# Effect of Solid-State Shear Milling on Structure and Properties of HDPE/UHMWPE Blends

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**ABSTRACT:** The structure and properties of HDPE/UHMWPE blends prepared through a pan-milling reactor in solid state at ambient temperature were compared with the blends made by melt mixing. The changes of structure and properties of the blends were investigated by FTIR, melt flow index, mechanical properties, dynamic rheological measurement, DSC, and WAXD. DSC measurement illustrated that after pan-milling treatment, the half-width of the melting temperature became smaller. The more content of UHMWPE added in the blend, the more evident change was observed. Combined with the dynamic rheological analysis, it was proved that, the pan-milling treatment can improve the compatibility of the HDPE/UHMWPE blends. X-ray diffraction analysis showed that after pan-milling treatment some ordered structure could be induced, but after heat treatment, the induced crystalline structure disappeared. The tensile properties of pan-milled HDPE/UHMWPE blends also achieved improvement after pan milling treatment. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39916.

## INTRODUCTION

Polyethylene (PE) is produced in many forms, each of which has different properties resulting from variations in structure. High-density PE (HDPE) is the most crystalline form, because the chains contain very little branching. UHMWPE is a simple super-molecular polymer that has been developed in recent decades. The outstanding properties of UHMWPE, such as toughness, high wear strength, and environment stress cracking resistance, provide not only new utility but also scientific interest.[1–3] For the poor flow of UHMWPE, it does not flow even when heated above its melting temperature. The blend of HDPE with UHMWPE is expected to combine excellent properties of UHMWPE while maintaining the processability of HDPE. But due to the viscosity mismatching, it is hard to get the homogeneous HDPE/UHMWPE blend.[4]

There are different techniques that have been reported in preparing UHMWPE blends. These include melt mixing, sequential loading, and coarse powder blending followed by compression molding solvent blending.[5–9] The solvent blending technique seems to provide good homogeneity in the incorporation of UHMWPE with the other polyethylenes, but is not efficient and environment-friendly. In melt mixing, the incomplete melting of UHMWPE was found to result in dispersed UHMWPE particles which greatly affect the final blend properties. Bosoletto

et al.[10] reported that UHMWPE was only partially dissolved in HDPE/UHMWPE blends during melt blending. Thus, an easy and environment friendly way is needed to be employed in preparing UHMWPE blends.

In recent years, it has been demonstrated that solid-state shear milling technology has many advantages over other conventional methods in plastic recycling and mixing of polymers and it has attracted a lot of interest.[11,12] In this study, we used a pan-mill equipment for solid-state shear milling. One of the distinct features of the pan-mill is that it can exert extremely strong shear forces on materials in-between because of its inlaid structure. In addition, the general moving path of materials in the pan-mill is spiral which increases residence time. Experiments have demonstrated that the pan-mill could be successfully applied to mix of polymers with very different viscosities. In this article, a stress field provided by pan-mill type reactor was introduced to HDPE/UHMWPE blends. The properties and structural of milled HDPE/UHMWPE blends were compared with the blends made by melt mixing.

## EXPERIMENTAL

### Materials
The material used in this study was HDPE with a melt index of 7.2 g/10 min (190°C, 2.16 kg). The HDPE, with the trademark

**Figure 1.** Digital camera picture of pan-mill type reactor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of DMDA8007, was supplied as pellets by Dow Chemical Industry Factory, and the UHMWPE was supplied as a powder by Beijing Second Subsidiary Additive Factory (Beijing, China), with an $M_w$ about 2500 kg/mol.

### Equipment

The main equipment used in this study was a pan-mill type reactor. The detailed external and inlaid structure was described in the previous articles.[12,13] Figure 1 is a digital camera picture of the pan-mill type reactor and Figure 2 shows the detailed structure of its key part, the milling pans. The equipment is composed by two pans. One is dynamic pan, driven by an electromotor, and the other one is static pan. The gap of between the two pans can be regulated by a transmission shaft. A chain transmission system was set to regulate the rotation speed of moving pan and a screw pressure system was imposed load, which can strictly control two major dynamic parameters of the milling, velocity and pressure. The heat generated during milling was taken away by cooling water circulation, so as to maintain the sample milling at ambient temperature, not elevated temperature.

### Sample Preparation

HDPE and UHMWPE were mixed together with UHMWPE composition (wt %) of 0, 10, 20, 30, and 40, respectively, and then milled through the pan-mill type reactor mentioned above. A cooling water system was added in so as to keep it running at ambient temperature. The materials were fed in the hopper set up at the center of the pan and discharged from the edge of the pan. The time of every milling cycle was 10 s. The milled HDPE/UHMWPE blends were collected by the

loading head and then fed into the hopper for the next milling cycle. The rotation rate of the movable pan was controlled at 30 r/min. The milled blends were recorded as M01, M02, and so on, and the number after letter M represented the milling cycle. For purpose of comparison, the HDPE/UHMWPE blends were also made by melt mixing in a Haake Torque Rheometer at 190°C for 10 min with the UHMWPE compositions (wt %) of 0, 10, 20, 30, and 40 which were named HU0, HU10, HU20, HU30, and HU40, respectively. In the preparation of all the melt mixing blends, the polymers were stabilized by addition of 0.5 wt % antioxidant to prevent thermal-oxidative degradation.

### Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The sample for FTIR analysis was prepared as follows: 2 mg powder obtained by treating HDPE/UHMWPE pellet with different cycles was mixed with 200–300 mg KBr. The required disc with a diameter of 1 cm was then obtained in a standard mold under a pressure of 4 MPa. The testing sample was dried before disc preparation and was subjected to FTIR analysis immediately afterwards. FTIR spectra were recorded on a Nicolet 560 spectrometer, the sample was scanned 32 times from 4000 to 400 $cm^{-1}$ with a resolution of 2 $cm^{-1}$.

### Melt Flow Index Measurement

The melt flow index of HDPE/UHMWPE blends was characterized with CS-127 melt flow rate meter. The charging barrel is with the diameter of 9.55 mm, the length of 8 mm, and the die diameter of 2.1 mm. The measurement condition is temperature $190 \pm 0.2°C$ and weight: 2.16 kg.

### Mechanical Properties

One millimeter thick samples of the milled blends were compression-molded in an electrically heated hydraulic press. Hot-press procedures involved preheating at 180°C for 5 min, followed by compression for 5 min at the same temperature and at a pressure of 10 MPa and subsequent cooling under pressure for 5 min. The samples were made into dumbbell specimens, and their mechanical properties were tested at room temperature in accordance with ASTM D 412 with an Instron Universal Testing Machine (Model 5567, Instron Corporation,
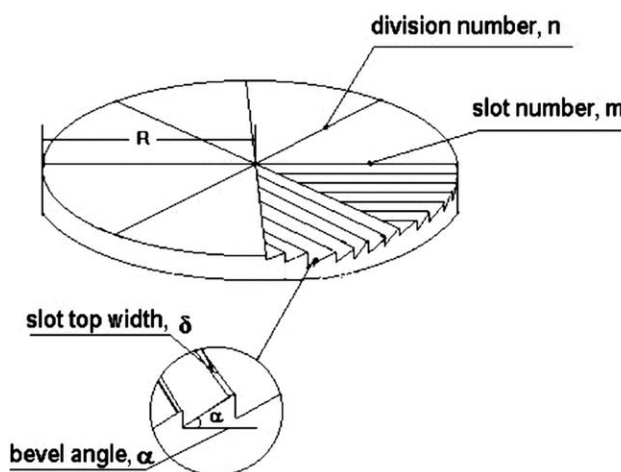


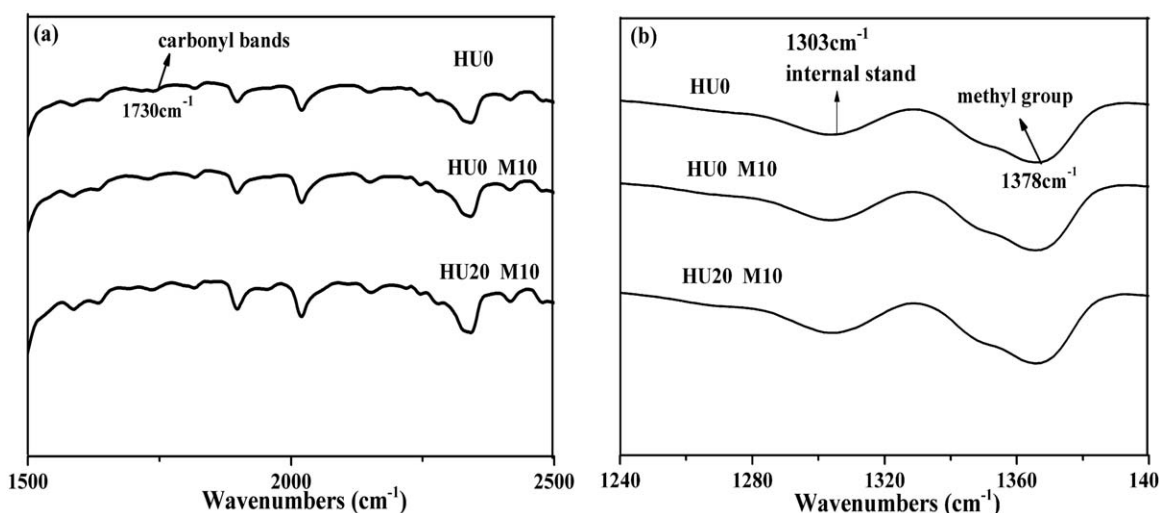**Figure 2.** Schematic diagram of inlaid milling pan.

**Figure 3.** FTIR spectra of the HDPE/UHMWPE blends that after pan-milling treatment.

Canton, MA) at a crosshead speed of 100 mm/min. The data were averaged over five specimens.

### Differential Scanning Calorimetry

DSC measurement was performed with a DSC204 equipment (Netzsch Com., Germany), fitted with a cooling system using liquid nitrogen and protect gas with nitrogen at a flow of 50 mL/min. The sample was first operated from ambient temperature to 180°C at a heating rate of 10°C/min, and was fixed at the temperature for about 5 min in order to eliminate heat history. The sample was then cooled down from 180°C to 30°C at a cooling rate of 10°C/min. Then the sample was heated from 30°C to 180°C again at the same heating rate, and the thermal trace was recorded for the analysis. The crystal weight fraction $X_c$, was assessed from the ratio of the melting enthalpy of the materials to that of a perfect PE crystal ($\Delta H_m = 289$ J/g).

### Wide-Angle X-ray Diffraction (WAXD) Analysis

The powder sample that after solid-state shear milling was compacted into a square groove of the slide, and then the surface was strike off for measurement. In addition, the powder sample that after heat treatment (180°C for 5 min) were also used for measurement. WAXD measurements were performed with a Philips analytical X'Pert X-diffractometer (Cu $K\alpha$ radiation, tube voltage = 40 kV, and tube current = 40 mA). WAXD data were collected from $2\theta = 5$–$50°$ with a step interval of 0.02°. The degree of crystallinity was obtained by resolution of the XRD patterns for the range $5° <$ Diffraction angle $< 50°$ into the diffraction area relative to the crystalline peaks ($I_c$) and relative to the amorphous halo ($I_a$). $X_c = I_c/(I_c + I_a) \times 100\%$.

### Dynamic Rheological Measurements

Dynamic rheological measurements were carried out in a Gemini 200 (Bohlin Instruments, UK) stress-controlled rheometer in constant-strain mode. The diameter of the plate was 25 mm, and the gap was about 1 mm. All of the samples were tested in the frequency range from 0.01 to 100 Hz at 190°C. To keep the response in the linear viscoelastic region, the applied strain was controlled at 1%. The thermal stability of the samples during rheological testing was checked by a time sweep and all of the tests were completed within 10 min.

## RESULTS AND DISCUSSION

### FTIR Analysis

In our experiment, the whole processing was operated in an open air circumstance, which always accompanied with the introduction of polar groups onto polymer chains. The FTIR analysis was measured to confirm whether any new functional group was produced during the pan-milling treatment. Figure 3 is the FTIR spectrum of HU0, HU0 M10, and HU20 M10. The absorbance curve labeled HU0 is for the HDPE. It is a typical FTIR spectrum of PE. From Figure 3(a), no new absorption peak appeared, illustrating that there is no carbonyl group generated during the pan-milling treatment and the oxidation has not took place during pan-milling.

Relative branching content can be determined by the content of polyethylene end group, which is methyl group.[14,15] In the infrared spectrum of polyethylene, the absorption peak situated at 1378 cm$^{-1}$ belongs to vibrational absorption of methyl group, the peak 1303 cm$^{-1}$ was used as the internal stand. As was shown in Figure 3(b) the intensity of this corresponding absorption peak did not changed during pan-milling treatment which showed that no branch was formed during pan-milling treatment.

### Effect of Pan-Milling on Melt Flow Index of HDPE/UHMWPE Blends

Figure 4 exhibits the melt flow index of HDPE/UHMWPE blends before and after pan-milling treatment. The melt flow index of HDPE/UHMWPE blends increased as a function of pan-milling cycle. After 10 milling cycles, the melt flow index of the blends kept stable. When an external force (solid shear stress) is exerted on the covalent bonds of polymer chains, they will deform and even to breakdown if the external energy is beyond the covalent bond energy. It is well known that break point of molecular chain is probably in the middle part. The possible reactions can be expressed as follows[16]:
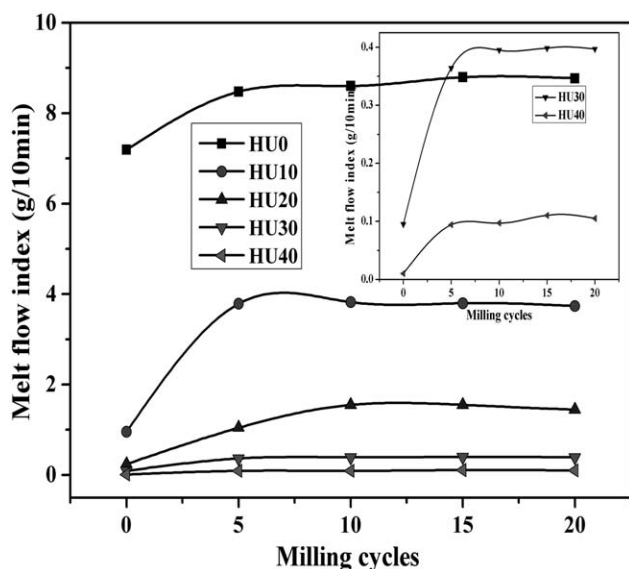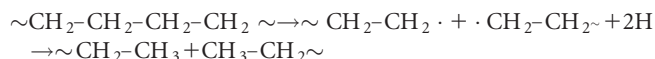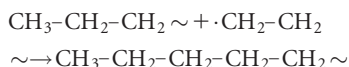
**Figure 4.** Effect of Pan-milling on melt flow index of HDPE/UHMWPE blends (190°C, 2.16 kg).

1. Direct chain scission:

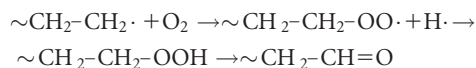$$\sim CH_2–CH_2–CH_2–CH_2 \sim \rightarrow \sim CH_2–CH_2 \cdot + \cdot CH_2–CH_{2\sim} + 2H$$
$$\rightarrow \sim CH_2–CH_3 + CH_3–CH_2 \sim$$

2. Formation of new chain:

$$CH_3–CH_2–CH_2 \sim + \cdot CH_2–CH_2$$
$$\sim \rightarrow CH_3–CH_2–CH_2–CH_2–CH_2 \sim$$

3. Formation of long chain branches:

$$\sim CH_2–CH_2–CH_2 \sim \rightarrow \sim CH_2–CH \cdot \text{-} CH_2 \sim CH_2–CH_2 \sim \rightarrow$$
$$\sim CH_2 \cdot \sim CH_2–CH \cdot \sim CH_2\text{-} + \sim CH_2 \cdot \rightarrow$$
$$\sim CH_2–CH(CH_2\sim)\text{-}CH_2 \sim$$

4. Oxidation:

$$\sim CH_2–CH_2 \cdot + O_2 \rightarrow \sim CH_2–CH_2–OO \cdot + H \cdot \rightarrow$$
$$\sim CH_2–CH_2–OOH \rightarrow \sim CH_2–CH{=}O$$
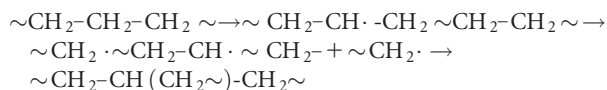
Combined with the above analysis, the formation of new chain and direct chain scission took the major role via the solid shear milling.

### Effect of Milling on Dynamic Rheological Behavior of HDPE/UHMWPE Blends

The dependence of elastic modulus ($G'$) on the frequency at 200°C for the HDPE/UHMWPE blends with different pan-milling cycles is shown in Figure 5. $G'$ means the elastic behavior of the material and can be viewed as a reflection of the entropic elasticity of the polymer chains. The UHMWPE fraction and molecular weight play an important role in the elasticity. The larger the molecular weight is, the higher $G'$ will be, because of the reduced motion of polymer chains. From Figure 5, we can see that although the blends after pan-milling had low molecular weight, at low frequencies its elastic modulus was large. The changes of $G'$ at low frequencies are related to the constraint effect produced by UHMWPE chain entanglements.[17] Therefore, it can be concluded that the UHMWPE constraint effect in milled blends was greater than that in the melting samples. This means that for the milled samples more UHMWPE chains can diffuse into the HDPE matrix than for the melt mixing samples, i.e., the pan-milling treatment can improve the compatibility of the blends.

### Effect of Milling on Crystalline Structure of HDPE/UHMWPE Blends

Figure 6 is the results of WAXD spectra of HU20 blends before and after pan-milling treatment (powder sample: directly from the milled sample). PE belonged to orthorhombic system, after pan-milling treatment, new peak at $2\theta = 19.5°$ appeared, which represented monoclinic system. Furthermore, the diffraction
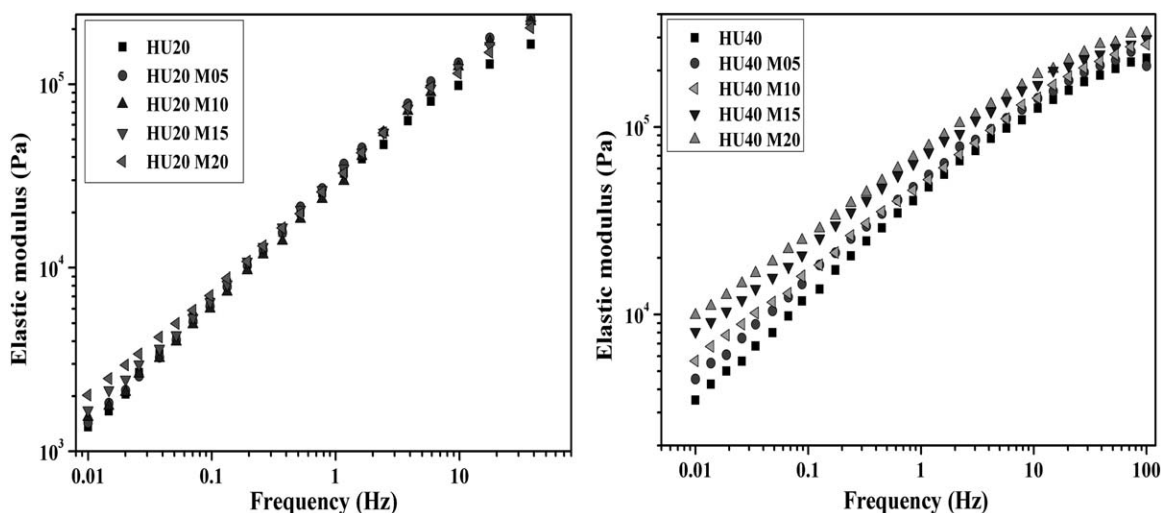


**Figure 5.** Elastic modulus curves plotted against frequency at 200°C for the HDPE/UHMWPE blends with different pan-milling cycles.
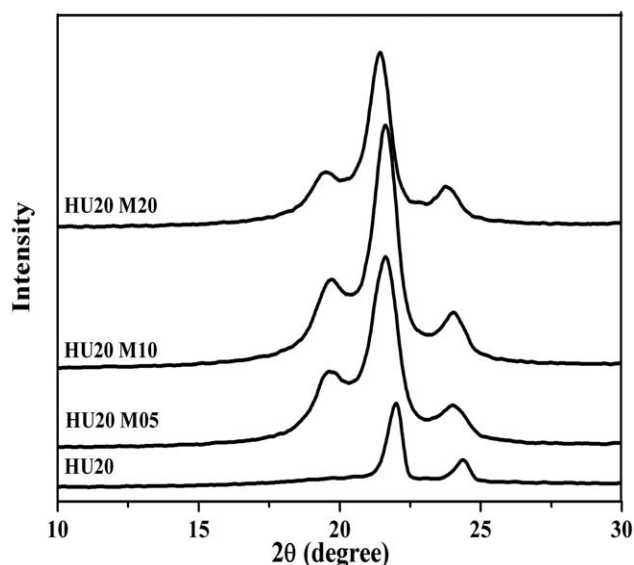
**Figure 6.** X-ray diffraction graph of HU20 that after pan-milling treatment.

**Table I.** Crystalline Size and Crystallinity of HDPE/UHMWPE Blends Before and After Pan-Milling Treatment

| Samples | $L_{110}$[a] (nm) | $L_{200}$[b] (nm) | $L_{001}$[c] (nm) | Crystallinity (%) |
|---|---|---|---|---|
| HU20 M00 | 14.8 | 14.2 | – | 45 |
| HU20 M05 | 8.5 | 7.5 | 6.7 | 56.1 |
| HU20 M10 | 9.3 | 9.0 | 7.7 | 49.9 |
| HU20 M20 | 10.1 | 9.6 | 8.4 | 49.1 |
| HU20 M10[d] | 14.6 | 13.8 | – | 45.9 |

[a] Lattice plane index (110) reflections.
[b] Lattice plane index (200) reflections.
[c] Lattice plane index (001) reflections.
[d] Heat treated.

intensity of the monoclinic system increased and then decreased with treating cycle.

In Figure 7, the new peak at $2\theta = 19.5°$ which represented monoclinic system disappeared after heat treatment (180°C for 5 min) for the sample HU20 M10. This result showed that the crystalline structure induced by solid-state stress was an unsteady metastable system.

The crystalline grain size of the blends could be calculated by Scherrer formula:

$$L_{hkl} = \frac{k\lambda}{\beta\cos\theta}$$

where $L_{hkl}$ designates the crystalline grain size of $hkl$ crystal face; $\lambda$ is the wavelength of incident X-ray; $\theta$ is the Bragg angle; $\beta$ is the width of the diffraction peak, and expressed as radian; $k$ is Scherrer form factor, and $k = 0.89$.

WAXD results of the powder sample (directly from the milled sample) were listed in Table I. The data illustrated that with the increase of treatment cycle, the crystallinity increased. Shear stress may result in crystal form transformation (orthorhombic form to monoclinic form) as reported in the literature.[18] However, this could not explain the experimental results that the total crystallinity of the blends after milling was even higher than the initial crystallinity of the blends without milling. The reason for the increase of crystallinity may be explained by the following proposed mechanism: in addition to the crystal form transformation from orthorhombic to monoclinic, a part of the short-range orderly structure in amorphous phase may be transformed into monoclinic crystal phase during pan-milling.

WAXD results of the heat treated sample (180°C for 5min) were listed in Table II. The data illustrated that after 10 cycles of pan-milling, the crystallinity of milled HDPE/UHMWPE blends increased slightly. This may due to the fact that the non-crystalline molecular chain would transform to ordered crystalline structure. After pan-milling treatment, the compatibility of the HDPE and UHMWPE components increased and the UHMWPE polymer chains can inhibit the HDPE from folding into growing crystal lamellae. Consequently, the crystalline grain size decreased as observed for the milled sample.
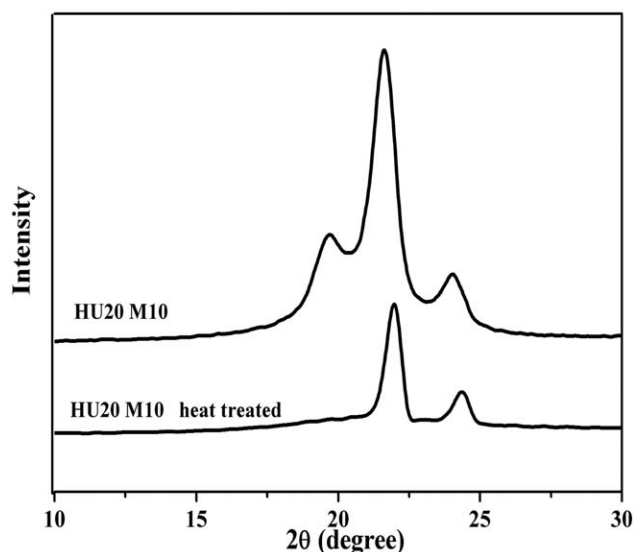


**Figure 7.** X-ray diffraction graph of HU20 M10 after heat treatment.

**Table II.** Crystalline Size and Crystallinity of HDPE/UHMWPE Blends Before and After Pan-Milling Treatment (Heat Treated)

| Samples | $L_{110}$[a] (nm) | $L_{200}$[b] (nm) | Crystallinity (%) |
|---|---|---|---|
| HU20 M00 | 14.8 | 14.2 | 45 |
| HU20 M10 | 14.6 | 13.8 | 45.9 |
| HU40 M00 | 15.9 | 15.3 | 41.3 |
| HU40 M10 | 15.6 | 15.2 | 42.1 |

[a] Lattice plane index (110) reflections.
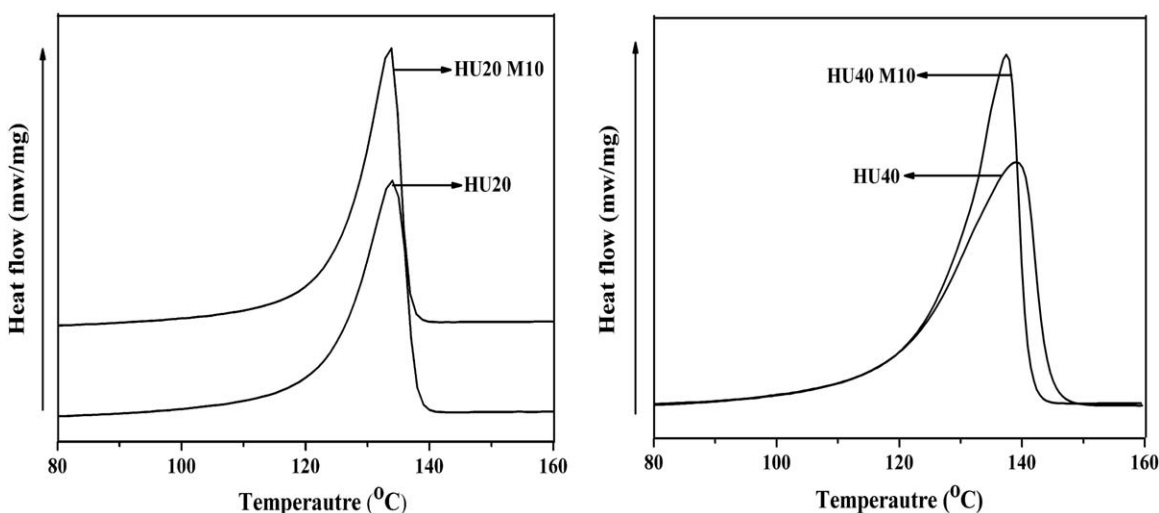[b] Lattice plane index (200) reflections.

**Figure 8.** Melting curves of pan-milled HDPE/UHMWPE blends.

## DSC Analysis of Pan-Milled HDPE/UHMWPE Blends

The melting curves of HDPE/UHMWPE blends before and after pan-milling treatment were indicated in Figure 8. In HDPE/UHMWPE system, only a single peak appears in the blends since the peaks of HDPE and UHMWPE are in close proximity. In such cases, the analysis on the melting temperature is inadequate for analysis the miscibility of the blends. Another parameter which may be sensitive to such situations is the half-width of the melting peak. Since the melting temperature of UHMWPE was some higher than that of the melting temperature of HDPE, one can expect to have a larger half-width if the two components form separate crystals. As was shown in Table III, the half-width of the melt mixing HDPE/UHMWPE blends increased with increasing UHMWPE content, which implies that separate crystals may be formed in HDPE/UHMWPE blends. But after pan-milling treatment, the half-width became smaller. The more content of UHMWPE added in the blend, the more evident change was observed. This indicated that the pan-milling treatment can improve the compatibility of the blends and the UHMWPE melting peak merged into the HDPE peak and the half-width and the melting temperature became smaller.

The analyzed DSC data were listed in Table III. As shown in Table III, the melting peak area of pan-milled samples was a little larger than that of un-milled samples. For the milled HU20 and HU40 blends, the crystallinity was increased, indicating the trend of the change agreed with the WAXD data well.

## Mechanical Properties of HDPE/UHMWPE Blends After Pan Milling

In general, the mechanical properties of polymer can be roughly classified into two categories: strength and toughness. Tensile strength can be considered as the material strength while tensile toughness such as elongation at break or impact strength is the material toughness. Generally, modification of a polymeric material seldom results in the improvement of strength and toughness simultaneously.[19–21]

It was well known that the yield stress exhibited a relationship to the crystallinity. Figure 9 gave the yield stress of the blends
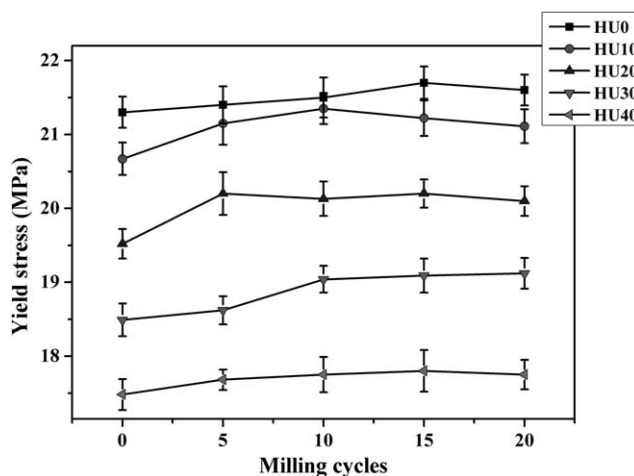
**Table III.** DSC Data of LDPE/UHMWPE Blends Before and After Pan-Milling Treatment

| Samples | Half-width of the melting temperature (°C) | Crystallinity $X_c$ (%) |
|---------|---------------------------------------------|-------------------------|
| HU20 M00 | 11.5 | 68.9 |
| HU20 M10 | 9.9 | 69.8 |
| HU40 M00 | 17.7 | 62.1 |
| HU40 M10 | 12.2 | 62.9 |
| HDPE | 10.1 | 78.3 |
| UHMWPE | 12.3 | 51.5 |



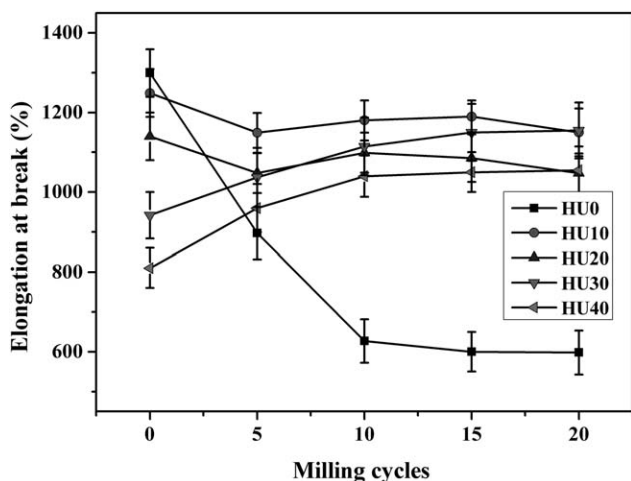**Figure 9.** Effect of Pan-milling on yield stress of HDPE/UHMWPE blends.

**Figure 10.** Effect of Pan-milling on of elongation at break HDPE/UHMWPE blends.

versus the milling cycles. As shown in Figure 8, after pan-milling treatment the yield stress slightly increased which is consistent with the variation of the crystallinity.

The effects of the milling cycles on the elongation at break and tensile strength of HDPE/UHMWPE blends were shown in Figures 10 and 11, respectively. The tensile strength and elongation at break increased with the cycles of pan milling, and the more content of UHMWPE led to more enhancements. For the sample HU0, the chain scission (reduce in the melt flow index) may the major factor that cause the elongation at break decreased significantly with mixing cycles. But for the sample HU40, after 10 cycles of milling, the tensile strength increased from 25.7 to 33.5 MPa, and the elongation at break increased from 810% to 1040%, about 1.30 times and 1.28 times of those of the melt mixing blends, respectively. However, further milling seemed to have little effect on the improvement of the mechanical properties after 10 cycles of milling.
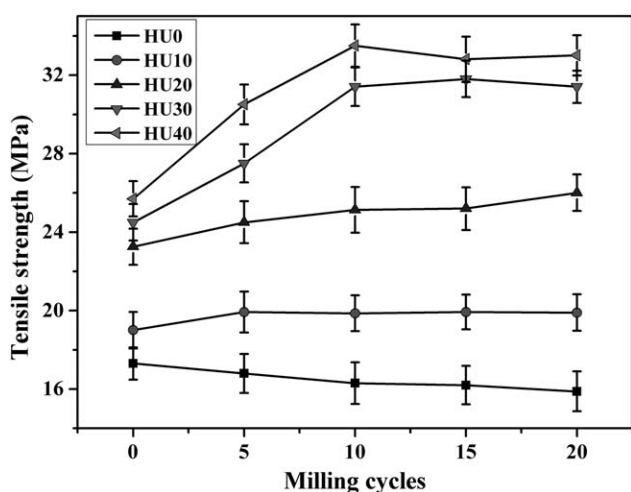


**Figure 11.** Effect of Pan-milling on tensile stress of HDPE/UHMWPE blends.

## CONCLUSIONS

HDPE/UHMWPE blends were prepared via solid-state shear milling and the structure and properties were compared with the melt mixing blends. After pan-milling treatment some ordered structure could be induced under the stress, but after the melting processing, the induced crystalline structure disappeared. The half-width of the melt mixing HDPE/UHMWPE blends increased with increasing UHMWPE content, which implies that separate crystals may be formed in HDPE/UHMWPE blends. But after pan-milling treatment, the half-width became smaller. The more content of UHMWPE added in the blend, the more evident change was observed. Combined with the dynamic rheological analysis, the pan-milling treatment can increase the compatibility of the blends. Furthermore, the pan-milling treatment can also simultaneously improve the strength and elongation at break of HDPE/UHMWPE blends.

In a word, pan-milling treatment is an efficient, clean, and environment-friendly method for preparing HDPE/UHMWPE blends, which can improve the compatibility and tensile properties.

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