

Effect of EPDM-g-MAH on properties of HDPE/OBC blends

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Abstract. In this paper, we take the HDPE as the matrix material, OBC as the toughening material, and EDPM-g-MAH as the compatibility agent, HDPE/OBC/EPDM-g-MAH blends were prepared by high speed mixing, melt extrusion, injection molding and so on. The effects of OBC and EPDM-g-MAH on mechanical properties, crystalline properties, fracture surface structure and rheological properties of HDPE were analyzed by universal tensile tester, melt mass flow rate test machine, DSC and SEM. Experimental results show that: with the addition of EPDM-g-MAH, the notched impact strength of the blends increased first and then decreased; HDPE/OBC blend containing 4% EPDM-g-MAH, OBC dispersion in the matrix is more uniform, particle size is significantly refined, melt flow has some improvement, Compared with HDPE/OBC blend materials, notched impact strength and elongation at break increased by 41.07% and 107.28% respectively, the toughness of the blend was greatly improved.

1. Introduction

HDPE is a kind of non polar and high crystallinity of the thermoplastic resin, inexpensive, lightweight, excellent moisture resistance and chemical stability and other advantages, is one of the most widely used polymer materials. However, due to the high crystallinity of HDPE and its own structural characteristics, it has many disadvantages, such as poor impact strength, etc. In order to widen the application field of HDPE, it is necessary to modify HDPE.

OBC has a unique “soft” and “hard” alternating block structure model of ethylene-octene block copolymer [1], compared with the other regulation of polyolefin copolymer, OBC has high temperature, excellent elasticity and compression deformation properties [2], is a new and efficient general plastic toughening agent.

In this paper, HDPE/OBC/EPDM-g-MAH was prepared with high speed mixing, melt extrusion and injection molding. The effect of EDPM-g-MAH content on the mechanical properties, melt flow rate, section structure, crystallization and melting behavior of HDPE/OBC blends was investigated.

2. Experimental part

2.1. Raw materials and reagents

HDPE, grade: DMDA 8920; OBC, grade: 9000; EDPM-g-MAH, grade: E-B12; Antioxidant1010.



2.2. Instruments and equipment

Extruder, XMTD-3001, Nanjing Zhicheng rubber machinery company; Injection molding, JN55-E, Chen Hung Machinery Factory Co., Ltd.; Electronic tension testing machine, CMT4204, Shenzhen SUNS Metering Technology Co. Ltd; Impact testing machine, ZBC1400-2, Shenzhen SUNS Metering Technology Co. Ltd; SEM, JSM-7500F, Japan JEOL company; DSC, DSC822e, Swiss Mettler-Toledo company; Melt mass flow rate tester, ZRZ1452, Shenzhen SUNS Metering Technology Co. Ltd.

2.3. Preparation of HDPE/OBC blend

2.3.1. *Sample formulation.* 0#: 99.5%HDPE(Mass fraction, the same below)+0.5% antioxidant1010; 1#: 81.5%HDPE+18%OBC+0.5% antioxidant1010; 2#: 99%1#+1%EPDM-g-MAH; 3#: 98%1#+2%EPDM-g-MAH; 4#: 97%1#+3%EPDM-g-MAH; 5#: 96%1#+4%EPDM-g-MAH.

2.3.2. *Sample preparation.* The HDPE and OBC were placed in the drying box at 75 °C for drying 4h, Then HDPE, OBC, EPDM-g-MAH, antioxidant 1010 according to a certain ratio at 65 °C evenly mixed in a high-speed mixer; then the initial mixture is placed in a double screw extruder for melt mixing, the extruder temperature was 132 °C, 137 °C, 142 °C, 150 °C, 155 °C and 152 °C, and then after cooling water cooling, granulator by extrusion pellets; blend in injection molding machine injection molding granulation after injection into standard samples, the temperature of 180 °C ~200 °C.

2.4. Performance testing

2.4.1. *Mechanical property test.* Tensile strength and elongation at break were tested by ISO 527-2: 2012; flexural strength were tested by ISO 178: 1993; notched impact strength were tested by ISO 179-2: 1997.

2.4.2. *Melt mass flow rate measurement.* Melt mass flow rate was measured by ISO 1133-1: 2011. Test temperature is 190 °C, load: 2.16 kg.

2.4.3. *SEM test.* The samples were frozen in liquid nitrogen for ten minutes, then etching at 80 °C of n-heptane for 5h, then using ethanol and distilled water cleaning section, by spraying treatment, observe the morphology of the sample section in scanning electron microscope.

2.4.4. *DSC test.* In nitrogen atmosphere, the gas flow rate is 50 ml/min, take the 3~6 mg in DSC thermal stage, rose from 170 °C to 30 °C at 10 °C /min, and then stay at 170 °C for 5min to eliminate the thermal history, and then at a rate of 10 °C /min from 170 °C to 30 °C, then heating at rate of 10 °C /min from 170 °C to 30 °C, record the crystallization and melting curve. $X(\%) = (\Delta H_c / \Delta H_m^0) \times 100\%$, Among ΔH_m^0 is the Melting enthalpy at 100% degree of crystallinity, $\Delta H_m^0 = 287.3 \text{ J/g}$ [3].

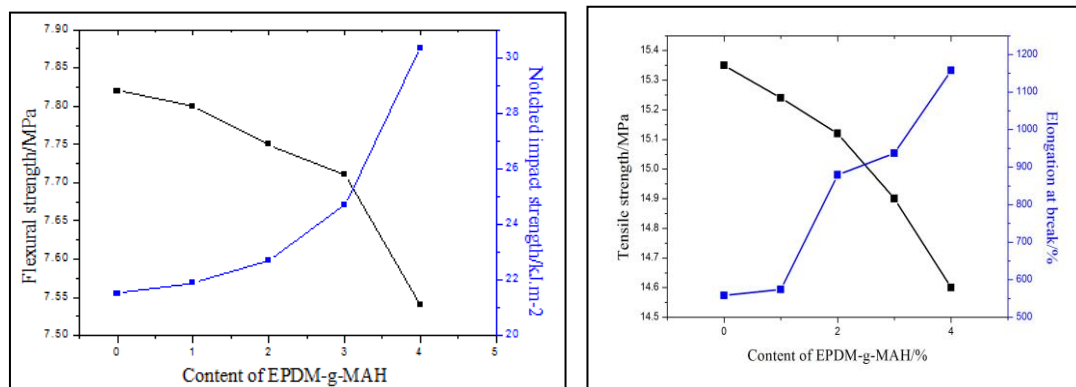
3. Results and discussion

3.1. Effects of OBC and EPDM-g-MAH on mechanical properties of HDPE

Effect of EPDM-g-MAH content on Mechanical property of HDPE/OBC blends are shown in Table 1 and figure 1. We can see from Table 1, adding 18%OBC (mass fraction, the same below), the notched impact strength of blends was 21.50kJ/m², while the elongation increased from 165.85% to 558.00%, the toughening effect is obvious, this is because the special structure of OBC ethylene octene copolymer, which makes the HDPE and OBC have good compatibility.

Table 1. Effect of OBC and EPDM-g-MAH content on mechanical properties of HDPE

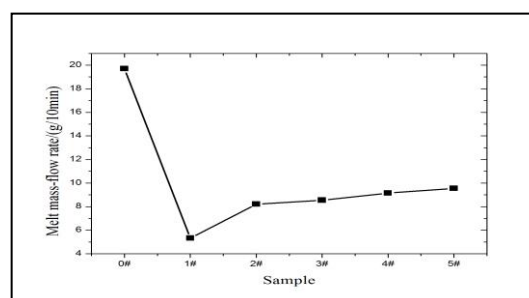
Sample	Tensile strength/MPa	Elongation at break/%	Flexural strength/MPa	Notched impact strength/ $\text{kJ}\cdot\text{m}^{-2}$
0 [#]	22.08	165.85	12.15	4.85
1 [#]	15.35	558.00	7.82	21.50
2 [#]	15.24	574.00	7.80	21.90
3 [#]	15.12	879.00	7.75	22.70
4 [#]	14.90	936.60	7.71	24.68
5 [#]	14.60	1157.60	7.54	30.33

**Figure 1.** Mechanical property VS. EPDM-g-MAH content

From Figure 1 we can see that the notched impact strength of blends increased with the increase of EPDM-g-MAH content, when adding 4% EPDM-g-MAH, the notched impact strength of blends reached 30.33 kJ/m^2 , higher than 1# 41.07%, the elongation is 1156.60%, higher than 1# 107.28%, the tensile strength and flexural strength were declined slightly. The reason, mainly the following two aspects: first, the non-polar part of EPDM-g-MAH is ethylene, propylene and non conjugated dienes copolymer, according to the similarity principle of compatibility, non polar part with HDPE and OBC has good compatibility [4]; Second, EPDM-g-MAH is an excellent synergistic toughening agent, so the impact strength and elongation of the blends increased, while the tensile strength and the bending strength does not change much.

3.2. Effects of HDPE and EPDM-g-MAH content on the melt flow rate of HDPE

The melt mass flow rate of OBC is 0.5 g/10min (Provided by DOW), the melt mass flow rate of pure HDPE is 19.7 g/10min, and the melt mass flow rate of 1# is 5.33g/10min, down by 72.94%, this is due to the low flow rate of OBC, melt the addition of OBC increases the blends in friction resistance, lead to the relative motion between polymer chains becomes difficult. From Figure 2 we can also see that the increase of EPDM-g-MAH content, melt flow rate of blends increases, this is because EPDM-g-MAH its good liquidity, driven by other components of the flow induced by [5].

**Figure 2.** Melt mass-flow rate of HDPE and its blends

3.3. SEM analysis of HDPE and its blends

Figure 3 is the SEM of HDPE and its blends. 0# is smooth, the cross section is smooth and the crack is not cross, which indicates that the toughness of pure HDPE is not good; 1# is HDPE/OBC blends after etching, etching holes is OBC particles left, 1# showed that OBC particles can be homogeneously dispersed in the matrix, indicating that HDPE and OBC dispersed phase compatibility between certain, but the pore size of different sizes, indicating that HDPE and OBC are partially compatible; 5# is refined and the pore distribution is more uniform, the addition of EPDM-g-MAH, the distribution of dispersed phase OBC is more uniform, improved HDPE and OBC interface compatibility, improve the toughness of the composites.

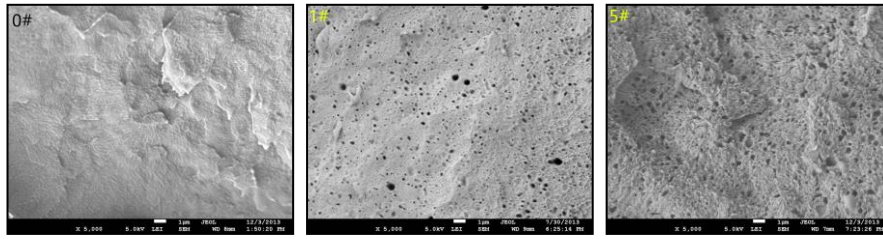


Figure 3. SEM of HDPE and its blends ($\times 5000$)

3.4. DSC analysis of HDPE/OBC/EPDM-g-MAH blends

Table 2 shows the pure HDPE (0#) crystallinity (X) 67.29%, HDPE/OBC (1#) crystallinity (X) 56.14%, this is due to the low crystallinity of block copolymer OBC; The crystallinity (X) of HDPE/OBC/EPDM-g-MAH (5#) was 51.93%, Crystallinity is still declining, This is because the addition of EPDM-g-MAH and EPDM segments in non conjugated dienes, the double bond under heat and force, resulting in a slight crosslinking, the flexibility of the molecular chain fell.

Table 2. DSC date of HDPE and HDPE/OBC/EPDM-g-MAH

Samples	$T_c^f / ^\circ\text{C}$	$T_c^p / ^\circ\text{C}$	$T_c^o / ^\circ\text{C}$	X/%	$T_m^o / ^\circ\text{C}$	$T_m^p / ^\circ\text{C}$	$T_m^f / ^\circ\text{C}$	ΔT
0#	112.17	117.88	119.52	67.29	126.33	131.15	135.49	13.27
1#	112.64	117.63	119.30	56.14	123.99	129.91	134.45	16.82
5#	112.73	117.33	119.12	51.93	124.40	130.96	134.25	13.63

Melting temperature $T_m = \Delta H / \Delta S$, among them, ΔH is the melting enthalpy change, ΔS is the melting entropy change [6]. From the above type: And the increase of ΔH or reduction of ΔS will increase the T_m . From Table 2 and Figure 4 shows that pure HDPE (0#) sample melting temperature is 131.15°C , HDPE/OBC (mass fraction of OBC is 18%) the melting temperature of blends is 129.91°C , decreased 1.24°C , this is because the addition of OBC, reduce the flexibility of the system, thereby reducing the molecular chain in the crystallization process of ordered surface nucleation rate, then reduce the crystallinity of blends. HDPE/OBC/EPDM-g-MAH (5#) sample melting temperature is 130.96°C , rise 1.05°C than the 1# sample, this is because the addition of EPDM-g-MAH, increase the interaction between molecular blends, the melting temperature increases. Degree of cooling ΔT is used to characterize the nucleation ability of the polymer molecular chain. The smaller the value is, the higher the nucleation ability of the polymer is, the faster the crystallization rate [7]. HDPE/OBC/EPDM-g-MAH blends have the biggest ΔT , the results show that the addition of EPDM-g-MAH can improve the nucleation ability of HDPE/OBC blends, and the blends are easier to crystallize.

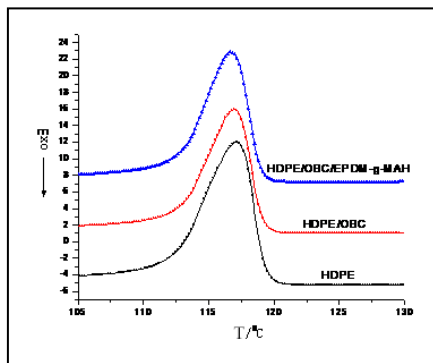


Figure 4. DSC crystallization curves of HDPE and its blends

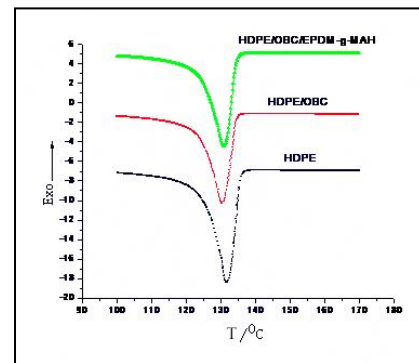


Figure 5. DSC melting curves of HDPE and its blends

4. Conclusion

- 1) New thermoplastic elastomer OBC and matrix HDPE has good compatibility, when adding 18% OBC, the notched impact strength of blends increased by 343.30%, the toughening effect is obvious.
- 2) When adding 4% EPDM-g-MAH, the notched impact strength of blends reached 30.33kJ/m², elongation was 1156.60%, compatibilization effect is obvious.
- 3) The addition of EPDM-g-MAH enhance the interface compatibility, making OBC more evenly distributed in the HDPE matrix, the size is refined and the crystallinity decreased.
- 4) With the addition of OBC and EPDM-g-MAH, the tensile strength and flexural strength of the blends decreased, the focus of future work is to find effective reinforcing material for HDPE/OBC.

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