Pan-Milling to Prepare Ultrafine High-Density Polyethylene Powder with Sodium Chloride Serving as Grinding Aid

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ABSTRACT: In this article, our self-designed pan mill equipment was used to pulverize high-density polyethylene (HDPE) to prepare its powder product. This pan mill based on three-dimensional shear forces shows much better pulverization effects on ductile polymer materials when compared with conventional pulverizing equipment based on impact force, and it can mill original HDPE pellets (particle size: 3–4 mm) into fine powder (particle size: 75 μm) at ambient temperature. To further improve the pulverization efficiency to obtain ultrafine HDPE powder, sodium chloride (NaCl), serving as a grinding aid, was comilled with HDPE. Taking the advantages of the cutting and isolating effects of NaCl crystals, HDPE can be pulverized into ultrafine powder with the particle size below 10 μm. Another advantage of NaCl as a grinding aid lies in an easy removal process through water wash, thus conveniently separating from hydrophobic HDPE powder. This technology provides a novel and efficient method to prepare the ultrafine powder of those polymers with high ductility and low melt point, and shows a promise in future commercial application. J Appl Polym Sci 105: 3426–3431, 2007

Key words: ultrafine powder; high-density polyethylene; pan mill equipment; pulverization; grinding aid

INTRODUCTION

Polymer ultrafine powder (particle size is generally below 10 μm) has wide application in powder coating, antiblocking, matting agent, cosmetics, filler with high performance, etc.,[1,2] and their preparation is being paid more and more attention in recent years. In comparison to the methods including emulsion polymerization, dispersion polymerization, and solution-precipitation method[3–6] to prepare polymer ultrafine powder, mechanical pulverization shows some obvious advantages due to a simple, efficient, environment-friendly, and low-cost preparation process without any limitation to those polymers hardly synthesized through emulsion or dispersion polymerization, as well as the difficulty when dissolved in a solvent. However, currently, the challenges to prepare the polymer ultrafine powder through mechanical pulverization are polymers' thermoplasticity (the heat generated during mechanical pulverization can cause softening or melting of polymer particle surface), elasticity, and stress relaxation (movable macromolecular chains make polymers possess high elasticity storage modulus, which can effectively convert imported mechanical energy into elastic potential energy of macromolecular chains, and the potential energy is subsequently converted into heat energy through the stress relaxation of macromolecular chains). During the pulverization of polymers, the occurrence of the adhesion of heated polymer particles and the considerable consumption of imported mechanical energy lead to difficult pulverization of polymer materials, and therefore it is hard to obtain polymer ultrafine powder by conventional mechanical pulverization. Although traditional pulverization equipment including vibromill, jet mill, ball mill, etc.,[7–12] have satisfactory pulverization effects on brittle inorganic materials such as minerals, they show inefficiency in pulverizing polymers at ambient temperature. To achieve ultrafine pulverization of polymers using the traditional equipment, deep cryogenic technology through liquid nitrogen is usually adopted; however, the high cost of this method restricts its extensive application.

In this article, we adopted our self-designed pan mill equipment to pulverize a typical ductile polymer, high-density polyethylene (HDPE), which is one of the most difficultly pulverized polymers because of its flexible macromolecular chains[13–15] as well as low melt point.

The detail structure of our pan mill equipment is shown in Figure 1. It consists of a pair of inlaid

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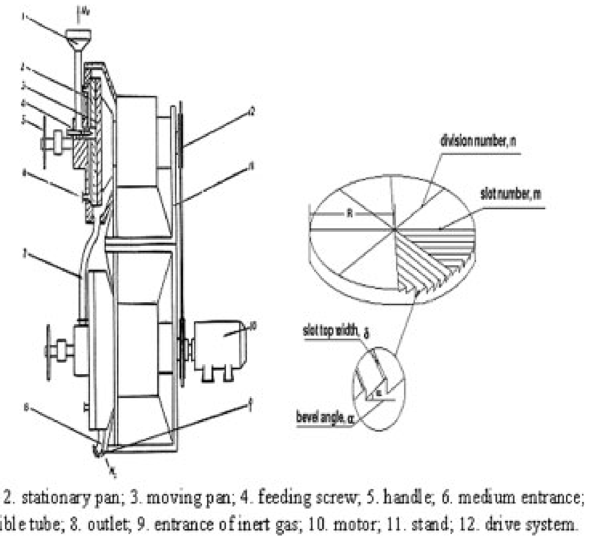


Figure 1 Schematic diagram of the pan-mill equipment.

round pans including a movable one and a stationary one placed together face to face. Every pan is divided into equal sectors by some diametrical lines and there are several bevels on each sector. The ridges of the bevels are parallel with the dividing lines and the ridges and bevels on both pans form many unit cells. The shape and volume of these unit cells are periodically changed with running of the movable pan. Correspondingly, the materials inbetween suffer from strong pressure and shear forces in circular and radial direction. The theoretical analysis[16–19] indicated that the action mechanism of pan-milling is like a pair of three-dimensional scissors. Based on this mode, pan-milling more easily pulverizes some ductile materials when compared with conventional pulverization equipment. Otherwise, a chain transmission system is set to regulate the rotation speed and the cooling water flowing through the hollow interior of the pan can take away the generated heat during pan-milling to maintain ambient temperature. During milling, the material particles are fed to the center of the pan from the inlet, driven by the shear force, and move along a spiral route toward edge of the pan till out from the outlet, thus one cycle of milling is finished (it takes about 30–60 s to finish one cycle).

Our investigations showed that through three-dimensional force field provided by pan-milling, HDPE can be effectively pulverized at ambient temperature. However, milling HDPE alone can only obtain fine powder with a limitation particle size of 70 μm and cannot satisfy ultrafine scale. To further improve the pulverizing efficiency, a grinding aid, sodium chloride (NaCl), was adopted to comill with HDPE. Due to the cutting effects of NaCl crystals, HDPE can be more finely pulverized, furthermore, as the results of the isolating effects of rigid NaCl particles, the adherence of interparticles of HDPE are weakened. Therefore, comilling with NaCl can greatly improve the pulverizing efficiency and prepare ultrafine HDPE powder. Another outstanding advantage of NaCl serving as grinding aid lies in its good solubility in water, thus water wash can easily remove it from hydrophobic HDPE powder after the milling to obtain pure HDPE ultrafine powder.

EXPERIMENTAL

Materials

HDPE, pellets with an average pellet diameter of 3–4 mm, was supplied by Du Shan Zi Petrochemical of China. NaCl was purchased from Chengdu Reagent of China.

Pan-milling to prepare HDPE fine (below 100 μm) powder

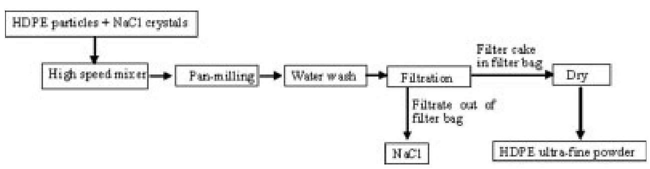
Original HDPE pellets were directly put into the running mill to be pulverized with different milling cycles (10–90 cycles), rotation speed (30–70 rpm) at ambient temperature (25°C).

Pan-milling to prepare HDPE ultrafine fine (below 10 μm) powder with NaCl serving as grinding aid

Original HDPE particles and NaCl crystals were mixed in a high speed mixer, and the obtained mixture were put into the running mill to be pulverized (milling cycles: 10–90 cycles, rotation speed: 30–70 rpm, milling temperature: 25°C). The comilled HDPE/NaCl mixture was placed in a filter bag and washed using water to remove the grinding aid. Then the purified HDPE ultrafine powder was dried to obtain the final product. The procedure is described in Scheme 1.

Characterization

The particle size of the HDPE powder was measured by a laser light scattering granulometer (Shimaduz 2001, Japan). The obtained HDPE powder was observed by a HITACHI X-650 scanning electron microscope (SEM).



Scheme 1 The procedure of pan-milling to prepare HDPE ultrafine powder, with NaCl serving as grinding aid.

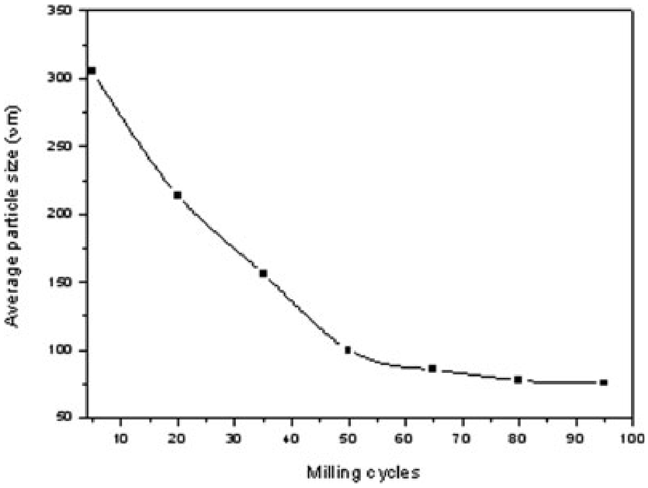


Figure 2 The influence of milling cycles on the average particle size of HDPE milled alone (rotation speed of the movable pan: 50 rpm).

RESULTS AND DISCUSSION

Pan-milling can effectively pulverize various polymers. In our previous investigations, some brittle polymers such as polypropylene (PP) and polystyrene were milled alone to prepare their ultrafine fine powder.[18,19] However, for some ductile polymers such as PE, the pulverization efficiency is still need to be improved.[20] Additionally, we also found that during comilling polymer/filler system to prepare their composite materials, the grinding aid effects of some fillers can remarkably accelerate the pulverization of polymers, thus obtaining much finer powder. For example, milling PP alone can only obtain micron scale particles, but comilling iron/PP can obtain nano scale ones.[21] Although these comilled systems were initially designed to prepare polymer-based composite materials by taking the advantages of good solid state blending and dispersing effects of pan-milling, they give us an illumination in preparing polymer ultrafine powder if we can conveniently remove those grinding aid fillers after comilling. In this article, we adopt pan-milling alone and comilling with easily removable grinding aid to prepare HDPE fine powder and ultrafine powder, respectively. It showed that the former can only obtain fine HDPE powder with the particle size below 100 μm, and the latter can obtain the ultrafine powder below 10 μm.

Pan-milling to prepare HDPE fine powder

Figure 2 is the curve of the particle size versus the milling cycles for HDPE milled alone. It can be seen that the particle size experienced prompt decrease in initial milling stage, and it reduced to below 100 μm after only 50 milling cycles. However, with further increase of the milling cycles, the pulverization efficiency obviously declined. When the number of the milling cycles was over 80, the obtained HDPE powder was close to a basically unchangeable limitation particle size (about 75 μm). The morphology observation also clearly reflected the decreasing process of the HDPE particle size, as shown in Figure 3. It

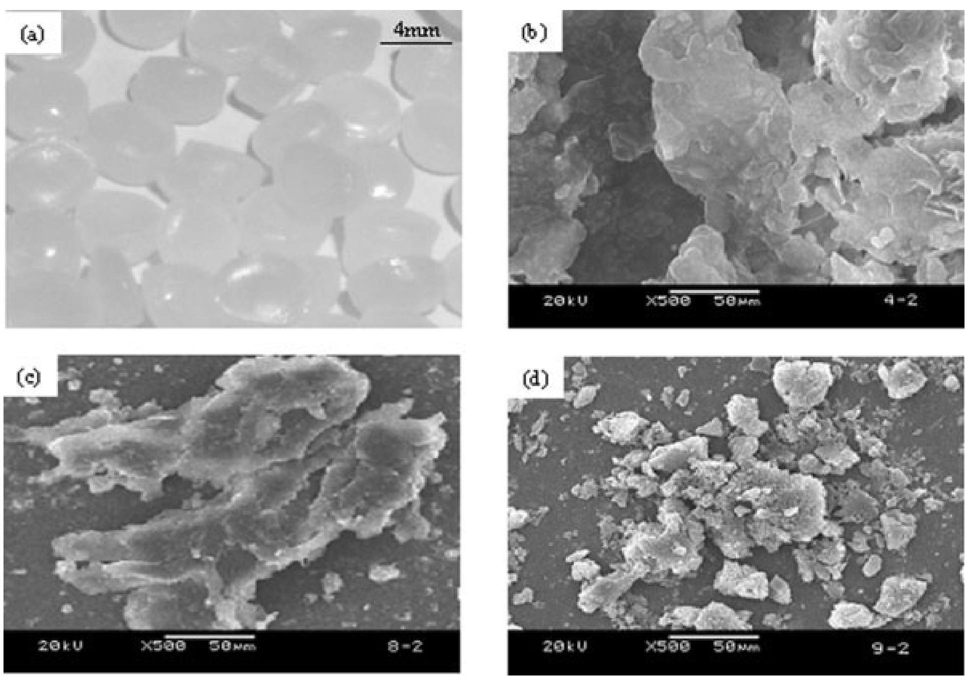


Figure 3 The morphology photographs of the HDPE powder milled alone: (a) original HDPE pellets, (b) 20, (c) 50, and (d) 80 milling cycles.

showed that original HDPE pellets were milled into sheets, and with increase of the milling cycles, the size of the sheets became smaller and smaller. Obviously, pan-mill equipment can effectively pulverize HDPE to obtain its fine powder.

The nature of the pulverization of materials is the breakage of the aggregation state of materials. This process is caused by high surface energy that is converted by imported mechanical energy, and therefore, pulverization takes place if surface energy accumulates high enough to overcome the cohesive energy of materials. For most inorganic materials, their atoms are located in crystal lattice and cannot freely move, thus leading to high rigidity and brittleness. However, polymer materials possess movable macromolecular chains, and show more elasticity and plasticity. During the pulverization of polymer materials, an amount of imported mechanical energy is converted into elastic potential energy through the extension and orientation of macromolecular chains. The elastic potential energy is consumed again through elastic recovery if only the relaxation time of macromolecular chains is long enough, thus greatly consuming the imported mechanical energy and decreasing the pulverization efficiency. On the other hand, the thermoplasticity of polymers makes those melting or softening particles easily adhere to each other, thus resulting in the conglomeration of pulverized polymer particles again. Accordingly, fine pulverization of those polymers with good macromolecular flexibility and low melt point (such as HDPE) is hard to be achieved.

The great difference in the pulverizing effects of pan-mill and traditional pulverization equipment is regarding with their different pulverization mechanisms. Traditional equipments such as vibromill, jet mill, etc., are mainly based on impact force that generates an instantaneous high load, however, such loading mode is discontinuous. The intermission of one and next impact load provides a relatively long relaxation time for macromolecular chains and leads to effective dissipation of the imported energy, thus disadvantageous to the pulverization of polymers. Different from the impact pulverization mechanism, pan-mill is mainly dependant on three-dimensional shear forces. As the shear forces are imposed on the materials in the whole milling process of the material particles along the spiral route, such continuous loading mode gives little relaxation time for the macromolecular chain, therefore, the continually increasing elastic deformation can quickly reach the limitation that macromolecular chains can endure and causes the rapid breakage of bulk materials. Except strong shear three-dimensional forces, low rotation speed of the pan is disadvantageous to the quick generation of the friction heat, which leads to the adherence of polymer particles surface. Based on the above pulverizing mechanism, pan-mill equipment shows outstanding advantage in pulverizing polymers with high ductility and low melt point like HDPE.

Pan-milling to prepare HDPE ultrafine powder with NaCl serving as grinding aid

Milling HDPE alone showed that the pan-mill equipment can effectively pulverize HDPE to fine powder with the particle size of 75 μm. However, it still cannot reach ultrafine scale below 10 μm. To further improve the pulverizing efficiency, comilling method is considered. It is well known that some grinding aids can accelerate the pulverization of materials, however, the selection of a proper grinding aid should satisfy the following two rules: (1) the grinding aid effects of the added filler should be good, and (2) the grinding aid filler itself is easily removed from HDPE powder after pan-milling. According to the rules, NaCl is chosen. As an ionic crystal, the combination of Na and Cl atoms through ionic bonds is very strong, which makes NaCl crystal its self possess high rigidity. Moreover, NaCl itself belongs to a cubical crystal and the pointedness of the crystal brim can effectively cut the HDPE particles. On the other hand, NaCl is a completely water-soluble compound, yet HDPE is a typical hydrophobic polymer, therefore the introduced grinding aid can be easily removed through dissolution in water and also conveniently recycled.

Figure 4 compares the particle size of the HDPE powder versus the milling cycles for HDPE milled alone and HDPE/NaCl comilled system. The latter showed much higher pulverizing efficiency than the

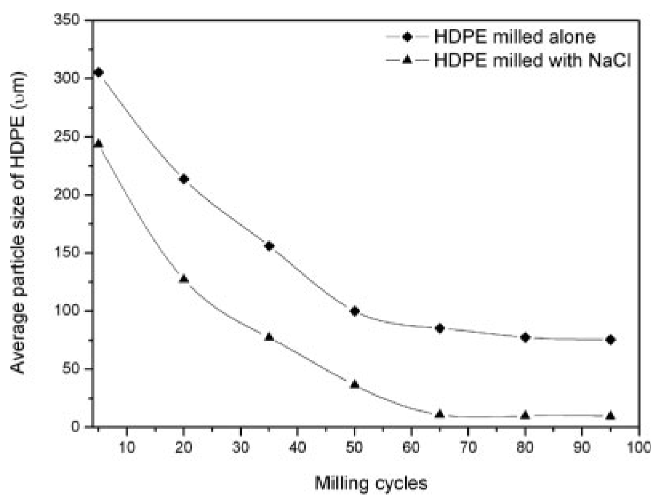


Figure 4 The curves of milling cycles versus average particle size of HDPE milled alone and milled with NaCl (NaCl content in comilled system: 50%; rotation speed of the pan: 50 rpm).

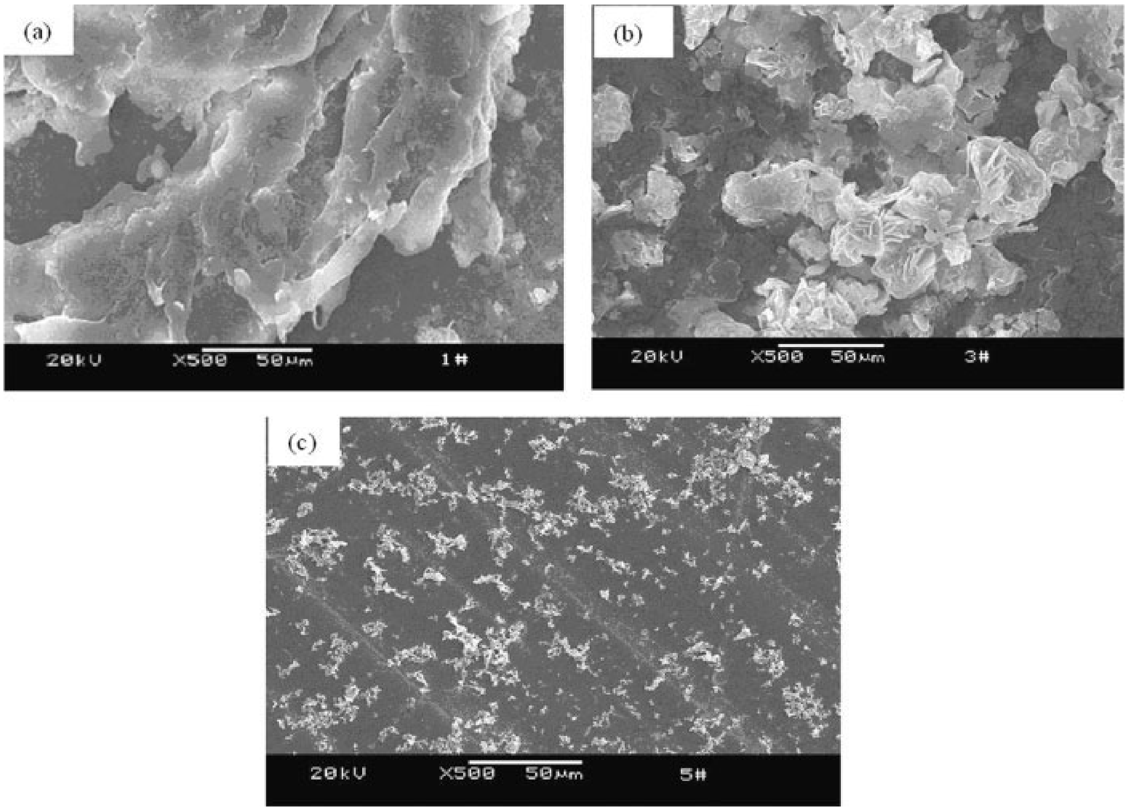


Figure 5 The morphology photographs of the HDPE powder milled with NaCl: (a) 20, (b) 50, and (c) 80 milling cycle.

former. It can be seen that after 80 milling cycles HDPE has been pulverized into 10.9-μm particles, and basically reached ultrafine scale. Over 80 milling cycles, the pulverization effects of comilled HDPE/NaCl system also reached a limitation (9.8 μm), much smaller than the limitation particle size (75.6 μm) of HDPE milled alone. This demonstrated that the introduction of NaCl effectively accelerated the pulverization of HDPE. Figure 5 is the SEM photographs of HDPE/NaCl system with different milling cycles. It can be seen that with increase of the milling cycles, the milled HDPE was tore into more and more smaller sheets. Compared with the photographs of HDPE particles milled alone, the particle size of the comilled system was obviously smaller with the same milling cycles.

To determine the optimum grinding aid content to prepare HDPE ultrafine powder, the relationship between NaCl content and the pulverization effects was investigated. From Figure 6, it can be seen that with increase of the NaCl content, the particle size showed rapid decline in the beginning. However, when over 50%, NaCl content seemed little influence on HDPE particle size. Accordingly, it was found that the effects of grinding aid also had a limitation, and excessive NaCl content cannot improve the pulverization efficiency any more, yet decreased productivity due to reducing the HDPE proportion.

We also investigated the rotation speed of the movable pan on the pulverizing effects as shown in Figure 7. It can be seen with increase of the rotation speed, the particle size of both the HDPE milled alone and HDPE/NaCl comilled system showed initial decline and subsequent increase, but the optimum rotation speed was different for the two systems.

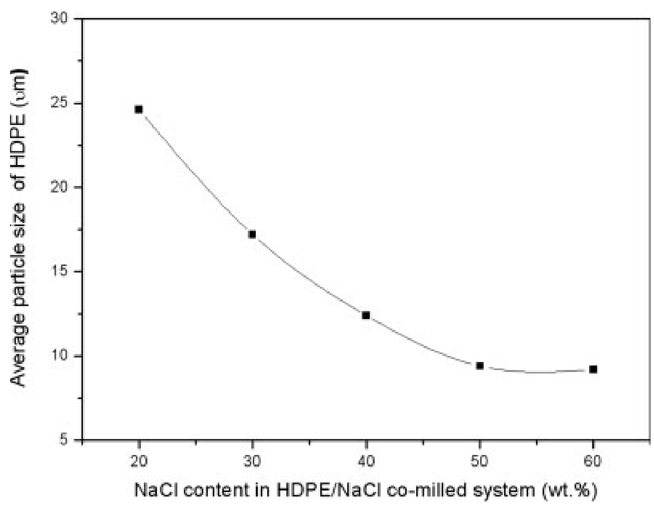


Figure 6 The influence of NaCl content on the average particle size of HDPE comilled with NaCl (rotation speed of the pan: 50 rpm; milling cycles: 80).

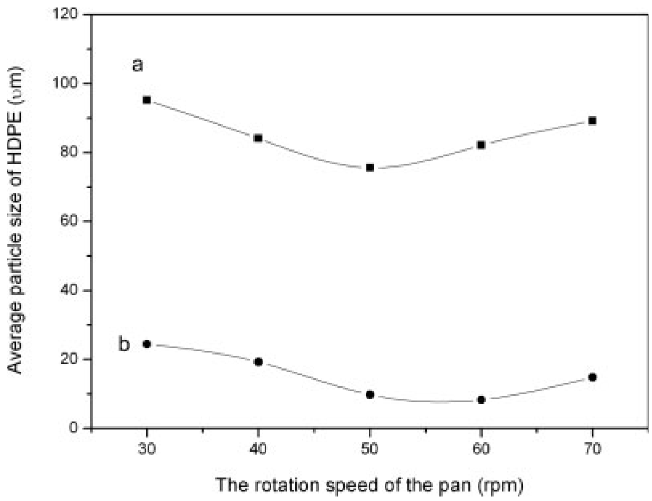


Figure 7 The curves of the rotation speed of the pan versus average particle size of (a) HDPE milled alone and (b) milled with NaCl (milling cycles: 80; NaCl content in comilled system: 50%).

Theoretically, the rotation speed of the pan has two sides influence on the pulverization. On one hand, a high rotation speed is advantageous to the enhancement of the loading frequency, which makes the stress relaxation more difficultly occur and promotes the breakage of materials. However, when the rotation speed is too high, the residence time of the materials in the pan-mill becomes shorter, moreover, more generated heat also accelerates the softening of the HDPE particles surface and interparticles adherence, thus decreasing the pulverization efficiency instead. As there was no grinding aid isolating the heated particles for the HDPE milled alone, the negative effects of the increasing rotation speed of the pan showed more obvious compared with the comilled system. Therefore, the particle size began to increase at 50 rpm for the former, however, 60 rpm for the latter.

CONCLUSIONS

Pan-mill based on three dimensional forces shows outstanding advantages in pulverizing polymer materials with high ductility and low melt point when compared with traditional pulverization equipment. Milling HDPE alone with enough cycles can obtain fine powder with an average particle size of 75.6 μm. Adopting easily removed water-soluble grinding aid, NaCl serving as grinding aid to comill with HDPE, can greatly improve the pulverization efficiency due to good cutting and isolating effects, and obtain ultrafine HDPE powder with an average size of 9.5 μm. The investigations also showed there was a limitation for the grinding aid effects, and when NaCl content was over 50%, the grinding aid effects were hardly improved. Additionally, the rotation speed of the pan had two side effects on the pulverization effects. Too low and too high rotation speed were disadvantageous to obtain ultrafine HDPE powder, and the optimum rotation speed was 60 and 50 rpm for HDPE/NaCl comilled system and HDPE milled alone, respectively.

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