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Synthesis and Characterization of Composites from Layered Silicates and Homo- and Copolymers of 2-Hydroxyethyl Methacrylate and P-Chloromethyl Styrene Obtained by *In Situ* Radical (Co)polymerization

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The hybrids 2-hydroxyethyl methacrylate – chlorometylstyrene – modified montmorillonite were synthesized by means of "in-situ" radical (co)polymerization. The composites were analysed by thermal analysis (DSC-TGA-MS), Fourier-Transform Infrared Spectroscopy (FT-IR), nuclear magnetic resonance (^{1}H-NMR), X-ray diffraction, and scanning electron microscopy (SEM). The influence of the polymerization conditions and compositions on the thermal stability and morphology of the obtained composites is discussed.

Keywords 2-Hydroxyethyl methacrilate; chlorometylstyrene; composite; layered silicate

Introduction

The composite materials are known since long time [1], but only after the first composite material marketed by Toyota group [2,3] the synthesis of organic-inorganic composites became a real challenge for the research community. The compatibility between an inorganic material (montmorillonite, silica particles, hectorite, kaolin, etc.) and one or more organic compounds (methacrylates, styrene and its derivates, lactides, etc.) is very difficult to be achieved. The main problem that needs to be considered is the physical and chemical interaction between the inorganic material and the organic matrix. The chemical interaction can be realized

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by the organomodification of the inorganic support using different methods (silanization [4], treatment with Lewis acids [5], etc.). On one hand, poor mechanical and thermal properties of the synthesized composites results when the physical interactions between the polymeric matrix and the inorganic support are weak [6]. On the other hand, strong interactions between composite components lead to uniform distribution of inorganic support in the polymeric matrix and, in consequence, the composite properties are better than in precursors cases. The easiest way to obtain an optimal physical interaction is probably the partial dispersion of the inorganic support in the polymeric matrix followed by in situ polymerization [7].

The inorganic supports are materials with remarkable properties that can be successfully used in different domains: biomaterials, thermoplastic materials, food industry, etc. One of the most used monomers for the synthesis of biomaterials is 2-hydroxyethyl methacrylate (HEMA) [8,9]. A problem that appears in this case is the behaviour of this monomer in the presence of different co-monomers.

4-Vinylbenzyl chloride, known also as chloromethyl styrene (CMS) [10] is one of the most important doubly functionalized monomer, characterized by high reactivity. This monomer can be used prior to or after the chemical modification of the chlorbenzyl group. The CMS copolymers [10] (with styrene, acrylates, etc.) are used in different fields: photo-cells, photo-resistant polymers, nonlinear optics, cholesterol trapping of human serum and polymeric prodrugs in drug delivery systems.

Starting from the above considerations, the present work aims at preparing silicate (Cloisite 30B) composites, employing HEMA and CMS as the monomers. Our previous results obtained for the copolymerization of CMS with different acrylates [11] are the main reason for using this copolymer pair. One should mention that, to the best of our knowledge, there are no studies in literature concerning the preparation of such materials up to now. The composites were characterized by thermal analysis (DSC-TGA-MS), Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (^{1}H-NMR), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Experimental

Materials

2-Hydroxyethyl methacrylate (HEMA, Sigma-Aldrich) was distilled at 5 mmHg and 75.5°C. Chloromethyl styrene (CMS, Aldrich), Cloisite 30B (Southern Clay Products) and 1,4-dioxane (Merck) were used as received. The initiator was lauroyl peroxide (PL, Sigma-Aldrich), purified by recrystallization from ethanol.

Cloisite 30B (Figure 1) is a montmorillonite organomodified with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium salt.

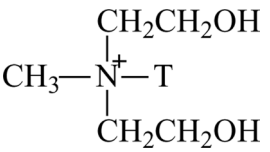

Figure 1. Methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium salt in Cloisite 30B.

Cloisite 30B Composites Synthesis

Cloisite 30B was dispersed in 1,4-dioxane using ultrasonic stirring for 20 minutes at room temperature. After this time, the monomers (HEMA and CMS) were added to the system and the ultrasonic stirring was continued for 10 minutes. In all cases the molar ratio between HEMA and CMS was 1:1, and the total monomer concentration was 3 mol/l. The initiator was then added, $[PL] = 3 \cdot 10^{-3}$ mol/l, using magnetic stirring for 10 minutes at room temperature. The polymerization started at 60°C, and the reaction time was 2 hours and 52 hours, respectively.

The obtained composite was separated by filtration and washed with diethyl ether, and then dried at 1 torr and 60°C for 24 hours.

Cloisite 30B-HEMA and Cloisite 30B-CMS composites were synthesized at 2 and 30 hours reaction time respectively. Homopolymer composites were separated following the above steps.

HEMA-CMS Copolymer Synthesis

For an easy characterization of the composites, the copolymer HEMA:CMS was synthesized in the absence of Cloisite 30B. The monomers (equimolar ratio, [Monomer] = 3 mol/l) were dispersed in 1,4-dioxane using ultrasonic stirring for 10 minutes at room temperature. The initiator was added ($[PL] = 3 \cdot 10^{-3}$ mol/l) using magnetic stirring for 10 minutes. The polymerization started at 60°C, and the reaction time was 52 hours.

The separation and the drying of the copolymer were performed following the steps presented above for the composites.

Characterization

All composites were characterized in solid state by FT-IR spectroscopy, using a Bruker VERTEX 70 instrument, equipped with a Harrick MVP2 diamond ATR device.

The homogeneous substrates, ungrafted on Cloisite 30B, were ^{1}H-NMR (300 MHz) analyzed using a Varian GEMINI 2000 in deuterated dimethyl sulfoxide (DMSO-D_6).

Thermal analysis was performed on a NETZSCH STA 449C Jupiter simultaneous TGA-DSC system, under He atmosphere.

X-ray diffraction (XRD) spectra of Cloisite 30B and of the obtained composites were collected on a Siemens XRD 6000 instrument at room temperature.

Textural investigation was realized by scanning electron microscopy (SEM) on a HITACHI S-2600 N apparatus.

Results and Discussions

The Cloisite 30B-HEMA-CMS composites were synthesized by in situ radical polymerization. For comparison, the silicate hybrids with the HEMA and CMS homopolymers and the HEMA-CMS copolymer in homogeneous system were synthesized under identical conditions. Table 1 shows the amount of reagents employed to synthesize the composites and the copolymer.

The data for the gravimetric determination of conversion showed small values for D2 and D4 than for D6. The conversion for the hybrid Cloisite 30B-CMS was

Table 1. Experimental conditions employed in the synthesis of the composites

Code	HEMA:CMS mole ratio	Conversion (%)	Polymerization time (h)
D1	1:1	37	52
D2*	1:0	20	2
D3*	0:1	**	2
D4*	0:1	11	30
D5*	1:1	8	2
D6*	1:1	36	52

*3 wt-% Cloisite 30B based on the total amount of the monomers.
**The obtained conversion was very small, negligible within the experimental errors.

small at 30 hours, probably due to the inhibitor content. The difficult purification of CMS, the fairly good purity (>90%) and the fact that the study does not try to characterize this system from the kinetics point of view, allowed the use of CMS without purification. The conversion values for D1 and D6 were close, hence, the copolymerization process of HEMA and CMS was not influenced by the use of the inorganic support.

The composite materials were characterized first by FT-IR spectroscopy. Figure 2 displays the IR spectra for the synthesized composites, in comparison with the spectra for Cloisite 30B and the HEMA:CMS copolymer without inorganic support. The substrates with HEMA showed the characteristic vibrations for this monomer: $\nu_{C=O} = 1750\,cm^{-1}$, $\nu_{OH} = 3412\,cm^{-1}$, at 1470 – 1380 cm^{-1} – the $-CH_2-$ vibration; $\nu_{CO(H)} = 1071\,cm^{-1}$; at 748 cm^{-1} – the CH_2 vibration from HEMA skeleton. Also IR analyses for the composites containing CMS in the substrate, revealed the characteristic vibrations for the monomer: $\nu_{CH\ aromatic} = 3100 - 3000\,cm^{-1}$; $\nu_{CH\ aliphatic} = 3000 - 2800\,cm^{-1}$; 1600 – 1450 cm^{-1} – C=C bond from the aromatic ring; $\nu_{C\text{-}Cl} = 671\,cm^{-1}$. The characteristic vibrations for Cloisite 30B are: 3630 cm^{-1} – Si-OH stretching vibration; 3350 cm^{-1} – stretching vibration of OH groups associated by hydrogen bonds; 1470 cm^{-1} corresponds to the deformation vibration of the tertiary amine group; 993 cm^{-1} – (Si-O)-Si vibration; 1120 cm^{-1}–(Si-O)-Me vibration; 915 cm^{-1} and 880 cm^{-1} – stretching peaks for the associated ions with two cations in the octaedric layer plane (Al_2OH and $Fe^{3+}AlOH$) [9,12]. For the HEMA-CMS copolymer the FT-IR analyse revealed the presence of the characteristic vibrations of the monomers.

In the case of D2, the interaction between the polymer and the silicate was proved by the shift of the Si-O-Si vibration at 1023 cm^{-1}, while for D3, the FT-IR spectra showed that the polymerization started, but the poly(CMS) vibrations could not be identified. In order to obtain a material that presents the vibrations for both inorganic support and poly(CMS), the polymerization time for this composite was risen at 30 hours. The IR spectra for D4 showed the presence of poly(CMS) vibrations and also the shift to the left at 1015 cm^{-1} of Si-O-Si vibration, revealing the interaction between poly(CMS) and Cloisite 30B. The smaller shift of Si-O-Si vibration for D4 case than for D2 is probably due to a weeker interaction between the polymer and Cloisite 30B in the first case than in the second.

The FT-IR spectrum for D5 revealed the presence of the characteristic vibrations for both monomer units, but the intensities of the signals were week. For the same composite synthesized at 52 hours, the characteristic vibrations of

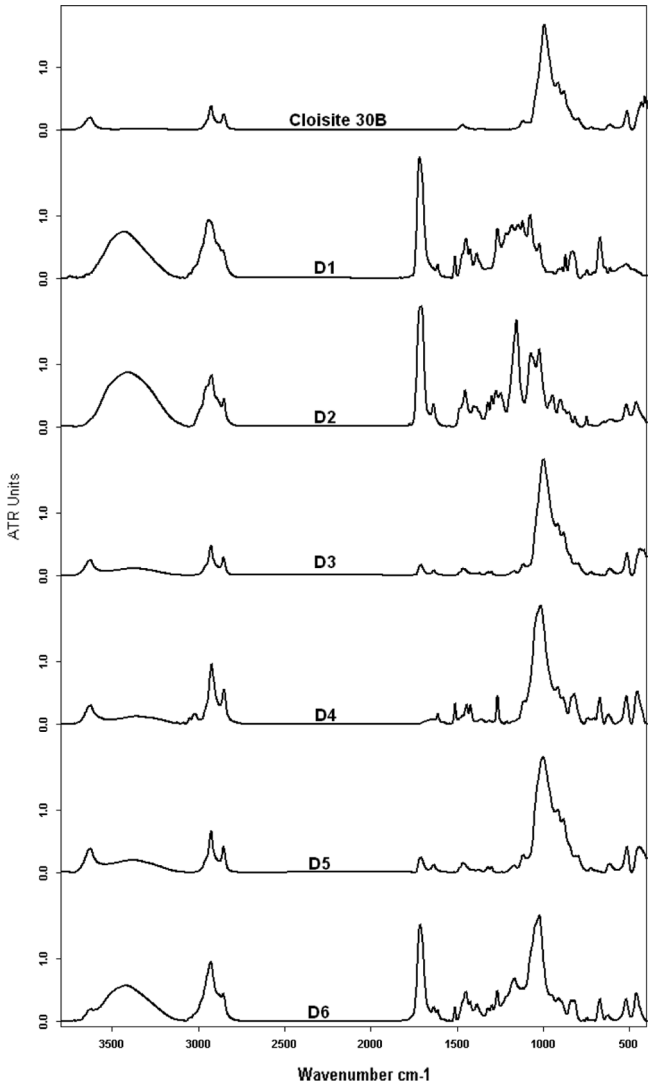

Figure 2. The FT-IR spectra of the synthesized materials.

the monomer units were well defined. The Si-O-Si vibration was shifted in D6 from 993 cm^{-1} to 1021 cm^{-1}. As reported in the literature [12], the shift of the Si-O-Si vibration toward higher wavenumbers proves the interactions between Cloisite 30B and the monomers, a modification of the layered silicate structure being also possible.

An additional evidence for the copolymerization of HEMA with CMS was obtained by the ^{1}H-NMR analyses in DMSO-D_6 of the synthesis material D1 (Figure 3). The spectrum revealed the presence of the monomers characteristics peaks: 4.42 ppm the hydroxyl group from HEMA, 4.66 ppm for benzyl chloride and 6.5–7.5 ppm the characteristic peaks for the aromatic ring protons from CMS. The presence of these signals in the ^{1}H-NMR spectrum is a proof for the synthesis of the HEMA-CMS copolymer.

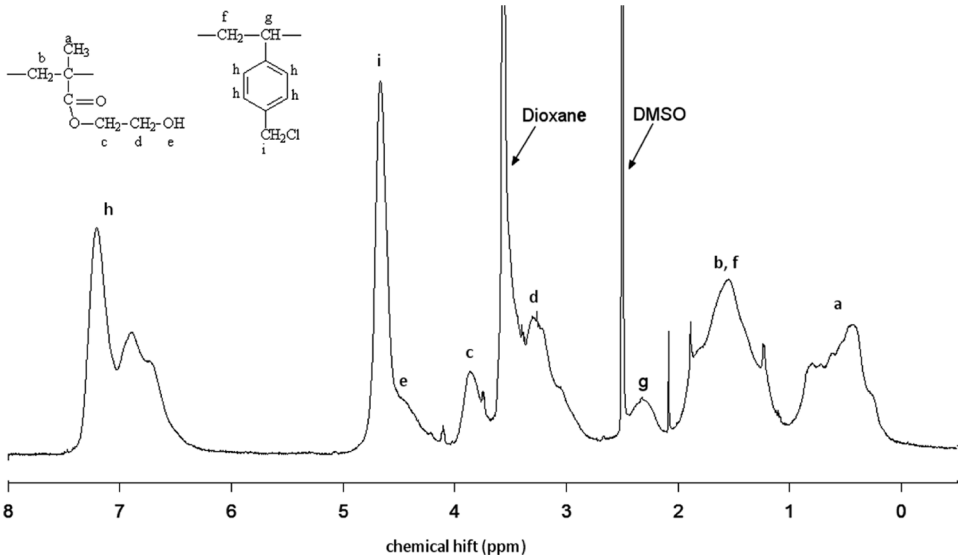

Figure 3. The ^{1}H-NMR analyses in DMSO-D_6 of the HEMA-CMS copolymer.

Further, all the synthesized materials were characterized from thermogravimetric point of view, the results being shown in Figure 4 in comparison with the original Cloisite 30B.

The TGA analysis of the copolymer HEMA-CMS revealed the presence of three degradation steps. The first step, between 116–306°C (11.80% weight loss) was due to some reactions of the functional groups, possible between benzyl chloride groups and the OH groups, with HCl elimination. The major degradation step of the copolymer was between 306–488°C (73.38% weight loss), and the final stage was in the range of 488–700°C (3.05% weight loss). At 700°C the copolymer thermal degradation was not complete, the weight loss being of 88.36%.

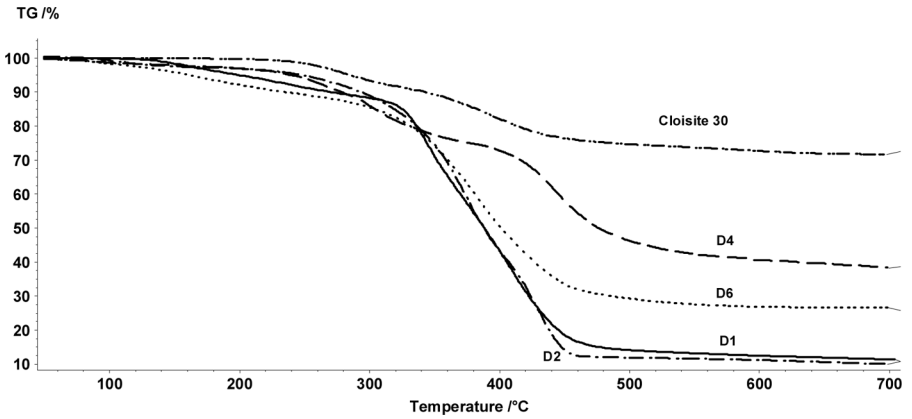

Figure 4. The thermogravimetric analyses of the synthesized composites and of the Cloisite 30B.

In the case of poly(CMS) the literature presents a degradation stage between 323–600°C, but there are no other explanations for the thermal behaviour [13]. The TGA curve of the composite Cloisite 30B-CMS is divided in four weight loss stages. The first degradation step, in the range of 40–134°C (1.72% weight loss), represents the loss of absorbed water. Two different stages represent the composite thermal degradation: 134–374°C with 22.86% weight loss, and 374–600°C with 34.58% weight loss. Probably, the presence of two different degradation stages in the composite case, comparatively with one for poly(CMS), was due to the superposition of the Cloisite 30B degradation with that of the homopolymer on one hand, and on the other hand to the interaction between the polymer and the silicate. The final degradation step, between 600–700°C, was not significant (2.39%) and represent the Cloisite 30B final degradation stage.

In D2 case, the first degradation stage between 40–134°C (weight loss 2.47%), represents the loss of water. The second stage 134–500°C (weight loss 85.97%) had two steps that can not be separated, representing the hybrid thermal degradation. The final step between 500–700°C (weight loss 1.9%) represents the Cloisite 30B degradation. The TGA curve for D2 displays the same pattern as for poly(HEMA) [14], but a difference between the final temperature of the principal degradation step – 500°C for D2 and about 400°C for poly(HEMA) could be observed. This behaviour was due, on one hand, to the fact that TGA analyses of poly(HEMA) was performed in air [14], and in D2 case the TGA analysis was performed in helium, and on the other hand to the presence of the inorganic support in the composite system.

The literature data reveals a residue of 37% for poly(CMS) [13] homopolymer and a residue of 0.2% for poly(HEMA) [14]. The used layered silicate yields a residue of 28.38% at 700°C. The maximum calculated residue that can be achieved at 700°C for the synthesized composites was evaluated considering firstly the Cloisite 30B content in the composite, determined with respect to monomer conversion, and secondly the thermal decomposition characteristics of the layered silicate and of the two homopolymers. In Table 2 are presented the calculated and experimental residue values. The two values for D2 are close, while for D4 the difference was small, proving the validity of the obtained data and the fact that Cloisite 30B does not quantitatively influence the two homopolymers decomposition. The calculated maximum residue for D6 was obtained by the method presented above, using this time the experimental residue for HEMA-CMS copolymer (11.4%) and the D6 conversion. In this case, the difference between the calculated value (16.5%) and the experimental residue (27%) is significant. A possible explanation for this result is the different composition of the copolymer, due to the presence of Cloisite 30B in the polymerization system, which can lead to different residue amounts obtained by the copolymer

Table 2. The experimental and calculated residue for the synthesized composites

Code	Experimental residue at 700°C (%)	Calculated residue (%)
D2	9,7	9,6
D4	38	44,5
D6	27	16,05

decomposition. In this case, the first degradation stage is between 50–256°C (11.38% weight loss). This stage is not characteristic for the other composites or for the inorganic support, but is present in the HEMA-CMS copolymer thermal degradation. This step represents the start of HEMA-CMS copolymer degradation, the loss of additional water and some reactions of the monomers functional groups, between them with HCl elimination, and with the layered silicate. The second stage, which is the most important, ranges between 256°C and 521°C (weight loss 60.18%), represents the thermal degradation of the synthesized material. This material presents also the stage between 512–700°C characteristic for Cloisite 30B thermal degradation. As observed for D2, the principal degradation step is not split due to the presence of Cloisite 30B in the system. This behaviour reveals the interaction between Cloisite 30B and the functional groups of the two monomers (the OH group from HEMA and the Cl from CMS), and probably the modification of layered silicate structure. The shape of the TGA curves for HEMA-CMS copolymer and for Cloisite 30B-HEMA-CMS composite are similar, showing that the influence of Cloisite 30B on the copolymer thermal behaviour was not significant.

The XRD analyses for the synthesized composites are presented in comparison with that of the original Cloisite 30B in Figure 5. In D2 case, one can notice the area of the characteristic Cloisite 30B signal at $2\theta = 4{,}89°$ decreased from $A = 765$ to $A = 42.39$. It is reported in the published literature that the structure of this nanocomposite is intercalated [9]. In our case, both FT-IR and XRD analyses reveal the interaction between poly(HEMA) and layered silicate with the obtaining of an intercalated nanocomposite. The interaction between poly(HEMA) and Cloisite 30B is also sustained by the TGA analysis. In D4 case, the XRD analysis reveals the interaction between the layered silicate and the poly(CMS), by decreasing the area of the characteristic peak at $A = 12.27$.

The XRD analysis of the D6 composite reveals the almost complete modification of the layered structure. The Cloisite 30B characteristic signal from $2\theta = 4.89°$ ($A = 765$) is shifted to lower angle at $2\theta = 4.70°$ and its area is significantly diminished $A = 11.3$. Both FT-IR and XRD analyses reveal the interaction between the HEMA-CMS copolymer and layered silicate with the obtaining of an intercalated nanocomposite. The modification of the layered silicate structure is sustained also by the TGA analysis.

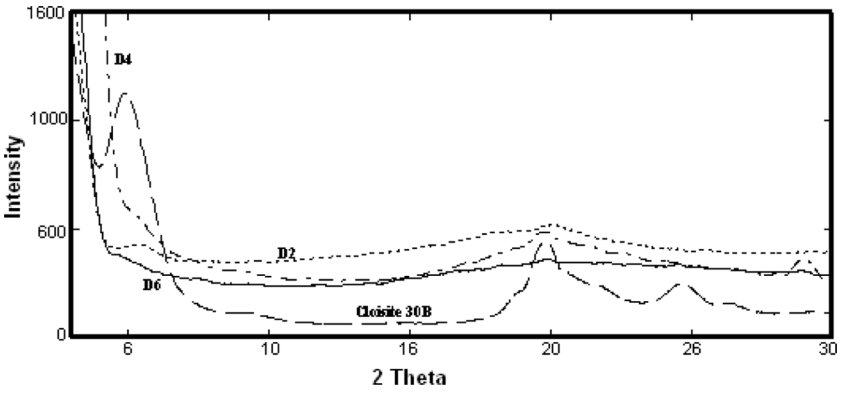

Figure 5. The XRD analyses of the synthesized composites and Cloisite 30B.

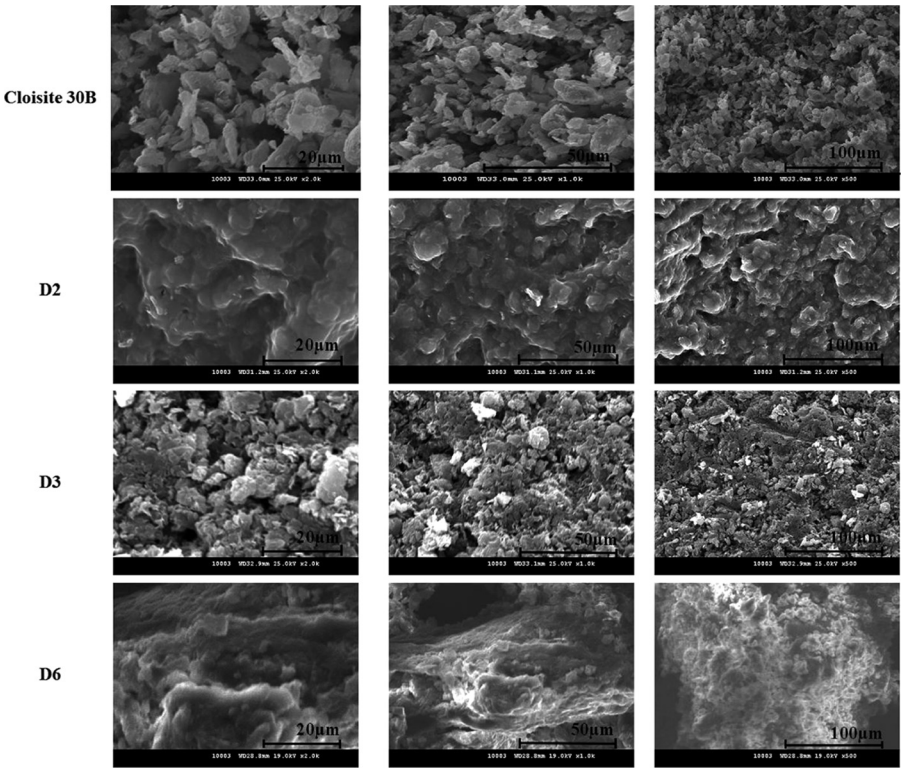

Figure 6. SEM images of Cloisite 30B, D2 and D3.

The SEM analyses (Figure 6) of the synthesized composites prove the homogeneity of the samples prepared.

Conclusions

Composites Cloisite 30B-HEMA-CMS, Cloisite 30B-HEMA and Cloisite 30B-CMS copolymer were synthesized through ''in situ'' radical polymerization. Comparatively, a HEMA-CMS copolymer was synthesized by radical homogeneous polymerization. The FT-IR analysis revealed the interaction between the layered silicate and the polymeric matrices. The obtaining of the HEMA-CMS copolymer was sustained by ^{1}H-NMR spectrum. For the Cloisite 30B-HEMA-CMS and Cloisite 30B-HEMA composites, the presence of the inorganic support did not influence the general thermal degradation behaviour. The TGA analyses for the Cloisite 30B composite with poly(CMS) matrix showed the split of the principal degradation step. By comparing the experimental TGA data with the calculated values for residue at 700°C, in the case of synthesized composites, it was shown that Cloisite 30B does not quantitatively influence the decomposition of the homopolymers. For Cloisite 30B-HEMA-CMS the difference between the calculated and the experimental residue values at 700°C was significant. This behaviour was due to the different composition, microstructure and morphology of the copolymer because of the presence of Cloisite 30B in the polymerization system that favours the coke formation. For the

three synthesized composites, the XRD and FT-IR analyses showed the modifications of the layered silicate structure. The SEM images showed the optimal dispersion of the layered silicate in the polymeric matrices.

Acknowledgments

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