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Effect of alkyl-disubstituted ureido silanes with different alkyl chain structures on tracking resistance property of addition-cure liquid silicone rubber

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A B S T R A C T

Ureido silane is considered to be a novel tracking resistance additive for effectively improving the tracking resistance property of addition-cure liquid silicone rubber (ALSR). In this work, a series of alkyl-disubstituted ureido silanes (ADUSs) with different alkyl chain structures were synthesized by the transetherification of allyl alcohol (AA) and alkyl-disubstituted ureido siloxanes from the nucleophilic addition between alkyl-disubstituted amides and 3-isocyanatopropyltriethoxysilane (ICPES). The effect of ADUSs with different alkyl chain structures on the tracking resistance property of ALSR was investigated by inclined plane test (IPT), thermogravimetry analysis (TGA), thermogravimetry-Fourier transform infrared spectrometry (TG-FTIR) and energy dispersive spectroscopy (EDS). The results showed that ADUSs could effectively improve the tracking resistance property of ALSR, especially for (γ-diisopropylureidopropyl) allyloxyethoxysilane (DIPUPAS), (γ-dibutylureidopropyl) allyloxyethoxysilane (DBUPAS) and (γ-diisobutylureidopropyl) allyloxyethoxysilane (DIBUPAS). ALSR incorporated with DIPUPAS, DBUPAS and DIBUPAS passed the inclined plane test (IPT) at the alternating voltage of 4.5 kV and the average erosion mass was only 3.8%, 3.4% and 4.4% of the virgin ALSR, respectively. TGA and TG-FTIR results revealed that DIPUPAS, DBUPAS and DIBUPAS could also effectively improve the thermal stability of ALSR. Accompanying with the weakened oxidation reactions of methyl groups in molecular chains, the formed cyclic oligomers decreased. Meanwhile, the release of methane and cross-linking reaction of the silicone rubber chains were enhanced, leading to the increase of residue under high temperature and the formation of a ceramic barrier layer to protect the silicone rubber matrix. EDS results showed that the carbon content in ceramic barrier layer decreased, which was beneficial to prohibit the development of tracking.

1. Introduction

With excellent advantages such as chemical resistance, electric insulation, weather resistance, hydrophobicity and hydrophobicity recovery, ALSR has been widely used in construction, aviation, high or extra-high voltage power electrical equipment, etc [1,2]. However, when ALSR is exposed to contaminated environment, leakage current will occur on the surface in strong electric field, leading to the water evaporation and arcing. Finally, the carbon pathway caused by arcing gives rise to tracking phenomenon which is not safe for the electric systems and apparatuses [3,4]. In order to improve the tracking resistance property of ALSR, inorganic fillers are usually added as tracking resistance additives, such as aluminium hydroxide (ATH) [5–8], magnesium hydroxide (MTH) [9,10], silica (SiO_2) [11,12], aluminium oxide (Al_2O_3) [13] and titanium dioxide (TiO_2) [14]. However, it needs a great number of fillers to achieve favourable effect, which is harmful to the processing and mechanical properties of ALSR.

To reduce inorganic fillers content, some organic additives owning arc-quenching capability are incorporated into the matrix. Arc-quenching materials, such as high nitrogen organic compounds, are capable of releasing gases which can change arcing medium atmospheres and provide a cooling effect on arc [15,16]. Lar and coworkers [17] combined melamine cyanurate with silica to

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Table 1
Types of disubstituted amine and the corresponding alkyl-disubstituted ureido siloxanes, ADUSs and vinyl group content.

Disubstituted amines	Alkyl-disubstituted ureido siloxanes	ADUSs	Vinyl group content (wt%)
DEA	(γ-diethylureidopropyl) triethoxysilane (DEUPES)	(γ-diethylureidopropyl) allyloxyethoxysilane (DEUPAS)	14.70
DPA	(γ-dipropylureidopropyl) triethoxysilane (DPUPES)	(γ-dipropylureidopropyl) allyloxyethoxysilane (DPUPAS)	13.27
DIPA	(γ-diisopropylureidopropyl) triethoxysilane (DIPUPES)	(γ-diisopropylureidopropyl) allyloxyethoxysilane (DIPUPAS)	14.71
DBA	(γ-dibutylureidopropyl) triethoxysilane (DBUPES)	(γ-dibutylureidopropyl) allyloxyethoxysilane (DBUPAS)	12.61
DIBA	(γ-diisobutylureidopropyl) triethoxysilane (DIBUPES)	(γ-diisobutylureidopropyl) allyloxyethoxysilane (DIBUPAS)	12.26
DPTA	(γ-dipentylureidopropyl) triethoxysilane (DPTUPES)	(γ-dipentylureidopropyl) allyloxyethoxysilane (DPTUPAS)	12.13
DHA	(γ-dihexylureidopropyl) triethoxysilane (DHUPES)	(γ-dihexylureidopropyl) allyloxyethoxysilane (DHUPAS)	11.41

improve tracking resistance and erosion resistance properties of silicone rubber, and found that the samples passed the IPT at 4.5 kV. However, the compatibility between melamine cyanurate and silicone rubber was poor due to the strong polarity of melamine cyanurate. Therefore, mechanical properties of silicone rubber obviously decreased. Our group [18] found that a small amount (2 phr) of the ureido silanes could effectively improve the tracking resistance and erosion resistance properties of ALSR. Meanwhile, thermal stability of ALSR was enhanced. It was shown that there was close relationship between tracking resistance property and thermal stability. Ureido silane enriched the species of tracking resistance additives and possessed the possibility to further improve the tracking resistance property of ALSR. Lai [19] found that the thermal stability of alkylcyclohexanes decreased with increasing side-chain length. Therefore, ureido silanes with different alkyl chain length in the substituted group may affect the tracking resistance property of ALSR. It is necessary to figure out their relationships to optimize the species of urea containing tracking resistance additives and enrich the applications.

In this work, seven ADUSs containing different alkyl chain length were synthesized and characterized by Fourier transform infrared (FTIR) spectroscopy and ^{1}H nuclear magnetic resonance (^{1}HNMR) spectroscopy. The effect of ADUSs on the tracking resistance property and the mechanical properties of ALSR were studied. The thermal stability and characterization of pyrolysis gases of ALSR samples were investigated by thermogravimetry analysis (TGA) and thermogravimetry-Fourier transform infrared (TG-FTIR) spectrometry. Energy dispersive spectroscopy (EDS) was also used to investigate surface elements of ALSR samples before and after IPT. Moreover, the possible suppression mechanism of the ADUSs on the tracking resistance and erosion resistance properties of ALSR was further explored.

2. Experimental

2.1. Materials

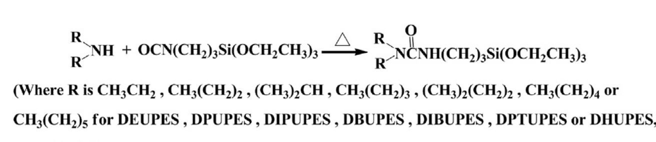
Allyl alcohol (AA, 99.8%) was supplied by Xiya Chemical Reagent Co., Ltd., China. Diethylamine (DEA, 98%), dibutylamine (DBA, 98%) and dihexylamine (DHA, 98%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. Dipropylamine (DPA, 98%), diisopropylamine (DIPA, 98%), diisobutylamine (DIBA, 98%) and dipentylamine (DPTA, 98%) were obtained from Shanghai Runjie Chemical Reagent Co., Ltd., China. 3-isocyanatopropyltriethoxysilane (ICPES, 97%) was purchased from Jiangsu Huasheng Chemical Reagent Co., Ltd., China. Acetone (99.8%) and methylbenzene (99.8%) were supplied by Guangzhou Chemical Reagent Co., Ltd., China. Tetrabutyltitanate (TBT, 99.8%) was offered by Tianjin Fuchen Chemical Reagent Co., Ltd., China. Vinyl-terminated poly(dimethylsiloxane) (VPDMS, viscosity was 20,000 mPa s and vinyl content was 0.12 wt%), ploy(hydromethylsiloxane) (PHMS, viscosity was 160 mPa s and hydride content was 0.70 wt%) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethydisiloxane complex (Karstedt's catalyst, Pt content was 3000 ppm) were provided by Guangzhou Tinci Silicon Technology Co., Ltd., China. 1-Ethynylcyclohexanol (99.8%) as inhibitor was offered by Shenzhen Xinzeye Technology Co., Ltd., China. Fumed silica (M-5, SiO_2) was purchased from Cabot Co., Ltd., USA.

2.2. Synthesis of alkyl-disubstituted ureido siloxanes

Disubstituted amine (0.5 mol) was dissolved in a certain amount of acetone in a 500 mL flask with a condenser pipe, a stirring paddle, a thermometer and a constant pressure funnel. The mixture was heated to 40 °C. ICPES (0.5 mol, 123.68 g) was added dropwise to the stirring mixture, and the reaction lasted for 3 h. Then, acetone was removed by rotary evaporation at 40 °C under reduced pressure and alkyl-disubstituted ureido siloxane was obtained. The types of disubstituted amine and alkyl-disubstituted ureido siloxane are listed in Table 1. The synthetic reactions of alkyl-disubstituted ureido siloxanes are shown in Scheme 1.

2.3. Synthesis of ADUSs

AA (1.5 mol, 151.79 g) and TBT (0.5 wt% of reactants) were dissolved in quantitative methylbenzene in a 500 mL flask with a condenser pipe, a stirring paddle, a thermometer and a constant pressure funnel. The mixture was heated to 80 °C. Then alkyl-disubstituted ureido siloxane (0.5 mol) was added dropwise into the mixture, and the reaction was maintained for 2 h. After that, the reaction lasted for another 2 h under the reduced pressure and the methylbenzene was removed by rotary evaporation at 75 °C under reduced pressure to obtain ADUS. The types of ADUS and the vinyl group content are listed in Table 1. The vinyl group content in ADUSs was determined by iodimetric titration [20]. The synthetic reactions of ADUSs are shown in Scheme 2.



Scheme 1. Synthetic reactions of alkyl-disubstituted ureido siloxanes.