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Monofunctional Epoxy-POSS Dispersed in Epoxy−Amine Networks: Effect of a Prereaction on the Morphology and Crystallinity of POSS Domains

Ileana A. Zucchi,[†] María J. Galante,[†] Roberto J. J. Williams,*[,†] Elsa Franchini,[‡] Jocelyne Galy,[‡] and Jean-François Gérard[‡]

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina, and Laboratoire des Matériaux Macromoléculaires, IMP UMR CNRS 5627, Institut National des Sciences Appliquées de Lyon, Bât Jules Verne, 20 Av. A. Einstein, F-69621 Villeurbanne Cedex, France

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ABSTRACT: Several studies have recently reported the use of monofunctional octahedral oligomeric silsesquioxanes (monofunctional POSS) to modify polymer networks. In most of these studies the final material is depicted as a network with pendent POSS units randomly dispersed in the structure. The aim of this paper is to show that this representation is generally not correct due to the occurrence of a polymerization-induced phase separation (PIPS) process. In this sense, monofunctional POSS are not different from different types of rubbers, thermoplastics, or liquid crystals used to modify polymer networks. Although some authors have noticed the occurrence of PIPS in particular systems, a comparative study of the effect of the chemical structure of POSS and its prereaction with one of the monomers on the morphologies generated has not been previously reported. Glycidyloxypropyl−heptaisobutyl POSS (iBu-GlyPOSS) and glycidyloxypropyl−heptaphenyl POSS (Ph-GlyPOSS) were used to modify an epoxy network based on diglycidyl ether of bisphenol A (DGEBA) and 4,4′-methylenebis(2,6-diethylaniline) (MDEA). POSS was introduced in the formulation either nonreacted or prereacted with MDEA (molar ratio POSS/MDEA: 1/10). While both nonreacted and prereacted iBu-GlyPOSS were soluble in the epoxy−amine precursors at the polymerization temperature (135 °C), only prereacted Ph-GlyPOSS could be dissolved in epoxy−amine precursors. For every case a polymerization-induced phase separation took place. For the nonreacted iBu-GlyPOSS this process led to a dispersion of spherical particles with sizes in the range of the micrometers that crystallized upon cooling. Both prereacted POSS led to different types of amorphous biphasic structures. Therefore, the nature of the organic inert group and the prereaction of a monofunctional POSS can be used to control the morphologies generated in the POSS-modified polymer network.

Introduction

Polyhedral oligomeric silsesquioxanes (POSS) are nanosized cage structures with formula $(RSiO_{1.5})_n$ ($n = 6, 8, 10, ...$), where R indicates an organic group. The most typical species is the octahedron ($n = 8$). POSS can be classified on the basis of the number of organic groups that bear reactive groups. Nonfunctional POSS do not contain reactive groups in the structure. Monofunctional POSS have only one reactive organic group in the structure (for octahedra seven of the organic groups are nonreactive). Multifunctional POSS contain two or more reactive organic groups in their structures.

POSS/epoxy blends have recently received considerable attention.[1−17] The use of multifunctional POSS as cross-linker units of the epoxy network often leads to a dispersion of POSS at a molecular level.[4,6,7,14,17] However, limited POSS aggregation was found in particular systems employing multifunctional POSS.[8,11] We will show that the situation is in general quite different when using monofunctional POSS to modify an epoxy network. The ideal structure consisting in pendent POSS cages homogeneously dispersed in the network that is often used in illustrations is frequently not achieved in practice due to the lack of compatibility of POSS with the organic network. In this sense, monofunctional POSS are not different from different types of rubbers, thermoplastics, or liquid crystals used to modify polymer networks. Some studies have already reported the presence of a phase separation in the course of polymerization.[5,14−16] But there is no previous study reporting the effect of a prereaction of the functional group and the nature of the inert organic groups on the phase separation process. These factors can be modified to exercise some control of morphologies generated including the possibility of producing either amorphous or crystalline POSS aggregates. This is in turn important to set thermal and mechanical properties of the hybrid materials.[11,12,15,16]

In this paper we analyze the effect of a prereaction on morphologies generated and crystallinity of POSS domains for two monofunctional epoxy-POSS—glycidyloxypropyl−heptaisobutyl POSS (iBu-GlyPOSS) and glycidyloxypropyl−heptaphenyl POSS (Ph-GlyPOSS)—that are used to modify an epoxy network based on diglycidyl ether of bisphenol A (DGEBA) and 4,4′-methylenebis(2,6-diethylaniline) (MDEA). The selected POSS contain two different types of inert groups: isobutyl or phenyl. On one hand, the isobutyl groups generate weaker POSS−POSS interactions than phenyl groups. This leads to a lower melting point of the corresponding monofunctional POSS that facilitates the prereaction with the diamine. But, on the other hand, isobutyl groups should be less compatible with the aromatic monomers (DGEBA and MDEA) than phenyl groups, a fact that should favor the phase separation of the corresponding POSS. The different morphologies generated by these competing effects will be analyzed.

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* Corresponding author. E-mail: williams@fi.mdp.edu.ar.
[†] INTEMA.
[‡] IMP.

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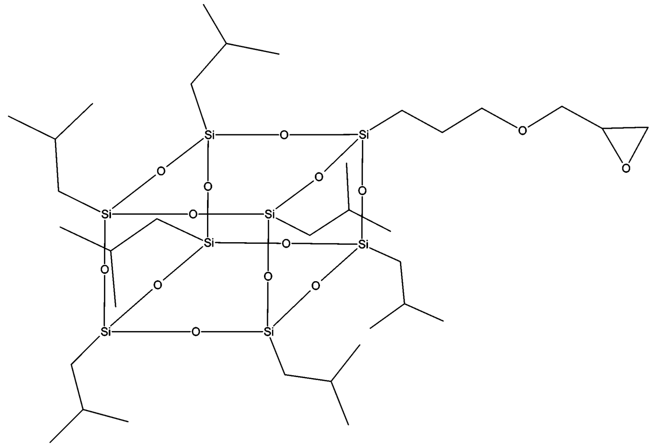
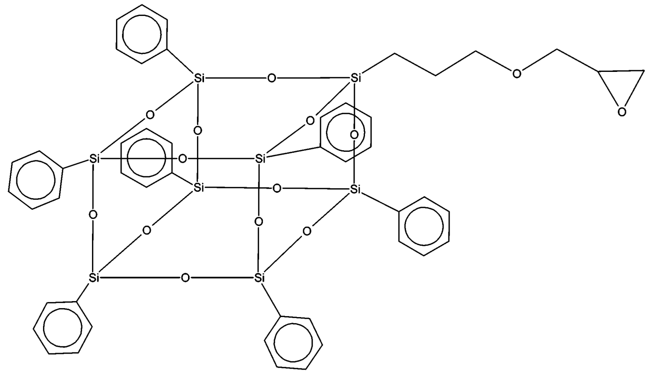
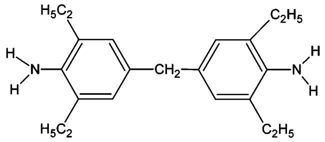


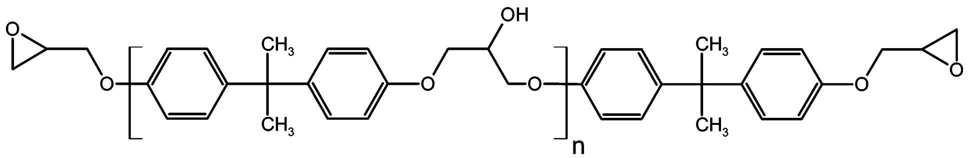
iBu-GlyPOSS



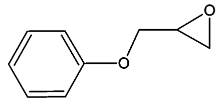
Ph-GlyPOSS



MDEA



DGEBA



PGE

Figure 1. Chemical structures of iBu-GlyPOSS, Ph-GlyPOSS, MDEA, DGEBA, and PGE.

Experimental Section

Materials. Chemical structures of different reactants are shown in Figure 1. Glycidyloxypropyl−heptaisobutyl POSS (iBu-GlyPOSS, EPO 418 Hybrid Plastics) was a crystalline powder with a molar mass of 931.6 g/mol. Two well-defined melting peaks at 112 and 132 °C are present in DSC (differential scanning calorimetry) thermograms of the commercial product.[5] After melting and recrystallization in mass, these peaks are shifted to 123 and 149 °C with a total melting heat of 15.9 J/g.[5] Glycidyloxypropyl−heptaphenyl POSS (Ph-GlyPOSS, EPO 425 Hybrid Plastics) was also a crystalline powder with a molar mass of 1071.5 g/mol. Like iBu-GlyPOSS, Ph-GlyPOSS is soluble in tetrahydrofuran (THF). However, it did not exhibit a melting peak in DSC scans up to the degradation temperature.

The selected diamine was 4,4′-methylenebis(2,6-diethylaniline) (MDEA, Lonza), a crystalline solid with a melting temperature of 96.5 °C. The diepoxy monomer was based on diglycidyl ether of bisphenol A (DGEBA, DER 330, Dow), with a weight per epoxy group equal to 180 g/mol ($n = 0.07$ in the chemical structure shown in Figure 1). Phenyl glycidyl ether (PGE, Sigma-Aldrich) was used to synthesize a reference polymer network where the monofunctional POSS was replaced by an equivalent amount of PGE.

Prereaction of POSS with MDEA. The prereaction of iBu-GlyPOSS (1 mol) with MDEA (10 mol) was carried out at 150 °C for 10 h in tubes sealed under vacuum. At this temperature both reactants were melted and form a homogeneous solution.

The prereaction of Ph-GlyPOSS (1 mol) with MDEA (10 mol) was much more difficult because this particular POSS could not be melted and dissolved in MDEA. Therefore, corresponding amounts of both components were dissolved in THF, and the solvent evaporated under vacuum at room temperature. Tubes were sealed under vacuum and heated at 150 °C for 5 h, followed by 1 h at 200 °C and 1 h at 220 °C. At these temperatures MDEA was melted, but the POSS remained as a crystalline material. Therefore, the reaction occurred in a heterogeneous medium.

Synthesis of POSS-Modified DGEBA−MDEA Networks. Networks were synthesized using the following molar ratios: POSS (1 mol), MDEA (10 mol), DGEBA (19.5 mol), leading to an overall stoichiometric proportion of epoxy and NH functionalities. The mass fraction of iBu-GlyPOSS in the final network was 8.4 wt % while that of Ph-GlyPOSS was 9.5 wt %. Both nonreacted and prereacted POSS were used to compare the morphologies generated. A reference network was also synthesized replacing the POSS by PGE (1 mol). In every case, the polymerization was carried out at 135 °C for 4 h, followed by a 4 h postcure at 190 °C.

Techniques. Size exclusion chromatography (SEC) was used to follow the distribution of reaction products during the prereaction of POSS with MDEA. A set of glass tubes containing known masses of the reacting mixture, in the range of 40 mg, were placed in an oil bath at the selected temperature cycle. Tubes were removed at predetermined times, their contents were dissolved in 2 mL of THF, and 10 μL of the resulting solutions was injected into the size exclusion chromatograph (SEC, Knauer K-501, RI detector Knauer K-2301, and a set of Phenomenex Phenogel 5 μm columns: 50A, 100A, and M2). THF was used as a carrier at 1 cm^3/min.

^{29}Si NMR spectra of the commercial POSS and of products obtained by prereaction with MDEA were performed in CDCl$_3$ using a Bruker 500 MHz NMR spectrometer with TMS as external reference. Inverse-gate proton decoupling was used with a delay $D_1 = 10$ s between pulses (pulse angle = 50°).

Transmission optical microscopy (TOM) was used to follow the phase separation process induced by polymerization. A Leica DMLB microscope provided with a hot stage (Linkam THMS 600) and a photodetector incorporated to the optical path was used for this purpose. The initial solution was placed between two glass covers separated by a 0.5 mm stainless steel spacer. The polymerization was carried out at 135 °C, and the light intensity transmitted through the sample was continuously monitored as a function of reaction time. The cloud-point time was determined at the onset of the decrease in the intensity of transmitted light. In order to replace the time scale by a conversion scale, a conversion vs time curve at 135 °C for a stoichiometric DGEBA−MDEA solution was obtained by differential scanning calorimetry (DSC, Pyris 1 Perkin-Elmer). The total reaction heat obtained from an isothermal scan at 135 °C was divided by the maximum reaction heat determined from a dynamic scan at 10 °C/min in order to obtain the maximum conversion at 135 °C (at this temperature the reaction was arrested by vitrification). Partial areas under the DSC thermogram at 135 °C could then be transformed into conversions at different selected times.

Morphologies of hybrid materials after the postcure at 190 °C were observed by scanning electron microscopy (SEM, Jeol 6460 LV and Jeol 1200EX; fracture surfaces coated by a fine gold layer). The presence of a crystalline fraction of POSS was assessed by polarized optical microscopy (POM, Leica DMLB microscope with crossed polarizers), by wide-angle X-ray diffraction (WAXS, Philips PW 1830/40, Co Kα radiation, $\lambda = 1.79$ Å; scanning rate = 1°/min), and by DSC (DSC50-Shimadzu at 20 °C/min). This last technique was also used to determine glass transition temperatures of the different materials (onset of the change in the specific heat measured in second scans).

Results and Discussion

Epoxy Networks Modified with iBu-GlyPOSS. The prereaction of POSS (1 mol) with MDEA (10 mol), at 150 °C, was followed by SEC (Figure 2). After 10 h the peak of POSS practically disappeared, forming a main reaction product assigned to the monosubstituted diamine, MDEA−(POSS)$_1$. The distribution of reaction products may be estimated by assuming that the four amine hydrogens have equal reactivity and there are no substitution effects (for an aromatic diamine substitution effects are however expected).[18] For the selected molar ratio of epoxy over amine hydrogens (1:40), the probability that an amine hydrogen had reacted at full conversion of POSS is 1/40 = 0.025. The probability that it had not reacted is 0.975. Therefore, the expected fraction of nonreacted MDEA is given by $(0.975)^4 = 90.4\%$, and that of the monosubstituted product is given by $4(0.975)^3(0.025) = 9.3\%$. The fraction of MDEA units covalently bonded to two or more POSS units is practically negligible, consistent with the fact that only one reaction product appeared in the SEC chromatogram.

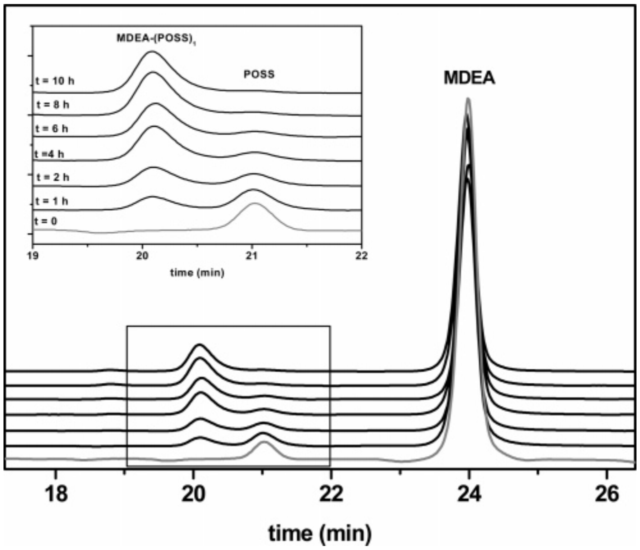


Figure 2. Evolution of SEC chromatograms during the prereaction of iBu-GlyPOSS (1 mol) with MDEA (10 mol), at 150 °C.

^{29}Si NMR spectra were recorded for the starting POSS and for the prereacted POSS. Both products exhibited a set of sharp peaks in the region comprised between −67 and −68 ppm (peaks at −67.32, −67.64, and −67.86 ppm were recorded for the starting POSS, while peaks at −67.24, −67.54, and −67.76 ppm were present in the prereacted product). This indicates that no opening of the POSS cage was produced in the course of the prereaction.

Stoichiometric formulations containing iBu-GlyPOSS:DGEBA:MDEA in a molar ratio 1:19.5:10, with the POSS either nonreacted or prereacted with MDEA, were homogeneous at 135 °C before the start of polymerization. However, a typical polymerization-induced phase separation occurred for both formulations as has been found for other systems containing nonfunctional and monofunctional POSS dissolved in the precursors of an epoxy network.[5,14−16] Figure 3 shows the variation of the intensity of light transmitted through the samples as a function of polymerization time at 135 °C. Vertical lines showing the conversion of the DGEBA−MDEA reaction are plotted based on the conversion vs time curve (Figure 4) obtained in an isothermal DSC scan, as described in the Experimental Section (it is assumed that the kinetics was not affected by the 8.4 wt % POSS dissolved in the sample or by the slight change in the molar ratio of DGEBA and MDEA). On the basis of the very slow reaction rate of iBu-GlyPOSS with MDEA at 150 °C (Figure 2), it may be expected that in the formulation containing the nonreacted POSS the only reaction at 135 °C will be that of DGEBA with MDEA.

For the formulation containing the nonreacted POSS a sharp phase separation process took place, starting at a conversion

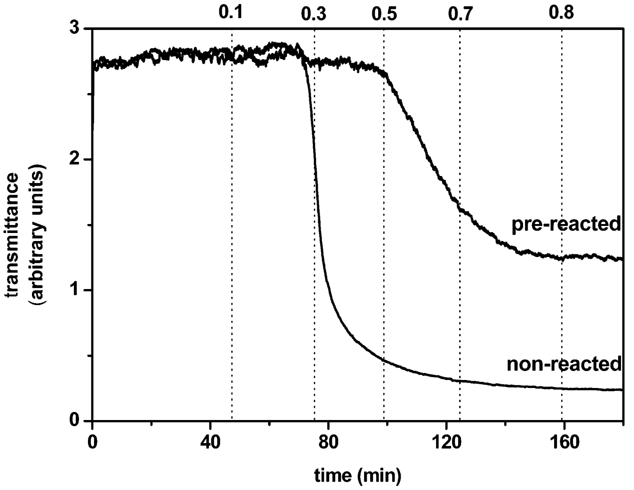


Figure 3. Variation of the light intensity transmitted through the samples as a function of polymerization time at 135 °C, for stoichiometric formulations containing iBu-GlyPOSS:DGEBA:MDEA in a molar ratio 1:19.5:10, with the POSS either nonreacted or prereacted with MDEA. Particular conversions of the MDEA−DGEBA reaction are plotted as vertical lines.

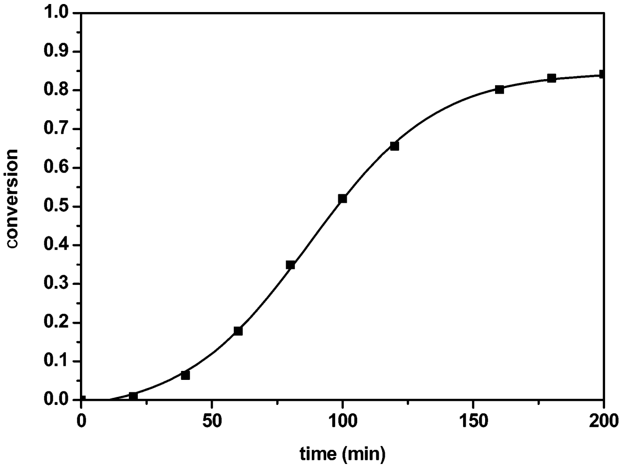


Figure 4. Conversion vs time curve for the DGEBA−MDEA reaction at 135 °C, derived from an isothermal DSC scan.

close to 0.28. For the formulation containing the prereacted POSS the start of the phase separation process was shifted to a conversion close to 0.50. This shift might be related to the higher compatibility of prereacted POSS compared to the nonreacted POSS, but it may also be a consequence of the smaller domains initially formed in the case of prereacted POSS that do not have the critical size necessary to scatter visible light. The decrease in the light intensity is more gradual in the case of prereacted POSS when compared to the nonreacted POSS. This reflects the slower aggregation rate of POSS units when they are covalently bonded to epoxy−amine species.

For a DGEBA−aromatic diamine formulation, the gel conversion is close to 0.60.[18] At this critical conversion most of the phase separation had already taken place for the nonreacted POSS but was still taking place for the prereacted POSS. In fact, light intensity continued to decrease up to conversions close to vitrification of the epoxy/amine network (the occurrence of vitrification is deduced from the significant decrease in the polymerization rate observed in Figure 4 at conversions close to 0.80).

The significant differences in phase separation processes for both formulations are also reflected in the final morphologies observed after the postcure step. Figure 5 shows SEM micrographs of the DGEBA−MDEA epoxy network modified with iBu-GlyPOSS, either nonreacted or prereacted. For the nonreacted POSS, dispersed domains are spherical with sizes in the range of several micrometers (Figure 5a). For the prereacted POSS phase separation led to the formation of irregular clusters composed by a set of small individual domains. A magnification of one of these clusters is shown in Figure 6.

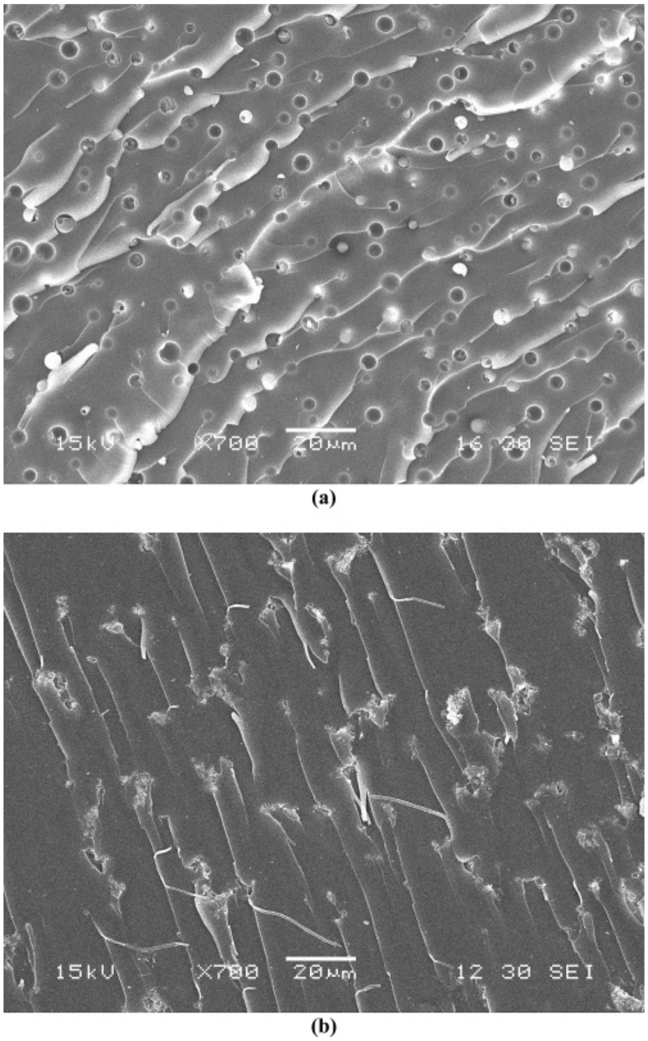


Figure 5. SEM micrographs of final morphologies generated in a DGEBA−MDEA epoxy network modified with iBu-GlyPOSS: (a) nonreacted iBu-GlyPOSS; (b) prereacted iBu-GlyPOSS.

The possibility that POSS could form a crystalline phase when cooling was investigated by WAXS and DSC. Figure 7 shows X-ray diffraction spectra of iBu-GlyPOSS and of DGEBA-MDEA epoxy networks modified with nonreacted iBu-GlyPOSS and prereacted iBu-GlyPOSS. The sharp peak present at 8.4° in the X-ray spectra of the network modified with the nonreacted POSS constitutes a clear indication that the spherical dispersed domains contain crystalline POSS. For the case of prereacted POSS, dispersed clusters are amorphous as evidenced by the appearance of an amorphous halo in Figure 7c. Therefore, the prereaction produced a significant change in the generated morphologies and in the nature (amorphous or crystalline) of the segregated POSS-rich domains.

Figure 8 shows a DSC scan of the DGEBA−MDEA network modified with nonreacted iBu-GlyPOSS. The melting peak of POSS crystals was evidenced at about 130 °C. The heat of fusion was 0.57 J/g, equivalent to 6.8 J/g POSS. This value may be compared to the heat of fusion of pure iBu-GlyPOSS crystallized

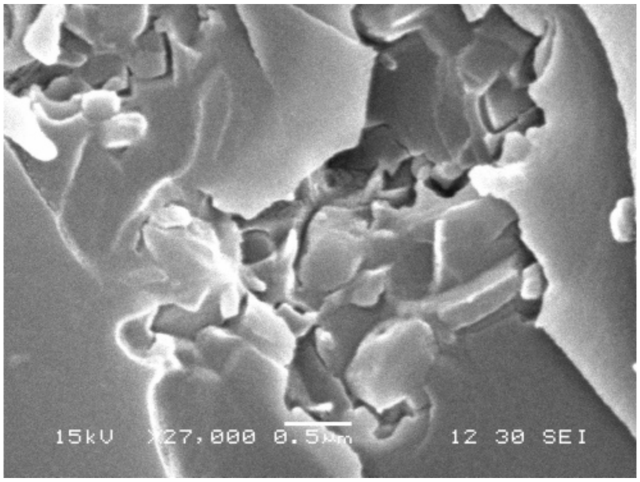


Figure 6. SEM micrograph showing a magnification of the irregular clusters generated when using prereacted iBu-GlyPOSS.

from the melt (15.9 J/g).[2] Therefore, the fraction of crystalline POSS was equal to 6.8/15.9 = 43% of the initial amount. These crystals should be formed by nonreacted POSS units (the experimental observation was that prereaction inhibited crystallization).

For both nonreacted and prereacted iBu-GlyPOSS, a fraction of the initially added amount remained in the epoxy matrix after the final postcure step. It is indeed possible that the initially nonreacted POSS that remained dissolved in the matrix was finally reacted with free amine groups during the postcure stage at 190 °C. The presence of POSS in the matrix can be qualitatively assessed by analyzing its effect on its glass transition temperature (T_g). Results are shown in Table 1. The neat DGEBA−MDEA network synthesized with a ratio of 10 mol of MDEA and 19.5 mol of DGEBA exhibited a $T_g = 171$ °C (the T_g of the stoichiometric matrix was 172 °C). This network contained 2.5% unreacted NH groups due to the initial stoichiometric imbalance. A stoichiometric network was also synthesized using 2.5 mol % epoxy groups contributed by monofunctional PGE. In this case, the 2.5% free NH groups were transformed into 2.5% pendent PGE units in the network. This network exhibited a $T_g = 163$ °C. In spite of the relatively rigid structure of PGE and the presence of an aromatic ring in its structure, its incorporation to the epoxy network produced a decrease of 8 °C in the glass transition temperature. The explanation must be related to the larger free volume associated with the presence of pendent PGE units in the network compared to the presence of unreacted NH groups. POSS units effectively incorporated to the network should produce a similar but even more significant effect than PGE due to the higher free volume contributed by nanosized cages.[14] Experimental values were $T_g = 162$ °C for the initially nonreacted iBu-GlyPOSS and $T_g = 159$ °C for the prereacted iBu-GlyPOSS. As the initially nonreacted POSS dissolved in the matrix should have reacted during the postcure step at 190 °C, the decrease in T_g for both systems can be compared. The larger decrease in T_g observed for the initially prereacted POSS may be associated with a smaller phase-separated fraction during polymerization.

In summary, both nonreacted and prereacted iBu-GlyPOSS were completely soluble in the epoxy−amine precursors and gave place to a polymerization-induced phase separation. The main difference is that the nonreacted POSS generated a typical dispersion of spherical domains with sizes in the range of the micrometers, whereas prereacted POSS produced clusters of very much smaller domains. While the former became crystalline upon cooling, the latter remained amorphous. The fraction of POSS present in the matrix was higher for the prereacted system and led to a higher decrease of the glass transition temperature.

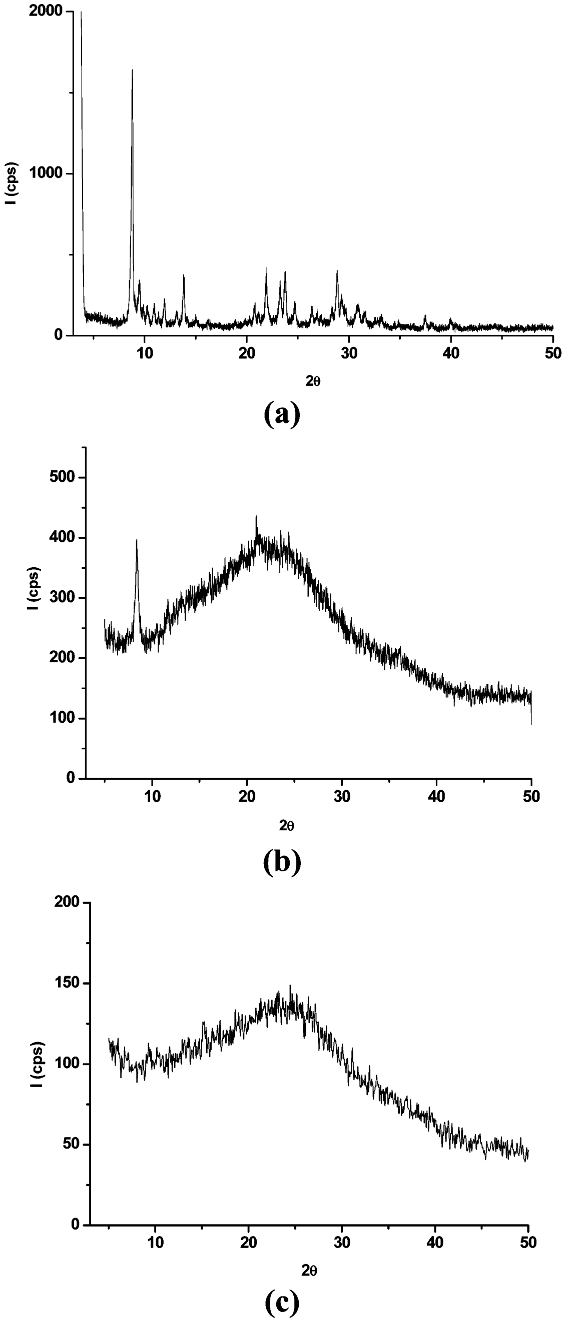


Figure 7. X-ray diffraction spectra of (a) iBu-GlyPOSS, (b) DGEBA−MDEA epoxy network modified with nonreacted iBu-GlyPOSS, and (c) DGEBA−MDEA epoxy network modified with prereacted iBu-GlyPOSS.

We will now analyze the case of the POSS with phenyl groups that are much more compatible with the aromatic epoxy−amine precursors.

Epoxy Networks Modified with Ph-GlyPOSS. The behavior of this particular POSS was determined by the impossibility of producing the melting of crystals in the temperature range preceding thermal degradation. To produce the prereaction, a molar ratio POSS:MDEA equal to 1:10 was dissolved in THF, and the solvent evaporated leading to a dispersion of crystals of both reactants. This mixture was heated to 150 °C producing the melting of MDEA but keeping the POSS in the crystalline

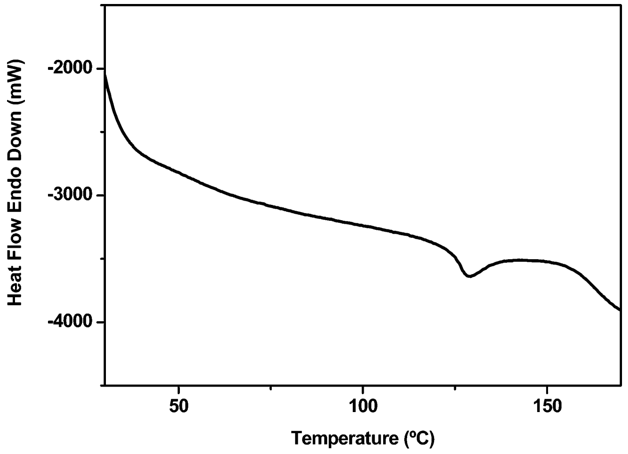


Figure 8. DSC scan of the DGEBA−MDEA epoxy network modified with nonreacted iBu-GlyPOSS.

Table 1. Glass Transition Temperatures of Epoxy Networks after the Postcure Stage

	initial formulation			
modifier (type)	MDEA (mol)	DGEBA (mol)	modifier (mol)	T_g (°C)
none	10	20	0	172
none	10	19.5	0	171
PGE	10	19.5	1	163
iBu-GlyPOSS (nonreacted)	10	19.5	1	162
iBu-GlyPOSS (prereacted)	10	19.5	1	159
Ph-GlyPOSS (nonreacted)	10	19.5	1	165
Ph-GlyPOSS (prereacted)	10	19.5	1	147

state. Reaction was conducted in the heterogeneous medium for 5 h. Figure 9 shows a SEC chromatogram of the reaction products obtained at this time.

Producing the prereaction in a heterogeneous medium had two main effects. First, a significant amount of POSS could not be reacted with MDEA. Second, apart from the main reaction product ascribed to the monosubstituted diamine, MDEA−(POSS)$_1$, other high-molar-mass products were present in the SEC chromatogram assigned to MDEA−(POSS)$_j$ (j = 2−4). A straight line resulted when plotting ln M vs elution time for the four peaks of MDEA species with different degrees of substitution (Figure 10).

The presence of multiple-reacted MDEA units can be explained by the heterogeneous nature of the reaction. Once a MDEA molecule reacts with a POSS unit located in the boundary of a crystal, it might react with more POSS units of the crystals due to the high strength of POSS−POSS interactions that makes difficult for the partially reacted species to diffuse away from the surface of POSS crystals. Increasing the reaction time at 150 °C did practically not change the distribution of reaction products. To increase conversion further after the first step (5 h at 150 °C), temperature was increased to 200 °C (1 h), followed by a heating at 220 °C (1 h). Figure 11 shows SEC chromatograms obtained after the heating at 200 °C and after the final heating at 220 °C. Increasing temperature led to a decrease in the fraction of nonreacted POSS, but it was not possible to attain complete conversion under these conditions.

^{29}Si NMR spectra were recorded for the starting POSS and for the prereacted POSS after the final stage at 220 °C. The starting POSS exhibited a set of sharp peaks at −64.86 ppm (1 Si), −78.23 ppm (3 Si), and −78.66 ppm (4 Si). Similar spectra were recorded for the prereacted POSS with peaks at −64.98 ppm (1 Si), −78.30 ppm (3 Si), and −78.71 ppm (4 Si). This indicates that no opening of the POSS cage was produced during prereaction.

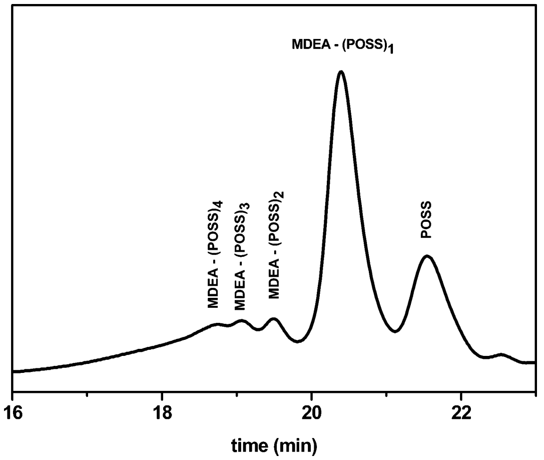


Figure 9. SEC chromatogram of the reaction products obtained in the reaction of Ph-GlyPOSS with an excess of MDEA (molar ratio Ph-GlyPOSS:MDEA = 1:10), at 150 °C for 5 h.

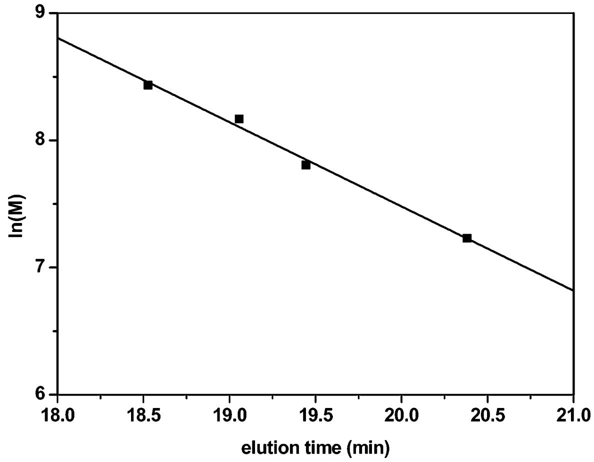


Figure 10. Correlation of ln M vs elution time for MDEA−(POSS)$_j$ (j = 1−4).

Stoichiometric formulations of nonreacted Ph-GlyPOSS: DGEBA:MDEA in a molar ratio 1:19.5:10 were heterogeneous at 135 °C, consisting of a dispersion of POSS crystals in the epoxy−amine precursors as observed by POM. Figure 12 shows the variation of the intensity of light transmitted through the sample as a function of reaction time at 135 °C. A partial solubilization of crystals may be inferred by the initial increase of light intensity with time. However, at a conversion close to 0.5 a polymerization-induced phase separation took place as indicated by the decrease of light intensity with conversion. As Ph-GlyPOSS is crystalline at 135 °C, the segregated phase should become part of the existing dispersion of POSS crystals. Figure 13 shows final morphologies present in this system after the postcure step. The SEM micrograph taken at a lower magnification reveals that the dispersion of crystals is nonuniform along the sample and that there is a broad distribution of crystal sizes. The glass transition temperature was T_g = 165 °C (Table 1), indicating that a fraction of the nonreacted POSS remained in the matrix after the postcure step.

The situation was quite different for the formulation prepared with the prereacted Ph-GlyPOSS using the thermal cycle up to 220 °C. In this case there was still a very small amount of POSS crystals in the initial formulation, observed by POM and ascribed to the small fraction of nonreacted POSS. Light intensity was also followed during polymerization, but no evidence of a phase separation was found possibly due to the small size of generated domains. A polymerization-induced phase separation did actu-

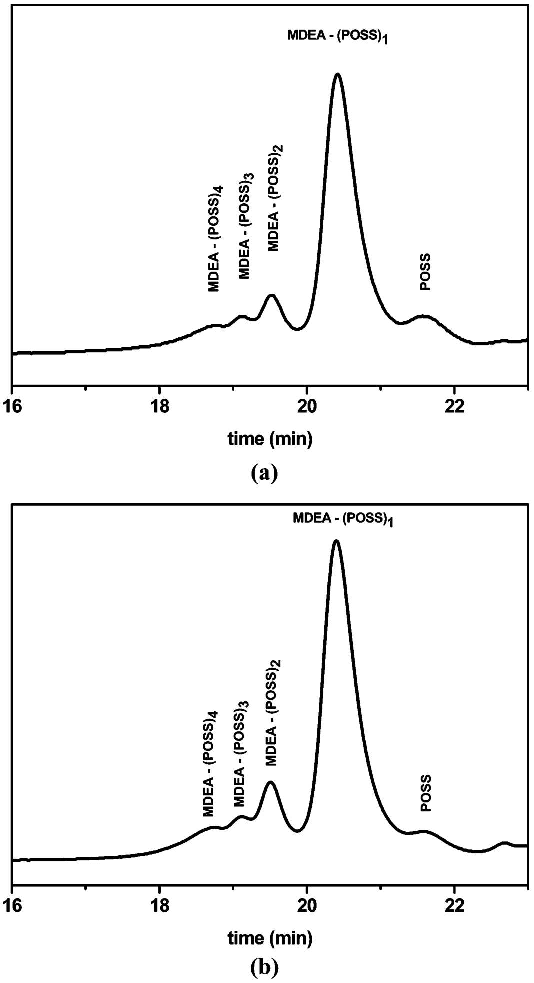


Figure 11. SEC chromatogram of the reaction products obtained in the reaction of Ph-GlyPOSS with an excess of MDEA (molar ratio Ph-GlyPOSS:MDEA = 1:10): (a) after 5 h at 150 °C + 1 h at 200 °C; (b) after 5 h at 150 °C + 1 h at 200 °C + 1 h at 220 °C.

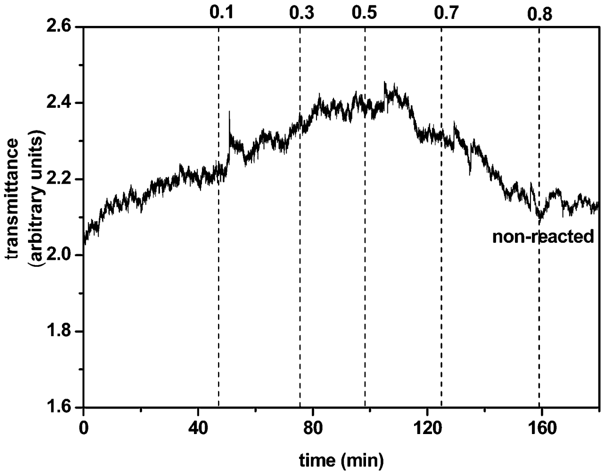


Figure 12. Variation of the light intensity transmitted through the sample as a function of polymerization time at 135 °C, for a stoichiometric formulation of nonreacted Ph-GlyPOSS:DGEBA:MDEA in a molar ratio 1:19.5:10. Particular conversions of the MDEA−DGEBA reaction are plotted as vertical lines.

ally take place in this formulation as inferred from the SEM micrograph shown in Figure 14. Two different phases are present in the micrograph. The smooth phase can be assigned to the neat matrix while the rough phase must be composed of POSS aggregates dispersed in the epoxy−amine matrix. The glass transition temperature of the matrix was T_g = 147 °C (Table 1), evidencing that a high fraction of POSS was not phase separated after the postcure step. (It is not possible to compare the decrease in T_g produced by Ph-GlyPOSS with that produced by iBu-GlyPOSS due to the different chemical structure of the inert organic groups and the different conversions of the epoxy functionalities after the postcure step.)

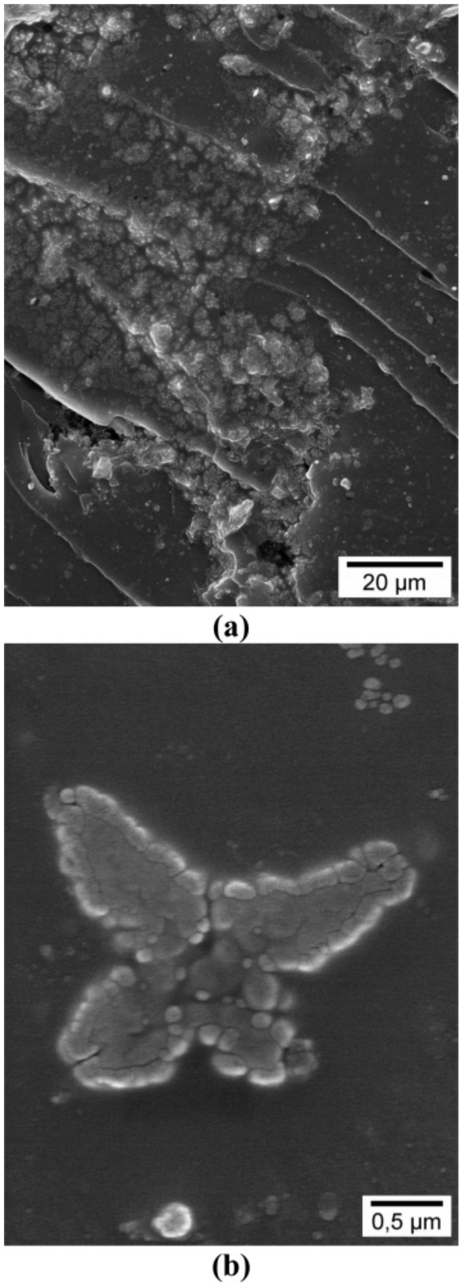


Figure 13. SEM micrographs of final morphologies generated in a DGEBA−MDEA epoxy network modified with nonreacted Ph-Gly-POSS at two magnification levels.

Figure 15 shows X-ray diffraction spectra of pure Ph-GlyPOSS and the networks modified by nonreacted and prereacted Ph-GlyPOSS. POSS crystals were present in the absence of a prereaction but practically disappeared when a prereaction was carried out.

In summary, in the case of Ph-GlyPOSS the lack of a prereaction led to a nonuniform dispersion of crystals in the epoxy matrix. A prereaction enabled to dissolve the POSS in the initial formulation. A polymerization-induced phase separation produced a complex morphology consisting of a smooth phase assigned to the neat matrix and a rough phase where

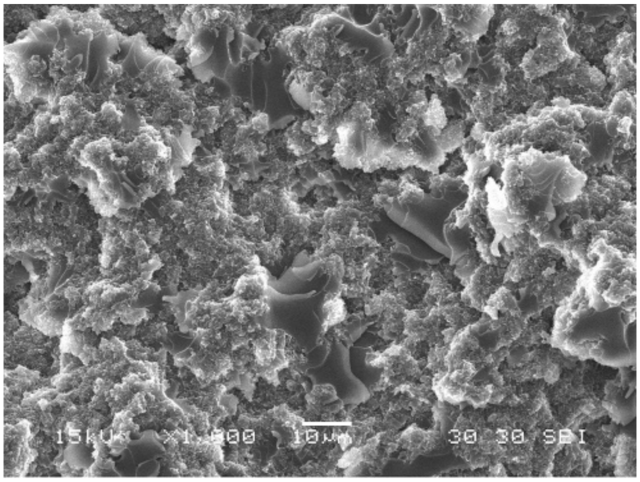


Figure 14. SEM micrograph of final morphologies generated in a DGEBA−MDEA epoxy network modified with prereacted Ph-Gly-POSS (thermal cycle up to 220 °C).

amorphous POSS domains are dispersed in the epoxy matrix. The better compatibility of the phenyl group with the epoxy−amine components compared with the isobutyl group led to a high fraction of residual POSS in the matrix inferred from the significant decrease of the glass transition temperature.

Conclusions

We selected two different monofunctional epoxy-POSS and analyzed the influence of their prereaction on the aggregation state and crystallinity of the POSS domains generated when POSS was used as a modifier of an epoxy−amine network. The difference between both POSS was the inert organic group present in the structure. One had seven isobutyl groups (iBu-GlyPOSS), and the other one had seven phenyl groups (Ph-GlyPOSS). POSS−POSS interactions were much strong in the case of Ph-GlyPOSS, giving place to crystals that could not be melted at temperatures preceding degradation.

It was found that both prereacted and nonreacted iBu-GlyPOSS could be dissolved in the precursors of the epoxy−amine network at the polymerization temperature, giving homogeneous solution containing 8.4 wt % POSS. In both cases phase separation took place during polymerization. In the case of nonreacted POSS most of the phase separation took place rapidly in the pregel region, giving place to a dispersion of spherical POSS particles with sizes in the micrometer range that could be crystallized upon cooling. In the case of prereacted POSS phase separation occurred more slowly in a range of higher conversions, producing irregular clusters of very small particles dispersed in the network. These POSS-rich domains remained amorphous upon cooling. The fraction of POSS that remained dissolved in the matrix at the end of the cure cycle produced a decrease in the glass transition temperature that was ascribed to the corresponding increase in the free volume.

For Ph-GlyPOSS a prereaction was necessary to produce its dissolution in the epoxy−amine precursors. In spite of the better compatibility of the phenyl group with the epoxy−amine components compared with the isobutyl group, a polymerization-induced phase separation did also take place for the prereacted POSS. This produced a complex morphology consisting of a smooth phases assigned to the neat matrix and a rough phase consisting of amorphous POSS domains dispersed in the epoxy matrix. However, a significant fraction of POSS remained in the matrix, producing a significant decrease in the glass transition temperature.

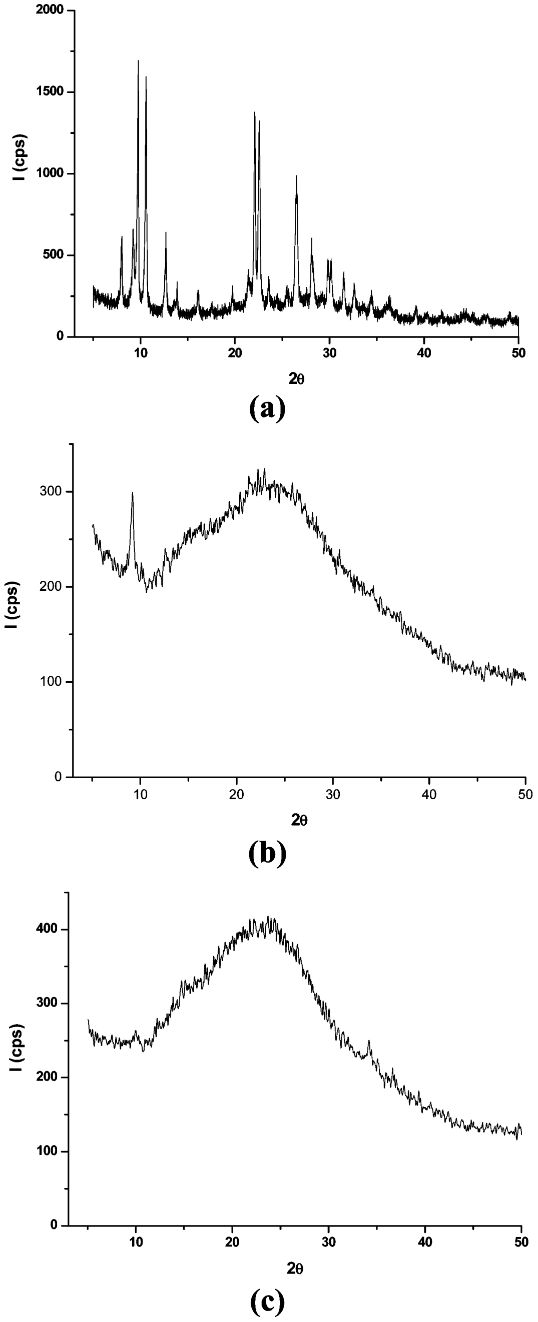


Figure 15. X-ray diffraction spectra of (a) Ph-GlyPOSS, (b) DGEBA−MDEA epoxy network modified with nonreacted Ph-GlyPOSS, and (c) DGEBA−MDEA epoxy network modified with prereacted Ph-GlyPOSS.

The general conclusion is that when monofunctional POSS are used as modifiers of polymer networks, phase separation should be expected either in the initial system or in the course of polymerization. The nature of the inert organic group and a prereaction of the epoxy functionality have a significant effect on the morphologies generated, the crystallinity of segregated POSS domains, and the amount of residual POSS in the polymer network.

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