

# Synthesis and Characterization of Epoxy Resin-Montmorillonite Nanocomposites Obtained by Frontal Polymerization

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**ABSTRACT:** Frontal polymerization, a method that allows to convert a monomer into a polymer exploiting the exothermicity of the self-same polymerization reaction, has been conveniently used for the easy and fast preparation of epoxy resin-montmorillonite nanocomposites. The obtained materials have shown characteristics similar or even better than those prepared by the conventional polymerization routes. The synthetic methods and the thorough characterization of the obtained nanocomposites are described. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 2204–2211, 2007  
**Keywords:** frontal polymerization; nanocomposites; synthesis; TEM; thermosets; X-ray

## INTRODUCTION

Frontal Polymerization (FP) is a method that allows to convert a monomer into a polymer exploiting the exothermicity of the self-same polymerization reaction. If the heat dissipated is not excessive, the quantity of energy left over may be sufficient to induce the polymerization of the monomer layer close to the zone heated by the reaction. As a result, a hot propagating and self-sustaining front can be observed (Fig. 1).

As it happens in many frontal reactions, FP runs are generally characterized by a constant velocity of the front ( $V_f$ , Fig. 2). In Figure 3, a typical FP temperature profile is depicted with the definition of  $T_{\max}$ ; this is the maximum tem-

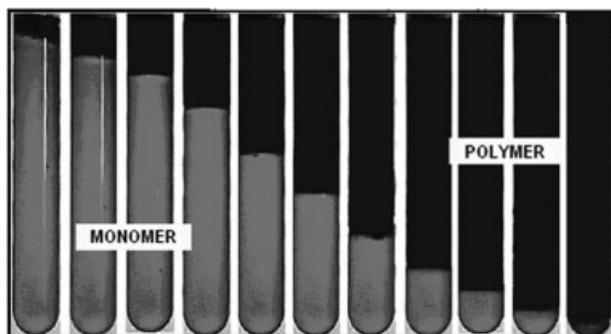
perature experimented by the thermocouple junction corresponding to the front temperature.

The first FP studies date back to the 70s when Chechilo and Enilkopyan frontally polymerized methyl methacrylate under high pressure.<sup>1,2</sup> Since then, several other fundamental studies have been pursued in this field; in particular, they dealt with: macrokinetic and dynamic behaviors,<sup>3–7</sup> frontal copolymerization,<sup>8</sup> the preparation of thermochromic composites,<sup>9</sup> IPNs,<sup>6</sup> polymer-dispersed liquid crystal materials,<sup>10</sup> functionally gradient materials,<sup>11–13</sup> composites,<sup>14</sup> nanocomposites,<sup>15,16</sup> hydrogels,<sup>17</sup> the design and synthesis of suitable glycidyl ethers that can be frontally polymerized.<sup>18</sup>

In recent years, our research group has embarked upon the study of the FP potentiality. We have studied new frontally polymerizable systems.<sup>19</sup> Namely, our research interests deal with polyurethanes,<sup>20,21</sup> polydicyclopentadiene,<sup>22</sup>

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**Figure 1.** Images acquired in temporal sequence of a self-propagating polymerization front. (Sample 02. Total time = 11 min; tube height = 10 cm.)

polyacrylates,<sup>23</sup> interpenetrating polymer networks,<sup>24</sup> unsaturated polyester resins,<sup>25,26</sup> and epoxy resins.<sup>27</sup>

Furthermore, we applied FP to the preparation of thin polymer dispersed liquid crystal films,<sup>28</sup> and to the consolidation of porous materials, in particular those potentially having interest in cultural heritage (stone, wood, paper).<sup>29–31</sup>

Among the advantages of such technique, we remind here, are as follows:

- FP runs are faster than the traditional polymerization routes (generally, a few minutes instead of hours);
- conversions are often almost quantitative;<sup>20,22,25,26</sup>
- thermal and mechanical properties are comparable or even better than those characterizing the materials traditionally obtained;
- FP is an environmentally friendly technique inasmuch as it does not need external energy supplying except that necessary to locally ignite it (ignition time takes only a few seconds).

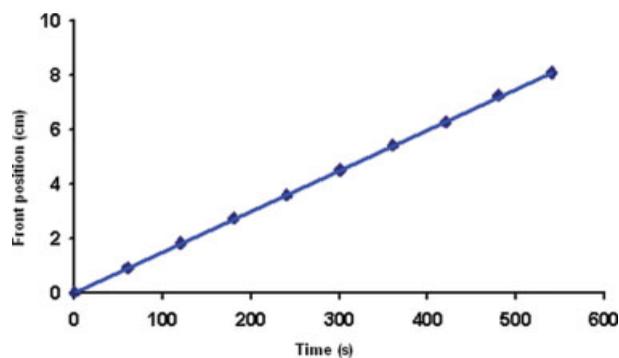
The continuous increase of the scientific production on composites and nanocomposites has suggested us to use FP for the synthesis of such materials. Indeed, several papers already concern FP performed in the presence of fillers as, thanks to the large quantity of heat released which characterizes FP runs, it is possible to incorporate an inert filler into a polymer matrix without negatively affecting front propagation. Thus, by using proper filling materials, it is possible to produce composites by FP. Some existing examples are

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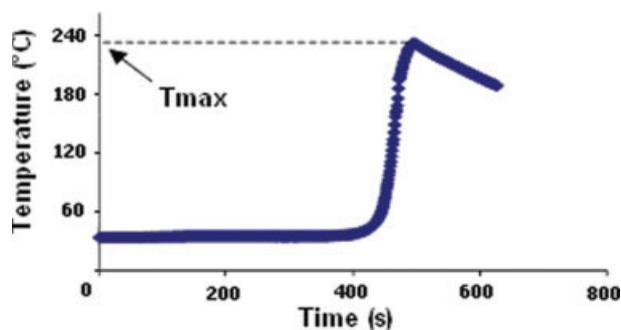
described in refs. 9 and 32 [in which thermotropic composites have been synthesized by incorporating a cobalt(II) salt in an acrylic matrix], ref. 10 (in which a nematic liquid-crystal has been embedded in an epoxy matrix), ref. 20 (in which nanoscopic silica-based agents with specific large surface area have been added for the production of polyurethanes), and ref. 15 (in which polyurethane-nanosilica hybrids have been prepared by encapsulating silica).

Nanocomposites are a relatively new class of composites in which at least one-dimension of the dispersed particles is in the nanometer range.<sup>33,34</sup> Three types of nanocomposite fillers can be distinguished. If the three-dimensions are all in nanometer range, it is the case of iso-dimensional nanoparticles (spherical silica nanoparticles, semiconductor nanoclusters, etc.). The second category includes nanotubes or whiskers as, for instance, carbon nanotubes or cellulose whiskers: these are characterized by two-dimensions in the nanometer scale whereas the third one is much larger, forming an elongated structure. The third type of fillers is characterized by only one-dimension in the nanometer range. In this case, the filler is present in the form of sheets that are few nanometer thick and hundreds to thousands nanometer long. These latter nanocomposites are almost exclusively obtained by intercalation of the polymer (or a monomer to be subsequently polymerized) inside the galleries of layered materials. As it is well-known, organically-modified phyllosilicates are the most widely used nanofillers among the species belonging to the third aforementioned class.<sup>33,34</sup>

As mentioned earlier, in situ intercalative polymerization is one of the techniques available



**Figure 2.** Front position as a function of time (sample 02). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 3.** Typical temperature profile recorded during a FP run (sample 02). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

for the synthesis of polymer-layered silicate nanocomposites. In particular, in this method a liquid monomer (or a monomer solution) infiltrates inside the silicate layers, swelling them and allowing the polymer formation in between the intercalated sheets.

A large variety of polymer systems are used in nanocomposite preparation with layered silicates:<sup>10</sup> vinyl polymers, epoxy resins, polyolefins, *N*-heterocyclic polymers, liquid crystalline polymers, hyperbranched polymers, biodegradable polymers being just some examples.

Taking into account all previous considerations, in the present work we explored the feasibility of preparing polymer/clay nanocomposite by means of in situ intercalative FP. The samples obtained were characterized and compared with analogous materials prepared by the classical method.

## EXPERIMENTAL

### Materials

Bisphenol A diglycidyl ether (DGEBA; FW = 340.4), diethylene triamine (DETA), tris(2-aminoethyl)amine (TREN) were purchased from Aldrich. Sodium montmorillonite (cloisite Na<sup>®</sup>, C—Na) and cloisite 30B<sup>®</sup> (C30B), characterized by particle size of less than 13  $\mu\text{m}$ , were supplied by Southern Clay. C30B is an organoclay, made organophilic by ion exchange of pristine alkaline cations with methyl, tallow, *bis*-2-hydroxyethyl quaternary ammonium chloride. C—Na has an exchange capacity of 92.6 meq/100 g clay. All materials were used as received, without further purification.

The temperature profiles of each synthesis were measured using a K-type thermocouple, the junction of which was placed at  $\sim 5$  cm from the upper surface of the mixture. The thermocouple was connected to a digital thermometer used for reading and recording of temperature. The position of the front (easily visible through the glass wall of test tubes, Fig. 1) against time was also measured ( $\pm 0.2$  mm).

Wide angle X-ray diffraction (WAXD) patterns were recorded using a Philips PW 1830 powder diffractometer (Ni-filtered Cu K $\alpha$  radiation). TEM measurements were performed by a high-resolution transmission electron microscope (GEOL 2010). Ultrathin sections, about 100-nm thick, were cut with a Power TOME X microtome equipped with a diamond knife and placed on a 200-mesh copper grid.

Starting from two sets of mixture compositions, a large number of experiments, both via FP and via Classic Polymerization (CP), were performed: no pretreatment was carried out on a first series (SET-0), whereas a second series (SET-1) was subjected to a specific pretreatment. For each set of FP runs, an analogous series of experiments was performed by the classic method. All curing reactions between epoxies and amines were accomplished at a fixed ratio between oxiranic rings and amino hydrogens. In addition, to be sure that all epoxy groups had reacted at the end of the curing process, all polymerizations were performed with an excess of aminic hydrogens (five aminic hydrogens for three epoxy rings).

SET-0 includes all reacting mixtures that are prepared as follows: DGEBA was poured into a glass test tube (inner diameter, 16 mm), and afterwards the desired amounts of clay were added. The mixture was homogenized, then the amine was poured into it and the mixture homogenized again. This mixture was placed in an ice bath for 20 min (to avoid spontaneous polymerization during the homogenization period); then it was removed from the bath, allowed to reach room temperature. Immediately, it was polymerized by the specific method (CP or FP).

SET-1 refers to all samples, which are prepared as follows: DGEBA was poured into a glass test tube (inner diameter, 16 mm), afterwards the desired amounts of clay were added. The mixture was homogenized and then placed (without the crosslinking agent) in an oil bath set at 90 °C (this operation is a well-known facilitating method to allow intercalation and/or

exfoliation processes in between the clay plies). After 1 h, the mixture was removed from the bath, allowed to reach room temperature, and then the amine was added. Also in this case, the mixture was placed in an ice bath for 20 min, afterwards it was removed and allowed to reach room temperature. Immediately, it was polymerized by the chosen technique (FP or CP).

To compare FP and CP, some mixtures (marked with an asterisk in Tables 1 and 2) were polymerized by two different classical batch methods. Method A: 4 h at 100 °C; 16 h at 150 °C; 12 h at 200 °C (SET-1A was pretreated; SET-0A was not). Method B: 24 h at room temperature, 4 h at 100 °C (SET-1B was pretreated; SET-0B was not).

All FP reactions were ignited by applying some heat to the portion of the mixture close to the upper surface using the tip of a soldering iron until the formation of a hot propagation front was noted.

## RESULTS AND DISCUSSION

### Synthesis

The aim of the present work concerns the exploitation of FP for the preparation of epoxy-based nanocomposites containing different amounts of C30B and C—Na.

Analogously to what was done in our previous works on FP, the characteristics of the samples synthesized by means of FP have been compared with those of the corresponding samples prepared by common batch polymerization methods (CP). At the same time, the effect of a thermal pretreat-

ment of the mixture has been investigated. As is well known, a phyllosilicate-containing nanocomposite shows typical thermal and mechanical characteristics that are related to the extent of intercalation and/or exfoliation of the filler.<sup>33</sup> A preliminary thermal treatment of the clay under stirring (typical procedure is 1 h at 90 °C, as adopted also in the present work) coupled, when necessary, to a sonication process of the same mixture, promotes the insertion of the monomer molecules between the clay plies.

DETA (one of the amines most widely used together with DGEBA) and TREN have been adopted as curing agents.

The experimental data relating to SET-0 and SET-1 are listed in Tables 1 and 2, respectively.

In Figure 4, the plots relating  $T_{\max}$  and  $V_f$  of the above sets of experiments as functions of the concentration of C30B (with DETA as curing agent), with and without pretreatment are shown. Figure 5 displays the corresponding graphs related to samples cured by TREN.

As can be seen in Figures 4 and 5, from a general point of view the increase of C30B content determines a decrease for both  $T_{\max}$  and  $V_f$ . Such trend is present independently of whether the samples had been subjected to the pretreatment or not, and independently of the kind of amine used as curing agent. Such trends are easily explainable in terms of the increase of clay content which to a first approximation, may be considered an inert material. As expected, increasing its amount results in a corresponding decrease in both  $T_{\max}$  and  $V_f$ . Indeed, the higher the amount of filler, the smaller the quantity of released heat per volume unit, and the larger the amount of dissipated heat.

**Table 1.** SET-0 of Composite Samples

DGEBA = $1.08 \times 10^{-2}$ mol, DETA = $7.20 \times 10^{-3}$ mol						DGEBA = $1.02 \times 10^{-2}$ mol, TREN = $6.00 \times 10^{-3}$ mol					
Sample	C30B (wt %)	$T_{\max}$ (°C)	$V_f$ (cm/min)	SET-0A	SET-0B	Sample	C30B (wt %)	$T_{\max}$ (°C)	$V_f$ (cm/min)	SET-0A	SET-0B
01	0.0	236	0.92			09	0.0	226	0.95		
02	1.0	233	0.90	*	*	10	1.0	232	0.92	*	*
03	2.0	232	0.85			11	2.0	221	0.80		
04	3.0	226	0.80	*	*	12	3.0	225	0.80	*	*
05	4.0	221	0.80			13	4.0	209	0.80		
06	5.0	223	0.80	*	*	14	5.0	210	0.80	*	*
07	7.5	203	0.78			15	7.5	213	0.80		

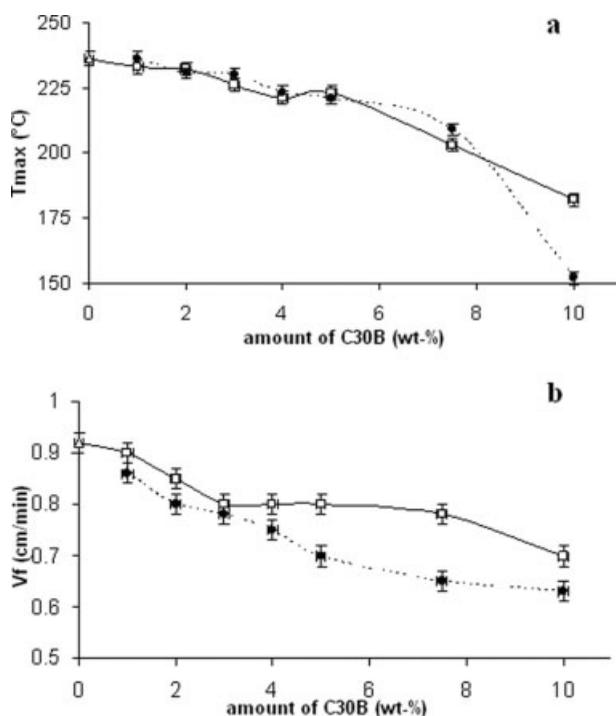
\*Sample obtained by CP (Method A: 4 h at 100 °C; 16 h at 150 °C; 12 h at 200 °C; Method B: 24 h at room temperature, 4 h at 100 °C).

**Table 2.** SET-1 of Composite Samples

DGEBA = $1.08 \times 10^{-2}$ mol, DETA = $7.20 \times 10^{-3}$ mol						DGEBA = $1.02 \times 10^{-2}$ mol, TREN = $6.00 \times 10^{-3}$ mol					
Sample	C30B (wt %)	$T_{\max}$ (°C)	$V_f$ (cm/min)	SET-0A	SET-0B	Sample	C30B (wt %)	$T_{\max}$ (°C)	$V_f$ (cm/min)	SET-0	SET-0B
17	1.0	236	0.86	*	*	24	1.0	220	0.80	*	*
18	2.0	231	0.80			25	2.0	215	0.78		
19	3.0	230	0.78	*	*	26	3.0	210	0.78	*	*
20	4.0	223	0.75			27	4.0	218	0.78		
21	5.0	221	0.70	*	*	28	5.0	210	0.68	*	*
22	7.5	209	0.65			29	7.5	188	0.66		
23	10.0	152	0.63	*	*	30	10.0	188	0.65	*	*

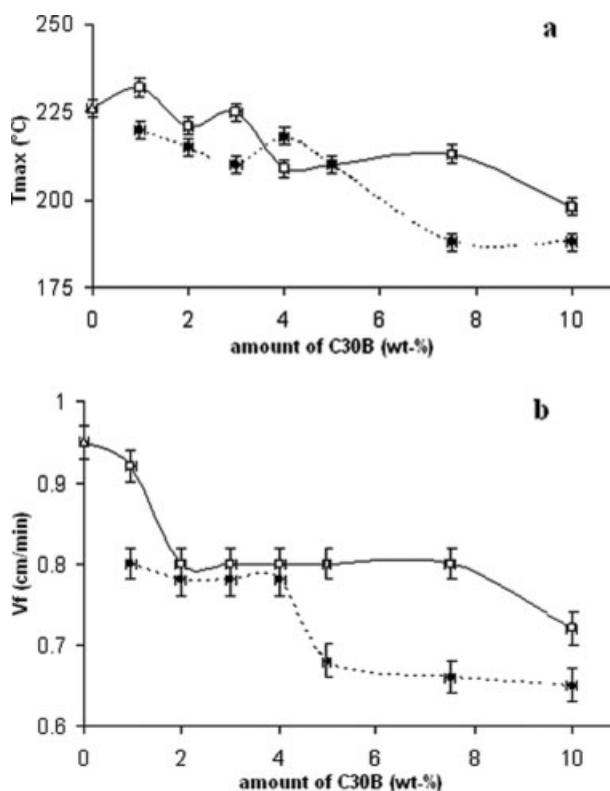
\*Sample obtained by CP (Method A: 4 h at 100 °C; 16 h at 150 °C; 12 h at 200 °C; Method B: 24 h at room temperature, 4 h at 100 °C).

In Figure 4(a) (curing agent: DETA) it is noteworthy that the pretreatment has a very low influence on  $T_{\max}$ ; in fact,  $T_{\max}$  data for thermally-treated or untreated samples are characterized by very similar values, the only significant discrepancy being found in the runs performed with 10.0 wt % of C30B (182 °C for sample 8, 152 °C for pretreated sample 23). Figure 5(a) (curing agent: TREN), besides dis-

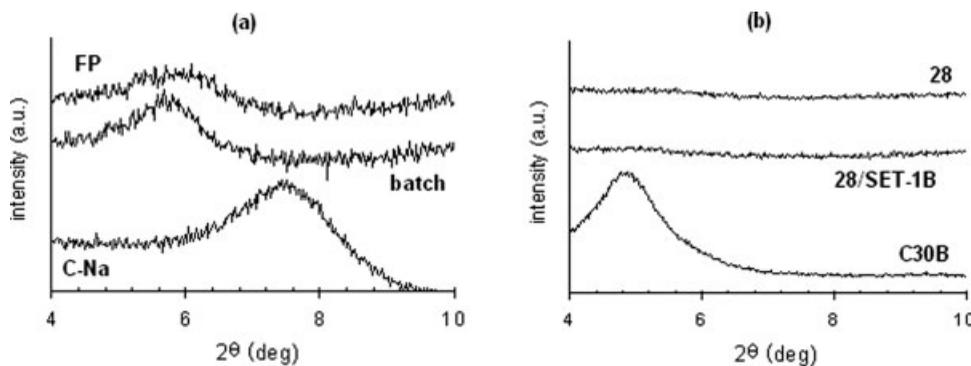


**Figure 4.**  $T_{\max}$  (a) and  $V_f$  (b) trends as functions of the C30B amount in frontal DGEBA/DETA-based nanocomposite syntheses starting from non pretreated (SET-0,  $\square$ ) and pretreated (SET-1,  $\bullet$ ) mixtures.

playing curves having again a decreasing trend of  $T_{\max}$  as C30B concentration increases, shows much less superimposition between the two sets of data, particularly at higher concentrations of clay (samples 15 and 16 for SET-0, 29 and 30 for SET-1).



**Figure 5.**  $T_{\max}$  (a) and  $V_f$  (b) trends as functions of the C30B amount in frontal DGEBA/TREN-based nanocomposite syntheses starting from non pretreated (SET-0,  $\square$ ) and pretreated (SET-1,  $\bullet$ ) mixtures.



**Figure 6.** (a) X-ray diffraction patterns of C—Na and of samples prepared via FP and batch with 5.0 wt % of C—Na; (b) X-ray diffraction patterns of C30B and of the samples 28 and 28/SET-1B.

From the data shown in Figures 4(b) and 5(b) it is evident that, in general, the pretreatment determines a larger decrease of  $V_f$  for clay contents higher than 4.0 wt %, with a corresponding larger amount of dissipated heat.

Differences between thermally-untreated and treated samples are rather large in the clay composition range from more than 4.0 to less than 10 wt %, with a maximum at 7.5 wt %, and become much less relevant around 10 wt %.

For the mixtures belonging to SET-0,  $V_f$  is characterized by a constant decrease when C30B concentration goes from 1.0 to 3.0 wt %, keeps almost constant up to 7.5 wt % and then, at 10 wt %, a further large decrease is noticed.

In Figure 4(b) (curing agent: TREN), for SET-0 an initial significant decrease of the  $V_f$ s is showed (from 0, 0.95 cm/min, up to 2.0 wt %, 0.80 cm/min), then  $V_f$  keeps almost constant (up to 7.5 wt %, 0.80 cm/min); afterwards a further decrease is found (0.72 cm/min at 10 wt %).

For the analogous pretreated samples (SET-1), in the range between 1.0 and 4.0 wt %  $V_f$ s are very similar to those of SET-0 (ranging between 0.80 and 0.78 cm/min), whereas for higher concentrations (5.0, 7.5, and 10.0 wt %) an appreciable decrease of  $V_f$  (0.68, 0.66, and 0.65 cm/min, respectively) was found.

By comparing the two trends, at 1.0 wt %,  $V_f$ s are rather different whereas between 2.0 and 4.0 wt % they are practically equal. On the other hand, for concentrations of C30B larger than 5.0 wt %, a neat differentiation between the two  $V_f$  series is clearly evident.

An analogous study performed by using C—Na achieved very similar results and thus is not reported here.

### Characterization

X-ray diffraction (WAXD) spectra allow to study the spacing between the clay layers and to evaluate nanocomposite formation.

Diffraction region between 3 and  $10^\circ$  of  $2\theta$  was studied. In Figure 6, the WAXD patterns of two clays (C—Na and C30B) are compared with those of the composite materials prepared using the two polymerization techniques.

C—Na shows a strong diffraction peak at  $2\theta = 7.6^\circ$  corresponding to an interlayer spacing of the (001) plane ( $d_{001}$ ) of 1.2 nm, as calculated from the Bragg law.

The (001) plane diffraction peak of the samples prepared via frontal and batch polymerization, respectively, shifts to lower angles, that is, to  $2\theta = 5.9^\circ$  (basal spacing of 1.5 nm) in both composites. This result indicates the formation



**Figure 7.** TEM micrograph of the composite sample 14 (FP).



**Figure 8.** TEM micrograph of the composite sample 28/SET-1B (CP).

of intercalated structures. On the light of this finding, we can conclude that the polymerization technique does not affect the C—Na dispersion in the polymeric matrix.

The WAXD patterns of C30B and of the composites made of this clay are reported in Figure 6(b). The diffraction peak of the organoclay disappears, indicating the formation of exfoliated or possibly intercalated structures, the latter being characterized by a diffraction peak not visible in the studied diffraction region.

To further validate and complement the results obtained by means of WAXD, TEM measurements were carried out on these samples.

TEM micrographs of the samples containing C—Na are given in Figures 7 (FP sample) and 8 (CP sample).

In the composite prepared via FP (Fig. 7) it is possible to identify some clay layers which show individual dispersion of delaminated sheets, as well as regions where a more regular stacking arrangement is maintained. Although in the latter regions the clay layers are organized in a parallel way, some deformations in this arrangement are visible. Furthermore, the basal spacing of C30B ( $d_{001} = 1.8$  nm) turns out to be much higher in the composite, as the layers are irregularly separated by approximately 2.0–6.6 nm of polymer. This finding proves that the nanocomposite prepared by FP is characterized by exfoliated and *quasi*-exfoliated structures.

Similar clay arrangement is visible in the TEM photographs of the CP sample 28/SET-1B (Fig. 8). Together with some individual delaminated sheets, a regular clay arrangement is

present. Although the similarities between the clay dispersion in the two composites, the spacing between the layers of the sample prepared via batch polymerization is lower than that of the previous sample ( $1.2 \text{ nm} < d_{001} < 4.3 \text{ nm}$ ).

TEM measurements reveal that FP allows to obtain a nanocomposite characterized by a higher degree of intercalation. This finding points out that, in the case of organoclay, the nanocomposite formation might be influenced by the polymerization conditions.

## CONCLUSIONS

Frontal Polymerization (FP) has been advantageously used for the preparation of epoxy resin-based nanocomposites with montmorillonite. This relatively new technique confirms to be a very promising alternative method for the preparation of polymeric materials. The obtained nanocomposites have shown characteristics similar or even better than those obtained by the conventional polymerization routes. However, the facility of the protocol and the extremely reduced preparation times allow one to consider FP as a privileged method to take in proper account before designing synthetic ways according to the classical techniques.

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