Polymer Bulletin 58, 711–722 (2007)
DOI 10.1007/s00289-006-0711-3

Polymer Bulletin

Preparation of HDPE/UHMWPE/MMWPE blends by two-step processing way and properties of blown films

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Received: 24 September 2006 / Revised version: 13 November 2006 / Accepted: 27 November 2006
Published online: 13 December 2006 –

Summary

Blends of high density polyethylene (HDPE) and ultra high molecular weight polyethylene (UHMWPE) were prepared by two-step processing way. Middle molecular weight polyethylene (MMWPE) as a fluidity modifier and compatilizer was added into UHMWPE in the first step, and then modified UHMWPE and HDPE were blending extruded to prepare the HDPE/UHMWPE/MMWPE blends used for blown films. The mechanical test of the blown films revealed that when the content of MMWPE in modified UHMWPE was 40wt% and the content of UHMWPE in the blends was 20 wt%, the film had the optimal mechanical properties. The tensile strength and tear strength of the film increased by 50% and 21%, respectively, compared with those of pure HDPE film. Rheological curves indicated that the melt torque and the apparent viscosity of the HDPE/UHMWPE/MMWPE blends made by two-step processing way both greatly reduced than other blends. The results from DSC suggested that the blends by two-step processing way may form more stable and perfect co-crystallization. PLM (polarized light microscopy) and SEM micrographs revealed that two-step processing way can improve the surface morphology of the films and make the dispersion of UHMWPE particles in HDPE increase.

Keywords

HDPE; UHMWPE; blown films; two-step processing way; MMWPE

Introduction

HDPE has widely been applied for various types of blown films, but it is still necessary to improve the tensile strength and tear strength for more application. UHMWPE has been used in many fields because of its good abrasion resistance, high toughness and excellent fatigue resistance. Due to its very high molecular mass (100×10^4~ 600×10^4), UHMWPE has the poor fluidity even above its melting temperature [1]. It is not suitable for conventional processing operations except for compression molding and ram extrusion, which seriously restricts the application fields of UHMWPE [2]. Some reports have shown that UHMWPE can improve the toughness and slow crack growth resistance of the polymers by blending with other polymers, such as polycarbonate, polyether sulfone and conventional polyethylene [3~6]. Thus the addition of UHMWPE to HDPE with different proportions hopefully improves the mechanical properties of HDPE film.

Some researchers have worked on HDPE/UHMWPE blends by direct compounding. [1, 3~6] They found that UHMWPE could improve the impact strength or tensile strain of HDPE [1, 6]. Their work mainly concentrated on the effect of the UHMWPE content on the mechanical properties of the HDPE/UHMWPE blends. The effects of fluidity modifier on the viscosity and the properties of the HDPE/UHMWPE blends were seldom discussed.

UHMWPE was usually dissolved in solvents to prepare the films, and the HDPE/UHMWPE films made by melt blending weren't studied up to the time of this report. In the present work, HDPE/UHMWPE blends were extruded in a twin screw extruder and the films were prepared in a blow film extruder. Due to the partial dissolution of UHMWPE [6], there were many fisheyes in the HDPE/UHMWPE films even at the processing temperature of 250°C. It seriously affected the surface morphology and mechanical properties of films. The entanglement of UHMWPE the ultra long molecular chains caused the incompletely fusion of the UHMWPE particles [6]. Therefore the key problem is to obtain the disentanglement of UHMWPE ultra length chain in certain degree. Here two-step processing way was used to prepare HDPE/UHMWPE/MMWPE blends and UHMWPE was modified by fluidity modifier MMWPE in the first step. The mechanical property of films and rheological property of the blends were determined. Melting and crystallization behavior of the blends, surface morphology of blown films and the fracture surface of the blends were also discussed.

Experimental

Materials

HDPE pellet was supplied by Guangdong Petrochemical Company Limited with a density of $0.95 g/cm^3$ and melt flow index (MFI) of 0.12g/10min (190°C, 2.16kg). UHMWPE powder with an average molecular weight of 1.5 million and no measurable MFI was supplied by Beijing No.2 Auxiliary Agent Factory. Middle molecular weight polyethylene (DMDB-8920) was supplied by Guangdong Petrochemical Company Limited and MFI was 7.36g/10min (190°C, 2.16kg).

Samples preparation

HDPE/UHMWPE and HDPE/UHMWPE/MMWPE blends (DBP) were prepared by direct blending in a twin screw extruder (TSE-35A, Nanjing Ruiya Polymer Equipment Corporation) followed by blowing films. HDPE/UHMWPE/MMWPE blends (TSP1~TSP5) made by two-step processing way with different proportions were prepared from the formulations shown in Table 1. The processing steps of two-step processing way were shown in Fig. 1. UHMWPE was first modified by MMWPE in the same twin screw extruder via melt mixing. The content of MMWPE in modified UHMWPE was 40wt%, 30wt% and 20wt%, respectively. The processing was carried out at a temperature of 240°C and a rotor speed of 180rpm. Secondly, modified UHMWPE was blended with HDPE in the same processing condition described earlier. The extruder pellets were used to prepare blown films in a blown film extruder (SJ-30, Guangdong Nanhai Light Industrial Machines Corporation), at a temperature of 240°C and a rotor speed of 50 rpm. The blow-up ratio of the films was about 2.0, and the average thickness was 50 um. The content of MMWPE and UHMWPE in TSP1~TSP5 blends was calculated by the ratio of their weight to that of the blends, respectively.

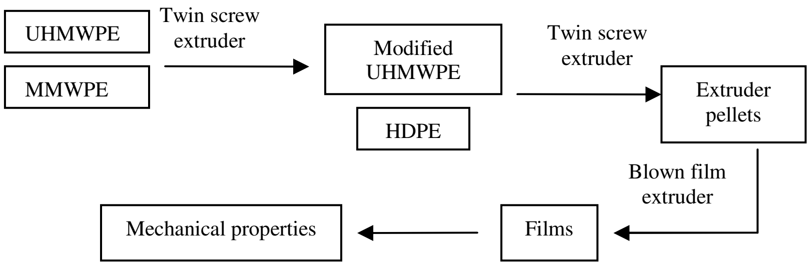


Fig. 1. The processing steps of two-step processing way

Table 1. The content of every component in the blends made by two-step processing way

Samples	UHMWPE content in blends(wt%)	MMWPE content in blends (wt%)	MMWPE content in modified UHMWPE (wt%)
TSP-1	10	6.7	40
TSP-2	20	13.3	40
TSP-3	30	20.0	40
TSP-4	20	8.5	30
TSP-5	20	5.0	20

The screws used in the twin screw extruder were especially designed. Some toothed disks and kneading blocks were used to improve the dispersion of UHMWPE in HDPE. The diameter of screws was 35mm and length-diameter ratio was 40/1.

The blown films were cut to dumbbell-shaped tensile test specimens according to ASTM D638 type II. Tear test specimens (right-angled, Die C) were made according to ASTM D624. The mechanical properties were measured on the GOTECH tensile test instrument (GT-TCS-2000).

The melt torque of the blends before extrusion was determined by HAAKE Rheolometor (Polylab System, Thermo Electron Corporation, USA) in the following processing condition: chamber temperature of 230°C, mixing time up to 25 min, and rotor speed of 40 rpm. The rheological examinations of the blends were carried out using a parallel plate (RDA3, Rheometric Scientific, USA). The diameter of disk was 25 mm and temperature was 200°C.

Differential scanning calorimetry (DSC) measurements were performed using a DSC 204F1 instrument made by German NETZSCH Corporation. Samples of about 6.0 mg were scanned to 250°C at a rate of 10°C/min in nitrogen atmosphere, and held for 5 min before cooling to 30°C at the same speed. The same step was repeated for the second scan.

The surface morphology of the films was examined by transmission polarized light microscope (Nikon SY2, Nanjing Jiangnan Photo-electricity Corporation), and pictures were taken using a Nikon 4500 digital camera at different magnifications.
The fracture surface morphology of the blends was observed via scanning electron microscopy (SEM) (JSM-6380LA, Japan Electron Optics Laboratory Co. Ltd). The specimens were fractured under liquid N_2 and the surfaces were gold-coated before observing.

Results and discussion

Mechanical properties of the films and modified UHMWPE

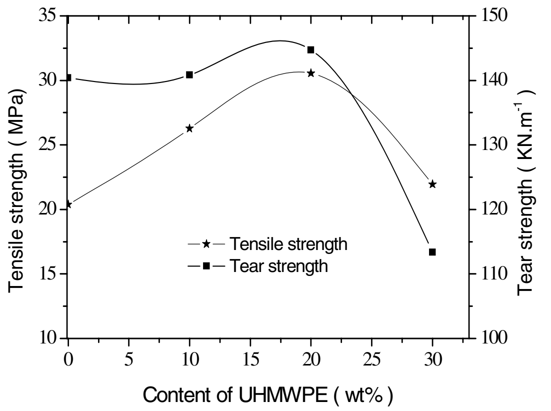


Fig. 2. Effect of the UHMWPE content on the tensile strength and tear strength of the HDPE/UHMWPE films

Some researchers have found that UHMWPE can improve the tensile strength and impact strength of HDPE [1, 3, 6].The effect of the UHMWPE content on the tensile strength and tear strength of the HDPE/UHMWPE films is depicted in Fig. 2. The tensile strength of the blown films improves by 38% than that of HDPE film as the UHMWPE content increases up to 20wt%, but the tear strength changes slightly. UHMWPE had a good interfacial affinity with HDPE and the fused UHMWPE particles produced the high plastics deformation when stress is applied [3~5]. When the UHMWPE content is 30wt%, the mechanical properties decrease. It is difficult for HDPE/UHMWPE blends to be blown the films. The surface of the blown films was rough and the unfused particles of UHMWPE could be seen by eyes. These particles easily initiated the rupture of the films [5]. UHMWPE has the ultra long molecular chains and they tangle each other resulting in the high melt viscosity. The large difference of the viscosity between UHMWPE and HDPE leads to the poor dispersion of UHMWPE in HDPE. The disentanglement of UHMWPE molecular chains is the key to resolve the problem. SEM micrographs of native UHMWPE showed that UHMWPE was composed of a large number of smaller units with the presence of micro-voids among them [6]. When UHMWPE was modified by small molecular modifiers, modifiers could penetrate into these voids and increase the activity of the molecular chains. Therefore MMWPE as a fluidity modifier was added into UHMWPE in the first step in two-step processing way in order to enhance the dispersion of UHMWPE in HDPE.

The corporation of MMWPE into UHMWPE usually helps to reduce the viscosity of UHMWPE, but it also impairs the mechanical properties of UHMWPE. When the content of MMWPE increases up to 40wt%, the impact strength and tensile strength decrease by about 13% and 9.5%, respectively, than those of pure UHMWPE. When MMWPE content is 50wt%, the impact strength decreases by about 30%. UHMWPE has excellent mechanical properties because of the entanglements of the long molecular chains. Excessive disentanglement would impair the mechanical properties of UHMWPE. The content of MMWPE in modified UHMWPE doesn't exceed 40wt% in order to maintain the mechanical properties of UHMWPE.

Adding MMWPE into HDPE/UHMWPE usually decreases the mechanical properties. Table 2 shows the mechanical properties of the blown films made by different blends. The tensile strength of blown films made by TSP-2 increases by 20% and 50%, respectively, compared with those of DBP and pure HDPE. The tear strength increases by 12% and 21% than those of DBP and HDPE, respectively. MMWPE as fluidity modifier could help UHMWPE molecular chains to slip and make their long chains easily orientate to absorb more energy. MMWPE doesn't impair the tensile strength of TSP-2 film in comparison with HDPE/UHMWPE film, but the tensile strength of DBP film decreases by about 19% than that of HDPE/UHMWPE film. It suggests that the degradation degree of UHMWPE molecular chains in the first step is slight. The dissolved molecular chains of UHMWPE have more positive effect on the mechanical properties as the dissolved degree of UHMWPE particles increases. Direct blends processing way just made MMWPE in the DBP blends stay between UHMWPE and HDPE chains, and the lower viscosity of MMWPE would affect the tensile strength of matrix. It also can be found that when the UHMWPE content in TSP blends is 20wt%, the film has the optimal mechanical properties. When the content of UHMWPE in TSP is up to 30 wt%, the higher MMWPE content in TSP-3 affects the tear strength of the film.

Table 2. The mechanical properties of the blown films made by different blends

Sample	Processing way	UHMWPE content in blends (%)	Tensile strength (MPa)	Tear strength (KN/m)
HDPE		0	20.4	140.4
HDPE/UHMWPE	Direct blends processing	20	30.5	144.7
HDPE/UHMWPE/ MMWPE (DBP)	Direct blends processing	20	24.7	151.5
TSP-2	Two-step processing	20	30.7	171.1
TSP-1	Two-step processing	10	29.1	165.5
TSP-3	Two-step processing	30	29.6	158.8

Table 3 shows the effect of the MMWPE content in modified UHMWPE mater batch on the mechanical properties of TSP series blends. The mechanical properties of the films gradually decrease by reducing the content of MMWPE in modified UHMWPE in the first step. It can be explained that as the content of MMWPE in modified UHMWPE decreases, the dispersion of UHMWPE powder became poor and dissolved degree of UHMWPE in HDPE decreased. The orientated chains of UHMWPE decreased and the absorbed energy decreased when stress was applied. The stress concentration effect caused by the unfused UHMWPE particles had exceeded the positive effect of the dissolved UHMWPE chains.

Table 3. Effect of MMWPE content in modified UHMWPE on the mechanical properties of the blown films made by TSP series

Sample	MMWPE content in modified UHMWPE (wt%)	MMWPE content in TSP (wt%)	Tensile strength (MPa)	Tear strength (KN/m)
TSP-2	40	13	30.7	171.1
TSP-4	30	9	26.5	160.0
TSP-5	20	5	25.7	158.3

UHMWPE contents in TSP series are all 20wt %

Rheological properties of the blends and modified UHMWPE

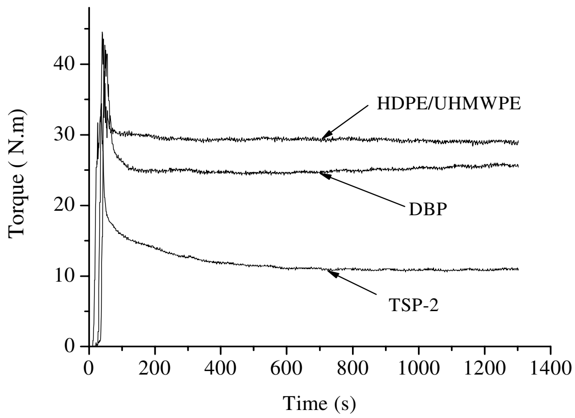


Fig. 3. Torque-time curves of the composites made by different processing ways

UHMWPE has extreme high viscosity which leads to the increasing of melt torque in processing. The typical torque-time curves of the HDPE/UHMWPE blends with different proportions have been reported [3]. Fig. 3 shows the torque-time curves of the blends by different processing ways. The melt torques at the stabilization zone of DBP and TSP-2 reduce by about 17% and 60% than that of HDPE/UHMWPE, respectively. Moreover the melt torque of TSP-2 is closed to that of pure HDPE. It shows that two-step processing way can effectively reduce the melt viscosity of HDPE/UHMWPE and improve the processability of the blends.

The relationship of apparent viscosity and shear rate of modified UHMWPE with different contents of MMWPE is compared in Fig. 4. Newtonian behavior is observed in the low shear rate range after which shear thinning is followed. The apparent viscosity of the blends increases as the content of MMWPE in modified UHMWPE deceases. Decreasing the content of MMWPE in modified UHMWPE can make the disentanglement degree of UHMWPE molecular chains decrease and the apparent viscosity of the blends enhance.

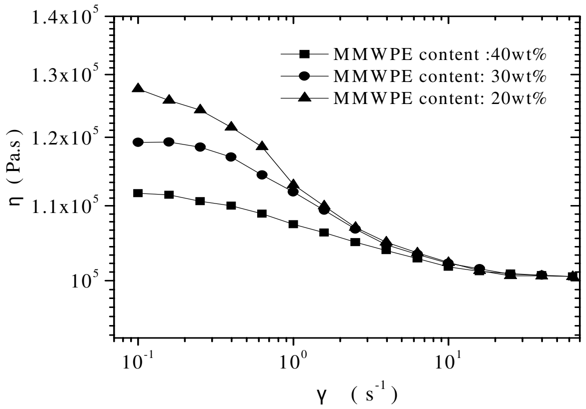


Fig. 4. The apparent viscosity versus shear rate of different contents of MMWPE in modified UHMWPE

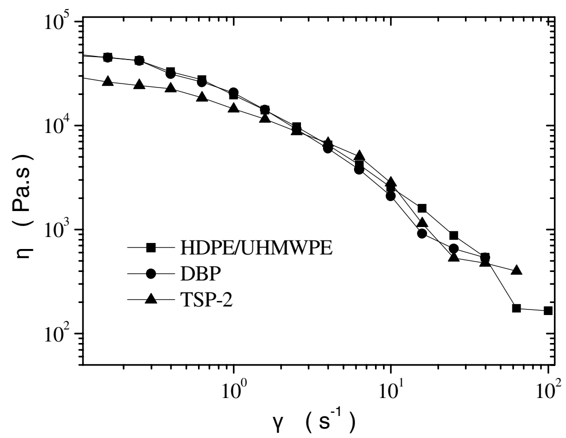


Fig. 5. The apparent viscosity versus shear rate of the blends made by different processing ways

Fig. 5 shows the apparent viscosity versus shear rate of extruder pellets made by different processing ways. It can be seen that MMWPE in DBP can't make the apparent viscosity of the blends obviously change. But after UHMWPE was modified by the same content of MMWPE, the apparent viscosity of TSP-2 greatly decreased, especially at the low shear rate. It suggests that two-step processing way effectively decreases the melt viscosity of blends. MMWPE can play the better dispersion role by the two-step processing way. The abnormal behavior at high shear rate may be caused by the experimental error.

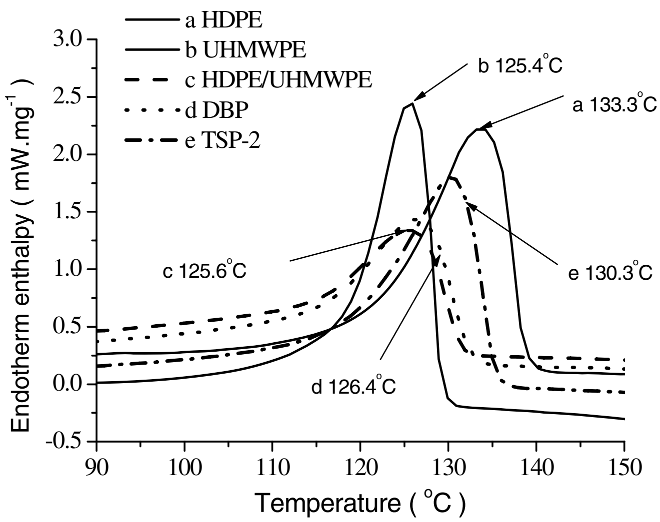


Fig. 6. DSC curves of HDPE, UHMWPE and the composites

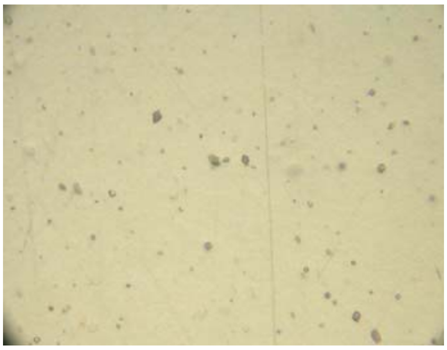
Fig. 6 displays the DCS curves of pure polymers and the blends made by different processing ways. Three blends all have single melting endotherm peak, and the peaks are all between the melting peak of HDPE and UHMWPE. It reveals that co-crystallization between HDPE and UHMWPE may form in the three samples according to many reports [3~8]. Some reports showed that HDPE/UHMWPE blends manifested two new melt endotherm peaks because of the poor mixing [5, 6]. Here the single melting endotherm peaks of HDPE/UHMWPE and DBP are due to the better dispersion gained by the especial screws structure in the twin screw extruder. The melt temperatures of HDPE/UHMWPE and DBP (125.6°C and 126.4°C) are closed to that of UHMWPE (125.4°C), which manifests that UHMWPE has an obvious influence on their melting-recrystallization procedures. The structure modification of their molecular chains in the crystallization procedure is similar with that of the UHMWPE chains [6, 8]. The melt endotherm peak of TSP-2 has higher melt temperature (130.3°C) and higher crystallization temperature (114.7°C in Table 4). It elucidates that TSP-2 may form more stable co-crystallization than other samples. From table 4 the width of crystallization peak of TSP-2 is smaller and the height of crystallization is bigger than those of HDPE/UHMWPE and DBP. Moreover the temperature range of crystallization of TSP-2 is narrower than others. It also confirms that TSP-2 may form

Table 4. Crystallization parameters of HDPE, UHMWPE and the composites

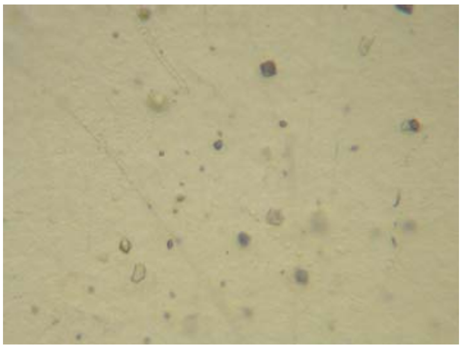
Samples	Tc (°C)	ΔH_c (J/g)	Width (mm)	Height (mm)	ΔTc (°C)
HDPE	114.7	170.7	10.4	2.6	13.1
UHMWPE	109.6	150.1	4.4	5.1	6.0
HDPE/UHMWPE	111.9	129.3	15.4	1.1	16.5
DBP	112.4	154.0	13.6	1.4	15.7
TSP-2	114.7	161.8	9.8	2.4	12.4

the more stable and perfect co-crystallization. It is still necessary to carry out further investigation to confirm the possibility of co-crystallization.

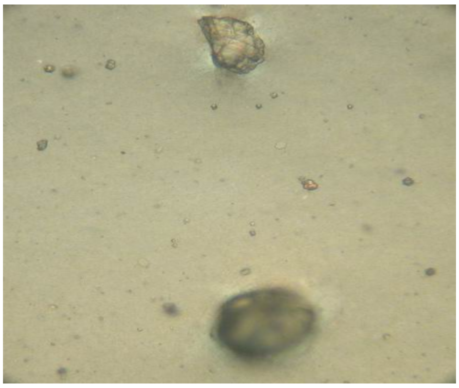
Surface morphology of the blown films



(a) 10wt%UHMWPE (at 100×magnification)



(b) 20wt%UHMWPE (at 100×magnification)



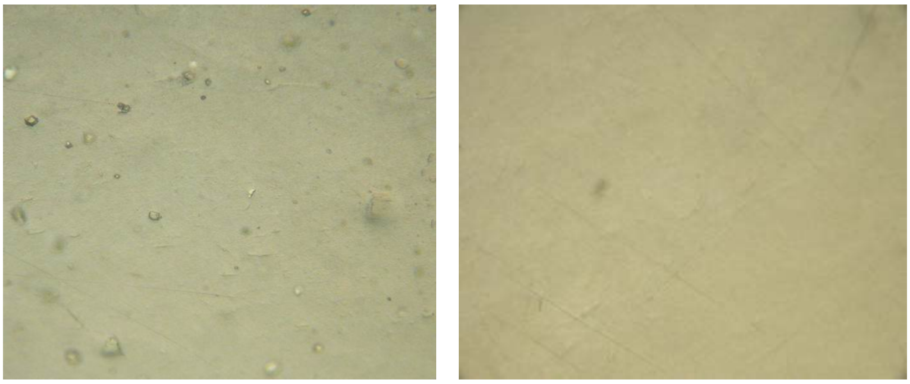
(c) 30wt%UHMWPE (at 100×magnification)

(d) 30wt%UHMWPE(at 400×magnification)

Fig. 7. Transmission polarizing micrographs of the HDPE/UHMWPE blown films

The poor surface morphology was the most important problem of the HDPE/UHMWPE blown films. UHMWPE existed as many unfused particles about 50~800um in the HDPE/UHMWPE films. Fig. 7 displays the polarizing micrographs of the films. From Fig. 7 (a) ~ (c), we can find that with increasing the content of UHMWPE, the size of UHMWPE particles increases. In Fig. 7 (c) and (d) the number of the UHMWPE particle clusters increases and the diameters are about 300~500um. These bigger unfused UHMWPE particles became stress concentration and made the local stress around the particles sharply increase. Fracture of blown films always happened on beside these particles. It is consistent with the front mechanical properties of films.

Fig. 8 shows the transmission polarized light micrographs of the films made by the different blends. Fig. 8 (a) displays the surface morphology of the film made by DBP. The diameters of UHMWPE particles are about 50um and some bigger particles still can't fuse completely. Fig. 8 (b) shows the surface morphology of the film made by



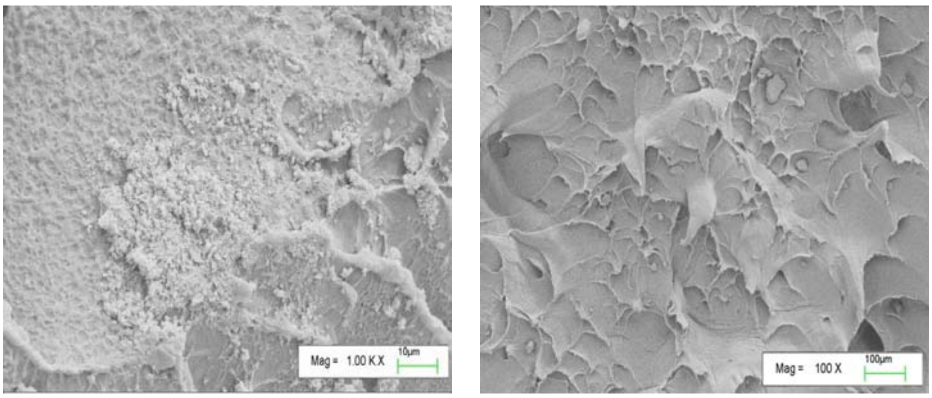
(a) (b)

Fig. 8. Transmission polarizing micrographs of the HDPE/UHMWPE/MMWPE blown films made by DBP (a) and TSP-2 (b) (at 100×magnification)

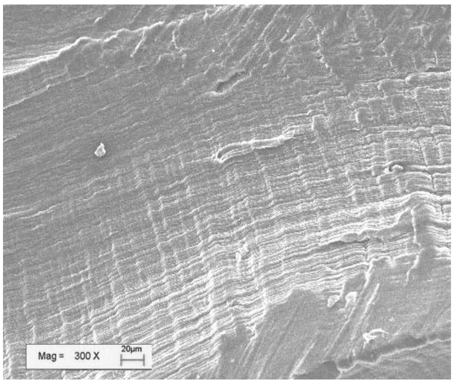
TSP-2. The surface of film is smooth and the unfused UHMWPE particles can be seldom seen. It suggests that the interfacial affinity between HDPE and UHMWPE become stronger and the fused degree of UHMWPE particles increase. The fused UHMWPE chains penetrated into HDPE molecular chains to form co-crystallization.

SEM micrographs

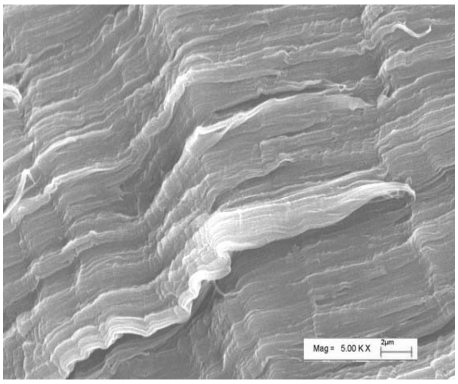
Fig. 9 shows the impact fracture surface of the blends made by different processing ways. Fig. 9 (a) is the micrograph of HDPE/UHMWPE, and the UHMWPE powder aggregates together. The smooth fracture surface of HDPE/UHMWPE indicates brittle failure characterization. In Fig. 9 (b) UHMWPE particles are dispersed in the flakelike fracture layer. The interface combination of UHMWPE particles and HDPE matrix is weak, but the fracture surface has shown slight plastics deformation. The fracture surface of TSP-2 [Fig. 9 (c)] reveals a number of crazing formation, and UHMWPE particles seldom can be seen. The corrugate surface of Fig. 9 (d) is attributed to the plastics deformation. It further manifests that the dissolved degree and dispersion of UHMWPE particles are both greatly improved by two-step processing way.



(a) HDPE/UHMWPE (at 100×magnification) (b) DBP (at 100×magnification)



(c) TSP-2 (at 300×magnification)



(d) TSP-2 (at 5000×magnification)

Fig. 9. SEM micrographs of the blends by different processing ways

Conclusions

The addition of UHMWPE into HDPE could improve the mechanical properties of the films. MMWPE was used as a fluidity modifier and compatibilizer and its content in modified UHMWPE didn't exceed 40wt% in two-step processing way. When the content of MMWPE in modified UHMWPE was 40 wt% and the content of UHMWPE in TSP blends was 20 wt%, the tensile strength and tear strength of blown film increased by 20% and 12% than those of the film made by DBP, and increased by 50% and 21% than those of HDPE film, respectively. The melt torque and apparent viscosity of TSP-2 greatly reduced compared with those of HDPE/UHMWPE and DBP blends.

The blends made by different processing ways all had single melting endotherm peak. It suggested that co-crystallization may form between UHMWPE and HDPE. Moreover the blends made by two-step processing way had more stable and perfect co-crystallization. The transmission polarizing micrographs of films showed that as the content of UHMWPE increased, the diameters of UHMWPE particles in HDPE/UHMWPE films increased. The surface morphology of film made by TSP-2 blends was better than other films. SEM micrographs revealed that the dissolved degree and dispersion of UHMWPE particles was greatly improved by two-step processing way.

Acknowlegements. Financially supported by the key project in Science and Technology of Guangzhou Province (No. 2005Z3-D0331)

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