

STUDY OF THE SOLVENTS INFLUENCE ON THE LAYERED SILICATES - CATION POLYMER HYBRIDS PROPERTIES

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Present paper studies the possibility to obtain polymer-clay nanocomposites using poly(3-methacrylamidopropyl (N,N-dimethyl) dodecyl ammonium bromide) and several commercial clays- Cloisite Na, Cloisite 30B, Cloisite 93A, Cloisite 20A, Cloisite 15A in three different solvents (ethanol, chloroform and propyleneglycol monomethyl ether). The reaction medium plays a key role in the synthesis of polymer-clay nanocomposites determining also the final consistence, properties and appearance of the final mixtures. The melting enthalpy, corresponding to 1g of polymer, increase in the presence of layered silicates. FTIR spectra obtained in different applied strain conditions showed that the increasing of layered silicate straining induce decreasing of wavelength for significant peaks in the 1000-1300 cm⁻¹ spectral region.

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1. Introduction

In the last three decades, polymer - layered silicates nanocomposites have received special attention from the researchers worldwide interested in the development and diversification of macromolecular compound applications [1-11]. Dispersion of the negative charged aluminosilicates layers into polymeric matrices was intensively investigated. The main problem is the polarity difference between partners: very polar layered silicates and nonpolar classic polymers.

Negatively charges of the clay layers are balanced by a cation (e.g. sodium), along with different amounts of water, which are positioned in the interlayer space. Using very well established treatments, metal cations can be replaced with organic cations with long chains which can expand the distance between layers [1-4] becoming more hydrophobic, thus increasing the compatibility with polymers. The intercalation of organic cations (mostly, quaternary ammonium salts) takes into consideration the cation exchange capacity (CEC) of the initial layered silicate. Quaternary ammonium salts chains can adopt mono and/or bilayer arrangements modifying the interlayer distance according with conformation and length of the hydrocarbonate chains [1-4].

There are numerous studies [12-20] where the metals from interbasal layer are replaced also with cationic polymers. Only a limited amount of polymer can be intercalated depending on the CEC of initial aluminosilicate [8, 12]. Thus, ultrastrong layered polymer nanocomposites were prepared by successive deposition technique (layer-by-layer) of some cationic polymers, e.g. poly(diallyl dimethyl ammonium chloride) [13], polyethylene imine [14].

Terminal amino groups [16, 20] of cationic blockcopolymers [19] and natural polymers,

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e.g. proteins [15, 16] or chitosan [17, 18], can interact by cation exchange with layered silicates. In most cases, using this kind of interactions, intercalated nanocomposites structures were obtained. Exfoliation of the clay layers to an organomodified layered silicate was achieved only with polystyrene-polyacrylamine blockcopolymers obtained in dioxane [19].

In a previous paper [21], the synthesis of polymer-silica nanocomposites using poly(3-methacrylamidopropyl (N,N-dimethyl) dodecyl ammonium bromide) was followed. These film forming composites showed antibacterial properties. Present paper studies the possibility to obtain nanocomposites based on polymer - layered silicates organomodified with different quaternary ammonium salts, suitable for antibacterial applications. Three organic solvents with different polarities were used as dispersion medium to put in evidence their influence even from the initial dispersion stages of partners: polymer and layered silicates [22, 23].

2. Experimental

Materials. The synthesis of polymer poly(3-methacrylamidopropyl (N,N-dimethyl) dodecyl ammonium bromide) was previously reported [21]. The layered silicates were provided by Southern Clay Products Inc. and are used in the sodium form (Cloisite Na; 92mg/100g) and organomodified with different ammonium salts (methyl, tallow, bis-2-hidroxyethyl)-(Cloisite 30B; 90 mg/100g), (methyl, dihydrogenatedtallow)-(Cloisite 93A; 90 mg/100g) and (dimethyl, dihydrogenatedtallow)-(Cloisite 20A; 95 mg/100g) and (dimethyl, dihydrogenatedtallow)-(Cloisite 15A; 125 mg/100g). The organic solvents, ethanol, chloroform, propyleneglycol monomethyl ether (MeOPrOH) (Fluka), were used as purchased.

Characterization methods. FTIR spectra of the final products were recorded in ATR mode, on a FTIR-Tensor 30 BRUCKER spectrometer, using Golden Gate unit, in the range of 400-4000 cm^{-1} . The X-Ray diffraction data were collected at room temperature. Data acquisitions were made with a DRON-2.0 X-Ray diffractometer, with horizontal goniometry, scintillation counter and Cu-K α ($\lambda=1.5418 \text{ \AA}$) radiation source, in the Bragg-Brentano reflexion geometry. The DSC analyses were realized with a Mettler Toledo DSC 823^e/700 instrument at a heating rate of 10°C/min, in nitrogen atmosphere.

Preparation of composites. In a glass vessel were successively introduced: 0.075 or 0.15 g layered silicate and 7.5 g solvent. The mixture was magnetically stirred for 1h and than ultrasonicated for 10 minutes. The composition was kept at room temperature 24h. 15 g polymer solution, which contains polymer (P, 1.5 g), was added and the mixture was magnetically stirred for 1h and ultrasonicated another 10 minute. The final mixture was transferred into polyethylene vials for solvents evaporation.

3. Results and discussions

The main purpose of the present study was to clarify how the syntheses medium influences the partner's compatibility in the process of obtaining polymer - layered silicates nanocomposites. The polymer contains dodecyl type side chains compatible with quaternary ammonium salt structure. These interactions can assure a favorable intercalation phenomenon between negative charges layers of aluminosilicates [24]. It was showed that the dispersion media induce different interactions state toward melt-cooled method using chloroform as solvent, for the obtaining of nanocomposites based on poly(3-dodecyl thiophene) and organomontmorillonite. These results were explained also by the favorable interactions between dodecyl side chains and quaternary ammonium salts located into the interbasal space of clay layers.

The first finding in this paper that evidences the solvent influence is the appearance of the final mixtures polymer-solvent-organomontmorillonite. In the case of ethanol, all final mixtures formed heterogeneous systems which deposited in time a precipitate in the bottom part. Mixtures have finally segregated in an inferior layer with gel aspect and a transparent superior layer in the case of chloroform- CHCl_3 or propyleneglycol monomethyl ether-MeOPrOH [22, 23]. The weight of separated gel depends on the solvent type which assures the initial swelling of the organoclay [22, 23]. Thus, the gel volume for chloroform decrease in the following order: Cl15A > Cl20A > Cl93A > Cl30B > ClNa. The order is changed in the case of MeOPrOH, following the

configuration: Cl30B > Cl20A > Cl15A > Cl93A > ClNa.

These experimental observations justify the interest to find the perfect dispersion medium for organic and inorganic partners that contribute to the obtaining of different nanocomposites. In the case of using chloroform for dispersion, the solvent assures a major interaction for most hydrophobic organomontmorillonite (Cl15A). This phenomenon will have as result the obtaining of dispersions with a high degree of exfoliated OMMT [22]. The best interaction with Cl30B is assured by MeOPrOH with a maximum amount of separated gel [23]. Very probably, this is due the -OH groups from quaternary salt used for the obtaining of organoclay.

X-ray diffraction. Figure 1 presents the XRD patterns of some inorganic partners and their composites. Figure 1A contains information about: OMMT - Cl15A type (I), polymer (III) and their composite with 20% Cl15A obtained in chloroform (II).

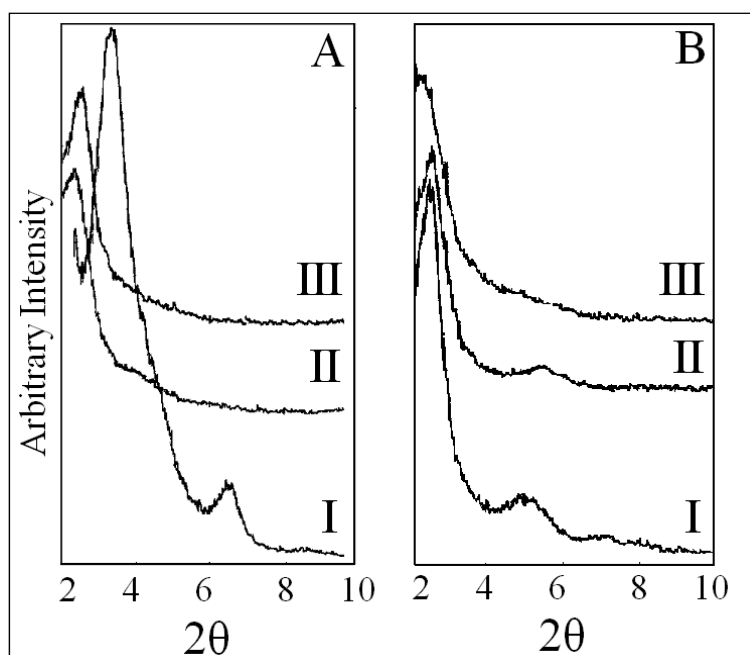


Fig. 1. XRD patterns for A: I-C115A, II- polymer-C115A (20 %), III- polymer separated from CHCl_3 ; B: polymer-C115A (10 %) hybrids obtained in I- EtOH, II- MeOPrOH, III- CHCl_3

The basal spacing (d_{001}) of the commercial Cl 15A is 31.7 Å which corresponds to intercalated quaternary ammonium salt. It was observed also a lower maximum peak at 12.4 Å which indicated the presence of some nonintercalated platelets, this value being very close to d_{001} obtained for ClNa (12.1 Å). The polymer presents a crystalline form at 34.9 Å due the association capacity of dodecyl chains.

The hybrid prepared with 20% Cl15A shared the characteristics peaks of both partners (Figure 1AII). It was observed a peak at 37.1 Å, which was attributed to the intercalated form of polymeric chains between organoclay layers. Also, it is observed a hump at 18.4 Å corresponding to the intercalated stage of layered silicate fraction. This behavior evidenced the presence of “interchain lamella” which was observed in the case of poly(dodecyl thiophene) –organomodified clay, too [24].

The results obtained in the presence of 10% Cl15A using the mentioned three solvents are very challenging (Figure 1B). For the systems prepared in alcohols, EtOH (Figure 1BI) and MeOPrOH (Figure 1BII), two peaks were observed at small sizes: 17.4 Å (EtOH) and 16.4 Å (MeOPrOH). The main peaks appear at 34.9 Å (EtOH) and at 34.5 Å (MeOPrOH) in intercalated range with higher size. The hybrid systems prepared in chloroform presented a different behavior (Figure 1BIII) and only one peak at 36.1 Å was observed. Complex studies regarding poly(3 dodecyl thiophene) –OMMT system [24] demonstrated that, in this case, an exfoliated structure was realized.

The table below shows the comparative analyses of the modification of the maximum diffraction peaks for the hybrids prepared in the presence of the mentioned solvents and five types of organomodified clays.

Table 1. Modification of the two peaks in the XRD patterns (sharp peak 18-30Å and small peak 12-13Å) for 10 % and 20 % layered silicates

| d_{001} | Cloisite type | 10% Cloisite | | | 20% Cloisite | | | |
|-----------|---------------|--------------|---------------------|--------|--------------|--------|---------------------|-----------|
| | | powder | P+CHCl ₃ | P+EtOH | P+MeOPrOH | powder | P+CHCl ₃ | P+MeOPrOH |
| 18-30Å | CI Na | 0 | 34.5 | 32.7 | 34.4 | 0 | 34.6 | 35.3 |
| | CI 30B | 18.07 | 34.9 | 34.5 | 34.5 | 18.07 | 35.8 | 34.5 |
| | CI 93A | 26.14 | 35.6 | 34.4 | 33.5 | 26.14 | 35.6 | 34 |
| | CI 20A | 25.8 | 34.6 | 35.2 | 35 | 25.8 | 37.8 | 34.1 |
| | CI 15A | 31.7 | 36 | 35.1 | 35.4 | 31.7 | 37.1 | 34.2 |
| 12-13Å | CI Na | 12.1 | 14.5 | 18.7 | 15.2 | 12.1 | 13.5 | 14.1 |
| | CI 30B | 12 | 15.4 | 13.3 | 16.3 | 12 | 15.8 | 16.4 |
| | CI 93A | 13.3 | 16.7 | 17.2 | 16.6 | 13.3 | 16.2 | 16.1 |
| | CI 20A | 12.6 | 0 | 17.6 | 16.6 | 12.6 | 17.7 | 16.1 |
| | CI 15A | 12.4 | 0 | 17.3 | 16.4 | 12.4 | 18.4 | 16.3 |

The changes observed for the sharp peak (~30 Å) are showed in Table 1 for both levels of inorganic partner (10% and 20%). In the hybrids case it was observed that the basal spacing of “interchain lamella” are superior compare with the partners sizes (layered silicates and polymer). For 10% clay no significant difference between the solvents used for synthesis, were observed.

In the case of hybrids that contain 20% clay, an increase of basal spacing obtained in chloroform for most hydrophobic OLS (CI93A, CI20A, and CI15A), was remarked. These results are in good agreement with the previous data's [22] that showed an advanced delamination of hydrophobic clays CI15A type, when CHCl₃ was used. In these conditions of advanced delamination, the separated gel weight is maxim after the partners contact. At high degrees of delamination of organomodified layered silicates, the side chains of polymer and of hydrophobic products have the possibility to form some structures which are larger after solvent evaporation.

The “small peak” which appears at around 15 Å changed according to the interactions between polymers and hydrophobic organic chains from clay. Hybrids with 10% LS, prepared using chloroform with unmodified layered silicate (CI Na) or more polar clay (CI30B, CI93A), contained intercalated structures with basal spacing superior of inorganic partners. Due to interaction between organoclays platelets and solvent molecule that induces a high degree of exfoliation of organoclays in dispersion, this maximum peak disappears in the case of CI20A and for CI15A indicating a high degree of dispersion. In the case of EtOH and MeOPrOH, the selective interactions through hydrocarbonated groups and through hydroxyl groups as well [23] induce superior sizes for EtOH. These results can be due to the polar groups which are in higher concentration in ethanol and also probable this alcohol is more volatile [24].

For the hybrids prepared with 20% clay, only the effect of chloroform and MeOPrOH, was followed. Using MeOPrOH (more polar solvent), higher intercalated degree was obtained for more polar clays: CI Na and CI30B. In the case of CI93A and CI20A, which experienced a higher delaminated degree in CHCl₃ [22], higher basal spacing was obtained. The disappearance of the “small peak”, remarked for 10% LS, was not observed in these conditions.

XRD studies demonstrated again the great interactions between layered silicates platelets and polymer, in the case of the hybrids obtained from solution.

DSC analyses. A recent study [24] revealed two melting points for poly(3-dodecyl thiophene): one corresponding to side chains and another, at higher temperatures, corresponding to principal chain. In the second part of this paper, following these suggestions, we studied the thermal behavior of polymer in the absence/presence of LS, at programmed heating rate in N₂. Figure 2 presents the thermal behavior of the hybrid prepared in chloroform with 10% CI15A. It was observed the presence of two melting domains with maximum at 102.83°C and 220.78°C.

According with the previous published results, the first melting point can be attributed to side chains and the second to the principal chain. These phenomena were remarked using repeated heating and cooling cycles.

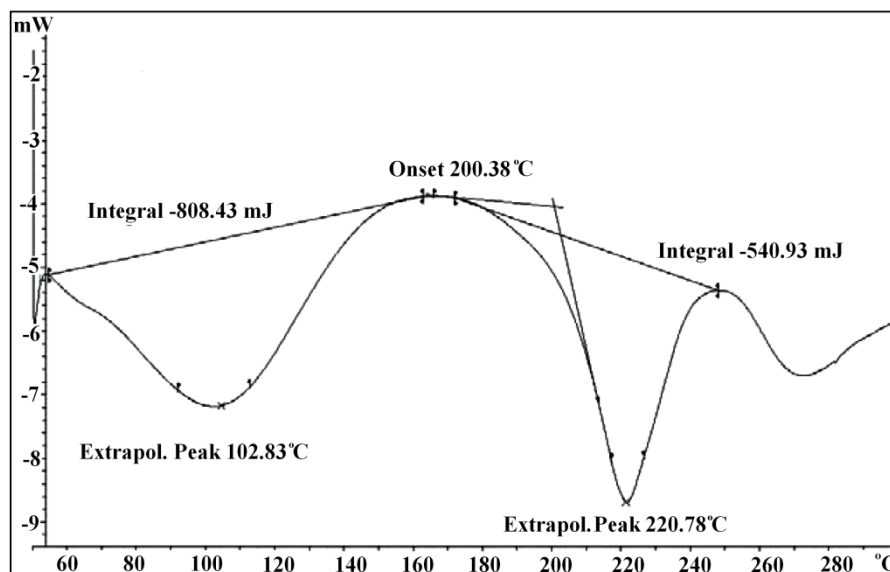


Fig. 2. DSC curve for 10 % CI15A hybrid obtained using CHCl_3

In order to show the influence of both, solvents and LS, the melting enthalpy corresponding to one gram of polymer, was calculated. Figure 3 presents the systematized observed modifications of the first peak which appears at 100°C , because in the second range ($\sim 200^\circ\text{C}$) appear weight losses, although the heating took place in N_2 .

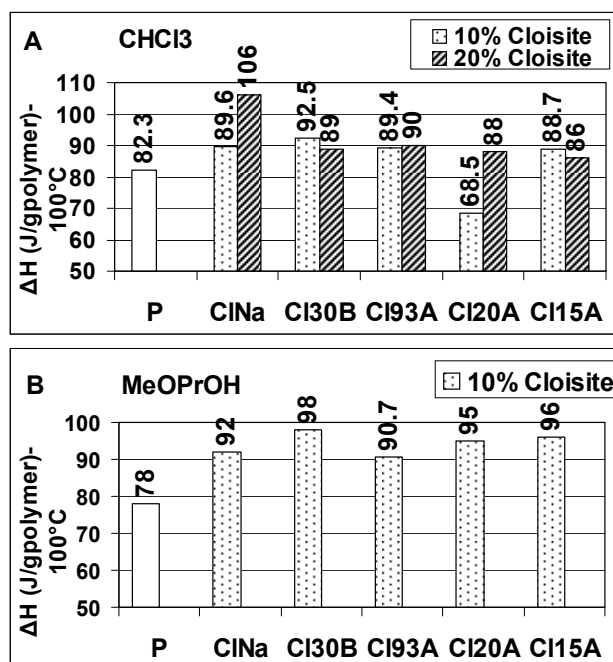


Fig. 3. Modification of ΔH ($\text{J/g}_{\text{polymer}}$) as function of solvent nature (A – CHCl_3 , B – MeOPrOH)

The first general observation is that the melting enthalpy, corresponding to one gram of polymer, increases in the presence of clay. The platelets of aluminosilicates increase the crystallinity, although, using organomodified clay, mix lamellas between side chains and quaternary salts used for hydrofobization can be formed. The highest melting enthalpy was

observed for the hybrid obtained with 20% ClNa using CHCl_3 . The mentioned solvent assures the delamination of platelets and subsequently a maximum interaction of the LS with the polymer (which is a quaternary salt), autonomously of the ammonium salts derived from OLS.

The second value of melting enthalpy was observed for the hybrid prepared with Cl30B in MeOPrOH (98 J/g). According with the previous data obtained in solution, the solvent and the quaternary salts which are present in the interlamellar layer, assure a good compatibility and probably a maximum density of chains with interlamellary compound.

In the case of other studied hybrids no remarkable differences were observed. One aspect should be noted, that the melting enthalpy obtained through evaporation from MeOPrOH is higher than that from CHCl_3 . This difference could indicate that the mixed crystallites which are formed between side chains and interlamellar lamellas are better organized in systems in which the exfoliation probability is smaller. Another explanation can be due the higher volatility of chloroform that cannot assure the necessary time for the formation of some more organized mixed lamellas [24].

FTIR results. The newest published results [24-27] have demonstrated that the IR spectroscopy is a very powerful tool to confirm the dispersion phenomena of clay in solvents or in polymer.

FTIR spectroscopy evidenced three maximum peaks in the region of SiO band $\sim 1000\text{ cm}^{-1}$ as follows: 1120, 1045 and 1015 cm^{-1} . For polypropylene hybrids appeared also a fourth peak after treatment with different additives and this because out of plane mode at 1080 cm^{-1} [25].

The comparative results between IR spectra obtained in different mathematical modeling or applied strain conditions are very interesting [26]. Increasing the LS strain induces the decrease of wavelength for the significant peaks in the spectral region $1000\text{-}1300\text{ cm}^{-1}$. The same effect was remarked also after the strong crushing of CaMMT [27].

An important observation for further studies is that even if the wavelength is changed with the mechanically induced tension or into composite, the behavior of the layered silicates can be observed through measuring of only one maximum peak ($\sim 1034\text{ cm}^{-1}$). This maximum peak decreases at 1026 cm^{-1} for a partially exfoliated form and to 1030 cm^{-1} for an intercalated morphology in case of poly(3-dodecyl thiophene)-OLS nanocomposites. Other peaks were observed at 515 and 460 cm^{-1} which were attributed to SiO stretching and bending (28, 29, 30). The polymer studied in this paper has quaternary ammonium salts, considered as side chains that can assure a better compatibility with organomodified clay.

Fig. 4A shows the modification of the IR spectra of Cl15A and of the composites prepared with 10% and 20% inorganic filler. It was observed that the peak absorbance from $\sim 1000\text{ cm}^{-1}$ decreased with the decrease of LS concentration. The corresponding polymer peaks were not evidenced; subsequently we can analyze the results through comparison. The polymer presented a peak at $\sim 1150\text{ cm}^{-1}$ attributed to C-N stretching vibrations. The absorbance of this peak decreased with the decreasing of polymer concentration in the prepared hybrid.

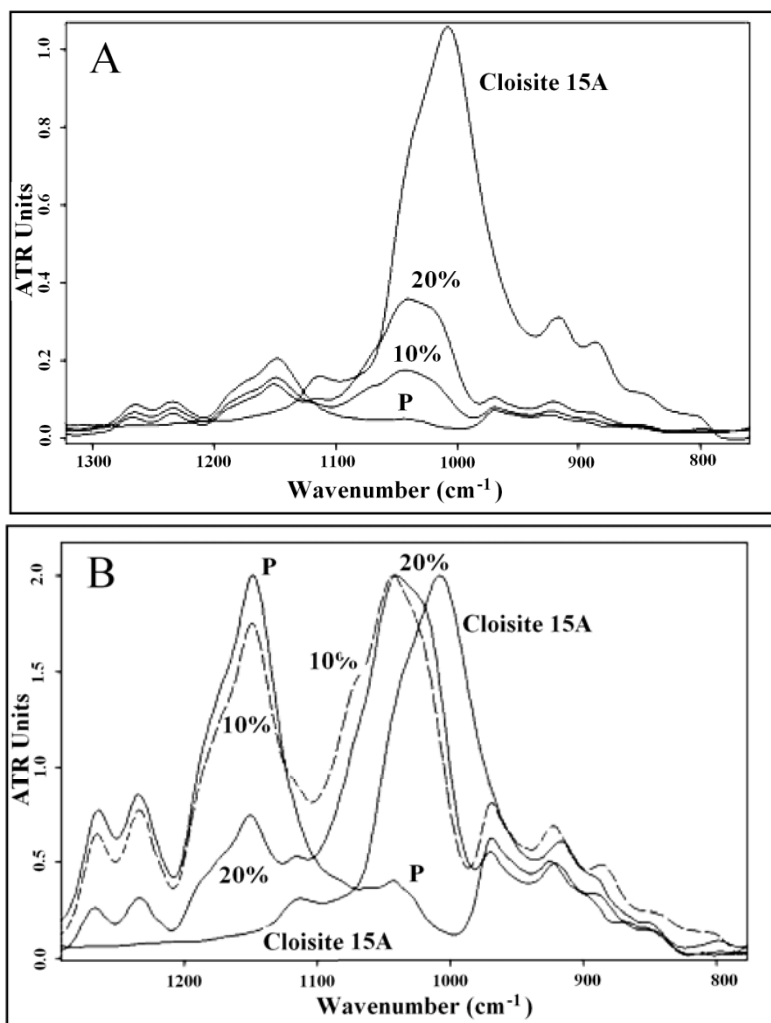


Fig. 4. FT-IR spectra of hybrids obtained with Cl15A using MeOPrOH (A – concentration effect of LS, B – normalized spectra)

Fig. 4B shows the normalized spectra. The wavelength corresponding to the maximum at ~ 1000 cm⁻¹ increased in the case of Cl15A hybrids. If the wavelength decreases in stress conditions [26] than this increasing can be assigned to the reversed phenomenon: the platelets of aluminosilicates are much relieved in hybrids than in its powder state.

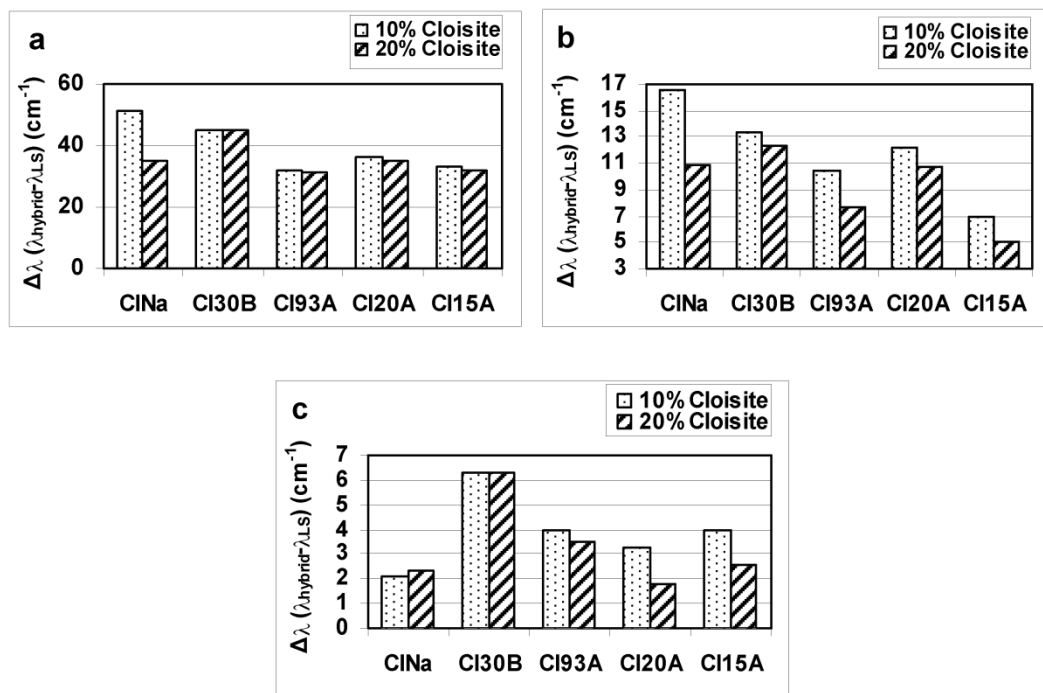


Fig. 5. The change of difference value between hybrid maximum wavelength and LS maximum obtained in MeOPrOH for the five types of used LS, for λ_{LS} : a) 1040 cm^{-1} , b) 460 cm^{-1} , c) 515 cm^{-1}

The comparative analysis of maximum wavelength modification regarding the hybrid and the layered silicates is showed in Figure 6. If we consider that the mechanism showed in Figure 4B is correct, than the most strained tactoids are formed in CINa case in comparison with its hybrids (the difference between hybrids wavelength and LS wavelength is maxim). One can notice, for the majority of the layered silicates showed in Figure 5, the relaxation maximum was obtained at 10% filler. At 20% filler, the wavelengths difference is smaller indicating a weaker strain relief. Similar results were obtained for hybrids prepared in CHCl_3 (Figure 6).

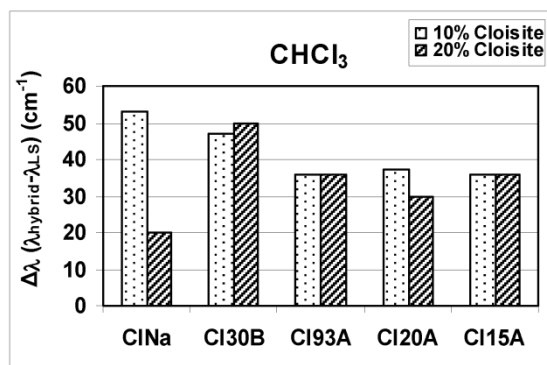


Fig. 6. The modification of the difference between wavelength of hybrids and of LS prepared in CHCl_3 .

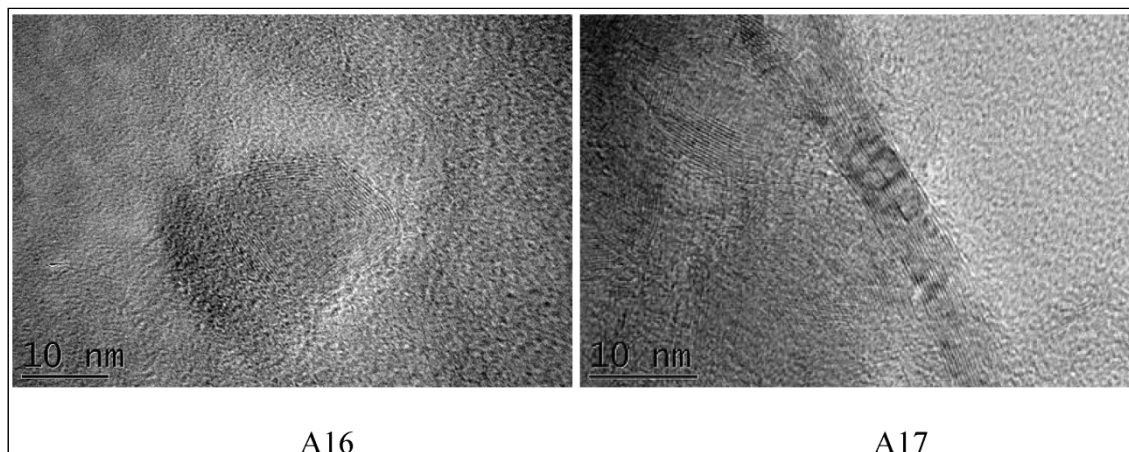


Fig. 7. TEM images of samples prepared in MeOPrOH with 10% LS (s.A16-CINa, s.A17-CI30B)

TEM images captured for two hybrids prepared in MeOPrOH confirmed the obtained results. The sample A16 has been prepared with 10% CINa. XRD diagrams showed one peak at 34.4Å for polymer and another one peak at 15.2Å for the LS. The sample A17 has been prepared with 10% CI30B. XRD diagrams presented one peak at 34.9Å for polymer and another one peak at 16.3Å for the LS. The DSC analyses and FTIR spectra evidenced the interactions between polymer matrix and layered silicate, the filler dispersion being incomplete. TEM images (Figure 7) validate these conclusions. Thus, the captured images showed domains where the silicate formed aggregates in the polymer matrix. The images captured at higher zoom confirmed the intercalation state between cationic polymer and layered silicate.

4. Conclusions

Composites based on poly(3-methacrylamidopropyl (N,N-dimethyl) dodecyl ammonium bromide) and different layered silicates in three different solvents, were obtained. The first finding was that the gel volume separated from the solvent is influenced by the clay and solvent types.

XRD results showed that the systems prepared in alcohols (EtOH and MeOPrOH) presented intercalated domain while for the hybrid prepared in chloroform exfoliated structure was realized.

The hybrids with 10% LS, prepared in the presence of chloroform with CINa or more polar silicates (CI30B, CI93A), contain intercalated structures with sizes which are superior compare with inorganic partners sizes. For the hybrids with 20% LS were observed a higher superior intercalated degree and higher sizes for more polar clays, CINa and CI30B, using MeOPrOH (more polar solvent). In the case of more hydrofobic OLS which have suffered a higher delamination degree in CHCl₃, final bigger sizes were obtained for CI93A and CI20A.

DSC studies show that the melting enthalpy obtained through evaporation from MeOPrOH is higher than that from CHCl₃. Thus, the mixed crystallites formed between side chains and interlamellar ammonium salts are better organized in systems which the exfoliation probability is smaller.

FTIR spectra revealed that the increase of the number of SiO bonds can be induced by the smaller stress of the platelets of aluminosilicates in polymer-clay hybrids comparing with the powder state.

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