

# Study of the Morphology and Granulometry of Polyethylene–Clay Nanocomposite Powders

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**Medium-density polyethylene (MDPE) matrix nanocomposites reinforced with different clay contents were produced by using a planetary ball mill. The morphology of all the milled samples, including pure polyethylene and the polyethylene–clay nanocomposites, was examined by scanning electron microscopy. To investigate the effects of milling time and clay content on the particle size of polyethylene powder, sieve analysis was used. The results showed that during milling, the regular shape of pure polyethylene powder converts into flake shapes and the average particle size of the powder increases upon increasing the milling time because the welding mechanism is predominant. Also, the presence of the clay can increase the maximum-particle size, and increasing the clay content can decrease the milling time required to reach the same maximum particle size. J. VINYL ADDIT. TECHNOL., 16:90–97, 2010. © 2009 Society of Plastics Engineers**

## INTRODUCTION

Polyethylene (PE) is commonly used in the plastics industry and especially for cable covering because of its abrasion resistance, flexibility, excellent electric insulation properties, low toxicity, and easy processing [1]. Medium-density polyethylene (MDPE) is a kind of PE defined by a density range of 0.926–0.940 g cm<sup>-3</sup>. It has good shock- and drop-resistance properties. It is also less notch-sensitive than high-density polyethylene (HDPE), and its stress-cracking resistance is better than that of HDPE. It is typically used in gas pipes and fittings, sacks, shrink films, packaging films, carrier bags, and screw closures.

Mechanical milling is a well-known technique and is extensively used in a wide range of processes. In mechanical treatments carried out by ball milling, powder particles are subjected to a severe plastic deformation due to the repetitive compressive loads arising from the impacts

between the balls and the powder. The properties of the resulting material depend on a large number of parameters involved in the milling process: (i) the intrinsic nature of the initial materials such as their mechanical properties, chemical constitution, and structural properties; (ii) the parameters of the ball-milling process such as ball-to-powder weight ratio, milling time, rotational speed, and type of motion of the vials; and (iii) the milling media, i.e., the milling atmosphere [2].

The field of nanocomposites has recently attracted considerable attention as researchers strive to enhance the properties of composites and extend their utility by using nanoscale reinforcements instead of the more conventional particulate-filled composites. Although smaller reinforcements have a better reinforcing effect than larger ones, applying the ball-milling technique for fabricating composites has some merits. Since ball milling is done at room temperature, the disadvantages of the liquid metallurgy method in producing undesirable materials can be avoided. Moreover, the ball-milling process can produce homogeneous nanocomposite powders instead of the more conventional coarse particulate-filled composites. Synthesizing nanocomposites by ball milling may receive much attention. This could occur because of the simplicity of the technique and the huge number of homogeneous composite powders that can be produced in an industrial scale at room temperature [3].

The dispersion of small quantities of nanometric inorganic materials in polymers and blends, generally, is achieved by using one of two approaches: (1) dispersion of nanoparticles in suitable monomers and subsequent polymerization or (2) direct incorporation of nanoparticles among the polymer chains from either solution or melt. For most natural or biodegradable polymers, these approaches are not always allowed. In fact, the melting temperatures of these polymers are too close to the temperatures at which thermal degradation takes place. The use of solvents is strongly limited by the problems connected with the gelation process [4]. To solve these problems, a “solid-state method” such as high-energy ball

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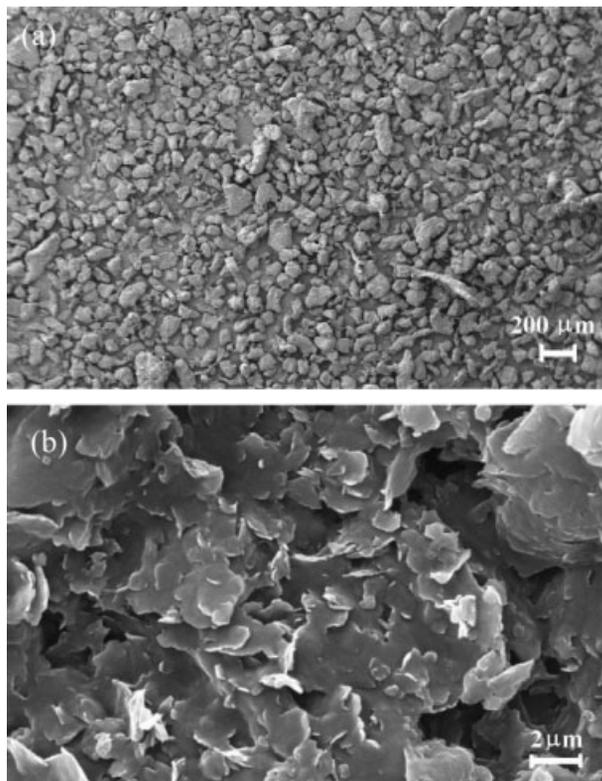


FIG. 1. Morphologies of the starting (neat or pristine) (a) polyethylene and (b) clay powder particles used in producing PE-clay nanocomposite.

milling (HEBM) might be an interesting alternative, not only because of its potential results, but also from an economical point of view [5].

Recently, it has been proved that HEBM can help in obtaining novel polymer nanocomposites with new characteristics, that are difficult to obtain by conventional techniques [6]. Mangiacapra et al. [7] prepared two composites of apple peel pectin (natural polymer) with 3% of organically modified montmorillonite clay by using HEBM. Fumed silica nanoparticles with a 14 nm diameter were blended with poly(methyl methacrylate) by means of an HEBM process [5]. Vertuccio et al. [4] used HEBM as a new preparation method for the fabrication of poly( $\epsilon$ -caprolactone)-starch-clay composites. The clay dispersion was promoted by the energy transfer between the milling balls and the polymer/clay mixture. The researchers studied the structural and physical properties and correlated them with the milling conditions. Zhang et al. [8] dispersed nano-SiO<sub>2</sub> particles into micron-sized polyether ether ketone powders by using an HEBM technique.

In our previous recent work [9], PE-clay nanocomposites (PECN) were fabricated by high-energy planetary ball milling. The nanocomposites produced were characterized by X-ray diffraction and transmission electron microscopy (TEM). Also, the effects of milling time and clay content on the degree of PE crystallinity were investigated [9]. To our best knowledge, there is no evidence for the effects of ball milling and clay content on MDPE

TABLE 1. Compositions of nanocomposites.

Composition (wt%)	Type of polyethylene-clay nanocomposite		
	PECN5	PECN10	PECN15
Clay	5	10	15
PE	95	90	85

morphology. Hence, the main goal of the current research has been concentrated on this issue. Briefly, the aim of this study was to gain new knowledge about the simultaneous effect of milling time and clay content on the morphology and granulometry of PE powders.

## EXPERIMENTAL DETAILS

A MDPE (density: 0.937 g cm<sup>-3</sup>, MFI: 4.2, Vicat softening point: 117) was used as a matrix resin. The pristine clay used was China clay. The pristine morphologies of the MDPE and clay are shown in Fig. 1.

The nanocomposites was prepared by mechanical milling of the MDPE and clay powders in a high-energy planetary ball mill. PE and 5, 10, and 15 wt% of clay were mechanically mixed first and then milled for different times. In all experiments, the milling times were 0, 10, 20, 40, and 60 h. The ball-to-powder weight ratio was chosen as 20:1, since in our previous work, we found that it was the best choice [10]. The milling was conducted by using hardened steel balls with different diameters. The milling speed was 300 rpm and the same milling times were used for the neat PE powder. The compositions of the PE-clay nanocomposites (PECN) produced are summarized in Table 1. Figure 2 shows a schematic illustration of the ball-milling process. In the milling procedure, when the vial is rotated, the powders are trapped between colliding balls as well as between the balls and the wall of the vial. Therefore, repetitive plastic deformations occur in the PE powders.

A transmission electron microscope (LEO 919 AB) was used to observe the dispersion of clay in the PE matrix. The sample was compressed by a hydraulic press in

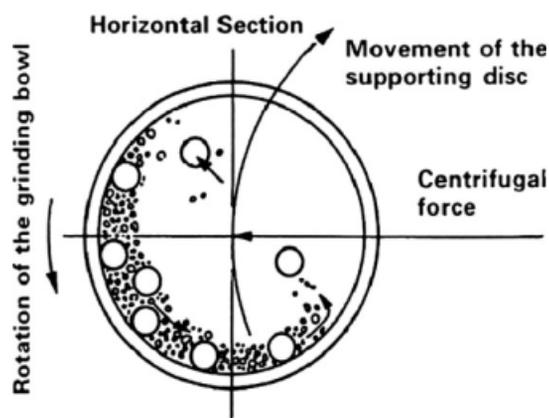


FIG. 2. Schematic illustration of the planetary ball-milling process [8].

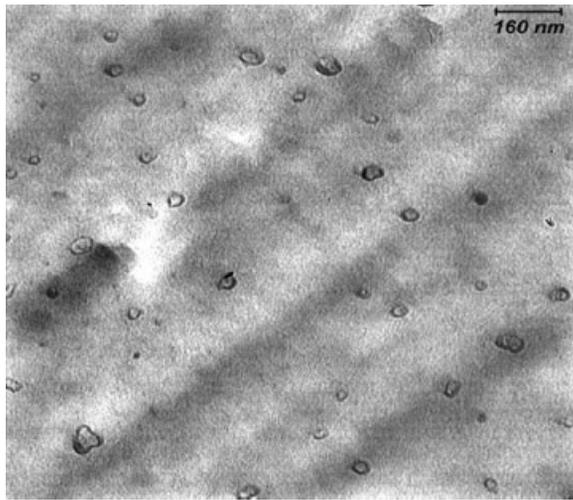


FIG. 3. TEM image of PECN15 after 60 h of milling time.

a cylinder model with a 10-mm diameter. Then it was heated for 10 min. Later, the sample was cut into small pieces and embedded in an epoxy intermediate resin (TAAB 812). The blocks were trimmed with a LEICA EM TRIM apparatus in order to form a trapezoid shape. Thin layers were cut with a glass knife by using a microtome (Leica ULTRACUTR). The morphologies of all the milled samples including pure PE and the PECN were examined by a scanning electron microscopy (SEM) (LEO 1450 VP Model). Before taking the micrographs, the samples were coated using a thin layer of gold/palladium by using a sputter coater (Polaron SC 7620). To investigate the effects of milling time and clay content on the particle size of the PE powder, sieve analysis was used. All samples were shaken for 15 min, and the mass of each sample was 2 g.

## RESULTS AND DISCUSSION

The TEM image of PECN15 after 60 h of milling is shown in Fig. 3. This figure shows that the clay particles have been dispersed homogeneously in the polymer matrix by using HEBM. The mean size of the clay was about 60 nm.

Figure 4 illustrates the energy dispersive X-ray spectroscopy analysis of 10-h-milled PECN10, that was performed on one of the small particles (marked with plus sign) for confirmation of the presence of clay in the PE matrix. Figure 4b shows that the composition included Si and Al matches with the clay compound. No other peaks, except those for Au and Pd due to coating, were observed. A micrograph of 20-h-milled PECN10 powder is shown in Fig. 5. The reinforcement particles are better seen with a backscattered electron image (BSE).

Figure 6 shows the effect of mechanical milling on the morphology of PE. As shown in Fig. 6, the PE powder used has an almost regular shape as well as different sizes. It is seen that a flaky particle (Fig. 6b) is formed

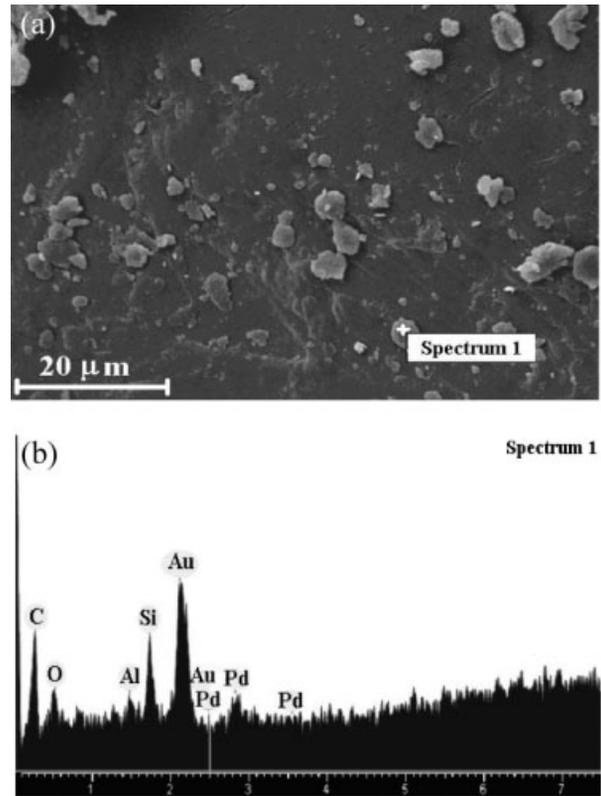


FIG. 4. (a) SEM image of 10-h-milled PECN10 sample at high magnification and (b) energy dispersive X-ray spectroscopy analysis of the marked small particle.

after 10 h, a result which indicates a possible preferred orientation. As milling proceeds, the particles are deformed and flattened, and the shape of the particles converts from regular into flake. This process occurs because of the mechanical impacts between ball-powder-ball and ball-powder-vial. These changes are followed by the fracture and rewelding of the powders, respectively. The size of the PE particles after 20-h milling is larger than that after 10 h as a result of the competition between the fracture and welding the phenomena. From an exacting look at the results, it is plausible to say that the welding phenomenon is the winner in this competition. Hence,

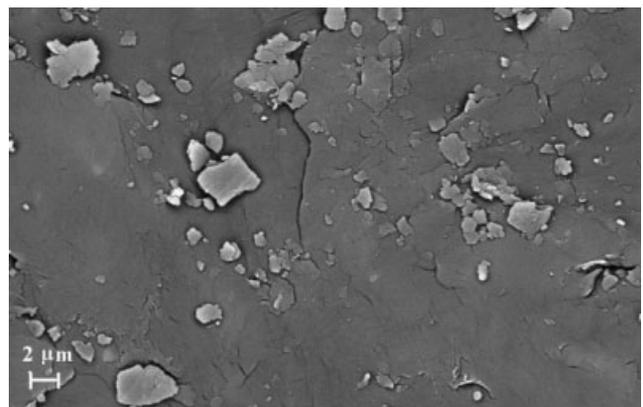


FIG. 5. BSE image of PECN10 after 20 h of milling.

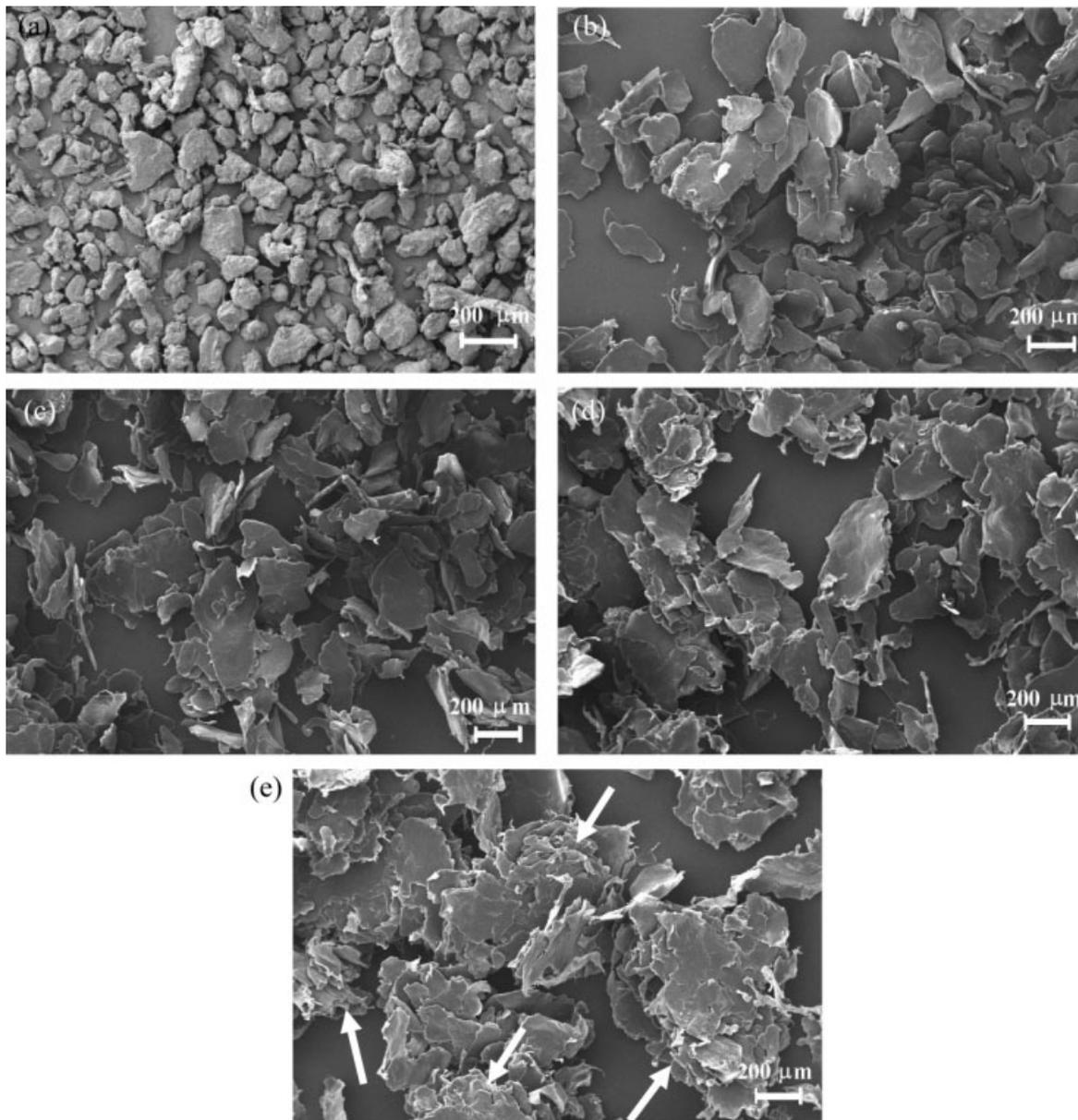


FIG. 6. SEM micrographs of polyethylene powder after milling times of (a) 0 h, (b) 10 h, (c) 20 h, (d) 40 h, and (e) 60 h.

by prolonging the milling process to 60 h, coarser particles are formed because the welding phenomenon plays the key role in the mechanism. The reason may be attributed to higher thermal conductivity of the clay compared with that of MDPE. In fact, the mechanism of ball milling for a ductile powder such as PE can be described as follows: first, the particles undergo deformation, and their morphology changes from equiaxed to flattened. Then, the welding mechanism predominates, thereby causing the equiaxed particles form. At this stage, oriented interfacial boundaries are observed. Then the welding and fracture mechanisms attain equilibrium, and particles with randomly oriented interfacial boundaries or, in other words, the random welding orientation are established. The final stage is characterized by a steady-state process in which

the microstructural refinement continues. Of course, the particle size and size distribution remain approximately the same [11].

The temperature experienced by the powder particles during milling is very important in determining the nature of the final powder product. It was reported that more than 90% of the mechanical energy imparted to the powders during milling is transformed into heat that raises the temperature of the powder [12]. Temperature has two different effects during mechanical alloying. One is the local temperature pulse due to the ball collisions. These local temperature pulses have a short duration, about  $10^{-5}$  s, approximately the same as the collision time between balls. The second effect is the overall temperature in a vial. Many experimental measurements have been

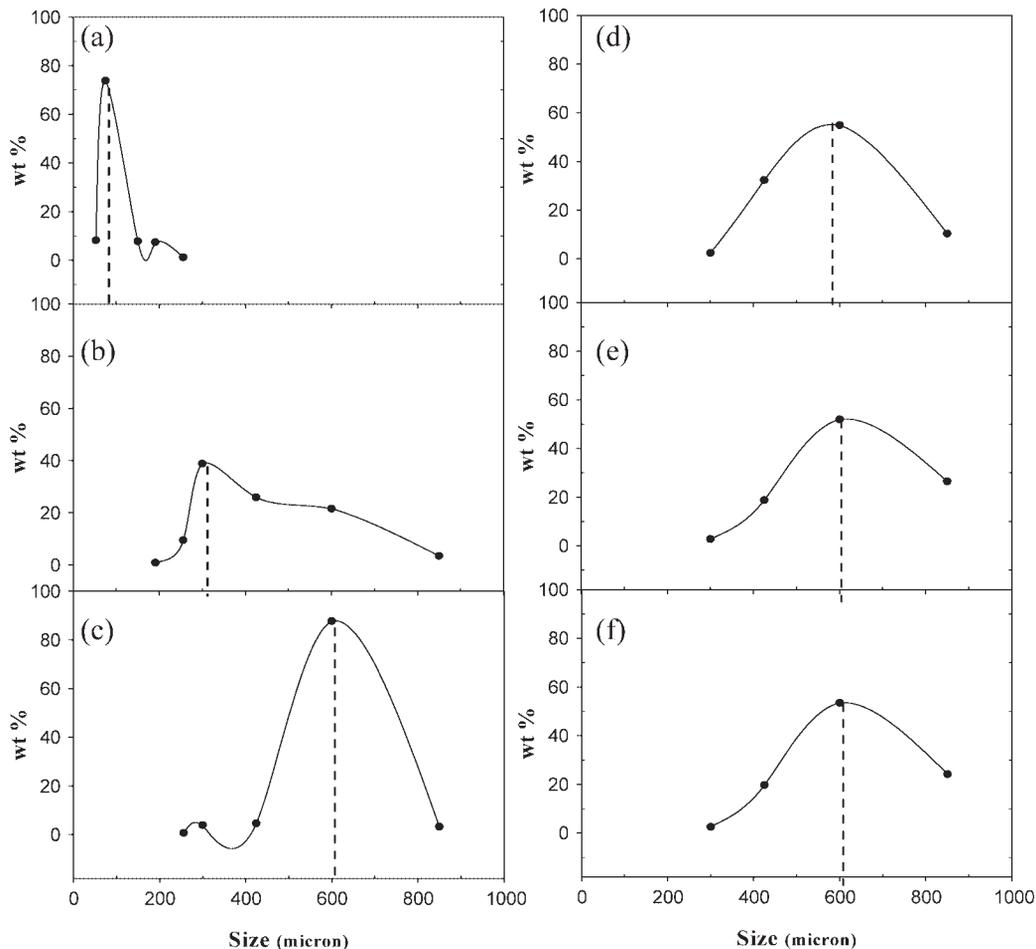


FIG. 7. Particle-size distribution of polyethylene powder after milling times of (a) 0 h, (b) 10 h, (c) 20 h, (d) 40 h, (e) 60 h, and (f) 100 h.

reported over the years, and the temperature varied from 50°C and 150°C [12]. Some investigators reported very large temperature rises. The maximum measured temperature was about 215°C, and more commonly it was about 100–120°C. It should be realized that this is the macroscopic temperature rise, even though it is recognized that local (microscopic) temperatures can be very high, often exceeding the melting points of some of the metals [12]. The temperature rise during milling is mainly due to ball-to-ball, ball-to-powder, and ball-to-wall collisions, and it is also due to frictional effects [12].

Powders of ductile materials such as PE can be easily deformed plastically under compressive loading, and hence they become flattened into flakes. The melting temperature of HDPE is typically in the range of 120–130°C, and the local temperature is very high. Therefore, ball-milling localized melting of the PE occurs, and flakes weld to each other.

The particle-size distribution of the milled powders is illustrated in Fig. 7. The average particle size of the ball-milled PE is higher than that of the pristine PE especially during the early stage of the ball milling (0–20 h). The average particle size of the powders increases upon increasing the milling time because the welding mechanism becomes predominant.

The presence of reinforcement particles mixed with PE changes the mechanical alloying/milling classification to a ductile–brittle component system. In Fig. 8, a possible scheme for the mechanical alloying process of this system is proposed. In the first stage of milling, the ductile particles undergo deformation, whereas brittle particles undergo fragmentation. Then when ductile par-

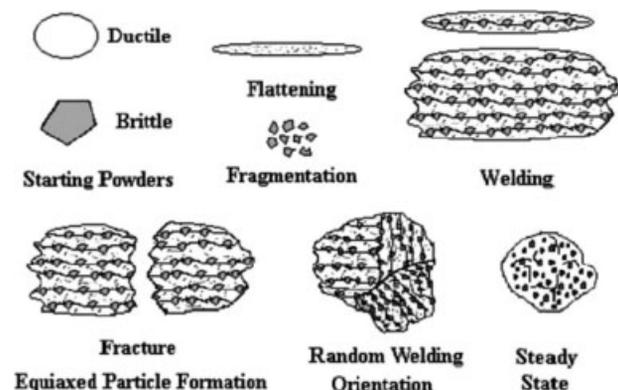


FIG. 8. The various stages of a ductile–brittle system during mechanical alloying.

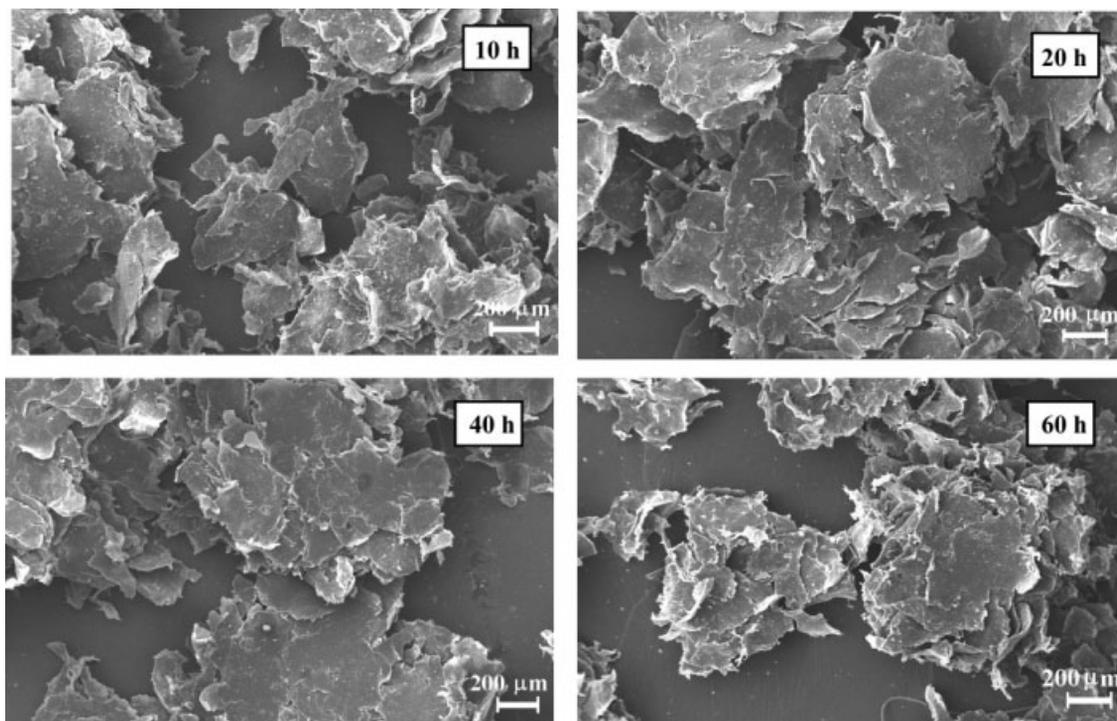


FIG. 9. Morphologies of PECN15 at different milling times.

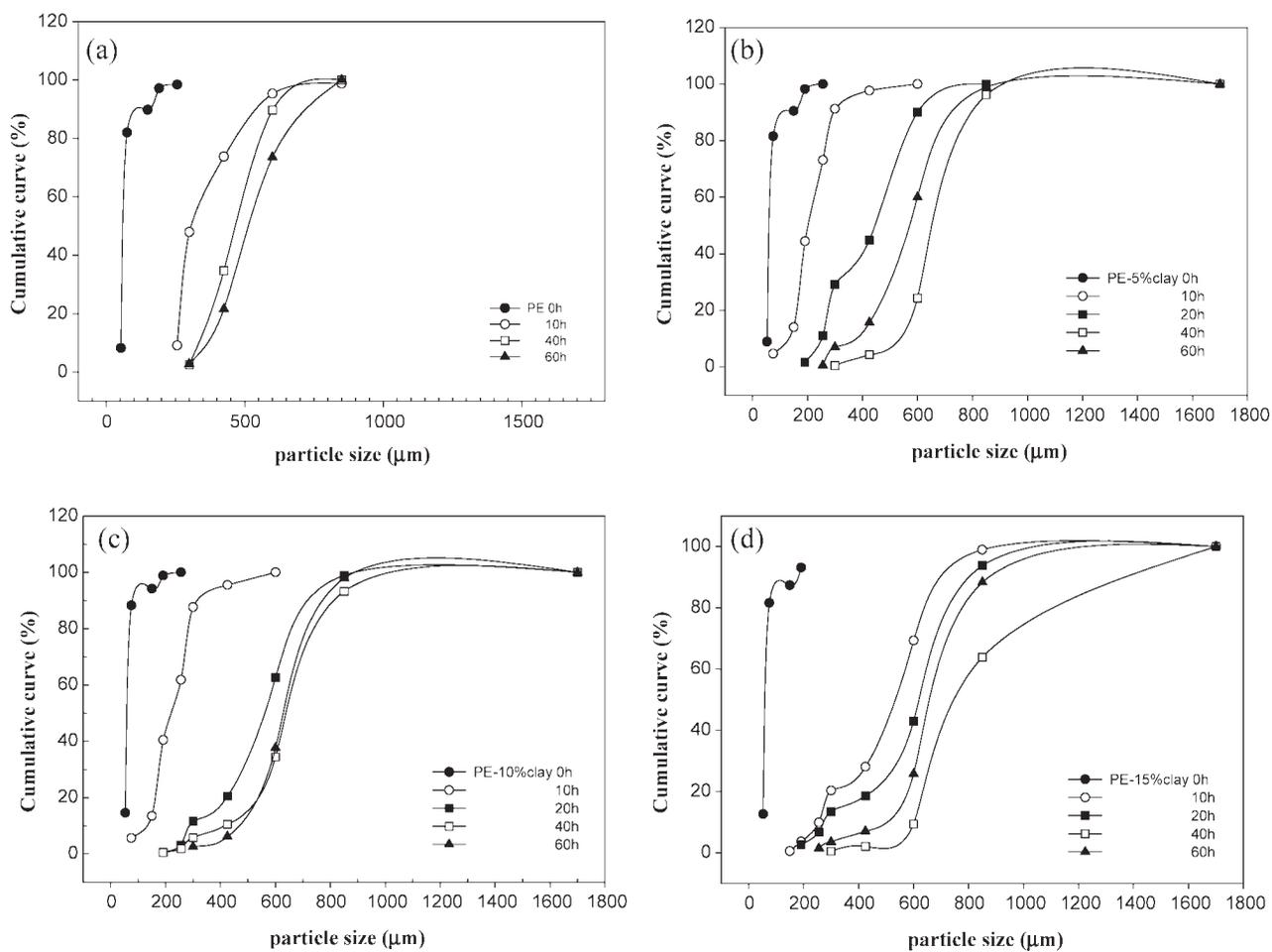


FIG. 10. Effect of milling time on the particle size distribution of PE-clay nanocomposites (a) Pure PE, (b) PECN5, (c) PECN10, and (d) PECN15.

TABLE 2.  $D_{20}$ ,  $D_{60}$ , and  $D_{80}$  values related to the particle-size distributions of PE, PECN5, PECN10, and PECN15 after 40 h of milling.

Sample	$D_{20}$ ( $\mu\text{m}$ )	$D_{60}$ ( $\mu\text{m}$ )	$D_{80}$ ( $\mu\text{m}$ )
PE	50–420	60–500	75–560
PECN5	50–590	60–675	75–740
PECN10	50–530	60–680	80–720
PECN15	50–640	60–800	70–1100

ticles start to weld, the brittle particles come between two or more ductile particles at the instant of the ball collisions. As a result, the fragmented reinforcement particles will be placed in the interfacial boundaries of the welded powder particles, and a real composite particle is formed. As the welding becomes the predominant mechanism in the process, the particles change their morphology. These phenomena, deformation, welding, and solid dispersion harden the material and increase the fracture process, which also contributes the equiaxed morphology. Welding and fracture mechanisms then attain equilibrium, thus promoting the formation of composite particles with randomly oriented interfacial boundaries [11]. Figure 9 shows the morphologies of the ball-milled PECN powders.

Figure 10 shows the particle-size distribution of PECN5, PECN10, and PECN15 at different milling times. The distribution in particle size is represented at 20, 60, and 80 cumulative percentage particle sizes, denoted as  $D_{20}$ ,  $D_{60}$ , and  $D_{80}$ , respectively. As particle size increases during milling, especially at the early stages, it is plausible to say that the welding of powders is the dominant mechanism rather than fracture. Figure 10a shows that the  $D_{20}$  size of the PE increases from 50 to 420  $\mu\text{m}$  and that the  $D_{80}$  size increases from 75 to 560  $\mu\text{m}$  at the same milling time. While the  $D_{20}$  size of PECN5 increases from 50 to 590  $\mu\text{m}$  after 40 h of milling, the  $D_{80}$  size increases from 75 to 740  $\mu\text{m}$  (Fig. 10b). Figure 10c shows that the  $D_{20}$  size of PECN10 increases from 50 to 530  $\mu\text{m}$  and that the  $D_{80}$  size increases from 80 to 720  $\mu\text{m}$  at the same milling time. Finally, for PECN15 at 40 h of milling, the  $D_{20}$  size increases from 50 to 640  $\mu\text{m}$ , and the  $D_{80}$  size increases from 70 to 1100  $\mu\text{m}$ . The particle-size distribution of pure PE (Fig. 10a) ranges from 50 to 250  $\mu\text{m}$  without milling to 300–850  $\mu\text{m}$  after 40 h of milling. For PECN5 and PECN10 (Fig. 10b and 10c), the particle-size distribution varies from 50 to 250  $\mu\text{m}$  without milling to 300–1700  $\mu\text{m}$  and 190–1700  $\mu\text{m}$  after 40 h of milling, respectively. Moreover, for PECN15, the particle-size distribution without ball milling is 50–200  $\mu\text{m}$

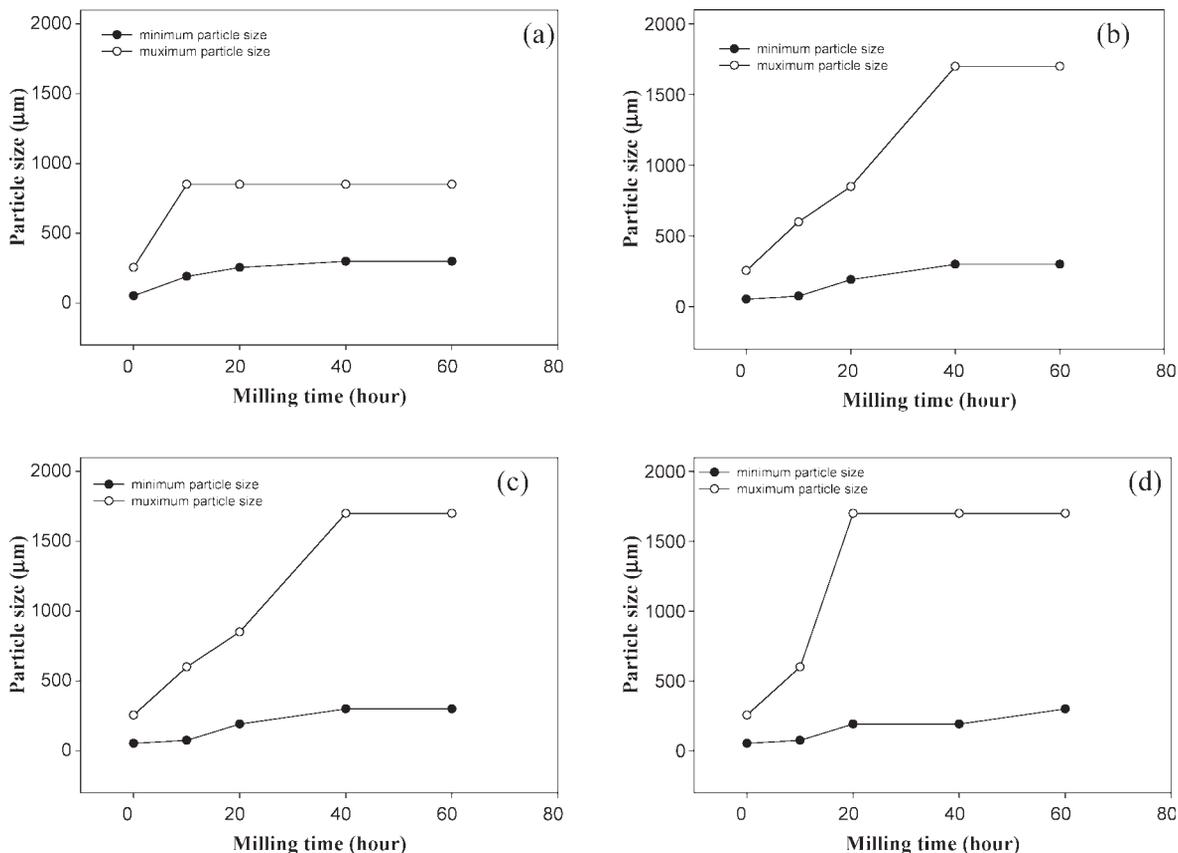


FIG. 11. Minimum and maximum sizes of PE and PE-clay nanocomposites as a function of milling time: (a) PE, (b) PECN5, (c) PECN10, and (d) PECN15.

and after 40 h of milling is 300 and 1700  $\mu\text{m}$ . It should be mentioned that the particle size of PECN has increased in comparison with that of pure PE and that the particle-size distribution has tended toward a larger size (Table 2).

Figure 11 illustrates the minimum and maximum sizes of the PE, PECN5, PECN10, and PECN15 samples as a function of milling time. It can be seen that the minimum-particle size of PE and the PECN increases slowly to  $\sim 300 \mu\text{m}$  with increasing milling time up to 40 h and then remained constant. On the other hand, the maximum-particle size of PE increases rapidly to 850  $\mu\text{m}$  with 10 h of milling (Fig. 11a). It appears that 10 h is the optimum milling time for neat PE. The maximum-particle size of PECN5, PECN10, and PECN15 increases to 1700  $\mu\text{m}$  with 40 h, 40 h, and 20 h of milling, respectively (Fig. 11b–11d). A further increase of the milling time up to 60 h causes almost no change in the maximum-particle size. As the optimum milling time increases from 10 h for neat PE to 40 h for PECN5 and PECN10 and to 20 h for PECN15, the maximum-particle size also increase from 850 for neat PE to 1700  $\mu\text{m}$  for PECN. The results show that the presence of clay can increase the maximum-particle size and that increasing the clay content can decrease the milling time required to reach the same maximum-particle size.

## CONCLUSIONS

Pure PE and PE with different percentages of clay were milled at different milling times. The morphology and particle size changes of pure PE and PECN were investigated by using SEM and sieve analysis. It seems to us that this work leads to the following conclusions:

1. The Nanocomposite powders containing clay nanoparticles in the polymer matrix are prepared after 60 h of milling. The fabricated nanocomposites have the highest dispersion and homogeneity of the clay.
2. The average particle size of the ball-milled PE is higher than that of the pristine PE. The major mechanism during mechanical alloying is welding.

3. The particle size of the PECN increases with increasing clay content after 40 h of milling.
4. The presence of the clay can increase the maximum-particle size and increasing the clay content can decrease the milling time required to reach the same maximum-particle size.

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