

Study on Processing of Ultrahigh Molecular Weight Polyethylene/Polypropylene Blends: Capillary Flow Properties and Microstructure

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ABSTRACT: The capillary flow properties and morphologies of ultrahigh molecular weight polyethylene/polypropylene (UHMWPE/PP) blends were studied. The results show that UHMWPE is difficult to process. The melts flowed unsteadily at lower shear rate. With 10 wt % PP contained in the UHMWPE/PP blends, the apparent melt viscosity was much lower than that of UHMWPE. When the PP content increased to 20 and 30 wt %, no pressure vibration occurred throughout the whole shear rate range. Microstructure analysis showed that PP prefers to locate in the amorphous or

low crystallinity zones of the UHMWPE matrix. The flowability of UHMWPE increased substantially with the addition of PP. The addition of PE could not effectively reduce the chain entanglement density of UHMWPE. The improvement of processability of UHMWPE by the addition of PE was rather limited. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3894–3900, 2004

Key words: rheology; ultrahigh molecular weight polyethylene (UHMWPE); morphology; blends; crystal structures

INTRODUCTION

Unsteady flow often occurs in the capillary flow of linear polymer melts that are entangled to a high degree.^{1–4} For example, ultrahigh molecular weight polyethylene (UHMWPE) is difficult to process because of its high molecular weight and very tight chain entanglement. Substantial pressure vibration and unusual flow of UHMWPE melt will occur during extruding. UHMWPE/kaolin composites prepared by a polymerization-filling method showed that the new materials had better steady and dynamic rheological properties.⁵ When the kaolin content was more than 15 wt %, the composite melts behaved like general polymer melts and could be extruded at low shear rate. However, when the kaolin content was less than 10 wt %, a common viscoelastic flow zone was absent from the flow curve of the composites. The stress vibration started at a low shear rate, and a coarse surface of the extrudate appeared.

Our previous study⁶ showed a surprisingly improved processability for the UHMWPE/polypropylene (PP) blend compared with that for UHMWPE and UHMWPE/HDPE blend. UHMWPE/PP blends still retain excellent mechanical properties at appropriate PP contents. The present article concerns systematic studies on the morphologies and capillary flow properties of UHMWPE/PP blends.

EXPERIMENTAL

Materials

UHMWPE (M-II), with an average molecular weight of 2.5×10^6 and a mean particle diameter of about 300 μm , was supplied by Beijing No. 2 Auxiliary Agent Factory (Beijing, China). PP (F401), with a melt flow rate (MFR) of 2.0 g/10 min (230°C, 2.16 kg load), was supplied by Lanzhou Chemical Industry Factory (Lanzhou, China). HDPE (5000S), with MFR = 1.2 g/10 min (230°C, 2.16 kg load), was supplied by Yanshan Petrochemical Corp. (Beijing, China).

Capillary flow properties

UHMWPE/PP blends for capillary flow experiments were prepared by extruding the blends with a single-screw extruder [$D = 25$ mm, length-to-diameter (L/D) ratio = 25], through a circle die ($D = 3$ mm, $L/D = 7$). The die temperature was 210°C and the screw rotation speed was 10 rpm. The extrudates were then made

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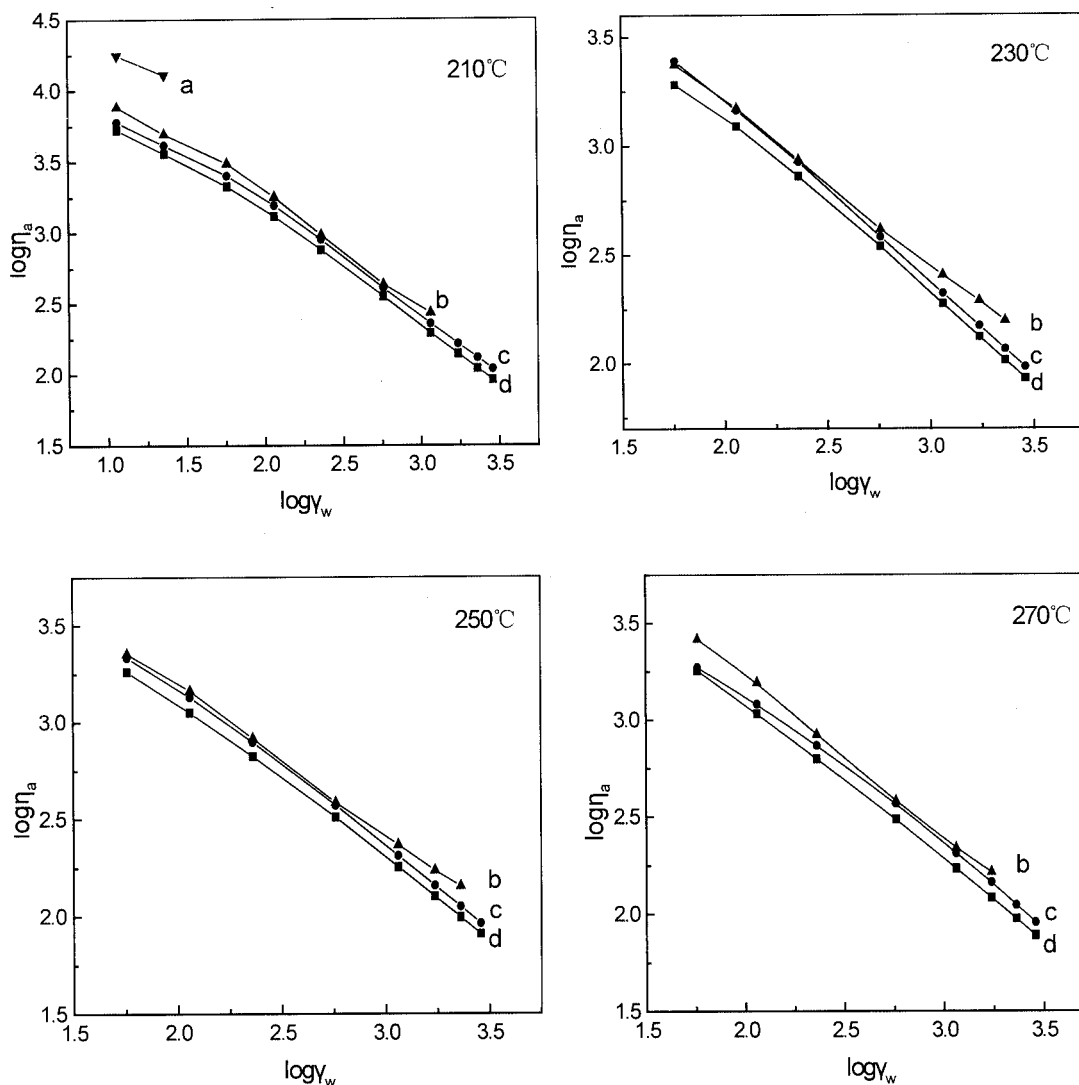


Figure 1 Apparent flow curves of UHMWPE/PP blends at different temperatures: (a) UHMWPE/PP; (b) UHMWPE/PP (90 : 10); (c) UHMWPE/PP (80 : 20); (d) UHMWPE/PP (70 : 30).

into pellets. The capillary extrusion experiments of the specimens were carried out on a Gottfert Rheograph 2002 rheometer (Univ. of Massachusetts, Amherst, MA) with cylinder dies of radius $R = 0.5$ mm, and length-to-radius ratios (L/R) of 20, 40, and 60 were used.

The thermal characteristics were studied on Netzsch DSC 204 (Netzsch-Gerätebau GmbH, Bavaria, Germany). The samples were heated under nitrogen atmosphere from 40 to 200°C at a rate of 10°C/min. A JSM 5900 LV scanning electron microscope (SEM; JEOL, Tokyo, Japan) was used to observe the morphology of UHMWPE/PP blends. Before the SEM observation, the specimens were prepared by brittle fracturing under liquid nitrogen, then etching in a solution of 1.3 wt % KMnO_4 dissolved in a $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ (10 : 4 : 1) mixture to eliminate the amorphous phase.

RESULTS AND DISCUSSION

Flow curves

The flow curves of pure UHMWPE and UHMWPE/PP blends at different temperatures, with capillary L/R ratios of 60, are shown in Figure 1. The data are presented without Bagley correction. UHMWPE is difficult to process. The melts flow unsteadily at lower shear rate, and no steady rheology data could be obtained at higher shear rates because of the pressure vibration. With 10 wt % PP content in the UHMWPE/PP blend, the apparent melt viscosity was much lower than that of UHMWPE, and the pressure vibration occurred only at a much higher shear rate. When the PP content increased to 20 and 30 wt %, no pressure vibration occurred throughout the whole range of shear rate. Moreover, as the PP content in the blends increased, the melt apparent viscosity of UHM-

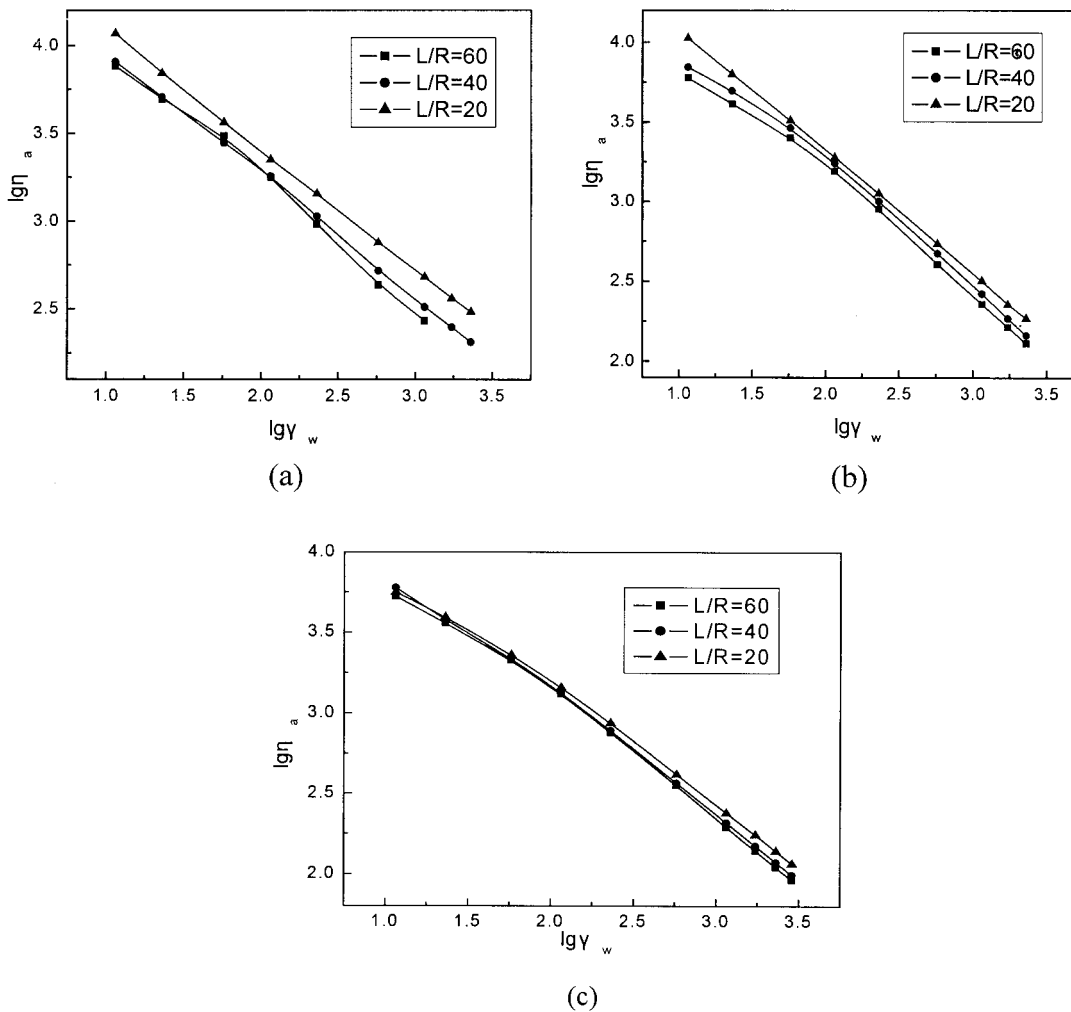


Figure 2 Apparent flow curves of UHMWPE/PP blends with different L/R ratios at 210°C: (a) UHMWPE/PP (90 : 10); (b) UHMWPE/PP (80 : 20); (c) UHMWPE/PP (70 : 30).

WPE/PP blends decreased under all chosen temperature conditions.

Figure 2 shows the melt flow curves of UHMWPE/PP blends extruded through dies of different L/R ratios. Because of the extra pressure drop, which was produced by the velocity profile adjusting at the entrance and the elastic energy storage in the viscoelastic fluid, the apparent flow curve obtained with a die of smaller L/R ratio was located at the higher apparent viscosity side. With 30 wt % PP contents in the blends, the influence of L/R ratio on the apparent viscosity of the melt decreased.

According to Bagley correction (or end correction) formula

$$\sigma = \frac{P}{2(L/R + n)} \quad (1)$$

where σ is the wall shear stress in the capillary for fully developed flow, P is the overall pressure drop,

and n is the end correction coefficient. Graphs of P versus L/R for different shear rates in the flow of UHMWPE/PP blends, known as Bagley plots, are shown in Figure 3. The shear rate range 1.15×10^2 to $2.88 \times 10^3 \text{ s}^{-1}$ is covered. Within experimental error, these plots are linear. The end correction coefficient n can be obtained by extrapolation of the line to $P = 0$.⁷

Figure 4 shows the variations of the end correction coefficient n , which is a measure of melt elasticity,⁸ with increasing apparent shear rate for UHMWPE/PP blends. Values of n increase with increasing shear rate $\dot{\gamma}$. The greater the content of PP in the blend, the lower the end correction coefficient n ; thus the melt elasticity of UHMWPE/PP blends decrease with increased content of PP in the blends.

DSC analysis of UHMWPE/PP blends

DSC thermograms of the specimens are depicted in Figure 5. The transition temperature and the corre-

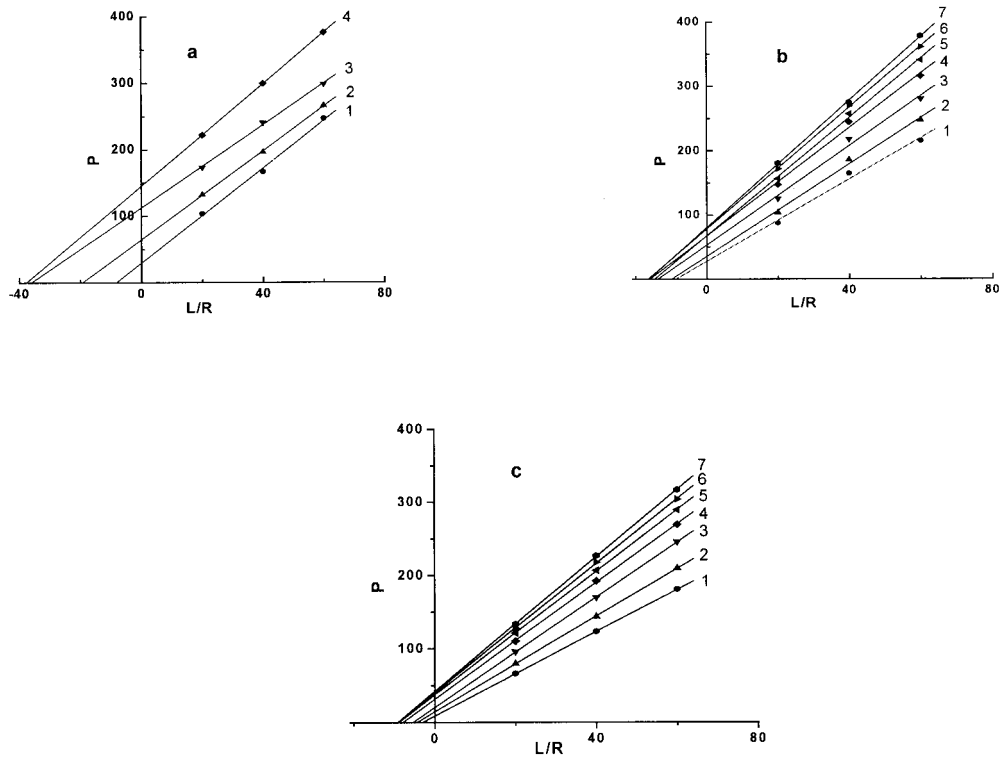


Figure 3 P - L/R curves of UHMWPE/PP blends at 210°C: (a) UHMWPE/PP (90 : 10); (b) UHMWPE/PP (80 : 20); (c) UHMWPE/PP (70 : 30). Shear rate: 1, 115.2 s⁻¹; 2, 230.4 s⁻¹; 3, 576.0 s⁻¹; 4, 1152 s⁻¹; 5, 1728 s⁻¹; 6, 2304 s⁻¹; 7, 2880 s⁻¹.

sponding transition enthalpy are listed in Table I. There are two peaks in the curves. The peaks at about 140 and 165°C are the melting peaks of crystallized UHMWPE and crystallized PP in UHMWPE/PP blends, respectively. This proves that UHMWPE/PP blends constitute a typical immiscible blending system. The addition of PP reduces the crystallinity of UHMWPE, and the crystallinity of PP in the blends is very low, as shown in Table I. The high chain entanglement density and low flowability of UHMWPE

molecules retard the movability of PP, and thus the crystallinity of PP in the blends is rather low.

Morphology observations

Figure 6 shows SEM micrographs of the cryogenically fractured surfaces of the specimens with etching of the

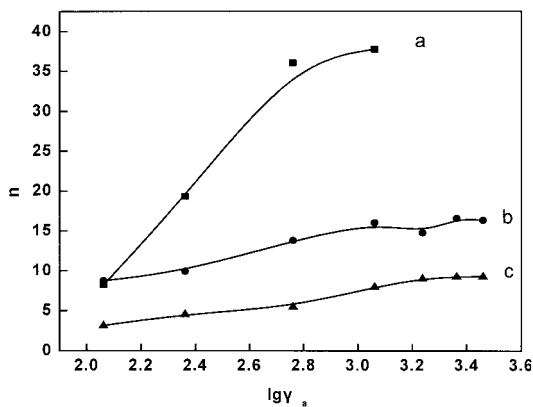


Figure 4 End correction values versus logarithm of shear rate of UHMWPE/PP blends: (a) UHMWPE/PP (90 : 10); (b) UHMWPE/PP (80 : 20); (c) UHMWPE/PP (70 : 30).

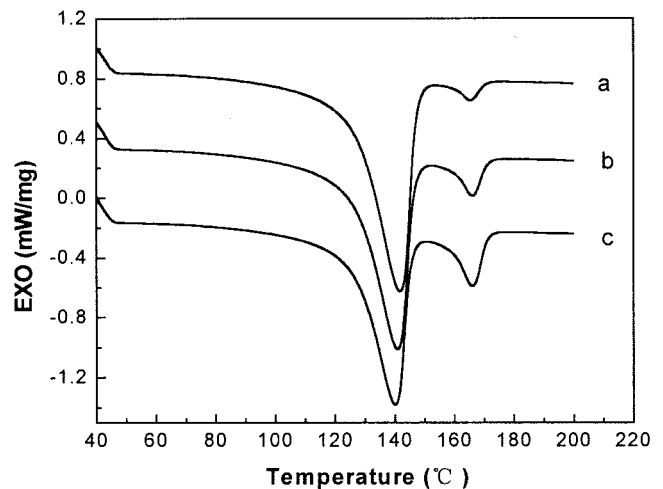


Figure 5 DSC curves of UHMWPE/PP blends: (a) UHMWPE/PP (90 : 10); (b) UHMWPE/PP (80 : 20); (c) UHMWPE/PP (70 : 30).

TABLE I
DSC Data of UHMWPE/PP Blends

PP (wt %)	UHMWPE			PP			Crystallinity (total) (%)
	T_{peak} (°C)	ΔH (J/g)	Crystallinity (%)	T_{peak} (°C)	ΔH (J/g)	Crystallinity (%)	
10	141.76	132.5	51.3	164.96	4.8	23.2	48.5
20	140.56	112.5	49.0	165.60	10.9	26.0	44.4
30	139.92	94.3	47.0	166.16	17.1	27.3	41.1

amorphous phase. UHMWPE shows a characteristic fibril-like crystal morphology [Fig. 6(a)]. Figure 6(b) indicates that HDPE has a crystal morphology similar to that of UHMWPE. The etched PP shows a typical spherical crystal morphology, as shown in Figure 6(c).

Figure 7 shows SEM morphology at two magnifications of UHMWPE/HDPE and UHMWPE/PP blends after etching. Figure 7(a) shows that the crystal morphology of UHMWPE/HDPE is almost the same as that of pure UHMWPE, as shown in Figure 6(a). HDPE crystal domains could not be distinguished. The melts of UHMWPE and HDPE, melts

of UHMWPE and HDPE penetrate into each other during processing for good miscibility of the two polymers, to form a perfect chain entanglement net. HDPE cannot effectively decrease the entanglement density of UHMWPE. Therefore, the improvement of processability of UHMWPE by the addition of HDPE is rather limited.

In UHMWPE/PP blends, the morphology of the etched specimens shows an abundance of blocks dispersed within the matrix, as shown in Figure 7(b)–(d). With increased content of PP in the blends, the size of the dispersed blocks decreases and the gaps between

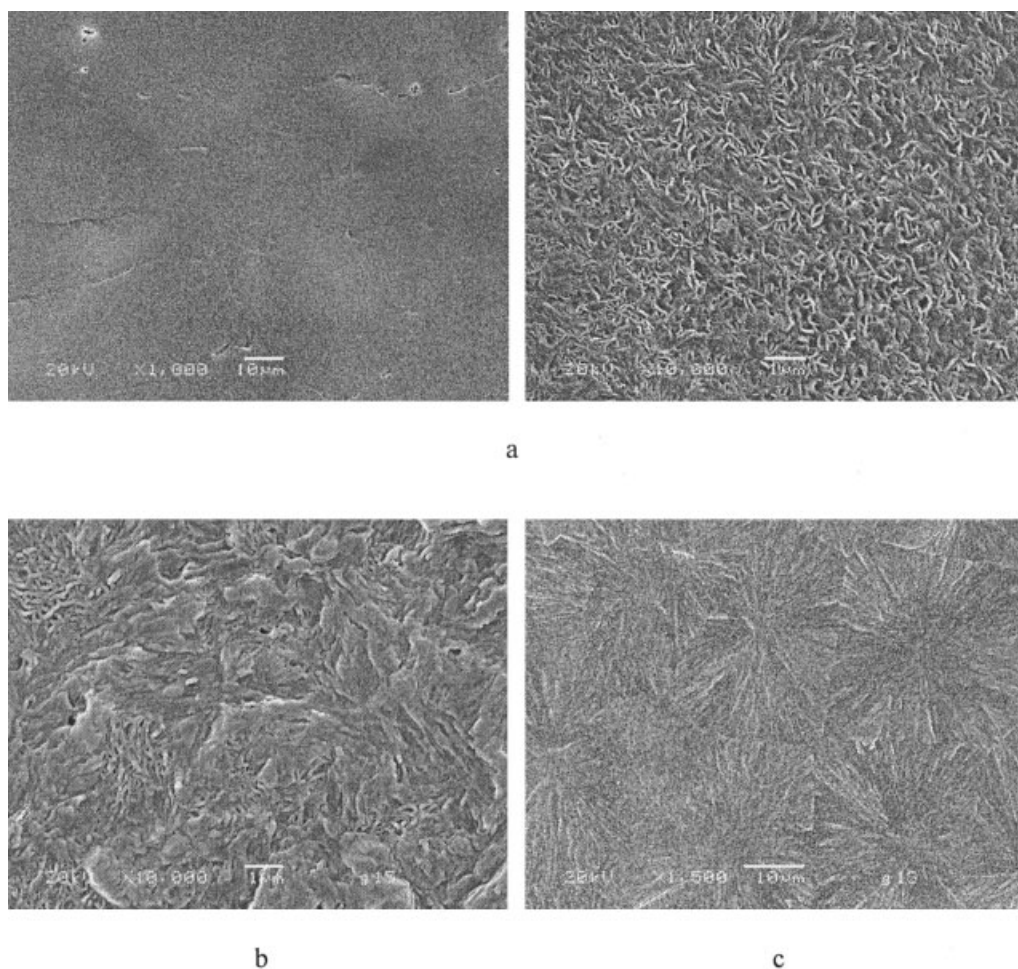


Figure 6 SEM micrographs of cryogenically fractured surfaces after etching: (a) UHMWPE; (b) PE(5000S); (c) PP.

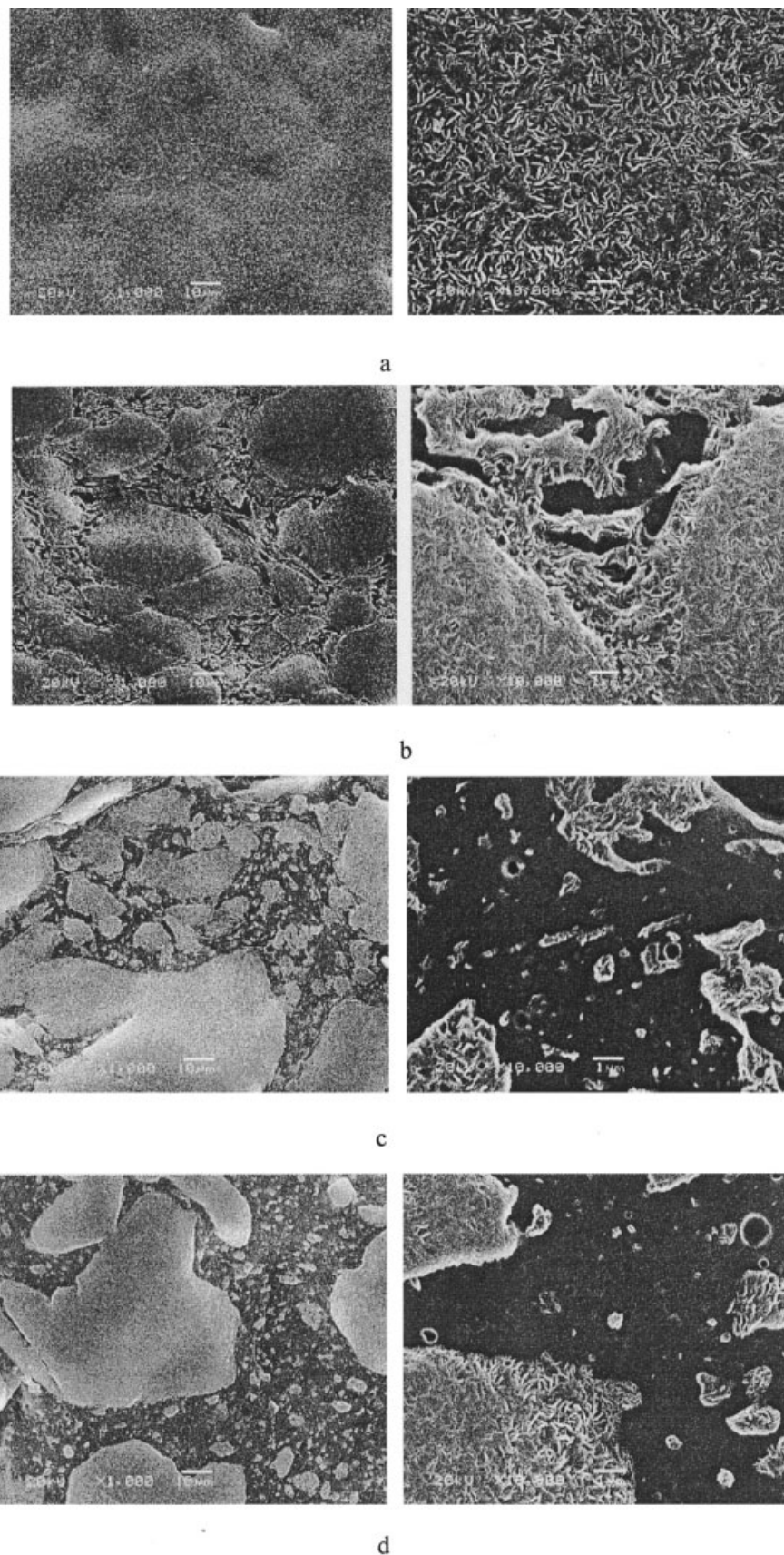


Figure 7 SEM micrographs of cryogenically fractured surfaces after etching: (a) UHMWPE/PE (80 : 20); (b) UHMWPE/PP (90 : 10); (c) UHMWPE/PP (80 : 20); (d) UHMWPE/PP (70 : 30).

the blocks increase. By careful observation it was determined that the dispersed blocks exhibit a morphology similar to that of pure UHMWPE. It was concluded that these dispersed blocks are the crystal domains of UHMWPE.

SEM observations of the original UHMWPE powder demonstrated that UHMWPE powder is composed of smaller, submicron particles. PP fills the gaps between the particles to act as a heat-transfer agent and adhesive during processing. DSC analysis of the investigated UHMWPE/PP blends revealed that the crystallinity of PP in the blend is rather low, and the total crystallinity of the blend decreased with the addition of PP. It is presumed that etching processing eliminates the entire amorphous zone of UHMWPE and the PP dispersed within it. Gaps between the UHMWPE crystal domains were thus observed. PP disperses between blocks of UHMWPE, and prefers to locate in the amorphous or low crystallinity zones of the UHMWPE matrix, which increases chain movability and causes the melt to flow more easily, such that the melt elasticity of UHMWPE decreases, and the flowability of UHMWPE increases substantially with increased PP content in the blend.

CONCLUSIONS

1. UHMWPE is difficult to process. The melts flow unsteadily at lower shear rate. With 10 wt % PP contained in the UHMWPE/PP blends, the apparent melt viscosity is much lower than that of UHMWPE. When the PP content increased to 20 and 30 wt %, no pressure vibration occurred throughout the whole shear rate range. The melt apparent viscosity of UHMWPE/PP blends decreases with the increase of PP content in the blends under all chosen temperature conditions.
2. The addition of PP decreases the end correction coefficient n of UHMWPE/PP blends. The greater the content of PP contained in the blend, the lower the end correction coefficient n .
3. Microstructure analysis shows that PP prefers to locate in the amorphous or low crystallinity zones of UHMWPE matrix. The flowability of UHMWPE increases substantially with the addition of PP. The addition of PE could not effectively reduce the chain entanglement density of UHMWPE. The improvement of processability of UHMWPE by the addition of PE is rather limited.

References

1. Denn, M. M. *Annu Rev Fluid Mech* 1990, 22, 13.
2. Larson, R. *Rheol Acta* 1992, 31, 213.
3. Kalika, D. S.; Denn, M. M. *J Rheol* 1987, 31, 815.
4. Hatzikiriakos, S. G.; Dealy, J. M. *J Rheol* 1992, 36, 845.
5. Wu, Q. Y.; Gao, W. P.; Hu, Y. L. *J Appl Polym Sci* 2001, 80, 2154.
6. Liu, G. D.; Li, H. L. *J Appl Polym Sci* 2003, 89, 2628.
7. Bagley, E. B. *J Appl Phys* 1957, 28, 624.
8. Fujiyama, M.; Kawasaki, Y. *J Appl Polym Sci* 1991, 42, 67.