

EFFECT OF PAN-MILLING ON RHEOLOGICAL PROPERTIES OF HIGH DENSITY POLYETHYLENE*

Hua Huang**

Polymer Research Institute, Sichuan University, Chengdu 610065, China

Abstract The effect of pan-milling on the rheological properties of high density polyethylene (HDPE) was studied. An innovative milling apparatus, viz. an inlaid pan-mill, was used. Melt indexer, capillary rheometer, Haake Rheocord 90 single-screw extruder and Brabender rheometer were used to evaluate the rheological properties of HDPE. HDPE with higher initial molecular weight and larger particle size was easier to degrade under pan-milling stress, as indicated by the melt index. Pressure oscillation in capillary flow occurred at significantly higher shear stress and shear rate for milled HDPE than for unmilled HDPE. The apparent shear viscosity of HDPE decreased with increasing times of milling. After milling, the flow activation energy decreased and thus the sensitivity of viscosity to temperature was reduced. Die pressure and torque during single screw extrusion were reduced significantly after milling. Plasticizing time as measured in a Brabender mixer decreased markedly with increasing milling times.

Key words High density polyethylene, Rheological properties, Pan-milling

INTRODUCTION

The effects of shearing forces in the molten state on the polymer properties including rheological properties have been the subject of intensive studies^[1-4]. The special flow behavior of HDPE, which exhibits a distinct discontinuity and pressure oscillations at the onset of gross melt fracture, has been investigated by a number of authors, and a variety of mechanisms have been proposed^[5-8].

Stress reactions are a major consideration for high molecular weight polymers^[9]. Application of stress to polymers may lead to changes in topology, chain entanglement and orientation, and crystalline structures. These will inevitably cause changes in the polymer properties including rheological properties. However, stress reaction in solid polyethylenes and its effects on the properties of polyethylenes are rarely studied because of equipment limitations. Only a few papers on the detection of free radicals resulted from ball-milling of polyethylene powder at liquid nitrogen temperature has been published^[10, 11].

Xu and Wang^[12] designed a type of innovative apparatus, an inlaid pan-mill, on the basis of traditional Chinese stone-mill. This kind of reactor can provide strong shear stress. Theoretical analysis and experimental results demonstrated that this innovative equipment is not only superior to traditional equipment in pulverizing brittle materials such as PS but also effective in pulverizing ductile materials such as HDPE^[13-15].

The purpose of this paper is to study the effect of pan-milling on the rheological properties of HDPE.

* The author acknowledges the financial support of this project by the National Natural Science Foundation of China and the State Education Commission of China.

** Corresponding author: Hua Huang (黄华), E-mail: huanghua@mail.sjtu.edu.cn; Permanent address: School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, China

Received August 19, 1999

EXPERIMENTAL

Materials

Unless otherwise stated, the HDPE used was HDPE6098 with a melt index of 0.1 dg/min and a density of 0.948 g/cm³, supplied by Qilu Petrochemical Company.

Pan-milling

An inlaid pan-mill type mechanochemical reactor with water cooling (room temperature) and a rotating speed of 25 rpm was used. Samples were taken at regular intervals during milling. The process from the beginning of feeding to the end of material discharge was considered as one cycle.

Analysis

The melt index of HDPE was measured at 190°C with 5 kg load unless otherwise stated according to ASTM D1238 E specifications, and its molecular weight and molecular weight distribution were determined by using a PL-GPC-210 gel permeation chromatography (GPC). Ortho-dichlorobenzene was used as the eluent with a flow rate of 1.0 mL/min at 160°C. Polystyrene was used as reference.

Flow curves were obtained by using a Göffert 2002 capillary rheometer. Dies with a diameter of 1 mm and L/D ratios of 10 and 30 were used.

A Haake Rheocord 90 single-screw extruder was used to measure the die pressure and torque at equilibrium during extruding.

Torque versus time curve was measured using a Brabender Rheometer during mixing.

RESULTS AND DISCUSSION

Effect of Pan-milling on Molecular Weight

Molecular weight and molecular weight distribution of the unmilled and the milled HDPE are shown in Table 1. Molecular weight decreased gradually with increasing number of milling cycles, confirming the degradation of HDPE during pan-milling. It can also be seen from the results that the molecular weight distribution of HDPE became narrower after milling. The changes of molecular weight and molecular weight distribution will inevitably affect the rheological behavior of HDPE.

Table 1. Effect of pan-milling on molecular weight and molecular weight distribution of HDPE

No. of milling cycles	0	4	8	15
M_n	31887	28175	26969	24200
M_w/M_n	19.50	19.13	17.72	17.04

Effect of Pan-milling on Melt Index

Figure 1 shows the melt indices of three kinds of HDPE after different times of milling. Melt indices all increased with increasing times of milling. Nevertheless, the extent of degradation was different for HDPEs with different initial melt index, which can readily be seen in Table 2. For HDPEs with higher initial molecular weights, HDPE7000F and HDPE6098, their melt index increased about 60% after 15 milling cycles; whereas the melt index of HDPE7006A (with lower initial molecular weight) increased less than 10%. These results indicate that HDPE with higher initial molecular weight is easier to degrade under stress field.

Table 2. Effect of initial molecular weight on the melt indices of HDPE

Sample	HDPE6098	HDPE7000F	HDPE7006A
Initial MI of HDPE (MI ₀ , dg/min)	0.47	0.21	8.12 (2.16 kg)
MI of HDPE milled for 15 cycles (MI ₁₅ , dg/min)	0.77	0.35	8.88 (2.16 kg)
(MI ₁₅ -MI ₀)/MI ₀	60%	63%	9.3%

Effect of Pan-milling on Capillary Flow Behavior

It has been known for HDPE that sharkskin roughness occurs (indicated on flow curves by a change of slope in

steady flow region) when the shear stress surpasses the first critical value (σ_{c1}), and the driving pressure and flow rate oscillate once the shear stress surpasses the upper critical value (σ_{c2}) while piston speed is in a certain range.

Figure 2 shows the apparent flow curve of the unmilled and the milled HDPE measured at 220°C using a die with a diameter of 1 mm and L/D ratio of 10 (Bagley correction was not performed). There was no significant difference in the low shear rate part of the flow curves of the milled and the unmilled HDPE. For HDPE milled for 15 times, pressure oscillation occurred at significantly higher shear stress and shear rate. Values of shear rate at which oscillating flow occurred, the first and upper critical shear stresses, were calculated and listed in Table 3. σ_1 was about the same at 0.11 MPa for both the unmilled and the milled HDPE. σ_{c2} was significantly higher for the milled HDPE than the unmilled HDPE. Oscillating flow occurred at a shear rate of 460 s^{-1} for HDPE after milling for 15 times, which was about two times of that for the unmilled HDPE.

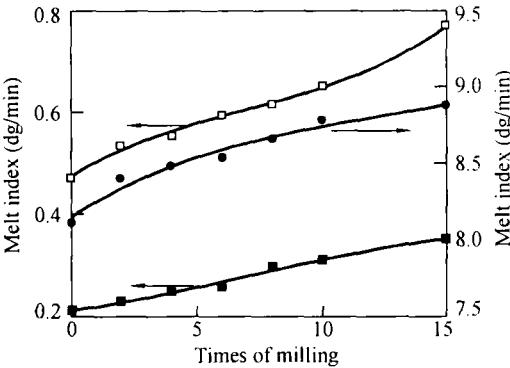


Fig. 1 Melt indices of various milled HDPE
□ HDPE60 98, 5 kg
■ HDPE7000F, 5 kg
● HDPE7006A, 2.16 kg

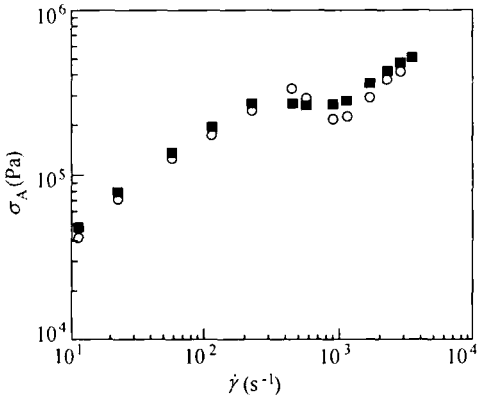


Fig. 2 Apparent flow curve of HDPE
 $D = 1.0\text{ mm}$; $L/D = 10$; $T = 220^\circ\text{C}$
■ Unmilled HDPE
○ HDPE milled for 15 milling cycles

Table 3. First critical stress (σ_{c1}), uppen critical shear stress (σ_{c2}), apparent shear rate at which oscillating flow occurs ($\dot{\gamma}_{A,O}$) of the milled and the unmilled HDPE

No. of milling cycles	0	8	15	30
σ_{c1} (MPa)	0.11	0.11	0.11	0.10
σ_{c2} (MPa)	0.26	0.28	0.33	0.29
$(\dot{\gamma}_{A,O})$ (s^{-1})	230	230	460	460

The period of oscillating flow was calculated from the length of smooth part over the whole length of extrudate in one cycle of oscillating extrusion and is listed in Table 4. The period of the oscillation increased with increasing times of milling and reached 0.73 after milling for 30 cycles.

Table 4. Period of oscillating flow of the milled and the unmilled HDPE as calculated from the length of smooth part over the whole length of extrudate in one cycle of oscillating extrusion

No. of milling cycles	0	8	15	30
Period of oscillating flow	0.40	0.60	0.62	0.73

The above oscillating phenomenon may be explained by the well-accepted slip-stick mechanism for flow instability. As the slip-stick mechanism explains, slip will occur above a critical shear stress because of lack of cohesion between melt fluid and capillary surface, and the possible rise of temperature resulting from slip and energy release will cause the melt fluid to stick again. Because of the slip-stick process, instability appears in the flow curve. The critical shear stress increases with the decrease of molecular weight. Our early research work showed that mechanochemical degradation of HDPE occurred under the stress fields of the pan-mill, the

molecular weight of HDPE was reduced and oxygen-containing groups were introduced into HDPE chains during milling^[16] which would increase the cohesion between melt fluid and capillary surface. Therefore, the upper critical shear stress (σ_{c2}) should be higher for the milled HDPE than for the unmilled HDPE and the period of the oscillation should increase with increasing number of milling cycles.

In the low shear rate branch where there is steady flow, the shear stress-shear rate relationship can be represented by a power-law expression:

$$\sigma = K\dot{\gamma}^n \quad (1)$$

The power-law constant K is the consistency of the fluids. The exponent n indicates the difference between Newtonian and non-Newtonian fluids. Non-Newtonian behavior of the fluids is more prominent with smaller values of n . The power-law constants of the milled and the unmilled HDPE before and after the sharkskin roughness were calculated from Fig. 2 and are listed in Table 5. Before the sharkskin roughness occurred, K decreased with increasing milling times due to the reduction in molecular weight, whereas n increased with increasing milling times as a result of narrower molecular weight distribution. After the sharkskin roughness occurred, K and n kept relatively constant. This indicates that changes in the molecular weight and the molecular weight distribution may only affect the rheological behavior before the occurrence of sharkskin roughness.

Table 5. Power-law constants (K) and exponents (n) before and after the occurrence of sharkskin roughness for the milled and the unmilled HDPE

No. of milling cycles	0	8	15	30
n_1 (Before sharkskin roughness occurs)	0.64	0.64	0.69	0.74
n_2 (After sharkskin roughness occurs)	0.47	0.47	0.45	0.46
$\lg K_1$ (Before sharkskin roughness occurs)	4.00	4.00	3.90	3.76
$\lg K_2$ (After sharkskin roughness occurs)	4.31	4.30	4.32	4.25

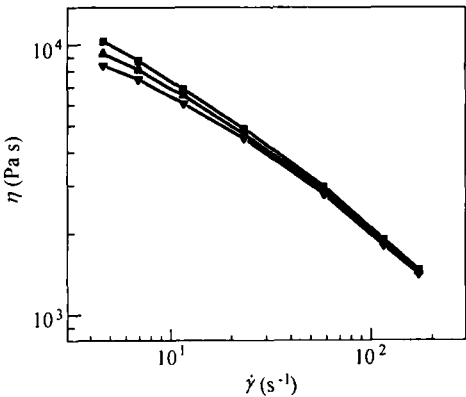


Fig. 3 Apparent shear viscosity of the milled and the unmilled HDPE
 $T = 190^\circ\text{C}$ and $L/D = 30$, numbers in the Figure stand for the number of milling cycles.
 ■ 0; ▲ 8; ▼ 15

Apparent shear viscosity of the milled and the unmilled HDPE is plotted in Fig. 3. When the shear rate was in the low shear rate branch of the flow curve, apparent shear viscosity decreased with increasing times of milling during the steady flow, which is consistent with the result of melt index. However, the difference in apparent shear viscosity between the milled and the unmilled HDPE became smaller at higher shear rates. This again

indicates that changes in the molecular weight and the molecular weight distribution of HDPE caused by milling stress only influence the rheological behavior of HDPE during steady flow (before sharkskin roughness occurs), but have little influence after the occurrence of sharkskin roughness.

$$\eta = A e^{\frac{E}{RT}}$$

(2)

Figure 4 shows the relationship between apparent shear viscosity and the reciprocal of absolute temperature for the unmilled HDPE and HDPE milled for 15 times. Flow activation energies (E) were calculated from the slopes of the linear portion of $\log \eta$ versus $1/T$ curves and are listed in Table 6. HDPE milled for 15 times had lower E than the unmilled HDPE at shear rate higher than 20 s^{-1} . This may be explained by the increase of the chain mobility of the milled HDPE as a result of chain scission. The apparent shear viscosity of the milled HDPE is therefore less sensitive to temperature than that of the unmilled HDPE.

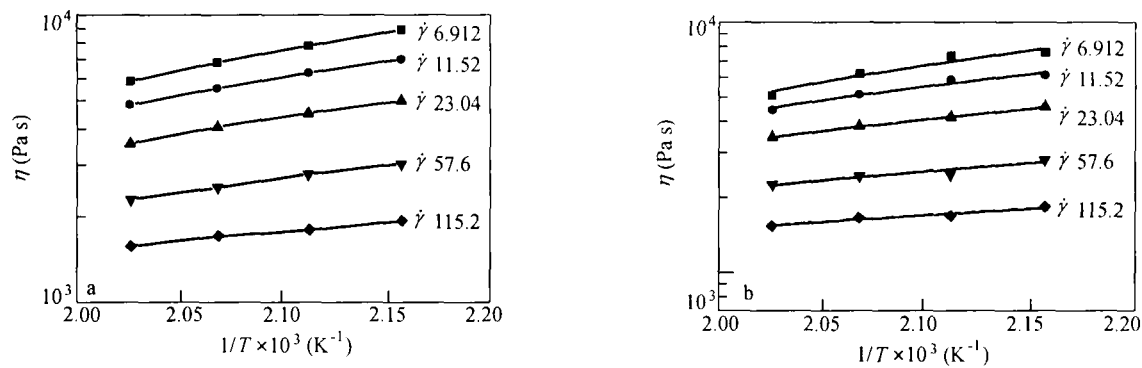


Fig. 4 Relationship between $\lg \eta$ and $1/T$ of the milled HDPE
a) Unmilled HDPE
b) HDPE milled 15 times

Table 6. Flow activation energy of the unmilled HDPE (E_0) and HDPE milled for 15 times (E_{15})

$\dot{\gamma}$ (s^{-1})	E_0 (kJ/mol)	E_{15} (kJ/mol)
6.912	27.7	35.0
11.52	24.7	26.8
23.04	23.1	18.0
57.6	18.8	9.52
115.2	12.3	8.79

Effect of Pan-milling on Rheological Behavior During Extrusion

Compared with the capillary flow, the melt flow in single screw extruder is a kind of dynamic flow and is similar to the practical processing situation. Figures 5 and 6 show the die pressure and torque of the unmilled HDPE and HDPE milled for 15 times at different rotor speeds in a single screw extruder. After milling for 15 times, both the die pressure and the torque decreased significantly. It was found through the observation of the extrudate that surface melt fracture appeared at a rotor speed of 50 rpm for the unmilled HDPE and 60 rpm for HDPE milled for 15 times. The difference in torque values (Fig. 6) for the milled and the unmilled HDPE decreased with increasing rotor speed. This is consistent with the above apparent shear viscosity curves as measured by capillary rheometer.

Effect of Pan-milling on Processing in a Brabender Mixer

Equilibrium torque and plasticizing time may be used to evaluate the processing properties of a polymer since torque values are in direct proportion to the apparent viscosity of polymer melt. Equilibrium torque (T_c) and plasticizing time (t) may be determined from the torque curves obtained during mixing as shown in Fig. 7. Equilibrium torque and plasticizing time of the unmilled and the milled HDPE are listed in Table 7. With

increasing milling times, plasticizing time is reduced markedly. After 15 milling cycles, less than half of the time is required for plasticizing. Equilibrium torque decreased slightly with increasing milling times as a result of HDPE degradation during milling. The reduction in plasticizing time and equilibrium torque is important in practical applications because less energy is required for processing.

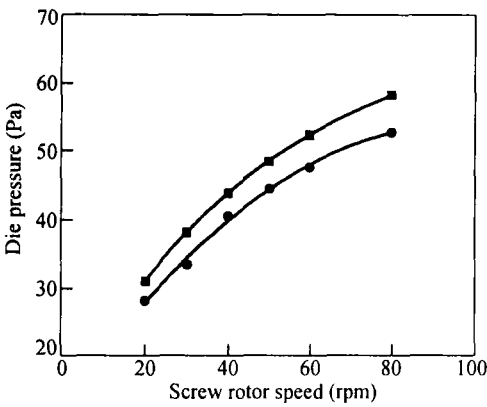


Fig. 5 Die pressure versus screw rotor speed curve of the milled and the unmilled HDPE
■ Unmilled HDPE
● HDPE milled 15 times

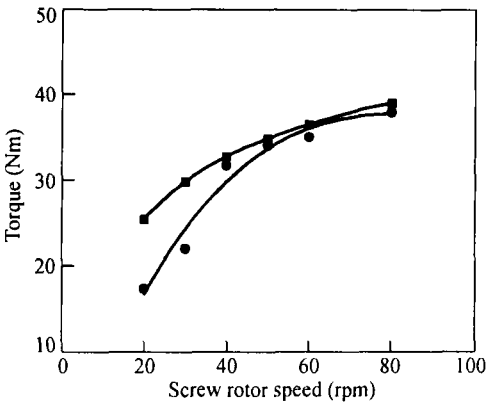


Fig. 6 Torque versus screw rotor speed of the milled and the unmilled HDPE
■ Unmilled HDPE
● HDPE milled 15 times

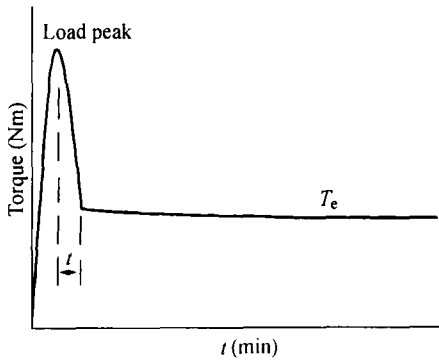


Fig. 7 Torque versus time curve of HDPE measured by Brabender rheometer
 T_e : Torque at equilibrium
 t : Time from load peak to minimum torque

Table 7. Plasticizing time (t) and equilibrium torque (T_e) of HDPE measured by Brabender mixer

No. of milling cycles	t (s)	T_e (Nm)
0	56	28.5
4	32	28.8
8	30	26.6
15	24	25.2

CONCLUSIONS

Mechanochemical degradation of HDPE occurred in the stress fields of pan-milling. The molecular weight of HDPE was reduced and its molecular weight distribution became narrower after milling.

HDPE with higher initial molecular weight and larger particle size was easier to degrade under pan-milling stress as indicated by the melt index.

Pressure oscillation in capillary flow occurred at significantly higher shear stress and shear rate for the milled HDPE than the unmilled HDPE. The apparent shear viscosity of HDPE decreased with increasing times of milling. After milling, flow activation energy decreased and thus the sensitivity of viscosity to temperature was reduced.

The die pressure and torque during single screw extrusion were reduced significantly after milling.

The plasticizing time as measured in a Brabander mixer decreased markedly with increasing milling times.

REFERENCES

- 1 Ar'er, A.M., *Int. Polym. Sci. Technol.*, 1981, 8(12): T/94
- 2 Rokudai, M. and Fujiki, T., *J. Appl. Polym. Sci.*, 1981, 26: 1343
- 3 Rudin, A. and Schreiber, H.P., *Polym. Eng. Sci.*, 1983, 23(8): 422
- 4 Rokudai, M., *J. Appl. Polym. Sci.*, 1979, 23: 463
- 5 Utracki, L.A., *J. Rheology*, 1984, 28(5): 601
- 6 Ramamurthy, A.Y., *J. Rheology*, 1986, 30(2): 337
- 7 Hatzikiriakos, S.G. and Dealy, J.M., *J. Rheology*, 1992, 36(5): 845
- 8 Hatzikiriakos, S.G. and Dealy, J.M., *J. Rheology*, 1992, 36(4): 703
- 9 Porter, R.S. and Casale, A., *Polym. Eng. Sci.*, 1985, 25(3): 129
- 10 Vivatpanachart, S., Nomura, H., Miyahara, Y., Kashiwabara, H. and Aakaguchi, M., *Polymer*, 1981, 22: 132
- 11 Benachour, D. and Rogers, C.E., *Amer. Chem. Soc. Symp. Ser.*, 1981, 151: 263
- 12 Xu, X. and Wang, Q., 1995, CN. Pat., 2217463y
- 13 Xu, X., Wang, Q., Kong, X. A., Zhang, X.D. and Huang, J.G., *Plast. Rubb. Comp. Process. Appl.*, 1996, 25(3): 152
- 14 Wang, Q., Cao, J.Z., Huang, J.G. and Xu, X., *Polym. Eng. Sci.*, 1997, 37(6): 1091
- 15 Wang, Q., Cao, J.Z., Huang, J.G. and Xu, X., *Polym. Inter.*, 1996, 41: 245
- 16 Huang, H., Ph. D., Thesis, Sichuan Union University, 1997