Atomic Force Microscopy Analysis of Morphology of Low Density Polyethylene Influenced by Al Nano- and Microparticles

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ABSTRACT: Spherulites are important morphological forms in semicrystalline polymers. Polarized optical microscope (POM) is a powerful tool for observing the spherulite morphology of semicrystalline polymers and their composites, but it can not resolve spherulites with average size smaller than 5 μm and also not be used to study the opaque nanocomposites film samples. Atomic force microscopy (AFM) is an excellent tool for observing spherulites comparatively small in size and not restricted by the transparency of the samples. In this work, AFM was used to investigate the impact of Al nano- and microparticles on spherulitic textures, lamellar thickness, and thickness distribution of low density polyethylene (LDPE). It was found that the spherulitic texture was seriously disordered by the nanoparticles, and that the LDPE in nanocomposites was found only to have poorly developed spherulite structure. The incorporation of microparticles can facilitate the growth of the lamellae but decrease the size of the spherulites. Furthermore, the lamellar thickness and its distribution did not alter so much with the addition of nano- and microparticles. Wide-angle X-ray diffraction (WXRD) was used to determine the crystal structure of LDPE, and the results show that both Al nanoparticles and microparticles do not change the unit cell parameters. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2494–2499, 2008

Key words: polyethylene (PE); Al nanoparticles; morphology; nanocomposites; thermal properties

INTRODUCTION

Semicrystalline polymers such as polyethylene consist of spherulites surrounded by amorphous regions.[1] The spherulite morphology can significantly influence the mechanical,[2] thermal,[3] electrical,[4] and optical properties of the polymers. The incorporation of fillers can result in the changes of degree of crystallinity,[5] rate of crystallization,[6] lamellar thickness, and its distribution,[7] melting and crystallization temperature,[8] supermolecular structure and crystalline phases,[9] modifying the macroscopic properties of the polymers mentioned above. The spherulitic nature (the folded chain crystallite lamellae and the interlamellar amorphous regions tying the lamellae together in a polymer bulk, the typical spherulites are 10^{-5} m in diameter, the lateral dimensions of a lamella are of the order of $10–20^{-6}$ m with a thickness of only 10×10^{-9} m) indicates that the fillers with different sizes (nanoscale and microscale) may have different effects on the crystalline structure of polyethylene.[10] In our previous work,[6] nonisothermal crystallization and melting behavior of low density polyethylene (LDPE) and LDPE/Al nano- and microcomposites were studied by differential scanning calorimetry (DSC). The DSC results show that the Al nanoparticles can either facilitate or hinder the crystallization of LDPE, depending on the dispersion of the nanoparticles in LDPE. The well-dispersed Al nanoparticles have been observed not to have any nucleating effects and to act mainly as obstacles in the crystallization process, whereas the agglomerates of Al nanoparticles have been found to act as nucleating agents and slightly accelerate the crystallization process of LDPE. The Al microparticles have nucleating effects and facilitate the crystallization process of LDPE. The spherulite morphology, however, can not be visualized by a polarized optical microscope because of the small size.

For polyethylene, the origin and the observation of spherulites are largely determined by catalyst, nucleation, crystallization process, and molecular weight of polymer, any of which can produce a dominant effect.[11] The information of spherulite morphology and crystallization process could be obtained by cycling experiments in an optical microscope with crossed polarizers. The average spherulite size of some LDPE, however, is too small to resolve. On the other hand, some nanocomposites filled with metal nanoparticles are opaque because of the unique

optical properties of metal nanoparticles, the film samples of these kinds of nanocomposites cannot be studied by a polarized optical microscope. Atomic force microcopy (AFM) is an effective and reliable method for visualization of the spherulite morphology of PE with a high resolution. Furthermore, AFM can present surface structures in the real space and the samples do not require such special treatments as transmission electron microscopy does.

This article discussed the influence of nano- and microparticles on the spherulite morphology of LDPE, lamellar thickness and its distribution of the spherulites. For this purpose, LDPE/Al nanocomposites and microcomposites were prepared by melting compounding. The crystal structure and degree of crystallinity were investigated by wide-angle X-ray diffraction (WXRD) and DSC, respectively. Atomic force microscopy (AFM) was used to observe the effects of Al nano- and microparticles on spherulitic texture of LDPE and lamellar thickness.

EXPERIMENTAL

Materials

The polyethylene (DJ200) with melt index 2.1 g/10 min and density 0.920 g cm^{-3} used is LDPE purchased from Shanghai Petrochemical (China). The LDPE was dried in vacuum oven for 8 h at 80°C before using.

The Al nanoparticles with the average diameter of 50 nm characterized with transmission electron microscopy were supplied by Shandong Origine Nanomaterial Engineering (China), and the Al microparticles with average diameter 5 μm were supplied by Jilin Petrochemical (China). Both the nanoscale and microscale particles were not subjected to any treatment before use.

Preparation of LDPE/Al nanocomposites

Both the microcompsites and nanocomposites were prepared by melting compounding of LDPE and 8.0 wt % Al particles using Haake Rheometer RC90 at the temperature of 130°C and the rotor speed of 60 rpm for 15 min. For the sake of convenience, the polymer composites were denoted using the following notation: particle scale-particle weight, thus N-8.0 and M-8.0 indicate the polymer composites with Al nano- and microparticles of 8.0 wt %, respectively.

Characterization

AFM

AFM images were obtained in ambient conditions using a Multimode Nanoscope IIIa (Digital Instrument, USA). The surface morphology observations were conducted in the tapping mode with an E scanner. Both height and phase images were collected and all the scans were carried out with a scan frequency below 1.5 Hz in air. The samples for AFM observations are films of the order of 500 μm in thickness. Preparation of the samples was conducted as follows: a film was placed on a clean glass wafer, the sample was first heated to 160°C using a Linkam-TMS94 thermal stage and held 10 min without pressure and then slowly cooled (1°C/min) down to the room temperature.

WXRD

WXRD patterns were recorded on a Rigaku D/MAX-2200/PC automatic diffractometer, all measurements were performed at the atmospheric pressure and room temperature with nickel-filtered Cu target Kα radiation at 40 kV and 20 mA with a scintillation counter system. The data was collected at a scanning rate of 6°/min with a step size of 0.02°. For the Al particles, the data were recorded by scanning the surface of the coating specimen after mechanical grinding. In the case of LDPE/Al composites, the samples were films of about 200 μm in thickness and the data was collected by scanning the top surfaces of the corresponding films.

DSC

The melting behavior was analyzed using a Perkin–Elmer Pyris-1 DSC. All the samples were accurately weighted (≈5.0 mg) and had the same shape and size - a circular film with the same diameter as the sample pan. The as-prepared samples were used to investigate the melting behavior: the samples were heated from 20 to 160°C at a heating rate of 20°C/min. The endothermic curves were recorded as a function of temperature. All DSC measurements were performed under N$_2$ atmosphere and the instrument was calibrated with an Indium standard.

RESULTS

Spherulite morphology

Spherulitic textures can provide the qualitative information pertinent to the average size of lamellar aggregates and the location of uncrystallized material.[9,12] Figure 1 presents the AFM images of the neat LDPE, the LDPE/Al nanocomposites and the LDPE/Al microcomposites. It can be seen that the neat LDPE exhibits the clear spherulitic texture [Fig. 1(a)], the diameter of the spherulites is found to be about 5 μ. According to the AFM images, it is easy to differentiate the growing front and interspherulitic boundaries, and the curved lamellae and lamellar bundles
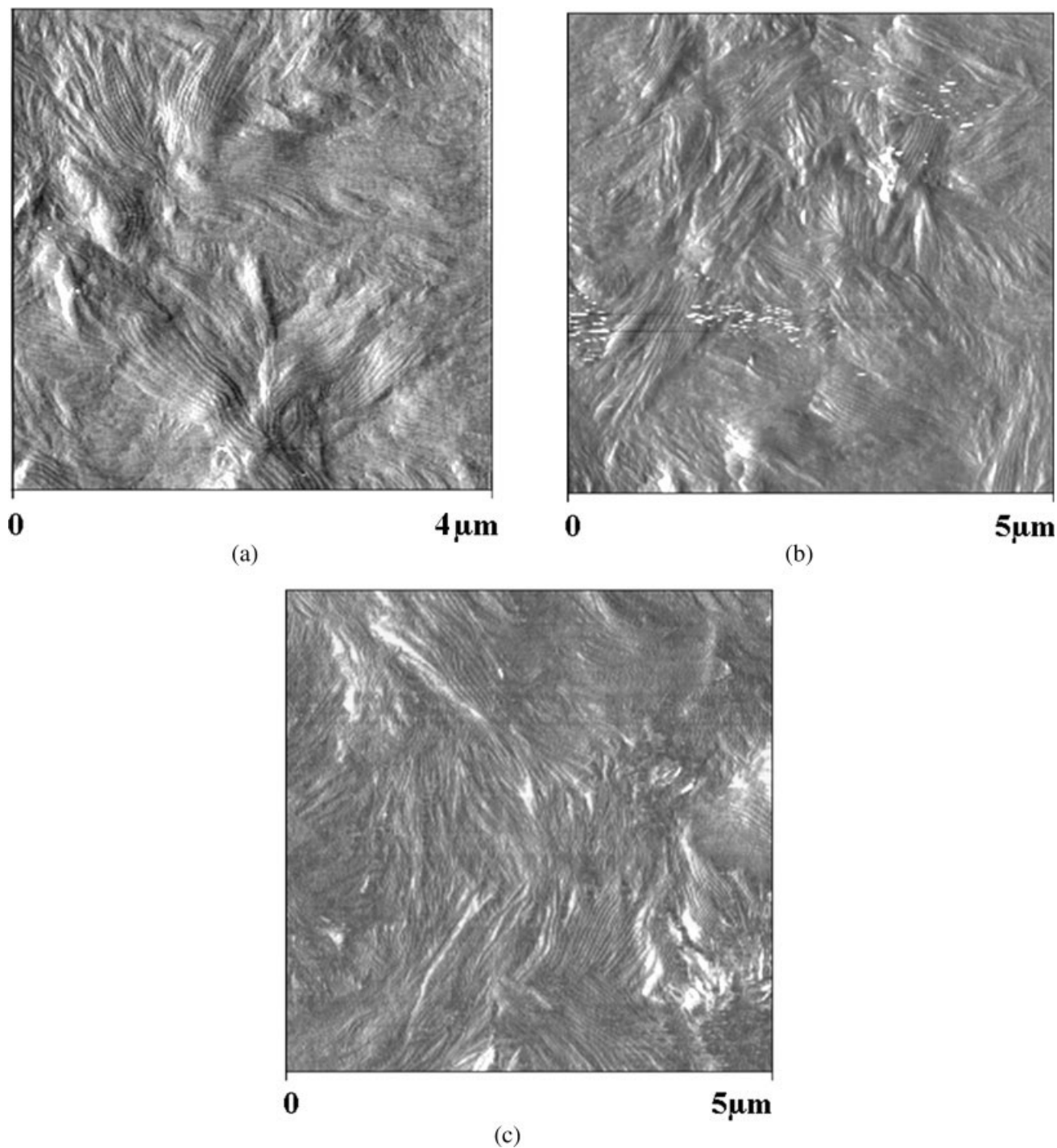
Figure 1 AFM tapping mode phase images: (a) neat LDPE, (b) LDPE/Al nanocomposites with an Al content of 8.0%, and (c) LDPE/Al microcomposites with an Al content of 8.0%.

can also be clearly observed. Nanocomposites exhibit coarser spherulitic textures [Fig. 1(b)], the lamellar bundles are arranged in a disordered way and it is difficult to resolve the individual spherulites. The image of the microcomposite [Fig. 1(c)] appears much finer in comparison with the nanocomposite, however it is also difficult to resolve the individual spherulites. Most of the lamellae shown in Figure 1 are

part of the spherulites growing outward from underneath of the observed surface, with the lamellae surface oriented vertically to the substrate surface.[9]

The spherulitic texture of LDPE is determined from the size of fillers and their dispersion state. In the case of the nanoparticles in small size, the individual particles can not nucleate,[6,8,13] on the contrary, they can hinder the movement of the chain
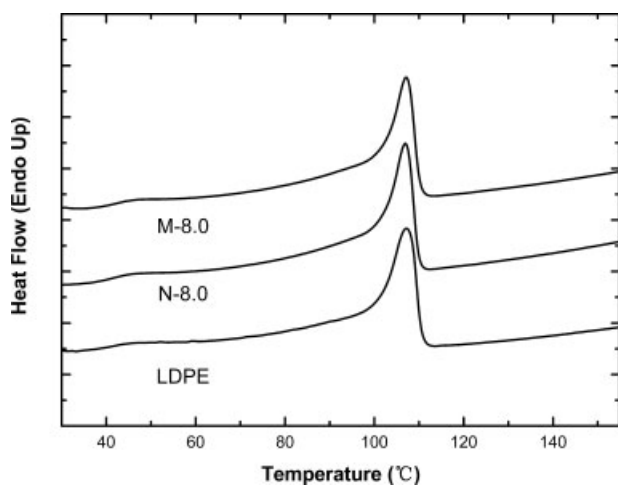
Figure 2 DSC melting curves for neat LDPE and LDPE/Al composites with 20°C/min.

segments of LDPE, and furthermore, the larger nanoparticle agglomerates can disrupt the spherulitic organization. Therefore, it is not strange to find poorly developed spherulites in nanocomposites. For the microcomposites, the growth of spherulites would be hindered and the spherulitic organization could be disrupted because the sizes of microparticles are comparable with the spherulite size of LDPE. The Al microparticles, however, can nucleate and facilitate the growth of the lamellae.[14] Therefore, the nanocomposites show a coarser spherulite texture in comparison to the neat LDPE, which exhibits the clear growing front and interspherulitic boundaries, the microcomposites show a finer spherulite texture than the nanocomposites.

Lamellar thickness

Lamellar thickness and its distribution can be helpful to account for the thermal, mechanical and electrical properties possessed by a specific polymer, and they are also affected by the chemical and crystallization processes of the polymer itself.[3] For a polymer nanocomposite, nanoparticles can reside in the interlamellar regions, which are tens of nanometers in size, aggregate into larger interfibrillar regions, or be excluded into an interspherulitic region of several microns in size in the crystallization process.[12,15] Therefore, it is important to evaluate the influences of nanoparticles on the lamellar thickness and its distribution of polymers. Because of its simplicity and rapidity, the DSC approach has been used as the principal route to obtain lamellar thickness and its distribution.[3] Gibbs-Thomson equation can be used to connect the melting temperature of a crystalline lamella, T_m, with the crystalline lamellar thickness, L. The Gibbs-Thomson equation is expressed as:

$$T_m = T_m^0\left(1 - \frac{2\sigma_e}{\Delta H_f L}\right) \qquad (1)$$

where $T_m^0 = 145.5°C$ is the equilibrium melting temperature of the crystalline lamella of infinite thickness; $\sigma_e = 90$ mJ m^{-2} is the basal surface energy of the crystalline lamella; $\Delta H_f = 290$ J cm^{-3} is the enthalpy of fusion for the crystalline phase.[3] This equation is only suitable to lamellae whose lateral dimensions are much larger than their thickness, while the crystallization behavior of polyethylene just fit in. The melting curves of the LDPE/Al nanocomposites at a heating rate of 20 °C/min are presented in Figure 2. The values of melting peak temperature T_m (Table I) and the final melting temperatures T_{mf} of all the samples are similar with one another, respectively, and the width of the melting peaks is almost the same, suggesting that the lamellar thickness distribution is not so considerably changed in comparison to LDPE. According to the Gibbs-Thomson equation, the lamellar thickness for all samples ranges from 18 to 25 nm, which is consistent with the direct AFM observation (Fig. 3). The above results produce a reasonable conclusion that both the nanoparticles and microparticles do not significantly affect the chain folding, which determines the lamellar thickness, and this conclusion is consistent with other studies. Ma et al. reported that the introduction of TiO_2 nanoparticles do not affect the average lamellar thickness of LDPE.[9] It was also found that the lamellar thickness of Nylon 6 is relatively independent of the presence of montmorillonite layers.[16]

Degree of crystallinity

On the basis of DSC melting curves (Fig. 2), the degree of crystallinity X_c can be determined with the following equation:

$$X_c^{DSC} = \frac{\Delta H_f}{\Delta H_m(1 - \phi)} \qquad (2)$$

where ΔH_f is the heat of fusion obtained from integrating the area under the normalized melting curves and ΔH_m is the enthalpy corresponding to the melting of a 100% crystalline sample and $\Delta H_m = 293$ J/g for PE. ϕ is the weight fraction of the particles in the composites. The calculated average degree of crystallinity based on the DSC thermograms (Fig. 2)

TABLE I
Degree of Crystallinity and Melting Temperature of LDPE and LDPE/Al Composites

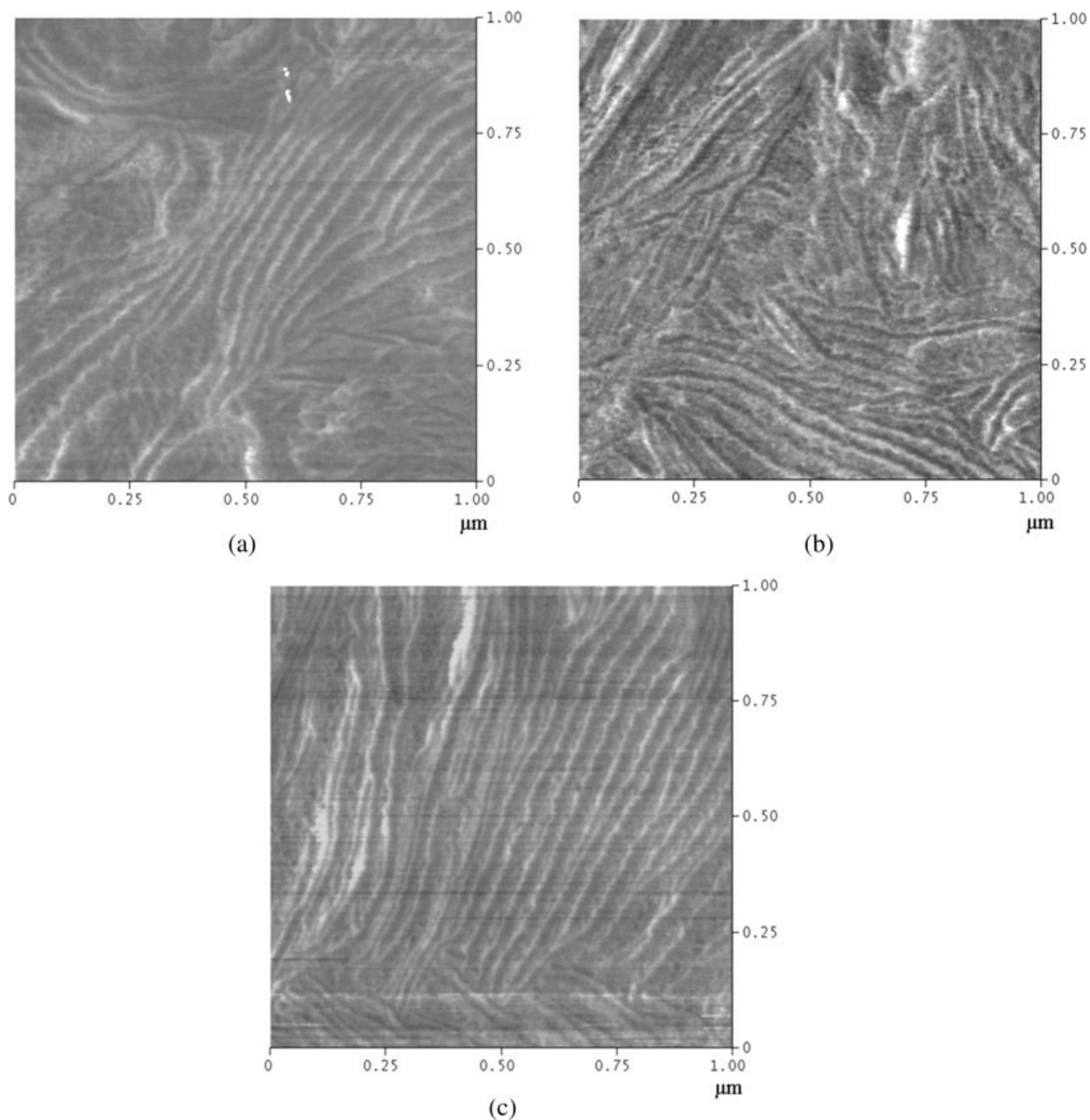| Sample	T_m (°C)	T_{mf} (°C)	X_c^{DSC} (%)
LDPE	107.2	110.6	28.9
N-8.0	107.2	110.2	27.6
M-8.0	106.9	109.8	30.9

Figure 3 AFM phase images showing lamellae in (a) neat LDPE, (b) LDPE/Al nanocomposites with an Al content of 8.0%, and (c) LDPE/Al microcomposites with an Al content of 8.0%.

for all samples ranges from 27.2 to 30.9%. Though the difference is not significant, it is easy to evaluate the effects of the particles in different sizes on the crystallization of LDPE. The nanoparticles hinder the crystallization of LDPE, whereas the microparticles have a positive effect on the crystallization of LDPE. Based on recent researches,[17] the nucleating and ordering effects of the fillers on polyethylene crystallization depend to a large extent on the nanostructure of its surface, in particular on the size of the atomically flat domains; small nanoparticles (below

100 nm) do not have any nucleating effect, moreover they act as obstacles for crystallization on polyethylene. Although the nanoparticle agglomerates may nucleate, the overall influence of the nanoparticles on the crystallization of LDPE can be considered to be the retardant effect, therefore, the degree of crystallinity of LDPE in nanocomposites is lower than that of the neat LDPE. The microparticles can nucleate because they can provide sufficiently large flat domains,[14,17] whereas the size of microparticles is comparable to the spherulite size of LDPE and thus

also hinder the spherulite growing, the degree of crystallinity of LDPE in microcomposites is not significantly larger than that of the neat LDPE.

Crystal structure and unit cell parameters

The WXRD patterns of neat LDPE, LDPE/Al nanocomposites and microcomposites are presented in Figure 4. All the samples show two distinct (110) and (200) reflection peaks related to the orthorhombic crystal structure of polyethylene. The amorphous peaks exhibit a broad halo and appear under the strong and sharp diffraction patterns. Very interesting is that the strength of amorphous halo of LDPE in microcomposites is weaker than that in the neat LDPE and the nanocomposites, suggesting that the size of the particles incorporated plays an important role in determining the crystal structure of LDPE. The microparticles can nucleate in the crystallization process of LDPE and increase the number of spherulites. The nanoparticle agglomerates may nucleate, therefore, the strength of amorphous halo of LDPE in nanocomposites decreases slightly with the increasing content of nanoparticles. The unit cell parameters and full width at half maximum (FWHM) are tabulated in Table II. The crystalline peaks of (110), (200) and (020) planes of the as-prepared LDPE are centered at 21.45, 23.77, and 39.19° and corresponds to d-spacings of 4.14, 7.48, and 2.48 Å, respectively. The values of FWHM are associated with the internal strains, crystallite size and the perfectness of the polyethylene crystallites. When the samples were annealed, the widths of the diffraction peaks become narrower.

CONCLUSIONS

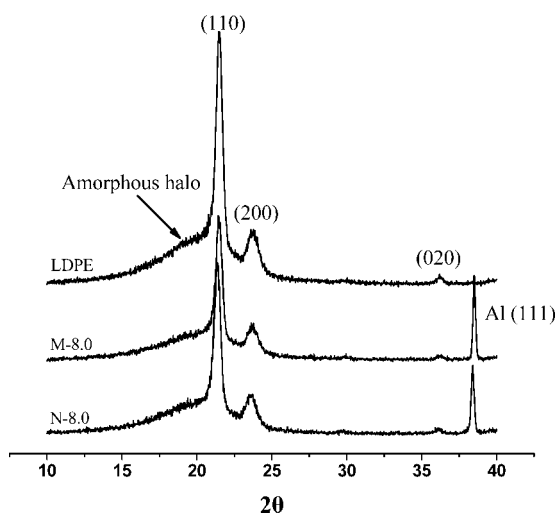The influence of Al nano- and microparticles on the morphology of LDPE was investigated. It has been

TABLE II
Unit Cell Parameters of LDPE and LDPE/Al Composites

Samples	(110)			(200)		
	2θ	d-spacing (Å)	FWHM	2θ	d-spacing (Å)	FWHM
LDPE[a]	21.45	4.14	0.47	23.77	7.48	0.64
LDPE[b]	21.34	4.16	0.45	23.64	7.52	0.58
LDPE[c]	21.36	4.16	0.44	23.57	7.54	0.58
N-8.0[a]	21.32	4.16	0.47	23.59	7.54	0.64
N-8.0[b]	21.46	4.14	0.45	23.66	7.51	0.58
N-8.0[c]	21.46	4.14	0.43	23.78	7.48	0.60
M-8.0[a]	21.42	4.14	0.47	23.68	7.51	0.66

[a] As-prepared.
[b] Annealed in 110°C.
[c] Annealed in 120°C.

found that both Al nanoparticles and microparticles do not change the degree of crystallinity of LDPE and the unit cell parameters. The lamellar thickness and thickness distribution do not significantly change with the addition of nano- and microparticles. The spherulitic texture of LDPE is observed to be seriously disordered by the nanoparticles, and LDPE in nanocomposites only exhibits poor developed spherulite structure. The incorporation of microparticles facilitates the growth of spherulites but decreases the size of the spherulites.

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Figure 4 WXRD patterns of neat LDPE, LDPE/Al nanocomposites and microcomposites.