

Influence of morphology and compatibilizer on burning behavior of PET/HDPE blend

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Abstract. Blending polymers offers a wide range of possibilities to tailor the properties of the components and to produce new materials. However, the most commonly used plastics are not compatible with each other. To increase compatibility between the phases, copolymer or compatibilizer has to be added to polymer blends, resulting in a finer morphology and better impact properties. Polymer blends are widely used in engineering where burning behavior can be a main criterion of application. It became clear that the fire resistance of blends can be improved by using flame retardant or different fillers. But the number of papers that examine the effects of morphological change or adding additives in polymer blends is quite few. In this paper polyethylene terephthalate (PET) and high density polyethylene (HDPE) were blended with styrene/ethylene/butylene/styrene block copolymer grafted with maleic anhydride (SEBS-g-MA), in order to present its effects on the morphology, rheology and burning characteristics.

INTRODUCTION

Blending polymers is useful to tailor the favorable properties of components. Blending two immiscible plastics can result in two different morphologies: if one component is significantly less than the other usually a dispersed phase/matrix structure forms; otherwise a co-continuous morphology forms, where both phases show a continuous structure. In many cases polymers are not compatible with each other and the properties of non-miscible polymer blends generally do not follow linear mixing rule, particularly in mechanical properties, where a negative deviation can be detected [1]. In order to achieve suitable dispersion between phases, copolymers or compatibilizers can be used [2, 3]. Polymer blends are widely used in automotive-, construction-, and electronic industry, where burning behavior can be a main criterion of application [4]. Nevertheless, plastics are easily flammable, which implies, it is important to enhance the fire resistance by using flame retardant [5, 6] and nanofillers [7, 8], or control the forming morphology in order to maximize the performance [1, 9]. It should be mentioned that despite our extensive research, we did not find any papers which have examined the effects of compatibilizers on fire behavior of polymer blends. However, it would be fairly important information since the use of polymer blends is increasingly popular.

Finding a relationship between morphological structure of blends, composition and fire behavior can promote the design of new polymeric materials with higher fire resistance [10]. However, the influence of the morphological structures on flammability has not been investigated widely. Sonnier et al. [1] found a relation between morphology

and fire behavior in binary blend, where the heat release rate and limiting oxygen index (LOI) of blends significantly changed in the range of phase inversion. Liang et al. [7] mentioned that linear burning rate depends on the thickness of specimens and the flame spreads mainly on the surface of specimens. Walters and Lyon [11] established a relationship between molar group contribution, heat-release capacity and ignitability of plastics. They measured the heat-release capacity (332 and 1676 J/gK) and total heat release (15.3 and 41.6 kJ/g) of polyethylene terephthalate (PET) and high density polyethylene (HDPE), and they found HDPE shows greater flammability than PET.

In this work it was attempted to reveal a connection between the morphology and burning properties, as linear burning rate and limiting oxygen index (LOI), of blends containing PET and HDPE, which are widely used in industrial fields. Further aim is to point out the negative effect of compatibilizer on fire behavior of blends.

EXPERIMENTAL

Materials

PET and two different flowability HDPE were blended during the study, where the HDPE with higher melt flow was Liten MB 87 (density 0.955 g/cm³; MFI=23 g/10 min (190°C/2.16 kg)) supplied by Unipetrol (Czech Republic, referred to as HDPE-UNI), while Tipelin BA 550-13 (density 0.955 g/cm³; MFI=0.35 g/10 min (190°C/2.16 kg)) produced by TVK (Hungary) had the lower flow rate (referred to as HDPE-TVK). PET was NeopET 80 (density 1.34 g/cm³; T_m=248°C, Intrinsic Viscosity 0.8 dl/g) produced by neogroup (Lithuania). Kraton FG1901X SEBS-g-MA compatibilizer (density 0.91 g/cm³; MFI=22 g/10 min, (230°C/5 kg)) was added to PET/HDPE blends in 4 vol%.

Equipment

PET was dried in an air drying oven at 160°C for 6 h. The extrusion took place in a Labtech Scientific LTE 26-44 twin screw extruder (temperature 250 to 275°C, rotation speed 40 rpm). The extrudates were cooled down in a water bath, followed by granulation. An Arburg Allrounder Advance 370S 700-290 machine was used to prepare the specimens with a 10x4 mm cross section, according to ISO 527-2 standard, where nozzle temperature was 275°C, mold temperature was 60°C, injection flow was 30-40 cm³/s, injection volume was 46 cm³, holding pressure was 400±100 bar. The viscosities were recorded using an AR2000 rheometer (TA Instruments) in plate-plate configuration, where 25 mm diameter discs were used to compression-mold the blends for 5 minutes at 275°C. After gold coating, JEOL JSM 6380LA scanning electron microscope (SEM) was used to compare the morphology of cryogenic fractured surface of PET/HDPE blends with and without SEBS-g-MA. Thermogravimetric analysis (TGA) was performed on TA Instruments TGA Q5000 IR at a heat rate of 10°C/min, where 6 to 10 mg of samples were examined under flowing nitrogen or air (50 ml/min) over a temperature range from 30°C to 600°C. According to ISO 4589 standard, limiting oxygen index (LOI) was measured on 10x4x80 mm specimens with ±0.5 accuracy. The linear burning rate of blends was calculated from the combustion length in mm and the burning time in minute, according to the requirement of UL 94 test (3 specimens, 75 mm distance). It should be mentioned that the flame extinguished before the 100 mm mark at specimens of 100 vol% PET, where linear burning rate was calculated from the damaged length and the elapsed time.

RESULTS AND DISCUSSION

Rheology

The viscosities of plastics (HDPE-UNI, HDPE-TVK and PET) at 275°C are shown as a function of shear rates in Fig. 1. The viscosity of HDPE-TVK was higher, while HDPE-UNI was lower than PET in the entire range of measurement (Fig. 1(a)), which result is consistent with the values of melt flow rates given by the suppliers.

Based on the results, the viscosity ratio of PET and HDPE (η_{PET}/η_{HDPE}) can be determined (Fig. 1(b)). Since the viscosity of HDPE-UNI is the lowest among the applied plastics, the viscosity ratio of PET and HDPE-UNI is higher than 1 in each data point, which suggests phase inversion will occur at higher PET content. On the other hand the viscosity ratio of PET and HDPE-TVK was less than 1 at every shear rate, accordingly the co-continuous morphology can be shifted towards lower PET content during the preparation of injection molded samples.

Morphology

Injection molded specimens were cryogenic fractured, where the core areas of different PET/HDPE blends were investigated (Fig. 2-3). In a range of 0-40 vol% PET content, the dispersed PET phases showed spherical shape in PET/HDPE-UNI blends. At 50 vol% PET content the dispersed morphology remained but the shape of dispersed parts changed into elongated, rod-like structure (Fig. 2(a)). From 55 to 60 vol% PET a coarsened co-continuous structure developed (Fig. 2(b)). After the phase inversion, from 70 vol% PET repeatedly dispersed structure formed and further increasing the PET content in PET/HDPE-UNI blends the dispersed HDPE phases become finer. If PET/HDPE-UNI blends are compared, it can be stated that blends with 4 vol% of SEBS-g-MA show a much finer distribution in the experiment range, and the co-continuous structure moves slightly toward to higher PET content (Fig. 2(c)-(d)). While blends without compatibilizer show co-continuous morphology at 55 vol% PET, in blends with 4 vol% SEBS-g-MA there can be found both dispersed and continuous parts. At 60 vol% PET a very fine co-continuous structure is visible in blend with additive (Fig. 2(d)), which suggests SEBS-g-MA was effective in PET/HDPE-UNI blends. By comparing the two blends a deviation of phase inversion can be seen. When the higher flowability HDPE-UNI blended with PET, phase inversion occurred at 55-60 vol% PET, until the co-continuous range formed at 30-40 vol% PET (Fig. 3(a)), when HDPE-TVK – characterized by low flow rate – was blended with PET. Already at 50 vol% PET content the phase inversion took place, wherein the matrix can be characterized by continuous PET phase in which large-scale and elongated HDPE phases located (Fig. 3(b)). In PET/HDPE-TVK blend with compatibilizer also can be observed a slight shift in phase inversion towards higher PET content. At 30 vol% PET blends with 4% SEBS-g-MA even more dispersed (Fig. 3(c)); and continuous parts were formed only at higher, 40 vol% PET content, besides dispersed phases (Fig. 3(d)). In blends of PET/HDPE-TVK the finer distribution of the phases were not observed, which can probably be explained by the small flow rate of HDPE-TVK, thereby finer dispersed or co-continuous structures were not able to develop.

Thermal stability

The applied TGA test conditions have no effect on PET, its initial decomposition temperature (T_{onset}) was around 390°C for both air and nitrogen atmospheres. Conversely, both HDPEs had a reduced thermal stability in air atmosphere, particularly for HDPE-UNI. The presence of SEBS-g-MA had no influence on thermal stability of PET, while a slight reducing effect was detectable in both HDPEs, mostly in air atmosphere (Table 1).

TABLE 1. The results from thermogravimetric curves of samples (heating rate: 10 °C/min in nitrogen or air)

Sample	nitrogen atmosphere				air atmosphere			
	T_{onset} (°C)	$T_{10\%}$ (°C)	T_{peak} (°C)	Char (%)	T_{onset} (°C)	$T_{10\%}$ (°C)	T_{peak} (°C)	Char (%)
HDPE-UNI	436.4	446.8	475.5	2.2	346.4	363.1	406.9	0.5
HDPE-UNI with 4% SEBS-g-MA	413.3	424.1	462.7	0.6	327.5	350.2	388.7	0.5
HDPE-TVK	439.5	449.3	477.8	1.7	408.2	413.2	429.6	0.3
HDPE-TVK with 4% SEBS-g-MA	430.4	439.7	471.3	0.0	330.1	376.9	413.9	0.1
PET	396.3	405.7	438.7	10.1	387.9	397.4	433.1	0.4
PET with 4% SEBS-g-MA	397.0	405.5	437.8	10.6	391.3	401.3	432.2	0.9
SEBS-g-MA	403.5	415.5	447.5	1.3	332.6	342.7	381.5	0.2

T_{onset} and $T_{10\%}$ are the temperatures where 5 and 10% mass loss occurred, respectively

T_{peak} is the peak of derivative thermogravimetric curve

$Char$ is the residue mass% at 600°C

Burning behavior

Comparing blends with two different viscosity ratios, it can be stated PET/HDPE-UNI blends can be characterized by higher burning rate, regardless of the SEBS-g-MA content (Fig. 4(a)). Moreover, PET/HDPE-UNI blends showed a high degree of dripping, particularly at lower PET content (0-40 vol%). It has rarely occurred that the downward flowing to metal grid extinguished the flame on the sample – in this case measurement was not taken into account. The linear burning rate was nearly constant, approximately 30 mm/min until the range of phase inversion (55 vol%

PET in PET/HDPE-UNI blend). After phase inversion in continuous PET matrix, a steady decline in burning rate was observed parallel with increasing PET content. In PET/HDPE-UNI blend with 4 vol% SEBS-g-MA a similar trend can be observed. By the end of the range of phase inversion, which slightly shifted towards higher PET content (60 vol%), the average linear burning rate was between 26-32 mm/min. Above 60 vol% PET the burning rate decreased steadily, similarly to PET/HDPE-UNI blend without SEBS-g-MA.

After increasing the PET content in PET/HDPE-TVK blend a slight decrease in burning rate (from 26 to 23 mm/min) was observed in a range of 0-20 vol% PET. In the early stage of co-continuous morphology (30 vol% PET), the burning rate was reduced under 20 mm/min and the slope of curve changed to almost constant until 60 vol% PET. In a range of 70-80 vol% PET content, the shape of dispersed HDPE phases changes from rod-like shape into spherical, which results in another reduction in burning rate of PET/HDPE-TVK blends. Comparing PET/HDPE-TVK blends without and with 4 vol% SEBS-g-MA it was detectable, that the presence of SEBS-g-MA increased the burning rate in the whole range of measurement. Apart from the lower, 0-30 vol% PET content stage with uncertainty in PET/HDPE-UNI, a similar phenomenon can be observed from 40 to 100 vol% PET, blends with compatibilizer showed higher burning rate. The difference was particularly significant after phase inversion (60-100 vol% PET).

The LOI values of blends are shown in Fig. 4(b). In PET/HDPE-UNI blends LOI did not change significantly (18.5-19.0) in a range of 0-50 vol% PET. At co-continuous structures (55-60 vol% PET) LOI was slightly increased to 20 and after phase inversion showed an increase with higher rate up to 100 vol% PET, where LOI was 26. Similarly in PET/HDPE-TVK, the first increase of LOI was detected besides co-continuous morphology (30-40 vol% PET), but steeper increase of LOI was only seen over 70 vol% PET content, when elongated, rod-like shape of dispersed HDPE changed to spherical. The negative effect of SEBS-g-MA on LOI values was also demonstrated in PET/HDPE blends when the matrix is formed by PET. While in case of lower PET content a significant effect of SEBS-g-MA was not detectable, until after phase inversion blends with SEBS-g-MA can be characterized by lower LOI values in each composition, regardless of usage of different HDPE during the blending. This phenomenon resulted in greater flammability in blends with PET matrix, and LOI decreased from 26 to 24 at 100 vol% PET.

CONCLUSIONS

In this work the influence of morphology and compatibilizer on burning behavior of PET/HDPE blend has been presented. Due to the different viscosity ratio, the phase inversion occurred under different composition in blends. The co-continuous morphology formed at 55-60 vol% PET in blend consists of HDPE with higher flow rate (referred as HDPE-UNI), while blending the lower flowability HDPE (referred as HDPE-TVK) to PET, 30-40 vol% PET was enough to reach the phase inversion. The presence of SEBS-g-MA compatibilizer in PET had no effect on thermal stability, while it had a slight reducing influence when introduced to HDPE. Comparing the burning rate of PET/HDPE blends, it can be stated that burning was faster with greater flammability when the matrix was formed by HDPE. Consistent results have been achieved in LOI studies, there was no significant change in LOI values in case of blends where HDPE showed continuous structure. Nevertheless, after phase inversion LOI was greatly increased. The negative impact of SEBS-g-MA was also appearing in blends. PET/HDPE blends with compatibilizer showed higher burning rate in most case, the difference was particularly significant after phase inversion.

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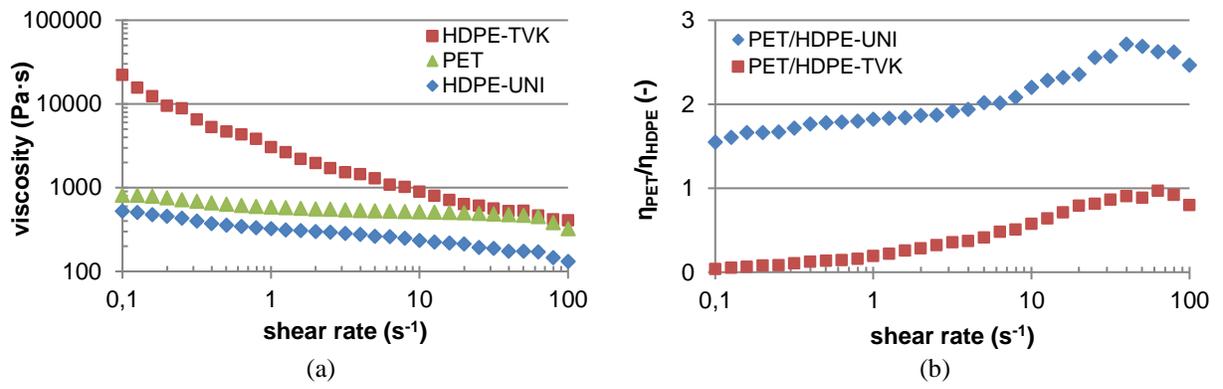


FIGURE 1. (a) Viscosity of (♦) HDPE-UNI, (■) HDPE-TVK, (▲) PET; (b) viscosity ratio of components: (♦) PET and HDPE-UNI, (■) PET and HDPE-TVK as a function of shear rate, at 275°C

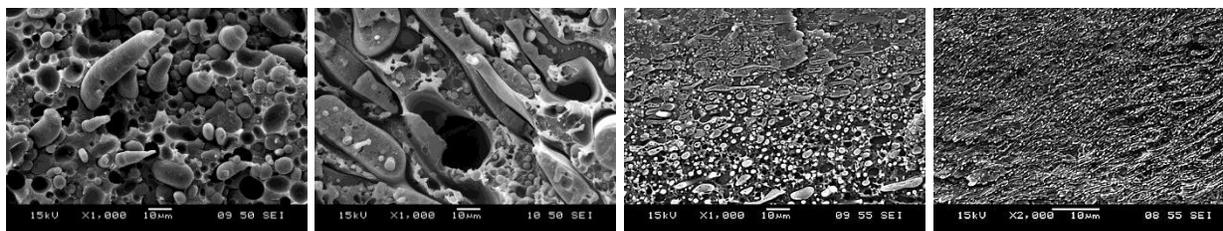


FIGURE 2. Morphology of cores of cryogenic fractured injection molded PET/HDPE-UNI blends (a) 50/50, (b) 55/45, (c) 55/45 with 4% SEBS-g-MA, (d) 60/40 with 4% SEBS-g-MA

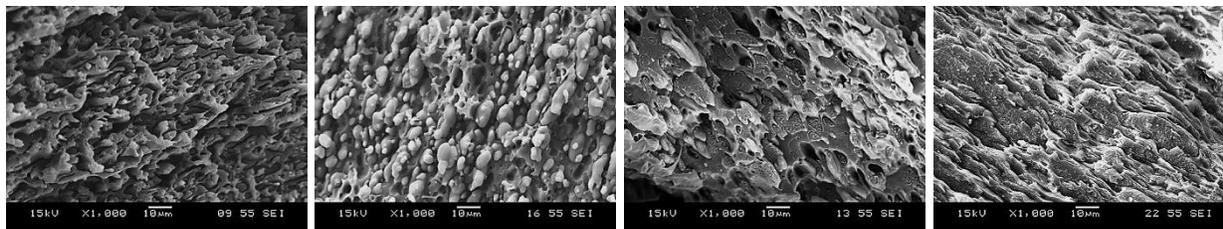


FIGURE 3. Morphology of cores of cryogenic fractured injection molded PET/HDPE-TVK blends (a) 30/70, (b) 50/50, (d) 30/70 with 4% SEBS-g-MA, (e) 40/60 with 4% SEBS-g-MA

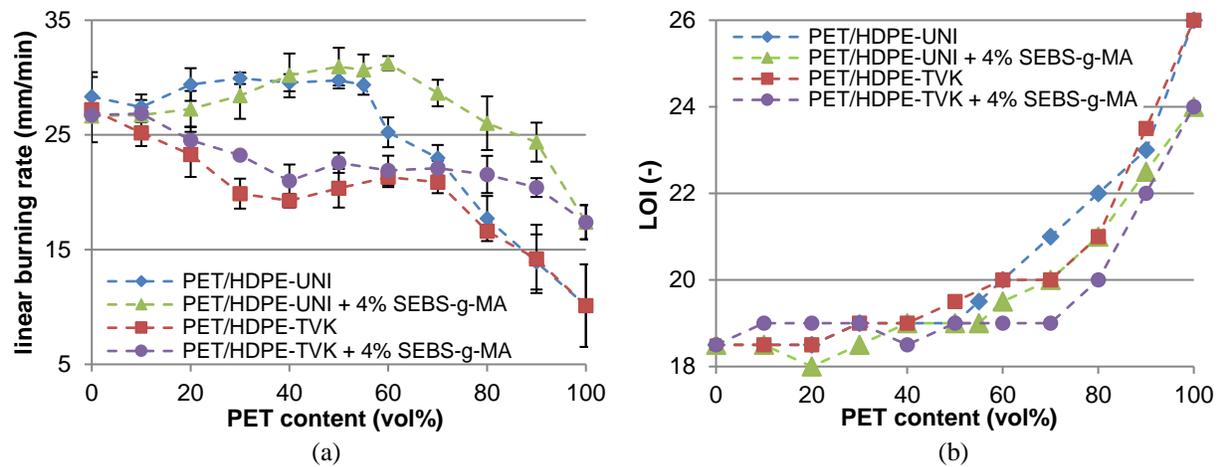


FIGURE 4. (a) Linear burning rate and (b) LOI of blends, shown with the following symbols: (◆) PET/HDPE-UNI, (▲) PET/HDPE-UNI + 4% SEBS-g-MA, (■) PET/HDPE-TVK and (●) PET/HDPE-TVK + 4% SEBS-g-MA