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ORIGINAL PAPER

Copolymerization in dispersion of divinyl benzene–maleic anhydride in the presence of silylated montmorillonite clays

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Abstract Sodium montmorillonite (NaMMT clay) derivatives were encapsulated in polymer particles obtained through dispersion copolymerization of divinyl benzene (DVB) with maleic anhydride (MA). To evidence the effect of alkyl monoalkoxysilanes upon MMT reaction, a variety of MMT clay functional derivatives were investigated. Particles with an increased size of modified MMT clay dispersed in dichloromethane were obtained using alkyl monoalkoxysilanes with a longer hydrocarbon chain. Relatively long hydrocarbon chains can exhibit a low substitution degree of MMT clay with alkyl monoalkoxysilanes. MMT class with a low substitution degree leads in the presence of alkoxysilanes to particles with average size between 700 and 1200 nm, and when DVB–MA copolymer is added the particles size decreases ($\sim$480 nm). The influence of layered silicates on the thermal stability of DVB–MA copolymer as a function of the used vinyl siloxanes derivatives for functionalization of MMT, on one hand, and the nonlinear variation of refractive index of used silanes on the other hand, pointing out the autoassociation during initial reaction of substitution.

Keywords Copolymer · Silane · Nanocomposites · Montmorillonite

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Introduction

The use of multilayered silicates as fillers, in the synthesis of the nanocomposites polymer-layered silicate, lead to the improvement of their mechanical, electrical, thermal stability, fire resistance, etc. properties [1–8]. The main problem that have to be solved in the synthesis of nanocomposites polymer-layered silicate is the optimal compatibilization of an extremely polar compound (the natural clay mineral) and a highly hydrophobic material (the polymer).

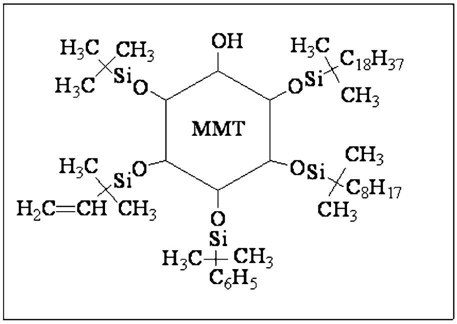
For achieving this goal, the clay mineral can be modified through ionic exchange between metals from the galleries with ammonium quaternary salts highly hydrophobic [1–8]. This type of silicates is known as organosilicates (organo-clay mineral).

The synthesis of polymer-silicates nanocomposites in disperse medium is a very tempting direction due to the possibility of mineral clay encapsulation in polymer particles from radical polymerization [9].

Several publications described the modification of organo-clay mineral [10–12] and clay mineral [10, 13–17] with chloroalkyl silane [17] or with alkoxysilanes [10, 11, 13–18]. As a dispersion medium were used alcohol [10, 13], chlorurated derivatives [10, 13], aromatic solvents [13, 15, 18, 19], pyridine [14], alcohol–water mixture and even water.

Despite some activity in this area, there are no systematic studies to reveal the effect of alkyl groups changing from alkyl monoalkoxysilanes on MMT reaction and on polymerization in dispersed medium. This study investigates sodium montmorillonite (NaMMT) modification using various monoalkoxysilane with different structures of alkyl derivatives. The MMT clay functionalization is carried out with the following derivatives: trimethylethoxysilane (Me_3ES), vinyldimethylethoxysilane (VMe_2ES), phenyldimethylethoxysilane ($PhMe_2ES$), octyldimethylmethoxysilane (C_8Me_2MS), and octadecyldimethyl methoxy silane ($C_{18}Me_2MS$). Reaction between side OH from clay mineral and alkoxy group from silane is followed by elimination of one molecule of alcohol and leads to MMT products with dimethyl side groups bind to Si, (RSiMMT), through methyl groups (MeMMT), vinyl (VMMT), phenyl (PhMMT), octyl (C_8MMT), and octadecyl ($C_{18}MMT$) (Scheme 1).

Scheme 1 Sodium montmorillonite modification using various monoalkoxysilanes



The association degree in the reaction medium, the coupling degree, the method to encapsulate derivatives in particles of polymer obtained through copolymerization in dispersion of divinyl benzene (DVB) with maleic anhydride (MA) are studied for these MMT clay products with different side organic groups. This copolymerization system was performed in organo-modified MMT presence, providing the possibility to obtain exfoliated hybrids [20].

Silicate layers have applications in building materials, as well as polymers, which can be used as additives in bitumen, cement, and asphalt concrete mixtures. Synthesized copolymers have a polyelectrolyte character, which can lead to the increase of the additives capacity to disperse in the concrete mixtures. The covalent bonding between silicate layers and copolymer additives can result in the formation of a complex additive structure, with special properties as a well dispersion in the synthesized matrix with bitumen, asphalt or cement concrete mixtures.

From our knowledge, this is the first attempt to compare different coupling products of MMT clay with monoalkoxysilane having various lengths of the hydrocarbon chains. VMMT can copolymerize by radical mechanism, PhMMT can interact with DVB through π–π interactions, and the rest of the monoalkoxysilanes can induce hydrophobic associations.

This article has two main objectives, first is the reaction between monoalkoxysilanes and mineral clay, and second is the encapsulation in DVB–MA copolymer of the previously synthesized products.

Experimental

Materials and methods

Diclormethane (Chimreactiv), methylethylketone (MEK) (Reactivul), and heptane (Fluka) were purified by distillation. Divinylbenzene (Aldrich) and maleic anhydride (Fluka) were purified by distillation, respective sublimation. Azoizobutyronitryle (AIBN) (Fluka) was purified by recrystallization. Sodium montmorillonite (MMT clay) (Southern Clay Inc.) was dried at 60 °C and kept at vacuum for 4 h.

Silanes: ethoxytrimethylsilane (Me_3ES) (Merk-Schuchardt), dimethyl-vinyl-ethoxysilane (VMe_2ES), dimethyl-phenyl-ethoxysilane ($PhMe_2ES$), dimethyl-octadecyl-methoxysilane ($C_{18}Me_2ES$) (Fluka), dimethyl-octhyl-methoxysilane (C_8Me_2MS) (Aldrich) were used without further treatment.

Analyses

Conversions were established gravimetrically.

The average particles size and Zeta potential were determined using a Zetasizer Nano ZS instrument (Malvern Instruments Ltd). The technique used for size measurements was dynamic light scattering DLS and for Zeta potential was Laser Doppler Velocimetry (LDV). The MMT clay particles synthesized with silane in dichloromethane (RSiMMT) were washed and then analyzed. The average diameters were also measured for modified layered silicates samples dispersed in polymerization mixture and for samples with polymer-RSiMMT hybrids from polymerization solvents mixture. The same samples obtained in water with ammoniac at 0.01% gravimetrically concentrations were analyzed.

FTIR spectra were registered by a FTIR-Tensor 30 BRUCKER instrument and SEM images were registered with a FEI Quanta 800 instrument. TEM analyses were performed on a Philips CM300-UltraTWIN instrument.

The thermal analyses were performed with a Du Pont 2000 instrument with heating rate of 20 °C/min in air.

X-ray diffraction diagrams (XRD) were obtained with a DRON-2 instrument provided with an horizontal goniometer and numbering of scintillations in continuous mode, using a Cu Kα ($\lambda = 1.5419$ Å) source of radiations and a Ni filter to eliminate K beta components.

Synthesis

MMT clay coupling with alkoxysilanes

Four grams of dried MMT clay and 250 mL CH_2Cl_2 were successively introduced in a flask with mechanical stirrer (350 rpm), condenser, and thermometer.

The mixture was stirred, kept under nitrogen for 30 min and then ultrasonated for 5 min. Meanwhile alkoxysilanes with different structures were added in drops, using a ratio of 5 mmol/1 g MMT clay.

The reaction mixture was heated at 40 °C and stirred for 8 h per day for 3 days. The mixture was let to rest for a few days in order to precipitate the modified clay mineral. The decanted solid was washed with 250 mL CH_2Cl_2. Samples were taken from the separated upper layer in order to perform the size measurements. After separation, the solid content was added in a polyethylene container and left to evaporate the solvent. The final solid was dried under vacuum and then analyzed by TGA, IR, and XRD.

DVB–MA copolymerization

Four grams of MA, 4 g of DVB, 0.5 g of MMT clay or RSiMMT, 40 mL of MEK, and 60 mL of heptane were successively introduced in a flask with mechanical stirrer (250 rpm), thermometer, and condenser. The mixture was purged with nitrogen under stirring (30 min) and ultrasonated (30 min). A sample of 5 mL was taken for DLS analyses. Then, the reaction mixture was heated at 70 °C under stirring and 0.2 g AIBN was added. After 2 h, another 0.2 g initiator AIBN was added, continuing heating for 2 h. The mixture was cooled down, diluted with MEK-heptane, and average particles sizes were measured. The reaction mixture was added in polyethylene containers and solvent and unreacted monomers were evaporated. Finally, the sample was dried under vacuum.

Results and discussion

Changes of sodium montmorillonite structure

Five dimethyl alkoxysilane were used in order to reveal the influence of hydrocarbon structure on the properties of the final products. The difference between the products consists in the hydrocarbon chain: methyl, vinyl, phenyl, octyl, octadecyl, and linked to Si and two methyl radicals. Considered alkoxy groups are ethoxy and methoxy. The alcohol is eliminated during the reaction of OH groups from the edges of clay sheets, and forms RSiMMT derivatives, different only by the radical R nature [10, 13–15, 19, 20].

The experimental work from a previous article presented the reaction between alkoxysilanes and MMT clay, at 40 °C in CH_2Cl_2 [21]. This solvent favors the pursued coupling reaction [10, 13].

During the layered silicates dispersion in fluids with different polarities, MMT clay tactoids tend to associate in different forms of higher dimensions which sediments [22–24].

The reaction of MMT clay with Me_3ES, after the second wash with CH_2Cl_2, leads to separation from the decanted solvent of almost 0.3% from the initial quantity of mineral clay. In this case, some of the grafting products of alkoxysilane on the clay mineral can remain unreacted in the solvent due to their functionalization.

We may assume that by association of the suspended entities, the separated precipitate is formed and used subsequently in the following process of polymerization.

DLS analyses of the organic upper layer confirm the existence of some particles with average sizes ranging between 700 and 1200 nm, depending on the type of coupling radical for MMT clay. Average sizes of the particles increase from MeMMT to C_{18}MMT. The intensity size distribution is bimodale. Two peaks can be seen in the intensity distribution curves [23]: a main peak and a secondary one—a complete generation of particles heaving high dimensions, possible formed after smaller particles aggregation. Figure 1 presents the values of the main size peak function of the substitute from silane.

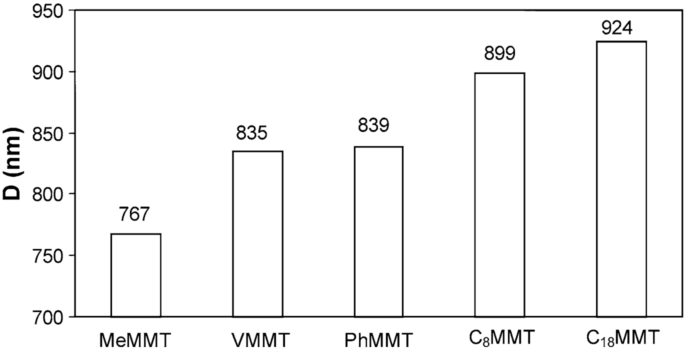


Fig. 1 Changes of the MMT clay particles sizes function of the used monoalcoxysilane

According to the DLS measurements, the particle size increases with the hydrocarbon chain length.

There is a slight difference of about 60 nm between particles sizes of methyl (767 nm) and octadecyl (924 nm) derivatives. Since we used the same quantity of MMT clay as associate, the difference might be due to the grafted alkyl groups, dispersed in solvent [10, 13, 15, 18, 19, 25].

Various aggregates with grafted groups of 1–18 carbons can lead to particles with differences sizes for only few nm, but this could not be the only reason of the dimensional difference [26].

The increased difference of aggregates dimensions shows that besides mineral clay platelets, autoassociation of alkyl groups may induce the aggregation phenomenon [22–24].

A previous attempt [27] had shown the possibility of octyltriethoxysilane to form nanoassociations in ethanol solutions, able to induce a nonlinear modification of the refractive index, function of the molar ratio.

The changes in refractive index for Me_3ES and $C_{18}Me_2MS$ solutions were determined as a function of silane molar ratio, in order to establish a possible similarity of the phenomenon using dichloromethane solutions. The results are represented in Fig. 2. It is obvious that nonlinear variation of the refractive index for both silanes shows strong associations induced by the alkyl groups, meaning that from the beginning of the reaction MMT clay + R_3SiOR, both partners autoassociate in specific ways. The final products tend to associate in two directions: clay tactoids and hydrocarbon chain.

Herrera [18] obtained similar results for condensation products of laponite with a monoalkoxysilane: the interfacial tension air–water decreases in water due to the hydrophobic demixture induced by the methacryloxy propyl radical; modified laponite is associated and mineral clay tactoids are autoassociated in frozen phase. The idea that MMT clay platelets (ca. 100 nm) are encapsulated in a liquid (monomer) which turns in polymer is far from reality, statement sustained by the published Herrera results.

TGA curves of the synthesized samples showed modifications of the mass loss in the temperature range 240–600 °C. These modifications correspond to the decomposition of organic moieties of the silane. Major modifications were observed at around 400 and 600 °C, these are due the loss of the trimethylsilyl groups. The

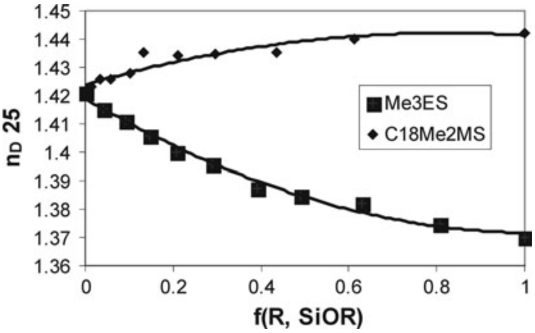


Fig. 2 The refractive index (n_D) variation function of the molar ratio of monoalcoxysilane in CH_2Cl_2 solutions

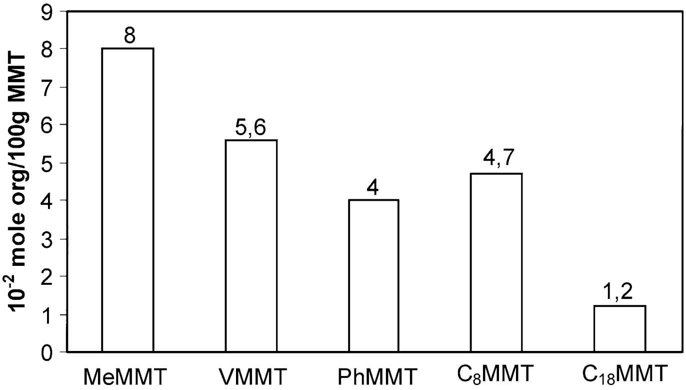


Fig. 3 The quantitative increase of grafted monoalcoxysilane on MMT clay function of the hydrocarbon chain

coupling degree was determined as a ratio of the difference between the weight loss at 240 °C and the weight loss at 600 °C divided to the weight loss at 140 °C (the solid content without water) [13].

The coupling degree (Fig. 3) of monoalkoxysilane on the edge of OH groups from MMT clay decreases with the increase of the hydrocarbon group's length bond to silane. This phenomenon is encountered for monoethoxysilane as well as for monomethoxysilane case. From our knowledge, the presented results are the first systematic analyses of grafting reaction of monoalkoxysilanes on MMT clay. This phenomenon is caused by different autoassociation of alkoxysilane groups during coupling reaction of silane with various concentrations. The results are also sustained by the dimensions of the aggregates formed in CH_2Cl_2 which are especially due to the hydrocarbon chain autoassociation despite the fact that the substitution degree with C_{18} group ($C_{18}Me_2MS$ reaction) is minimum (Fig. 3). It can be mentioned that the results for the quantitative increase of grafted monoalkoxysilane on MMT clay are reproducible, grafting conversion is low, and lead to insignificant changes if the quantity of MMT clay from reaction is double.

FTIR spectroscopy confirmed the structure of modified MMT (Fig. 4). Regarding MeSiMMT, we calculated the ratio of peaks intensities for alkyl (2957 cm^{-1}) and MgOH (3632 cm^{-1}). It can be observed an increased density of alkyl groups with the increase of the grafted silane moles number) (Table 1).

The absorption band corresponding to stretching vibration of C=C double bond for VSiMMT overlaps with OH deformation band at 1645 cm^{-1} due to the physisorbed water [20].

The encapsulation of synthesized MMT clay products in DVB–MA copolymer particles

The synthesis of DVB–MA copolymer in the presence of organo-clay mineral using as solvent heptane/MEK mixture is reported in one of our recent studies [24].

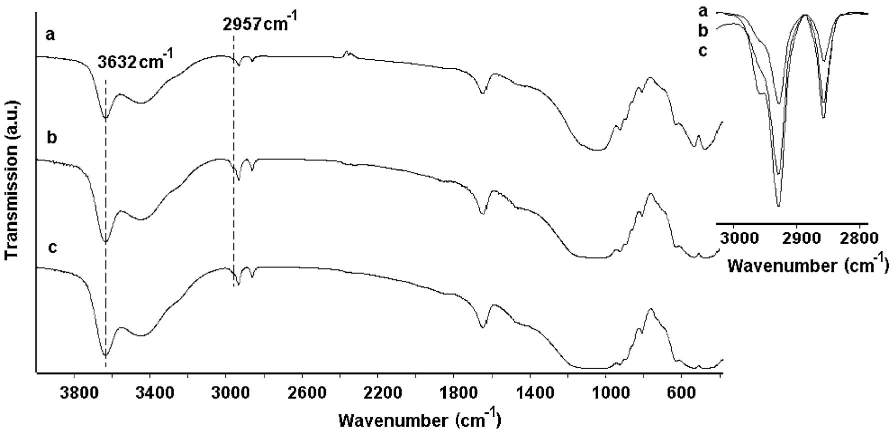


Fig. 4 FT–IR spectra of the monoalkoxysilanes modified with MMT clay

Table 1 FT–IR intensity ratio calculated for sample MeMMT

Sample	ICH_3 ($\lambda = 2957\ cm^{-1}$)	IMgOH ($\lambda = 3632\ cm^{-1}$)	ICH_3/ IMgOH
NaMMT (a)	0.97102	0.3386	2.86
RSiMMT (b) (0.0634 mol/100 g)	0.94118	0.1607	5.85
RSiMMT (c) (0.08 mol/100 g)	0.91324	0.1296	7.04

The study presented a possibility to obtain hybrids, with exfoliation of organo-clay mineral in the particles of alternating copolymers.

We focused on modified layered silicates grafted with alkyl silane groups with different chemical structures. The vinyl group from VMMT participates at alternating copolymerization with MA, and the phenyl group from PhMMT participates at π–π interactions with DVB.

The alkyl groups can stabilize the particles as in the polymerization in nonaqueous medium, due to the interaction with heptane [18, 19].

At the beginning of the process, the reaction mixture without clay mineral is a homogenous solution. The mixture becomes opaque after adding MMT clay or RSiMMT. The inorganic particles deposits in time. DLS analyses of the particles from the initial nonaqueous suspension (Fig. 1) showed the existence of some aggregates of higher dimensions than the ones measured after synthesis of RSiMMT (Fig. 5). It is obvious that RSiMMT the same as organo-montmorillonite, interact with monomers and forms increased associations which deposit in time [28].

If stirring and heating of the polymerization mixture in AIBN presence continuous, the reaction system becomes opaque. The monomer conversion at 4 h was in most of the cases over 98%. Only in two cases the polymerization took place at low conversions (D34, D36), the values are presented in Table 2.

DLS analysis allows the determination of the hybrid particles sizes after dilution with a mixture of solvents heptane/methyl ethyl ketone or in water with ammonia (Fig. 5).

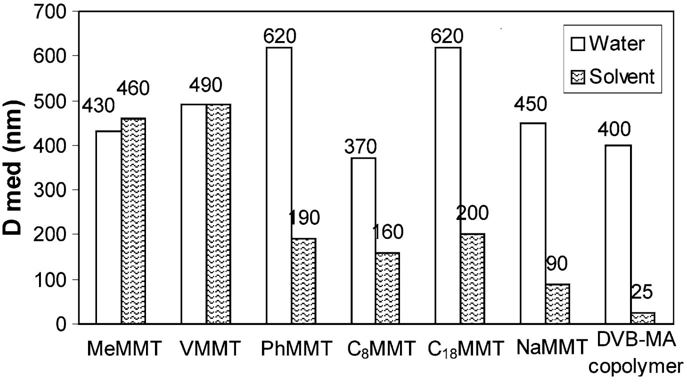


Fig. 5 Average sizes of the DVB–MA particles formed through polymerization in RSiMMT presence

Table 2 Conversions of the synthesized nanocomposites

Sample	D34	D35	D36	D37	D38	D39	D40	D41	D42
Cop. DVB/MA with	NaMMT	Me_3ES	C_8Me_2MS	$C_{18}Me_2ES$	VMe_2ES	$PhMe_2ES$	NaMMT	–	C_8Me_2MS
Conversion %	39	99	44	84	97	99	98	97	99

It can be noticed the changes of average particle sizes in respect with the modified or unmodified type of layered silicates present in the polymerization mixture. The average particle size decreases with the decrease of the mineral clay substitution degree. There is a similarity between the decreasing sizes of the particles measured in 0.01% dilution in heptane/methyl ethyl ketone mixture after polymerization and the degree of grafting with MMT clay hydrocarbon groups (Fig. 3). The results show that the increase of polymer particles takes place as a result of a strong interaction with RSiMMT. Therefore, the inorganic particles play a template role in polymer particles produced from the initial homogenous medium.

Maleic anhydride groups' hydrolysis and polymer particles became cross-linked polyelectrolyte after dispersion in water with ammonia. Average size particles obtained in this way increase, contrary to the particles measured from the polymerization solvent mixture (Fig. 5). The increase in mean diameter can be the results of the particles hydration and maybe of the increased probability of aggregation in a polar medium as water.

After dispersion in water the particles became cross-linked polyelectrolyte, result proved by the negative value of the Zeta Potential (Fig. 6). The maximum value of Zeta Potential (−41 mV) obtained for DVB–MA–VSiMMT copolymer can be interpreted by the capacity of the layered silicates modified with vinyl groups to copolymerize. Ternary copolymerization assures a covalent bonding between polymeric chains and modified layered silicates, leading to the increase of negatively charged groups in and on the surface of hybrid particles. The rest of

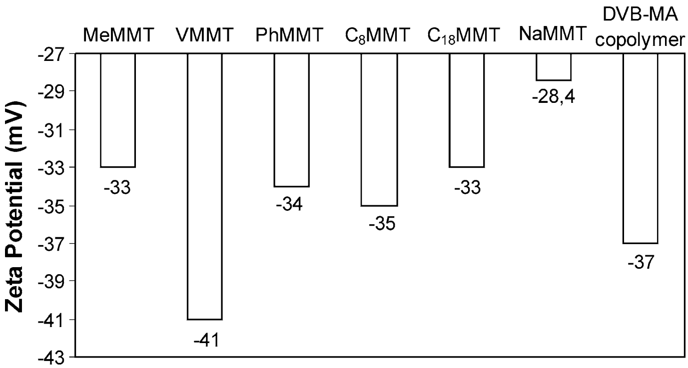


Fig. 6 Zeta potential values of the DVB–MA copolymer particles function of R radical from the silane used for the coupling with MMT clay

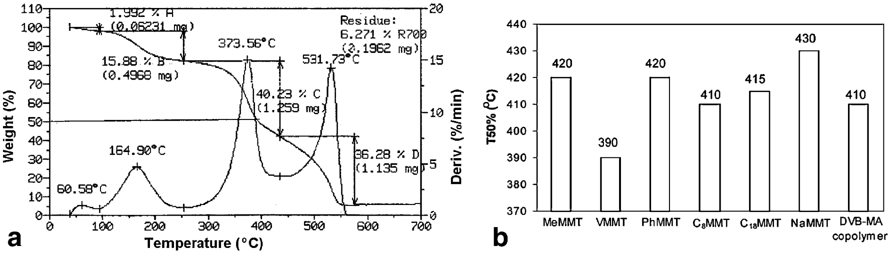


Fig. 7 **a** TG curve for DVB–MA–VMMT copolymer; **b** the T50% variation function of the layered silicate type

hybrids can partial separate the polymeric and inorganic components which lead to a decreased mean potential. A special attention was given to analyses of the synthesized polymers after solvents evaporation.

After RSiMMT synthesis, a part of the modified layered silicates quantity was separated by decantation. Solvent and unreacted silanes were eliminated in vacuum, resulting solid products, analyzed by TG to determine the quantity of coupled organic compound. This method was also used in other published studies [10, 13, 14, 17–19].

In this study, RSiMMT does not form gels, which is different from the case when organo-montmorillonite is used [28]. RSiMMT particles deposited in time and can be easily redispersed.

DTG and TG curves for DVB–MA–VSiMMT copolymer are presented in Fig. 7a. There are three main stages of weight decreasing. Similar with the previous published data for DVB–MA copolymer obtained in organo-montmorillonite presence [24], the first two stages are the result of side groups decomposition (T = ca 165 °C, respective 370 °C). The final stage ($T \sim 530$ °C) represents the thermal decomposition of main polymeric chain.

Thermal stability of DVB–MA copolymer dependence of layered silicates type is shown also in Fig. 7b. To compare temperatures was measured the decomposition temperature (T50%) for half of the copolymer total quantity.

Comparatively to the copolymer without inorganic component (T50% = 410 °C), the lowest decomposition temperature is obtained for ternary copolymer DVB–MA–VMMT (T50% = 390 °C) and the highest is obtained for the hybrid with MMT clay (T50% = 430 °C).

Vinyl groups of VMMT can participate in alternating copolymerization with MA leading to covalent bonding to DVB–MA copolymer chains. This process can start at lower temperatures as a result of the initial decomposition of side chains at a programmed heating rate. TG curves of VMMT obtained in order to establish the substitution degree of MMT clay presents the maximum value of the thermal decomposition at 363 °C.

DVB–MA copolymer obtained in MMT clay holds different interactions evidenced by T_{50} maximum value. A weak dispersion due to the polarity of the layered silicate can be shown after the copolymer formation. A part of the tactoids could remain associated and could offer a protective barrier for oxygen access in thermal decomposition process.

The other four hybrids shown in Fig. 7b (MeMMT, PhMMT, C_8MMT, and C_{18}MMT) have specific dispersion and relative stability as result of the hydrocarbon chains bonded by MMT clay which lead to T_{50} medium values.

From literature data [29, 30], result that the thermal stability of MMT hybrids is affected by two key processes, the barrier effect induced by the nanofilling and the catalytic effect which occurs due to hydroxyl groups present in the MMT. The data presented in Fig. 7b can be explained by these two aspects. For the hybrids modified with NaMMT, the barrier effect is stronger due to weak dispersion of the layered silicate platelets. DVB–MA–VMMT ternary copolymer forms a covalent bond between the matrix and the reactive filling, and the catalytic effect causes a decrease in temperature at which loss of 50% quantity of the matrix occurs.

The other composites have an increased stability compared to the copolymers without nanofillings, probably due to the barrier effect. Intermediate values obtained between 390 and 420 °C are due to specific interactions between MMT and DVB–MA.

X-ray analysis performed on solids nanocomposites revealed the presence of MMT clay specific peak (12.7 Å). NaMMT with low conversion has d_{001} value at 12.68 Å and with higher conversion> 98% $d_{001} = 12.83$ Å (Fig. 8). The same phenomenon can be observed for the hybrids with C_8Me_2MS $d_{001} = 12.7$ Å at low conversions and $d_{001} = 12.92$ Å at high conversions. The others hybrids have d_{001} value in the same range, without noticeable changes. The modifier did not influence the basal spacing significantly. Therefore, XRD spectra confirmed the incorporation of montmorillonite in the polymer matrix.

Figure 9 presents a comparison between NaMMT, copolymer DVB–MA, and the final nanocomposite between copolymer DVB–MA with NaMMT. The nanocomposite FT–IR spectra confirm the presence of the Si–O and Si–O–Si groups from NaMMT, between 400–600 and at 1052 cm^{-1}. DVB–MA copolymer has several strong peaks between 1750 and 1800 cm^{-1} assigned to C=O stretching vibration,

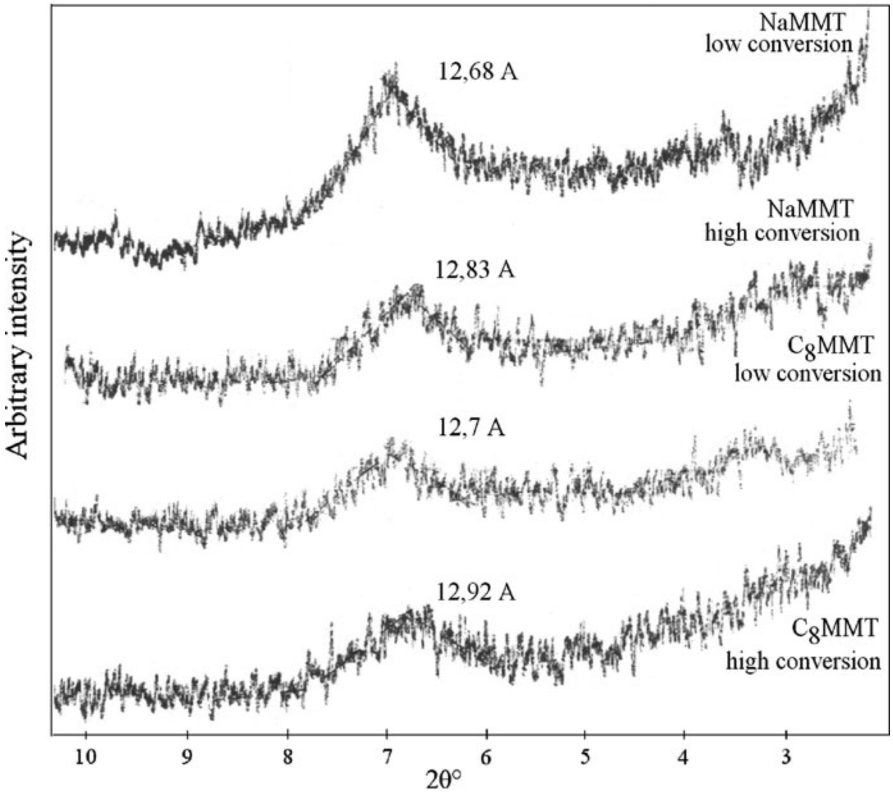


Fig. 8 X-ray analyses of the DVB–MA nanocomposites with NaMMT and C_8MMT

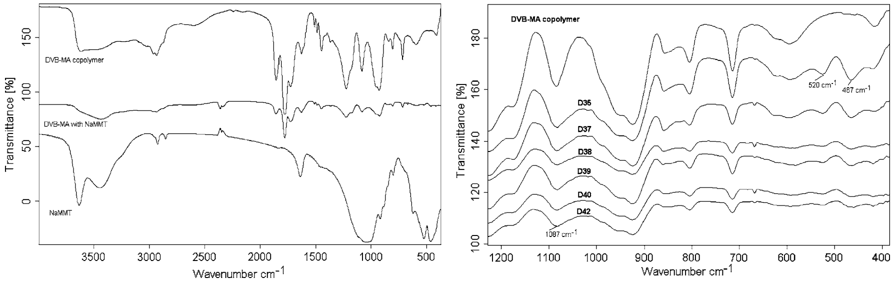


Fig. 9 FTIR spectra of: **a** the nanocomposite with NaMMT at low conversion and **b** the synthesized nanocoposites

which presence is also observed in the nanocomposite structure, but with a weaker intensity.

According to Fig. 9, FTIR spectra of all the samples also confirms the presence of Si–O–Si groups at 1087 cm^{-1} stretching vibration and Si–O groups at 467 and 520 cm^{-1} for bending, respective stretching vibration. An important observation is

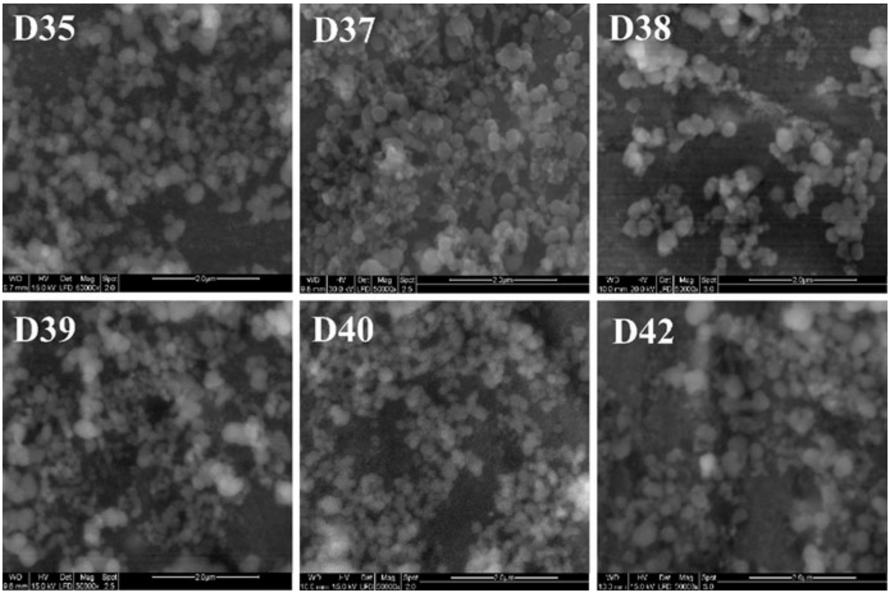


Fig. 10 SEM images for synthesized copolymers (Table 2)

that the strong peak around 1080 cm^{-1} has a synergetic contribution characteristic both to maleic semiester from DVB–MA copolymer, and from the silica Si–O–Si groups.

Organic molecules in general present next to inorganic layers possess different molecular conformations which depend on the specific interaction. In the case of the intercalated chains in clay structures, the molecular conformation is strongly influenced also by the overall variable degree of order [31]. This molecular conformation can be evidenced by following the shifts or modifications of the hydrocarbonated chain absorption bands. This modification occurs mainly on the asymmetric –CH_2 stretching and bending vibrations as well as for the –CH_3 bending vibrations, presented in our case at 2930 cm^{-1} respective at 1447 cm^{-1}.

Environmental scanning electron microscopy analyses of synthesized particles can offer additional information on the location of the clay platelets. Figure 10 shows spherical particles with a minor percentage of nonspherical particles. The presence of clay platelets inside of the particles apparently has an influence on the hybrid particles shape. In concordance with the results published by van Herk's group, the platelets are presented at the particles interface, and have spherical shapes.

Variation of the particle shape could be the result of the broad size distribution of modified MMT: particles containing smaller MMT platelets tend to be spherical. The surface of the particles is smooth, which differs with the rugged surface observed for clay covered particles as organo-montmorillonite [24]. The result confirms that clay platelets are not located at the surface of the particles, being completely encapsulated inside the particles.

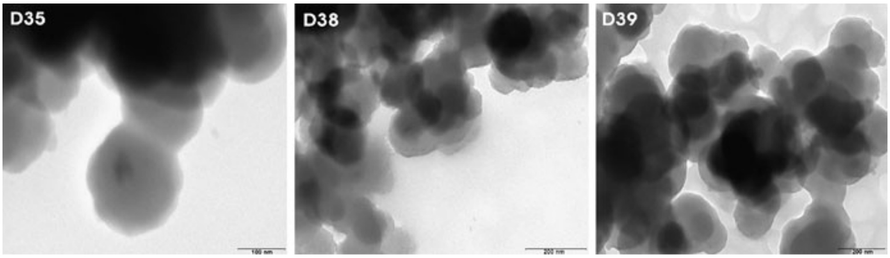


Fig. 11 TEM images of synthesized samples with different silane alkyl groups (Table 2)

Some of the spherical particles are free of clay platelets (nonetheless, the spherical shape does not necessarily imply the absence of clay platelet inside). It is very difficult to determine exactly the amount of particles with or without clay inside. TEM (Fig. 11) may offer an indication of the number of particles with clay, but the visibility of clay by TEM observation depends on its basal plane orientation, making the counting of clay-containing particles very difficult [10, 13].

Polymer particles have spherical and well countered shape. The TEM images show the modified presence of silicates in some areas (darker ones). It is obvious that not every polymer particles contains silicates, results also showed in the published papers.

Conclusions

The dispersion copolymerization developed in this article is an effective procedure for preparing MMT clay derivatives grafted with different organic groups for encapsulating in divinylbenzene-maleic anhydride. The surface of the particles is smooth, proving that clay platelets are not located at the surface of the particles, being completely encapsulated inside the particles without exfoliation.

The substitution degree of MMT clay with alkyl monoalkoxysilanes decreased with the increase of hydrocarbon substitute length. The particle size diameter of the copolymer DVB–MA decreased with the substitution degree of MMT clay.

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