



Synthesis and characterization of novel room temperature vulcanized (RTV) silicone rubbers using Vinyl-POSS derivatives as cross linking agents

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ABSTRACT

Two kinds of novel POSS cross-linkers were firstly prepared via hydrosilylation of Vinyl-POSS and trimethoxysilane. And two types of novel polydimethylsiloxane (PDMS) polymer composites as RTV silicone rubbers were prepared using Vinyl-POSS derivatives as cross-linkers in the presence of organotin catalyst. To completely exhibit superiorities of two kinds of novel cross-linkers, RTV silicone rubbers prepared with two proportions of different cross-linkers were assessed. The chemical inclusion of novel POSS into PDMS networks by hydrolytic condensation reaction was verified by attenuated total reflection (ATR) infrared spectroscopy. Morphologies, thermal properties, mechanical properties and hardness of these novel RTV silicone rubbers were studied. The results exhibited significantly enhanced effects of POSS on thermal stabilities, mechanical properties and hardness as compared to the PDMS polymers prepared with the traditional tetra-functional TMOS and TEOS cross-linkers. The striking improvements in thermal properties, mechanical properties and hardness could be attributed to the synergistic effect of the increase of dimensionality of cross-linked networks in novel RTV silicone rubbers resulting from special three-dimensional structure of novel POSS cross-linkers, plasticization of self-cross-linked POSS cross-linkers and uniform distribution of POSS cross-linkers.

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1. Introduction

Polyhedral oligomeric silsesquioxanes (POSS) with their combined inorganic–organic chemistry properties have attracted considerable attention in the field of organic/inorganic hybrid nano-materials over the past decades. POSS molecules with a generic empirical formula $(\text{RSiO}_{1.5})_n$ (where n is an even number, $n > 4$) are a type of building blocks, and their sizes range from 1 to 3 nm, which can be thought of as the smallest spherical silica. The substituent groups (R) connected with the Si atoms in the cage can be divided into hydrogen, reactive organic groups and inert organic groups. POSS with $n = 8$ nano-structured cage has been explored extensively, and several reviews [1–3] have been published recently.

Due to the modifiable substituent groups (R), POSS derivatives can be easily incorporated into common polymer systems via chemical bonds or physical blending as enhancement nano-filler [4]. The incorporation of POSS derivatives into polymeric materials can obviously enhance polymer properties, such as used temperatures, decomposition temperatures, oxidation resistance, surface hardening, mechanical properties, flammability resistance, heat evolution and so on [1]. These improvements have been shown to apply to a wide range of polymeric systems. Some specific examples were enumerated as the following, such as polystyrene [5–10], polyimide [11–14], polyurethane [15–17], poly(methyl methylacrylate) [18,19], poly(ϵ -caprolactone) [20], polyvinylchloride [21], poly(ethylene oxide) [22] and polybenzoxazine [23–26]. However, due to insurmountable disadvantages of incompatibility and aggregation of POSS monomers, like the above enhanced polymer composite materials are difficult to be prepared by simply physical blending. The incorporation of POSS into polymeric materials by chemical bonding may be the best alternative for material scientists when they encounter these insurmountable problems, so synthesis of the novel POSS derivatives with reactive functionalities for polymerization or grafting into polymer is a new research focus for scientists.

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Moreover, the above enhancements of POSS have also been applied to polymeric PDMS system. Up to present, PDMS still has been intensively explored for its unique properties, such as high permeability, low viscosity, low surface free energy, unexpected mesophase, low gas transition temperature, excellent thermal stability, low toxicity and low chemical reactivity [27–32].

However, a few researches on hybrid materials of polysiloxane/POSS have been reported. Pan et al. [33] also reported mechanical properties of enhancing polydimethylsiloxane (PDMS) elastomers prepared by physical blending with monovinyl-POSS or inert four linked POSS and chemical bonding with monovinyl-POSS, respectively. Isayeva et al. [34] also investigated mechanical properties and thermal oxidative stabilities of novel tricomponent amphiphilic membranes consisting of hydrophilic poly(ethylene glycol) and hydrophobic HPDMS segments and octasilane-POSS cages prepared by cohydrosilylation followed by hydrolysis/condensation. Subsequently, Liu et al. [35] investigated crystallization and morphology of poly(methylvinylsiloxane) elastomer composites with octaisobutyl-POSS prepared by melt blending. Similarly, Baumann [36] also reported the synthesis and mechanical properties of novel elastomeric nano-composites containing POSS as both the cross-linker and filler within a polydimethylsiloxane (PDMS) polymer matrix.

The aforementioned investigations mostly involve mechanical properties of high-temperature vulcanized silicone rubbers (HTV), addition-type curable (ATC) silicone rubbers and room temperature vulcanized (RTV) silicone rubbers. POSS monomers are generally incorporated into silicone rubbers via either simply physical blending with inert POSS or chemical bonding with reactive POSS, but the reports of preparation, morphologies and thermal degradation properties of RTV silicone rubbers prepared by chemical bonding with reactive POSS are rare. Therefore, it is necessary to investigate preparation, morphologies and thermal stability properties of novel RTV silicone rubber composites with reactive POSS.

In our work, our goal is to use freshly prepared Vinyl-POSS derivatives as both the cross-linkers and fillers in HPDMS system to design novel RTV silicone rubbers with improved thermal stabilities and enhanced mechanical properties. In this paper, we firstly reported the preparation of Vinyl-POSS derivatives and their application in the RTV silicone rubbers as both cross linking agents and fillers. The novel POSS cross-linkers were chemically bonded into HPDMS polymer matrix by hydrolytic condensation to form three-dimensional cross-linked networks in PDMS polymers, which were also confirmed by infrared spectroscopy, extraction/swelling experiments. The morphologies, thermal stabilities, mechanical properties and hardness of novel RTV silicone rubbers were investigated by means of scanning electron microscopy, thermal gravimetric analysis, universal tensile testing machine and shore A durometer, respectively. It was found that the novel POSS cross-linkers were favorable to enhancement in the thermal stabilities, mechanical properties and hardness of the RTV silicone rubbers as compared with conventional tetra-functional cross-linkers (TMOS and TEOS).

2. Experimental

2.1. Materials

Vinyl-POSS was prepared in our laboratory. Vinyltrimethoxysilane, tetraethoxysilane (TEOS), tetramethoxysilane (TMOS), trimethoxysilane and $\text{H}_2[\text{PtCl}_6]$ were supplied by Wuhan University Silicone New Material Co., Ltd, Wuhan, China. Hydroxyl terminated polydimethylsiloxane (HPDMS) (107#, viscosity, 4500 cst, $M_w = 49\,000$ g/mol) 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. Concentrated hydrochloric acid 37% (AR) was obtained from Shanghai Reagent Plant, China. The above starting materials were used as received except $\text{H}_2[\text{PtCl}_6]$ was dissolved in anhydrous isopropanol. Ethyl ether, acetone, pentane and dichloromethane were purchased from Tianjin BoDi Chemical. 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 octavinyl-POSS (Vinyl-POSS)

1350 mL of acetone and 133.5 g of vinyltrimethoxysilane (0.90 mol) were charged into a 2 L flask, which was equipped with a magnetic stirrer. The mixture of 225 mL of concentrated hydrochloric acid and 259.2 mL of deionized water was added dropwise into the reaction mixture, stirred and refluxed at 40 °C for 48 h. White solid was deposited on the wall of the flask, meanwhile the reaction mixture turned brown. The solvent mixture was decanted into a pre-prepared 2000 mL beaker to be reused in the next experiment. The white powder can be obtained from centrifugal separation, washing with ethanol and drying at 60 °C in vacuum drying oven. The total crude product was recrystallized from the mixed solvents of dichloromethane and acetone (volume ratio 1:3) to afford 23.7 g of Vinyl-POSS with 33.3% of yield. FTIR (KBr, cm^{-1}): 3067, 3024 (ν C–H), 1604 (ν C=C), 1409, 1276 (δ C–H), 1112, 465 (ν Si–O–Si), 585 (δ Si–O–Si), 779 (ν Si–C); ^1H NMR (CDCl_3): δ 5.86–6.14 (m, $\text{H}_2\text{C}=\text{CH}-$, 24H); ^{13}C NMR (CDCl_3 , ppm): δ 128.93 ($\text{CH}=\text{CH}_2$), 137.18 ($\text{CH}=\text{CH}_2$); ^{29}Si NMR (CDCl_3 , ppm): δ –80.21; MS (ESI): 663 ($\text{M} + \text{CH}_3\text{O}^+$, adduct ion).

2.3. Synthesis of octa[(trimethoxysilyl)ethyl]-POSS (OPS)

The hydrosilylation catalyst ($\text{H}_2[\text{PtCl}_6]$) (0.1 mol L^{-1} in Pr^iOH , 10 drops) and trimethoxysilane [$\text{HSi}(\text{OCH}_3)_3$ (23.42 g, 98.9%, 189.6 mmol)] were charged respectively into a 500 mL three-necked flask with a solution of Vinyl-POSS (5.00 g, 7.90 mmol) in diethyl ether (250 mL). The reaction mixture was refluxed for 8 h, and continued to stir at 20 °C for 15 h. Activated carbon was added to this flask, and the resulting mixture had been kept on refluxing for 0.5 h. The black ether solution was filtered through silica gel and celite, the filtrate was collected and the volatile materials were removed under vacuum. Subsequently, 300 mL of pentane was added to the residue and stirred for 1 h, and then the mixture was filtered through celite to provide a clear colorless solution. Finally, OPS (12.41 g, 97.6% of yield) was obtained by moving pentane under a reduced pressure, which is highly viscous pale liquid and soluble in common organic solvents, such as tetrahydrofuran, chloroform and petroleum ether. The OPS product was used in the following steps without further purification. FTIR (cm^{-1}) with KBr powder: 2950, 2843 (ν C–H), 1465, 1409, 1276 (δ C–H), 1093, 476 (ν Si–O–Si), 829 (δ Si– OCH_3), 781 (ν Si–C); ^1H NMR: (CDCl_3 , ppm) 3.52 (s, $-\text{OCH}_3$, 72H), 0.58 (m, Si– CH_2 , 32H); ^{13}C NMR: (CDCl_3 , ppm) 50.71 (Si– OCH_3), 3.47 (Si– CH_2 – CH_2 –Si(OCH_3) $_3$), 0.72 (Si– CH_2 – CH_2 –Si(OCH_3) $_3$); MS (ESI): 1631 ($\text{M} + \text{Na}^+$, adduct ion).

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

The hydrosilylation catalyst ($\text{H}_2[\text{PtCl}_6]$) (0.1 mol L^{-1} in Pr^iOH , 30 drops) and trimethoxysilane [$\text{HSi}(\text{OCH}_3)_3$ (17.6 g, 98.9%, 142.2 mmol)] were charged respectively into a 1 L three-necked flask with the solution of Vinyl-POSS (15.0 g, 23.7 mmol) and diethyl ether (750 mL). The mixture was refluxed for 8 h, and continued to stir at 20 °C for 15 h. Activated carbon was added to this flask, and the resulting mixture had been kept on refluxing for 0.5 h. The black ether solution was filtered through silica gel and celite, the

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