Preparation of High Barrier and Exfoliated-Type Nylon-6/Ultrafine Full-Vulcanized Powdered Rubber/Clay Nanocomposites

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In recent years, there has been considerable interest in polymer−clay nanocomposites,[1−8] such as nylon-6,[1,2] polystyrene,[3] epoxy resin,[4] polycaprolactone,[5] polyurethane,[6] poly(ethylene terephathalate),[7] and polyolefin[8] nanocomposites. One of the most successful composite systems is nylon-6/clay nanocomposite based on clay minerals and nylon-6, wherein silicate layers are exfoliated into about 1 nm thick monolayers and homogeneously dispersed in nylon-6 matrix. There are several methods for the preparation of nylon-6/clay nanocomposites. A polymerization method was first reported by a research team from Toyota, in which caprolactam was polymerized in the presence of organophilic montmorillonite.[1] Later, incorporation of organoclays into nylon-6 by the melt compounding process attracted a great deal of industry attention.[2] In these compounding processes, it is necessary to use organoclay to obtain the exfoliated-type nanocomposites. The organo-modification process of silicate layers is complex, which makes the above two compounding methods costly. Therefore, it is of great industrial value to develop a general compounding process for the production of polymer−clay nanocomposites by using unmodified natural clay minerals. Recently, some researchers from Toyota reported that good property nylon-6/clay nanocomposites could be prepared by using Na−montmorillonite slurry without organic treatment by extruder with special structure.[9] In this Communication, we propose a novel and economical approach to form well-exfoliated nylon-6 nanocomposites by using conventional polymer melt compounding process with a new compound powder of ultrafine full-vulcanized powdered rubber/montmorillonite (UFPRM). Noteworthily, Na−montmorillonite silicate layers without organic modification are exfoliated into nylon-6 matrix.

UFPRM consists of natural montmorillonite and ultrafine full-vulcanized powdered rubber (UFPR). UFPR itself can be used as a toughening agent for plastics. UFPR can be prepared by using rubber latex with irradiation sensitives as raw material followed by irradiation cross-linking and drying before obtaining full-vulcanized powdered rubber with basically same sized particles in rubber latex.[10−14] The latex particles in most chosen rubber latexes are 50−150 nm in size, so we call all the full-vulcanized powdered rubber with size much less than micron scale as ultrafine full-vulcanized powdered rubber. It can be inferred from its manufacturing process that the surface part of UFPR has higher cross-linking degree than the interior due to a higher concentration of irradiation sensitives near the surface part as well as more reactions with excited molecules and ions in water produced by the irradiation. Therefore, the reversible agglomeration UFPR not only has good rubber properties but also can be easily dispersed in plastics when blended with plastics.[12] In our previous work, carboxylated styrene−butadiene UFPR was used to toughen nylon-6. It could greatly improve the toughness of nylon-6 and TEM micrographs showed that UFPR particles were well dispersed in the matrix with a diameter of 150 nm.[13] It is well-known that the clay minerals, such as Na−montmorillonite, exfoliate in water to form clay slurry. On the basis of the clay slurry and irradiated rubber latex, we prepared the special compound powder, ultrafine full-vulcanized powdered rubber/montmorillonite (UFPRM). It is expected that UFPR can help clay without surface treatment better exfoliate in the nylon-6 matrix.

Interest in the nylon-6/clay nanocomposites stems from their various superior properties such as high strength, high modulus, high heat distortion temperature, and low gas permeability compared to those of nylon-6 resin.[1] According to Nielsen, filler particles such as platelets, spheres, and cubes can reduce gas permeability of polymer, owing to a very tortuous path for gas molecules traveling through a filled polymer.[15] The nylon-6/clay nanocomposites are those where the layered clay platelets are delaminated and dispersed as single platelets in the nylon-6 matrix. Individual clay platelets have a high aspect ratio, and thus a high barrier effect to gas is obtained. For example, compared with nylon-6, oxygen permeability of nylon-6/clay nanocomposites reduced by 35% and hydrogen permeability decreased by 30%.[9,16] In this work, we have found that nylon-6/UFPRM nanocomposites have superior low gas permeability.

Figure 1 illustrates the scheme for preparation of nylon-6/UFPRM nanocomposites. The preparation of UFPRM is similar to that of UFPR. First, Na−montmorillonite powder was dispersed into water by using an emulsifier for 30 min to prepare clay slurry, and the clay content in the slurry was 2 wt %. The irradiated butadiene styrene vinylpyridine rubber latex (average single latex particle size, ca. 150 nm) was added into the clay slurry at a certain dry weight ratio and stirred for 60 min to form uniform mixture, in which the clay layers and the latex particles were interpenetrated each other. The mixture was then spray-dried to obtain UFPRM. Finally, the nylon-6/UFPRM nanocomposites were compounded with the conventional melt blending method by using a corotating twin-screw extruder.[17] Two samples of nylon-6 nanocomposites, PA-1 and PA-2 (see Table 1), were prepared for further research.

Figure 2A,B shows transmission electron micrographs (TEM) of the uniform mixture (the irradiated butadiene styrene vinylpyridine rubber latex and clay slurry at a dry weight ratio 4/1). The dark lines in the figures correspond to the clay silicate layer with a thickness of 1 nm. It indicates that the silicate layers are exfoliated

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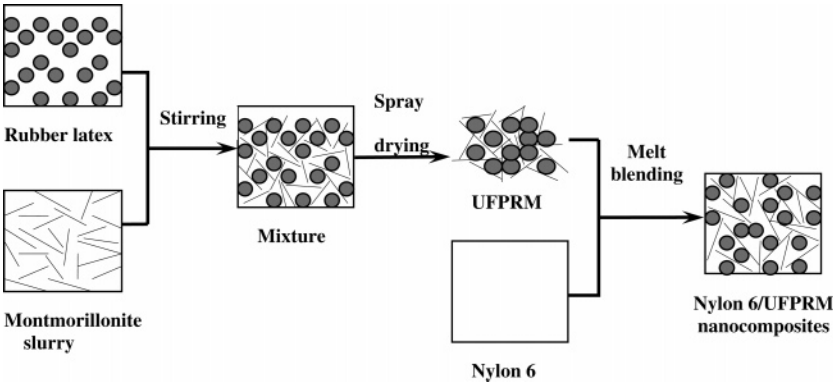

Figure 1. Schematic illustration for the preparation of nylon-6/UFPRM nanocomposites.

Table 1. Composition of Two Samples: PA-1 and PA-2

sample code	composition (wt)		
	nylon-6	UFPR	UFPRM (UFPR/MMT = 4/1, wt/wt)
PA-1	100	15	
PA-2	100		15

into monolayers in the mixture. The black shadow in TEM images can be related to rubber latex particles. Figure 3a,b shows X-ray diffraction (XRD) patterns of Na−montmorillonite and UFPRM powder. The Na−montmorillonite exhibits an apparent peak at $2\theta = 7.1°$ corresponding to the 001 diffraction peak. The interlayer spacing of Na−montmorillonite is 1.25 nm. On the other hand, there is no peak in XRD pattern of the UFPRM. It indicates that the silicate layers of Na−montmorillonite in UFPRM are stacked irregularly. The results show that, owing to the separating effect of rubber latex particles to silicate layers, the dispersed microstructure in the mixture is retained after spray drying. That is to say that the UFPR particles and exfoliated silicate layers interpenetrated each other in UFPRM.

To observe the morphology of nylon-6/UFPRM nanocomposites, OsO_4 was used to stain the ultrathin sections of PA-2 for TEM to differentiate rubber particles from the nylon matrix. As shown in the TEM micrographs of Figure 2C, there are many black particles, i.e., UFPR particles, and a lot of dark lines (clay silicate layers) in PA-2. It is evident that most UFPR particles are well dispersed in the nylon matrix. At the same time, the clay silicate layers are exfoliated into about 1 nm thick monolayers and randomly dispersed in the matrix among the UFPR particles. Moreover, no peak in XRD pattern of the nylon-6/UFPRM nanocomposites (Figure 3C) can be seen. It suggests that the clay silicate layers are exfoliated in nylon matrix, which agrees well with that of TEM observation. According to the TEM and XRD results, it is believed that the exfoliated silicate layers in UFPRM do not aggregate in nylon-6, possibly due to the separating effect of UFPR to silicate layers in UFPRM. Therefore, with the help of UFPR, the silicate layers are successfully exfoliated in the nylon-6 matrix, whereas without UFPR, the clay without organic treatment cannot be delaminated.

The nitrogen permeability coefficient (P_g) of nylon-6 and its nanocomposites was tested according to the GB/T 1038-2000 method.[18] The data are listed in Table 2. P_g of PA-1 is only 1/5 that of pure nylon-6. It indicates that UFPR can reduce gas permeability of nylon-6. Interestingly, P_g of PA-2 becomes 1/26 that of nylon-6. As mentioned above, both UFPR and clay platelets exhibit barrier effect to gas. It is evident that the sample modified with UFPRM which contains UFPR and mont-

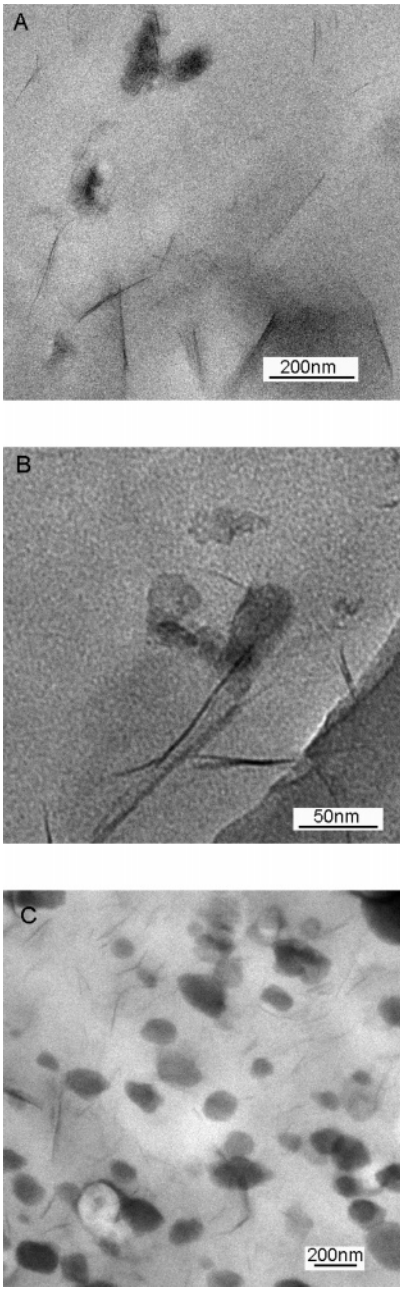

Figure 2. TEM image of (A, B) the mixture (the irradiated butadiene styrene vinylpyridine rubber latex and clay slurry at a dry weight ratio 4/1) and (C) PA-2 (nylon-6/UFPRM, 100/15, wt).

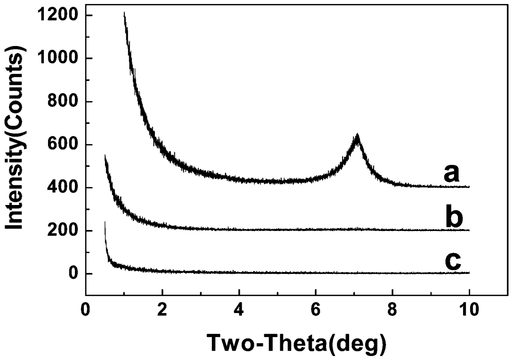

Figure 3. X-ray diffraction patterns of (a) Na−montmorillonite powder, (b) the UFPRM powder, and (c) PA-2 (nylon-6/UFPRM, 100/15, wt).

Table 2. Nitrogen Permeability Coefficient (P_g) of Nylon-6 and Nylon-6 Nanocomposites

sample code	composition: nylon-6/UFPR/MMT	nitrogen permeability coeff P_g [10^{-15} cm^3 cm/ (cm^2 s Pa)]
nylon-6	100/0/0	17
PA-1	100/15/0	3.6
PA-2	100/12/3	0.66

morillonite shows much lower gas permeability than single UFPR component does at the same loading content, i.e., a synergistic barrier effect to gas. Therefore, UFPRM is very effective in further increasing barrier effect of nylon-6. The reason for the synergistic barrier effect of nylon-6/UFPRM nanocomposites to gas needs to be further studied.

In summary, we have demonstrated a facile route for the preparation of exfoliated-type nylon-6/UFPRM nanocomposites by using a novel compound powder, UFPRM. The clay layers of Na−montmorillonite without any organic treatment are exfoliated in nylon-6 with the help of UFPR. In addition, we have found that nylon-6/UFPRM nanocomposites have excellent barrier effect to gas, which provides us a new idea to prepare polymer material with superior low gas permeability.

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(17) PA-1 and PA-2 were compounded according to the following process: nylon-6, UFPRM (or UFPR), and Irganox 1010 were mixed uniformly in a high-speed mixer at a certain weight ratio. And then the mixture was fed into a corotating twin-screw extruder (ZSK-25, Werner and Pleiderer, $L/D = 30$) at a barrel temperature of 230−240°C, a screw speed of 300 rpm, and a feed rate of 10 kg/h. In addition, 0.3 wt % Irganox 1010 was added as stabilizer. Prior to mixing, nylon-6 was dried at 100 °C for 6 h in an air oven.

(18) The films for nitrogen permeability coefficient (P_g) test were prepared by using a compression molding machine (T-3S, Toho Int., Inc.). The materials (nylon-6 or nylon-6 nanocomposites) were first preheated at 235 °C for 7 min, then molded at 235 °C under a pressure of 1.5 MPa for 2 min, and finally cold molded at 30 °C under 2 MPa for 10 min to form 90 μm thick test films. Prior to molding, nylon-6 (or nylon-6 nanocomposites) was dried at 100 °C for 6 h in an air oven.

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