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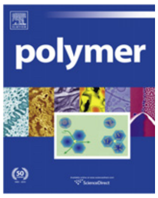

Synthesis and characterization of novel room temperature vulcanized (RTV) silicone rubbers using Vinyl-POSS derivatives as cross linking agents

Dongzhi Chen [a,b], Shengping Yi [a,b], Weibing Wu [a], Yalan Zhong [a], Jun Liao [b,*], Chi Huang [a,b,**], Wenjuan Shi [a]

[a] *College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, 430072, PR China*
[b] *Engineering Research Center of Organosilicon Compound and Material, Ministry of Education of China, Wuhan, 430072, PR China*

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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.

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 $(RSiO_{1.5})_n$ (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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* Corresponding author.

** Corresponding author. College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, 430072, PR China. Tel.: +86 027 68752701; fax: +86 027 68754067.

E-mail addresses: junliao@whu.edu.cn (J. Liao), chihuang@whu.edu.cn (C. Huang).

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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 $H_2[PtCl_6]$ 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 $H_2[PtCl_6]$ 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); ^{1}HNMR ($CDCl_3$): δ 5.86–6.14 (m, $H_2C{=}CH{-}$, 24H); ^{13}CNMR ($CDCl_3$, ppm): δ 128.93 ($\mathbf{C}H{=}CH_2$), 137.18 ($CH{=}\mathbf{C}H_2$); ^{29}SiNMR ($CDCl_3$, ppm): δ −80.21; MS (ESI): 663 (M + CH_3O^-, adduct ion).

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

The hydrosilylation catalyst ($H_2[PtCl_6]$) (0.1 mol L^{-1} in Pr^iOH, 10 drops) and trimethoxysilane [$HSi(OCH_3)_3$ (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); ^{1}HNMR: ($CDCl_3$, ppm) 3.52 (s, $-OCH_3$, 72H), 0.58 (m, $Si{-}CH_2$, 32H); ^{13}CNMR: ($CDCl_3$, ppm) 50.71 ($Si{-}O\mathbf{C}H_3$), 3.47 ($Si{-}\mathbf{C}H_2{-}CH_2{-}Si(OCH_3)_3$), 0.72 ($Si{-}CH_2{-}\mathbf{C}H_2{-}Si(OCH_3)_3$); MS (ESI): 1631 (M + Na^+, adduct ion).

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

The hydrosilylation catalyst ($H_2[PtCl_6]$) (0.1 mol L^{-1} in PriOH, 30 drops) and trimethoxysilane [$HSi(OCH_3)_3$ (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 filtrate was collected, and concentrated. Subsequently, 1200 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, DVPS (29.5 g, 91.1% of yield) was obtained by moving pentane from this solution under a reduced pressure, 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 (ν H—C=C), 2950, 2843 (ν C—H), 1598 (ν C=C), 1403, 1270 (δ C—H), 1137, 472 (ν Si—O—Si), 829 (δ Si—OCH_3), 784 (ν Si—C), 549 (δ Si—C=C); ^{1}HNMR ($CDCl_3$, ppm): δ 5.82–6.10 (m, H_2C = CH—, 6H), 3.56 (s, —OCH_3, 54H), 0.67 (m, Si—CH_2, 24H); ^{13}CNMR ($CDCl_3$, ppm): δ 129.63 ($\mathbf{C}H{=}CH_2$), 136.49 ($CH{=}\mathbf{C}H_2$), 50.71 (Si—$O\mathbf{C}H_3$), 3.43 (Si—$\mathbf{C}H_2$—CH_2—Si$(OCH_3)_3$), 0.68 (Si—$\mathbf{C}H_2$—$\mathbf{C}H_2$—Si$(OCH_3)_3$); MS (ESI): 1387 (M + Na^+, adduct ion).

2.5. *Preparation of room temperature vulcanized silicone rubber*

The general preparation procedures of RTV silicone rubbers are as follows. HPDMS polymer was charged into a three-necked flask, and stirred at 130 °C for 2 h under dry nitrogen by mechanical stirrer. After the mixture was cooled to room temperature under vacuum, the ethyl ether solution of OPS and curing catalyst (101#) was added into flask with vigorously stirring, and the mixture was obtained after stirring for 15 min, then volatile compounds were removed in vacuum around 15 min. The mixture was poured into a Teflon mold subsequently, and cured for about 2 d at room temperature to give an about 3 mm thick sheet of RTV silicone rubber with smooth surface.

A variety of PDMS composites were prepared respectively using cross linking agent (such as DVPS, TEOS and TMOS) as a substitute for OPS cross-linker according to the same approach above, and their formulations were listed in Table 1.

2.6. *Characterizations and measurements*

^{1}H NMR 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 $CDCl_3$ (0.05% TMS as an internal standard). Mass spectra were obtained from a Waters (Miford, MA, USA)-ZQ electrospray ionization (ESI)-quadrupole mass spectrometer. X-ray diffraction (XRD) analysis was carried out on a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα radiation, and the steps size and scan rate were 0.02° and 6°/min, respectively. Infrared (IR) spectra of the solid samples were measured using KBr pellet technique with a Nicolet AVATAR 360FT infrared analyzer. IR spectra of rubber specimens were carried out on a Nicolet NEXUS 670 Spectrometer by ATR (attenuated total reflection). Thermal gravimetric analysis (TGA) coupled with IR was performed on SETSYS-1750 (SETARAM Instruments). About 10 mg of sample cut as small pieces was heated in an Al_2O_3 crucible in air atmosphere from ambient temperature to 650 °C at a heating rate of 10 °C/min, and in nitrogen atmosphere from ambient temperature to 800 °C at a constant rise of temperature (10 °C/min). Mechanical tensile tests were performed on a universal testing machine (Shimadzu, AGS-J, capacity 10 kN), at 25 °C and around 60% RH. The tensile strength, elongation at break and modulus were measured by using a 50 mm/min cross-head speed. The dumbbell-shaped specimens were obtained from vulcanized sheet, and an average of at least three measurements for each sample was recorded. The shore A Hardness is the relative hardness of elastic materials such as rubber can be determined with an instrument called a Shore A durometer (LX-A) according to ASTM D1415-88 (1999). Morphological studies were preformed on an FEI Quanta 200 scanning electron microscope (SEM) at a voltage of 30 kV. The cured samples were placed into liquid nitrogen for 5 min and then fractured into two pieces to create fresh surfaces. The fractured surfaces of all the samples were placed in scanning electron microscope after they were coated with gold.

Table 1
The formulations of RTV silicone rubbers and TG results for the RTV silicone rubbers obtained in N_2.

Sample	cross-linker		Temperature for 5% weight loss (°C)	Temperature for 10% weight loss (°C)	Temperature of peak degradation, T_{max} (°C)	Residual yield at 800 °C (%)
	Alkoxyl groups (mmol)	Wt%				
TM-1	78.8	10.0	367	402	492	0.7
TE-1	57.6	10.0	387	419	486	0.8
OP-1	44.7	10.0	466	497	580	11.1
DVP-1	39.5	10.0	434	460	510	4.1
TE-2	78.8	13.7	374	423	504	0.6
OP-2	78.8	17.6	447	460	467, 499	1.4
DVP-2	78.8	19.9	453	481	510, 573	14.4

2.7. *Extraction and swelling experiments*

Extraction/swelling experiments in toluene were used to estimate the cross linking density. Samples approximately 1 × 1 cm were cut from the 3 mm thick sheet and then were weighed (W_o'). The samples were immersed in toluene (20.00 mL) in stoppered bottles for 120 h, and the toluene was refreshed each 24 h. The swelled-samples were then removed from the bottles, excess solvent was removed by blotting with tissue paper, and the weights (W_{sw}) of the toluene-swollen samples were determined. The toluene-swollen samples were dried in a vacuum oven until at a constant weight (W_o). The magnitude of the sol fraction was determined by Eq. (1):

$$s = \frac{W_o' - W_o}{W_o'} \times 100\% \tag{1}$$

where S is the soluble fraction (%), and the degree of swelling (d_{sw}, %) was also calculated according to the following Eq. (2):

$$\mathrm{dsw} = \frac{W_{sw} - W_o}{W_o} \times 100\% \tag{2}$$

3. Results and discussion

In this work, novel materials were prepared through hydrolysis under moisture and condensation between HPDMS and POSS cross-linkers freshly prepared in the presence of organotin catalyst. The cross linking process between HPDMS and cross-linkers was very sensitive to changes in several factors such as the concentration of cured catalysis, weight fraction of cross linking agents relative to amount of used HPDMS and types of HPDMS, moisture and temperature under ambient circumstance. Hence, in this study only one type and concentration of cured catalyst, one type of HPDMS polymers were used, and all experimental samples were prepared in the same conditions.

Before novel RTV silicone rubbers were prepared, we had done a lot of controlling experiments on conventional RTV silicone rubbers prepared using cross-linkers (TEOS and TMOS). As a result, we found that conventional RTV silicone rubbers prepared using 10 wt% cross-linker (TMOS) relative to the amount of HPDMS had better thermal stability and mechanical property, compared with using the other weight fractions. Hence, we designed the following experiments according to this weight fraction (10 wt% TMOS relative to amount of used HPDMS).

To investigate the effect of different types of cross-linkers on thermal stabilities and mechanical properties of PDMS polymer systems, samples of novel RTV silicone rubbers containing equivalent mass fraction (10%) and equimolar amount (78.8 mmol) of alkoxy groups of different cross linking agents were prepared. The concentration of HPDMS and cured catalyst was kept constant and the cured reaction was performed at room temperature in the presence of air.

The network structures of the novel RTV rubbers were confirmed by ATR Infrared spectroscopy and the extraction/swelling experiment. And morphology, thermal stabilities properties, mechanical properties and hardness properties of novel RTV silicone rubbers were studied by scanning electron microscopy, thermal gravimetric analysis experiments, universal tensile testing experiments and shore A durometer, respectively. These results would be discussed in the following sections in detail.

3.1. Synthesis of novel RTV silicone rubbers with Vinyl-POSS derivatives

Vinyl-POSS was firstly prepared by hydrolytic polycondensation of vinyltrimethoxysilane in the presence of strong acid (HCl). The structure of Vinyl-POSS powder was characterized by mean of X-ray diffraction analysis. Fig. 1 displays XRD pattern of Vinyl-POSS. The Vinyl-POSS shows a sharp intense peak at 2-theta of 9.8°, with the other characteristic peaks at 2-theta of 13.0°, 19.5°, 21.0°, 22.8°, 23.6° and 29.6°. This indicated that the Vinyl-POSS powder was highly crystalline.

However, the syntheses of novel cross linking agents are very crucial to preparation of novel RTV elastomers. In the present work, we have successfully synthesized the two kinds of Vinyl-POSS derivatives through hydrosilylation of Vinyl-POSS with trimethoxysilane for the first time. The catalyst is chloroplatinic acid, which is classical hydrosilylation catalyst [37,38]. In this hydrosilylation reaction, steric hindrance of α-addition (terminal) would be bigger than that of β-addition, and the addition reaction was generally carried out as a result of both a small amount of α-addition and primarily β-addition of trimethoxysilane to Vinyl-POSS, which was confirmed via ^{13}CNMR experimental technique. Therefore, the resulting novel cross-linkers (DVPS and OPS) are mixtures.

DVPS was synthesized through controlling the molar ratio of silane to Vinyl-POSS (about 6:1), and meanwhile a mixture of POSS with different degree of vinyl substitutions was also obtained. The positive-ion mode ESI mass spectrum of the mixture of DVPS cross-linker (Fig. 2a) reveals a major ion peak at $m/z = 1387$ with 100% of relative intensity, which can be attributed to DVPS plus sodium ion. The peaks at m/z = 1145, 1266 and 1511 indicate sodium ion adducts of POSS with different degree of vinyl additions. The average number of the remaining vinyl groups per cage is estimated to be 2 by ^{1}HNMR, which is corresponding with the molar ratio we employed. And OPS cross-linker was also prepared through adding a larger excess molar ratio of silane to Vinyl-POSS under the same condition. In this addition reaction, adding an excess molar ratio of trimethoxysilane to Vinyl-POSS was to overcome steric hindrance to promote the hydrosilylation reaction completely. In this case, steric hindrance was caused by the two factors such as Vinyl-POSS cage and reacted vinyl groups during further hydrosilylation reaction. The peaks at m/z = 1631, 1632, 1633 and 1634 should be assigned to a sodium ion adduct of OPS, as showed in Fig. 2b, and this characteristic peak at $m/z = 1632$ also appears in Fig. 2a. This implied that the mixture of cross-linker DVPS also contained a trace amount of OPS. A similar approach was adopted in synthesizing mesoporous organic–inorganic hybrid materials with hierarchical structure using predefined Vinyl-POSS derivative as the only building blocks [39] by Zhang et al., and they weaved the POSS cages into an infinite mesoporous structure by a block-copolymer-assisted co-assembly method.

The PDMS composites were synthesized through the hydrolytic condensation reaction between the cross linking agents and HPDMS at room temperature in the catalysis of organotin (101#). In this curing reaction, the cross linking network was achieved by the hydrolyzation of Si–OCH$_3$ groups and the condensation of Si–OH groups. The relative humidity of ambient circumstance also can promote crosslink of HPDMS polymer systems, therefore the curing mold should be set over the water bath of which the temperature was controlled at 25 °C for a constant relative humility of ambient circumstance.

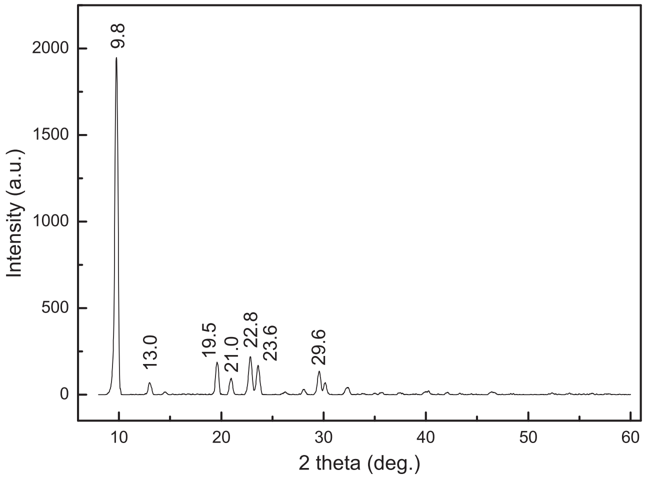


Fig. 1. The X-ray powder diffraction pattern of Vinyl-POSS.

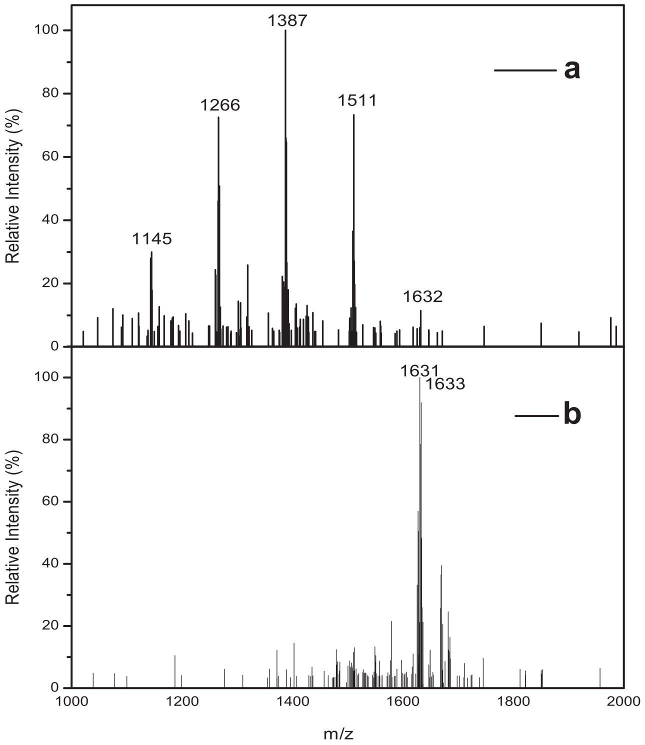
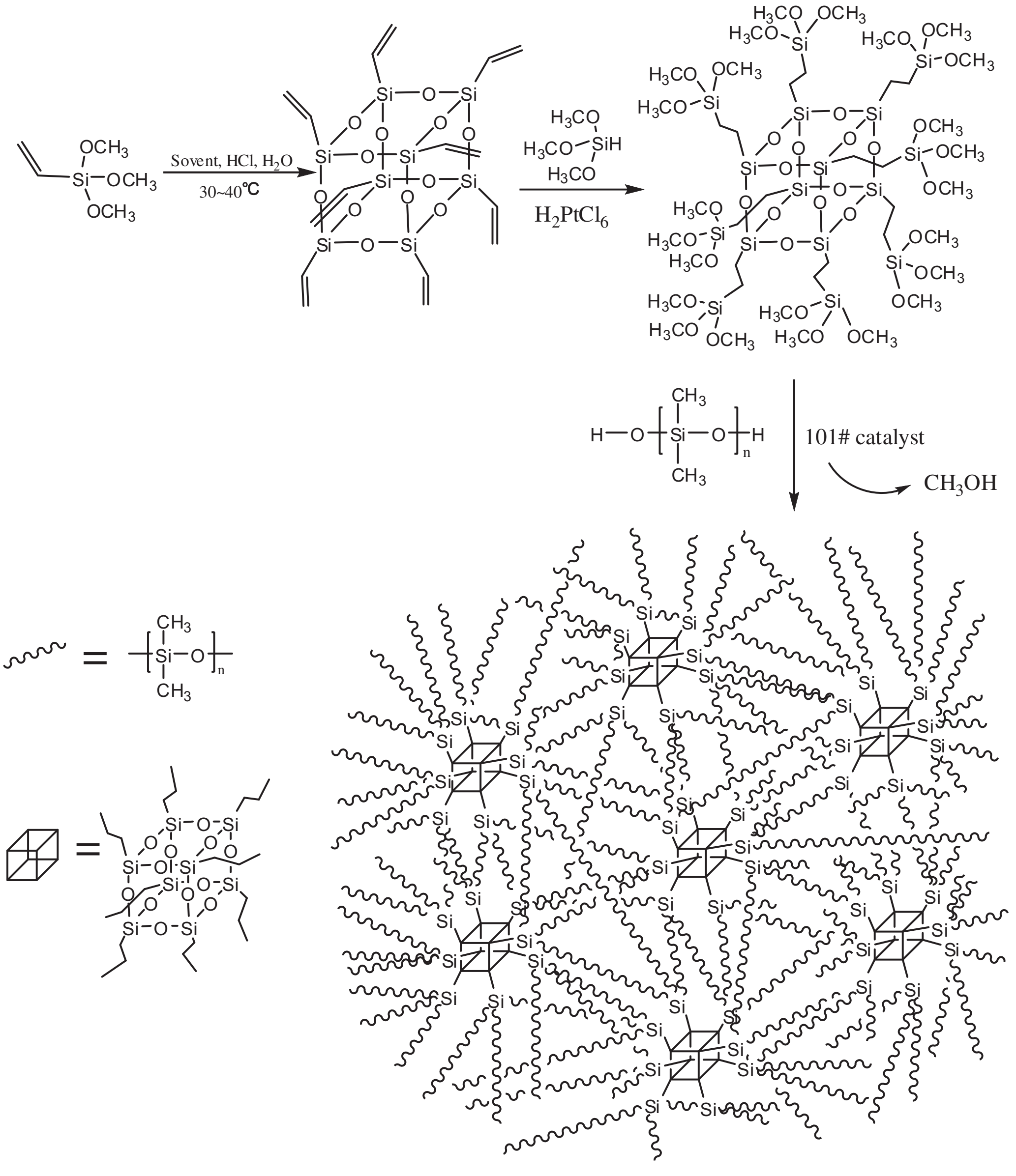


Fig. 2. Positive-ion mode ESI mass spectra of (a) DVPS and (b) OPS.

The prepared processes of novel RTV silicone rubbers (OP) using OPS as cross-linker were showed in Scheme 1. Replacement cross-linker OPS with DVPS, samples of another novel RTV silicone rubbers (DVP) were prepared according to the same approach. As reference materials, our groups also synthesized PDMS polymer systems using conventional tetra-functional cross-linkers (such as TMOS and TEOS) with the same mass fraction and equimolar amount of alkoxy groups, respectively. Meanwhile, we attempted to synthesize RTV silicone rubbers by simple physical blending novel cross-linker (OPS and DVPS) with HPDMS without curing catalyst (101#). Unfortunately, these reference materials hadn't been prepared successfully because these mixtures remained viscous liquid and couldn't vulcanize into elastomers at RT, even after curing times were extended (several weeks). The abbreviations for each PDMS polymer systems are as follows: PDMS composites prepared with the cross linking agent TMOS, TEOS, OPS and DVPS are respectively denoted as TM, TE, OP and DVP. A variety of PDMS composites prepared with different cross-linkers were listed in Table 1.

3.2. Characterization of novel RTV silicone rubbers with Vinyl-POSS derivatives

The cross-linked network structure of the select RTV silicone rubbers can be measured by FTIR. The samples were studied by ATR infrared spectroscopy measurements on the silicone elastomeric surface. The infrared spectra of cured PDMS were dramatically changed as compared with that of uncured PDMS. The differences between cured and uncured PDMS cured were shown in Fig. 3. Although the two types of novel cross-linkers had hydrolyzed partly, the changes of mainly characteristic bands can be discerned clearly in Fig. 3. A broad peak at 3448 cm^{-1} and a weak peak at 1630 cm^{-1} of HPDMS (107#) spectrum are attributed to stretching and deformation vibration of silanol (Si—OH), respectively, which completely disappeared after HPDMS was cured. The two sharp bands at 2964 cm^{-1} and 2905 cm^{-1} are due to asymmetric and symmetric C—H stretching vibrations of Si—CH_3. And the band at about 2840 cm^{-1} is assigned to the C—H stretching vibrations of Si—O—CH_3 structure of novel cross-linkers, which utterly



Scheme 1. Prepared procedures of novel RTV silicone rubber using POSS as cross-linker.

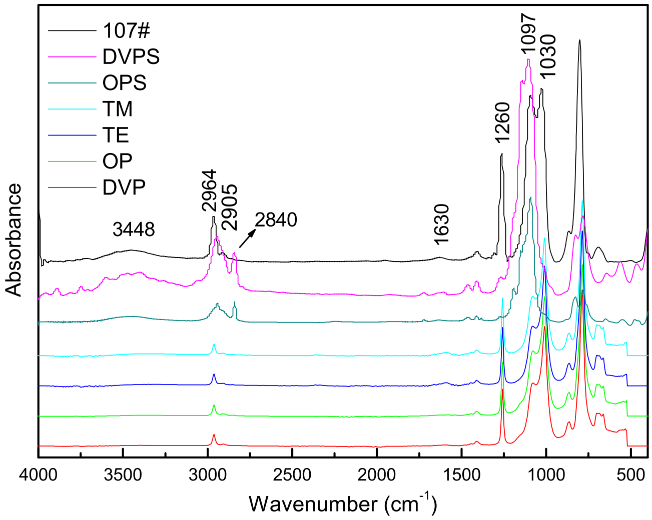


Fig. 3. Infrared spectrum of uncured and cured PDMS (DVP, OP, TM and TE denote PDMS prepared with DVPS, OPS, TMOS and TEOS, respectively).

disappeared after HPDMS was cured. It could be said that silanol of HPDMS and Si–O–CH_3 of novel cross-linkers reacted completely. Moreover, the asymmetric Si–O–Si stretching vibration band around 1097 cm^{-1} of all cured samples (DVP, OP, TE and TM) becomes weaker, and the band at 1030 cm^{-1} of all cured samples likely resulting from the random structure of the asymmetric Si–O–Si stretching vibration [2] becomes sharper as compared with those of HPDMS, which suggest that silanol had reacted completely with cross-linkers, and new cross-linked networks of Si–O–Si had formed in the matrix of PDMS. The infrared spectra also confirmed the design of preparation in Scheme 1.

3.3. *Morphologies of the novel RTV silicone rubbers: SEM characterization*

In this study, these DVPS and OPS cross-linkers were chemically incorporated into PDMS polymeric system to prepare novel RTV silicone rubbers. The conventional RTV silicone rubbers prepared with tetra-functional cross-linkers (TMOS and TEOS) were transparent, but the novel RTV silicone rubbers were semi-transparent, which indicated that the novel cross-linkers (DVPS and OPS) were incompatible with the PDMS polymer, and possible phase separation was induced by the cross linking process. To improve on transparence of novel RTV silicone rubbers, novel cross-linker (OPS or DVPS) was added into HPDMS before cured catalyst was added. It was found that the mixtures of novel cross-linker (OPS or DVPS) and HPDMS without the cured catalyst appeared pale. And all of these mixtures became vaguer after the cured catalyst was added. After curing completely, the transparence of novel RTV silicone rubbers became weak, and semi-transparent RTV silicone rubbers were again obtained. Unfortunately, we failed to improve on the transparence of novel RTV silicone rubbers, but the further works on improvement in their transparence are in progress.

The distribution of POSS moieties in polymer matrices had great effect on both thermal and mechanical properties of resultant composite systems [40–43]. And subsequent morphologies of the novel RTV silicone rubbers were investigated by means of scanning electron microscopy (SEM). Fig. 4 presented the SEM images (on fractured surfaces) of two types of novel RTV silicone rubbers. Various micron-sized spherical domains (bright part) and holes in

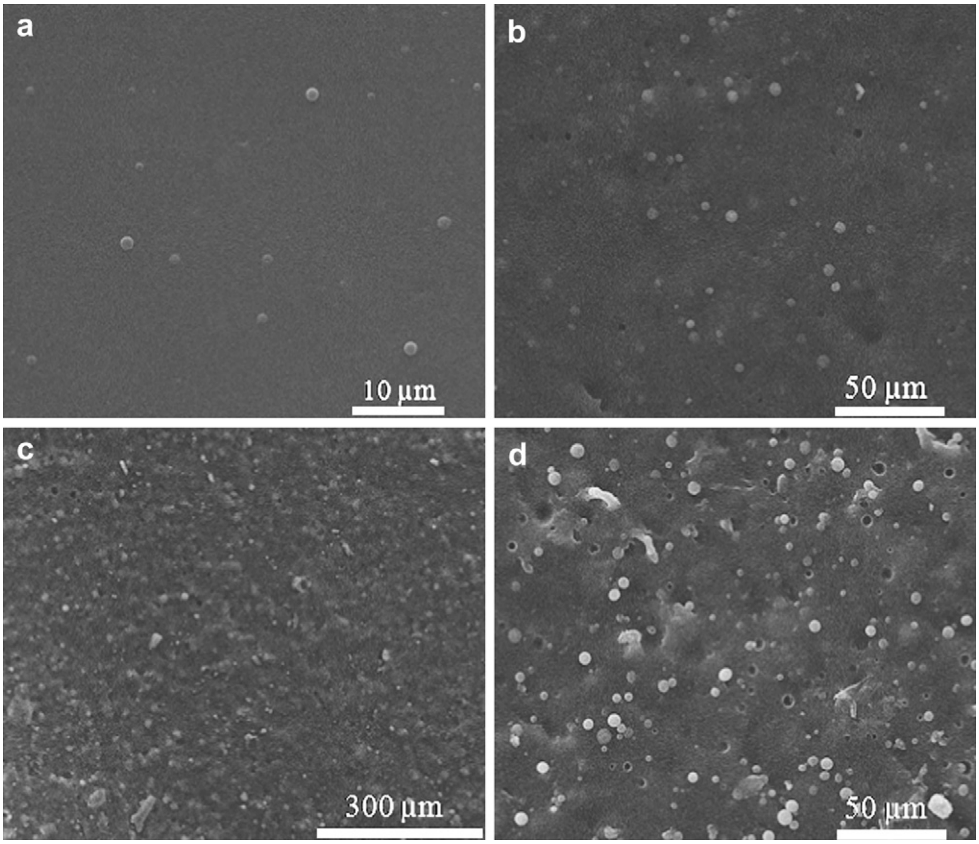


Fig. 4. SEM micrographs of the fractured surfaces of the novel RTV silicone rubbers: (a) DVP-1, (b) OP-1, (c) DVP-2 and (d) OP-2.

the novel RTV silicone rubbers were observed in each of these micrographs in Fig. 4. The micron-sized spherical domains were likely to be POSS-rich clusters [42,44], which were ascribed to aggregation of self-cross-linked DVPS and OPS cross-linkers. A large number of the micron-sized white spheres were almost embedded into the RTV silicone rubbers, but some ones were nearly bare on the fractured surfaces. The numerous holes on the fractured surfaces should be due to remaining space resulting from the fracture of the aggregated phase domains when the samples were fractured in liquid nitrogen. In the novel RTV silicone rubbers prepared with equivalent weight fraction of DVPS and OPS cross-linkers, these aggregated cross-linked DVPS and OPS domains were significantly small and uniformly dispersed in the novel RTV silicone rubbers, as shown in Fig. 4a and b. The micron-sized spheres (white dots) in the novel RTV silicone rubbers prepared with equimolar amount of alkoxy groups of DVPS and OPS cross-linkers became much more than those of the ones prepared with equivalent weight fraction of DVPS and OPS cross-linkers, as demonstrated in Fig. 4c and d. In addition to the regular micron-sized spheres, some irregular and heterogeneous domains also appeared. The appearances of the irregular and heterogeneous domains were likely caused by aggregation of the excess of self-cross-linked POSS cross-linkers relative to HPDMS in the presence of catalyst.

3.4. *Thermal degradation stability*

Two types of novel RTV silicone rubbers were successfully prepared through hydrolytic condensation between HPDMS and Vinyl-POSS derivatives under moisture at room temperature. To investigate improvement effect of PDMS polymer system incorporating with Vinyl-POSS derivatives, the thermal properties of RTV silicone rubbers with equivalent weight fraction of different cross linking agents and equimolar amount of alkoxy groups of cross linking agents were evaluated by thermal gravimetric analysis experiments respectively.

Initially, the thermal degradation behaviors of RTV silicone rubbers with the equivalent weight fraction of different cross linking agents (DVP-1, OP-1, TE-1 and TM-1) in nitrogen atmosphere were investigated. In nitrogen atmosphere, only a single degradation step was also observed in Fig. 5 and the important characteristic data were summarized in Table 1. For instance, the temperatures of 5% mass loss for TM-1 sample, TE-1 sample and DVP-1 sample were 367 °C, 387 °C and 434 °C, respectively, but 466 °C for OP-1 sample, which was the highest among all of these PDMS polymers. The initial thermal stabilities of the cross linking PDMS polymers maximally increased by 99 °C from 367 to 466 °C when novel cross-linkers (Vinyl-POSS derivatives) were used instead of conventional cross linking agents (such as TEOS and TMOS). The TG curves of TM-1 and TE-1 samples almost overlapped, which indicated that both samples had the same thermal stabilities. The characteristic temperatures of 10% weight loss were delayed from 402 °C (TM-1 sample) to 497 °C (OP-1 sample). The temperatures of maximum peak degradation were also delayed from 486 °C (TE-1 sample) to 580 °C (OP-1 sample). And two small humps at around 530 °C (OP-1) and 567 °C (DVP-1) were observed respectively in Fig. 6. These humps probably implied that both OP-1 and DVP-1 samples underwent different degradation mechanisms during the course of depolymerization as compared to the samples (TM-1 and TE-1). Moreover, the degradation remaining residues of the tested samples at 800 °C are much different. TM-1 and TE-1 samples hardly degraded completely at 800 °C in nitrogen, but DVP-1 and OP-1 samples retained 4.1% and 11.1% of the initial mass, respectively. From the discussions above, it could be concluded that Vinyl-POSS derivatives has a significant improvement on thermal stability of the cross-linked PDMS prepared with equivalent mass fraction of different cross-linkers.

Additionally, the thermal degradation behaviors of these PDMS polymers prepared with equimolar amount of alkoxy groups of different cross-linkers (DVP-2, OP-2, TE-2 and TM-1) in nitrogen were also investigated. The superior thermal stabilities of these novel PDMS polymers prepared with novel cross-linkers (DVPS and OPS) over those of the PDMS prepared with conventional cross-linkers (such as TEOS and TMOS) are immediately apparent, as shown in Fig. 7, and the important characteristic data were presented in Table 1. Although the curves of all these PDMS polymers exhibited one similar trend of degradation, the characteristic temperatures of onset degradation were delayed. For example, the temperatures of 5% weight loss for TM-1 sample, TE-2 sample and OP-2 sample were 367 °C, 374 °C and 447 °C respectively, but 453 °C for DVP-2 sample, which was highest among all of these PDMS polymers. And the temperatures of 10% weight loss also exhibited a similar regularity of 5% weight loss. Moreover, it was interesting that novel RTV silicone rubbers (samples DVP-2 and OP-2) exhibited two characteristic temperatures of peak degradation, but only one for conventional RTV silicone rubbers (samples TE-2

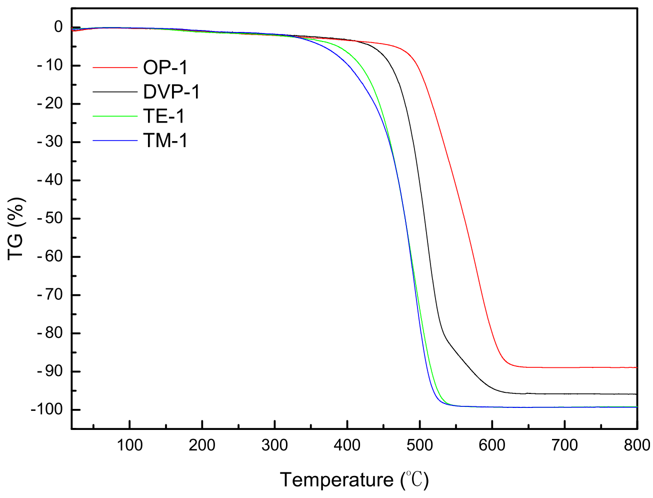


Fig. 5. TG curves for RTV silicone rubber containing the equivalent mass fraction of different cross linking agents in nitrogen atmosphere.

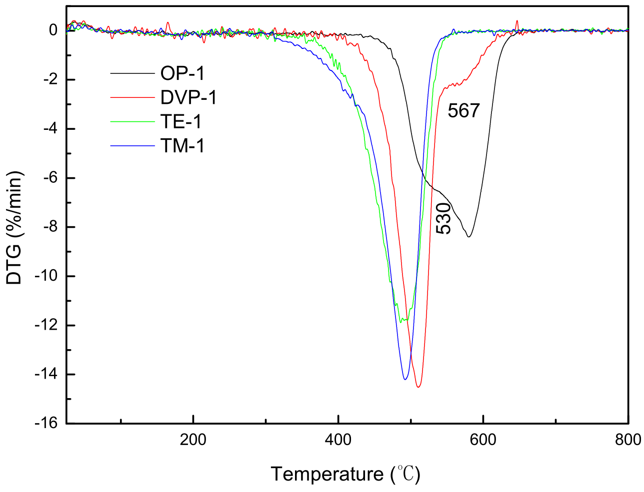


Fig. 6. DTG curves for RTV silicone rubber containing the equivalent mass fraction of different cross linking agents in nitrogen atmosphere.

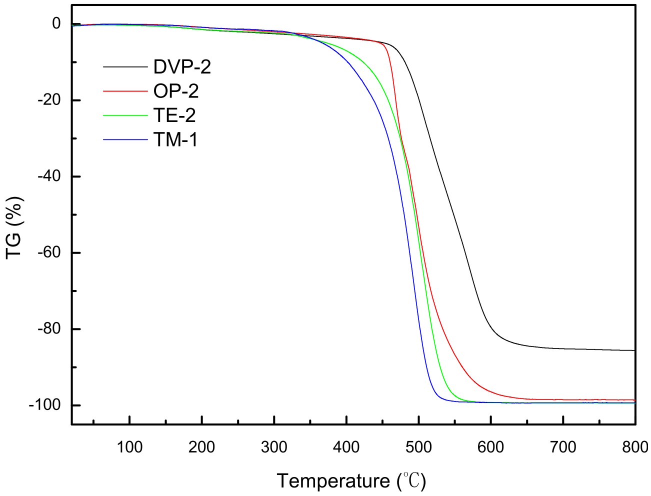


Fig. 7. TG curves for RTV silicone rubber containing the equimolar amount of alkoxy groups of different cross linking agents in nitrogen atmosphere.

and TM-1), as shown in Fig. 8 and Table 1. These changes of characteristic temperatures of peak degradation between novel RTV silicone rubbers and conventional RTV silicone rubbers probably also implied the existence of different degradation mechanisms. The degradation mechanism would be discussed in the below section. Additionally, all of these PDMS polymers had hardly residual mass at 800 °C except DVP-2 sample with 14.4 wt%, which suggested that DVP-2 sample had the best thermal resistance among all of PDMS polymers, and DVPS had a significant improvement on thermal stability of the PDMS polymer system. Due to the superiorities above, Vinyl-POSS derivatives could be developed as a novel type of thermal resistance material.

In nitrogen atmosphere, the enhancement effect of thermal stability on RTV silicone rubbers prepared with equivalent mass fraction of different cross linking agents (DVP-1, OP-1, TE-1 and TM-1) is attributable to special three-dimensional caged structures of POSS cross-linkers and uniform dispersion of self-linked POSS cross-linkers. In other words, both OPS and DVPS have many active sites, which facilitate formation of new spatial three-dimensional networks during the vulcanized process of HPDMS and Vinyl-POSS derivatives, and the linear HPDMS are facile to crosslink into novel branched PDMS. The new three-dimensional networks of PDMS polymer decrease the flexibility of the PDMS chain, hinder the formation of cyclic oligomers and delay the temperatures of thermal degradation of the PDMS polymer. Similar study was also found that the thermal stability of the branched PDMS is higher than that of the linear one, which indicated that the branched structure benefits the formation of a crosslink in the solid residue [28]. On the other hand, uncured hydroxyl groups in chains of PDMS or POSS cross-linkers also have an important influence on the thermal stability of RTV silicone rubbers. OP-1 sample has the best thermal stability and the highest residual yield among all of these PDMS samples, which is likely due to forming the structure of the effective three-dimensional networks and the least molar amount of uncured hydroxyl groups in sample OP-1. As compared with sample OP-1, sample DVP-1 has more molar amount of remaining hydroxyl groups (a small hump around 3400 cm^{-1}), as shown in Fig. 9, which low the thermal stability of PDMS considerably, and therefore less residue was left after sample DVP-1 degraded. This effect of the remaining hydroxyl groups on thermal stability of PDMS polymer is consistent with the result of previous studies [45,46].

However, the changes of RTV silicone rubbers prepared with equimolar amount of alkoxy groups of different cross-linkers (DVP-2, OP-2, TE-2) are not always similar to those of the ones prepared with equivalent mass fraction of different cross linking agents (DVP-1, OP-1, TE-1 and TM-1). But the RTV silicone rubbers prepared with novel POSS cross-linkers have better thermal stability than the ones prepared with TEOS and TMOS from the overall trends of degradation. The observed improvement effect of thermal stability on RTV silicone rubbers prepared with equimolar amount of alkoxy groups of different cross-linkers (DVP-2, OP-2, TE-2 and TM-1) is attributed to heavily cross-linked PDMS and uniform distribution of POSS-rich domains (as evidenced by the results of SEM) in addition to the effective spatial three-dimensional networks. The remaining vinyl groups of cross-linked PDMS prepared using DVPS as cross-linker also can favor to crosslink into heavily cross-linked phase through some radicals formed in the process of thermal depolymerization of PDMS chains. The heavily cross-linked PDMS resulting from coupling of macro radicals decreases the flexibility of the PDMS chains and hinders splitting of cyclic oligomers still further [47]. OP-2 sample has no remaining vinyl groups and couldn't form the heavily cross-linked phase during degraded process, compared with DVP-2 sample. The

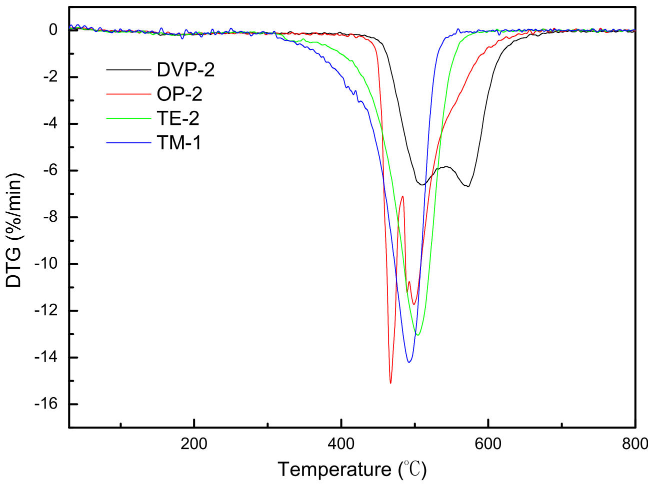


Fig. 8. DTG curves for RTV silicone rubber containing the equimolar amount of alkoxy groups of different cross linking agents in nitrogen atmosphere.

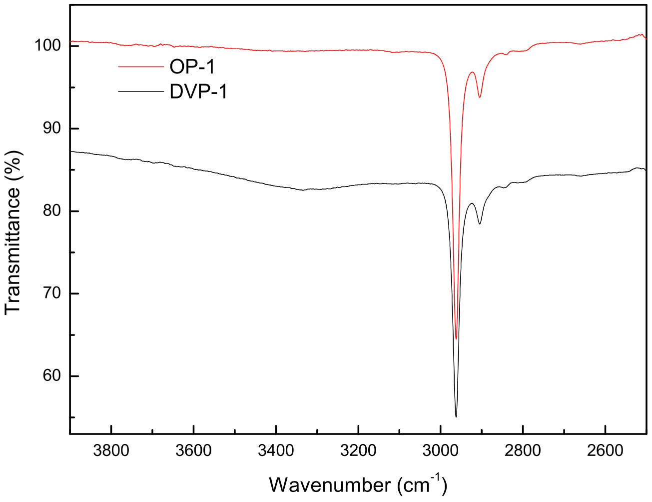


Fig. 9. Partly characteristic IR spectra of the novel RTV silicone rubbers containing the same mass fraction of different cross-linkers.

heavily cross-linked phase likely results in an increase in residue and improvement in thermal stability of the DVP-2 sample. However, the distribution of POSS-rich domains in PDMS polymer also has a great effect on thermal stability of resultant RTV silicone rubbers. The uniform distribution of POSS-rich domains is favorable for improvement in thermal stability of the resultant RTV silicone rubbers. The distribution of POSS-rich domains in the OP-2 sample couldn't be so uniform as that of ones in the DVP-2 sample. The cross-linker OPS has more reactive sites than the cross-linker DVPS, which likely leads to a non-uniform distribution of POSS-rich domains in the OP-2 sample. Hence, the DVP-2 sample has better thermal stability and higher residual yield as compared with the OP-2 sample.

3.5. *Thermo-oxidative stability*

The thermo-oxidative behavior of the examined PDMS is obviously more complex than the aforementioned thermal degradation behavior in nitrogen atmosphere. Two degradation steps are observed in Figs. 10–13. The first degradation step around between 330 and 400 °C has weight loss of about 10%, and the greatest amount of weight loss occurs in the second degradation step between 400 and 580 °C.

First of all, the thermally oxidative behaviors of RTV silicone rubbers with the equivalent mass fraction of different cross linking agents (DVP-1, OP-1, TE-1 and TM-1) in air atmosphere were also studied, and the most important features of characteristic mass loss temperatures and residues were presented in Table 2. In the first degradation step, a low weight loss of around 10% was observed, and the temperatures of 10% weight loss were delayed from 388 °C (TM-1 sample) to 436 °C (DVP-1 sample). In the second degradation step, the greatest amount of weight loss took place between 400 and 580 °C, as shown in Figs. 10 and 11. For instance, the characteristic temperatures of 30% weight loss were 469 °C for OP-1 and 488 °C for DVP-1 respectively. However, the characteristic temperatures of 50% weight loss were 557 °C for OP-1 and 527 °C for DVP-1 respectively. The thermal oxidative stability of DVP-1 sample was likely affected by the remaining vinyl groups and hydroxyl groups. This degraded process probably involved a complex competition between enhancement and reduction of thermo-oxidative stability. The remaining vinyl groups in DVP-1 were easily involved in the further cross linking in air, and favored to improve its thermo-oxidative stability, but the remaining hydroxyl groups in DVP-1 (confirmed by Fig. 9) were favorable to low its thermo-oxidative stability. The effect of remaining vinyl groups on thermo-oxidative stability of DVP-1 likely predominated at low temperature, but the effect of remaining hydroxyl groups on thermo-oxidative stability likely predominated at high temperature. In Table 2, it was also found that the thermal stabilities of novel RTV silicone rubbers were all improved as compared with those of the conventional RTV silicone rubbers. Moreover, the residual yields at 600 °C were improved. OP-1 sample had the highest residue yield (49.4%) among all of these cross-linked PDMS polymers, which was 6.2% higher than that of DVP-1 sample.

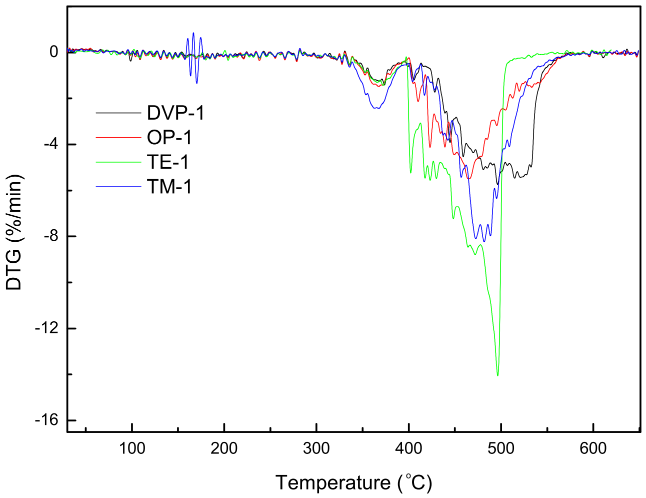


Fig. 11. DTG curves for RTV silicone rubber containing the equivalent mass fraction of different cross linking agents in air atmosphere.

The overall degraded processes of these RTV silicone rubbers prepared with equimolar amount of alkoxy groups of different cross linking agents are similar to the ones prepared with equivalent weight fraction of different cross-linkers, as demonstrated in Figs. 12 and 13. The DTG curves in Figs. 11 and 13 are less smooth than those of these polymers obtained in nitrogen atmosphere (Figs. 6 and 8) due to vigorously oxidative reaction in air. Although the initial thermal stabilities of these polymers PDMS (DVP-2, OP-2, TE-2 and TM-1) are approximately similar, the final resistant thermo-oxidative stabilities of these PDMS polymers have many

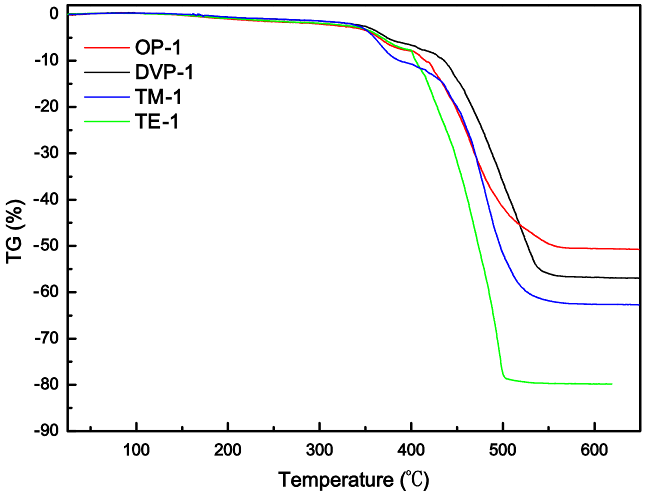


Fig. 10. TG curves for RTV silicone rubber containing the equivalent mass fraction of different cross linking agents in air atmosphere.

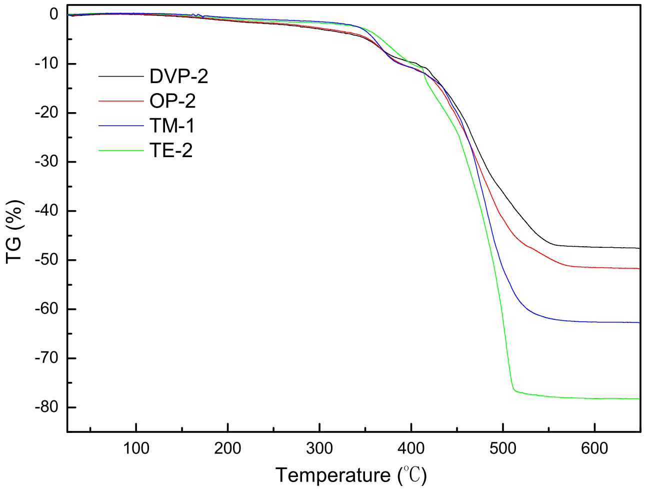


Fig. 12. TG curves for RTV silicone rubber containing the equimolar amount of alkoxy groups of different cross linking agents in air atmosphere.

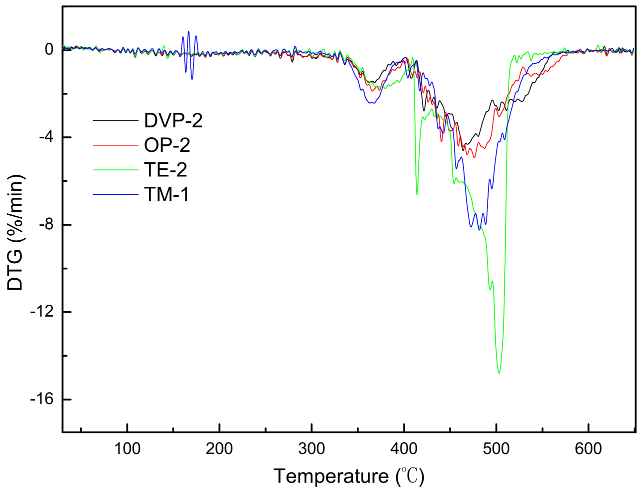


Fig. 13. DTG curves for RTV silicone rubber containing the equivalent mole amount of alkoxy groups of different cross linking agents in air atmosphere.

differences. For example, the temperatures of 5% mass loss for the novel RTV silicone rubbers are lower than those of conventional RTV silicone rubbers, which can be seen clearly in Table 3. Among all of these PDMS polymers, TE-2 sample has the lowest characteristic temperature of 30% and 50% mass loss and the lowest residue yield at 600 °C (21.8% of the initial mass), which indicate that TE-2 sample has the lowest resistant thermo-oxidation behavior. However, the resistant thermo-oxidation stabilities of novel RTV silicone rubbers are better as compared with those of conventional RTV silicone rubbers, especially, sample DVP-2 has the highest degradation residual mass at 600 °C, about 52.6 wt%, which is 4.1 wt% more than that of sample OP-2. As for sample TM-1, the degradation residue yield at 600 °C is 11.1% less than that of sample OP-2.

Moreover, it is interesting that the amount of degraded residue obtained in air was substantially higher than that obtained in nitrogen. The reason for this phenomenon is that in air, cross-linked oxidized structures are formed, which protect the residue from further exhaustive thermal degradation [34]. From the discussed above, using Vinyl-POSS derivatives (OPS and DVPS) as cross-linkers are indeed beneficial to improving on thermo-oxidative stabilities of these PDMS polymers when using TEOS and TMOS as cross linking agents. In this case, the improvements in thermo-oxidative stabilities should be attributed to the three-dimensional networks of cross-linked PDMS polymers resulting from three-dimensional cages of Vinyl-POSS derivatives, uniform distribution of POSS-rich domains and heavily cross-linked oxidized structures.

3.6. *The degradation mechanism*

Up to the present, four mainly different mechanisms have been proposed for thermal degradation of PDMS in inert atmosphere due to variations in the method of preparation, the level of impurities and residual catalyst, and the degradation of conditions: (a) the end-initiated unzipping mechanism; (b) the random main chain scission mechanism; (c) the externally catalyzed mechanism for polymers containing impurities and residual catalyst [48]; and (d) molecular mechanism [47,49]. The mechanisms stated above don't take place independently, but they go on simultaneously sometimes, which are complex and reported in recent studies [45,49].

Table 2
TG data of RTV silicone rubbers with equivalent mass fraction of different cross-linkers obtained in air.

Sample no.	Temperature for 10% weight loss (°C)	Temperature for 30% weight loss (°C)	Temperature for 50% weight loss (°C)	Residue at 600 °C (%)
TM-1	388	470	497	37.4
TE-1	405	448	473	20.2
OP-1	416	469	557	49.4
DVP-1	436	488	527	43.2

Table 3
TG data of RTV silicone rubbers with equimolar amount of alkoxy groups of different cross-linkers obtained in air.

Sample no.	Temperature for 5% weight loss (°C)	Temperature for 30% weight loss (°C)	Temperature for 50% weight loss (°C)	Residue at 600 °C (%)
TM-1	360	470	497	37.4
TE-2	368	461	489	21.8
OP-2	354	472	555	48.5
DVP-2	352	479	–	52.6

It is well-known that hydroxyl terminated PDMS (107#) depolymerizes mainly from chain ends with an appreciable contribution of random degradation as well, and the extent of random degradation increases with the increase of temperature [45], as shown in Fig. 14. The maximum degradation peak at 518.0 °C was assigned to the end-initiated degradation, and a followed small hump was due to random degradation.

However, it is interesting that novel RTV silicone rubbers also exhibit two characteristic temperatures of peak degradation in their overall thermal degradation process in nitrogen, but only one for conventional RTV silicone rubbers, as shown in Figs. 6 and 8. In these cases, it was reasonable that two different degradation mechanisms existed in their degradation processes. The positions of the first DTG peaks of all novel RTV silicone rubbers overlapped the position of the DTG curves of conventional ones, which indicated that the degradation reactions were probably initiated in a similar way [48]. The DTG curves of conventional RTV silicone rubbers (TM and TE) without the small humps were due to trace of residual hydroxyl groups in cross-linked PDMS, which could accelerate decomposition of the cross-linked PDMS. Based on the above analysis, we proposed that a mainly ionic catalyzed mechanism occurred for these novel cross-linked PDMS polymers containing organotin cured catalyst, which could form active depolymerization centers (tin-siloxane centers) [50], and catalyze the depolymerization of these cross linking PDMS polymers. The

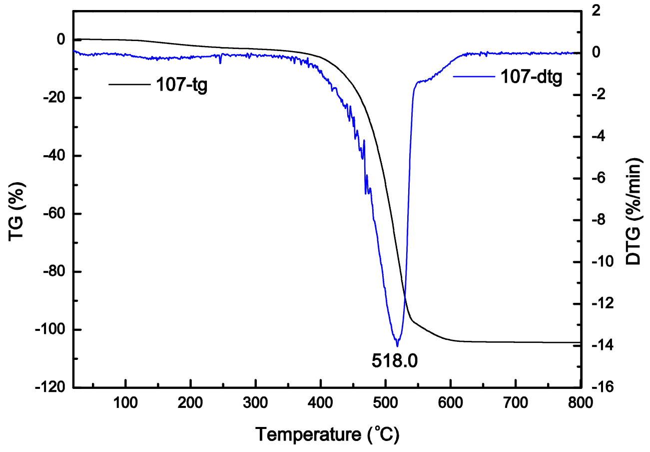


Fig. 14. TG and DTG curves for hydroxyl terminated PDMS (107) obtained in N_2 atmosphere.

DTG curves for all novel RTV silicone rubbers in Figs. 6 and 8 showed that a degradation peak followed another one, which provided convincing evidences that another mechanism governed mainly the degradation process at higher temperatures. This mechanism could be attributed to the random degradation mechanism because the increase chain mobility and molecular motion at higher temperatures might facilitate random degradation [45].

Thermal decomposition process of OP-1 sample was monitored by real-time FTIR being coupled with TGA, and the important characteristic absorbance bands of degraded products were shown in Fig. 15. It is clearly showed that cyclic dimethylsiloxanes (2970, 1265, 1095, 1026 and 814 cm^{-1}) [47] were the main products during the course of thermal degradation. The degraded process can proceed indefinitely with a chain until the residual linear structure is too short to cyclize. The cross-linked PDMS polymers (TE and TM samples) hardly depolymerized completely in nitrogen, as a result, few black solid residues were remained. But many of black residues were obtained in nitrogen for novel RTV silicone rubbers, which indicated that the novel RTV silicone rubbers were more stable at high temperature as compared with the cross-linked PDMS polymers prepared with the conventional cross-linkers. The black solid residues were probably silicon-oxycarbide [28,47,51], which were formed in the process of thermal degradation of heavily cross-linked PDMS. Methane gas was found in degraded process of DVP and OP samples. In this case, another radical mechanism likely occurred through homolysis $Si-CH_3$ bonds scission. This radical mechanism was illustrated in the previous literature [47].

Generally speaking, PDMS polymer undergoes the two major decomposition procedures (such as thermal oxidative and thermal depolymerization) in air atmosphere. Thermal oxidative degradation of PDMS polymer in the presence of air gives results much different from their thermal degradation in nitrogen. It has been found that there are mainly two steps of degradation in air atmosphere. However, a small unnoticeable weight loss was observed prior to the onset of the main decomposition processes in Figs. 5, 7, 10 and 12, which was attributed to low temperature decomposition processes attributable to the presence of ionic impurities or residual polymerization catalysts before the main depolymerization process began [45].

The results of TG curves obtained in air show that a new step appeared when compared with those got in high pure nitrogen, which should be assigned to the thermo-oxidative process of the methyl side groups. The TG results also indicate that the thermal oxidative process occurs predominantly at a lower temperature than the thermal depolymerization in spite of the fact that the two mechanisms overlap to some extent. The first degradation step is likely due to the thermo-oxidative effect, for this thermo-oxidative process probably predominates around 380 °C and involves methyl group oxidative and crosslink formation [49]. The second high temperature process is the thermal depolymerization of the basic chains of the PDMS polymers, which probably predominates around a comparable temperature (above 400 °C) and involves a complex competition between oxygen diffusion and solubility on one side and degraded products evaporation on the others. In degraded steps, the major degradation products are a similar mixture of cyclic oligomers as in nitrogen with additional CO_2 and water. The two steps feature of the process can be assuming that oxygen catalyses the depolymerization reaction of PDMS to volatile cyclic oligomers, leading to a lower temperature for 10% of weight loss than the one obtained in nitrogen [51], as shown in Table 1 and 2. During the course of oxygen catalyzing depolymerization, radical created in the peroxidation chain may also couple with each other, which also leads to the formation of the black stable residue. The black residue is difficult to detect, being finely dispersed in an overwhelming amount of white silica, so residues remain pale.

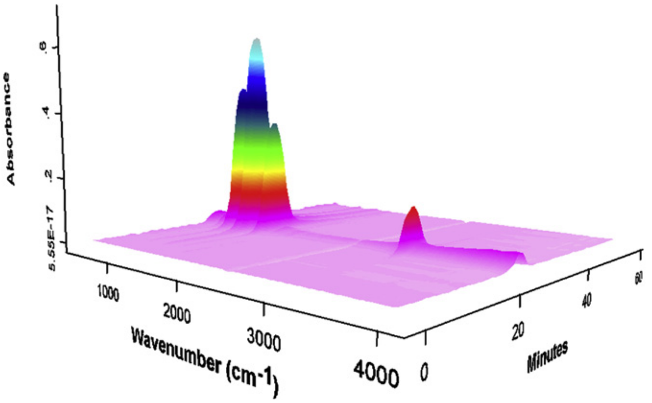


Fig. 15. Real-time FTIR spectra of the OP-1 sample thermal degradation (condition: 20 °C/min and N_2 atmosphere).

3.7. Mechanical properties, swelling properties and hardness

To investigate mechanical reinforcement effect of PMDS polymer systems incorporating with Vinyl-POSS derivatives, the tensile properties and hardness of two different proportions of RTV silicone rubbers were assessed.

The results of mechanical properties such as tensile strength, elongation at break, modulus and hardness of samples were presented in Table 4. The tensile strength and elongation at break improved greatly as the RTV silicone rubbers prepared with Vinyl-POSS derivatives. Especially, the tensile strength of OP-2 and DVP-2 samples increased twice, and their elongation at break almost improved three times, compared with those of TM-1 sample.

Moreover, OP-1 sample has the best mechanical properties among all of the RTV silicone rubbers prepared with equivalent mass fraction of different cross-linkers (10%), which is attributed to form the effective three-dimensional networks and uniform dispersion of micron-sized POSS-rich domains in PDMS matrix. These POSS-rich domains act as enhanced cores as well as cross-linkers in PDMS matrix. Although the improvement effect of Vinyl-POSS derivative on modulus of RTV silicone rubbers is unnoticeable, this also increases from 0.315 to 0.454 MPa. And this subtle increase in modulus of the composites could be due to the rigidity of the bonded three-dimensional networks [33]. The increased dimensionality of the Vinyl-POSS derivatives molecules (i.e., both OPS and DVPS have many reactive groups at the vertices) relative to traditional chemical cross-linkers (four reactive groups) should allow for improved network formation in these PDMS system, which results in improvements in tensile properties, and this enhancement results are consistent with recent report [36].

The mechanical properties of OP-2 sample is close to that of DVP-2 except for hardness, the sol fractions and the swollen degree, which can be seen clearly in Table 4. In this case, the mechanical reinforcement of the cross-linked PDMS polymers likely results

Table 4
Mechanical properties of the RTV silicone rubbers.

Sample	Tensile Strength (MPa)	Elongation at break (%)	Modulus (MPa)	The sol fraction (%)	Degree of Swelling (%)	Shore hardness (A)
TM-1	0.500	125.5	0.430	5.14	297	22
TE-1	0.469	192.8	0.315	5.28	338	18
OP-1	0.914	353.3	0.413	5.84	327	25
DVP-1	0.559	180.4	0.385	4.12	284	25
TE-2	0.514	194.7	0.347	5.12	338	20
OP-2	1.050	368.8	0.451	12.74	623	25
DVP-2	1.105	359.8	0.454	6.78	418	27

from plasticization of self-cross-linked POSS cross-linkers in addition to the formation of special three-dimensional networks. Shore hardness of the novel RTV silicone rubbers are close to 25A, and their tensile strength, elongation at break also increase, which indicate an existence of plasticization effect. On the other hand, the distribution of POSS cross-linkers should be taken into account in explanation of this improvement effect [36]. The large amount of POSS cross-linkers relative to terminal hydroxyl groups of HPDMS are likely unfavorable to the distribution of POSS-rich domains during the cross linking process due to many reactive sites. And the non-uniform distribution of POSS cross-linkers is supported by the results of the aforementioned SEM. Moreover, it is found that the novel RTV silicone rubbers prepared with equimolar amount of alkoxyl groups of different cross-linkers have larger degree of swelling and soluble fraction, compared with those of the ones prepared with equivalent mass fraction of cross-linkers. The soluble fractions of novel RTV silicone rubbers in toluene also increased from 4.12% to 12.74%, as summarized in Table 4. High soluble fractions and large degree of swelling imply networks imperfect distribution of POSS [34], such as self-cross-linked POSS-rich domains.

Therefore, from the aforementioned above, it is concluded that the enhanced mechanical properties of the RTV silicone rubbers prepared with novel POSS cross-linkers can be attributed to the synergetic action of the increased dimensionality of effective cross-linked networks of 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-rich domains.

4. Conclusions

In this paper, we report synthesis, characterization of novel RTV silicone rubbers using Vinyl-POSS derivatives as cross linking agents. These novel POSS cross-linkers have been prepared through hydrosilylation of Vinyl-POSS and trimethoxysilane for the first time. The novel PDMS polymer composites were prepared through hydrolysis under moisture and condensation between HPDMS and freshly prepared POSS cross-linkers in the presence of organotin catalyst. The chemical incorporation of novel POSS derivatives into HPDMS network by condensation was verified by ATR infrared spectroscopy. Morphologies, thermal properties, mechanical properties and hardness of these novel RTV silicone rubbers have been characterized by scanning electronic microscopy, thermal gravimetric analysis, universal tensile testing machine and shore hardness tester, respectively. The results showed that the novel cross-linkers (DVPS and OPS) had significant improvements on thermal stabilities, mechanical properties and hardness of these RTV silicone rubbers, compared with traditional cross-linkers (TMOS and TEOS). These enhancements in comprehensive properties were ascribed to the synergistic effect of increasing dimensionality of effective three-dimensional networks in PDMS matrix resulting from special three-dimensional structure of novel POSS cross-linkers, plasticization of self-cross-linked POSS cross-linkers and uniform distribution of POSS-rich domains.

Acknowledgments

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