Extrusion of Ultrahigh Molecular Weight Polyethylene Under Ultrasonic Vibration Field

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ABSTRACT: The effects of polypropylene (PP) and ultrasonic irradiation on the processing and mechanical properties of ultrahigh molecular weight polyethylene (UHMWPE) are studied. The results show that PP can effectively improve the fluidity and mechanical properties of UHMWPE. The Izod notched impact strength increases from 92 kJ/m^2 for pure UHMWPE to 109.2 kJ/m^2 for the blend of UHMWPE with 10 wt % PP. The Young's modulus increases from 528 MPa for pure UHMWPE to 1128 MPa when 25 wt % PP is contained in the blend, and the yield strength also rises when PP is added. The application of ultrasonic vibrations during extrusion can prominently decrease the die pressure and apparent viscosity of the melt, thus increasing the output of extrudate. An appropriate ultrasonic intensity and irradiation time can further promote the mechanical properties, while an overdose of irradiation destroys them. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2628–2632, 2003

Key words: ultrahigh molecular weight polyethylene; polypropylene; single-screw extruder; ultrasonic vibration

INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) may be defined as PE with a molecular weight in excess of approximately 1 million. These extremely high molecular weight PEs provide a number of technically important properties including notched impact strength, energy absorption capacity at high loading rates, resistance to stress cracking, and extremely low embrittlement temperatures. At this high molecular weight, the PE has a high solution viscosity and pronounced viscoelastic characteristics in the melt. Therefore, it is not suitable for conventional processing operations, except for compression molding and ram extrusion.[1,2] Numerous efforts have been made to reduce the viscosity by solution or gel processing.[3–5] An alternative route to reduce the melt viscosity is to dilute the UHMWPE with conventional PE that generally has a lower average molecular weight[6–8] or add some lubricants such as stearate, PE wax, styrene, and so on. However, effective amounts of these agents cause a marked decrease in some of the most desirable properties of UHMWPE, such as the impact strength and abrasion resistance. In addition, the instability and transference of these low molecular agents to the surface of the extrudate is very harmful, especially in surgical areas where UHMWPE often plays an important role. For this reason, the addition of intermediate molecular weight PE to UHMWPE does not in itself present a practical way to improve the melt processability of UHMWPE. Although some reported that the addition of a nucleating agent can counteract the bad effect of these processing aid agents, in fact, the effect is rather moderate.[7] The addition of a thermotropic liquid crystalline polymer (TLCP) to UHMWPE increases the mechanical strength and stiffness, as well as the flowability, of UHMWPE, because of the strong shear-thinning effect and molecular orientation of TLCP along the flow direction. However, the incompatibility of the processing temperatures of UHMWPE and LCP and the high cost of LCP make this unacceptable.

Except for the optimization of the processing technique, much work has been done on the amelioration of the extruder. UHMEPE can be extruded by a single-screw extruder by digging grooves in the extruder barrel and by devising a special screw structure to improve the mixing effect and to cope with the hard-feeding problem that often happens with conventional single-screw extruders. However, improving the processing equipment is not always easy in a factory.

On the other hand, polymer processing aided by ultrasonic vibration has attracted attention for many years. Isayev and coworkers reported that during extrusion a high-intensity ultrasonic vibration could reduce the pressure and die swell and postpone melt fracture.[9–11] Oda[12] applied a 20–100 kHz ultrasound vibration in a direction vertical to the rubber discharging direction through an extrusion and attained rubber sheets with better dimensional accuracy. Peshkovskii et al.[13] described a method for eliminating the unstable flow of a polybutene melt by the application of ultrasonic irradiation, and they discovered the average size of fillers was smaller and the size distribution was more homogeneous with ultrasonic treatment than without ultrasonic treatment in kaolin clay filled high-density PE.

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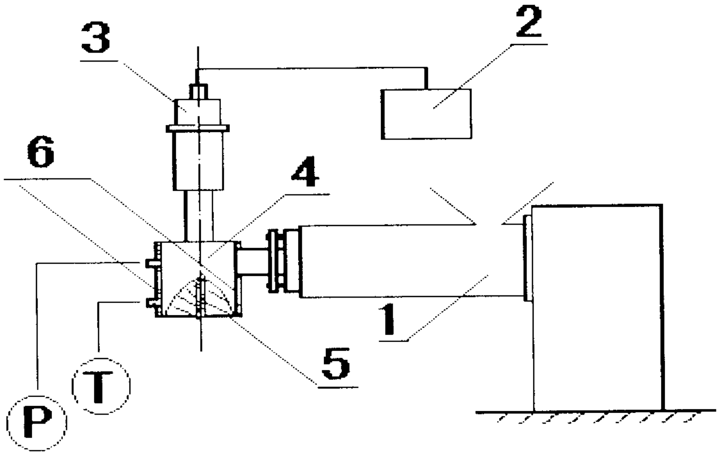


Figure 1 A schematic of the ultrasonic wave extrusion system: 1, extruder; 2, ultrasonic generator; 3, piezoelectric transducer; 4, die; 5, melt; 6, electric heaters; P, pressure transducer; T, thermocouple.

In this study, we first increase the fluidity of UHMWPE to make it processable by a conventional single-screw extruder, and the mechanical properties can also be improved to some extent. We then employ ultrasonic vibration during extrusion to further enhance its processability.

EXPERIMENTAL

Materials

UHMWPE (M-II) with an average molecular weight of 2.5×10^6 was supplied by Beijing No. 2 Reagent Plant (Beijing, China). Polypropylene (PP, F401) was produced by Lanzhou Chemical Industry Factory (Lanzhou, China) with a melt flow rate (MFR) of 2.0 g/10 min (230°C, 2.16-kg load).

Extrusion

All the blends were extruded by a single-screw extruder (D = 25 mm, L/D = 25) with a cross-section capillary die (D = 3 mm, L/D = 7), a high-temperature melt pressure transducer, and an ultrasonic generator (Fig. 1). The ultrasonic frequency is 20 kHz and the power ranges from 0 to 300 W. The direction of ultrasonic vibration coincides with that of the melt flow, and the die temperature is 210°C.

Mechanical properties evaluation

The extrudates were compression molded at 195°C and 13 MPa for 5 min to achieve 1 and 4 mm thick plates. The samples for the mechanical tests were cut from the plates. Pure UHMWPE testing specimens were prepared from the original UHMWPE powder under the same conditions.

The tensile strength was measured on an Instron 4302 tensile tester according to GB 1040-79 with a crosshead speed of 100 mm/min. The Izod notched impact strength was measured according to GB 1843-80 on a XJ-40A impact tester. The MFR was measured at 230°C (12.16 kg) on a CS-127 MFR instrument.

RESULT AND DISCUSSION

Mechanical and fluidity properties

Figure 2 shows that the addition of PP does improve the fluidity of UHMWPE; the MFR increases almost linearly with the increase of the PP content. When only 5 wt % PP was added, the flow rate was almost undetectable. When the PP concentration was increased to 25 wt %, the MFR increased to 0.66 g/10 min.

The mechanical properties of these blends were improved, except the elongation at break, as shown in Table I. When 25 wt % PP is added, the Young's modulus increases from 528 MPa for pure UHMWPE to 1128 MPa, which more than doubled the former. The yield strength also rises when PP is added. Both the

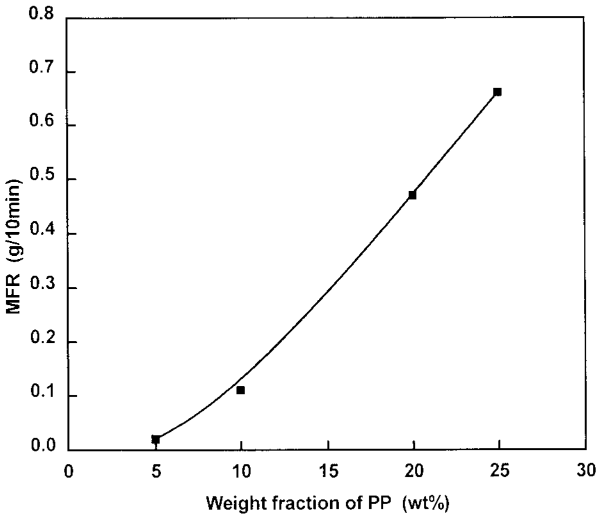


Figure 2 The melt flow rate (MFR) of UHMWPE/PP blends versus the weight fraction of PP.

TABLE I
Mechanical Properties of Various UHMWPE/PP Blends at 10 rpm Extrusion Speed

Mechanical Properties	Pure UHMWPE	UHMWPE/PP		
		90:10	80:20	75:25
Yield strength (MPa)	23.0	25.3	26.6	26.0
Strength at break (MPa)	36.1	39.1	37.0	30.7
Izod notched impact strength (kJ/m^2)	92.0	109.2	90.3	78.1
Elongation at break (%)	395.3	334.7	324.0	293.5
Young's modulus (MPa)	528	700	1032	1128

strength at break and the Izod notched impact strength are the highest at a 10 wt % PP concentration. Generally speaking, the yield strength and Young's modulus of PP are much higher than those of UHMWPE, the increase of the yield strength and Young's modulus with the increase of PP in the blends is reasonable according to the linear additivity rule, but the increase of the impact strength at 10 wt % PP is a strange occurrence. The melt viscosity of PP is much lower than that of UHMWPE, and PP may be well dispersed in the UHMWPE matrix as a reinforcement material in the blend system.

The MFR and mechanical properties data clearly show that the addition of PP to UHMWPE can effectively increase the fluidity of UHMWPE, and the mechanical properties of the blends are also improved to some extent.

Processability and rheology under ultrasonic vibration

The relative die pressure drop under various ultrasonic intensities indicates that a higher ultrasonic intensity and lower rotation speed both contribute to the larger reduction of pressure. In the case of a 15 rpm screw rotation speed and 250-W ultrasonic intensity, the pressure drop is 35% (Fig. 3). Furthermore, ultrasonic vibration during extrusion increases the throughput of the extrudate. The flow rate increases with the increase of the ultrasonic intensity, as shown in Figure 4. All these demonstrate that ultrasonic vibration can significantly improve extrusion efficiency.

A series of rheological curves of these blends could be obtained by treating the extruding die as a dynamic capillary rheometer (Fig. 5). The apparent viscosity of these blends decreases with the increase of the PP concentration. Ultrasonic irradiation during extrusion can further decrease the viscosity for all the blends; and the lower the shear rate or the stronger the ultrasonic irradiation, the more the apparent viscosity decreases under ultrasonic irradiation. At a low shear rate, the less PP contained in the blend, the more sensitive is the apparent viscosity to ultrasonic irradiation. All the blends appear to have similar shear-thinning curves when the ultrasonic intensity is lower than 200 W, but the difference appears when the irradiation intensity is higher than 200 W. The less PP (relatively low molecular weight compared with that of UHMWPE) contained in the blend system, the stronger the shear-thinning phenomenon appearing at a lower shear rate and the lower the irradiation intensity needed to cause this phenomenon. In the case of 10 wt % PP contained in the blend [Fig. 5(A)], when the ultrasonic intensity is 200 W, a strong shear-thinning phenomenon exists at low shear rate. Moreover,

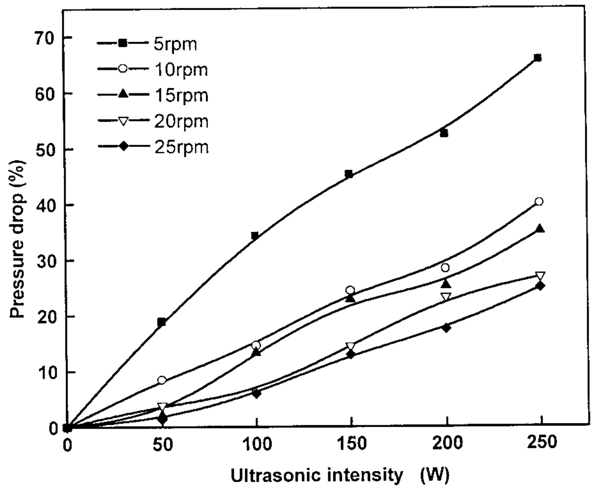


Figure 3 The variation of the die pressure drop of the UHMWPE/PP (80:20) blend with the ultrasonic intensity at various extrusion speeds.

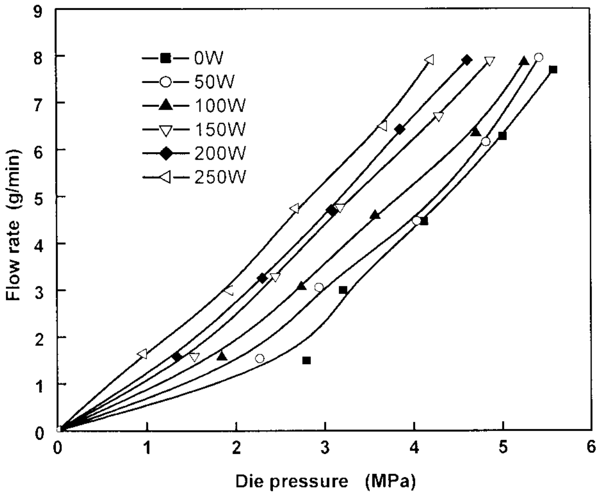
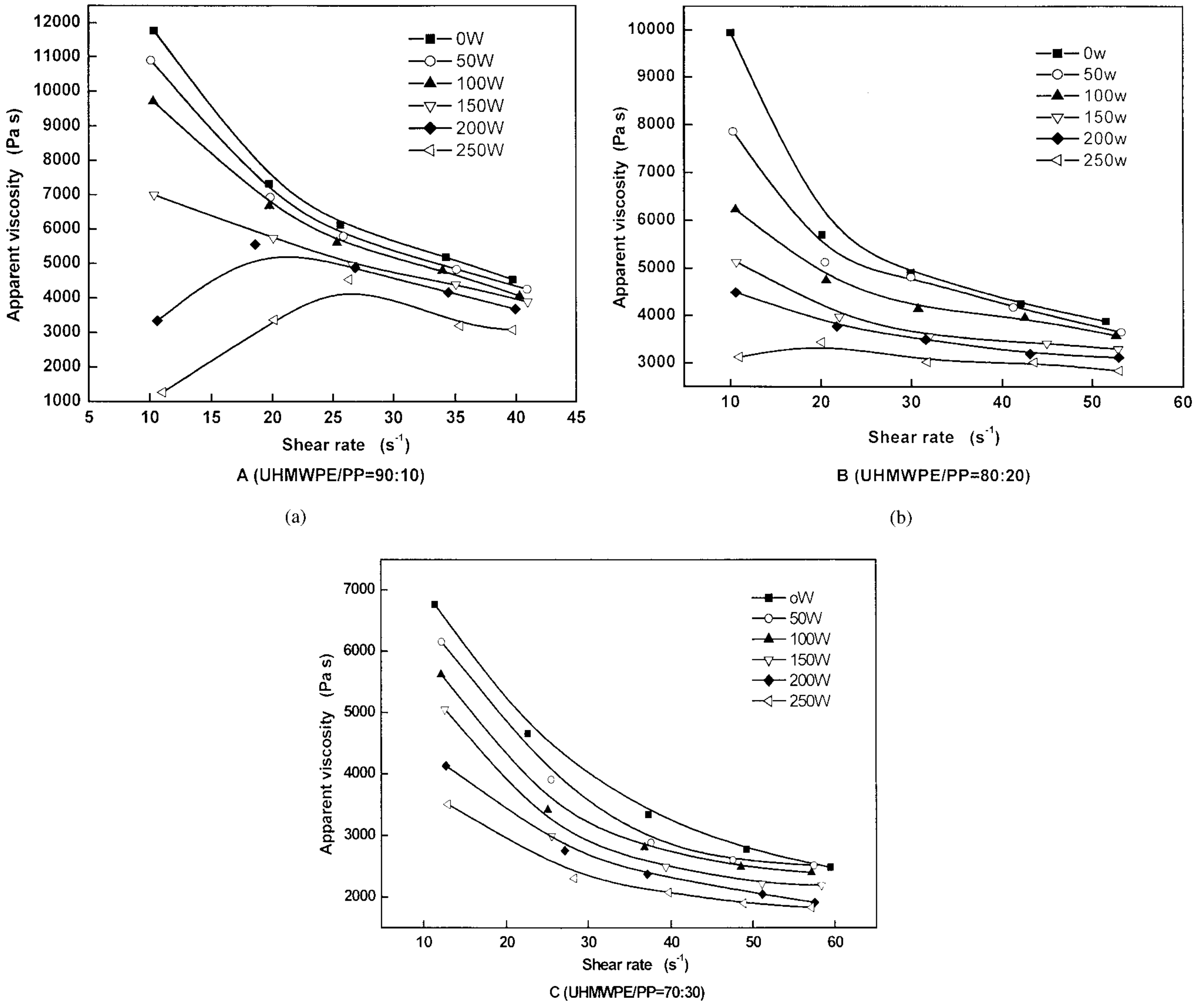


Figure 4 The variation of the flow rate of the UHMWPE/PP (80:20) blend with the die pressure under various ultrasonic intensities.



(a) (b)

(c)

Figure 5 The variation of the melt apparent viscosity with the shear rate under various ultrasonic intensities for UHMWPE/PP blend ratios of (A) 90:10, (B) 80:20, and (C) 70:30.

when the PP content is increased to 30 wt % in the blend [Fig. 5(C)], the shear-thinning phase does not exist in the whole shear rate area. These phenomena indicate that, because of its very long molecular chain, UHMWPE is very sensitive to ultrasonic vibration under high irradiation intensity and a long exposure time (lower shear rate); more molecular chains may be broken; and more entanglements may be disentangled, which causes a sharp drop in the apparent viscosity. As the shear rate increases, the irradiation time decreases. Both the smaller molecular decomposition and less disentangling of the UHMWPE molecular chain make the apparent viscosity rise, which surpasses the amount of reduction caused by the shear rate increase, so the whole apparent viscosity increases as the shear rate increases. As the shear rate continues to increase, the shear-thinning effect plays the main role, so the curve appears in the normal shear-thinning form again. With the increasing of PP content in the blend, there may be enough PP dispersed into the UHMWPE molecular net under the ultrasonic vibration, which may affect the rheological characteristics of UHMWPE. Thus, no shear-thinning phase appeared at a higher PP concentration.

Mechanical properties of extrudate after ultrasonic irradiation

Figure 6 shows that the yield strength of the UHMWPE/PP (80:20) blend remains almost unchanged when tultrasonic intensity is lower than 150 W. When the ultrasonic irradiation intensity is higher than 150 W, the yield strength begins to decrease. In addition, the lower the extrusion speed, the more

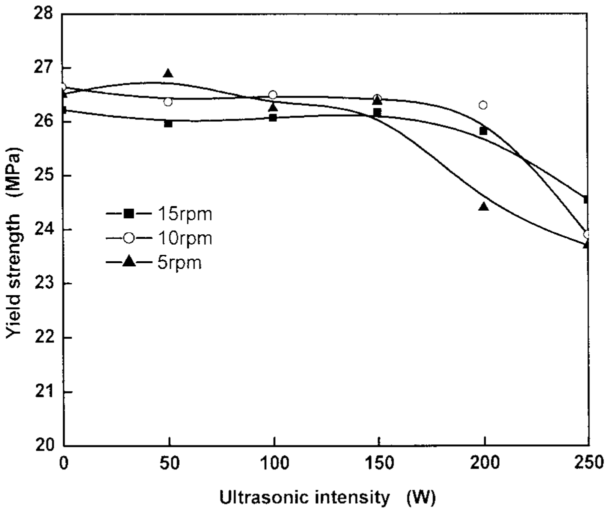


Figure 6 The variation of the yield strength of the UHMWPE/PP (80:20) blend with the ultrasonic intensity at various extrusion speeds.

sharply the yield strength decreases, which coincides with the rheology analysis above that high irradiation intensity and a long residence time may destroy the structure and therefore the properties.

When the ultrasonic intensity is 50 W, the Izod notched impact strength appears to slightly increase after ultrasonic irradiation at all three extrusion speeds (Fig. 7). With the increase of the irradiation intensity, the Izod notched impact strength at 5 rpm begins to decrease and that at 10 rpm remains nearly unchanged until the irradiation intensity increases to 150 W, whereas at 15 rpm an apparent decrease does not exist in the whole range of ultrasonic intensities.

Figure 8 shows the variation of the Young's modulus with the ultrasonic irradiation intensity. As a whole, the Young's modulus increases with the increase of irradiation intensity at all extrusion speeds.

In short, an appropriate ultrasonic intensity and irradiation time can improve the Izod notched impact strength and Young's modulus, but the yield strength remains almost unaffected. This effect may be ascribed to the vibration, orientation, disentangling, and dispersion roles of ultrasonic vibration. However, an irradiation intensity that is too high and an irradiation time that is too long will damage the properties.

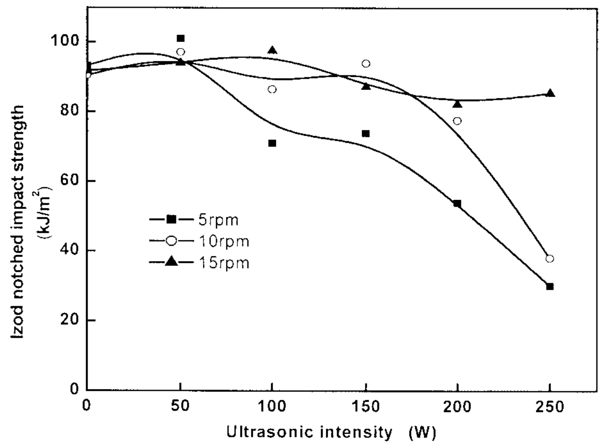


Figure 7 The variation of the Izod notched impact strength of the UHMWPE/PP (80:20) blend with the ultrasonic intensity at various extrusion speeds.

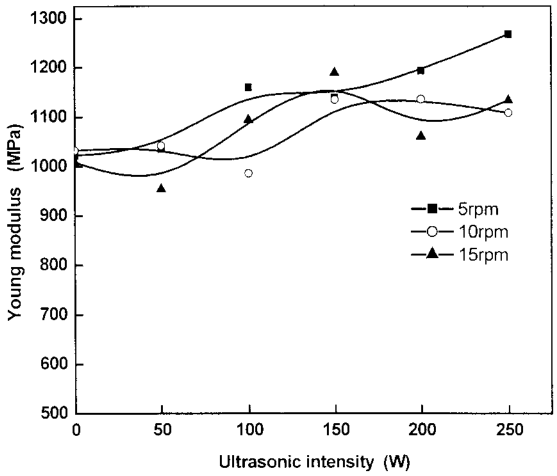


Figure 8 The variation of the Young's modulus of the UHMWPE/PP (70:30) blend with the ultrasonic intensity at various extrusion speeds.

CONCLUSION

UHMWPE/PP blends can be processed by a conventional single-screw extruder, and their mechanical properties are improved compared to UHMWPE. When PP is in the blends, it acts as a reinforcement material, as well as a processing aid agent. Ultrasonic vibration applied near the die can effectively reduce the die pressure and the melt apparent viscosity and thus increase the extrusion effect of UHMWPE/PP blends. An appropriate ultrasonic intensity and extrusion rate can further improve the Young's modulus and Izod notched impact strength, but an overdose of irradiation will harm the impact and yield strengths.

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