

Polymeric Nanocomposites Containing Polyhedral Oligomeric Silsesquioxanes Prepared via Frontal Polymerization

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Received 12 February 2007; accepted 24 April 2007

DOI: 10.1002/pola.22185

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Frontal polymerization (FP) has been successfully applied, for the first time, to obtain polymeric nanocomposites containing polyhedral oligomeric silsesquioxanes (POSS) in an amine-cured epoxy matrix. Variations of maximum temperature (T_{\max}) and front velocity (V_f) have been studied. A comparison of these products with the corresponding materials, obtained by the classical batch polymerization technique, demonstrated that FP allows a higher degree of conversion than batch polymerization. The products have been characterized in terms of their thermal behavior with DSC analysis. SEM and X-ray analyses revealed the morphology and the structures of the nanocomposites. The nanocomposites obtained by FP have the same characteristics of those synthesized, in much longer times, by batch polymerization. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 4514–4521, 2007

Keywords: electron microscopy; epoxy resin; frontal polymerization; nanocomposites; polyhedral oligomeric silsesquioxanes (POSS); X-ray

INTRODUCTION

The organic–inorganic nanocomposites, obtained by incorporating inorganic or organometallic blocks having nanoscale dimensions into organic polymers, combine the advantages of inorganic materials (mainly, stability and rigidity) with those of organic polymer (mostly, flexibility and processibility);^{1–4} for this reason, in the last decades the preparation of these materials has attracted considerable interest. These materials can be made via the sol-gel process,^{4–8} by inter-

calation and exfoliation of layered silicates with organic polymers,^{8–10} and by embedding polyhedral oligomeric silsesquioxanes (POSS).^{11–21} In POSS technology, a variety of polymerizable (or reactive) POSS macromers have been employed; sometimes, when reactive groups were present on the POSS structure, they were used to prepare copolymers with organic monomers thus affording organic–inorganic nanocomposites.^{11,12}

Silsesquioxanes are compounds with general formula $(\text{RSiO}_{1.5})_n$, where R is an organic group or hydrogen.^{12,22–26} They can have various geometrical structural architectures, including random, ladder, and cage structures; the latter are generally known as POSS. They can be considered as the smallest particles of organosilicon

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 45, 4514–4521 (2007)
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currently available, and their structure is an organic–inorganic hybrid, in which compatibility with the polymer matrix is ensured by the presence of the organic pendent groups linked to the inorganic POSS cage.

POSS have been used for a variety of applications, from low dielectric constant materials to new resists for electron beam lithography materials and high temperature lubricants.²⁷ Among the various applications of POSS, the preparation of polymer nanocomposites and hybrids, with the aim of obtaining multifunctional materials with intermediate properties, comprised between those of organic polymers and of ceramics, is actually one of the most important fields. Indeed, POSSs have been successfully used to improve polymer properties such as oxidation resistance, temperature, and mechanical properties; in some cases, an interesting reduction of polymer flammability was reached.^{28,29}

In the present article, we describe the first preparation of nanocomposites containing POSS by using frontal polymerization (FP). FP uses the exothermicity of the polymerization reaction to promote the conversion of the monomer into polymer. If the amount of dissipated heat is not too large, a sufficient amount of energy able to induce the polymerization of the monomer close to the hot zone is provided. The result is the formation of a hot polymerization front capable of propagating through the reactor.

Among the advantages of this method one can mention: high reaction rate, short reaction time, low energy consumption, and the possibility of conducting polymerization in an ecologically friendly way, avoiding additional solvent (if conversion is sufficiently high so that no solvent-based purification is required).

Initially investigated by Chechilo et al.,³⁰ FP was lately extensively studied by Pojman and coworkers who polymerized acrylic monomers^{31–33} and epoxy resins.³⁴ In recent years, Mariani and coworkers have extended the use of the FP technique to other polymerizing systems, specifically dicyclopentadiene,³⁵ polyurethanes^{36,37} interpenetrating polymer networks³⁸ an unsaturated polyester/styrene.³⁹ Several applications of FP have been proposed: White and coworkers investigated the curing of epoxy-based materials,⁴⁰ Pojman and coworkers prepared thermochromic composites⁴¹ and polymer-dispersed liquid crystal (PDLC) materials,⁴² Morbidelli and coworkers obtained homogenous polymer blends⁴³ and copolymers,⁴⁴ Washington and Steinbock

synthesized hydrogels,⁴⁵ Mariani et al. prepared PDLC films⁴⁶ and applied FP to the consolidation of porous materials.⁴⁷ There are several patents relating to frontal polymerization.^{48–54} Pojman et al. demonstrated FP with thiol-ene chemistry.⁵⁵ McFardland et al. studied FP with microencapsulated initiators.^{56,57}

Crivello studied the design and synthesis of glycidyl ethers that undergo frontal polymerization.^{58,59} Recently, Hu frontally copolymerized urethane-acrylates.⁶⁰

A current comprehensive bibliography of frontal polymerization can be obtained at <http://pojman.com/FP.html>.

In this work, we report the synthesis of epoxy resins containing POSS by FP and classical (batch) polymerization and their characterization with differential scanning calorimetry (DSC), SEM, and X-ray analysis.

EXPERIMENTAL

Front temperature measurements were made with a K-type thermocouple connected to a digital thermometer reader Delta Ohm model DO 9416. DSC measurements were obtained with a DSC Q100 Waters TA Instruments in a temperature range between -100 and $+250$ °C, with a heating rate of 10 °C/min, under argon atmosphere.

The Si distribution was determined by SEM-EDS analysis using a Leo Steroscan-440 scanning electron microscopy, equipped with an EDS system (Oxford Link-Gem). Samples were prepared by freezing pieces of the extruded strand in liquid nitrogen followed by high-speed impact to create fresh fracture surfaces and coated with carbon before analysis.

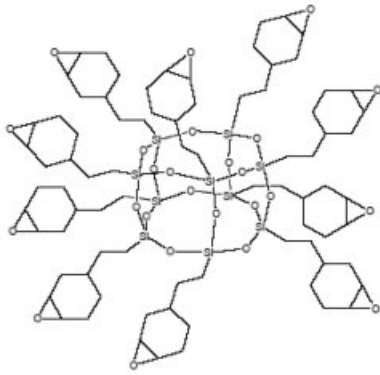
X-ray analysis was performed on an X-Ray Diffractometer (PHILIPS by Bragg-Brentano geometry using Ni-filtered Cu $K_{\alpha 1}$).

Wide angle X-ray diffraction (WAXD) patterns were recorded using a Philips PW 1830 powder diffractometer (Ni-filtered Cu K_{α} radiation).

TGA measurements were performed using a TA Instrument thermobalance, TGA 2050, under either nitrogen or air flow, at a heating rate of 10 °C/min. Samples prepared by using both FP and batch polymerizations are characterized by the same degradation behavior, namely they decompose in nitrogen in a single step at 360 °C, while in air the degradation consists of two peaks (360 and 560 °C).

Materials

All materials were used as received.

<p>EP0408.0503</p> <p>EpoxyCyclohexyl-POSS Cage Mixture, 60%</p> <p>$n = 8$ (15%), 10 (67%), 12 (18%) ($n = 10$ shown)</p> <p>$C_{80}H_{130}O_{25}Si_{10}$</p> <p>Appearance: glassy, yellow, solid</p> <p>M_w average: 1791</p> <p>from <i>Hybrid Plastics</i></p>	
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Methodology

In the system, the epoxy groups are not only from DGEBA but also from polyhedral oligomeric silsesquioxanes (POSS). The ratio of epoxy to amine hydrogens was maintained at (4:5), but the proportion of epoxy groups derived from DGEBA and POSS was allowed to vary. Different mixtures of DGEBA, DETA, and POSS were prepared, with variable content of the epoxy groups: 0, 1, 3, 5, 7, 10 mol % of epoxy groups deriving from POSS (Table 1). Pot life of the mixture at room temperature exceeded 4 h.

Each mixture was used for two kinds of synthesis: frontal polymerization and batch (classical) polymerization (oil bath, 80 °C, 1 h).

The POSS resin was not pure but contained a large quantity of impurities (40% of “unknown resin,” hereinafter UR), reported to be chemically inert. All the stoichiometric calculations take this fact into account. The resin interacted physically with the system, by removing heat

from the polymerization front, varying the total C_p , and influencing T_g values of the final polymers. The effect was more evident as the POSS content increased. For example, in sample F1, the content of inert resin was 0.6 wt % only; whereas, F10 contained 5.50 wt % of inert resin.

Only mixtures having a POSS content ranging from 0 to 10% allowed FP to be carried out. For larger quantity FP stopped due to: (i) convective fingering; (ii) increase of inert resin concentration, which slowed the rate of reaction by both lowering the concentration of reagents and by absorbing heat and thus lowering the front temperature (Table 1).

Frontal Polymerization

In a typical run, a nonadiabatic glass test tube (inner diameter: 0.8 cm, length: 5.3 cm) was loaded with an appropriate quantity of a DGEBA/DETA/POSS mixture (mixture height was always 4.0 cm).

Table 1. Quantity of Reagents Used

Samples		Epoxy Groups Deriving from POSS (mol %)	POSS (wt %)	UR (wt %)	POSS + UR (wt %)
FP	Batch				
F0	B0	0	0	0	0
F1	B1	1	0.90	0.60	1.50
F3	B3	3	2.67	1.78	4.45
F5	B5	5	4.40	2.94	7.34
F7	B7	7	6.08	4.05	10.13
F10	B10	10	8.24	5.50	13.74

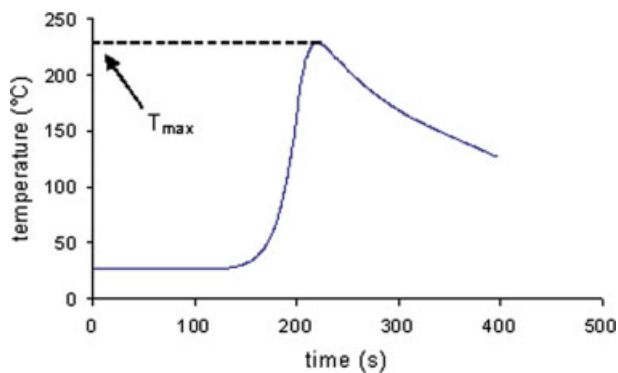


Figure 1. Temperature profile of a self-propagating front (sample F1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

A K-type thermocouple was placed into the above mixtures and located at about 1 cm from the bottom of the tube. Temperature was monitored with a digital thermocouple reader. FP reactions were ignited by heating the external wall of the tube in correspondence of the upper surface of the mixture until the formation of the traveling front became evident. Position of the front as a function of time was recorded from the first centimeter of propagation, and V_f calculated.

Batch Polymerization

The same DGEBA/DETA/POSS mixtures were also polymerized by the standard batch method in reactors placed in a thermostatic oil bath set at 80 °C for 1 h.

RESULTS AND DISCUSSION

Figure 1 shows a typical temperature profile. As can be seen, the temperature value recorded by

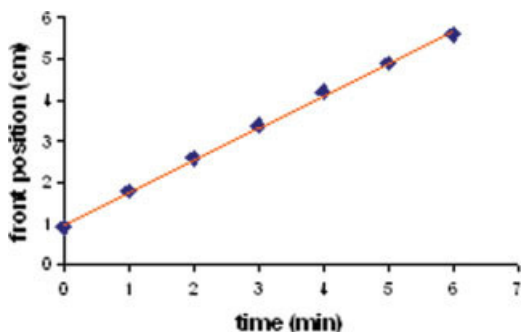


Figure 2. Front position as a function of time (sample F1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

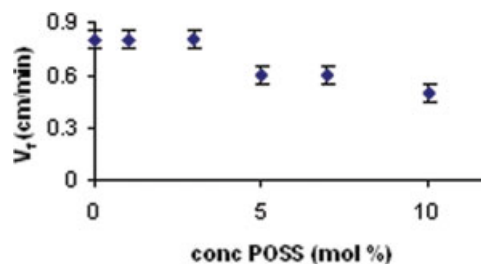


Figure 3. Front velocity as a function of POSS content (mol %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the thermocouple remains constant until front crosses its junction. This indicates that pure FP is occurring. Indeed, if it were not the case, due to the exothermicity of a possible simultaneous polymerization reaction, a progressive temperature increase should be observed. The maximum temperature reached by the front, T_{max} , one of the main parameters generally taken into account in this kind of study, is also indicated and defined.

As can be seen in Figure 2, which refers to a typical example (sample F1), the front velocity (V_f) remained constant during the entire experiment, further confirming that pure frontal polymerization was occurring without batch polymerization.

For each FP run, V_f and T_{max} were recorded. Figures 3 and 4 show the behaviors of these parameters as functions of POSS content.

V_f values range from 0.8 cm/min (0% POSS mixture) to 0.5 cm/min (10% POSS mixture) thus becoming lower as the POSS concentration increases. T_{max} values decrease from 239 °C (0% POSS mixture) to 187 °C (10% POSS mixture).

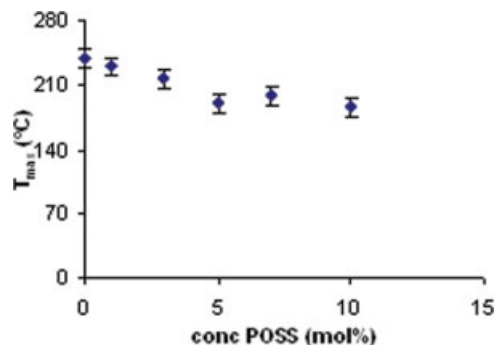


Figure 4. Front maximum temperature as a function of POSS content (mol %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

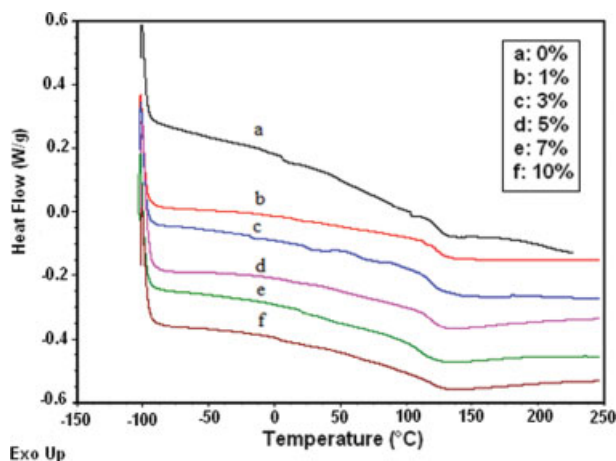


Figure 5. DSC first scans on the FP samples at different content of POSS. Percentage indicates the mole percentage of epoxy groups deriving from POSS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

This occurs for two reasons. These results are consistent with the 40% of the POSS resin that is inert acting as a heat sink and as a diluent to the second-order epoxy-amine reaction.

Characterization of the Nanocomposites

We investigated some of their thermal properties of nanocomposites obtained by FP and those prepared by batch polymerization. For each FP and BATCH sample, two heating ramps were carried out, from -100 to 250 °C. The first scans

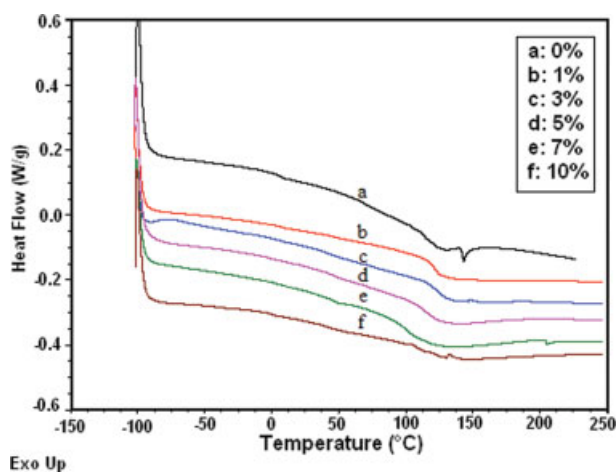


Figure 6. DSC first scans on the BATCH samples at different content of POSS. Percentage indicates the mole percentage of epoxy groups deriving from POSS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

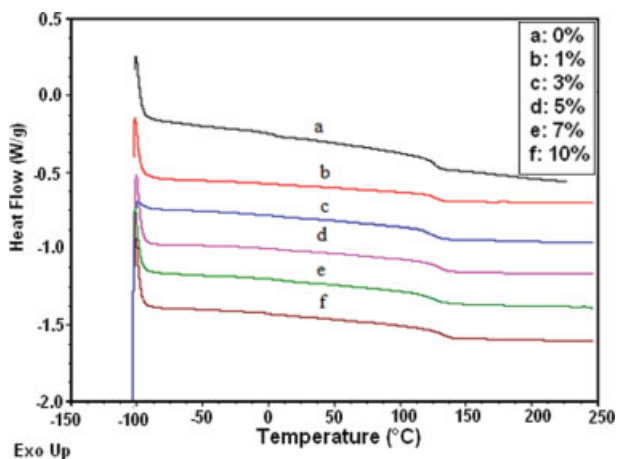


Figure 7. DSC second scans on the FP samples at different content of POSS. Percentage indicates the mole percentage of epoxy groups deriving from POSS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(Figs. 5 and 6) were performed to determine the residual polymerization enthalpy for calculating the degree of conversion. The second scans (Figs. 7 and 8) were done to determine glass transition temperatures (T_g).

In Figures 5–8, two transition temperatures are evident: T_{g1} , at lower temperatures (in the range from -3 to 23 °C), and T_{g2} , at higher temperatures (in the range from 100 to 134 °C). In the first scans of both FP and BATCH composites (Figs. 5 and 6, respectively), some irregularities are evident; they are probably due to the presence of impurities and/or unreacted low mo-

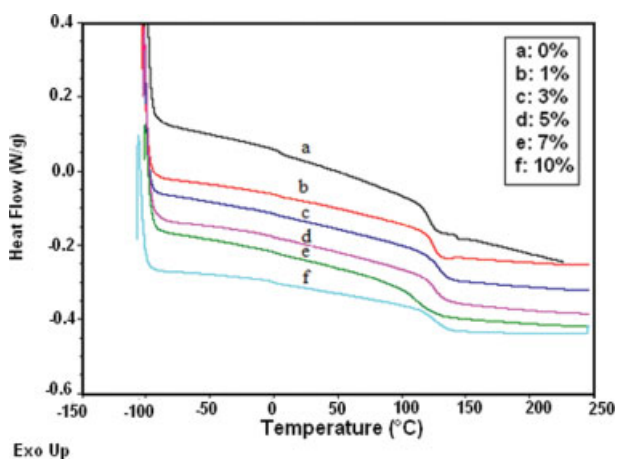


Figure 8. DSC second scans on the BATCH samples at different content of POSS. Percentage indicates the mole percentage of epoxy groups deriving from POSS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

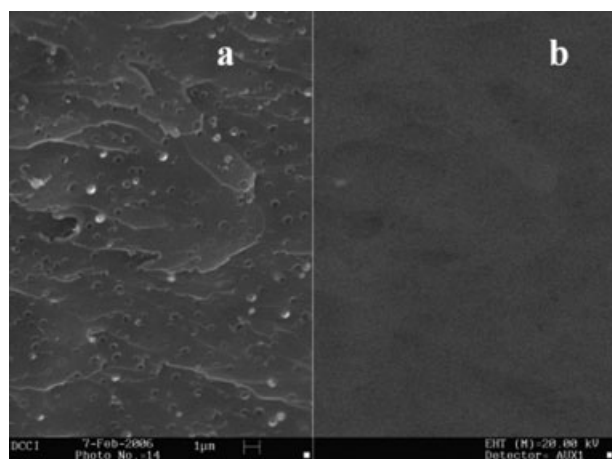
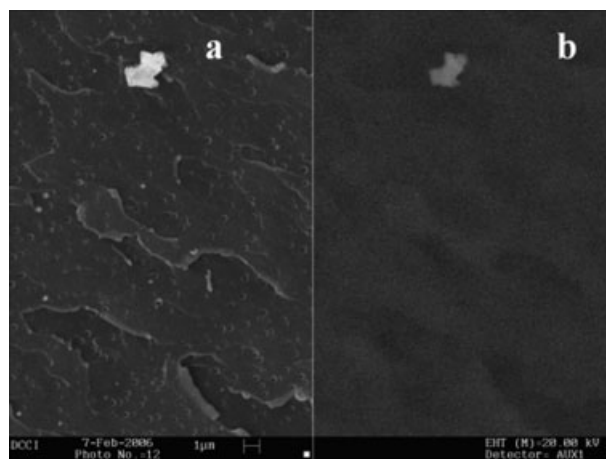
Table 2. Residual Polymerization Enthalpy

Polymer	Residual ΔH (J/g)	Total ΔH (J/g)	Degree of Conversion (%)
B0	0	-553.8	100
F0	0	-553.8	100
B1	0	-507.6	100
F1	0	-507.6	100
B3	0	-503.0	100
F3	0	-503.0	100
B5	-2.44	-522.9	99.5
F5	0	-522.9	100
B7	-2.87	-476.9	99.4
F7	-2.59	-476.9	99.5
B10	0	-475.8	100
F10	0	-475.8	100

lecular weight molecules that act as plasticizers. These irregularities disappear in the second scan (Figs. 7 and 8), since the low molecular weights products can react, thus being included in the polymer chains, or evaporate.

Some differences can be noticed between the scans: (i) T_{g1} decreases; (ii) T_{g2} increases. This latter finding can be explained by the total conversion and, more generally, to the possible elimination of low molecular weight products achieved during the first heating. No explanation can be proposed for the corresponding T_{g1} behavior.

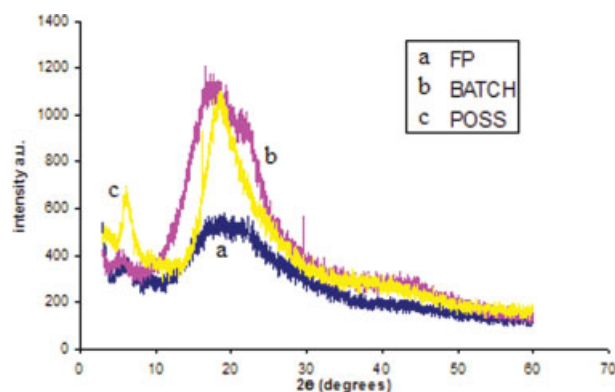
By comparing FP and BATCH nanocomposites, it can be stated that the former show T_g values that are slightly higher than those obtained by BATCH polymerization. Since these data cannot be explained in terms of different

**Figure 9.** SEM micrograph of sample B5: (a) SE emission, (b) BS emission.**Figure 10.** SEM micrograph of sample F5: (a) SE emission, (b) BS emission.

conversion (see below) and are reproducible, they will be object of future research.

DSC measurements were done to calculate conversion. The results are listed in Table 2, which shows that quantitative yields were obtained independently of the polymerization method. However, it is noteworthy that FP samples were prepared in significantly less time (about 5 min, depending on the composition) than the batch samples (1 h).

Samples prepared by FP and batch polymerization, characterized by various content of POSS (B3 and F3, B5 and F5, B10 and F10), have been examined in detail by scanning electron microscopy (SEM). Figures 9 and 10 compare the micrographs of B5 and F5 by secondary electron emission (SE) and those by back scattering (BS) emission. BS emission allowed us to identify the presence and distribution of Si in

**Figure 11.** X-ray diffraction pattern of the F5 (a), B5 (b), and of POSS (c) samples.

the polymer matrix and hence to study POSS dispersion.

As shown in the above figures, independent of the POSS content, in all samples no Si aggregates are present in the composite. Moreover, the inorganic filler seems to be uniformly distributed. Similar results have been obtained analyzing the other mentioned composites. Although more analysis of the Si dispersion is necessary, these findings indicate formation of nanostructured materials. It is relevant to underline that, as far as POSS distribution is concerned, both polymerization methods produced similar materials.

To study the organization of the POSS molecules in the polymer matrix, X-ray measurements were performed. We focused on the characterization of the neat POSS used (Fig. 11, curve c). The low number and the broadness of the peaks of the epoxy silsesquioxane X-ray diffraction pattern demonstrates its low degree of crystallinity and indicates, once again, the low purity of the sample.

Figure 11 shows the X-ray diffraction pattern of the samples B5 (curve b) and F5 (curve a). The comparison of the above spectra with that of the neat POSS indicates that the crystalline peaks at around 6° and 19° of 2θ in the composite diffraction patterns are POSS signals.

This finding indicates the presence of POSS aggregates, which maintain their crystalline organization and, due to their small dimension, are not visible by SEM. Nevertheless, it is relevant to point out that a similar crystalline organization of POSS was found also in nanostructured materials, such as nanocomposites based on polyethylene (PE),⁶¹ and polyamide 6 (PA6).⁶² In these cases, POSS units, incorporated as pendant groups to the PE backbone or as one end of each PA6 chain, turned out to aggregate and crystallize as nanocrystals. On this basis, WAXD characterization has always to be considered in conjunction with SEM analysis.

CONCLUSIONS

We prepared for the first time by frontal polymerization, polymeric nanocomposites containing POSS in an amine-cured epoxy matrix. The POSS molecules contained epoxy groups that were copolymerized with diglycidyl ether of bisphenol A and diethylenetriamine. Samples prepared by frontal polymerization had higher

T_g s than those prepared by batch polymerization at 80°C . The distribution of the POSS was the same for both types of samples, as revealed by SEM. X-ray analysis indicated the presence of POSS aggregates.

We thank Hybrid Plastics (Hattiesburg, MS) for the POSS-epoxy monomer.

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