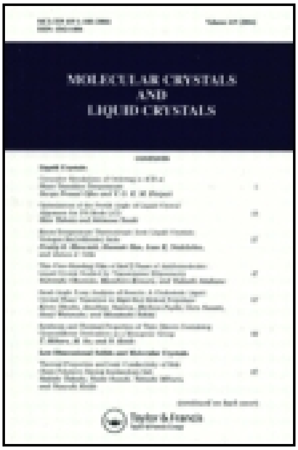

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Electrical Insulating and Heat-Resistive Properties of PDMS-TEOS Hybrid with Different Molar Ratio of TEOS to PDMS

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The hybrids prepared from polydimethylsiloxane (PDMS) and tetraethoxysilane (TEOS) have been well known to be rubbery hybrid materials. In this report, the authors have investigated the electrical insulating and heat resistive properties of the hybrids by changing the molar ratio of TEOS to PDMS. The electrical insulating properties are evaluated by volume resistivity and AC breakdown strength at room temperature. The resistivity is about 10^{13} Ω·m and AC breakdown strength is about 25 kV/mm irrespective of the molar ratio. Heat-resistive properties are evaluated by the weight loss after keeping for 480 h at 200°C in air. The weight loss becomes smaller as the TEOS content increases, and it is less than 3%. It has been clarified that the hybrids have good electrical insulating and heat-resistive properties.

Keywords: electrical insulating property; heat-resistivity; organic-inorganic hybrids; polydimethylsiloxane

1. INTRODUCTION

The demand for a new class heat resistive electrical insulating materials gets higher from a cost and environmental problem in electrical

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power and industrial apparatus. The heat resistive rank of epoxy resin is classified into F class where the maximum temperature of conductor is limited less than 155°C. If a new material with a higher heat resistive rank is applied to the apparatus, it is possible to employ a higher current density through conductors, leading to saving energy and a high efficiency. From the point of view of actual apparatus, insulating materials are in the form of composites with mica and conducting filler. Thus, how mechanical and electrical insulating properties are improved by introducing fillers into the new material is important in addition to the heat resistive property. Thus, the authors have focused on PDMS-based organic-inorganic hybrids for a reason that the hybrid has the potential to fulfill demands of high thermal conductivity and flexibility by adding fillers, because a sol state of the hybrid is able to contain a lot of functionalizing fillers [1–2].

There are some studies on the characterization and mechanical properties of organic-inorganic hybrids [2–5]. Optical transparency and mechanical property of PDMS-TEOS based hybrids were discussed by changing acid and TEOS contents where the average molecular weight was less than 1,700 g/mol [3]. Huang *et al.* found that the hybrids show more homogeneous and higher extensibility when TEOS content is 48% or 60 wt% [3]. An increase of the TEOS content causes a tighter network with higher modulus. However, in that case, cracking and shrinkage raise problems in making thick monolithic materials. Mackenzie *et al.* have studied the PDMS-TEOS based hybrids prepared by varying the molar ratio of TEOS to PDMS and incorporating fumed silica into the hybrids where the molecular weight is below 4,200 g/mol [2]. With a low PDMS content, the hybrids are harder, stiffer and stronger than those with higher content of PDMS [2]. They found that hybrids made with fumed silica are much more stable than commercial rubbers at elevated temperatures [2]. Iwamoto *et al.* have studied the sol-gel reaction mechanism of the hybrids made with PDMS and TEOS by liquid state ^{29}Si NMR spectroscopy [4]. They have found that the higher the reaction temperature (room temperature to 70°C), the more copolymerization between PDMS and TEOS occurs. Katayama *et al.* have studied the hybrids made with PDMS of molecular weight of 3,000 g/mol and chemically modified metal alkoxides [5]. They have found that the inorganic components in the hybrids are present as oxide-like clusters with sizes of 2–3 nm or below and are chemically attached to PDMS via Metal-O-Si bonds. The flexibility of the hybrids was kept at least to 200°C for 100 h in N_2. However, it is not clear how this thermal stability is held if the hybrids are kept in air. It should be also discussed the difference of mechanical properties between the hybrids made with zirconium n-butoxide and tantalum ethoxide from the point of view of the difference of the reaction rate of metal alkoxide through the sol-gel reaction.

Because the molecular weight of PDMS was less than 4,200 g/mol in previous papers [2–5], there is some room for improvement of their heat-resistive property by employing a larger molecular weight of PDMS. From the point of view of the application of the hybrids to electrical power apparatus, electrical insulating and heat-resistive properties have not been studied so much. Generally, heat-resistive property has been evaluated by thermo-gravimetric analyzer (TGA). Because the measurement of TGA is usually carried out only within several hours, it will not give a true heat-resistive property which is strongly required in engineering fields. In this paper, the authors have investigated the electrical insulating and consecutive heat-resistive properties of the hybrids with different molar ratios of TEOS to PDMS. In order to evaluate the electrical insulating property, volume resistivity and AC breakdown strength are examined. Heat-resistive property has been estimated with the changes of weight loss and mechanical strength by keeping 480 h at 200°C in air.

2. EXPERIMENTAL

Sample Preparation

Liquid silanol-terminated PDMS with an average molecular weight of 20,000 g/mol was used as a precursor for the organic component, and TEOS ($Si(OC_2H_5)_4$) was used as a precursor for the inorganic component. 2-ethoxyethanole was the solvent, and acetic acid (CH_3COOH) was used as a catalyst. Deionized water (H_2O) was used for the hydrolysis of TEOS. PDMS was purchased from GE Toshiba Silicones Co., Inc. TEOS was purchased from Kanto Chemical Co., Inc. 2-ethoxyethanole and acetic acid were purchased from Wako Pure Chemical Industries, Ltd.

Hybrid was prepared through a sol-gel method. TEOS and PDMS and 2-ethoxyethanole were mixed in the molar ratio of TEOS: PDMS:2-ethoxyethanole $= 1 : x : 2$ ($x = 0.1, 0.2, 0.5, 1$). This solution is called liquid A hereafter. The value of x was changed in order to examine the effect of the TEOS content on mechanical and electrical insulating properties of the hybrids. H_2O and 2-ethoxyethanole and CH_3COOH were mixed with in the molar ratio of H_2O : 2-ethoxyethanole : $CH_3COOH = 4 : 1 : 0.05$. This solution is called liquid B. At first, liquid A was heated to 90°C by mixing with a hot stirrer. This heating procedure makes a possible to employ the large molecular weight of PDMS in this experiment. After the temperature of liquid A reached 90°C, liquid B was poured into liquid A drop by drop by mixing. The solution was mixed for 30 min at 90°C after pouring. Then, the mixed solution was cooled to room temperature by leaving without heating. The solution was poured into a teflon petri dish and covered with aluminum-foil. The solution in the teflon petri dish was allowed to gel at 150°C for 24 h and then heat-treated at 250°C for 5 h to give a PDMS-TEOS hybrid sheet.

Measurements

Resistance R was measured with a 6430 SUB-FEMTOAMP REMOTE SourceMeter (KEITHLEY Co.). Reading current I_T was taken at 15 min after applying voltage V_I. The volume resistivity ρ was calculated by $\rho = E/J = (V_I/d)/(I_T/S)$, where d is thickness of sample and S area of electrode.

AC breakdown strength E_B was conducted using a sphere to plane electrode system. The diameter of the sphere is 5.5 mm and the diameter of the plane was 50 mm with 2.5 mm in curvature. The AC voltage was applied to the sheet sample in fluorinated inert liquid (Fluorinert^{TM}). A frequency of applied voltage is 50 Hz. The breakdown voltage V_B was estimated from a profile of voltage across the sample. The value of E_B was estimated by $E_B = V_B/d$.

In order to estimate the heat-resistive property of hybrids, a measurement of weight loss was carried out at room temperature after heating them for 480 h at 200°C in air. The weight loss of hybrids was evaluated by $(W_b - W_a)/W_b{*}100$, where W_b is the initial weight and W_a the weight at each time of the exposure till 480 h.

Mechanical properties were carried out with a tension tester (AGS-J: Shimadzu Co.) at room temperature. Dumbbell-shaped samples prescribed in JIS K6251 [6] were employed. The crosshead speed was 500 mm/min.

Differential scanning calorimetry (DSC) was performed with a DSC6200 (SEIKO Instrument, INC). Aluminum pans were used and the amount of sample was approximately 9 mg. An empty aluminum pan was used as a reference. At first, the cell containing a sample was cooled to –150°C and then held for about 30 min to allow the system to attain thermal equilibrium. DSC measurement was carried out at a cooling or heating rate of 3°C/min.

3. RESULTS AND DISCUSSION

Electrical Insulating Property

Figure 1 shows the change in volume resistivity ρ and AC breakdown strength E_B as a function of the molar ratio of TEOS to PDMS. From

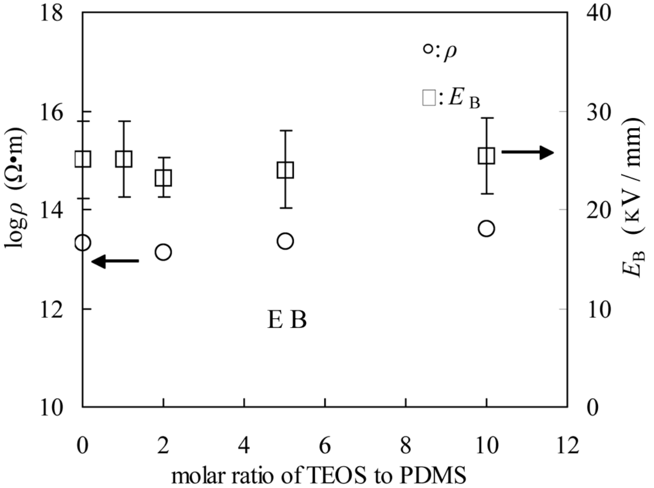

FIGURE 1 Change in volume resistivity ρ and AC breakdown strength E_B as a function of the molar ratio of TEOS to PDMS.

the results in Figure 1, the value of ρ is above $10^{13}\ \Omega \cdot m$ and the value of E_B is about 25 kV/mm irrespective of the molar ratio. It is well known that adding micro-fillers into electrically insulating resin introduces weak points due to voids formed at interface between filler and resin, leading to reduced breakdown strength [7]. Also, an introduction of electrically conducting filler into resin causes a steep decrease in breakdown strength where the way of the change for the breakdown strength is governed by a power law with a critical exponent as a function of the distance from the volume fraction of filler to the percolation threshold [8]. In Figure 1, the breakdown strength doesn't show a distinct difference for the molar ratio. Thus, it is expected that PDMS and TEOS are uniformly-dispersed and they are chemically combined [3,5], leading to no defects at interface between PDMS and TEOS.

Heat-Resistive Property

Weight loss after keeping for 480 h at 200°C is shown in Figure 2. As the reasons of the weight loss, vaporizations of low molecular moieties of PDMS and water formed through further dehydration and condensation polymerization may be expected. From Figure 2, it can be seen that the weight loss becomes smaller as increasing TEOS content, and it is less than 3% in the molar ratio range. The inset in Figure 2 shows the weight loss of the sample (the molar ratio of TEOS/PDMS = 10)

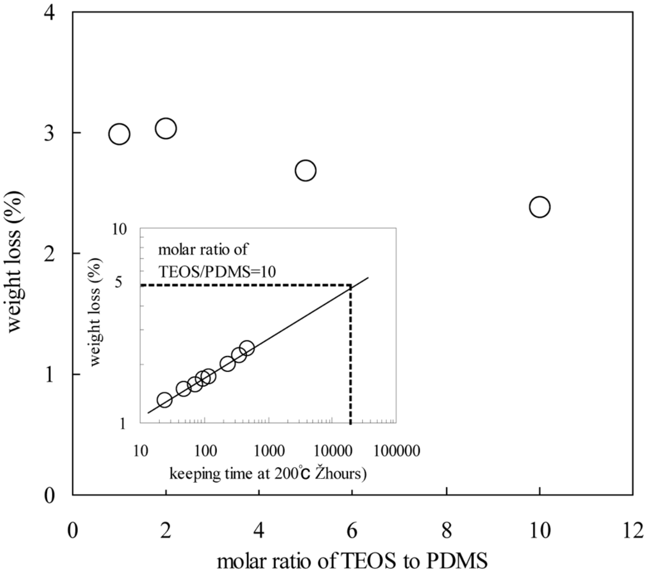

FIGURE 2 Weight loss of the hybrids after keeping for 480 h at 200°C as a function of the molar ratio of TEOS to PDMS. The inset shows the weight loss of the sample (TEOS/PDMS = 10) as a function of keeping time at 200°C.

as a function of keeping time at 200°C on double logarithm plot. In the inset, a linear solid line is the guide to eye and the slope of it is about 0.002. It can be expected that the weight loss even after keeping for 20,000 h at 200°C is about 5% from the extrapolated line. This value is fully satisfied with a requirement for heat-resistive materials. The change of weight loss for the molar ratio shall be discussed together with the results obtained from the measurements of mechanical property.

Figure 3 shows the change of mechanical properties as a function of the molar ratio of TEOS to PDMS. In the figure, open and closed circles stand for the properties before and after heating for 480 h at 200°C, respectively. As TEOS content increases, elastic modulus and stress at break are more enhanced and, on the other hand, elongation at break becomes smaller. Because of the improvement of elastic modulus and stress at break with the TEOS content, the results indicate that more introducing TEOS into PDMS causes more cross linking points [2]. It has been found that the elastic modulus and stress at break of hybrid are improved after keeping for 480 h at 200°C as shown in Figure 3. It can be suggested that further cross linking takes

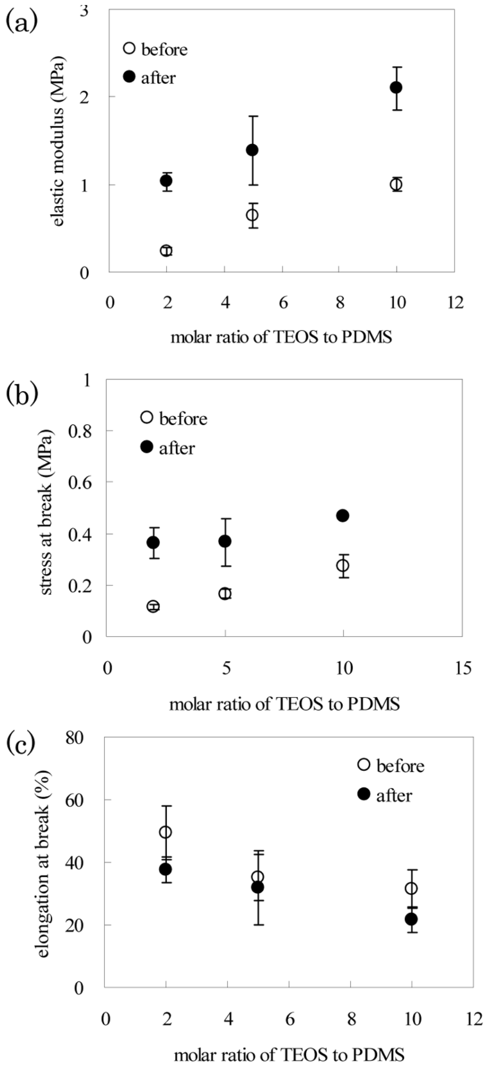

FIGURE 3 Change of mechanical properties of hybrids as function of the molar ratio of TEOS to PDMS. (a) elastic modulus, (b) stress at break, and (c) elongation at break.

place through the ageing because of the improvement of mechanical properties. As shown in Figure 3, the elongation at break is getting smaller with increasing TEOS content which is due to much formation of cross linking. However, the lowest value of elongation at break of

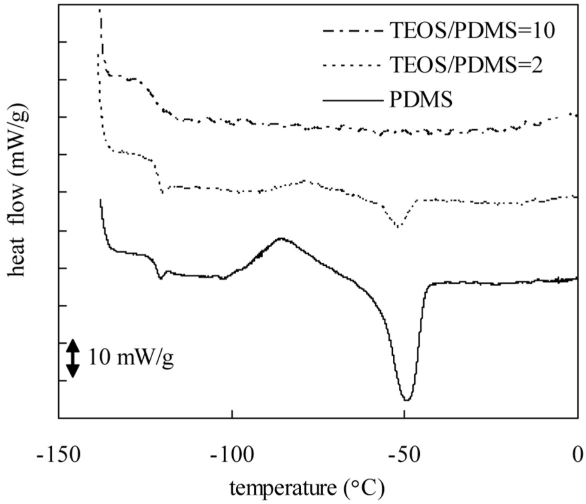

FIGURE 4 DSC curves of hybrids with various molar ratios of TEOS to PDMS.

our hybrids is much better than the best value of the previous paper [2]. Moreover, the data of elongation at break of our samples are superior to those of the previous paper [2] even after keeping for 480 h at 200°C.

A degree of crosslinking between TEOS and PDMS was also evaluated with DSC measurement. The DSC curves of the hybrids are shown in Figure 4. The figure shows that the exothermic peak around −80°C to −70°C and the endothermic peak at −50°C become smaller and finally disappear as the TEOS content increases. In the previous paper [9], these exothermic and endothermic peaks are ascribed to a ordering and disordering of free PDMS chains. Thus, the introduction of TEOS into PDMS also brings about a restriction to the motion of free PDMS chains by a cross linking mechanism, leading to a less weight loss for heating at 200°C.

It can be concluded that the improvements of weight loss and mechanical strength can be obtained by employing an average molecular weight 20,000 g/mol of PDMS.

4. CONCLUSIONS

The change in electrical insulating and heat-resistive properties of hybrids made with TEOS and PDMS through the sol-gel methods with different molar ratios was studied. The electrical insulating properties of volume resistivity and AC breakdown strength of the hybrids changed a little in the range of the molar ratio. Weight loss of the hybrids after keeping for 480 h at 200°C becomes smaller as the TEOS content increases. This weight loss is caused by vaporization of low molecular component and dehydration. Weight loss after keeping for 20,000 h at 200°C is estimated less than 5%. These results lead us to the conclusion that the hybrids have good electrical insulating and heat-resistive materials. The curing condition and application by adding fillers will be presented in a future publication.

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