

Modification of liquid silicone rubber by octavinyl-polyhedral oligosilsesquioxanes

Hongqiang Bai,¹ Chi Huang,^{2,3} Liao Jun,³ Houbin Li¹

¹School of Printing and Packaging, Wuhan University, Wuhan 430079, China

²College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

³Engineering Research Center of Organosilicon Compounds and Materials, Ministry of Education of China, Wuhan 430072, China

Correspondence to: L. Jun (E-mail: liaojun001@sina.com) and H. Li (E-mail: lhb@whu.edu.cn)

ABSTRACT: To develop an efficient, simple, and biocompatible method for improving the thermal and mechanical properties of an addition-type liquid silicone rubber (LSR), octavinyl-polyhedral oligosilsesquioxane (OPOSS) modified LSR samples were prepared through the addition of 0.5–4.0 wt % OPOSS as a modifier to a platinum-based silicone curing system before vulcanization. The characterization and measurement of the OPOSS and LSR samples were carried out by Fourier transform infrared spectroscopy, X-ray diffraction, NMR, gas chromatography/mass spectrometry (electron impact ionization), scanning electron microscopy, thermogravimetric analysis/differential scanning calorimetry, and universal testing. The experimental results show that the crosslinking of the OPOSS and LSR polymer had a significantly positive effect on the thermal and mechanical properties. Compared with the unmodified sample, its tensile strength was enhanced by 423–508%, its tear resistance was increased from 22 to 44%, the residue at 600 °C was increased by 36–75% in an N₂ atmosphere and 8–65% in an air atmosphere, respectively. These results were obviously superior to those from other similar reported methods that used larger molecular or nonreactive polyhedral oligosilsesquioxane (POSS) derivatives as modifiers at similar POSS loadings. Furthermore, a significant correlation was found between the loading rate of OPOSS and the thermal properties. However, the mechanical properties seemed negatively correlated with the OPOSS content within the experimental range; this may have been due to a material defect caused by the uneven distribution and agglomeration. The results of this study proved that the incorporation of OPOSS into an LSR polymer matrix by a hydrosilylation reaction could be an efficient way to improve the mechanical properties, thermal stability, and biocompatibility of LSR in the future. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43906.

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INTRODUCTION

Addition-type liquid silicone rubber (LSR) is a promising silicone elastomer with high technique and added value that has been developed rapidly in past decades. Compared with other kinds of synthetic rubbers, LSR has attracted considerable attention in recent years because of its lack of byproducts generated during vulcanization, excellent biocompatibility, permeability properties, electrical insulation resistance, corrosion resistance, small shrinkage, and ability to be deeply vulcanized; thus, it is widely used in biomedical materials, baby pacifiers and nipples, aerospace applications, electronic appliances, and the automotive industry.^{1–4}

Silicone elastomers without reinforcement treatment can hardly be used because of its poor physical properties.⁵ Therefore, many kinds of fillers, usually inorganic fillers, such as fumed

silica, carbon black, clay, TiO₂, and polyhedral oligosilsesquioxane (POSS) derivatives, have been researched and used to overcome this deficit.⁷ However, there have been further problems brought on by inorganic fillers, including the (1) negative effect of the surface polarity of inorganic fillers in LSR raw materials and (2) hazardous impurities and residual byproducts of the filler surface treatment, which has limited the reinforcement results and downstream application expansion. Most reinforcing fillers, including some POSS derivatives, in the aforementioned research were introduced into the polymer physically and were not chemically inert with the polymer system. Anyway, most of these methods have not been able to fulfill the quality needs of high-end applications in medical industry, aviation, and so on.

POSSs are a category of organosilicon compounds with an internal cage structure that is similar to that of nano-SiO₂ materials surrounded with organic groups; this provides POSSs

with a good compatibility, high reactivity, and solubility with organic chemicals. This peculiar molecular structure, which is usually described as a hybrid, endows POSSs with both organic and inorganic chemical properties and gives researchers more choices and opportunities to modify POSS molecules.¹⁷ These advantages has caused POSSs to receive considerable attention from the nanomaterial and polymer fields for decades. In recent research, POSS derivatives with different reactive groups were used as modifiers, with a mechanism corresponding to that of polymerization or vulcanization.

A few studies have started to incorporate POSS derivatives into silicone elastomers, including LSR, by a different mechanism. Chen *et al.*⁸ studied the thermal and mechanical properties of novel room-temperature-vulcanized silicone rubbers using divinyl-hexa[(trimethoxysilyl)ethyl]-POSS or octa[(trimethoxysilyl)ethyl]-POSS as a crosslinker and studied the synergistic effect between POSS and fumed silica on the thermal stability and mechanical properties of room-temperature-vulcanized silicone rubbers. Vartika *et al.*¹⁸ studied the dispersion of different nonreactive POSSs and fumed silica in silicone elastomer nanocomposites and their combined effects on hydrodynamic reinforcement and the rheological properties. Zhao *et al.*¹⁵ studied the performance of heptaphenyl-vinyl-polyhedral oligosilsesquioxane (PVPOSS)/addition-type curable silicone rubber hybrid materials and proved positive effects of the incorporation of phenyl-vinyl-POSS into a polydimethylsiloxane (PDMS) network on the thermal and mechanical properties. However, there have not been any reports on the chemical incorporation of octavinyl-polyhedral oligosilsesquioxane (OPOSS), which has much more reactive groups, a small molecule size, and no byproducts, into LSR by the hydrosilylation reaction.

The goal of this study was to develop an efficient, simple, and biocompatible way to improve the thermal and mechanical properties of LSR to fulfill the quality needs of high-end applications. In this study, OPOSS and modified LSR samples were prepared. Both the thermal and mechanical properties of the modified and unmodified samples were measured and analyzed. The role of OPOSS and its effects on the reinforcement and thermal properties were evaluated in detail. The structures of the LSR, OPOSS, and modified LSR are shown in Figure 1.

EXPERIMENTAL

Materials

The OPOSS and deionized water were prepared in our laboratory. Vinyltrimethoxysilane was supplied by WD Silicone Co., Ltd. (Wuhan, China). Vinyl dimethicone (VPDMS; 10,000 cSt, vinyl = 0.05%), hydrogen dimethicone (PMHS; hydrogen: 0.1%), and a platinum complex [platinum-1,3-divinyltetramethyldisiloxane (DVTMS); 2 wt % Pt in xylene] were obtained from Andisil Silicones (Nantong, China). Concentrated hydrochloric acid (37%, analytical reagent) was obtained from Shanghai Reagent Co., Ltd. (Shanghai, China). The aforementioned starting materials were used as received. Tetrahydrofuran was purchased from Tianjin Bo Di Chemical Co., Ltd. All of these solvents were analytically pure and were used without long-term storage. Toluene and tetrahydrofuran were dehydrated according to a classic literature procedure.

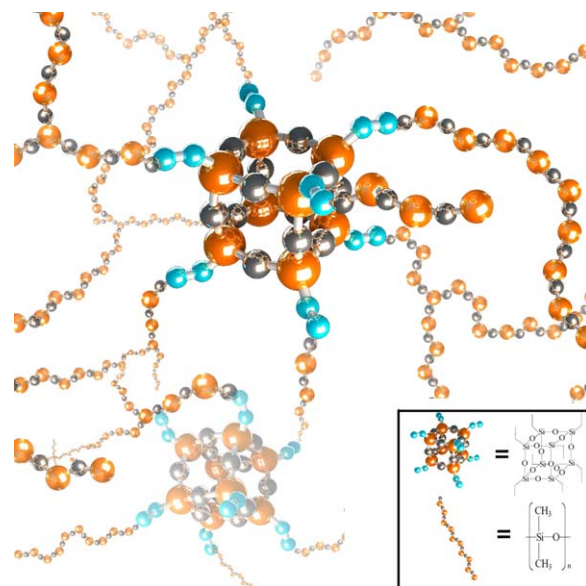


Figure 1. Structures of the LSR, OPOSS, and modified LSR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Preparation of OPOSS

OPOSS was prepared according to Chen's method.⁷ Vinyltrimethoxysilane (250 g) and acetone (2000 g) were charged into a 5-L flask equipped with a magnetic stirrer, and then, 900 g of a 17 wt % solution of hydrochloric acid was added dropwise into the flask. The solution was stirred and refluxed at 40 °C for 48 h. A white solid powder was observed on the wall of the flask, and the reaction mixture turned brown. The white powder was obtained via centrifugal separation, washed with ethanol, recrystallized in a mixture of acetone and dichloromethane (volume ratio = 3:1), and dried at 60 °C in a vacuum drying oven for 12 h. The final OPOSS product obtained weighed 39.5 g with a yield of 29.6%.

Preparation of the OPOSS-Modified LSR

Various amounts of OPOSS, moderate DVTMS and tetrahydrofuran, PMHS, and VPDMS were added successively into a flask equipped with a magnetic stirrer at room temperature. The mixture was stirred vigorously to ensure complete dispersion. The solvent was then removed by evacuation until no new bubbles rose. The liquid mixture was transferred onto a polytetrafluoroethylene plate, which was placed on a horizontal table for 4 h and then into a curing oven for approximately 4 h at 80 °C. The LSR samples (denoted as P0.5–P4) were obtained subsequently. A unmodified sample (denoted as P0) was prepared under the same condition but without OPOSS. The formulations of the prepared samples with various amounts of OPOSS are given in Table I.

Sample Characterization

Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet Avatar 360 FTIR analyzer via the KBr pellet technique. X-ray diffraction (XRD) analysis was carried out with a Shimadzu X-ray diffractometer (XRD-6000) with Cu K α radiation; the step size and scan rate were 0.02 and 6°/min,

Table I. Formulations of the Modified LSR Samples

Sample	PMHS/(VPDMS + OPOSS) (mol)	OPOSS (wt/total %)
P0	1.3	0
P05	1.3	0.5
P10	1.3	1.0
P20	1.3	2.0
P40	1.3	4.0

respectively. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were obtained with a Varian Mercury VX-300 spectrometer at 300.131 and 75.476 MHz in CDCl_3 . $^{29}\text{Si-NMR}$ spectra were recorded with a Varian Unity-Inova 600 spectrometer in CDCl_3 . For the analysis, 0.05% TMS was chosen as the internal standard.

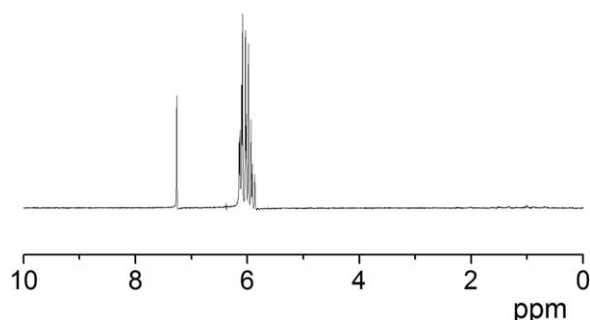
Gas chromatography/mass spectrometry (electron impact ionization) [GC/MS(EI)] was performed with a Shimadzu GC2010 Plus analyzer at a starting temperature of 170°C and a heating rate of $20^\circ\text{C}/\text{min}$; the ionization peaks appeared at 280°C and maintained a stable temperature for 6 min.

Morphological studies were performed with an FEI Quanta 200 scanning electron microscope at 30 kV. The cured samples were placed into liquid nitrogen for 5 min and then fractured into two pieces to create a fresh surface to coat with gold.

Thermal stability studies were done with a simultaneous thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) instrument Setsys Evolution 1750 (Setaram).

An amount of 8 mg of each LSR sample was cut into small pieces and heated in an Al_2O_3 crucible under both a nitrogen atmosphere from room temperature to 800°C and an air atmosphere from room temperature to 600°C at the same heating rate of $10^\circ\text{C}/\text{min}$. Dehydrated OPOSS powder with a weight of 0.3 mg was also heated in an Al_2O_3 crucible under a nitrogen atmosphere from room temperature to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$.

Mechanical tensile tests were performed with a Shimadzu universal testing machine (AGS-J) at room temperature and an

**Figure 3.** $^1\text{H-NMR}$ of OPOSS.

approximately 40% relative humidity. Dumbbell-shaped specimens were obtained from the vulcanized sheet, and an average of at least three measurements was recorded for each sample.

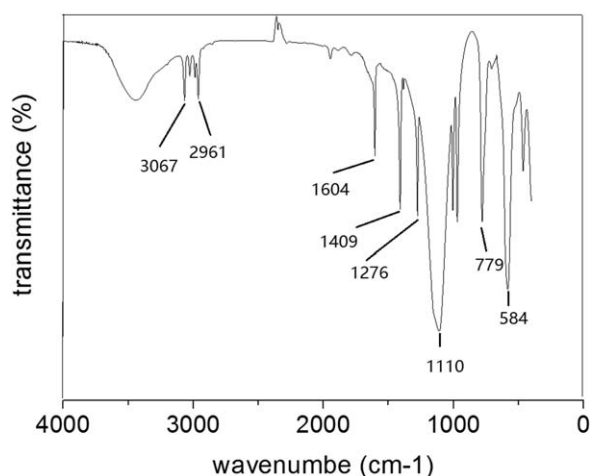
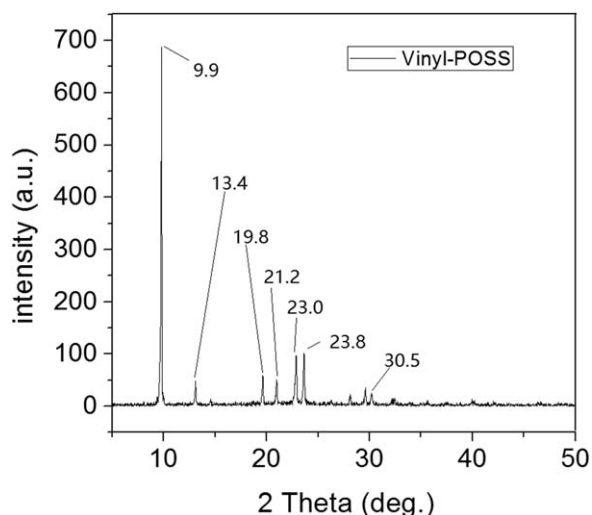
RESULTS AND DISCUSSION

FTIR spectroscopy (KBr , cm^{-1}): 3067, 3027 (ν C—H); 1604 (ν C=C); 1409, 1276 (δ C—H); 1110, 463 (ν Si—O—Si); 582 (δ Si—O—Si); 779 (ν Si—C). $^1\text{H-NMR}$ (CDCl_3 , δ): 5.86–6.14 (m, $\text{H}_2\text{C}=\text{CH}-$, 24H). $^{13}\text{C-NMR}$ (CDCl_3 , δ , ppm): 128.93 ($\text{CH}=\text{CH}_2$), 137.18 ($\text{CH}=\text{CH}_2$); $^{29}\text{Si-NMR}$ (CDCl_3 , δ , ppm): -80.21 . Mass spectrometry (electron spectroscopic imaging): 663 ($\text{M} + \text{CH}_3\text{O}^-$, adduction). XRD: $2\theta = 9.8, 13.1, 19.6, 21.0, 22.9, 23.6, \text{ and } 29.6^\circ$. GC/MS(EI): 632, 605, 577, 551, 525, 499, 471, and 455.

For the IR spectra of OPOSS, see Figure 2. For the $^1\text{H-NMR}$ spectra (b), see Figure 3. For XRD, see Figure 4. For GC/MS(EI), see Figure 5. For the IR spectra of the modified LSR, see Figure 6.

Morphology

Figure 7 presents the scanning electron microscopy (SEM) images of the fractured surfaces of representative LSR samples. The unmodified sample P0 had a smooth surface, whereas the other samples had particle strips on the surface. The particle strip dispersion was reasonably homogeneous when the amount of modifier was relatively low. The size of the strips appeared

**Figure 2.** IR spectra of OPOSS.**Figure 4.** XRD patterns of OPOSS.

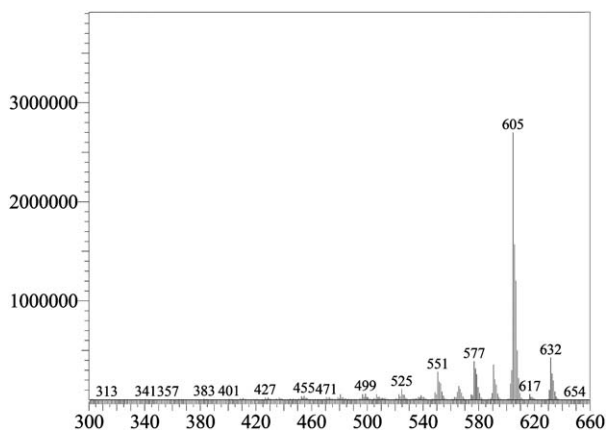


Figure 5. GC/MS(EI) spectra of OPOSS.

irregular, between 0.1 and 1 μm , because of particle agglomeration when the OPOSS loading reached 4%.

Thermal Stability

The thermal degradative behaviors of the OPOSS, modified LSR, and unmodified sample were evaluated via TGA. As shown in Figure 8, we found easily that OPOSS in an N_2 atmosphere started to lose weight as follows: 1% at 232 $^\circ\text{C}$, 5% at 260.5 $^\circ\text{C}$, and 98.5% at 322 $^\circ\text{C}$. It sublimated completely from 322 to 800 $^\circ\text{C}$ with a very low residue.

Moreover, only one sharp peak was observed in the DSC curve on 305.5 $^\circ\text{C}$, which proved that most of the OPOSS sublimated before 322 $^\circ\text{C}$; this left a very small amount, which was carbonized into a solid gray residue.

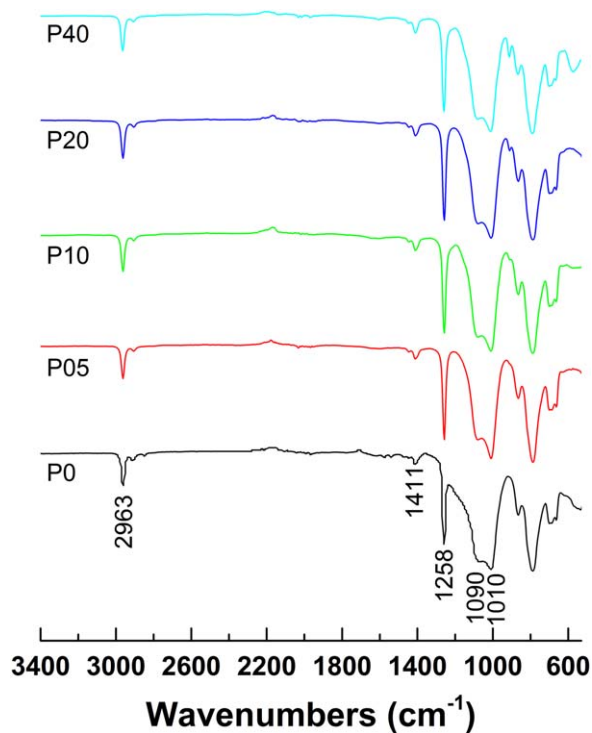


Figure 6. IR spectra of the modified LSR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

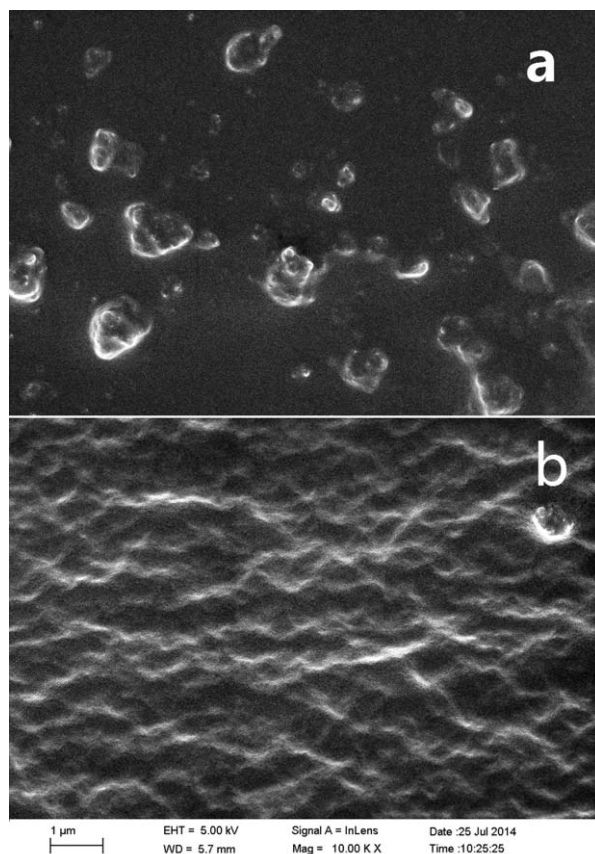


Figure 7. SEM micrographs of the modified LSR: (a) P40 and (b) P05.

As shown clearly in Figure 9, only one degradation step was found in each TGA curve under an N_2 atmosphere. The unmodified sample without OPOSS had the lowest residues, and the sample with the highest OPOSS proportion had the highest residual yield. Meanwhile, both the residue at 800 $^\circ\text{C}$ and the characteristic degradation temperature of the modified samples were improved with increasing OPOSS loading. Only one similar degradation reaction was assumed to occur among all of the samples because only one significant degradation peak appeared in the derivative thermogravimetry (DTG) curves, as shown in Figure 10. These results prove the partial grafting of OPOSS into the polymer matrix; this resulted in more physical and chemical crosslinking in the polymer matrix and, thereby, retarded the degradation of the polymer chains. Moreover, the presence of vinyl groups in LSR indeed favored the chemical crosslinking between PDMS chains at high temperatures¹⁹; this made the crosslinked three-dimensional networks more solid and retarded the free motions of the decomposing PDMS chains with increasing vinyl-polyhedral oligosilsesquioxane (vinyl-POSS) to restrain volatilization. In addition, the results also revealed that the crosslinked three-dimensional networks, which were mainly caused by the partly crosslinked OPOSS, were more thermally stable than the unmodified sample. The thermogravimetry (TG) data of the modified LSR samples with equivalent mass fractions under an N_2 atmosphere are shown in Table II.

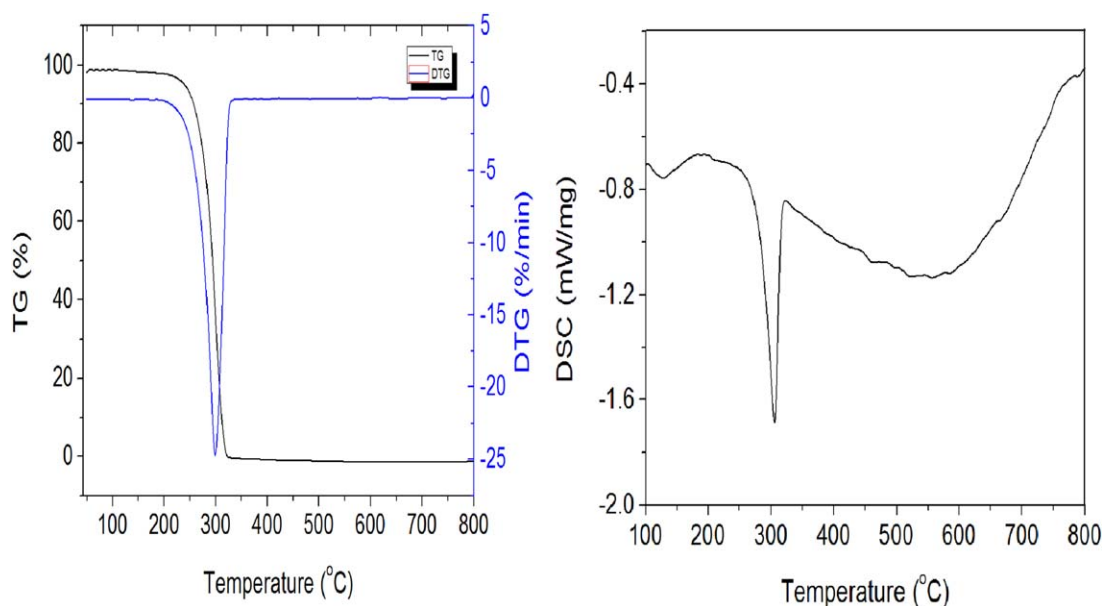


Figure 8. TGA/DSC curve of OPOSS in an N_2 atmosphere obtained with a simultaneous TGA/DSC instrument. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The thermooxidative behavior was obviously complex, and the TGA and DTG curves of the modified LSR under an air atmosphere are shown in Figures 11 and 12.

Each TGA curve demonstrated two steps under an air atmosphere, with the first step from around 320 to 400 °C and the second from around 400 to 550 °C. In the first step, each of the samples lost approximately 15% of its weight. When the process entered the explosive decomposition at approximately 400–450 °C, the samples lost approximately 20–35% of their weights. The DTG curves also confirmed the phenomenon, as shown in Figure 11. In addition, the residual yields of the modified samples after the second step were higher than that of the unmodified sample. This degradation process probably involved a complex competition between enhancement and a reduction in the thermooxidative stability.²⁰ However, the results suggest that

OPOSS was an effective modifier for improving the thermooxidative stability of the modified LSR by maintaining high residual yield under a wide proportion.

Obviously, the incorporation of the OPOSS cage structure improved the crosslinking density and reduced the relative slide among strands of molecule chains inside the polymer system significantly; this made the polymer multidimensional and more stable compared with the reference system. This was proven by the aforementioned thermal stability studies.

Mechanical Properties

The Shore A hardness, tensile strength, and tear resistance of the modified LSR and unmodified sample were assessed. The test results are shown in Figure 13 and Table III. The Shore A hardness, tensile properties, and tear resistance of all of the

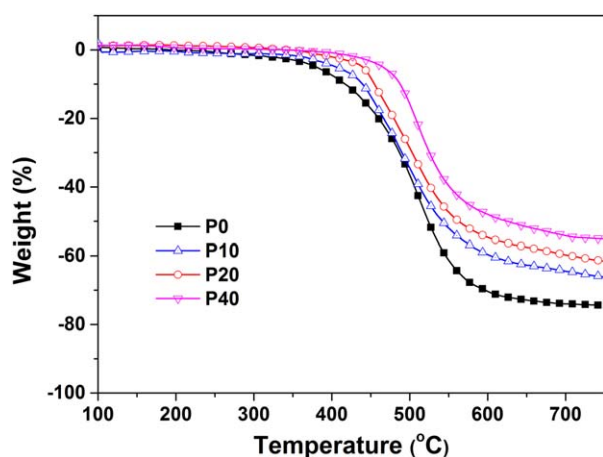


Figure 9. TGA curves of the modified LSR in an N_2 atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

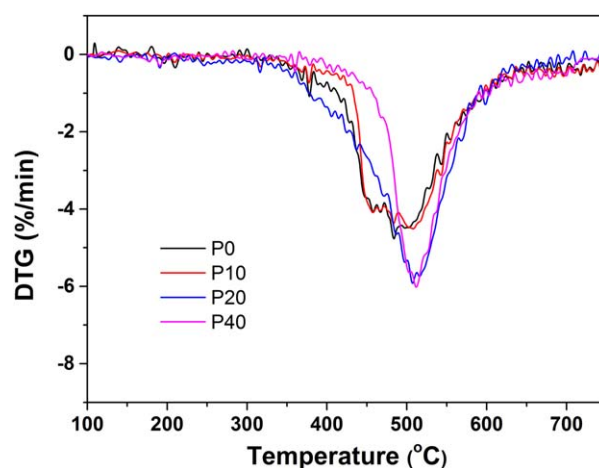


Figure 10. DTG curves of the modified LSR in an N_2 atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Comparison of the Thermal Properties of Modified LSR Samples in an N₂ Atmosphere

Sample	Temperature at 10% weight loss (°C)	Temperature at 30% weight loss (°C)	Temperature at 50% weight loss (°C)	Residue at 600°C (%)	Residue at 750°C (%)
POSS	257	281	293	0	0
P0	417	487	524	29.7	25.6
P10	440	490	542	40.4	33.9
P20	455	503	563	45.4	38.5
P40	488	525	626	52.0	44.9

modified LSRs were higher than those of the unmodified sample. Figure 13 shows a rapid increase in the Shore A hardness and a rapid decrease in the elongation rate. For the tensile strength and tear resistance, a peak appeared at a low OPOSS proportion (0.5%) and then declined steadily.

Studies with ¹H-NMR imaging demonstrated the presence of microvoids in the polymer matrix.²¹ Figure 7 shows representative SEM microphotographs of the fractured surfaces of the modified LSR and the unmodified sample. For the high-loading modified sample, obvious OPOSS aggregations with different sizes covered the fracture surface, and the so-called cross-hatched pattern was observed. However, these solid aggregation particles could change the stress field, increase the local strain of the chains, and lead to local heterogeneities and lower mechanical properties.²² This phenomenon also showed another fact: that a good dispersion of OPOSS in the polymer matrix occurred with low loading via this experimental method.

The uneven distributions and aggregation of POSS molecules are a key disadvantage in this polymer system. SEM microphotographs proved the increased agglomeration of OPOSS when the POSS loading increased. The FTIR results also show that vinyl and Si-H groups existed in the modified rubber samples. These results reveal that the dispersion and proportion of POSS had a significant influence on the thermal and mechanical property enhancements of the samples. First, POSS particles or

aggregations on the polymer surface easily gave rise to tiny crannies, and this was very harmful for the mechanical properties of the samples. Second, POSS particles or aggregations that got vaporized easily around 305 °C may have caused numberless microvoids or defects in the samples and expanded the gas solid contact area surface quickly before the polymer itself decomposed thermally to decrease the thermal performance. Furthermore, the solubility of POSS in the VPDMS and PMHS mixture also caused a similar problem, especially when the POSS loading increased, as we experienced; this indicated that the method for introducing the POSS as a raw material also needs to be optimized.

The reaction between Si-H groups from the PMHS and vinyl groups from OPOSS could be easily and hypothetically affected by steric hindrance in several ways. First, the PMHS molecules reacted with OPOSS and blocked other PMHS molecules from hydrosilylation with residual vinyl groups on these POSS molecules. Second, Si-H groups in short-chain PMHS molecules could react with the same POSS molecules to decrease the reaction opportunity between the OPOSS and polymer matrix. These reactions limited the crosslinking density and left more residue vinyl and Si-H groups; this also accelerated the decomposition.²³

However, compared with a PVPOSS/addition-type curable silicone rubber system with abundant phenyl groups,¹⁵ with the

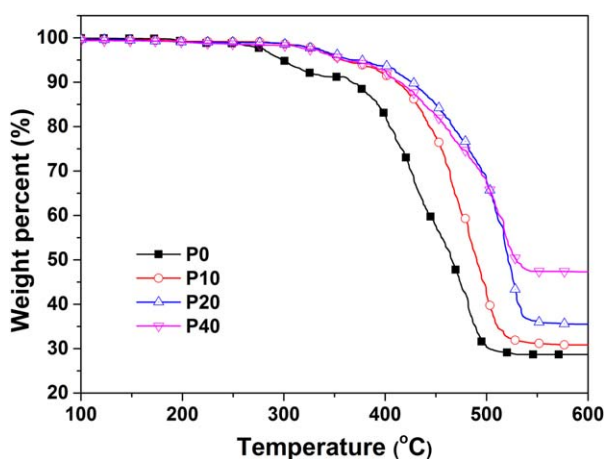


Figure 11. TGA curves of the modified LSR in an air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

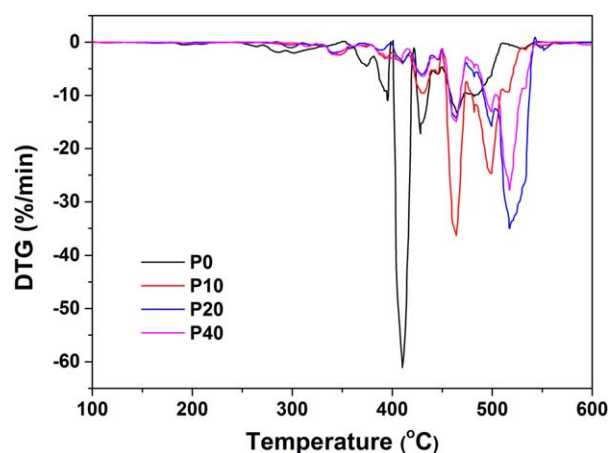


Figure 12. DTG curves of the modified LSR in an air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

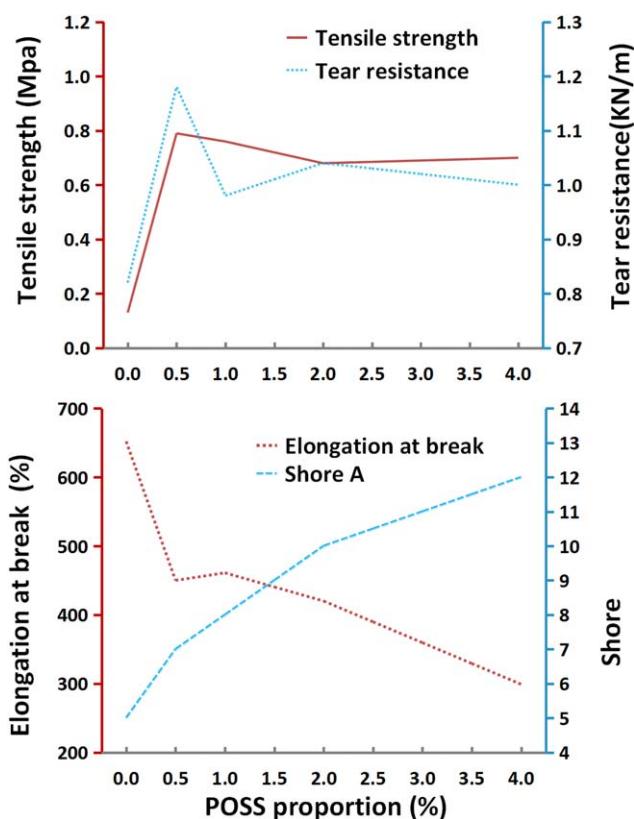


Figure 13. Mechanical properties of the modified LSR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

OPOSS-modified LSR in this study, we got much better mechanical and thermal properties results with a lower POSS loading (see Table IV). This was generally credited to the smaller molecular size of OPOSS and the higher crosslink density of the OPOSS-modified polymer. On the other hand, PVPOSS had a higher tendency to agglomerate and formed large chunks of POSS structures because of the great interaction between the phenyl rings of different OPOSS molecules; therefore, it did not disperse well into the PDMS matrix and was set as a separate phase in the matrix. This led directly to lower mechanical and thermal stabilities of the system.¹⁸ Also, PVPOSS-modified LSR will not be accepted by the biomedical industry because phenyl groups are biotoxic.

Table III. Comparison of the Mechanical Properties of the Modified LSR Samples

Sample	Tensile strength (MPa)	Tear resistance (KN/m)	Elongation at break (%)	Shore A
P0	0.13	0.82	652	5
P05	0.79	1.18	450	7
P10	0.76	0.98	461	8
P20	0.68	1.04	420	10
P40	0.70	1.00	299	12

Table IV. Comparison of the Mechanical and Thermal Properties of OPOSS/LSR and PVPOSS/LSR

Sample	POSS loading (%)	Tensile strength (MPa)	Elongation at break (%)	Initial decomposition temperature in an N ₂ atmosphere (°C)
OPOSS/LSR	2.0	0.68	420	424
PVPOSS/LSR	2.5	0.47	124	344
OPOSS/LSR	4.0	0.70	299	455
PVPOSS/LSR	5.0	0.52	149	349

CONCLUSIONS

In this article, we reported the synthesis and characterization with FTIR spectroscopy, XRD, NMR, GC/MS(EI), SEM, TGA/DSC, and universal testing of LSR with OPOSS as a modifier. The experimental results prove that the chemical incorporation of OPOSS into the polymer matrix caused LSR to have significant positive effects on the thermal and mechanical properties. The results were obviously superior to others using PVPOSS or nonreactive POSS as a modifier at similar POSS loadings. Furthermore, a significant correlation was found between the loading rate of OPOSS and the thermal properties. However, the mechanical properties seemed negatively correlated with the OPOSS content within the experimental range; this may have been due to the material defect caused by uneven distribution and agglomeration. In conclusion, OPOSS could become an efficient, simple, and biocompatible modifier to produce high-quality LSR by further optimization in the future.

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