDMS. The molar ratio of metal alkoxide, PDMS, EAcAc, H_2O and ethanol was 1 : 0.25 : 2 : 2 : 4. After stirring the mixture for 30 min, the obtained solution was allowed to gel at 70°C and then heat-treated at 150°C to produce a hybrid.

UV-VIS transmittance spectra of sols and hybrids with a thickness of about 1mm were measured with a Hitachi U-4000 spectrophotometer. XPS was performed with a Physical Electronics 5500MT ESCA spectrometer using a monochromated Al K α source (1486.6 eV). During the experiments, the pressure inside the analysis chamber was about 6.7×10^{-8} Pa.

ESR spectra of gels prepared at 70°C and hybrids heat-treated at 150°C were recorded at room temperature on a JEOL JES-RE 2X ESR spectrometer equipped with an X-band microwave unit and 100 kHz field modulation. The g -values were determined by referring to ESR spectra of Mn^{2+} doped in MgO. The spin concentrations were obtained by using 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in benzene as a standard material. Spectral integrations were carried out on a JEOL ES-PRIT 375 ESR data system. The spin concentrations were determined from double integrations of the spectra.

3. Results and discussion

Figure 1 shows the representative hybrids containing the inorganic components derived from Al, Ti and Ta alkoxides.

Fig. 1. Inorganic/organic hybrids containing the inorganic components derived from Al, Ti and Ta alkoxides.

ides, which are denoted as Al-O-PDMS, Ti-O-PDMS and Ta-O-PDMS hybrids, respectively. The hybrids were flexible and transparent, although they were slightly colored. The color was varied by the inorganic component derived from metal alkoxides. The Al-O-PDMS, Ti-O-PDMS and Ta-O-PDMS hybrids had yellowish, wine-red and orange colors, respectively.

Optical transmittance measurements were conducted during the formation process of the hybrids. Figure 2 shows UV-VIS spectra of sols and hybrids containing the inorganic components derived from Al, Ti and Ta alkoxides. Sols containing inorganic species derived from Al, Ti and Ta alkoxides had an absorption peak of around 280, 300 and 300 nm, respectively, corresponding to the $\pi-\pi^*$ transition in the chelate ring of EAcAc.^{10),11)} No absorption was observed in the visible region, although the Ti-O-PDMS had a broad band from the UV to visible regions and an absorption peak corresponding to chelating EAcAc. The broad band of the Ti-O-PDMS hybrid arises from the oxygen-coordinated polyhedron of Ti^{4+} ions, which is similar to the characteristics of TiO_2 . Gels prepared at 70°C also exhibited a weak absorption peak around 300 nm corresponding to the $\pi-\pi^*$ transition in the chelate ring of EAcAc. The presence of the chelating EAcAc groups has been revealed by the IR studies,^{6),9)} in which the gels have chelating EAcAc species.

The hybrids synthesized by heat treatment at 150°C were transparent in the visible region, especially in the long-wavelength region. In all the hybrids, however, a broad absorption appeared from the visible to UV regions, leading to the color from yellow to wine-red as shown in Fig. 1. The Al-O-PDMS, Ti-O-PDMS and Ta-O-PDMS hybrids had an absorption edge around 550, 620 and 650 nm, respectively. Although the presence of an absorption peak of chelating EAcAc was not confirmed because of overlapping of the broad absorption, the IR study has already revealed that the hybrids have no EAcAc species.^{6),8)} It is, therefore, considered that the coloration does not directly result from the absorption concerning the $\pi-\pi^*$ transition in the chelate ring of EAcAc.

From the fact that the color and absorption edge of the hybrids depended on the inorganic components, the in-

Fig. 2. UV-VIS spectra of sols and hybrids containing the inorganic components derived from Al, Ti and Ta alkoxides.

organic components derived from metal alkoxides may be responsible for the coloration.

The chemical bonding state of the inorganic components

Fig. 3. Al2p, Ti2p and Ta4p XPS spectra of hybrids containing the inorganic components derived from Al, Ti and Ta alkoxides, respectively.

was investigated by XPS. The XPS spectra of the hybrids are shown in Fig. 3. Al2p, Ti2p and Ta4p XPS spectra correspond to the Al-O-PDMS, Ti-O-PDMS and Ta-O-PDMS hybrids, respectively. The Al2p XPS peak of the Al-O-PDMS hybrid was observed at a binding energy of approximately 75.3 eV, which was slightly higher than that of typical Al_2O_3 (73–74 eV). Aluminum is likely present as an oxide but the higher binding energy suggests the possibility of a specific chemical state of Al ions in the hybrid. The Ti-O-PDMS hybrid had not only Ti2p peaks similar to TiO_2 but also unknown Ti2p peaks that were suited to neither TiO_2 nor Ti_2O_3 peaks. Titanium is primarily seen as an oxide, likely in the form of TiO_2 , which accounted for approximately 86% of the Ti signal. The remaining ~14% of the Ti signal corresponded to the unknown Ti2p peaks, which appeared at a binding energy between those of TiO_2 and Ti_2O_3 . This means that some Ti ions in a specific state are present in the hybrid, although it may also be attributed to the low valence Ti ions produced by Ar ion etching. The Ta4p peaks of the Ta-O-PDMS hybrid were consistent with those of Ta_2O_5 . Thus, no specific chemical state of Ta ions in the hybrid was observed from the result of XPS. Al, Ti and Ta ions derived from metal alkoxides exist in a form similar to oxides in each of the respective hybrids. However, Al ions detected on the Al-O-PDMS hybrid appear at an uncommonly high binding energy and some of Ti ions in the Ti-O-PDMS hybrid appear intermediately between the binding energies of TiO_2 and Ti_2O_3 . These observations suggest a certain amount of metallic ions in the inorganic components is present in a specific chemical state that is distinct from a simple oxide. A large C1s XPS peak of hydrocarbons with a trace amount of oxygen functionality (C–O) in all the Al-, Ti- and Ta-O-PDMS hybrids was observed. The hydrocarbons can be attributed to methyl groups of PDMS. A small amount of carbons corresponding to C–O may be present in a remaining organic compound produced by decomposition of EAcAc, although no remaining organic compound was observed in the IR spectra.^{6),8)}

ESR spectra of gels prepared at 70°C and hybrids synthesized by heat treatment at 150°C are shown in Fig. 4, in which both the signal ($g=2.034$) at the lower field and that ($g=1.981$) at the higher field are due to Mn^{2+} doped in MgO. ESR signals were observed around 330 mT in the Ti-O-PDMS gel, Al-O-PDMS hybrid and Ti-O-PDMS

Fig. 4. ESR spectra of gels prepared at 70°C and hybrids synthesized by heat treatment at 150°C.

hybrid, although they were hardly detected in the Ta-O-PDMS gel and hybrid. The intensity of the ESR signal for the hybrids synthesized by heat treatment at 150°C was higher than that for the gels prepared at 70°C. The heat treatment caused the increase in intensity of the ESR signal, as well as the coloration with an absorption edge of 550–650 nm. The intensity of the ESR signal was also affected by the inorganic components derived from metal alkoxides. The Ti-O-PDMS hybrid exhibited the ESR signal having the highest intensity among the gels and hybrids. Table 1 shows ESR parameters of g -value, peak-to-peak linewidth (ΔH_{pp}) and spin concentration. The Ti-O-PDMS hybrid provided a slightly higher g -value than the Al-O-PDMS hybrid. It is, however, considered that the radicals in both hybrids are present in a similar chemical state because of their similar g -value. In the case of the Ti-O-PDMS hybrid, the formation of trivalent titanium by reduction can generally be assumed because one $3d$ electron produces an ESR signal and an optical absorption in the visible region corresponding to the ${}^2T_{2g}-{}^2E_g$ transition. However, the g -values observed in the hybrids were higher than those of Ti^{3+} ions ($g=1.961-1.968$)¹²⁾ and similar to those of free electron ($g_e=2.0023$). It can at least be said that the ESR signal of the hybrids does not arise from an electron localized in titanium ion such as Ti^{3+} . On the other hand, anion radicals such as O_2^- and O^- , which arise from a reduction of oxygen molecules in air, can be considered to be radicals with a similar g -value.^{13),14)} The hybrids prepared and heat-treated in N_2 atmosphere also showed the same g -value signal and spin concentration as those synthesized in air. It is, therefore, considered that the ESR signal can not be attributed to anion radicals such as O_2^- and O^- formed from oxygen molecules in air. It was reported that sol-gel-derived oxides exhibited an ESR signal near $g=2.003$ corresponding to carbon particles,^{15),16)} which is similar to the ESR signal of the hybrids. The ESR signal of carbon particles in sol-gel derived oxides only appeared at high firing temperatures above 600°C, which cause the pyrolysis of organic compounds to form carbon particles. The hybrids were synthesized at a lower temperature of 150°C so that hardly any carbon particles were formed. The XPS spectra of the hybrids also showed no peak of free carbons. It is, therefore, considered that the ESR signal of the hybrids can not be attributed to carbon particles formed by pyrolysis of organic compounds. However, the ESR signal of the hybrids may result from carbons in an organic compound produced by decomposition of

EAcAc, because the XPS spectra showed the presence of a small amount of carbons corresponding to C-O in the hybrids. Considering that EAcAc groups bonded to metal alkoxides are released during the formation of the inorganic components in the hybrids,⁶⁾ the intensity of the ESR signal for carbons in an organic compound produced by decomposition of EAcAc can be related to the inorganic components derived from metal alkoxides.

From the viewpoint of the g -value ($g\sim 2.003$) and the dependence of the inorganic components on the intensity of the ESR signal, the ESR signal of the hybrid may also result from the localized electrons in the inorganic components derived from metal alkoxides. In the formation of the hybrids, chemically modified metal alkoxides are hydrolyzed to react with not only the terminal silanol groups of PDMS but also another hydrolyzed metal alkoxide.⁶⁾ Thus, the inorganic components in the hybrids are thought to be a very small aggregate formed by the condensation of some hydrolyzed metal alkoxides. In the inorganic components with a small aggregate structure, localized electrons may be present and produce the ESR signal. In one possible case, the electrons, trapped in a very small aggregate derived from metal alkoxides, behave like free electrons ($g=2.0023$). In another case, the electrons like those of anion radicals of O_2^- and O^- ($g\sim 2.004$),^{13),14)} which are derived from oxygen atoms of precursors and stabilized in the coordination sphere of metal ions, are present in the structure of the inorganic components. These localized electrons may be formed by transfer of electrons from reduced Al, Ti and Ta ions in the inorganic components. The formation of the electrons detectable by ESR occurred in the gels prepared at 70°C, even though the spin concentration was low. This is possibly because the formation of small aggregates derived from hydrolyzed metal alkoxides has already started in the gels, although some EAcAc groups are attached to hydrolyzed metal alkoxides as a chelating ring. The spin concentration was remarkably increased by about one order of magnitude by the heat treatment at 150°C, possibly because of the formation of a complete small aggregate structure of the inorganic components without EAcAc groups.

The spin concentration depended on the color and absorption edge of the hybrids, which were varied by the heat treatment and the inorganic components derived from metal alkoxides. Therefore, the formation of the electrons detectable by ESR might be responsible for the coloration of the hybrids. Although the coloration may result from a

Table 1. ERS Parameters (g -Value, ΔH_{pp} and Spin Concentration) for Gels Prepared at 70°C and Hybrids Synthesized by Heat Treatment at 150°C

Metal alkoxide used for inorganic component	Heating temp.	g -value	ΔH_{pp} (G)	Spin concentration ($\times 10^{14}$ spins/gr)
Al alkoxide	70 °C	-	-	~ 0
	150 °C	2.003 ⁸	9.7	27
Ti alkoxide	70 °C	2.003 ²	5.4	4.9
	150 °C	2.002 ⁹	5.6	40
Ta alkoxide	70 °C	-	-	~ 0
	150 °C	-	-	~ 0

transition of π electrons in an organic compound produced by decomposition of EAcAc and organic impurities, a transition of the localized electrons is instead thought to provide the coloration by the formation of a transition state in the specific structure of the inorganic components or the carbons in an organic compound produced by decomposition of EAcAc.

4. Conclusions

The coloration occurred during the formation process of the inorganic/organic hybrids from PDMS and metal alkoxides modified with EAcAc. Although the hybrids were transparent in the long-wavelength visible region, a broad absorption was observed from the visible to UV regions, leading to the color from yellow to wine-red. The color and absorption edge of the hybrids depended on the inorganic components derived from metal alkoxides. The XPS study revealed that a certain amount of metallic ions in the inorganic components derived from metal alkoxides is present in a specific chemical state that is distinct from a simple oxide. The ESR study showed the presence of specifically localized electrons in the specific structure of the inorganic components derived from metal alkoxides or in an organic compound produced by decomposition of EAcAc. The spin concentration depended on the color and absorption edge of the hybrids, which were varied by the heat treatment and the inorganic components. A transition of the localized electrons may be responsible for the coloration of the hybrids.

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