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*Journal of Composite Materials* 2009; 43; 2821 originally published online Aug 26, 2009;

DOI: 10.1177/0021998309345307

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# Crystallinity Behavior of MDPE–Clay Nanocomposites Fabricated using Ball Milling Method

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**ABSTRACT:** Polymer–clay nanocomposites were fabricated from medium-density polyethylene and organically modified Na-montmorillonite (MMT) using the planetary ball milling as a new method. The materials were characterized using scanning electron microscopy, transmission electron microscopy, and X-ray diffraction (XRD). The crystalline size of polyethylene (PE) filled with MMT was studied using XRD. These studies indicated that the addition of MMT decreases the crystalline size of the polymer. Moreover, the degree of crystallinity of both ball-milled and un-milled PE and PE–clay nanocomposites was measured by applying the XRD technique. The results show that both milling time and clay content decrease the degree of crystallinity of PE.

**KEY WORDS:** polyethylene–clay nanocomposites, planetary ball milling, XRD technique, degree of crystallinity.

## INTRODUCTION

**P**OLYETHYLENE (PE) WITH almost one-third of the world plastic production is one of the most popular polymers [1]. It is one of the most important commodity thermoplastic used in many industrial applications such as packaging, wire, and cable industries [2]. This is due to its low specific weight, high chemical resistance, low cost, high mechanical flexibility, low dielectric constant, low losses, and good processability [3,4]. Medium-density polyethylene (MDPE) is a kind of PE defined by a density range of 0.926–0.940 g/cm<sup>3</sup>. MDPE has good shock- and drop-resistance properties. Its notch sensitivity is lesser than high-density polyethylene (HDPE), but its stress-cracking resistance is better than HDPE. MDPE is typically used in gas pipes and fittings, sacks, shrink films, packaging films, carrier bags, and screw closures.

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Clays have been recognized only very recently as important nanoparticle fillers of different polymers leading to a new class of materials called polymer–clay nanocomposites [4]. Polymer–clay nanocomposites are a class of plastic materials that has gained increasing attention in the past few years. In fact, quite recently, it has been discovered that a number of properties of commercially available thermoplastic polymers may be improved considerably by the addition of small amounts of clays, provided they are conveniently dispersed in the polymer matrix in the form of nanoscale platelets [5]. Improvement in mechanical properties such as tensile strength, tensile modulus, decrease in thermal expansion coefficient, increase in solvent resistance, outstanding diffusion barrier properties, and flame retardant capability are a few selected examples illustrating the advantages provided by this new class of materials [6].

Clay–polymer nanocomposites have received a great deal of attention, not only because of their potential industrial applications, but also from their fundamental point of view [6]. The first industrially successful and significant development of polymer–clay nanocomposites was pioneered by Toyota’s researchers for high-performance reinforced plastics applications in automobiles [7]. Then, General Motors Corporation (GMC) developed a step-assist component for 2002 GMC Safari and Chevrolet Astro vans, which is made of thermoplastic polyolefin–clay nanocomposite. This material is lighter and stiffer, more robust at low temperatures, and easily recyclable. GMC has also used the nanocomposites in the lateral protection wire of the 2004 Chevrolet Impada since the polymer–clay nanocomposites are 7% lighter in weight and present a better surface appearance. New applications of polymer–clay nanocomposites are envisaged by the automotive industry for commercialization: polypropylene–clay for bodywork with anti-scratch properties, panes of doors, consoles, and interiors decoration due to its aesthetics, recyclability, and weight-saving properties; nylon–clay for bumpers with enhanced mechanical and weight-saving properties (Toyota) and so on. Apart from the above applications, it has been reported that widespread use of polymer–clay nanocomposites by the US automotive industry could save 1.5 billion liters of gasoline in 1 year of automotive production and reduce related carbon dioxide emissions by more than 10 billion pounds. Furthermore, for environmental applications, nanoclays are used as effective reinforcing agents in ‘green nanocomposites’ [8] and they are attractive materials used as substitutes for petroleum feedstock in the manufacture of biodegradable plastic for the commercial market [9].

Till now, several methods have been developed for the fabrication of polyethylene (PE)–clay nanocomposites including: *in situ* polymerization, the solution, and melt intercalation methods. Shin et al. [10] prepared PE–clay hybrid nanocomposite using *in situ* polymerization with bifunctional organic modifiers. Kuo et al. [11] reported the preparation of *in situ* blends of metallocene polyethylene (mPE) with montmorillonite (MMT). They have investigated the crystallization behavior, morphology, and molecular motion of mPE–clay nanocomposites. Zanetti et al. [12] produced polymer nanocomposites based on organically modified clay (organoclay) and PE by melt processing using poly (ethylene-co-vinyl acetate) (EVA) as compatibilizer and studied the thermal degradation behavior of nanocomposite. Morawiec et al. [13] synthesized nanocomposites based on low-density polyethylene (LDPE), containing of 3 or 6 wt% of organo-modified montmorillonite nanoclay (MMT-ODA) and maleic anhydride-grafted LDPE as a compatibilizer by melt mixing. Araújo et al. [14] obtained PE–MMT clay nanocomposites via direct melt intercalation in order to study the effect of salts and organoclay on thermal stability and mechanical properties of PE. No significant differences were found in the organophilic

properties of clay modified with different types of quaternary ammonium salts. Ou et al. [15] fabricated poly(ethylene terephthalate) (PET)–MMT nanocomposites by solution intercalation method. They investigated the nonisothermal crystallization and the morphology of PET–MMT nanocomposite.

The high-energy ball milling (HEBM) technique has emerged as a nonexpensive route to produce nonequilibrium phases in several varied forms, such as nanostructured, amorphous materials, nanocomposites, and extended solid solutions [16]. It has many advantages such as low cost, simple operation, high efficiency, and so on [17]. To the best of our knowledge, and in spite of simplicity of ball milling method, it has not been under more attention to produce PE–clay nanocomposites. Thus, the main goal of this study is to fabricate PE–clay nanocomposites by HEBM as a new method. As reported in previous studies, severe deformation has a significant effect on crystallinity behavior of semicrystalline polymer such as PE, polypropylene, etc. But the subject is still under debate, the role of both ball milling and clay content on the degree of crystallinity or the crystallinity behavior of MDPE has not been clarified.

It is worth noting that the degree of crystallinity is an important parameter for semicrystalline polymers [18]. Many physical and mechanical properties of polymers are significantly dependent on the degree of crystallinity. It is well known that the degree of crystallinity can be determined by a variety of physical methods, for example, X-ray diffraction (XRD), differential scanning calorimetry (DSC), density measurements, infrared spectroscopy (IR), and nuclear magnetic resonance (NMR). In the present work, the degree of crystallinity of PE and its nanocomposite have been evaluated by XRD method. The influence of both ball milling time and clay content on the degree of PE crystallinity has been also investigated.

## EXPERIMENTAL PROCEDURE

### Materials

MDPE was used as a composite matrix resin and the used clay was organomodified Na-MMT. These two commercial chemicals were used as received without further purification. The specifications of these materials have been summarized in Table 1. Also, Figure 1 shows the SEM micrographs of MDPE and clay powders before milling. It can be seen that the morphology of clay is flake-like and PE powders are almost regular with different sizes. The average size of MDPE powder varied between 40 and 200 nm.

**Table 1. Some properties of the MDPE and organoclay.**

Materials	Type	Properties
Organoclay	Na-MMT	Swelling agent: dioctadecyldimethylammonium chloride
Resin	MDPE	Density: 0.937 (g/cm <sup>3</sup> ) MFI: 4.2 Vicat softening point: 117

## Milling Conditions

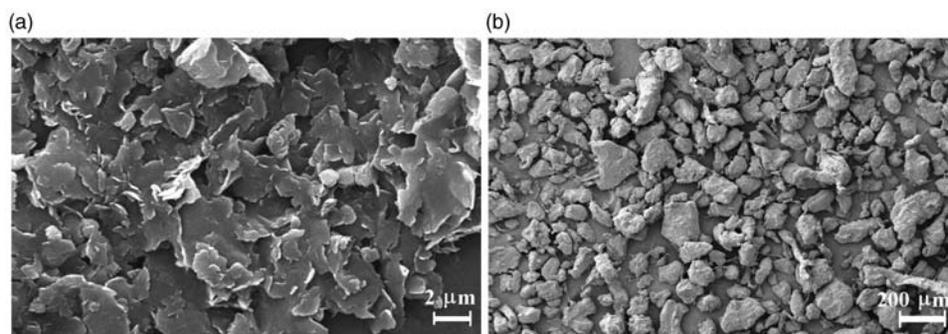
HEBM was performed in a stainless steel container (vial) charged with stainless steel balls at the speed of 300 rpm. The powder to ball mass ratio was kept 1 : 20 with a powder mass of 10 g MDPE and clay particles were first mixed mechanically before ball milling to achieve three different nanocomposites. Table 2 provides the details of the composition of each nanocomposite studied in this work. Prepared samples were milled in ambient atmosphere without any additive (i.e., dry milling). The milling time was varied from 10 to 100 h. Unfilled MDPE was also similarly processed at the same times for comparison.

## Characterization

XRD is the most commonly used technique to characterize nanocomposite structure. The structure of pure MDPE and MDPE in the nanocomposite, before and after ball milling has been investigated by XRD. The XRD patterns were obtained using a Bruker/D8 ADVANCED diffractometer with  $\text{CuK}_\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) in the range of  $2\theta = 4^\circ - 70^\circ$  by the step of  $0.02^\circ$ .

## Morphological Analysis

The morphologies of pristine MDPE and organoclay were observed using scanning electron microscopy (SEM) (LEO 1450 VP model). Transmission electron microscopy (TEM) is considered as a powerful technique to observe the clay mineral layers and the PE–clay nanocomposites. A TEM, LEO 919 AB, was used to observe the dispersion of clay in nanocomposite.



**Figure 1.** The SEM micrographs of (a) clay and (b) pure PE before milling.

**Table 2.** The details of the composition of each nanocomposite studied in this work.

Composition	Type of PE–clay nanocomposites		
	PECN5	PECN10	PECN15
Clay (wt%)	5	10	15
PE content	95	90	85

## RESULT AND DISCUSSION

Figure 2 presents the TEM micrograph obtained from MDPE filled with 15 wt% organoclay after 40 h milling. As this figure shows, the clay layers have been dispersed in MDPE matrix using HEBM. In fact, Na-MMT can undergo cation exchange with organic molecules, leading to the intercalation of organic molecules into their galleries. Because of the nonpolar nature of the alkyl chain (i.e., dioctadecyldimethylammonium chloride), the electrostatic interactions between the silicate layers were reduced, thus diffusion of the PE into the clay layers is facilitated.

The XRD pattern of pristine MDPE with two crystalline peaks at  $2\theta$  of  $21.67^\circ$  and  $24.04^\circ$  and one amorphous peak at  $2\theta$  of  $19.81^\circ$  are shown in Figure 3. These two crystalline peaks correspond to 110 and 200 spacing.

Figure 4 illustrates the XRD of MDPE for various milling times. The position of the maximum peaks in the patterns of MDPE before and after ball milling is similar, but the

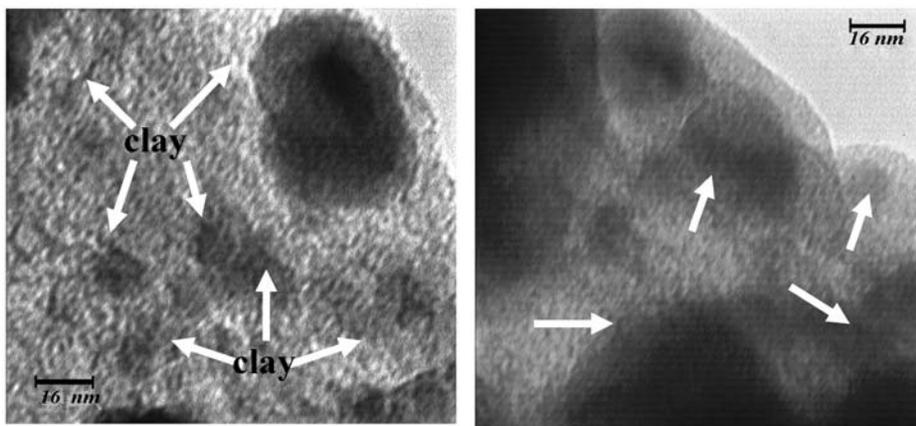


Figure 2. The TEM image of PECN15 after 40 h milling.

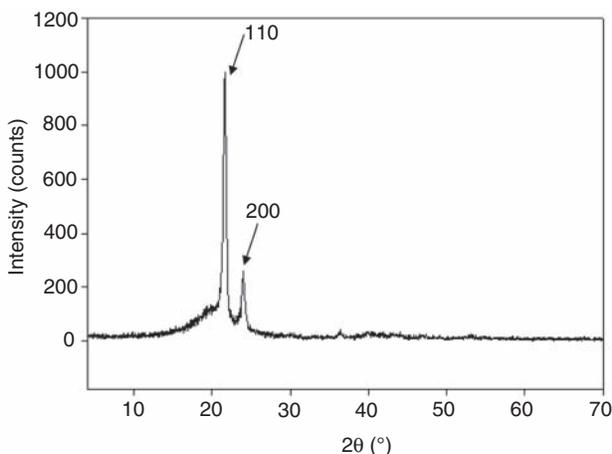
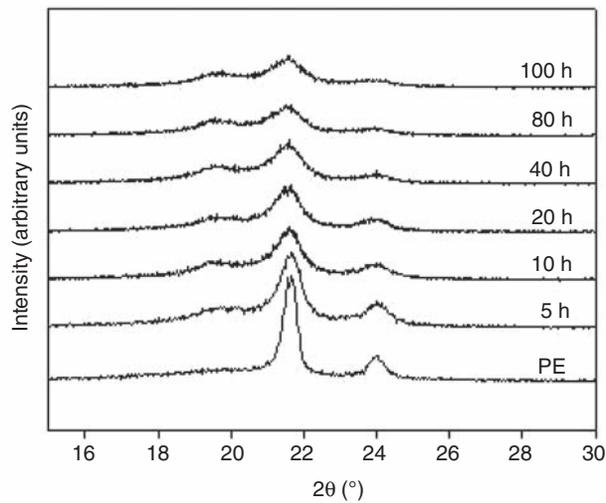


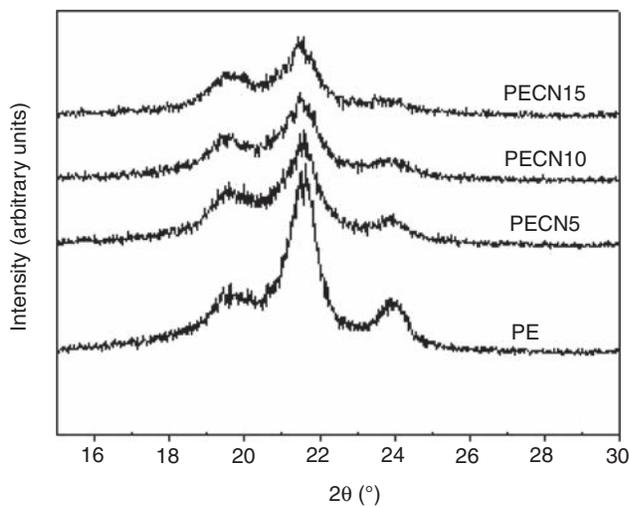
Figure 3. XRD patterns of PE before milling.

intensity of peaks has remarkably decreased after 10 h of milling time. After further ball milling (between 20 and 100 h), no considerable change in the intensity of peaks of MDPE were observed. It indicates that the ball milling can influence the degree of crystallinity of MDPE, especially during the early stage of milling (10 h). Since MDPE is a semicrystalline polymer thus the XRD spectrum consists of two region parts (crystalline and amorphous). It can be seen that the intensity of two crystalline peaks decreases as the milling time increases unlike amorphous peak.

The XRD patterns of the ball milled powders for 20 h with various clay amounts are shown in Figure 5. As this figure shows, the peaks of MDPE do not shift by adding



**Figure 4.** XRD patterns of PE as well as ball-milled PE at different times (hour).



**Figure 5.** XRD patterns of ball-milled PE, PECN5, PECN10, and PECN15 samples for 20 h.

different amounts of clay. There is no significant distinctable difference between MDPE and MDPE–clay nanocomposite and both have the same crystalline structure. At the early stages of clay loading (5 wt%), the Bragg peaks have become wider and their intensities have considerably decreased. It indicates that the degree of crystallinity of PE has been decreased. During the clay loading to 15 wt%, these peaks have become a little broader. It shows that the crystallinity of MDPE has decreased as the clay contents have increased. It is considerable that the intensity of XRD peaks decreases by only 5 wt% clay. After 5 wt% clay loading, the intensity of major peak decreases 40.45% but further clay loading from 5 to 15 wt% decreases the intensity of this peak by just 28.30%.

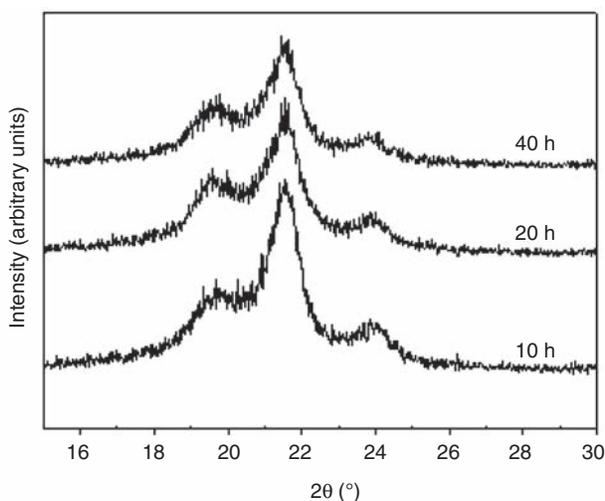
Figure 6 presents the XRD patterns of PECN10 powder after selected ball milling time. The intensity of the Bragg peaks decreases after 20 h of the milling time, whereas the peak positions do not change. Further milling up to 40 h causes the intensity of peaks decreases but it is not dramatic.

### Crystalline Size

According to the Debye–Sherrer equation [19], the crystalline size of PE ( $L_{hkl}$ ) can be calculated via:

$$L_{hkl} = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where  $L_{hkl}$  is the microcrystalline dimension (nm),  $\theta$  is an angle of incidence,  $\lambda$  is the wavelength of X-ray ( $\lambda = 0.15406$  nm),  $\beta$  is the full width at half maximum (FWHM). The results for  $L_{110}$  and  $L_{220}$  have been given in Table 3. As Table 3 shows, the crystalline size of the PE has decreased as the milling time increases, especially during the first stage of milling (10 h). Also, by adding the clay the crystalline size of MDPE decreases. The reason for this variation can be attributed to the fact that the presence of filler particles may provide solid surfaces as heterogeneous nuclei for crystallization, the reduced mobility of the chains, on the other hand, hinders the growth of crystals.



**Figure 6.** XRD patterns of PECN10 nanocomposites with different milling times.

**Table 3. The crystalline size  $L_{hkl}$  (nm) of PE and PE–clay nanocomposites.**

Sample	PE		PECN15	
	$L_{110}$	$L_{200}$	$L_{110}$	$L_{200}$
0	19.395	17.135	–	–
10	11.571	10.450	8.536	7.582
20	10.857	10.657	10.365	11.954
40	10.813	9.900	10.007	8.664

**Table 4. The degree of PE crystallinity.**

Milling time (h)	$X_c$
0	34.51
5	27.62
10	25.56
20	25.13
40	24.72
80	21.19
100	19.32

### The Degree of Crystallinity

The concept of semicrystallinity is important because PE can be considered to be a composite of crystalline and noncrystalline regions. In fact, if PE is considered to be completely crystalline material, it would be brittle and in the case of totally amorphous, the sample would be highly flexible. In practice, PE is a tough and resilient material. Neither pure crystalline nor pure amorphous PE samples are available, so the properties of each phase must be extrapolated from those of partially crystalline samples. There are many methods for determining of the degree of crystallinity of polymer, such as DSC, XRD, etc. The XRD pattern of MDPE shows two crystalline peaks at  $2\theta$  of  $21.67^\circ$  and  $24.04^\circ$  and one amorphous peak at  $2\theta$  of  $19.81^\circ$ , respectively. These two crystalline peaks correspond to 110 and 200 spacing (Figure 3).

The degree of crystallinity of samples was quantitatively estimated using the method of Nara and Komiya [20]. The equation is as follows:

$$X_c = \frac{A_c}{A_c + A_a} \quad (2)$$

where  $X_c$  refers to the degree of crystallinity,  $A_c$  and  $A_a$  stand for the crystallized area and the amorphous area on the X-ray diffractogram, respectively.

Tables 4 and 5 show the degree of crystallinity of MDPE and MDPE–clay nanocomposite, respectively. The degree of crystallinity of all materials including neat MDPE and its nanocomposites decreases as milling time increases. The interesting result achieved in the current study is that both milling time and clay content can affect on crystallinity of MDPE, especially during the early stage of milling (10 h) and clay loading. It is noticeable that the degree of crystallinity depends strictly on clay content because addition of clay acts like a barrier against crystal growth.

**Table 5. The degree of MDPE–clay nanocomposites crystallinity.**

Milling time (h)	$X_c$		
	PECN5	PECN10	PECN15
10	21.42	20.53	19.56
20	20.08	19.20	17.83
40	19.04	18.52	17.60

## CONCLUSIONS

The method of HEBM has been used to fabricate PE–clay nanocomposites containing different clay contents (0–15 wt%). The XRD of neat MDPE, ball-milled MDPE, and MDPE–clay nanocomposite showed that:

- (1) The milling time and the addition of clay have not affected on the crystal structure of MDPE matrix.
- (2) The microcrystalline dimension  $L_{hkl}$  of MDPE–clay nanocomposite is less than that of MDPE. The addition of clay reduces the crystalline size of MDPE. Ball milling is also effective in reducing the crystallite size of MDPE.
- (3) The ball milling has influence on the crystallinity of MDPE, especially during the early stage of milling.
- (4) The crystallinity of MDPE decreases as the clay contents increase. It can reduce the intensity of XRD peaks by only 5 wt% clay.

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