



Synergistic effect between POSS and fumed silica on thermal stabilities and mechanical properties of room temperature vulcanized (RTV) silicone rubbers

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ABSTRACT

In this paper, both divinyl-hexa[(trimethoxysilyl)ethyl]-POSS (DVPS) and fumed silica were firstly introduced into polydimethylsiloxane (PDMS) system using as the cross-linker and the reinforcing filler respectively. And a series of novel RTV silicone rubbers synergistically enhanced by DVPS and fumed silica were prepared. The cross-linked networks in the novel RTV silicone rubbers have been studied by attenuated total reflection infrared spectroscopy, and the dispersions of POSS and fumed silica in these novel RTV silicone rubbers have been observed by means of scanning electron microscope (SEM). And thermal stabilities, thermo-oxidative stabilities and mechanical properties of these novel RTV silicone rubbers were studied by means of thermal gravimetric analysis and universal tensile testing machine, respectively. From the obtained results, it was found that synergistic effect between POSS-rich areas and fumed silica on thermal stability and mechanical property of RTV silicone rubber indeed existed. And the experimental results also exhibited that the thermal stabilities and mechanical properties of the novel RTV silicone rubbers were far better than those of the reference materials (DVPR and MTRF). The striking enhancements in thermal properties and improvements on mechanical properties of novel RTV silicone rubbers were likely attributed to the synergistic effect between POSS-rich domains and fumed silica. Meanwhile, it was found that the mechanical properties of RTV silicone rubbers prepared with a given amount of POSS cross-linker were enhanced with the increment of the loading amount of fumed silica.

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1. Introduction

Polyhedral oligomeric silsesquioxanes (POSS) combined organic/inorganic material properties have received considerable attention in the field of organic/inorganic hybrid nano-materials over the past decade. POSS molecules with 1–3 nm in diameter are a new type of nano-sized building blocks. Their empirical formulas are $(\text{RSiO}_{1.5})_n$ (n is an even number, $n > 4$), and the inert inorganic caged framework of POSS is made up of silicon and oxygen $(\text{SiO}_{1.5})_n$, and the cage can be thought of the smallest spherical silica. The substituent groups (R) connected tightly with the cage can mainly be divided into hydrogen, reactive organic groups and inert organic groups, so POSS nano-structured

chemicals can be easily incorporated into common polymer systems as enhanced nano-filler via chemical bonds, or Van der Waals interaction between substituent groups (R) and polymer chains. POSS with $n = 8$ nano-structured cage have been explored extensively, and several related reviews [1–6] have been published recently.

POSS are a new class of lightweight, high performance hybrid materials, which are commonly used to modify various polymeric systems as nano-structured filler [4]. And many related researches have been reported that the incorporation of POSS into polymeric matrixes can improve comprehensive properties of composites, such as service temperatures, decomposition temperatures, oxidation resistance, surface hardening, mechanical properties, flammability resistance, heat evolution and so on [1]. These enhancements have also been shown to apply to polymeric PDMS systems. Till now, PDMS composites still have been intensively studied for their unique properties, such as high permeability, good electrical properties, low surface free energy, weather resistance, low glass transition temperature, low toxicity and low chemical reactivity [7–9].

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Although unfilled PDMS has a good flexibility, it usually shows weak mechanical property, which is unable to meet the practical requirements of commercial applications. To meet these applied requirements, adding enforcing filler is widely used method that improves mechanical properties of PDMS composites. Up to the present, POSS have been used as a new generation of reinforcing nano-filler. However, there are a few researches [10–16] on PDMS composites with POSS have been reported. Moreover, the reported investigations mostly focused on mechanical properties of high temperature vulcanized silicone rubbers (HTV), addition type curable (ATC) silicone rubbers and room temperature vulcanized (RTV) silicone rubbers except our recent works [14–16].

Based on our recent work [14], we also further introduced fumed silica into novel RTV silicone rubber to study the synergistic reinforcement of POSS and fumed silica. It is well known that fumed silica is mainly used as an enhancing filler in industry to improve mechanical properties [17–22] of silicone rubber, such as tensile strength and hardness. To our knowledge, there is no report in this area which researches the synergistic effect between fumed silica and POSS in RTV silicone rubbers. This study was initially carried out to determine if the synergistic effect between fumed silica and POSS in RTV silicone rubbers existed. Meanwhile, we also studied the synergistic effect between fumed silica and POSS on improving thermal stabilities and mechanical properties of RTV silicone rubbers.

In this paper, we firstly reported the preparation and characterization of the novel enhanced RTV silicone rubbers using divinyl-hexa[(trimethoxysilyl)ethyl]-POSS (DVPS) and fumed silica as the cross-linker and reinforcing filler respectively. The three dimensional cross-linked networks of the select RTV silicone rubbers have been characterized by attenuated total reflection (ATR) infrared spectroscopy and the extraction/swelling experiment. And the morphologies, thermal stabilities and mechanical properties of the novel enhanced RTV silicone rubbers were investigated by scanning electron microscope, thermal gravimetric analysis and universal tensile testing machine, respectively.

2. Experimental

2.1. Materials

Divinyl-hexa[(trimethoxysilyl)ethyl]-POSS (DVPS) was prepared in our method [14,15], and the ideal structure was shown in Fig. 1. The fumed silica (SiO_2) employed in this study was Cabot-O-Sil fumed silica LM-150 obtained from Cabot Corporation (USA). The specific surface area of the fumed silica is $150 \text{ m}^2/\text{g}$ and its average

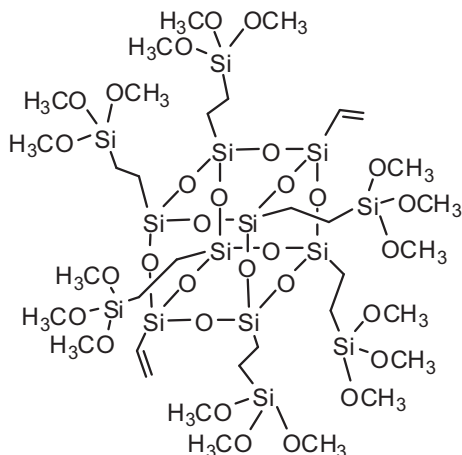


Fig. 1. The ideal structure of DVPS cross-linker.

particle size is 5–30 nm, which was used after drying at 120°C for 24 h. Methyltrimethoxysilane (MTMOS) was supplied by Wuhan University Silicone New Material Co., Ltd, Wuhan, China. Hydroxyl-terminated polydimethylsiloxane (HPDMS) (107#, viscosity, 5000 cSt), methyl silicone oil (viscosity, 500 cSt) and curing catalyst (mixture of dibutyltin diacetate and stannous 2-ethyl hexanoate, 101#) were provided by Hubei Wuhan University Photons Technology Co., Ltd., Suizhou, China. Ethyl ether and toluene were purchased from Tianjin BoDi Chemical reagent Co., Ltd. All of the above solvents are of analytical purity and were used as received except that ethyl ether was dehydrated according to classic literature procedure.

2.2. Synthesis of divinyl-hexa[(trimethoxysilyl)ethyl]-POSS (DVPS)

The cross-linker DVPS was prepared according to our recent work [14,15], which is highly viscous pale liquid and soluble in common organic solvents, such as tetrahydrofuran, chloroform and petroleum ether. The DVPS product was used in the following experiments without further purification. FTIR (KBr, cm^{-1}): 3067, 3034 ($\nu \text{ H}-\text{C}=\text{C}$), 2950, 2843 ($\nu \text{ C}-\text{H}$), 1598 ($\nu \text{ C}=\text{C}$), 1403, 1270 ($\delta \text{ C}-\text{H}$), 1137, 472 ($\nu \text{ Si}-\text{O}-\text{Si}$), 829 ($\delta \text{ Si}-\text{OCH}_3$), 784 ($\nu \text{ Si}-\text{C}$), 549 ($\delta \text{ Si}-\text{C}=\text{C}$); ^1H NMR (CDCl_3 , ppm): δ 5.82–6.10 (m, $\text{H}_2\text{C}=\text{CH}-$, 6H), 3.56 (s, $-\text{OCH}_3$, 54H), 0.67 (m, $\text{Si}-\text{CH}_2$, 24H); ^{13}C NMR (CDCl_3 , ppm): δ 129.63 ($\text{CH}=\text{CH}_2$), 136.49 ($\text{CH}=\text{CH}_2$), 50.71 ($\text{Si}-\text{OCH}_3$), 3.43 ($\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OCH}_3)_3$), 0.68 ($\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OCH}_3)_3$); ^{29}Si NMR (CDCl_3 , ppm): δ -66.51, -66.64, -80.63; MS (ESI): 1387 ($\text{M} + \text{Na}^+$, adduct ion).

2.3. Preparation of RTV silicone rubbers

The general preparation of RTV silicone rubber is as follows. HPDMS polymer was charged into the kneading chamber of the kneader (IKA HKD-T0, 6), and the HPDMS polymer was mixed to move volatile components at 130°C for 2 h under vacuum. The fumed silica was added into the kneading chamber when the HPDMS polymer was cooled to RT under vacuum. The mixture was continued to knead under vacuum at RT until it became light blue, and then the ethyl ether solution of DVPS and curing catalyst (101#) was added into the kneading chamber, and the new mixture was obtained after kneading for 15 min, then volatile compounds were removed under vacuum around 15 min. This new mixture was rapidly transferred into a packing rubber tube, and then this packing rubber tube was sealed with a piston. Subsequently, the mixture could be squeezed out by caulking gun, and cured for about 2 d at room temperature to give an enhanced RTV silicone rubber.

As reference material, we also synthesized RTV silicone rubbers using conventional tri-functional cross-linker (such as MTMOS) according to the same approach above, and we also prepared the blank material without fumed silica (DVPR). The abbreviations for each filled PDMS polymer systems are as follows: PDMS composites prepared with the cross-linker MTMOS and fumed silica were denoted as MTFR, those prepared with DVPS and fumed silica were denoted as DVPF. The curing formulations were as follows: HPDMS polymer (107#), cross-linker (DVPS), methyl silicone oil and cured catalyst were 100, 20, 10 and 0.90, respectively. And the RTV silicone rubber formulations with various weight percent of fumed silica were listed in Table 1.

2.4. Characterizations and measurements

^1H and ^{13}C NMR spectra were recorded with a Varian mercury VX-300 spectrometer at 300.081 and 75.455 MHz in CDCl_3 (0.05% TMS as an internal standard) at RT, respectively. ^{29}Si NMR spectra were recorded with a Varian Unity-Inova 600 spectrometer in

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