



# An efficient strategy for simultaneously improving tracking resistance and flame retardancy of addition-cure liquid silicone rubber



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## ABSTRACT

How to effectively improve tracking resistance and flame retardancy of silicone rubber is one of the key problems needed to be resolved in the development of high performance silicone rubber insulating materials. In this work, a novel functional silane containing hindered amine and urethane groups, named PPAS, was synthesized by using 1,2,2,6,6-pentamethyl-4-piperidinol, (3-isocyanatopropyl) triethoxysilane and allyl alcohol via the nucleophilic substitution and *trans*-etherification. The effects of PPAS on the tracking resistance, flame retardancy and thermal stability of addition-cure liquid silicone rubber (ALSR) were investigated. It was found that PPAS could effectively enhance the tracking resistance and flame retardancy of ALSR simultaneously. When the content of PPAS was only 3.0 phr, ALSR/PPAS could pass the 1A4.5 kV level in the inclined plane (IP) test and had outstanding electrical erosion resistance, which showed great potential in exterior insulator. In particular, the limiting oxygen index (LOI) of the ALSR/PPAS was 30.0%, and it had a good self-extinguishing capability. Meanwhile, the risk of fire measured by cone calorimeter was also significantly reduced. The mechanism for these phenomena were further studied and revealed: PPAS could effectively quench the peroxy radicals and suppress the oxidation degradation of Si-CH<sub>3</sub> groups, eliminate the Si-OH groups and promote the cross-linked reaction during the thermal degradation of ALSR.

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## 1. Introduction

Silicone rubber (SR) is increasingly being used as exterior insulator in electrical and electronic applications, such as high voltage transmission lines, bushings and cable terminations, due to its advantages of light weight, high insulation and superior resistance to contamination [1–3]. However, when being employed as exterior insulator in polluted environment, the pollutant and moisture covered on the surface of SR will result in leakage current and arc discharge. Due to dry band arcing, SR is prone to tracking and even smoldering combustion, which severely threatens the reliability of the insulation system [4–6]. In order to resolve the problems, many anti-tracking additives such as metal hydroxides

[7,8], metal oxide [9,10], silica [11] and melamine cyanurate (MC) [12] have been incorporated into SR. The most commonly used are metal hydroxides, which can simultaneously improve the tracking resistance and flame retardancy of SR. When being attacked by dry band arcing, crystalline water released from metal hydroxides can quench the arc and cool the polymer surface, thus suppressing the thermal degradation and combustion of ALSR. However, the high loading ( $\geq 50$  wt%) of metal hydroxides severely worsen the mechanical properties and processability of SR [13,14]. In our previous work [15,16], the anti-tracking additive containing urea and urethane groups showed high anti-tracking efficiency in SR. Only a small amount of the organic additive could make ALSR achieve 1A4.5 kV level in the inclined plane (IP) test, due to the arc-quenching capability of the urea group. Besides, the urea group could promote the cross-linking of ALSR to form the compact ceramic barrier, which effectively protected the underlying material. However, the less desirable flame retardancy of the ALSR mixture was still a big challenge.

N-alkoxy hindered amines (NORs) are considered to be a good candidate to address this problem, because of its excellent free-radical quenching capability and high flame-retardant efficiency

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[17]. As reported by literature [18] and [19], NORs can seize the free-radicals such as alkyl radicals and peroxy radicals produced by polymer to endow the matrix with better thermostability and flame retardancy. In our recent work [20], 1,2,2,6,6-pentamethyl-4-piperidinol hindered amine showed a significant improvement on the flame retardancy and thermal stability of ALSR, because it could effectively quench the free-radicals which produced by ALSR and prevent the polymer from degradation. Therefore, the combination of hindered amine and urethane groups in one molecule proposed here would be a promising way to simultaneously promote the tracking resistance and flame retardancy of ALSR.

Herein, a novel functional silane containing hindered amine and urethane groups, named PPAS, was synthesized by using 1,2,2,6,6-pentamethyl-4-piperidinol, (3-isocyanatopropyl) triethoxysilane and allyl alcohol via the nucleophilic substitution and *trans*-etherification. The effects of PPAS on the tracking resistance, flame retardancy and thermal stability of ALSR were investigated. The results showed that PPAS could effectively enhance the tracking resistance and flame retardancy of ALSR simultaneously. The possible mechanism of PPAS on the thermal stability of ALSR was also proposed. This work provides an efficient way to simultaneously improve the tracking resistance and flame retardancy of ALSR, which has good potential applications in high voltage transmission lines, insulator, bushings and cable terminations.

## 2. Experimental

### 2.1. Materials

1,2,2,6,6-pentamethyl-4-piperidinol (PMPO) was supplied by Tiangang Auxiliary Co., Ltd., Beijing, China. Allyl alcohol (AA), ( $\gamma$ -isocyanatopropyl) triethoxysilane (ICPES), tetrabutyl titanate (TBT) and 1-ethynylcyclohexanol were supplied by Shanghai Macklin Biochemical Technology Co., Ltd., China. Vinyl-terminated polydimethylsiloxanes (VPDMS, 20000 mPa s, Vi: 0.12 wt%), polyhydromethylsiloxane (PHMS, 160 mPa s, Si-H: 0.50 wt%) and platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Pt (dvs), 3000 ppm) were purchased from Guangzhou Tianci Silicon Technology Co., Ltd., China. Fumed silica (M – 5) was purchased from Cobot Co., Ltd., USA. Toluene and acetone were purchased from BoDi chemical, Tianjin, China.

### 2.2. Synthesis of PPAS

Exactly 8.56 g (0.05 mol) PMPO, 12.37 g (0.05 mol) ICPES and 50 mL acetone were added in a 150 mL round bottom flask. The mixture was stirred and reacted at 40 °C for 2 h under nitrogen atmosphere. After that the solvent was removed by rotary evaporation under reduced pressure and then PPES was obtained. 8.71 g (0.15 mol) AA, 0.15 g TBT (0.5% of the total mass of reactants) and 100 mL toluene were added in a 250 mL round bottom flask, then the mixture was stirred at room temperature. 20.93 g (0.05 mol) PPES was dropped slowly into the flask, and the reaction lasted for 2 h at 80 °C after PPES was finished. Afterwards, the reaction was maintained for another 2 h under the reduced pressure. Finally, the toluene was removed to obtain PPAS. The synthetic route of PPAS was shown in Fig. 1. By using iodometric titration method [21], it could be obtained that the content of vinyl groups was 12.59 wt%.

### 2.3. Preparation of the ALSR samples

VPDMS, SiO<sub>2</sub>, PHMS, PPAS, Pt (dvs) and 1-ethynylcyclohexanol were mixed uniformly by a kneader reactor. After that, the mixture was vulcanized at 120 °C for 10 min under 8 MPa to obtain the ALSR samples. The formula of ALSR is listed in Table 1.

## 2.4. Characterization

### 2.4.1. Fourier Transform Infrared Spectrometry (FTIR)

FTIR spectra of the samples were measured with a resolution of 4 cm<sup>-1</sup> on a Tensor 27 spectrometer (Bruker Optics, Germany) using KBr disks or pellets at room temperature.

### 2.4.2. <sup>1</sup>H magnetic resonance spectrometry (<sup>1</sup>H NMR)

The <sup>1</sup>H NMR spectrum of the sample was performed on an AVANCE AV-400 Fourier transform superconducting magnetic resonance spectrometer (Bruker, Germany).

### 2.4.3. Limiting oxygen index (LOI)

The LOI test was measured on an oxygen index meter (HC-2, Jiangning Analysis Instrument Co., China) according to ASTM D2863-2008 with 65 mm × 6.5 mm × 3.0 mm specimens.

### 2.4.4. Vertical burning (UL-94) test

UL-94 test was performed on a vertical burn instrument (CFZ-3, Jiangning Analysis Instrument Co., China) according to ASTM D2863-2008 with 100 mm × 100 mm × 3.0 mm specimens.

### 2.4.5. Cone calorimetric test (CCT)

The CCT was performed on a cone calorimeter (Fire Testing Technology Co., UK) according to ISO5660 with 100 mm × 100 mm × 4 mm specimens. The external heat flux was 45 kW/m<sup>2</sup>.

### 2.4.6. Thermogravimetry analysis (TGA)

TGA was performed on a thermogravimeter (TG209, Netzsch Instruments, Germany). Samples with a weight of 5–10 mg were heated from 25 to 800 °C with a heating rate of 20 °C · min<sup>-1</sup> under air.

### 2.4.7. Thermogravimetry-Fourier Transform Infrared Spectrometry (TG-FTIR)

The TG-FTIR was performed using a thermogravimeter instrument (TG209, Netzsch Instruments, Germany) that was interfaced to a Fourier transform infrared spectrometer (Tensor 27, Bruker Optics, Germany). About 15 mg samples was heated from 25 to 800 °C with a heating rate of 20 °C · min<sup>-1</sup> under air.

### 2.4.8. Inclined plane test

According to IEC 60587 standard method [22], the inclined plane (IP) test setup used in this study was shown in Fig. 2 and had been previously described in literature [23]. The ALSR samples with dimensions of 120 × 50 × 6 mm<sup>3</sup> was mounted at an angle of 45°. The applied voltage was 4.5 kV AC and the resistance of the series resistor was 33 kΩ. During the test, the samples were wetted by solutions contained 0.1 wt% ammonium chloride and 0.2 wt% iso-octylphenoxypolyethoxyethanol. Five samples were needed for each test. At the end of the test, the eroded compound of tested specimen was cleared away and the decreased mass of specimen was recorded as the eroded mass.

## 3. Results and discussion

### 3.1. FTIR and <sup>1</sup>H NMR spectra

Fig. 3 shows the FTIR spectra of ICPES, PMPO, PPES, AA and PPAS. ICPES was mainly characterized by the absorptions of 2974–2889 cm<sup>-1</sup> (ν<sub>C-H</sub>), 2272 cm<sup>-1</sup> (ν<sub>N=C=O</sub>) and 1086–955 cm<sup>-1</sup> (ν<sub>Si-O-C</sub>) [24]. For PMPO, the main characteristic peaks were listed as follows: 3500–3400 cm<sup>-1</sup> (ν<sub>OH</sub>), 2966–2939 cm<sup>-1</sup> (ν<sub>C-H</sub>) and 1217–1185 cm<sup>-1</sup> (stretching vibration of pentamethyl piperidinyl) [20]. As illustrated in Fig. 3(c), when ICPES reacted with PMPO, the

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