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Nanotailoring of epoxy adhesives by polyhedral-oligomeric-sil-sesquioxanes (POSS)

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Abstract

The development and commercialization of nanoparticles such as nanoclays, carbon nanotubes and polyhedral-oligomeric-sil-sesquioxanes (POSS) offer new possibilities to tailor adhesives in the nanoscale range. Due to the large surface area of the nanosized particles, only small amounts are needed to cause significant changes in properties of adhesives. Properties affected include shear and peel strengths, thermal characteristics, etc.

Experimental results showed that only small amounts of POSS (<5 wt%) were needed to enhance the shear strength of epoxy adhesives and double the peel strength compared with that of the neat epoxy adhesive. The glass transition temperature was increased significantly when the POSS moiety contained reactive groups. In all cases, the increase in properties was obtained at low concentrations of POSS. Above the optimal concentration of POSS, the properties decreased. The mechanical and thermal results were complemented with atomic force microscopy (AFM) characterization of the fracture surfaces of the POSS/epoxy adhesives. AFM results indicated that the surface roughness changed with concentration of POSS. At low levels of POSS, the typical roughness was low and the roughness increased with concentration of POSS. The results led to the conclusion that incorporation of tailored POSS particles in adhesives could improve structural adhesives and composite matrices.

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Keywords: A. Epoxy; C. Atomic force microscopy; D. Mechanical properties of adhesives; E. Poss

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1. Introduction

With the emergence of commercial nanoparticles such as nanoclays, carbon nanotubes and hybrid organic–inorganic copolymers-polyhedral-oligomeric-sil-sesquioxanes (POSS), new potential routes have been opened to nanoscale tailoring of adhesives. The nanosized particles are characterized by large surface area (hundreds of m^2/g). The enhancements in properties of adhesives attained with these materials are higher than predicted with conventional materials. Moreover, the small size of the particles ensures that many atoms of the particles will be at the surface and the reactivity of the surface atoms can be quite different from those in the bulk. The potential of nanofillers for adhesive formulations is promising, provided chemical and physical interactions develop between the particle surface and the resin matrix rather than between one particle and another (agglomeration). Thus, a small amount of nanoparticles may cause significant changes in the nanostructure with consequences to the macroscopic properties [1].

POSSs are inorganic silica-like nanocages of 1.5 nm in size that have organic substituents (Fig. 1). Inactive organic substituents make the POSS physically compatible with relevant polymers promoting dispersion in a polymer at a molecular level [3], while substituents that are reactive, promote curing or grafting reactions [2]. There are two methods by which the silica-like cages can be incorporated into the polymer [4]. In the first method

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the silsesquioxane cages are mechanically dispersed in the organic matrix like a filler without covalent bonding. In the other method the silsesquioxane cage is functionalized and covalently linked to the polymer. The functionalization can be by a single functional group or multiple functional groups. POSS has been incorporated into thermosets such as epoxy resins [5–9] and has shown improvements in thermal and rheological properties.

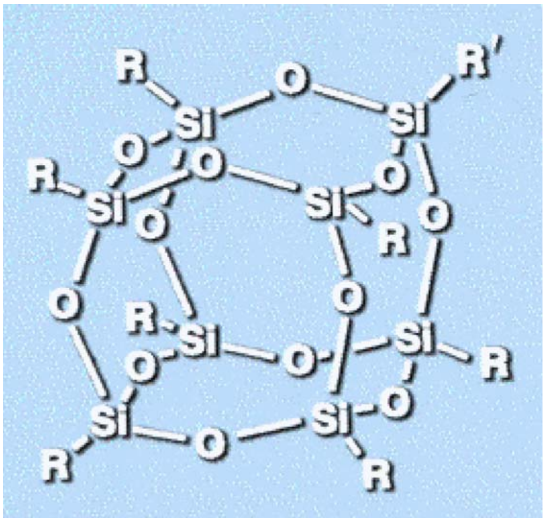


Fig. 1. General structure of POSS.

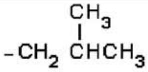
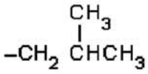
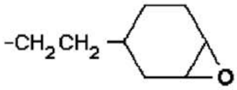
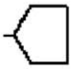
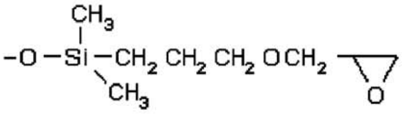
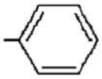
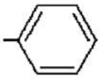
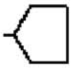
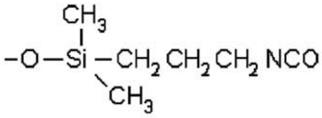
The use of nanofillers for tailoring of adhesives has not received a great deal of attention. Consequently, the current study is aimed at studying the effects of POSS that contains chemical functionalities on epoxy adhesives and on their adhesion strengths (shear and peel) and microstructure.

2. Experimental

POSS with five different types of functionalities have been included in the study, as described in Table 1. The first is an amino group, the second an epoxycyclohexyl group, the third a glycidyl group, the fourth an octaphenyl group, and the fifth an isocyanate group.

The epoxy resin used in this study was diglycidyl ether of bisphenol-A (DGEBA) (Epon 828 from Shell Co.). Its epoxide equivalent weight was 187 g/mol, the curing

Table 1
POSS substituents

Name	R	R′
POSS-(3-(2-Aminoethyl)amino)propyl-Heptaisobutyl substituted	 $-CH_2\overset{CH_3}{\overset{\mid}{C}}HCH_3$	$-CH_2CH_2CH_2NHCH_2CH_2NH_2$
POSS-(2-(3,4-Epoxycyclohexyl)ethyl)-Heptaisobutyl substituted	 $-CH_2\overset{CH_3}{\overset{\mid}{C}}HCH_3$	
POSS-Glycidoxypropyldimethylsilyloxy-Heptacyclopentyl substituted		
POSS-Octaphenyl substituted		
POSS-Isocyanatopropyldimethylsilyloxy-Heptacyclopentyl substituted		 $-O-\underset{CH_3}{\overset{CH_3}{\overset{\mid}{Si}}}-CH_2CH_2CH_2NCO$

agent used was polyamidoamine (Versamide 140 from Cognis Co.) and the mixing ratio used was 70:30 w/w. The POSSs were incorporated into the epoxy resin with intensive mixing. The curing agent was added to the mixture to form a homogeneous blend. Air was removed and curing at 80 °C for 12 h followed. The epoxy-POSS formulations were analyzed by means of differential scanning calorimetry (DSC) on a DSC-7 (Perkin Elmer) to obtain the glass transition temperature (T_g) and to study the curing kinetics. Dynamic scans were carried out at heating rates of 2, 5, 10 and 20 °C/min. The temperature range scanned was 15–300 °C. The activation energy was calculated according to ASTM E-698-99 from

$$E_a = -2.19R[\mathrm{d}\log\beta/\mathrm{d}(1/T)], \tag{1}$$

where E_a is the activation energy (kJ/mol), $R = 8.314$ (J/mol), β is the heating rate (K/min), and T is the peak temperature (K).

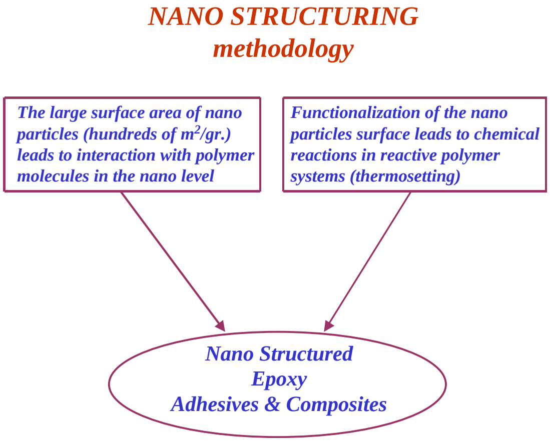


Fig. 2. Nanotailoring methodology.

Dynamic mechanical analysis (DMA) was carried out on a DMA-7e (Perkin Elmer) according to ASTM-D 5023, by three-point bending mode, at a frequency of 1.0 Hz in the temperature range from 0 to 130 °C. Sample bars of dimensions 1 × 3 × 20 mm were used. Lap shear (ASTM D-1002-72) and peel (ASTM D-1876-72) strengths of selected formulations were evaluated. The adherends were aluminum 2024-T3 treated with unsealed chromic acid anodization according to MIL-B-8625. The bonded joints were loaded at a crosshead speed of 2 mm/min for shear and 200 mm/min for peel. The mode of failure was determined visually.

The morphology of specimens fractured in liquid nitrogen was investigated by means of atomic force microscopy (AFM) on an instrument from Auto Probe Research Thermo Microscopes—Veeco. The contact mode and lateral force mode were used. Lateral force microscopy is a scanning probe microscopy technique that identifies and maps relative differences in surface frictional characteristics.

3. Methodology

Fig. 2 describes the methodology that was followed in the current study. Nanoparticles possess a large surface area, and a large portion of the atoms in the particles is located at the surface. As indicated, uniform dispersion and avoidance of agglomeration of nanoparticles is a key in high-quality polymer nanocomposites. It is postulated that these can be achieved if the surface of the nanoparticle is functionalized in accordance with the chemical characteristics of the host polymer matrix, to obtain chemical interaction. In this study, the effectiveness of POSS containing a variety of functional groups was evaluated. Different concentrations were also

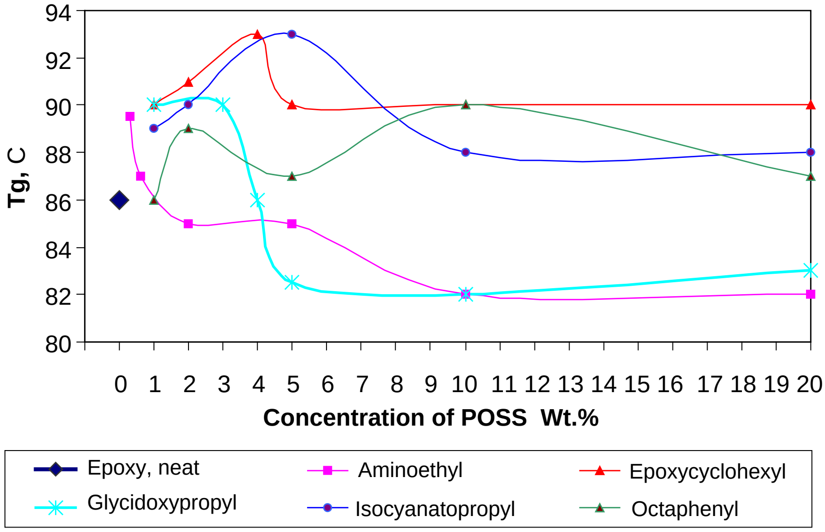


Fig. 3. The effect of POSS type and concentration on T_g.

studied. The effect of these tailored particles on the morphology, thermo-mechanical, bulk and adhesion shear and peel properties was investigated.

4. Results and discussion

4.1. Bulk properties

The effect of functionalized POSS on the bulk thermal and mechanical properties was investigated first. Fig. 3 depicts the variation of the T_g of the nanoepoxy formulations with functionality type and concentration. As can be observed, the T_g increased in the cases where the functionalities were compatible with the epoxy resin. It should be emphasized that the increase in T_g takes place in the concentration range of 0.5–5%. The maximum increase in T_g was 9 °C compared with the neat epoxy formulation. High amounts of POSS caused a reduction in the T_g. Furthermore, the maximum in T_g with respect to POSS concentration depends on the POSS functionality. The more reactive the chemical group toward the epoxy, the lower the concentration required to obtain the maximum T_g.

Table 2 describes the results obtained from the kinetics study. As evident, the activation energy, E_a, of the compatible functionalized POSSs were about 10% lower than that of the POSS free epoxy formulation and about 14% lower than that of the non-reactive octaphenyl-grafted POSS. The changes observed in the activation energies can be attributed to the chemical reaction between the functional group on the POSS and the constituents of the epoxy/curing agent mixture.

Table 2
Activation energy of POSS/epoxy formulations

POSS type	Concentration (%)	Activation energy (kJ/mol)
Neat	—	62.0
Glycidoxy	1	58.1
Epoxyhexyl	4	56.7
Isocyanate	5	55.5
Octaphenyl	10	64.8

Fig. 4 depicts the variation of storage modulus with temperature for various aminoethyl POSS concentrations. It can be seen that 0.5% of the latter POSS caused a significant enhancement while higher concentrations reduced the storage modulus as a function of temperature. The same behavior was obtained for epoxycyclohexyl functionalized POSS, as shown in Fig. 5. The results in Fig. 5 are not completely consistent with the T_g results (Fig. 3). In this case storage modulus increase is not accompanied by an increase in T_g. This is attributed to experimental error. The effect of POSS type and concentration on storage modulus at 25 and 110 °C are illustrated in Figs. 6 and 7, respectively. The octaphenyl functionality has the most dominant effect on the storage modulus at elevated temperature due to the aromatic groups contribution to the thermo-mechanical stability. Moreover, it was noticed that higher the reactivity of the functional group, lower was the concentration of POSS needed to obtain the maximum increase in storage modulus and stability at an elevated temperature.

4.2. Nanostructure

AFM images in the nano range can be seen in Figs. 8a and b. Figs. 8a and b depict the AFM images of epoxycyclohexyl POSS/epoxy formulations. Table 3 summarizes the roughness measured by AFM for epoxycyclohexyl, aminoethyl and octaphenyl POSSs, for a variety of concentrations. As can be seen that the surface roughness varies from 28 to 175 nm and it increases with POSS concentration in the epoxy matrix. Epoxycylohexyl POSS at 0.5% results in a typical roughness of 65 nm (Fig. 8a); epoxycyclohexyl POSS at 5% in roughness of 175 nm (Fig. 8b). As summarised in table 3, aminoethyl at 0.2% exhibited a typical roughness of 27 nm; at 0.5%, a roughness of 39 nm; at 3%,

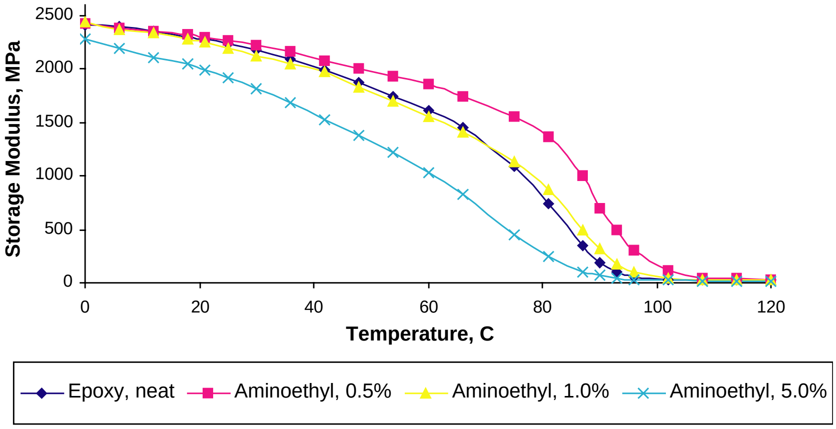


Fig. 4. The effect of aminoethyl POSS on storage modulus.

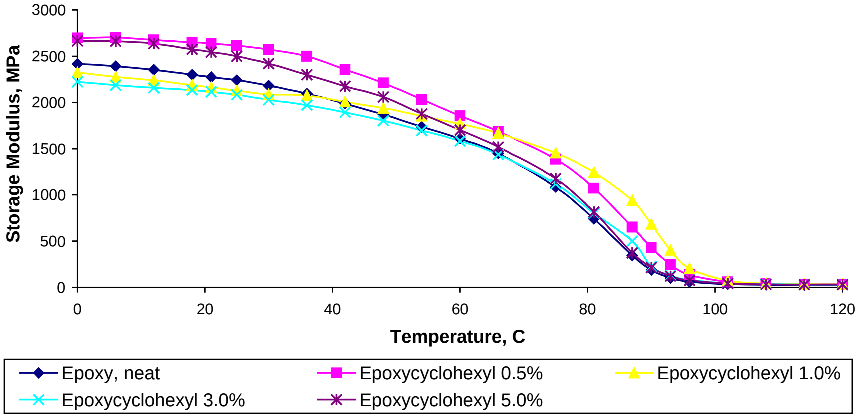


Fig. 5. The effect of epoxycyclohexyl POSS on storage modulus.

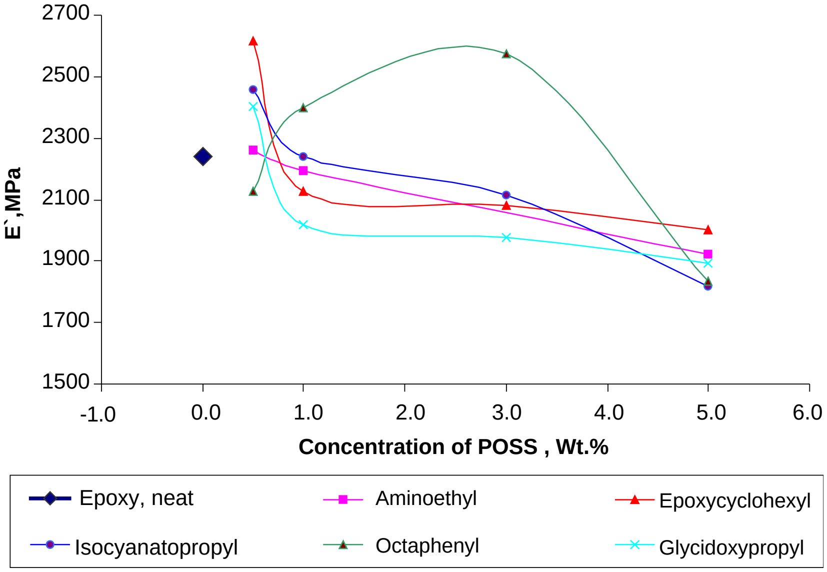


Fig. 6. The effect of POSS type and concentration on storage modulus at 25 °C.

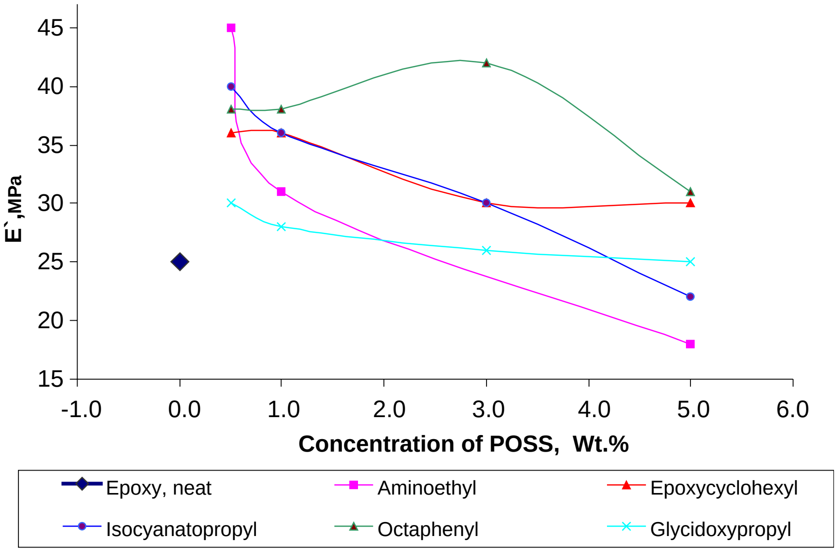


Fig. 7. The effect of POSS type and concentration on storage modulus at 110 °C.

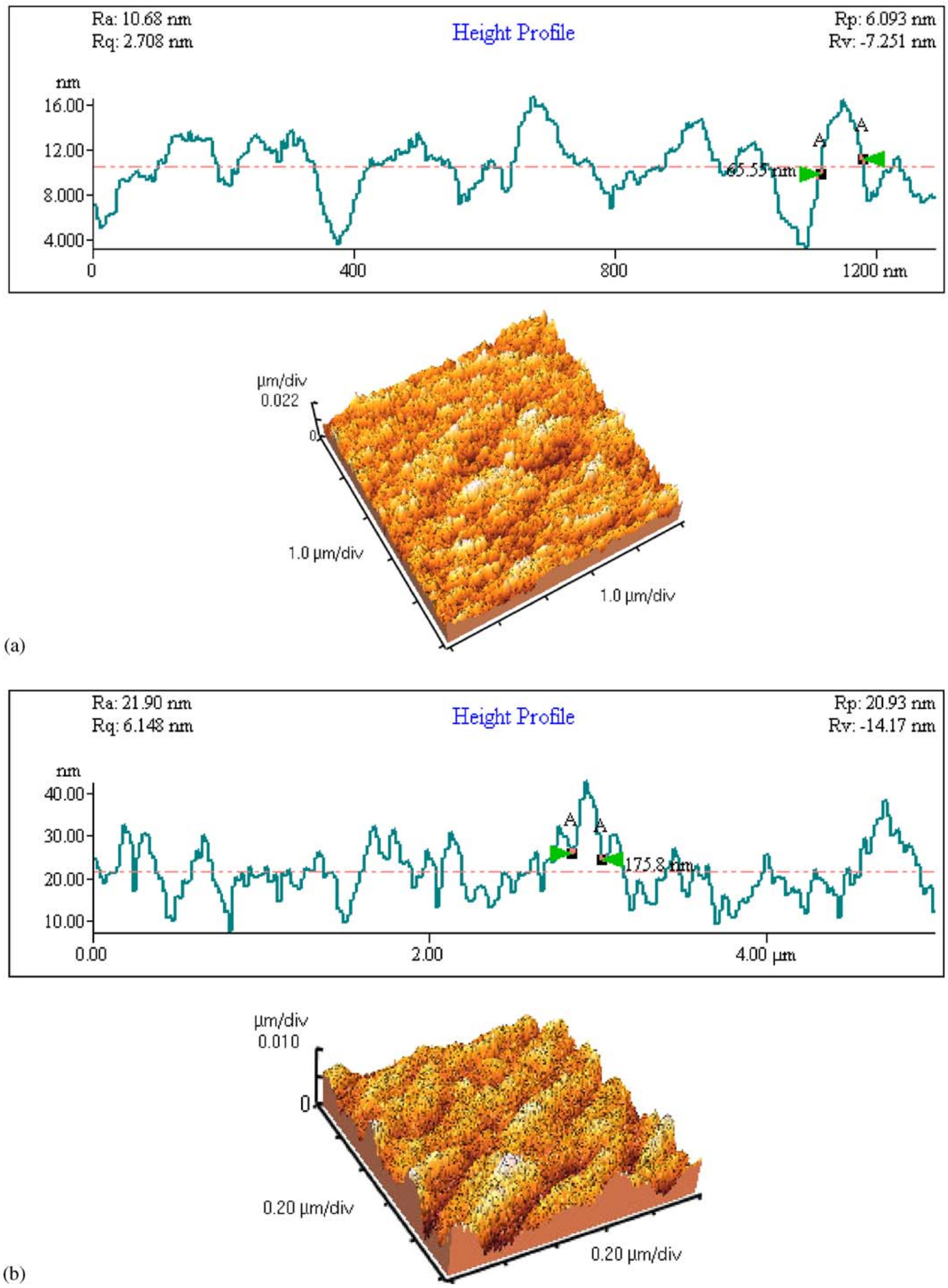


Fig. 8. (a) AFM of 0.5% epoxycyclohexyl POSS, (b) AFM of 5% Epoxycyclohexyl POSS.

a roughness of 40 nm; and at 5%, a roughness of 94 nm. In the case of octaphenyl POSS, 0.5% lead to a typical roughness of 28 nm and 5% lead to a typical roughness of 97 nm were measured. Consequently, it was concluded, that as the concentration of the POSS increased, a larger nanoscale structure is formed that might be attributed to agglomeration. Moreover, the size of the nanostructure was influenced by the reactivity of the functional group as well as by the steric hindrance from the peripheral groups of the POSS (Table 1). An example is given by comparison of cyclopentyl with isobutyl groups. It is worth noticing that the changes in nanoscale roughness associated with changes in concentration are also related to the values of T_g and storage modulus. As the surface roughness is increased above a certain threshold value, the values of T_g and storage modulus decrease. This may be due to plasticization effects at high concentrations. In addition, the

Table 3
Roughness from AFM results

POSS type	Composition (wt%)	Particle diameter (nm)	RMS (nm)
Epoxycyclohexyl	0.5	65.55	2.708
Epoxycyclohexyl	5	175.80	6.148
Aminoethyl	0.2	27.34	2.367
Aminoethyl	0.5	39.06	3.388
Aminoethyl	3	40.56	5.489
Aminoethyl	5	94.50	4.324
Octaphenyl	0.5	28.20	4.619
Octaphenyl	5	97.66	7.737

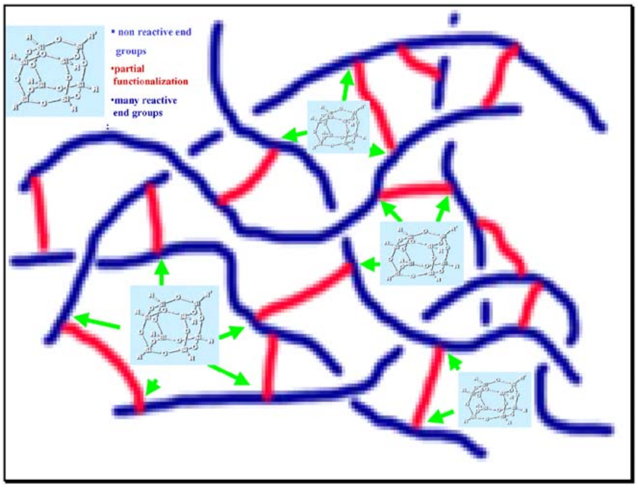


Fig. 9. Schematic nanostructure model of POSS/ in Epoxy molecular Network.

AFM results indicate that the grafted groups on the POSS can affect the roughness. The roughness was the largest in the case of epoxycyclohexyl POSS/ epoxy adhesive (65 nm for 0.5 wt% and 175 nm for 5 wt%). For 0.5 wt% of aminoethyl POSS, the roughness was on the order of 39 nm and for 0.5 wt% octapheny POSS the roughness was 28 nm.

4.3. Adhesion properties

The shear and peel strengths of selected POSS epoxy formulations were characterized (Table 4). The POSS concentration levels in the formulations were at values where a maximum in the T_g was obtained (see Fig. 2). As can be seen in Table 4, an increase of 20% was obtained in shear strength in the selected formulations compared with the neat epoxy formulation. Furthermore, a significant increase in peel strength was obtained when the functionalities of the POSS were compatible with the epoxy system. The higher shear and peel values were obtained for isocyanatopropyl and octaphenyl functionalities. In both cases, combined strengthening (shear) and toughening (peel) is evident in addition to higher T_g. It should be emphasized that in the case of the reactive POSS functionalities, toughening is obtained at relatively low concentrations (<4 wt%).

Table 4
Shear and peel strengths of POSS/epoxy (cohesive failure)

POSS type (wt%)[a]	T_g[b] (°C)	Shear strength[c] (MPa)	Peel strength[c] (N/mm)
Neat epoxy	86.0	21	0.19
Aminoethyl (0.3)	89.5	19	0.38
Epoxycyclohexyl (4)	92.9	16	0.27
Glycidoxypropyl (1)	90.0	18	0.32
Isocyanatopropyl (5)	92.9	24	0.49
Octaphenyl (10)	89.9	24	0.43

[a] Weight concentration at maximum T_g.
[b] Standard deviation: ±1 °C.
[c] standard deviation: ±5%.

4.4. Mechanism

It is proposed that the nanostructuring of the epoxy molecular network is the result of incorporating POSS into the network as illustrated schematically in Fig. 9. The level of reaction depends on the degree of functionalization (either fully or partially substituted) of the POSS. The reaction of the functional group with the epoxy resin or the amidoamine curing agent controls the degree of compatibility of the POSS with the cross-linked epoxy. For every case, there is an optimal concentration of POSS as a function of the reactive groups and the peripheral groups. The steric hindrance provided by the peripheral group also has a dominant effect. There are threshold values where optimal bulk and adhesion properties are obtained; beyond these optimal levels a decrease of properties occurs.

5. Conclusions

Functionalization of POSS is the decisive factor in nanostructuring and tailoring of epoxy systems. Due to the large surface area of POSS, only relatively small amounts are needed to cause significant changes. Optimal concentration exists for each functional derivative. Excess amount results in plasticization. The type of the functional groups (reactive or nonreactive) of the POSS is the dominant factor in the formation of the molecular network.

Further studies are planned to elucidate the nanostructure of POSS containing adhesives and its relationship to macro properties. Furthermore, additional adhesives as well as mixtures of various nanomoieties will be investigated.

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