

Structure and Tensile Properties Change of LDPE/UHMWPE Blends via Solid State Shear Milling

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ABSTRACT: LDPE/ultrahigh molecular weight polyethylene (UHMWPE) blends were prepared through a pan-milling reactor in solid state at ambient temperature. The changes of structure and properties of LDPE/UHMWPE blends were investigated by melt flow index, mechanical properties, scanning electronic microscope (SEM), differential scanning calorimetry (DSC), and wide-angle X-ray diffraction. SEM photos showed that after pan-milling treatment the dispersed approximately equiaxed UHMWPE particle became rodlike. DSC measurement illustrated that after pan-milling treatment, the peaks of UHMWPE shift to lower temperatures while the peaks of LDPE kept stable. The more content of UHMWPE led to more evident shift. X-ray diffraction analysis showed that the crystallinity of milled LDPE/UHMWPE blends decreased lightly, but the crystalline grain size decreased only for high content UHMWPE blends. The tensile properties of pan-milled LDPE/UHMWPE blends also achieved significant improvement after pan milling treatment. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2487–2493, 2013

KEYWORDS: blends; morphology; phase behavior; polyolefins; properties and characterization

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INTRODUCTION

>Ultrahigh molecular weight polyethylene (UHMWPE) is one of the leading plastics that have been developed in recent decades. The outstanding properties of UHMWPE, such as toughness, high wear strength, and abrasion resistance, provide not only new utility but also scientific interest.^{1–3} Study on blends of UHMWPE with conventional polyolefins is of continued interest. It has been well documented that a number of physical properties and process-ability of polyolefins can be improved by blending.^{4,5} One of the most important developments in the field of polyolefin design in recent years is the production of polyolefin with a bimodal molecular weight distribution. Mainly produced by operating two polymerization reactors under different conditions in series, this material is a polymer blend consisting of two fractions with average weights that differ significantly. The potential danger of in-homogeneities within the material even in case of an identical chemical composition of both high and low molecular weight fractions had been reported.⁵ Furthermore, it has been established that polyolefin–polyolefin blends show almost no synergetic effect. The final mechanical properties of these blends are usually intermediate between the parent polymers, and are also affected by processing.⁶

Because of the poor flow of UHMWPE, there are different techniques that have been employed in preparing UHMWPE blends.

These include melt mixing, sequential loading, coarse powder blending followed by compression molding solvent blending and shear controlled orientation injection molding. The advantages and disadvantages have been discussed in other reports.^{6–10} 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. Kyu and Vadhar⁸ have reported that cocrystallization takes place in the blends of UHMWPE/HDPE blends. However, separate crystals are formed in UHMWPE/LDPE blends.¹¹ Thus, a simple and effective way is needed to be employed in preparing UHMWPE blends.

The research and development of the solid-state shear pulverization technology has grown significantly since 1990 from the development of a new plastics recycling process to a much broader polymer processing method that allows intimate mixing of polymers with very different viscosities, solid-state dispersion of additives, including pigments, and continuous production of powder with unique shapes and large surface areas.¹² Because of the unique structure of the solid-state shear milling equipment, it acts as three-dimensional scissors during milling, exerting very strong shear forces on the materials in between, and showing a multifunction such as pulverization, dispersion, mixing as

Table I. Characteristics of the Polyethylene Studied

Sample	Density (g/cm ³)	Melt index ^a (g/10 min)	Mw (g/mol)
LDPE 2210H	0.919	1.8	8.2e4
UHMWPE	0.937	Not measurable ^b	2.5e6

^aUnder the condition 190°C, 2.16 kg, ^bClose to zero that hard to measure.

well as activation. In this paper, a stress field provided by pan-mill type reactor was introduced to LDPE/UHMWPE blends. The properties and structural changes of milled LDPE/UHMWPE blends were investigated simultaneously.

EXPERIMENTAL

Materials

The materials used in this article were LDPE with the trademark of 2210H was supplied as pellets by Lanzhou Petrochemical Corporation China; UHMWPE was supplied as a powder type by Beijing Second Subsidiary Additive Factory. All the molecular and physical parameters are listed in Table I.

Equipment

The main equipment used in this work was a pan-mill type reactor. The detailed external and inlaid structure was described in the previous papers^{13,14}. 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



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.]

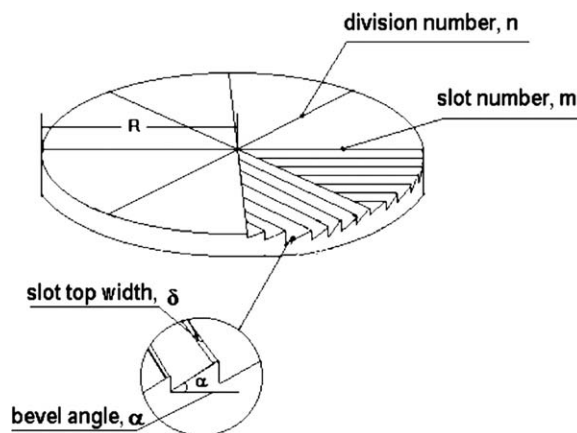


Figure 2. Schematic diagram of inlaid milling pan.

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

LDPE and UHMWPE were mixed together with UHMWPE composition (weight percentage) 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 setup 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 LDPE/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 mPE was recorded as M00, M01, M02 et al, and the number after letter M represented the milling cycle. For purpose of comparison, the pure LDPE/UHMWPE blends were also made by melt mixing in a Haake Torque Rheometer at 190°C for 10 min, and were named LU0, LU10, LU20, LU30, and LU40, respectively.

Melt Flow Index Measurement

The melt flow index of LDPE/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 ± 0.2°C, weight: 2.16 kg.

Scanning Electronic Microscope

Morphology of LDPE/UHMWPE blends before and after pan-milling treatment were observed with a scanning electron microscope (SEM) (JSM-5900LV, Japan). The samples were cryogenically fractured in liquid nitrogen, and then all the surfaces were gold-coated to enhance image resolution and to avoid

electrostatic charging. SEM was operated at an accelerating voltage of 5 kV.

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

Differential Scanning Calorimetry

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 Analysis

One millimeter thick samples of the milled blends were compression-molded in an electrically heated hydraulic press and then Wide-angle X-ray diffraction (WAXD) measurements were performed with a Philips analytical X'Pert X-diffractometer (Cu K α radiation, tube voltage = 40 kV, and tube current = 40 mA). WAXD data were collected from $2\theta = 5^\circ$ to 50° with a step interval of 0.02° . The degree of crystallinity was obtained by resolution of the XRD patterns for the range $5^\circ <$ diffraction angle $< 50^\circ$ into the diffraction area relative to the crystalline peaks (I_c) and relative to the amorphous halo (I_a). $X_c = I_c / (I_c + I_a) * 100\%$.

RESULTS AND DISCUSSION

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

Figure 3 exhibits the melt flow index of LDPE/UHMWPE blends before and after pan-milling treatment. The melt flow index of LDPE/UHMWPE blends increased as a function of pan-milling cycle. After 10 milling cycles, the melt flow index of the blends kept stable and was almost twice more than that of original blends. The MFI results showed that pan-milling treatment can activate the molecular chain of PE and the melt flow rate can be enhanced effectively. In general, mechanical properties go in a direction opposite to processibility. Thus the challenge in material engineering is to combine good properties with acceptable processing conditions.

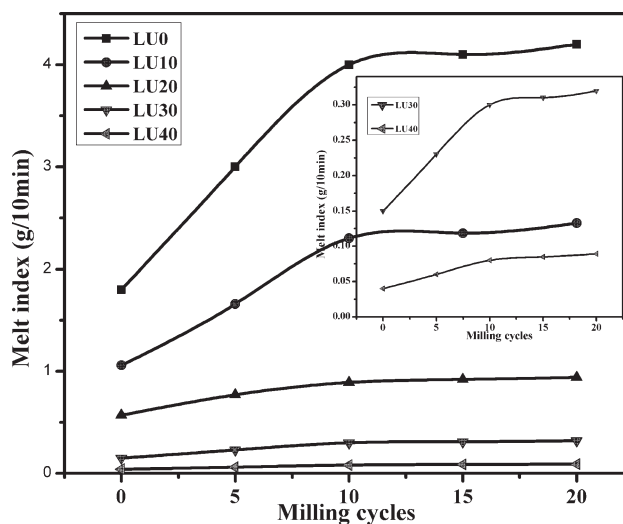


Figure 3. Effect of Pan-milling on melt flow index of LDPE/UHMWPE blends.

Morphology Analysis

It is believed that the interaction between two phases is one of the key factors deciding the degree of dispersion. There is a little change in the morphology for the sample LU10 after pan-milling treatment as was shown in Figure 4(a,b) due to the low content of the dispersion phase. Thus the mechanical properties of LU10 may be affected little by pan-milling treatment. But, as shown in Figure 5(a), the melt mixing LDPE/UHMWPE blend (LU40) exhibited very big approximately equiaxed domains, which may be formed by UHMWPE, and were nonuniformly distributed throughout the whole system, resulting from the high interfacial tension and weak adhesion between LDPE and UHMWPE. Generally speaking, an effective compatibilizer endows polymer blend with finer phase domain size, larger interfacial contact area, and stronger interfacial adhesion.¹⁵ As expected, pan-milling treatment resulted in decreasing and much more homogeneous size of the dispersed UHMWPE particles. The dispersed particles changed to rod-like shape in the mean time and the extent is enhanced with the content of UHMWPE. On the other hand, the treatment also makes the boundary between LDPE and UHMWPE phases much dimmer. The fractured surface of LU40 M10 became rougher and the trace of plastic deformation appears [Figure 5(b)]. Many rod-like UHMWPE particles were dispersed in the matrix and the particle size was decreasing obviously. These demonstrated the decrease of interfacial tension and strengthening of the interfacial adhesion between LDPE and UHMWPE, which is beneficial to the improvement of the mechanical properties of the blends.

Effect of Milling on Crystalline Structure of LDPE/UHMWPE Blends

WAXD results were listed in Table II. The data illustrated that after 10 cycles of pan-milling, the crystallinity of milled LDPE/UHMWPE blends decreased slightly. Under pan-milling stress, a part of crystals may be destroyed into amorphous phase, resulting in the decrease of crystallinity. Shear stress may also result in crystal form transformation (orthorhombic form to monoclinic form) as reported in the literature,¹⁶ but the crystalline

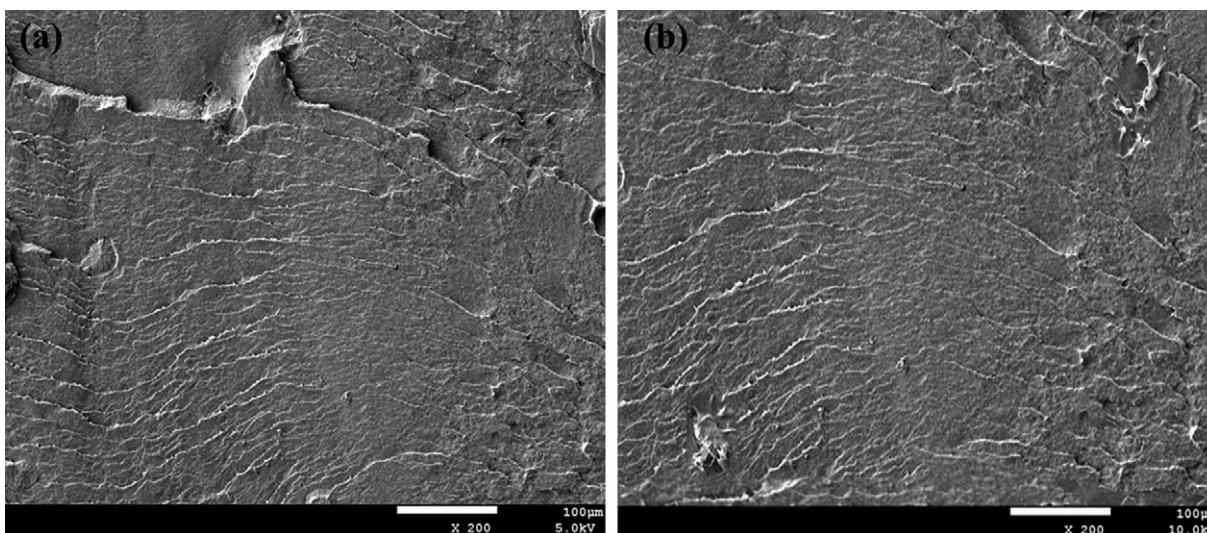


Figure 4. SEM photos of unmilled LU10 (a) and pan-milled LU10 (b).

structure induced by solid-state stress was an unsteady metastable system, the monoclinic system induced by stress disappeared after heat treatment.

The crystalline grain size of LDPE/UHMWPE blends could be calculated by Scherrer formula:

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

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

The crystalline grain sizes of the milled LDPE/UHMWPE were also listed in Table II. After pan-milling treatment, the compatibility of the LDPE and UHMWPE components increased and the size of dispersed phases become smaller, resulting in larger interface areas and stronger interfacial adhesion that inhibit the

polyethylene chains from folding into growing crystal lamellae. Consequently, the crystalline grain size decreased as observed for LU40 M10 sample. But for the sample LU0 M10 and LU10 M10, the crystalline grain size changed a little, this may be because of the low content of UHMWPE.

DSC Analysis of Pan-Milled LDPE/UHMWPE Blends

The melting and crystallization curves of LDPE/UHMWPE before and after pan-milling treatment were indicated in Figures 6 and 7, respectively. Blends of LDPE/UHMWPE show two or three endothermic peaks. An intermediate peak between the UHMWPE and the LDPE peaks has been associated with the fusion of a co-crystal, formed from linear and branched polyethylenes. Figure 7 also shows that the crystallization temperature of both LDPE and UHMWPE are depressed by the other component instead of closing to each other. The well-separated melting and crystallization temperature peaks of the LDPE/UHMWPE blends before and after pan-milling treatment are indicative of immiscibility of the component polymers. The

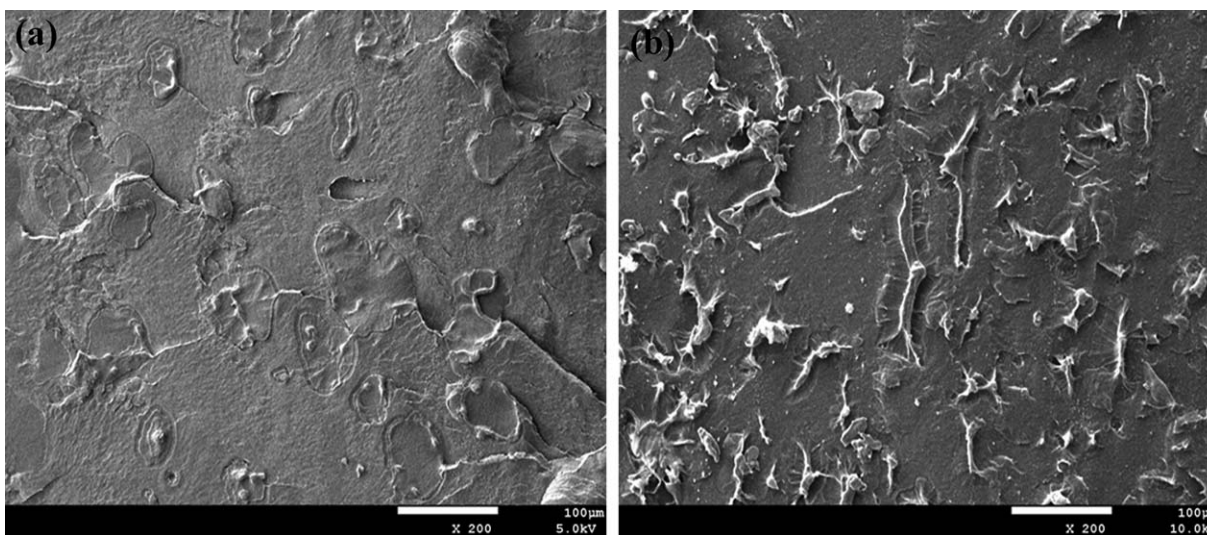


Figure 5. SEM photos of unmilled LU40 (a) and pan-milled LU40 (b).

Table II. Crystalline Size and Crystallinity of LDPE/UHMWPE Blends Before and After Pan-Milling Treatment

Sample	L_{110}^a (nm)	L_{200}^b (nm)	Crystallinity (%)
LU0 M00	14.9	9.3	42
LU0 M10	15.0	9.6	40.1
LU10 M00	14.5	9.6	43.9
LU10 M10	14.8	9.6	42.8
LU40 M00	16.1	12.2	49.2
LU40 M10	14.7	11.0	48.1

^aLattice plane index (110) reflections, ^bLattice plane index (200) reflections.

analyzed data were listed in Table III. As shown in Table III, the melting peak area of pan-milled samples was a little smaller than that of un-milled samples. For the milled LU10 and LU40 blends, the crystallinity was decreased, indicating the trend of the change agreed with the WAXD data well.

After pan-milling treatment, the melting peaks of UHMWPE shift to lower temperatures, whereas the peaks of LDPE kept stable. The more content of UHMWPE led to more evident shift. There is some co-crystallization between LDPE and UHMWPE. The pan-milling treatment can improve the structure of interface but little influence on the LDPE phases. Because in the melting curves the shoulder at the UHMWPE peak (co-crystallization between LDPE and UHMWPE) merged

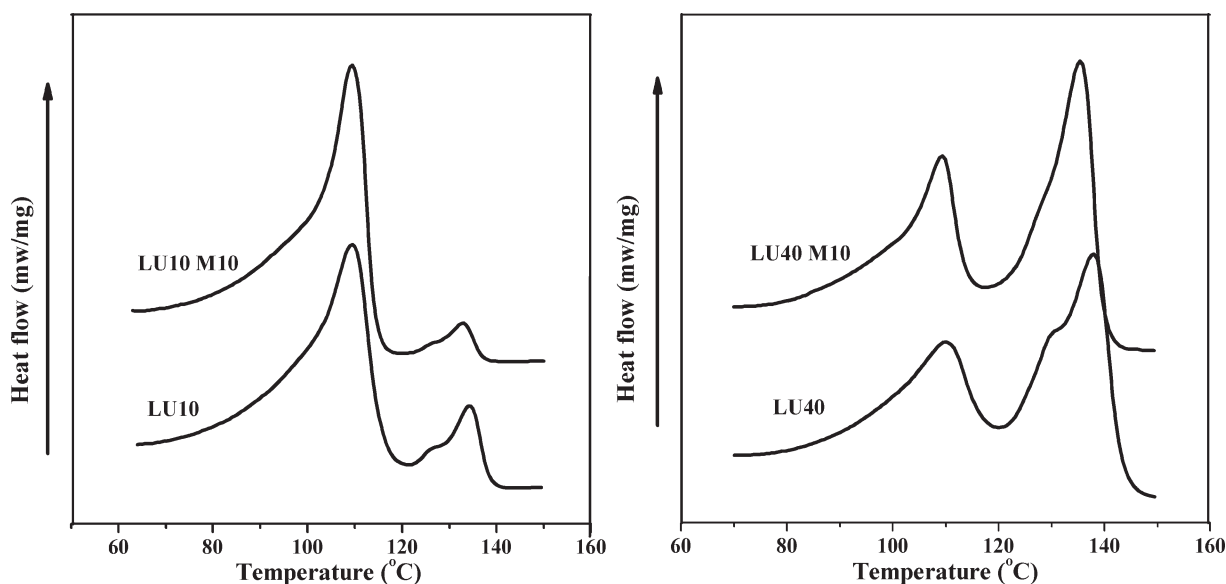


Figure 6. Melting curves of pan-milled LDPE/UHMWPE blends.

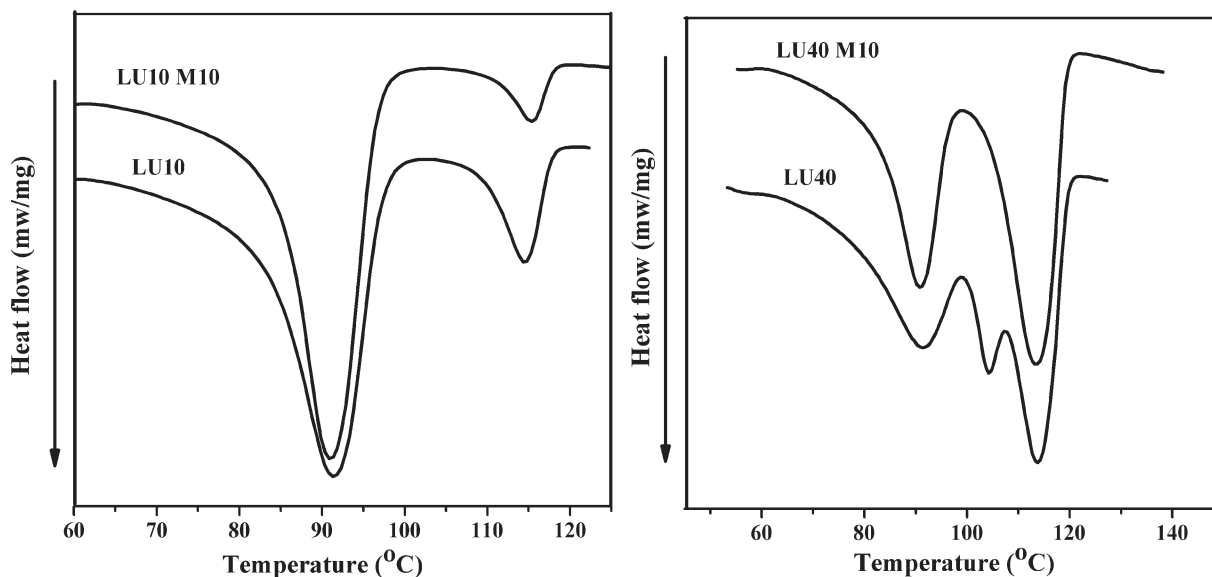


Figure 7. Crystallization curves of pan-milled LDPE/UHMWPE blends.

Table III. DSC Data of mPE Before and After Pan-Milling Mechanochemical Treatment

Sample	T_{m1} (°C)	T_{m2} (°C)	ΔT_m (°C)	X_c (%)
LU10 M00	109.5	134.5	25	32.1
LU10 M10	109.5	134	24.5	28.1
LU40 M00	109.6	138	28.4	41.4
LU40 M10	109.4	135.4	26	40.2

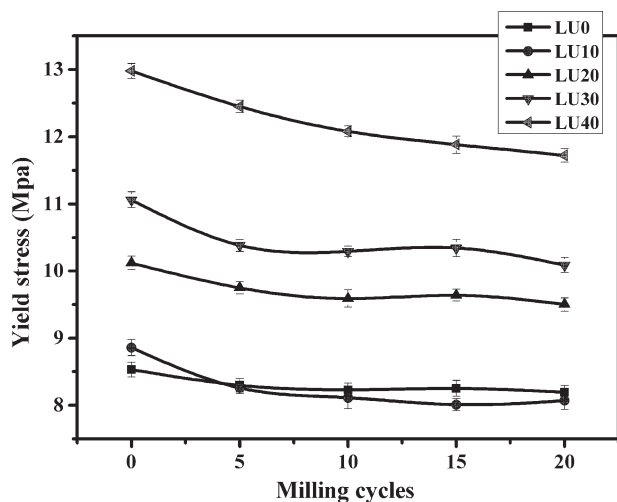
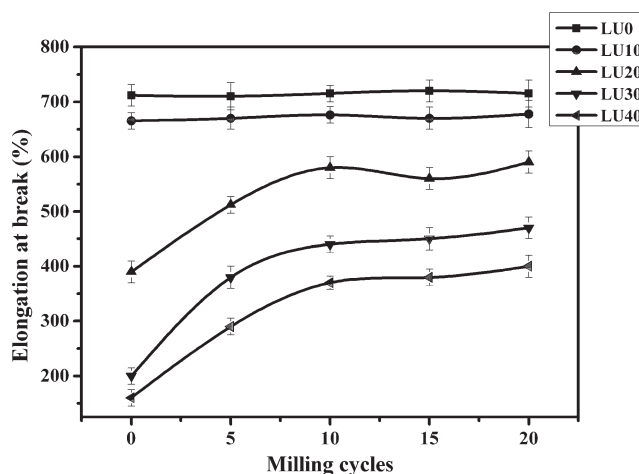
into the UHMWPE peak after pan-milling. This phenomenon confirmed that the immiscible system became more miscible because of the enhanced interaction between LDPE and UHMWPE phases.

Mechanical Properties of LDPE/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, whereas 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.^{15,17,18}

It was well known that the yield stress exhibited a relationship to the crystallinity. Figure 8 gave the yield stress of the blends versus the milling cycles. As shown in Figure 8, after pan-milling treatment the yield stress decreased a little, which is consistent with the variation of the crystallinity, this implied that pan milling had little effect on the stiffness of the material.

The effects of the milling cycles on the elongation at break and tensile strength of LDPE/UHMWPE blends were shown in Figures 9 and 10, 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 LU40, after 10 cycles of milling, the tensile strength increased from 11.7 to 13.5 MPa, and the elongation at break

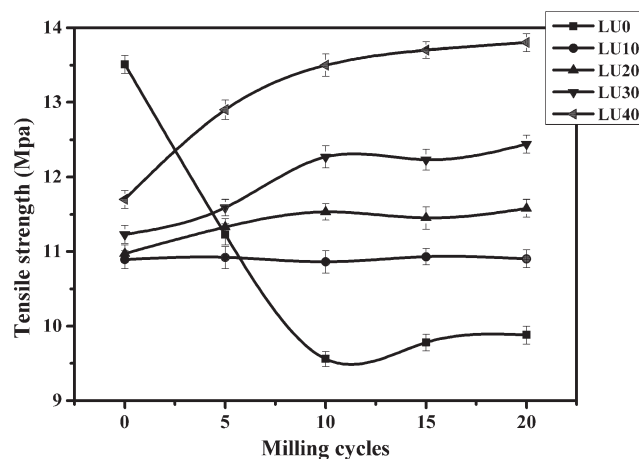
**Figure 8.** Effect of Pan-milling on yield stress of LDPE/UHMWPE blends.**Figure 9.** Effect of Pan-milling on of elongation at break LDPE/UHMWPE blends.

increased from 160% to 370%, about 1.15 times and 2.3 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.

CONCLUSIONS

LDPE/UHMWPE blends were prepared via solid-state shear milling. Pan-milling treatment resulted in decreasing and much more homogeneous size of the dispersed UHMWPE particles. The dispersed particles changed to rod-like shape in the mean time and the extent is enhanced with the content of UHMWPE. Furthermore, the pan-milling treatment can also simultaneously improve the strength and toughness of LDPE/UHMWPE blends.

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

**Figure 10.** Effect of Pan-milling on tensile stress of LDPE/UHMWPE blends.

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