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ORIGINAL PAPER

The effect of irradiation on morphology and properties of the PET/HDPE blends with trimethylol propane trimethacrylate (TMPTA)

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Abstract The mechanical properties of poly(ethylene terephthalate)/high-density poly(ethylene) (PET/HDPE) blends were improved by γ-ray irradiation combined with using a cross-linking agent—trimethylol propane trimethacrylate (TMPTA). The effect of the weight ratio of PET/HDPE, the content of TMPTA and the absorbed dose on the phase morphology and the mechanical properties of the PET/HDPE blends were investigated through scanning electron microscopy (SEM), gel fraction, Fourier transform infrared spectroscopy (FTIR), tensile and impact tests. SEM images showed that the phase structure changed significantly as TMPTA coexistence. The results of tensile and impact tests indicated that their mechanical properties depended on their structures. FTIR spectra suggested that a new structure of HDPE-g-PET was generated. When the weight ratio of PET/HDPE blend was 80/20, the content of TMPTA was 1 wt% and the absorbed dose was 30 kGy, the tensile strength, elongation at break and impact strength of irradiated blends were improved greatly compared with non-irradiated blends.

Keywords PET/HDPE · TMPTA · Irradiation ·
Morphology and mechanical properties

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Introduction

The development of new materials is traditionally achieved by synthesis of new polymers or combination of polymers with additional properties. Moreover, blending of commercially available polymers to produce improved materials have been paid more attention rather than synthesis of new polymers. However, it is very difficult to obtain good phase dispersions in polymer blends due to their inherent low entropy of mixing in long chain molecules. This incompatibility often results in blends having a microscopically phase-separated structure, large interfacial tension, unstable morphology and poor mechanical properties [1].

The thermoplastic poly (ethylene terephthalate) (PET) and polyolefin (HDPE, LDPE, PP, etc.) are extensively used as packaging materials (bottles, films, containers, etc.), being the most found in urban waste streams. Current environmental policies for pollution abatement encourage the recycling of these plastics [2–5]. It would be highly convenient, in economical terms, to blend both polymers. The blends of PET and HDPE have been investigated widely [6], because HDPE can modify the rheological properties and impact properties of PET and increase the speed of crystallization, while PET can improve the mechanical properties and thermostability of HDPE. As mentioned above, they are not thermodynamically miscible. If blended mechanically, the incompatibility of these two polymers may give rise to bad morphology and a lack adhesion between the phases, resulting in poor mechanical properties.

In the past two decades, many researchers have focused on the control of the morphology and interfaces of PET/HDPE blends to improve their compatibility. Li et al. [7, 8] reported in situ microfibrillar PET/PE blends (MRB) fabricated by slit–die extrusion–hot stretching–quenching. The tensile modulus and strength of MRB were significantly enhanced with appropriate PET concentrations and a comparatively high hot stretching ratio. Most of researchers improved the compatibility and mechanical properties with addition of compatibilizers consisting of a graft or block copolymer. Usually, one side of the copolymer is miscible with HDPE, the other reacts with the functional groups of PET during reactive extrusion, such as PE-g-GMA [9–12], PE-g-MA [11, 12], PE-g-BHI [13, 14], SEBS-g-MA [9, 15], EVA based graft-copolymers [16] and ionomers [17, 18]. Among these compatibilizers, PE-g-GMA is considered as a very suitable compatibilizer, and its compatibilizing effectiveness is higher than that of polyolefin grafted with maleic anhydride (MA) or other monomers [9–11]. Although both of improved morphology and better mechanical properties have been observed by using some of these compatibilizers, complicated compatibilizers need to be first synthesized. Fasce et al. [19] improved the elongation at break and fracture toughness of 50:50 PET/HDPE blends significantly by adding a commercial grade of ethylene/methacrylic acid copolymer (EMA, 7%) as compatibilizer combination with inducing fibrillation of PET phase in the HDPE matrix by extruding the blends under adequate conditions.

It is well known that high energy radiation is a powerful technique for the modification of polymers [20–22]. The miscibility of blends could be improved by the cross-linking of one or both of the polymers via irradiation, leading to stable morphology and good mechanical properties. In the system of PET/HDPE blends, HDPE was easily cross-linked while PET was hard to be cross-linked due to aromatic group. Until now, there are a few reports about the radiation effect of PET/HDPE blends. Burillo and co-workers [23, 24] had tried to improve the compatibility of PET with radiation-oxidized HDPE. HDPE was oxidized by irradiation in air, then heated to destroy peroxides formed by this irradiation and to form polar groups in the HDPE, and then reacted with PET by extrusion, but the improvement of mechanical properties is still limited.

In order to promote the reaction at the interface and to improve the miscibility of the blend, it is useful to add cross-linking agent which could facilitate the cross-linking of PET by decreasing the gel dose and the absorbed dose necessary to obtain maximum gel. In this paper, we report a facile method to improve the mechanical properties of PET/HDPE blends by γ-ray radiation with addition of cross-linking agent—trimethylol propane triacrylate (TMPTA). The interfacial adhesion is supposed to be improved by the formation of the cross-linked copolymers at the presence of TMPTA and irradiation. The SEM images, FTIR spectra and gel fraction of those blends are presented. Their tensile and impact strengths are also tested.

Experimental

Materials

PET was supplied by Degao plastics technology Co. Ltd., Yuyao, China. HDPE (5000S) was from CNPC Lanzhou Chemical Company. TMPTA was purchased from Orient Organic Chemical Plant, China. Hexafluoroisopropanol (HFIP) and dimethylbenzene (DMB) used for extraction were from Zeus Flours Technology Shanghai Co. Ltd., and Beijing Chemical Plant, respectively.

Sample preparation and irradiation

Before blending, PET was dried at 120 °C for 10 h. The blends of PET/HDPE at various compositions (80/20, 70/30 and 50/50 wt%) were prepared, then each composition was added with TMPTA by 0.5, 1, 2 and 3 wt%, respectively. Extrusions were carried out in a Haake Polylab System (RC500P) with twin-screw extruder at a temperature range of 240–270 °C under a screw speed of 100 rpm. The pallets from extrusion were used to obtain specimens for mechanical properties by injection molding. Blends of PET/TMPTA and HDPE/TMPTA were prepared in a Haake Rheomix 600 internal mixer with TMPTA by 0.5, 1, 2 and 3 wt%, respectively. Finally, the specimens were irradiated by γ-ray with the absorbed doses of 10, 30, 50 and 70 kGy, respectively, at room temperature.

Determination of gel fraction

The samples covered with nickel-mesh were extracted by solvent in a Sokhlet apparatus for 30 h, and then dried to a constant weight in vacuum at 120 °C after washing with alcohol. For PET/TMPTA blends, HFIP was used to eliminate PET that did not cross-linked, while DMB was used to eliminate HDPE that did not cross-linked in HDPE/TMPTA blends. For PET/HDPE blends, the samples were extracted by HFIP, DMB and HFIP in turn. The gel fraction was calculated by following formula:

$$G = \frac{W_1}{W_0} \times 100\%$$

where G is the gel fraction (%), W_1 and W_0 are the masses of the samples after and before extraction, respectively.

Mechanical properties

Tensile strength and elongation at break of irradiated samples with different doses were tested with an Instron universal testing instrument (INSTRON1121). The extension rate is 50 mm min^{-1} at room temperature. Izod impact strength was determined by UJ-40 without notch.

Scanning electron microscope (SEM)

The blends morphology was examined by XL30 scanning electron microscope (SEM). The samples were fractured under liquid nitrogen and vapor coated with gold for microscopy.

Fourier transform infrared spectroscopy (FTIR)

To observe the chemical structure of gel, FTIR measurement was carried out at room temperature using a BRUKER Vertex 70 FTIR. The ATR-FTIR spectra of gel and HDPE were recorded in the range of 400–4,000 cm^{-1}, with the resolution of 4 cm^{-1} and the number of sample scans was 128, while the resolution of TMPTA was 2 cm^{-1} and the number of sample scans was 32.

Results and discussion

SEM

Figure 1 shows the cryofractured surfaces of PET/HDPE (80/20 by weight) blends with different content of TMPTA at 30 kGy. Without TMPTA, the smooth craters left in the PET matrix (Fig. 1a) when HDPE is pulled out during fracture, which is typical morphology of poor interfacial bonding. With the addition of TMPTA, the morphology of blends changes significantly. The HDPE domain dimension is reduced remarkably and dispersed more evenly, resulting in the blurry interface of blends, which is not as clear as those without TMPTA. The change of morphology indicates that the compatibility of PET and HDPE is improved greatly in the

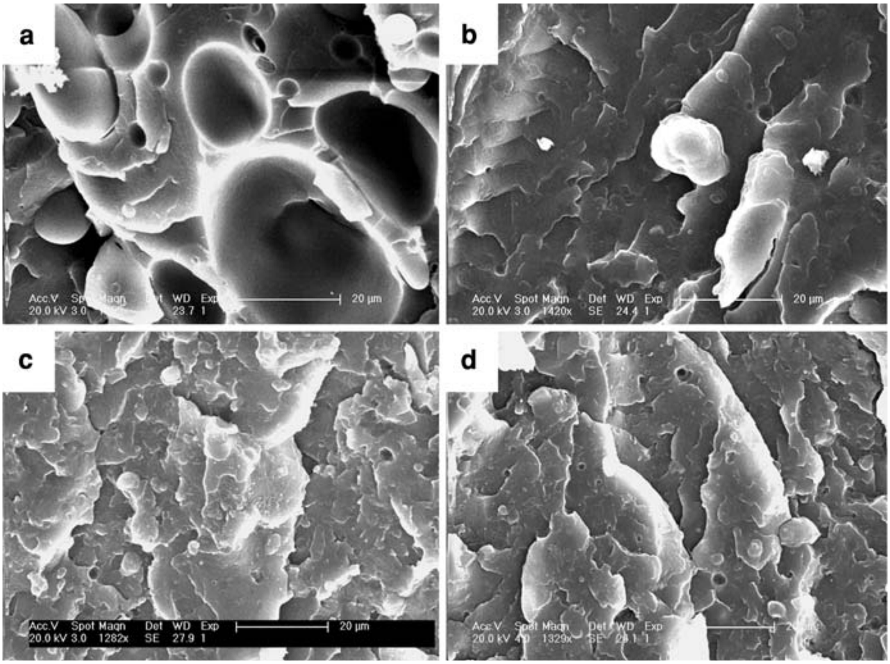

Fig. 1 SEM photos of cryofractured surfaces of PET/HDPE blends at 30 kGy, PET/HDPE/TMPTA: **a** 80/20/0; **b** 80/20/1; **c** 80/20/2; **d** 80/20/3

presence of TMPTA. However, when the content of TMPTA increases further, the change of morphology isn't obvious (comparing Fig. 1c with d).

The cryofractured surfaces of PET/HDPE blends (70/30 and 50/50 by weight) with 1 wt% TMPTA at 30 kGy are shown in Fig. 2. Compared to Fig. 2a and b with Fig. 1b, it can be found that the morphology of blends changed with the increment of content of HDPE. The domain dimension of HDPE increased gradually with the content of HDPE, then it became to the continuous phase when its content reached

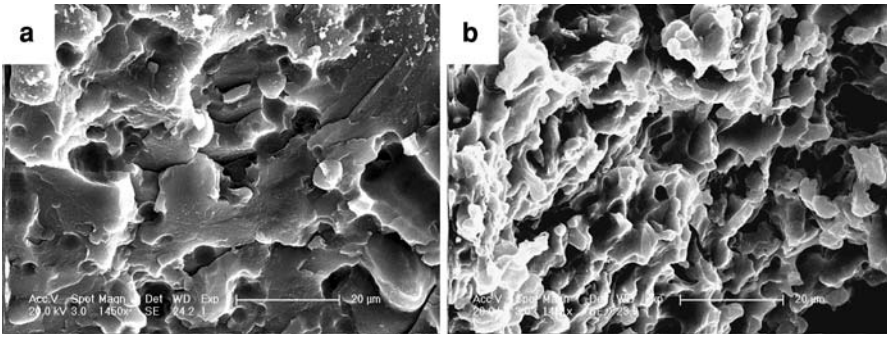

Fig. 2 SEM photos of cryofractured surfaces of PET/HDPE blends at 30 kGy, PET/HDPE/TMPTA: **a** 70/30/1; **b** 50/50/1

to 50 wt%. So the properties of sample in Fig. 2b are different from those of the others in this paper. Figure 2 also showed that the interface of blends becomes clear with the increase of the content of HDPE, which indicates the poor interaction of the two phases. These results suggested that the mechanical properties of PET/HDPE = 80/20 maybe the best among three samples.

Gel fraction

Figure 3 shows the comparison of the additive and experimental gel fraction of PET/HDPE (80/20 by weight) as a function of absorbed doses with different content of TMPTA. The additive gel fraction is calculated by following formula:

$$G_{\mathrm{A}} = G_{\mathrm{HDPE}} \times P + G_{\mathrm{PET}} \times (1 - P)$$

where G_{A} is the additive gel fraction of the PET/HDPE blends, G_{HDPE} and G_{PET} are the gel fraction of HDPE/TMPTA and PET/TMPTA blends at different absorbed doses, respectively. P is the weight percent of HDPE in PET/HDPE blends. For PET/HDPE (80/20 by weight), P is equal to 20%. It is seen that the gel fraction of PET/TMPTA is close to zero because aromatic group of PET makes PET hard to be cross-linked. When the content of TMPTA is less than 1 wt%, the gel fraction of

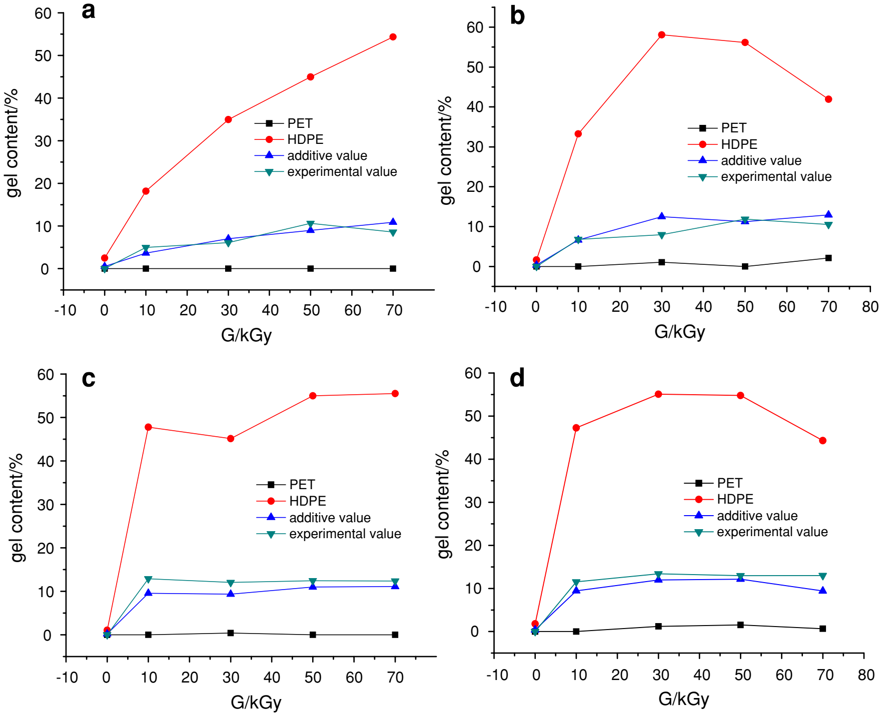

Fig. 3 Comparison of additive and experimental gel fraction of PET/HDPE (80/20 by weight) blends as a function of absorbed doses with the content of TMPTA: **a** 0.5%, **b** 1%, **c** 2%, and **d** 3%

PET/HDPE blends is close to the additive value, which indicates that PET hardly enters the cross-linking network of HDPE. When the content of TMPTA is more than 1 wt%, the gel fraction of blends is obviously larger than the additive value, hinting that PET has entered the HDPE cross-linking network. The percent of PET content in the cross-linked HDPE/PET gel could be up to 3.59%. The reasons may be that during irradiation, the vinyl group of TMPTA which disperses at the interface can react with the macromolecule radicals from two components to generate a PET-g-HDPE structure, resulting in the improved compatibility of PET/HDPE blends. This kind of structure will be also verified by infrared spectra of gel later.

FTIR

The infrared spectra of HDPE, gel and TMPTA are shown in Fig. 4. Comparing Fig. 4b with Fig. 4a and c, the peaks at 1,580 and 1,507 cm^{-1} due to in-plane aromatic ring vibrations and the peak at 873 cm^{-1} due to aromatic ring C–H out-of-

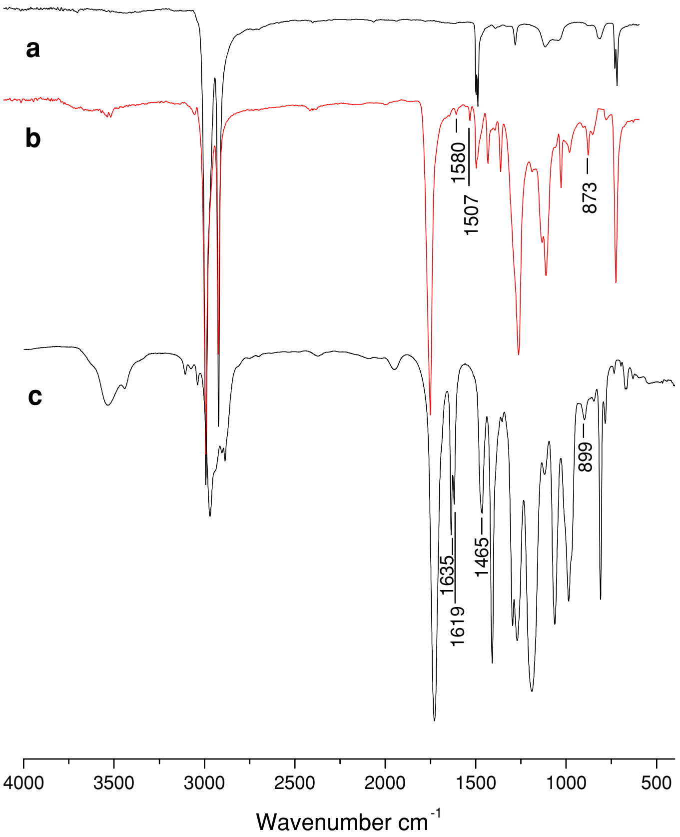

Fig. 4 Infrared spectra: **a** HDPE, **b** gel of PET/HDPE (80/20 by weight) blend at 50 kGy with 3% TMPTA, **c** TMPTA

plane deformations were found in the spectrum of gel. The results indicate that PET enters HDPE cross-linking network, generating a PET-g-HDPE structure. This kind of block polymer improves the compatibility of PET/HDPE blends, which is consistent with the conclusion of gel fraction and SEM.

Mechanical properties

The mechanical properties of PET/HDPE blends with and without TMPTA at different absorbed doses are shown in Table 1. As it is seen, the mechanical properties of blends are improved greatly with TMPTA and irradiation. As the content of HDPE increase, the mechanical properties of blends decrease gradually. These results were in agreement with the previous results of SEM, from that PET is dispersed phase in PET/HDPE (50/50 by weight) blends (Fig. 2b), while in PET/HDPE (80/20 by weight) and PET/HDPE (70/30 by weight) blends PET is continuous phase.

For PET/HDPE blends (80/20 and 70/30 by weight), the tensile strength increases with the content of TMPTA at first, and up to the maximum at 0.5–1 wt%, then decreases under the same absorbed doses. On the other hand, when the absorbed dose is more than 30 kGy, the tensile strength changes little. The tensile strength of PET/HDPE (80/20 by weight) blend with 1 wt% TMPTA at 30 kGy is the highest, reaching 47.15 MPa. The elongation at break and impact strength of PET/HDPE blends have a similar change tendency with that of tensile strength. When the content of the TMPTA is 1 wt% and the absorbed dose is 30 kGy, the elongation at break and impact strength of PET/HDPE (80/20 or 70/30 by weight) blends are the highest, reaching 300% and 117.8 kJ m^{-2}, respectively. The improvement of mechanical properties is a consequence of the increase in interfacial adhesion between phases, because the structure of PET-g-HDPE is generated at the interface at the presence of TMPTA and under irradiation.

However, for PET/HDPE blends (50/50 by weight), the effect of content of TMPTA and absorbed doses on mechanical properties is not obvious. It's probable that the cross-linking of HDPE played an important role in the improvement of mechanical properties, rather than the increase in interfacial adhesion, owing to the continuous phase for HDPE (Fig. 2b) when its content reaches 50%. As we known, HDPE is easily cross-linked. Figure 3 shows that the gel content of HDPE is about 50% when the absorbed doses higher than 10 kGy, and the gel content changed little as the content of TMPTA and absorbed doses increase. Therefore, the increase of content of TMPTA and absorbed doses has little effect on the mechanical properties for PET/HDPE blends (50/50 by weight).

Conclusions

The PET/HDPE (80/20 by weight) blend with 1 wt% TMPTA at 30 kGy presents the best mechanical properties: the tensile strength is 47.15 MPa, the elongation at break is more than 300%, and the Izod impact strength reaches 117.8 kJ m^{-2}. SEM images show that the interface of blends with TMPTA is not as clear as the blends

Table 1 Mechanical properties of PET/HDPE blends with and without TMPTA at different absorbed doses

Doses (kGy)	TMPTA (%)	PET/HDPE(80/20)			PET/HDPE(70/30)			PET/HDPE(50/50)		
		Tensile strength (MPa)	Elongation (%)	Impact strength (kJ m^{-2})	Tensile strength (MPa)	Elongation (%)	Impact strength (kJ m^{-2})	Tensile strength (MPa)	Elongation (%)	Impact strength (kJ m^{-2})
0	0	39.9	4.19	13.9	36.75	3.61	15.6	29.55	3.70	7.6
10	0.5	45.48	14.49	11	40.85	31.89	24.9	33.12	4.66	12.6
	1	45.92	201.3	46.9	41.14	26.41	27.2	33.41	4.81	12.3
	2	45.20	68.06	44.5	40.01	7.72	30.1	32.02	4.35	–
	3	45.09	34.56	55.5	40.32	7.72	36.3	32.30	4.63	19.8
30	0.5	46.05	16.73	36.3	42.46	30.53	41.5	33.68	4.68	–
	1	47.15	320.9	117.8	41.95	67.64	42.9	32.74	4.02	12.2
	2	46.46	59.77	34.4	41.62	7.15	35.7	31.29	3.97	12.9
	3	46.45	64.63	55.3	40.81	8.30	34.7	34.52	5.22	18.7
50	0.5	46.05	19.54	27	42.33	33.01	29	33.50	4.52	17.1
	1	46.38	61.48	55.6	42.42	58.63	36.6	33.79	4.47	13.5
	2	46.56	113.8	47.4	41.46	8.73	33	32.92	4.25	16.7
	3	46.11	34.26	12.6	41.42	7.35	32.4	34.54	5.44	13.3
70	0.5	46.14	20.02	43.4	42.29	6.61	17	35.06	4.85	15.9
	1	46.43	112.3	93.2	42.24	29.86	42.1	33.81	4.57	13.8
	2	46.18	48.87	54.3	41.51	7.87	28.5	32.58	4.42	–
	3	46.31	48.25	32.4	41.33	7.98	37.9	34.15	4.72	15.7

without TMPTA. The change of morphology indicates that the compatibility of PET and HDPE is improved greatly with the addition of TMPTA by irradiation. On the other hand, the gel fraction data and FTIR spectra suggest that a new structure of PET-g-HDPE is formed at the interface of blends caused by the radiation-induced cross-linking. This kind of block polymer improves the interfacial adhesion and reduces the interfacial tension, resulting in good mechanical properties. Therefore, the radiation modification can be suggested as a prospective method for developing new materials with fine physical properties.

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