

Effect of Solid-State Stress Induced Reaction on Morphology and Structure of Metallocene Polyethylene

Huawei Zou, Yang Chen, Mei Liang, Pengbo Liu

The State Key Lab of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China
Correspondence to: H. Zou (E-mail: hwzou@163.com) or M. Liang (E-mail: liangmeiww@163.com)

ABSTRACT: Metallocene-catalyzed polyethylene (mPE) powder was prepared through a mechanochemical reactor in solid state at ambient temperature. The changes of morphology and structure of mPE were investigated by SEM, FTIR, DSC, viscosimetry, GPC, WAXD, dynamic rheometer, and high pressure capillary rheometer methods. FTIR measurement illustrated that the branching degree of mPE increased after mechanochemical reaction. Combined with the dynamic rheological analysis, it was proved that the rupture and combination of macromolecular chain undergo strong shear resulted in the formation of long chain branches. X-ray diffraction analysis showed that the crystal form of mPE transferred from rhombic to monoclinic system partly, and the crystalline degree increased slightly in the initial mechanochemical reaction period. Viscometer test results exhibited that molecular weight of mPE dropped during the mechanochemical treatment. Rheology measurement indicated that the critical shear rate of the shark-skin failure enhanced and the extruded stands exhibited smooth face for the mPE after mechanochemical treatment. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1691–1699, 2013

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INTRODUCTION

Metallocene-catalyzed polyethylenes (mPE) are polymers with higher tacticity and narrower molecular mass distribution than other traditional polyolefins. These special structure characters endow them with excellent performances as impact strength, puncture resistance, solvent resistance, and low heat-sealing temperature. Due to the unique molecular structure, mPE in general suffers from a poor processability compared to conventional polyolefins of higher polydispersity.¹ The melt of mPE has high melt viscosity and low melt strength, which results in melt fracture, shark-skin and high torque under the melt processing.^{2–4} Literature on eliminating these flow instabilities have pointed out that mPE could be prepared by the improvement of synthesis techniques, using composite catalyst to produce bimodal or broad molecular weight distribution of mPE,^{5–7} blending with similar chain structure polymers such as HDPE, LDPE, LLDPE, long chain branched PE, and UHMWPE,^{8–12} filling with flow modifier^{13–15} or amending the processing equipment of polyolefins.^{16,17}

Mechanochemical modification is an easy and efficient method for improving rheological properties of mPE. When an external force 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, which will produce macro-

radicals. The radicals are to be an active center to initiate a series of reactions in which branching or micro-crosslinking structure can be formed by disproportionation and combination termination.^{18–20} In this article, a stress field provided by mechanochemical reactor was introduced to mPE macromolecular chains to realize the promising reactions. The morphological and structural changes of milled mPE were investigated simultaneously. The mPE treated by this method will be used as flow modifier of mPE to improve the rheological stability during the subsequent melt processing.

EXPERIMENTAL

Materials

Metallocene-catalyzed linear low density polyethylene (below is shorted as mPE) used in this study was obtained commercially from Exxon Com., and the trademark was Exact 1327. The number-average molecular weight is 5.24×10^4 , and the melt flow index is 1.91 g/10 min (230°C, 2.16 kg). Hydroquinone (AP), a free radical terminator, was purchased from Chengdu Kelong Chemical Plant and was used to avoid crosslinking during the mechanochemical treatment.

Equipment

The main equipment used in this study was a mechanochemical reactor and the detailed external and inlaid structure was



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

described in the previous articles.^{21–25} Figure 1 is a digital camera picture of the mechanochemical 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 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 mechanochemical reaction was taken away by cooling water circulation, so as to maintain the sample treated at ambient temperature, not elevated temperature.

Sample Preparation

mPE and 0.5 wt % of free radical terminator (hydroquinone) were mixed together, and then milled through the mechanochemical 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 treated cycle was 10 s. After one mechanochemical treatment cycle, the mPE was collected by the loading head and then fed into the hopper for the next reaction cycle. The rotation rate of the movable pan was controlled at 30 r/min. The treated mPE was recorded as M00, M01, M02, etc., and the number after letter M represented the treatment cycle.

Scanning Electronic Microscope

Morphology of mPE before and after mechanochemical treatment and tensile fracture surface of the specimen were observed

with a scanning electron microscope (Hitachi LTDX-650, 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 20 kV.

Molecular Weight and Molecular Weight Distribution

The molecular weight and molecular weight distribution measurements were performed by high temperature gel permeation chromatography (Agilent 1100LC). The eluting solvent is dimethyl benzene and the reference polymer is polystyrene.

Viscosity-Average Molecular Weight

The mPE solution viscosity was determined by Ubbelohde viscometer with the solvent of tetrahydronaphthalene at the temperature of 135°C. The viscosity-average molecular weight was calculated according to ASTM D 4020-96.

Fourier Transform Infrared (FTIR) Spectroscopy Analysis

The sample for FTIR analysis was prepared as follows: 2 mg mPE powder 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} .

WAXD Analysis

Wide-angle X-ray diffraction (WAXD) measurements were performed with a Philips analytical X'Pert X-diffractometer (Cu $K\alpha$ radiation, the tube voltage was 40 kV, and the tube current was 40 mA). WAXD data were collected from $2\theta = 5^\circ$ to 50° with a step interval of 0.02° . The powder sample was compacted into a square groove of the slide, and then the surface was striked off for measurement.

Differential Scanning Calorimetry (DSC)

DSC measurement was performed with DSC204 equipment (Netzsch Com., Germany). 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

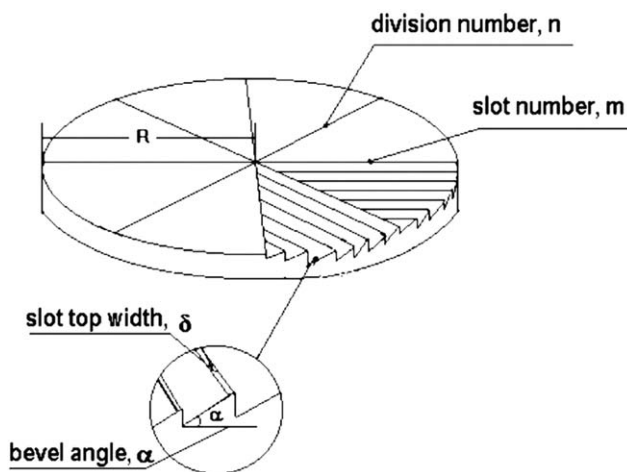


Figure 2. Schematic diagram of inlaid milling pan.

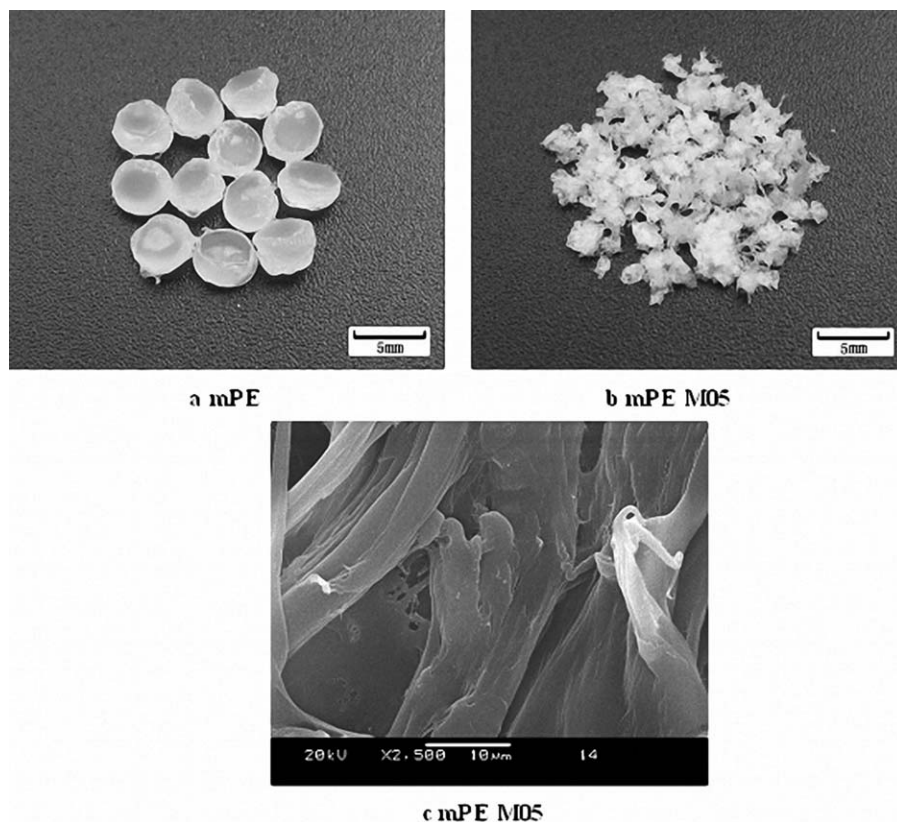


Figure 3. SEM photos of mPE (a) before and (b,c) after mechanochemical treatment.

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.

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,

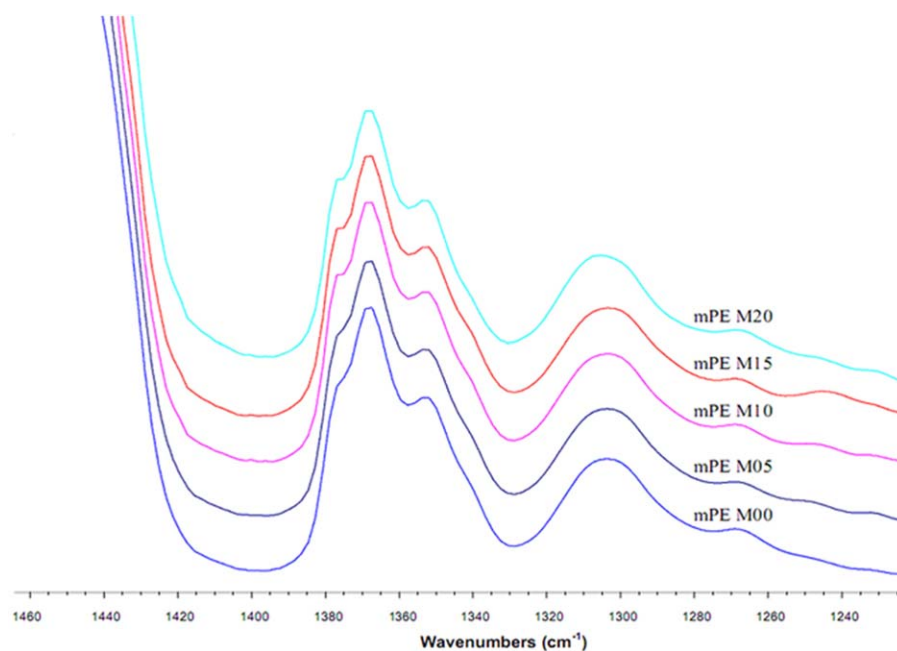


Figure 4. FTIR spectra of mPE that after mechanochemical treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Relative Branching Content of mPE Before and After Mechanochemical Treatment

Sample	Branching degree ($n_{-CH_3}/1000C$)
mPE M00	2.55
mPE M05	2.73
mPE M10	3.35
mPE M15	3.89
mPE M20	3.63

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 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.

High pressure capillary measurements were performed on a capillary rheometer (GOTTERT Rheograph 2002, Germany) at 190°C. A round-hole die of 1 mm diameter with a length-diameter (L/D) ratio of 30 was used. The range of apparent shear rate was from 10 to 3000 s^{-1} . The rheological data were calculated directly by the rheometer.

RESULTS AND DISCUSSION

Morphology Analysis of mPE that After Mechanochemical Treatment

The morphological change of mPE before and after mechanochemical treatment can be estimated according to optical and electron microscopic observation. Figure 3(a, b) are optical microscope photos of mPE with different treatment cycle. Figure 3(a) shows the morphology of initial mPE is uniform pellet with particle size of about 4 mm. mPE is a high ductile plastic and is difficult to be pulverized into powder with traditional methods. But through the unique-designed mechanochemical equipment, the mPE pellet can be treated into flake-like powder just after five treatment cycles, as shown in Figure 3(b). Figure 3(c) is SEM photo of mPE M05. In Figure 3(c), the pellet was

stretched and distorted into irregular powder after undergoing strong stress. Some oriented lines along the stress direction were observed on the treated mPE powder surface.

FTIR Analysis

In our experiment, the whole mechanochemical treatment process was operated in an open air circumstance, which always accompanied with the introduction of polar groups onto polymer chains.²⁶ The FTIR analysis was measured to confirm whether any new functional group was produced during the mechanochemical reaction. Figure 4 is the FTIR spectrum of mPE with different treatment cycles. The absorbance curve labeled mPE M00 is for the original mPE. It is a typical FTIR spectrum of mPE. From the treated mPE FTIR curves, no new absorption peak appeared, illustrating that there is no other functional group generated during the mechanochemical reaction.

Relative branching content can be determined by the content of polyethylene end group, which is methyl group. In the infrared spectrum of polyethylene, the absorption peak situated at 1378 cm^{-1} belongs to vibrational absorption of methyl group, which overlapped with peaks at 1388 cm^{-1} and 1358 cm^{-1} of $-CH_2-$ group. The CH_3- content can be calculated with following formula^{27,28}:

$$K'_{1378}(\text{Methyl group}) = K'_{1378}(\text{All}) - 0.741 K'_{1303} - 2.6$$

where $K' = A/\rho$, A is the intensity of corresponding absorption peak, and ρ is the density of the sample (g/cm^3), and b is thickness of the film (cm). If octadecanoic alkyl was used as reference, the density of methyl group can be calculated as:

$$\text{Methyl group number (n) / 1000(carbon atom)} = 1.00 \times [K'_{1378}(\text{All}) - 0.741 K'_{1303} - 2.6]$$

The relative branching content of treated mPEs is listed in Table I. mPE has a relative branching content of 2.55 methyl groups every 1000 carbon atom. The value of relative branching content increased with treatment cycle, and then leveled off during the later treatment cycle.

It is well known that break point of molecular chain is probably in the middle part results in direct chain scission¹⁹ or formation

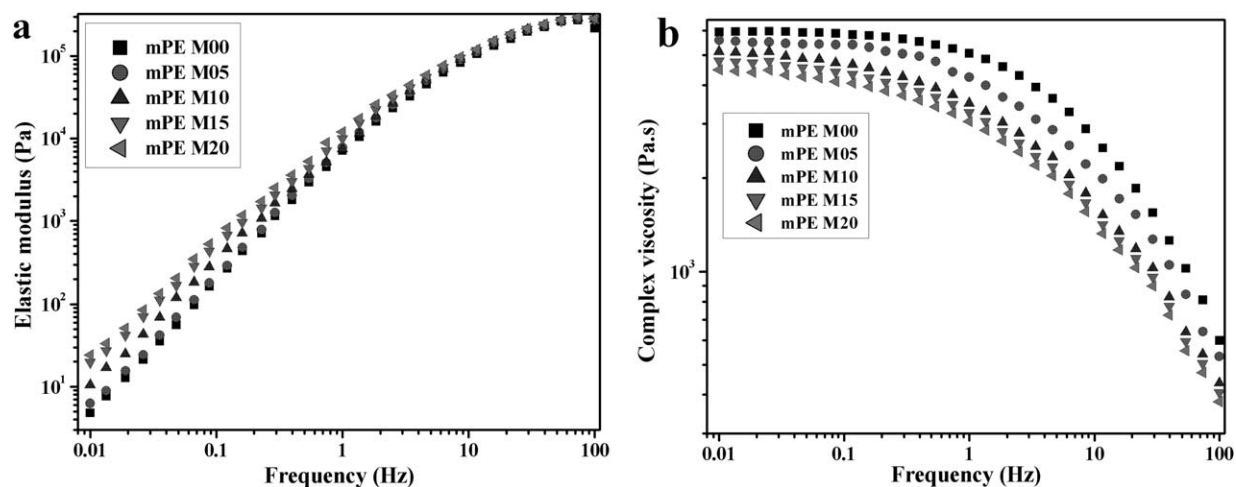
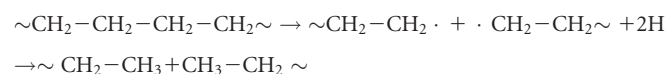
**Figure 5.** (a) Elastic modulus and (b) complex viscosity curves plotted against frequency at 190°C for mPE with different mechanochemical reaction cycles.

Table II. Molecular Weight and Its Distribution of mPE Before and After Mechanochemical Treatment

Sample	Dispersion index	$\overline{M}_w \times 10^{-4}$
mPE M00	2.6	13.77
mPE M05	2.5	12.54
mPE M10	2.5	12.03
mPE M15	2.6	10.22
mPE M20	2.5	10.20

of new branching chain. The new branching chain is mainly long-branching chain, which is benefit to subsequent processing.²⁹ The possible reactions can be expressed as follows:

(1) direct chain scission



(2) formation of long chain branches:

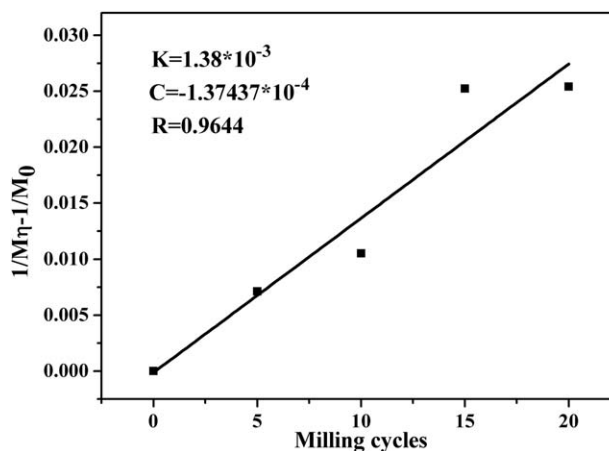
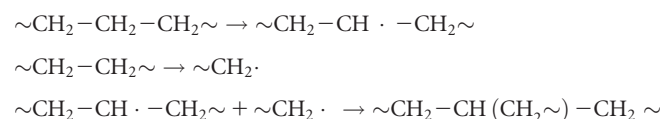


Figure 6. Kinetics of mechanochemical degradation of mPE during mechanochemical reaction.

Effect of Mechanochemical Reaction on Dynamic Rheology Properties of mPE

Storage modulus G' is a measure of stored energy of a polymer. In the terminal region, for linear monodisperse chains, G' decreases more rapidly than loss modulus G'' . However, an introduction of LCBs on the linear chains retards relaxation or

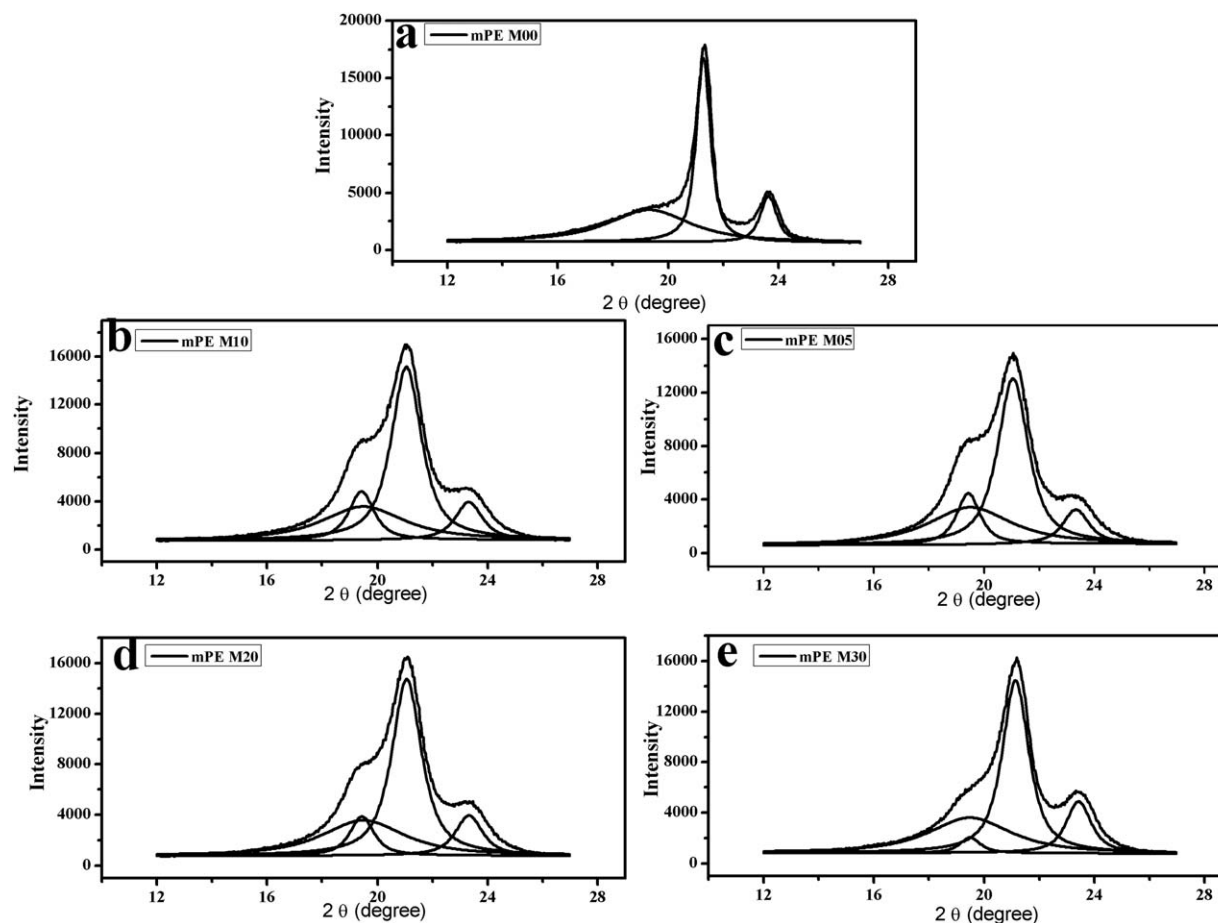


Figure 7. X-ray diffraction graph of mPE that after mechanochemical treatment.

Table III. Crystalline Structure Development of mPE During Mechanochemical Reaction

Sample	W_c (%)	$W_{\text{rhombohedral}}$ (%)	$W_{\text{monoclinic}}$ (%)	W_a (%)
mPE M00	65.53	65.53	0.00	34.47
mPE M05	76.03	66.43	9.59	23.97
mPE M10	78.80	69.32	9.48	21.20
mPE M20	77.71	70.46	7.26	22.29
mPE M30	75.57	72.81	2.76	24.43
mPE M10 ^a	66.87	66.87	0.00	33.14

^aHeat treated.

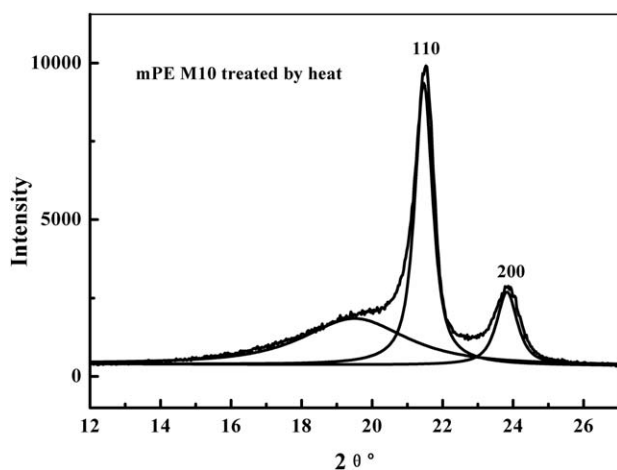
migration, and so their G' is larger than that for the linear chains.³⁰

In Figure 5(a), we see the increase in G' in the terminal region for the milled mPE. Combined with the FTIR measurement, this indicates that there is a minute increase in the number of LCBS in mPE after mechanochemical reaction. In our experiment, the hydroquinone was used to obtain the degradation effect. If not, is hard to distinguish the macromolecular radicals experiencing coupling termination or disproportionation termination. Thus, the formation of long chain branches is limited, but the chain scission may take the major role. This is indicated by decreases in complex viscosity [Figure 5(b)] in the low-frequency region due to mechanochemical reaction.

Effect of Mechanochemical Reaction on Molecular Weight and Its Distribution of mPE

Macromolecular free radical is produced by the chain rupture induced by solid-state stress. The macro-radicals may combine to form a new macromolecule or initiate monomer to form grafting copolymer, or may be annihilated by radical terminator. Table II listed the molecular mass change with treatment cycles. The data showed that after mechanochemical treatment, the molecular weight distribution remained unchanged.

The kinetics of mechanochemical degradation of polymers has been studied by some scientists for decades.^{19,20} In this article,

**Figure 8.** X-ray diffraction graph of mPE M10 after melt processing treatment.**Table IV.** Crystalline Size of mPE Before and After Pan-Milling Mechanochemical Treatment

Sample	L_{110} (nm)	L_{200} (nm)	L_{001} (nm)
mPE M00	12.93	11.32	-
mPE M05	6.05	7.02	7.72
mPE M10	6.05	6.87	7.26
mPE M20	6.17	6.79	7.65
mPE M30	6.94	7.34	8.81
mPE M10 ^a	13.15	11.43	-

^aAfter melt processing.

the relationship between $(1/M_n - 1/M_0)$ of mPE and treatment cycle were investigated. Where, the M_n designated the viscous-average molecular weight of mPE mechanochemical treatment for n cycles and the M_0 was initial viscous-average molecular weight of mPE. The fitted regression line of experimental data was shown in Figure 6. The relative coefficient of the linear regression line was 0.9644, indicating the fitted result was credible. Therefore, the degradation kinetics equation could be expressed as:

$$(1/M_n - 1/M_0) = 1.38 \times 10^{-3}n + (-1.37437 \times 10^{-4})$$

By differentiating both sides with respect to n , the upper equation could be deduced as follows:

$$-dM_n/dn = 1.38 \times 10^{-3}M_n^2$$

The equation indicated that the degradation rate of mPE was proportional to the square of the viscous-average molecular weight of mPE.

Effect of Mechanochemical Reaction on Crystalline Structure of mPE

Figure 7(a–e) is peak-fitting results of WAXD spectra of mPE before and after mechanochemical treatment. mPE belonged to orthorhombic system [Figure 7(a)], after mechanochemical reaction, new peak at $2\theta = 19.5^\circ$ appeared, which represented monoclinic system [Figure 7(b–d)]. Furthermore, the diffraction intensity increased and then decreased with treating cycle [Figure 7(d,e)].

The spherocrystal structure was destroyed by the stress and squeeze produced by mechanochemical reactor. The oriented lamellar lattice was tensioned and distorted which would result in the leaning and slippage of the molecular chains and the transformation of monoclinic system from orthorhombic system.

WAXD results were listed in Table III. The data illustrated that with the increase of treatment cycle, the crystallinity of treated mPE increased. When the treatment cycle reached 10 treatment cycles, the crystallinity of mPE decreased slightly. The rhombic system content increased with treatment cycle and the monoclinic system increased at five treatment cycles, which indicated that non-crystalline molecular chain would transform to ordered crystalline structure.

In Figure 8, the crystalline structure of heat treated sample of mPE that after mechanochemical treatment recovered to that of

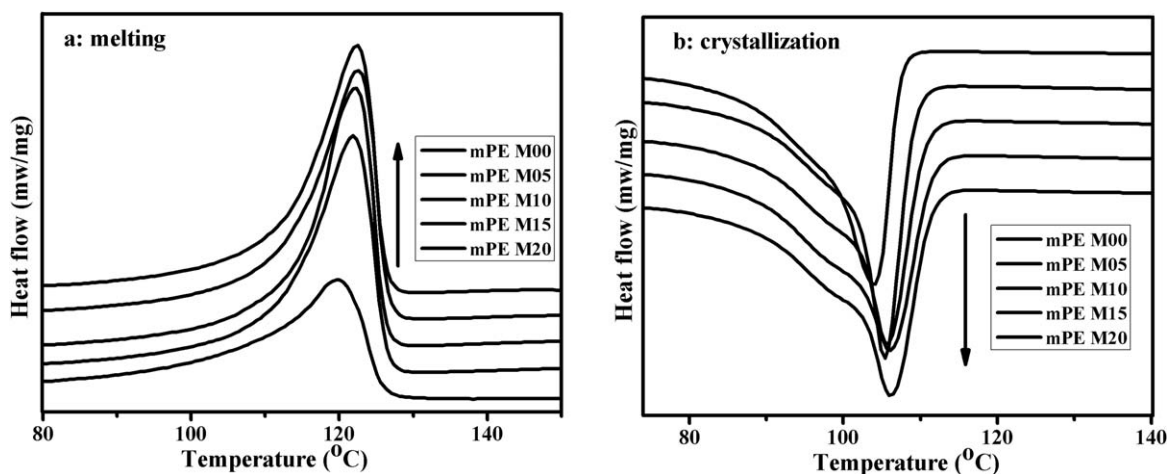


Figure 9. DSC curves of mPE that after mechanochemical treatment (a: melting curve; b: crystallizing curve).

untreated mPE. The monoclinic system induced by stress disappeared after heat treatment. This result showed that the crystalline structure induced by solid-state stress was an unsteady metastable system.

The crystalline grain size of mPE could be calculated by Scherrer formula³¹:

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

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

The crystalline grain sizes of the mPE that after mechanochemical treatment were listed in Table IV. At initial mechanochemical reaction period, the rhombic crystalline grain decreased rapidly, and then got level. However, for monoclinic system, the crystalline grain would not change when they were formed. The crystalline grain size of mPE M10 was bigger than that of it after heat treatment.

DSC Analysis of mPE that After Mechanochemical Treatment

The DSC curves were indicated in Figure 9. In Figure 9(a), the melting peak area of mPE that after mechanochemical treatment was bigger than that of un-treated mPE. The analyzed data were listed in Table V. For the treated mPE, the crystallinity was increased with treatment cycle, indicating the trend of

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

Sample	T_m (°C)	X_c (%)	T_m^* (°C)	X_c^a (%)	T_c (°C)
M00	119.8	37.1	120.0	37.0	103.9
M05	121.9	45.2	118.9	37.7	105.4
M10	122.2	45.6	119.3	37.4	105.7
M15	122.6	46.2	119.5	37.8	106.0
M20	122.4	44.0	119.4	37.3	106.1

^a After heating treatment.

the change agreed with the WAXD data well. But, for sample after heat history elimination, the crystallinity was lower than unheated sample, which showed that the heat treatment counteracted molecular regularity produced by mechanochemical reactor partly. The mechanochemical reaction resulted in the activation of molecular chain, decreased the molecular weight, and increased the crystalline ability.

Effect of Mechanochemical Reaction on Melt Flow Properties of mPE

Table VI listed melt flow index (MFI) of mPE before and after mechanochemical treatment. The melt flow index of mPE increased as a function of treatment cycle. After 20 treatment cycles, the melt flow index of mPE M20 improved to 4.16 g/10 min, almost twice than that of original mPE. The MFI results showed that mechanochemical treatment can active the

Table VI. Effect of Mechanochemical Reaction and Mechanochemical Treatment on Melt Flow Index of mPE

Sample	Melt flow index (g/10 min)
mPE M00	1.91
mPE M05	2.74
mPE M10	3.28
mPE M15	3.72
mPE M20	4.16

Temperature: 230°C, weight: 2.16 kg.

Table VII. Critical Shear Rate for the On-Set of the Melt Instability

Sample	Critical shear rate (s ⁻¹)
mPE	1152
mPE M05	1728
mPE M10	2880
mPE M20	2880

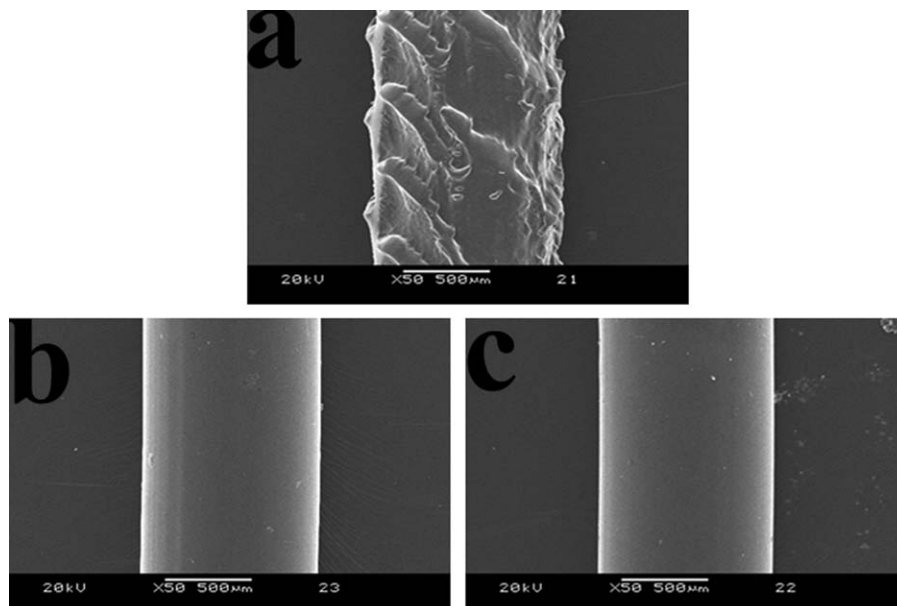


Figure 10. Surface morphology of mPE extrudate before and after mechanochemical treatment (a) mPE M00, (b) mPE M10, (c) mPE M20, 230.4 s^{-1} ; $L/D = 30/1$; $T = 190^\circ\text{C}$.

molecular chain of mPE and the melt flow rate can be enhanced effectively.

Table VII listed the critical shear rate of mPE ($L/D = 30/1$, $T = 190^\circ\text{C}$) before and after mechanochemical treatment. The onset shear rate of the shark-skin failure for the treated mPE is higher than the shear rate of un-treated mPE. The SEM photographs of the extruded stands are shown in Figure 10 (a–c). It is found from the figure that mPE [Figure 10(a)] shows shark-skin failure even if at low shear rate (230.4 s^{-1} , $L/D = 30/1$, $T = 190^\circ\text{C}$), whereas all the treated samples [Figure 10(b,c)] do not show shark-skin failure at the same shear rate in this experiment, suggesting that the mechanochemical modification is an easy and efficient method for improving rheological properties of mPE.

CONCLUSIONS

mPE powder was prepared via mechanochemical route. The morphological and structural changes were investigated by many measurements. The main conclusions made from this study are as follows: (1) undergoing the strong stress, initial mPE pellets were stretched and distorted into irregular flake-like powder. Through mechanochemical reaction, the branching degree of mPE increased with the treatment cycle; (2) the molecular weight of mPE decreased at the initial reaction stage, and then leveled off. The molecular weight distribution remained unchanged; (3) in amorphous phase, some ordered structure could be induced by the mechanochemical reaction, but after the melting processing, the induced crystallinity disappeared; (4) the mechanochemical modification is an easy and efficient method for improving rheological properties of mPE.

In a word, mechanochemical treatment is an efficient, clean, and environment-friendly method for preparing mPE powder,

which could be used as the flow modifier of mPE to improve the rheological stability during its subsequent melt processing.

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