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Synthesis and thermal properties of modified room temperature vulcanized (RTV) silicone rubber using polyhedral oligomeric silsesquioxane (POSS) as cross linking agent

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Incompletely condensed tetra-silanol-phenyl-/polyhedral oligomeric silsesquioxane (TOPO) were synthesized first and then copolymerized with hydroxy terminated polydimethylsiloxane (HPDMS) as cross linking agent to prepare room temperature vulcanized (RTV) silicone rubber (TOPO-PDMS). The structure of TOPO was characterized with matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) and nuclear magnetic resonance (NMR). The fourier transform infrared spectroscopy (FT-IR) spectra suggested successful bonding of TOPO silanols and HPDMS. Scanning electron microscopy (SEM) and wide angle X-Ray diffraction (WAXD) analysis showed that POSS could dissolve in silicone rubber at the molecular level. Thermal stability of TOPO-PDMS was investigated by thermo gravimetric analysis (TGA) and results demonstrated that the chemical incorporation of POSS into polydimethylsiloxane (PDMS) networks significantly enhanced the thermal stability of modified RTV silicon rubber. The degradation mechanism(s) was further monitored by TGA coupled with FTIR. Results suggest that the remarkable improvement in thermal stability can be attributed to (a) the consumption of OH in the condensation reaction between TOPO and HPDMS which decline the 'back biting' reaction and (b) the nanoreinforcement effect of the POSS cage that retard polymer chain motion. Additionally, the characteristic temperatures of 5%, 20% and maximal rate of weight loss exhibit different trends with content increase of cross-linker TOPO and the cause has been discussed in detail.

1. Introduction

Organic/inorganic hybrid materials with specially designed structures and excellent properties deserve particular attention for their practical application. Polyhedral oligomeric silsesquioxane (POSS), owing to their well-defined nanostructures: cube-octameric molecules consisting of a rigid, inner inorganic Si-O-Si framework and organic substituent groups at corners, offer the potential as precursors to inorganic–organic hybrid materials with advantageous properties.[1,2] The unique structure also endows POSS molecules superior properties[3-8] in the construction of POSS-containing polymeric species,[9-15] as compared to other traditional inorganic agents. In addition, the problems caused by changes at the interface between inorganic filler and polymer in conventional systems can be overcome, for the organic groups at corners can provide the POSS molecules with desired reactivity and solubility, and help POSS molecules to be well dispersed in hybrid polymers. In the past reports, a variety of POSS-based hybrid materials have been successfully prepared via copolymerization, chemical coupling or physical blending for different systems with promising properties such as improved thermal properties, dielectric constants and oxidation resistance.[16-24]

Polysiloxane is a commercially used elastomeric material for its unique properties such as low combustion heat, low gas transition temperature and low chemical reactivity. It is also worth mentioning that polysiloxane is derived from non-petrochemical route and can be widely applied to promote the low carbon economy. In spite of having a large range of advantages and useful properties, introducing a filler phase into linear polysiloxane is the main approach to enhance the thermal properties for high temperature continuous applications.[25-29] In traditional inorganic filler modified polysiloxane system, phase separation is found to be the major problem to hinder the improvement of physical properties.[30-33] Therefore incorporating POSS species containing reactive groups into polysiloxane via chemical bonding creates the possibility to promote uniform dispersions in the material. A few POSS-based polysiloxane systems have been prepared and possess a number of desirable properties up to the present.[34-36] However, Previous studies into the properties of POSS/polysiloxane were subsequently investigated in a cursory way. To the best of our knowledge, researches on thermal degradation properties for POSS/polysiloxane composites, especially those of POSS with reactive groups resulting in particular network architectures, have rarely been reported.

Our recent work presented thermal degradation properties and mechanisms of modified room temperature vulcanized (RTV) silicon rubbers prepared by blocking POSS in the main chain[37] and grafting onto the side chain,[38] respectively. In this study, we firstly report the preparation of incompletely condensed tetra-silanol-phenyl-POSS (TOPO) and the designation of modified RTV silicon rubber (TOPO-PDMS) using TOPO as cross linking agents. It is the intent of this study to provide an examination of the thermal degradation properties for structurally and compositionally well-defined PDMS networks based on POSS building blocks. Using X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA) coupled with FTIR analyses, some thought-provoking results are reported firstly.

2. Experimental

2.1 Materials

Tetra-silanol-phenyl-POSS (TOPO) used in this study were prepared in our laboratory. Hydroxyl-terminated PDMS (HPDMS) (107#, 3000±300cs) was supplied by Jiangxi Xinghuo chemical Co., Ltd, Jiangxi, China. Dibutyltin dilaurate was provided by Zhuorui New Material Co., Ltd, Shanghai, China. Poly(hydrosiloxane) and methyltris(methylethylketoxime)silane were obtained from Taly Chemical Industrial Co., Ltd, Chengdu, China. The above starting materials were used as received. Toluene, chloroform, methanol, and tetrahydrofuran (THF) were purchased from Chengdu Haihong Chemical. All of the above solvents are of analytical purity, in addition toluene and THF were dehydrated according to classic literature procedure.

2.2 Synthesis

2.2.1 Synthesis of tetra-silanol -phenyl-POSS (TOPO) [$Ph_8Si_8O_{10}(OH)_4$]

A 250-ml three-necked flask equipped with a reflux condenser and a dropping funnel was charged with 120 mL 2-propylalcohol, 0.14 mol deionized water, and 0.42 mol sodium hydroxide respectively, and sealed under dry nitrogen. 0.12 mol phenyltrimethoxysilane was added dropwise from the dropping funnel at room temperature in about 60 minutes while stirring by means of a magnetic stirrer. The reaction mixture was refluxed for 4 h, and continued to stir at 20 ^{0}C for 15 h. A deposited precipitate was separated by a pressure filter equipped with a membrane filter. The precipitate was washed once with 2-propyl alcohol and taken to dryness under vacuum at 70 ^{0}C for 5 hours to obtain a colourless solid product in 83.5% yield. 11.6 g solid product thus obtained and 120 mL THF were charged into a 250 mL flask while stirring by means of a magnetic stirrer. Then 2.4 mL glacial acetic acid was quickly injected and continued to stir at room temperature for at least 15 min. 50 mL deionized water was added to neutralize extra acid. The reaction mixture thus obtained was transferred to a separating funnel, The organic fraction was washed with 1N hydrochloric acid or saturated sodium bicarbonate solution (aqueous) until the pH reached 7, then further washed three times with ion-exchanged water. The organic layer was isolated and dried over $MgSO_4$ for 20 min. Finally, white powder was obtained by moving the solvent and the volatile via rotary evaporation at 70 ^{0}C, which was further dried in vacuum at 70 ^{0}C for 5 h to get a constant weight, and 6.82 g pale powder was obtained with the yield of 59%.

2.2.2 Synthesis of modified RTV silicon rubber using POSS as cross linking agents (TOPO-PDMS)

A series of TOPO-PDMS was prepared according to the procedures described in Scheme 1, We have prepared a series of TOPO-PDMS copolymers for thermal properties investigations. And typical experimental procedures are given below.

In a typical reaction, TOPO and HPDMS were dissolved in sufficient toluene via agitation in a 250 mL flask with a magnetic stirrer, and then 0.15 g dibutyltin dilaurate as catalyst was added. The reaction mixture was stirred at room temperature for 1 h to access a complete reaction. A constant amount of methyltris(methylethylketoxime)silane was then charged and stirred for 15 min. The mixture was then poured into a Teflon mould subsequently, and cured for about 2 d at room temperature to get a sheet of RTV silicone rubber with smooth surface.

As reference material, we also synthesized RTV silicone rubbers named PDMS according to the same approach above.

2. 3 Measurements

^{29}Si NMR spectra was recorded on a Bruker AV 11-400 spectrometer at 400 MHz in $CDCl_3$ (0.05%TMS as an internal standard) at RT. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) analysis was carried on a Bruker micoFlex spectrometer emitting at 337 nm wavelength of nitrogen laser(concentration of 0.5~1.0 mg/mL in THF).FTIR spectra were measured with a spectral resolution of 2 cm^{-1} on a Nicolet Magna 560 infrared analyzer using KBr disks or pellets at room temperature. Scanning electron microscopy (SEM) was performed on a JSM-5900LV scanning electron microscope at a voltage of 20 kV. Samples were first fractured in liquid nitrogen and then coated with a gold coating film of about 100 Å thick and photographed in the microscope. The Wide Angle X-Ray Diffraction (WAXD) was used to investigate the distribution of POSS in the silicone rubber. The WAXD measurements were conducted with a Philips X' Pert Graphics & Identify. Thermo gravimetric analysis (TGA) coupled with FTIR were carried out using a Perkin-Elmer and Nicolet Magna 560. About 10 mg of sample cut as small pieces was loaded in alumina pans in nitrogen and in air atmosphere from ambient temperature to 800 ^{0}C at a constant rise of temperature (10 ^{0}C min^{-1}).

3. Results and discussion

3. 1 Charaterization of incompletely condensed POSS (TOPO)

The synthesis of novel cross-linking agent TOPO was successfully achieved by alkali-catalyzed hydrolysis and condensation of phenyltrimethoxysilane. To identify the chemical structure of the product TOPO, MALDI-TOF MS and ^{29}Si NMR were performed. Results from MALDI-TOF MS analysis show that two peaks could be observed in Fig.1 among which, peak at *m/z* 1092.0(TOPO+Na) matches the molecular weight of TOPO (*m/z* 1068.09) with additional Na. ^{29}Si NMR provides structural information concerning the type of silicones present in the cage-like framework. Two chemical shifts at about -69.66 and -79.81 ppm appear in the ^{29}Si NMR spectrum of TOPO as shown in Fig.2. These signals can represent two types of silicones; one is lie conjoint hydroxyl groups and the other comprises T structure in the cage-like frame. More specifically, we find in the ^{29}Si NMR spectra a 1:1 integration ratio, which is consistent with the molar ratio of the different two types of silicone atoms in the TOPO exactly.

3. 2 Characterization of modified RTV silicon rubber using POSS as cross linking agents (TOPO-PDMS)

The TOPO-PDMS composites were prepared by condensation of Si-OH groups between the cross-linking agent TOPO and HPDMS at room temperature in the presence of curing catalysis (dibutyltin dilaurate) and co-crosslinker (methyltris(methylethylketoxime)silane) under atmospheric humidity, which could promote cross-link of HPDMS polymer systems. The preparation procedures of novel RTV silicone rubber using TOPO as the cross-linker are shown in Scheme 1.

To establish the network structures of modified RTV silicone rubber, FTIR was performed. Fig.3 shows the FTIR spectra of PDMS, the TOPO monomer, and the modified RTV silicon rubber TOPO-PDMS. The broad and strong peaks at 950-1300 cm^{-1}, as well as the new peaks around 1500-1800 cm^{-1} which can be observed in spectrum of TOPO-PDMS composites, are attributed to stretching vibration of the asymmetric Si-O-Si and Si-Ph in POSS cages, respectively. On the other hand, the intensity of the stretching and deformation vibration at 3016 cm^{-1}, which is the characteristic bands of silanol (Si-OH) of TOPO monomer, decrease. It can be considered that Si-OH groups between PDMS and TOPO are reacted. We are satisfied that POSS are indeed incorporated into modified RTV silicon rubber rather than as a mixture. The infrared spectra can also confirm the design of preparation in Scheme 1.

3. 3 Morphology analysis

In this study, TOPO cross-linker was chemically incorporated into PDMS polymeric system. However, the possible existence of incompletely reacted POSS might result in aggregation and phase separation in the matrix, which is of great importance to the physical properties of composites. Therefore the investigation in the distribution of fillers in matrix is necessary. In this work, the morphology of POSS in modified RTV silicon rubber was evaluated by means of SEM. And the dispersions of POSS in modified RTV silicon rubber was of further interest to the study by WAXD measurements.

Fig. 4 presents the fractured surfaces (broken under liquid nitrogen) of modified RTV silicone rubbers. It is found that several micron-sized spherical domains (bright part) in the modified RTV silicone rubbers can be observed. The micron-sized domains are approximately to be spherical POSS-rich particles[39,40] with sizes of ~50 nm, which are ascribed to aggregation of self-cross-linked TOPO. In addition, these aggregated cross-linked TOPO domains are significantly small, which illustrates that the molecular level dispersion of POSS that can be achieved in polysiloxane via compounding, as shown in Fig. 4b, c and d. Results of SEM indicate that POSS is uniformly dispersed in RTV silicone rubber without any large aggregates when POSS is tethered to PDMS as cross linking points.

Figure 5 displays the resulting X-ray diffraction curves from cured PDMS rubber and TOPO-PDMS composites. Strong diffraction peaks at 2θ=7.30° and 19.39° can be observed in the pattern of TOPO, suggesting an ordered crystal form of TOPO. While, only two diffuse amorphous reflections approximately appear at 2θ=11.55° and 2θ=22° in that of PDMS. Similarly, no crystalline peaks or any large-scale ordered structure for POSS crystal are detected in the pattern of TOPO-PDMS composites at room temperature condition. Besides, it is more interesting to note that condensation of polysiloxane with TOPO leads the amorphous reflections to shift to right as the content of TOPO increase, illustrating that incorporating POSS into the new cross linking networks can enhance the rigidity of TOPO-PDMS molecular chains and form a portion-range ordered structure. Therefore, the framework distance decreases appreciably with the interchain distance of TOPO-PDMS decreases for cross linking points TOPO and the regularity increases, according to $2d\sin\theta = m\lambda$, (m = 0, 1, 2…)(d, θ and λ represent for distance, scattering angle and wavelength, respectively). Thus in combination with the results of SEM, POSS molecules display an excellent dispersion capability in polysiloxane matrix for (a) the chemical bonding forces between the POSS molecules and polysiloxane chains and (b) the compatibility from the organic substituents.

3. 4 Thermal degradation behaviour

Thermogravimetric analysis of the TOPO-PDMS composites was carried out in nitrogen atmosphere at 10 °C/min to estimate the thermal degradation properties, as presented in Figs.6 and 7. Only a single degradation step is observed under nitrogen for pure TOPO, while two characteristic degradation peaks appear on the first derivative (DTG) curves for all PDMS polymers. According to the TGA measurement, it can be certainly envisaged that different degradation processes exist within the experimental temperature range.

In order to visualize the trends in the TGA data more clearly, the degradation temperatures calculated from the 5%, 20% and maximal rate of weight loss curves have been plotted for all PDMS systems in figure 8. The results present that the thermal stability for covalently bound TOPO-PDMS system increases along with the increase of the TOPO cross-linker loadings. For instance, the temperature of 5% weight loss has delayed from 340 to 379°C for TOPO-PDMS with 5 wt% TOPO. However, the characteristic temperatures of 20% weight loss and maximal rate of weight loss exhibit a different trend with content increase of cross-linker, compared to that of 5% weight loss. As shown in Fig. 8, there are little discrepancies between 1, 5 and 10% loading levels at the temperatures of 5% weight loss; while the content of TOPO is 10 wt%, the temperature of 20% weight loss decreases compared with that of 5 wt% TOPO-PDMS; on the other hand, temperatures of maximal rate of weight loss rise superior with the content increase of TOPO. Interstingly, in combination with the data of DTG, the temperatures of 20% weight loss for the three loadings of TOPO-PDMS (1 wt%, 5 wt% and 10 wt%) appear at 403, 425, and 410 °C, respectively, which correspond to the temperatures of first degradation peak exactly; while actually the maximal rate of weight loss appears on the second degradation stage for all TOPO-PDMS systems, suggesting the existence of different decomposition mechanism. Additionally, residual yields obtained in N_2 at 800 °C exhibit an increasing trend with the increase of POSS cross-linking agent loadings, which are clearly seen in Fig. 9. The PDMS has the lowest residual yield (0.19 wt %) at 800 °C among all of RTV silicone rubbers. The residual yields of modified RTV silicone rubber with 10 wt% TOPO reaches 19.9%. These results suggest that the chemical incorporation of POSS cages has a detrimental impact on the thermal stability of the PDMS polymer system.

3. 5 Degradation mechanism

In general, analysis of the decomposition process would provide insight into decomposition mechanism(s) of the TOPO-PDMS composites, which could aid the design of future POSS polymers with enchanced thermal stability. Therefore, the unclear thermal decomposition mechanism(s) of TOPO-PDMS composites was performed by measurements of thermal gravimetric coupled with IR.

Curves with two different degradation stages were observed in the overall thermal degradation process for cross-linking TOPO-PDMS composites, as shown in Fig. 7, suggesting the existence of different degradation mechanisms. The thermal decomposition of 5 wt% TOPO-PDMS sample was monitored by real-time FTIR coupled with TGA in nitrogen, as shown in Fig. 10. It is clearly to note that cyclic dimethylsiloxanes[41] (2970，1265，1095，1026，814cm^{-1}) are the main products during the first weight-loss region from 332 to 456 °C, and the relative concentration of cyclic dimethylsiloxanes is almost constant at this stage. However, the concentration of dimethylsiloxanes begin to increase distinctly along with the intensity of peaks at 2970, 1265, 1095, 1026 and 814 cm^{-1} increase obviously when the temperature rises to 486°C, and a small amount of methane(3016 cm^{-1})appears during the second degradation stage, implying that another mechanism governs mainly the degradation process at higher temperature.

Essentially, different degradation mechanisms occur for different PDMS, among which mainly four 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.[42] The four mechanisms include, (a) the end-initiated unzipping mechanism;[43–46] (b) the random main chain scission mechanism;[45] (c) the externally catalyzed mechanism for polymers containing impurities and residual catalyst;[47] and (d) molecular mech-anism.[45,46,48] Similarly, cyclic dimethylsiloxanes generate and keep increasing slightly during the first degradation stage of TOPO-PDMS, showing the identical behaviour of PDMS with incompletely reacted hydroxyl terminal which can participate in a 'back biting' reaction in accordance with the end-initiated unzipping mechanism.[42,45,49] At the second degradation stage of TOPO-PDMS from 468 °C to 683 °C, the concentration of dimethylsiloxanes increases distinctly and methane generates owing to the random degradation mechanism of PDMS main chain, which is caused by increasing chain mobility and molecular motion as the temperature elevated. In this mechanism, a flexible chain would be more easily degraded than a rigid chain, since the probability of chain motion should be dependent of chain flexibility.

Additionally, the temperatures of two degradation stages move to higher regions in contrast to that of PDMS, convincing that using POSS as cross linking agents significantly affects the thermal stability of the TOPO-PDMS system. Since the reaction with the TOPO silanols, the influence of Si-OH on the thermal stability of PDMS polymers decline to a certain extent. The degradation initiated by hydroxyl-terminal is diminished, and thus the thermal stability of the modified RTV silicone rubbers in nitrogen is greatly improved. The enhancement of the second degradation step of the TOPO-PDMS composites can be ascribed to the nanoreinforcement effect of POSS on the macromolecular networks. Using rigid bulky TOPO cages as cross linking agents can form new networks of PDMS polymers and retard the polymer chain motion,[50] hinder the formation of cyclic oligomers in the course of degradation, exert nanoreinforcement effect, and finally delay the temperatures of thermal degradation of the TOPO-PDMS composites.

However, as aforementioned, the characteristic temperatures of 5%, 20% and maximal rate of weight loss exhibit different trends with increased TOPO cross-linker loadings. This lack of a consistent trend may be attributed to incompletely reacted POSS within the TOPO-PDMS composites. Low levels of POSS loadings (≤ 5 wt%) can be uniformly dispersed in RTV silicone rubber and most of the silanols groups of TOPO seem to sufficiently bind hydroxyl-terminated PDMS to decline the 'back biting' reaction, which is the dominative mechanism for the first degradation stage. As the concentration of TOPO is high (10 wt%), aggregation of self-cross-linked TOPO appears besides, the excessive unreacted silanols groups of TOPO can cause pyrolysis of the TOPO-PDMS chains, resulting in the lower temperatures of 20% weight loss as the content of TOPO is 10 wt%, in contrast to that of 5 wt% TOPO-PDMS. The temperatures of second degradation step of the modified RTV silicone rubbers increase along with the increase of the TOPO cross-linker loadings. As the concentration of TOPO increase from 5 to 10 wt%, the number of molecularly dispersed POSS molecules grows large and the rigid bulky TOPO cages chemically bonding to PDMS networks can restrict the molecular mobility, exert nanoreinforcement effect, hinder the random degradation and finally delay the degradation temperatures.

4. Conclusion

In summary, we have successfully synthesized incompletely condensed tetra-silanol -phenyl-POSS (TOPO), which was designed as cross linking agent for the synthesis of modified RTV silicon rubber (TOPO-PDMS). SEM and XRD results have shown that POSS is uniformly dispersed in RTV silicone rubber without any large aggregates when POSS is tethered to PDMS as cross linking points. Significant improvement on thermal stability of the RTV silicon rubber can be achieved by incorporating TOPO into new networks of PDMS polymers. The thermal decomposition mechanisms of TOPO-PDMS composites is investigated by real-time FTIR coupled with TGA and results show that reaction with the TOPO silanols can diminish the degradation initiated by hydroxyl-terminal during the first degradation stage, and the nanoreinforcement effect of POSS on the PDMS networks can delay the temperatures of the second thermal degradation stage. At low concentrations of POSS (≤ 5 wt%), most of the Si-OH groups of TOPO seem to sufficiently bind hydroxyl-terminated PDMS to decline the 'back biting' reaction, while the excessive unreacted silanols groups can cause pyrolysis of the TOPO-PDMS chains as the concentration of TOPO is high (10 wt%). On the other hand, the increase of the TOPO cross-linker loadings can retard the polymer chain motion and exert nanoreinforcement effect; on this condition higher temperatures are demanded for the random degradation of the second weight-loss region as the concentration of TOPO increased from 5 wt% to 10 wt%.

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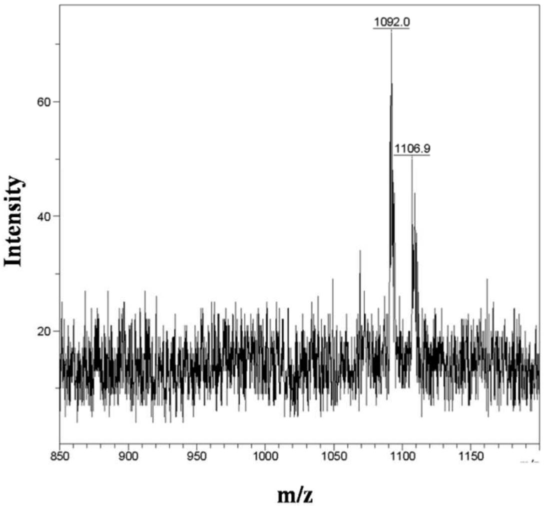


Fig. 1 Enlarged sections of MALDI-TOF MS spectra of TOPO monomer

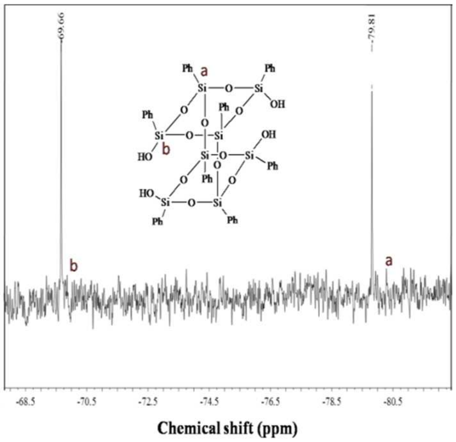
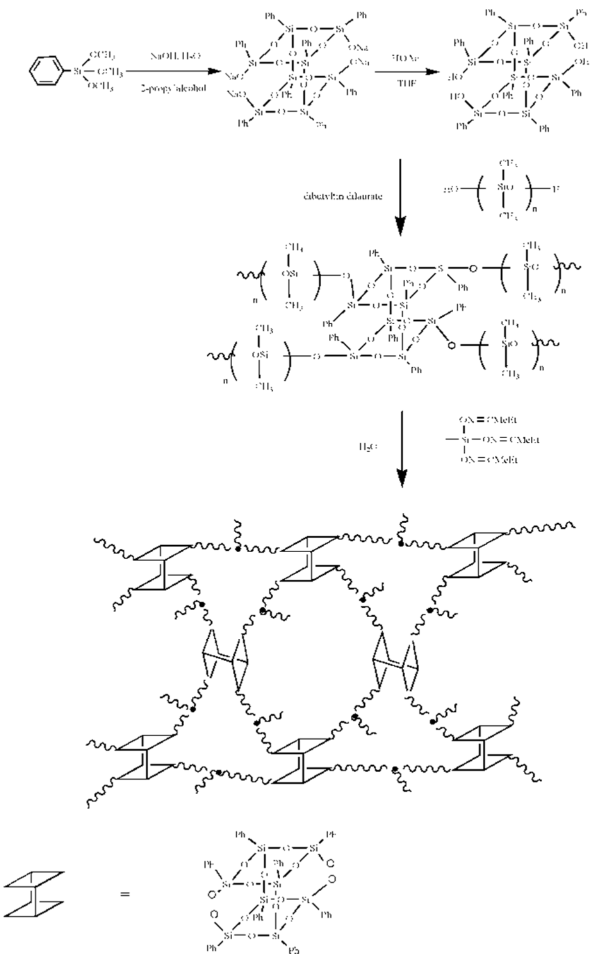


Fig. 2 ^{29}SiNMR spectra of TOPO monomer



Scheme 1 Preparing routes of modified RTV silicon rubber TOPO-PDMS

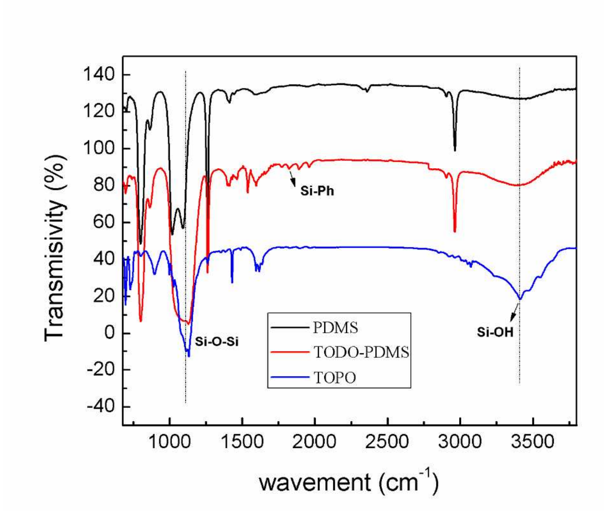


Fig. 3 FTIR spectra of TOPO and PDMS before and after reaction

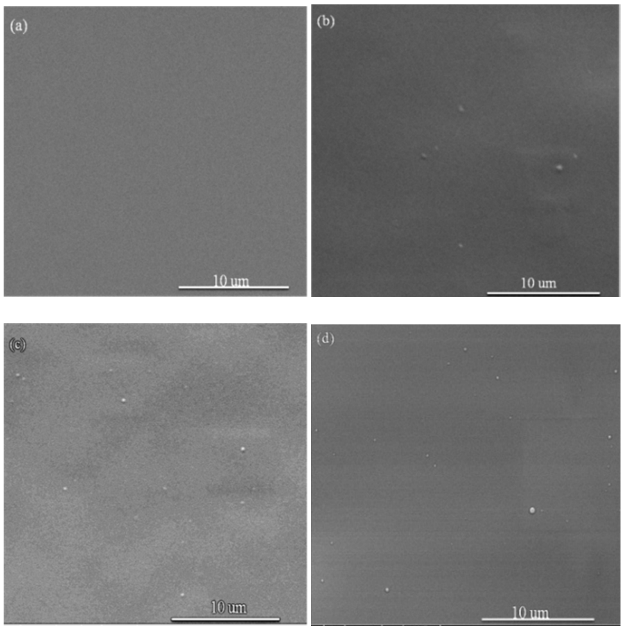


Fig. 4 SEM micrographs of the fractured surfaces of the RTV silicone rubbers: (a) PDMS, (b) 1 wt% TOPO-PDMS, (c)5 wt% TOPO-PDMS and (d)10 wt% TOPO-PDMS

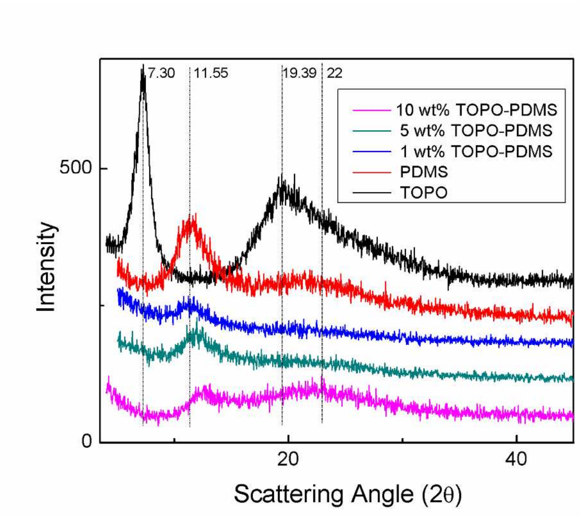


Fig. 5 WAXD patterns of TOPO and PDMS before and after reaction

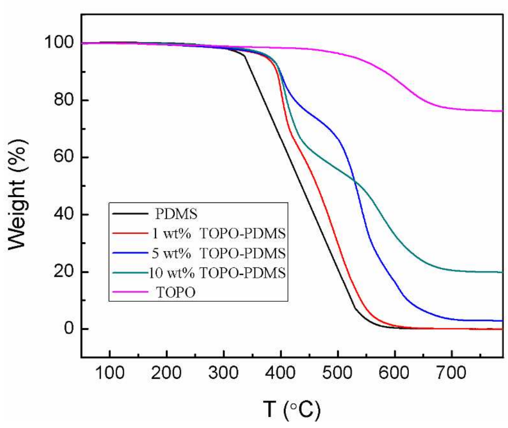


Fig. 6 TGA curves of pure TOPO, PDMS and RTV silicon rubber TOPO-PDMS obtained in nitrogen atmosphere

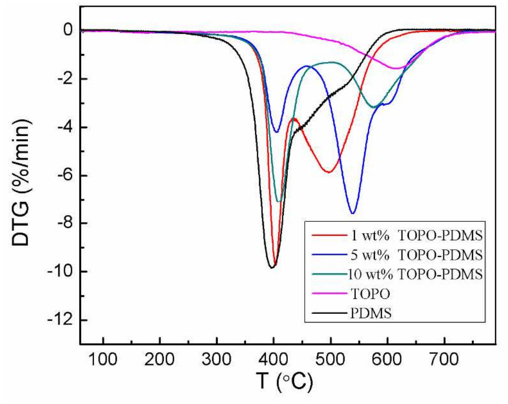


Fig. 7 DTG curves of pure TOPO, PDMS and RTV silicon rubber TOPO-PDMS obtained in nitrogen atmosphere

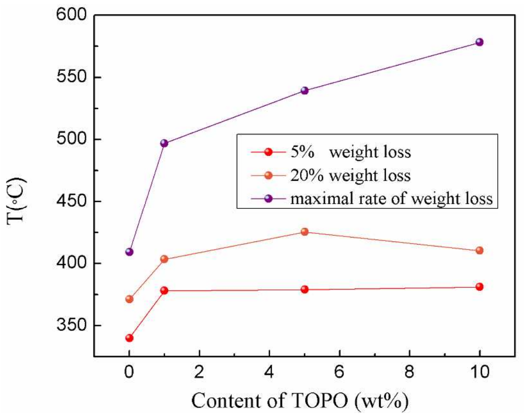


Fig. 8 Effect of TOPO content on select characteristic degradation temperatures of RTV silicone rubbers: 5% weight loss, 20% weight loss and the maximal rate of weight loss in nitrogen atmosphere

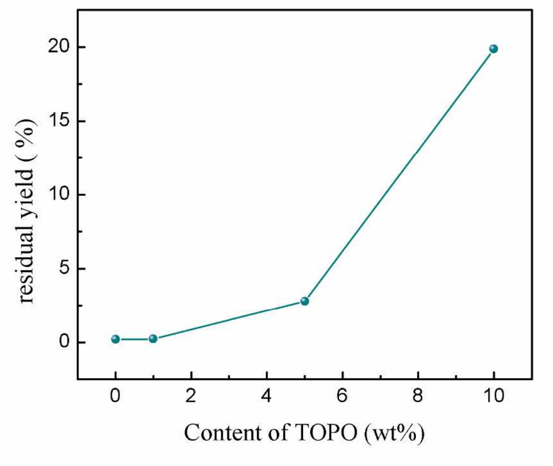


Fig. 9 Effect of TOPO content on residual yield of the RTV silicone rubbers: residual yields obtained in nitrogen atmosphere at 800 °C

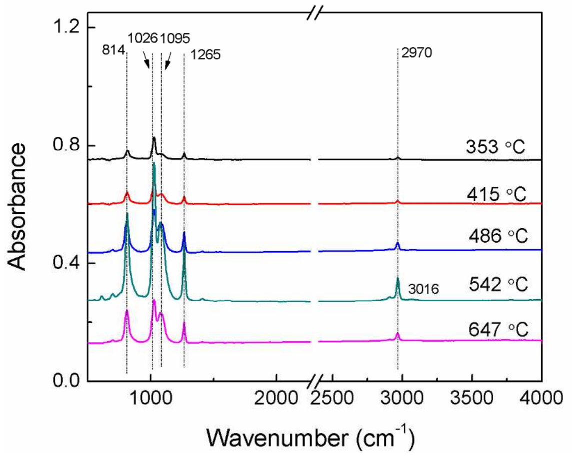


Fig. 10 FTIR spectra of thermal degradation products for 5 wt% TOPO-PDMS sample at different temperature in nitrogen atmosphere