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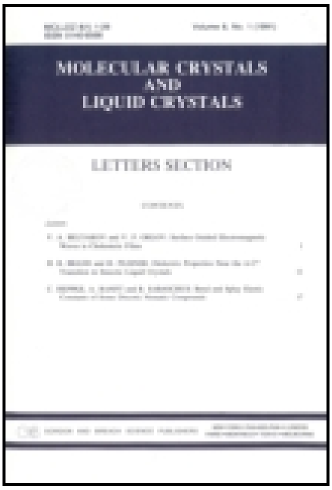

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Preparation and Characterization of Highly Heat-Resistant Organic-Inorganic Hybrid Materials Made from Two-Component Polydimethylsiloxane

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Preparation and Characterization of Highly Heat-Resistant Organic–Inorganic Hybrid Materials Made from Two-Component Polydimethylsiloxane

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Organic–inorganic hybrid materials made from polydimethylsiloxane (PDMS) have been studied as encapsulation materials for high-power devices because of their high dielectric strength, high heat resistance, and flexibility when compared to conventional elastomers. To improve the heat-resistant property, hybrid materials made from two PDMS components, PDMS terminated with silicon alkoxide $Si_5O_4(OC_2H_5)_{12}$ *(A-PDMS) and PDMS terminated with ethyl-acetoacetate-modified titanium alkoxide* $Ti(OCH_2CH(C_2H_5)C_4H_9)_4$ *(T-PDMS), were prepared. We found that the heat-resistant property of a hybrid material could be improved by adjusting the molar ratio between A-PDMS and T-PDMS. After heat treatment at 250°C for 1,000 h, the hardness and weight loss of the hybrid material made from A-PDMS and T-PDMS were under 60 degrees (on an Asker C durometer) and under 5.0%, respectively. The excellent long-term thermal stability of the hybrid material made from A-PDMS and T-PDMS can be attributed to the improved homogeneity of inorganic clusters and the decrease in unreacted functional groups in hybrids by using T-PDMS as a raw material.*

Keywords Organic–inorganic hybrids; polydimethylsiloxane; long-term thermal stability

Introduction

Polydimethylsiloxane (PDMS)-based organic–inorganic hybrid materials have been studied as encapsulation materials for high-power devices. Compared with conventional elastomers, they possess unique characteristics that include high heat resistance [1], flexibility [2–5], and high dielectric strength [6–10]. In a previous paper [9], we clarified that hybrid materials made from titanium alkoxide and alkoxysilane-terminated PDMS provide higher electrical insulation than conventional hybrid materials made from hydroxyl-terminated PDMS and tetraethyl orthosilicate (TEOS). They have a problem in long-term thermal stability, however. This may be attributed to aggregation of titanium alkoxide, which reduces the heat resistance of materials by lowering the crosslinking density and increasing the

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unreacted moieties in materials. In order to prevent aggregation of titanium alkoxide, we synthesized PDMS terminated with chelated titanium alkoxide (T-PDMS). For the study presented here, we prepared hybrid materials made from two PDMS components: PDMS terminated with silicon alkoxide (A-PDMS) and T-PDMS. We investigated the thermal stability of hybrid materials made from A-PDMS under non-isothermal and ithothermal heating; we also compared the thermal stability of the hybrid made from A-PDMS and T-PDMS with the thermal stability of various conventional PDMS-based hybrid materials.

Experimental

Sample Preparation

PDMS terminated with silicon alkoxide (also called alkoxysilane, $Si_5O_4(OC_2H_5)_{12}$), with an average molecular weight of 27,000, was synthesized according to the literature [6]. PDMS terminated with ethylacetoacetate-modified titanium alkoxide was synthesized as follows. Titanium alkoxide (tetrakis (2-ethylhexyloxy) titanium, also referred to as TA, $Ti(OCH_2CH(C_2H5)C_4H_9)_4$) was chelated with ethylacetoacetate (EAcAc) by mixing in a EAcAc/TA molar ratio of 2:1 at room temperature. Next, hydroxy-terminated polydimethylsiloxane (PDMS) with an average molecular weight of 38,000 (XF3057, Momentive Performance Materials Inc.) was mixed with EAcAc at different charged molar ratios (EAcAc/PDMS = 1, 4, 8, 35, 70, 100, 140). The chelated titanium alkoxide was slowly released dropwise into the PDMS–EAcAc solution, which was maintained at 120°C. The temperature was then increased to 250°C for 1 h to complete the reaction and evaporation of residual EAcAc and cyclic siloxanes in the solution. After completion of the reaction, the titanium alkoxide was introduced to the end of the PDMS chain and all alkoxy groups of Ti became chelated. The chemical structures of A-PDMS and T-PDMS are shown in Fig. 1. A-PDMS and T-PDMS with different molar ratios (T-PDMS/A-PDMS = 0.7, 1, 3, 5, 10) were mixed by a conditioning planetary mixer (THINKY CORPORATION, ARE250); the mixture was then poured into a pot of molten aluminum to a depth of 3 mm and then heat-treated at 250°C for 2 h to yield hybrid materials.

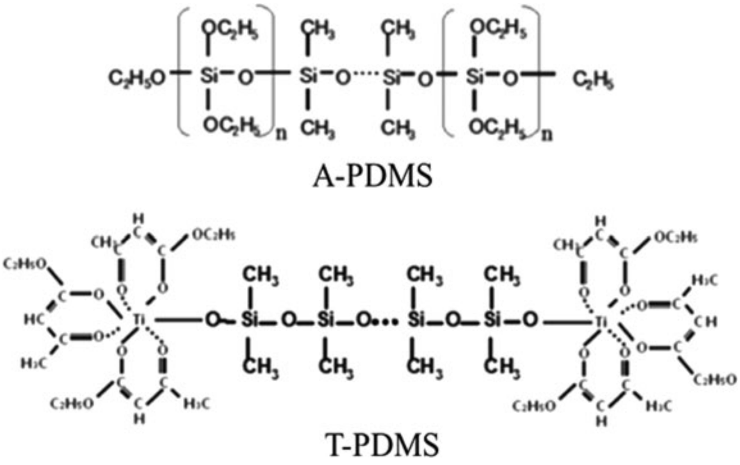


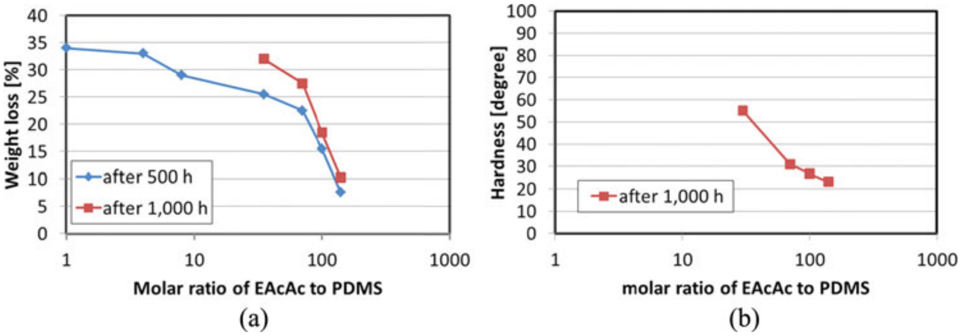
Figure 1. Chemical structures of PDMS terminated with silicone alkoxide (A-PDMS) and PDMS terminated with chelated titanium alkoxide (T-PDMS).

Characterization

The long-term isothermal analysis was performed as follows. Both samples were placed in an air-circulating oven maintained at 250°C. Samples were extracted at selected time intervals, and their weight-loss ratio and hardness were evaluated. The weight of the samples was measured by an electronic balance (AUX220, Shimadzu Co.). The hardness was evaluated by using a durometer for soft-type rubber (Asker Type C2L, Kobunshi Keiki Co.). All measurements were carried out at room temperature. The samples were exposed to 250°C for more than 1,000 h. The non-isothermal analysis of thermal degradation was performed using a thermogravimetric analysis (TGA) measurement system (TG-60, Shimadzu Co.). All samples were heated from room temperature to 600°C at a rate of 10°C/min in air. The flow rate of air was kept constant at 50 mL/min. Samples that weighed about 8 mg each were evaluated.

Results and Discussion

The curing temperature of T-PDMS was investigated to evaluate its reactivity. All T-PDMS synthesized with different molar ratios of EAcAc/PDMS developed a skin within a few hours after exposure to 250°C, and the hardness increased with exposure time. Figure 2 shows the weight-loss ratio and hardness following 500 h and 1,000 h of isothermal heating at 250°C for hybrid materials made from T-PDMS synthesized with different charged molar ratios of EAcAc to PDMS. The hardness of the sample became lower than the measurable hardness after 500 h of isothermal heating. The hybrid made from T-PDMS synthesized with an EAcAc/PDMS molar ratio of less than 35 began to shrink and cracked with the lapse of heat-treatment time. The increase in hardness and weight loss with time are attributed to the increase in crosslinking density of T-PDMS. The crosslinking reaction of T-PDMS occurred slowly because the hydrolysis and polymerization of chelated Ti terminating the end of PDMS chains were deferred owing to ligands, and the reaction could only occur only when some parts of the chelating ligand was broken off by heat treatment at 250°C. The hardness of the hybrids decreased with the increase in molar ratio of EAcAc to PDMS, suggesting that T-PDMS was further stabilized by adding more chelating agent EAcAc in



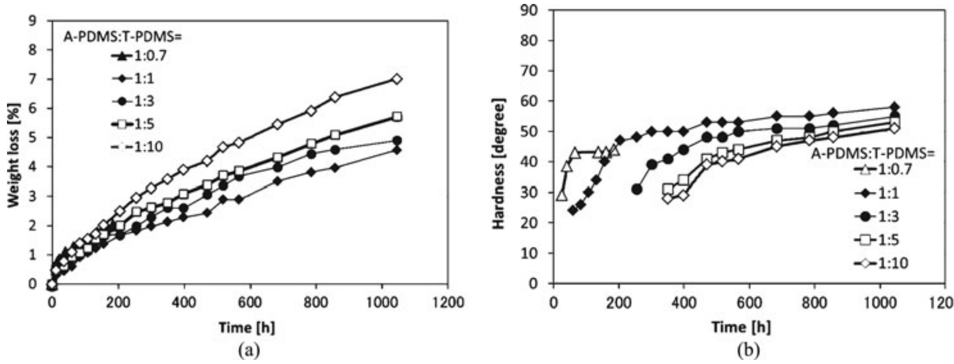
(a) (b)

Figure 2. (a) Weight-loss ratio and (b) hardness following 500 h and 1,000 h of isothermal heating at 250°C for the hybrid made from T-PDMS synthesized with different charged molar ratios of EAcAc to PDMS (weight average molecular weight of PDMS is 38,000). The weight-loss data after 1,000 h of heating for the hybrid with EAcAc/PDMS molar ratios of <35 were eliminated because all samples shrank and cracked. The data of hardness after 500 h were not plotted because the hardness of the samples became lower than the measurable hardness.

the synthesis. It was realized that an EAcAc/PDMS molar ratio exceeding the stoichiometric ratio was necessary to stabilize T-PDMS because titanium alkoxide has a strong reactivity. The change in the inclination of the plot showing the relationship between the exposure time at 250°C and the weight loss shows that the appropriate molar ratio of EAcAc to PDMS for synthesizing the stabilized T-PDMS was 70 and higher.

Figure 3 shows the weight-loss ratio and hardness versus exposure time at 250°C for the hybrid made using different A-PDMS/T-PDMS molar ratios. All samples became tack-free after heat treatment for 2 h at 250°C. The hardness of the sample became lower than the measurable hardness in the initial heating stage. The hardness of the hybrids increased and then became a stationary value with time. The hybrid prepared by mixing the starting materials in a T-PDMS/A-PDMS molar ratio of under 1.0 cracked within 200 h at 250°C. With the increase in molar ratio of T-PDMS/A-PDMS, the hardness decreased and the weight-loss ratio increased. In other words, there was a tradeoff between the hardness and weight loss, and it was found that the appropriate molar ratio of T-PDMS to A-PDMS was 1:1 to 1:3.

The non-isothermal and isothermal analyses of thermal degradation were carried out for various PDMS-based hybrid materials. Here, PDMS, PDMS + TA, and A-PDMS + TA denote the cured elastomer consisting of hydroxy-terminated polydimethylsiloxane, the hybrid made from hydroxy-terminated polydimethylsiloxane and titanium alkoxide (PDMS/TA = 1:2) [9], and the hybrid made from alkoxysilane-terminated PDMS and titanium alkoxide (A-PDMS/TA = 1:2) [9], respectively. Figure 4 shows TGA curves of the various hybrids. The initial weight-loss temperature of the hybrid made from T-PDMS and A-PDMS became higher than the other hybrids. Table 1 lists the presence or absence of peeling and cracking, hardness degree, and weight loss after 1,000 h of isothermal heat treatment of various hybrid materials. The cracking or peeling, or both cracking and peeling of the materials occurred in hybrids prepared from PDMS, PDMS + TA, A-PDMS, and A-PDMS + TA within the first 24–72 h. After the heat treatment at 250°C for 1,000 h, the weight loss and hardness of the hybrid made from only T-PDMS was 11% and 23 degrees, respectively; the weight loss and hardness of the hybrid material made from A-PDMS and T-PDMS was 4.3% and 58 degrees, respectively. The hybrid made from T-PDMS maintained its softness but its weight loss became large. By contrast, the hybrid made from



(a) (b)

Figure 3. (a) Weight-loss ratio and (b) hardness versus time at 250°C for hybrid materials made using different molar ratios of A-PDMS/T-PDMS. The data of weight-loss ratio were eliminated after shrinkage and cracking occurred in the samples. The data of hardness were not plotted because the hardness of the samples became lower than the measurable hardness in the initial heating stage.

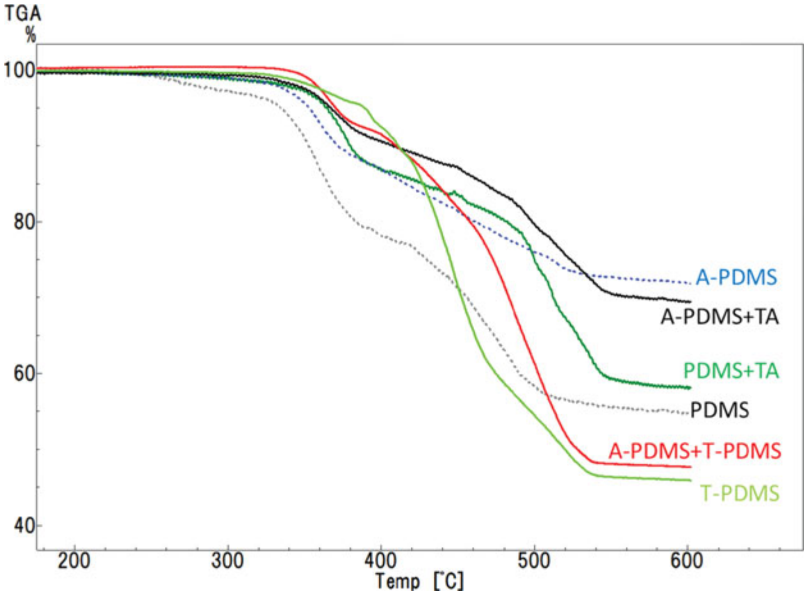


Figure 4. TGA curves of various hybrids.

A-PDMS and T-PDMS showed high resistance to heat while maintaining its flexibility and softness compared with conventional PDMS-based hybrid materials.

The thermal stability of materials made from PDMS is governed mainly by their molecular structure and network structure. PDMS-containing functional groups, i.e., hydroxyl groups, alkoxy groups, or hydroxyl–alkoxy groups are principally depolymerized by an unzipping mechanism [11]. Therefore, it is important to decrease the concentration of these types of end-groups remaining in the materials in order to improve the thermal stability of hybrids. Moreover, the formation of the cross-linked network structure can suppress the degradation by inter- or intra- molecular redistribution reactions that occur randomly between the siloxane bonds of the PDMS backbone via a random scission mechanism at higher temperature. The reason that conventional hybrid materials showed large residual weight at over 500°C by TGA, but large degradation under isothermal heat treatment at 250°C, is attributed to the existence of many unreacted functional groups in the material. TGA showed that the hybrid made from T-PDMS had a large weight-loss at over 450°C.

Table 1. Long-term thermal stability of various PDMS-based hybrid materials.

Sample	Presence or absence of peeling and cracking	Hardness [deg]	Weight loss [%]
PDMS	Presence (within 24 h)	—	45
PDMS + TA	Presence (within 36 h)	—	38
A-PDMS	Presence (within 48 h)	—	22
A-PDMS + TA	Presence (within 72 h)	—	48
T-PDMS	Absence	26	11
A-PDMS + T-PDMS	Absence	58	4.3

It is assumed that the hybrid made from T-PDMS was easy to degrade by random scission reaction because of its low crosslinking density. The good thermal stability shown by TGA at temperatures below 400°C and isothermal heating of 250°C in the hybrid prepared from T-PDMS and A-PDMS can be attributed to the improvement in homogeneity of inorganic clusters and the decrease in unreacted functional groups.

Conclusion

Hybrid materials were prepared from two PDMS components: PDMS terminated with silicon alkoxide and PDMS terminated with chelated titanium alkoxide. The heat-resistant property of hybrid materials could be improved by adjusting the molar ratio of A-PDMS to T-PDMS. After the heat treatment at 250°C for 1,000 h, the hardness and weight loss of the hybrid materials were under 60 degrees (on an Asker C durometer) and under 5.0%, respectively. The hybrid made from T-PDMS and A-PDMS had high heat resistance while maintaining its flexibility and softness compared with conventional PDMS-based hybrid materials. These properties can be attributed to the improvement in homogeneity of inorganic clusters and the decrease in unreacted functional groups in the hybrids.

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