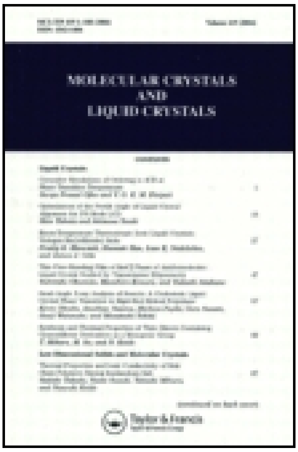

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Electrical Treeing Characteristics in Polydimethylsiloxane-Based Organic-Inorganic Hybrid Materials

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Electrical treeing characteristics of hybrid materials made from titanium alkoxide $Ti(OCH_2CH(C_2H_5)C_4H_9)_4$ and alkoxysilane-terminated polydimethylsiloxane (PDMS) in different TA/PDMS ratio was investigated. The development of AC tree of sample was mounted on a glass substrate with needle electrode was observed by CCD camera and computer. The tree inception voltage increased and tree growth speed decreased with increase in TA/PDMS ratio of the hybrid. It is suggested that the variation of crosslinking density and homogeneity of dispersion of silica clusters influenced on their tree propagation characteristic. We found that the hybrid made from the alkoxysilane-terminated PDMS and TA has good electrical insulating property compared with conventional PDMS-based hybrid materials and silicone rubber.

Keywords organic-inorganic hybrids; polydimethylsiloxane; electrical tree propagation; electrical insulating property; sol-gel method

Introduction

Polydimethylsiloxane (PDMS)-based organic–inorganic hybrid materials prepared by in-situ sol-gel method have showed unique features in thermal stability [1] and flexibility [2–5]. According to such features, the hybrid materials have been studied as electrical insulating material [6–9]. In particular, we have studied the material for electric vehicle and hybrid electric vehicle because it requests high electrical insulation property, high thermal endurance, and flexibility because they must support high resistance toward to mechanical vibration, and thermal shock at the wide temperature. In the previous paper [9], we clarified that the hybrid materials made from titanium alkoxide and alkoxysilane-terminated PDMS provide high electrical insulation property than the conventional hybrid materials made from hydroxyl-terminated PDMS and TEOS, and the dielectric strength of them was improved with increase in TA/PDMS ratio. However, the aging property of electrical insulation of the hybrid did not have been clarified for details. For the estimation about the aging of electrical insulation, an electrical treeing is an important factor since the occurrence of electrical tree is precursory phenomenon of the electrical breakdown in polymer insulating materials and the tree structure varies with the structure of polymer materials. In this study, we investigated the electrical treeing characteristics of

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PDMS-based hybrid made from different molar ratio of TA and alkoxysilane-terminated PDMS. In order to initiate electrical tree, we applied AC voltage with the frequency of 60 Hz through the needle electrode. We observed the structure and growth speed of electrical tree by CCD and computer. We also investigated tree characteristic of SiR, conventional hybrid materials made from TA and sillanol-terminated PDMS, and silica-filled PDMS rubber for comparison purpose.

Experimental

Sample Preparation

PDMS based hybrid materials are made from titanium alkoxide (TA: $Ti(OCH_2CH(C_2H_5)C_4H_9)_4$) and Silanol-terminated PDMS with an average molecular weight of 20,000 or PDMS end-linked with $Si_7O_6(OC_2H_5)_{16}$ (alkoxysilane-terminated PDMS) with an average molecular weight of 27,000 according to the literature [9]. TA was mixed with PDMS at different molar ratio (TA/PDMS = 0, 1, 2) in IPA solutions. 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 materials. Hybrid materials made from silanol-terminated PDMS and alkoxysilane-terminated PDMS are denoted hybrid O_n and hybrid E_n respectively. Here, subscript n indicates the molar ratio of TA to PDMS. Silicone rubber (Shinetsu chemical co., Ltd. KE44RTV) and PDMS rubber filled with silica contain 5% weight of fumed silica (Degussa-Aerosil 200) was employed for comparison. The solution of silica- filled PDMS is also stirred by using magnetic stirrer. The filled PDMS was vulcanized by same condition with the hybrid materials.

Characterization

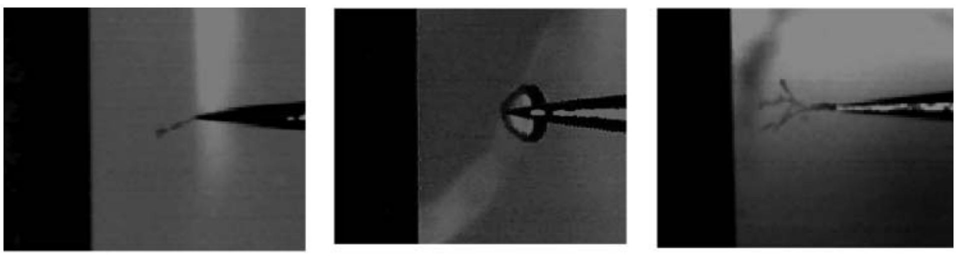
Two-dimensional (2-D) sample with polished needle electrode and counter electrode was used to visualize tree propagation [10]. A tungsten needle electrode was 0.6mm in diameter and 20 mm in length. The needle tip is formed by electrolytic polishing. Its tip radius and tip angle were 3 μm and 15 degree, respectively. The counter electrode was same tungsten wire with 0.6 mm diameter. The hybrid sol was poured into the space between two electrodes and was heated under the condition as described above. The gap inter-electrode is 200 μm. AC voltage was applied and increased by 2.0 kVrms/min. A frequency of applied voltage is 60 Hz. When tree incepted, the applied voltage was kept constant during the tree developed. The time to breakdown from tree inception time are measured. The tree was observed and monitored by CCD camera with zoom lens and a computer. The number of testing sample is 12. All measurements were carried out at room temperature.

Result and Discussion

The typical profiles of electrical trees namely bubble tree, tube tree, branch tree, were observed in our experiment specimens for hybrid O_n and E_n as shown in Figs 1(a)–2(c). The tree inception voltage and proportion of shape of electrical tree occurred in the hybrid O_n and E_n with different molar ratio of TA/PDMS is shown in Table 1. Here, the crosslinking density of hybrid O_0 was low and hybrid O_0 was not hardened, therefore the hybrid O_0 is excluded from the measurement. Figure 2 shows the typical relationship between the length of tree and the treeing time after tree initiation. As for hybrid O_n, the tree inception voltages are lower than that of hybrid E_n, and the shape of tree is all tube. The tree

Table 1. Proportion of tree shape and tree inception voltage of hybrid O_n and E_n.

Sample	Shape of tree pattern	Proportion [%]	Tree inception voltage [kV]
O_1	tube	100	2.8
O_2	tube	100	3.2
E_0	tube	33	4.5
	bubble	67	4.4
E_1	bubble	33	4.9
	branch	67	5.0
E_2	bubble	16	5.0
	branch	84	5.2
silicone	branch	100	2.2
PDMS+silica	branch	100	2.5



(a) tube tree (b) bubble tree (c) branch tree

Figure 1. Typical profiles of electrical trees.

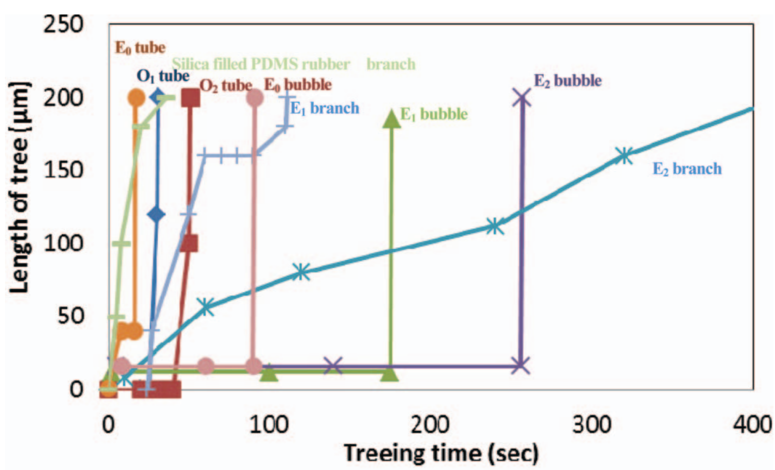


Figure 2. Typical relationship between the length of tree and the treeing time in hybrid O_n and E_n with different molar ratio of TA/PDMS. Voltage applied to hybrid O_1, O_2, E_0, E_1, E_2, and silica filled PDMS rubber are 2.5 kV, 3.0 kV, 4.4 kV, 4.9 kV and 5.0 kV, and 2.5 kV, respectively.

inception occurred by the fatigue process such as repeated process of electron injection, scission process of polymer chain by injected election, oxidation of formed free radicals, auto-oxidation, and void formation due to Maxwell stress [11] and the electrical tree was developed by erosion that occurred by partial discharge in the tree tube. The increase in crosslinking density of PDMS means that more bonds have to be broken and makes both the initiation and propagation of electrical tree more difficult. The structure of hybrid O_n and E_n was estimated from gel fraction and mechanical property obtained from stress-strain test as reported in previous paper [9]. The gel fractions of O_1, O_2 were 75%, 82%, respectively. The crosslinking density of hybrid O_n was too low to suppress tree propagation, thus, the shapes of the tree became tube tree. It is reported that the tube tree is observed in silicone gel [12,13]. A tube tree grew rapidly and developed to the counter electrode directly at first stage, and then flashover occurred in a short time as shown in Fig 2.

The gel fractions of hybrid E0, E1, and E2 were almost equal and the values of them were 98%, 99%, and 99%, respectively. However, there is a remarkable difference in the network structure between hybrid E_0 and $E_n(n > 0)$ [9]. We have found that hybrid E_0 has three-dimensional dense network structure formed through the intermediary of the amorphous silica cluster, which were derived from alkoxysilane terminated with PDMS chains. As the results, the different tree propagation characteristic are observed between hybrid E_0 and $E_n(n > 0)$ as shown in Table 1. In hybrid E_0, there were two structures, bubble and tube tree, and the former occupied over 67%. In addition, the tree inception voltage of hybrid E_0 is smaller value than that of hybrid E_1 and E_2. Since the hybrid E_0 was so brittle and had weak adhesiveness to the tip electrode, the degradation would advance at the interface between the electrode and the hybrid materials, and then bubble tree grew up at the front of a tip. Here, since the hybrid E_0 has a high crosslinking density, the decomposition gas generated by partial discharge remained in the bubble and the pressure increased in the tree pipe, the gas discharge would not be maintained and the growth of the bubble tree became slow down. However, after the stagnation of the tree propagation from several seconds to several minutes, the pressure dropped due to the increase of cavity volume and/or the dispersion of the gas in the bubble, the gas discharge could occur again and tree would start to grow again, and then flashover occurred At the moment, the tube tree was observed. The occurrence of the tube tree indicated the insufficient homogeneity of dispersion of the silica cluster and/or the existence of unexpected defects in hybrid E_0. The time to electrical breakdown by bubble tree propagation seems to be long, however, the difference of the breakdown time between samples is large from several seconds to several minutes. Thus the hybrid E_0 lacks in the reliability of electrical insulation.

In the hybrid E_n $(n > 0)$, the dominant structure was branch tree. With the increase in TA/PDMS ratio in hybrid E_n, the proportion of bubble tree decrease and that of branch tree increased as shown in Table 1. In the sample which the branch tree was occurred, the speed of tree growth was slower than other trees as shown in Fig. 2. As mentioned above, crosslinking density plays on the variation of the tree propagation, and in general, it is known that the tree profiles of polymer material change from tube to branch with increase in crosslinking density [14]. However, hybrid E_n $(n > 0)$ has looser network structure that is formed by the linear PDMS chains which has silica clusters in the main chain backbone as reported in previous paper [9]. However, the branch tree was observed in hybrid $E_n(n > 0)$ in spite of its lower crosslinking density. This is attributed to the barrier effect [15] by well-dispersed clusters of silica without aggregation in hybrid En $(n > 0)$. Since the silica cluster would be more resistant against partial discharge compared to the PDMS moiety, and play a role of obstruction to the straight tree propagation, thus the shape of tree would become branch. In hybrid E_n, the homogeneity of dispersion of silica clusters is believed to be improved by introducing the silica clusters to the main chain backbone of PDMS. We also observed that the tree inception voltage increased and the number of branch of tree increased with the increase in molar ratio of TA/PDMS in hybrid E_n. These results indicated that the homogeneity of dispersion of silica cluster was improved by increase in molar ratio of TA/PDMS in hybrid E_n. This supposition about the dispersion of silica clusters agrees with that supposed from stress-strain test.

On the other hand, the speed of tree growth in silica-filled PDMS rubber became faster than that in hybrid E_2. It is attributed to the difference of silica aggregation. In silica-filled silicone rubber, formation of well-dispersed silica cluster in the matrix polymer is difficult without surface treatment of silica and/or mixing process by mixer machines. By contrast, in-situ silica filling by utilizing alkoxysilane-terminated PDMS can easily make hybrid materials dispersed silica without aggregation. Tree propagation characteristic of SiR is also shown in Table 1. We realized that the tree inception voltage of the SiR is lower than that of hybrid O_n and E_n. These results suggest that the hybrid made from the alkoxysilane-terminated PDMS and TA is good insulating materials compared with conventional SiR.

Conclusion

We investigated electrical treeing characteristics of PDMS-based hybrid materials made from titanium alkoxide and alkoxysilane-terminated PDMS in different TA/PDMS ratio. We observed the development of AC tree of 2-D specimens with needle electrode system by CCD camera and computer. We found that the shape of tree is bubble tree and branch tree. With increase in molar ratio of TA and alkoxysilane-terminated PDMS in the hybrid, the dominant shape of tree became branch tree, namely, the tree inception voltage increased and growth speed decreased. We found that the tree propagation was suppressed with the increase in TA/PDMS ratio in hybrid E_n. It is suggested that the variation of crosslinking density and homogeneity of dispersion of silica clusters in hybrid materials influenced on their tree propagation characteristic. We found that the hybrid made from the alkoxysilane-terminated PDMS and TA has good electrical insulating property compared with conventional PDMS-based hybrid materials and silicone rubber.

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