U.P.B. Sci. Bull., Series B, Vol. 68, No. 3, 2006

POLYMER-CLAY HYBRIDS SYNTHESIS FROM WATER DISPERSIONS

M. C. COROBEA, D. DONESCU, G. HUBCA, C. RADOVICI, M. GHIUREA,
Violeta STEFAN[*]

Au fost obținute nanocompozite polimer-argilă din dispersii apoase utilizând silicați stratificați. Pentru solubilizarea heterofazelor a fost folosit un sistem de tip miniemulsie. Sintezele au loc prin procedeul discontinuu de polimerizare în emulsie a unor monomeri vinilici şi acrilici (stiren, acetat de vinil, acrilat de butil). A fost urmarită influența tipului de monomer asupra dimensiunilor particulelor hibride. S-au studiat de asemenea conversiile monomerilor, stabilitatea latexurilor, structura materialelor solide. Materialele obținute au fost caracterizate prin analize DLS, FTIR, XRD şi SEM

Polymer-Clay nanocomposites were synthesised from water dispersion systems using layered silicates. For the heterophases solubilization a miniemulsion system was chosen. Syntheses occur in one step free radical emulsion polymerization of some vinyl and acrylic monomers (styrene, vinyl acetate, butyl acrylate). The influence of the monomer type was followed regarding the hybrid particles size before and after polymerization. It was studied also the monomer conversion, latex stability, solid materials structure. The obtained materials were characterized by DLS, FTIR, XRD and SEM analyses.

Keywords: nanocomposites, emulsion polymerization, montmorillonite.

Introduction

Polymer-clay nanocomposites (PCN) are a relatively new class of materials which provided better physico-chemical properties and smaller cost than classical composite materials [1-3]. Although if the intercalation chemistry proved to offer some interesting ways for the interfaces problems between inorganic layered materials and organic species [4], the recent intensive development of nanocomposites started in the 80's by the report of Toyota research group of a

---

[*] PhD Student - Technology for Organic Substances and Polymer Science, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania; PhD. Eng. National R-D Institute of Chemical Research, Bucharest, Romania; Prof., Technology for Organic Substances and Polymer Science, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania; PhD. Chemist, National R-D Institute of Chemical Research, Bucharest, Romania, PhD Student Physicist, PhD Student Chemist, University of Bucharest, Romania

Nylon-6/montmorillonitenanocomposites [5]. A lot of clay minerals and layered silicates (LS) such as montmorillonite (the most commonly used), hectorite, saponite, fluoromica, fluorohectoritte, vermiculite, kaolinite, magaditte, etc. are used for inorganic filler to improve polymers stiffness, toughness, barrier properties, resistance to fire, corrosion resistance, etc. [1]. These properties are very much influenced by the PCN structure which can be for example intercalated or exfoliated or a combination of these two. LS are a nature source. For LS and polymers compatibilization usually the inorganic partner is organically modified by the ion exchange with quaternary ammonium salts of the cations present in the interlayers spaces. The sodium montmorillonite (NaMMT) can be suspended in dispersion media like water by a strong hydratation of the interlayers cations, which implies a significant increase of basal spacing (the space between the bases of two layers) and even a partially dissociation [6].

Emulsions can be efficient media for LS stabilization and a proved way to achieve advanced materials with double structured phases [7-11]. By this technique one structuration is provided by the dispersion of the LS in the polymer matrix and other achieved by the dispersion form in water as hybrid latex nanoparticles. We reported also some personal contribution [12- 14] regarding the emulsion polymerization of vinyl acetate in the presence of organo-modified and unmodified clay. But for the miniemulsion technique we didn’t found in the literature too many references [15].

Miniemulsions can offer a very low interfacial tension that might be a way for a better solubilisation of LS layers [16]. Miniemulsion polymerization is an extension of conventional emulsion polymerization. The system assumes a water-insoluble component called costabilizer, in the comparison with conventional emulsions. The costabilizer reduces the diffusional degradation phenomena (Ostwald ripening) of a monomer/water emulsion, also the monomer droplet size below 500nm [16] and droplets become the primary loci of particle nucleation. This technique used for LS encapsulation may be an efficient route for nanocomposite synthesis.

The use of unmodified clays is a big challenge regarding the compatibility with common polymers which are quite hydrophobic phases. Solving efficiently this problem can bring a series of advantages regarding the over all technology for nanocomposite and advanced materials obtaining.

In this study we used the miniemulsion polymerization in order to obtain hybrids polymer-nanoclay materials, by encapsulation of MMT in different polymer matrixes: polystyrene (PSt) and for the first time from our knowledge polyvinylacetate (PVAc), polybutylacrylate (PBuA). The monomer nature was followed in relation with the initial and final particle size, measured by dynamic light scattering (DLS). The solid materials obtained after water removal were characterized regarding the solid state structure by XRD, FTIR and microstructure by SEM analyses.

1. Experimental

Regeants

The monomers: styrene (St), butyl acrylate (BuA), vinyl acetate (VAc), commercial products, were purified by rectification.

The LS were provided by Southern Clay Products Inc. and were used in the sodium form (Cloisite®Na; 92 meg/100g) and organomodified with a methyl, tallow, bis-2-hidroxyethyl quaternary ammonium salt (Cloisite® 30B; 90 meg/100g) (OMMT).

The cetyl alcohol (CA), (Merck), hexadecyl-trimethylammonium bromide (CTAB), (Fluka), were used without other purifications. A nonyl phenol with 25 moles of ethylene oxide ($NPEO_{25}$) was used as nonionic surfactant, with structure verified by NMR.

The initiator α, α'-azo-isobutyronitril (AIBN) (Fluka), was used without other purifications

Distilled water was used as dispersion media.

Instrument

The mean diameter of particles was analyzed by dynamic light scattering (DLS), using a NICOMP 270 instrument, using a He-Ne 2000 V laser source. Measurements were done at room temperature (22 ^{0}C) without additional dilution. For the particle size evaluation, a Nicomp-Intensity Module was used.

A DRON-20 X-ray diffractometer with horizontal goniometer and scintillation counter was used for structure determination. Cu Kα (λ=1.5418Å) radiation was filtered with Ni for the kβ component removal, in the Bragg-Brentano (by reflexion) system.

IR Spectra were recorded on a FTIR-Tensor 30 BRUCKER spectrometer from KBr pellets using 40 scans with 4 cm^{-1} resolution.

Scanning electron microscopy (SEM) was performed with a FEI Quanta 200.

Procedure

The hybrids were obtained by using a four necks glass flask with round bottom, coupled to a thermostated bath. A reflux refrigerator and a thermometer were also connected to glass flask. First a mixture of monomer, MMT, costabilizer (CA), CTAB, and initiator (AIBN), was made by strong mechanical stirring in a water bath with ice, for 2 hours. It is very important to keep a low temperature by adding ice in the water bath for the initiator thermal stability. A second mixture was prepared by adding the second surfactant $NPEO_{25}$ in water, after very well mixing the system was cooled also in a water bath with ice. After these procedures the two mixtures were added in an ultrasound bath also cooled with ice. The polymerization mixture was kept under ultrasound stirring for 30 min. Then another mechanical stirring for about 10 min. at room temperature was performed. The polymerization started by rising the temperature at 65 ^{0}C, and the system was kept under mechanical stirring. After 4 hours the systems were cooled under stirring and the latexes were collected for analyses. The conversions were estimated by the gravimetric method. The latexes particles mean diameters were analyzed by DLS. The latexes stability was evaluated by the static method. A small amount of latexes were deposed on a polyethylene foil for water evaporation, which was performed at room temperature for several days. After the complete water removal the solid materials were analyzed by FTIR, XRD and SEM.

Results and Discussions

The miniemulsion polymerization system is a very complex one in comparison with classical emulsions. The systems used for hybrids syntheses are presented in Table 1. The role of each one of the component was carefully considered before starting the syntheses. The inorganic component was chosen to be soluble in the same phase with the monomer to promote a certain adsorption in the LS galleries. This thought was in sight to achieve a possible growing of macromolecular chains into LS interlayer spaces. To see if such a phenomenon could happend in previous reports [13,14] we presented the swelling capacity of NaMMT and OMMT with different monomers. The results showed different adsorption capacity by the polarity of the monomer used and the hydrophobia of the inorganic partner. The highest adsorption capacity in the case of unmodified MMT (NaMMT), was showed by BuA, and the poorest in the case of St (the most hydrofobic, and less polar). If an organically modified LS is used the adsorption capacity in the case of VAc can be even more then double. Even in the case of NaMMT, the swollen capacity is quite good considering that more than 100 wt.% of the monomer related to MMT, can be swelled. These experiments showed that the adsorbtion of the monomer is possible, but if the inorganic partner is more hydrophobic this process could be strongly increased. That is why we used a cationic surfactant with an ammonium salt head, CTAB, which is thought to improve the interaction between monomer and LS.

Table 1

Compositions used for hybrids syntheses

Sample	Monomer (g)	MMT (g)	CTAB (g)	CA (g)	$NPEO_{25}$ (g)	H_2O (g)	AIBN (g)
162	St (20)	NaMMT (1)	1	2.4	2	100	0.6
163	AcV (20)	NaMMT (1)	1	2.4	2	100	0.6
164	BuA (20)	NaMMT (1)	1	2.4	2	100	0.6
165	AcV (20)	OMMT (1)	1	2.4	2	100	0.6

It is quite known in the literature that NaMMT can be suspend in water and even with formation of small amount of individual dispersed layers [17]. But the stability of NaMMT in water is rather poor, after the stirring stops, in a few hours the inorganic tactoids re-associates and forms a white precipitate. By analyzing the three main generations of separated LS particles phases (Fig. 1), it was obvious why this instability occurred. In fact after LS crystallites (tactoids) are dispersed in water, after hydratation, they associates in bigger aggregates by searching a thermodynamically preferred state and the large ones (over 1000nm) precipitate, because of the larger specific weight related to water. Only a small amount of LS are stable in water suspension as a superior phase of the analyzed dispersions. But if we want bigger amounts of NaMMT to use in the process we need to improve the stability by adding a surfactant. This is the second role of the surfactant system. We reported the possibility to obtain stable polyvinyl acetate (PVAc)-NaMMT hybrid latexes by using $NPEO_{25}$ as surfactant [12]. CTAB can offer improving the partners interaction, and also a cooperative effect for the negatively charged silicate particles [17]. CA is used as costabilizer to prevent Oswald ripening and the $NPEO_{25}$ for particles stabilization. By performing this complex stabilization system stable emulsions were achieved (Fig. 2). Also the mean diameters of the particles are dramatically decreased related to NaMMT-water system. The highest particle sizes observed in the case of VAc both with NaMMT and OMMT after stabilization (226 nm and 289 nm), could be explained by the hydrophilic character of the VAc induced by the monomer polarity. The smallest particles are obtained by using St (153nm). All the emulsions obtained by this procedure were stable after the stirring removal. These results could be related with the swollen capacity of the monomers, because as the NaMMT swollen capacity increase with the different types of monomers the particles sizes are increasing. This behavior can occur due the specific volume of clay tactoids which increase because of the swollen monomer in the galleries.

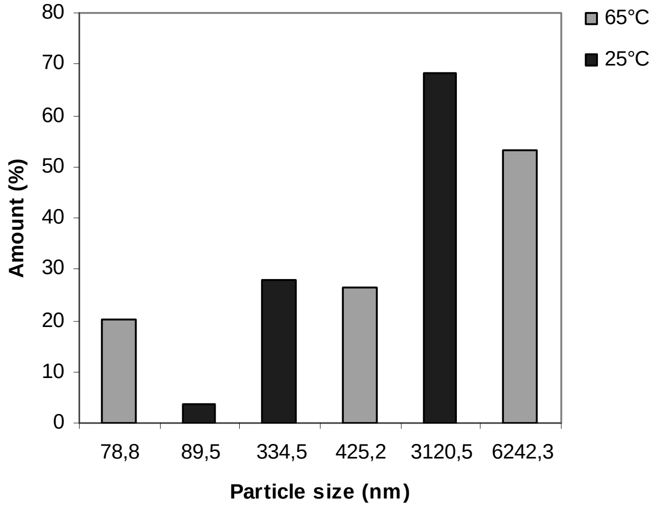

Fig. 1. NaMMT (1%wt.) particles size suspended in water after a static sedimentation process for a few hours

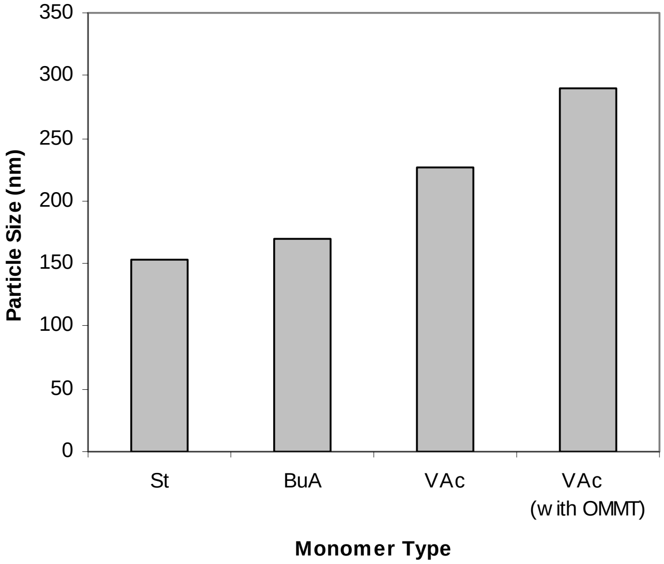

Fig. 2 Particles mean diameters using the proposed stabilization system before polymerization, related to the monomer type used for syntheses

The polymerizations occur at conversions over 52% (Fig. 3). The monomer conversion depends on the monomer type. The smallest conversion is registered to St while the biggest is showed by VAc (over 68%). In the case of using OMMT the conversion of VAc is decreased, but was still over 58 %. This behavior can be explained by the transfer reactions with the double bond present in the tallow chain of the modification agent used for OMMT. Considering that the vinyl group present in the OMMT is attached on C_{14-18} hydrocarbonated chain, the reactivity of this group can be considered rather poor for a copolymerization process, but regarding the VAc macromolecular chains propagation, a transfer reaction can be very probable. After finishing the polymerization time, the overall stability was good, except the case of BuA hybrid polymer, which showed big amounts of precipitated latex. The particles size was evaluated immediately after the polymerization (Fig. 4). The smaller particles were obtained in the case of using St as monomer. The particle size is in good correlation with the polarity of the polymers, that is why in the case of using VAc which generates an insoluble polymer but water swelling, the particles have a bigger mean diameters. After polymerizations end the stable phases were collected in tight glass vials in order to observe the stability in time, by the static method. Latexes were stable for several months (Fig. 5). After 6 months the probe containing VAc begins a gel transition, this behavior was similar with the VAc hybrids latexes obtained by emulsion polymerization in presence of nonionic surfactant like $NPEO_{25}$ [12]. After 9 ½ months the latexes with St hybrid polymer starts the gel transition. But in both cases no phase separation was observed. The phase separation occurs after 3 months only in the case of using VAc and OMMT, when a white gel like precipitate as lower phase is present. The upper phase was still milky like and did not show any clear phase above. The gel formation is quite a normal phenomena which appears on the clay particles level [18]. This behavior occurs due the favorable positioning, by forming ramifying flocs termed “card-house”, or “book-house”, of the clay platelets. The platelets formation occurs by the preferential positioning (“edge-edge”) of the clay lamellae, on the interface with an organic partner.

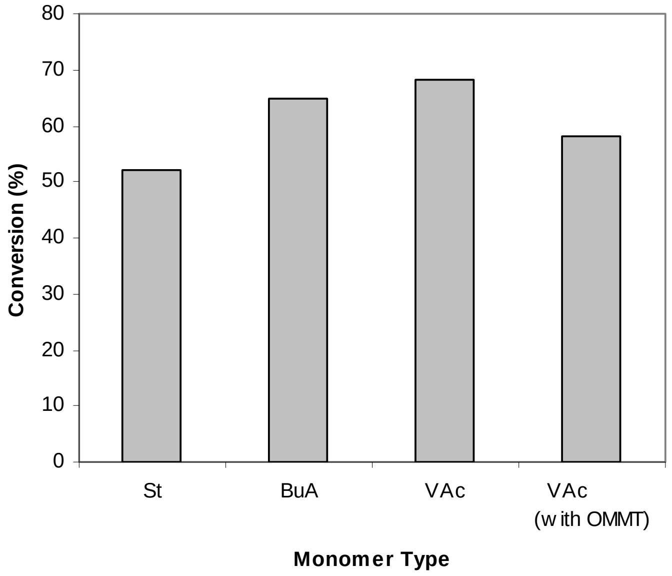

Fig. 3 Monomers conversions after 4 hours of polymerization related to the different monomers

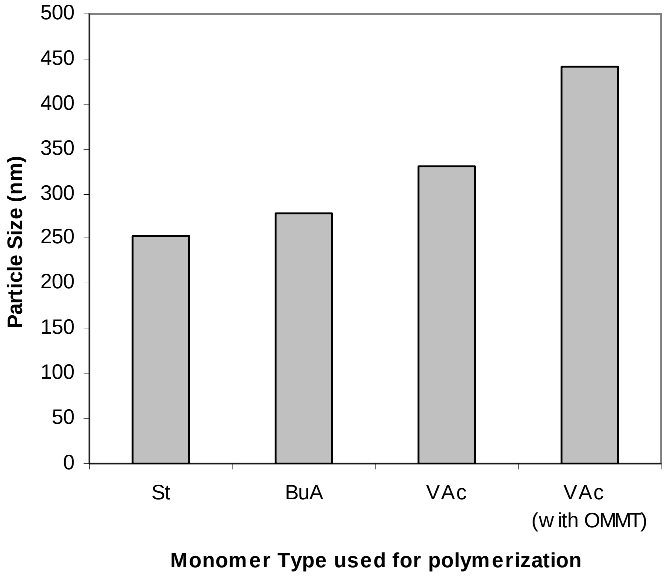

Fig. 4 Particles size after the polymerization time

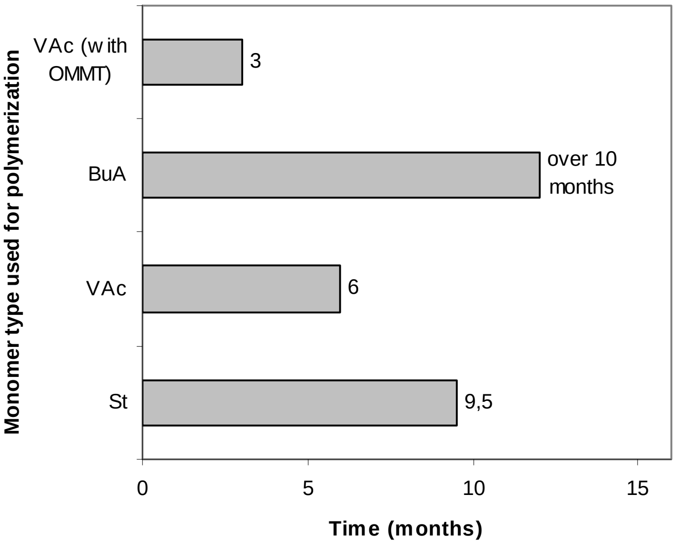

Fig. 5 Latex stability after the polymerization time

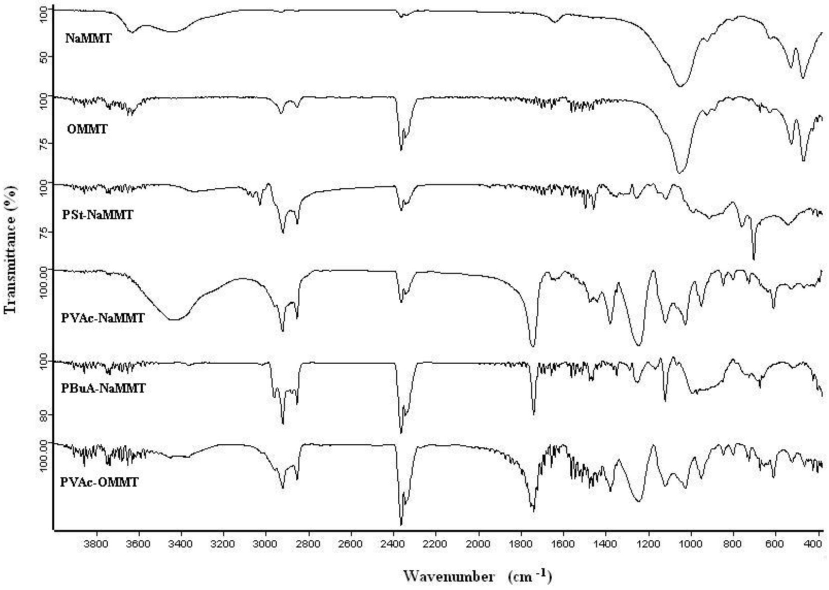

Fig. 6 FTIR spectra for the solid hybrid materials obtained after water evaporation

The incorporation of the inorganic component showed also by the FTIR spectra (Fig. 6). The specific peaks of polymers and MMT are present in the hybrid samples. Even if the attributions for groups specific bands of the polymers, did not showed evident modifications, in the cases of NaMMT and OMMT some specific peaks are modified, this kind of interaction between the organic and the inorganic partners is probably due secondary shield valence which can induces Van der Waals forces and OH bridges. In the case of PSt the 1044 cm^{-1} peack of the NaMMT, Si-O stretching vibration is a little shifted and modified with 9 cm^{-1} the others bands are a little modified 525 cm^{-1} to 538 cm^{-1} Al-O bending and 467 cm^{-1}-419 cm^{-1}Mg-O bending, the surprising 619 cm^{-1} Si-O bending almost vanishes. This behavior is induced by the macromolecular chains oriented next to the elementary lamellae crystals, which adsorbs some vibrations present on the lattice groups levels. In the case of PVAc-NaMMT hybrid the 1044 cm^{-1} Si-O stretching vibration shifts towards 1024 cm^{-1} and 619 cm^{-1}-604 cm^{-1} Si-O bending, this behavior can be associated also with the modification of acetate groups specific bands from 1745 cm^{-1} -1724 cm^{-1}. But in the case of PVAc-OMMT hybrids the 1745 cm^{-1} shifts to 1756 cm^{-1} this over all comportment may be ascribed also to OH interactions in good correlation with the decrease of the free water (3400 cm^{-1}) present in the hybrids and the increase of the OH bonded water 2800-3000 cm^{-1}). The Si-O in the case of PBuA hybrid appears almost at 1100 cm^{-1}, the Si-O bending shifts from 619-669 cm^{-1} and in the PVAc-OMMT the Si-O specific bands almost disappears.

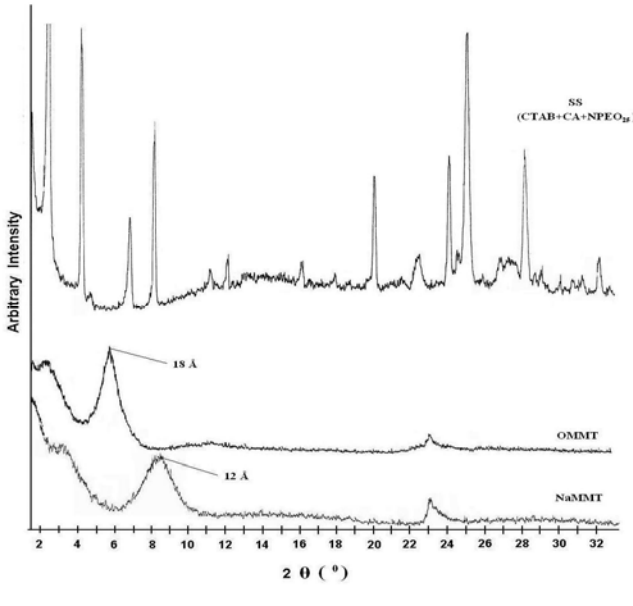

Fig. 7 XRD diffraction patterns for the clays used in the synthesis procces (NaMMT and OMMT) and for the stabilization system (SS=CTAB+CA +NPEO$_{25}$) obtained by physical mixing

The structure was very difficult to examine because of a high ordination degree which corresponds to the surfactants (CTAB and $NPEO_{25}$) and costabilizer (CA). The specific peaks of the surfactants were much closed to the clay tactoids and layers maxima (Fig. 7). That is why further procedures were required for the stabilization system removal. The hybrids were washed in hot water and separated by ultracentrifugation for several times. After these procedures the samples were analyzed (Fig. 8). The structure evidenced by XRD patterns corresponds to exfoliated nanocomposites by the disappearing of clay tactoids specific maxima (about 12 Å for NaMMT and 18 Å for the OMMT) (Fig. 7, 8). The presences of the 23 degree θ peak in the hybrids structure indicate the presence of the layers in the polymers matrix. The small intensity maxima present at 2 degree θ is also proper to clay presence. In the case of PBuA hybrid the peaks showed in Fig. 8 at 7 degree θ corresponds very probable to stabilizing system (SS) traces unremoved after washing. This argument can be sustained one: by the presence of the SS specific peaks present at over 24 degree θ (25, 27, 29 degree θ) and second: by a strong peak then for the clay present between 2 and 3 degree θ.

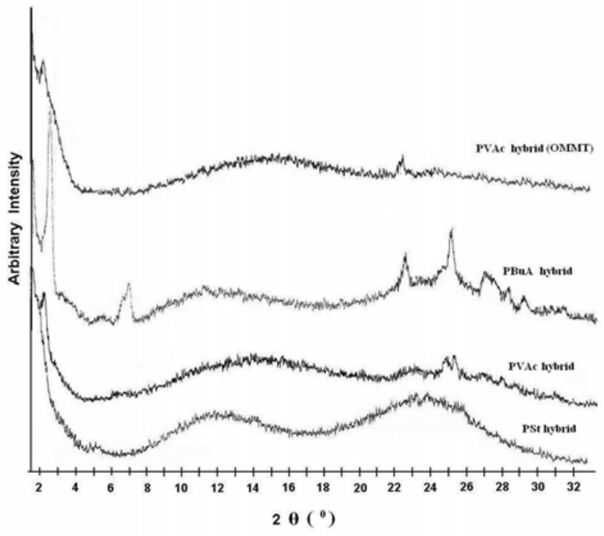

Fig. 8 XRD diffraction patterns for the hybrids obtained after the stabilization system removal

SEM analyses brought supplementary information, involving the microstructure morphology. The fractures analyses of the solid hybrid materials were analyzed in Fig. 9. A closer look to the hybrids fracture showed a typically nanocomposite behavior to stress [19,20]. The images showed specific polymer matrix filled with clay layers which are acting as stress concentrators, and induces the fracture propagation. The fractures are marked by plastic deformation because of the preferential planes induced by the inorganic partner.In the case of using

PBuA (Fig. 9 c), a very soft elastic material became as a smoth thin fiber when was mechanicaly stresed. But a more accurate look at the bottom (the interface between fiber and the bulk phase) revealed a fracture with a certain plastic deformation. This behavior is showed by the fracture path which is likely obtained by multiple shear deformation of the matrix ligaments [19]. In the case of PVAc and OMMT the fractures are quite similar with the one of PVAc-NaMMT (Fig. 9 b,d), with the same behaviour of the deformation planes. The shear deformation is restricted by OMMT presence. The shear deformation is restricted by OMMT particles.

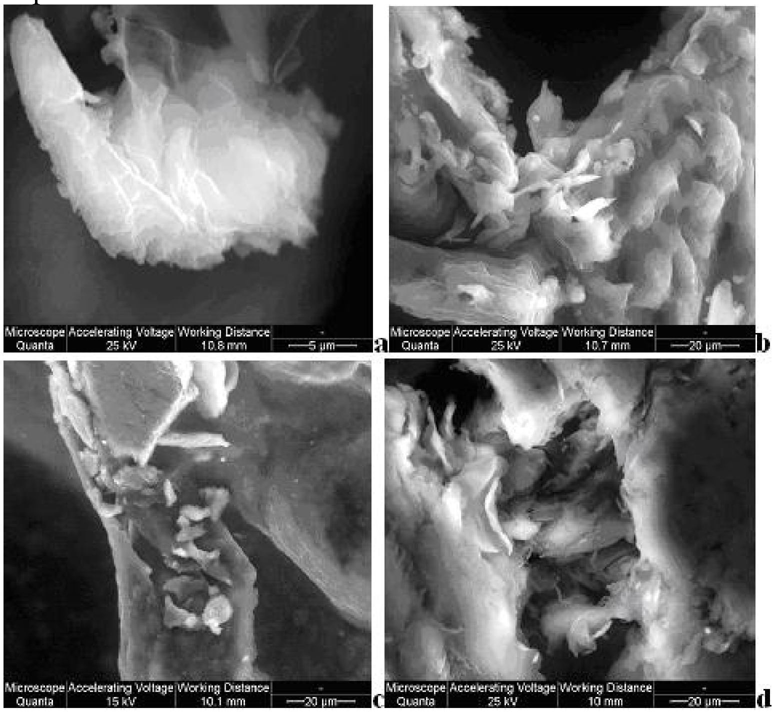

Fig. 9 SEM fractures for the solid state hybrids (a-PSt-NaMMT, b-PVAc-NaMMT, c-PbuA-NaMMT, d-PVAc-OMMT)

After an overall view of the experimental results water dispersions like miniemulsions systems are proved to be not only efficient media for clay layers stabilization but also an interesting way to achieve stable hybrid latexes and very probable exfoliated nanocomposites. Is very important also that by this method the compatibility between organic partners (both monomer and polymer) and unmodified clays (with hydrophilic character – NaMMT) is no longer a problem. In future works a more accurate investigation by transmission electronic microscopy (TEM), related to hybrids structure could be very useful for morphologic confirmation of the X-ray diffraction structure, cryo-TEM technique for nanoparticles structure in latex and solid states as well as an NMR study for a better understanding of the interfacial interactions between layers and polymer chains wich were evidenced for the moment by FTIR.

Conclusions

Nanoclay particles can be stabilized by miniemulsion water dispersions. Also stable water borne hybrid latexes are achievable by polymerization with different monomers like vinyl acetate, styrene and butyl acrylate.

The particle sizes are affected by the monomer respectivly the polymer nature. The nanoclay can be used also without organofillization even with hydrophobic monomers like styrene. The final conversions in presence of clay increase with the monomer polarity.

The presence of the polymers chains next to clay layers is very probable induced by physical interactions. The hybrids structure coresponds to exfoliated nanocomposites. The inorganic filler acts as stress concentrator inducing plastic fractures in the solid materials obtained after water evaporations.

REFERENCES

1. *M. Alexandre, P. Dubois*, “Polymer-layered silicates nanocomposites: preparation, properties and uses of a new class of materials”, Materials Science and Engineering, 28, 2000, 1-63.
2. *L. A. Ultracki, M. R. Kamal,* “Clay-containing polymeric nanocomposites”, The Arabian Journal for Science and Engineering, 27, no. IC, 2002, 43-67.
3. *S. S. Ray, M. Okamoto,* “Polymer/layered silicates nanocomposites: a review from preparation to processing”, Progress in Polymer Science, 28, 2003, 1539-1641.
4. *B.K.G. Theng*, The Chemistry of Clay-Organic Reactions, Ed. Wiley, New York, 1974.
5. A. *Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi, O. Kamigaito*, “Synthesis and properties of nylon-6/clay hybrids” Ed. D.W. Schaefer, J.E. Mark. Polymer based molecular composites. MRS Symposium Proccedings, Pittsburg, 171, 1990, 45-50.
6. *H. Huang, W. Brittain*, “Synthesis and characterization of PMMA nanocomposites by suspension and emulsion polymerization”, Macromolecules, 34, 2001, 3255-3260.
7. *Y.S. Choi, M.H. Choi, K.H. Wang, S.O. Kim, Y.K. Kim, J.J. Chung*, “Synthesis of exfoliated PMMA/Na-MMT nanocomposites via soap-free emulsion polymerization”, Macromolecules, 34(26), 2001, 8978-8985.
8. *Y.S. Choi, K.H. Wang, M. Xu, I.J. Chung*, “Synthesis of exfoliated polyacrylonitrile/NaMMT nanocomposites via emulsion polymerization”, Chemistry of Materials., 14(7), 2002, 2936-2940.
9. *Y.K. Kim, K.S. Choi, K.H. Wang, I.J. Chung*, “Synthesis of exfoliated PS/Na-MMT nanocomposites via emulsion polymerization”, Chemistry of Materials., 14(12), 2002, 4990-4995.
10. *M.H. Noh, L.W. Jang, D.C. Lee*, “Intercalation of styrene-acrylonitrile copolymer in layered silicate by emulsion polymerization”, Journal of Applied Polymer Science,74(1), 1999, 179-188.
11. *M.W. Noh, D.C. Lee*, “Synthesis and charaterization of PS-clay nanocomposite by emulsion polymerization”, Polymer Bulletin, 42, 1999, 619-626.

12. *M.C. Corobea, D. Donescu, C. Radovici, S. Serban*, "Hybrids Poly(vinylacetate)–Montmorillonite by Emulsion Polymerization" in "13th Romanian International Conference on Chemistry and Chemical Engineering", Bucharest, Romania, September 16-20, 2003.
13. *D. Donescu, M.C. Corobea, S. Serban, C. Ducu, V. Malinovschi, I. Stefanescu*, "Polymer-Nanoclay Hybrids Obtained by Emulsion Polymerization of Vinyl Acetate in Presence of Polyvinyl Alchol and Organically Modified Montmorillonite", in "European Materials Research Society Conference E-MRS 2005 Spring Meeting", Strasbourg, France, May 31 – June 3, 2005.
14. *M. C. Corobea, D. Donescu, S. Serban, C. Radovici, V. Uricanu, E. Constantinescu*, "Obtinerea unor Nanocompozite prin Polimerizare din Sisteme Disperse Apoase de tip Emulsie", in "Priorities of Chemistry for a Sustainable Development-International Symposium", Bucharest, Romania, 20-21 octombrie 2005.
15. *Q. Sun, Y. Deng, Z. L. Wang*, "Synthesis and Characterization of Polystyrene-Encapsulated Laponite Composites via Miniemulsion Polymerization", Macromolecular Materials and Engineering, 289, 2004, 288–295
16. *K. Landfester*, "Polyreactions in Miniemulsions", Macromolecular Rapid Communication, 22, 2001, 896-936
17. *F. Tiarks, K. Landfester, M.Antonietti*, "Silica Nanoparticles as Surfactants and Fillers for Latexes Made by Miniemulsion Polymerization", Langmuir, 17 (19), 2001, 5775 -5780.
18. *S. Yariv, H. Cross*, "Organo-Clay Complexes and Interactions", Ed. Marcel Dekker, Inc., New York, Basel, 2001, 39-111
19. *J. Karger-Kocsis, O. Gryshchuk, J. Fröhlich, R. Mülhaupt,* "Interpenetrating vinylester/epoxy resins modified with organophilic layered silicates", Composites Science and Technology, 63, 2003, 2045-2054
20. *M. E. Walter, C. Zeng, W. Li, J. J. Lannutti, L. J. Lee*, "Damage formation during fracture of polystyrene/clay and polystyrene/nanoporous silica nanocomposites" in 2003 ASME International Mechanical Engineering Congress, Washington, D.C., U.S.A., 15–21 November, 2003