The Effects of Organotin Catalysts on Hydrolytic Condensation of Polymethylsiloxane Oligomer and Moisture Cure of the Coatings

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Abstract

The polymethylsiloxane oligomer (P-MTS) was synthesized by the hydrolytic condensation of trimethoxy (methyl) silane. The effect of mono- and bis-type organotin carboxylate catalysts on hydrolytic condensation of P-MTS was investigated in relation to pot life time and tack free time of P-MTS coating in the presence of catalysts. The viscosity variations and tack free time of P-MTS on aging were measured with IR and NMR spectral analysis. It was observed that the condensation reaction proceeds faster with bis-type catalysts than mono-types depending on the concentration of active species generated from the hydrolysis of the organotin catalysts. On the other hand, the tack free time was found to be correlated with the functional group of organotin carboxylates. Due to the steric hindrance of the functional group, dibutyltindilaurate is less easily hydrolyzed to the inactive dibutyltinoxide compared to dibutyltindiacetate. This results in the lauroyloxy group taking part more effectively in catalytic action than the acetoxy group.

From these results, it was revealed that the structure of organotin catalysts plays an important role on the condensation of the P-MTS and the cure of its coating.

1. Introduction

Recently organosilicone polymers have been applied to several kinds of coatings, because their advantages are distinguished from organic analogs in their superior film performances of thermal stability, resistance to solvent, water, and environmentalst (moisture, temperature, ultraviolet radiation, etc.). Silicone coatings are applied as moisture cure paints with catalysts (acids, amines, and organometallic compounds). In the curing process, catalysts play an important role to control the degree of crosslinkage of resins. Especially organotin compounds are often used as a catalyst for RTV1) (Room Temperature Vulcanization) of silicone rubbers, but the mechanism has not been made clear in detail.

We have experienced that appreciable differences are observed in pot life and tack free time depending on organotin catalysts in moisture cure silicone oligomer system. In this work, therefore, hydrolytic condensation of P-MTS was investigated with the four catalysts of dibutyltindiacetate (DBDA), dibutyltindilaurate (DBDL), bis(acetoxydibutyltin)oxide (BADO) and bis (lauroyloxydibutyltin)oxide (BLDO). The catalysts BADO and BLDO correspond to the dimer of DBDA and DBDL, respectively. These catalysts are divided into the mono-type (DBDA and DBDL) and bis-type (BADO and BLDO) and also into DBDA and BADO with acetoxy group and DBDL and BLDO with lauroyloxy group.

The catalytic effect of mono-type organotins with the functional groups has been investigated2). However, no study has been done from the stand point of the catalytic effect comparing mono-type with the bis-type. Moreover, the moisture cure of oligosiloxane P-MTS have not been investigated in detail. In this work, organotin-catalyzed condensation process of P-MTS in the state from liquid to solid and/or the mechanism will be discussed.

2. Experiments

2.1 Synthesis for P-MTS

The oligosiloxane P-MTS was synthesized by the hydrolytic polycondensation of trimethoxy(methyl)
silane (MeSi(OMe)₃) under the acid condition. Into a 500ml reactor equipped with a reflux condenser and a stirrer, 272.0g (2 mol) of MeSi(OMe)₃ was added and cooled under 5°C with stirring. Then, a mixed solution containing 27.5g of deionized-water and 10.0g of 0.1 N HCl was dropwise added over a period of an hour at 5°C. The temperature was raised to 65°C and maintained at that temperature for 3 hours. After then 135g of methanol was removed under reduced pressure.

The oligomer P-MTS showed 33mPa-s in viscosity at 20°C and Mn=910, Mw=1500 in molecular weight which was determined by using gel permeation chromatography with monodisperse polystyrene as a standard. The ¹H-NMR spectra of oligomer showed that the molar ratio of structure unit was CH₃-Si/CH₃ O-Si=1/1.

2.2 Organotin compounds

The four different organotin compounds such as dibutyltindiacetate (DBDA), dibutyltindilaurate (DBDL), bis(acetoxydibutyltin)oxide (BADO) and bis (lauroxyl dibutyltin)oxide (BLDO) were used as the catalyst. The structure of catalysts was shown in Figure 1. The commercially available catalysts were used without further purification.

2.3 Trace of condensation process of P-MTS

According to the formulations in Table 1, P-MTS and organotin catalyst were mixed to give a homogeneous solution. The condensation of P-MTS was followed by measuring the viscosity, IR (Simazu : FTIR-8300), and NMR(Varian : UNITY-400) spectra on aging the solution stirring at the rate about 100rpm in 200ml (diameter : 6cm) beaker without any covers at 25°C under R. Hs. (Relative Humidity) 50% and 80%, respectively.

The coating film prepared with the above mentioned solution on the tin plate sheet using 4 mil applicator was cured at 25°C under R. Hs. 50% and 80%, and tack free time was evaluated by JIS K 5600-1-1 method, while the condensation on the cure process of P-MTS in the state from liquid to solid was also followed by IR and ²⁹Si Solid-State NMR spectral analysis.

3. Results and discussions

3.1 Organotin-catalyzed hydrolytic condensation of P-MTS and the mechanism

The viscosity of P-MTS with or without (Blank) the catalysts was measured under the above mentioned conditions (2.3). In the experiments, the catalyst was added at the same molar equivalent weight of tin atom.

Figure 2 shows the viscosity of P-MTS on aging under R. H. 50%. A slight increase is observed in the Blank, while it remarkably increases depending on the catalyst, which indicates the relative order of viscosity increase is as follows:

BADO>BLDO>DBDA>DBDL>Blank
(without catalyst)

The viscosity with the bis-type catalysts (BADO and BLDO) increases gradually up to 150 mPa-s on aging for four hours followed by a rapid increase. With the mono-type catalysts (DBDA and DBDL), on the other hand, it takes around six or seven hours to reach 150 mPa-s and then a further gradual increase is observed. With the bis-type, there appears a little difference in viscosity increase between BADO and BLDO, while the viscosity with DBDA increases faster than that with DBDL. From the results, it is clearly revealed that the relationship between the structure of catalyst and the viscosity increase and/or the relative ease of condensation is as follows:
(RCOOSn(C₆H₅)₂)₂O > (RCOO)₂Sn(C₆H₅)₂
R : CH₃ > C₁H₂₃

Under R. H. 80%, the same tendency was observed for the viscosity variation with the catalysts except that viscosity increased more rapidly. The condensation reaction was also followed by IR spectral analysis.

Figure 3 showed the IR spectra of P-MTS with or without DBDL on aging under R. H. 80%. In the case of the Blank, the absorption peak intensities at 3500 cm⁻¹ and 900 cm⁻¹ due to Si-OH bond increase with time, while those of 2850 cm⁻¹ and 850 cm⁻¹ due to Si-OCH₃ bond decrease. With DBDL, on the other hand, the absorption peaks due to Si-OH are almost not seen, and the peak ascribed to Si-O-Si stretching vibration (v₁=[O-Si-O]) at 1020 cm⁻¹ is clearly observed. The same tendency was confirmed with the other catalysts. The results on the variation due to Si-OH and Si-O-Si bond suggest that the absence or presence of catalyst greatly affects the hydrolysis of P-MTS and the following condensation under the experimental conditions, with almost no condensation taking place without catalyst. Thus the condensation process of P-MTS was investigated in detail by NMR spectral analysis.

Figure 4 shows the ²⁹Si-NMR spectra of P-MTS with or without DBDL in the liquid state under R. H. 50% just after addition of catalyst and 3 hours’ aging under stirring, respectively. The signals appear in the three regions at −48 ppm as the sharp signal due to $T₁$, −58 ppm as those coalesced with the sharp and broad signal to $T₂$, and around −66 ppm as the broad one to $T₃$. The sharp signal ($T₁$) at the lower field should be assigned to the terminal groups. The sharp and broad one ($T₂$) are expected of the structures resulted from cyclic and branched linear or cyclic types. The broad signals ($T₃$) at the higher field would be assigned to branched linear or condensed cyclic structures. Therefore, P-MTS is obtained as the mixture of cyclic and branched linear oligosiloxanes.

Figure 5 indicates the integrated intensity variations...
of structure units T₁, T² and T³ with time where the ²⁹Si-NMR spectra of P-MTS with BADO and BLDO on aging for five hours were not measured because of gelation. Without the catalysts (Blank), T² increases as T₁ decreases, but T³ stays unchanged, which means that T₁ condenses with each other to form T², but the condensation between T₁ and T² or that between T² does not occur, that is, the unit structure T² is formed by the condensation between terminal groups. Therefore, the viscosity increase in the Blank is resulted from a molecular weight increase by the condensation to form higher molecular weight polysiloxanes. Obviously marked variations of T₁, T², and T³ are observed in the presence of catalyst compared with in the absence of catalyst. Regardless of catalysts, T₁ decreases while T² and T³ increase, and especially T³ increases significantly. The relationship between the T³ and viscosity variations evidently reveals that the absorption peak at 1020 cm⁻¹ due to νSi-O-Si is associated with the unit structure T³.

Based on the experimental results, the reaction mechanism for the organotin carboxylate-catalyzed hydrolytic condensation of P-MTS was discussed. According to Wei³, at first, the catalysts are hydrolyzed to form active and unstable intermediate (3) according to eqs. 1) and 2) in Scheme 1. In Scheme 2.

Scheme 1  The hydrolysis reaction of the organotin catalyst

Scheme 2  Organotin-catalyzed hydrolytic condition of P-MTS
the reaction of thus formed intermediate with P-MTS provides the active group-terminated product (5) in eq. 3 which is in turn hydrolyzed to give the silanol group-terminated product (6). This has been also present as a hydrolysis product. Then the subsequent condensation between (5) and (6) yields polysiloxanes with higher molecular weight in eq. 5).

The viscosity variations in Fig. 2 clearly shows that the relative activity order is as follows, and obviously the bis type is more active than mono-type:

\[ \text{BADO} > \text{BLDO} > \text{DBDA} > \text{DBDL} \]

Mono-type tin carboxylate generates same equivalent mole of active species to be hydrolyzed in eq. 1) as shown in Scheme 1. On the other hand, as eq. 2) in Scheme 1 shows, bis-type generates two equivalent mole of active species with same quantity of water, and consequently the difference in the viscosity increase and/or condensation rate with the catalysts will result from the concentration of active species depending on the type of catalyst. The hydrolyzability is known to be dependent on the steric factor of functional group of catalyst. Actually, it was observed that when the ethanol solutions of DBDA and DBDL were added to water, the former was hydrolyzed to give an acidic solution and white precipitates while the latter showed no change. As the experimental results show, the viscosity increase is faster in the case of the catalyst with acetoxy group than that with lauroyloxy group, which suggests that the hydrolysis is faster in the former than the latter so that the concentration of active species increases faster in the former to accelerate the condensation.

3.2 Curing of P-MTS films

The tack free time of P-MTS films with the catalysts under R. Hs. 50% and 80% is summarized in Table 2.

Table 2  Tack free time (Hour) of P-MTS films with catalysts

<table>
<thead>
<tr>
<th>Humidity</th>
<th>Blank</th>
<th>DBDA</th>
<th>DBDL</th>
<th>BADO</th>
<th>BLDO</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 %</td>
<td>9.0</td>
<td>&gt;9.0</td>
<td>&gt;9.0</td>
<td>&gt;9.0</td>
<td>5.0</td>
</tr>
<tr>
<td>80 %</td>
<td>8.5</td>
<td>5.5</td>
<td>8.0</td>
<td>3.5</td>
<td></td>
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</tbody>
</table>

Without the catalyst, no condensation took place regardless of curing conditions. Under R. H. 50%, no appreciable difference was observed even with the catalyst, but P-MTS films were found to be distinctly cured depending on the catalyst under R. H. 80%. The early sequence of tack free time under R. H. 80% is as follows:

\[ \text{BLDO} > \text{DBDL} > \text{BADO} > \text{DBDA} \]

This shows the different tendency with that of viscosity variation:

\[ \text{BADO} > \text{BLDO} > \text{DBDA} > \text{DBDL} \]

However, the results show that the catalyst with the lauroyloxy group is more active than that with acetoxy group and also bis-type is superior to mono-type. This may be ascribed to the fact that although the diffusion rate of the active species in the condensed siloxane network has to be considered, BADO and DBDA are easily hydrolyzed compared with BLDO and DBDL to form dibutyltin dioxide without catalytic activity according to the reactions in Scheme 3. It is confirmed from the different hydrolyzability of DBDA and DBDL as described in the section 3.1 and the preliminary experimental result that no condensation of P-MTS with dibutyltin dioxide took place. Therefore, DBDA forms the active species faster than does DBDL but it...
easily turns to the species without catalytic activity, that is, the difference in tack free time of P-MTS films with catalysts results from the relative hydrolyzability of catalyst depending on the structure of functional group and mono or bis type.

It was also confirmed by the IR and NMR spectral analysis that the catalytic activity was reflected in the degree of condensation of P-MTS. Figure 6 represents the IR spectra of P-MTS films on aging for 6 and 24 hr under R. H. 50% using KRS. The peak intensity at 1020 cm\(^{-1}\) (T3) obviously increases with time. On the other hand, Figure 7 shows the \(^{29}\)Si solid-state NMR spectra of P-MTS films with BLDO and BADO on curing for one month under R. H. 50%. The structure unites T2 (-54 ppm) and T3 (-63 ppm) appear while T1 disappears, and the relative intensity of T2 against T3 increases in BLDO compared with BADO, which indicates that the degree of condensation and/or crosslinkage of siloxane bond is dependent on the catalysts.

4. Conclusion

The oligosiloxane P-MTS was prepared by the hydrolysis of trimethoxy (methyl) silane. The effect of organotin carboxylate on further hydrolytic condensation of P-MTS and curing of the coating films was investigated by measuring the viscosity and tack free time of P-MTS accompanied by the IR and NMR spectral analysis. The results revealed that the condensation of P-MTS depends on the concentration of active species formed from the catalysts while the curing of films is closely associated with the stability to hydrolysis of the active species which results from the steric hindrance of alkylolxy groups. Subsequently it was clarified that the structure of catalyst is the key factor to control the condensation of P-MTS and curing of the films.

References

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ポリメチルシロキサンオリゴマーの加水分解重合および塗膜の硬化に及ぼす錫触媒の影響

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要　旨

メチルトリメチオキシシラン (MeSi(OMe)₃) の加水分解重合によりシロキサンオリゴマー (P-MTS) を合成した。モノ (Mono) およびビス (Bis) タイプ鍍カルボキシレート存在下における P-MTS の可洗時間および塗膜の半硬化時間を明らかにすると共に、加水分解による生成物の性質に影響を及ぼす錫触媒の影響を検討した。P-MTS溶液の粘度および塗膜の半硬化時間の時間経過におとなく、変化を IR NMR スペクトルで追跡した結果、P-MTS の重組合はモノタイプよりビスタイプで顕著に速く、触媒の加水分解で生じる活性種の濃度によることがわかった。一方、塗膜の半硬化時間は触媒のカルボキシレートのアルキル基がメチルよりもラウリル基で活性がいちじるしく高いことが観察された。これは、活性種がアルキル基の立体因子によっても加水分解性的差により錫オキシドとなり失活するためを推測された。以上の結果より、錫触媒の鍍カルボキシレートの構造が P-MTS の重組合と塗膜の硬化に顕著な影響を及ぼすことが明らかにされた。

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