

## Polyhedral oligomeric silsesquioxanes nanoreinforced methacrylate/epoxy hybrids

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**ABSTRACT:** The aim of this study was to design novel binary and ternary copolymers based on methacrylate and/or epoxy monomers reinforced with 10 wt % mono-/octafunctional polyhedral oligomeric silsesquioxanes (POSS) compounds bearing one or eight epoxy or methacrylate moieties. The experimental parameters such as temperature and time of reaction, comonomer ratio and the incorporation of various types of POSS that strongly influences the curing behavior, polymerization kinetics, glass transition temperature ( $T_g$ ), thermostability and morphological structure of the obtained copolymers were investigated through DSC, FTIR, DMA, TGA, and SEM techniques. The obtained results evidenced that the complex kinetic mechanisms of curing reactions for the binary and ternary copolymers  $\pm$  POSS influence the thermomechanical and morphological properties of the materials. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42912.

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### INTRODUCTION

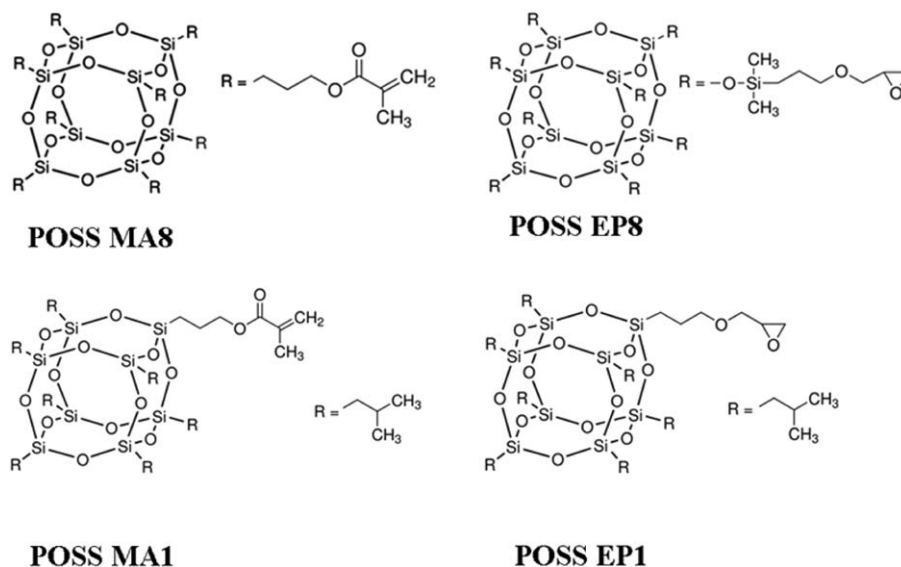
Over the past few years much attention has been given to generate new synergetic properties of organic polymers by incorporation of different types of inorganic nanoparticles. Recently, polyhedral oligomeric silsesquioxane (POSS) compounds were considered as modern chemical structures to prepare reinforced organic–inorganic polymer nanocomposites. Silsesquioxane is the general term used for all structures with the formula  $(RSiO_{1.5})_m$  where R can be hydrogen or any alkyl, alkylene, aryl, arylene, or organic functional derivative groups.<sup>1–5</sup>

The preparation of nanocomposites containing POSS nanostructured compounds is a new fascinating and interesting field of materials research based on both polymer and silicon chemistry. POSS compounds with diameters of 1–3 nm can be possibly considered the smallest silica nanoparticles. Unlike silica or other fillers, POSS molecules contain either functionalized or nonfunctionalized substituents at all silicon atoms located at each corner. Therefore, POSS has been used as silica nanoparticles molecularly surface modified with organic substituents.<sup>6</sup> Thus, POSS compounds as versatile nanobuilding blocks can be used both as reinforcing agents due to the inorganic Si–O–Si

nanocages as well as comonomers due to their reactive functional groups.

Previously, many researchers have incorporated different multi-, mono- or nonfunctional POSS compounds into various types of thermosetting polymers to achieve organic–inorganic polymer based nanocomposites with improved thermomechanical properties.<sup>7–10</sup> In the last years we have also published several studies regarding the influence of methacrylate or epoxy substituted POSS on the thermomechanical properties of both methacrylic or epoxy thermosetting matrices.<sup>11–17</sup> These substituents control the miscibility between POSS compounds and organic monomers as well as the reactivity of the methacrylate and epoxy POSS respectively. We successfully proved that the degree of POSS dispersion within the polymer matrix is a key factor, which is strongly influenced by the organic substituents grafted onto the POSS cages. Moreover, we recently have reported the synthesis and characterization of simultaneous interpenetrating polymer networks (IPNs) based on dimethacrylate/diepoxy resins via *in situ* polymerization reinforced with different POSS compounds.<sup>18</sup>

Previously published investigations were mainly focused on the IPNs containing only organic components without



**Figure 1.** The chemical structure of mono-/octafunctional methacrylate and epoxy POSS compounds.

nanostructured compounds. Therefore, based on the above findings, adding of POSS compounds within methacrylate–epoxy based copolymers seems to be an interesting approach to synergistically combine favorable properties of nanoreinforcements in thermosets. Thus, to explore new principles for creating novel materials with distinct and improved properties, herein we report the synthesis and characterization of novel nanocomposites based on ternary copolymers consisting a mixture of three distinct difunctional monomers (dimethacrylate, diepoxy, and a methacrylate–epoxy containing monomer) reinforced with POSS macromers bearing one or eight methacrylate or epoxy moieties. Radicalic and anionic initiators were used to simultaneously cure the methacrylate and epoxy groups. To the best of our knowledge the combination of free radical and anionic polymerization for the used comonomers and their POSS nanocomposites were not reported elsewhere. The resulted properties of the obtained systems were fully investigated using a wide range of experimental techniques (DSC, FTIR, DMA, TGA and SEM). Various types of POSS derivatives (fully or partially functionalized) were selected in an effort to understand the nanoreinforcement effects of POSS within the suitable host comonomer. Moreover, the incorporation of various POSS moieties within the polymer networks through copolymerization of POSS compounds with the monomers could be a unique opportunity to tailor nanoreinforced organic–inorganic hybrids with superior features.

## EXPERIMENTAL SECTION

### Materials

The methacrylic monomer, bisphenol A diglycidyl ether dimethacrylic (**B**) and the monomer with dual functionality, containing both methacrylic and epoxy groups (glycidyl methacrylate, **G**) were purchased from Sigma-Aldrich Chemicals. The liquid epoxy resin D.E.R.<sup>TM</sup> 332, a high purity bisphenol A diglycidylether (**D**) with an epoxy equivalent weight (EEW) of 171–175 g/eq was supplied by Dow Chemical. The azoinitiator,

azobis(isobutyronitrile) (AIBN) was received from Merck and the anionic initiator, 1-methyl imidazole (**1-MeI**) was supplied by Sigma-Aldrich Chemicals.

Four distinct POSS derivatives commercially available were selected for this study and purchased from Sigma-Aldrich Chemicals: **POSS MA8** (octamethacryl-POSS cage mixture  $n = 8, 10, 12$ )  $M_w = 1433.97$  g/mol, **POSS MA1** (1-propylmethacrylate)-heptaisobutyl substituted POSS  $M_w = 943.64$  g/mol, **POSS EP8** (POSS-Octa(3-glycidyloxypropyl)dimethylsiloxy)  $M_w = 1931.11$  g/mol and **POSS EP1** (POSS-(3-Glycidyl)propoxy-Heptaisobutyl substituted) with  $M_w = 931.63$  g/mol. The chemical structures of the used POSS compounds are further showed in Figure 1. All chemicals were used as received without further purification.

### Formulation of Methacrylate-Epoxy Binary and Ternary Copolymers $\pm$ POSS

Binary copolymers were first synthesized by mixing **B** or **D** respectively (80 wt %) with **G** (20 wt %). For ternary copolymers the initial comonomers mixture was **B** (40 wt %), **G** (20 wt %) and **D** (40 wt %). To initiate the polymerization of methacrylic groups from both **B** and **G** comonomers, azobis(isobutyronitrile) (AIBN) was used at 1 wt % concentration based on the mass of the methacrylate component.<sup>19</sup> To cure the epoxy functionalities from **D** and **G**, 1-Methyl imidazole (**1-MeI**) was employed at a level of 2 wt % based on the mass of the epoxy component. Further, to obtain nanoreinforced organic–inorganic hybrids, 10 wt % of methacrylate or epoxy mono- or octafunctionalized POSS was incorporated within the binary and ternary mixtures (Table I). All POSS compounds were covalently bonded to the polymer matrix via methacrylate or epoxy group's copolymerization.

To prevent any self-condensations of POSS nanocages within the organic host, the obtained monomer mixtures were sonicated 1 h on ice using an ultrasonic processor UP100H type.<sup>20</sup> After mixing the components, both initiators were added. The

**Table I.** Formulation of Binary or Ternary Copolymers  $\pm$  POSS

Copolymers	POSS reinforcing agents	Hybrid nanocomposites
80B:20G	Methacrylated POSS (MA8/MA1) Epoxy POSS (EP8/EP1)	80B:20G/10POSS
80D:20G	Methacrylated POSS (MA8/MA1) Epoxy POSS (EP8/EP1)	80D:20G/10POSS
40B:20G:40D	Methacrylated POSS (MA8/MA1) Epoxy POSS (EP8/EP1)	40B:20G:40D/10POSS

resulting viscous blends were then cast into Teflon molds and the polymerization was further carried out using the following experimental temperature protocol: 120°C for 2 h and postcured at 160°C for another 3 h. All performed experiments were conducted in triplicate to verify the reproducibility. A schematic representation of the approach used to synthesize all the studied specimens is shown in Figure 2.

### Methods

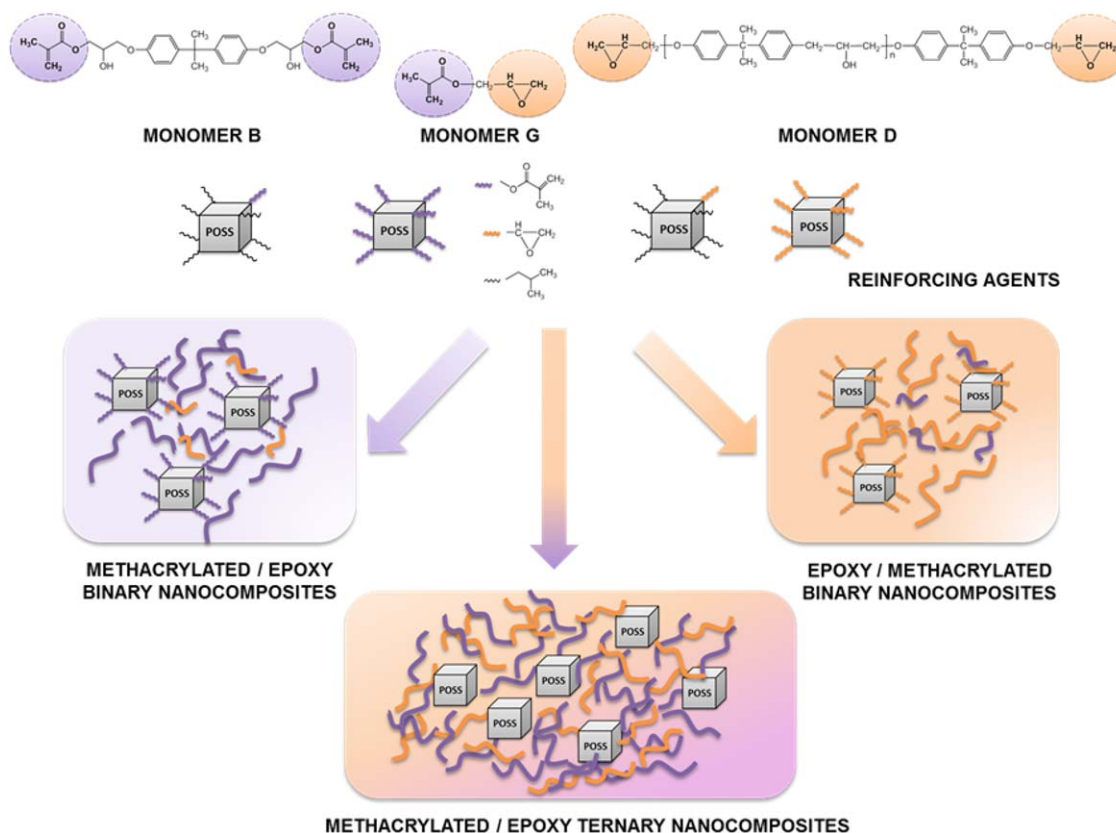
**Differential scanning calorimetry (DSC).** The calorimetric measurements were carried out on Netzsch DSC 204 F1 Phoenix equipment, using a heating rate of 5°C/min. The sample was heated within the temperature range of 20–250°C under constant nitrogen flow rate (20 mL/min).

**Fourier Transform Infrared (FTIR)** spectra were registered on a Vertex 70 Bruker FTIR spectrometer equipped with an

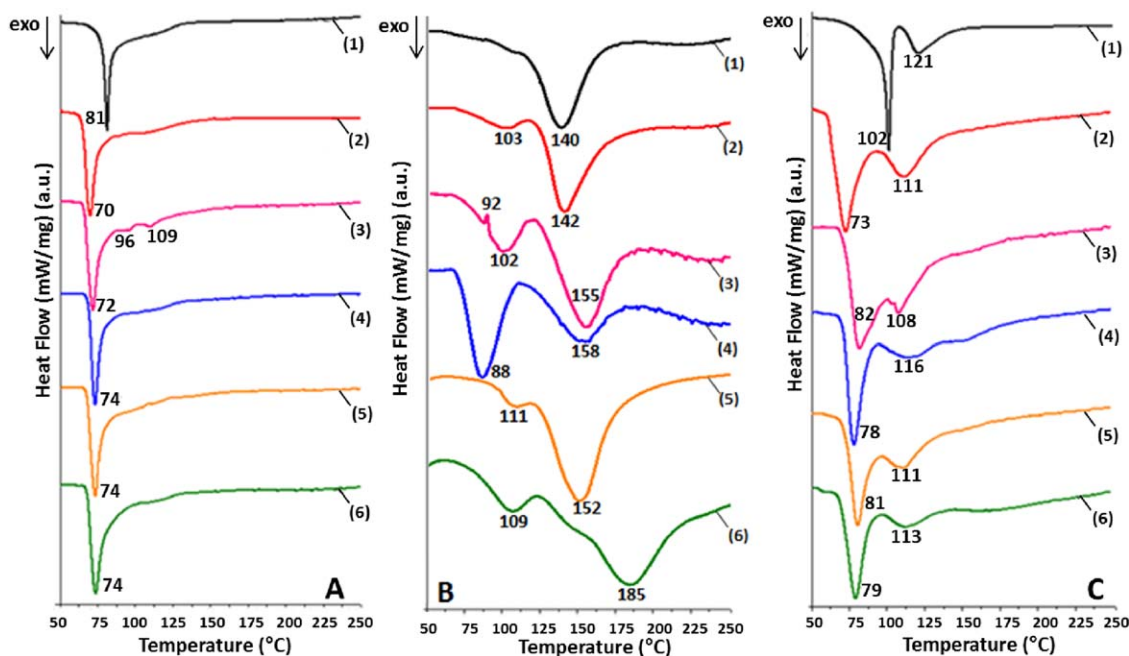
attenuated total reflectance (ATR) accessory to determine the chemical structure and also the curing degree of all the studied specimens. All FTIR measurements were performed in the ATR-FTIR cell on Ge crystal, at room temperature using 32 scans in 600–4000  $\text{cm}^{-1}$  wavenumber region.

The *dynamic mechanical analyses (DMA)* were followed on a Tritec 2000 (Triton Technology) instrument using 10 mm  $\times$  2 mm  $\times$  20 mm rectangular specimens in a single cantilever bending mode.  $\tan \delta$  was calculated as a function of temperature ranging from  $-100$  to 250°C using 5°C/min heating rate at a frequency of 1 Hz. The displacement amplitude was 0.05 mm.

The *thermogravimetric analyses (TGA)* results 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



**Figure 2.** A schematic illustration of POSS nanoreinforced methacrylate–epoxy binary or ternary copolymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** DSC curves of: Panel A: B homopolymer (1), 80B:20G (2), 80B:20G/10POSS MA1 (3), 80B:20G/10POSS MA8 (4), 80B:20G/10POSS EP1 (5), 80B:20G/10POSS EP8 (6); Panel B: D homopolymer (1), 80D:20G (2), 80D:20G/10POSS MA1 (3), 80D:20G/10POSS MA8 (4), 80D:20G/10POSS EP1 (5), 80D:20G/10POSS EP8 (6); Panel C: G homopolymer (1), 40B:20G:40D (2), 40B:20G:40D/10POSS MA1 (3), 40B:20G:40D/10POSS MA8 (4), 40B:20G:40D/10POSS EP1 (5), 40B:20G:40D/10POSS EP8 (6). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

rate of 10°C/min under a constant nitrogen flow rate (balance flow 10 mL/min, oven flow 90 mL/min).

The morphological structure of the nanoreinforced organic–inorganic hybrids was established by *scanning electron microscopy (SEM)* using a Quanta Inspect F SEM device equipped with a field emission gun (FEG) providing a resolution of 1.2 nm; gold coating was performed for enhanced surface conductivity.

## RESULTS AND DISCUSSION

Various types of POSS derivatives such as *octafunctional POSS compounds* substituted with eight methacrylate (POSS MA8) or epoxy groups (POSS EP8) and *monofunctional POSS compounds* substituted with one methacrylate (POSS MA1) or epoxy group (POSS EP1) respectively were used to synthesize novel nanocomposites.

Methacrylic and epoxy substituted POSS compounds were deliberately selected for nanocomposites synthesis in order to achieve multiple crosslinking points within the polymer host. Thus POSS MA8 or POSS MA1 containing functional methacrylic groups could chemically react with methacrylic groups from both B and G monomers during curing. In the case of POSS EP8 or POSS EP1, the crosslinking points with the polymer matrix are caused by the chemical reaction with epoxy groups from the chemical structure of both D and G monomers during the polymerization reactions.

According with Kuo and coworkers, depending on the number of POSS functional groups, various architectures of polymer/

POSS nanocomposites can be obtained.<sup>6</sup> Thus, monofunctional POSS can be covalently incorporated as a pendant group along a polymer chain through copolymerization whereas multifunctional POSS containing several functional groups can form more homogeneous hybrids due to the multiple POSS–polymer network junctions. Hence, due to the numerous crosslinking points the POSS moiety could be molecularly dispersed within the organic host.<sup>21</sup> Besides the methacrylate or epoxy reactive moieties, the monofunctional POSS compounds (POSS MA1/POSS EP1) are heptasubstituted with unreactive isobutyl groups that can improve the compatibility of POSS molecules with the used hydrophobic monomers.

### Curing Kinetic Studies Using DSC and FTIR Techniques

The reaction mechanisms and the kinetics of the curing process for methacrylate and epoxy resins were further detailed using both calorimetry (DSC) and spectrometry (FTIR) techniques. The influence of methacrylate or epoxy POSS incorporation on the curing behavior of the binary or ternary methacrylate–epoxy copolymers could be due to the complex local molecular interactions, which may affect in different ways the resulting polymer chain mobility.<sup>22–26</sup>

Thus, to investigate the effect of POSS type on the reactivity of methacrylate or epoxy groups during the copolymerization reactions, non-isothermal DSC scan were performed in the temperature range 20°C - 250°C (Figure 3). This method gives an assessment of curing degree by monitoring the heat changes associated with polymerization reactions that occurs as a function of time and temperature.<sup>27,28</sup>



From Figure 3 panel A and B, curve 1, it can be noticed that in the presence of their specific initiators, neat B and D exhibit single exothermic peaks ( $T_{max}$ ) at 81°C and 140°C respectively, assigned to the maximum polymerization enthalpies of methacrylic and epoxy groups.

As we expected, in the case of dual functionalized G monomer initiated with both AIBN and 1-MeI, two exothermic peaks appear in the DSC plot [curve 1 from Figure 3(C)]. The first peak (102°C) is assigned to methacrylate polymerization and the second peak from 121°C corresponds to epoxy polymerization. Analyzing the curve 1 from Figure 3(C) one may observe that the peak assigned to methacrylate polymerization exhibits a higher intensity than the peak corresponding to epoxy polymerization even if the anionic initiator (1-MeI) was added in a higher concentration than azoinitiator (AIBN). This behavior could be ascribed to the redox reactions that occur between AIBN and 1-MeI. These reactions lead to enhancement of AIBN dissociation and as a consequence the methacrylic polymerization exhibits with a higher rate.<sup>29–31</sup>

The incorporation of G within the used methacrylate (B) or epoxy (D) monomers, and also in their mixtures, exhibits a significantly influence on the methacrylic or epoxy groups polymerization behavior. Moreover when POSS compounds are used as nanoreinforcing agents both in binary and ternary copolymers the curing reactions exhibit more complex kinetic mechanisms of the investigated functional groups.

In the first panel [Figure 3(A)] an acceleration of the methacrylate polymerization was observed when G was incorporated within B to obtain the binary copolymer. In this case the curing exothermic peak appears to be shifted toward lower temperatures with 10°C from 81°C to 70°C [Figure 3(A) plot 2]. This behavior could confirm that the imidazole acts as an accelerator of methacrylate polymerization causing enhanced radical production of the AIBN. Also the presence of G may act as spacer between B molecules, which leads to a lower viscosity of B, enabling a high mobility of methacrylic chains increasing thus the attack of AIBN radicals to the methacrylic groups.

The introduction of POSS compounds within the 80B:20G binary copolymer causes a lower reactivity of methacrylic groups,  $T_{max}$  being slightly shifted toward higher temperatures [Figure 3(A) plots 3–6]. This effect is probably due to the restricted mobility of the polymer matrix chains in the vicinity of the POSS cages, these chains being less available for the polymerization.

As one may notice from Figure 3(A) curve 3 the binary copolymer reinforced with POSS MA1 (80B:20G/10POSS MA1), besides the major exothermic peak from 72°C exhibits another two smaller peaks at 96°C and 109°C. The appearance of these two small peaks suggests that AIBN produces radicals with different activities that initiate the curing reactions of the remaining methacrylate groups.<sup>29–32</sup>

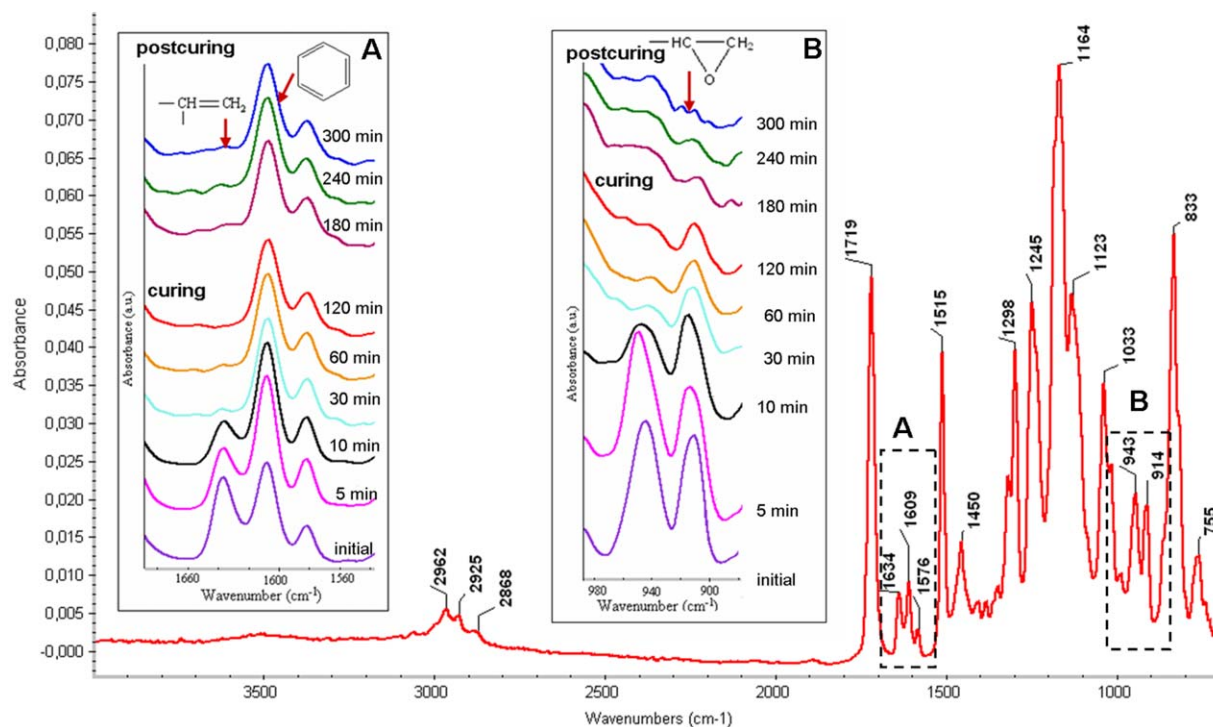
On the other hand, no exothermic peaks attributed to epoxy polymerization were observed. The methacrylate network previously formed hinders the polymerization of the low amount of epoxy groups provided by G monomer. This is due to the

competition between the anionic polymerization of epoxy groups and radical polymerization of methacrylate bonds. The latter exhibit a higher rate so that the methacrylic network is almost done when the epoxy polymerization just starts.

In the second panel [Figure 3(B)] it can be noticed that two exothermic peaks appear, when D is combined with G to obtain the corresponding binary copolymer: first at 103°C corresponding to methacrylic polymerization from G and the second at 142°C attributed to polymerization of epoxy groups from both D and G comonomers [Figure 3(B) plot 2]. In this case the number of methacrylic groups able to form the network is low and therefore the lower density of methacrylic network will not hinder anymore the anionic polymerization of epoxy groups, but will lead to a lower rate of epoxy polymerization. The exothermic peak of D homopolymer appears at 140°C but when G was incorporated within D, the  $T_{max}$  obtained for epoxy polymerization is slightly shifted toward higher temperatures (142°C) which is consistent with the effects of dilution.

DSC thermograms of **80D:20G binary copolymers** reinforced with mono- or octafunctional methacrylated POSS compounds (POSS MA1 or POSS MA8) are further illustrated in Figure 3(B) plots 3, 4. POSS MA1 nanocages bearing a single methacrylic group on the POSS cages exhibit no significant influence on the methacrylic polymerization, while POSS MA8 increase the overall reactivity of methacrylic groups, the peak being shifted downward from 103°C to 88°C which is almost similar in behavior as a pure methacrylic compound. This behavior could be attributed to the higher reactivity of methacrylate groups belonging to POSS MA8 cages in comparison with the reactivity of methacrylic groups from G monomer. As we already reported in a previous work POSS MA8/AIBN exhibits an exothermic peak at ~90°C assigned to the maximum polymerization enthalpy of the methacrylate groups from POSS MA8.<sup>18</sup> Moreover, from Figure 3(B) curves 3–4 it may be observed that the peak assigned to the maximum polymerization enthalpy of methacrylic groups increases in height with the content of methacrylic groups grafted onto the POSS cages. So, the highest intensity of this peak was obtained for POSS MA8 based nanocomposites. Furthermore, the addition of methacrylic POSS compounds gives a higher density network of methacrylic groups, which delays the opening of epoxy groups. In this case, the peak assigned to epoxy polymerization decreases in height and is shifted toward higher temperatures with increasing the number of methacrylic groups from the POSS cages. This is more significant for POSS MA8 that determines the polymerization of epoxy groups to occur at 158°C [Figure 3(B) plot 4].

When 80D:20G binary copolymer is reinforced with POSS with one or eight epoxy groups (POSS EP1 and POSS EP8), the temperatures at which the polymerization enthalpy of epoxy groups is maximum ( $T_{max}$ ) are shifted to higher temperatures which is probably a consequence of the hindrance effect caused by the presence of the bulky POSS cages. Moreover, a significant influence of the number of epoxy groups from POSS nanocages against the curing behavior of the resulted nanocomposites was noticed. By comparison between POSS EP1 based



**Figure 4.** Evolution of (A) methacrylic and (B) epoxy groups during curing of 40B : 20G : 40D/10POSS MA8 nanocomposite using FTIR spectrometry. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

nanocomposite [Figure 3(B) curve 5] and the one reinforced with POSS EP8 [Fig. 3(B) curve 6] the lowest reactivity was obtained for the nanocomposite with POSS EP8. Thus, POSS EP1 bearing only one reactive group exhibits a high agglomeration tendency leading to partially POSS cages agglomeration, which may hinder the attack of the initiator (1-MeI) to the epoxy groups being the reason for the lower epoxy groups reactivity. In the case of POSS EP8 the epoxy polymerization occurs at much higher temperature [185°C, Figure 3(B) plot 6] caused by the difficulty in alignment of the reactive sites from 80D:20G with POSS EP8 since the eight epoxy reactive groups from POSS compound are distributed in a star shape.<sup>16</sup> Furthermore, the reactivity of epoxy groups grafted onto POSS EP8 is much lower than for the reactivity of epoxy groups from the polymer matrix. As we previously reported, in the case of POSS EP8/1-MeI the exothermic peak assigned to the maximum polymerization enthalpy of the epoxy groups appears at 194°C.<sup>18</sup>

From Figure 3(B) (plots 5, 6) it can be noticed that the presence of epoxy POSS leads to a lower reactivity of methacrylic groups. The maximum polymerization enthalpies of methacrylic groups appears at 111°C for 80D:20G/10POSS EP1 and at 109°C for 80D:20G/10POSS EP8. This behavior can be a consequence of the dilution effect caused by the presence of the other components.

The recorded **DSC curves for the ternary copolymers** are shown in the **third panel** [Figure 3(C)]. For the unreinforced 40B:20G:40D copolymer [Figure 3(C), plot 2] two distinct peaks are noticed, one at 73°C assigned to radical polymerization of methacrylic groups and another one at 111°C attributed to epoxy

rings opening. The peak assigned to epoxy polymerization is shifted with about 30°C to lower temperatures in comparison with the binary copolymer probably due to the catalytic effect of OH groups from B on epoxy cure of D and/or G with 1-MeI.<sup>33</sup>

From Figure 3(C) (curves 3–6) it may be observed that the incorporation of POSS compounds bearing one or eight methacrylic or epoxy groups within 40B:20G:40D leads to a lower reactivity of methacrylic groups and this behavior is more pronounced for monofunctionalized POSS compounds (POSS MA1 or POSS EP1), which determine the methacrylic polymerization to occur at 82°C and 81°C respectively. In general, these types of POSS being functionalized with only one reactive group (methacrylate or epoxy) and seven unreactive isobutyl groups exhibit a high tendency to self-assemble and to form POSS aggregates which may hinder the attack of the initiator to the methacrylic groups.

As one can notice from Figure 3(C) curve 3 the ternary copolymer reinforced with POSS MA1 (40B:20G:40D/10POSS MA1) exhibits a similar behavior as the binary copolymer (80B:20G/10POSS MA1) reinforced with the same type of POSS. In this case, besides the major peaks assigned to methacrylate and epoxy polymerization (82°C and 108°C) another small peak appears between them at ~105°C which is probably caused by the presence of AIBN isomers that enable the curing of the remaining methacrylate groups.<sup>19</sup>

The addition of methacrylic POSS leads to a higher crosslinking density of methacrylic groups, which probably cause a delay of the epoxy polymerization. This behavior is more significant for POSS MA8, which determines the polymerization of epoxy groups to occur at 116°C (E. 3C plot 4).

The incorporation of POSS EP1 within 40B:20G:40D copolymer exhibits no influence on the reactivity of epoxy groups but when octaepoxy POSS was used the polymerization of epoxy groups occurs with at a lower temperature (113°C) comparing with the unreinforced 40B:20G:40D matrix (111°C). This behavior may be a consequence of the high content with a lower reactivity of epoxy groups from the POSS cages.

**FTIR spectrometry** was further used to establish the conversion degree of methacrylate/epoxy groups during the polymerization of binary or ternary copolymers reinforced with POSS nanostructured compounds (Figure 4). The significant bands for methacrylate and epoxy groups are detailed in A and B insets of Figure 4.

The band at  $1634\text{ cm}^{-1}$  results from the stretching vibration bands of methacrylic groups while the stretching vibration band for epoxy groups appears at  $914\text{ cm}^{-1}$ . These bands were further used to predict the dependencies of conversion against time of both methacrylate and epoxy moieties. The band of Si—O—Si cage at  $1123\text{ cm}^{-1}$  assigned to the POSS molecule was observed in the chemical structure of all the studied specimens including POSS compounds.

During the polymerization process, the methacrylate and epoxy ring vibration bands exhibit a significantly decrease. From Figure 4 it can be observed that the epoxy polymerization starts when the methacrylate polymerization is almost complete (20–30 min). A postcuring reaction at elevated temperature is additionally carried out to crosslink the remained epoxy groups and to achieve better thermomechanical features. Completion of the reaction was confirmed by the disappearance of methacrylate and epoxy peaks from FTIR spectra. The band at  $1608\text{ cm}^{-1}$  assigned to aromatic C=C stretching vibration was used as reference to calculate the progress of curing reaction using eq. (1):

$$\eta = \left[ 1 - \frac{\left( \frac{A_{\text{polym}}}{A_{\text{ref}}} \right)_t}{\left( \frac{A_{\text{polym}}}{A_{\text{ref}}} \right)_0} \right] \times 100 \quad (1)$$

in which:

$$\eta = \text{conversion (\%)}$$

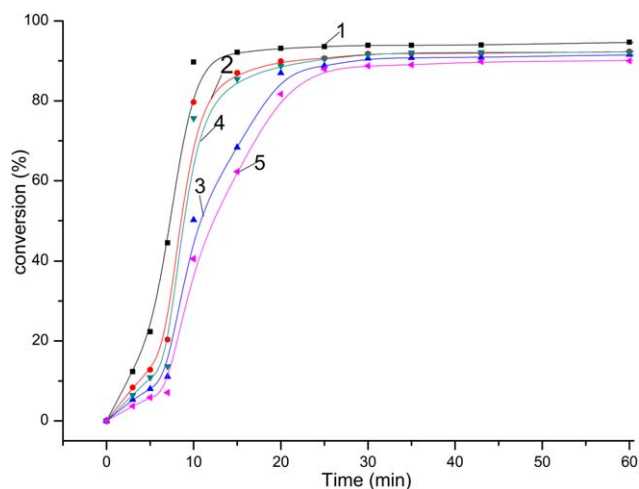
$A_{\text{polym}}$  = the area of signal corresponding to polymerization of methacrylate ( $1634\text{ cm}^{-1}$ ) or epoxy ( $914\text{ cm}^{-1}$ ) groups

$A_{\text{ref}}$  = the area of reference signal corresponding to aromatic C=C vibration.

#### The Effect of POSS Nanoreinforcement on the Curing Kinetics of methacrylate-Epoxy Binary and Ternary Copolymers ± POSS

The conversion degree of POSS based binary and ternary copolymers is quite dependent on both type and number of organic substituents located on the Si—O—Si nanocages. The reactivity of mono- and octafunctional POSS bearing methacrylate or epoxy groups strongly influences the interactions with polymer compounds.

From Figures 5 and 6, it may be observed that the inclusion of organic-inorganic POSS compounds within the binary copolymers (80B:20G and 80D:20G) reduces the overall conversion



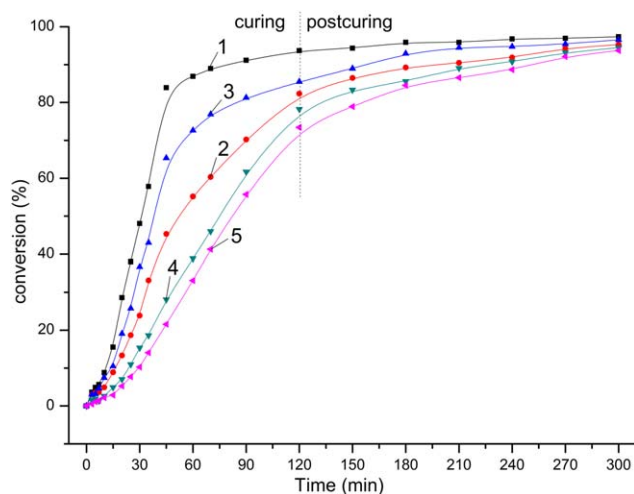
**Figure 5.** The dependence of methacrylic groups conversion against time for 80B : 20G sample (1) and the respective nanocomposites with POSS MA1 (2); POSS MA8 (3); POSS EP1 (4); POSS EP8 (5). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

degree of methacrylate or epoxy reactive groups from the obtained nanocomposites. No matter what type of POSS is used, the reactivity of methacrylate or epoxy groups respectively is diminished. Therefore, the initiation process is delayed ( $\sim 10$  min for methacrylate groups;  $\sim 30$  min for epoxy groups) and thus the polymerization of functional groups occurs with a lower rate.

From Figure 5 curves 2-3, one may notice that the incorporation of POSS compounds with one or eight methacrylic groups decreases the methacrylic polymerization rate as a consequence of the hindrance effect caused by the presence of voluminous POSS cages.<sup>12,13,16,18,34</sup> When the reaction goes on, the crosslinking density becomes higher since more methacrylic groups are involved. Thus, POSS MA8 based nanocomposites exhibit a high crosslinking density of the final network due to the high content of methacrylic groups from the POSS molecules. In this case the access of AIBN molecules to methacrylic groups becomes more difficult which leads to a lower conversion of the system with POSS MA8 in comparison with the one with POSS MA1 in which the formed network exhibit a lower crosslinking density. This behavior is probably caused by the agglomeration tendency of POSS MA1.

The inclusion of POSS compounds with one or eight epoxy groups (Figure 5 curves 4-5) within the binary 80B:20G copolymer leads also to a decrease of methacrylic groups conversion. In this system, the content of methacrylic groups is higher than that of epoxy groups. Thus, higher conversions were obtained for the POSS EP1 reinforced nanocomposite, which include only one epoxy group (Figure 6 curve 4). In this case most of the epoxy groups belonging to POSS EP1 cages react with the epoxy groups from G comonomer. When octaepoxy POSS is included within the binary 80B:20G system, the low amount of epoxy moieties from the binary copolymer are not enough to react with all epoxy groups from POSS EP8 and thus the remaining unreacted epoxy groups from the POSS cages could homopolymerize and form POSS aggregates which may act as a





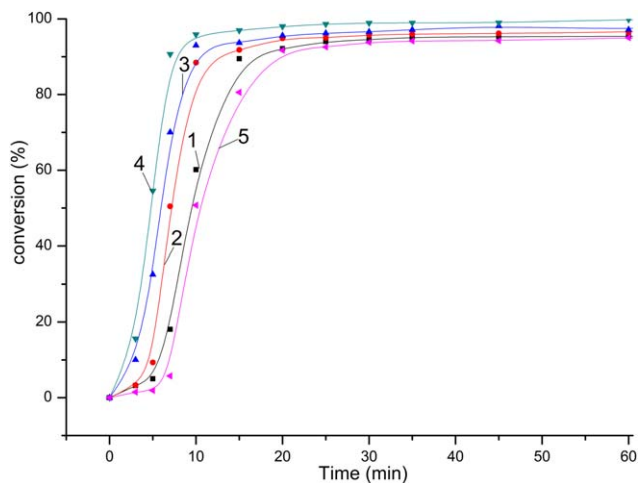
**Figure 6.** The dependence of epoxy groups conversion against time for 80D : 20G sample (1) and the respective nanocomposites with POSS MA1 (2); POSS MA8 (3); POSS EP1 (4); POSS EP8 (5). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

barrier against the polymerization of methacrylic groups. Moreover, as we already described the reactivity of epoxy groups from POSS EP8 cages is very low being necessary a high temperature to reach full cure. As a consequence a large content of these epoxy groups may remain unreacted and act as a plasticizer for the more rapidly reacting component (methacrylic groups), which subsequently lead to a lower conversion degree of methacrylic groups.

Among POSS based **80D:20G binary copolymers** it may be noticed that POSS compounds with one or eight methacrylate groups exhibit a restraining effect on the epoxy polymerization rate (Figure 6 curves 2-3). This effect can be attributed to the low amount of methacrylic groups from the polymer matrix (80D:20G) which are not able to polymerize with all available methacrylic groups attached to POSS cages. As a consequence the remained unreacted methacrylic groups from POSS cages could react between them and form large POSS aggregates that may hinder the attack of 1-MeI to epoxy groups and thus lower epoxy conversions were obtained. In this case the methacrylic POSS compounds act as a plasticizer not as a reinforcing agent. A similar plasticization behavior was noticed when epoxy POSS were incorporated within the binary 80B:20G copolymer.

When POSS functionalized with one or eight epoxy groups are loaded within 80D:20G copolymer, the rate of epoxy polymerization is reduced as the number of epoxy groups from the POSS cages increases. Thus, the epoxy polymerization was significantly retarded ( $\sim 30$  min) when POSS EP8 is loaded. These results are well correlated with DSC results indicating a lower reactivity of epoxy groups from POSS EP8 in comparison with epoxy groups corresponding to D. Therefore the majority of epoxy rings from POSS EP8 will remain probably unreacted and subsequently lower conversions were obtained.

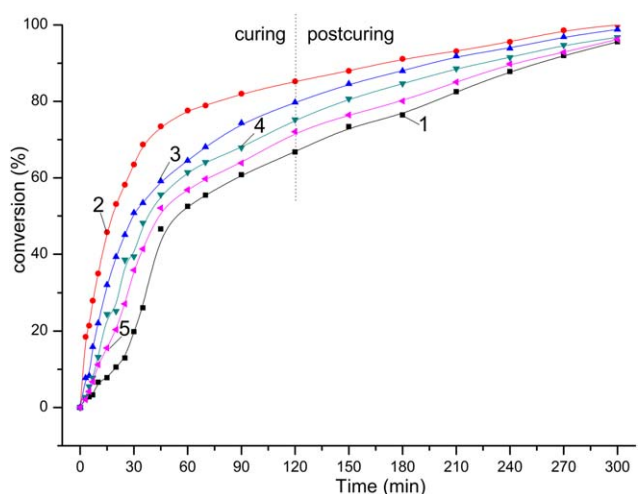
The influence of POSS type on the conversion degree of methacrylate or epoxy groups during the preparation of **POSS-based ternary nanocomposites** is displayed in Figures 7 and 8.



**Figure 7.** The dependence of methacrylic groups conversion on time for 40B : 20G : 40D sample (1) and the respective nanocomposites with POSS MA1 (2); POSS MA8 (3); POSS EP1 (4); POSS EP8 (5). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

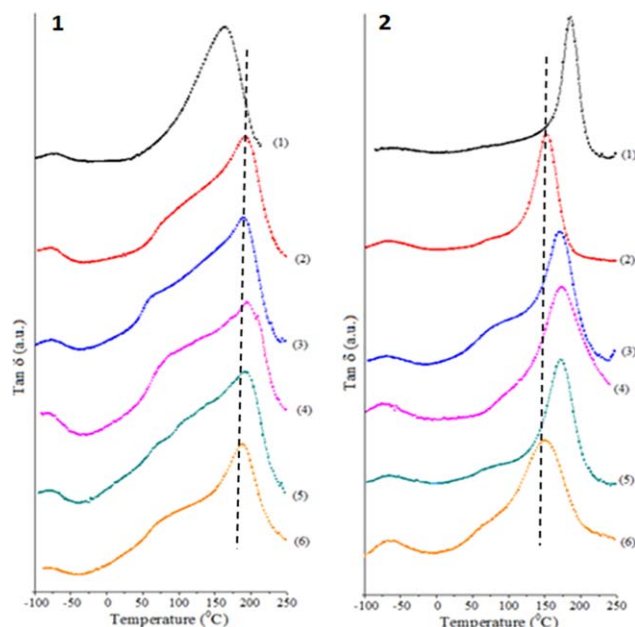
As it was expected the polymerization rates of methacrylic and epoxy groups from 40B:20G:40D without POSS are lower than those of the unreinforced binary systems (80B:20G, 80D:20G) due to the dilution effect of the reactants.<sup>19</sup> Concerning the evolution of methacrylic conversion against time for ternary system including methacrylate POSS compounds, it can be noticed that generally an increase of conversion occurs (Figure 7).

Contrary to our expectations the incorporation of POSS 1EP within the ternary copolymer leads to an increasing of methacrylic conversion degree. The reason for this behavior is unclear, but could be caused by the presence of the flexible unreactive isobutyl groups from the POSS cages enabling a high mobility of the polymer chains and as a consequence the polymerization of methacrylic groups occurs with a higher rate.



**Figure 8.** The dependence of epoxy groups of 40B : 20G : 40D sample (1) and the respective nanocomposites with POSS MA1 (2); POSS MA8 (3); POSS EP1 (4); POSS EP8 (5). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 9.** The dependences of  $\tan \delta$  against temperature for all the binary copolymers and their corresponding nanocomposites: Panel 1: B homopolymer (1), 80B : 20G (2), 80B : 20G/10POSS MA1 (3), 80B : 20G/10POSS MA8 (4), 80B : 20G/10POSS EP1 (5), 80B : 20G/10POSS EP8 (6); Panel 2: D homopolymer (1), 80D : 20G (2), 80D : 20G/10POSS MA1 (3), 80D : 20G/10POSS MA8 (4), 80D : 20G/10POSS EP1 (5), 80D : 20G/10POSS EP8 (6). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

POSS EP8 exhibits an opposite effect on the conversion degree of methacrylic groups. As was already discussed in a previous section, the presence of the eight epoxy rings belonging to POSS cages reduces the flexibility within the system and as a consequence a large number of methacrylate groups remain trapped in the formed network, these groups being less available for the polymerization. This effect could be caused by the much lower reactivity of epoxy groups from the POSS EP8 cages, which need higher temperatures for complete polymerization. Moreover, the presence of epoxy groups from D and G that exhibit a higher reactivity than epoxy rings of POSS cages leads to impossibility of epoxy rings opening from POSS EP8 molecules which are already entrapped between the epoxy network developed between D and G comonomers from the ternary copolymer. Therefore the epoxy rings from POSS EP8 will remain probably unreacted and may act as a plasticizer for the methacrylic component, which subsequently lead to lower conversions of methacrylic groups.

The incorporation of methacrylic-POSS compounds within the ternary copolymer leads to a gradually increase of methacrylic conversion with increasing the number of methacrylic groups from the POSS cages. The higher the number of methacrylic groups the faster the polymerization occurs.

Regardless of the POSS type, the epoxy groups conversion from ternary 40B:20G:40D system increases in the presence of POSS. Among POSS based nanocomposites, higher conversions were obtained when methacrylic POSS compounds were used. The

highest conversion degree was obtained for POSS MA1 based nanocomposites and could be attributed to the presence of the flexible isobutyl groups from the POSS cages which increase the mobility of the polymer chains and thus the epoxy groups become more available for the attack of the initiator.

The incorporation of POSS with epoxy groups within the ternary copolymer leads to lower conversions of epoxy groups than POSS with methacrylate. As DSC evidenced, this behavior could be ascribed to the lower reactivity of epoxy groups from the POSS cages.

### Thermomechanical Behavior of Binary or Ternary Copolymers $\pm$ POSS

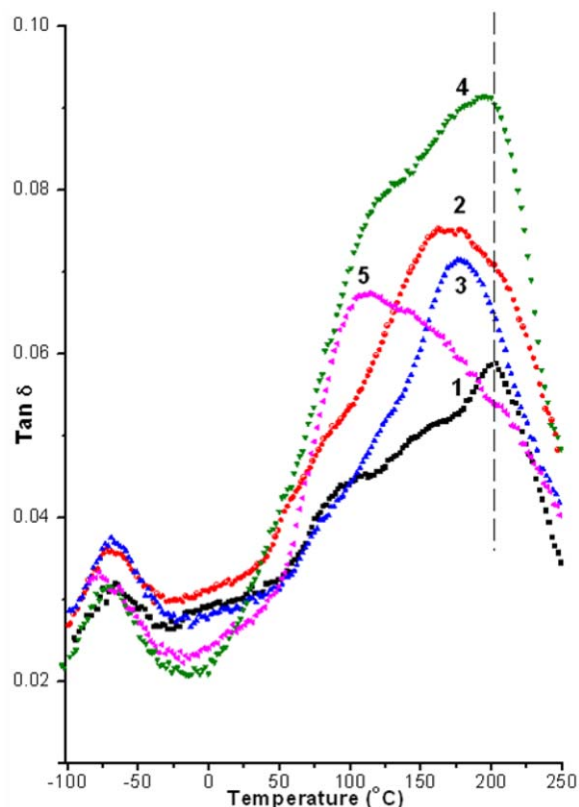
The thermal properties of all the studied copolymers were further investigated by DMA and TGA respectively. Figure 9 shows the plots of  $\tan \delta$  against temperature for all the studied binary copolymers and their POSS hybrids.

The DMA curves exhibit a low relaxation temperature, denoted as  $\beta$  transition that occurs in the range  $-100/-50^\circ\text{C}$  and  $\alpha$  relaxation transition attributed to glass transition temperature ( $T_g$ ) in the experimental domain  $50-200^\circ\text{C}$ . Both B and D homopolymers displayed a single well-defined  $T_g$  peak centered at  $161^\circ\text{C}$  and  $186^\circ\text{C}$  respectively. If 20%w G is loaded within B the DMA thermograms displayed also a single  $T_g$  but shifted to higher temperature ( $193^\circ\text{C}$ ). This is due to the partially cross-linked structure which may be formed through the G molecules bonding different B chains. The  $\tan \delta$  peak of the B:G hybrids containing 10% POSS are broader than those of the corresponding neat organic host. The  $T_g$  of the POSS nanocomposites varies very similarly as the unreinforced matrix.

On the contrary, the incorporation of 20%w G in D decreases the  $T_g$  value with  $\sim 20^\circ\text{C}$ , from  $186^\circ\text{C}$  to  $153^\circ\text{C}$  due to the decrease of the overall content of aromatic rings which thus diminishes the rigidity of the system. The introduction of monofunctional (methacrylic or epoxy) or octamethacrylate POSS will increase again the value of  $T_g$  due to the effect of nanoreinforcement of POSS cages that could restrict the motions of macromolecular chains. A similar phenomenon was also found in other POSS-containing nanocomposites.<sup>26,35,36</sup>

In contrast, the incorporation of POSS EP8 within 80D:20G copolymer exhibits a different behavior, the obtained  $T_g$  value being lower than for the other copolymers reinforced with POSS. The decrease of the  $T_g$  value for 80D:20G/10POSS EP8 is probably caused by the impossibility of epoxy rings opening from POSS EP8 molecules which are already entrapped between the epoxy network of D. This is proved also by the lower reactivity of epoxy rings from POSS EP8 and D as DSC measurements reveal. Due to the agglomeration of Si—O—Si cages, the attack of 1-MeI to the epoxy rings of POSS-EP8 is more hindered in comparison with the attack of 1-MeI to the epoxy rings from D.<sup>18</sup> As we already described in the FTIR section for this specimen the lowest curing degree was obtained; as a consequence the  $T_g$  value for 80D:20G/10POSS EP8 system is quite low.

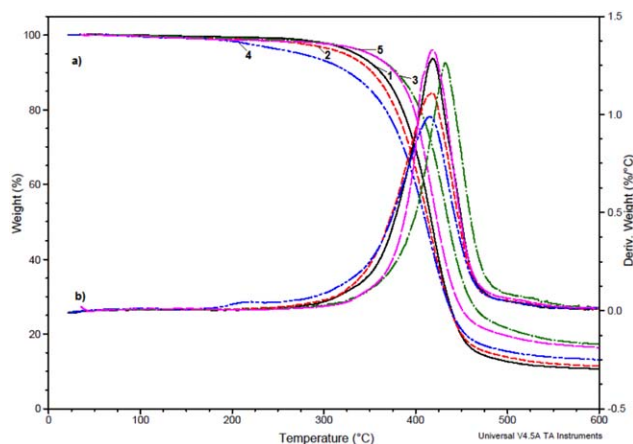
Parallel DMA investigations were also conducted for ternary copolymers 40B:20G:40D and their POSS hybrids (Figure 10). The inorganic nanofillers can dramatically alter the chain



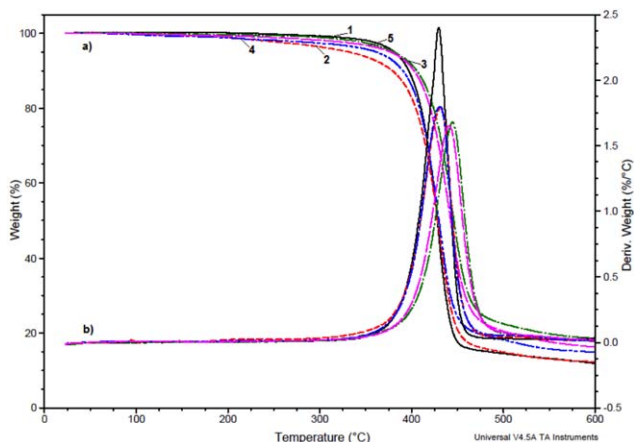
**Figure 10.** Tan  $\delta$  against temperature curves of ternary copolymers and their nanocomposites: 40B : 20G : 40D (1), 40B : 20G : 40D/10POSS MA1 (2), 40B : 20G : 40D/10POSS MA8 (3), 40B : 20G : 40D/10POSS EP1 (4), 40B : 20G : 40D/10POSS EP8 (5). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

kinetics due to the interface interactions of polymer chains with the POSS moieties.<sup>37–41</sup>

The  $\beta$  relaxation transition caused by the combined mobilities of the methacrylate and epoxy polymer chains appears to be well defined in comparison with binary systems.



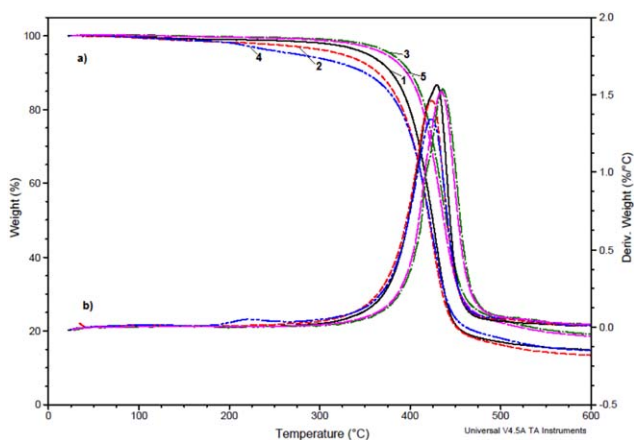
**Figure 11.** (a) TGA and (b) DTG plots of 80B : 20G sample (1) and the corresponding nanocomposites with POSS MA1 (2); POSS MA8 (3); POSS EP1 (4); POSS EP8 (5). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



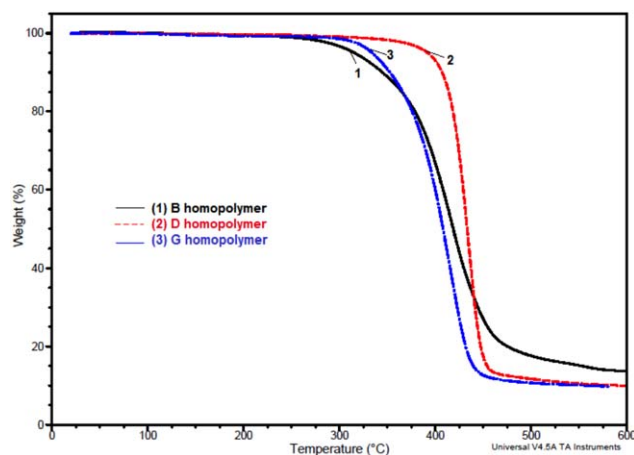
**Figure 12.** (a) TGA and (b) DTG plots of 80D : 20G sample (1) and the corresponding nanocomposites with POSS MA1 (2); POSS MA8 (3); POSS EP1 (4); POSS EP8 (5). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

One single broad  $T_g$  peak of methacrylate and epoxy components can be observed in the ternary copolymers and their nanocomposites. The tan  $\delta$  peaks of the hybrids containing POSS were markedly broader compared with the corresponding neat methacrylate/epoxy system. It was also found that the  $T_g$  of POSS based copolymers is dependent on the type (methacrylate/epoxy) and number of the organic substituents (mono, octa) on Si—O—Si cages.

Thus the incorporation of methacrylic POSS compounds within ternary copolymer (40B:20G:40D) leads to a decrease of  $T_g$  value. This can be explained by the high number of bonds established between methacrylic groups from POSS compounds and those from the copolymer, which leads to a higher degree of flexibility. This is more likely to occur than the explanation already reported,<sup>39–41</sup> according to which the bulky POSS cages could act as an internal plasticizer.



**Figure 13.** (a) TGA and (b) DTG plots of ternary copolymers and their nanocomposites: 40B : 20G : 40D (1), 40B : 20G : 40D/10POSS MA1 (2), 40B : 20G : 40D/10POSS MA8 (3), 40B : 20G : 40D/10POSS EP1 (4), 40B : 20G : 40D/10POSS EP8 (5). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 14.** TGA plots of B, D and G homopolymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

When POSS with epoxy groups were added to 40B:20G:40D ternary copolymer the  $T_g$  values are also decreased. In the presence of POSS EP8 the ternary copolymer gives the lowest value of  $T_g$  among all POSS reinforced ternary copolymers. This behavior is also attributed to the lower reactivity of epoxy groups attached to the POSS EP8 cages being consistent with DSC data.

The POSS-containing binary/ternary copolymers were also subject to **thermal analysis**. Figures 11–13 depict the TGA/DTG curves of the obtained binary and ternary copolymers and their POSS based nanocomposites in the temperature range from 30°C to 600°C.

All the curves have similar degradation shapes within the experimental temperature domain. The thermal decomposition, which occurs in one single step, demonstrates the compatibility between the used monomers. Moreover the presence of POSS cages does not significantly alter the degradation mechanism of the ternary copolymer matrix. Regarding the DTG plots of thermal decomposition no significant differences were observed.

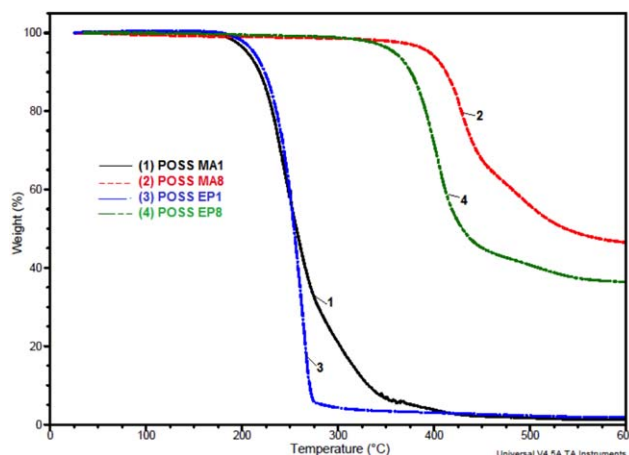
Firstly we have investigated the thermal degradation of the neat homopolymers in order to establish their thermostabilities (data shown in Figure 14). As we expected B homopolymer starts to degrade earlier ( $T_{\text{onset}5\%} = 315^\circ\text{C}$ ) than D homopolymer ( $T_{\text{onset}5\%} = 392^\circ\text{C}$ ) for the used curing/postcuring experimental protocol. G homopolymer exhibits an intermediary  $T_{\text{onset}}$  value ( $340^\circ\text{C}$ ).

From the Table II it can be observed that ternary copolymer 40B:20G:40D exhibits an intermediary thermostability between the two binary systems 80B:20G and 80D:20G.

**Table II.** Thermostability of the Obtained Organic–Inorganic Nanocomposites

	POSS MA1	POSS MA8	POSS EP1	POSS EP8	
$T_{\text{onset}5\%}$ (°C) <sup>a</sup>	295	395	212	358	
80B : 20G	335	323	349	275	350
80D : 20G	381	332	383	362	377
40B : 20G : 40D	353	325	380	275	372

<sup>a</sup>  $T_{\text{onset}} = 5\%$  weight loss temperature



**Figure 15.** TGA plots of mono- and octafunctional POSS compounds. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

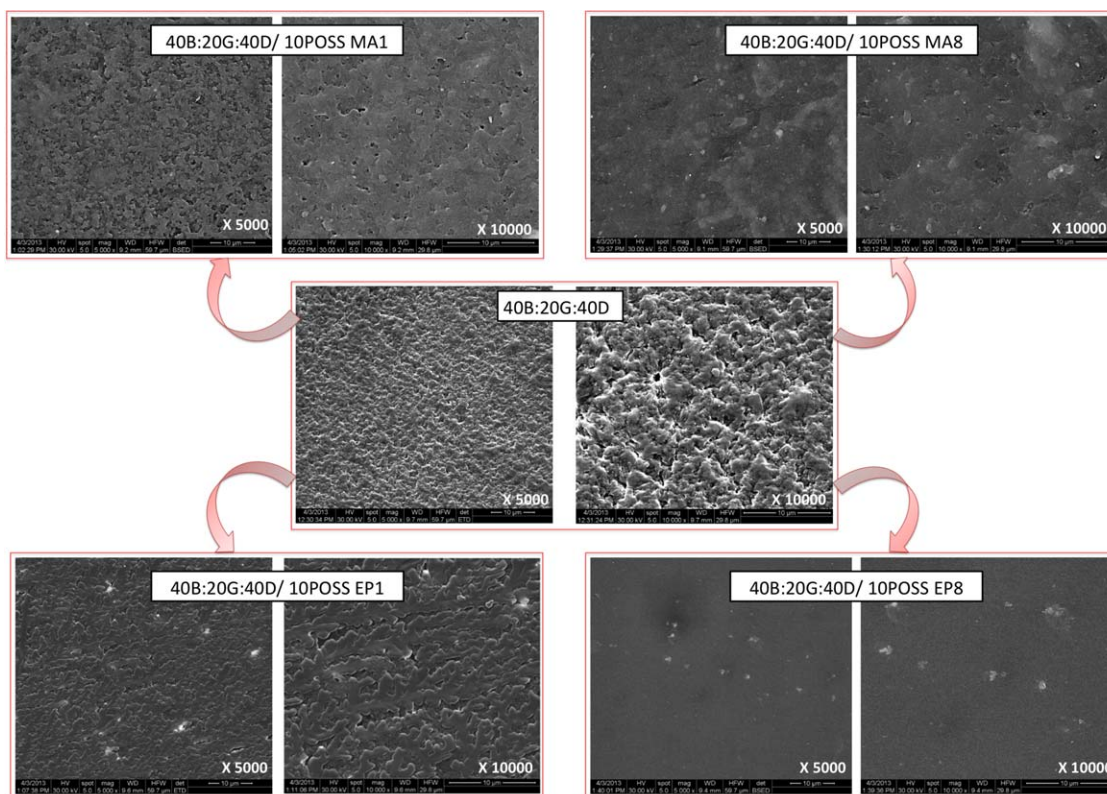
The selected mono-POSS compounds exhibit lower thermostabilities ( $295^\circ\text{C}$  for POSS MA1 and  $212^\circ\text{C}$  for POSS EP1) compared with octafunctional POSS units that show an enhanced thermal resistance ( $395^\circ\text{C}$  for POSS MA8 and  $358^\circ\text{C}$  for POSS EP8) (Figure 15).

The thermostability of the obtained nanocomposites is thus reduced when monofunctional POSS bearing methacrylate or epoxy reactive moieties are loaded within the binary or ternary copolymers. This behavior is the result of lower thermostability of mono-POSS compounds towards the neat polymeric matrices. The incorporation of POSS MA8, which possesses a good thermal stability, into the polymeric networks (binary or ternary) leads to the increase of thermostability. This improvement is due to multiple crosslinking points formed by the octafunctional POSS with the methacrylate chains from the matrix, this being the same reason for which the thermostability significantly increases for methacrylic binary system if POSS EP8 is added.

Concerning the ternary copolymers, the presence of octafunctional methacrylic or epoxy POSS compounds will cause an increase of thermostability confirming the hypothesis according to which a high number of bonds are formed between the POSS moieties and the functional groups from the monomers.<sup>42,43</sup>

SEM was further used to investigate the influence of POSS cages bearing one or eight methacrylate or epoxy reactive groups on the morphology of ternary copolymers. The SEM micrographs





**Figure 16.** SEM micrographs of the fractured samples of ternary copolymers and their corresponding nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

for all fractured surfaces frozen under cryogenic conditions using liquid nitrogen are displayed in Figure 16. SEM images exhibit different morphologies indicating that the functionality of silsesquioxane cages plays a significant role in the formation of covalent bonds with polymer matrix, which therefore can influence the final morphology of the studied samples. Thus by controlling both the type and the reactivity of the functional groups from the POSS cages, methacrylate-epoxy nanocomposites with different morphologies can be synthesized.

From SEM images it could be noticed that both unreinforced copolymer and their corresponding nanocomposites based on monofunctional POSS (POSS MA1 or POSS EP1 exhibit similar morphologies which means that similar polymer networks are formed. The most compact structure is gained for POSS EP8 based nanocomposite.

The most important parameter to achieve a well-dispersed polymer nanocomposite is the compatibility between POSS molecules and polymer matrix. In general, POSS molecules display a better dispersion with polymers than conventional fillers due to the presence of the organic substituents on the Si—O—Si cages.

An overall inspection of the SEM images suggests pronounced tendency to aggregate when POSS MA8 and POSS EP8 were loaded. The size and distribution of the POSS aggregates strongly depend on the type and strength of the intermolecular interactions. The interactions between POSS MA8 or POSS EP8

and the polymer matrix are unable to hinder the attraction force among of the POSS cores even if a premixing process was applied to promote uniform dispersion of the POSS derivatives.

POSS MA1 and POSS EP1 exhibit a better dispersability within their corresponding nanocomposites. Since each POSS molecule has a  $\text{Si}_8\text{O}_{12}$  cage covered with seven unreactive isobutyl groups and one methacrylate or epoxy reactive group, it is believed that better dispersion may result both from the chemical bonding of reactive POSS groups to polymer matrix and to an increased interaction between side unreactive groups and the organic matrix.

## CONCLUSIONS

To synthesize novel materials with distinct and improved properties, different methacrylate or epoxy POSS (POSS MA1, POSS MA8, POSS EP1, POSS EP8) were incorporated within methacrylate-epoxy binary or ternary copolymers (80B:20G, 80D:20G, 40B:20G:40D).

DSC and FTIR studies have been undertaken to establish the influence of POSS compounds on the curing behavior of methacrylate or epoxy functionalities from the resulting hybrid copolymers. The results reveal that both type and number of the organic groups from the POSS cages exhibit a significant influence on the curing behavior of methacrylic and epoxy groups from all the studied POSS-based copolymers. The polymerization of methacrylate groups from the ternary copolymers



is almost similar being less influenced by the formation of the crosslinked epoxy network. On the contrary the epoxy polymerization is significantly affected by the formation of crosslinked chains of methacrylate and moreover it is hindered by POSS cages agglomeration.

This strongly influences the final thermomechanical properties of the nanocomposites. Thus, the incorporation of POSS nanoparticles within the binary copolymers leads to an increase of  $T_g$  due to the effect of nanoreinforcement of POSS cages that could restrict the motions of macromolecular chains. For the ternary copolymers the presence of POSS compounds leads to a decrease of the  $T_g$  value for the synthesized nanocomposite regardless of the type or number of functional groups from the POSS cages.

Concerning the thermostability of the synthesized nanocomposites it may be concluded that this depends on the thermostability of POSS compounds. The thermostability of the obtained nanocomposites is thus reduced when monofunctional POSS are loaded within the binary or ternary copolymers due to the lower thermostability of mono-POSS compounds towards the neat polymeric matrices. The incorporation of octafunctional POSS, which possesses a good thermal stability, into the polymeric networks (binary or ternary copolymers) leads to nanocomposites with enhanced thermostability, which is probably due to the multiple crosslinking points formed by the octafunctional POSS with the reactive groups from the polymer matrix.

SEM images show that higher size of the POSS agglomerates is achieved for using octafunctional POSS within ternary copolymers even if multiple interactions are established between POSS functionalities and those from the monomers.

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