"One-Pot" Preparation of Polymer/Clay Nanocomposites Starting from Na$^+$ Montmorillonite. 1. Melt Intercalation of Ethylene−Vinyl Acetate Copolymer

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Polymer/clay nanocomposites currently give rise to a tremendous interest from both academics and industries. Indeed, by dispersing at the molecular level a tiny amount of clay (usually less than 5 wt %) within a polymeric matrix, a large array of properties can be significantly improved (large increase in the polymer Young's modulus and in heat deflection temperature, improved barrier properties, and fire retardancy).[1,2] To promote the molecular and stable dispersion of the clay layers, clays previously organo-modified with onium salts are most often needed.[1−4] Some nanocomposite preparations starting directly from non-organo-modified clays have been reported as well but they are limited to hydrophilic polymers such as poly(ethylene oxide) (PEO)[5,6] or poly(vinyl alcohol),[7] sufficiently polar to be intercalated between the aluminosilicate layers of the clay. Another alternative relies upon the emulsion polymerization carried out in the presence of water-dispersed, nonmodified clays as described for polymethyl methacrylate (PMMA),[8] polystyrene (PS),[9] epoxy resin,[10] and styrene−acrylonitrile copolymer.[11] In each case, a true intercalated nanocomposite was obtained, characterized by single extended polymer chains sandwiched between the silicate sheets. However, these techniques do not lead to exfoliation/delamination of the non-organo-modified silicate layers.

An interesting approach to produce nanocomposites from natural clay with some extent of exfoliation has been very recently proposed.[12] In this method, diblock copolymers constituted by a polar hydrophilic block (PEO) and a hydrophobic block (PS, PMMA) were used to compatibilize the natural clay and a hydrophobic matrix (PS and PMMA, respectively).

While melt intercalation of polymers in organo-modified clays has been known for a long time,[1] this communication aims at reporting on the preparation of nanocomposites in an original "one-pot" reactive process, starting directly from natural (Na$^+$-based) clay. For so doing, a cationic surfactant such as an ammonium salt bearing long alkyl chains, has been considered as a polymer/clay reactive compatibilizer.

Ethylene−vinyl acetate copolymer (Escorene UL00328, Exxon) containing 27 wt % vinyl acetate has been used as a model in this study. Such type of copolymer has demonstrated its ability to promote nanocomposite formation by melt blending with organoclays.[1,13,14]

Purified sodium montmorillonite (Cloisite Na$^+$, Southern Clay Products) with a cationic exchange capacity of 92 mequiv/100 g and an interlayer spacing of 12.6 Å has been used as the nanofiller precursor. Dimethyl dioctadecylammonium bromide (DMDODABr) (used as received from Acros) has been studied as the potential clay/matrix reactive compatibilizer.

For the sake of comparison, Cloisite Na$^+$ has been organo-modified with DMDODABr, using the general method described in the literature.[15] Thermogravimetric analysis (TGA) of this DMDODA-modified Cloisite carried out under helium at a heating rate of 10 K/min allows the amount of ammonium (DMDODA) incorporated in the organo-modified clay to be evaluated, that is, 46.2 wt % of DMDODA corresponding to 83.5 mequiv of DMDODA/100 g of organoclay. Three EVA-based composites filled with the same amount of inorganics (ca. 3.5 wt % of clay) were prepared on a two-roll mill (Agila) operating at 130 °C for 7 min: one from DMDODA-modified Cloisite (**1**), one from Cloisite Na$^+$ (**2**), and the last one from a mixture of Cloisite Na$^+$ and DMDODABr (**3**), using an amount of ammonium bromide equivalent to the amount found in the organo-modified clay ("one-pot" process)(see Table 1). In this case, DMDODABr was added at the beginning of the blending procedure, that is, directly after EVA was molten, and then after 3 min. Cloisite Na$^+$ was added to the DMDODABr/EVA molten mixture. For the sake of comparison, an EVA sample blended with the same

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Table 1. Tensile Properties of EVA and EVA-based (nano)Composites Filled with Ca. 3.5 wt % Cloisite (relative to the organic fraction)

compound	clay[a] (wt %)	compatibilizer DMDODABr (wt %)	stress at break (MPa)	strain at break (%)	Young's modulus (MPa)
1	DMDODA-modified Cloisite[b] (3.4)		28.77 ± 0.47	1365.2 ± 11.2	21.42 ± 1.75
2	Cloisite Na^+ (3.6)		27.74 ± 2.37	1423.9 ± 34.6	12.61 ± 0.68
3	Cloisite Na^+ (3.5)	3.5	29.10 ± 1.15	1367.3 ± 10.9	17.44 ± 0.74
4		3.5	25.36 ± 0.39	1419.1 ± 16.2	13.86 ± 0.70
5[c]			28.66 ± 0.73	1406.4 ± 28.2	12.41 ± 1.31

[a] wt % (relative to the inorganic fraction) in the (nano)composite. [b] DMDODA relative content in the nanocomposite ≈3.0 wt %. [c] EVA Escorene UL00328 alone.

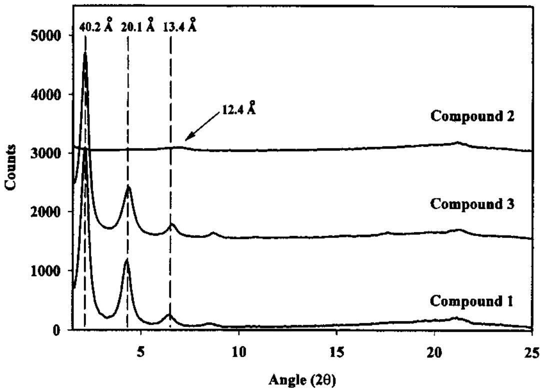

Figure 1. X-ray diffraction analysis of compound **1** (EVA + DMDODA-modified Cloisite), **3** (EVA + DMDODABr + Cloisite Na^+), and **2** (EVA + Cloisite Na^+).

amount of DMDODABr as for **3** was prepared as well (**4**). It is worth pointing out that the slight difference in the filler weight fraction (from 3.4 to 3.6 wt %, relative to the inorganic content of the clay filler) reported for the composites **1**−**3** (Table 1) comes from the presence of NaBr salt in the compatibilized composite. Clearly, such a limited variation in the filler relative content cannot be responsible for the differences in measured tensile properties (vide infra).

Morphology studies have been carried out on both compounds **1** and **3**. X-ray diffraction analysis has been carried out (Cu Kα radiation $\lambda = 0.15406$ nm, between $2\theta = 1.5°$ and 25°) on both materials and is compared in Figure 1 with the result obtained for **2**. From this analysis, it is clear that the same intercalated morphology is obtained for both **1** and **3**, characterized by a main diffraction peak (d_{001}) corresponding to an interlayer distance of 40.2 Å and two registries (d_{002} and d_{003}), with an apparent interlayer distance of respectively 20.1 and 13.4 Å. Compound **2** exhibits only a weak peak corresponding to an interlayer distance of 12.4 Å, assimilated to the interlayer distance of the nonmodified clay.

Both composites have been observed by transmission electron microscopy (TEM) on ultrathin sections (≈80 nm) of the composites. Compound **3** displays an intercalated−exfoliated morphology with a dispersion of small 20-nm-thick stacks (Figure 2a at high magnification and 2b at lower magnification), even if isolated particles are observed to a lesser extent as compared to the nanocomposite directly obtained with the organo-modified clay.[13]

The tensile properties were measured according to ASTM D638 type V norm for soft materials on dumbbell-shaped specimens cut from compression-molded 3-mm-thick plates (Table 1). When the mechanical properties are compared, and especially the Young's modulus, the best value is obtained for nanocomposite **1**, produced using the DMDODA-modified clay. However, compound **3**, produced by the "one-pot process", shows also a relatively high modulus, significantly higher than those observed for the other compounds, that is, the microcomposite **2** and EVA, either alone (**5**) or blended with DMDODABr (**4**), indicating that the observed substantial increase in modulus is not induced by any of the two additives (Na^+ clay or DMDODABr) alone but by their synergistic combination. Similarities between compounds **1** and **3** are also observed for the stress and

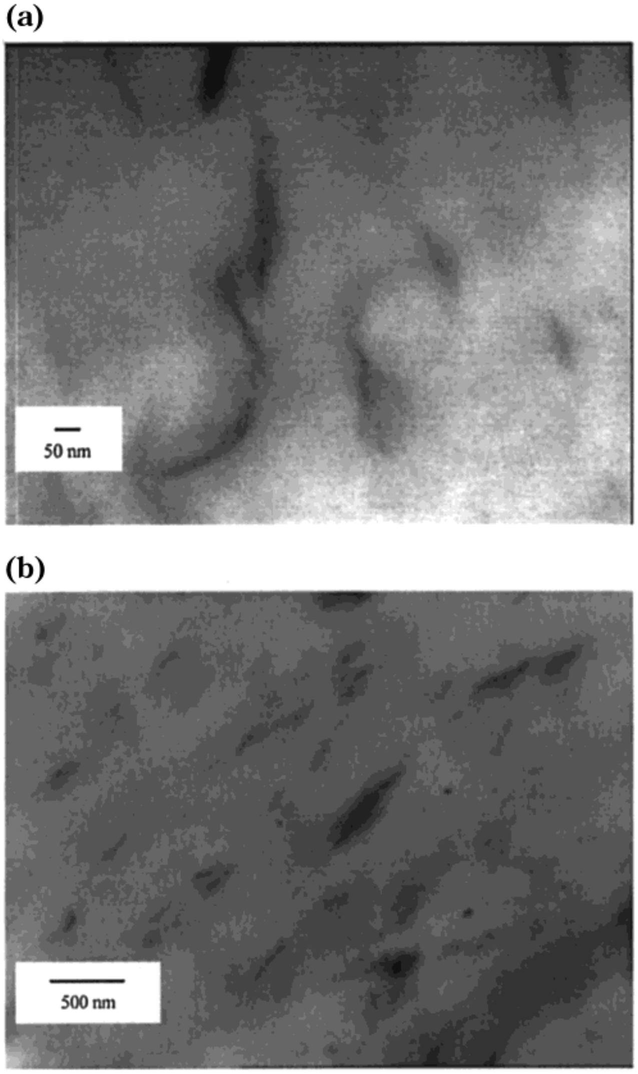

Figure 2. Transmission electron microscopy micrographs of nanocomposite **3** (EVA + DMDODABr + Cloisite Na^+): (a) low magnification; (b) high magnification.

strain at break, significantly different from the other compounds. DMDODABr dispersed alone within the EVA matrix (**4**) appears to be detrimental to the stress at break while the introduction of such a small amount of Cloisite Na^+ alone (**2**) in the EVA matrix does not virtually modify its properties. However, it may be noticed that the elastic modulus for compound **3** is a little bit lower than the value recorded for nanocomposite **1**. This variation in modulus may be explained by the difference in structure observed between the two nanocomposites as the amount of individual clay platelets responsible for the large increase in modulus[1] is smaller in the case of nanocomposite **3**. This behavior might result from a limited diffusion of the ammonium salts within the molten EVA, inducing a modification of the clay interlayer not sufficient to achieve the best clay compatibilization. Indeed, when the process is upscaled using a much more efficient kneader such as a BUSS kneader (throughput = 12 kg/h), the one-pot process has allowed Young's modulus to reach a value almost as high as that recorded for the previously organo-modified clay, that is, 20.5 MPa compared to 21.4 MPa, with 3.0 wt % clay (relative to the inorganic fraction).

Thermal stability under air is another property for which the nanocomposite morphology plays an important role, especially for EVA/clay nanocomposites.[1,14] This behavior has been observed again for the nanocomposites **1** and **3** analyzed by TGA under air flow from 25 to 625 °C at 20 K/min. Indeed, an increase of $\approx$35−40 K is observed during the second weight loss for all nanocomposites compared to the microcomposite **2**, in perfect agreement with the improvement reported for partially intercalated partially exfoliated EVA-based nanocomposites.[1,13]

This study has demonstrated the ability to prepare EVA-based nanocomposites by melt intercalation starting from Na^+ montmorillonite by adding, in a “one-pot” reactive process, a surfactant able to compatibilize the clay platelets with the polymer matrix. Various variables such as the nature of the onium salt, its proportion relative to the clay, the addition order of the components, and the melt-blending processes used will be presented in a forthcoming paper in addition to the use of this “one-pot” technique with other polymer matrixes such as nylons, polyesters, and polyurethanes.

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