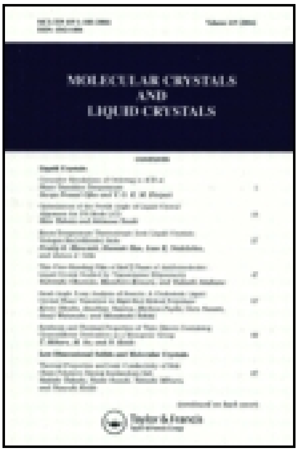

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Electrical Insulating and Heat-Resistive Properties of Organic-Inorganic Hybrid Materials Made from Alkoxysilane-Terminated Polydimethylsiloxane

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Hybrid materials made from titanium alkoxide (TA) ($Ti(OCH_2CH(C_2H_5)C_4H_9)_4$) and alkoxysilane-terminated polydimethylsiloxane (PDMS) in different TA/PDMS ratio was prepared and characterized. Gel fraction, mechanical strength, dielectric strength and thermal endurance of hybrids made from TA and alkoxysilane-terminated PDMS increased more than that of conventional hybrids made from silanol-terminated PDMS. Tensile strength, dielectric strength, and thermal endurance were improved with increase in TA/PDMS ratio. These results suggest that utilizing alkoxysilane-terminated PDMS and TA as raw material is useful for improving the electrical insulating property, thermal endurance, and mechanical property of PDMS-based hybrids.

Keywords Electrical insulating property; organic-inorganic hybrids; polydimethylsiloxane; sol-gel method; thermal endurance

Introduction

Advancing electrical insulating materials for electric vehicle and hybrid electric vehicle request not only high electrical insulating property, high thermal endurance, but also flexibility because they can support high resistance toward to mechanical vibration, and thermal shock at the wide temperature. We have paid attention to polydimethylsiloxane (PDMS)-based organic–inorganic hybrid materials as a material that achieves such a characteristic. The hybrids prepared by in-situ sol-gel method have showed unique features in thermal stability [1] and flexibility [2–4]. In particular, the hybrids prepared from silanol-terminated PDMS and titanium alkoxide had large elongation and tensile strength [4]. In the synthesis process of the hybrid, the titanium alkoxide was stabilized by chemical modification with ethyacetoacetate in order to prevent the precipitation of titanium oxides or hydroxide during hydrolysis owning to high activity of transition-metal alkoxide [4]. However, the chemical modification can become a problem because it

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complicated the synthetic process, caused the coloring of the hybrids [5], and rose the heat-treatment temperature to produce the hybrids.

In this study, we have prepared the hybrid materials made from titanium alkoxide and alkoxysilane-terminated PDMS in order to prepare hybrids that formed a network-structure with well-dispersed inorganic particles without chemical modification of metal alkoxide. The changes of the properties of hybrids by using alkoxysilane-terminated PDMS as raw materials were investigated by stress-strain measurement, dielectric strength test, and thermogravimetric analysis (TGA).

Experimental

Sample Preparation

Silanol-terminated PDMS with an average molecular weight of 20,000 was commercially obtained from Momentive Performance Materials Inc. PDMS end-linked with $Si_7O_6(OC_2H_5)_{16}$ (alkoxysilane-terminated PDMS) with an average molecular weight of 27,000 was synthesized according to the literature [6]. Titanium alkoxide (TA) was $Ti(OCH_2CH(C_2H_5)C_4H_9)_4$ (Matsumoto Trading Co.). TA was mixed with PDMS at different molar ratio (TA/PDMS = 0, 1, 2, and 3) in IPA solutions. The mixed solution was poured into a Teflon Petri dish and covered with aluminum-foil. The solution was allowed to gel at 150°C for 1hour and then heat-treated at 250°C for 2 hours to produce the hybrids sheet. Hybrid made from silanol-terminated PDMS or alkoxysilane-terminated PDMS is denoted O_n and E_n respectively. Here, subscript n indicates the molar ratio of TA to PDMS.

Characterization

The degree of crosslinking density of PDMS chains is estimated by gel fraction as described in literature [7]. Mechanical properties were measured by stress-strain measurement with a tension tester at room temperature. Dumbbell-shaped samples prescribed in JIS K6251 were employed [8]. The crosshead speed was 5.0 mm/min. AC breakdown strength E_B was conducted using a plane-to-plane electrode system. The diameter of the plane was 10 mm with 5.0 mm in curvature. The AC voltage was applied to the sheet sample in fluorinated inert liquid (Fluorinert^{TM}). A frequency of applied voltage is 60 Hz. Thermogravimetric analysis (TGA) measurement was carried out in order to examine the thermal characteristics of the hybrids using TGA measurement system (DTG-60, Shimazu co.) by heating at 10°C/min in air from room temperature to 600°C in air.

Result and Discussion

The each hybrid O_n and E_n was transparent with no visible particle, thus considered as molecular-level hybrids. The gel fraction of O_0, O_1, O_2, O_3 was 61%, 75%, 82%, and 87%, respectively. It is observed that gel fraction of Hybrids O_n increase with the TA content. This indicates that the introduction of TA content yields to increase crosslinking density. The gel fraction of E_0, E_1, E_2, E_3 was 98%, 99%, 99%, and 99%, respectively. It is clear that the gel fraction of hybrid E_n is independent of TA content and indicates a higher crosslinking degree than hybrids O_n.

Table 1 lists the average mechanical properties obtained from stress-strain test. The changes in mechanical properties of hybrid O_n suggest a development of

Table 1. Mechanical properties of hybrid O_n and E_n with different molar ratio of TA to PDMS

Sample	Young's modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]
O_1	0.53	0.51	510
O_2	0.62	0.66	465
O_3	0.85	0.98	386
E_0	1.92	1.16	66
E_1	1.80	1.32	101
E_2	1.73	2.90	192
E_3	1.63	1.64	128

network structure of PDMS with the increase of inorganic contents [5]. Hybrid E_0 was stronger and stiffer than hybrid O_n. This suggests that hybrid E_0 has three-dimensional dense network structure formed through the intermediary of the alkoxysilane terminated with PDMS chains. With the increase in TA to PDMS ratio (of up to 2) in hybrids E_n, Young's modulus decreased, and the tensile strength and elongation at break increased. The decrease in modulus means decrease in crosslinking density. Thus the hybrid E_1, E_2, and E_3 have looser network structure than hybrid E_0. Since the interaction between TA and alkoxysilane terminated with PDMS's end is stronger than that between alkoxysilanes, the introduction of TA tend to form the linear PDMS chains, which has inorganic moiety in the main chain backbone. Consequently, the average molecular weight between crosslinking points in the network of hybrid E_n increases with the increase in TA content, however the gel fraction does not decrease. Thus the hybrid E_n become soft, flexible, and insoluble. In addition, the tensile strength of E_n was influenced by interaction between titanium element and silica moiety, and increased with the increase in TA content. The tensile strength and elongation at break of E_2 are higher than those of E_1 and E_3, and the values of E_2 became more than double for those of E_1 and E_3. This indicates that the hybrid E_2 has a better network structure through the well-dispersed inorganic particles without formation of aggregate. However, the strength degraded when the molar ratio of TA to PDMS was 3 or more.

Figure 1 shows the characteristics variation in AC dielectric breakdown strength of hybrid O_n and E_n. The thickness of specimens was 20 μm. The increase in molar ratio of TA to PDMS showed the increase in breakdown voltage on the hybrid O_n. The increase in dielectric strength with the TA content in hybrid O_n is attributed to the increase in crosslinking density and the decrease in the free volume [9]. The strength of hybrid E_n was higher than that of the hybrid O_n. The result suggests the free volume of hybrid decrease with the increase of crosslinking density by changing silanol-terminated PDMS to alkoxysilane-terminated PDMS. The increase in TA/PDMS ratio (of up to 2) showed the increase in breakdown voltage in spite of decrease in crosslinking density on the hybrid E_n. We guess that the improvement of dispersion of inorganic particle with increase in TA contents influenced on dielectric strength. Due to dispersed inorganic particle, the electrons accelerated by electric field transfer their energy to the particles, and cannot gain momentum to involve in the breakdown, thus the dielectric strength increases when the dispersion of the inorganic particle is improved by introducing TA content. However, when the molar

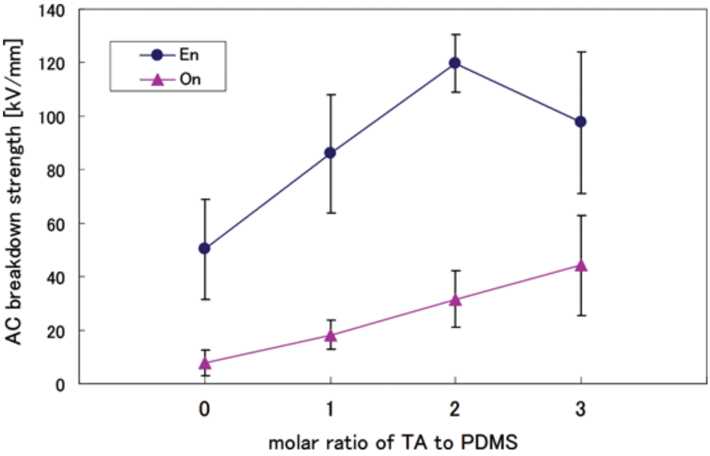

Figure 1. Change in AC dielectric breakdown strength of hybrid O_n and E_n as a function of molar ratio of TA to PDMS.

ratio of TA to PDMS is increased above certain value, the chance of aggregate formation in structure is high. The degradation of the dielectric strength and mechanical property of hybrid E_3 is attributed to stress concentration caused by the aggregate, which acted as additional crack initiation site under electrical and mechanical stress.

Figure 2 shows TGA curves of the hybrids. The weight loss exothermally occurred within the temperature rage of 250°C to 500°C. This is attributed to the thermo-oxidative degradation of PDMS. Weight loss of pure PDMS (hybrid O_0) occurred around 250°C, is attributed to the decomposition of methyl groups [10]. The decomposition temperature of hybrid O_n and E_n rose with TA content. Residual weight of E_0 was larger than that of other hybrids because E_0 had the densest network

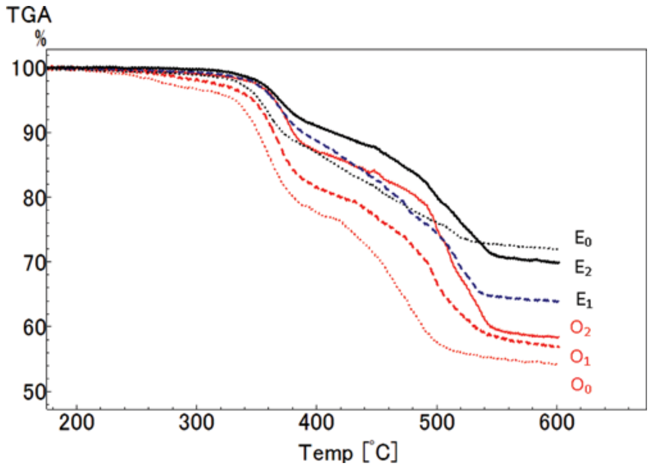

Figure 2. Thermogravimetric analysis curves of hybrid O_n and E_n with different molar ratio of TA to PDMS in air.

structure. Residual weight of E_n at 600°C increased with TA content, and was larger than that of hybrid O_n. Therefore we consider that the alkoxysilane terminated with PDMS can help to form three-dimensional network structure which restricted siloxane redistribution reaction on a free radical mechanism [11]. It was realized that the thermal endurance of hybrid was improved by incorporation of alkoxysilane and TA to the PDMS.

Conclusion

The hybrid materials made from titanium alkoxide (TA) ($Ti(OCH_2CH(C_2H_5)C_4H_9)_4$) and in the different TA/PDMS ratio was prepared and characterized. Gel fraction, mechanical strength, dielectric strength and thermal endurance of hybrids made from TA and alkoxysilane-terminated PDMS increased more than that of conventional hybrids made from silanol-terminated PDMS. The tensile strength and dielectric strength were improved with the increase in TA/PDMS ratio. In particular, the hybrids prepared TA and alkoxysilane-terminated PDMS with the TA/PDMS ratio of 2 showed distinct improvement of the properties. These results indicate that the silica component formed from the alkoxysilane terminated to PDMS's end is homogeneously dispersed in hybrids with the increase in TA content. TGA studies indicated that increase in TA/PDMS ratio shows rise of decomposition temperature of hybrids. These results suggest that utilizing alkoxysilane-terminated PDMS and TA as raw material is useful for improving the electrical insulating property, thermal endurance, and mechanical property of PDMS-based hybrids. As a result, we suppose that the alkoxysilane-terminated PDMS based hybrid materials have a potential for application as the industrial electrical insulating materials.

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