

Morphological and Dielectric Properties of Vinyl PDMS-Polyhedral Oligomeric Silsesquioxanes Composites

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Abstract - Polyhedral oligomeric silsesquioxanes (POSS) are a class of important nanosized cage-like molecules, derived from hydrolysis and condensation of tri functional organosilanes. Incorporation of nano sized POSS macromers into polymers has produced significant improvement in the thermal stability, mechanical strength and the dielectric properties of the polymer. This paper presents the development of a hybrid polymer dielectric nanocomposite as a better dielectric material than the existing polymer such as polydimethyl siloxane (PDMS). It investigates the effect of addition of a synthesized monofunctional POSS into a vinyl terminated polydimethyl siloxane (PDMS) Incorporation of different weight loadings of the synthesized monofunctional POSS into vinyl terminated PDMS and curing via addition cure mechanism using platinum as catalyst, resulted in the polymer composite with enhanced dielectric properties. The incorporation of POSS into PDMS is done by two routes (1) mechanical route (2) ultrasonication route. The dielectric and morphological properties of the cured polymer composites obtained from the two different routes are compared. The Fourier Transform Infrared Spectroscopy (FT-IR) results confirm the curing of the PDMS resin via chemical incorporation of mono functional POSS. A scanning electron microscopy image taken from the POSS reinforced polymers illustrates the molecular level dispersion of mono functional POSS that can be achieved in silicone resin via compounding. The studies have shown that the POSS incorporated vinyl PDMS exhibit better dielectric properties than the neat vinyl PDMS resin. The LCR meter was used to measure the dielectric constant and loss tangent of the polymer nanocomposites at different frequency. This paper discusses the possibilities of the dielectric elastomers using polyhedral oligomeric silsesquioxanes being used as a dielectric layer in dielectric actuators.

Keywords: Polydimethyl siloxane, polyhedral oligomeric silsesquioxanes, morphological and dielectric properties

I. INTRODUCTION

There is a continuous rise in the usage of polymers as an electrical insulating material. Silicone elastomers are known to be excellent dielectrics [1]. Poly dimethylsiloxane (PDMS)

is one such silicone elastomer. PDMS based thin films have excellent application in insulation purpose. The incorporation of the nano-filler into the silicone resin, for example PDMS, may enhance its dielectric properties. Polyhedral oligomeric silsesquioxanes (POSS) is a nano-filler having diameter in the range 1-3 nm. POSS is a hybrid having chemical composition, intermediate ($\text{RSiO}_{1.5}$) between that of silica (SiO_2) and silicone (R_2SiO), derived from hydrolysis and condensation of trifunctional organosilanes or chlorosilanes [2-4]. Further exploration of the dielectric properties of the POSS incorporated thermoplastics and thermosets have been done and reported earlier [5-15]. The various factors which affect the improvement in dielectric properties are particle-polymer nanoscopic structure, change in polarity due to presence of the nanoparticles and large particle-polymer interfacial area [16]. The use of polydimethyl siloxane (PDMS) as a dielectric elastomers have been reported earlier [17, 18], due to its excellent thermal stability and stiffness. But it has certain limitation due to low electrical permittivity which could be enhanced with the addition of POSS. The POSS incorporated PDMS could be a potential candidate as a dielectric layer in the Dielectric Elastomer Actuators (DEA) due to its improved electrical permittivity and electrical strength [19]. Several parameters need to be considered for the usage of polymer as a dielectric layer in the dielectric elastomer actuators [20-24]. The present paper focuses on studying the morphological and dielectric properties of the monofunctional POSS incorporated vinyl PDMS composites. Monoallyl heptaphenyl POSS is synthesized and characterized using Fourier Transform Infrared Spectroscopy. Vinyl PDMS is basically a thermosetting polymer. The purpose of our research is to investigate the effect of the chemical incorporation of Monoallyl heptaphenyl POSS into the vinyl terminated PDMS by studying its dielectric and morphological properties. Different weight loadings of MAHP POSS is incorporated into vinyl PDMS by two different routes (1) mechanical

mixing (2) ultrasonication. The obtained POSS-PDMS composite is subjected to addition cure mechanism using platinum as catalyst and a crosslinker, polydimethyl-co-methylhydrogen-trimethylsilyl terminated. The dielectric and the morphological properties of the polymer nanocomposite prepared by two different routes are compared. The dielectric properties such as dielectric strength, dielectric constant and loss factor of the POSS incorporated PDMS specimens are measured. Scanning Electron Microscopy is used to determine the morphological properties of the POSS incorporated PDMS system.

II. EXPERIMENTAL

MATERIALS USED

Phenyltrimethoxysilane (98%), were purchased from Aldrich Co., USA and used as received. Allyl trichlorosilane (97%) was purchased from Alfa Aesar and used as such. Sodium Hydroxide, Tetrahydrofuran (THF) and triethylamine (TEA) were purchased from Qualigens and used as received. Poly(dimethyl-co-methylhydrogensiloxane) trimethylsilyl terminated was purchased from Anabond, Chennai, India and used as such. The structure of Poly(dimethyl-co-methylhydrogensiloxane) trimethylsilyl terminated is shown in figure 2.1.

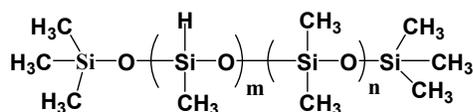


Figure 2.1: The structure of crosslinker-
Poly(dimethyl-co-methylhydrogensiloxane)
trimethylsilyl terminated

SYNTHESIS OF MONOALLYL HEPTAPHENYL POSS

Heptaphenyl tricycloheptasiloxane trisodiumsilanolate [$\text{Na}_3\text{O}_{12}\text{Si}_7(\text{C}_6\text{H}_5)_7$] was synthesized by following the method reported in literature according to [25] (scheme 1). Typically, Phenyltrimethoxysilane [$\text{C}_6\text{H}_5\text{Si}(\text{OMe})_3$] (35.258 g, 178.1 mmol), THF (195 ml), deionized water (4.064 g, 225.8 mmol) and sodium hydroxide (3.080 g, 77.0 mmol) were charged to a flask equipped with a condenser and a magnetic stirrer. After refluxed for 5 hours, the reactive system was cooled down to room temperature and held at this temperature with vigorous stirring for additional 15 hours. All the solvent and other volatile compounds were removed via rotary evaporation and white solids were obtained. After being dried at 60°C in vacuum for 24 h, the product (12.262

g) was obtained with the yield of 98.5%. The corner capping reaction between $\text{Na}_3\text{O}_{12}\text{Si}_7(\text{C}_6\text{H}_5)_7$ and Allyl trichlorosilane was carried out. Typically, $\text{Na}_3\text{O}_{12}\text{Si}_7(\text{C}_6\text{H}_5)_7$ (10.030 g, 10.04 mmol) and Triethylamine (1.3 ml, 8.8 mmol) were charged to a flask equipped with a magnetic stirrer and then 250 ml of anhydrous THF was added with vigorous stirring. The flask was immersed into an ice-water bath and purged with highly pure nitrogen for 1 h. After that, Allyl trichlorosilane (3.11 g, 12.12 mmol) dissolved in 20 ml of anhydrous THF was slowly dropped within 30 minutes. The reaction was carried out at 0°C for 3 h and at room temperature for 24 h. The insoluble solids (i.e., sodium chloride) were filtered out and the solvents together with other volatile compounds were removed via rotary evaporation to obtain the white solids. The solids were washed with 50 ml methanol for three times and dried in vacuum at 30°C for 24 h and the product (6.997 g) was obtained with the yield of 62.3%.

PREPARATION OF VINYL PDMS-MAHP POSS HYBRID POLYMERS

Mechanical Route

Various amounts of Allyl capped heptaphenyl POSS were blended into vinyl-terminated PDMS resin before crosslinking. For better mixing, a small portion of acetone (amounting to 10 wt% vinyl PDMS) was added to dissolve the POSS, before it was mixed with PDMS resin. The mixture was stirred vigorously, and the solvent was removed by evacuation. To the resulting solution, Platinum complex was added and mixed thoroughly. Finally it is mixed with crosslinker-Poly(dimethyl-co-methylhydrogensiloxane) trimethylsilyl terminated, keeping the vinyl : silane ratio of 1. The resulting solution was poured into Teflon moulds and kept at room temperature for curing.

Ultrasonication route

Various amounts of Allyl capped heptaphenyl POSS were blended into vinyl-terminated PDMS resin before crosslinking. For better mixing, a small portion of acetone (amounting to 10 wt% vinyl PDMS) was added to dissolve the POSS before it was mixed with PDMS resin. The mixture is then taken into a ultrasonicator and mixed for 30 minutes under amplitude of 50 Hz. To the resulting solution, Platinum complex was added and mixed thoroughly. Finally it is mixed with crosslinker-Poly(dimethyl-co-methylhydrogensiloxane) trimethylsilyl terminated, keeping the vinyl : silane ratio of 1. The resulting solution was poured into Teflon molds and kept for room temperature curing.

MEASUREMENT AND TECHNIQUES

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was obtained using Perkin Elmer Spectrum GXA FTIR spectrometer for wave number range of 4000-400 cm^{-1} . The instrument employed a pyroelectric detector (DTGS detector) and each interferogram was generated by signal averaging of 4 scans at a resolution of 0.5 cm^{-1} .

Scanning Electron Microscopy

Carl Zeiss EVO 50 Extended Pressure Scanning Electron Microscope having resolution of 4nm was used to take SEM image of the samples. The variable pressure mode was up to 300 Pa. and the accelerating voltage was up to 40 kV. The filament used was tungsten and lanthanum boride.

LCR meter

The dielectric constant and the loss tangent measurements of the samples were carried out using Quadtech 7600 LCR meter having test frequency of 10 Hz to 2 MHz with a basic measurement accuracy of 0.05 %. The maximum power requirement of the LCR meter was 100 W.

Dielectric strength testing instrument

The transformer oil breakdown strength testing instrument, having minimum 60 kV power supply, was used to measure the dielectric strength of the samples. The samples were cut into 4 cm x 4 cm dimension having thickness of 1mm. The samples were placed between two spherical electrodes. The electrodes were made spherical to avoid flashover in the edges. The whole electrode setup was completely immersed into paraffin oil to avoid flashover in air.

III. RESULTS AND DISCUSSIONS

FTIR SPECTRUM ANALYSIS

Figure 3.1 shows the FT-IR spectra curve overlay of a) MAHP POSS b) Neat Vinyl PDMS c) Si-H crosslinker and d) Vinyl PDMS + 10% MAHP POSS. As discussed in literature [26], the $-\text{CH}=\text{CH}_2$ and Si-O-Si absorption bands of the PDMS resin are shown at 1600 cm^{-1} and 1300-1000 cm^{-1} , respectively. Two distinct changes can be observed in the spectrum curve of Vinyl PDMS + 10 % MAHP POSS. The absorption peaks of the $-\text{CH}=\text{CH}_2$ groups at 1600 cm^{-1} decrease in intensity obviously. This suggests that the

addition reaction of the $-\text{CH}=\text{CH}_2$ group in POSS and silicone resin on to $-\text{Si}-\text{H}$ have taken place. Another distinct change is the peak intensity between 1000 and 1300 cm^{-1} . The intensity of the Si-O-Si absorption band increases with the incorporation of POSS. These results further confirm that the POSS is indeed incorporated into the silicone resin rather than as a mixture. In the FTIR spectrum of MAHP POSS, characteristics peaks due to allyl group ($-\text{CH}=\text{CH}_2$) is seen at 1600 cm^{-1} while the bands at 3030 and 3065 cm^{-1} are assigned to the C-H stretching vibrations of the $-\text{CH}=\text{CH}_2$ units in the vinyl groups, respectively. Si-O-Si absorption bands are observed at 1300-1000 cm^{-1} . The peaks at 697 and 746 cm^{-1} are related to out-of-plane vibrations of phenyl groups.

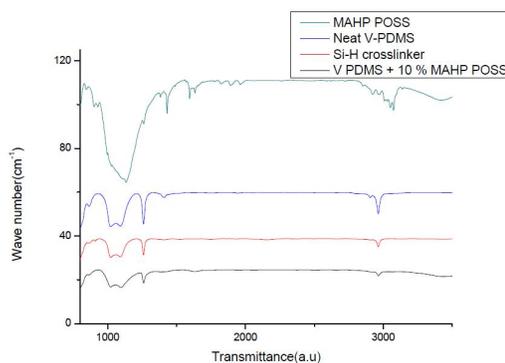


Figure 3.1 FTIR spectrum of a) MAHP POSS b) Neat Vinyl PDMS c) Si-H crosslinker d) Vinyl PDMS + 10% MAHP POSS

MORPHOLOGY

The morphology of the reference Vinyl PDMS and MAHP POSS – PDMS hybrid polymer were studied with scanning electron microscope (SEM). The moulded vinyl PDMS samples were broken in liquid nitrogen and the fracture surface was analyzed by SEM. The fracture surfaces of reference vinyl PDMS and 10 % wt MAHP POSS -PDMS (mechanical route and ultra sonication route) are presented in the figure 3.1-3.3. The fracture surface of reference neat vinyl PDMS, as shown in Figure 3.1, was observed to be rough. The fracture surface of 10 % wt MAHP POSS- PDMS shows some amount of nanoparticles of approximately 150 nm size. Figure 3.2 indicates the SEM image of the mechanically prepared Vinyl PDMS + 10% MAHP POSS composites. The fracture surface displays adequate amount of rough surface and some amount of nanoparticles. Figure 3.3 indicates the SEM image of the ultrasonicated Vinyl PDMS + 10% MAHP POSS composites. The fracture surface displays adequate amount of nanoparticles and some amount of rough surface. This could be attributed to proper dispersion of POSS in vinyl PDMS resin matrix being

obtained better in ultrasonication route as compared to mechanical route.

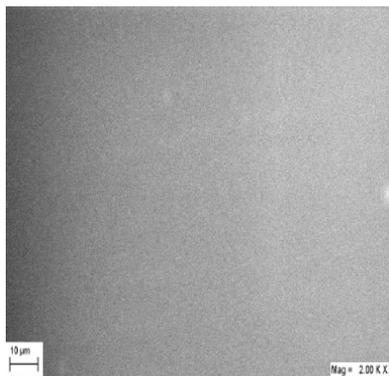


Figure 3.2 SEM image of reference neat Vinyl PDMS

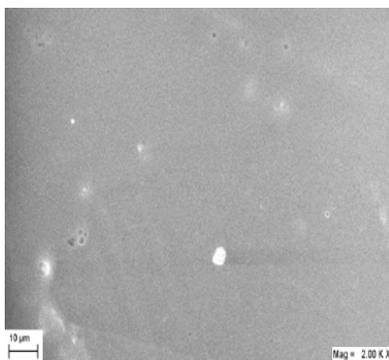


Figure 3.3 SEM image of Vinyl PDMS + 10% MAHP POSS (mechanical route)

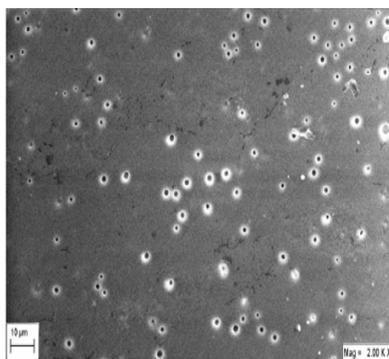


Figure 3.3 SEM image of Vinyl PDMS + 10% MAHP POSS (mechanical route)

DIELECTRIC PROPERTY

Dielectric Strength

The results of the dielectric strength measurements for different wt% of POSS incorporated in vinyl PDMS resin are presented in Table 1. The table presents the comparison of the dielectric strength values of the POSS- vinyl PDMS composites prepared by mechanical mixing and

ultrasonication. The dielectric strength increases with the increase of the POSS content into the vinyl PDMS resin. The tabular results give a clear interpretation of the insulating property of PDMS being increased with the increase of POSS content which ultimately increases the dielectric strength. Figure 6 provides the graphical representation of the dielectric strength as the function of the different wt% of POSS content.

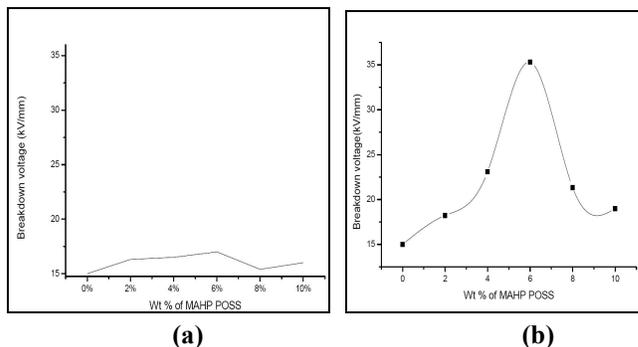


Figure 3.4 Dielectric strength values for a) Mechanically prepared samples b) Ultrasonically prepared samples

Table 1 Dielectric strength values for varying concentration of POSS

Wt % of MAHP POSS	Dielectric strength (kV/mm) (Mechanically prepared)	Dielectric strength (kV/mm) (Ultrasonically prepared)
0% MAHP POSS	15.0 kV/mm	15.0 kV/mm
2% MAHP POSS	16.3 kV/mm	18.23 kV/mm
4% MAHP POSS	17.3 kV/mm	23.1 kV/mm
6% MAHP POSS	19.0 kV/mm	35.3 kV/mm
8% MAHP POSS	15.3 kV/mm	21.33 kV/mm
10% MAHP POSS	17.0 kV/mm	19.0 kV/mm

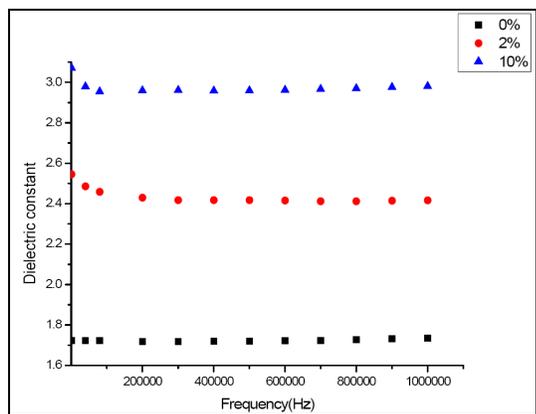
Dielectric constant and Dielectric loss

The dielectric constant and dielectric loss are the two important indexes to characterize the dielectric properties of materials [19]. Figure 7 shows the dielectric constant ϵ as a function of the POSS content for POSS-PDMS hybrids at different testing frequencies. The value of dielectric constant increases with the increase in wt % of POSS content into PDMS. The figure also compares the dielectric constant values of the POSS-PDMS composites prepared by mechanical mixing and ultrasonication. Table 2 presents the

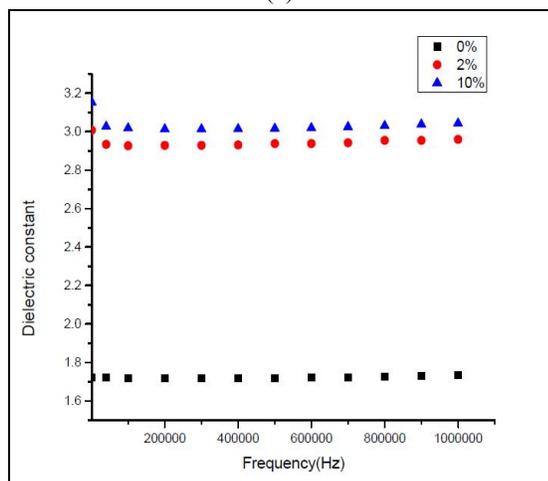
dielectric constant values at 1 kHz frequency for different wt % of POSS into PDMS. According to the table, the dielectric constant values of the ultrasonicated POSS + vinyl PDMS is more than the mechanically mixed POSS + vinyl PDMS at 1kHz.

Figure 8 presents the graphical representation of the dielectric loss as the function of different wt% of POSS into PDMS resin. The figure also compares the dielectric loss values of the POSS-PDMS composites prepared by mechanical mixing and ultrasonication. According to the figure, the dielectric loss values of the mechanically mixed POSS - vinyl PDMS increased with the different wt % addition of POSS. The dielectric loss values of the ultrasonicated POSS - vinyl PDMS remained at the same level as that of the reference neat PDMS.

Wt % of MAHP POSS	Mechanical route	Ultrasonication route
V PDMS + 0% MAHP POSS	1.7	1.7
V PDMS + 2% MAHP POSS	2.52	3.01
V PDMS + 10% MAHP POSS	3.09	3.15



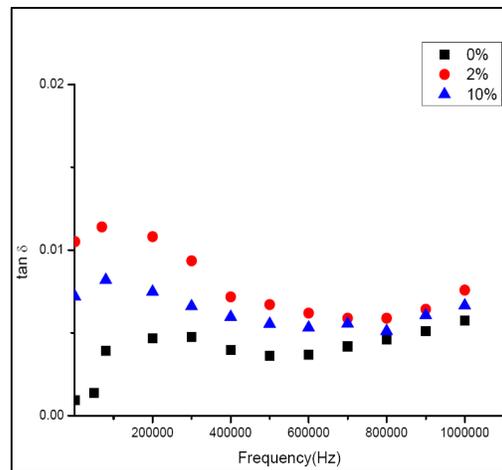
(a)



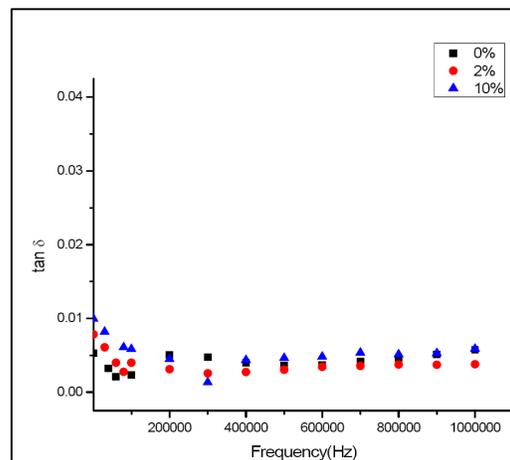
(b)

Figure 3.5 Dielectric constant values for (a) Vinyl PDMS + MAHP POSS (mechanical route) (b) Vinyl PDMS + MAHP POSS (ultrasonication route)

TABLE 2 Dielectric constant values for varying concentration of POSS at 1 kHz frequency



(a)



(b)

Figure 3.6 Loss tangent values for (a) Vinyl PDMS + MAHP POSS (mechanical route) (b) Vinyl PDMS + MAHP POSS (ultrasonication route)

IV. DISCUSSION

According to the morphological measurement presented in the paper, the proper dispersion of the MAHP POSS into the vinyl PDMS could be obtained by ultrasonication method as compared to the mechanical mixing. The dielectric

measurement presented in the paper interprets that the dielectric strength of the POSS based nanocomposites increases with the increase in addition of POSS. The POSS can strengthen the PDMS resin by foraging charges temporarily under high electric field. POSS molecules may restrict electrons from speeding up in the insulation and so it increases the dielectric strength. We presume that by improving the dispersion of compounds more towards nanoscale, better dielectric properties for the insulation can be achieved. The dielectric strength of the ultrasonicated samples were better than the mechanically mixed samples. This could be attributed to the proper dispersion of POSS molecules into the resin being obtained in the ultrasonication method. The dielectric constant of the PDMS/POSS composites increased with the addition of 2 and 10% wt of MAHP POSS. The ultrasonicated PDMS/POSS composites displays higher increase in dielectric constant for different %wt of MAHP POSS as compared to mechanically prepared composites. This can be due to the improved dispersion of the POSS molecules into the PDMS resin by ultrasonication route. The dielectric loss of the PDMS/POSS composites prepared by mechanical mixing increased with the addition of different % wt of MAHP POSS. The ultrasonicated PDMS/POSS composites displayed dielectric loss values same as the reference neat PDMS.

It seems that the ultrasonicated PDMS/POSS composites have shown the better morphological and dielectric results as compared to the mechanically prepared composites. The dielectric constant relatively increased with the addition of POSS and the dielectric loss of the PDMS/POSS composites remained same as that of the reference PDMS

V. CONCLUSION

A series of MAHP POSS/PDMS hybrids containing different contents of MAHP POSS have been prepared by mechanical and ultrasonication method which is followed by platinum addition curing. Based on FTIR results it is concluded that the POSS/PDMS hybrid has been completely cured using Platinum catalyst and Poly(dimethyl-co-methylhydrogensiloxane)trimethylsilyl crosslinker as catalyst. The incorporation of POSS into PDMS leads to increase in dielectric constant & dielectric strength. This ultimately leads to improvement in dielectric property of the PDMS. The dielectric properties of the samples obtained by ultrasonicated route are better than the mechanical route. SEM results conclude the dispersion of POSS content in vinyl PDMS. The dispersion of POSS content in PDMS through ultrasonication route produces better dispersion than

the mechanical route. The SEM results confirm this inference.

VI. REFERENCES

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