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Crystallization and morphology study of polyhedral oligomeric silsesquioxane (POSS)/polysiloxane elastomer composites prepared by melt blending

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Abstract

Composites of poly(methylvinylsiloxane) (‘‘silicone’’) elastomers with polyhedral oligomeric silsesquioxane (POSS) were prepared by melt blending. One goal was to establish conditions that would lead to morphologies different from that of a simple filler dispersed in a polymer matrix for the purposes of reinforcement. To this end, the study focused on the dispersion and state of POSS in silicone rubber blends as determined by X-ray diffraction (XRD), polarizing optical microscopy (POM), scanning electron microscopy (SEM), and analysis using a rubber processing analyzer (RPA). Of particular interest were the thermal stability of POSS macromers, and the effects of mixing temperature and subsequent vulcanization of the polysiloxane. The results showed that highly crystalline POSS macromers could undergo condensation reactions at 230 °C in air, leading to partially amorphous structures. Also, POSS crystals apparently dissolved in the polysiloxane at high temperatures and POSS crystals with hexahedral or flake-like structures recrystallized out upon cooling. Both crystallites and POSS molecules co-existed in these blends, with the amount of dispersed molecular POSS being increased at higher temperatures. The POSS molecules exhibited some physical interactions with the polysiloxane uncross-linked chains, but phase separation was induced by the process of cross-linking. In this curing process, POSS molecules could react with the polysiloxane, resulting in decreases in cross-link density. The original POSS crystals could also be dissolved in the polysiloxane during the initial curing stages, but recrystallization upon cooling gave regenerated crystals that were roughly spherical.

Keywords: POSS; Polysiloxane elastomers; Crystallization

1. Introduction

Polyhedral oligomeric silsesquioxane (POSS) is a three-dimensional structurally well-defined cage-like molecule represented by the formula $(RSiO_{1.5})_n$ (where the R's are organic groups at the corners of the cage and $n = 6$, 8, 10 or higher). These POSS ‘‘macromers’’ have an inorganic silica-like core surrounded by organic groups and the size of the typical POSS cage is about 1.5 nm. Because of its hybrid nature and nanometer scale size, POSS is a promising material for the preparation of nanocomposites. A variety of polymers have been used in these composites [1–6] and the subject has been reviewed a number of times [7–13]. Simulations have also been carried out on the POSS particles themselves [14] and on POSS nanocomposites [15].

The R organic substituents can be either reactive or nonreactive, and this gives rise to three methods for incorporating POSS macromers into polymers [7–13]. First, POSS containing unreactive functional groups can be simply blended into

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the polymer in a typical ex situ technique. If one of the groups is reactive, the cages can be bonded onto the polymer backbones as side chains. In the case of two reactive R groups, the cages can be incorporated as comonomeric units, and three or more reactive groups per molecule can be used to provide cross-linking. One departure from this simple picture arises from the fact that POSS molecules tend to crystallize at room temperature, which results in one type of phase separation. Even for POSS containing reactive functional groups, very small POSS domains often form as POSS aggregates instead of bonding to the polymer backbones or otherwise dispersing into the polymer matrix [16−19]. The incorporation of POSS cages into a polymer backbone may result in dramatic improvements in polymer properties, including increases in maximum use temperature, oxidation resistance, and surface hardness, improvements in mechanical properties, and reductions in flammability and heat evolution [20]. These enhancements have been shown in wide range of thermoplastics and a few thermoset systems. Some specific examples are polysiloxanes [21], poly(methyl methylacrylate) [22], polystyrene [1], epoxies [23], polyurethane [24], polyimide [25], and polynorbornene [26]. One relevant observation was the fact that simply blending in POSS containing the non-reactive organic groups gave smaller improvements, possibly due to partial incompatibility of POSS with some polymers [27].

Some recent reports have described such nanocomposites prepared by the ex situ blending with non-reactive POSS. Fina et al. [28] reported isotactic polypropylene (iPP) reinforced with POSS having R groups of various lengths that had been prepared by melt blending in a Brabender internal mixer. A good dispersion was obtained, particularly at low loadings of POSS molecules that contained longer organic chains. The POSS influenced the crystallization by acting as a nucleating agent and also induced some PP polymorphism.

The non-isothermal crystallization of high-density polyethylene (HDPE) in POSS nanocomposites was studied by Joshi and Butola [29]. The HDPE/POSS materials had been prepared in a twin-screw extruder by melt mixing. The POSS molecules exhibited nucleation activity only at 10 wt% loading in HDPE, but were not effective nuclei at lower loadings.

Fu et al. [30] reported crystallization studies in quiescent and shear states in isotactic polypropylene (iPP) containing nanostructured POSS molecules. The samples had been mixed on a Brabender apparatus at 177 °C for 20 min and were characterized by differential scanning calorimetry (DSC) and in situ small-angle X-ray scattering (SAXS). In quiescent states, the addition of POSS increased or reduced the crystallization rate of iPP depending on the POSS concentration. Under shear, the POSS (possibly acting as a weak cross-linker) significantly increased the crystallization rate.

Similarly, octamethyl POSS composites with ethylene−propylene (EP) copolymers with POSS loadings from 10 to 30 wt% were prepared by melt mixing in a twin-screw device [31]. Results obtained using wide-angle X-ray diffraction (WAXD) showed that the majority of POSS molecules in the EP melt were present in the crystalline form. Oscillatory shear results showed that POSS caused physical gelation in EP copolymers. Dynamic mechanical analysis (DMA) results indicated that the presence of POSS increased their Young's modulus as well as their glass transition temperatures T_g.

The above studies focused on polyolefins blended with POSS but apparently there have not been similar investigations on silicone rubber composites prepared by melt blending. The present work is thus concerned with such POSS/silicone blends with as fine a state of dispersion as possible. In this study, polysiloxane consisting of methyl and vinyl substitutions is used as the matrix. The polymer [$-Si(CH_3)_2O-$] has a backbone composed of alternate silicon and oxygen atoms, and this composition and structure make it very similar to POSS itself, suggesting good miscibility of the two components.

The present work focuses on revealing crystallization features and morphologies of POSS/silicone rubber blends prepared in a Haake Banbury mixer. The influences of some processing parameters on the dispersion of POSS macromers in the elastomeric matrix are studied. The dispersion of the POSS macromers in the matrix is investigated using X-ray diffraction (XRD), polarizing optical microscopy (POM), scanning electron microscopy (SEM), with additional analysis using a rubber processing analyzer (RPA). Also of interest is the possible solubility of POSS crystals in silicone rubber and how this might influence crystallization and melt behavior.

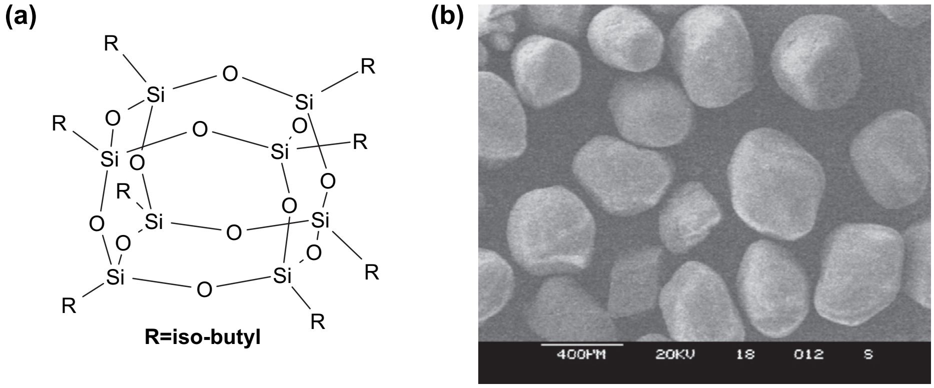
2. Experimental

2.1. Materials

A sample of silicone rubber having 0.15% vinyl substituents and a molecular weight of 640,000 g/mol was purchased from the Second Chemical Factory of Beijing. The POSS used in this study was octaisobutyl-POSS ($C_{32}H_{72}O_{12}Si_8$). It was in the form of a white powder with a molecular weight of 873.60 g/mol and was supplied by the Hybrid Plastics Company, Fountain Valley, California. Its structure is shown in Fig. 1A. As can be seen, the POSS molecule contains a polyhedral silicone−oxygen nanostructured cage, surrounded by eight isobutyl organic R groups. Fig. 1B shows the shape of the particles to be roughly spherical, with a size of approximately 300 μm.

2.2. Preparation of POSS/silicone rubber blends

POSS/silicone rubber blends were prepared by melt mixing in a Haake Banbury mixer (American Thermo Corporation), which was a small laboratory mixer with counter-rotating rotors. Haake software was used for monitoring the mixing conditions for each composition and for storing data. First, silicone rubber was placed into the chamber of the mixer and then the POSS powder was added. In order to investigate the effect of mixing condition on incorporating the POSS into the rubber, blends were prepared by varying the mixing temperature. After mixing was completed, the blends were kept at ambient temperature for at least 24 h before any of their properties were measured.



Molecular structure of octaisobutyl-POSS

SEM micrograph of octaisobutyl-POSS

Fig. 1. Structure and size of the octaisobutyl-POSS.

The curing formulation in parts per hundred (phr) was follows: POSS/silicone rubber, 100 and curing agent (2,5-bis-*tert*-butyl-2,5-dimethylhexane peroxide), 1.5. Both were directly mixed with an open two-roll mill for 15 min, followed by vulcanization on a hot press at 160 °C and a pressure of 150 kgf/cm^2. This was continued for the optimal cure time t_{90} (corresponding to 90% of the maximum torque), which had been determined using a torque rheometer.

2.3. Characterization

2.3.1. Curing characteristics of the rubber composites

The cure parameters were determined with a P3555B2 oscillating disc rheometer (ODR) made by the Beijing Huanfeng Machinery Factory. The curing dynamics of the rubbers were characterized at 160 °C, an angular displacement of 3°, and a test frequency of 1.7 Hz. The rheometer tests were run for 30 min, after which the torque values and the optimal cure time t_{90} were calculated.

2.3.2. X-ray diffraction (XRD)

X-ray diffraction (XRD) analyses were carried out on a Rigaku D/Max 2500VBZC/PC X-ray diffractometer with Cu Kα radiation. The 2θ angle ranged from 3° to 40°, and the step size and scan rate were 0.02° and 5°/min, respectively.

2.3.3. Gel permeation chromatography (GPC)

GPC analyses were run at room temperature in tetrahydrofuran (THF) (at a flow rate of 1 ml/min) on a Waters 510 HPLC pump with a series of columns using a Waters 410 RI-detector. The injection volume was 20 ml of a 2 wt% solution of POSS macromers in THF.

2.3.4. Thermogravimetric analysis (TGA)

A NETZSCH thermal gravimetric analyzer (STA 449C) was used to investigate the thermal stability of POSS. The sample was heated under air atmosphere from ambient temperature to 500 °C at the heating rate of 10 °C/min.

2.3.5. Differential scanning calorimetry (DSC)

DSC measurements were run using a NETZSCH DSC204F1 instrument under a flow of nitrogen and with a heating rate of 10 °C/min. A transition temperature was taken at the maximum peak position for the transition.

2.3.6. Polarizing optical microscopy (POM)

It turned out to be difficult to use scanning electron microscopy on these blends before vulcanization since they were very viscous fluids. Therefore, the phase and crystalline morphologies of the blends were examined using a polarizing optical microscope (Olympus BX-51, Japan). In this technique, the samples were heated and cooled with a hot-stage (THMS-600) and associated temperature controller.

2.3.7. Scanning electron microscopy (SEM)

Scanning electron microscopy was preformed on an AS-250-III scanning electron microscope at a voltage of 20 kV. The cured samples were placed into liquid nitrogen for 5 min and then fractured into two pieces to create fresh surfaces. The samples were then coated with gold, examined and photographed in the microscope.

2.3.8. Rubber processing analysis

The storage moduli of the composites and their dependence on scanning strain were measured on a RPA2000 rubber processing analyzer made by American Alpha Corporation. Each sample (approximately 6 g) was tested at 60 °C, and the frequency used was 1 Hz.

3. Results and discussion

3.1. Characterization of octaisobutyl-POSS and silicone rubber

The octaisobutyl-POSS sample employed was a crystalline material with a high melting point, but was found to oxidize in air at high blending temperatures. Such crystallization, melting, recrystallization, and oxidation could obviously strongly affect the dispersion of POSS in silicone elastomers during

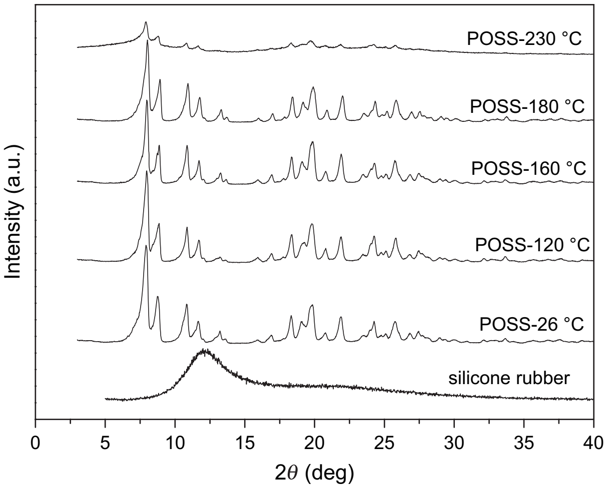


Fig. 2. X-ray diffraction patterns of octaisobutyl-POSS and silicone rubber.

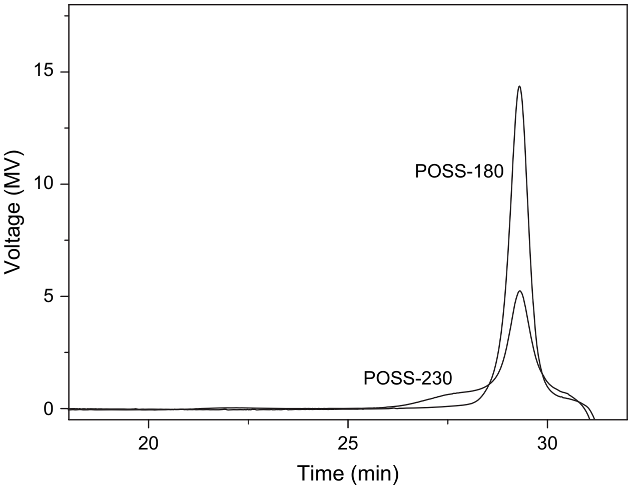


Fig. 4. GPC chromatograms of POSS heated at 180 and 230 °C in air.

melt blending, especially at higher temperatures. Hence, it was essential to first characterize the crystallization and the thermal stability of POSS.

In this regard, the POSS was heated in air at 120, 160, 180, and 230 °C for 30 min and X-ray diffraction patterns were obtained from the resulting materials. Fig. 2 shows the diffraction patterns for the POSS from 26 to 230 °C and for the neat silicone rubber. A very intense main diffraction peak at a 2θ of 11.7° was attributed to the amorphous silicone rubber. As Fig. 2 illustrates, the octaisobutyl-POSS showed sharp peaks, with two major intensity peaks at 2θ of 7.9° and 8.8°. This indicated that the material was highly crystalline and these peak positions and intensities did not change with increasing the temperature from 26 to 180 °C. However, when the temperature was raised to 230 °C, the characteristic peaks decreased and broadened significantly, indicating the conversion of the materials from a crystalline to the amorphous state.

It has been reported that POSS macromers showed a propensity for sublimation and octaisobutyl-POSS evaporated upon melting at a maximum rate at 265 °C in a nitrogen atmosphere [32,33], but in air the isobutyl-POSS was sensitive to oxygen, promoting the occurrence of oxidation reactions in competition with the evaporation process [33]. The thermal stability of the octaisobutyl-POSS in air was therefore further determined by TGA and GPC. Fig. 3 indicates that the maximum rate of the major weight loss in air occurred at 266 °C, as in nitrogen, but a slight weight loss had already begun at 200 °C. The molecular weights of POSS heated in air at 180 and 230 °C for 30 min (labeled samples POSS-180 and POSS-230) were measured, with the results shown in Fig. 4. The POSS-230 sample had become yellow, and moreover did not completely dissolve in THF (unlike the POSS-180 sample). Compared with POSS-180, POSS-230 appeared to have a higher molecular weight ($M_n = 3{,}144$ g/mol) and broader molecular weight distribution. The results suggested that octaisobutyl-POSS began to sublime at 200 °C; when the temperature was further increased, oxidation occurred. Because the Si–O bond energy (451 kJ/mol) is higher than those of the C–C bond (345 kJ/mol) and the Si–C bond (318 kJ/mol), the degradation of POSS macromers in air should start by initial cleavage of the organic corner groups on the POSS

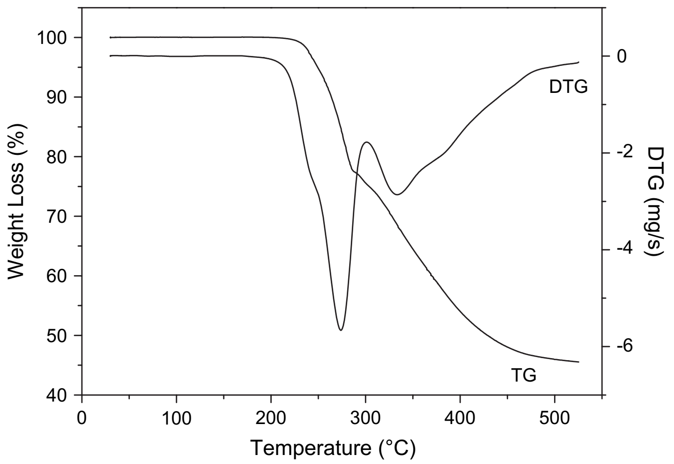


Fig. 3. TGA and DTG curves under air atmosphere for octaisobutyl-POSS.

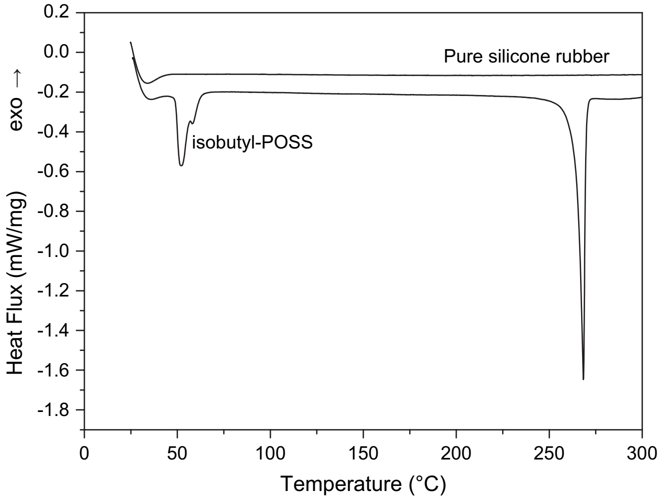


Fig. 5. DSC curves for the isobutyl-POSS and silicone rubber.

Table 1
Characteristics of various POSS/silicone rubber blends

POSS content (wt%)	Silicone rubber content (wt%)	Mixing temperature (°C)	Designation	Transparency of blend during mixing
0	100		SiR	Transparent
0	100	230	SiR-230	Transparent
5	95	40	P5-40	Opaque
5	95	80	P5-80	Opaque
5	95	120	P5-120	Opaque
5	95	160	P5-160	Transparent
5	95	180	P5-180	Transparent
5	95	230	P5-230	Transparent

cage. Octaisobutyl-POSS therefore decomposed somewhat through partial loss of organic substituents at 230 °C. In this process, condensation might have occurred, converting POSS into a less tractable resin.

The transition temperatures of isobutyl-POSS and silicone rubber were determined by DSC. The results, presented in Fig. 5, indicate that the silicone rubber did not show any thermal transition at temperatures up to 300 °C, but isobutyl-POSS had two transition peaks at 52 and 268 °C. The former peak could be due to breaking up of weak aggregates of isobutyl-POSS macromers and the latter was obviously due to melting. POSS could thus be melted in 230 °C, which was close to the temperature at which POSS started to oxidize, and the resulting fragments started to condense. Of course, POSS would recrystallize during cooling, and not necessarily into the same morphology. For these reasons, the subsequent experiments on the dispersion of POSS involved melt blending temperatures in the range from 40 to approximately 230 °C. In the process of the blending of POSS with the silicone rubber, POSS was embedded in the rubber, making the sublimation of POSS negligible.

3.2. Effect of blending temperature on the dispersion of POSS

The blends were prepared using a Haake Banbury mixer, with careful attention to the processing parameters. Increasing

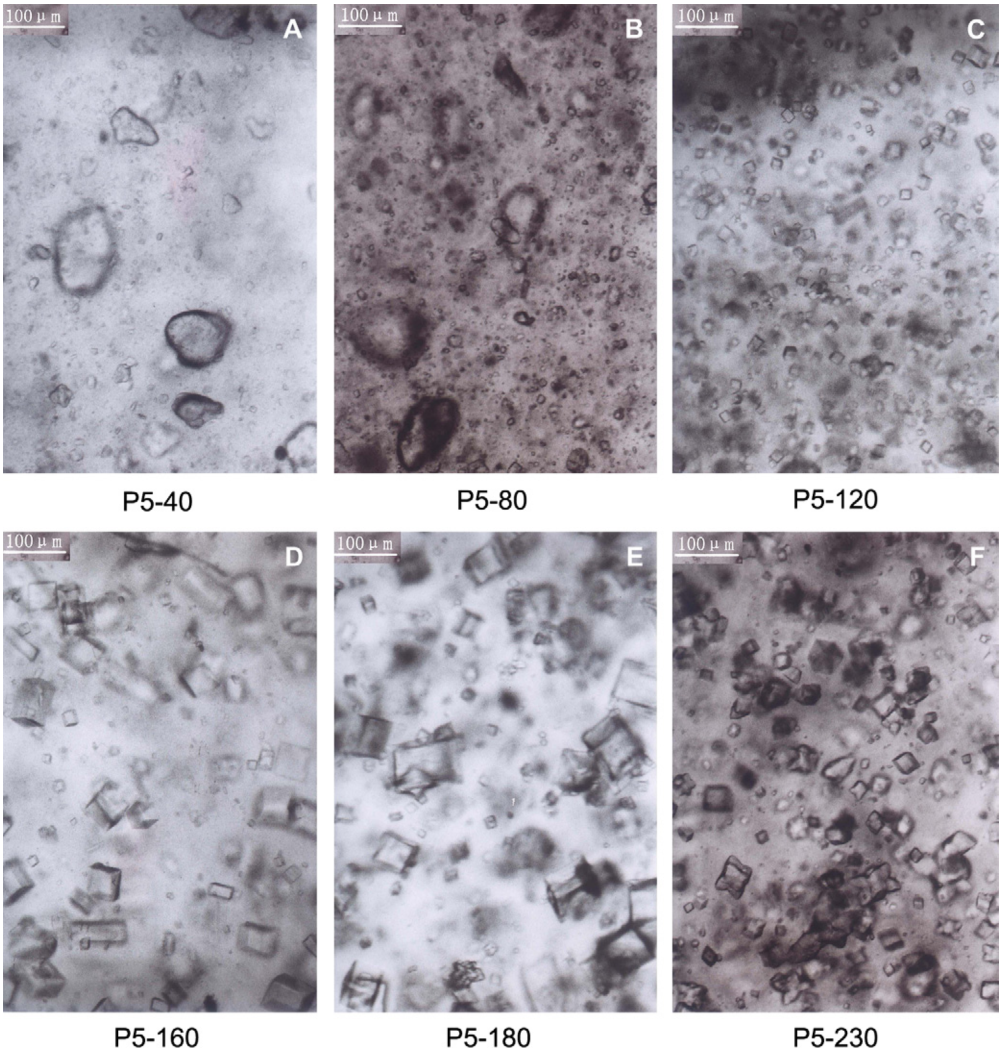


Fig. 6. Photographs of POSS/silicone rubber blends prepared at different temperatures.

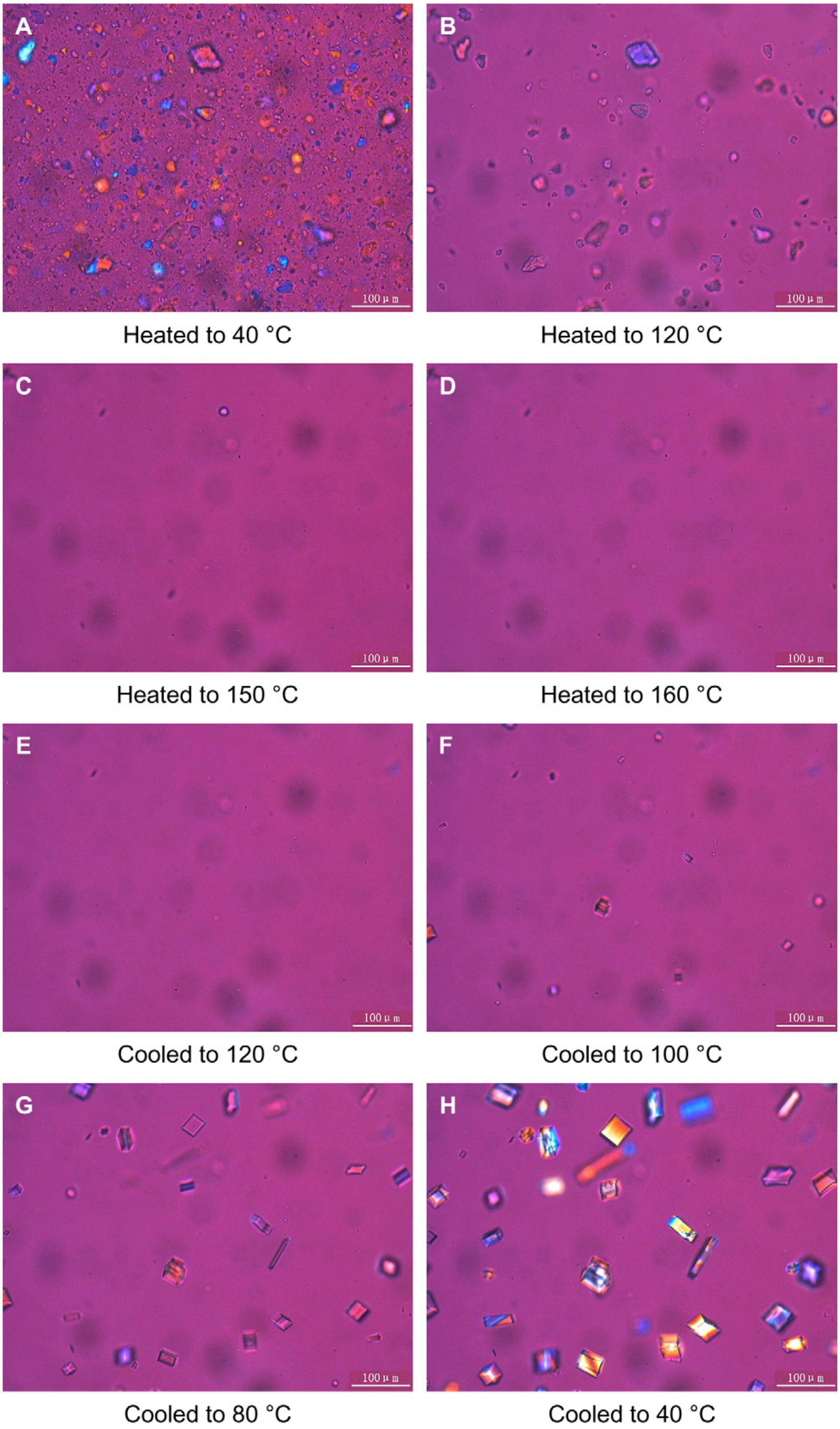


Fig. 7. POM images of the sample P5-40 during heating and cooling process (10 °C/min).

the blending temperature should be an effective way to disperse POSS in rubber compounds such as silicones. Since the silicone rubber was stable to at least 300 °C (judging from Fig. 5), the blending temperatures chosen were 40, 80, 120, 160, 180, and 230 °C. The POSS was present at a loading of 5 wt%, the rotational speed during blending was 80 r/min, and the mixing time was 30 min. Further details are given in Table 1. During mixing, it was observed that the blends in the chamber of the mixer at low mixing temperature were opaque, implying that POSS crystals were poorly dispersed in the silicone rubber. When the processing temperature was increased to 160 °C, the blend gradually became transparent. The transparency was a rough indication of the quality of the POSS dispersion in the rubber, which meant that POSS could apparently be dispersed nearly at the molecular level at these elevated temperatures.

An optical microscope permitted visual observation of the state of the dispersion of the POSS in the blends prepared at different temperatures. A camera was installed at the top of the optical microscope to take photographs, some of which are shown in Fig. 6. The size of the pure POSS crystals in the absence of silicone rubber was about 300 μm, as can be seen from Fig. 1B, which showed POSS crystals in large aggregates. Parts A and B of Fig. 6 show that the POSS crystals became smaller during processing and some large aggregates up to 100 μm were present at low mixing temperatures. At a mixing temperature of 120 °C, the POSS crystals suddenly became as small as approximately 20 μm, and their shapes seemed more regular. Also interesting was the fact that at higher mixing temperatures, the shape of the POSS crystals became hexahedral or flake-like (Fig. 6D–F). It seems that the POSS crystals at higher temperatures (about 160 °C) were first highly dissolved in the silicone rubber, but then recrystallized out in the form of new crystals when the mixture was cooled.

In order to test this speculation, a part of the POSS/silicone rubber blend P5-40 was placed between two glass plates. It was heated to 160 °C from 40 °C (with a heating rate of 10 °C/min), kept at this higher temperature for 3 min, and then cooled to 40 °C (at 10 °C/min). The morphology evolvement of the sample as recorded using a polarizing optical microscope, is shown in Fig. 7. (Dark spots in the background were from the instrument, not from the sample.) The original crystals of POSS in sample P5-40 had an irregular shape (as can be seen in Fig. 7A), and with heating their number gradually decreased. Since the temperature of 160 °C was far below the melting temperature of POSS crystals and no shear force was exerted on the blend, this strongly suggested that the POSS crystals dissolved in silicone rubber matrix (presumably because of structural similarities between these two components, leading to good compatibility between POSS and silicone rubber). Such solubility of POSS in the silicone polymer was seen to increase with temperature, as expected. The POSS crystals completely disappeared at 160 °C (Fig. 7D), which implied that the POSS was totally dissolved in the silicone matrix. Upon subsequent cooling, crystals nucleated and tiny crystals could be observed at 120 °C (Fig. 7E). When the temperature was further decreased, more crystals began to form and grew larger. These results also explained why the blends became transparent when the processing temperature rose to 160 °C, which was well below the melting point of POSS.

According to the above POM observation, the changes in shape of POSS crystals in Fig. 6 could also be explained.

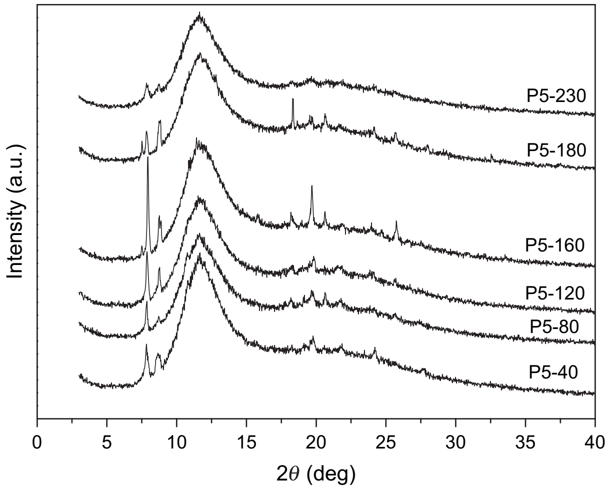


Fig. 8. The X-ray diffraction profiles of the POSS/silicone rubber blends prepared at different mixing temperatures.

For the blends prepared at low mixing temperatures (such as P5-40 and P5-80), the original POSS aggregates were broken up and the POSS aggregate sizes were changed by the shear stress from the rotating rotors of the Haake Banbury mixer, so the POSS crystal shapes were irregular. With increasing mixing temperatures (such as in the case of P5-120), partial POSS crystals began to dissolve in the silicone matrix, which resulted in lessening of the size and number of large POSS aggregates. During the cooling process, the decrease in solubility led to dissolved POSS molecules being crystallized out. Because of the absence of full crystal growth, tiny crystal units were formed. In this kind of blend at 120 °C, both numerous small POSS crystal aggregations with irregular shapes and tiny POSS crystal units with hexahedral or flake-like structures from recrystallization co-existed in the silicone matrix. When the mixing temperature continued to increase (such as in the cases of P5-160 and P5-180), POSS aggregates completely dissolved in the silicone rubber. With cooling, POSS crystals

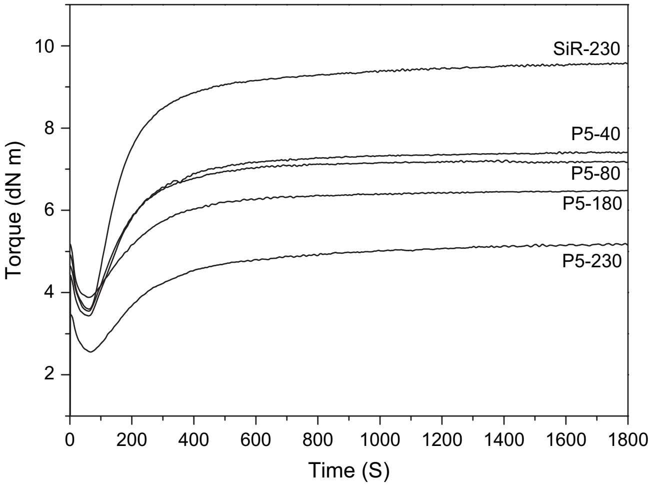


Fig. 9. The relation between the torque and time of blends prepared at different mixing temperatures during curing process.

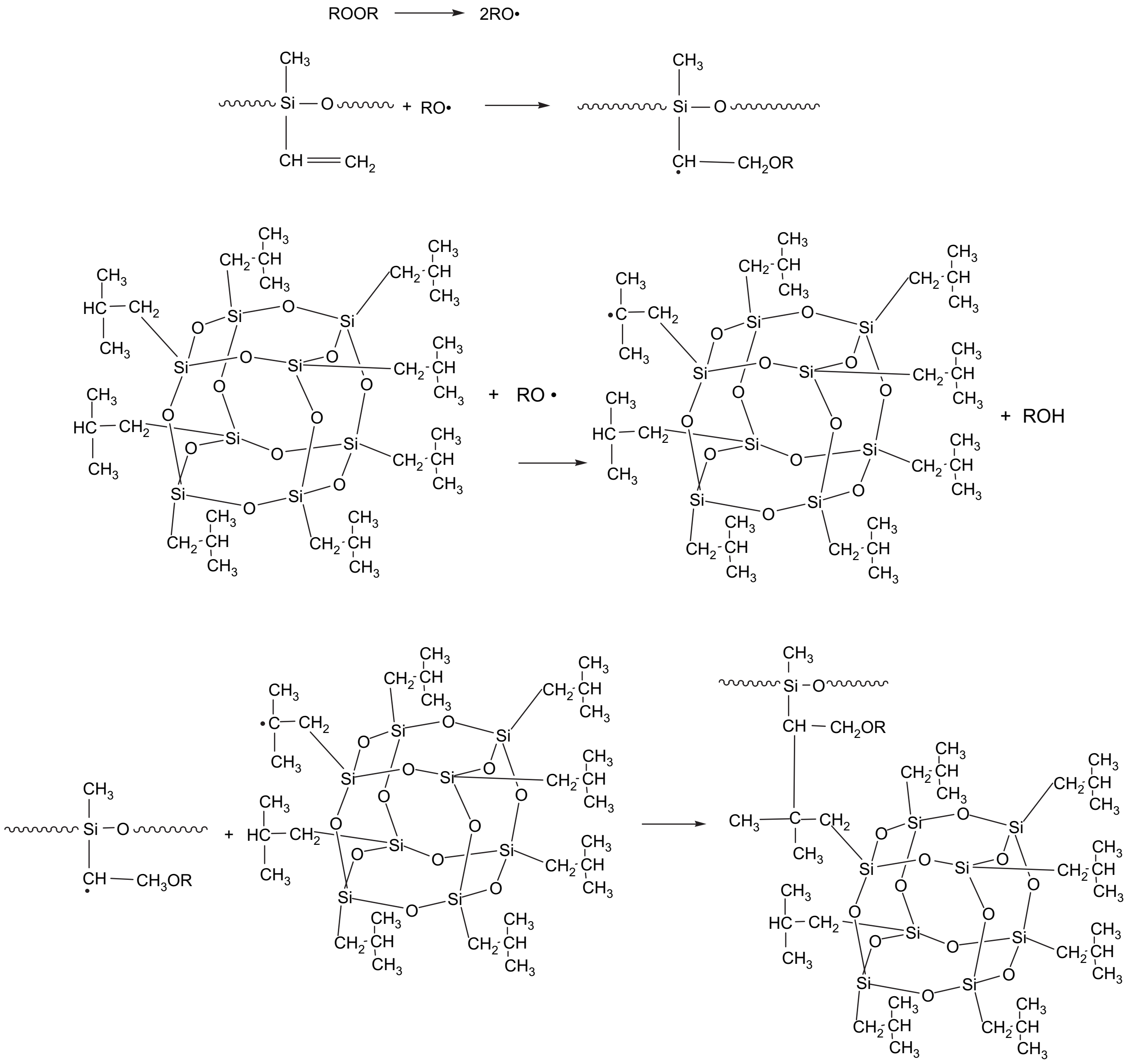


Fig. 10. Scheme of possible reaction between peroxide and silicone rubber chain and POSS molecules.

with hexahedral or flake-like structure grew and the crystal size became larger.

The dispersion state of the POSS in silicone rubber was further studied by XRD. Fig. 8 depicts the XRD patterns of blends prepared at different mixing temperatures. (After mixing was completed at different mixing temperatures, all samples were immediately taken out from the Haake Banbury mixer and cooled to room temperature in air.) Three major peaks appeared in the XRD patterns. First, a very broad peak appeared at a value of 2θ of 11.7°, corresponding to the amorphous structure peak of the silicone rubber. The other two peaks occurred at 2θ values of 7.9° and 8.8°, which correspond to the POSS characteristic peaks found for the as-received POSS powder. The existence of characteristic peaks of POSS crystals in XRD patterns of un-cross-linked blends meant that POSS was dispersed in particle form even for blends made at high temperatures. This was consistent with the morphologies shown in Figs. 6 and 7. Relevant here was the fact, shown in Fig. 8, that the intensity and breadth of the POSS characteristic peaks had changed with mixing temperature. When the blends were prepared at lower mixing temperatures (40 and 80 °C), the dispersion of isobutyl-POSS in the silicone rubber matrix was poor and much of the POSS existed in large crystal aggregates. This was a result of the lower solubility of POSS in silicone rubber at the lower temperatures, and the fact that the blending temperature was far below the POSS melting temperature. With increased mixing temperature (120 and 160 °C), the POSS characteristic peaks became more pronounced and sharper. These peaks were from the POSS that recrystallized from the silicone matrix during cooling. These crystallites probably possessed fewer defects and more regular shapes. Moreover, a new peak at $2\theta = 7.6°$ appeared (in samples P5-160 and P5-180), also indicating some changes in the POSS crystal structure. This peak could be attributed to different crystalline forms of POSS from recrystallization. When the mixing temperature was increased to 180 °C, the intensity of the POSS characteristic peaks suddenly decreased. At the higher mixing temperatures, the dispersed POSS molecules could interact with silicone rubber chain due to the increasing thermal movement, which hindered the POSS molecules from migrating toward each other during cooling so that some POSS molecules was left in silicone matrix and fewer POSS crystals precipitated.

3.3. Effect of vulcanization on the dispersion of POSS

After the experiments described above, the POSS/silicone rubber blends prepared at different mixing temperatures were vulcanized using peroxide thermolysis. Curing curves of these blends obtained using an oscillating disk rheometer are shown in Fig. 9. Higher values of the torque correspond to higher cross-link densities of the silicone rubber. There was a noticeable decrease in the cross-link density when the POSS was added, which indicated that the POSS adversely affected the cross-linking. Moreover, the decrease in cross-link density was larger at the higher mixing temperatures. This indicated that the more molecularly dispersed POSS in the silicone rubber, the larger will be its effect on the curing process. There were two possible reasons: the plasticizing effect of dissolved POSS molecules and the chemical reaction of POSS molecules with curing agent. It was seen from Fig. 9 that the minimum torque of P5-180 was higher than that of SiR-230, although the maximum torque of P5-180 was obviously lower than that of SiR-230. This showed that the decrease in cross-link density with the addition of POSS should be ascribed to the chemical reaction of POSS molecules with the curing agent. More specifically, POSS molecules could have bonded to the silicone rubber chains in a way that inhibited network formation. Decomposition of the curing agent into free radicals could form macromolecular free radicals through addition reactions. The free radicals could capture the hydrogen from the isobutyl groups on the POSS molecules to form isobutyl free radicals, as illustrated in Fig. 10. The isobutyl free radicals could react with vinyl free radicals on the silicone rubber chain, and the reduced numbers of vinyl free radicals could then lead to the observed decreases in cross-link density.

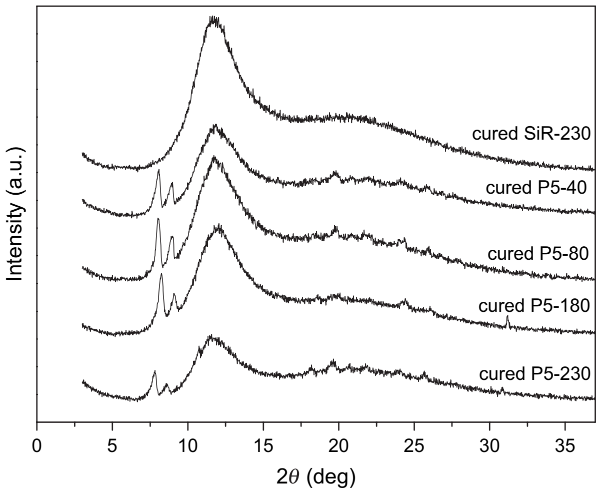


Fig. 12. The X-ray diffraction profiles from the cured blends prepared at different mixing temperatures.

The dynamic storage moduli of the cured blends as a function of strain are shown in Fig. 11. Increased mixing temperature decreased the storage moduli, especially in the case of sample P5-230. The decreases in moduli were caused by the already mentioned decreases in cross-link density and confirmed the conclusions reached from the above analysis of the curing curves.

Fig. 12 depicts the XRD results for the cured POSS/silicone rubber blends. (After the vulcanization was finished at 160 °C,

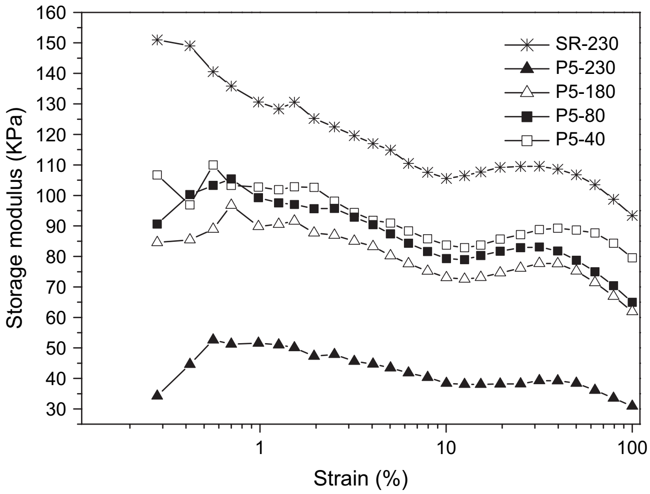


Fig. 11. The relation between the storage modulus and strain of cured blends prepared at different mixing temperatures.

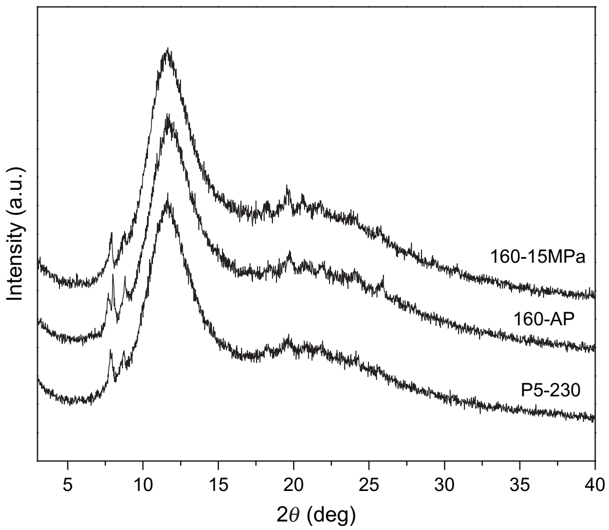


Fig. 13. The effect of temperature and pressure on XRD patterns of the sample P5-230.

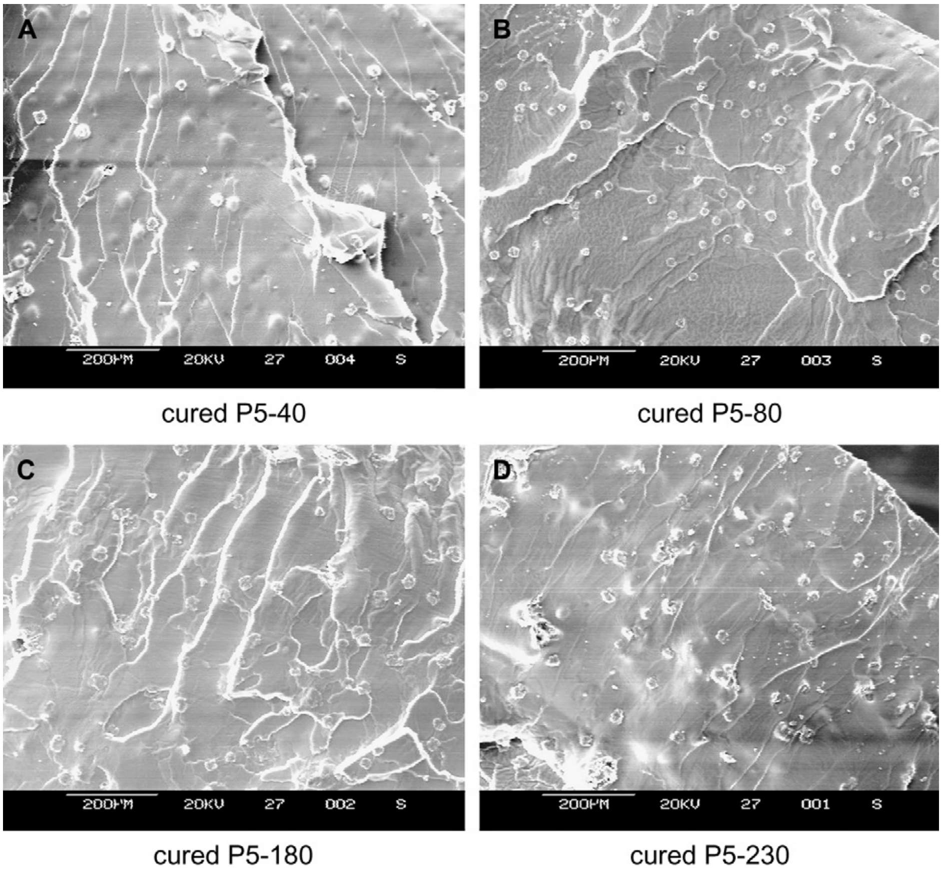


Fig. 14. SEM micrographs of cured blends prepared at different mixing temperatures.

all samples were immediately taken from hot press, cooled to room temperature in air, and held for the same time as the POSS/silicone rubber blends before the XRD measurements were made.) Comparison of these results with those in Fig. 8 showed that the POSS characteristic peak intensities significantly increased after the vulcanization, possibly because of more pronounced crystallization. The effects of temperature and pressure on the POSS dispersion were also investigated. Sample P5-230 without curing agent was heated to 160 °C at atmospheric pressure (AP) and designated as sample 160-AP. In contrast, sample P5-230 without curing agent was heated to 160 °C under high pressure, specifically at 150 kgf/cm^2 and designated as 160-15MPa. Fig. 13 represents the influence of temperature and pressure on the XRD patterns of the sample P5-230. It can be seen that there were no significant changes observed in the intensities of the POSS characteristic peaks, which meant that the pressure and temperature during vulcanization were not key factors leading to high crystallization of POSS in rubber matrix, but the formation of network could be the important factor.

The morphology of the cured blends prepared at different mixing temperatures was also investigated by SEM (Fig. 14). The POSS crystals in the cured silicone rubber were roughly spherical, while those in the uncured blends were hexahedral or flake-like. In addition, the crystals in the cured blends prepared at high mixing temperatures seemed larger than those in the cured blends prepared at low mixing temperatures. To clarify these changes, part of blend P5-40 containing curing agent was sandwiched between two glass plates. It was then heated from 30 to 160 °C at a heating rate of 100 °C/min, kept at this temperature for the optimum cure time t_{90}, and then cooled to 30 °C at a rate of 10 °C/min. The sample was observed through polarizing optical microscope at whole process. Fig. 15 shows that the POSS crystal aggregates were in the process of dissolving, but this leveled off after approximately 3 min. During cooling, the POSS crystallites began to precipitate, starting at around 80 °C. In unvulcanized blends, the POSS crystals readily grew into perfect hexahedral or flake-like crystals, while in the vulcanized blends, the POSS crystals were constrained by the network structure and tended to aggregate into small, roughly spherical shapes.

As was shown in Fig. 7D, some POSS crystal aggregates had already diminished in the blends at elevated temperatures of 160 °C, but some aggregates still remained after curing was complete (Fig. 15B–D). This confirmed the conclusions that the POSS solubility decreased due to the formation of the network structure. During the beginning of the curing process, dissolved POSS molecules could react with vinyl free radicals on the silicone chains, which would affect the network formation. For the blends prepared at low mixing temperatures, POSS crystals existed in the form of larger aggregates, which

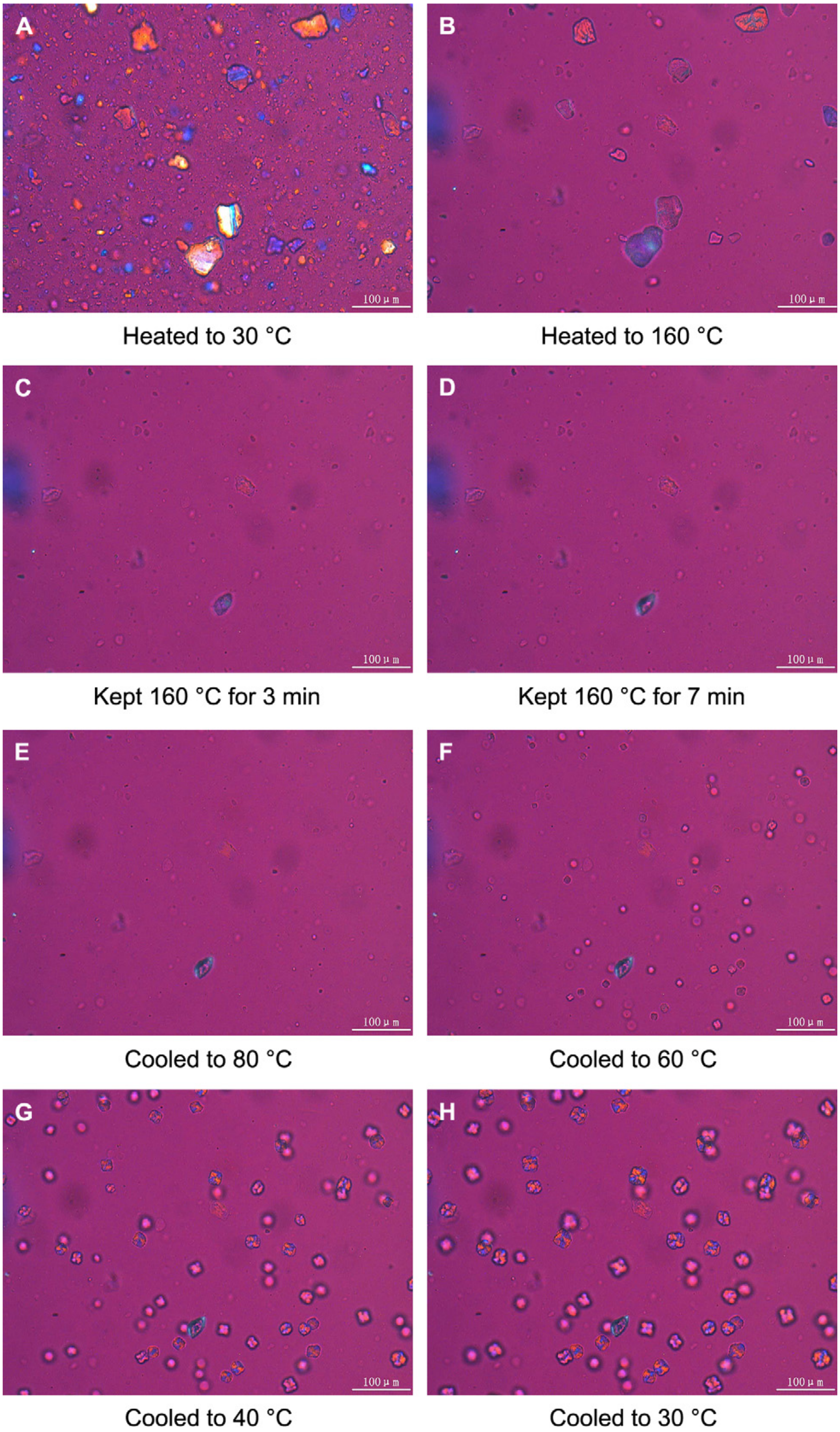


Fig. 15. POM images of the sample P5-40 containing curing agent during heating and cooling process.

first had to be dissolved for reactions with the silicone rubber. For the blends prepared at high mixing temperatures, there were already POSS molecules dissolved in the silicone so the probability of such reactions would be larger than in the blends prepared at low mixing temperature. This would explain some of the rheometer torque results shown in Fig. 9.

4. Conclusions

Melt mixing was used to prepare blends of a silicone rubber with octaisobutyl-POSS, a polyhedral oligomeric silsesquioxane that was highly crystalline and stable over the range 26–180 °C. Oxidation at high temperatures occurred through partial loss of the isobutyl organic substituents, which could lead to condensation into a POSS resin. For the blends prepared at low mixing temperatures, the POSS crystals were dispersed in the silicone rubber as large crystal aggregates with irregular shapes. For the blends prepared at high mixing temperatures, the increased thermal energy caused some of the POSS crystals to dissolve into the silicone rubber. During subsequent cooling, some dissolved POSS molecules crystallized out in hexahedral or flake-like structures. At the higher mixing temperatures, some POSS molecules could interact with the silicone chains so that fewer POSS crystals precipitated during cooling. During curing of the silicone, POSS molecules could react with the silicone chains, which could hinder the silicone network formation, which resulted in decreases in rheometer torque during curing. POSS crystals began to dissolve during the initial curing stages, but the solubility limit was apparently decreased by the network formation. During subsequent cooling, roughly spherical POSS crystals crystallized out and the presence of the network structure could have an effect on this process as well.

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