

# Organic/inorganic hybrid latexes colored with azoic dyes

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Stable hybrid nanolatexes based on styrene, butylacrylate or methylmetacrylate with alkoxy silane in the absence/presence of an azoic dye, with/without layered silicate, using microemulsion copolymerization procedure, were obtained. Type of monomer, dye concentration and the presence of layered silicate influences the average diameter of the particles and the Zeta potential appeared on the particle - disperse medium interface, inclusive the maximum wavelength, as it was shown by DLS and UV-VIS analyses. In order to evidence the inorganic partners presence (silica, layered silicates) in the polymer matrix, FTIR and X-Ray fluorescence, were performed.

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**Keywords:** Hybrid latexes, Silica, dye, Layered silicates, Microemulsion

## 1. Introduction

Special interest was paid to the obtaining of nanocomposites materials because of their exceptional properties offered by both organic and inorganic components [1-5]. In previous studies we showed the influence of inorganic partner, obtained by sol-gel reaction [6,7] and/or layered silicate [8,9], on the properties of the final latexes. There are studies that show the behavior of organic-inorganic matrices in the presence of some organic dyes like rhodamine B, methylene blue, crystal violet, Congo red [10-15]. These materials containing dye molecules are of considerable interest from a fundamental point of view as well as for potential applications such as: optics, catalysis, biosensors, etc. [16-18].

We consider interesting the continuation of the mentioned studies by the introduction of a new component which is an azoic dye with Si-OR groups which can participate also at sol-gel processes and is utilized to grow a network in polymer matrices (composite) or to create inter-polymer network among polymer chains (hybrid).

The aim of this work is to synthesize colored hybrid latexes through microemulsion copolymerization procedure of monomers with different polarities (styrene (St), butylacrylate (BuA) and methylmetacrylate (MMA)) with a sol-gel precursor that has vinyl group metacryloxypropyltrimethoxysilane (MPTS), in the presence of an azoic dye with Si-OR groups. This dye was previously obtained by the reaction of izocyanopropyltriethoxysilane (NCOTEOS) with an azoic dye ((HESA) hydroxyethylsulphonaniline reacted with N-ethyl-N-benzyl-aniline). In order to minimize premature sol-gel process, the copolymerization occurred in buffer solution (pH=7). The polymerization was followed by sol-gel process in the presence of ammonia.

Supplementary, the behavior of these systems in the presence of layered silicate, montmorillonite type was studied. When dyes are embedded in a clay mineral

matrix, they can improve the thermal and chemical stability being very useful for nanoscale devices of optical memory systems, optical switching systems, amplifiers, energy storage devices and solar cells [19].

If some studies present the adsorption of single chromophores and aggregates on different substrates, synthesis and characterization of heterogeneous fluorescent nanocomposites is still in its infancy [20] and from the best of our knowledge this combination polymer-silica-dye-layered silicate wasn't studied before.

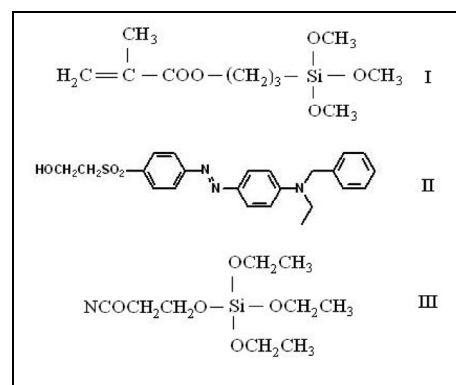


Fig. 1. Chemical structure of:  
I. Metacryloxypropyltrimethoxysilane (MPTS).  
II. Hydroxyethylsulphonaniline (HESA) reacted with N-ethyl-N-benzyl-aniline.  
III. Izocyanopropyltriethoxysilane (NCOTEOS).

## 2. Experimental

### 2.1 Materials

Monomers: styrene (St), butylacrylate (BuA), methylmetacrylate (MMA) – were purified through rectification; metacryloxypropyltrimethoxysilane (MPTS) – used without further purification; commercial products

(Fluka). The dye was previously obtained by the reaction of izocyanopropyltriethoxysilane (NCOTEOS) with an azoic dye ((HESA) hydroxyethylsulphonaniline reacted with N-ethyl-N-benzyl-aniline) (private results).

Buffer solution (natrium tetraboricum/kaliumdyhydrogenphosphate, pH=7) was used as dispersion media and 25% NH<sub>3</sub> solution to start the sol-gel process. The surfactant, sodium dodecylsulphate (SDS, Fluka) and the initiator, ammonium persulphate (APS, Loba Feinchemie), were used without other purifications. The layered silicate was provided by Southern Clay Products Inc. and is used in the sodium form (Cloisite ®Na).

## 2.2 Procedures

The latexes were obtained by using Erlenmeyer recipients (with lid, cork) coupled to a thermostat bath with magnetically stirrer. In the first stage, the surfactant (8 g SDS) was dissolved in buffer solution (40 ml, pH=7) at 30°C temperature, after that layered silicate was added (0.5 g Cloisite). The mixture was magnetically stirred for 15 min. and ultrasonicated for 5 min. A mixture of monomers and dye [4 ml (St, BuA, and MMA)], 0.4 ml (MPTS), 0.1-0.4 ml HESA-SiOR (in THF solution)] was added and the reaction mixture was heated at 65°C. The polymerization started by adding the initiator (APS, 0.15 g). The system was kept under magnetically stirring. After 3 hours the system was cooled and 25% NH<sub>3</sub> solution was added, in order to start the sol-gel process. The final latexes were analyzed through DLS and UV-VIS. A small amount of latexes were deposited on a polyethylene foil for water evaporation, which was done at room temperature for several days. The resulted materials were washed with water to extract the surfactant (through centrifugation) and analyzed through FTIR and X-Ray fluorescence.

## 2.3 Measurements

Particles hydrodynamic diameters and Zeta potential were determined by Dynamic Light Scattering (DLS) with Zetasizer Nano ZS, ZEN3600, produced by Malvern International Ltd. The samples were prepared using a 0.01M NaCl solution (0.1 ml latex/25 ml sol. 0.01M NaCl).

UV-VIS absorption spectra of the final latexes were acquired in the range of 350-800 nm using an UV-VIS spectrophotometer (Nicolet Evolution 500 from Thermo Electron Corporation).

FTIR spectra of final products resulted after water evaporation and surfactant removal, were recorded in transmission mode, on a FTIR-Tensor 30 BRUCKER spectrometer, in the range of 400-4000 cm<sup>-1</sup>, from KBr pellet using 40 scans with 4 cm<sup>-1</sup> resolution.

X-Ray fluorescence (XRF) analyses were performed on a PW4025-MiniPal-Panalytical type EDXRF Spectrometer. The determinations have been carried out in helium atmosphere, for a period of 300 sec., without any filter, at 20kV voltage and automatically adjusted current

intensity; for the construction of the cap a 3.6 µm Mylar film was used.

## 3. Results and discussion

The hybrid latexes obtained as a result of polymerization and sol-gel reactions, were characterized through UV-VIS and DLS analyses. It was found one peak in every UV-VIS absorption spectra; this is due to the monomeric form of the dye. Maximum wavelengths of the colored latexes based on styrene, butylacrylate and methylmethacrylate with MPTS, were extracted from UV-VIS absorption spectra and are presented in Fig. 2. In all of the cases, (St, BuA, MMA) – MPTS (Fig. 2), it was observed that the absorbance (not shown) increases and absorption maximum shifts at higher values with the increase of dye concentration (0.2, 0.3, 0.4 ml), a red shift ( $\pi$ - $\pi$  transitions) which proves that dye concentration influences the chromophore properties of the final hybrid latex. This fact could be explained through the possible interactions occurred between dye and the components of the system (monomer/polymer, alkoxy silane). The polarity of the medium as well as the length of macromolecular chain influences the maximum wavelengths [15]; red shift was registries and the values increase in the following order: PSt-PBuA-PMMA at all concentrations of dye used in the synthesis (0.2, 0.3, and 0.4 ml). These shifts to higher wavelengths with dye concentration increase were explained as a consequence of the enhancement of the polarizability in the dye-surrounding environment that results from the close packing of the dye moieties in aggregates [20, 21].

The smallest values obtained for the system based on styrene could be due to the presence of ammonium persulphate as initiator. At a higher concentration (5 times bigger) it was observed a discoloration of the latex and therefore a minimum wavelength gave by the consumption of the dye by the excess amount of SO<sub>4</sub><sup>2-</sup> species [22]. When added a higher concentration of dye the values tend to stabilize, at 0.4 ml no significant difference being visualized as a function of monomer type.

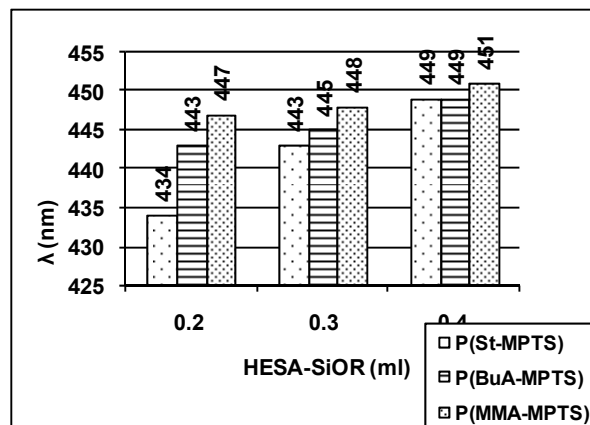


Fig. 2. Modification of maximum wavelength of UV absorption spectra of (PSt-PBuA-PMMA) - MPTS at several dye concentration.

The presence of alkoxy silane (MPTS) also affects the absorption maximum (Fig. 3). It was observed a blue shift, given very probably by carbonyl group, oxygen electrons respectively, from MPTS ( $n-\pi$  transitions). This phenomenon is called “metachromasy” and the dyes which exhibit this effect are “metachromatic dyes” [23,24].

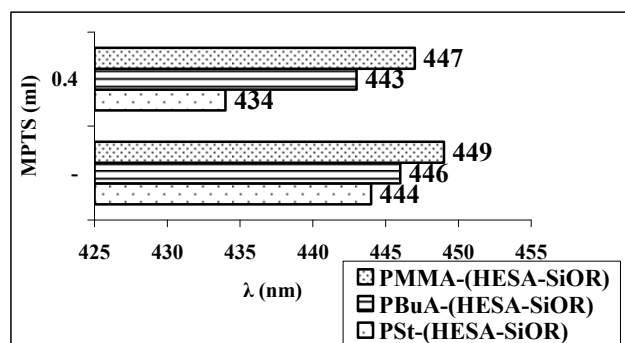


Fig. 3. Modification of maximum wavelength of UV absorption spectra of (PSt – PBuA – PMMA) – (HESA – SiOR) with/without MPTS.

When the layered silicate was added to our polymer – alkoxy silane – dye system (Fig. 4), it was observed a slightly increase in maximum wavelength, more obvious for the latexes based on polystyrene (from 434 nm to 443 nm). This can be attributed to the interactions that can take place between clay minerals and phenyl rings of organic dye, which can cause changes in the optical, spectral and chemical properties of the chromophores ( $\pi-\pi^*$  transitions).

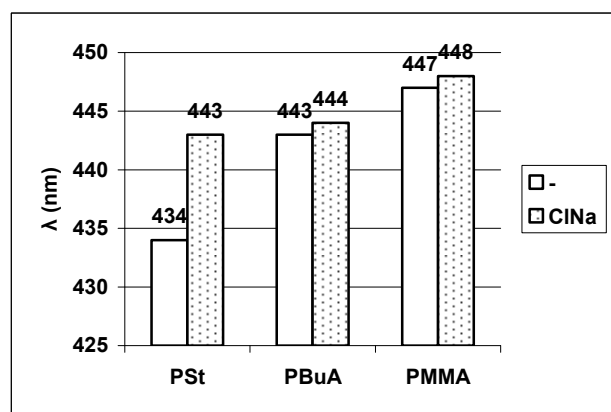


Fig. 4. Maximum wavelengths obtained for the latexes based on PSt, PBuA, PMMA with MPTS and HESA-SiOR in the absence/presence of layered silicate.

In previous studies, DLS analyses for the hybrid polymer-silica latexes, showed modifications in the particle dimensions and surface charges as a result of sol-gel process [6, 9]. In the present paper we focused on the changes that appear in the presence of HESA-SiOR dye. Some results are presented in figure 5 and table 1. It can be remarked from Fig. 5, that medium diameters don't differ too much with dye concentration. But for the samples obtained with 0.3 and 0.4 ml HESA-SiOR it was

observed a bimodal distribution, the first peak being around 25 nm and the second one between 300-400 nm; this behavior could be explained by the aggregation of dye with macromolecular chains. The medium diameters grow as a function of monomer type in the order (PSt-PMMA-PBuA) – MPTS with different dye quantities. It can be noticed that the dimensions ranges from 20 to 30 nm, this fact allows for the excellent optical transparency as it was seen for another dye (rhodamine B dispersed in hybrid silica gel glasses) [20]; this is very important for various applications.

Zeta potential measurements reveal higher absolute values when dye concentration increase (Table 1); negative values are given by the surfactant presence [6-8] and silica charges. Thus, the presence of a higher concentration of dye can be favorable for the stability of the polymer – alkoxy silane system. Regarding the zeta potentials for latexes obtained with 0.2 ml HESA-SiOR it can be observed an increase of the values in the presence of MPTS, the alkoxy silane having a positive effect on the stability of the latexes as it was shown in our previous studies [6, 7].

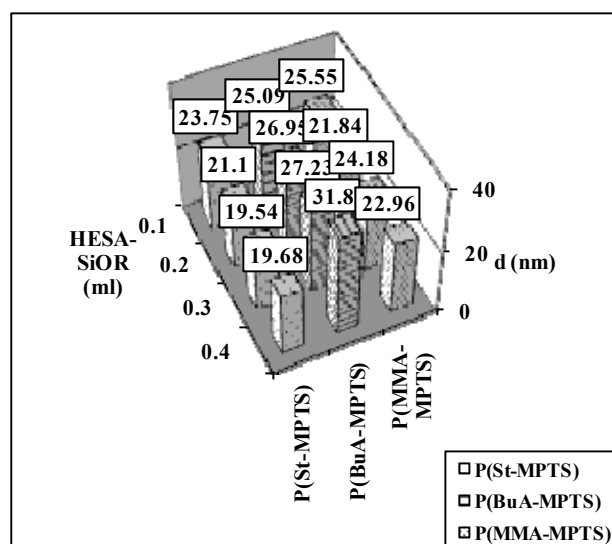


Fig. 5. Medium diameters obtained for the (PSt, PBuA, PMMA) - MPTS latexes with different dye concentrations.

Table 1. Zeta potentials (mV) for (PSt, PBuA, PMMA) - MPTS latexes with different dye concentrations.

HESA-SiOR (ml)	PSt	PBuA	PMMA
0.2 (-)	-17,6	-20	-10,2
0.1 (0.4mlMPTS)	-26,1	-28	-23,5
0.2 (0.4mlMPTS)	-28,8	-29	-26,1
0.4 (0.4mlMPTS)	-41,7	-36,4	-42,3

Regarding (PSt, PBuA, PMMA) latexes with 0.4 ml MPTS and 0.1 ml HESA-SiOR, it can be remarked an increase of medium hydrodynamic diameters in the presence the layered silicate (Fig. 6). The distribution was bimodal, the first peak being around 30 nm and the second

one around 500 nm. This behavior was observed before for other systems obtained in the presence of layered silicates, the modification of medium diameters being a consequence of the layers localization in/outside of the latex particles [25,26].

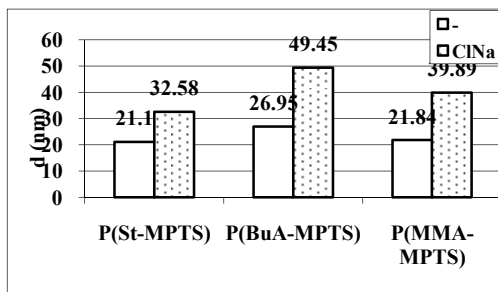


Fig. 6. Medium hydrodynamic diameters obtained for the latexes based on PSt, PBuA, PMMA with MPTS and HESA-SiOR in the absence/presence of layered silicate.

The Zeta potential is modified also in the presence of silicate to more negative values (Table 2); this is because of the stabilization effect induced by the silicate lamellas, similar behavior with Pickering emulsions [27].

Table 2. Zeta potentials (mV) obtained for the latexes based on PSt, PBuA, PMMA with MPTS and HESA-SiOR in the presence of several layered silicate.

Layered silicate	P(St-MPTS)-(HESA-SiOR)	P(BuA-MPTS)-(HESA-SiOR)	P(MMA-MPTS)-(HESA-SiOR)
-	-28,8	-29	-26,1
ClNa	-41,7	-37,7	-45,9

The presence of inorganic partners in the polymer matrix was emphasized by FTIR (Figs. 7-10) and X-Ray fluorescence analyses. FTIR spectra's of the solid materials obtained after surfactant removal showed the polymer specific peaks; for polystyrene (Fig. 7) - 3020-3100  $\text{cm}^{-1}$  CH aromatic stretching vibration, 2850-2940  $\text{cm}^{-1}$   $\text{CH}_2$  asymmetric stretching vibration, 1450  $\text{m}^{-1}$  shearing vibration, 1220  $\text{cm}^{-1}$  CH aromatic deformation vibration, 950-1050  $\text{cm}^{-1}$  vibration at aromatic nucleus, 790  $\text{cm}^{-1}$  CH bending vibration; for polyacrylates (Fig. 8 and Fig. 9) - 1737  $\text{cm}^{-1}$  C=O stretching vibration, 1163  $\text{cm}^{-1}$  C-O-C asymmetric stretching vibration and 2960-2870  $\text{cm}^{-1}$   $\text{CH}_3$  stretching vibration [28]. The characteristic bands of MPTS units are in the 1717-1724  $\text{cm}^{-1}$  domain for the carbonyl group [28, 29]. It can be observed also the peak of silica obtained through sol-gel process of the MPTS or HESA - SiOR, at 1000-1200  $\text{cm}^{-1}$ . Regarding the specific peaks for silica, these are present in the FTIR spectra for polymer-MPTS and also polymer-HESA-SiOR; this fact can be prove that the sol-gel process took place at alkoxy silane edges as well at HESA-SiOR extremities. In the case of (PSt-PBuA-PMMA)-MPTS-(HESA-SiOR) nanocomposites with layered silicates, specific peaks are found: 3635  $\text{cm}^{-1}$  OH stretching of lattice water, 1045  $\text{cm}^{-1}$  Si-O-Si stretching vibration and (400-600)  $\text{cm}^{-1}$  Si-O bending and stretching vibration (Fig.

10). Thus, the existence of PSt, PBuA, PMMA and layered silicates peaks in nanocomposites FTIR spectra, is ascribed to the inclusion of the clay layers in the polymer matrix [2, 3, 4].

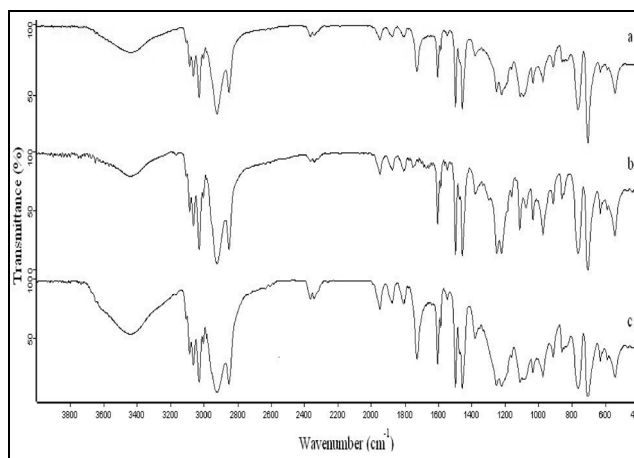


Fig. 7. FTIR spectra of the hybrid materials based on: a) PSt-MPTS; b) PSt-(HESA-SiOR); c) PSt-MPTS-(HESA-SiOR).

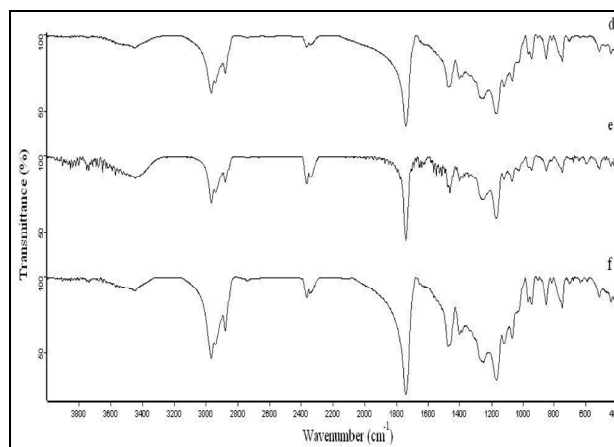


Fig. 8. FTIR spectra of the hybrid materials based on: d) PBuA-MPTS; e) PBuA-(HESA-SiOR); f) PBuA-MPTS-(HESA-SiOR).

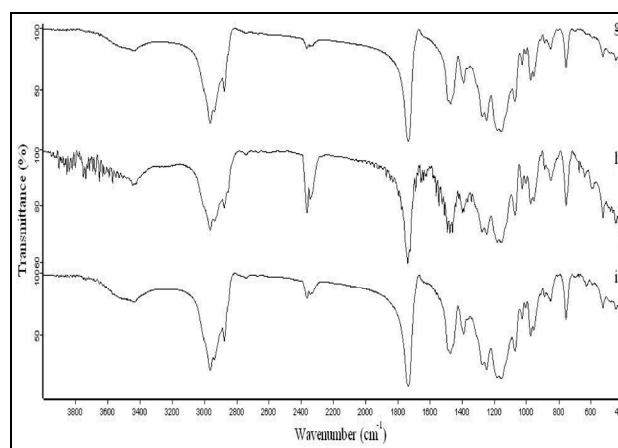


Fig. 9. FTIR spectra of the hybrid materials based on: g) PMMA-MPTS; h) PMMA-(HESA-SiOR); i) PMMA-MPTS-(HESA-SiOR).

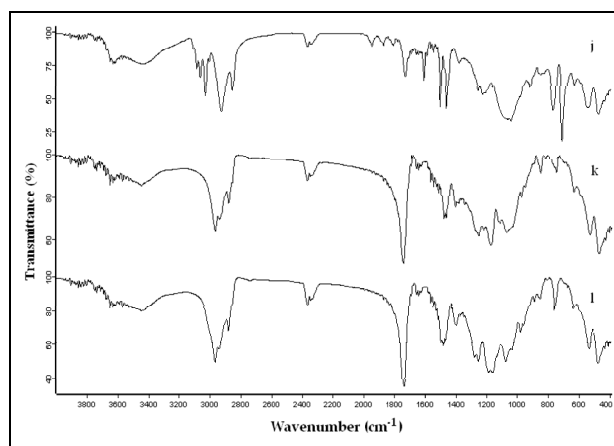


Fig. 10. FTIR spectra of the nanocomposites materials obtained in the presence of Cl Na for the samples based on: j) PSt; k) PBuA; l) PMMA.

The presence of silicon in the final materials was emphasized by X-ray fluorescence spectroscopy, too. Some of the spectra are presented in Figs. 11- 13.

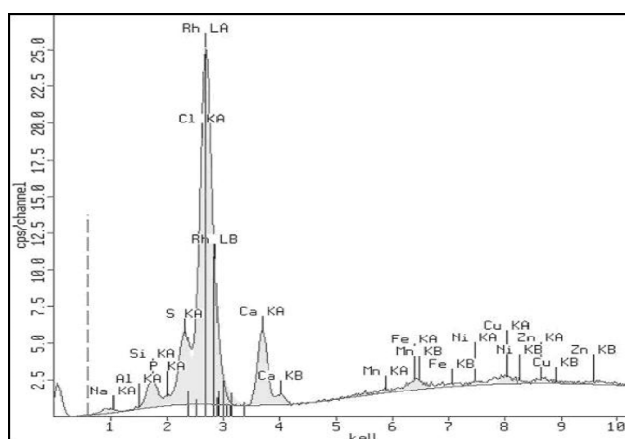


Fig. 11. X-Ray fluorescence spectra for the sample based on PBuA-MPTS.

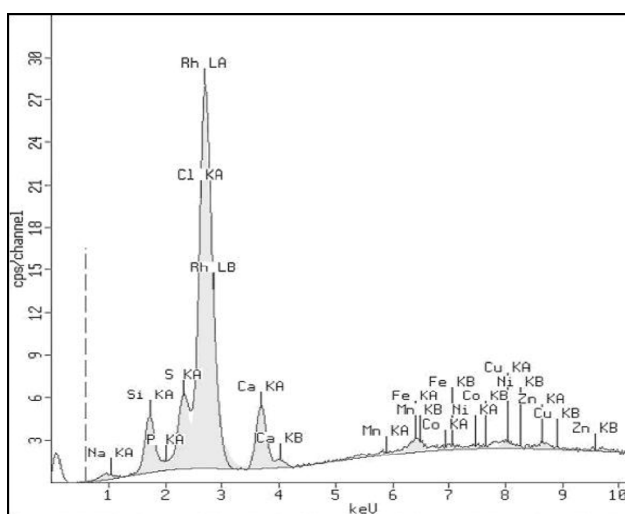


Fig. 12. X-Ray fluorescence spectra for the sample based on PBuA-MPTS-(HESA-SiOR).

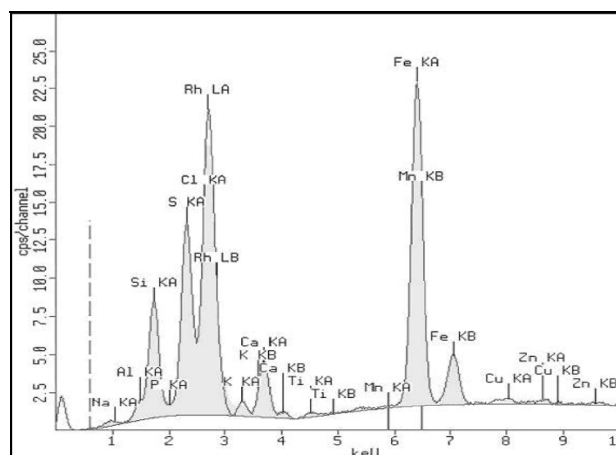


Fig. 13. X-Ray fluorescence spectra for the sample based on PBuA-MPTS-(HESA-SiOR)-Cloisite Na.

The analyses performed for PSt - MPTS, PSt -MPTS - (HESA - SiOR) and PSt - MPTS - (HESA - SiOR) - Cl Na, showed the presence of silicon in polymer - silica hybrids and polymer- silica - layered silicates samples. The silicon percentage grew from 16% silicon deriving from MPTS (Fig. 11) to 27.8% silicon resulting from MPTS and HESA-SiOR (Fig. 12). When the layered silicate was added, the percentage grew again to 33.2% silicon, deriving from MPTS, HESA-SiOR and Cloisite Na (Fig. 13). These results are in good accordance with FTIR analyses and sustain the hypothesis of silica and layered silicates inclusion in the polymer matrix.

#### 4. Conclusions

Polymer - inorganic hybrid latexes colored with azoic dyes using microemulsion polymerization procedure, were obtained. The UV-VIS analyses revealed that the interactions occurred between dye and the system components lead to modifications in absorption specters. Particle size analyses didn't showed significant changes in function of dye concentration but as monomer type. Zeta potential instead, is more negative with increasing dye concentration.

Layered silicates presence affects also the particle sizes and Zeta potential of the colored hybrid latexes. FTIR analyses performed for polymer - silica hybrids, polymer - layered silicates nanocomposites and polymer-silica- -layered silicates samples, showed the presence of silica as well as layered silicates in the polymer matrix; X-Ray fluorescence determinations confirmed the silica presence in the obtained samples, being in good agreement with FTIR results.

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