

Effect of High-Density Polyethylene-*g*-Maleic Anhydride on the Morphology and Properties of (High-Density Polyethylene)/(Ethylene-Vinyl Alcohol) Copolymer Alloys

Qifei Wang, Rongrong Qi, Yanhan Shen, Qiaochu Liu, Chixing Zhou

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

Received 11 July 2006; accepted 29 December 2006

DOI 10.1002/app.26097

Published online 15 August 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: High-density polyethylene (HDPE)/(ethylene-vinyl alcohol) (EVOH) copolymer alloys were prepared through reactive extrusion method with high-density polyethylene-*graft*-maleic anhydride (HDPE-*g*-MAH) as a compatibilizer to improve the compatibility of the blending system. The results of the morphologies and properties of HDPE/EVOH blends show that the size of dispersed EVOH phase in HDPE/EVOH/HDPE-*g*-MAH blends is greatly diminished, the crystallization of EVOH is retarded and the impact strength of the blends is improved, which

mean that specific interactions could be existed between the functional groups of the EVOH and HDPE-*g*-MAH. Rheological experiments and FTIR spectra reveal that network structures are formed in the blends when the content of compatibilizer is >20%. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3220–3226, 2007

Key words: (ethylene-vinyl alcohol) copolymer; HDPE-*g*-maleic anhydride; hydrogen bond; compatibility; network structure

INTRODUCTION

Polyethylene (PE) is one of the most widely used resins because of its low absorption of humidity, good electrical resistance, easy processing, low cost, and high toughness at low temperature.^{1–3} On the other hand, ethylene-vinyl alcohol (EVOH) is one of the most important thermoplastic materials with outstanding properties of gas barrier and resistance to solvents and hydrocarbons.^{4,5} However, EVOH must be coextruded or blended with other polymers because of its brittle and easy water-absorption properties,^{6–14} moreover, the blend of HDPE and EVOH prepared through simple melt blending process would lead to morphologically unstable and brittle products because of their incompatibility. It has been proved that the addition of a compatibilizer is one of the most effective methods to improve the mechanical properties and final morphologies of blends, and some work has been done on the blends of EVOH/HDPE. For example, EVOH/HDPE blends have been prepared with EVOH/HDPE-*g*-HI (HDPE grafted with 2-hydroxyethyl methacrylate-isophorone) as compatibilizer,⁷ and the compatibilization of HDPE/EVOH was studied with SEBS-*g*-MA and Zn²⁺ ion-

omer of ethylene-methacrylic acid-isobutyl acrylate terpolymer as compatibilizers.^{9,12} The relationship of morphology and mechanical properties of the compatibilized HDPE/EVOH blends was studied by Prasad and Jackson in one of their communications,¹¹ and phase separation was observed. However, to obtain good performance of HDPE/EVOH blends, detailed studies are necessary. In this manuscript, compatibilized HDPE/EVOH blends were prepared with HDPE-*g*-MAH as compatibilizer, and the structural changes were studied by rheological and FTIR methods. The results show that network structures are formed and interphases are indistinct when the content of compatibilizer is >20%. The thermal, mechanical, and barrier properties of the blends are further studied.

EXPERIMENTAL

Materials

HDPE, EVOH, and HDPE-*g*-MAH were used after being dried in vacuum at 60°C for 24 h. EVOH (EVAL G170, vinyl alcohol content = 52 mol %) was purchased from Karury (Japan). HDPE is the product of Yanbet in Saudi Arabia with a melt index of 8 g/10 min (HDPE 80064: notched impact strength, 6.7 kJ/m²; tensile strength 27.9 MPa; elongation 730%; T_m = 133.2°C). HDPE-*g*-MAH, made by our group (notched impact strength, 6.2 kJ/m²; tensile strength, 29.2 MPa; elongation, 670%; T_m = 132.7°C), contains 1.2% maleic

Correspondence to: R. R. Qi (rrqi@sjtu.edu.cn).

Contract grant sponsor: Natural Science Foundation of China; contract grant number: 50390095.

anhydride by weight and has a melt index of 2.5 g/10 min (ASTM D1238).

Preparation of the blends

Blends of HDPE, EVOH and HDPE-g-MAH were prepared in 80/20/0, 75/20/5, 70/20/10, 65/20/15, 60/20/20, 55/20/25, 0/20/80 HDPE/EVOH/HDPE-g-MAH weight ratios. All components were premixed and simultaneously fed into the twin-screw extruder (C. W. Brabender compounder DSK 42/7). The blends were prepared at a constant rotating speed of 40 rpm, at temperature profiles of 185, 190, 195, and 200°C.

Thermal analysis

DSC measurements were conducted in a Perkin-Elmer PYRIS-1 differential scanning calorimeter (DSC). Transition temperatures were calibrated using indium and zinc standards. Samples (about 5 mg) were heated from room temperature to 190°C at a rate of 10°C/min and held for 5 min to destroy any residual nuclei before being cooled to room temperature at 10°C/min, and then reheated in the melting range in the same conditions. All DSC measurements were performed under an inert (N₂) atmosphere at a heating rate of 10°C/min.

Field emission scanning electron microscopy

Morphological analysis was carried out on frozen fractured samples, and the corresponding cross sections were examined by field emission scanning electron microscope (JSM-7401F, JEOL, Japan). The surface of samples was dried under vacuum and then coated with a conductive gold layer before FESEM analysis.

Infrared spectroscopic analysis

Fourier transform infrared (FTIR) spectra were performed by a Perkin-Elmer spectrometer model PARAGON 1000 on compression-molded films, at a resolution of 1 cm⁻¹ (10 scans collected).

Mechanical testing

The tensile strength of the blends was studied by an Instron machine under controlled humidity and temperature conditions according to the ASTM D882 testing method (testing rate: 50 mm/min). Several specimens (an average at least 5) of each sample were tested to determine the mechanical parameters.

The Izod notch impact strength was measured by Izod instrument (Ray-Ran). All materials were injection molded in 100 mm × 40 mm × 2 mm specimen according to ASTM D256. The notch was cut by a notch instrument (Ray-Ran).

Oil permeability measurements

Oil permeability measurements were conducted according to ASTM D2684-89 standard with dimethylbenzene as penetrant. All the samples were cut into the same size and measured the original weight (W_0), then dipped into dimethylbenzene and maintained at 20°C for 7, 14, 35 days, and finally obtained the saturated weight W_s , respectively. The permeation ratio is expressed by the following equation:

$$\text{Absorption Ratio} = \frac{W_s - W_0}{W_0} 100\% \quad (1)$$

Rheological measurements

The rheological properties of the blends were measured in a rotational rheometer (Gemini 200HR Rheometer, Bohlin Instruments, UK) equipped with a parallel plate geometry. The plate was 25 mm in diameter and the gap between two plates was 2.0 mm. The tests were carried out in the frequency ranging from 0.01 to 100 rad/s at 190°C. All tests were conducted under nitrogen atmosphere.

RESULTS AND DISCUSSION

Morphological analysis

It is well-known that HDPE is one kind of hydrophobic polymers, while EVOH has hydrophilic property, and they are immiscible. To improve the compatibilization of HDPE and EVOH, compatibilizer (HDPE-g-MAH) is used to reduce the interfacial tension and to increase the adhesion of the two immiscible phases. Figure 1 shows the FESEM micrographs of cryofractured surfaces of blends with varying amounts of HDPE-g-MAH. We can see that the domain size of dispersed phase is very large without HDPE-g-MAH [Fig. 1(a)], and a discrete interface between two phases can be also observed, which suggests poor interfacial adhesion between HDPE and EVOH. When 10 phr HDPE-g-MAH is used as a compatibilizer, the domain size of EVOH distinctly decreases in the HDPE matrix [Fig. 1(b)], and the phase boundaries disappears as the HDPE-g-MAH content is further >20 phr [Fig. 1(c,d)]. From the above observation, we can conclude that HDPE-g-MAH plays as an effective compatibilizer between the immiscible components of HDPE and EVOH. These micrographs also clearly show that the structures of the blends are changed from a droplet-matrix type of morphology to a cocontinuous morphology with large, interpenetrating network structures. As will be discussed under "Rheological properties," it is suggested that this kind of network structure may affect the rheological behavior of the compatibilized HDPE/EVOH blends compared with HDPE/EVOH blend without HDPE-g-MAH.

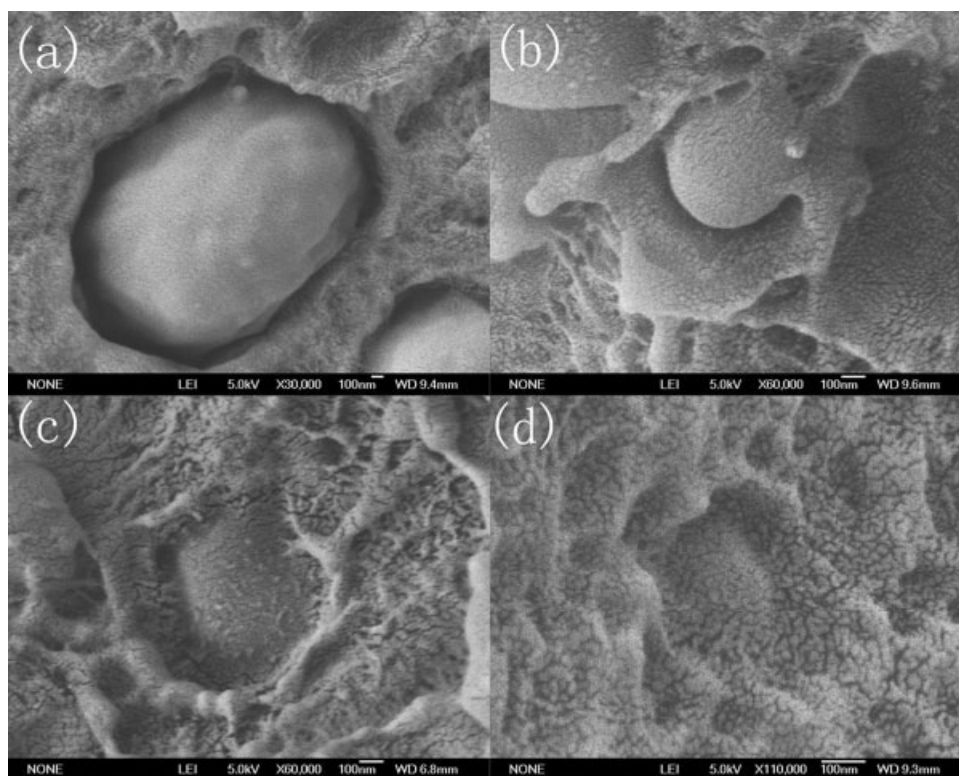


Figure 1 FESEM photographs for cryofractured surfaces of HDPE/EVOH/HDPE-g-MAH blends. (a) 80/20/0; (b) 70/20/10; (c) 60/20/20; (d) 55/20/25.

FTIR analysis

A physicochemical nature occurred in the compatibilization process, that is, the hydrogen donor–acceptor interactions involving the carbonyl groups of MAH (acceptor) and hydroxyl groups of the EVOH (donor) providing the acidic hydrogen. Similar intermolecular interaction was also detected in the EVOH-PE-SEBS-

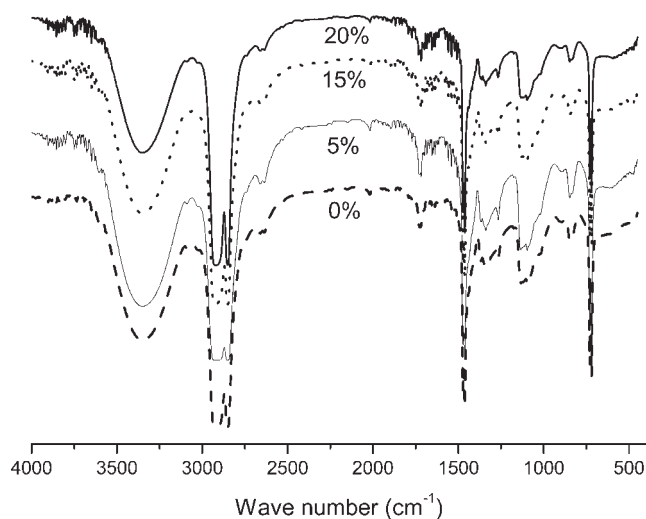


Figure 2 FTIR spectra of HDPE/EVOH blend and HDPE/EVOH blends containing different amount of compatibilizer.

g-MA blend.⁸ It has been known that the fundamental stretching vibration of a “free” hydroxyl group, which is not engaged in hydrogen bonding, corresponds to a sharp spectral peak in the neighborhood of 3600 cm^{-1} . When the hydroxyl group acts as donor in a hydrogen bond, three changes may be observed in the —OH peak with the increase of hydrogen bonding: moving to a lower frequency, becoming less

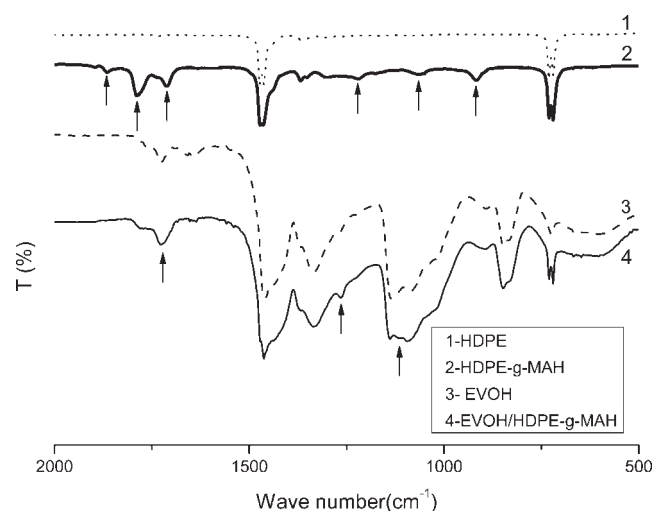


Figure 3 FTIR spectra of HDPE, HDPE-g-MAH, EVOH, and EVOH/HDPE-g-MAH blend.



Scheme 1 Potential reaction between the carbonyl groups of MAH and hydroxyl group of EVOH.

sharp and a consequent increasing in intensity.¹⁵ The FTIR spectra of HDPE/EVOH blends are shown in Figure 2. From Figure 2, we can see that the absorption band of —OH is at 3400 cm^{-1} ; the Figure also indicates that the hydrogen bond formed by EVOH itself or the interaction between the —OH group of EVOH and the carbonyl groups of MAH. However, no changes could be directly observed in the FTIR spectra for the blends with or without compatibilizer because of the low grafting degree of MAH (1.2 wt %). To further study the interaction between the functional groups of the EVOH and HDPE-g-MAH, some parallel experiments were conducted. New peaks (Fig. 3) appeared in HDPE-g-MAH besides the characteristic absorption peaks of HDPE, such as absorption peaks in $1864\text{--}1860\text{ cm}^{-1}$ for the asymmetric stretching of carbonyl $V_{\text{as}}(\text{C}=\text{O})$, in $1786\text{--}1780\text{ cm}^{-1}$ for the symmetric stretching of carbonyl $V_{\text{s}}(\text{C}=\text{O})$, at 1710 cm^{-1} for $V(\text{C}=\text{O})$ of carboxylic acid dimer, at 1224 cm^{-1} for the asymmetric ring stretching $V(\text{=C—O—C=})$, at 1064 cm^{-1} for the symmetric ring stretching $V(\text{=C—O—C=})$, and at 919 cm^{-1} for the ring stretching vibration of saturated cyclic five-membered anhydride. These results implied that MAH had been successfully grafted onto the HDPE backbone. We can find that the peaks (assigned to carboxylic acid) of EVOH/HDPE-g-MAH in $1864\text{--}1860\text{ cm}^{-1}$, 1710 cm^{-1} , and 919 cm^{-1} disappeared compared with that of HDPE-g-MAH. Further observation also shows that the shape of the peak at $1000\text{--}1100\text{ cm}^{-1}$ (assigned

to C—O of EVOH) slightly changed, in contrast to that of pure EVOH. The above results further implied that a possible reaction between the —OH group of EVOH and the carbonyl groups of MAH was formed according to the Scheme 1.¹⁶ These results are also consistent with the observation from the SEM that network structure is formed in the blends due to the addition of HDPE-g-MAH.

Rheological properties

The morphology of immiscible polymer blend is closely related to its rheological properties. Therefore, the rheological properties of HDPE, EVOH and the blend composites have been studied, and significant changes of the rheological property are observed when HDPE-g-MAH is used as a compatibilizer for the HDPE/EVOH blends. Figure 4 shows the complex viscosity of pure HDPE, EVOH, and the blends, respectively. Shear thinning behaviors, which is the typical behavior of non-Newtonian fluid, are observed for all samples. We can also find that the complex viscosities of the blends are more than those of pure HDPE or pure EVOH at low frequency. Further observation reveals that the complex viscosities of the HDPE/EVOH/HDPE-g-MAH blends are also higher than those of the HDPE/EVOH blends without HDPE-g-MAH and increase with increasing HDPE-g-MAH. It implies that the addition of HDPE-g-MAH compatibilizer is very sensitive to the rheological

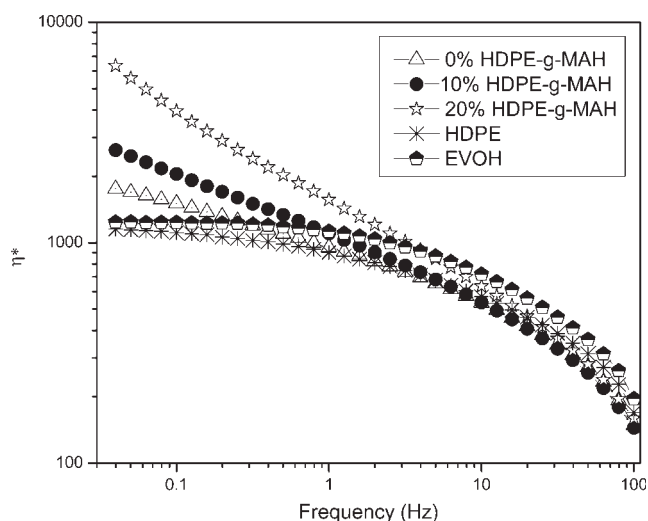


Figure 4 Complex viscosity versus frequency for the blends containing varying amounts of compatibilizer.

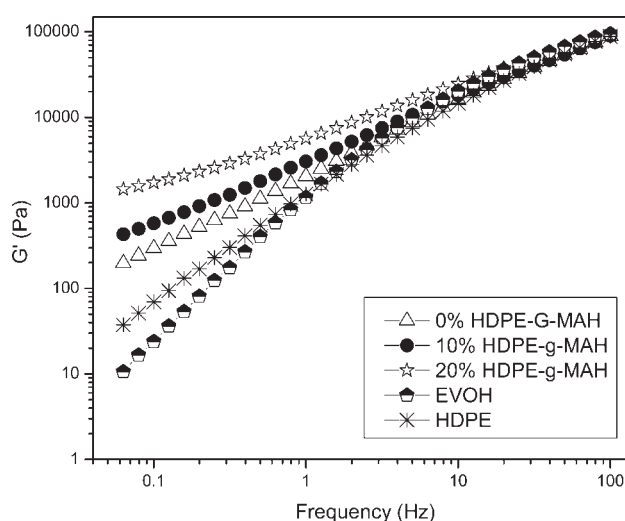


Figure 5 Storage modulus versus frequency for the blends containing varying amounts of compatibilizer.

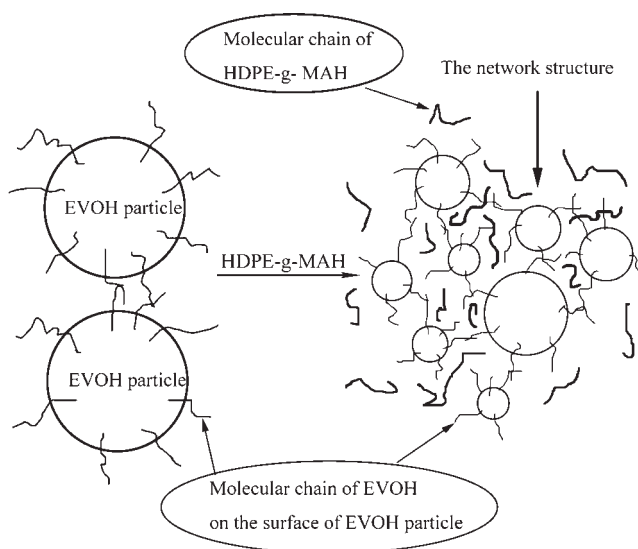


Figure 6 Formation scheme of network structure.

properties of the compatibilized blend. When HDPE-g-MAH was used as compatibilizer for HDPE/EVOH blend, the viscosity of the blends strongly increased as a result of the graft formation reaction between the EVOH —OH groups and the HDPE-g-MAH anhydride groups. Furthermore, the viscosity does not reach a plateau value at low frequencies. This suggests that a network structure is existed in the blends. Such phenomenon could be also confirmed by the fact that the storage moduli G' (in Fig. 5) tends to reach a plateau value at low frequencies in solid or gel-like structure.¹⁷ This behavior is also consistent with that of SEM and FTIR, as explained in Figure 6. When HDPE-g-MAH is used as compatibilizer, the dispersed EVOH particles dwindle in size because the molecular chains containing functional —OH groups on the surface of the particle could interact each other through intermolecular hydrogen bond or ester bond due to the motion of molecular chains in melt state, and the network structure forms when the blend is cooled down.

Crystallization and melting behavior

Melting temperature T_m , crystallization temperature T_c of HDPE and EVOH are shown in Table I. The reg-

ular T_m and T_c depression of EVOH is noticeable, whereas the T_m and T_c of HDPE remain constant values with the addition of HDPE-g-MAH. This further suggests that the specific interaction between hydroxyl groups of EVOH and carbonyl groups of MAH are formed and it further hinders the crystallization of EVOH. The results also agree with the work of Lee and Kim on the system of PP/PA6/PP-g-MAH¹⁸ and the work of Du et al. on the system of LDPE/EVOH.¹⁹

Mechanical property

In general, the mechanical properties of material can roughly be classified into two categories: strength and toughness. Tensile strength could be considered as the material strength, while Izod impact strength can represent material toughness. To investigate the effect of HDPE-g-MAH on the mechanical properties of HDPE/EVOH blends, tensile strength and notched Izod impact strength are measured using universal testing machine according to the standard methods.

Figure 7 shows the tensile strength of HDPE/EVOH blends with different HDPE-g-MAH content. Because of the incompatible properties of EVOH and HDPE, the tensile strength of binary blend of EVOH and HDPE is low. When 5 wt % compatibilizer is added, the tensile strength is effectively improved, which indicates that HDPE-g-MAH acts as an effective compatibilizer to improve the compatibilization between the dispersed EVOH and HDPE matrix. The tensile strength remains essentially constant when the content of HDPE-g-MAH is increased >5 wt %. This is because the addition of HDPE-g-MAH may yield a finer dispersion of EVOH phase and improves the adhesion between EVOH and HDPE phases (Figs. 1 and 6), which may further improve the tensile properties of the compatibilized blends.

Figure 8 shows the relationship of the impact strength and blend composition. The notched Izod impact strength of the blend increases significantly with the content increasing of HDPE-g-MAH. When the content of compatibilizer reaches 25 wt %, the notched Izod impact strength is nearly three times higher than that of the HDPE/EVOH blend without HDPE-g-MAH. It is because the network structure

TABLE I
 T_m and T_c of the HDPE/EVOH/HDPE-g-MAH Blends

HDPE-g-MAH (phr)	T_{m1} ; HDPE (°C)	T_{m2} ; EVOH (°C)	T_{c1} ; HDPE (°C)	T_{c2} ; EVOH (°C)
0	133.647	155.866	119.421	137.329
5%	133.188	154.900	120.113	137.359
10%	133.182	154.223	120.420	136.515
15%	133.490	153.377	120.428	136.166
20%	132.849	152.888	120.918	135.088

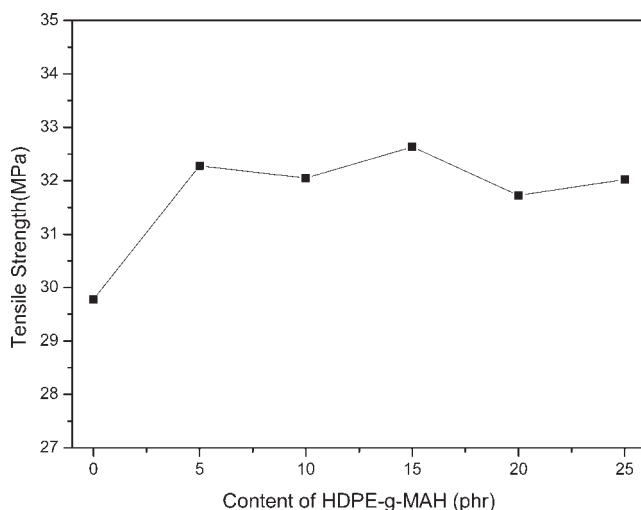


Figure 7 Tensile properties of HDPE/EVOH/HDPE-g-MAH blends.

formed during melt blending (Fig. 6) leads to strengthen the interaction between the EVOH dispersion phase and HDPE matrix, and further increases the impact strength. This result also accords with the results of rheological and FTIR measurements.

Barrier properties

It is well-known that the excellent barrier property of one kind of material arises from intense bonding provided by the hydroxyl group. From the barrier properties of the blends with different amount of HDPE-g-MAH (Table II), we can see that the barrier properties of compatibilized HDPE/EVOH blends decrease compared with that of noncompatibilized HDPE/EVOH blend.

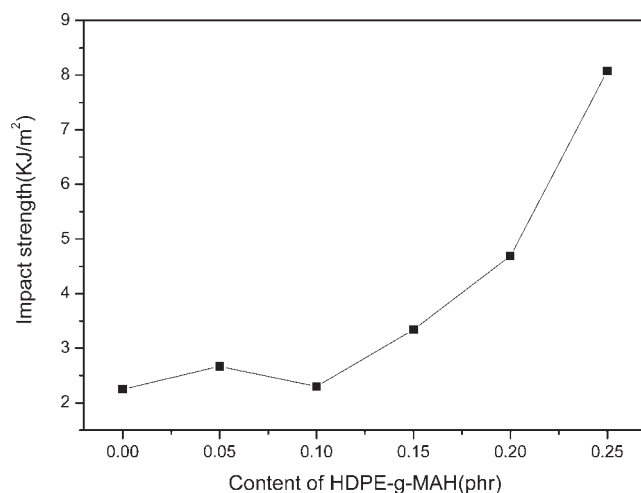


Figure 8 Notched Izod impact strength of HDPE/EVOH/HDPE-g-MAH blends.

TABLE II
Barrier Properties of HDPE/EVOH Blends with Different Amounts of HDPE-g-MAH

HDPE-g-MAH (phr)	7 days	14 days	35 days
0	6.15079	6.48148	6.08466
5	6.23892	6.84155	6.77065
10	6.36516	6.83417	6.83417
15	6.2403	6.42658	6.42658
20	6.73044	6.90126	6.96959
25	6.38441	6.55242	6.58602
EVOH	0	0.1967	0.2950
HDPE	6.9869	15.1017	15.0874

CONCLUSIONS

Blends of the HDPE and EVOH compatibilized with HDPE-g-MAH copolymer were prepared by twin-screw extruder. Morphological, thermal, rheological, FTIR, mechanical, and barrier properties of the blends were investigated. The important results are summarized as follows:

1. HDPE-g-MAH plays as an effective compatibilizer between the two immiscible components of HDPE and EVOH.
2. Rheological results prove that a network structure is formed when the content of HDPE-g-EVOH is up to 20%, which is formed through decreasing the hydrogen bonds of EVOH itself and forming the ester bonds or the hydrogen bonds between the dispersed EVOH phase and HDPE-g-MAH phase.
3. Tensile and impact properties of HDPE/EVOH blends are greatly improved with the addition of HDPE-g-MAH, while barrier property of the blends is not greatly harmed with the addition of compatibilizer.
4. DSC results show that the crystallization behavior of EVOH is retarded when HDPE-g-MAH is used.

References

1. Zhang, H. X.; Hourston, D. J. *J Appl Polym Sci* 1999, 71, 2049.
2. Legros, A.; Carreau, P. J.; Favis, B. D.; Michel, A. *Polymer* 1997, 38, 5085.
3. Lee, D. S.; Doo, J. K.; Kim, B.; Kim, J. *J Polym Eng* 1998, 18, 17.
4. Finch, C. A. *Polyvinyl Alcohol*; John Wiley: New York, 1993.
5. Takahashi, M.; Tashiro, K.; Amiya, S. *Macromolecules* 1999, 32, 5860.
6. Yeo, J. H.; Lee, C. H.; Park, C. S.; Lee, K. J. *Adv Polym Tech* 2001, 20, 191.
7. Park, S. H.; Lee, G. J.; Im, S. S.; Suh, K. D. *Polym Eng Sci* 1998, 38, 1420.
8. Lagaron, J. M.; Gimenez, E.; Gavara, R.; Saura, J. J. *Polymer* 2001, 42, 9531.
9. Kaleoglou, N. K.; Samios, C. K.; Papadopoulou, C. P. *J Appl Polym Sci* 1998, 68, 589.

10. Finlayson, K. M. *Plastic Film Technology*; Technomic: Lancaster, 1989.
11. Prasad, A.; Jackson, P. *Polym Mater Sci Eng* 1996, 75, 281.
12. Samios, C. K.; Kalfoglou, N. K. *Polymer* 1998, 39, 3863.
13. Lagaron, J. M.; Cava, D. *Macromol Symp* 2004, 205, 225.
14. Guiu, A.; Shanahan, M. E. R. *Int J Adhesion Adhesives* 2002, 22, 415.
15. Dai, L. X.; Ying, L. N. *Macromol Mater Eng* 2002, 287, 509.
16. Hert, M. *Angew Makromol Chem* 1992, 196, 89.
17. Tola, R. T.; Groeninckxa, G.; Vinckierb, I.; Moldenaersb, P.; Mewisb, J. *Polym* 2004, 45, 2587.
18. Lee, S. Y.; Kim, S. C. *J Appl Polym Sci* 1998, 68, 1245.
19. Du, W. C.; Zhong, W.; Lin, Y. J.; Shen, L.; Du, Q. G. *Eur Polym J* 1987 2004, 40.