JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 15, No. 5- 6, May – June 2013, p. 578 - 582

Miniemulsion polymerization of styrene in the presence of different commercial clays

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Stable nanocomposite latexes based on styrene with/without layered silicate using miniemulsion polymerization procedure, were obtained. The presence of the clays influences the average diameter of the particles and the size distribution, as it was shown by DLS analyses. In order to evidence the inorganic partner's presence as well as the intercalation/exfoliation of clay layers in the polymer matrix, FTIR and XRD analyses were performed. Thermal behavior of the obtained nanocomposites by TGA and DSC was followed. The morphology of the final latex was observed by ESEM.

(Received February 4, 2013; accepted June 12, 2013)

Keywords: Nanocomposites, Polystyrene, Miniemulsion, Layered silicates, Latexes

1. Introduction

Polymer-clay nanocomposites have gained special interest because of their enhanced properties compared with traditional composites like increased modulus, thermal stability, inflammability, better barrier properties, chemical resistance and electrical conductivity [1-5]. These properties are conferred by the synergetic combination at nanoscale between organic and inorganic partners [6-9]. Miniemulsion polymerization is a powerful tool able to synthesize polymer-clay nanocomposites and this is because of the distinct aspect of monomer droplet nucleation [9, 10]. Therefore, via miniemulsion polymerization three structures of polymer/clay nanocomposites can be obtained: irregular dispersion on clay in polymer matrix, clay armored polymer particles and clay encapsulated inside the polymer particles [11].

The most commonly clay used in the synthesis of polymer nanocomposites is montmorillonite [2-5, 10, 12]. The building blocks of montmorillonite are silicon-oxygen tetrahedral ($Si_2O_5^{-2}$) and aluminum octahedra ($Al(OH)_6^{-3}$. The MMT has a thickness about 1nm and a length of 100nm or higher conferring the much higher surface area of the clay platelets. Although the encapsulation of spherical inorganic particles using miniemulsion polymerization has been extensively studied, clay particles have a platy morphology making dispersion and encapsulation more difficult to achieve. It is well known that montmorillonite is easy to disperse in water due to its hydrophilic nature and this is an advantage regarding ecological aspects, but causes problems when dispersing in hydrophobic monomers/polymers [2-4, 13]. To obtain a better compatibility with the polymer matrices, organically modified montmorillonite were used in the synthesis [3, 4, 7, 10]. Their modification can be achieved either by edge covalent bonding with silanes (sol-gel reaction with chloro or alkoxysilanes involving edge SiOH groups) or by replacing inorganic cations with quaternized ammonium or phosphonium compounds preferably with long alkyl chain [14-18]. Previous studies already proved the influence of the organomodification of montmorillonite in the polymerization process of several polymers [6, 7, 19-21].

The goal of our present study is to obtain polymer-clay nanocomposites using miniemulsion polymerization of styrene in the presence of several commercial clays modified with different quaternary ammonium salts. The influence of the silicate nature on the structure and morphology of the final latex/material was also studied.

Polymer-clay nanocomposites obtained by miniemulsion polymerization are still in its infancy and from the best of our knowledge this system polymer-surfactant-clay wasn't studied before.

2. Experimental

2.1 Materials

Styrene (Acros Organics) was purified by distillation under reduced pressure before use. The surfactants, sodiumdodecylsulphate and Brij96V (Fluka), ammonium persulphate (APS) from Loba Feinchemie, and n-hexadecane from MERCK-Schuchardt were used as supplied. The layered silicates were provided by Southern Clay Products Inc. and are used in the sodium form (Cloisite Na; 92meg/100g) and organomodified with different ammonium salts (methyl, tallow, bis-2-

hidroxyethyl)-(Cloisite 30B; 90 meg/100g), (methyl, dihydrogenatedtallow)-(Cloisite 93A; 90 meg/100g) and (dimethyl, dihydrogenatedtallow)-(Cloisite 20A; 95 meg/100g) and (dimethyl, dihydrogenatedtallow)-(Cloisite 15A; 125 meg/100g). Distilled water was used as dispersion media.

2.2 Procedures

The latexes were obtained by using a three neck glass flask with round bottom, coupled with a thermostat bath with mechanical stirrer. A reflux refrigerator and a thermometer were also connected to the glass flask. In the first stage, A mixture of 0.3 g Brij 96V, 0.49 g n-hexadecane, 9.99 g styrene, and 0.5 g ClNa or modified Cloisite (5.005 % wt to monomer) was sonicated for 5 min, then vigorously stirred (500 rpm) for 30 min under nitrogen atmosphere. The mixture was sonicated again for 5 min on an ice bath. Next, a solution of 0.3 g SDS in 40 g of distilled water (DW) was added to the mixture and the temperature was raised to 70^{o}C. The polymerization was initiated by adding a solution of 0.15 g of APS in 10 g of DW water. After 5 h of polymerization, the latex was cooled to room temperature. Monomer conversions were determined by the gravimetric method. Small amounts of latexes were deposed on a polyethylene foil for water evaporation, which was done at room temperature for several days. The final latexes were analyzed through DLS and ESEM. The resulted materials analyzed through FTIR, TGA, and XRD.

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).

FTIR spectra of final products resulted after water evaporation and surfactant removal, were recorded in ATR mode, on a FTIR-Tensor 30 BRUCKER spectrometer, in the range of 400-4000 cm^{-1}.

XRD analyses were performed using a RIGAKU Ultima IV Instrument with Parallel Beam geometry and Ultima IV In-plane Goniometer at 40 kV/30 mA (Cu Ka), in 2h range: 1_–30_ and 5_ scanning speed.

TGA analyses were performed with a SDT Q600 instrument. The samples were heated, in helium atmosphere 100ml/min with a rate of 20 ^{o}C/min. Differential scanning calorimetry (DSC) thermographs were recorded with the same instrument at a heating rate 1st Heating: 20°C/min RT to 200°C; Isothermal for 1 min; 2nd Heating: 20°C/min RT to 200°C.

Diluted latex samples were cast on aluminum stubs and copper grids and were investigated by scanning electron microscopy (SEM-FEI Quanta 200).

3. Results and discussion

Polymer-clay nanocomposites were obtained as a result of in-situ polymerization of polystyrene. The latexes were characterized through DLS analyses (figure 1). For polystyrene latex the distribution was narrow, unimodal with a medium hydrodynamic diameter of 105 nm which corresponds to polystyrene elementary particles. A bimodal distribution was observed for the composite latexes. The first generation contains polystyrene particles (100nm); the second one is related to polystyrene-clay aggregates (2500-5200nm) which are formed because of the hydrophilic-hydrophobic behavior of the modified layered silicate. This phenomenon was observed also by other researchers who obtained hybrid structures of clay inside/outside polymer particles [9, 10, 15, 18].

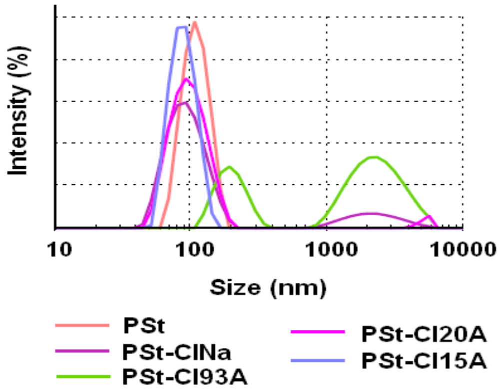

Fig. 1 Size distribution by intensity of PSt and PSt composite latexes prepared by miniemulsion polymerization

It can be noticed that for the latex with Cl 93A, the proportion of the particles generations are comparable. Thus, we have the first generation around 200nm and the second around 2500nm. This fact can be due the presence of the anion sulfate (SO_4^-) in the structure of the quaternary ammonium salt which modifies the clay and possibly gives a different behavior beside the other clays.

The presence of inorganic partners in the polymer matrix was emphasized by FTIR (figure 2) and X-Ray diffraction analyses (figure 3). FTIR spectra's of all solid materials obtained after water evaporation showed the specific peaks of polystyrene - 3020-3100 cm^{-1} CH aromatic stretching vibration, 2850-2940 cm^{-1} CH_2 asymmetric stretching vibration, 1450 m^{-1} shearing vibration, 1220 cm^{-1} CH aromatic deformation vibration, 950-1050 cm^{-1} vibration at aromatic nucleus, 790 cm^{-1} CH bending vibration. For all PSt nanocomposites, the specific peaks of montmorillonite are found: around 1045 cm^{-1} Si-O-Si stretching vibration and (400-600) cm^{-1} Si-O bending and stretching vibration (figure 2) [9, 10, 16, 22]. The existence of PSt and layered silicates peaks in nanocomposites FTIR spectra, was attributed to the inclusion of the clay layers into polymer matrix [2, 3, 4].

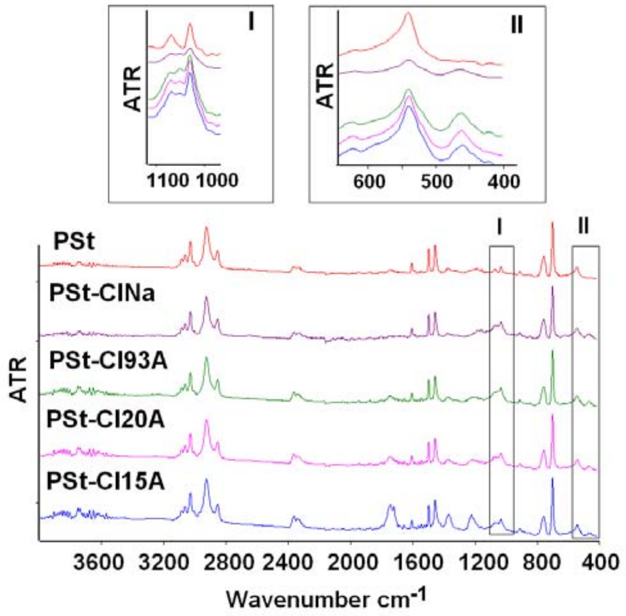

Fig. 2 FTIR spectra of PSt and PSt compositess prepared by miniemulsion polymerization

XRD is a common technique used for examining expansion of clay layers after in situ polymerization of the monomer [1-4, 23, 24]. The basal spacing (d_{001}) of the commercial clays are: 11.7 Å for ClNa, 23.6 Å for Cl 93A, 24.2 Å for Cl 20A and 31.5 Å for Cl 15A (according to the product bulletin). The XRD patterns of polystyrene composite material are shown in figure 3. It can be observed that the clay interlayers were modified as a result of the polymerization process XRD analyses presenting a shift of d(001) peak at lower 2θ values. The following diffraction peaks were obtained: 5.1 Å for Cl Na, 4.5 Å for Cl 93A, 4.66 Å for Cl 20A and 4.6 and 3.02 Å for Cl 15A. It can be noticed that the values decrease with the hydrophobicity of the modified clays from Cl Na to Cl 15A. Thus, according to XRD patterns mostly intercalated composites were synthesized via miniemulsion polymerization of polystyrene in the presence of clays.

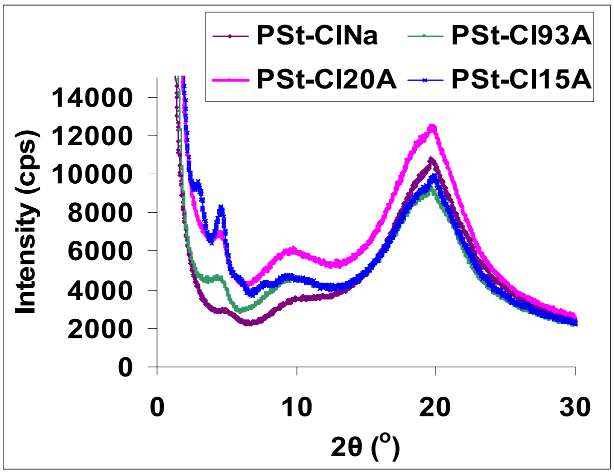

Fig. 3 XRD patterns of PSt composites prepared by miniemulsion polymerization.

The degree of intercalation/exfoliation influences as well the thermal behavior of the polymer-clay nanocomposites [17, 24, 25] was observed. In our case, the presence of the inorganic partner led to higher maximum decomposition temperatures (Tmax) for all nanocomposite materials obtained (Figure 4). Thus, the nanocomposite with Cl Na presents the highest Tmax=446°C, with 12°C higher than the pure polymer (Tmax=432.6°C). The better thermal stability of the nanocomposites was attributed to the formation of a char that acts as a barrier for the decomposition products [17, 19].

The residue obtained at 700°C also attests the incorporation of clay into polystyrene; the residue increased from 0.4% for PSt to around 5% for PSt-clay.

Very interesting is the Tmax decreasing tendency from Cloisite Na to Cloisite 15A (TmaxCl Na= 446.01°C; TmaxCl 93A= 442.04°C; TmaxCl 20A= 439.09°C; TmaxCl 15A= 435.09°C). This phenomenon can be explained in two ways: by different types of quaternary ammonium salt presence which degrades at lower temperatures and behaves as emulsifiers [23] lowering also the glass transition temperature (second heating) (in the same manner from Cl Na to Cl 15A); or through the intercalation/exfoliation degree of layered silicates into the polymer matrix being in good agreement with XRD analyses.

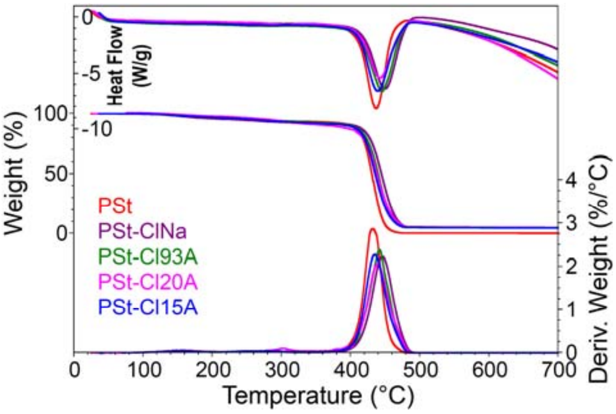

Fig. 4 TGA-DTG and Heatflow curves obtained for PSt composites prepared by miniemulsion polymerization

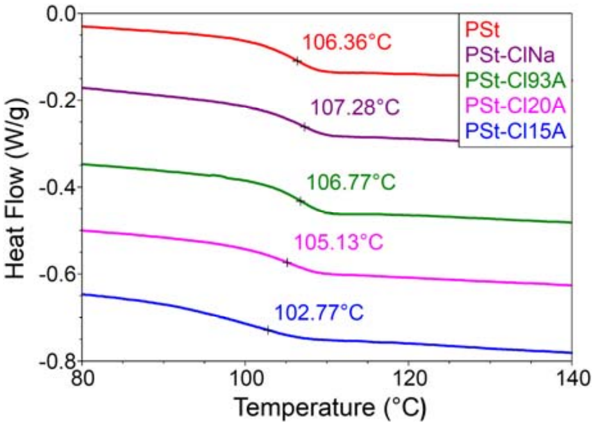

Fig. 5 The glass transition temperature (second heating) of the obtained nanocomposites.

ESEM images showed the presence of elementary polystyrene particles for the blank latex with dimensions around 100nm being in good relation with DLS analyses. For the composite latexes, the images revealed the presence of polymer-clay aggregates [2, 20, 21, 26, 27].

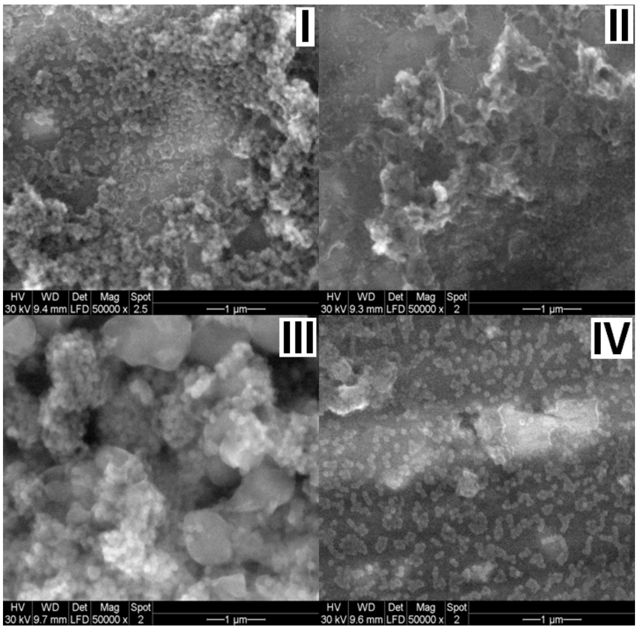

Fig. 6 ESEM images obtained for: PSt (I), PSt-Cl Na (II), PSt-Cl93A (III), PSt-Cl15A (IV) latexes prepared by miniemulsion polymerization

4. Conclusions

Nanocomposites based on styrene and four different commercial clays were successfully synthesized via miniemulsion polymerization procedure. The layered silicate modified the average diameter of the particles as well as the size distribution by intensity. FTIR spectra of the nanocomposites proved the existence of the specific peaks of the clays and X-Ray diffraction patterns suggested mostly an intercalated structure of polymer-clay nanocomposites. Thermal analyses evidenced an increased thermal stability in the presence of clay, the silicate layers acting as a barrier against thermal degradation. Glass transition temperature was also affected by the clay and especially by the quaternary ammonium salt which modifies the clay. The morphology of the latex was changed in the presence of inorganic partner as revealed by ESEM pictures.

Aknowledgement

Cristina-Lavinia Nistor acknowledges the financial support of European Social Fund – „Cristofor I. Simionescu" Postdoctoral Fellowship Programme (ID POSDRU/89/1.5/S/55216), Sectoral Operational Programme Human Resources Development 2007 – 2013.

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI– UEFISCDI, project number 3.2-1391.

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