

Influence of Poly(ethylene glycol)-Containing Additives on Extrusion of Ultrahigh Molecular Weight Polyethylene/Polypropylene Blend

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ABSTRACT: The influence of poly(ethylene glycol) (PEG)-containing additives on the extrusion behavior of ultrahigh molecular weight polyethylene/polypropylene (UHMWPE/PP) blend was studied. It was found that the addition of small amounts of PEG to UHMWPE/PP blend resulted in significant reduction of die pressure and melt viscosity, and obvious increase of the flow rate at a given die pressure, while PEG/diatomite binary additives enhanced the improvement in the processability of UHMWPE/PP blend. When pure HDPE was extruded with the die through which UHMWPE/PP/PEG blend was previously extruded, the extrusion pressure of HDPE increased with the extrusion time gradually. This meant that PEG might migrate to the die wall surface and coat it in the extrusion of UHMWPE/PP/PEG blend. FTIR spectra and SEM micrographs of the

UHMWPE/PP/PEG extrudates indicated that PEG located not only at the surface but also in the interior of the extrudates. So, the external lubrication at the die wall, combined with the internal lubrication to induce interphase slippage of the blend, was proposed to be responsible for the reduction of die pressure and viscosity. In addition, an ultrahigh molecular weight polysiloxane and a fluoropolymer processing aid were used as processing aids in the extrusion of UHMWPE/PP as control, and the results showed that only minor reduction effects in die pressure and melt viscosity were achieved at their suggested loading level. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1282–1288, 2006

Key words: ultrahigh molecular weight polyethylene; poly(ethylene glycol); extrusion; additive; viscosity

INTRODUCTION

In recent decades, increasing interest has been devoted to ultrahigh molecular weight polyethylene (UHMWPE) because of its outstanding properties, especially excellent toughness, high abrasion resistance, low friction, good chemical resistance, and biocompatibility. UHMWPE could be used in many fields, but its poor processability limits its application. Due to its extremely high molecular weight, melt viscosity of UHMWPE is extremely high and it can hardly flow above its melting point. So the conventional thermoplastic processing technique cannot be used for its processing except compression molding or ram extrusion.

To improve the melt fluidity of UHMWPE, conventional polyethylenes (LLDPE, LDPE, and HDPE) were blended with it.^{1–4} However, small quantities of conventional polyethylenes did not improve the flow of UHMWPE sufficiently to render it amenable to conventional melt processing, while the mechanical and tribological properties of UHMWPE would be decreased by blending with effective amounts of conventional polyethylene. It was also reported that mixtures of 70–90% UHMWPE and 10–30% polypropylene (PP) can be extruded by a conventional single extruder, and its mechanical and tribological properties were as good as or even better than that of pure UHMWPE.⁵ However, the melt fluidity of the UHMWPE/PP blend is still low, for example, the melt flow rate of the UHMWPE/PP (75/25) was 0.66 g/10 min under the condition of 230°C and 21.6 kg load.

Recently, fluoroelastomer and liquid crystalline polymer, which usually acted as processing aids for many other polymers were used to improve the processability of UHMWPE.⁶ It was reported that the die pressure and torque of UHMWPE in twin-screw extrusion processing was reduced when small amounts of these processing aids were added. However, the detailed effects of these aids on the properties of the UHMWPE need to be studied. The addition of calcium

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stearate was proved to produce dense packing of UHMWPE particles in direct compression molding, which resulted in better mechanical properties and better resistance to oxidative degeneration.⁷ But the calcium stearate addition is harmful to the medical application of UHMWPE. Poly(ethylene glycol) (PEG) was reported to be biocompatible, which is usually used as a coating in the field of biomaterials.⁸ PEG also proved to be effective in reducing the surface roughness of the LLDPE extrudate and the extrusion pressure when it was used together with poly(vinylidene fluoride-co-hexafluoropropylene) or polysiloxane or organic fillers.^{9,10}

In this work, PEG and PEG/diatomite binary additives were used as processing aids in the single-screw extrusion of UHMWPE/PP blend. The effect of PEG and PEG/diatomite binary additives on the die pressure, flow rate, and melt viscosity of the UHMWPE/PP blend were investigated.

EXPERIMENTAL

Materials

Base resin

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) was supplied by Lanzhou Chemical Industry Factory (Lanzhou, China) with a MFR of 2.0 g/10 min (230°C, 2.16 kg load). HDPE (6098A) was supplied by Qilu Petrochemical Corp. (Shandong, China) with a MFR of 7.8 g/10 min (230°C, 2.16 kg load).

Additives

Poly(ethylene glycol) (PEG) with an average molecular weight of 6000 was supplied by Aoke Chemical limited company (Liaoyang, China). Diatomite was supplied by Nahui desiccating agent company (Shanghai, China). PEG/diatomite binary additives were first blended for 10 min by a two-roll mill and then pulverized. The PEG/diatomite binary additives with weight ratio 1 : 1 and 1 : 4 were donated as PPA1 (1 : 1) and PPA1 (1 : 4), respectively. The ultrahigh molecular weight polysiloxane aid (donated as PPA2) in the form of white powder was supplied by a plastics company (China). The suggested loading for PPA2 is 0.5–2.0%. The fluoropolymer aid (donated as PPA3) in the form of white powder was supplied by a new materials company (China). The suggested loading for PPA3 is 500–1000 ppm.

Extrusion and characterization

All the blends were extruded by a general three-section single-screw extruder ($D = 20$ mm, $L/D = 25$)

with a cross sectional capillary die ($D = 3$ mm, $L/D = 8$) and a high-temperature melt pressure transducer. The temperatures were 100, 190, and 230°C for every section of the barrel, respectively, and 210°C for the die.

The die pressure was measured by the pressure transducer at the entrance of the capillary; the flow rate was got by measuring the extrudate weight per second, and the apparent melt viscosity was obtained by treating the extruding die in a dynamic capillary rheometer.

After the extrusion of UHMWPE/PP/PEG (80/20/1), HDPE was extruded at 30 rpm (revolution per minute) without cleaning of the die to analyze the coating of PEG on the die wall.

FTIR analysis of the surface layer and the internal layer of the UHMWPE/PP/PEG (80/20/1) extrudate was carried out with NICOLET-560 FTIR instrument. The surface layer and the internal layer of the UHMWPE/PP/PEG (80/20/1) extrudate were separated carefully with a fresh razor and then heat-pressed into a thin film for FTIR analysis. The morphology of the cryogenically fractured surfaces of the extrudates was analyzed with a JSM 5900 LV scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Die pressure of UHMWPE/PP(80/20) blends

The die pressures of UHMWPE/PP blends containing PEG or PEG/diatomite additives are shown in Figure 1. Adding small amounts of PEG induced an apparent drop of die pressure of UHMWPE/PP blends. And the drop of die pressure of UHMWPE/PP increased with the increase of PEG concentration. When 0.3 phr (part per hundred parts resin) PEG was incorporated, the die pressure of UHMWPE/PP dropped from 5.56 to 3.80 MPa at the screw rotation speed of 20 rpm, obtaining a die pressure reduction of 32% [Fig. 1(a)]. When 1.0 phr PEG was added, the percentage reduction of the die pressure of UHMWPE/PP increased to 60% at 20 rpm [Fig. 1(b)]. For a given PEG concentration, the effect of PEG on the die pressure reduction of UHMWPE/PP varied very little with the increase in screw rotation speed from 10 to 50 rpm, as seen in Table I.

When the same amount of PEG was contained in the UHMWPE/PP blend, the PEG/diatomite binary additives showed better effect on die pressure reduction of UHMWPE/PP than when PEG was used alone; and the weight ratio of PEG to diatomite influences the effect of binary additives. PEG/diatomite binary additive with weight ratio of 1 : 4 (PEG to diatomite) was more effective on die pressure reduction of UHMWPE/PP than PEG/diatomite with a higher weight ratio of 1 : 1

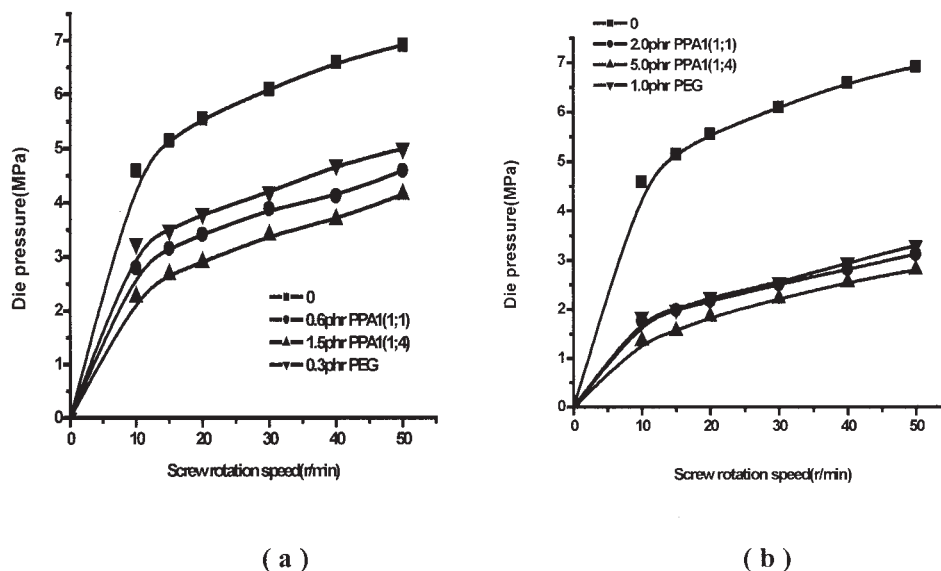


Figure 1 The variation of the die pressure with the screw rotation speed for UHMWPE/PP (80/20) blends with different additive concentrations: (a) 0.3 phr PEG, 0.6 phr PPA1 (1 : 1) and 1.5 phr PPA1 (1 : 4), (b) 1.0 phr PEG, 2.0 phr PPA1 (1 : 1) and 5.0 phr PPA1 (1 : 4).

Flow rate of UHMWPE/PP(80/20) blends

The large drop in die pressure provides the substantial potentiality for increasing production rate by speeding up screw rotation and reducing energy cost. At die pressure of 4.7 MPa, the flow rate of UHMWPE/PP (80/20) blend containing 0.3 phr PEG was 12.6 g/min, which was three times that of UHMWPE/PP (80/20) blend at the same die pressure. For a given flow rate, the die pressure of UHMWPE/PP blend with 0.6 phr PPA1 (1 : 1) was smaller than that of UHMWPE/PP blend with 0.3 phr PEG. For 1.5 phr PPA1 (1 : 4), the corresponding die pressure decreased further, as shown in Figure 2(a). A similar experimental result was obtained when higher amounts of PEG or PEG/diatomite binary additives were added, as shown in Figure 2(b).

Apparent viscosity of UHMWPE/PP(80/20) blends

Figure 3 showed that the addition of PEG reduced the apparent viscosity of UHMWPE/PP (80/20) blend in the whole shear rate range investigated. And with more addition of PEG, more viscosity reduction of

UHMWPE/PP occurred. In comparison with PEG, PEG/diatomite binary additives promoted the viscosity reduction effect of the UHMWPE/PP blend. When 0.3 phr PEG was added, the apparent viscosity reduction of UHMWPE/PP was about 20–30% in the shear rate range investigated. When 0.6 phr PPA1 (1 : 1) or 1.5 phr PPA1 (1 : 4) was used, the apparent viscosity reduction increased to 29–40% and 37–56%, respectively. In the case of 1.0 phr PEG or 2.0 phr PPA1 (1 : 1) or 5.0 phr PPA1 (1 : 4), the corresponding value was 42–55%, 53–63%, and 52–69%, respectively.

Compared with a polysiloxane aid and a fluoropolymer aid

Figures 4 and 5 showed that the ultrahigh molecular weight polysiloxane aid PPA2 and the fluoropolymer aid PPA3 had little effect on improving the die pressure and apparent viscosity of UHMWPE/PP blend. When 1 phr PPA2 was added, the reduction of die pressure of UHMWPE/PP was less than 10%. As far as viscosity was concerned, the addition of PPA2 had almost no effect on viscosity reduction of UHMWPE/PP. In the case of UHMWPE/PP with 0.5 phr PPA3, the die pressure reduction and the viscosity reduction of UHMWPE/PP was about 10% and 5%, respectively.

Proposed mechanisms

The significant effect of PEG-containing additives on the reduction of die pressure and melt viscosity of UHMWPE/PP blend may result from two factors: external lubrication of extrudate on the die wall sur-

TABLE I
Percentage Reduction of the Die Pressure of UHMWPE/PP(80/20) Blend at Different Screw Rotation Speed

PEG concentration (phr)	Screw rotation speed (rpm)					
	10	15	20	30	40	50
0.3	29	32	32	31	29	28
1.0	60	61	60	58	55	52

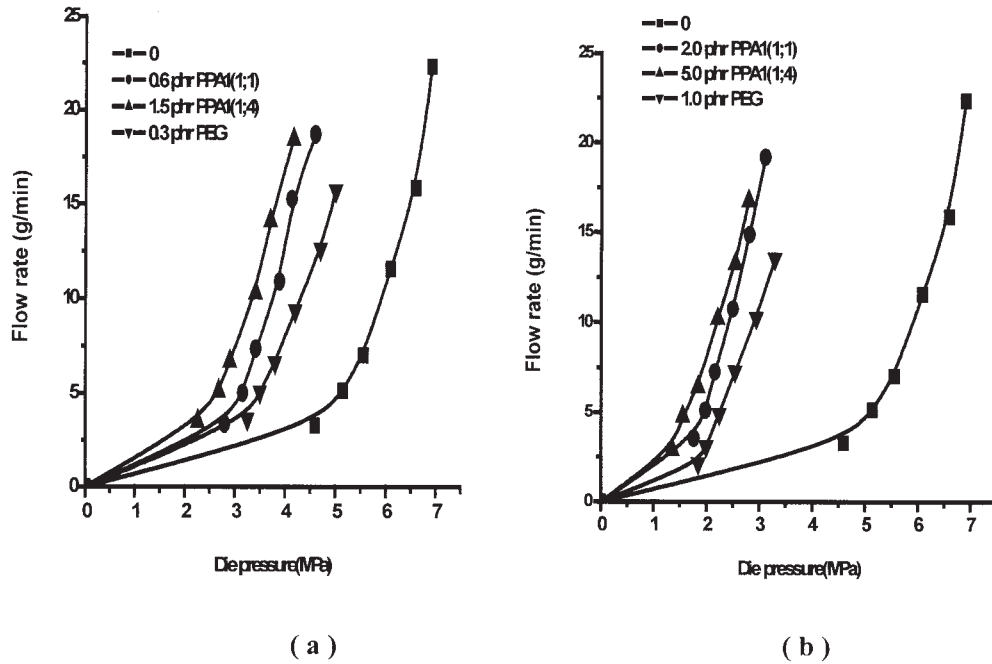


Figure 2 The variation of the flow rate with the die pressure for UHMWPE/PP (80/20) blends with different additive concentrations: (a) 0.3 phr PEG, 0.6 phr PPA1 (1 : 1) and 1.5 phr PPA1 (1 : 4), (b) 1.0 phr PEG, 2.0 phr PPA1 (1 : 1) and 5.0 phr PPA1 (1 : 4).

face and the internal interphase lubrication in the melt.

In the extrusion of UHMWPE/PP blend with PEG-containing additives, PEG tended to segregate in the interface between the metal die wall and the polymer melt. The driving force came from two aspects. Firstly, as PEG has higher surface energy than UHMWPE and

PP(their surface tensions can be seen in Table II¹¹), it tended to migrate to the die wall surface with high energy (the surface of the metal die is in fact covered by a layer of metal oxide and the surface tension of a typical metal oxide Fe₂O₃ is as high as 1357 mN/m)¹² to minimize the free energy of the system. Secondly, the viscosity of PEG is much lower than that of UH-

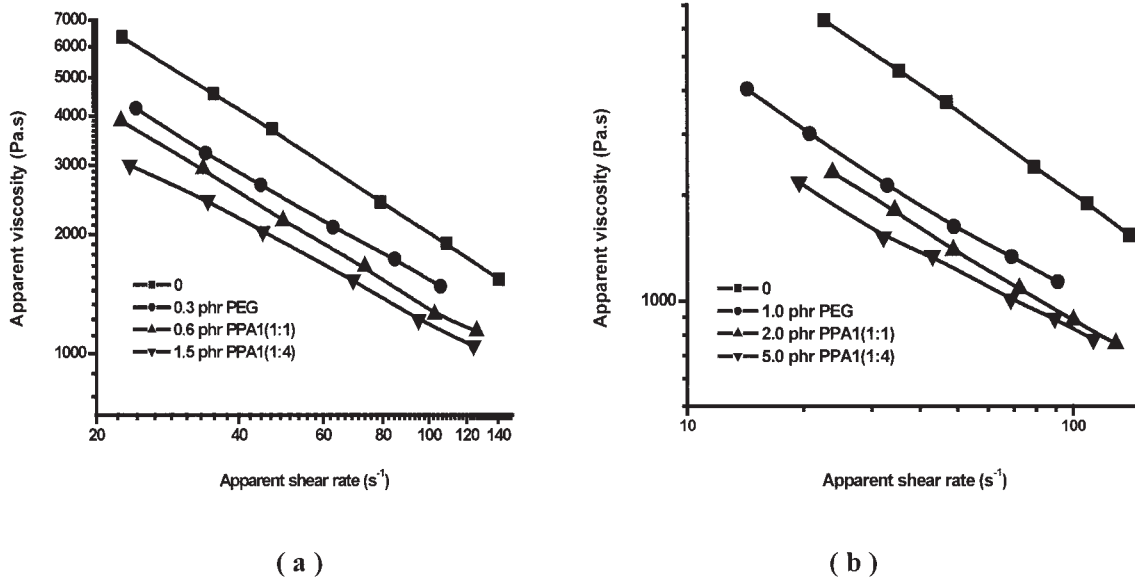


Figure 3 The variation of the apparent viscosity with the apparent shear rate for UHMWPE/PP (80/20) blends with different additive concentrations: (a) 0.3 phr PEG, 0.6 phr PPA1 (1 : 1) and 1.5 phr PPA1 (1 : 4), (b) 1.0 phr PEG, 2.0 phr PPA1 (1 : 1) and 5.0 phr PPA1 (1 : 4).

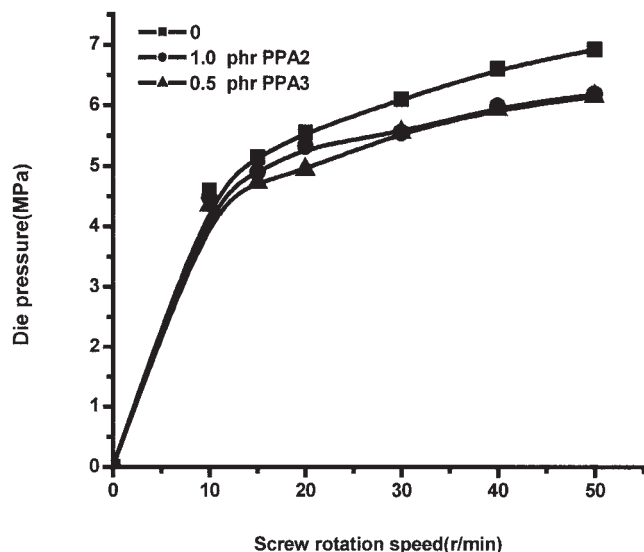


Figure 4 The variation of the die pressure with the screw rotation speed for UHMWPE/PP (80/20) blends containing PPA2 and PPA3.

MWPE and PP. To minimize viscous dissipation, PEG tends to migrate to the skin layer of the melt where the shear rate is maximum. To study the migration and coating of PEG on the die wall, HDPE was first extruded at 30 rpm with clean die and the equilibrium die pressure recorded was 4.7 MPa. After the extrusion of UHMWPE/PP/PEG (80/20/1), HDPE was extruded at 30 rpm without cleaning the die used previously, and the die pressure was recorded as the function of extrusion time. Figure 6 showed that it took 30 min for the die pressure of HDPE to go up gradually from 3.7 to 4.7 MPa. This phenomenon in-

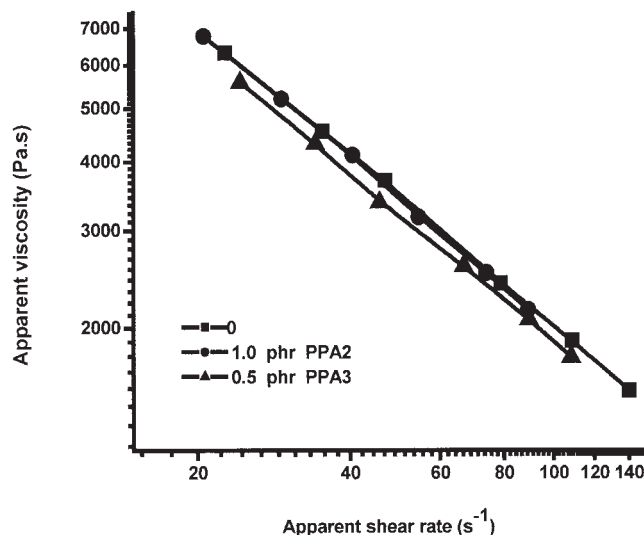


Figure 5 The variation of the apparent viscosity with the apparent shear rate for UHMWPE/PP (80/20) blends containing PPA2 and PPA3.

TABLE II
Surface Tension of Polymer Involved in the Blend System

Polymer	r^a (20°C) (mN/m)	$-dr/dT^a$ (mN/m°C)	r^b (210°C) (mN/m)
UHMWPE	36.8	0.056	26.16
PP	30.1	0.058	19.08
PEG	42.9	0.076	28.46

^r Surface tension.

^T Temperature.

^a The data are from reference.¹¹

^b The data are calculated from reference.¹¹

dicates that a PEG-enriched layer did exist at the die wall surface, acting as a lubricant to promote the slippage of the polymer melt on the wall.

While, it seemed that external lubrication effect was not the whole story, FTIR spectra showed that PEG (peak at $\sim 1100\text{ cm}^{-1}$) not only existed at the surface layer but also appeared in the internal section of the UHMWPE/PP (80/20) extrudate (Fig. 7). SEM micrographs (Fig. 8) also showed that some PEG was contained in the interior of the extrudate of UHMWPE/PP/PEG (80/20/1) blend.

Figure 8(a) is the micrograph of the fractured surface of UHMWPE/PP (80/20) extrudate. It can be observed that the UHMWPE/PP (80/20) blend was immiscible, with PP particles dispersed in UHMWPE matrix. While, for the fractured surface of UHMWPE/PP/PEG (80/20/1) extrudate [Fig. 8(b)], lots of holes were observed which resulted from the pulling out of the dispersed phase during the fracture. It was presumed that PP with higher melt viscosity forms the dispersed particles with large size, i.e., of micron to decamicon, while PEG with very low viscosity forms the particles with small size, i.e., of submicron.

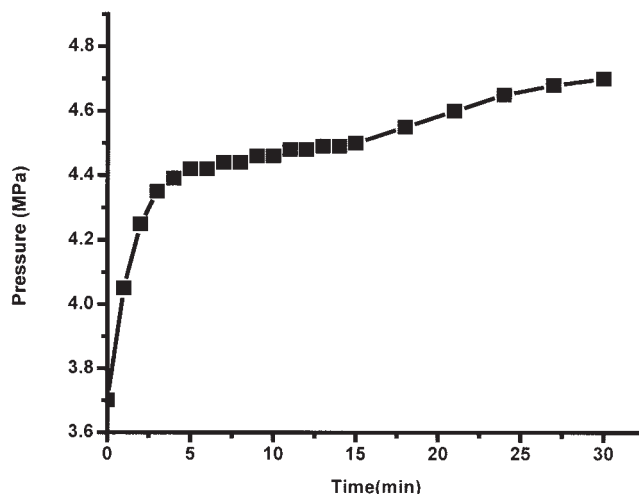


Figure 6 Die pressure as a function of time during the extrusion of pure HDPE after the extrusion of UHMWPE/PP/PEG (80/20/1) blend.

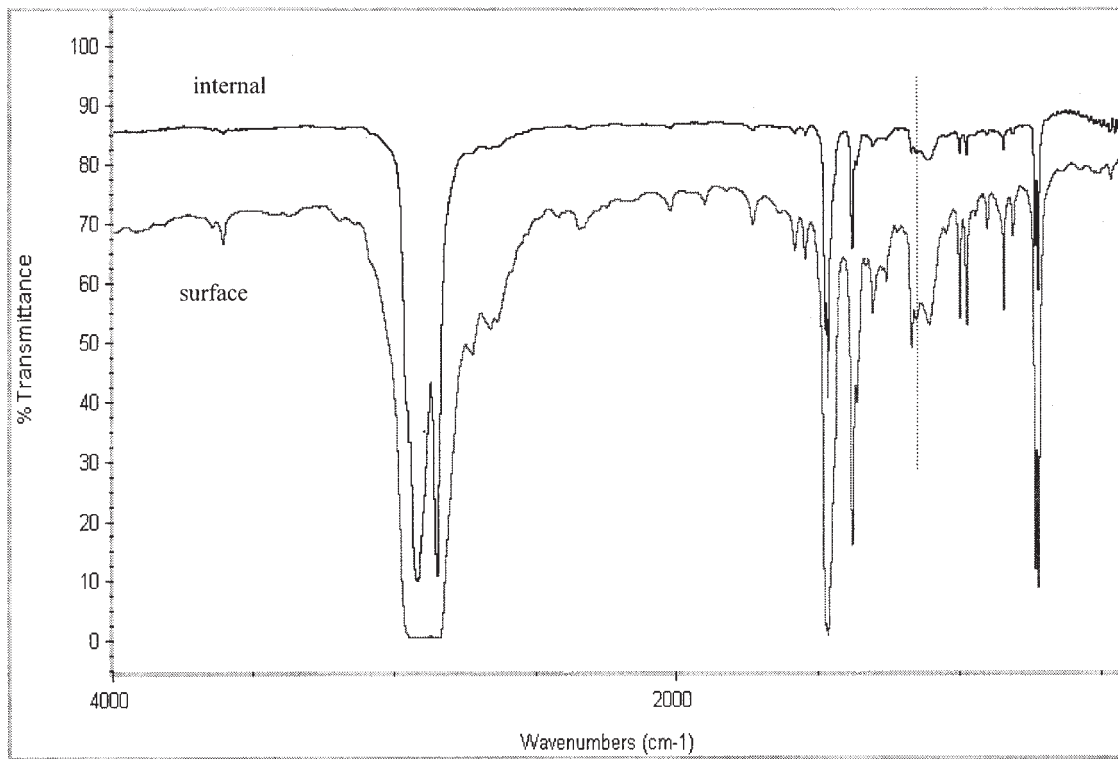
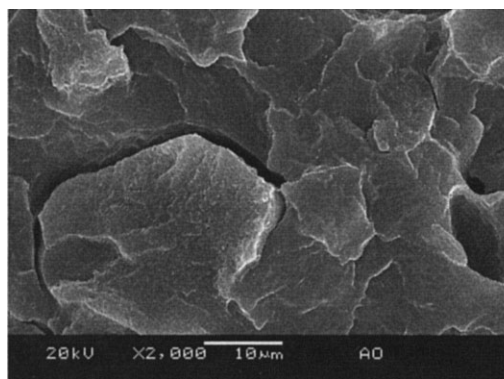


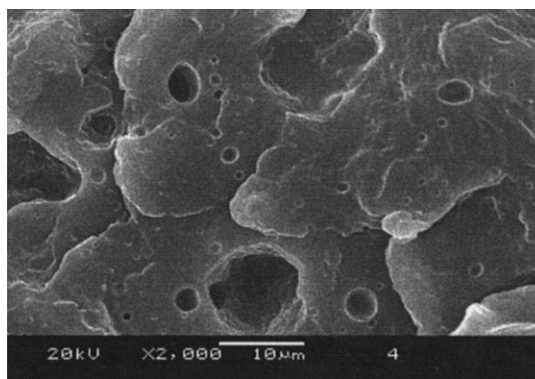
Figure 7 FTIR spectra of UHMWPE/PP/PEG(80/20/1) extrudate at different locations.

Both FTIR and SEM results indicated that a certain part of PEG was left in the interior of the extrudate during the extrusion of the UHMWPE/PP (80/20) blend with PEG-containing additives. It is well known that PEG has very low viscosity and good lubricating property, and PEG is incompatible with UHMWPE and PP. It will act as an internal lubricant to induce interphase slippage of the blend.

When PEG/diatomite binary additives were added, the amount of PEG which migrated to the die wall surface reduced, because a certain part of PEG was anchored by diatomite. So more PEG was left in the interior of the extrudate and the effect of interphase slippage was enhanced. In other words, synergistic effect of PEG and diatomite on reducing the die pressure and viscosity was achieved. In the case of equiv-



(a)



(b)

Figure 8 SEM micrographs of fractured surfaces of extrudates (a) UHMWPE/PP(80/20) blend, (b) UHMWPE/PP(80/20) blend containing 1 phr PEG.

alent PEG contained, PPA1 (1 : 4) was more effective than PPA1 (1 : 1) in viscosity reduction, because there was more diatomite in PPA1 (1 : 4), which would anchor more PEG.

Polysiloxane and the fluoropolymer were often used as processing aids to improve the processability of conventional polyethylene. While in this work, the ultrahigh molecular weight polysiloxane aid (PPA2) and the fluoropolymer aid (PPA3) had minor effects on reducing the pressure and viscosity of UHMWPE/PP blend, especially compared with PEG-containing additives. The reasons why PPA2 and PPA3 could not act effectively as processing aids in the extrusion of UHMWPE/PP blend were unclear, and further investigation is going on.

CONCLUSIONS

The addition of a small amount of PEG was found to reduce the die pressure and melt viscosity of UHMWPE/PP blend significantly. The effect of PEG depended on its concentration. With the increase in PEG concentration, more reduction of die pressure and viscosity of UHMWPE/PP blend were induced. In the case that involved equivalent PEG, PEG/diatomite binary additives exhibited better effect on reducing the die pressure and viscosity of UHMWPE/PP blend than PEG. And it was also found that, when the same amount of PEG was contained in the UHMWPE/PP/PPA1 blends, the PPA1 (1 : 4) showed more obvious effects on reducing the die pressure and viscosity of

UHMWPE/PP blend than PPA1 (1 : 1). The significant reduction of die pressure and viscosity of UHMWPE/PP blend with PEG-containing additives was attributed to the external lubrication at the die wall as well as the internal lubrication in the extrudate.

The effect of an ultrahigh molecular weight polysiloxane aid and a fluoropolymer aid on the extrusion behavior of UHMWPE/PP blend was studied for comparison. The results showed that both the polysiloxane aid and the fluoropolymer aid at their suggested loading level had minor effects on reducing the die pressure and melt viscosity of UHMWPE/PP blend.

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