



Synergistic effect and mechanism of platinum catalyst and nitrogen-containing silane on the thermal stability of silicone rubber



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ARTICLE INFO

Article history:

Received 13 December 2015
Received in revised form 9 February 2016
Accepted 10 March 2016
Available online 15 March 2016

Keywords:

Silicone rubber
Platinum catalyst
Nitrogen-containing silane
TG-FTIR
Thermal stability
Degradation mechanism

ABSTRACT

Platinum (Pt) catalyst and nitrogen-containing silane (NS) were introduced to improve the thermal stability of silicone rubber. The effects of Pt and NS on thermal stability and degradation mechanism of silicone rubber were investigated by thermogravimetry (TG), thermogravimetry-Fourier transform infrared spectrometry (TG-FTIR), scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDXS) and Fourier transform infrared spectrometry (FTIR). A significant synergism was found between Pt and NS for improving the thermal stability of silicone rubber. When 6.67 ppm of Pt and 1.4 phr of NS were introduced, the temperature of 10% and 20% weight loss under nitrogen atmosphere were respectively increased by 36 °C and 119 °C. Meanwhile, the residue weight at 900 °C was doubled to 68% in the presence of Pt/NS. The synergistic mechanism might be that the nitrogen atom coordinated with Pt and improved the catalytic efficiency of Pt. Additionally, NS preserved the catalytic activity of Pt under air atmosphere. Hence, Pt/NS efficiently catalyzed thermal crosslinking and suppressed degradation of silicone chains. Moreover, it revealed that the presence of Pt/NS protected silicone chains from oxidation. Thus, the unzipping depolymerization by silanol groups was reduced significantly.

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1. Introduction

Currently, silicone rubbers are rapidly developing to substitute traditional materials in many fields, due to their unique characteristics, such as hydrophobicity, transparency, chemical resistance, insulation properties and wide temperature adaptability [1–4]. However, as the requirement for high performance of materials enhances, how to effectively improve the thermal properties of silicone rubber has become a significant topic [5]. Especially in field of aerospace, electrical equipment and automation, materials would suffer temperature as high as 900 °C and even above 1000 °C. On such condition, high degradation temperature and residue weight of materials are necessary to ensure safety [6–8]. Traditional method to improve the thermal stability involves adding inorganic fillers. Indeed, heat conductive fillers, like BN, Al₂O₃ and MgO, facilitate heat transfer and relieve thermal degradation of silicone rubber [9–11]. Additionally, some of the calcium and aluminum-based fillers decompose at high temperature and react with silicone matrix to form barrier layer which can suppress thermal degradation of silicone rubber [12,13]. Nevertheless, high loading contents

of inorganic fillers are needed to meet the requirement for thermal stability of silicone rubber, which may severely deteriorate its mechanical properties. Another way to enhance thermal stability of silicone rubber is adding metal oxides, such as Fe₂O₃, CeO₂, SnO₂ and CuO, which suppress radical decomposition [14]. However, metal oxides have poor compatibility with silicone rubber and only work for the thermal oxidative stability. Besides, the introducing of silicone compounds with specific structures [15–18], like polyhedral oligomeric silsesquioxanes and silicon resins, can also improve the thermal stability of silicone rubber. Such silicone compounds reduce the regularity of silicone chains and thus retard the random scission reaction during hydrolysis. However, those compounds are relatively complicated to prepare.

The platinum compounds are widely used in silicone rubber. The Karstedt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex) is one of the optimal catalysts for hydrosilylation, due to its high solubility in polysiloxane and high catalytic efficiency [19]. It was reported that platinum compounds were efficient in fire retardancy and improvement of thermal stability [20,21]. Delebecq revealed that containing over 50 ppm of Pt, silicone rubber showed increased residue at high temperature; higher content of Pt would further increase the residue and degradation temperature [22]. However, high content of Pt may increase the cost. Additionally, it was reported that the role of platinum

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depended on the filler type. Pt-containing silicone rubber showed high residue up to 75%, when filled with 30% vinyl-modified silica. The synergistic mechanism was that platinum catalyzed crosslinking of silicone chains via vinyl on the silica to form ceramic layer [22]. Despite those efforts, mentioned investigations about thermal stability of Pt-containing silicone were made under inert atmosphere.

Some patents used small contents of Pt and azo compounds to prepare fire retarded silicone, in the absence of modified silica [20]. Our previous work [23] found that urea-containing silane could significantly elevate the residue of silicone rubber under air atmosphere and increase the thermal degradation temperature under nitrogen atmosphere. However, Pt, adding as the cure catalyst in this system, had not been taken into account and the synergistic effect of platinum and nitrogen compound on thermal stability had not been investigated.

In this work, a small content of platinum catalyst (Karstedt catalyst) and nitrogen-containing silane (NS, γ -aminopropyltriethoxy) were employed to improve the thermal stability of silicone rubber. The thermal stability of silicone rubber under nitrogen and air atmosphere was investigated by thermogravimetry (TG). The combined effect of Pt and NS on the degradation mechanism was revealed by thermogravimetry-Fourier transform infrared spectrometry (TG-FTIR), Fourier transform infrared spectrometry (FTIR) and scanning electron microscope-energy dispersive X-ray spectrometry (SEM-EDXS).

2. Experimental

2.1. Materials

Polydimethyl/methylvinylsiloxane (PDMS, 600,000 g/mol and 0.18 mol% vinyl) gums were purchased from Nanjing Dongjue Silicone Group Co. Ltd., China. Fumed silica (SiO_2 , with a specific surface area of $200 \text{ m}^2/\text{g}$) was produced by Tokuyama Chemical Co. Ltd., China. The hydroxyl silicone oil (6 wt% hydroxyl groups) and methyl hydrogen silicone oil (1.2 wt% hydrogen groups) were provided by Shenzhen Senri Silicone Group Co. Ltd., China. 2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane (DBPMH) was the product of Shin-Etsu Chemical Corporation, China. The Karstedt catalyst, namely platinum(0)-1,1,3,3-tetramethyldisiloxane (3000 ppm of Pt) was provided by Guangzhou Tinci Silicon Technology Co. Ltd., China. γ -aminopropyltriethoxysilane was supplied by Dongguan Bettely New Materials Technology Co. Ltd., China.

2.2. Preparation of silicone vulcanizates

According to ISO 2393, hydroxyl silicone oil, SiO_2 and methyl hydrogen silicone oil were blended into polydimethyl/methylvinylsiloxanes in a two-roll mill (XK-168, Dongguan Lina Machinery Industrial Co., Ltd., China) to obtain a transparent compound. Then, the compound went through heat treatment in a ventilated oven at 150°C for 2 h. After that, γ -aminopropyltriethoxysilane, Karstedt catalyst and DBPMH, were introduced into the compound via the two-roll mill. The obtained mixture was vulcanized under compression (8 MPa, 165°C) for an optimal cure time, which was tested by the UR-2030 rheometer. The secondary vulcanization was conducted at 200°C for 4 h [24]. Formulations of the silicone vulcanizates are shown in Table 1.

2.3. Testing and characterization

2.3.1. Thermogravimetry (TG)

Thermogravimetric analysis was conducted on TG209 (Netzsch Instruments Co., Germany) from 30°C to 900°C . The heating rate was $20^\circ\text{C}/\text{min}$. 5–10 mg of samples was measured in an alumina

crucible under a nitrogen flow or a synthetic air flow of $40 \text{ mL}/\text{min}$. The synthetic air flow consisted of 21% oxygen gas and 79% nitrogen gas.

2.3.2. Thermogravimetry-Fourier Transform Infrared Spectrometry (TG-FTIR)

The thermogravimetry-Fourier transform infrared spectrometry (TG-FTIR) was applied to investigate the volatile products of silicone rubber during thermal degradation, which was composed of a thermogravimeter (TG209, Netzsch Instruments Co., Germany), a Fourier transform infrared spectrometer (Tensor 27, Bruker Optics, Germany) and a transfer tuber with inner diameter of 1 mm connecting them. About 15 mg samples were heated from 30°C to 900°C at a heating rate of $20^\circ\text{C}/\text{min}$, under nitrogen or synthetic air atmosphere. The synthetic air atmosphere was composed of 21% oxygen gas and 79% nitrogen gas. During the process, the volatile products were continuously transferred to Tensor 27 for IR testing through the connected tube with a temperature of 230°C .

2.3.3. Scanning electron microscopy-energy dispersive X-ray spectrometer (SEM-EDXS)

The morphology of silicone rubber residues heated from room temperature to certain temperature in a furnace under nitrogen atmosphere was characterized by scanning electron microscopy (SEM, EVO18, Carl Zeiss Jena, Co., Germany). The surface of residue was coated with a gold layer (several nanometers in thickness) for observation. The elemental analysis of residues was conducted by energy-dispersive X-ray spectrometer (EDXS, Oxford Inca250, Oxford Instruments Co., Britain), an integrated tool in SEM.

2.3.4. Fourier Transform Infrared Spectrometry (FTIR)

The spectra of silicone rubber residues heated from room temperature to certain temperature in a furnace under air atmosphere were measured by Fourier transform infrared spectroscopy (FTIR, Tensor 27, Bruker Optics, Germany), after mixing the samples with spectroscopy grade potassium bromide powder. The recorded ranges were from 4000 cm^{-1} to 400 cm^{-1} . Only the spectra of silicone rubbers were obtained by attenuated total reflection method in the range from 4000 cm^{-1} to 600 cm^{-1} .

3. Results and discussion

3.1. Thermal stability

The thermal stability of silicone rubbers under nitrogen atmosphere was investigated by TG. The TG curves and their derivative (DTG) curves are shown in Fig. 1. The characteristic parameters are displayed in Table 2. As demonstrated, the characteristic temperatures of 10% weight loss (T_{10}) were delayed for only 5°C and 16°C , after adding Pt or NS, respectively. However, the combined addition of Pt and NS (Pt/NS) improved T_{10} and temperature of 20% weight loss (T_{20}) for 36°C and 119°C , respectively. Additionally, the residue of PDMS/Pt/NS at 900°C was 68%, which was much higher than 30% for PDMS. Fig. 1b shows that the addition of Pt/NS greatly reduces the degradation rate. The maximum degradation rate during the first stage ($R_{\text{max}1}$) was decreased from 6.98 wt\%/min to 2.13 wt\%/min , when Pt/NS was introduced to PDMS. Besides, the $R_{\text{max}1}$ of PDMS/Pt was 3.90 wt\%/min , which was also lower than $R_{\text{max}1}$ of PDMS. It might be that Pt catalyzed thermal crosslinking of silicone chains, so tightly crosslinked network was formed to resist degradation of silicone chains. [21] Besides, the formation of tight network reduced mobile chains which tended to degrade in first stage [22], thus $R_{\text{max}1}$ was decreased significantly. Moreover, nitrogen atoms were easy to coordinate with Pt through lone pair electrons. Those Pt-NS coordination complexes were stable at

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