

POLYMER-NANOCLAY HYBRIDS OBTAINED BY EMULSION POLYMERIZATION OF VINYL ACETATE IN THE PRESENCE OF AN ORGANICALLY MODIFIED MONTMORILLONITE

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A new polymer-nanoclay hybrid based on polyvinyl acetate (PVAc)-organically modified montmorillonite (OMMT) has been developed via emulsion polymerization technique. By establishing the swollen capacity of Na montmorillonite and an organically modified montmorillonite with vinyl acetate (VAc), we deduced that compatibility between partners is related to hydrophobic interaction depending on monomer and montmorillonite hydrophobic nature. The hybrid materials were synthesized by one-step emulsion polymerization of VAc in the presence of OMMT using polyvinyl alcohol (PVA) as stabilizing agent. Conversions of VAc are not significantly affected by the OMMT load in the polymerization system. The maximal reaction rates were also evaluated. APV-OMMT hybrids were prepared *via* solution intercalation to be compared with PVAc-OMMT hybrids obtained by emulsion polymerization using PVA. TGA and XRD analyses were performed firstly to evaluate the hybrids, and also the TEM for morphological determination, and structure confirmation.

INTRODUCTION

In the last years, nanocomposites gave a new perspective of hybrid materials due to their special properties.¹ The different types of nanocomposites from thermoplastic materials or films, to structures with different levels of dispersion, bring superior properties (thermal, mechanical, anticorrosive, etc.) than the classical composite materials.²

Layered silicates (LS), especially of montmorillonite type (MMT), are commonly used in the synthesis of nanocomposites. MMT is a natural mineral clay processed at industrial level. The MMT structure presumes layers formed by two layers of tetrahedral silica and between them positioned head to head octahedral layers of aluminum or magnesium hydroxide. This crystalline structure is complexed on basal surfaces by Na⁺, Ca²⁺, etc. complex ions. The crystallites consist in stacks with about 10 to 100 layer type entities parallel to each other at equal distances of 1 nm. This morphology can evolve in two ways in the synthesis process: intercalated structures (insertion of polymer chains into interlayer spaces) and exfoliated structures (delaminating of crystallites and layers dispersion in polymer array). These morphologies are ideal structures but practically it is impossible to obtain an absolute dispersed phase, for thermodynamically reasons.

The interactions based on a hydrophobic-hydrophilic balance are very important for phase dispersion. Modified LS are used frequently for optimal interactions between phases. Melt intercalation, solution intercalation and *in situ* polymerization are the most important methods for the preparation of such materials. In the last years, the synthesis by *in situ* polymerization in oil/water emulsion was very studied.³⁻⁶ Another interesting technique described in the literature⁷ is the *in situ* polymerization using LS directly in the synthesis.

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In this paper we synthesize nanocomposite materials based on polyvinyl acetate (PVAc) emulsion polymerization. We also made materials by solution intercalation of polyvinyl alcohol (PVA). These are used beforehand, as protection colloids in emulsion polymerization with organically modified montmorillonite (OMMT). Another route proposed in this paper is the synthesis in one step of vinyl acetate (VAc), in the presence of PVA, OMMT and ammonium persulfate (APS). We followed the monomer conversion and kinetics of reaction vs. reaction time and OMMT quantity in the system. Materials were characterized by TGA, DSC, XRD and TEM.

RESULTS AND DISCUSSION

The interaction of OMMT with the protective colloid (PVA) is established most probably by the OH groups. These hybrids are easily obtained by the solution intercalation method from water solutions. Final materials obtained as films showed flexibility and transparency at small loads of OMMT (0.1g/1.1gPVA). In Table 1 are presented the general characteristics of films obtained on polyethylene support.

Table 1

Compositions and films characteristic of PVA-OMMT hybrids

Sample	OMMT (g)	PVA (g)	H ₂ O (g)	d ₀₀₁ (Å)	Characteristic
121dd	0.1	1.1	15	19.85	film, transparent flexible
122dd	0.5	1.1	15	19	film, semitransparent friable
123dd	1	1.1	15	18.8	film, opaque friable (agglomeration)
124dd	0.2	1.1	15	20	film, opaque (agglomeration)

Hybrid structure formation was put into evidence by the thermal behavior (TGA) (Fig. 1). The inorganic partner increases the thermal stability of PVA.

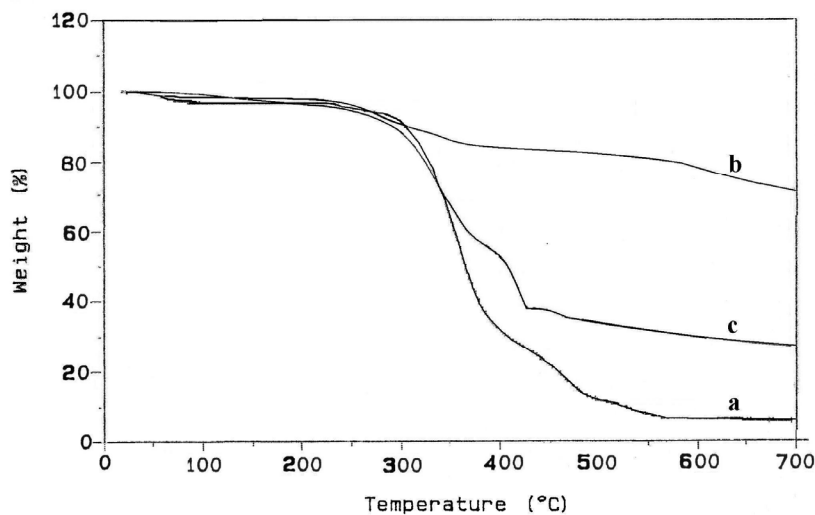


Fig. 1 – Thermal behavior of the PVA-OMMT hybrid (a-PVA, b-OMMT, c-123dd hybrid).

The thermal behavior of hybrids also showed a decrease of the characteristics maximal rates of decomposing (T1 and T2) related to the OMMT load (Fig. 2). Temperature T1 is associated with the decomposing of chain groups and T2 with the destruction of the hydrocarbonated chain. This behaviour could be explained by the catalytic effect of the quaternary ammonium salt from OMMT induced on PVA decomposing.

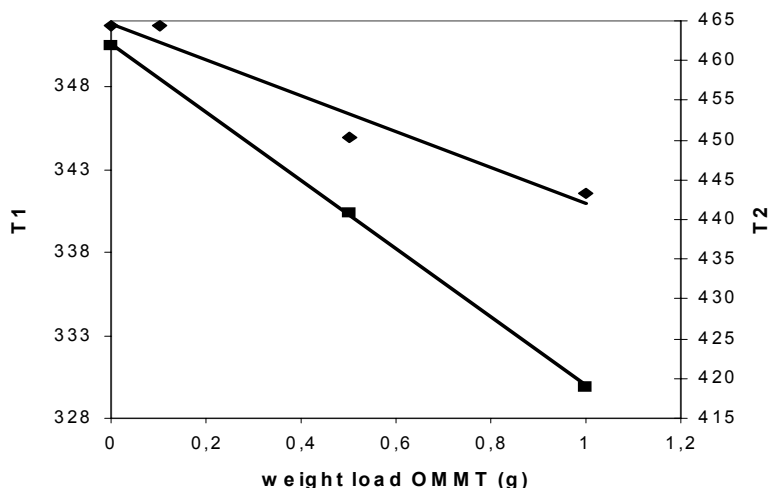


Fig. 2 – Influence of OMMT load on the decomposition temperatures of hybrids.

The structure of hybrids is supported by X-ray diffraction, which showed the intercalation of PVA in OMMT interlayers space. The weak increase of basal spacing of OMMT is showed in Fig. 3. Is also obvious that the basal spacing is not considerably affected by the phase compositions.

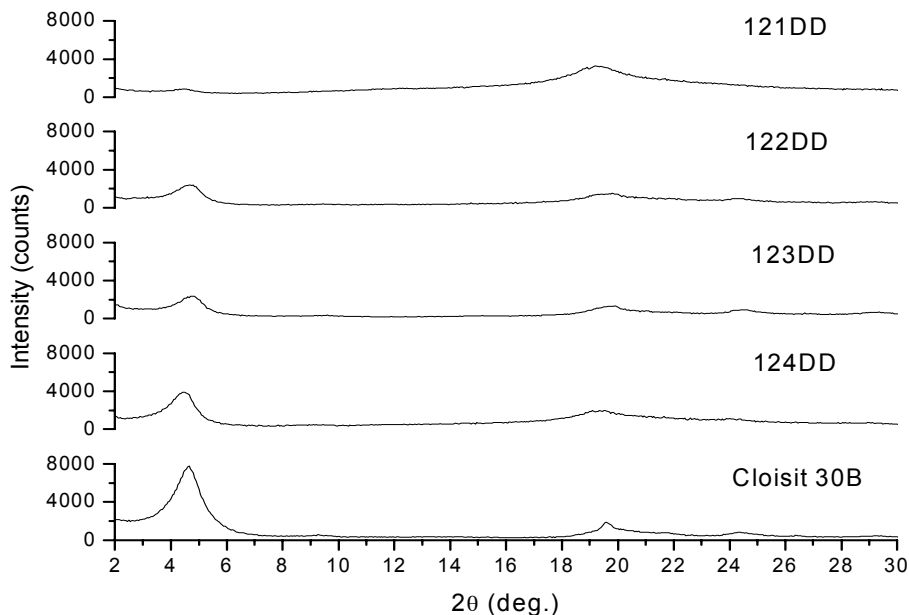


Fig. 3 – XRD patterns of Cl30B and 121DD-124DD samples obtained by the solution intercalation method.

The interaction between the organic and inorganic partners is obviously very important. OMMT offers a good swelling capacity for organic monomers. To verify the swelling capacity we prepared some dispersions of OMMT in different vinyl monomers with a constant 1:1 weight: composition ratio (Fig. 4).

These dispersions were magnetically stirred at room temperature for 4 h and then separated by ultracentrifuge. The adsorbed monomers were determined by the gravimetric method. As we expected, the interaction depends on the monomers nature and polarity, but also on the OMMT nature. A good swelling capacity is revealed on the VAc adsorption on the inorganic substrate. These could be explained by the small difference of polarity between VAc and the alkyl ammonium salt which contains a tallow chain with a double linking and two chains with C_2H_5-OH groups.

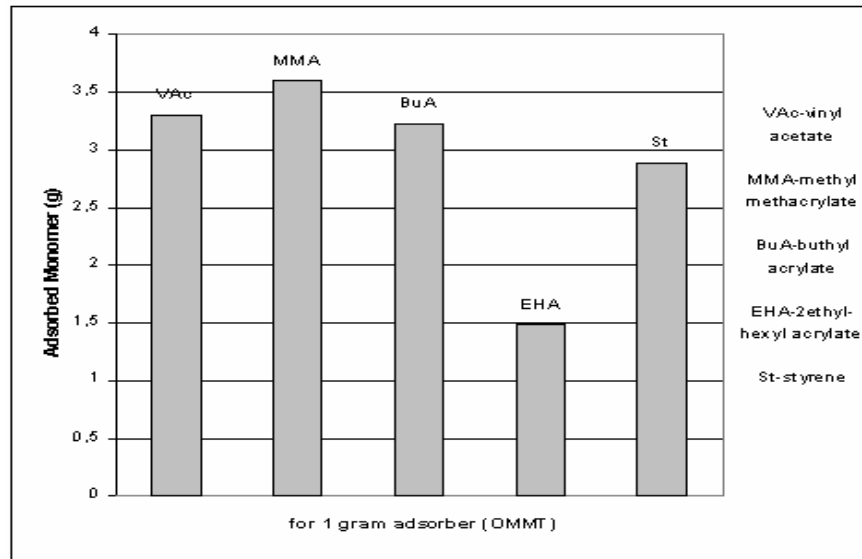


Fig. 4 – Swelling capacity of OMMT with different vinyl monomers.

Table 2

Films characteristics obtained by direct synthesis and analyzed by DSC

Sample	g of OMMT/20gPVAc	T _g (°C)	Characteristics	Observations
84	0	37.12	film, transparent friable	PVA swelling method
101	0.5	48.07	film, transparent friable	PVA swelling method
102	2.5	46.58	film, low transparency friable	PVA swelling method
103	1	47.11	film, transparent friable	PVA swelling method
104	5	46.37	film, opaque friable	PVA swelling method
105	1	46.92	film, transparent friable	monomer swelling method

Hybrids synthesis by emulsion polymerization of VAc in the presence of PVA and OMMT occurs at high conversions, over 95% (Fig. 5). The final conversions are not much affected by the presence of OMMT.

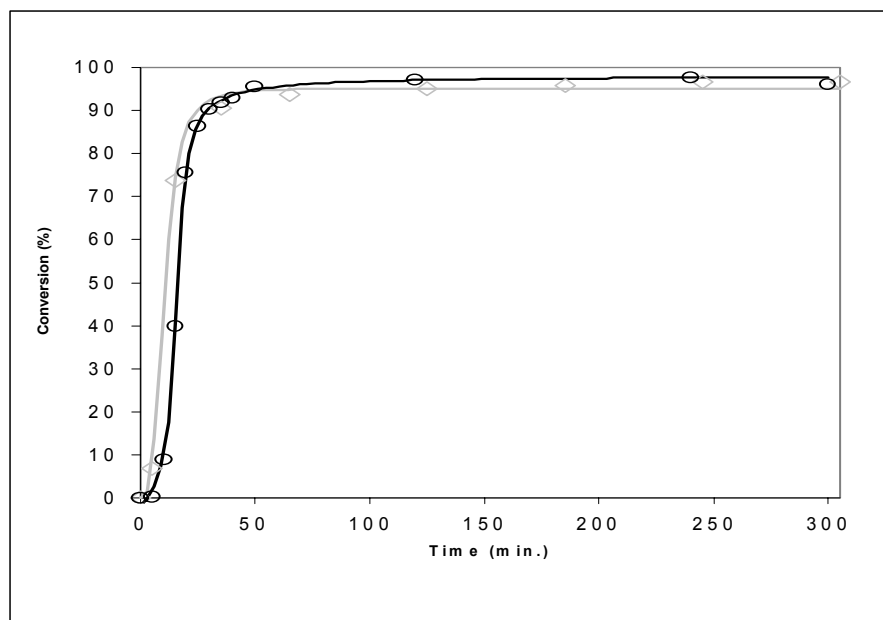


Fig. 5 – Conversion of 20 g VAc by free radical emulsion polymerization and in the presence of 2,5 g OMMT.

In the case of maximal reaction rates, a significant variation is shown related to OMMT load for a constant amount of VAc in the polymerization system (Fig. 6). For the same recipe (with 1 g OMMT), we also used another way for swelling on OMMT, thus, OMMT was swelled into the monomer overnight and then added to the PVA solution. In this case the maximal reaction rate was about 1.44 g/min, a little different from the one obtained with the standard procedure presented in the experimental section. The kinetic behavior is related with the one of using nonionic and anionic surfactants.^{8,9}

The first information about PVAc-PVA-OMMT hybrids formation is established by the thermal behavior. Similar to PVA-OMMT hybrids, the thermal stability of the polymer is significantly improved (Fig. 7). The variation in the 370°C region represents the same result of the catalytic activity of the alkyl ammonium salt.

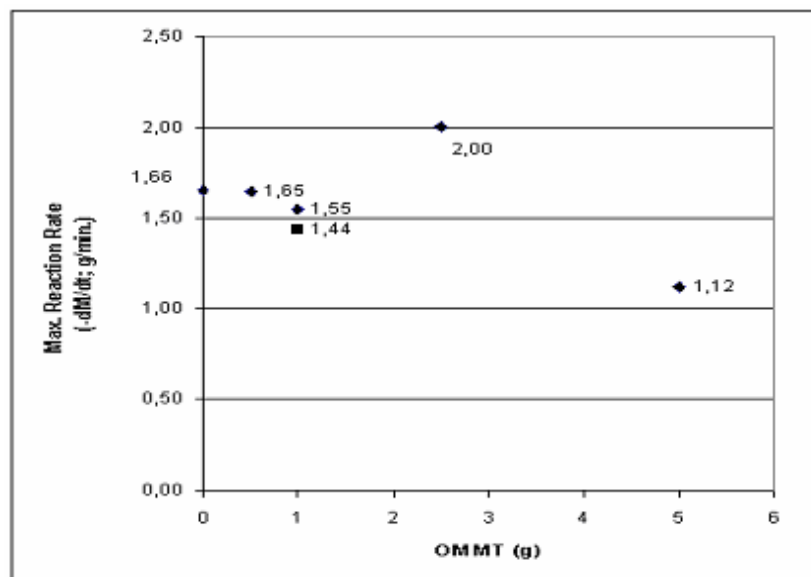


Fig. 6 – Maximal reaction rates at different OMMT weight load.

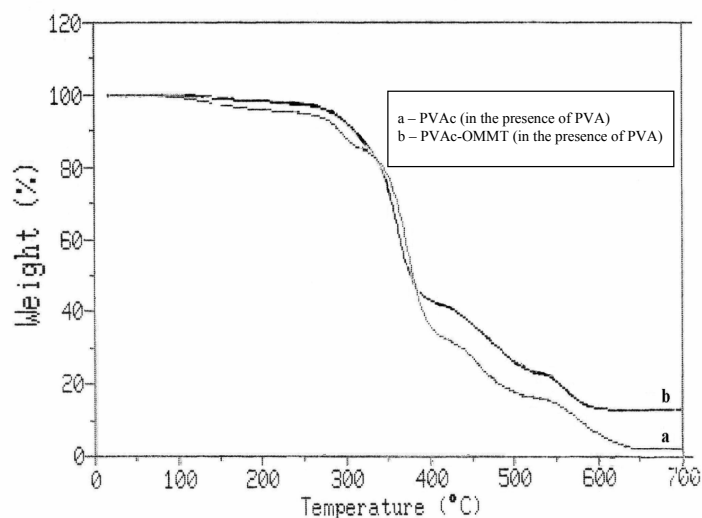


Fig. 7 – Thermal behavior of the PVAc – (2.5g OMMT) hybrid related to PVAc obtained in the same condition without layered silicate.

The first information about the structure of these materials is provided by the major modification of the glass transition temperature T_g provided by DSC analyses (Table 2). The considerable increase of T_g 's of

about 10⁰C, implies an important interaction between the mezophases. In this context the existence of one single Tg shows a high degree of homogenization between partners for the analyzed films. This behavior is in good correlation with the structural XRD analyses, which have proved the OMMT exfoliation.

Films structural analyses, XRD, confirm the unitary behavior shown by the DSC analyses. If in the case of PVA-OMMT hybrids intercalation occurs, in the case of PVAc-OMMT hybrids no diffraction peak for the crystalline phase was shown and the system becomes totally amorphous after the synthesis (Fig. 8). In these conditions totally exfoliated naocomposites are achievable. One single exception was obtained in the case of use of the biggest amount of OMMT (5 g) in this study, when a peak of weak intensity is present for a 33 Å basal spacing. This peak is associated with a polymer intercalated phase of OMMT (basal spacing increase from 18.5 Å to 33 Å). A possible mechanism could be founded by the totally dispersed OMMT in a first stage and because of the polymerization propagation the system exfoliates. The polymer networks by the acetate groups can provide by a polarity interaction a thermodynamically better situation for layers reorganization.

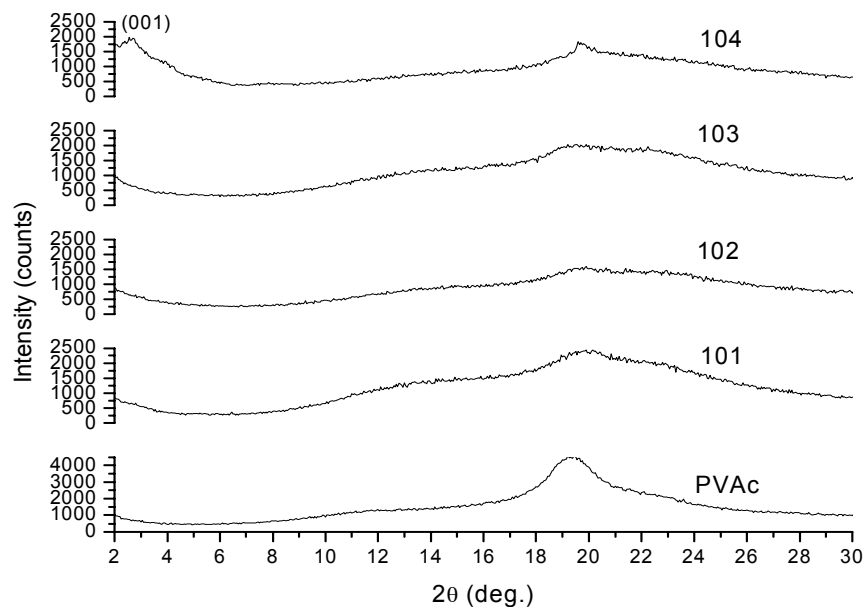


Fig. 8 – XRD patterns of PVAc and 101-104 samples obtained by the direct synthesis method.

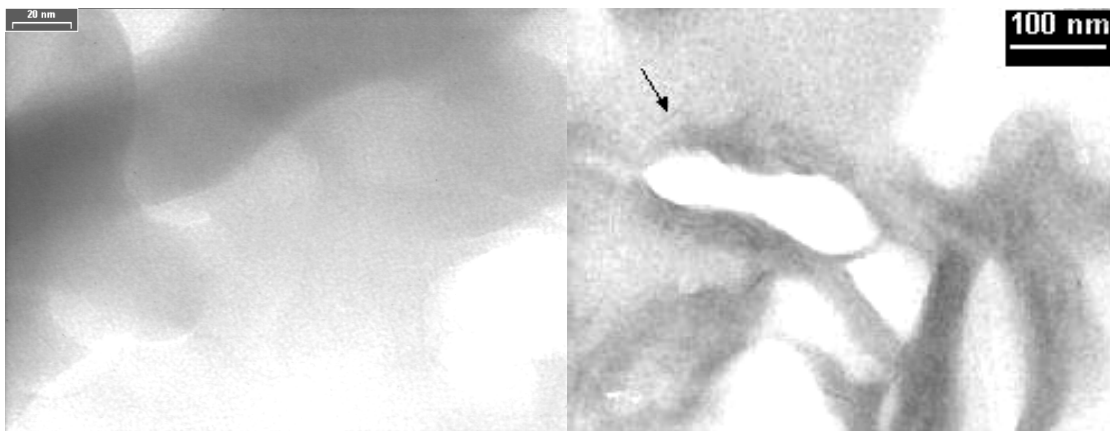


Fig. 9 – TEM image of sample 101 (0.5g OMMT) exfoliated structure.

At high concentration of OMMT in fact the intercalated phase coexists with the exfoliated one. This behavior is in good relation with the nanocomposites general properties which are better at small loads of inorganic component in the polymer matrix.

TEM analyses confirmed the exfoliation. In Fig. 9 the darker phase is represented by the OMMT which showed a good dispersion and layers orientation in the polymer matrix.

EXPERIMENTAL

Materials

OMMT is a cloisite 30B as provided by Southernclay Inc. used without purification obtained by ion exchange with a methyl, tallow, bis 2-hydroxyethyl quaternary ammonium chloride salt ($d_{001}=18.5 \text{ \AA}$). PVA is a commercial product with $M_w=120000$ and 88% degree of hydrolysis. VAc is a commercial product purified by rectification. APS was provided by Loba Feinchemie and used without further purification.

Preparation of PVA-OMMT hybrids

A typical procedure was followed for the preparation of PVA-OMMT hybrids. The hybrids were obtained by solution intercalation, using 10 g of PVA 10% solution in water, by adding it on different quantities of OMMT (between 0.1-1g OMMT), dispersed in 5 g of water. These dispersions were magnetically stirred at room temperature for 5 hours. Thin films were deposited on glass and polyethylene. Films drying occur at room temperature for several days.

Preparation of PVAc-PVA-OMMT hybrids

PVAc-PVA-OMMT hybrids were synthesized by free radical emulsion polymerization of vinyl acetate in the presence of OMMT. A TLA 30 autoclave with mechanical stirring, stirring controller, back-flow condenser, heating jacket, connected to a Lauda E100 thermostat was used for synthesis.

OMMT was dispersed in 100 g solution of PVA 10% for about ½ h and then 100 g of water was added and stirred for another ½ h. The monomer (20 g) was added to this mixture and stirred for 1 h. All stirring operations were done at 200 rot./min. Polymerization starts after temperature stabilization at 65 °C and APS (0.25 g) adding. Polymerization time was about 5 h. The reaction mixture was then cooled and the hybrid latex was used directly for film forming.

Different samples were analyzed during the polymerization for conversion estimation. Different weight loads of OMMT (0.5; 1; 2.5; 5 g) were used to observe the influence on monomer conversion and reaction rates. Conversion and reaction rates were estimated by the gravimetric method.

Measurements

TGA and DSC analysis of all samples was carried out at a heating rate of 20°C min⁻¹, respectively 10°C min⁻¹ in air using a Du Pont 2000 instrument.

The X-ray diffraction data were collected at room temperature. Data acquisitions were made with a DRON UM1 diffractometer connected to a PC. A horizontal powder goniometer in Bragg-Brentano focusing geometry with graphite monochromator was used. The incident Cu-K α radiation, $\lambda=1.54178 \text{ \AA}$, at 35 kV and 30 mA was used. The typical experimental conditions were: 5 sec. for each step, range angle $2\theta = 2^{\circ}$ -50 $^{\circ}$, step 0.02 $^{\circ}$. The spectra obtained in these conditions were used to make qualitative phase analysis [8].

A Philips CM 120, was used for TEM analyses. The probes were sliced to a microtome with diamond knife in 30 nm sections and analyzed without additional staining.

CONCLUSIONS

OMMT structure exfoliation is provided by the free radical emulsion polymerization of VAc. OMMT exfoliation is related more to PVAc formation and less to the protective colloid PVA.

Although the conversion is not very much affected by the presence of OMMT, the VAc kinetics is influenced by the OMMT load in the system.

PVAc- OMMT hybrids showed the increase of PVAc specific Tg's.

This synthesis method offers a lot of advantages like obtaining of: hybrid nanocomposites latexes, nanocomposites films, waterborne hybrid latexes, exfoliated nanocomposites materials, etc.

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