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Copolymerization of DVB with MA in non aqueous dispersion

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Copolymerization of divinyl benzene (DVB) with maleic anhydride (MA) was studied to obtain functional particles. UV spectra of monomer mixtures DVB+MA put in evidence charge-transfer complexes like styrene-MA. Copolymerizations were performed in the presence of monomaleates of nonylphenol ethoxylated with 4 moles of ethylene oxide (MEMNPEO$_4$) and dodecyl alcohol ethoxylated with 4 moles ethylene oxide (MEMC$_{12}$EO$_4$). Particle sizes and Zeta Potential decreased with increasing MEM concentrations in the presence of layered silicates like montmorillonite (MMT), Na montmorillonite (NaMMT) and organo modified montmorillonite (OMMT), the Zeta potential decreased too, proving the presence of a part of aluminosilicates on the surface of the particles. IR spectra and TGA confirmed the presence of MMT in copolymers. XRD diagrams put in evidence that the modification of the state of MMT in the copolymer matrix is affected by the chemical structure of organo modifier. SEM images suggested that particles with spherical shapes were obtained in the presence of MEMNPEO$_4$, MEMC$_{12}$EO$_4$ and NaMMT. In the presence of OMMT only agglomerated particles were obtained.

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Keywords: Divinye bezene, Maleic anhydride, Organoclay, Copolymerization, Nanocomposites, Synthesis, Dispersions, particles

1. Introduction

The change of polymer particles - liquid composites properties causes the interest for the way in which the dispersant phase nature affects the system (1, 2). Although the particle stabilization in the mentioned composites can be obtained through copolymerization with monomers (1), the divinyl-benzene (DVB) – maleic anhydride (MA) copolymers particles are very interesting, due to capacity of side groups to be chemically modified for stabilization. This type of copolymers DVB-MA is mentioned in the previous publications (3).

The present study is focused on the modification of the DVB-MA polymer particles, obtained in non aqueous dispersion, through copolymerization with macromers of reactive surfactants type (4, 5). Another method to modify the particles surface will be the intercalation of these copolymers into the interlamellar spaces of layered silicates of hydrophobic modified montmorillonite (MMT) (6).

2. Experimental

2.1 Materials

Divinyl Benzene (Aldrich) and Maleic Anhydride (Fluka) were purified by distillation, sublimation. Heptan (C$_7$) (Merk), Methyl Ethyl Ketones (MEK) (Reactivul), azo izo butyronitrile (AIBN) (Fluka) were used without supplemental purifications. Nonylphenyl ethoxylated with 4 moles of ethylene oxide (NPEO$_4$) and dodecyl alcohol ethoxylated with 4 molls of ethylene oxide (C$_{12}$EO$_4$) were used as technical products. Their composition was established by NMR spectroscopy. Were used layered silicates, products of Southern Clay Prod. Inc. Na Montmorillonite (Cloisite Na 92.6 meq/100g), Cloisite 30B (methyl, tallow, bis-2-hydroxyethyl quaternary ammonium 90meq/100g), Cloisite 20A (dimethyl dihydrogenated tallow quaternary ammonium 95meq/100g), Cloisite 15A (dimethyl dihydrogenated tallow quaternary ammonium 125 meq/100g) were the inorganic components used in obtaining of copolymers particles DVB-MA.

2.2 Copolymerization conditions

The conditions mentioned in (3) for syntheses were used. In a glass vessel with mechanically agitation (350 rot/min), refrigerant and thermometer, were introduced successively: 60cc C7, 40 cc MEK and a mixture of 4g of MA, 4g of DVB, 0.2 g of AIBN.

The mixture is homogenized, purged with nitrogen and heated at 70 C for 4 hours. In the copolymerization with MMT case, the inorganic component is introduced in homogeneous mixture at room temperature, then ultrasonicated for 30 min., and finally heated under agitation. The reactive surfactants, the maleic monoester of NPEO$_4$ (MEMNPEO$_4$) and C$_{12}$EO$_4$ (MEMC$_{12}$EO$_4$) were synthesized through the mentioned procedure (4, 5). They were added before heating, under agitation of the homogenous mixture (monomers+C7+MEK).

After polymerization, the whole reaction mixture is poured in polyethylene vessels for the solvent evaporation at room temperature.

2.3 Analyses of the polymer

The conversions were established gravimetrically.

UV spectra were measured with an UV Nicolet 500 in normal vials of 10 mm at 25 C in acetone.

IR spectra were measured on tablets of KBr which contains copolymers, using an Tensor 37 (Bruker) type instrumet. The particles size and Zeta potential were established with an Zetasizer Nano ZS (Malvern) instrument. Before measurement, the samples were dispersed in water with ammonia and then ultrasonicated. Polymers concentration in water was 0.01 % gravimetric.

SEM images were obtained with an instrument FEI Quanta 200.

The thermal analyses were done with an Du Pont 2000 instrument with a heating rate of 20°C/ min. Diffraction diagrams of X rays (XRD) were obtained with an DRON-2 instrument provided with an horizontal goniometer and numbering of scintillations in continuous mode, with Cu K alfa (λ=1.5419 A) source of radiations and a Ni filter to eliminate K beta components.

3. Results and discussion

The maleic anhydride copolymerization with styrene and its derivatives has as result the obtaining of alternant copolymers (3, 7 and 8). These monomers pairs form complexes with charge transfer (CT) (7, 8). During this complexes formation, the styrene comonomers can be competitive with the interactions between the solvents and MA.

This is the reason why we tried to establish if, in the polar solvents as acetone, DVB forms charge transfer complexes as in the case of St.

UV spectra of mixtures with different ratio between monomers, with total concentration constant, were studied.

The comparative modification of the mixtures St-MA and DVB-MA spectra, for λ=330 and 340 nm, is represented in Fig. 1.

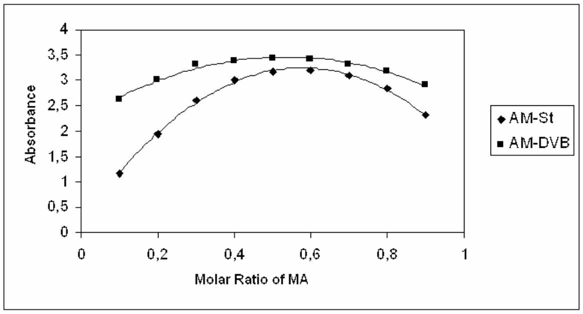

Fig. 1. The UV spectra modification for the DVB-MA (DVB+ MA = 0.1 mol/l, 25°C).

It is certain that the charge transfer complexes are formed between the monomers studied in this work DVB-MA. The maximum absorbance was shown at a molar ratio of DVB-MA=1:1.

The DVB-MA copolymers conditions of syntheses are mentioned in Table 1. One of the first conclusions of this table is the fact that the conversions in all syntheses were very high, over 95 %. The final mixture is a white polymer, finely dispersed in the solvent mixture, the polymer being as sediment. In the case of MMT additions were obtained agglomerated mixtures, which in some cases deposits on the walls of the reactor vessel and on the agitator.

Tab. 1. The particle size and Zeta potential modification, function of syntheses conditions (4g MA + 4g DVB + 40cc MEC + 60 cc C7) 70 °C; (0,2g AIBN + 0,2 g AIBN) 4 h.

Sample no.	Sample / g	Conversion (%)	Size Dmed (nm)	Zeta Potential (mV)
D18	$NFEO_4$ / 1,8	95	683	-39,1
D19	Cl 20 A / 1,0	100	617	44
D20	Cl 30 B / 1,0	96	629	45,1
D21	Cl 93 A / 1,0	97	506	46,3
D 22	$MEMNFEO_4$ / 0,5	96	599	40,6
D23	$MEMNFEO_4$ / 1,0	96	823	-43
D24	-------	99	995	-43,5
D25	Cl Na / 1,0	99	1020	44,7
D26	Cl 15A / 1,0	96	509	46,7
D27	$MEMNFEO_4$ / 0,8	100	364	-43,2
D28	$MEMC_{12}EO_4$ / 1,0	100	613	45,2
D29	$MEMC_{12}EO_4$ / 0,5	100	712	45,6
D30	$MEMC_{12}EO_4$ / 0,8	100	545	47,4
D31	$MEMNFEO_4$ / 1,0 Cl 20 / 1,0	98	604	50,2
D32	$MEMNFEO_4$ / 1,10 Cl 30 B /_1,0	99	840	47,9
D33	$MEMNFEO_4$ / 1,0 Cl Na / 1,0	100	266	48,2

For the $MEMNPEO_4$ and $MEMC_{12}EO_4$ reactive surfactants can be noticed a decrease of particles medium diameter with the increase of the stabilizer concentration, till a concentration of 0.8 g is reached (Fig.2). The distributions of particles dimensions are mono modal. Once the concentration of maleic semester goes over 0.8 g, the particles dimensions increase keeping the mono modal character of the distribution (Fig.3). The increase of particles medium diameter with the surfactant maximum concentration indicates a stronger interaction between the primary particles obtained due to the chemically bonded surfactant through copolymerization. The final particles are the result of agglomeration during the evolution of the process (3).

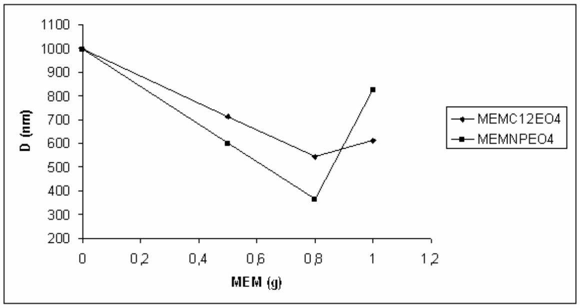

Fig. 2. The variation of medium diameter of copolymer particles function of MEMNPEO$_4$ (a), MEMC$_{12}$EO$_4$ (b).

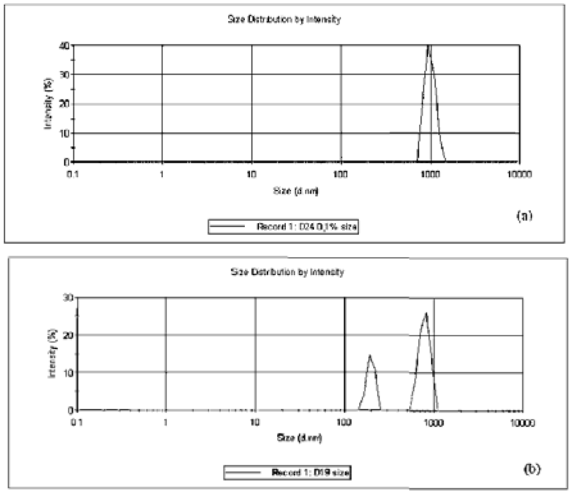

Fig. 3. The distribution of copolymer (C=0.01 %) particles; a. DVB-MA copolymer (D24), b. DVB-MA copolymer obtained in presence of Cloisite 20A (D 19).

The dimensions of particles obtained with MEMNPO$_4$ are smaller than those obtained with the other reactive surfactant. The difference could be due to a stronger interaction with the maleic monoester, which contains NPEO$_4$ because of presence of benzene nucleus in the structure of the stabilizer and of the copolymer DVB-MA. This favoring interaction could be the cause of the negatively Zeta potentials when MEMNPEO$_{25}$ is used (Fig.4).

In the both cases, Zeta potential decreases with the maleic semiester concentration increase, fact which demonstrates the dissociated carboxyl groups' existence on the particles surface after copolymerization. It is noticeable the fact that for the copolymers obtained only in the presence of NPEO$_4$, the Zeta potential is identical with that for the non modified particles with reactive surfactant (sample.18, 24-Tab.1). The obtaining of the particles with modifiable Zeta potential depending of the conditions of synthesis leads to the affirmation that they could be considered interesting even for systems which form liquid crystals in aqueous environment (9).

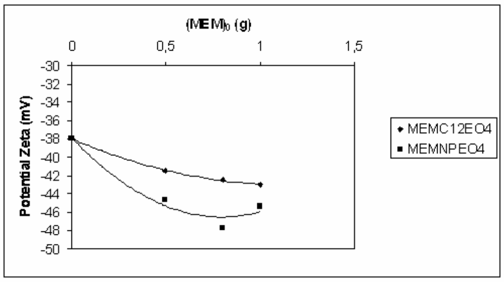

Fig. 4. The decrease of Zeta potential with the increase of concentration of reactive surfactant (a - MEMNPEO$_4$, b - MEMC$_{12}$EO$_4$).

The addition effect of montmorillonite inorganic compounds on the distribution of copolymer particles dimensions (Tab.1, Fig. 3b) and their medium diameter (Fig. 5) is very interesting. These additions presence generates particles with a bimodal distribution of their dimensions. In all the cases with hydrophobic layered silicates (Cl30B, Cl93A, Cl15A), a generation of particles between 140-220 nm dimensions and another generation of particles with higher dimensions has been shown. It is possible that the MMT hydrophobic agent's quaternary salts to permit stabilization of this smaller particles generation.

The medium calculated diameter decreases toward the copolymer without inorganic compound for those types of MMT hydrophobic modified (Fig. 5).

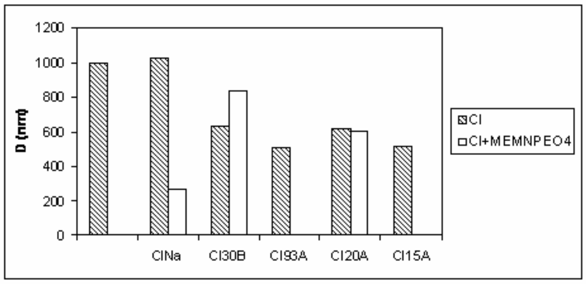

Fig. 5. The modification of medium diameters of copolymer DVB-MA particles in the presence of addition of MMT type and MMT+ MEMNPEO$_4$).

In the case of NaMMT due to a strong hydrophobic character (10) it's not noticed a decrease of medium diameter (Fig. 5). The particles dimensions distribution is monomodal as in the case of standard polymer (Tab.1-samples 19, 33, 24). A decreasing effect of the particles medium diameter was noticed only when ClNa-MEMNPEO$_4$ is used (Tab.1, Fig.5). The intercalation of the polyethylene oxide groups in the inter-basal space of layered silicates can change MMT in a modified hydrophobic compound. This modification effect is a better stabilization of particles, then a decrease of medium diameter from 1020 nm to 266 nm (Fig.5).

The aluminosilicates presence, which in aqueous medium are negatively charged (10), induces a Zeta potential decrease for the particles (Fig.6). The

MEMNPEO$_4$ addition, which in ammonia solution is negatively charged decreases with the Zeta potential value increase. These remarks permit to consider that a part of MMT and the maleic monoester are present on the particles surface in the interaction with the dispersion aqueous medium.

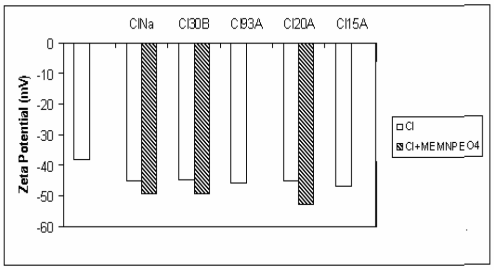

Fig.6. The decrease of Zeta potential for copolymers DVB-MA particles with the addition of MMT and MMT+MEMNPEO$_4$.

Because our purpose was to recommend these copolymer particles to form nanocomposites with liquid crystals, the properties of the polymers obtained in a dried state were studied. Fig.7 represents the weight lost through heating the DVB-MA (a) and DVB-MA-Cl93A (b). Four stages of losing weight were noticed for both types of products. Until 100°C the water absorbed on the polymer particles is lost and until 300°C the decomposition products of the surfactant and of the hydrofobization agents with MMT are lost (11). The main stage of losing weight is noticed over 350°C and is corresponding to side groups of the structural units losing. Over 450°C takes place the thermal decomposition of the main chains of the crosslinked copolymers. The inorganic residuum increase in the case of the products obtained with MMT (Fig. 7b) is an indicator of inorganic-polymer nanocomposites forming.

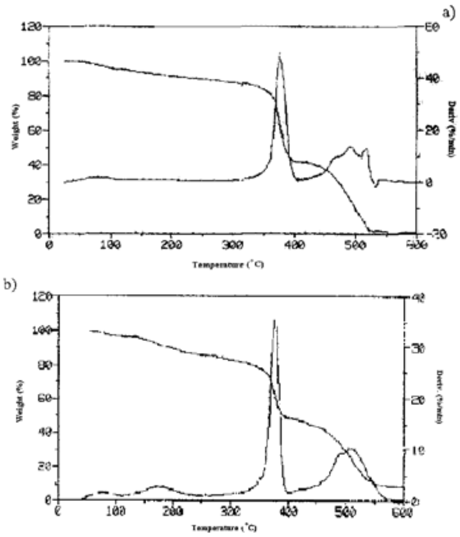

Fig. 7. TGA curve for MA-DVB copolymer (a) (D24) and copolymer MA-DVB-Cl93A (b) (D21).

The decomposition maximum temperature value around 350°C is not affected by the nature of surfactant used to synthesize the reactive surfactants (Fig.8). The highest value for T max was obtained at the maximum concentration of the reactive surfactant (1, 0 g) (Fig.8). In the MMT presence was not noticed a spectacular increase of T max value (Fig.9). The highest value was obtained for Cloisite 93A, a product which has by itself a high value of weight losing temperature due to Hoffman degradation of organophilization compound (11).

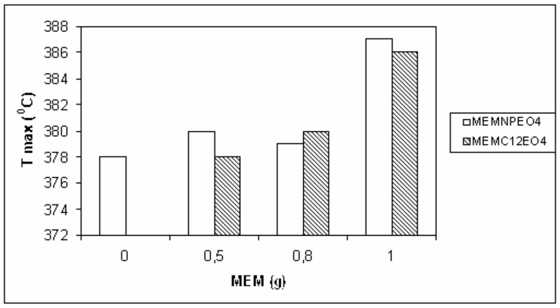

Fig. 8. Modification of temperature corresponding to maximum rate of thermal decomposition (T max) for DVB-MA obtained in presence of MEMNPEO$_4$, MEMC$_{12}$EO$_4$, MEM 0=0-1g.

The MEMNPEO$_4$ addition increases the T max value only for nanocomposites obtained with Cloisite Na which can give intercalated products of the surfactant in the interlamellar layer of MMT (Fig.9).

Information about the accuracy of the experimental work can be obtained by IR spectra analyses of the synthesized polymers.

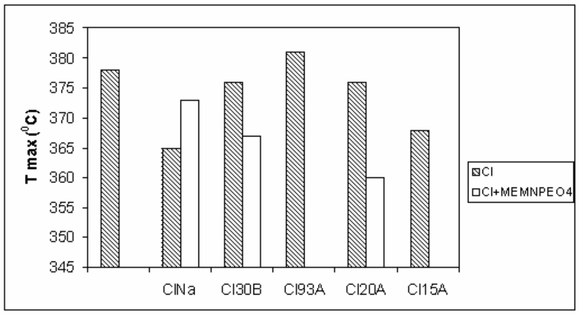

Fig. 9. Variation of T max value for copolymers obtained in MMT and in (MMT+ MEMNPEO$_4$).

FT-IR spectra are used to characterize the polymeric nanocomposites, proving the formation of the modified DVB-MA copolymers. The inorganic component presence in composites is sustained also through FTIR analyses. The spectrum presented in fig.10 confirms the existence of an absorption maximum specific to silicates Si-O-Si:

elongation vibration at 1045 cm^{-1} and Si-O bending vibration at 600-400 cm^{-1}. The maximum absorption specific to residual maleic anhydride is at 1782 cm^{-1} and 1720 cm^{-1} for maleic semiester.

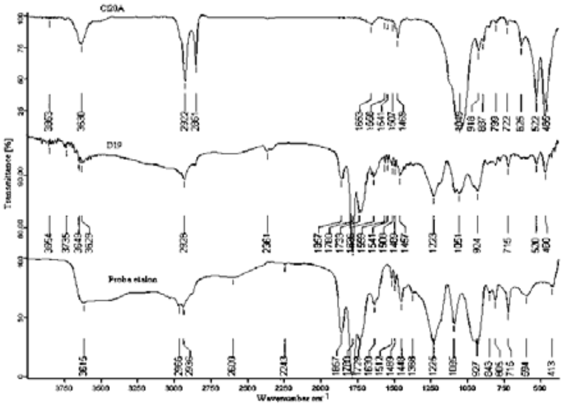

Fig. 10. FT-IR spectra of synthesizes copolymers (Cl 20A- Cloisite 20A, D24- copolymers DVB-MA, D19- Copolymers DVB+MA+Cl20A).

To obtain information about the state of layered silicates in interaction with DVB-MA copolymers were studied by X (XRD) diffraction diagrams (Fig.11). Due to amorphous state of cross linked DVB-MA copolymers, these do not present a maximum of diffraction (sample 24). The obtained copolymer in presence of ClNa presents a maximum at 12, 5 Å, similar to that of initial silicate. In case of Cl20A addition (sample 19) is noticed a shoulder at 22.19 Å. The maximum shown in Fig.11 indicates a small interaction between polymer and aluminosilicate. The same phenomenon, weak maximum approximately to initials, was noticed also for Cl93A, Cl15A. To simplify the figures, these diagrams are not presented in Fig.11.

A completely different behavior has the composite obtained with Cl30B. There is no maximum, fact which suggests an advanced dispersion of the tactoids in the polymer matrix. The cause of this phenomenon is the possibility of the anhydride groups from the MA structural units to react with hydroxyethyl groups of the MMT hydrophobic component. The effect of this strong interaction is the maximum dimension of the water dispersed particles diameters, obtained with Cl30B (Fig. 5).

$MEMNPO_4$ effect on the XRD diagrams of the inorganic polymer nanocomposites is represented in Fig.11b. If the syntheses takes place in the presence of ClNa a diffraction maximum appears at 17.5 Å, characteristic for the polyethylene glycol chains intercalation in the interlamellar layer (12). The obtained polymers with Cl30B (sample 32) or Cl20A (sample.31) does not present a maximum of diffraction. These findings indicate an advanced dispersion of MMT plates in the polymer matrix.

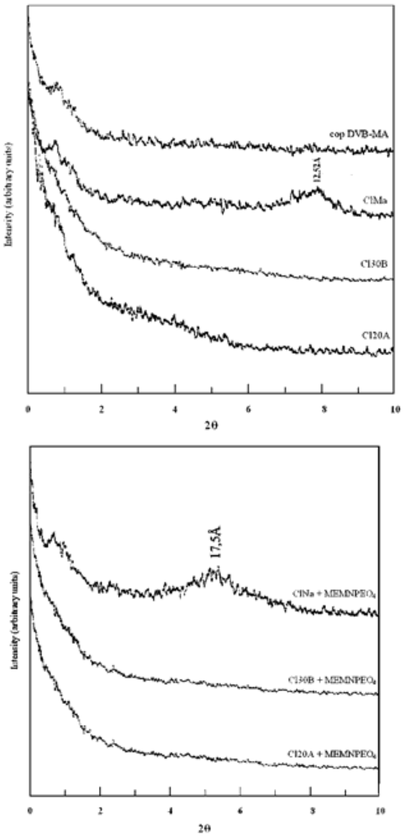

Fig. 11. Diffraction X rays diagrams for: a. DVB-MA copolymers (sample 24) , DVB-MA + MMT cop.(sample 25) (ClNa), 20 (Cl30B), 19 (Cl20A)), b. DVB-MA-$MEMNPEO_4$ copolymers (sample 33 (ClNa), 32 (Cl 30B), 31 (Cl20A).

In Fig. 12 are included SEM imagines for all synthetic polymers as in Tab.1. It is found that in all cases without an inorganic phase, well defined contour particles were obtained, homogenous and with similar dimensions to those previously reported (3).

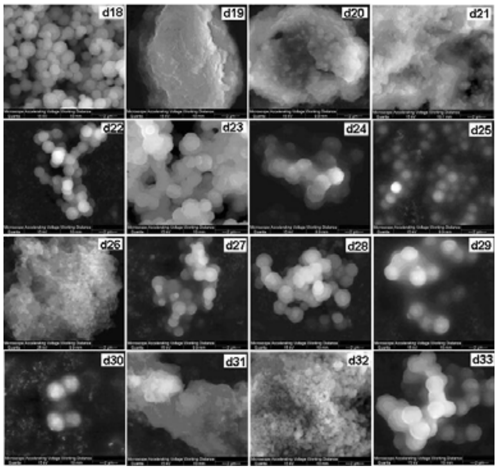

Fig.12. SEM images for synthesized samples in accordance with Table 1.

The original element of imagines from Fig.11 is the fact that all nanocomposites which in aqueous dispersion have a bimodal dispersion of the particles dimensions, in dried state do not evidences contoured particles. It is probable that the particles with smaller dimensions to be included in the inter spaces between the bigger once and when dried to strongly associate due to the MMT lamellas existence on surface. It is very interesting the effect of layered silicate without hydrophobization agent - ClNa. In the absence of $MEMNPEO_4$ (sample 25) as well as in its presence (sample 33), well contoured particles are obtained.

4. Conclusions

Through polymerization in non aqueous dispersions were obtained DVB-MA copolymers with particle dimensions which depend on the nature and on the concentration of two reactive maleic semiesters. The concentration increase of these two semiesters decreases the Zeta potential of the water dispersed particles, fact which indicates the presence of the carboxylic groups on the surface. Hybrids with bimodal distribution of the particles are obtained in the presence of some layered hydrophobic silicates, and after drying the particles agglomerate without individualized particles in SEM images.

The layered silicates increase the Zeta potential of particles.

The IR spectra and the thermal analyses confirm the presence of an inorganic component in the polymer matrix.

The dispersion of layered silicates depends of the type of MMT hydrophobic component.

In the case of the aluminosilicate with OH groups as hydrophobic component are obtained materials with a high degree of inorganic components dispersion due to the reaction with anhydride groups from the structural units of MA.

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