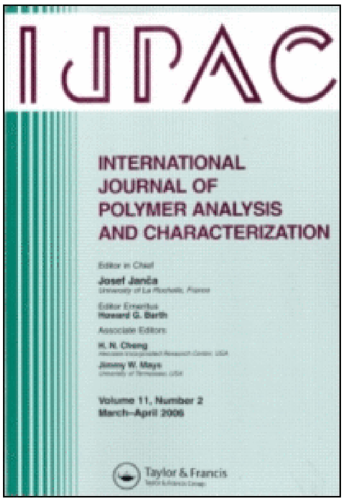

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Characterization of Novel Epoxy Composites Based on Hybrid Inorganic/Organic Polyhedral Oligomeric Silsesquioxane

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CHARACTERIZATION OF NOVEL EPOXY COMPOSITES BASED ON HYBRID INORGANIC/ORGANIC POLYHEDRAL OLIGOMERIC SILSESQUIOXANE

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New nanocomposites were synthesized by the reaction between a polyhedral oligomeric silsesquioxane (POSS) with eight epoxy groups (epoxy-POSS) and diglycidyl ether of bisphenol A (DGEBA) using Jeffamine D230 as curing agent. The reactivity of the systems was extensively studied by Raman spectroscopy. The hybrid materials were characterized by different techniques like thermogravimetric analysis, dynamical mechanical analysis, X-ray photoelectron spectroscopy, differential scanning calorimetry, and scanning electron microscopy. The "Si–O–Si" cages of the POSS component form aggregates, which was shown by the conversion data obtained from the Raman spectra and confirmed by the DSC curves, XPS spectra, and SEM images.

Keywords: Glass transition; Polyhedral oligomeric silsesquioxane (POSS); Raman spectroscopy; X-ray photoelectron spectroscopy (XPS)

INTRODUCTION

Epoxy resins are used on a large scale as protective coatings or in other applications like electronic materials, polymer composites, paints, and adhesives. The cured resins provide excellent mechanical strength and toughness, chemical resistance, good thermal adhesion, low shrinkage on cure, and electrical properties.[1–3]

In recent years, epoxy nanocomposites filled with nanoscaled particles have become more and more important because of their outstanding properties.[4–9]

For the hybrid materials synthesis, a new class of compounds with special properties, polyhedral oligomeric silsesquioxane (POSS), was used. The POSS molecules with the formula $(RSiO_{1,5})_n$ include an inorganic part consisting of a cage formed by oxygen and silicon atoms and an organic part given by the substituents on the inorganic cage. These molecules may play a double role, either as monomers because of the substituents on the inorganic cage that include reactive epoxy groups or as nanometric reinforcing agents due to the inorganic cage that exhibits low size, 1.2 nm.[10–14]

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By introducing POSS molecules in an epoxy-based composite material, some properties like oxygen permeability, viscosity during processing, and mechanical strength are improved. Also, the flammability and the dielectric constant are reduced and the glass transition temperature (T_g) is modified.[15,16]

The aim of our work was to synthesize and characterize nanocomposites based on diglycidyl ether of bisphenol A (DGEBA) and a POSS compound with eight epoxy groups (epoxy-POSS) so that both components are finally inter- and intra-molecularly cross-linked by a polyether amine, Jeffamine D230. Moreover, the epoxy-POSS component will contribute to better thermal properties and T_g, due to the compact "Si–O–Si" cages.

EXPERIMENTAL PART

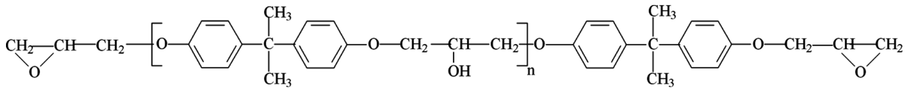
Materials

Diglycidyl ether of bisphenol A (Epilox A 19) was supplied by Dow Chemical and used as received.

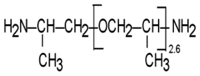
The polyetheramine Jeffamine D230 was provided by Huntsman.

Epoxy-POSS compound (POSS-Octa[(3-propylglycidylether)dimethylsiloxy] was received from Sigma-Aldrich and used without further purification.

The chemical structures of the raw materials are shown in Scheme 1.

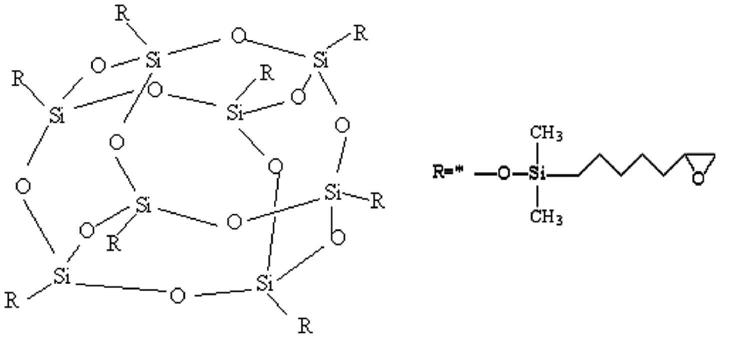


Diglycidylether of bisphenol A (DGEBA)



$H_2N{-}\underset{CH_3}{CH}{-}CH_2{-}[OCH_2{-}\underset{CH_3}{CH}]_{2.6}{-}NH_2$

Jeffamine D230



POSS-Octa[(3-propylglycidylether)dimethylsiloxy]

Scheme 1. Chemical structures of the raw materials.

Table I. Concentration of DGEBA and epoxy-POSS used for hybrid materials synthesis

Hybrid	Epoxy-POSS (wt.%)	DGEBA (wt.%)
1	0	100
2	20	80
3	50	50
4	80	20
5	100	0

Nanocomposite Synthesis

The nanocomposites were synthesized using epoxy-POSS and DGEBA in various concentrations (Table I). The mixture of DGEBA and epoxy-POSS was sonicated, the cross-linking agent (D230) was stoichiometrically added, the mixture was poured into molds, and then it thermally cross-linked at 60°C for 2 h.

The conversion of the cross-linking reaction was calculated using the following equation, taking into account the absorptions from the Raman spectra:

$$\alpha = \left[1 - \frac{\left(\frac{I_{3000}}{I_{1601}}\right)_t}{\left(\frac{I_{3000}}{I_{1601}}\right)_0} \right] *100$$

where α = conversion (%);

$\left(\frac{I_{3000}}{I_{1601}}\right)_t$ = the ratio between the peaks intensity at 3000 cm^{-1} and 1601 cm^{-1} at time t;

$\left(\frac{I_{3000}}{I_{1601}}\right)_0$ = the ratio between the peaks intensity at 3000 cm^{-1} and 1601 cm^{-1} at the initial moment.

The band at 3000 cm^{-1} was assigned to epoxy ring vibration and the band at 1601 cm^{-1} was assigned to the vibration of C–C bonds from aromatic rings.

Nanocomposite Characterization

Raman Spectroscopy. The Raman spectra were recorded on a DXR model Raman microscope, equipped with Omnic 8 software from Thermo Fisher Scientific USA (Madison, Wis.). The excitation laser wavelength was 532 nm using a laser power level of about 8.0 mW. The Raman shift range was between 50 and 3550 cm^{-1}.

Differential Scanning Calorimetry (DSC). The DSC curves were registered on a Netzsch DSC 204 F1 Phoenix, using a heating rate of 10°C/min. The sample was heated from 20° to 400°C under a constant nitrogen flow rate (40 mL/min).

Dynamic Mechanical Analysis (DMA). The DMA curves were recorded on a TRITEC 2000 instrument, at various frequencies, from 25° to 180°C using a heating rate of 5°C/min.

Thermogravimetric Analysis (TGA). The TGA results were obtained on a Q500 TA instrument. A typical sample was heated from 20° to 750°C at a heating rate of 10°C/min under a constant nitrogen flow rate (100 mL/min).

X-Ray Photoelectron Spectroscopy (XPS). The XPS spectra were registered on Thermo Scientific K-Alpha equipment, fully integrated, with an aluminum anode monochromatic source (1486.6 eV). The charging effects were compensated by an argon flood gun.

Scanning Electron Microscopy (SEM). A scanning electron microscope (SEM Quanta Inspect F) was used to study the morphologies of final hybrids at an accelerating voltage of 30 kV.

The samples were also analyzed by energy dispersive X-ray analysis (EDX) to identify the presence of POSS in the bulk.

RESULTS AND DISCUSSION

The cross-linking process and the reactivity of epoxy groups from both DGEBA and epoxy-POSS components were extensively studied by Raman spectroscopy (Figure 1).

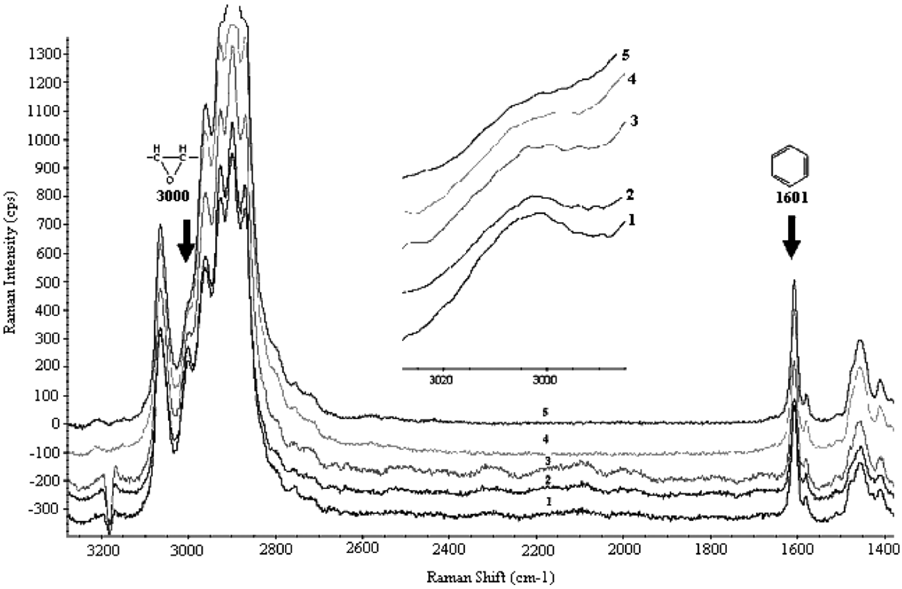


Figure 1. Raman spectra for the hybrid system 50% epoxy-POSS-50% DGEBA-D230 at different reaction times (1, 0 min; 2, 30 min; 3, 60 min; 4, 120 min; 5, 150 min).

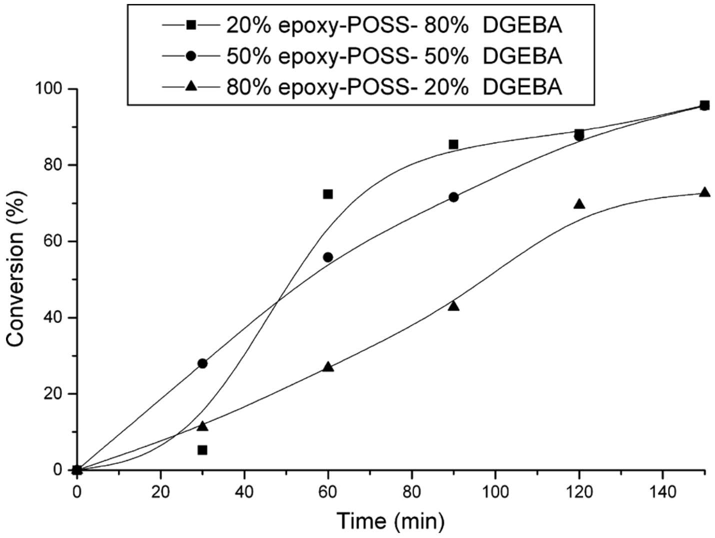


Figure 2. Dependence of the conversion calculated from the Raman spectra on time for different hybrid systems.

From Figure 1 one may notice two significant bands, one around 3000 cm^{-1}, assigned to the vibration of the epoxy ring, and the other at 1601 cm^{-1}, assigned to the vibration of the C–C bond from the aromatic ring.

The reactivity of the hybrid systems strongly depends on the concentration of the epoxy-POSS, as may be observed from Figure 2. Therefore, the system based on 20% epoxy-POSS and 80% DGEBA exhibits a higher reactivity, while the hybrid system that contains 80% epoxy-POSS and 20% DGEBA gives a lower reactivity.

However, the conversion data calculated from the Raman spectra suggest that a competition always occurs between the increased number of the epoxy groups from the increased number of epoxy-POSS molecules, which gives a higher reaction rate, and the barrier effect of the epoxy-POSS aggregates, which is more significant as the epoxy-POSS concentration increases, giving a lower rate. Thus the higher conversion reached in the final stages for the hybrid system including a low epoxy-POSS concentration may be explained.

The reactivity of the hybrid systems was also studied by DSC (Figure 3). From Figure 3 and Table II one may observe that the presence of the epoxy-POSS in the classical system based on DGEBA leads to a decrease of the DGEBA reactivity in the cross-linking reaction, revealed as an increase of the temperature (T_{max}) at which the cross-linking heat exhibits the maximum value. This fact may be due to the sterical hindrance caused by the presence of the “Si–O–Si” cages, which are partially aggregated. Therefore the epoxy-POSS molecules act as barriers against the amino groups, which meet difficulties in reaching the epoxy groups of DGEBA. Thus, the obtained DSC data are in good agreement with the Raman spectra.

The presence of the aggregates from the POSS cages was also pointed out by SEM analysis (Figure 4). Thus, the SEM images at different magnifications suggest the formation of aggregates with various sizes from 57.7 to 280.3 nm. The elemental

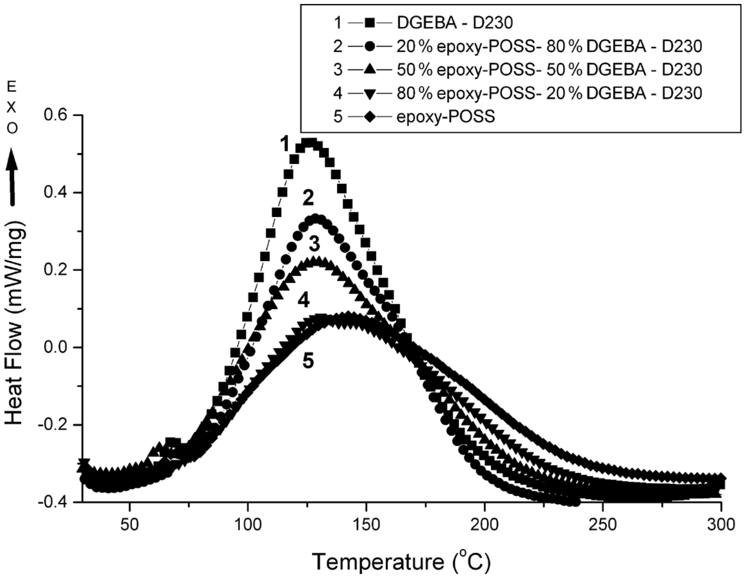


Figure 3. DSC curves for the hybrid systems based on DGEBA and epoxy-POSS in different ratios.

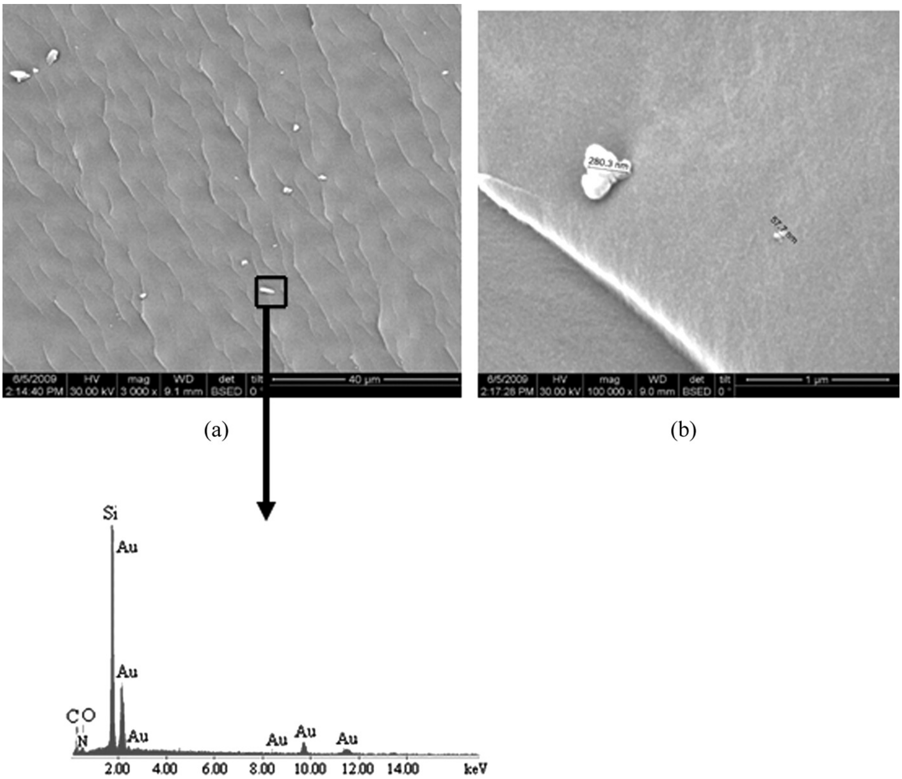
composition of these aggregates is given by the EDX spectra, which show high silicon content.

Other evidence for the presence of epoxy-POSS molecules in the synthesized hybrids is given by the XPS spectra (Figure 6). As the epoxy-POSS content increases, the silicon content (Si% in Table III) increases.

More details can be determined from the XPS deconvolution spectra (Figures 5 and 6). By comparing Figures 5 and 6 it can be noticed that in the case of the hybrid system including epoxy-POSS, the oxygen signal is deconvoluted into three signals. The first signal, at 532.2 eV, is assigned to C–OH bonds formed by the epoxy rings opening reaction during the cross-linking process. The second signal, at 533.1 eV, is related to the Si–O–Si bonds from the inorganic cages within the epoxy-POSS molecules, strong evidence for the presence of POSS compound in the final structure of the hybrid material. The third signal, at 531.1 eV, is assigned to the epoxy rings that remain in the final material, this being in good agreement with conversion data revealed by the Raman spectra, which did not reach 100% for all the studied hybrid materials.

Table II. Enthalpy values for the different hybrid systems

Epoxy/hybrid system	Enthalpy (J/g)	T_{max} (°C)
DGEBA-D230	317.3	126.7
20% epoxy-POSS-80% DGEBA-D230	286.8	129.0
50% epoxy-POSS-50% DGEBA-D230	246.9	129.3
80% epoxy-POSS-20% DGEBA-D230	245.5	131.1
Epoxy-POSS-D230	239.4	180.7



(a) (b)

Figure 4. SEM images (a), (b) and EDX spectrum (c) of 80% epoxy-POSS-20% DGEBA-D230 hybrid system. (a) 3000×; (b) 100000×.

The influence of epoxy-POSS concentration on the thermostability of the synthesized hybrid systems was studied by TGA (Table IV).

As the epoxy-POSS concentration increases within the mixture, the thermostability of the obtained hybrid material increases, which is shown by the decrease of weight loss and the increase of T_{onset} value. Also, the maximum degradation rate is reached at higher temperature. This behavior is due to the multiple "Si–O–Si" cages from the epoxy-POSS structure, which acts as a true reinforcing agent.

The influence of the epoxy-POSS on the glass transition temperature of the hybrids was revealed by DMA (Table V).

Table III. Composition of the hybrid systems revealed by XPS

Epoxy/hybrid system	C(%)	O(%)	N(%)	Si(%)
DGEBA-D230	92.8	5.8	1.4	–
20% epoxy-POSS-80% DGEBA-D230	84.7	9.0	1.8	4.5
50% epoxy-POSS-50% DGEBA-D230	64.7	19.7	1.8	13.8
80% epoxy-POSS-20% DGEBA-D230	50.9	28.6	1.9	18.6
Epoxy-POSS	43.2	32.6	1.7	22.5

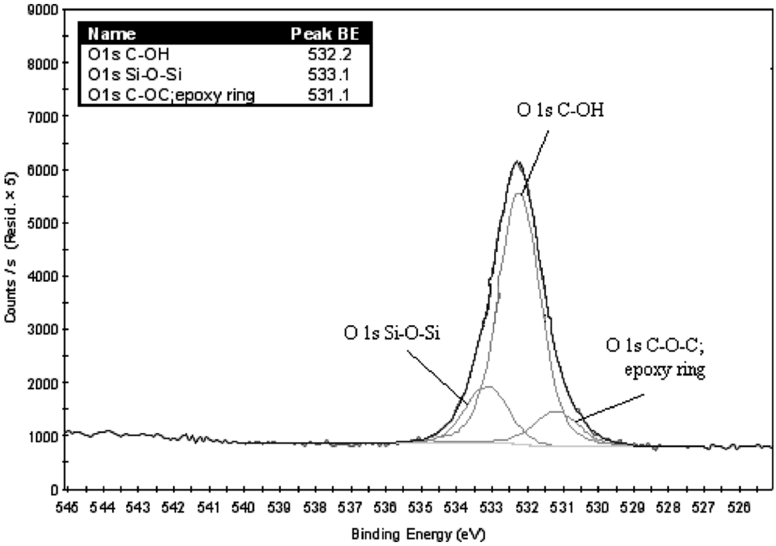


Figure 5. XPS deconvolution spectrum for oxygen. Hybrid system: 50% epoxy-POSS-50% DGEBA-D230.

From Table V one may observe the decrease of the T_g value as the concentration of epoxy-POSS increases in the mixture. This may be due either to the flexibility of the epoxy chains from the "Si–O–Si" cages or to the excess of amine that remains after the cross-linking process occurs and acts as a plasticizer. This is in good agreement with the Raman data, which show that not all the epoxy groups were opened by the reaction with D230, probably due to the compact cage structure

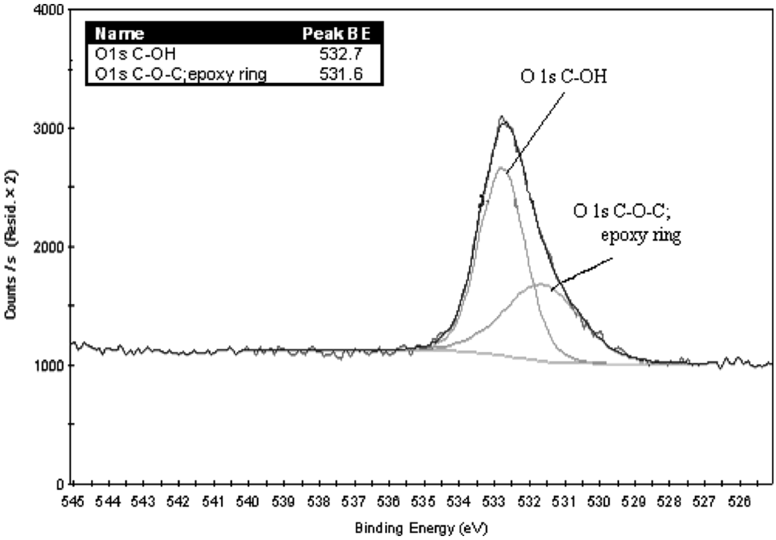


Figure 6. XPS deconvolution spectrum for oxygen. System: DGEBA-D230.

Table IV. TGA results for the hybrid systems based on epoxy-POSS

Epoxy/hybrid system	Weight loss (%)	T_{onset} (°C)	Temperature corresponding to maximum degradation rate (°C)
DGEBA-D230	91	359	373
20% epoxy-POSS-80% DGEBA-D230	82	364	379
50% epoxy-POSS-50% DGEBA-D230	75	377	390
80% epoxy-POSS-20% DGEBA-D230	67	380	400

Table V. T_g values of the synthesized hybrid materials

Epoxy/hybrid system	T_g (°C)
DGEBA-D230	88.0
20% epoxy-POSS-80% DGEBA-D230	68.7
50% epoxy-POSS-50% DGEBA-D230	59.4
80% epoxy-POSS-20% DGEBA-D230	32.0

of the epoxy-POSS compound, which does not allow all the epoxy groups to be available for the cross-linking process.

CONCLUSIONS

The conversion of the epoxy groups from both components of the mixture, DGEBA and epoxy-POSS, given by Raman spectra showed that the increase of the epoxy-POSS concentration leads to a decrease of the overall reactivity due to the aggregates formed by “Si–O–Si” cages, which makes the access of aminic groups from the cross-linking agent to the epoxy groups difficult.

The decrease of reactivity for larger epoxy-POSS component combined with DGEBA was also underlined by the DSC tests. Thus, the total enthalpy of the epoxy ring opening process is lower as the epoxy-POSS concentration is higher.

Both Raman spectra and XPS deconvolution spectra for oxygen showed that not all the epoxy groups are opened during the cross-linking process, probably due to the aggregation of the inorganic cages from POSS, which hinders the aminic groups in reaching the epoxy groups.

The main goal of using the epoxy-POSS component in combination with DGEBA was achieved by the increase of thermostability for the synthesized hybrids due to the reinforcing action of the “Si–O–Si” cages. However, the T_g values of the hybrids decrease, probably due to the organic radicals from the cages, which act to increase the overall flexibility.

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