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Full Length Article

Efficiently enhancing the tracking and erosion resistance of silicone rubber by the synergism of fluorine-containing polyphenylsilsesquioxane and ureido-containing MQ silicone resin

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ABSTRACT

It is of great interest and challenge to simultaneously improve the anti-pollution and tracking resistance of silicone rubber for its application in outdoor high voltage insulation. In this work, we proposed an efficient approach to address this issue by incorporating fluorine-containing polyphenylsilsesquioxane (F-PPSS) and ureido-containing MQ silicone resin (U-MQ) into addition-cure liquid silicone rubber (ALSR). F-PPSS/U-MQ significantly improved the tracking resistance and hydrophobicity of ALSR. By adding 2 phr F-PPSS and 1 phr U-MQ, ALSR passed the 1A 4.5 level inclined plane test with merely 0.2% eroded mass, and had a water contact angle as high as 121°. The synergism of F-PPSS and U-MQ on suppressing the ALSR degradation was further revealed and demonstrated. Our findings exhibited great potentials for fabricating silicone rubber with prominent tracking and erosion resistance by the combination of prevention and inhibition of tracking damage, endowing it with excellent long-term stable service performance.

1. Introduction

Silicone rubber (SR) has been extensively utilized in outdoor high voltage insulation and is gradually replacing the conventional insulators made by glass or porcelain, because of its advantages of light weight, excellent electrical insulation, outstanding hydrophobicity and pollution flashover resistance [1–4]. However, its surface is inevitably contaminated by the accumulation of dirt, salt fog and other contaminant during service, causing the hydrophobicity deterioration, leakage current and pollution flashover [5]. Moreover, concentrated dry band arcing discharge will result in the formation of "hot spot" and carbonaceous track on the SR surface, further leading to the electrical failure of SR [6], which seriously threatens the security and stability of the high voltage transmission system.

Basically, inorganic fillers, such as aluminium hydroxide ($Al(OH)_3$) [7], silica (SiO_2) [8] and boron nitride (BN) [9], are commonly employed anti-tracking additives. However, a large amount (> 40 wt%) of addition is usually required to reach desirable tracking resistance. Due to their high surface polarity and poor compatibility with SR, the processability and mechanical properties of SR were seriously deteriorated. Our previous works illustrated that the tracking and erosion resistance of SR was greatly improved by incorporating a slight addition (< 5 phr) of nitrogen-containing silane (NS) and platinum complex [10–12], which was highly efficient and had no negative effect on the processability and mechanical properties of SR. But NS was mainly consisted of the high polarity ureido groups or urethane groups, for which the hydrophobicity of SR was deteriorated, limiting its applications in the heavily polluted environments. Recently, we found that the low surface energy fluorine-containing compounds not only enhanced the tracking resistance of ALSR, but also improved its hydrophobicity [13]. Duan et al. [14] reported that direct fluorination enhanced the surface adsorbing energy and surface resistivity of polymer insulators while its surface secondary electron emission coefficient was decreased. Hence, the surface flashover voltage and dielectric capability of polymer insulators were greatly improved, resulting in a better anti-flashover performance. Du and co-workers [15] indicated that the fluorinated SR surface had a better dissipation of electric charge because of the high electronegativity of fluorine atom and the highly polarized C—F bond. The superficial fluorinated layer could trap quantities of electrons and act as a shielding layer, which prevented further accumulation of space charge and thereby mitigated arc discharge. Whereas, for direct fluorination, greater demands are being placed on the manufacturing equipment, and it is relatively difficult for large-scale production. Besides, fluorine (F_2) is an actively irritant, corrosive and oxidizing gas,

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which may bring about certain security risks. Such disadvantages limit the further applications of direct fluorination.

Given the above, the tracking and erosion resistance of SR could be effectively improved by two methods: (i) introducing nitrogen-containing compounds and platinum complex, which facilitated the formation of dense ceramic barrier layer on the SR surface [16–18], (ii) incorporating fluorine-containing compounds or direct fluorination, which improved the hydrophobicity and anti-flashover performance of SR. Although decent tracking and erosion resistance could be realized by one of the above approaches alone, to the best of our knowledge, simultaneously adopting these two mechanisms had not been reported yet.

In consideration of the mechanism of nitrogen- and fluorine- containing compounds, incorporating both compounds into SR may be an efficient method to synergistically improve the hydrophobicity and tracking resistance of SR. This will serve as a novel combination of prevention and inhibition aiming at tracking and erosion. Accordingly, we herein prepared addition-cure liquid silicone rubber (ALSR) with desirable hydrophobicity and tracking resistance, realized by incorporating our synthesized fluorine-containing polyphenylsilsesquioxane (F-PPSS) and ureido-containing MQ silicone resin (U-MQ). ALSR/F-PPSS/U-MQ exhibited outstanding tracking resistance and prominent hydrophobicity. Besides, it was demonstrated to have excellent anti-plasma irradiation performance and thermal stability. This work provided a new and feasible strategy to manufacture long-term stable silicone rubber with excellent tracking and erosion resistance.

2. Experimental section

2.1. Materials

Perfluorooctyltriethoxysilane (FAS) was purchased from Evonik Industries AG, Germany. Phenyltriethoxysilane (PhTES) was obtained from Hubei Jianghan Fine Chemical Co., Ltd., China. Vinyltriethoxysilane (ViTES) was supplied by Qufu Chenguang Chemical Co., Ltd., China. Diisopropylamine (DIPA) was purchased from Shanghai Richjoint Chemical Reagent Co., Ltd., China. 3-Isocyanatopropyltriethoxysilane (ICPES) was provided by Jiangsu Huasheng Fine Chemical Co., Ltd., China. Tetraethoxysilane (TEOS) was obtained from Guangzhou Chemical Reagent Factory, China. Vinyl-terminated poly(dimethylsiloxanes) (VPDMS, vinyl content was 0.28 wt % and viscosity was 24320 mPa·s) was obtained from Midgold Fine Performance Materials Co., Ltd., China. Poly(hydromethylsiloxane) (PHMS, hydride content was 0.75 wt%) was obtained from Shandong Dayi Chemical Co., Ltd., China. 1-Ethynylcyclohexanol, Karstedt's catalyst (platinum content was 2000 ppm) and poly(dimethylsiloxanes) with high vinyl content (HVPDMS, vinyl content was 8.7 mol% and viscosity was 2095 mPa·s) were purchased from Guangzhou Xiyou New Material Technology Co., Ltd., China. Fumed silica (SiO_2, QS-25, specific surface area was 250 m^2/g) was supplied by Tokuyama Corp., Japan.

2.2. Synthesis of fluorine-containing polyphenylsilsesquioxane

Fluorine-containing polyphenylsilsesquioxane (F-PPSS) was synthesized according to our developed one-step acid-catalyzed sol-gel reaction [13]. Ethanol (0.57 mol), HCl (0.01 mol) and deionized water (0.30 mol) were added to a 250 mL four-neck round bottom flask. Afterwards, FAS (0.025 mol), ViTES (0.012 mol) and PhTES (0.088 mol) were dissolved in ethanol (0.43 mol), and the solution was then added dropwise to the flask under stirring at 30 °C. The mixture was first stirred for 3 h at 60 °C, and then heated to 150 °C. The reaction lasted for another 24 h. Reduced pressure distillation was applied to remove the ethanol, and F-PPSS was obtained. The synthetic scheme is shown in Scheme 1, and Fig. S1 presents the FT-IR spectra of FAS, PhTES, ViTES and F-PPSS. The characteristic peaks of the ^{1}H-NMR spectrum for F-PPSS (600 MHz, $CDCl_3$, δ, ppm) were as follows: 5.2–5.4 $(-C\underline{H}{=}C\underline{H}_2)$, 3.2–4.0 $(-OC\underline{H}_2CH_3)$, 0.5–1.5 $(-OCH_2C\underline{H}_3)$, 6.5–7.8 $(-C_6\underline{H}_5)$, 5.6–6.3 $(-O\underline{H})$, 1.5 $(-CF_2C\underline{H}_2CH_2-)$. The ^{29}Si-NMR spectrum of F-PPSS is exhibited in Fig. S2. F-PPSS was in glassy state at room temperature and its glass transition temperature (T_g) was 65 °C.

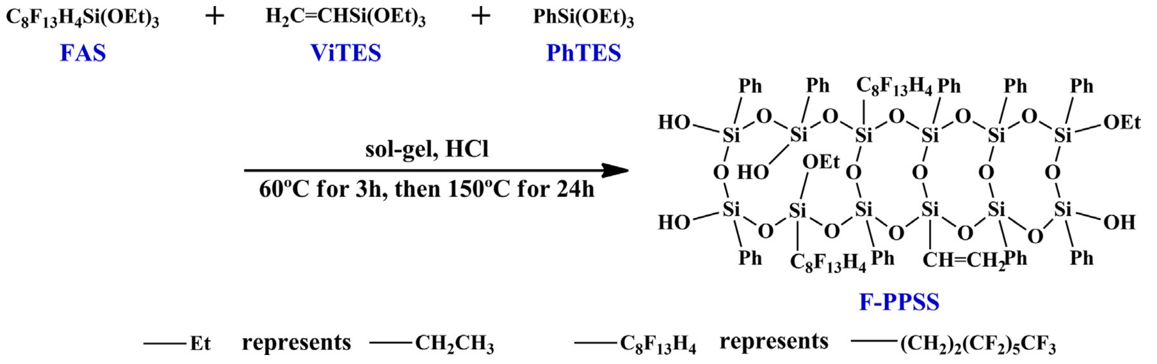
Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apsusc.2018.08.021.

2.3. Synthesis of ureido-containing MQ silicone resin

The synthesis of ureido-containing MQ silicone resin was based on our previous literature [19]. Firstly, as shown in Scheme 2(a), (3-diisopropylureido)triethoxysilane (DIPUPES) was prepared by the addition reaction of DIPA (0.35 mol) and ICPES (0.30 mol). Subsequently, the co-hydrolysis condensation reaction of DIPUPES (17.4 g), TEOS (28.3 g), MM (13.6 g), $M^{Vi}M^{Vi}$ (3.0 g) was conducted, illustrated in Scheme 2(b). As a pale yellow viscous liquid, ureido-containing MQ silicone resin (U-MQ) was obtained after the process of toluene extraction, ammonia neutralization, water washing and reduced pressure distillation. The FT-IR spectra of ICPES, DIPUPES and U-MQ are displayed in Fig. S3. The characteristic peaks of the ^{1}H-NMR spectrum for U-MQ (600 MHz, $CDCl_3$, δ, ppm) were as follows: 5.4–6.0 $(-C\underline{H}{=}C\underline{H}_2)$, 4.4 $(-NCON\underline{H})$, 3.2 $(-NCON-C\underline{H}_2-)$, 1.6 $(-NCON-CH_2-C\underline{H}_2-)$, 0.6 $(-NCON-CH_2-CH_2-C\underline{H}_2-)$, 1.1–1.3 $(-CH(C\underline{H}_3)_2)$, 0–0.7 $(-C\underline{H}_3$ on the Si—O—Si chain). Fig. S4 presents the ^{29}Si-NMR spectrum of U-MQ.

2.4. Preparation of the ALSR samples

VPDMS, SiO_2, hexamethyldisilazane and HVPDMS were uniformly mixed in a kneader for obtaining the ALSR masterbatch. A suitable quantity of the masterbatch, F-PPSS, U-MQ, PHMS, 1-ethynylcyclohexanol and Karstedt's catalyst were vigorously stirred by an electric mixer. Subsequently, the mixture was first vulcanized at 120 °C for



Scheme 1. F-PPSS was synthesized via the one-step acid-catalyzed sol-gel reaction.