Polyhedral oligomeric silsesquioxane/silica/polydimethylsiloxane rubber composites with enhanced mechanical and thermal properties

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ABSTRACT: Composites of polydimethylsiloxane (PDMS) rubber modified by three kinds of polyhedral oligomeric silsesquioxanes (POSSs) as well as fumed silica were prepared through solution blending and then open two-roll mill blending with curing agent. Subsequently, the influences of POSS on mechanical and thermal properties of the resulting composites were investigated in detail. The addition of POSS significantly enhanced the tensile strength and elongation at break of the composite but lowered the tensile modulus, which could be ascribed to the interruption of silica–silica and silica–PDMS interactions. Octamethylsilsesquioxane (OMS)/ silica/PDMS and octaphenylsilsesquioxane (OPS)/silica/PDMS composites did not show desirable mechanical and thermal properties. Nevertheless, heptaphenylvinylsilsesquioxane (VPS)/silica/PDMS composite with 5 wt % VPS exhibited enhanced glass transition temperature (T_g), mechanical properties, and thermal stability. Further studies revealed that more VPS unfavorably affected properties of the composite. Scanning electron microscope and X-ray diffraction demonstrated that owing to the grafting reaction, 5 wt % VPS in the rubber matrix could form microcrystal domains the most effectively. Thus, the improved mechanical properties and thermal stability just resulted from the the formation of microcrystal domains and the increase in stiffness of PDMS chains because of the graft of VPS onto PDMS. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42173.

INTRODUCTION

As oil resources are drying up, organic silicone materials, which come from nonoil routes, are paid more and more attention. Thereinto, polydimethylsiloxane (PDMS) rubber is among the most focused new materials. PDMS rubber possesses an inorganic [—Si—O—Si—] structure in the backbone and organic substituents in the outer space. It is endowed with some exceptional properties such as high and low temperature resistance, ultraviolet resistance, weatherability, electric insulativity, atomic oxygen resistance, and so on.[1–3] Nevertheless, its poor mechanical properties tremendously restrict its practical application, so PDMS merely can be used after the addition of fillers.

Among all the fillers, silica is the most universally used one.[4,5] Dewimille *et al.*[6] reported that PDMS/silica nanocomposites synthesized through sol–gel technique showed prominently improved mechanical properties. Moreover, in PDMS silica nanocomposites, Fragiadakis *et al.*[7] observed two α relaxations which were separately assigned to unrestricted PDMS chain segments and PDMS chain segments whose relaxation was restrained by silica. Thus, silica could enhance mechanical properties of PDMS by restricting the motion of PDMS chain segments.

Known as the smallest possible silica particles,[8] polyhedral oligomeric silsesquioxane (POSS) has been attracting a great deal of attention during the past decades. Owing to the surrounding organic groups, POSS is compatible with most polymers, such as polyethylene,[9] epoxy,[10] polyurethane,[11] chlorinated polyethylene,[12] polyamide,[13] and polystyrene[14]. However, the morphology of POSS in polymer matrix, which is responsible for the modification effect, intensively depends on the incorporation method of POSS. Explicitly, POSS without reactive groups can only physically blend with polymers, whereas POSS containing reactive groups can be grafted onto polymer matrix, be copolymerized into polymer main chain or act as cross-linking point.[15,16]

Because of the similar chemical composition, POSS is also explored to be incorporated into PDMS to get composites with enhanced thermal resistances, mechanical properties, dielectric

properties and so on. In our previous researches, two kinds of POSSs were respectively grafted onto and block copolymerized with PDMS oligomers to prepare room temperature vulcanized (RTV) silicone rubbers.[17,18] The resulting rubbers showed remarkably modified thermal properties in both nitrogen and air. Pan et al.[19] found that incorporating POSS-based filler into PDMS by simply blending had little effect on mechanical properties of the resulting composite, but when POSS was partially bonded to PDMS network, the mechanical properties could be improved. As is much more expensive than silica, POSS is impractical to be used as largely as silica. Nevertheless, PDMS composites only incorporate a little POSS still do not have comparable mechanical properties with that incorporate large numbers of silica, but blending both POSS and silica might achieve an excellent effect.

An exclusive study concerning PDMS composited with both POSS and silica was presented by Joshi et al.[20] In their work, fumed silica was firstly treated by aliphatic and aromatic groups, and then the resulting silica and two kinds of nonreactive POSSs were physically incorporated into RTV silicone rubber. The nanocomposites with silica treated by similar groups as the POSS showed higher tensile strength and modulus, and the nanocomposites incorporated with phenyl-based POSS displayed higher thermal stability than that with methyl-based POSS. However, as mechanical and thermal properties of the above RTV silicone rubber based nanocomposites were still not good enough to meet the requirement of practical use, they should be further improved.

In this article, two nonreactive POSSs and one reactive POSS were respectively incorporated into high temperature vulcanized (HTV) PDMS loaded with fumed silica. Owing to the diversities in microstructures of POSSs derived from distinctions in compatibility of PDMS and POSSs with different functional groups, the resulting composites displayed quite different properties with each other. At a certain content of POSS, composite of PDMS incorporated with reactive POSS showed obviously enhanced mechanical properties and thermal stability. The article investigated the relationships between morphologies of POSSs and properties of the resulting composites, and thus could provide guiding significance for the preparation of high-performance PDMS-based composites which can meet practical application.

EXPERIMENTAL

Materials

In this study, octamethylsilsesquioxane $[(CH_3SiO_{1.5})_8$, OMS], octaphenylsilsesquioxane $[(C_6H_5SiO_{1.5})_8$, OPS], heptaphenylvinylsilsesquioxane $[CH_2=CH(C_6H_5)_7(SiO_{1.5})_8$, VPS], and PDMS having 0.18% vinyl substituents and a molecular weight of 528,429 g/mol were all synthesized in our laboratory.[21,22] Fumed silica (abbreviated as silica) which has been pretreated was provided by Zhonglan Chenguang Chemical Research Institute. Toluene was obtained from Kelong Chemical, Chengdu, China. The peroxide vulcanizing agent, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (DBPH) was purchased from Dongyang Chemical, Haian, China. OMS: FTIR (KBr, cm^{-1}): 2971 (vC—H), 1410 (ωC—H), 1116 (vSi—O—Si), 1269.71 (vSi—C); ^{29}Si NMR

(C_3D_6O, ppm): -67.03 (**Si—CH$_3$**). OPS: FTIR (KBr, cm^{-1}): 1136 (vSi—O—Si), 3073 (vC—H of phenyl), 998, 1029, 1431 (Si—Ph), 697 (βC—H of phenyl), 742 (γC—H of phenyl), 428 (τSi—O—Si), 501 (δSi—O—Si); ^{29}Si NMR (C_3D_6O, ppm): -75.90 (**Si—Ph**). VPS: FTIR (KBr, cm^{-1}): 1136 (vSi—O—Si), 3074 (vC—H of phenyl), 1610 (vC=C), 1409 (βC=C); ^{29}Si NMR (C_3D_6O, ppm): -78.2(s, 4**Si**), -78.4 (s, 3**Si**), -79.2(s, 1**Si**).

Preparations of POSS/Silica/PDMS Composites

In present study, PDMS was blended with silica and the three types of POSSs. For each kind of POSS, composites with different POSS loadings were prepared and labeled as M-x, P-x or V-x (M-x, P-x and V-x correspond to OMS/silica/PDMS, OPS/silica/PDMS, and VPS/silica/PDMS composites with POSS loadings of x wt % based on PDMS, respectively). A sample of PDMS only composited with silica named MVQ was also prepared for comparison. All the samples were prepared in the same way including MVQ. POSS and PDMS were dissolved in toluene respectively and stirred adequately, and then the two kinds of solution were mixed directly. After being ultrasonic processed and mechanical stirred, the mixture was placed to vacuum oven at 100°C for 48 hours to discharge solvent. In two days, the above mixture, silica (50 wt % of PDMS) and DBPH (2 wt % of PDMS) were mixed with an open two-roll mill to get a good distribution. Subsequently, the obtained product was placed to plate vulcanizing press at 165°C and a pressure of 10 MPa for 12 min, followed by postcuring at 180°C for 4 hours.

Measurements

Scanning electron microscopy (SEM) was preformed on a JSM-5900LV scanning electron microscope at a voltage of 20 kV. The vulcanized samples were placed into liquid nitrogen for some time and then fractured into two pieces to create fresh surfaces. The samples were then coated with a gold coating film of about 100 Å thick, examined and photographed in the microscope.

The mechanical tests were carried out using an XL-250A universal tensile testing machine at room temperature and a relative humidity of 50%. Each sample was trimmed into a dumbbell of 5 cm in length, 1 cm in width, and the narrow section was cut into 2 cm in length, 0.4 cm in width. All the samples are 0.3 mm in thickness. The crosshead speed was 200 mm/min. All measurements were repeated five times and the results reported were the average values.

Thermo gravimetric analysis (TGA) was studied on a Mettler Toledo TGA/DSC1 thermogravimetric analyzer. The samples were heated from 30°C to 800°C at a heating rate of 10°C/min under a flow of nitrogen (50 mL/min).

Dynamic mechanical analysis (DMA) was performed on a TA Q800 (TA Instrument, USA) analyzer. The measure temperature ranged from -135°C to 0°C and the heating rate was 3°C/min. The tests were carried out at a frequency of 1 Hz.

X-ray diffraction (XRD) spectra analyses were carried out on the Philips X'Pert Graphics and Identify with Ni-filtered Cu Ká radiation. The 2θ angle ranged from 5° to 45°, and the scanning rate was 2.4 deg/min.
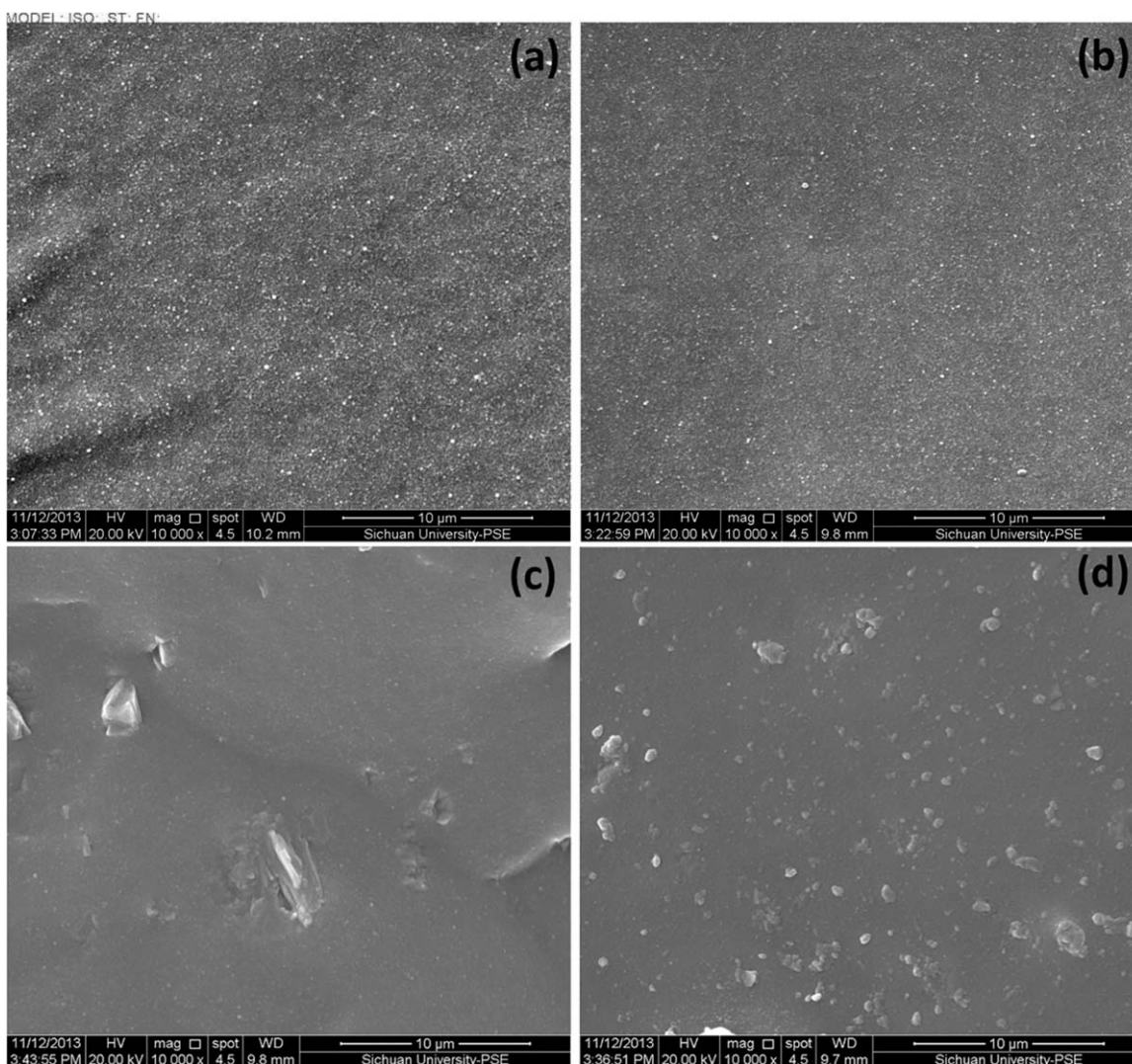
Figure 1. SEM images of (a) MVQ, (b) M-5, (c) P-5, and (d) V-5.

RESULTS AND DISCUSSION

SEM Characterization

The SEM images of dispersion state of POSS and silica in PDMS are illustrated in Figure 1. Obviously, silica and POSS are dispersed quite uniformly in PDMS matrix. Wherein, nearly no agglomerate can be detected in the samples MVQ and M-5. However, agglomerates can be observed in the samples P-5 and V-5, among which agglomerates in P-5 are much larger than that in V-5. Subsequently, the influences of such microstructures on properties of the composites are discussed in the following sections.

Mechanical Properties

It is well known that reinforcement of PDMS rubber is the most important problem, so the influences of POSS on mechanical properties of POSS/silica/PDMS composites are studied first of all. The stress–strain curves of MVQ, M-5, P-5, and V-5 are all displayed in Figure 2, and at the same time the values of three relevant parameters are listed in Table I.

As can be seen, compared with the results in previous literature, the composites have superb mechanical properties. With the addition of POSS, an evident decrease in tensile modulus can be observed, which is ascribed to the impairment of the weak Si...O and Van der Waals interactions between silica and PDMS, within silicas and within PDMS chains.[23] What is inspiring is that both tensile strength and toughness of the composites are distinctly enhanced by the addition of POSS. Wherein, because of the lubrication action of OMS derived from its small size, M-5 shows the best elongation at break. Nevertheless, tensile modulus and tensile strength of P-5 and V-5 are higher than that of M-5 because of the inherent stability of phenyl. In general, the agglomeration of fillers tends to decrease tensile strength of the resulting composite because the agglomerates act as strong stress concentrators.[24] As verified by Meng et al.,[25] it is an effective way for double bond-containing POSS to be grafted onto PDMS chains by such in situ grafting reaction. By contrast, just because of the graft of VPS onto PDMS chains, V-5 displays better tensile strength and smaller agglomerates appear in V-5 than in P-5. Simultaneously, V-5 shows higher elongation at break which means better toughness maybe because of the increase in free volume caused by the
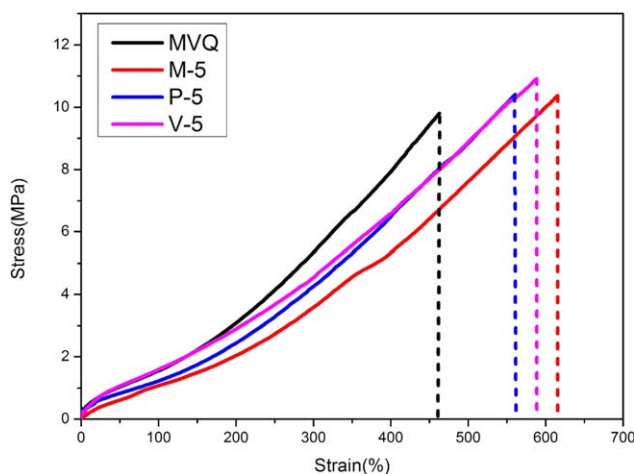
Figure 2. Stress–strain curves of MVQ, M-5, P-5, and V-5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

extension in distances between PDMS chains with the graft of POSS. On the other hand, the graft of VPS tends to increase the stiffness of PDMS chains, so the overall result is that tensile modulus, tensile strength, and elongation at break of V-5 are all ideal.

Thermal Stability

Thermal stability is always dominated by analogical causes with mechanical properties, so thermal stability tests were also conducted to evaluate the modification effect of POSS on the composites. TG curves of the three kinds of POSSs and the four kinds of composites are displayed in Figure 3, and corresponding parameters are listed in Table II.

As shown in Figure 3, OMS begins to lose weight at about 200°C and ends at 320°C with almost nothing left. However, Tamaki et al.[26] found that OMS does not decompose until 415°C, so the weight loss at such a low temperature is ascribed to sublimation.[27] By comparison, OPS and VPS show better thermal stability where VPS starts to decompose earlier than OPS and also the residual yield of VPS is lower than that of OPS. The excellent thermal stability of OPS derives from the intense phenyl–phenyl interactions; while for VPS, as a phenyl is substituted by hydrogen, phenyl–phenyl interactions are impaired, which results in worse thermal stability.

TG curves (Figure 3) of MVQ and P-5 are quite comparative with each other where P-5 shows slightly higher residual yield than MVQ. In the two samples, only silica was left. M-5 begins

Table I. The Strain–Stress Results of MVQ, M-5, P-5, and V-5

Sample	Ultimate tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
MVQ	9.9 ± 0.3	2.98 ± 0.13	472.3 ± 33.7
M-5	10.2 ± 0.2	2.23 ± 0.20	634.5 ± 20.1
P-5	10.4 ± 0.4	2.41 ± 0.12	560.3 ± 24.7
V-5	10.7 ± 0.3	2.40 ± 0.08	593.3 ± 41.8
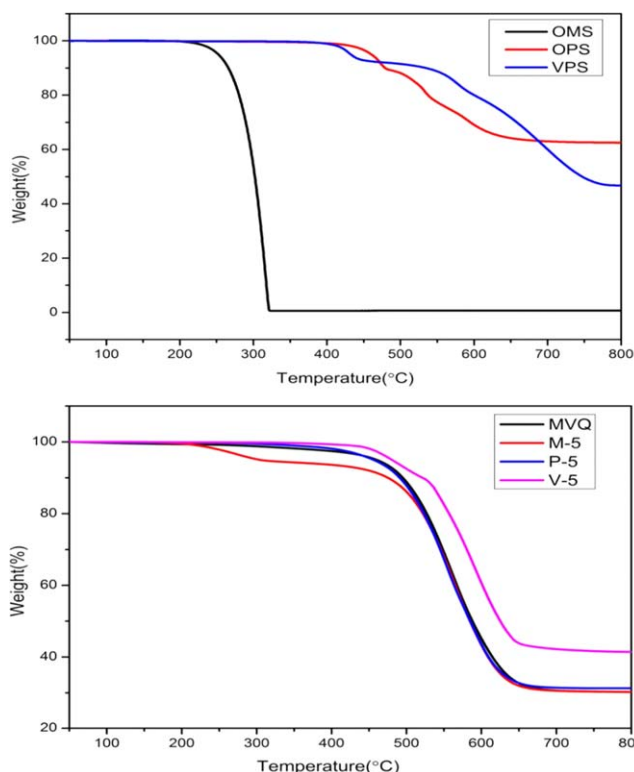
Figure 3. TG curves of POSSs and composites in N_2 atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to lose weight at a much lower temperature which just corresponds to the weight loss of OMS, so this situation also derives from the sublimation of OMS. Interestingly, TG curve of M-5 is consistent with that of MVQ at higher temperatures, which indicates that the addition of OMS does not affect the degradation of PDMS matrix.

Nevertheless, the thermal stability of PDMS could be dramatically enhanced by incorporating VPS. For V-5, the initial degradation temperature which corresponds to 5% weight loss (T_i) is improved from 460°C to 480°C, the temperature of the greatest amount of weight loss (T_m) is boosted from 560°C to 593°C, and the degradation residual yield is enhanced from 30.3% to 41.4%. So we may consider that except for the extra silica, some new matters are also left. The origin of the improvement in thermal stability can be explained through exploring the thermal degradation mechanism.

The wellknown thermal degradation mechanism of silicone rubber is illustrated in Figure 4. When PDMS is heated in N_2, the trimer cyclic oligomer (D_3) comes into being abundantly, accompanied by higher oligomers, such as tetramer (D_4), pentamer (D_5), etc.[28] During the degradation process, the cyclic transition state can be formed anywhere in the PDMS chains until the chains are too short.[29] Camino et al.[30] further proposed that the formation of cyclic transition state is the rate-determining step and the flexibility of PDMS chains favors the formation of cyclic transition state. When VPS is grafted onto PDMS chains, the flexibility of PDMS chains is overwhelmingly

Table II. Thermal Properties of POSSs and Composites in N2 Atmosphere

Sample	The initial degradation temperature (°C)	The temperature of the greatest amount of weight loss (°C)	The degradation residual yield (%)
OMS	252	–	0.6
OPS	460	–	62.5
VPS	432	–	46.7
MVQ	460	560	30.3
M-5	304	564	30.2
P-5	455	556	31.3
V-5	480	593	41.4

Figure 5. Variation of E' as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]
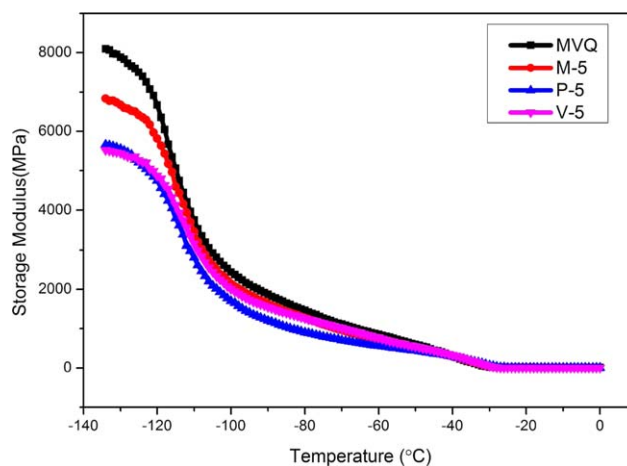
reduced, resulting in that the formation of the cyclic transition state becomes much difficult, so the degradation process comes to an end ahead of schedule.

Dynamic Mechanical Analysis

Both mechanical properties and thermal stability of the composites are macro reflections of microstructures. As a medium to associate macro performances with microstructures, DMA was applied to verify the changes in microstructures with the incorporation of POSS which lead to the above modifications in properties.

The temperature dependence of storage modulus (E') for the composites is displayed in Figure 5. With the elevation of temperature, E' values remain stable first and then drop sharply, which is ascribed to the glass transition of PDMS. Before glass transition, samples with POSS show lower E' values than MVQ. The decrease of E' value is also caused by the interruptions of interactions within silicas and PDMS chains with the addition of POSS.

The curves of tan δ versus temperature in Figure 6 illustrate the glass transition behaviors of the composites more explicitly. M-5 and P-5 show higher tan δ values than others during glass transition where the case for M-5 may be dominated by the intense restriction from OMS filler network to PDMS chain segments which originates from the good distribution of OMS in PDMS matrix, and that for P-5 is primarily ascribed to the friction between amorphous PDMS and OPS agglomerates. Regarding V-5, although it displays almost equal tan δ value as MVQ

during glass transition, it presents the highest glass transition temperature (T_g). Similar to the mechanical properties, the improved T_g also can be attributed to the increase of stiffness of PDMS chain segments which derives from the hindrance to the motion of PDMS chain segments from the giant grafted VPS. Moreover, the tan δ curve of V-5 demonstrates the widest glass transition section, which stems from the heterogeneity of relaxation modes of PDMS chains owing to the graft of VPS.

X-ray Diffraction Characterization

In brief, not only the kinds of groups in POSS, but also the incorporation methods determine the microstructures of the composites. So XRD studies were performed to provide further information on aggregation structure of POSS in the composites.

The XRD spectra of OMS, OPS, VPS, MVQ, M-5, P-5, and V-5 are shown in Figure 7. As can be seen, the three kinds of POSSs are all crystalline: OMS shows a strong reflection at 2θ of
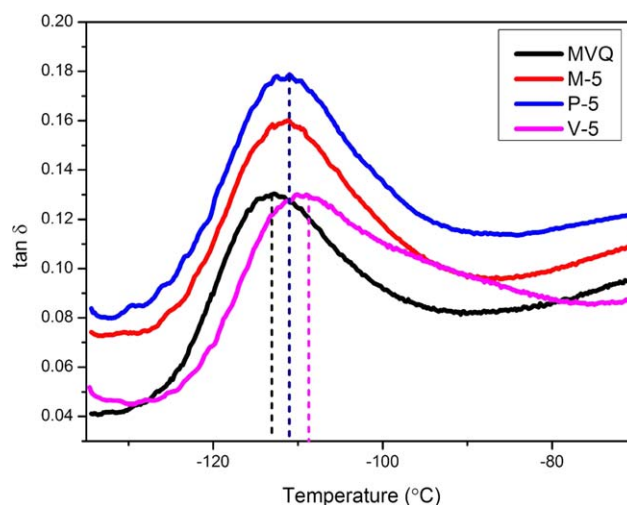
Figure 6. Variations of tan δ as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Figure 4. Thermal degradation mechanism of silicone rubber in inert atmosphere.
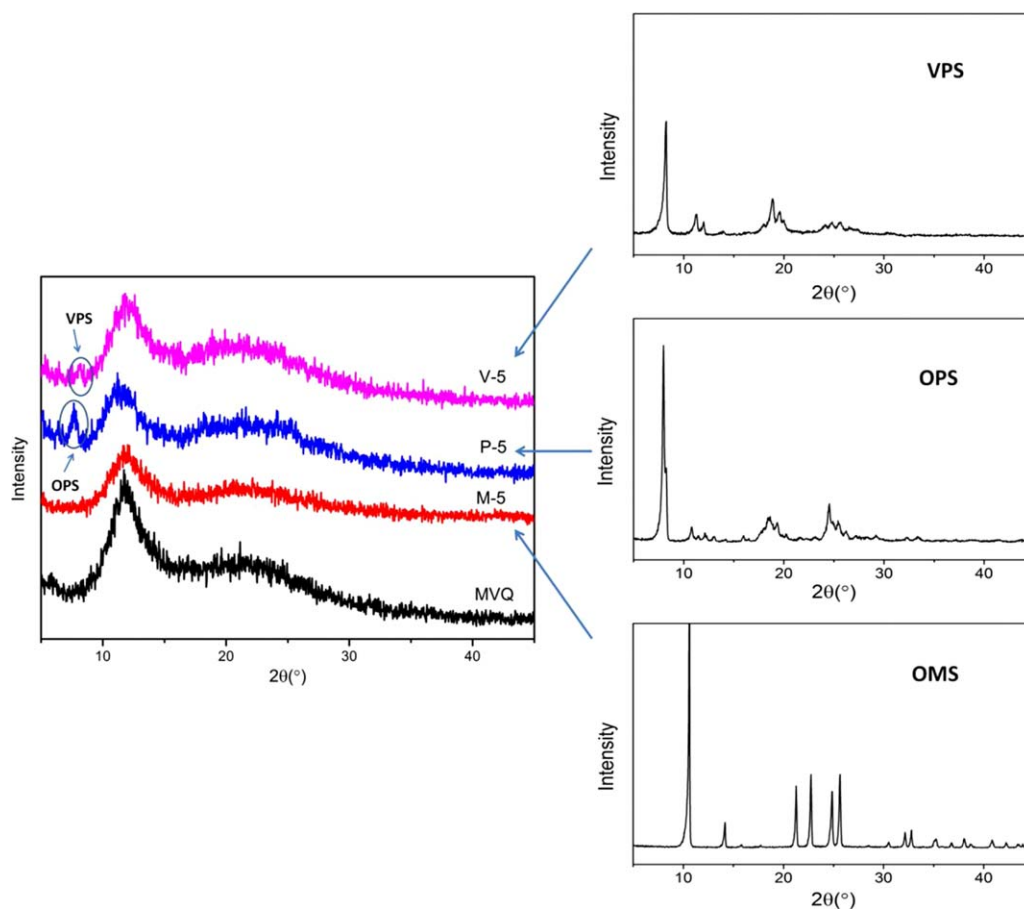
Figure 7. XRD spectra of OMS, OPS, VPS, MVQ, M-5, P-5, and V-5. [Color figure can be viewed in the online issue, which is available at wileyonlineli-brary.com.]

10.59° and some weaker reflections at 14.16°, 21.27°, 22.74°, 24.86°, and 25.65°; OPS shows a strong reflection at 2θ of 7.99° and some weaker reflections at 10.80°, 18.63°, and 24.54°; VPS shows a strong reflection at 2θ of 8.22° and some weaker reflections at 11.22°, 12.00°, 17.99°, 18.87°, and 24.09°.

In the composites, a very broad peak at 2θ of about 11.7° corresponding to the amorphous structure of PDMS is striking. However, the peak intensities of the samples with POSS are weaker than that of MVQ, indicating that the regularity of PDMS molecular chains is reduced. Comparing the three kinds of composites, the reflection of OMS is not detected in M-5, which means a molecular level distribution of OMS. However, an obvious peak and a vague peak can be respectively detected in P-5 and V-5.[25] This is because OPS molecules in P-5 are more apt to aggregate and form crystal regions, while since most VPS in V-5 has been grafted onto PDMS chains, only a small amount of VPS crystallizes by itself and the crystal areas are much smaller. The above results are coincident well with SEM results.
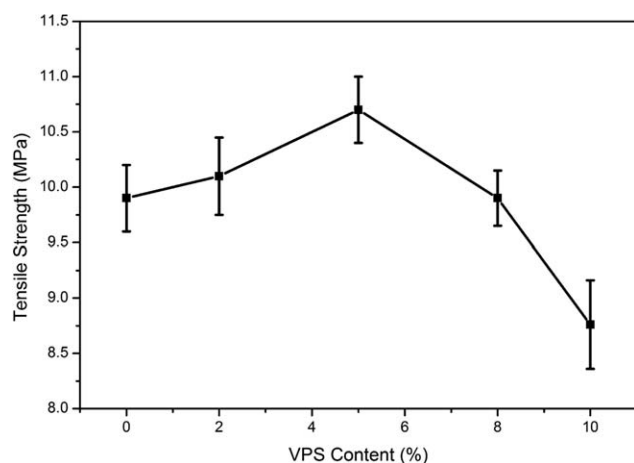
Influence of POSS Content on Properties of POSS/Silica/PDMS Composites

Previous analyses have confirmed that large crystal regions of OPS are adverse to the enhancement in mechanical properties,

whereas small crystal domains of VPS still exist in V-5 which shows enhanced mechanical properties and thermal stability. Then whether larger or smaller amount of VPS is more favorable to the composites? We attempt to explore the problem thoroughly in the following.

Firstly, the effect of VPS content on tensile stength is investigated. As shown in Figure 8, with the increase of VPS content, tensile strength of the composites first rises and then goes down sharply. Moreover, the turning point appears when 5wt % VPS is incorporated.
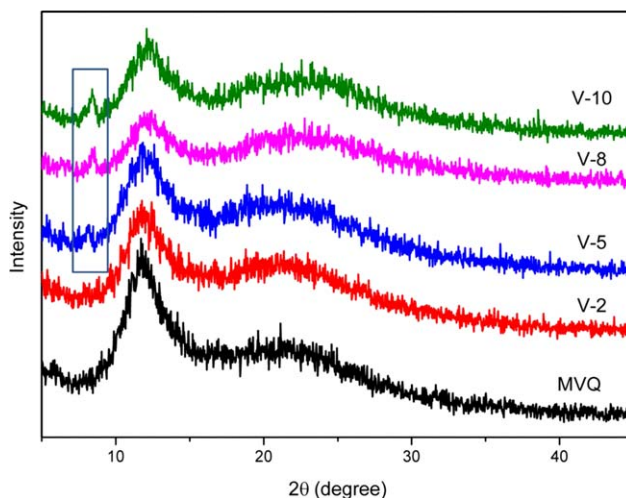
XRD patterns of composites with different contents of VPS are displayed in Figure 9 to demonstrate the reason of the above changes. One can observe that the peak of VPS begins to appear at 2θ of about 8.2° when VPS content reaches 5wt % and subsequently, the peak intensity increases with the further increase of VPS content. As to microstructures of the composites, before VPS content reaches 5wt %, most VPS can be tethered to PDMS chains and therefore, the tensile strength is elevated by the change of chain structure. Whereas, when more VPS is incorporated, as restricted by limited grafting points and the large steric hindrance provided by VPS which has already been grafted onto PDMS chains, a portion of VPS can only be free from PDMS chains. Because of the intense π–π interactions

Figure 8. Effect of VPS content on tensile strength of VPS/silica/PDMS composites.

Figure 9. XRD patterns of composites with different contents of VPS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

among phenyls in VPS, VPS has a strong tendency to aggregate, so that the resulting agglomerates act as strong stress concentrators and decrease tensile strength of the composite, which is similar to that of OPS.

Nevertheless, the crystalline peak of VPS in the sample V-5 is evident in XRD patterns (Figure 9), but V-5 displays the best mechanical properties, which seems contradictory with the above conclusions. The difference between V-5 and the composites with higher amount of VPS is shown in Figure 10. As less VPS is incorporated in V-5, the aggregation of VPS cannot form crystal regions but microcrystal domains. The microcrystals formed by VPS tethered to PDMS chains can act as physical crosslinking points[21] which reduce the mobility of chemically bonded PDMS chains, resulting in improved mechanical properties.[31] While for the composites with more VPS, the agglomerates tend to be larger and form crystal regions. As a result,

although microcrystal domains which favors the enhancement in mechanical properties may still exist, the large crystal regions abound and lower the tensile strength.

In addition, the relation between thermal stability of the composites and VPS content are also discussed. Two parameters about thermal stability are illustrated in Figure 11. T_i of the composites can be significantly improved by the initial addition of VPS, but it drops slightly when VPS content is beyond 5wt %, which may be interpreted as the degradation of ungrafted VPS because of the unstable C=C double bond. In the meantime, the formed microcrystal domains which make PDMS chains stiffer also favor the enhancement in thermal stability.[32] Furthermore, the residual yield increases steeply with the initial
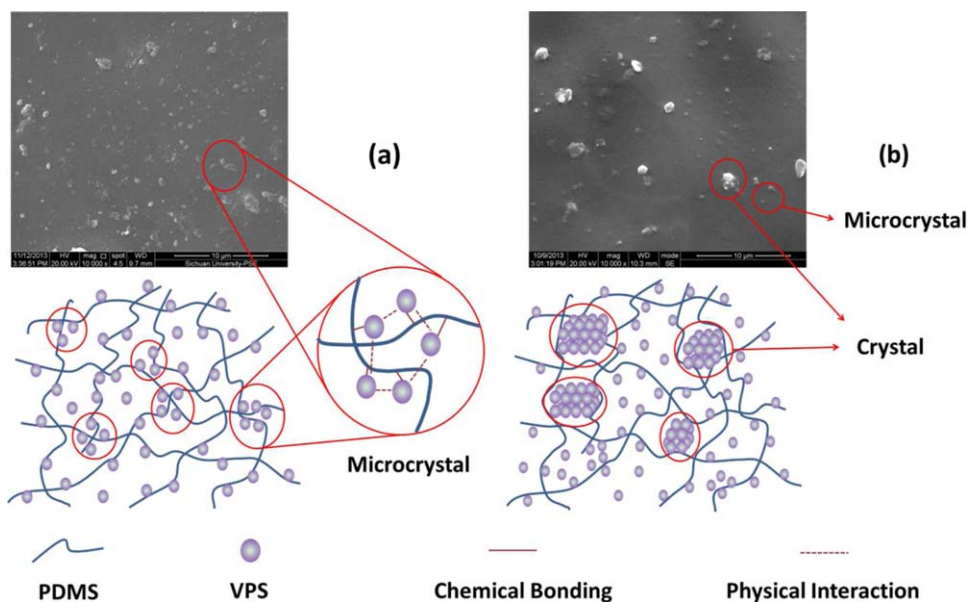
Figure 10. Schematic diagrams of (a) VPS dispersion state in the sample V-5 and (b) samples with higher VPS contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
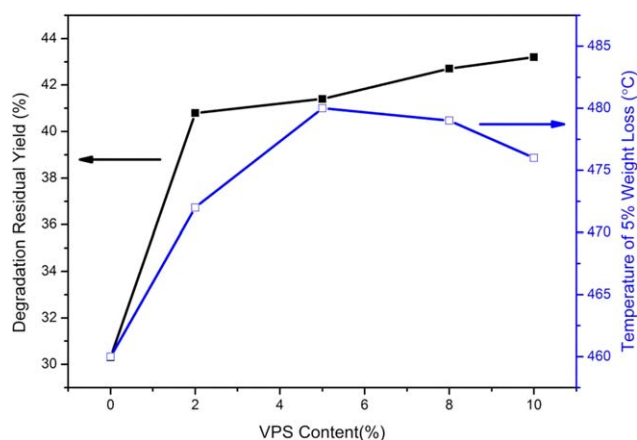
Figure 11. Changes of parameters on thermal stability with VPS content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

addition of VPS, but it only shows slight increase when more VPS is incorporated for the increase is only dominated by VPS in that case.

CONCLUSION

In this work, three kinds of POSS/silica/PDMS composites were prepared through solution blending, open two-roll mill blending and vulcanizing. SEM images revealed that OMS was dispersed quite uniformly in PDMS matrix, while tiny agglomerates and large agglomerates appear in composites incorporated with VPS and OPS, respectively. In contrast, because of the sublimation of OMS, OMS/silica/PDMS composite displayed the worst thermal stability. OPS/silica/PDMS composite exhibited poorer mechanical properties because the large crystal regions of OPS acted as stress concentrators. Owing to the graft of VPS onto PDMS chains, the modification effect of VPS in mechanical properties and thermal stability was better than that of OMS and OPS. Nevertheless, it was not that the more VPS was incorporated into PDMS, the better. Factually, the composite containing 5wt % VPS performed the best because of the formation of microcrystal domains.

ACKNOWLEDGMENTS

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