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Novel nanocomposites based on epoxy resin/epoxy-functionalized polydimethylsiloxane reinforced with POSS

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ABSTRACT

The purpose of the present study is to develop novel nanocomposites based on diglycidylether of bisphenol A (DGEBA) combined with diglycidylether-terminated polydimethylsiloxane (DG-PDMS), reinforced with 10 wt.% (mono-/octa) epoxy POSS nanocages (MEP or OEP-POSS). DG-PDMS and POSS compounds were covalently incorporated into DGEBA resin via copolymerization of epoxy groups. The effect of both DG-PDMS and POSS nanoparticles on the curing reaction, glass transition temperature (T_g), thermal stability, hardness and morphology of DGEBA/DG-PDMS ± POSS nanocomposites were studied by DSC, FTIR, DMA, TGA, SEM/EDX, AFM and contact angle measurements. SEM/EDX and AFM results prove that OEP-POSS is well dispersed within DGEBA/DG-PDMS polymer matrix, while MEP-POSS forms large POSS aggregates. The thermo-mechanical properties of POSS based nanocomposites are also in good correlation with morphology features. MEP-POSS based nanocomposite with heterogeneous dispersion of POSS aggregates exhibits lower T_g value and thermal stability in comparison with OEP-POSS nanocomposite which exhibits a nanoscale dispersion of the POSS cages. The obtained T_g of OEP-POSS based nanocomposite increases with 31 °C in comparison with the unreinforced matrix. Moreover, this nanocomposite shows the highest storage modulus (E') and hardness.

1. Introduction

Over the past decade, advanced researches have been focused on the development of polymer based nanocomposites, reinforced with well-defined nanostructured compounds, which are expected to provide high performance materials, with potential application in a wide range of technological areas [1].

Recently, polyhedral oligomeric silsesquioxanes (POSS) nanostructures have gained considerable attention as they possess a synergistic combination of constituent properties of conventional inorganic materials and organic polymers, resulting in a new generation of hybrid materials with superior properties [2–5]. POSS molecules architecture is based on a well-defined polyhedral cage (1.5 nm), with general formula $(RSiO_{3/2})_n$, n varying from 6 to 18. These macromers have an inorganic silica-like core with a precise geometry, surrounded by organic ligands (R) covalently bonded to each Si atoms placed at the vertices of the polyhedral cage. R may be hydrogen or any alkyl, alkylene, aryl, arylene groups, or organofunctional derivatives. Unlike silica, silicones and other conventional inorganic fillers, the POSS compounds exhibit advantages like monodisperse size, low density, and synthetically well-controlled functionalities. The functional groups from the organic substituents bring chemical versatility to POSS nanoparticles and make POSS widely compatible with various organic polymers [6–8].

Epoxy resins, the well-known class of thermosetting polymers, have been widely used as adhesives, electronic encapsulating compounds, and organic phase of composite materials due to their high mechanical strength, high chemical and corrosion resistance, excellent electrical insulation and simplicity in processing [9,10]. For further improvements of the general properties of epoxy resins,

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different POSS compounds containing epoxy, hydroxyl and amino reactive functionalities which can generate covalent bonding with the base polymer to reduce the agglomeration effect, have been employed. In general, the obtained results showed that the incorporation of POSS nanounits within epoxy resins improves the performances of the obtained networks [11–13]. However, even for POSS containing reactive groups, small POSS aggregates can form within the base polymer that lead to lower thermo-mechanical properties [14]. Moreover their highly cross-linked structures exhibit a brittle behavior, poor crack resistance, and low fracture toughness.

One of the most promising approaches used to modify the features of such brittle polymers consists in adding of flexible polymers like polysiloxanes, used as spacers between POSS and polymer matrix during the preparation of POSS/polymer nanocomposites. This method has been demonstrated to be efficient in order to prepare nanocomposites with good dispersion and enhanced thermo-mechanical properties [15–19]. Polysiloxanes have been extensively used to improve the epoxy resins properties due to their excellent thermal stability [20]. Moreover, these compounds were also used in the preparation of different POSS/polysiloxane composites. Chen and coworkers demonstrated that the incorporation of POSS nanoparticles into polysiloxane elastomers can improve the thermal stability of the obtained composites [21].

Recently, we have reported the synthesis and characterization of simultaneous interpenetrating polymer networks (IPN) based on dimethacrylic/epoxy resins via *in situ* polymerization reinforced with octafunctional POSS (with methacrylate or epoxy groups) [22]. In this study, we successfully proved that the degree of POSS dispersion within the polymer matrix is a key factor that is strongly influenced by the organic substituents grafted onto the POSS cage. The obtained results show that the incorporation of OEP-POSS within the used epoxy resin lead to a decrease of thermo-mechanical properties (T_g and thermal stability) of the obtained nanocomposites.

Thus, based on our previous experience [23–31] we intended to design different organic-inorganic hybrid materials with good dispersion and enhanced thermo-mechanical properties by combining diglycidyl ether of bisphenol A (DGEBA) with a small quantity (2 wt.%) of diglycidyl ether terminated poly(dimethylsiloxane), (DG-PDMS). As reinforcing agents, (mono-/octa) epoxy POSS (POSS-(3-Glycidyl) propoxy-Heptaisobutyl substituted (MEP-POSS) and POSS-Octa-(3-glycidyloxypropyl) dimethylsiloxy) (OEP-POSS)) were included into DGEBA/DG-PDMS organic host. To improve the dispersion of POSS during the preparation of POSS/polymer nanocomposites, DG-PDMS was used as a spacer between POSS molecules and DGEBA, enabling a high mobility of the epoxy chains which may contribute to a better dispersion of POSS units within the polymer matrix.

To the best of our knowledge, all previously studies were focused mainly on synthesis of different POSS/epoxy resin and POSS/PDMS nanocomposites, while DGEBA/DG-PDMS nanocomposites reinforced with epoxy POSS compounds remain unexplored [12–16,32–35]. Thus, we focused our research to evaluate the effect of DG-PDMS and epoxy POSS nanostructures on the properties of epoxy network. The curing behavior of DGEBA/DG-PDMS reinforced with epoxy POSS was analyzed by DSC and FTIR spectroscopy. The thermal stability and morphology of the obtained nanocomposites are evaluated by DMA, TGA, SEM/EDX, AFM and contact angle measurements. The hardness of the studied materials was also investigated through the AFM nanoindentation tests.

2. Experimental section

2.1. Materials

The studied networks possess in their structures a mixture of diglycidyl ether of bisphenol A (**DGEBA**), D.E.R.™ 332 (epoxy equivalent weight of 171–175 g/eq) and diglycidyl ether terminated poly(dimethylsiloxane), (**DG-PDMS**) (epoxy equivalent weight of 490 g/eq and a M_n ~ 800 g/mol). Two types of epoxy POSS (POSS-(3-Glycidyl)propoxy-Heptaisobutyl substituted with $M_w = 931.63$ g/mol (**MEP-POSS**) and POSS-Octa(3-glycidyloxypropyl)dimethylsiloxy) with $M_w = 931.11$ g/mol (**OEP-POSS**)) were used as reinforcing agents. 1 methyl imidazole (**1MeI**) was the anionic initiator for the high temperature polymerization reaction of epoxy groups. All reagents, were supplied by Sigma-Aldrich Chemicals, and used without further purification. The chemical structures of the raw materials are further illustrated in Scheme 1.

2.2. Formation of POSS based DGEBA/DG-PDMS nanocomposites

As represented in Scheme 1, two types of POSS based DGEBA/DG-PDMS nanocomposites were synthesized. Firstly, DGEBA/DG-PDMS polymer matrix was prepared by mixing the liquid epoxy resin (DGEBA) with the epoxy functionalized polydimethylsiloxane (DG-PDMS) in 98/2 weight ratio. Further, 10 wt.% MEP or OEP POSS was incorporated within DGEBA/DG-PDMS organic host. To achieve a good dispersion of both DG-PDMS and POSS nanocages within DGEBA resin, the obtained mixture was sonicated 1 h at room temperature using an ultrasonic processor UP100H. After mixing the components, 5 wt.% 1MeI was added. The resulting blends were degassed to remove the entrapped air during mixing, poured into Teflon molds, cured at 120 °C for 2 h, and postcured at 160 °C for another 3 h. After cooling, the obtained hybrids were removed from the mold and characterized. DGEBA homopolymer was also prepared in the same conditions.

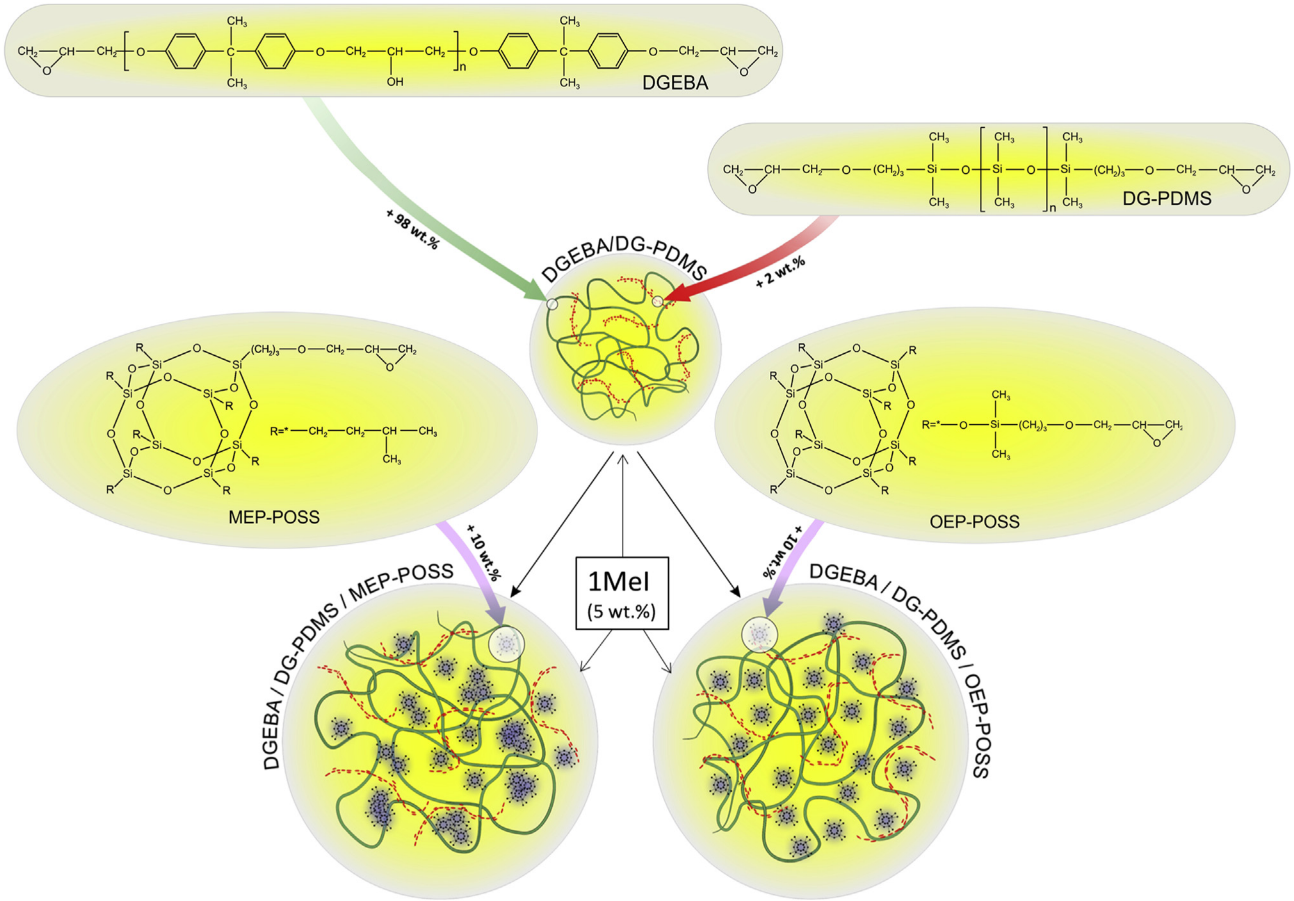
In order to check the efficiency of the network formation and to remove any traces of unreacted compounds, the synthesized samples were Soxhlet extracted with a suitable solvent for 2 h and subsequently were dried at room temperature for minimum 24 h. After extraction, no shape deformation was observed for any specimen.

2.3. Characterization

Differential scanning calorimetry (DSC). The calorimetric measurements were performed on a Netzsch DSC 204 F1 Phoenix differential scanning calorimeter under a constant nitrogen flow rate (20 mL/min). All the samples (about 4 mg in weight) were non-isothermally heated from 20 to 350 °C and the DSC curves were recorded at a heating rate of 10 °C/min.

Fourier transform infrared (FTIR) spectra were registered on a Vertex 70 Bruker FTIR spectrometer equipped with an attenuated total reflectance (ATR) accessory in order to determine the chemical structure and also the curing degree of all the studied specimens. All FTIR measurements were performed in the ATR-FTIR cell on Ge crystal, at room temperature. The FTIR spectra were recorded using 32 scans in 600–4000 cm^{-1} wavenumber region.

The dynamic mechanical behavior of the samples after postcuring was followed on a Tritec 2000 (Triton Technology) instrument using 10 mm × 2 mm × 20 mm rectangular specimens in a single cantilever bending mode. Tan δ was calculated as a function of the temperature ranging from -130 to 200 °C using 5 °C/min heating



Scheme 1. The synthesis route of DGEBA/DG-PDMS ± POSS nanocomposites.

rate at a frequency of 1 Hz. The displacement amplitude was 0.05 mm. The experiment was performed in triplicate.

The *thermogravimetric analysis (TGA)* curves were achieved on a Q500 TA instrument. A sample of about 2.5 mg was placed in a platinum crucible and heated from 20 to 650 °C at a heating rate of 10 °C/min under a constant nitrogen flow rate (balance flow 10 mL/min, oven flow 90 mL/min). Three different experiments were run for each sample.

Scanning electron microscopy (SEM) and Si mapping of DGEBA/DG-PDMS ± POSS hybrids were carried out using a Zeiss EVO50 scanning electron microscope equipped with a Carl Zeiss NTS energy-dispersive X-ray detector (EDX). Before analysis, cryogenic fracture surfaces were covered with a thin gold layer.

Atomic force microscopy (AFM). Surface topography was examined by using MultiMode NanoScope IIID Controller Atomic Force Microscope (Digital Instruments Veeco Metrology Group, Santa Barbara, CA, USA) working in the so-called tapping mode. Images were achieved using a TESP (0.01–0.025 Ohm-cm Antimony (n) doped Si) tip at 1 Hz scan rate. All the measurements were performed in ambient environment. Images were flattened using first order fitting to remove any background tilt. All images were achieved at 10 μm, 5 μm and 2.5 μm size scale. In order to characterize the roughness of these samples, a 5 × 5 μm^2 surface area was analyzed. The roughness measurements were performed over the entire image. A minimum of five specimens were tested for each sample and the average values are reported. The hardness of all the studied specimens was also investigated by nanoindentation measurements. Nanoindentation tests were performed at room temperature using the MultiMode NanoScope IIID Controller atomic force microscope. A DNISP diamond tip mounted on a stainless steel cantilever (spring constant, k = 227 N/m) was used for both indentation test as well as for AFM imaging. Nanoindentation hardness was defined as the maximum indentation load (F) divided by the projected area (A). The projected area was determined from the tip shape of the indenter using AFM NanoScope V531r1 software and Heron formula [36–38]. The indentation load was set to 98 μN and kept constant for all measurements. A 2 × 2 array of indentation was made on each sample, in three different areas, using the same force and parameters. The hardness was obtained as an average of twelve measurements.

Contact angle measurements. The surface wettability was determined using KSV Instruments's CAM 100 by measuring the contact angle on the surface of the films with small water droplets. The contact angles reported represent the mean of three tests.

3. Results and discussion

3.1. The influence of POSS type on the DGEBA/DG-PDMS curing behavior studied by DSC

To investigate the effect of both DG-PDMS and POSS type on the reactivity of epoxy groups during copolymerization reactions of DGEBA/DG-PDMS ± POSS nanocomposites, non-isothermal DSC scans were performed. Fig. 1 shows the DSC curves before curing for DGEBA and hybrids based on DGEBA/DG-PDMS ± POSS (MEP or OEP-POSS).

The curve 1 from Fig. 1 reveals that DGEBA homopolymer exhibits an exothermic peak at 142 °C, assigned to the temperature at

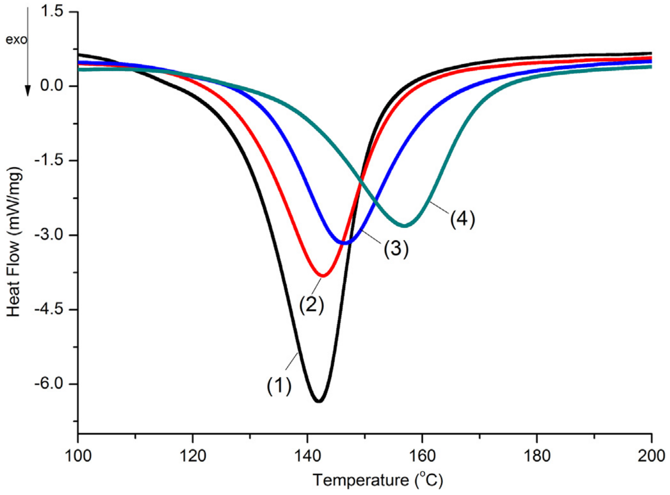


Fig. 1. DSC curves for: (1) DGEBA; (2) DGEBA/DG-PDMS; (3) DGEBA/DG-PDMS/MEP-POSS; (4) DGEBA/DG-PDMS/OEP-POSS.

which the polymerization enthalpy of epoxy groups is maximum (T_{max}). As one may notice from Fig. 1 (curve 2), the presence of DG-PDMS exhibits no significant influence on the polymerization of epoxy groups from pure DGEBA. The introduction of (mono-/octa) epoxy POSS nanocages (MEP or OEP-POSS) within DGEBA/DG-PDMS matrix, causes an increase of T_{max} which depends mainly on the number of the epoxy groups belonging to the POSS cages. Thus, the inclusion of MEP-POSS within DGEBA/DG-PDMS matrix, leads to a slightly increase of T_{max} from 143 °C to 147 °C (curve 3). This type of POSS bearing only one reactive group exhibits a high agglomeration tendency which may lead to a partial POSS cages agglomeration which hinders the attack of the initiator (1-MeI) to the epoxy groups.

When OEP-POSS is used, the epoxy polymerization occurs at a higher temperature (157 °C, Fig. 1 curve 4) probably due to the restricted mobility of the DGEBA chains in the vicinity of the POSS cages, these chains being less available for the polymerization. The reactivity of epoxy groups belonging to this type of POSS is much lower than for neat DGEBA. In the case of OEP-POSS/1MeI the exothermic peak assigned to the maximum polymerization enthalpy of the epoxy groups appears at 194 °C, as we previously reported [22].

3.2. *FTIR studies during the polymerization of POSS based DGEBA/DG-PDMS nanocomposites*

FTIR studies were used to monitor the curing reactions of the epoxy groups. The FTIR spectra shown in Fig. 2, were performed during the curing process of DGEBA/DG-PDMS hybrid and reveal that the peak assigned to the epoxy groups (915 cm^{-1}) significantly decreases at higher reaction times. After the postcuring treatment the corresponding absorption band disappeared, indicating that the curing reaction of epoxy groups is complete.

Under the same curing and postcuring conditions similar results were obtained for POSS-containing nanocomposites. The characteristic peak in the infrared region for the epoxy ring disappeared, indicating that the curing reactions in the nanocomposites were carried out to completion. The band at 1608 cm^{-1}, assigned to aromatic C=C stretching vibration was used as a reference.

The conversion degree of epoxy groups was calculated by means of Equation (1) from the ratio of the epoxy groups absorbance peak area (915 cm^{-1}) relative to that of the aromatic C=C stretching vibration (1608 cm^{-1}), for the cured and uncured specimens.

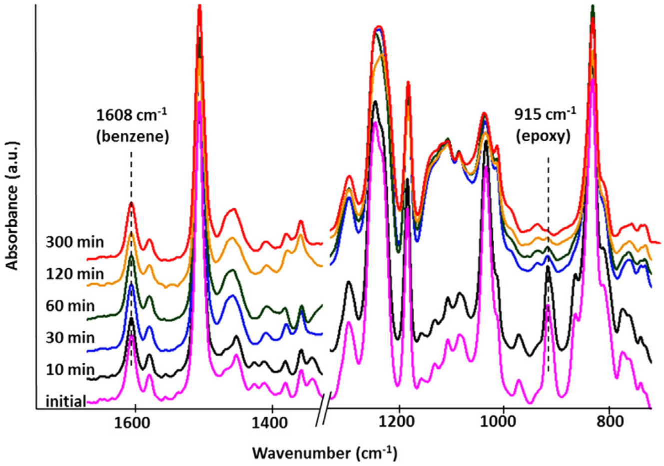


Fig. 2. FTIR spectra of DGEBA/DG-PDMS system at different polymerization times.

$$\eta = \left[1 - \frac{(A_{915}/A_{1608})_t}{(A_{915}/A_{1608})_0}\right] \times 100 \tag{1}$$

where:

η – conversion, %;
A_{915} = 915 cm^{-1} peak area;
A_{1608} = 1608 cm^{-1} peak area;
t = the reaction time (min);
0 = initial moment of the reaction (uncured mixture).

The obtained conversion degrees for DGEBA/DG-PDMS ± POSS nanocomposites are shown in Fig. 3.

From the conversion results, it may be observed that the conversion degree of epoxy groups is strongly influenced by the presence of both DG-PDMS and POSS compounds (Fig. 3).

From Fig. 3 curve 2, one may noticed that the incorporation of a small amount of low molecular weight DG-PDMS into DGEBA epoxy resin leads to lower conversions than for neat DGEBA probably due to the chains of DG-PDMS which may partially hinder the attack of 1MeI molecules to the epoxy groups.

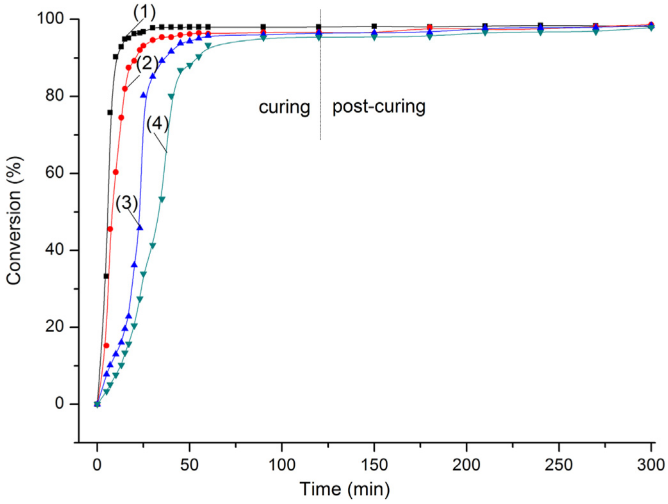


Fig. 3. The conversion degree of the epoxy groups against time for: (1) DGEBA; (2) DGEBA/DG-PDMS; (3) DGEBA/DG-PDMS/MEP-POSS; (4) DGEBA/DG-PDMS/OEP-POSS.

The inclusion of POSS compounds, bearing one or eight epoxy moieties, decreases the rate of epoxy polymerization especially at the early stages, which is probably a consequence of the hindrance effect due to the bulky POSS cages [22–24,39]. Moreover, a significant influence of the number of epoxy groups from the POSS cages against conversion was noticed. Thus, in the early stages of the reaction this influence is not noticeable since the network formation is just at the beginning. However, when the reaction goes on, the crosslinking density becomes higher since more epoxy groups are involved. As a consequence, OEP-POSS based nanocomposites exhibit a high crosslinking density of the final network due to the high content of epoxy groups from the POSS molecules. In this case the access of the 1MeI molecules to the epoxy groups becomes more difficult which leads to a lower conversion of systems with OEP-POSS in comparison with those with MEP-POSS in which the formed network exhibit a lower crosslinking density. This behavior is probably caused by the agglomeration tendency of MEP-POSS. More details about morphology will be further described in morphology section.

To achieve a complete cure for all the studied specimens, a postcuring treatment at a higher temperature was also performed. At the end of the postcuring process, all the systems were almost completely cured (Fig. 3).

3.3. *Thermo-mechanical properties*

To establish the influence of DG-PDMS and POSS on the T_g and storage modulus (E') of the cured DGEBA/DG-PDMS ± POSS networks, DMA tests were performed in the temperature range $-130 \div 200$ °C (Fig. 4, Table 1).

From the tan δ curves it may be observed that the neat epoxy network (Fig. 4(a) curve 1) shows two transitions: one at 137 °C assigned to the α-relaxation and corresponds to the glass transition of the epoxy network. The transition at low temperature (-130 °C to -20 °C) is attributed to the β-relaxation of the epoxy chain, and is due to the motion of the glycerol groups in DGEBA [40,41].

The incorporation of 2 wt.% of low molecular weight DG-PDMS within DGEBA leads to a lower T_g of the cured DGEBA/DG-PDMS network (127 °C) in comparison with DGEBA homopolymer. This behavior is caused mainly by the high flexibility of DG-PDMS chain. It is also clearly seen that DGEBA/DG-PDMS hybrid displayed a single well-defined T_g, which indicates that the epoxy terminated PDMS form a homogeneous phase with the epoxy resin [16,42,43].

Table 1
Thermomechanical results for DGEBA/DG-PDMS ± POSS hybrid materials.

DGEBA/DG-PDMS ± POSS	DMA	TGA		
	T_g[a], (°C)	$T_{d5\%}$[b], (°C)	$T_{d50\%}$[c], (°C)	Weight loss[d], (%)
DGEBA	137	383	438	87
DGEBA/DG-PDMS	127	400	440	88
DGEBA/DG-PDMS/MEP-POSS	132	318	440	83
DGEBA/DG-PDMS/OEP-POSS	158	335	445	80

[a] T_g = glass transition temperature (maximum of tan δ);
[b] $T_{d5\%}$ loss = the temperature at which the weight loss is 5%.
[c] $T_{d50\%}$ loss = the temperature at which the weight loss is 50%.
[d] The percentage of the weight loss at 600 °C.

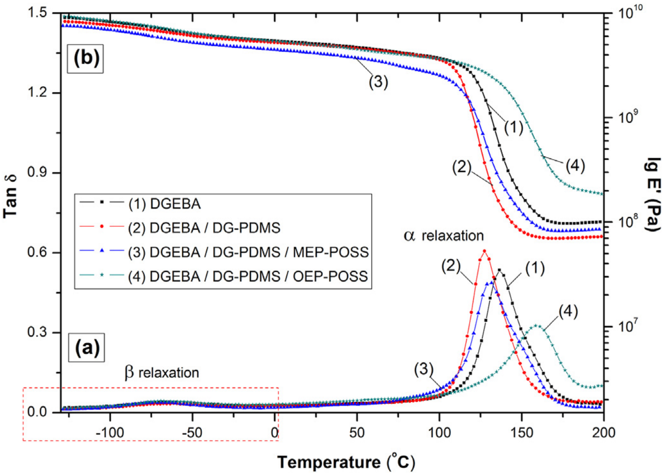


Fig. 4. The dependences of tan δ (a) and storage modulus E′ (b) curves against temperature for DGEBA/DG-PDMS ± POSS nanocomposites.

The dynamic mechanical behavior of the obtained PDMS/epoxy hybrids was determined using the storage modulus (E′) results. From Fig. 4(b) curve 2 it may be observed that the inclusion of the flexible DG-PDMS chains within DGEBA resin, leads to a lower E′ of the obtained hybrid network, in comparison with E′ of DGEBA neat matrix. For these types of hybrid networks a lower crosslinking density was achieved which lead to a lower E′ in the rubbery region [31].

The incorporation of MEP-POSS within the polymer matrix, leads to a slightly increase of T_g of the obtained nanocomposites in comparison with the unreinforced DGEBA/DG-PDMS organic host. This type of POSS bearing only one reactive group exhibits a self-assembly tendency which may lead to a partial POSS cages agglomeration which subsequently leads to a lower crosslinking density.

When OEP-POSS is used, the obtained value for the T_g of the corresponding nanocomposite is shifted with 31 °C towards higher temperature compared with the polymer matrix. The effect of raising the T_g by the introduction of POSS cages into the organic host suggests that the polymeric matrix can be reinforced on the nanoscale level by the POSS cages which are covalently bonded to the polymer networks [8,44]. OEP-POSS seems to be the best candidate to form a highly crosslinked network due to the presence of multiple epoxy groups. The rigid and bulky structure of POSS cages could restrict the motions of macromolecular chains which additionally enhance the T_g of the OEP-POSS based nanocomposites.

Moreover, for OEP-POSS based nanocomposites, it was noted that the tan δ curve was significantly decreased in height and becomes broader. This suggests higher limitations on freedom of chain mobility in the samples probably due to an increased crosslinking density [31,43].

Concerning the dynamic mechanical properties of the POSS reinforced systems, it was interesting to note that in the glass state region the storage modulus of MEP-POSS reinforced nanocomposites is lower than DGEBA/DG-PDMS. This behavior is probably caused by the heterogeneous structure of the obtained nanocomposites in which the POSS compounds form large aggregates. Moreover, the presence of bulky POSS aggregates leads to an increase in the free volume between the polymer chains thus acting like a plasticizer.

In the rubbery domain, the dynamic storage modulus E′ appears to be improved, no matter what type of POSS was used.

The highest storage modulus was achieved for the nanocomposites containing OEP-POSS which can easily react with epoxy groups from both DGEBA and DG-PDMS resulting nanocomposites with higher crosslinking density. These networks exhibit a higher stiffness even in comparison with DGEBA pure matrix.

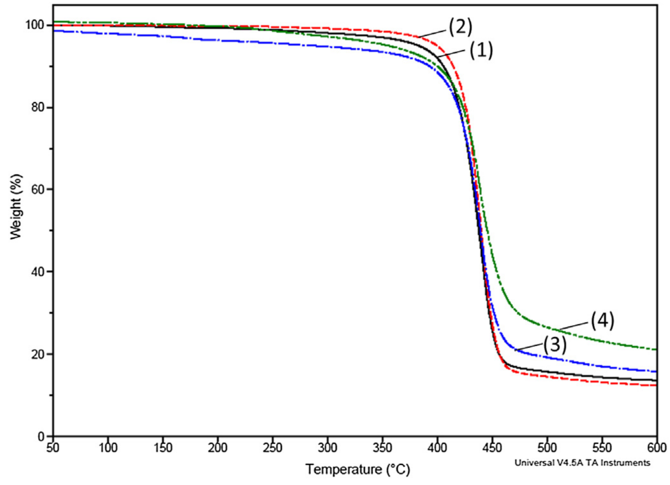


Fig. 5. TGA plots for: (1) DGEBA; (2) DGEBA/DG-PDMS; (3) DGEBA/DG-PDMS/MEP-POSS; (4) DGEBA/DG-PDMS/OEP-POSS.

3.4. Thermal stability

The thermal stability of the DGEBA/DG-PDMS ± POSS hybrid materials was revealed through TGA measurements (Fig. 5). Within the experimental temperature range all the TGA curves are unimodal, displaying only one degradation step, suggesting that the incorporation of DG-PDMS and epoxy POSS exhibits no significantly influence on the thermodegradation mechanism of the epoxy polymer matrix.

From the TGA curves, it can be calculated that the $T_{d5\%}$ value obtained for DGEBA/DG-PDMS hybrid is 17 °C higher compared with the $T_{d5\%}$ registered for DGEBA homopolymer. This behavior clearly indicates that the incorporation of DG-PDMS within epoxy resin increases the thermostability of the obtained DGEBA/DG-PDMS hybrid. The presence of Si—O—Si inorganic backbone on the DG-PDMS structure contributes to the increase of the thermostability due to the high Si—O bond dissociation energy (460 kJ/mol) compared with the C—O (345 kJ/mol) or even with Si—C (318 kJ/mol) bonds [45].

The nanocomposites reinforced with POSS (10 wt.%) were also subject to thermal analysis. The TGA results show that the MEP-POSS/OEP-POSS based nanocomposites exhibit lower initial thermal stability compared with the unreinforced network, DGEBA/DG-PDMS. Among POSS based nanocomposites, the lowest temperature corresponding to the weight loss of 5% was obtained in the case of MEP-POSS nanocomposite which is probably due to the low crosslinking density of the network established between MEP-POSS and epoxy matrix.

Although the initial thermal stability is significantly decreased, at higher temperatures, the degradation degree ($T_{d50\%}$) is almost similar for POSS based nanocomposites as for the unreinforced material. As Fu et al. previously reported [46], this behavior can be attributed to the yields of silicon-rich residues, which make the materials more stable at elevated temperatures. Therefore, the thermal degradation behavior of epoxy resins is strongly influenced by the presence of POSS compounds due to the self-decomposition and self-condensation processes which occur at relatively low temperatures and form protective layers that increase the thermostability at higher temperatures.

It should be emphasized that the lowest degradation degree at higher temperatures was observed for the nanocomposite reinforced with OEP-POSS, among all the POSS based nanocomposites. This improvement could be the result of the formation of tightly crosslinked structure between the polymer matrix and POSS cages. In this case, the POSS cages are probably dispersed at nanoscale level in epoxy matrix.

For the nanocomposite with MEP-POSS, the degradation rate at higher temperatures ($T_{d50\%}$) remains unchanged in comparison with unreinforced matrix. This type of POSS exhibits a strong tendency toward aggregation and thus its presence tends to reduce the epoxy crosslinking density. Therefore, the decomposition

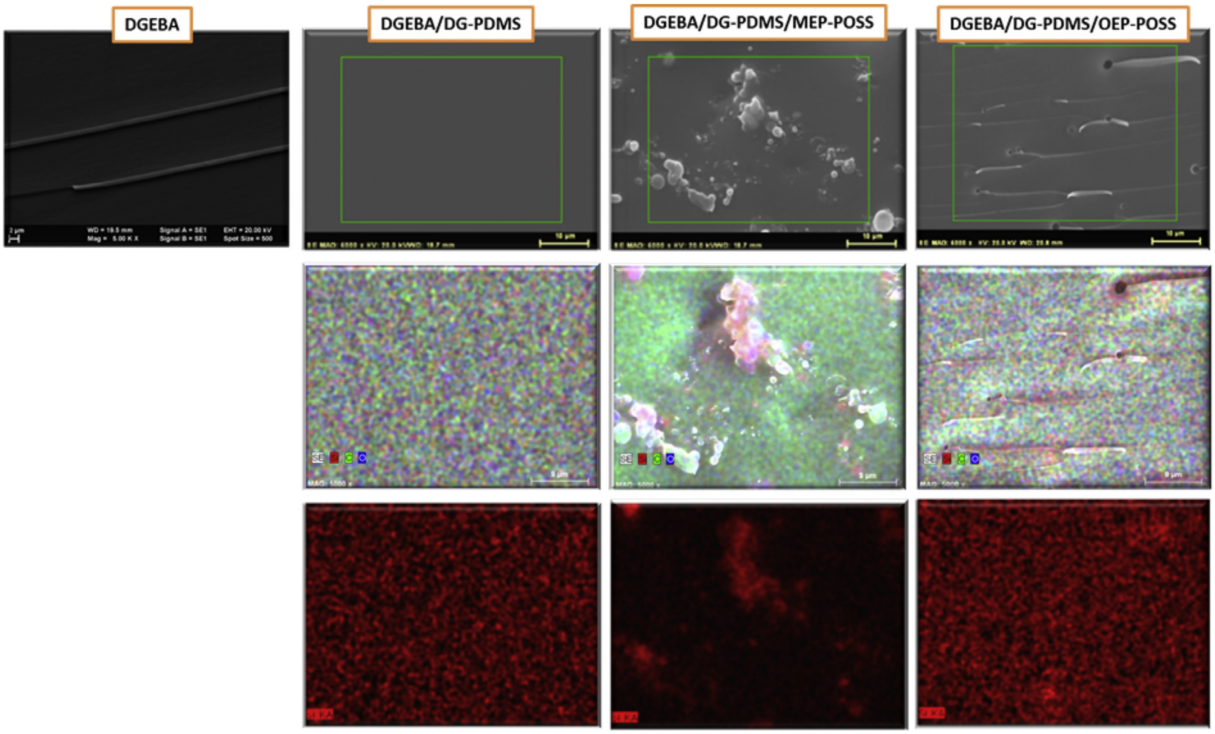


Fig. 6. SEM and EDX Si mapping micrographs of the fractured surface of POSS based DGEBA/DG-PDMS nanocomposites.

temperature of the epoxy resin will decrease. These results are in good agreement with DMA tests.

As we expected, the char yield increases for the POSS based nanocomposites, because of the presence of the inorganic moiety.

3.5. Morphological characterization

To establish the morphology of the DGEBA/DG-PDMS ± POSS hybrid materials, SEM with EDX Si map distribution and AFM analyses were performed and the obtained results are displayed in Figs. 6 and 7(a–d), respectively.

The SEM and Si mapping images, show that DG-PDMS is homogenously distributed in the corresponding epoxy matrix. SEM and EDX Si mapping micrographs are also performed for the POSS based nanocomposites. The obtained results reveal that the OEP-POSS seems to be well dispersed in the network, and no aggregates were observed. This good dispersion of OEP-POSS hybrid nanobjects can be attributed to the miscibility of the POSS within the resin mass and to the covalent bonds formed between the eight epoxy functionalities belonging to POSS nanocages and the epoxy groups from the base matrix.

Studying the morphology of MEP-POSS containing networks, it is obviously that this type of POSS exhibits a highly agglomeration

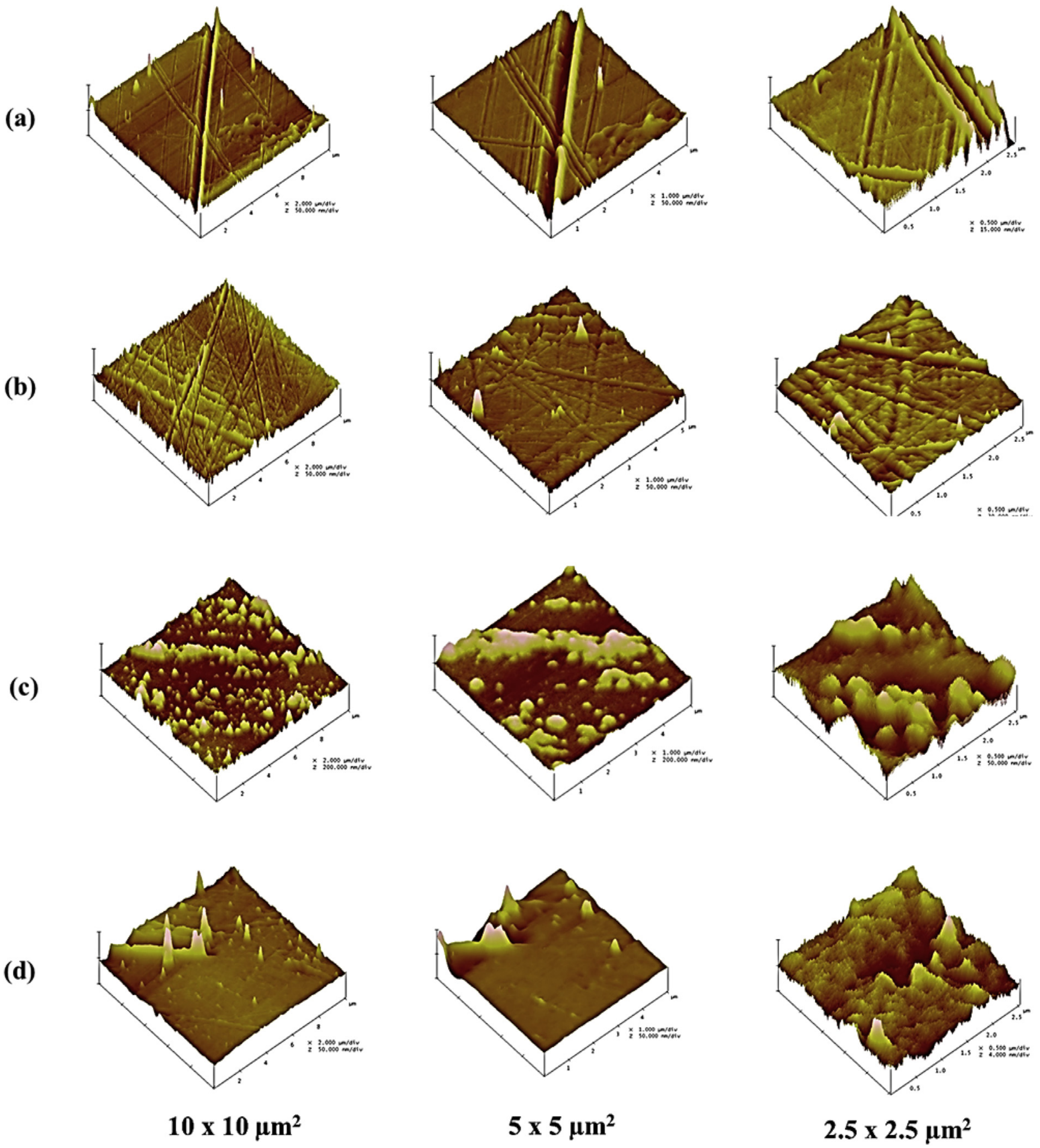


Fig. 7. The AFM micrographs of (a) DGEBA; (b) DGEBA/DG-PDMS; (c) DGEBA/DG-PDMS/MEP-POSS; (d) DGEBA/DG-PDMS/OEP-POSS.

tendency that leads to a phase segregation in the matrix which is in good agreement with DMA results. The obtained results are also in good agreement with those reported by Boček et al. [47].

To fully understand the morphology of the POSS based materials, AFM analyses were performed on all the synthesized nanocomposites and the obtained 3D images are displayed in Fig. 7(a–d). AFM is also a useful tool for studying the surface roughness at the nanoscale level. To characterize the roughness of the studied samples, 5 μm^2 surface areas were analyzed and the obtained average roughness (Ra) values are illustrated in Fig. 8. Applying special investigation modes, AFM can additionally be used to measure mechanical properties such as nanoindentation hardness. The results of hardness measurements performed for the studied samples are illustrated also in Fig. 8 along with the roughness values.

From the 3D AFM images shown in Fig. 7a–b and from the average roughness (Fig. 8), it may be observed that DGEBA/DG-PDMS hybrid and DGEBA homopolymer exhibit similar surface topographies and similar roughness values indicating that DG-PDMS is well dispersed within DGEBA epoxy matrix and no phase segregation occurs.

For the POSS based nanocomposites different morphologies were obtained (Fig. 7c–d). The incorporation of MEP-POSS into DGEBA/DG-PDMS matrix yields to a considerable increase in the surface roughness as shown in Fig. 7c and Fig. 8. MEP-POSS being functionalized with one epoxy group and seven unreactive isobutyl groups, exhibits a high tendency to self-agglomerate at the surface of the obtained nanocomposite.

Our results for MEP-POSS are completely consistent with the results obtained by Dodiuk et al. [48] who describes that an increased roughness is accompanied with a reduced T_g and storage modulus. In this case, POSS nanocages act more like a plasticizer than as reinforcing agent. Consecutively, it was concluded, that a poor compatibility is obtained between this type of POSS and the polymer matrix.

The nanocomposite with OEP-POSS exhibits a roughness value similar with the unreinforced samples, which means that this POSS is well dispersed in the polymer matrix due to the eight epoxy groups attached to Si—O—Si cages. In this case a higher compatibility between the POSS molecules and the polymer matrix was achieved.

Concerning the nanoindentation hardness features, it was noticed that the presence of 2 wt.% of the polysiloxane monomer generate minor modifications [16]. As expected, the addition of 10 wt.% POSS into neat DGEBA/DG-PDMS matrix has a great effect on the nanohardness. The obtained results are in good agreement with the results reported by Yari et al. [49].

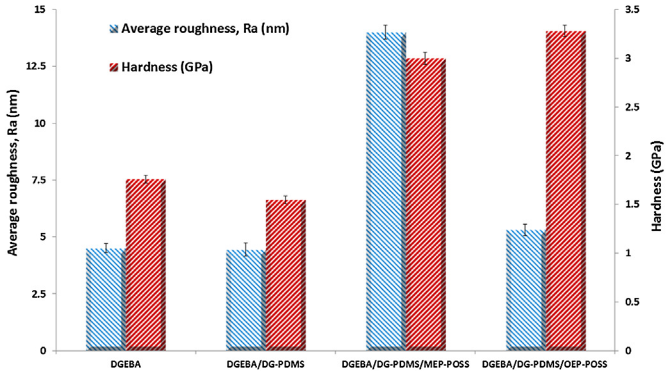


Fig. 8. The AFM average roughness and nanohardness measurements of: DGEBA; DGEBA/DG-PDMS; DGEBA/DG-PDMS/MEP-POSS; DGEBA/DG-PDMS/OEP-POSS.

The increase in hardness can be correlated with the storage modulus data: the samples become more rigid as POSS with higher functionalities was used. The reinforcing effect of the POSS was thus confirmed and a good interfacial adhesion between polymeric matrix and POSS compounds was gained in the tested composites.

The contact angle measurements were also performed and no significant differences were observed between the synthesized samples. When POSS was added, a slight increase of the surface hydrophobicity was observed probably to the hydrophobic nature of -Si-O-Si- linkage. In the case of MEP-POSS based nanocomposites, the tendency to form agglomerations is supplementary confirmed also by the contact angle measurements.

4. Conclusions

To prepare DGEBA/DG-PDMS/POSS nanocomposites with good dispersion and improved thermo-mechanical properties, a low amount of epoxy functionalized polydimethylsiloxane (DG-PDMS) together with POSS bearing one or eight epoxy groups (10 wt.%) were covalently introduced within DGEBA epoxy matrix through copolymerization of epoxy groups. The presence of DG-PDMS as a spacer between POSS molecules and DGEBA leads to a nanoscale dispersion of OEP-POSS within the polymer matrix. Thus, for this nanocomposite the highest thermo-mechanical properties were obtained.

According to DSC data, the introduction of (mono-/octa) epoxy POSS nanocages (MEP or OEP-POSS) within DGEBA/DG-PDMS matrix, leads to an increase of the temperature at which the polymerization enthalpy of epoxy groups is maximum (T_{max}) and depends mainly on the number of the epoxy groups belonging to the POSS cages. The inclusion of OEP-POSS within DGEBA/DG-PDMS matrix, leads to a significantly increase of the maximum polymerization enthalpy of the epoxy groups, the exothermic peak being shifted from 143 °C to 157 °C. In this case the polymerization reaction occurs with a lower rate.

The DSC data are in good agreement with the FTIR kinetic studies which demonstrate that the inclusion of both DG-PDMS and POSS compounds reduces the polymerization rate curing process of DGEBA/DG-PDMS/POSS nanocomposites, but after the postcuring treatment, all the studied specimens exhibit complete cure.

The DMA results show that the presence of DG-PDMS reduces the glass transition temperature indicating that DG-PDMS forms a homogeneous phase with the epoxy resin.

Moreover, the average roughness obtained from the AFM measurements evidenced that DGEBA/DG-PDMS hybrid and DGEBA homopolymer exhibit similar surface topographies and similar roughness values indicating that DG-PDMS is well dispersed within DGEBA epoxy matrix and no phase segregation occurs. Similar results were obtained from the SEM and Si mapping images.

The incorporation of POSS functionalized with one or eight epoxy groups (10 wt.%) within DGEBA/DG-PDMS networks exhibits a significantly influence on the morphology and thermo-mechanical properties (T_g, storage modulus, thermal stability and hardness) of the obtained nanocomposites.

Among POSS based nanocomposites enhanced thermo-mechanical properties were obtained for those reinforced with OEP-POSS. These features could be ascribed to the nanoscale reinforcement effect of OEP-POSS on the DGEBA/DG-PDMS matrix. This statement is supplementary sustained by the SEM/EDX and AFM micrographs that emphasize the higher compatibility between OEP-POSS and the selected polymer matrix, this type of POSS being well dispersed in the polymer matrix due to the eight epoxy groups attached to POSS molecules.

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