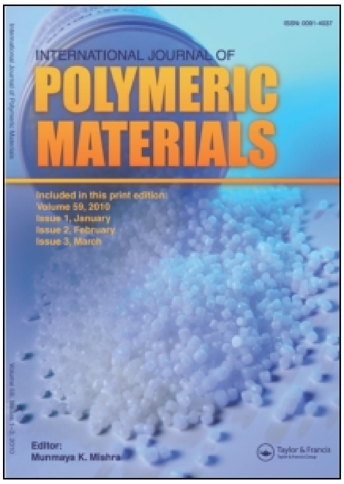

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Film Forming Nanohybrids Obtained with Polyethers

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Film Forming Nanohybrids Obtained with Polyethers

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New hybrid materials based on polyether polyols were prepared by using a sol-gel reaction of alkyltriethoxysilanes, in the presence of propylenoxide-ethylenoxide trifunctional block copolymers. The resulting composites are transparent and have a filmogene behavior. Two types of filler systems were used: one based on silane precursors and one based on both the silane precursors and nanoclay (sodium montmorillonite). FT-IR spectra were evaluated to prove both the covalent interaction at the functional groups level and the presence of silica nanodomains formed by sol-gel process. The polarity changes were analyzed in the UV spectra, which shift according to the nature of different cationic dyes. Polyether hybrids were also obtained in the presence of some layered silicates. The X-ray diffraction reflects the changes in basal spacing of the Cloisite Na^{+}, when it is added to different formulations. The modification of film morphology, depending on the reactants nature, can be observed in the SEM images.

Keywords: cationic dyes, functionalized polyether polyols, organic-inorganic hybrids, silicate nanocomposites, sodium montmorillonite

INTRODUCTION

Previous studies [1–2] reported the preparation of filmogene materials with controllable polarities by sol-gel process of some substituted triethoxy siloxanes. The substituents able to polymerize through different radical mechanisms allow the preparation of materials

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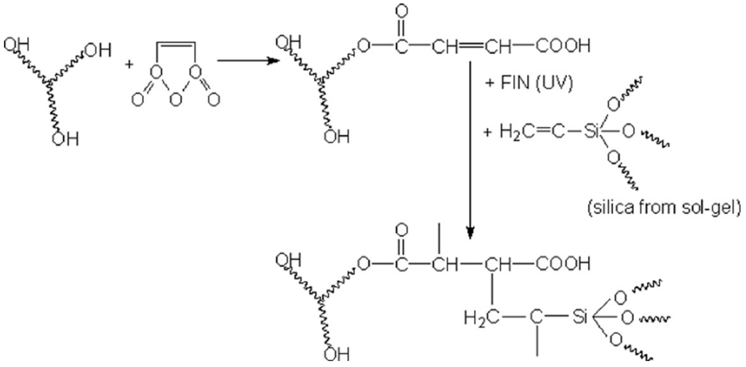
capable of crosslinking between the hydrocarbon chains and the silica network [1].

The modification of the hydrophobicity of the triethoxysilanes derivative substituents allows the obtaining of filmogene materials with different polarities [2]. These polarities can be distinguished from the fluorescence spectra modification for Rhodamine B [2]. The presence of some filmogene polymers in the sol-gel systems makes possible the preparation of polymer-inorganic materials [3].

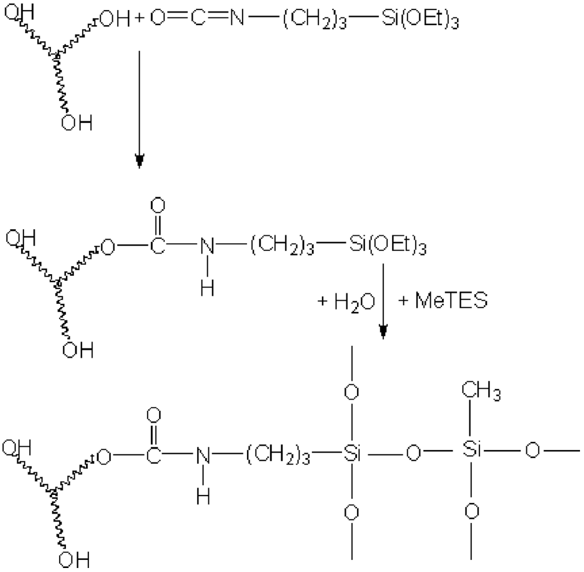
The main aim of this work was to synthesize polymer-inorganic hybrid films by the sol-gel process, in the presence of polyether polyols [1–2]. The polyether polyol was used as such and functionalized with maleic anhydride (MA) and (3-isocyanatopropyl)triethoxysilane (NCOTEOS), respectively. Then, the filmogene hybrids obtained in the presence of propylene oxide-ethylene oxide (PEO-EO) block copolymers and layered silicates were investigated. This type of block copolymers play a role of templates in the sol-gel processes and exhibits a good compatibility with the inorganic networks [4–8].

By functionalizing the block copolymers, covalent bonds between the polymeric chains and the silica network were formed. Thus, when functionalizing the polyether chains with maleic acid semi esters, double bonds are introduced in the molecular structure of the PEO-EO block copolymer. Also, double bonds are introduced in the silica network, which is functionalized by the sol-gel process with triethoxyvinylsilane. That double bonds allow the formation (through radical polymerization) of covalent bond between the polyether polyol and the silica network (Scheme 1).

When the polyether polyol chains are functionalized with (3-isocyanatopropyl)triethoxysilane (NCOTEOS), urethane linkages are



SCHEME 1 Polymerization through double bonds.



SCHEME 2 Polymerization through isocyanate groups.

formed from the reaction of –OH terminal groups from the polyol and the –N=C=O functional groups from NCOTEOS (Scheme 2).

The presence of terminal group from the trialkoxysilane class will enable the covalent bonds formation (through sol-gel process) between block copolymers and the silica networks.

The study of film polarities modifications, as a function of the nature and concentration of the partners, was performed by UV-VIS spectroscopy, using four cationic dyes. This type of dyes (being cationic) provides a good interaction with the silica and the negatively charged layered silicate. The UV-VIS spectra are very sensitive to the modification of the micro-vicinity polarities [2,9–13].

The modifications of the filmogene materials in the presence of the layered silicates (Cloisite Na+) were also investigated. Both block copolymers and the alkoxysilanes can generate strong interaction by intercalation or exfoliation of sodium montmorillonite [14–23].

EXPERIMENTAL

Materials

The sol-gel precursors: triethoxymethylsilane (MeTES) (Merck/Suchardt), triethoxyvinylsilane (VTES) (Merck/Suchardt) and tetraisopropylorthotitanate (TIP) (Fluka) were used as silica and titani sources. A three chains block polyether polyol (PETOL 36-3BR (PE)), initiated by glycerol, having PO (85%) and EO (15%) units, and with a average molecular mass of 5000 g/mol, produced by Oltchim, Romania, was used as polymeric component. The maleic anhydride (MA) (Fluka) and (3-isocyanatopropyl)triethoxysilane (NCOTEOS) (also known in literature as ICPTES) (Fluka) were the functionalization agents for polyether. The nanoclay added in some sample formulations was Cloisite Na^+ (ClNa, a Na^+ montmorillonite) (Southern Clay Products, Gonzales, Texas, USA). Benzoinedimethylacetal (FIN) (ICPAO) was added to the base sol-gel formulation as UV photo initiator.

Preparation of Functionalized Polyether Polyols

In order to obtain polyetheric chains containing double bonds that are able of radical polymerization during the sol-gel process, the authors used the reactions of polyether terminal hydroxyl groups with maleic anhydride, a reagent containing double bonds in its structure. MA reacts quantitatively with hydroxyl groups at moderate temperatures (60–7°C) for 1 h, with the formation of half esters of maleic acid. The reaction mixture was continuously stirred and maintained in neutral conditions (in N_2 atmosphere).

In a similar way the polyether polyol (PE) functionalized with 3-(isocyanatopropyl) triethoxy silane (NCOTEOS) was obtained. In this case the aim was to connect to the polyether backbone the triethoxy functional groups of an usual sol-gel precursor (NCOTEOS). As is further proved through FTIR spectra, the reaction between the NCOTEOS and the polyether successfully took place, with the formation of a urethane linkage ($1531 cm^{-1}$, $3355\,cm^{-1}$).

Technique Used for the Film Preparation

The hybrids were prepared by a two step sol-gel method because TIP hydrolyzes at a much higher rate than the MeTES and VTES. Thus, in all preparations, MeTES and VTES were prehydrolyzed in acid condition with ethanol and water for 1 h, under continuous stirring, at room temperature. Beside this sol-gel precursors, the polyether (PETOL 36-3BR as such or functionalized) were added in different concentrations (0.006 mol/l, 0.012 mol/l and 0.024 mol/l). When Cloisite Na^+ was used, the layered silicate was mixed, in the first step, with the polyether. Furthermore, to promote swelling and expansion of the interlayer spacing of clay for polymer intercalation, the clay

TABLE 1 Typical Compositions for Preparing the Hybrid Films

MeTES (mol/1)	VTES (mol/1)	EtOH (mol/1)	H_2O (mol/1)	TIP (mol/1)	FIN (mol/1)	PE as such or functionalized (mol/1)
1.292	1.316	5	5.55	0.158	0.092	0.006 0.012 0.024

dispersed in polyether (PE) was sonicated for ~1 h, using an ultrasound bath.

As a second step, the TIP and the FIN were added to the solution, together with the second portion of water, the mixture being stirred for another hour. From the resulted solution, equal amounts were taken and mixed with different cationic dyes, and stirred 15 min. Hybrid films were deposited on glass slides by dip coating.

Note: For all the hybrid samples, the base formulation (comprising the sol-gel precursors and FIN only) was noted with **M**, in order to simplify the figure legends.

Typical compositions adopted in this study are shown in Table 1. Samples of the hybrid films were taken for SEM, UV-VIS, FTIR, X-ray, and thermogravimetric analysis (TGA).

Characterizations

FTIR spectra were obtained with a TENSOR 37 spectrometer (Bruker), on KBr pellets. The materials were also analyzed by **XRD**-DRON-2.0 X-ray diffractometer with horizontal goniometer; the patterns were automatically recorded at small angles ($2\theta°$). A Nicolet Evolution 500 instrument (Thermo Electron Corporation) was used for obtaining the **UV-VIS** spectra. Thermal behavior of the non-supported films were determined by thermogravimetric analysis (**TGA**) on a Du Pont 2000 instrument, with a 20°C/min heating rate, for the purpose of correlating their properties with the processing conditions. From the differential curves, the temperatures with higher rate of thermal decomposition (T_{max}) were evaluated. Scanning electron microscopy (**SEM)** was performed with a FEI QUANTA 200 microscope, without coating the samples.

The degree of crosslinking was evaluated by extraction in isopropyl alcohol, assuming that the grafted species are not soluble in this solvent. The grafted species was gravimetrically evaluated after previously drying of the sample for several days in air and then for a night at low vacuum.

RESULTS AND DISCUSSION

FTIR Spectra

The structural groups in the obtained hybrids were analyzed by Fourier Transform Infrared (FT-IR) Spectroscopy. Figures 1a and b show the FTIR spectra of the pure components and of their hybrids.

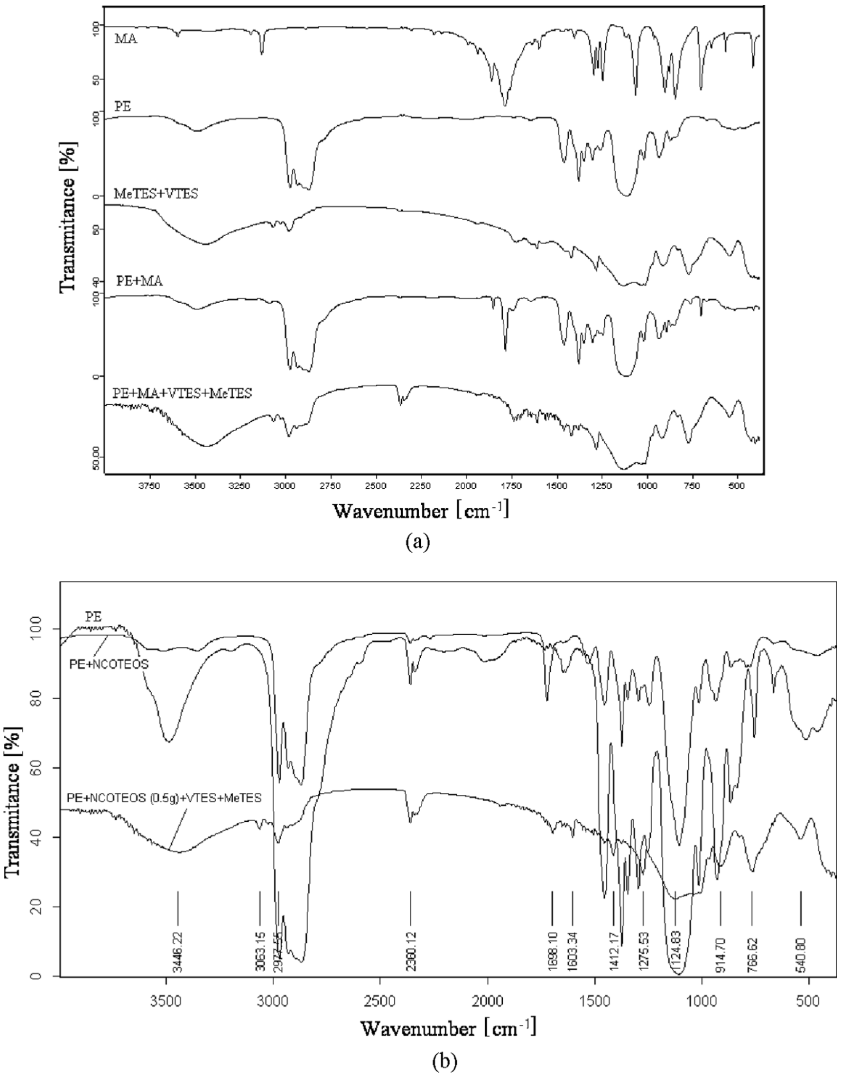
Evaluating all the peaks from the spectrum of the hybrid film based on polyether polyol (as such), with the peaks obtained using the functionalized polyether polyols (both cases: with MA and NCOTEOS, respectively), no difference occurred. In all three situations all peaks are the same. However, the spectra of the unmodified polyether polyol and the functionalized PE (without adding the sol-gel precursors) are different.

Thus, the spectrum of the PE functionalized with maleic anhydride (PE + MA) contains some specific bands arising from the MA spectrum: 406,696, 887, 1239, 1736, 1779, 1848, and 1934 cm^{-1}. The displacement to higher frequency of most of the bands can also be observed: 408, 697, 898, 1242, 1717, 1781, and 1856 cm^{-1}. However, the presence of the MA specific peaks in the spectra of the functionalized PE and the presence of the 1717 cm^{-1} absorption band (assigned to maleic acid semi esters) indicate that the reaction between MA and PE did take place.

The FTIR spectrum of the polyether polyol modified with NCOTEOS contains absorption peaks located at ca. 2270 and 1723 cm^{-1}, attributed to asymmetric and symmetric stretching of –N=C=O, respectively. These peaks are due to the unreacted –N=C=O functional groups. The absorptions at 1531 cm^{-1} and 3355 cm^{-1} are assigned to urethane (–R–NH–(C=O)–O) linkage formed by the reaction between NCOTEOS and PE.

The spectra of PE–silica organic-inorganic network showed no evidence of direct formation of Si–O–C linkages between the silica and PE [24]. Peaks at 765, 1277, and 1413 were assigned to Si–C (CH_2 rocking vibration, C–H symmetric deformation vibration, and C–H asymmetric deformation vibration, respectively). The spectra of the obtained nanohybrids in the presence of the sol-gel precursors show peaks at 769 and 1028 cm^{-1} (Si–O–Si symmetric and asymmetric stretching vibration). A strong absorption can also be observed at 1100 and 1220 cm^{-1} related to Si–O–Si and Si–OH absorption [24]. Water and –OH absorption bands are present too at 3062, 3441, 3648, 3735, and 3853 cm^{-1}.

The specific absorption bands of the polyether chains are a little bit shifted, which can be induced by the interaction with the cations from the intergalleries of the layered silicate.



(a)

(b)

FIGURE 1 (a) FTIR spectra of the hybrids obtained with polyether polyol functionalized with MA; (b) FTIR spectra of the hybrids obtained with polyether polyol functionalized with NCOTEOS.

X-Ray Diffraction

The influence of added nanoclay, sodium layered silicate, on the structure of the composites formed by the organic-inorganic hybrids

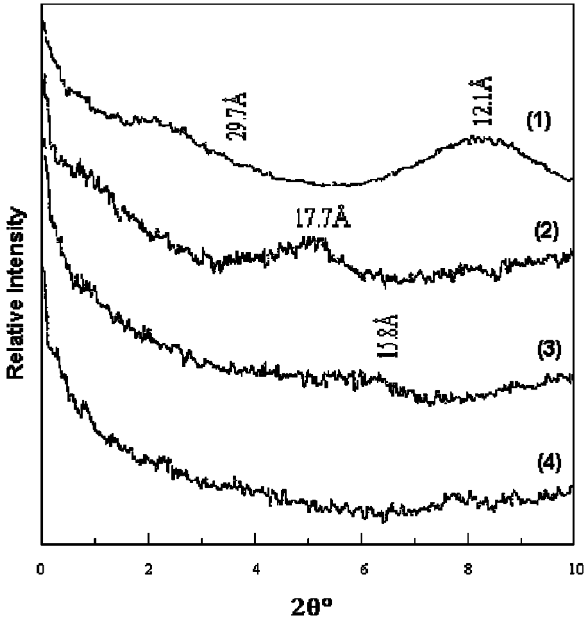


FIGURE 2 XRD pattern of the films obtained in the presence of Cloisite Na$^+$.

was investigated by X-ray diffraction **(XRD)**. Figure 2 reflects the change in basal spacing of the Cloisite Na$^+$ (1), when added to different formulations: (2) Cloisite Na$^+$ with **M** and polyether (PE); (3) Cloisite Na$^+$ with the sol-gel precursors (**M**) only and (4) Cloisite Na$^+$ (ClNa) with **M** and maleic anhydride (MA). The basal spacing of pure air dried Cloisite Na$^+$ is 12 Å. From this value, the basal spacing of the clay increases to 15.8 Å when used with the sol-gel precursors (**M**) only.

The X-ray diffraction pattern of PE/**M**/Cloisite Na$^+$ hybrid shows a modification in intensity of the peaks corresponding to the PE-intercalated silicate. The primary repeat unit (*basal spacings*) of 17.7 Å is identical to that previously obtained for PEO intercalation [25]. This behavior is attributed to the specific way the polyetheric chains interact with Na$^+$ montmorillonite, where strong coordination of the polyether chain to the surface of Na$^+$ cations promotes ether crown conformations [26].

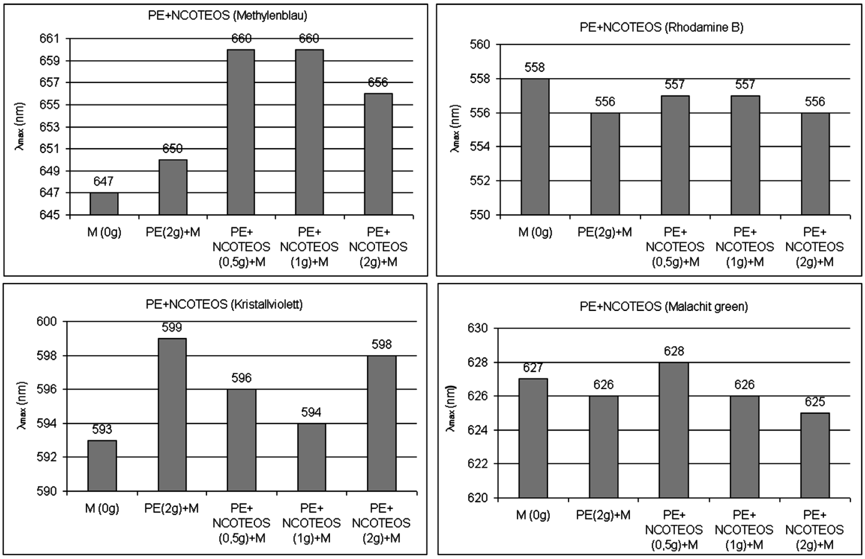
Studying the diffraction pattern of **M**/MA/Cloisite Na$^+$ hybrid, the absence of the 12 Å diffraction peak was observed, providing strong evidence that the clay nanolayers have been exfoliated in the sol-gel process.

UV-VIS Spectra

UV-VIS spectra reveal the polarity modification induced by the interaction between the inorganic network and the polyether. Depending on the dye structure, the phase repartition is probably different. From Figures 3a and b one can conclude that the crosslinkable functional groups are not exhibiting a major influence over the modification of the dyes behavior in hybrids. The nature of the polyether backbone is important.

For the four cationic dyes solutions in ethanol/water mixture at different ratios, the effect of the decrease of the average polarity is the reduction of the λ_{max} value. This is a very complex phenomenon and the nonlinear variation of λ_{max} in the alcohol/water systems is a sign of the different forms of association resulting from hydrophobic demixing of the ethyl chains from the organic solvent.

In the case of the voluminous dyes (Malachite green and Cristalviolet), this effect is well distinguished only when using alcohols with long molecular chains (for example, t-buthanol/water system) [27]. From the UV-VIS diagrams it can be seen that the two dyes, Malachite green and Cristalviolet (which have nonlinear structures), manifest a



(a)

FIGURE 3 (a) UV-VIS diagrams for the films obtained with polyether polyol functionalized with NCOTEOS; (b) UV-VIS diagrams for the films obtained with polyether polyol functionalized with MA; (c) UV-VIS diagrams for the films obtained in the presence of Cloisite Na^+.

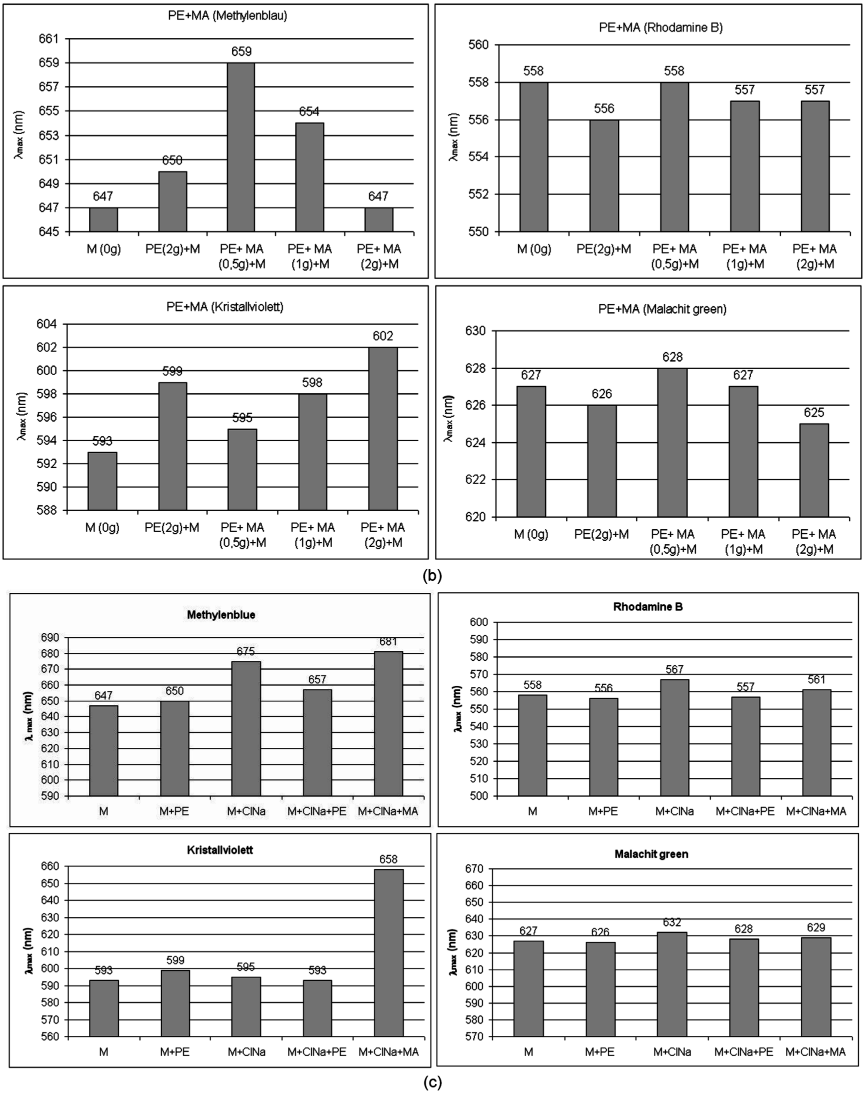


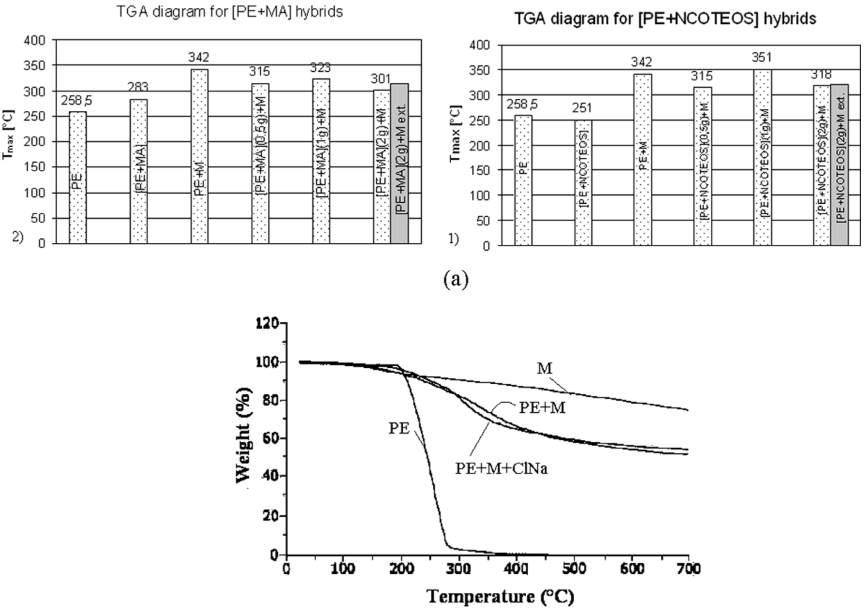
FIGURE 3 Continued.

different behavior from the other two, Rhodamine B and Methyleneblue (with linear structures). Due to the presence in its structure of three functional groups and because of its voluminous structure, the Malachite green is more anchored in the silica network. As a consequence, the difference between the $\lambda_{\max}$ value of the reference sample and those of the other composites is smaller for this cationic dye [2,9–13].

After analyzing Figure 3c, a conclusion can be reached regarding the effect of the presence of a layered silicate (Cloisite Na^+) over the dyes behavior. In the case of Rhodamine B, Methyleneblue and Cristalviolet, an important decrease of the absorbance in the presence of the polyether polyol and a displacement of the λ_{max} toward lower values can be observed. This is due to the polarity modification of the colorant micro-vicinity and to its trapping in the polymeric matrix. The exception is the Malachite green that, as previously mentioned, is the most voluminous. Another finding is that in the presence of MA a more polar medium is created than in the case of PE, λ_{max} moving for higher values.

Thermal Stability (TGA Analysis)

Useful information was also obtained from the TGA studies of thermal stability. The T_{max} diagrams of the hybrids obtained with the functionalized polyether polyols (Figure 4a) indicate that the



(a)

(b)

FIGURE 4 (a) T_{max} modification for the hybrids obtained with functionalized polyether polyols: (1) with maleic anhydride (MA) and (2) (NCOTEOS); (b) thermal stability of the hybrids composites, in the presence of Cloisite Na^+.

thermal stability varies with the concentration of functionalized PE added in the preparation process. Although the thermal stabilities of the hybrids based on PE functionalized with NCOTEOS are slightly higher than in the case of the hybrids derived from PE functionalized with MA, in both situations the thermal behavior is similar. Thus, the concentration of functionalized PE seems to achieve an optimum value at 0.012 mol/l. When the polyether concentration is above that value, the excess of non-grafted polyether will induce a decrease of the thermal stability.

In both diagrams is also represented the T_{max} for the hybrids obtained with 0.024 mol/l of functionalized PE, but after extraction in isopropyl alcohol. As expected, after the removal of the unchained polyether, the thermal stability increases. Due to its lower crosslinking degree (only 45%), comparing with the one for PE functionalized with NCOTEOS hybrid (60%), the sample based on PE functionalized with MA shows a higher increase.

Figure 4b shows a comparison between the samples containing PE. The effects of the presence of the sol-gel precursors and of the layered silicate over the thermal stability of the polyether are illustrated. Thus, when analyzing TGA curves of the sample containing PE + sol-gel precursors (**M**) and of the sample based on PE + **M** + Cloisite Na^+, an increase of the thermal stability can be observed in the second situation, but only for temperatures lower than 240°C. Beyond this temperature the thermal stability of the sample is lower than that of the compared one. It is also clear that the PE thermal stability increases by adding the sol-gel precursors.

SEM Images

Representative examples of the morphologies of the hybrid film based on PE (as such and functionalized) are presented in Figure 5a. Most obvious is the increase of the homogeneity of the film surface when adding PE. Image 5 shows the morphology of a typical intercalated structure, obtained by adding Cloisite Na^+ to polyether in the preparation process. The cross-section of this film is presented in image 2 from Figure 5b.

The Figure 5b shows a comparison between the cross-section of three films. The coherent stacking of silicate layers can be observed in image 1. In image 2, the local parallel alignment of fractures planes is preserved, in spite of adding the polyether. The presence of the intercalated polyether does not affect the fracture morphology.

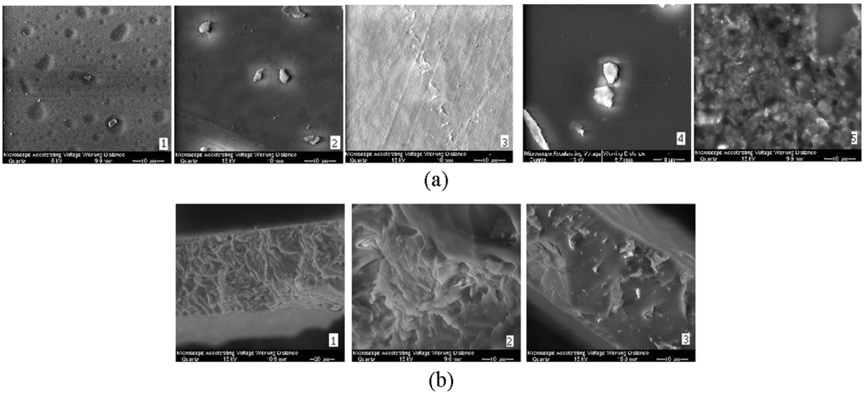


FIGURE 5 (a) SEM images of hybrid films surfaces: 1. **M**; 2. **M** + PE; 3. **M** + PE functionalized with MA; 4. **M** + PE functionalized with NCOTEOS; 5. **M** + PE + Cloisite Na^+; (b) cross section in films obtained with Cloisite Na^+: 1. **M**+ Cloisite Na^+; 2. **M**+ Cloisite Na^+ + PE; 3. **M**+ Cloisite Na^+ + MA.

Thus, in the first two images the "mica-like" aspect of the aggregates structure can be observed.

In contrast, image 3 (the case of the hybrid based on **M**/MA/Cloisite Na^+ system) shows a totally different fracture morphology. From the XRD analyses one can assume that dispersed individual silicate layers are imbedded in the organic-inorganic network. The morphology is totally different from the first two cases, a continuous phase occurring (also "rocky," but more uniform). The aggregates of the primary particles are disrupted, resulting in a micron-scale arrangement of the primary particles in the organic-inorganic matrix. The induced fracture planes are fewer in this case and the apparent number of stress accumulation regions is smaller.

CONCLUSIONS

Films of polyether polyol and functionalized polyether polyol organic-inorganic hybrids were obtained. For the higher amount of PE the crosslinking degree was smaller for MA ($\sim$45%) than for NCOTEOS ($\sim$60%).

Thermal stabilities were measured by means of **TGA**. In the case of using functionalized PE the thermal stability varies with the amount of functionalized PE. When the amount of polymer is higher than 0.012 mol/l, the excess of ungrafted polyether induces a decrease of the thermal stability. By adding silicates to PE, the thermal stability increases.

The **FTIR** studies show that the reaction of MA and NCOTEOS with the polyether polyol occurred and the functionalized polyether reacted further in the sol-gel process.

The effect of Cloisite Na^+ fillers on the structure of PE based hybrid films was evaluated by **XRD**. In the presence of the nanoclay and polyether, the system based on polymer–inorganic hybrid is intercalated. For the sample without polyether, the XRD pattern for **M**/MA/Cloisite Na^+ showed no diffraction peak proving that the clay nanolayers have been exfoliated in the sol-gel process.

The SEM image in Figure 5a of the dip-coated films shows an increase of the homogeneity of the film surface when adding the polyether polyol. The film surface morphology depends on the inorganic precursor nature. In the presence of nanoclay, the fracture morphology is dramatically affected. For the films obtained in the presence of MA and nanoclay the stacked morphology is retained, but the fracture planes are numerically fewer (Figure 5b). The "rocky" like and "mica"-type aspect of the aggregates can be observed.

Hybrid polymer-inorganic systems, in the presence of some cationic dyes, were also prepared through the sol-gel method, evaluating their spectral properties through **UV-VIS** spectroscopy. The polarity changes affect the spectral properties of the included cationic dyes.

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