Effect of Polyvinyl Chloride Coated Skin Composition on Curing of Additive Silicone Model

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Abstract. The silicone model is an important part in the making of plastic molds. This paper studies the curing kinetics of two-component addition silicone in polyvinyl chloride (PVC) coated skin using the rheological method. Meanwhile, this paper analyses the components in the PVC coated skin causing the two-component addition silicone not to cure by using infrared spectroscopy, nuclear magnetic resonance, inductively coupled plasma mass spectrometry, and inductively coupled plasma spectrometer. Result shows that phosphorus (P), sulfur (S), Plumbum (Pb), chromium (Cr), mercury (Hg), and arsenic (As), especially P in the PVC coated skin can cause platinum catalyst poisoning.

1. Introduction
As an integral part of the car interior, the dashboard is usually covered with a layer of textured polyvinyl chloride (PVC) coated skin for decoration and comfort. The PVC coated skin is generally made by processing PVC powder in the plastic mold, which affect the surface texture of the PVC skin\cite{1}. To make the plastic mold, it is necessary to cast silicone on the wrapper model coated with PVC coated skin with texture on the surface and then obtain the textured silicone model after demolding. This step is crucial to the texture of the dashboard\cite{2}. The silicone used here is generally a two-component addition silicone composed of vinyl rubber, hydrogen-containing silicone oil, and platinum catalyst. Literature shows that the platinum catalyst in the addition of silicone will fail when it encounters a certain type of PVC coated skin, making the silicone unable to be completely cured on the contact surface of the two, thus clear texture cannot be reproduced. This phenomenon is called platinum catalyst poisoning\cite{3}, which results in a significant waste of materials and an increase of production costs. Recent years have seen more on the types of substances that cause platinum catalyst poisoning\cite{4}. However, the component in the PVC coated skin that causes the addition of silicone not to be cured is still unclear.

In order to optimize production and improve economic benefit, this paper takes the rheological method to study the curing kinetics of two-component addition silicone in the PVC coated skin and the curing of silicone on PVC coated skin. Meantime, this paper adopts a variety of means to identify the components in the PVC coated skin that poison the platinum catalyst.
2. Experiment

2.1. Reagents
Epoxy resin type 460 was purchased from Shenzhen Hongwang Co., Ltd. PVC coated skins I and II for automobile dashboard wrapper model were from Changchun FAW Faway Johnson Controls Automotive Metal Components Co., Ltd. Two-component addition silicone DY6840 was purchased from Shenzhen Dayou Silicone Mould Co., Ltd., in which A contains platinum catalyst and vinyl (-CH=CH₂) functional group while B contains silicon-hydrogen bond (-Si-H) and a vinyl (-CH=CH₂) functional group.

2.2. Rheology experiment
In order to study the effect of the components contained in PVC on the curing of silicone, it is necessary to fix the PVC on the rheometer fixture. Since PVC cannot be firmly bonded with metal fixture, it is necessary to process the 460 epoxy resin into a rheometer flat plate clamp with a diameter of 25 mm, and then use a special glue to adhere the PVC coated skin wafer with uniform thickness and a diameter of 25 mm to the epoxy resin fixture, as shown in Figure 1.

Figure 1. (a) Aluminum geometry of rheometer (b) homemade geometry of rheometer with PVC layer at the surface.

Mix A and B of the two-component addition silicone DY6840 at 1:1, stir it for 5 minutes, and then left it under vacuum for 5 minutes to remove bubbles in the sample. Then immediately test it in AR-2000ex rotary rheometer made by TA in the US. The fixture used was 25 mm plate fixtures (as shown in Figure 1), which are 1 mm distant from each other. The frequency of the time scanning experiment was 10 rad/s, the strain was 2% (in the linear strain zone), and the temperature was 25 °C.

2.3. Characteristics of sample compositions
VERTEX 70 Fourier Transform Infrared Spectrometer (FTIR) from Bruker, Germany was adopted in the infrared spectroscopy test; AVANCE III 400 NMR spectrometer (NMR) from Bruker, Switzerland was adopted in the 13C NMR test; Xseries II inductively coupled plasma mass spectrometer (ICP-MS) and iCAP6300 inductively coupled plasma optical emission spectrometer (ICP-OES) from ThermoScientific was adopted in elemental analysis.

3. Result and discussion

3.1. Curing kinetics of addition silicone in the PVC coated skin
Curing kinetics of silicone was analyzed by using a rotary rheometer. The temperatures of silicone in different fixtures at 25 °C were shown in Figure 2. It can be seen that the loss modulus G” of the two groups of silicone is greater than the storage modulus G’ at the initial stage of the reaction, which is in a liquid-like state. As the reaction progresses, G’ and G” increased, indicating that cross-linking point gradually increases. In the later stage, G’ is larger than G", which is in a solid-like state. When the silicone is cured in I fixture, the silicone was fully cured as it reaches the plateau after 15000 s, and. But in II fixture, though the silicone is still solid-like in the late stage, G’ and G” are still slowly increasing without forming a plateau. In this situation, the final storage modulus of the silicone is less
than that in the former situation.

![Storage modulus G' and loss modulus G'' versus reaction time.](image)

**Figure 2.** Storage modulus G' and loss modulus G'' versus reaction time.

### 3.2. Morphology of the addition silicone on PVC coated skin

The morphology of silicone cured on PVC coated skin for 24 h is shown in Figure 3. It can be seen that when silicone is cured on I skin, it was completely cured with a clear surface pattern but no silicone remains. However, the silicone cured on II skin was solid on the surface but remained to be in a viscous flow state without a clear surface pattern. Meantime, there was viscous silicone residual on the PVC fixture. The result indicates that when the addition silicone encounters a certain component of the II skin, platinum catalyst poisoning will occur, resulting in the incomplete curing of silicone[5].

![Morphology of silicon rubber after vulcanization between different geometry with PVC.](image)

**Figure 3.** Morphology of silicon rubber after vulcanization between different geometry with PVC.

### 3.3. Composition analysis of PVC coated skin

In order to determine whether PVC coated skin contains unsaturated functional groups such as alkynyl and vinyl that can poison the platinum catalyst, this paper adopts FTIR to analyze the two PVCs (see Figure 4). Spectrum indicates that the two dashboard skins show the characteristic peaks of PVC: 698 and 607 cm$^{-1}$ are the extensional vibration peak of C-Cl bond in PVC; 960 cm$^{-1}$ is the bending vibration peak of C-H bond; 1067 cm$^{-1}$ is the stretching vibration peak of the C-C bond; 1425 cm$^{-1}$ is the stretching vibration peak of the CH$_2$-Cl bond; 1462 cm$^{-1}$ is the bending vibration peak of the methylene CH$_2$; 2925 and 2855 cm$^{-1}$ are the stretching vibration peak of the methylene CH$_2$. However, the sample did not show an absorption peak at 3072, 3005, and 1640 cm$^{-1}$, indicating that it did not contain a vinyl functional group[6]. Meantime, the sample did not show an absorption peak at 2120 cm$^{-1}$, indicating that it did not contain an alkynyl functional group[6].
Figure 4. FTIR spectra of 2 types of PVCs.

Figure 5 is a $^{13}$C NMR spectrum of two PVCs, showing the characteristic peak of PVC: there is a distinct peak at 56.8 ppm, which is the characteristic chemical shift of C on CH-Cl; there is a distinct peak at 31.9 ppm, 23.0 ppm, 14.3 ppm, which is the characteristic chemical shift of C on R-CH$_2$CH$_2$CH$_3$; there is no characteristic chemical shift peaks of C in the alkylnyl functional group at about 100 ppm or in the vinyl functional group at about 110 ppm[7].

Figure 5. $^{13}$C NMR of 2 types of PVCs.

In summary, $^{13}$C NMR and IR produce the same results. The absorption peaks of the two PVC coated skins are almost identical with the same functional group. They do not contain unsaturated functional groups such as vinyl and alkylnyl groups, making platinum catalyst poisoning impossible.

Table 1 shows the ICP-MS and ICP-OES results of two PVC coated skins. It can be seen that the two skins do not contain N, Bi, Sn, and Sb elements, therefore, these element and their compounds do not poison the platinum catalyst by these elements. In addition, both skins contain elements which can poison the platinum catalyst, such as S, P, Pb, Cr, Hg, and As. The mole percentages of the above respective elements for platinum catalyst poisoning can be calculated based on Table 1, as shown in Table 2. From the two tables, it can be seen that the proportion of P element in I accounts for 74.83%, higher than that in II. Meanwhile, the difference between the proportion of Pb, Cr, Hg, As and other elements is small. In summary, P, S, Pb, Cr, Hg, and As in PVC coated skin will poison the platinum catalyst, during which P plays a major role.
Table 1. The mass fraction of catalyst poisoning elements in the PVC coated skin.

|     | N  | S   | P   | Pb  | Cr  | Hg  | As  | Bi  | Sn  | Sb  |
|-----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|     |    |     |     |     |     |     |     |     |     |     |
| I   | 0.00 | 25.33 | 28.19 | 4.12 | 7.44 | 0.21 | 0.18 | 0.00 | 0.00 | 0.00 |
| II  | 0.00 | 29.93 | 120.60 | 3.66 | 6.52 | 0.32 | 0.13 | 0.00 | 0.00 | 0.00 |

Table 2. The elements in the PVC coated skin that cause platinum catalyst poisoning account for all mole percent of possible poisoning elements.

|     | P   | Pb  | Cr  | Hg  | As  | S   |
|-----|-----|-----|-----|-----|-----|-----|
|     |     |     |     |     |     |     |
| I   | 43.06 | 6.29 | 11.36 | 0.32 | 0.27 | 38.70 |
| II  | 74.83 | 2.27 | 4.05  | 0.09 | 0.20 | 18.57 |

4. Conclusion

In the manufacturing of the plastic mold, when the PVC coated skin contains 74.83% P, S, Pb, Cr, Hg, and As, the curing rate the two-component addition molding is slower with smaller G′ and less crosslinking points. The platinum catalyst in the silicone is poisoned and cannot be completely cured.

This article provides a guide for factory production. First, it tests the elements of the PVC coated skin to see whether the three types of elements poisoning the catalyst are contained and conduct quantitative analysis of these elements. When it is proved that PVC will not cause catalyst poisoning, it is time to make the wrapper model and cast silicone to save costs and optimize the production process.

References

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