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Modified high-density polyethylene films: preparation, composition and their physical properties

WEI-LI WU* and YI-WEN WANG
College of Materials Science and Engineering, Qiqihar University, Qiqihar 161006, People's Republic of China
*Author for correspondence (wuweili2001@163.com)

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Abstract. To prepare high-density polyethylene (HDPE) films with excellent mechanical properties and lower haze, HDPE was modified by using linear low-density polyethylene (LLDPE) and polypropylene (PP), and their characterizations were performed by melt index, light transmittance/haze, dart impact and elongation at break, infrared (IR) spectra, scanning electron microscopy image and IR image analyses. The results showed that the modifying effect of the 10% PP/30% LLDPE/60% HDPE composition was the best; the haze was reduced 6% and the translucency, dart impact strength, elongation at break and tensile strength were increased 1, 27.3, 29.4 and 1.0%, respectively. The blend of 10% PP/30% LLDPE/60% HDPE had good compatibility, and PP, LLDPE and HDPE were only the physical entanglement, and no chemical reaction, the modified HDPE films can partly replace polyvinyl chloride and LLDPE films.

Keywords. High-density polyethylene film; modification; preparation; composition.

1. Introduction

Currently, polyvinyl chloride (PVC) products have been restricted in food-packaging films and medical devices due to their toxicity, linear low-density polyethylene (LLDPE) films are gradually replacing PVC films [1]. With the increased production of LLDPE films [2], the high cost involved has not been solved [3]; therefore, the attention of researchers has been shifted to the use of high-density polyethylene (HDPE) [4] due to its outstanding mechanical properties, abundant raw materials and low cost. Compared with low-density polyethylene (LDPE) [5], LLDPE and many other polymer materials [6], HDPE has higher tensile strength, high and low temperature resistance [7] and production capacity [8], however, its haze, dart impact and elongation at break are worse than those of PVC and LLDPE. In this study, the melt index (MI), mechanical properties and haze of modified HDPE films were studied by adding LLDPE and polypropylene (PP) as the modifying agents, and replaced the PVC film with the modified HDPE film and the application range of the modified HDPE films has been widened.

2. Materials and methods

HDPE (5000S, pellets with a density of 0.963 g cm^{-3}, melt flow index of 0.96 g/10 min; purchased from the National Petroleum Corp., China) was mixed with PP (T30S, pellets with a Vicat-softening point of 153°C, melt flow index of 3.1 g/10 min; purchased from the National Petroleum Corp., China) and LLDPE (HPR18H10AX, pellets with a density of 0.933 g cm^{-3}, melt flow index of 4.0 g/10 min; purchased from the National Petroleum Corp., China) in a mixing machine (HRS-50A, Ylang Environmental Technology Co., Ltd., China) at various ratios, and then extruded using a twin-screw extruder (SKR-65, Foshan Shengkalrul Plastic Specialized Equipment Co., Ltd., China). The temperatures of the twin-screw extruder were set to 172, 182, 183, 183 and 178°C (die). It was extruded into a granulator (SJG-65, Yuyao Jingang Industrial Equipment Co., Ltd., China) for granulation. At last, the HDPE mixture was blown using a film blowing machine (XCH-1, Jilin University Science and Education Instrument Plant, China); the temperature of the film extruder die was set to 220°C, the screw diameter was 20 mm, the drawing speed was 23 rpm and the blow up ratio was 3.5 and the thickness of the prepared film was 0.1 mm. The elongation at break of the samples (50 × 10 × 0.1 mm^3) was determined by using a CSS-2200 universal testing instrument (Zhongji Application Technical Institute, China) according to the ISO37 method. Dart impact tests were carried out by using a JBS-300B impact testing machine (Jinan Kesheng Experimental Equipment Co., Ltd., China) according to ASTMD1709-03 on a 30 mm × 30 mm film. Haze and light transmittance were tested by using a light transmittance/haze meter (WGT-S, Shanghai Jingke Co., Ltd., China), in which the film samples were placed in the photoelectric haze metre at

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20°C and a relative humidity of 39%. The melt flow index of the samples was tested by using an SRZ-400E melt flow rate meter (Changchun Intelligent Instrument Equipment Co., Ltd., China) at 230°C under a 2,160 g load. The film samples were fractured in liquid nitrogen, and the fracture surfaces of the specimens were examined by using an S-4300 scanning electron microscope (SEM; Hitachi Ltd., Japan). The film samples (5 × 5 × 0.1 mm^3) for infrared (IR) analysis were dried, and then IR spectra and IR image were recorded by using a Spectrum One Fourier transform infrared spectrometer (Perkin Elmer Co., Ltd., USA), and the IR images in the range from 150 to 0 μm of the samples were obtained.

3. Results and discussion

As we know, the flexibility of HDPE is poor and its viscosity is notable, the material made of this film must first solve the problem of its toughness. The flexibility of LLDPE is better, and the side group of the PP can decrease viscosity and increase flexibility of the HDPE blend, and HDPE, PP and LLDPE are non-polar crystalline polymers, so that PP and LLDPE were selected as modifiers to decrease the viscosity and increase the flexibility of the HDPE blend. For a given chemical structure of a resin, the lower the MI is, the greater the viscosity, the more difficult to process. The MI of HDPE is higher, so it is too difficult to prepare the film. In addition, the haze and transmittance are also important indexes; the higher haze would limit the application of HDPE films. The MI, haze and transmittance of the modified HDPE films are shown in figure 1. The MI of HDPE modified with PP and LLDPE was increased due to the higher MI of the PP and LLDPE used, so that the MI of the modified HDPE films was much higher than that of HDPE. The MI of 10% PP/30% LLDPE/60% HDPE was the highest (2.6 g/10 min) among all samples, so that 10% PP and 30% LLDPE were used as a modifying agent.

It can also be observed that the haze of HDPE was 30.1%, and that of LLDPE and PP was 24.6 and 25.1%, respectively. The haze of the modified HDPE film decreased with the addition of LLDPE and PP and thereby the hazes (24–25.5%) of all samples being similar to that of PP and LLDPE except for 20% LLDPE/80% HDPE (haze: 26.7%); the haze and transmittance of 10% PP/30% LLDPE/60% HDPE were the best among all samples, the haze was reduced 6%, and the translucency was increased by 1% (92.5–91.5). The reason may be that the transmittance of LLDPE and PP was better than that of HDPE, both could improve the transmittance and reduce the haze.

Because the changes in MI and haze do not show whether PP and LLDPE modified HDPE, the effects of PP and LLDPE on the mechanical properties of HDPE were examined and the results are shown in table 1. It was anticipated that the flexibility would increase if the elongation at break increases. The elongation at break and tensile strength of the PP and LLDPE modified HDPE films were much higher than those of HDPE, and the dart impact strengths were also higher than that of pure HDPE. In addition, the elongation at break, tensile strength and dart impact strength of LLDPE-modified HDPE were far better than those of PP-modified HDPE, and PP/LLDPE-modified HDPE was found to be the best.

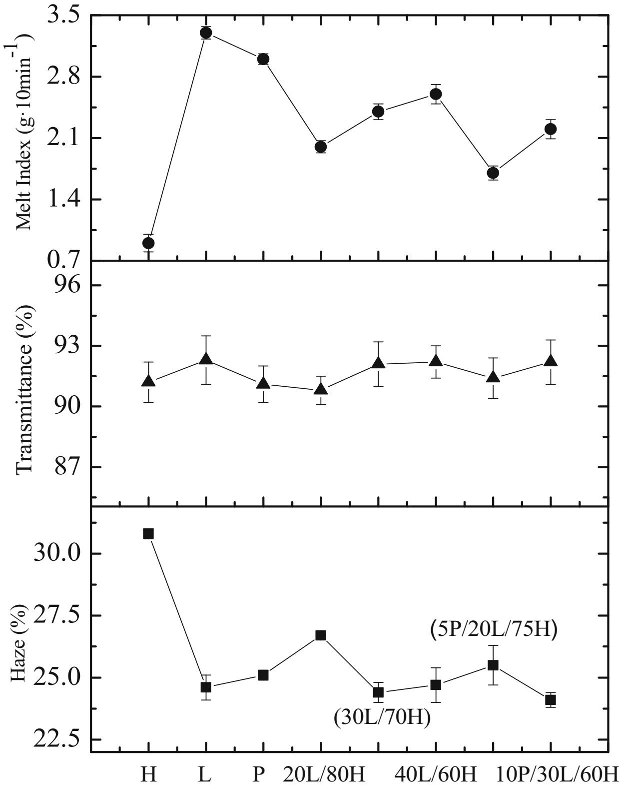

Figure 1. Haze, transmittance and MI of the modified HDPE films. On the *X* axis, H is 100 phr of HDPE, L is LLDPE and P is PP for all samples.

It could be observed that the melting temperature of PP was too high to mix fully with the other ingredients. For the LLDPE/HDPE film, the elongation at break and tensile strength increased significantly with the addition of LLDPE; when the mass fraction of LLDPE components exceeded 30%, the elongation at break and tensile strength showed a trend of slow growth from 30% LLDPE/70% HDPE to 40% LLDPE/60% HDPE. It could be explained by using the modifying mechanism of thermoplastic materials [9]. When the interface strength between LLDPE and HDPE was decreased and the stress was weak, a good bond between LLDPE and HDPE was conducive to stress transfer. Under the action of greater stress, the polymer chain segment on the interface would debond or slide and produce greater strain to resist the stress and to finally yield. The molecular chain of LLDPE is soft, can be closely integrated with HDPE, the force between HDPE and LLDPE was higher, so the tensile strength and elongation at break were increased with the addition of LLDPE. When the amount of LLDPE was more

Table 1. Elongations at break, dart impact strength and tensile strength of the modified HDPE films.

Components (%)	Tensile strength (MPa)	Elongation at break (%)	Dart impact strength (g)
100HDPE	21.3	455	55
100PP	29.4	200	55
100LLDPE	15.8	602	120
5PP/95HDPE	21.9	459	55
10PP/90HDPE	21.3	460	55
20PP/80HDPE	19.8	458	60
30PP/70HDPE	18.4	457	60
5LLDPE/95HDPE	20.8	458	59
10LLDPE/90HDPE	20.0	498	60
20LLDPE/80HDPE	19.4	534	65
30LLDPE/70HDPE	18.8	565	65
40LLDPE/60HDPE	18.2	570	65
5PP/20LLDPE/75HDPE	19.8	553	65
10PP/10LLDPE/80HDPE	21.0	542	65
10PP/20LLDPE/70HDPE	20.6	540	65
10PP/30LLDPE/60HDPE	21.5	589	70

than 30%, the combining site of the molecular chain was not so much, and slowly increased. Similarly, the addition of PP could generate gaps between HDPE and/or PP, LLDPE to increase the mean square end-to-end distance of the blend, so PP can play a role in the decrease of viscosity and increase of flexibility of the blend due to its side group, thereby increasing the mechanical properties of the modified HDPE. When PP content was more than 10%, the interaction between HDPE and PP would reduce, resulting in the decrease of mechanical properties. This can also be demonstrated by the IR images. As can be observed from figure 2, the individual LLDPE or PP in the HDPE was not evenly dispersed in an island, the LLDPE was in a strip shape and the PP was in a round shape. From the 3D view of light scattering, the light scattering 0.44 of the 10% PP/30% LLDPE/60% HDPE film was smaller than 0.48 of pure HDPE, and much smaller than 0.60 of the 30% PP/70% HDPE and 30% LLDPE/70% HDPE films, and the surface of the 10% PP/30% LLDPE/60% HDPE film was more smooth. The results of IR images also proved that the effect of the 10% PP and 30% LLDPE modified HDPE films was good, and the individual PP or LLDPE was scattered in the matrix of HDPE in a heterogeneous fashion, only the combination of PP and LLDPE can modify the HDPE film, the smaller the light scattering was, the smaller the haze and more applied value.

For actual commercial production, the PE films are evaluated according to the data of dart impact strength. The dart impact strength of the pure HDPE film was 55 g, that of pure LLDPE film could reach 120 g and that of the PP film was 55 g. On comparing the dart impact strength of several modified HDPE films, only the dart impact strength of the 10% PP/30% LLDPE/60% HDPE film was higher than that of pure HDPE, various LLDPE/HDPE, PP/HDPE and the other PP/LLDPE/HDPE films, reaching a maximum of 70 g. Therefore, the dart impact strength of the modified HDPE film was increased by 27.3%, similarly, the elongation at break and tensile strength were increased by 29.4 and 1.0%, respectively.

To understand the compatibility between several polymers in the modified film, their SEM characterization is shown in figure 3. It was observed that the surface of the pure HDPE film was smooth due to the presence of components, but the film was very thick, its light transmission was poor and was largely hazy, which could only be applied to low-grade packing materials. When 30% PP was added, the surface of the modified HDPE film was rough and tree-like folds, the compatibility between PP and HDPE was bad. When 30% LLDPE was added, the surface of the 30% LLDPE/70% HDPE film was smooth, but the compatibility between HDPE and LLDPE was bad, and there was some crack on the surface of the film. With the addition of 10% PP and 20% LLDPE, its surface morphology was the same as the 30% LLDPE/70% HDPE film. When 10% PP and 30% LLDPE were added to the HDPE, the surface of the modified HDPE film was smooth, the compatibility among the three materials was better and the film was thinner, making translucency to increase and haze to decrease. This reason was consistent with the original idea, namely LLDPE was in the physical tangles function, and PP played a role of open PEs' intermolecular accumulation, and made the LLDPE easy to be evenly distributed, thereby improving the mechanical properties of the HDPE, and reduced the haze. Thus, we found that the 10% PP/30% LLDPE/60% HDPE film would replace PVC and LLDPE films.

However, for certification, the IR spectrum analysis was carried out on the modification of the HDPE film as shown

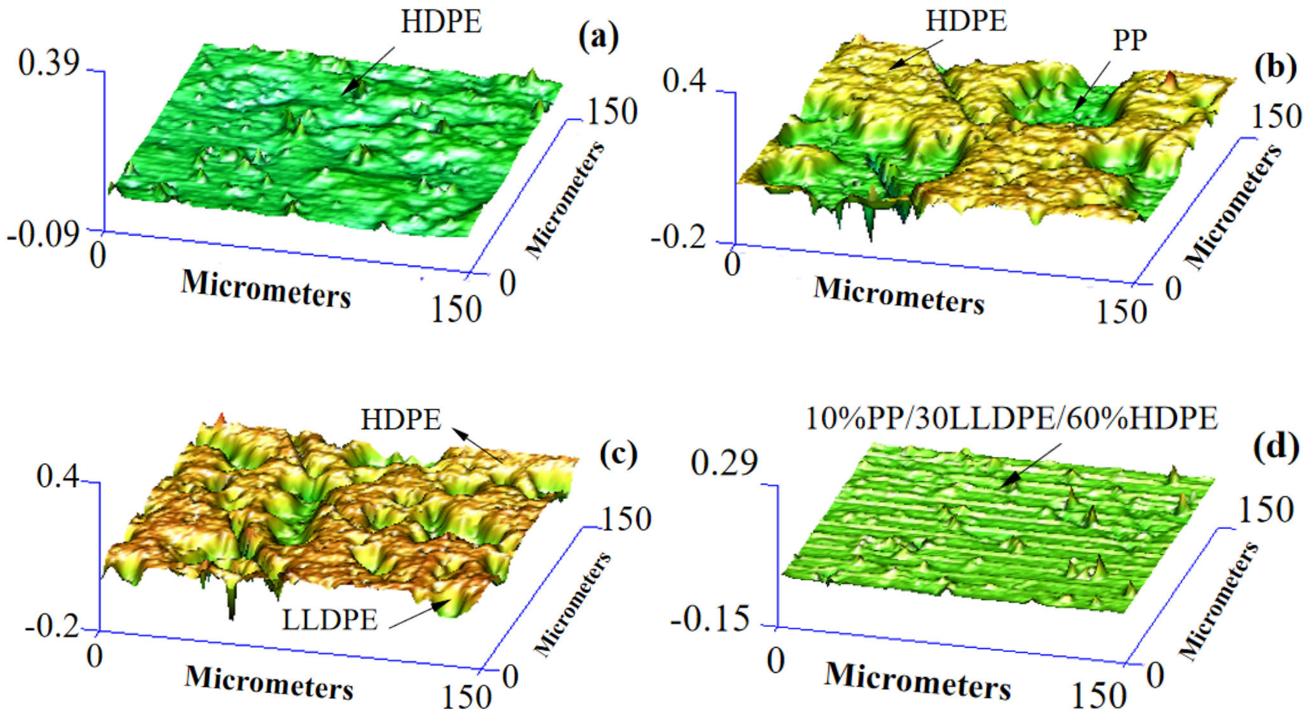

Figure 2. IR images of (**a**) pure HDPE film, (**b**) 30% PP/70% HDPE, (**c**) 30% PP/70% HDPE and (**d**) 10% PP/30% LLDPE/60% films.

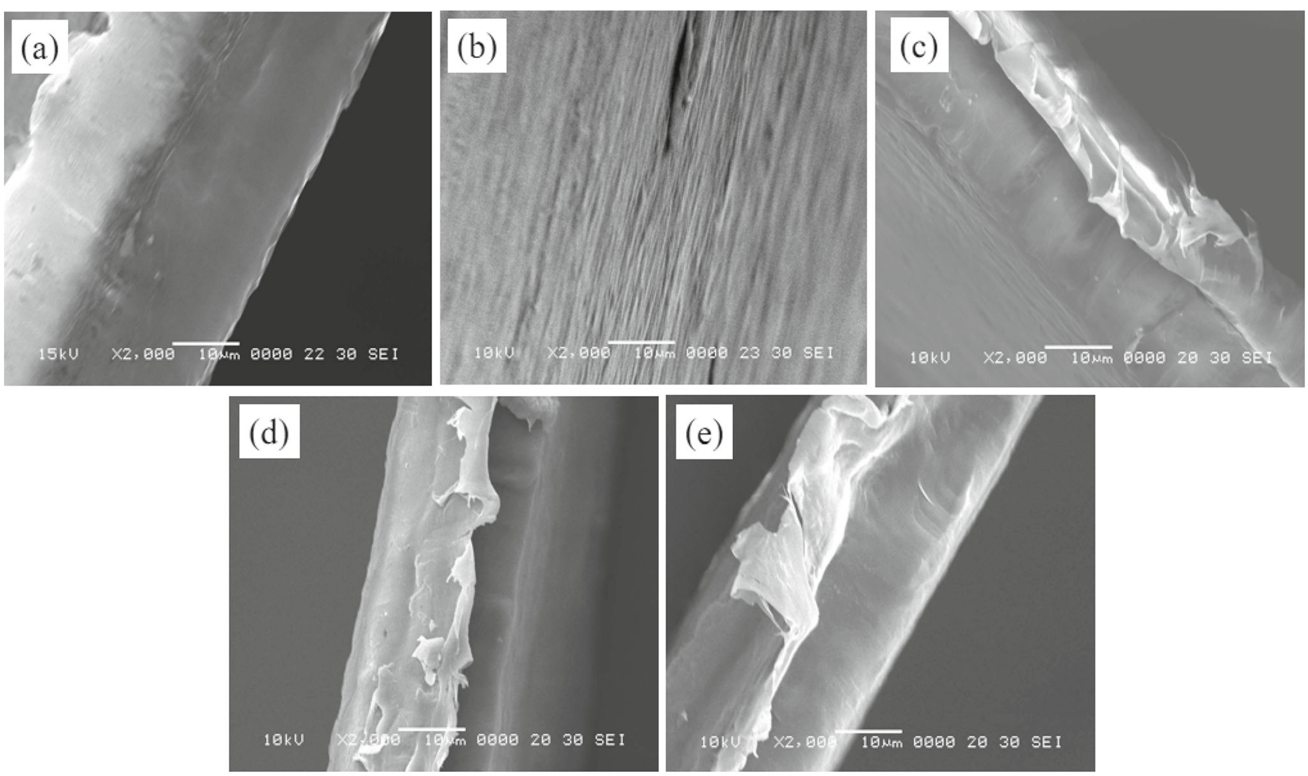

Figure 3. SEM of (**a**) pure HDPE, (**b**) 30% PP/70% HDPE, (**c**) 30% LLDPE/70% HDPE, (**d**) 10% PP/20% LLDPE/70% HDPE and (**e**) 10% PP/30% LLDPE/60% HDPE films.

in figure 4. The methylene absorption peak –CH_2– at 2,850–2,900 cm^{-1} and 1,463 cm^{-1}, –CH– at 730 cm^{-1} and methyl characteristic peak at 1,368 cm^{-1} are provided in figure 4; there was no new vibration peak, the position of some peak drifted and size changed, there was no chemical reaction between polymers [10], the PP, LLDPE and HDPE

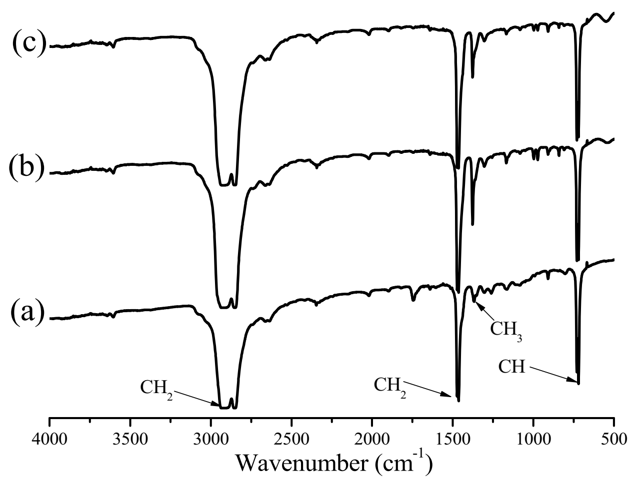

Figure 4. IR curves of (**a**) HDPE, (**b**) 30% LLDPE/70% HDPE and (**c**) 10% PP/30% LLDPE/60% HDPE films.

were just the physical entanglement. This result was consistent with the above analysis.

4. Conclusion

HDPE was modified with LLDPE and PP; when the mass ratio was 10% PP/30% LLDPE/60% HDPE, the modifying effect was the best; the translucency, dart impact strength, elongation at break and tensile strength were increased 1, 27.3, 29.4 and 1.0%, respectively, and the haze was reduced 6% and MI was higher. The blend of 10% PP/30% LLDPE/ 60% HDPE had good compatibility. The PP, LLDPE and HDPE were only the physical entanglement, and no chemical reaction; the modified HDPE films can partly replace PVC and LLDPE films.

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