Preparation of Organosiloxane-Based Inorganic/Organic Hybrids with High Affinity toward Engine Oil

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1. Introduction

The nano-combination of inorganics and organics is attracting attention because of the possibility for not only summing properties of both inorganic and organic materials but also providing novel properties arising from the synergistic interaction of the individual constituents. Therefore, promising applications are expected in many fields, optics, electronics, mechanics, ionics, membranes, sensors, catalysis, biology, and others. The sol–gel process is generally used for nano-combining the inorganics and organics to provide inorganic/organic hybrids or nanocomposites because of the low-temperature route for the formation of inorganic oxide networks such as siloxane networks.

There have been many works to investigate the inorganic/organic hybrids for many applications such as protective coatings, low-k dielectrics, optical coatings, sensors, and membranes. Some of the authors have investigated the hybrid structures and properties as mechanical, optical and chemical materials. However, there is no study on the friction property of inorganic/organic hybrids. Inorganic/organic hybrids have also the possibility for an application to tribological materials. The authors have investigated the lubrication properties of organosiloxane-based inorganic/organic hybrids, aiming at the development of low friction materials under boundary and fluid lubrication conditions for application to automobile components. The presence of phenyl groups in organosiloxane-based hybrids was more effective for the high wettability with oil than other organic groups such as alky1 and fluoro-alkyl groups with different carbon-chain length. In order to readily obtain hybrid films without cracks, dimethyl groups were incorporated into the phenylsiloxane-based hybrid. The hybrid films were found to have the good wettability with oil up to the heat-treatment temperature of 400°C. In the C₆H₅Si(OC₂H₅)₃:(CH₃)₂Si(OC₂H₅)₂ ratios of 20 : 80 to 10 : 90, the hybrid films were found to keep a relatively good wettability with oil although the content of phenyl groups decreased.

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2. Experimental

Organotriethoxysilanes (RSi(OC₂H₅)₃, R = CH₃-, CH₃CH₂-, CH₃(CH₂)₂-, CH₃(CH₂)₃-) and organosiloxane-based hybrids containing phenyl groups showed the high wettability with oil and the good friction property. Therefore, it was considered that the measured values of contact angles had no contribution of the surface roughness in this experiment. The contact angle measurements were carried out without any treatment of hybrid film surface. FT–IR spectra were recorded on a Perkin-Elmer System 2000 FT–IR Spectrometer.

3. Results and discussion

Figure 1 shows the contact angles with oil and liquid paraffin for organosiloxane-based inorganic/organic hybrid films. The organosiloxane-based hybrid films prepared from RSi(OC₂H₅)₃, R = CH₃-, CH₃(CH₂)₂-, CF₃(CH₂)₂-, CF₃(CF₂)₂C₂H₄-, and C₆H₅-, were heat-treated at 200°C for

4. Conclusion

The nano-combination of inorganic/organic hybrids with high wettability toward engine oil have been prepared, aiming at the development of low friction materials under boundary and fluid lubrication conditions for application to automobile components. The presence of phenyl groups in organosiloxane-based hybrids was more effective for the high wettability with oil than other organic groups such as alkyl and fluoro-alkyl groups with different carbon-chain length. In order to readily obtain hybrid films without cracks, dimethyl groups were incorporated into the phenylsiloxane-based hybrid. The hybrid films were found to have the good wettability with oil up to the heat-treatment temperature of 400°C. In the C₆H₅Si(OC₂H₅)₃:(CH₃)₂Si(OC₂H₅)₂ ratios of 20 : 80 to 10 : 90, the hybrid films were found to keep a relatively good wettability with oil although the content of phenyl groups decreased.
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3 h in air. The organosiloxane-based hybrid films prepared from RSi(OC₂H₅)₃, R = CH₃CH₂- and CH₃(CH₂)₂-, were heat-treated at 150 and 200°C for 3 h in air. Looking at the oil contact angles of the hybrid films prepared from RSi(OC₂H₅)₃ with simple alkyl groups of methyl, ethyl, propyl and octyl groups, the hybrid films containing long alkyl groups, except octyl group, provided lower contact angle with oil than hybrid films containing methyl group. The contact angles with liquid paraffin, which was simple hydrocarbons of alkenes, showed the similar tendency. The oil used in this experiment was typical and simple engine oil, which had a very small amount of or no additives such as oiliness agents, stabilizers, antioxidants, and specific lubricants.

As shown in Fig. 2, FT–IR spectra of both the oil and liquid paraffin were very similar, except that the oil had extremely small absorption peaks at 1710 and 1610 cm⁻¹ corresponding to carboxy groups and carboxy-anions, respectively. In the case of simple alkyl groups with normal chain, it may be generally predicted that the wettability of long alkyl groups with oil is higher than that of methyl groups from the standpoint of the high affinity resulting from the similarity in chemical structure between long alkyl groups and oil, so-called “chain matching effect.” However, in the hybrid films containing ethyl and propyl groups, samples prepared by the heat-treatment at 200°C exhibited higher contact angle with oil than that of hybrid films containing methyl group. This is due to the thermal decomposition of the alkyl groups because the decomposition temperature of ethyl and propyl groups in siloxane networks is in the range of about 200 to 300°C, which is lower than that of methyl groups. Since methyl groups in siloxane networks are thermally stable up to about 400°C, the value of the contact angle with oil is not so much varied by the heat-treatment. The high contact angle of the hybrid films containing octyl groups may be due to the small number of octyl groups on the surface, which resulted from the ineffective configuration of octyl groups on the surface and/or the thermal decomposition of several octyl groups.

The hybrid films containing fluoro-alkyl groups exhibited high contact angle with both oil and liquid paraffin. This result arises from the very low affinity of fluoro-alkyl groups toward any substances, that is, the low dispersion force in van der Waals forces, because fluorocarbons’ electrons are held so tightly by the highly electronegative fluorine atoms. It is well known that fluoropolymers, for example polytetrafluoroethylene, have the extremely low coefficient of friction under solid lubrication condition. Also in the hybrid films containing fluoro-alkyl groups, the low coefficient of friction under solid lubrication condition may be expected but the high wettability with oil is more important factor under boundary and fluid lubrication conditions. The difference in contact angle between oil and liquid paraffin was observed in the cases of CF₃(CF₂)₅C₆H₄- group. The oil gave lower contact angles than liquid paraffin. This may be due to an aid of some additives such as fatty acids and fatty acid salts, which were at least confirmed by both the FT–IR
The hybrid films containing phenyl groups exhibited the lowest contact angle with oil among our experiments. The contact angle with liquid paraffin was also low but higher than that with oil. The principal ingredient of the engine oil is aliphatic hydrocarbons. Liquid paraffin is also saturated hydrocarbons, alkanes. On the other hand, phenyl group in siloxane networks is aromatic. Although the chemical structure of phenyl group is very different from that of oil and liquid paraffin, many phenyl compounds such as benzene, toluene, and xylene have also the high affinity toward aliphatic compounds through their lipophilic nature. Therefore, the high wettability with oil and liquid paraffin is likely due to the high affinity of phenyl groups toward aliphatic hydrocarbons by the lipophilic nature and/or the effective configuration of phenyl groups on the surface. Also in the case of phenyl groups, the difference in contact angle between oil and liquid paraffin may be due to an aid of some additives such as fatty acids and fatty acid salts. In addition, phenyl groups in siloxane networks are most thermally stable among organic groups of organosiloxane-based hybrids. Thus, the incorporation of phenyl groups into organosiloxane-based hybrids is suitable for applying the hybrids to low friction materials under boundary and fluid lubrication conditions at high temperatures.

Since the organosiloxane hybrids containing only phenyl groups as an organic component has ladder and cage structures, which are rigid and brittle, it is difficult to make thick films and bulk bodies. Subsequently, we investigated the phenylsiloxane hybrids containing dimethyl groups as a flexible component. In this system, a thick film has been obtained for the friction test. Figure 3 shows the effect of heat-treatment temperature on the contact angle with oil and water. The organosiloxane-based inorganic/organic hybrid films were prepared from C₆H₅Si(OCH₃)₃ and (CH₃)₂Si(OCH₃)₂ in the C₆H₅Si(OCH₃)₃/(CH₃)₂Si(OCH₃)₂ molar ratio of 50:50. The contact angle with oil increased with increasing heat-treatment temperature although the hybrid films just dried at 70°C had a relatively high contact angle with oil possibly because of the insufficient formation of organosiloxane networks. On the other hand, the contact angle with water abruptly decreased from 300 to 500°C. These changes in contact angle are thought to be related to the presence of phenyl groups and hydroxyl groups in the hybrid films, which was evaluated by FT-IR spectra shown in Fig. 4. The hybrid films heat-treated at 70–400°C had an absorption peak around 1270 cm⁻¹ corresponding to methyl groups and absorption peaks around 1130 and 1430 cm⁻¹ corresponding to phenyl groups. In the case of 400°C, the peaks of phenyl and methyl groups became smaller when the absorption peak of siloxane around 1100 cm⁻¹ was a standard. This is due the decomposition of several phenyl and methyl groups. The hybrid films heat-treated at 500°C had only a trace amount of the peaks and the hybrid films heat-treated at 600°C had no peaks of methyl and phenyl groups. In contrast, a considerable absorption peak corresponding to hydroxyl groups was observed around 3400 cm⁻¹ in these hybrid films. It is considered that the contact angle with oil is dependent on the presence of phenyl and dimethyl groups and the contact angle with water is dependent on the presence of hydroxyl groups.

The lower heat-treatment temperatures, at which organic groups are present in siloxane networks, is preferred as good wettability with oil. However, the higher heat-treatment temperatures are need to make a strong film, in which organosiloxane networks is more completely formed. Therefore, the appropriate heat-treatment temperature is thought to be around 400°C.

Figure 5 shows the effect of the starting material composition, C₆H₅Si(OCH₃)₃/CH₃)₂Si(OCH₃)₂, on the contact angle with oil and water. The hybrid films were heat-treated at 400°C. The contact angle with oil slightly increased with decreasing the amount of C₆H₅Si(OCH₃)₃ in the C₆H₅Si(OCH₃)₃/(CH₃)₂Si(OCH₃)₂ ratios of 50:50 to 10:90. The contact angle with water increased with decreasing the amount of C₆H₅Si(OCH₃)₃ in the C₆H₅Si(OCH₃)₃/(CH₃)₂Si(OCH₃)₂ ratios of 50:50 to 20:80 and decreased in the C₆H₅Si(OCH₃)₃/(CH₃)₂Si(OCH₃)₂ ratios of 20:80 to 10:90.

Figure 6 shows FT-IR spectra of these hybrids. According to the starting material composition of C₆H₅Si(OCH₃)₃/(CH₃)₂Si(OCH₃)₂, the absorption peaks of
phenyl and methyl groups were changed in the ratios of 50:50 to 20:80. Despite the large amount of \((\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2\) in the ratio of \(\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3:(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2=10:90\), however, the peak of methyl groups became smaller and in addition the peak of hydroxyl groups around 3400 cm\(^{-1}\) became larger. This is due to the decomposition of many organic groups during the heat-treatment. Although phenyl groups can stabilize organosiloxane networks, the thermal stabilization effect of phenyl groups on organosiloxane networks is thought to be smaller because of the low content of phenyl groups.

Although some organic groups were thermally decomposed at the heat-treatment temperature of 400°C, the following discussions can be done by assuming that the starting material composition is related to the hybrid composition. In the ratio of \(\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3:(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2=10:90\), the low contact angle with water is likely caused by the formation of many hydroxyl groups, which have the strong interaction with water via hydrogen bonds. In the \(\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3:(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2\) ratios of 50:50 to 20:80, the decrease in wettability of organosiloxane-based hybrids with water may be due to the decrease in number of hydrogen bonding sites such as Si–O–Si and/or Si–OH. The ratio of Si–O–Si:\((\text{C}_6\text{H}_5–\text{Si} + \text{CH}_3–\text{Si})\) is formally varied from 62:5:37.5 to 55:45 with the \(\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3:(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2\) ratios of 50:50 to 20:80.

The wettability of organosiloxane-based hybrid films with oil slightly decreased with decreasing the amount of \(\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3\), but it was high even in the ratio of \(\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3:(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2=10:90\). In this ratio, some organic groups were thermally decomposed but thermally more stable phenyl groups may preferentially remain during the heat-treatment. Oil is thought to have no interaction with hydroxyl groups because of no chemical structure to make hydrogen bonding, but the strong interaction with organic groups, especially phenyl groups. Thus, the wettability of organosiloxane-based hybrid films with oil is dependent on the amount of \(\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3\) in the \(\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3:(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2\) ratios of 50:50 to 10:90.

4. Conclusions

Processing of organosiloxane-based inorganic/organic hybrids with high wettability toward engine oil has been investigated for application to low friction materials under boundary and fluid lubrication conditions.

It was revealed that the presence of phenyl groups in organosiloxane-based hybrid films was effective for the high wettability with oil as compared with organosiloxane-based hybrid films containing other organic groups such as alkyl and fluoro-alkyl groups with difference carbon-chain length. Organosiloxane-based hybrid films containing both phenyl and dimethyl groups were prepared. The hybrid films were found to have the good wettability with oil up to the heat-treatment temperature of 400°C. The hybrid films without cracks were found to be readily obtained by the incorporation of dimethyl groups into phenylsiloxane-based hybrids in the region of the starting material composition \(\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3:(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2=50:50\) to 10:90. In this range, the hybrid films had a relatively good wettability with oil although the content of phenyl groups decreased.

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