

# The effect of structure on thermal stability and anti-oxidation mechanism of silicone modified phenolic resin



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## ARTICLE INFO

### Article history:

Received 4 November 2015

Received in revised form

11 December 2015

Accepted 16 December 2015

Available online 19 December 2015

### Keywords:

Silane

Phenolic

Structure

Thermal stability

Anti-oxidation mechanism

## ABSTRACT

In order to improve the thermal properties of the phenolic resin, silane with different degree of polymerization was introduced into phenolic resin by controllable reactions. Silicone phenolic resin was first synthesized via esterification reaction between methyltrimethoxysilane and novolac phenolic resin; then the degree of self-polymerization of silane was controlled by the hydrolyzation reaction. The designed structure of the hybrids was confirmed by Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (<sup>1</sup>H-NMR and <sup>29</sup>Si-NMR), and curing of the hybrids was performed to obtain samples for microstructure observation and anti-oxidation evaluation. In situ self-polymerization of the silane during both the hydrolyzation and the curing processes led to phase separation in the cured hybrids, and the size of the phase structure increased with the increase of self-polymerization degree of the silane. Thermogravimetric analysis and high-temperature oxidation test were performed, and silane introduction was found to be beneficial to the enhancement of both thermal stability and oxidation resistance. Anti-oxidation mechanisms for the phenolic resin modified with silanes at different polymerization degree were compared and discussed.

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## 1. Introduction

Phenolic is a class of thermosetting resin with excellent mechanical and thermal performances, and was widely used as matrix for thermal insulation, flame retardant and ablative materials [1–3]. However, its oxidation resistance at high temperatures needs to be further improved for the application in ablative and refractory materials [4,5]. Inorganic elements, such as boron [6–9], titanium [2,10] and silicon [1] were found to exhibit excellent oxidation resistance, and have been successfully introduced into to phenolic resin (PR), enhancing its oxidation performance.

The merit of organic silicone is their attractive integrated properties including thermal stability [11,12], flame retardancy [13], toughness [14] and moisture resistance [15]. It is of great interest to introduce silicone into organic polymers [16–20] to endow the hybrids with excellent properties from both components. Many studies proved that silicone is an effective component in improving the anti-oxidation properties of polymers [12,17,20,21]. K.

Haraguchi and co-workers [21,22] prepared phenolic/silica hybrid by in-situ polymerization of silicon alkoxide, and both mechanical and thermal properties were enhanced. Silicone and phenolic resin were incompatible, and phase separation would always occur in the hybrids [12,23,24]. The phase structure (including dispersion state [25], particle size [14,26] and interface of the phases [21]) would affect the properties of the hybrids.

Microstructure was responsible for the properties, and its relationship with mechanical properties was intensively studied. Unfortunately, less effort was made on the effect of microstructure on the thermal properties. Yong Nie et al. [16] claimed that the epoxy dispersed with nanoscale polyhedral oligomeric silsesquioxane (POSS) cages has better anti-oxidation properties than that possessing microscale separated phase structures. Researchers have revealed that the anti-oxidation mechanism is complicated and greatly depended on the microstructure (including interfaces [27,28], holes and cracks [29,30], etc) and chemical structure [31,32] of the materials. As far as we knew, such understanding for silicone modified phenolic system was rarely reported, which would benefit the structure design of anti-oxidative silicone modified phenolic resin.

To obtain different phase structure, the control of polymerization degree of the silane in phenolic resin may be an effective

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method [33,34]. Here in this report, we controlled the ratio between grafted and self-polymerized silane within silicone phenolic resin by a two-step synthesis process. Silicone phenolic resin was first synthesized via esterification reaction between methyltrimethoxysilane and novolac phenolic resin, then the degree of self-polymerization of silane was controlled by the hydrolyzation reaction. The in situ self-polymerization of silane in hybrids led to the changing of the structure and morphology. The thermal stability and oxidation resistance of silicone phenolic resin was studied by thermogravimetric analysis and high-temperature oxidation test. The anti-oxidation mechanism for the hybrids with different structures was proposed and discussed.

## 2. Experimental

### 2.1. Materials

Novolac phenolic resin (PF-8013) was supplied by Shandong Jinan Shengquan Co. Ltd, China. Methyltrimethoxysilane was purchased from Hubei New Blue Co. Ltd, China. Acetic acid was purchased from Beijing Chemical Works, and hexamethylene tetramine (HMTA), the curing agent for the novolac resin and hybrids, was obtained from Sinopharm Chemical Reagent Co. Ltd.

### 2.2. Preparation of the hybrid resin

#### 2.2.1. Synthesis of the silicone modified novolac phenolic resin (SN)

SN was synthesized in a 250 mL three-neck round-bottom flask reactor equipped with a thermometer, a stirrer, and a reflux condenser. Novolac phenolic resin (NR) (103.3 g), methyltrimethoxysilane (136.0 g), and acetic acid (1.03 g) were stirred and gradually heated to 100 °C, and then kept heating for 20 h. At the end of the reaction, the unreacted methyltrimethoxysilane and byproducts were distilled under reduced pressure at 130 °C for 40 min, and then SN was obtained. The synthesis route for SN is shown in Scheme 1.

#### 2.2.2. Hydrolyzation and condensation reaction of SN

Different amount of water was added to the SN ethanol solutions, and refluxed at 80 °C for 10 h. At the end of the reaction, the resin was distilled under reduced pressure at 100 °C to remove the byproducts and solvent. The reaction route is shown in Scheme 2. The water amount was 2 wt%, 6 wt%, 10 wt% of SN and the obtained hybrid resin was designated as SN-2% $H_2O$ , SN-6% $H_2O$  SN-10% $H_2O$ , respectively.

#### 2.2.3. Preparation of cured specimens

The curing agent, HMTA, was then added into the hybrid ethanol solutions with a loading level of 10 per hundred ratio of the hybrids by weight. The solvent was removed at room temperature under vacuum to get hybrid resins containing curing agent. The samples were cured following the procedure 80 °C (4 h) +120 °C (2 h) +180 °C (4 h).

### 2.3. Measurements

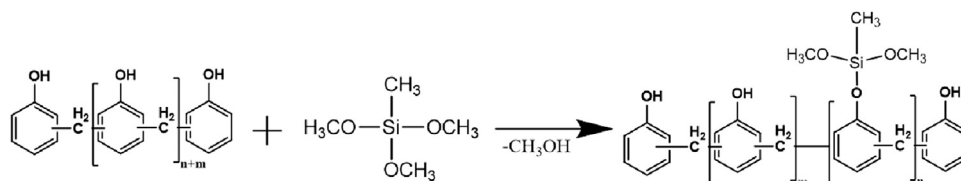
Fourier Transform Infrared Spectroscopy (FTIR) measurements were performed on a Tensor-27 spectrometer at room temperature. Samples were grinded, mixed with KBr and pressed into small flakes for testing.  $^1H$ -NMR and  $^{29}Si$ -NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrophotometer. Thermogravimetric analysis (TGA) was carried out from ambient temperature to 900 °C on a Netzsch STA409PC at a heating rate of 10 °C  $min^{-1}$  in nitrogen and air atmosphere, respectively. The samples were quenched and cracked in liquid nitrogen, and fracture surface of the hybrids was observed on a Hitachi S-4800 scanning electron microscope (SEM) at an accelerating voltage of 10 kV. Energy dispersive X-ray spectroscopy (EDX) was performed on an Oxford INCAx-sight 7593 system attaching to the SEM apparatus. High-temperature oxidation test was performed in a muffle furnace; the furnace was heated to the desired temperature before the powdered samples were put into the furnace and kept for 30 min. X-ray photoelectron spectroscopy (XPS) measurement was performed using an ESCALAB250XI instrument. The Raman spectra were recorded on a Renishaw inVia plus using the 633 nm excitation line of an Argon-ion laser.

## 3. Results and discussion

### 3.1. Structure characterization of the hybrids

FTIR and NMR were used to characterize the structure of hybrid resins, and the spectra were shown in Fig. 1 and Fig. 2. It can be seen that Si–O–ph signals at 949  $cm^{-1}$  was formed after the esterification reaction between novolac and methyltrimethoxysilane. With the amount of water increasing, the signal intensity at 949  $cm^{-1}$  (ascribed to Si–O–ph) became weak, while the peak intensity at 1057  $cm^{-1}$  (corresponding to Si–O–Si vibration [17]) became stronger. The decreased Si–O–ph signal revealed that the Si–O–ph was not stable and would decompose to a certain extent after the hydrolyzation reaction; the breaking down of Si–O–ph would weaken the interactions between silane and phenolic. The increased Si–O–Si signal suggested the self-condensation of silane. According to  $^1H$  NMR shown in Fig. 2, the integral ratio (R) between the proton signals of Si–OCH<sub>3</sub> and that of –CH<sub>2</sub>– decreased with the increase of water content, which further confirmed the hydrolyzation and condensation reaction of Si–OCH<sub>3</sub>. The degree of both breaking down of Si–O–ph and polycondensation of Si–OCH<sub>3</sub> could be controlled by varying the amount of water. The bulk samples of SN and SN-2% $H_2O$  were both transparent; the SN-6% $H_2O$  was translucent, and the SN-10% $H_2O$  was opaque, which might be related to phase separations within the hydrolyzed hybrids [22].

The  $^{29}Si$ -NMR spectrum was displayed in Fig. 3. The signal at –45 ppm was attributed to the Si–O–phenyl, suggesting that most MTMS was grafted onto the phenol groups of phenolic resin in the first reaction. When 2 wt% water was added, the intensity of the signal for Si–O–ph decreased and new signals at –57 and –66 ppm appeared, which corresponded to T<sub>2</sub> and T<sub>3</sub> groups, respectively [35,36], as shown in Scheme 2. It further confirmed that the



Scheme 1. The synthesis reaction for SN.

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