Novel Polymer Nanocomposites from Templated Mesostructured Inorganic Materials

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Polymer nanocomposites (PNCs) consist of inorganic particles with nanometric dimensions dispersed in a single phase or a multiphase polymeric matrix. Most of the polymer nanocomposites reported in the literature use nanoclays of sodium montmorillonite class (Na−MMT) that are commercialized in the form of micronic agglomerates of lamellae structured in the form of sandwich-type structure with a thickness of 0.3−1 nm and a length of 50−100 nm for each layer. The dispersion of the nanometric layers in the host polymeric matrix is obtained through two steps: (i) intercalation and (ii) exfoliation. Intercalation (expansion of the interlamellar spacing to up 3−6 nm) is usually obtained via ion exchange using organic amines or quaternary ammonium salts $RNH_3^+Cl^-$. Exfoliation is generally obtained through reactive chemical compounding or by intensive melt mixing MMT with the polymeric matrix. Because of their high aspect ratio (typically >50−100), volume fractions of nanoparticles as small as 2−7 wt % are enough to impart the PNCs with mechanical properties comparable to those obtained upon 30−50 wt % addition of glass fibers, without greatly altering the density and the transparency of the matrix. High barrier, conductive and thermal resistance properties have been reported for PNCs without changing the classical machinery used for thermoplastics.

However, the ultimate properties of such PNCs are restricted by the limited intrinsic properties of clays that are difficult to modify due to the high interaction energy between the individual layers.

We propose here the first completely synthetic nanoparticles made from mesostructured materials (other than clay-based nanocomposites[1−3]). These materials are very known in the catalysis field and are obtained by self-assembly of surfactant molecules that self-organize in supramolecular structures (liquid crystals assembly of cylindrical, spherical, or lamellar micelles) which may act as templates for mesostructured inorganic materials.[4,5] Using this concept, a variety of ordered mesostructured and mesoporous inorganic materials with hexagonal, cubic, and lamellar symmetries[6−12] were obtained. For instance, the family of M41S[10,13] has silica or alumina−silica inorganic phases and cationic surfactants such as CETAC ($C_{16}H_{33}N(CH_3)_3^+Cl^-$). Three types of structures are obtained: hexagonal (MCM-41), cubic (MCM-48), and lamellar (MCM-50). The lamellar structure is the easiest to obtain, and researchers working in the catalysis field tend to avoid this structure due to its collapsing upon calcination and that imparts the material with low surface area. However, in the field of PNCs, such a structure is the most suitable due to its high aspect ratio. In addition, there is no need for the intercalation step since the organic/inorganic hybrid materials are synthesized in a one-step operation that generates well-intercalated nanolamellae.

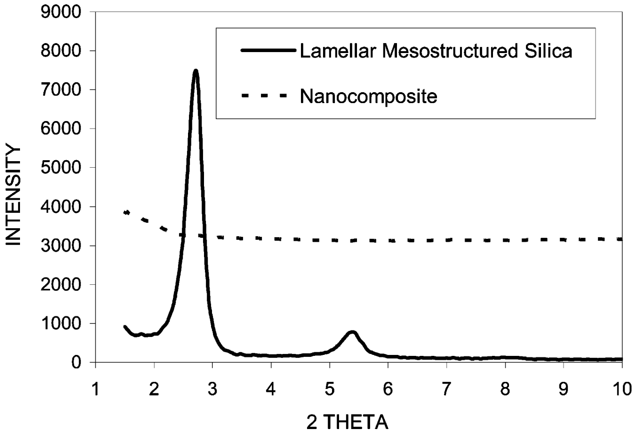

Figure 1. X-ray diffraction patterns of lamellar mesostructured silica and nanocomposite material.

The polymer nanocomposites (PNCs) reported in the present work were prepared by mixing the LMS nanoparticles with polypropylene grafted with maleic anhydride moieties (MODIC-P300F resin, density 0.90 × 10^{-3} kg m^{-3}, melting temperature 161 °C, crystallinity 36%, elongation at break 547%) provided by Mitsubishi Chemical Co., Japan (designated here as PP-*g*-MA).[14] The LMS nanoparticles were synthesized in our laboratory.

As shown in Figure 1, the average interlayer spacing of the (001) (d_{001}) for the LMS nanoparticles obtained by XRD (X-ray diffraction) measurement is about 3.25 nm ($2\theta \sim 2.7°$). For the PNC material, such a peak is not observed (a basal spacing > 8.8 nm would correspond to $2\theta < 1°$), which may imply exfoliation of the lamellae due to shear process and diffusion of polymer chains inside the spacing of the lamellar galleries. The intercalated/exfoliated structure was also confirmed by TEM (transmission electron microscopy) observations. Figure 2 shows the typical structure of the obtained PNC. The nanographs show in fact an intercalated/exfoliated morphology with a clear increase of the gallery spacing of the silica layers compared to the 3.25 nm value of the pure LMS nanophase. As observed by Pinnavaia and Wang[15] for clay nanocomposites, this gallery spacing will be affected by both the nature of the intercalated polymer and the tail length of the surfactant.

Three steps are needed to obtain partial or full exfoliation of the nanoparticles inside the bulk of the polymeric hosting matrix: (i) diffusion of the macromolecular chains inside the relatively open interlamellar galleries (typical spacing of 3−6 nm), (ii) interactions between the nanoparticles surfaces and the diffusing macromolecular chains, and (iii) delamination of the

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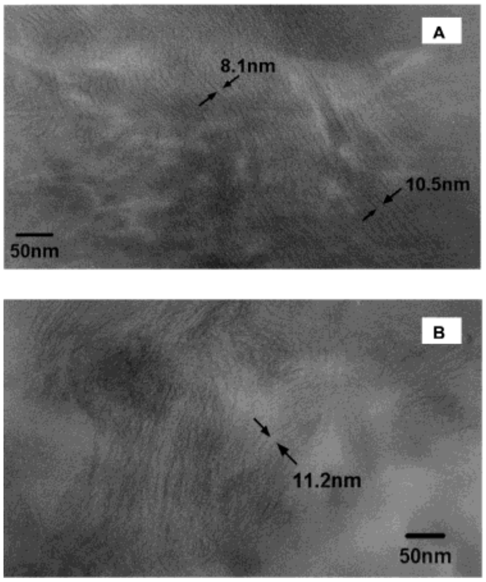

Figure 2. TEM micrographs showing the formation of exfoliated layers of mesostructured silica in a PP-*g*-MA matrix.

nanoparticles layers due to external strong stresses. The most convenient stresses are of shear type (only little is known about elongational or other type of stresses). The diffusion process may take place under quiescent conditions by Brownian motion (partial exfoliation in this case is very long and may take weeks to occur) or preferably under flow conditions where the forced diffusion and the delamination processes occur simultaneously. The term interaction is taken here in the broad sense: it may be physical such as entanglements, chemical such as covalent bonding, or physicochemical such as hydrogen or electrostatic bonding. Entanglements would require a surfactant molecular weight (M) larger than the critical entanglement molecular weight (M_c) of the hosting matrix. Since this is not the case of the surfactant used here as template, favorable interactions between the surfactant tails and the PP macromolecules should be promoted by specific interactions other than entanglements. In our case such specific interactions were obtained through maleic anhydride groups. In fact, LMS nanoparticles blended under the same conditions with pure nongrafted polypropylene (PP) matrix did not show any exfoliation. This is likely due to the absence of interactions between the hydrophobic PP matrix and the hydrophilic surface of the LMS nanoparticles.

The specific interactions may also be induced by any unsaturated carboxylic acids, anhydrides, or esters thereoff or by polymers containing these groups such as maleic acid, methacrylic acid, acrylic acid, ethacrylic acid, fumaric acid, phthalic acid, maleic anhydride, phthalic anhydride, glycidol methacrylate, diethyl maleate, itaconic acid, and alike.

This Communication is a preliminary report of the first synthetic layered nanostructured particles exfoliated in PNC materials. The strategy is obviously not limited to silica particles but may be extended to any of the other nanolamellar materials that have been synthesized by supramolecular assembly. These encompass oxides of transition metals,[6] aluminophosphates,[7] borophosphates,[8] sulfides,[9] etc., which can impart the PNC materials with a whole spectrum of useful properties.

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Supporting Information Available: Full experimental details of the preparation and characterization of lamellar mesostructured silica and nanocomposite material. This material is available free of charge via the Internet at http://pubs.acs.org.

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