Oil wettability improvement of inorganic/organic hybrid prepared from methyltriethoxysilane in a low temperature processing

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Abstract: Inorganic/organic hybrid gel was prepared using methyltriethoxysilane (MTES) and various metal alkoxides such as Ti(O-iso-C₅H₄)₄, Al(O-sec-C₅H₄)₃, and Nb(O-C₅H₅)₅, modified with acetylacetone via a sol-gel process. The objective of this study is to fabricate organic/inorganic hybrids bulk and to measure ²⁹Si nuclear magnetic resonance spectroscopy to analyze structure. The catalytic activity increases in the order of Al < Nb < Ti by ²⁹Si nuclear magnetic resonance spectroscopy. Simultaneously, the oil wettability of oil on SUS board coated hybrid gel increased in the order of Al < Nb < Ti.

Keywords: organic/inorganic hybrid, methyltriethoxysilane, metal alkoxide Sol-gel method

1. Introduction

Organosiloxane-based inorganic/organic hybrids have unique mechanical properties such as thermal resistance, flexible properties and oil wettability. Fig.1 shows model of organosiloxane-based inorganic/organic hybrid. Improving oil wettability and sliding property of inorganic/organic hybrids leads to excellent mileage performance of the car. Some attempts have already been made to synthesize inorganic/organic hybrid, polydimethylsiloxane (PDMS) was used as the precursor for such hybrid materials in most studies.

Accordingly in this report, to control characteristic of hybrids effectively inorganic/organic hybrid was prepared using low molecular precursor such as methyltriethoxysilane (MTES) via a sol-gel process. Sol-gel techniques have been widely used for the preparation of inorganic/organic hybrid materials [3]. The inorganic framework is mostly obtained from metal alkoxides through hydrolysis and condensation reactions in the sol-gel process. Using this process, characteristics of the hybrids were draw by adding various metal alkoxides in MTES.

This report emphasizes the relationship between oil wettability and the metal component in inorganic/organic hybrid processed at low temperatures.

2. Experimental

2.1. Fabrication of inorganic/organic hybrids

The following chemical reagents were used in this experiments. Organosiloxane was MTES (CH₃Si(OCH₃)₃; Shin-Etsu Chemical Co., Ltd.,Tokyo). The metal alkoxides (M(OR)₃) were Ti(O-iso-C₅H₄)₄, Nb(O-C₅H₅)₅ (Kojundo Chemical Laboratory Co., Ltd.), and Al(O-sec-C₅H₄)₃ (Kanto Chemical Co., Inc.).

Because reactivity of transition metal alkoxides is high the metal alkoxides themselves easily cause hydrolysis even with atmospheric water. Therefore acetylacetone (AcAc) was used as a chemical modifier of these metal alkoxides in order to stabilize [2]. Mixing molar ratio of metal alkoxides (Ti, Nb) : AcAc was 1 : 2. As for alkoxy of Al, the molar ratio of Al alkoxide : AcAc : 2-butanol were 1 : 0.5 : 20. 2-butanol was used for Al alkoxide to be stabilized effectively.

Then ethanol, HCl, MTES, H₂O were added to the stabilized metal alkoxides mentioned above. The molar ratios of MTES : metal alkoxides : ethanol : HCl : H₂O were 1 : 0.05 : 3 : 0.005 : 2. HCl was used as an acid catalyst. The mixed solution was stirred for 1h at room temperature, followed by aging conducted under 60 °C for 3 hours. After that the solution was divided into 2 for coating and for bulk. In the case of the former, coating on SUS substrates was conducted drying at 40 °C or 80 °C for 48 hours. The latter, hybrid bulk was also dried at the same condition.

2.2. Structural analysis

To inspect coordination state of a carbon atom and an oxygen atom around the silicon atom, ²⁹Si-solid CP/MAS nuclear magnetic resonance (NMR) (ECA-700MHz) analysis was carried out for the crashed bulk materials. In the measurement, the chemical shifts for obtained spectra were given with reference to tetramethylysilane (TMS).

2.3. Lipophilic character measurement

A drop of 0.2 µl of oil was placed on the prepared coating film. Both of synthetic oil of POE and SAE10W-30 were used. Then area just after placing and area 1 minute later were measured with a digital CCD microscope. Lipophilic character of coating film was evaluated as follows

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\text{(Area ratio)} = \frac{\text{(Area 1 minute later)}}{\text{(Area just after placing)}}
\]
3. Results and discussion

Fig. 2 shows the photographs of inorganic/organic hybrid bulk bodies; (a) MTES, (b) MTES+Ti, (c) MTES+Al dried at 40 °C. Hybrid bulk fabricated in this study are about 10 cm in diameter and about 0.5mm in film thickness. In addition, these hybrids were transparent, crack-free and large size compared to previous reported ones [4]. As observed in Fig.2, a large hybrid added metal alkoxides were formed successfully compared to hybrid fabricated only by MTES. This can conclude that addition of metal alkoxides makes polycondensation effectively.

Fig. 3 shows the $^{29}$Si-CP/MAS NMR spectra of hybrids dried at 40 °C. The large peak detected at around -65 ppm is ascribed to the $T^3$ unit which indicates Silicon is in condition to have one methyl radical and three siloxane bond; CH$_3$SiO$_3$ [5]. In addition the small peak detected at lower magnetic field than large peak is ascribed to $T^2$ unit; CH$_3$Si(OH)O$_2$. Focused on the data of Al and Ti, in the presence of Al, the peak ascribed to $T^2$ unit was detected at lower magnetic field than others. On the contrary in the presence of Ti, the peak ascribed to $T^2$ unit was getting more shift to the peak ascribed to $T^3$ unit compared to the others. This results revealed that adding Al in MTES could suppress the polycondensation reaction and adding Ti in MTES could accelerate polycondensation reaction. Consequently, the catalytic effect of these alkoxides was found to be different between hybrid gel incorporated Ti alkoxide and Al alkoxide in the low temperature processing. Fig. 4 shows the difference of $^{29}$Si-CP/MAS NMR spectra between hybrids dried at 40 °C and hybrid dried at 80 °C. And Fig. 5 shows dynamic wettabilities with oil for hybrids including various metal alkoxides dried at 40 °C and 80 °C. In all hybrid dried at 80 °C, the peak ascribed to $T^2$ unit shifted to the right slightly compared to hybrid dried at 40 °C. This indicated fractional progress of polycondensation and evaporation of ethanol took place by 80 °C treatment. Therefore, area ratio in 80 °C process higher than that in 40 °C process. Besides, it is reasonable to suppose that high wettability of oil in Ti and Nb alkoxides attributes to the broad peak of them ascribed to $T^2$ unit in Fig. 4.

4. Conclusions

In this experiment, the inorganic/organic hybrid bulk that was transparent and crack-free could be obtained by using MTES as a precursor in sol-gel processing. The catalytic activity of metal alkoxides increases in the order of Al < Nb < Ti by $^{29}$Si nuclear magnetic resonance spectroscopy. That is to say, this results suggests that the polycondensation can be controlled by the metal alkoxides.

With regard to lipophilic character, as is the same order in $^{29}$Si NMR analysis the oil wettability on SUS board coated with hybrid increased in the order of Al < Nb < Ti.
References

Fig. 4 $^{29}$Si-CP/MAS NMR spectra of hybrids dried at 40 $^\circ$C(left) and 80 $^\circ$C(right).

Fig. 5 Dynamic wettabilities with oil for hybrids including various metal alkoxides dried at 40 $^\circ$C and 80 $^\circ$C.