Preparation of Nanocomposites by Exfoliation of ZnAl Layered Double Hydroxides in Nonpolar LLDPE Solution

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In recent years, the exfoliation of layered materials has been extensively used in preparing polymer/inorganic nanocomposites. These layered materials involved in this field include silicate clay minerals,[1] manganese oxides,[2] molybdenum sulfide,[3] titanates,[4] layered phosphates,[5] and layered double hydroxides (LDHs).[6] Up to now, however, previous studies on the layered materials have been mainly focused on the layered silicates and the polymer/layered silicates exfoliated nanocomposites[1,7−9] because of the relatively low layer charge density and the easy exfoliation of montmorillonite-type layered silicate compounds. On the other hand, there are only a few reports on the exfoliation of LDHs and the polymer/LDHs exfoliated nanocomposites. Forano and co-workers[10] used a two-step method to exfoliate 1.5 g of ZnAl LDH per liter by exchanging with dodecyl sulfate anions and then refluxing in butanol. Hibino and Jones[11] have exfoliated 3.5 g of LDH per liter by intercalation of glycine into a MgAl LDH and reflux in formamide. O'Hare et al.[12] delaminated 10 wt % LDH by mixing $Mg_2Al(OH)_6(C_{12}H_{25}SO_4)$ with polar acrylate monomers under high shearing, and the subsequent polymerization of monomers in the dispersion systems, resulting in polyacrylate/MgAl LDH exfoliated nanocomposites. All the above three exfoliations of LDHs took place in polar systems, which limits the application of LDHs in preparing polymer/LDH exfoliated nanocomposites. Therefore, the studies of the exfoliation of LDHs in nonpolar solutions of polymers and the preparation of polymer/LDH exfoliated nanocomposites with high LDHs loading are of great significance. In our recent work, $Mg_3Al(OH)_8(C_{12}H_{25}SO_4)$ was exfoliated in a xylene solution of polyethylene grafted with maleic anhydride (PE-*g*-MA) and obtained the PE-*g*-MA/MgAl LDH exfoliated nanocomposites containing up to 5 wt % $Mg_3Al(OH)_8(C_{12}H_{25}SO_4)$ with enhanced thermal and flame-retardant properties.[13] In this communication, we report the exfoliation of $Zn_3Al(OH)_8(C_{12}H_{25}SO_4)$ [named $Zn_3Al(DS)$] in a nonpolar xylene solution of linear low-density polyethylene (LLDPE) without modification and the synthesis of LLDPE/ZnAl LDH exfoliated nanocomposites containing up to 20 wt % $Zn_3Al(DS)$.

The $Zn_3Al(DS)$ was synthesized by a spontaneous self-assembly method according to the literature.[14] The pH value of 30 mL of aqueous solution containing $Zn(NO_3)_2$ (0.03 mol), $Al(NO_3)_3$ (0.01 mol), and $C_{12}H_{25}SO_4Na$ (3.0 g) was adjusted to about pH = 10 with 1 mol/L NaOH aqueous solution. The obtained slurry was aged for 3 days at 80 °C, then filtered, and washed by distilled water. A white $Zn_3Al(DS)$ powder was obtained by drying at 60 °C in an oven. The LLDPE/ZnAl LDH exfoliated nanocomposites were obtained by refluxing the above $Zn_3Al(DS)$ powder in 50 mL of xylene solutions of desired amount of LLDPE with stirring under a N_2 atmosphere for 24 h. Then the mixture was poured into 50 mL of ethanol. The precipitate was filtered, washed by ethanol, and dried at 120 °C under vacuum for 12 h. The compositions and structural features of the related nanocomposite samples in this study are summarized in Table 1.

The X-ray diffraction (XRD) patterns of $Zn_3Al(DS)$ and LLDPE/ZnAl LDH composites are shown in Figure 1 in the range of $2\theta = 1.5-10°$. These diffraction patterns reveal the structural changes of the samples with different loadings of $Zn_3Al(DS)$. The basal spacing of the original $Zn_3Al(DS)$ powder sample (Figure 1a) is measured to be 2.55 nm from the (003) diffraction peak at $2\theta = 3.46°$. The (003) diffraction peak of the $Zn_3Al(DS)$ component of the S95 sample (Figure 1b) has shifted to $2\theta = 3.60°$, corresponding to a reduced basal spacing of 2.45 nm after refluxing in the xylene solution of LLDPE, which can be due to the loss of water harbored in the galleries of $Zn_3Al(DS)$. These results suggest that the LLDPE chains were not intercalated into the galleries of $Zn_3Al(DS)$ in the S95 sample. However, the LLDPE chains in the S50 sample have been intercalated into the galleries of $Zn_3Al(DS)$ with the expansion of basal spacing to about 3.5 nm determined from the peak at $2\theta = 2.5°$ (Figure 1c). This very broad and weak diffraction peak indicates that the $Zn_3Al(DS)$ layers are partially exfoliated in 50 wt % LLDPE matrix. The (003) diffraction peak of the $Zn_3Al(DS)$ component in NC20 (Figure 1d) and NC2 (Figure 1e) samples completely disappeared when the LLDPE component in the xylene solution increased to above 80 wt % of the total amount of LLDPE and $Zn_3Al(DS)$. The diffraction peak at about 9.5° for NC2 in Figure 1e is caused by the crystals of pure LLDPE, which is shown more clearly in Figure 2a. Figure 2 shows the XRD patterns of pure LLDPE and NC20 in the range of $2\theta = 8-70°$. In comparison with

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Table 1. Compositions and Structural Features of the Related Nanocomposite Samples

sample code	loading of $Zn_3Al(DS)$ in composite (wt %)	composition in xylene solution LLDPE (g)	composition in xylene solution $Zn_3Al(DS)$ (g)	structure of LDH determined from XRD pattern
S95	95	0.05	0.95	DS intercalated
S50	50	0.20	0.20	LLDPE intercalated and partially exfoliated
NC20	20	0.80	0.20	exfoliated
NC10	10	1.80	0.20	exfoliated
NC5	5	1.90	0.10	exfoliated
NC2	2	2.45	0.05	exfoliated

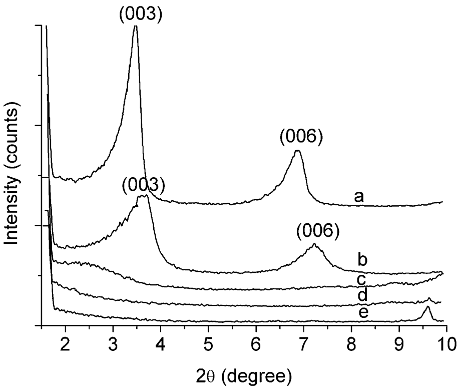

Figure 1. X-ray diffraction patterns of (a) $Zn_3Al(DS)$, (b) S95, (c) S50, (d) NC20, and (e) NC2 in the range of $2\theta = 1.5-10°$.

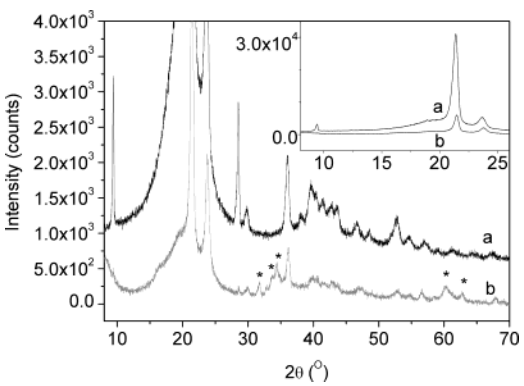

Figure 2. X-ray diffraction patterns of (a) LLDPE and (b) NC20 in the range of $2\theta = 8-70°$.

patterns of LLDPE, there are some additional peaks for NC20 marked by an asterisk (*) in Figure 2b, which are due to the existence of $Zn_3Al(NO_3)$.[6,15] Nevertheless, taking the intensity of these peaks into account, the amount of $Zn_3Al(NO_3)$ is so tiny that its effect on the exfoliation process can be neglected. These results obtained from the NC20 to the NC2 samples show that the $Zn_3Al(DS)$ layers have been completely exfoliated in the LLDPE matrix and the parent nonpolar xylene solution of LLDPE after refluxing. The obtained LLDPE/ZnAl LDH exfoliated nanocomposites with the different loadings of $Zn_3Al(DS)$ from 2 wt % up to 20 wt % are listed in Table 1.

The transmission electron microscopy (TEM) image of a S50 sample is shown in Figure 3. The intercalated structure of $Zn_3Al(DS)$ component is obviously observed from Figure 3a, in which about 20−40 layers of $Zn_3Al(DS)$ are stacked with a distance of 3.5−4.0 nm. The stacking distance is much larger than the original 2.54-nm basal spacing of $Zn_3Al(DS)$, which gives positive evidence that the LLDPE chains have been intercalated into the interlayers of $Zn_3Al(DS)$ during refluxing in the nonpolar xylene solution. In addition to the intercalated structure, some exfoliated layers of $Zn_3Al(DS)$ are also observed in the S50 sample. The disconnected dark lines in Figure 3a indicate that the layers of $Zn_3Al(DS)$ might be broken into small parts while they were exfoliated. It can be seen that the two exfoliated layers parallel to the section surface are sandwiched between two individual layers vertical to the section surface, which is marked with the circle in Figure 3a. Figure 3b illustrates the forming process of this sandwiched structure. The middle $Zn_3Al(DS)$ layer of the three layers might rotate and thus be broken into two parts during the exfoliation process caused by the intercalation of LLDPE chains when refluxing $Zn_3Al(DS)$ in the xylene solution of LLDPE.

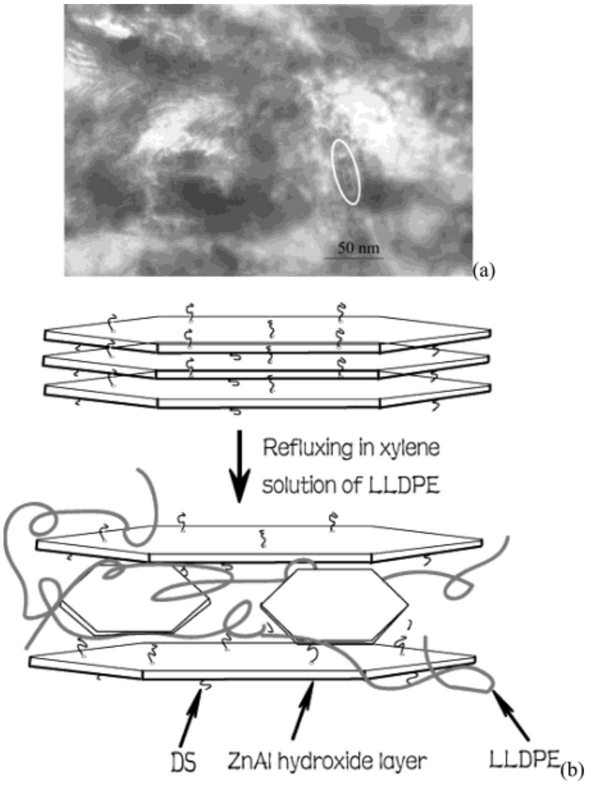

Figure 3. (a) TEM image of S50 sample and (b) the formation process of the sandwiched structure as shown in the circle in Figure 3a.

Figure 4 presents the TEM image of NC20 sample. No intercalated structures of $Zn_3Al(DS)$ component are observed directly from the TEM image. The exfoliated ZnAl hydroxide sheets combined with DS anions are dispersed in a disordered fashion in the LLDPE matrix. The position pointed by an arrow in Figure 4 shows an individual ZnAl hydroxide layer nearly vertical to the section surface of the TEM specimen. Most of the exfoliated ZnAl hydroxide nanolayers are tilted at some large angle with respect to the section surface. These results give positive evidence that the exfoliated ZnAl hydroxide layers are molecularly dispersed in the LLDPE matrix with a high loading of 20 wt % $Zn_3Al(DS)$ in the NC20 sample. The thickness and width/length

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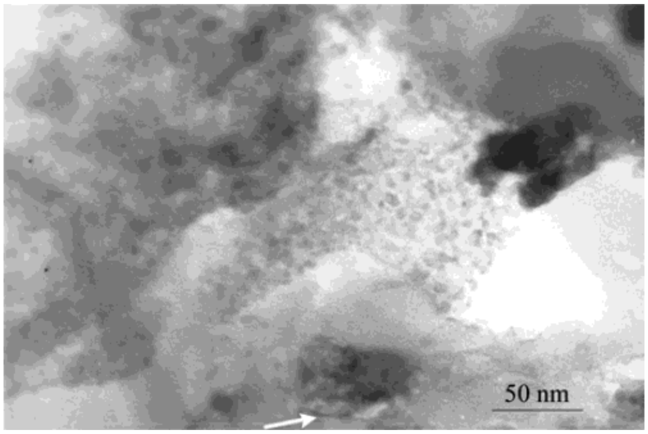

Figure 4. TEM image of NC20 sample.

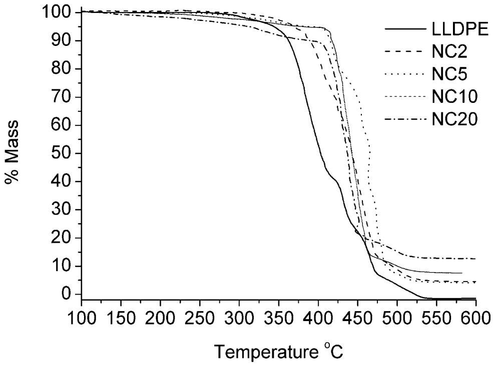

Figure 5. Thermogravimetric curves of LLDPE and LLDPE/ZnAl LDH exfoliated nanocomposites under air flow.

of the individual exfoliated $Zn_3Al(DS)$ layers (combined with DS ions) are determined to be 1.5−2.5 and 15−20 nm, respectively.

The thermogravimetric curves of pure LLDPE and the four LLDPE/ZnAl LDH exfoliated nanocomposite samples are shown in Figure 5. The degradation rate for pure LLDPE becomes very quick after 350 °C, while all the LLDPE/ZnAl LDH exfoliated nanocomposites show much slower degradation rates before 400 °C. There is around 10% weight loss with each LLDPE/ZnAl LDH exfoliated nanocomposite in the temperature range from 200 to 400 °C due to the dehydration of ZnAl hydroxide sheets, thermal degradation of DS alkyl chains, and the volatilization of thermo-oxidative product of LLDPE. It has been found that an efficient charring process in flame retardant polymeric materials must occur at a temperature higher than the processing temperature of polymer but much lower than the decomposition temperature of polymer.[16] Therefore, this kind of weight loss at the first step of decomposition is highly advantageous for promoting the charring process and enhancing the fire safety of nanocomposites. When 30% weight loss was selected as a point of comparison, the thermal decomposition temperatures for pure LLDPE, NC2, NC5, NC10, and NC20 samples are determined as 384, 421, 449, 432, and 426 °C, respectively. Although the above thermal decomposition temperatures of NC10 and NC20 samples are lower than that of the NC5 sample, they are more stable than the NC5 sample above 475 °C. The pure LLDPE has almost no residues above 530 °C, whereas the corresponding residue amounts of NC2, NC5, NC10, and NC20 samples are about 5%, 5%, 8%, and 13%, respectively, and are kept stable until 600 °C. It is worth noting that the char residues of NC2 sample are almost the same as that of NC5 sample at 600 °C, which means that even a very small amount of ZnAl layered double hydroxides can promote the charring process during the degradation process of LLDPE. The enhanced thermal stability of exfoliated nanocomposites can be attributed to the molecular dispersion of ZnAl hydroxide nanolayers in the LLDPE matrix and the promoting formation of charred layers in the first decomposition step.

On the basis of the above data analysis, it can be concluded that the LLDPE/ZnAl LDH exfoliated nanocomposites can be prepared by refluxing in a nonpolar xylene solution of LLDPE. This exfoliation method is promising for the preparation of other polymer/LDH nanocomposites, such as polypropylene, polystyrene, poly(1,3-diene) rubbers, and those polymers with polar groups.

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