Effect of Functionalization on Dispersion of POSS-Silicone Rubber Nanocomposites

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ABSTRACT: The nanocomposite of PDMS using functionalized fumed silica and nonreactive POSS as fillers were prepared by blend method in a planetary mixer. Fumed silica was functionalized by aliphatic and aromatic groups to study the filler–filler interactions with the aliphatic and aromatic POSS fillers and consequently their influence on the properties in the PDMS matrix. Transmission electron microscope (TEM) showed a good dispersion in the systems having the silica and POSS fillers with similar modifications. However, aliphatic and aromatic filler combinations showed more aggregated structures. Moreover, aliphatic POSS despite of good dispersion at higher loadings, act as lubricant, which is attributed to the disturbance in the PDMS- silica filler interaction and also the filler–filler interaction within fumed silica. There is a decrease in complex viscosity with the functionalization of fumed silica and with the aromatic/aliphatic POSS fillers. The thermal stability of aromatic functionalized fillers improves owing to the thermally stable phenyl groups. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 92–99, 2013

INTRODUCTION

Silicone rubber is an inorganic synthetic rubber made of polydimethylsiloxane (PDMS), which offers excellent weatherability, good chemical stability, oxidation resistance, good flow properties, thermal stability, low temperature toughness, electrical insulation properties, low surface energy, and low toxicity.[1–3] As a result it is widely used in applications like, lubricants, sealants, adhesives, and medical implants.[4,5] However, an unfilled silicone elastomer usually has poor mechanical properties, low thermal, and electrical conductivity that can be significantly improved by the use of reinforcing nanofillers.[6–8] The effectiveness of the filler depends on the filler characteristics such as quality of the dispersion, particle size, and shape and more significantly on the strength of the polymer filler interactions.[9,10] Various types of silica structures such as fumed silica,[11] nano silica[12] and colloidal silica are commonly used as fillers in PDMS matrix for the improvement of its mechanical properties.

One of the nanoscopic forms of silica is polyhedral oligomeric silsesquioxane (POSS), which can be dispersed in the polymer matrix at the level of individual molecules, and is much smaller in size than average dimension of the conventional fillers.[13–15] These can be considered therefore as molecular particles with

organic substituent at each silicon atom. Variations of these organic groups can be used to control the compatibility with different matrix polymers in order to form blends or nanocomposite materials.[16] Recently, the incorporation of POSS into polymer matrix by chemical bonding has been reported to overcome the disadvantages of incompatibility and aggregation of POSS.[17–19] However, there are only very few reports[20] regarding the preparation of nanocomposites using nonreactive POSS in the silicone matrix e.g., those containing nonreactive alkyl groups compared with the chemically incorporated POSS/polymer nanocomposites. Pan et al.[21] showed no significant improvement on the mechanical properties by simply blending these POSS-based fillers into silanol-terminated PDMS compared with the chemical bonding to PDMS that provided considerable reinforcement at lower loadings of POSS about 3 wt %. When there is no polymer–filler bonding available through chemical crosslinking as in the case of non reactive POSS, the hydrodynamic reinforcement that arise from the inclusion of rigid particles could be achieved by using a coupling agent that could increase the polymer–filler interactions.[22]

In this work, we report the dispersion, rheological, thermal, and mechanical properties of silicone elastomer nanocomposites,

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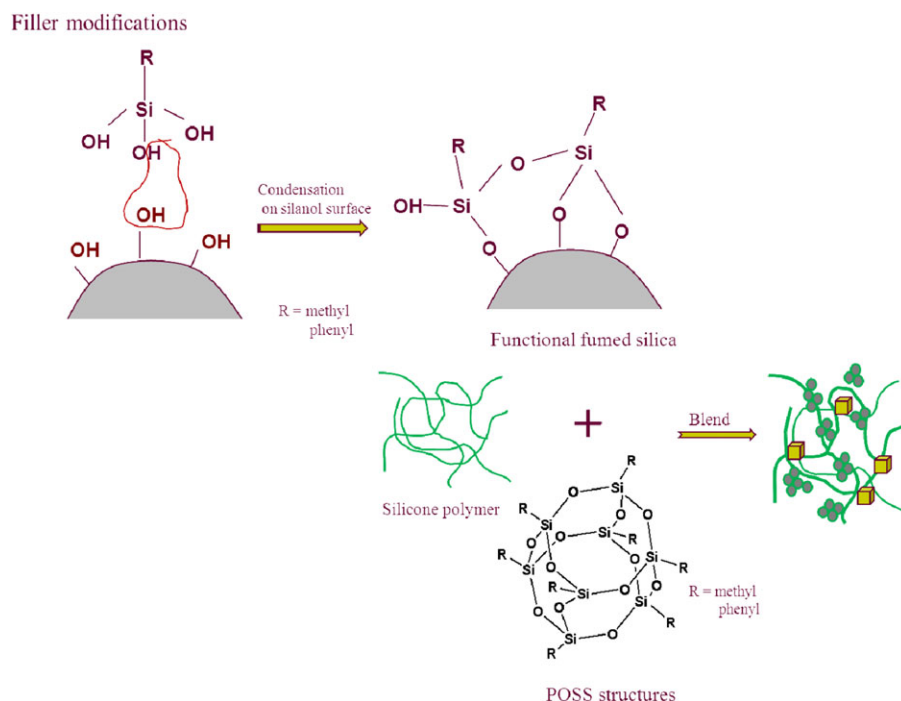
Figure 1. Schematic representation of the PDMS/Functionalized fumed silica/POSS nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

prepared by the incorporation of different types of nonreactive POSS structures namely Octamethyl POSS (OM-POSS) and Octaphenyl POSS (OP-POSS) in the presence of aliphatic and aromatic surface treated fumed silica particles (Figure 1). The role of functionalized fumed silica particles in compatibilizing the nonreactive POSS and their combined effect on the hydrodynamic reinforcement and the rheological properties are evaluated in detail.

EXPERIMENTAL

Materials

The commercially available vinyl terminated polydimethylsiloxane (PDMS) (molecular weights 57,200 g/mol and 47,600 g/mol) with trade name Siloprene, hydride terminated−PDMS (7.3 mmol of hydride) as curing agent and platinum complex catalyst (Karstedt's catalyst) were provided by Momentive Performance Materials, Bangalore. Octamethyl POSS (OM-POSS) and Octaphenyl POSS (OP-POSS) were purchased from Sigma-Aldrich. Fumed silica (AEROSIL R 300 grade) obtained from Evonic. Methyl trimethoxy silane (MTMS) and phenyl trimethoxy silane (PTMS) were obtained from Sigma-Aldrich.

Preparation of Silicone Rubber/POSS Nanocomposites

In this work, physical blending method has been used to prepare the silicone rubber/POSS nanocomposites. Since fumed silica has low compatibility with organic components, modification of silica surface by silane coupling agent has been mainly pursued to improve the miscibility and thereby improving the dispersion in silicone rubber. Two types of nonreactive POSS, octamethyl POSS (OM-POSS) and octaphenyl POSS (OP-POSS) have been used where, former is an aliphatic substituted and latter has aromatic substituted groups.

The functionalization of fumed silica was done prior to the addition of fumed silica into polymer. The functionalizing agents [methyl trimethoxy silane (MTMS)/phenyl trimethoxy silane (PTMS), each 0.048 moles] was mixed with siloxane to functionalize 75–90% silanol group present on the fumed silica surface. Nanocomposties were prepared by blending PDMS, fumed silica, and POSS in several installments in a planetary mixer. The temperature was varied from ambient to 110°C during the course of blending at 1 atm pressure for 4 h.

Curing of the elastomer was done with hydride terminated PDMS crosslinker in presence of platinum complex catalyst using hand blender. The blended mixture was cured in a mold at 165°C under 100 bar pressure for a compression time of 10 min.

The samples are designated in a general way as POSS Functional Silica (PFS)-functionalizing agent for fumed silica-wt% POSS type, e.g., PFS-MT-2.5OM represents PDMS with MTMS functionalized fumed silica and 2.5 wt % octamethyl POSS (Table I). In all these cases 20 wt % fumed silica was added and the POSS addition was varied as 2.5, 5, and 10 wt %. The remaining weight percent was the vinyl terminated polysiloxane polymer.

Characterization

Morphological examinations of the samples were done using transmission electron microscopy (TEM). Sample was prepared by taking a small part of the elastomer, which was cut using a scalpel and was faced on a Leica Ultracut microtome at cryo temperature. Final microtomy was carried out on microtome at −140°C to obtain 100 nm sections. These tests were performed

Table I. Designation of the Silicone Rubber Systems

Designation	Polymer matrix	Functional silica filler	Functional POSS filler
PFS-MT-OM-POSS	PDMS	MTMS functionalized silica	Octamethyl POSS
PFS-MT-OP-POSS	PDMS	MTMS functionalized silica	Octaphenyl POSS
PFS-PT-OM-POSS	PDMS	PTMS functionalized silica	Octamethyl POSS
PFS-PT-OP-POSS	PDMS	PTMS functionalized silica	Octaphenyl POSS

on Tecnai G2 instrument and experimental conditions were bright field, transmitted mode.

Rheological properties of nanocomposites were measured using Haake Rheostress-600. Viscosity was measured at constant shear rate of 10/s at 25°C. Storage modulus and loss modulus were measured in parallel plate rheometer RDA111 Rheometrics (25 mm plate diameter) frequency sweep mode at 3.5% shear strain, the frequency ranging from 0.1 to 100-rad/s and 170°C temperature.

The mechanical tests were carried out using Instron 3356 instrument at room temperature (22°C). Sample dimensions and testing procedure were in accordance with DIN 53504. The gauge length of the specimens was 4 mm × 2 mm. The crosshead speed was 200 mm/min. All measurements were repeated five times and the values averaged.

Thermogravimetric analysis of POSS/Polysiloxane nanocomposites was carried out using Auto TGA2950 V5 HR. 4A, with 15–25 mg samples under a purge flow of 40 mL min^{-1} nitrogen at a heating rate of 10°C/min from ambient to 800°C.

RESULTS AND DISCUSSION

Microstructure Characterization

Dispersion of POSS filler in presence of fumed silica in siloxane/POSS nanocomposite was studied by TEM. The effect of POSS filler loadings in siloxane/functionalized fumed silica nanocomposite is shown in Figure 2. A better dispersion of the 10 wt % loading of the POSS molecules in the matrix is seen compared with the lower loadings, which could be attributed to the high shear produced by the dense crowd of fumed silica and POSS molecules during the compounding process, which led to their partial disaggregation.[23]

In general, the addition of OP-POSS shows bigger aggregates (Figures 2 and 3) in the PDMS when compared to the OM-POSS especially at lower loadings when blended with both the aliphatic and aromatic functionalized fumed silica. However the compatibility is seen to be better in the case of blending of OP-POSS with aromatic functionalized fumed silica [Figure 2(c)] at higher loadings (PFS-PT-10OP) when compared with the lower loadings of both aromatic and aliphatic functionalized fumed silica systems. It could be speculated for the incompatibility of the aromatic octaphenyl POSS in the PDMS-fumed silica matrix due to the high π-π interaction among the phenyl rings. Figure 3 shows the effect of the compatibility of the filler particles in their dispersion in the polymer matrix. Filler particles having same interface properties as that of the surrounding polymer (e.g., both aliphatic functionalization) show better adhesion with the polymer. This results in improved wetting of

the fillers and hence the better dispersion.[24] Whereas, the bigger the difference of the surface energies of filler and polymer, the higher is the thermodynamic driving force of the filler particles to aggregate. Therefore, a surface modification of the filler particles can suppress the tendency of filler aggregation in a rubber mixture.[25]

Rheological Measurements

Understanding the rheological properties of reinforcing filler containing elastomer is of great interest since the filler particles enormously change the viscoelastic behaviors of these materials. The effect of fumed silica modification and the loading of POSS molecules on the frequency dependence of the dynamic shear storage modulus of the elastomers are studied.

Figure 4 shows the storage modulus curves for PDMS blends with MTMS, and PTMS modified fumed silica in presence of 2.5 wt % OM-POSS where the particle–particle interactions of the two different fillers influence the rheological behavior. The storage modulus of MTMS modified fumed silica shows a higher value when compared with the PTMS functionalized fumed silica. This is attributed to a strong interaction between the PDMS chain and the methyl functional silica filler that increases the elasticity and the storage modulus. In the case of PTMS, the aliphatic and the aromatic filler combinations lead to aggregations of two different types that do not improve the polymer–filler interaction showing lower storage modulus value resulting in probably self-sorted structure. The marginal improvement of G' in the entire frequency range, which is a typical rheological behavior of micro-particles filled polymers[26–28] shows the existence of aggregates in both cases where the filler–filler interaction predominates.

Also the nearly frequency independent nature ($G' \sim$ (angular frequency)^0) in the low frequency range, which is a characteristic solid-like behavior could be related to filler–filler interactions and to the consequent formation of a percolated network structure as seen in Figure 2 by the physical aggregation of the silica particles fused together as clusters of 1–1.5 μm. It is possible to hypothesize that the solid-like behavior is formed by the silica-POSS, silica-silica, and POSS-POSS interactions and the agglomerates interact to create a space filling network and able to block the flow of PDMS.

In Figure 5(a), there is a comparison of the unmodified fumed silica filler with the variation of the OM-POSS loading with MTMS modified fumed silica. Unmodified fumed silica system showed G' to be greater than the functionalized fumed silica which is due to the filler–filler interactions that arise from the hydrogen bonds between the silanol groups on the silica surface
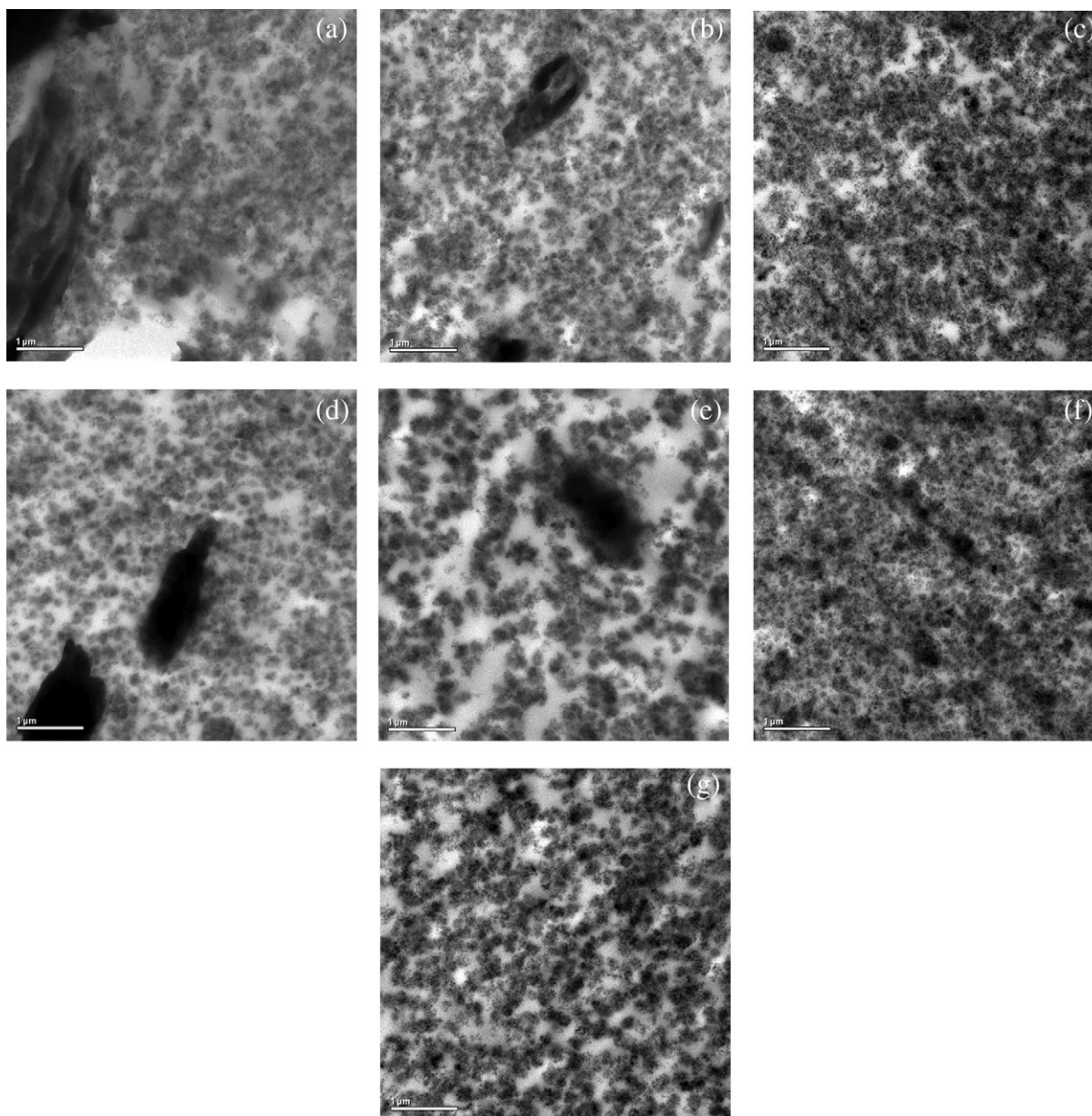
Figure 2. TEM images: Effect of various loadings of POSS fillers in siloxane/fumed silica nanocomposite. (a) PFS-PT-2.5OP. (b) PFS-PT-5OP. (c) PFS-PT-10OP. (d) PFS-MT-2.5OM. (e) PFS-MT-5OM. (f) PFS-MT-10OM. (g) PFS.

and the PDMS.[29] Despite the better dispersion seen from the TEM, a noticeable decrease in the modulus with the addition of OM-POSS could be hypothesized as a defect owing to their small size acting as a lubricant disrupting the weak Si…O and van der Waals interactions between the fumed silica and the PDMS thereby improving the filler–filler interactions.[30] In all the loadings especially at higher frequencies, there is not much change in G' with frequency sweep that confirms the existence of strong particle–particle interaction and the formation of filler network in the host polymer.[31,32]

On the other hand the PDMS/OM-POSS blend with PTMS modified fumed silica [Figure 5(c)] showed a reverse behavior than the aliphatic modified fumed silica where the increase in the POSS filler concentration increases the modulus. But these

observations are in agreement with the existing scientific literature on the rheological properties of nanoparticles-filled systems.[33,34] The increase in the OM-POSS concentration increases the storage modulus though they could not match the moduli of the unmodified fumed silica with no POSS additive. This could be attributed to the incompatibility of the PTMS modified filler with the polymer matrix thereby forming pockets of agglomerates along with the OM-POSS thus raising the effective volume fraction of filler. Even though the effective G' value is lowest in this case they follow the general trend of increased G' with increased filler loadings.

The similar trend was observed in the case of PDMS/aliphatic/aromatic modified fumed silica with different loadings of OP-POSS [Figures 4(b,d)]. Here, the systems show solid-like
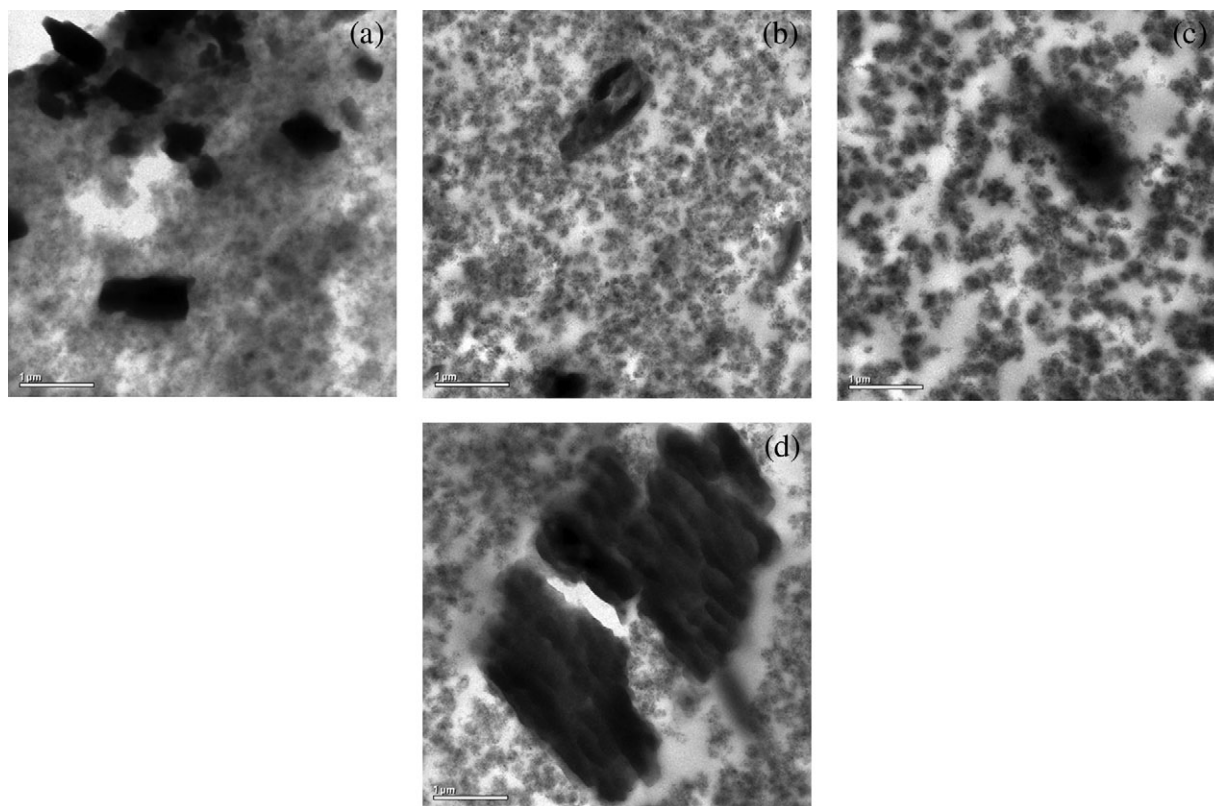
Figure 3. TEM images: Effect of the POSS structures at 5 wt % loading in siloxane/fumed silica nanocomposite. (a). PFS-PT-5OM. (b) PFS-PT-5OP. (c) PFS-MT-5OM. (d) PFS-MT-5OP.

behavior especially in the highly filled cases of 10 wt % OP-POSS where the storage modulus is high and varies less with frequency which is clear behavior of aggregates that are formed by the incompatibility of the filler in the polymer matrix. The inherent stability of the phenyl system could also be a reason for the improved modulus of these systems when we compare the aliphatic and aromatic fumed silica filled systems.

Figure 6 reports the frequency dependence of the complex viscosity of the PDMS/10 wt % POSS blends with modified fumed silica. The systems showed a pseudo plastic behavior where the complex viscosity decreases with frequency. The higher value of the complex viscosity in the MTMS modified fumed silica systems shows the higher resistance to flow due to the comparatively greater interaction with the PDMS matrix when compared with the PTMS-modified fumed silica systems.

Mechanical Properties

The PDMS system with unmodified fumed silica (PFS) shows the highest tensile strength (Table II) due to the better polymer filler interaction through the hydrogen bonding via the silanols. There is not much change with the increased loading of POSS and also the functionalized fumed silica does not play a significant role as a coupling agent to increase the polymer filler interactions to improve the mechanical properties. Generally, filler particle size has significant effect on the tensile strength of the composites owing to the interfacial area per unit volume and the efficient stress transfer when there are nanodispersions.

However, particle agglomeration tends to reduce the strength of the material acting as strong stress concentrators and the decrease in tensile strength can be attributed to the agglomeration of particles.[35]
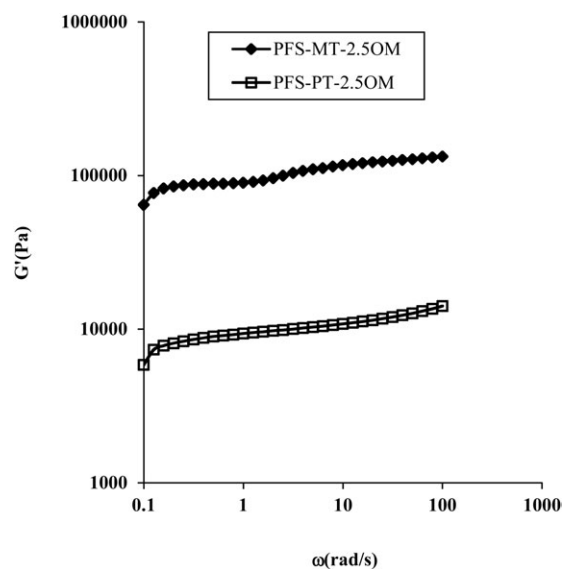

Figure 4. Rheograms of the storage modulus variation with frequency for the functionalized silica-2.5 wt % OM-POSS fillers containing liquid silicone rubbers.
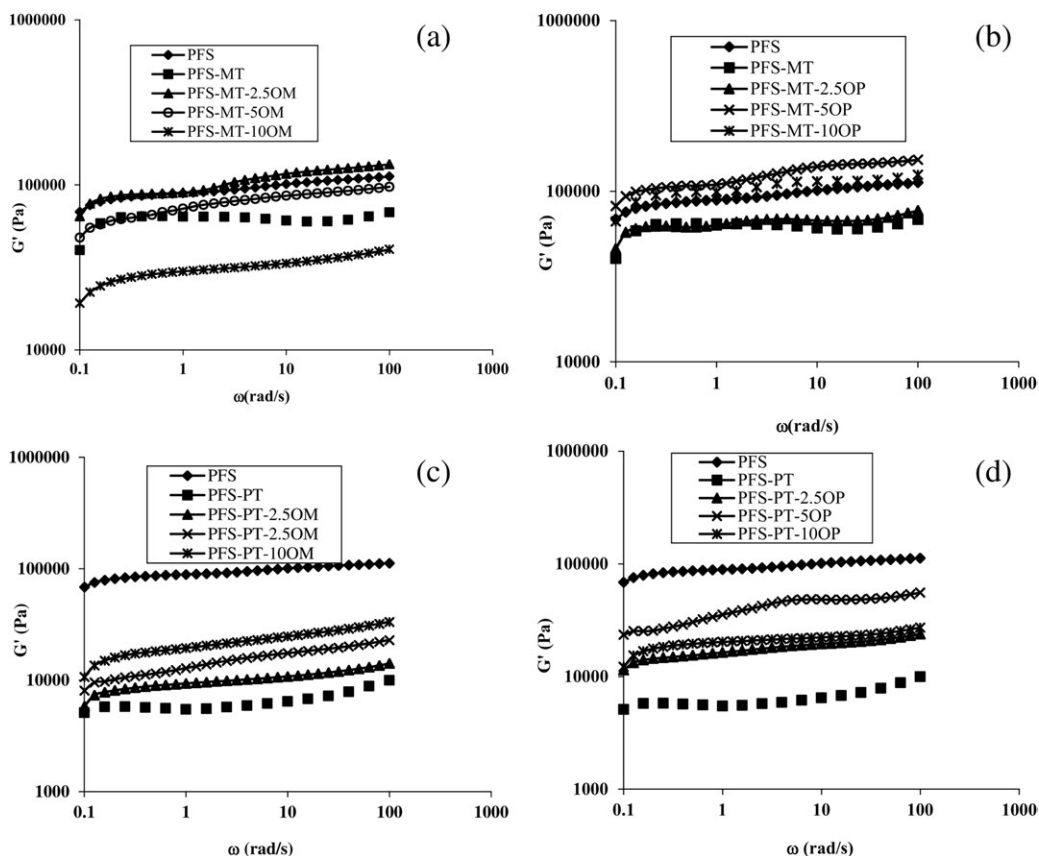
Figure 5. (a) Rheograms of the storage modulus variation with frequency for the system OM-POSS loading with MTMS modified fumed silica. (b) Rheograms of the storage modulus variation with frequency for the system OP-POSS loading with MTMS modified fumed silica. (c) Rheograms of the storage modulus variation with frequency for the system OM-POSS loading with PTMS modified fumed silica. (d) Rheograms of the storage modulus variation with frequency for the system OP-POSS loading with PTMS modified fumed silica.

In the case of better compatible aliphatic POSS systems (Table II), they are so compatible with the matrix that they do not act as reinforcing filler and reduces the PDMS-silica filler interac-

Figure 6. Rheograms of the complex viscosity variation with frequency for the unmodified/functionalized silica-10 wt % functionalized POSS fillers containing silicone rubbers.

tions. Also, due to this, there will be a competition between the POSS and fumed silica fillers in interacting with the PDMS matrix and this destroys the existing filler–filler interaction within silica, which was actually responsible for the strength of the material and forming new POSS-silica interactions as well resulting in the aggregates. Similar to the rheology measurements, MTMS modified fumed silica showed a slightly higher modulus than the PTMS systems (Table III).

Thermal Properties
The filler nature and morphology plays an important role in determining the thermal stability of a nanocomposite. The thermal stability of the silicone rubber/POSS nanocomposite was
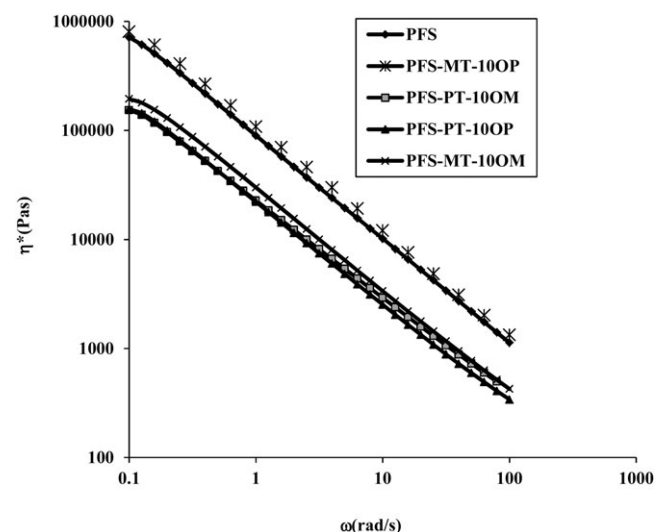
Table II. Mechanical Properties of the OM-POSS Loadings with MTMS-Modified Silica Nanocomposite

Nanocomposite	Tensile strength (MPa)	Modulus @100% elongation (MPa)
PFS	6.3	1.86
PFS-MT-2.5 OM	5.1	2.06
PFS-MT-5 OM	4.6	2.04
PFS-MT-10OM	3.8	1.7

Table III. Mechanical Properties of the OM-POSS Loadings with PTMS-Modified Silica Nanocomposite

Nanocompostie	Tensile strength (MPa)	Modulus @100% elongation (MPa)
PFS-PT-2.5 OM	4.8	1.63
PFS-PT-5 OM	4.6	1.76
PFS-PT-10OM	4.1	1.7
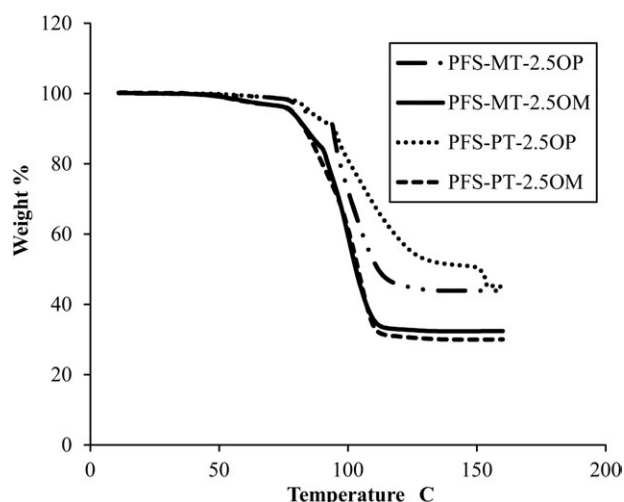
Figure 7. TGA curves for the 2.5 wt % POSS loading to PTMS/MTMS functionalized fumed silica

evaluated by the thermogravimetric analysis. Figure 7 shows the effect of aromatic and aliphatic functionalized fumed silica with the 2.5 wt % loading of POSS. It is observed that the PTMS modified fumed silica with the phenyl POSS showed the highest thermal stability as well as the highest char yield. All the samples showed higher char yield of about 30% owing to the fact that more Si—O—Si network is formed at high temperatures on hydrophobization of the fumed silica. On the other hand, with the loading of OM-POSS to the PDMS/PTMS fumed silica system, the thermal stability decreases and this trend is more with increase in the POSS loading. This could be due to the inherent low thermal stability of the OM-POSS which is less than 300°C when incorporated into highly stable PDMS/fumed silica system reduced its thermal stability by reducing the silica-polymer interactions and chopping the thermally stable Si—O networks. Even though there is existence of strong π-π interactions among phenyl rings,[36,37] the higher loading of OP-POSS showed a reduction in the thermal stability due to the fact of immiscibility of the OP-POSS in the host matrix thereby not contributing to the thermal stability. Nevertheless, it showed better thermal stability than the OM-POSS.

CONCLUSIONS

The effect of filler–filler and PDMS–filler interactions of the functionalized fumed silica/ aliphatic and aromatic POSS blends in PDMS matrix and their effect on the rheological, mechanical, and thermal properties were studied. The surface treatment of

the fumed silica reduces the viscosity of the blends thereby improving the processability and dispersion of filler. With the nonreactive POSS structures, the MTMS showed better compatibility and acted as a flow promoter when compared to its aromatic counterpart PTMS. The rheological trend shows that the OM-POSS owing to the small size and good compatibility, acts as a lubricant thereby reducing the filler–filler and polymer-fumed silica interactions. OP-POSS has higher tendency to agglomerate and forms large chunks of POSS structures because of high π-π interaction between phenyl rings of different OP-POSS molecules, therefore does not disperse well into PDMS matrix and sets as separate phase in the matrix. This could be the reason for observed lowered mechanical and thermal stabilities of OP-POSS/PDMS nanocomposites. However, the thermal stability for phenyl POSS blends is higher than for methyl POSS blends.

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