

POLY(VINYL ACETATE)-MONTMORILLONITE COMPOSITES PREPARED VIA EMULSION POLYMERIZATION WITH NONIONIC SURFACTANT

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Received February 22, 2006

Hybrid materials containing poly(vinyl acetate) and montmorillonite (MMT) were prepared using an one-batch emulsion polymerization recipe, assisted by nonionic surfactant. The amount of clay used in the recipes and its relative concentration with respect to the other reaction partners drastically influence the morphological units in the end-products. For low MMT concentrations, well-defined, spherical particles are formed. At the other extreme, for high MMT amounts, production of polymeric, water-swollen aggregates is favored. A small amount of reformed MMT tactoids was detected in all casted hybrid films, indicating that most of the inorganic is dispersed in the organic phase.

INTRODUCTION

Recently, polymer-clay hybrid materials have received significant attention because the mutual interactions between polymer and clay are considered to affect their properties. As compared to with conventional microcomposites, greatly improved physical and mechanical characteristics were found for hybrids based on thermoplastic matrices containing a nano-scale dispersion of layered silicates.¹⁻⁵ The properties of the hybrid materials are directly related to their internal morphology and, in this respect, the state of dispersion of the inorganic phase is very important.⁵ At low clay content, exfoliated nanocomposites are encountered. For these composites, individual clay platelets are separated by a continuous, more or less thick polymer matrix. As the inorganic load becomes higher, flocculated and / or intercalated hybrids are formed.

In this paper, we explore the possibility to obtain polymer-MMT hybrids using a one-batch recipe, with growing of the polymeric phase via a radicalic (emulsion) polymerization, after dispersion of the MMT tactoids in water. The starting monomer is vinyl acetate (VAc) and the reaction is assisted by a nonionic surfactant, with a medium-long (30 units) ethyleneoxide tail. Several experimental techniques were used to elucidate the phenomena taking place in the wet as well as the dried state of the end-products.

RESULTS AND DISCUSSION

The list of all formulations with polymer is given in Table 1. Based on the monomer conversions at different moments from the beginning of the polymerization, we were able to calculate the reaction rate and found that it depends on the amount of Na-MMT present in the recipe. At high enough MMT concentrations,

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the growing oligomeric radicals can be affected by transfer reactions with the mineral crystals edges,⁶ hence decreasing the conversion towards the macromolecular chains.

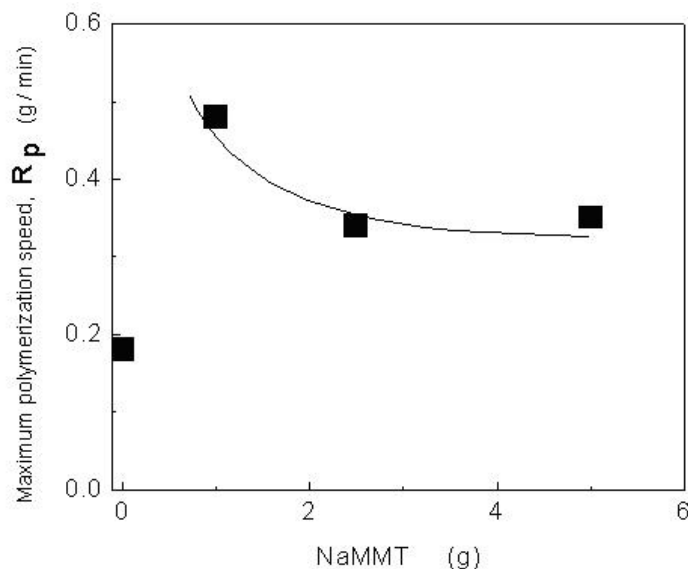


Fig. 1 – The effect of added inorganic on the maximum polymerization rate reached in the polymerization reaction.

Also, more MMT in the recipe was seen to affect the average hydrodynamic diameter of the PVAc latex particles (see Table 1). The ascendent trend could have two explanations:

(i) for higher [MMT], more NPh₃₀EO is involved in the interaction with the clay, leaving less surfactant available for particle stabilization. In this case, the reaction will favor the formation of a smaller number of particle, but with bigger diameters, or

(ii) physical (clay-surfactant-polymer) interactions tend to destabilize the dispersion and, instead of independent latex particles, the DLS measures aggregates (i.e. larger units).

Table 1

Index of the hydrid preparations, with the average diameter for the PVAc particles measured using dynamic light scattering (DLS).

Sample	Na-MMT (g)	Average diameter (nm)	Comments
H0	-----	240	Stable latex, no sedimentation /phase separation for more than 3 years.
H1	1	337	Stable latex, no sedimentation or phase separation for around 2 years.
H2	2.5	383	The latex was stable for ~ 8 months after which the lower region starts building a gel-like phase which grows up to 1/3 from the total sample volume.
H3	5	753	The dispersion as prepared is extremely viscous and the transition towards a gel starts after 2 weeks. The gelation proceeds for 3 weeks and, at its end, the whole dispersion is gelled.

For the clay-surfactant interaction, the hydrophilic tail of the surfactant is important.^{5, 7-8} The chemical structure (ethoxyl groups) of the tail favors ion-dipole and hydrogen bonding of the oxygen atoms with the 2:1 clay. These specific interactions have been already used in making hybrids with: EO-surfactants,^{7, 8} EO-monomers⁹ or with PEO as pure polymer^{7, 10-13} or as copolymer.¹⁴⁻¹⁶

Our results (see Fig. 2) confirm the high-adsorption of NPh₃₀EO onto the clay, in agreement with previously published data.¹⁷

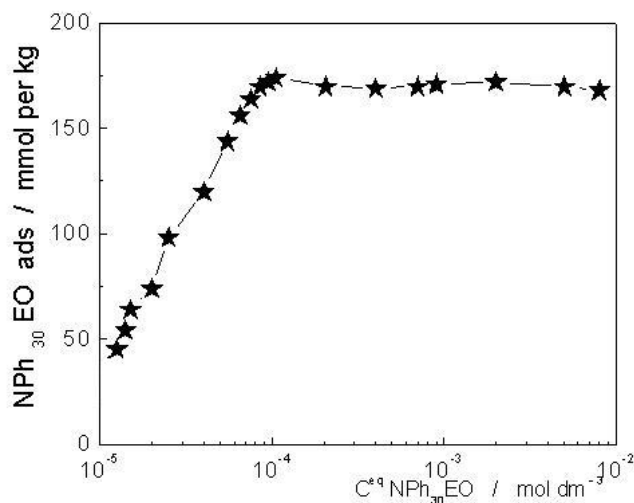


Fig. 2 – Adsorption isotherm (Langmuir-type) for the surfactant onto Na-MMT.

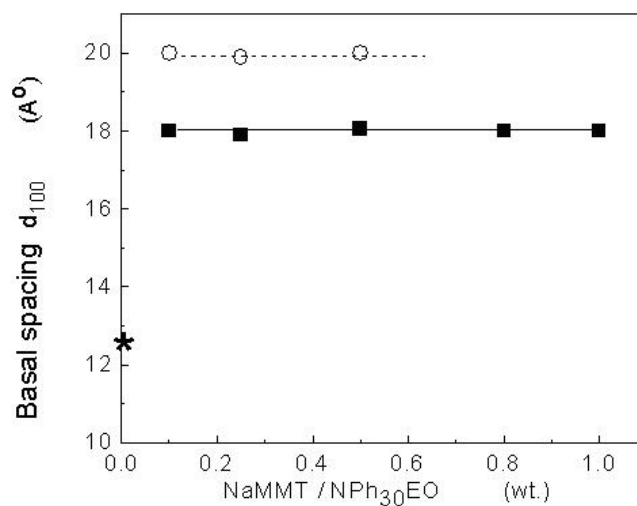


Fig. 3 – Basal spacing (d_{001}) for dried NPh₃₀EO – NaMMT mixtures (full symbols) and for hybrids with surfactant and PVAc (open symbols). The value measured for pure NaMMT is indicated by the star.

When the surfactant-MMT mixtures are dried, one can also estimate (from the position of the (001) peak in the XRD pattern) the modifications in the basal spacing of the montmorillonite due to NPh₃₀EO insertion between the platelets. Compared with the initial 12.5 Å value, a swollen state, with higher interlamellae distances = 18 Å is found for all compositions. This value increases even more (to 20 Å) if the PVAc chains are in the dried mixture (Fig. 3). Also, the intensity of the XRD main diffraction peak decreases very much, which suggests a rather small percentage of the reformed tactoids in the films. The small increase in the interbasal spacing in the composite films excludes the existence of ‘sandwiches’ in which both polymer and surfactant are trapped simultaneously in the clay inner-galleries. Actually, it seems that in the hybrids there is a preferential interaction of the macromolecular chains with the clay surface and we detect exactly its influence via the XRD diffraction patterns.

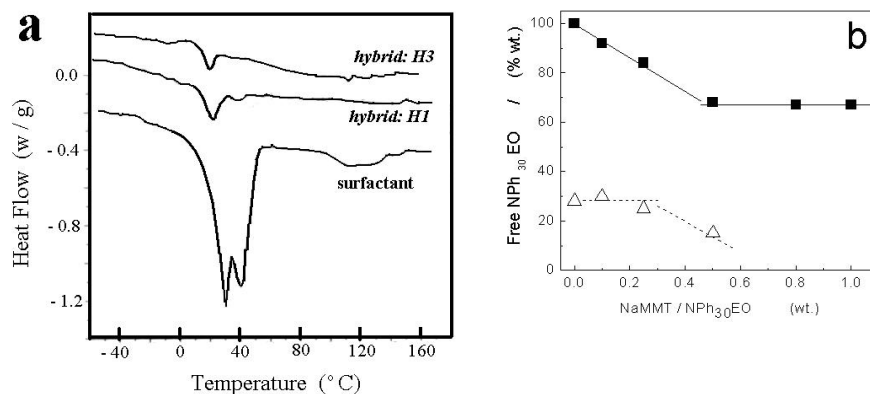


Fig. 4 – Results of the films analysis using differential scanning calorimetry (DSC).

(a) DSC curves measured for the pure surfactant and the hybrids H1 and H3.

(b) Calculated free-surfactant which remains unconstrained by the interaction with the other compounds. Closed symbols: physical mixtures containing clay and surfactant. Open symbols: results for hybrids. The lines are drawn only for eye guidance.

Also, the endothermic peaks of the surfactant become less prominent and almost disappeared (see Fig. 4a) in the DSC curves obtained on the dried hybrids. The same was observed also for clay-surfactant mixtures (data not shown). These trends could be explained by a decrease of the ordered association of the NPh₃₀EO molecules in the presence of the other components, saying that the surfactant chains are highly constrained by the presence of Na-MMT and / or PVAc. If one assumes that the melting enthalpy per unit mass of the free-surfactant has the same value in all the physical mixtures and polymer-containing composites, the DSC method provides an alternative to calculate the amount of free-surfactant, in the dried state. The results are plotted in Fig. 4b. As the inorganic / surfactant ratio increases, a saturation is reached in the amount of free-surfactant. When the mixtures have also polymer, the saturation was not seen for the compositions used in the present work.

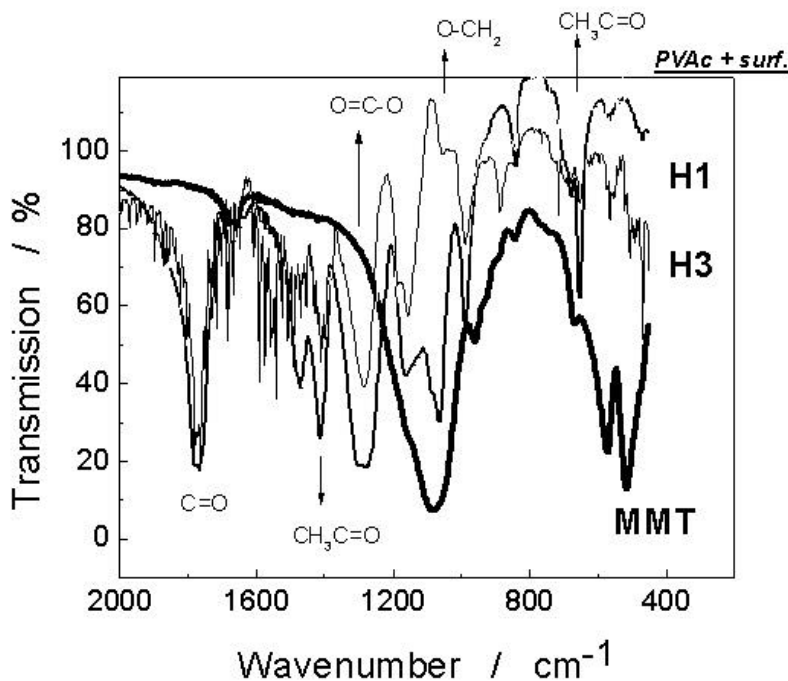


Fig. 5 – Selected FTIR spectra for the inorganic (thick line) and the hybrids: H0(=PVAc+surfactant), H1 and H3.

Exploring further the composite films, we used FTIR spectroscopy to get more evidence for mutual inter-elements interactions. The typical bands for the Na-MMT groups¹⁸ were found in the FTIR spectra of

pure inorganic phase (Fig. 5): the Si-O (1070 cm^{-1}) and Al-O (524 cm^{-1}) stretching and Si-O bending (at 466 cm^{-1}). For poly(vinyl acetate) in the H0 formulation, one can easily recognize the peaks of the polymer: a very strong peak at 1736 cm^{-1} (C=O) and the signature for the $\text{CH}_3\text{C}=\text{O}$, at 1374 and 606 cm^{-1} , associated with a weak doublet: $^{19} 629 - 650\text{ cm}^{-1}$. Adding clay in the preparation recipe induces a strong reduction of the vibrations for the $\text{CH}_3\text{C}=\text{O}$ and the blocking of the O- CH_2 group (vibration located at 1415 cm^{-1}).

It was proven that the interaction of MMT with fully hydrolised poly(vinyl alcohol) is driven by hydrogen bonding between the vinyl alcohol group of the PVA and the silicate oxygens, hence dominating the cleavage plane of the clay.²⁰⁻²³ Our FTIR results (Fig. 5) indicate that the ester group of the vinyl acetate interacts strongly with the surface of the MMT platelets also.

The thermal stability of the surfactant (pure or with clay) and of the composite films was determined by TGA as weight loss during a programmed heating. As observed in Fig. 6a, the pure NPh_{30}EO exhibits two weighted-loss steps. The first step, around 270°C (peak I, in Fig. 6a), can be attributed to degradation of chains in amorphous conformations. The second degradation (peak II), with the maximum at $\sim 360^\circ\text{C}$, corresponds to surfactant in cristalline arrangements. When in mixture with Na-MMT, a third degradation step occurs (peak III in Fig.6b), confirming the existence of surfactant entrapped between the clay lamellae.

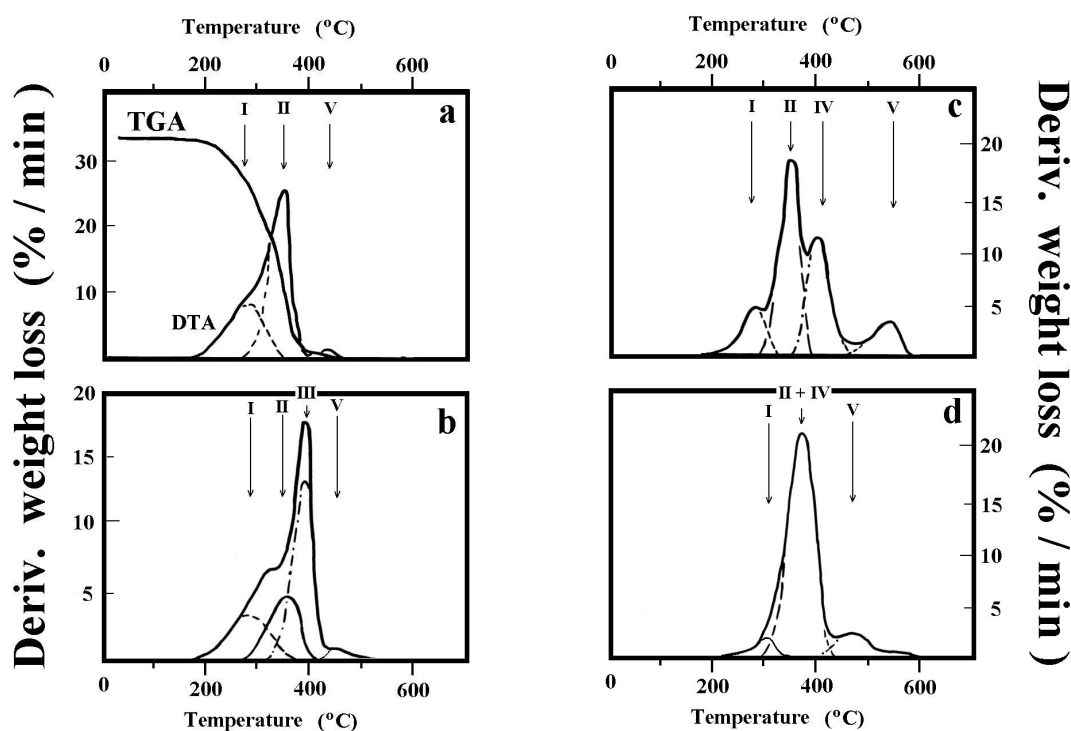


Fig. 6 – Derivative thermogravimetric analysis (DTA) on the dried samples for: (a) pure surfactant, (b) surfactant with clay, (c) PVAc latex polymerized with surfactant and (d) hybrid H3, containing polymer, surfactant and clay. For the mixtures in (b) and (d), the same ratio: $\text{NaMMT} / \text{NPh}_{30}\text{EO} = 0.5$ was used. To simplify the graphs, we have included the original TGA curve only in (a). The arrows indicate the positions of the major degradation peaks, as found after deconvolution.

For a PVAc latex prepared with surfactant and without inorganic, the degradation of the polymeric chains (peak IV, $\sim 410^\circ\text{C}$, Fig. 6c) can be easily distinguished from surfactant contribution. However, in hybrids, we are faced with an interesting situation. The PVAc-contribution is shifted to lower temperatures and we find a combined peak (peak II+IV, Fig.6d). The effect (of a less thermally stable polymer) was seen before^{24,26} and can be attributed to a less polymerized structure of the PVAc in the final composite. It means that in hybrids with high clay concentration (as H3), the molecular weight of the polymeric chains is lower than in formulations with none or low clay amounts. In all DTA curves, the thermal degradation ends with a more or less detectable contribution (peak V) from structure (*i.e.*, ashes) collapse, with burning of the former ‘protected’ organics.²⁴

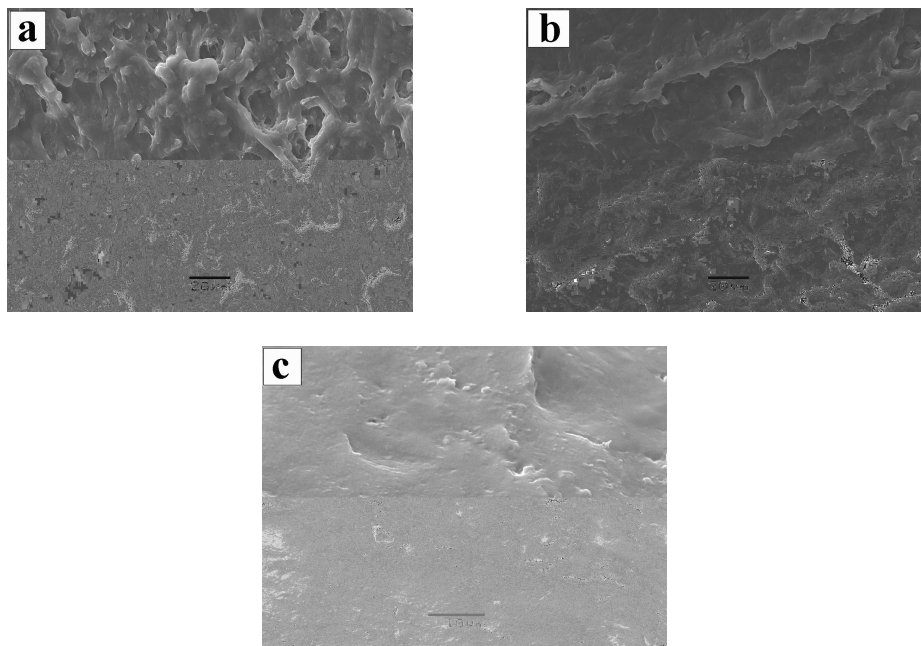


Fig. 7 – Scanning electron microscopy images for the composites: H1 (a), H2 (b) and H3 (c), in fractures.

Inspecting (with scanning electron microscopy) the fractures of the composite films, we encountered a variable morphology, clearly depending on the amount of Na-MMT used in the initial formulations. Since all the films have an identical fabrication history, the differences in the SEM images could only be explained by a variation in the ‘starting units’, as explained in what follows. The PVAc has a low T_g ($\approx 27.5^\circ\text{C}$) and the particles obtained via emulsion polymerization of the vinyl acetate monomer are hairy.²⁵ Also, when casting the films at room temperature, the surfactant has a plastifying effect. The two above-mentioned factors contribute synergetically to partial fusion of the latex spheres. Remains of the initial particles can be still recognized in the fracture of the H0 film (Fig.7a). As the clay amount increases, there is a visible transition to smoother fractures (Fig.7c).

Based on all the data obtained using different analysis techniques in the wet phase (DLS, adsorption isotherms) and dried films (SEM, TGA, FTIR, DSC and XRD), one can advance a coherent scenario which explains all the experimental findings.

In normal emulsion polymerization of vinyl acetate with nonionic surfactant, at the end of the reaction, a good dispersion of spherical, particles is obtained. These particles show a rather narrow size distribution and have an average hydrodynamic diameter ≈ 240 nm. Casting films from PVAc latexes will result in films with only partial preservation of spherical units.

If increased amounts of Na-MMT are added in the formulations, a collection of physical interactions drive the system. Multiple effects could be then expected. The clay- NPh_{30}EO interaction, with a direct contact between the ethylene oxide and the inorganic surfaces, gives an increased hydrophobe character to the MMT platelets. We can not exclude that an increased hydrophobicity would actually make the platelets more attractive as interaction partners for vinyl acetate groups, as monomer or as growing polymeric chains.

Also, due to clay-surfactant initial coupling, there is less surfactant left in the aqueous phase (hence the DSC results, Fig.4a-b). This turns the balance during the polymerization towards formation of larger latex particles (like in H1, H2) or even PVA spheres with a high water/polymer ratio. These last entities are more close to super-swollen polymer aggregates than to classical, dense polymeric spheres. Such entities will have larger diameters (see the DLS result for formulation H3) and will shrink and fuse very easily when dried (see the SEM image in Fig.7c). Also, these large units use some of the PVAc chains for stabilization, which increases the probability of interaction with surfactant (i), with clay-surfactant complexes (ii) and eventual bridging via free PVAc chains (iii). Since the monomer has a relative high solubility in water: around 2 % wt., polymerization in the aqueous phase will always provide a certain percentage of free PVAc molecules. Further, if they grow beyond a critical length, these oligomeric molecules will collapse in aggregates, or interact with other partners (like single or surfactant-modified clay platelets). The diversity (in structure) at

the end of the polymerization step in formulations with high clay content (as in H3) is the base for completely different rheological properties. In this case we do not have a latex comprised from individual, well-dispersed particles, but rather a mixture of elements with a high tendency for associative interactions. The H3 formulation is the extreme example (from the recipes used in the present work) for a mixture which is very viscous and turns relatively soon (2-3 weeks) after preparation into a whole gel (see Tab. 1).

EXPERIMENTAL

Materials

Sodium-montmorillonite (Cloisite Na-MMT) was generously donated by Southern Clay Products, Inc., USA. Vinyl acetate (VAc, Chimopar - Roumania) was purified by rectification. The initiator: ammonium persulphate (LOBA-Feinchemie) and the surfactant: NPh₃₀EO (nonylphenol poly(oxyethylene) with 30 OE units) from ICI, UK) were used without further purification.

Hybrids Formulation

In the batch polymerization, the surfactant (10 g. NPh₃₀EO) was first dissolved in water (200 g). Further on, under continuous stirring, a given amount of the monomer (VAc, 20 g.) was added and the mixture was heated up to 65°C, after which the initiator (0.25 g APS) was added. For kinetics determinations, small aliquots were taken and analysed every 15 min., during the entire reaction time (6 h). When clay-organic recipes were prepared, the Na-MMT was first mixed with water, under stirring, for 1 h, before adding the surfactant. After preparation, aliquots were taken from all the *wet* phases, deposited on poly(ethylene) sheets and dried room temperature (25°C), for 2 weeks, followed by 24 h drying under vacuum. Before measurements in the resulting dried state, the poly(ethylene) substrate was peeled off.

Techniques

Monomer conversion (during polymerization) was calculated based on gravimetric measurements of the polymer phase, after water elimination. Hydrodynamic diameters in the final PVAc latex dispersions were determined by dynamic light scattering (DLS), using a NICOMP 370 equipment.

Adsorption isotherms (onto MMT) were determined at 25°C, by mixing a known amount of the clay with a constant volume of calibrated surfactant solutions in 50 ml. centrifuge tubes. After equilibration, the mixtures were centrifuged for 45 minutes at 15,000 rpm. The final concentration of the surfactant in the supernatant was determined spectrophotometrically from the optical density at 276 nm. At this wavelength the absorbance in the UV spectra is due only to the phenyl ring of the hydrophobic head-group.

Thermogravimetric analysis (TGA, with a speed of 20°C/min) and differential scanning calorimetry (DSC, 10°C/min) were performed with a Dupont 2000 instrument. X-ray diffraction (XRD) studies were done using a DRON-2 instrument with horizontal goniometer and a Cu K α ($\lambda = 1.5418$ Å) radiation source. After coverage with a thin (20 nm, sputtered) gold layer, the fractured surfaces of the dried polymer-clay composites were observed by scanning electron microscopy (SEM), using a JEOL-5610 equipment operated with a high-tension voltage of 20 kV.

CONCLUSIONS

From the results obtained so far, it can be concluded that polymer-clay nanocomposites can be successfully synthesized using a smectic clay, modified by interaction with nonionic surfactant, by a simple emulsion polymerization technique. The amount of clay used in the recipes (i) and its relative concentration with respect to the other reaction partners (ii) incline the reaction equilibria in different directions. Hence, in the final dispersions, the morphological units could belong to a variety of forms, spread between: well-defined, spherical particles at one extreme and polymeric, water-swollen aggregates at the other extreme. Most probably, at intermediate MMT concentrations, combinations between the two extremes will be found. A small amount of reformed tactoids was detected in all casted hybrid films, indicating that a large percentage of the inorganic is dispersed in the organic phase.

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