ARTICLE

In-situ Enhanced Toughening of Poly(ethylene terephthalate)/elastomer Blends via Gamma-Ray Radiation at Presence of Trimethylolpropane Triacrylate

Li-zhao Xie, Le-chen Chen, Mo-zhen Wang, Qi-chao Wu, Xiao Zhou, Xue-wu Ge

a. CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China
b. Guangdong Tianan New Material Co., Ltd., Foshan 528000, China

(Dated: Received on May 12, 2016; Accepted on June 6, 2016)

Gamma-ray radiation has always been a convenient and effective way to modify the interfacial properties in polymer blends. In this work, a small amount of trimethylolpropane triacrylate (TMPTA) was incorporated into poly(ethylene terephthalate) (PET)/random terpolymer elastomer (ST2000) blends by melt-blending. The existence of TMPTA would induce the crosslinking of PET and ST2000 molecular chains at high temperatures of blending, resulting in the improvement in the impact strength but the loss in the tensile strength. When the PET/ST2000 blends were irradiated by gamma-ray radiation, the integrated mechanical properties could be enhanced significantly at a high absorbed dose. The irradiated sample at a dose of 100 kGy even couldn’t be broken under the impact test load, and at the same time, has nearly no loss of tensile strength. Based on the analysis of the impact-fractured surface morphologies of the blends, it can be concluded that gamma-ray radiation at high absorbed dose can further in situ enhance the interfacial adhesion by promoting the crosslinking reactions of TMPTA and polymer chains. As a result, the toughness and strength of PET/ST2000 blend could be dramatically improved. This work provides a facile and practical way to the fabrication of polymer blends with high toughness and strength.

Key words: Toughened PET blend, Interfacial interaction, Gamma-ray radiation, Radiation crosslink, Trimethylolpropane triacrylate

I. INTRODUCTION

With the rapid development of modern polymer industry, polymer blends have attracted considerable scientific and industrial interest since their properties can be finely tuned by varying the composition and the type of the components [1–4]. However, due to the unfavorable enthalpy of mixing, macro-phase separation occurs in most polymer blends, which leads to the deterioration in the integrated mechanical properties [5–7]. Therefore, many methods have been developed to manipulate the interface properties of polymer blends to realize the exceptional properties that the blending can offer [8–13].

In general, the introduction of macromolecular compatibilizers, such as graft, block or star copolymers, can lower the interfacial tension between the partially miscible or immiscible phases so as to improve the interfacial affinity [14–16]. In our previous work [17], poly(acrylic acid) (PAA) grafted poly(ethylene terephthalate) (PET) resins (PET-g-PAA) prepared by γ-ray radiation was introduced in PET/ethylene-methyl acrylate-glycidyl methacrylate random terpolymer (ST2000) blend (PET/ST2000) as the compatibilizer. The ternary PET/PET-g-PAA/ST2000 blend with only 6 wt% of PET-g-PAA has an improved impact strength, twice that of PET/ST2000. PET resins grafted with other polymers such as methyl acrylate [18], could also have the similar effect on improving the mechanical properties of PET/ST2000 blends. However, the disadvantages of this method are obvious. First, the copolymeric compatibilizer themselves have little contribution to the strength and stiffness of polymer blends because they are generally composed of “soft” chain segments. In some cases, their introduction even brings in the fatal loss of the strength of the blends [19, 20]. Second, the preparation and introduction of these copolymeric compatibilizers will inevitably increase the synthetic and processing cost of the blends [21–23].

With the development of the radiation grafting and crosslinking technique, high energy radiation has been widely used in the modification and processing of single polymers or polymer blends [24–28]. Li et al. prepared the quinary mixtures of high den-
sity polyethylene (HDPE), poly(vinyl chloride) (PVC), and polystyrene (PS) using poly(ethylene-co-vinyl acetate) (EVA) and poly(styrene-b-ethylene/butyrene-styrene) (SEBS) as the compatibilizers, and investigated the effects of γ-ray radiation on the mechanical properties of the blends. The results showed the impact strength of HDPE/PS/PVC/EVA/SEBS (90/5/5/7.5/7.5) could be enhanced dramatically after γ-ray radiation at an absorbed dose above 100 kGy [29]. Deng et al. melt-blended PET and poly(ethylene octene) (POE) with various amounts of trimethylol-propane triacrylate (TMPTA). The impact strength of the PET/POE (85/15, W/W) blend with 2wt% of TMPTA could increase approximately 3.4 times after the blend was irradiated by γ-ray radiation at an absorbed dose of 30 kGy [30]. The similar radiation enhancement effect occurred in another polymer blend system, PET/HDPE blend containing a small amount of TMPTA (≤3wt%) [24]. The readily crosslinking of POE and HDPE by the crosslinking agent TMPTA under γ-ray radiation was considered to be the main contribution for the enhancement of mechanical properties of the radiated blends [24, 30].

In this work, we focused on the effect of γ-ray radiation on the mechanical properties of widely-used PET/ST2000 blends at the presence of TMPTA. The change in the morphologies of PET/ST2000 blends and mechanical properties with different content of TMPTA was then investigated in detail. It was found that the toughening effect of ST2000 on PET can be further in situ enhanced under γ-ray radiation at the presence of TMPTA. The toughness mechanism was also discussed with the micro-voiding and plastic deformation theories.

II. EXPERIMENTS

PET resin (CB651, [η]=0.75 dL/g) and ethylene-methyl acrylate-glycidyl methacrylate random terpolymer (ST2000, 1.5wt% of glycidyl methacrylate) were purchased from Far Eastern Industry (Shanghai, China) and Shanghai Xiuhu Chemical Co., Ltd., respectively. Analytical reagents, including phenol, tetrahydrofuran (THF), and tetrachloroethane, were purchased from Shanghai Chemical Reagents Co., Ltd. TMPTA (95%, technical grade) was supplied by Laiyu Chemical (Shangdong, China).

Before the preparation of PET/ST2000 blends, the raw PET granules were dried at 90 °C for 24 h and ST2000 granules were dried at 50 °C for 12 h. The dried PET and ST2000 were firstly premixed together with TMPTA in a homogenizer (WJ-30) at room temperature. The premixed blends were then added into a feeding device and transported to a co-rotating twin-screw extruder (TE-35, China) with a screw diameter of 35 mm and an overall L/D of 37. The feed rate was 300 r/min. The temperatures of the first to the seventh regions were set as 140, 200, 260, 260, 260, and 260 °C. The die temperature was also 260 °C. The screw speed was 300 r/min. The extrudates were cooled in water. After being pelletized, the extrudates were dried at 90 °C for 24 h, then injection-moulded into the standard specimens for the tensile and notched Izod impact strength measurement using an injection-moulding machine (HTF800X1, China). The temperatures of the first to the sixth regions were set as 265, 260, 260, 260, 255, and 25 °C, respectively. The injection pressure was 80 MPa. The screw rate was 20 r/min. The retention time was 35 s. The weight content of ST2000 in all samples was fixed as 20%. The as-prepared standard specimens were then thermally sealed into plastic bags filled with nitrogen gas and exposed in the radiation field of 60Co γ-ray at a dose rate of 83.3 Gy/min. The 60Co source with a radioactivity of 1.37×10^15 Bq is located in University of Science and Technology of China. The absorbed dose ranged from 10 kGy to 150 kGy.

The gel fractions of the radiated samples for impact tests were measured by the solvent extraction method. The samples (0.2–1.0 g) wrapped with nickel mesh were extracted in a Soxhlet extractor with THF at 66 °C for 24 h. The THF extracted samples were immersed in 30 mL of phenol/tetrachloroethane mixed solvent (1/2, W/W) under magnetic stirring for 24 h at 110 °C. Finally, the extracted samples were taken out and dried in vacuum oven at 100 °C till a constant weight. The gel fraction, G, was calculated by the following equation:

\[
G/\% = \frac{W_1}{W_0} \times 100
\]

where \(W_0\) and \(W_1\) are the weights of the samples before and after extraction, respectively.

Fourier-transform infrared (FT-IR) spectra of the solvent-extracted samples were recorded on a Nicolet-8700 infrared spectrometer (Thermo Scientific Instrument Co., USA) at a resolution of 1 cm^{-1}. The samples were prepared by mixing the grinded gel with KBr and pressing into a thin film.

The notched Izod impact strengths of all samples were tested on a Memory Impact Test machine (JJ-20, Intelligent Instrument Equipment Co., Ltd.) at room temperature according to GB/T 1843-2008 (ISO 180: 2000). The tensile properties of all samples were conducted on an electronic universal testing machine (WSM-20KB, Intelligent Equipment Co., Ltd.) at room temperature. The dumbbell-shaped specimens were stretched until they were broken at a crosshead rate of 50 mm/min according to GB/T1040.2-2006 (ISO 527-2: 1993). A minimum of five tensile and impact specimens were tested for each reported value.

The microstructure of the samples before and after the impact test was observed by field-emission scanning electron microscopy (SEMJEOL JSM-6700, Japan, 5 kV). The samples before impact test were observed after being fractured in liquid nitrogen. After the fractured surfaces were etched by THF at 66 °C for 12 h
FIG. 1 (a) Impact strength, (b) tensile strength, and (c) elongation at break of PET/ST2000 blends with different content of TMPTA before and after being irradiated by $\gamma$-ray at various absorbed doses. The impact samples of PET/ST2000 blends with 2wt% TMPTA irradiated at 100 and 150 kGy didn’t break under the same impact test condition.

III. RESULTS AND DISCUSSION

A. Effect of $\gamma$-ray radiation on the mechanical properties of PET/ST2000 blends at the presence of TMPTA

The impact strength, tensile strength, and elongation at break of PET blends with different content of TMPTA before and after $\gamma$-ray radiation at various absorbed doses are shown in Fig.1. It is seen from Fig.1(a) that the introduction of a little amount of TMPTA (1–2wt%) can slightly increase the impact strength of PET/ST2000 blend. However, the impact strength of PET/ST2000 blend with more content of TMPTA (>2wt%) falls instead. At the same time, the elongation at break increases slightly with the content of TMPTA (Fig.1(c)), also indicating the improvement in the toughness of PET/ST2000 blends. But the tensile strength drops with the content of TMPTA (Fig.1(b)). TMPTA molecule has three active C=C bonds. The grafting or crosslinking of polymer chains by TMPTA will occur during the melt-blending process at high temperatures [31]. When the content of TMPTA is low, a little amount of copolymer composed of PET and ST2000 chains connected by TMPTA will be produced during the melt blending process, and can act as the compatibilizer to enhance the interfacial interaction between PET and ST2000, resulting in the increase of the toughness of the PET/ST2000 blend. But excessive TMPTA may lead to a high crosslinking degree in the blends, and weaken the integrated mechanical property of PET/ST2000 blends.

After being irradiated by $\gamma$-ray radiation at an absorbed dose above 10 kGy, all of the PET/ST2000 blends exhibit improved impact strength. The relationships between the impact strength and the content of TMPTA for the irradiated PET/ST2000 blends are similar to that for the un-irradiated PET/ST2000 blend, i.e. 2wt% of TMPTA can reach the highest impact strength for all the irradiated PET/ST2000 blends. However, the rate of increase in the impact strength is dramatically high when the absorbed dose is above 100 kGy as listed in Table I since the PET/ST2000 blends with 2wt% of TMPTA irradiated at 100 and 150 kGy even cannot break under the impact test condition. But the tensile strengths for these two samples almost have little change, which indicates the $\gamma$-ray radiation produces an in situ enhanced toughening and strengthening effect on PET/ST2000 blend.

The storage modulus is a measure of the stiffness for polymer [32], thus DMTA was carried out to evaluate the mechanical properties, as exhibited in Fig.2. All the irradiated blends have a higher storage modulus than the un-irradiated sample. The glass transition temperature ($T_g$) can be determined as the peak temperature on the tan$\delta$ curves. It was obvious that the $T_g$ of PET in all studied PET/ST2000 blends have little change due to the macro-phase separation between PET and ST2000. And the $T_g$ of ST2000 in irradiated samples is hardly distinguished, which should be attributed to the crosslinking of ST2000 under $\gamma$-ray radiation or at high temperatures.

Since $\gamma$-ray radiation can produce free radicals randomly on any polymer chains and TMPTA molecules, it can be expected that the crosslinking between polymer chains can be in situ enhanced under $\gamma$-ray radiation. The gel fractions in the raw PET ($G_{PET}$), raw ST2000 ($G_{ST}$), and the PET/ST2000 ($G_{PET/ST}$) blends with 2wt% TMPTA treated with the same melting blend condition were measured and are shown in Fig.3. It can be seen that ST2000 could be fully crosslinked at high temperatures at the presence of 2wt% TMPTA, while...
TABLE I The impact strength of PET/ST2000 blends with different content of TMPTA at various absorbed doses.

<table>
<thead>
<tr>
<th>Dose/kGy</th>
<th>Without TMPTA</th>
<th>1wt% TMPTA</th>
<th>2wt% TMPTA</th>
<th>3wt% TMPTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>32.5±0.2</td>
<td>37.6±0.2</td>
<td>45.1±0.2</td>
<td>36.0±0.2</td>
</tr>
<tr>
<td>10</td>
<td>33.9±0.1 (4.3%)</td>
<td>37.5±0.2 (−0.3%)</td>
<td>45.8±0.1 (1.6%)</td>
<td>36.8±0.3 (2.2%)</td>
</tr>
<tr>
<td>30</td>
<td>38.0±0.3 (16.9%)</td>
<td>42.4±0.1 (12.8%)</td>
<td>45.9±0.2 (1.8%)</td>
<td>37.5±0.2 (4.2%)</td>
</tr>
<tr>
<td>50</td>
<td>38.6±0.1 (18.8%)</td>
<td>48.1±0.2 (27.9%)</td>
<td>48.9±0.3 (8.4%)</td>
<td>43.5±0.4 (20.8%)</td>
</tr>
<tr>
<td>100</td>
<td>44.9±0.3 (38.2%)</td>
<td>50.6±0.1 (34.6%)</td>
<td>Sample unbroken</td>
<td>55.4±0.2 (53.9%)</td>
</tr>
<tr>
<td>150</td>
<td>46.1±0.2 (41.8%)</td>
<td>48.6±0.2 (29.3%)</td>
<td>Sample unbroken</td>
<td>52.3±0.2 (45.2%)</td>
</tr>
</tbody>
</table>

Note: The values in parentheses are the rates of increase in the impact strength relative to that of the corresponding un-irradiated samples.

FIG. 2 DMTA curves of PET/ST2000 blends with 2wt% of TMPTA at different absorbed doses.

FIG. 3 Gel fractions of the PET, ST2000, and PET/ST2000 blends with 2wt% of TMPTA before and after being irradiated at different absorbed doses. All the samples were treated with the same blending condition.

FIG. 4 FTIR spectra of neat PET, ST2000, TMPTA, and the gel of PET/ST2000 blends with 2wt% of TMPTA irradiated at a dose of 100 kGy.

only a little part of PET (15 wt%) can be crosslinked at the same condition without γ-ray radiation. The result is easy to understand as shown in many thermoplastic elastomers-based dynamic vulcanization systems [33]. There are about 35% of gel in PET/ST2000 blend incorporated with 2wt% of TMPTA, which makes a remarkable increase in the impact strength of the blend. When all the samples were exposed under the γ-ray radiation, the \( G_{PET} \) and \( G_{PET/ST} \) slightly increased with the absorbed doses till a constant above 100 kGy, indicating that the PET and ST2000 chains at the phase interface can be further crosslinked by TMPTA so as to enhance the affinity of the phase interface resulting in the improvement of the impact strength of the blends.

The FTIR spectrum of the gel extracted from PET/ST2000 blends is shown in Fig.4, compared with those of pure PET, ST2000, and TMPTA. As the ST2000 could be fully crosslinked either at high temperatures or under γ-ray radiation, so the gel extracted...
In-situ Enhanced Toughening of PET/Elastomer Blends

from PET/ST2000 blends must contain the ST2000 component. In the spectrum of PET, the characteristic peaks of benzene rings in the PET chains could be found at 727 and 875 cm\(^{-1}\) which were assigned to the aromatic ring C–H out-of-plane bending vibrations and deformation vibrations, respectively \[34, 35\]. The peaks at 1577 and 1506 cm\(^{-1}\) were due to the in-plane aromatic ring vibrations \[24\]. All of these characteristic peaks of PET could not be found in the spectra of TMPTA and ST2000 but in the gel. From the gelation analysis and FTIR characterization, we confirmed the existence of both ST2000 and PET chains network formed after radiation. Due to the high mobility, TMPTA acted as a bridge connecting PET matrix and ST2000 phase, leading to the enhanced interfacial interaction.

B. Morphologies and toughening mechanism of PET/ST2000 blends at the presence of TMPTA

Figure 5 exhibits the morphologies of the cryofractured samples of PET/ST2000 blends with 2wt% of TMPTA before and after \(\gamma\)-ray radiation. There are no observable changes in the size and size distributions of the dispersed ST2000 particles after the samples were irradiated by \(\gamma\)-ray radiation.

However, the morphologies of the impact-fractured surface of the same samples are quite different, typically shown in Fig.6. In order to give clear morphological variations along the propagation direction of impact energy, the impact-fractured surface was divided into three zones, i.e. the crack initiation zone (zone A), the transmission zone (zone B), and the later stage of crack propagation (zone C), as indicated in Fig.6 \[36\]. For neat PET, a typical brittle-fractured surface morphology without any obvious plastic deformation was observed all along the propagation direction of impact energy. For the un-irradiated PET/ST2000 blend with 2wt% of TMPTA (0 kGy), slightly plastic deformation in the early stage of zone A can be observed. But the fractured surface became coarse and much small micro-voids appeared due to the interfacial debonding of the ST2000 particles. The plastic deformation on the fractured surface became more intense in zone B and zone C, and the voids become larger, indicating a large quantity of impact energy had been dissipated in this zone through the deformation of polymer chains and the debonding of dispersed phase. After the PET/ST2000 blend was irradiated by \(\gamma\)-ray radiation at a low absorbed dose (10 kGy), the morphologies of the three zones were similar to those of un-irradiated sample, indicating the radiation with a low absorbed dose has little influence on the structure and intermolecular interactions in the blends even at the presence of TMPTA. However, after being irradiated at a dose of 100 kGy, the notched blend specimen cannot be broken under the impact load. It can be seen that relatively high degree of plastic deformations appears in zone A and zone B, which consumed most of impact energy. Evidently, the great improvement on the impact strength under \(\gamma\)-ray radiation at a high dose should be attributed to the crosslinking reactions in the ST2000 phase and at the interfaces between PET and ST2000 due to the existence of TMPTA, which effectively enhanced the interfacial adhesion, as illustrated in Scheme 1.

IV. CONCLUSION

In this work, the effect of \(\gamma\)-ray radiation on the mechanical properties of widely-used PET/ST2000 blends incorporated with a small amount of the crosslinking agent TMPTA has been investigated. PET, ST2000 (20wt%), and TMPTA were melt-blended by a co-rotating twin-screw extruder. The existence of TMPTA would induce the crosslinking of PET and ST2000 molecular chains at the high temperature of blending and produce a small amount of gel in the blend system, resulting in the improvement in the impact strength but the loss in the tensile strength. However, excessive TMPTA may lead to a high crosslinking degree in the blends, and weaken the integrated mechanical property of PET/ST2000 blends. The optimum content of TMPTA is 2wt%. After the PET/ST2000 blend containing 2wt% of TMPTA was irradiated by \(\gamma\)-ray ra-

FIG. 5 SEM images of PET/ST2000 with 2wt% of TMPTA at different absorbed doses. (a) 0 kGy, (b) 10 kGy, (c) 30 kGy, (d) 50 kGy, (e) 100 kGy, and (f) 150 kGy. The weight content of ST2000 is 20wt% for all the samples.
FIG. 6 SEM images of the impact-fractured surface at zone A, B, and C of PET and PET/ST2000 blends with 2wt% of TMPTA before (0 kGy) and after being irradiated at different doses (10 and 100 kGy).

Scheme 1 The *in-situ* enhanced toughening mechanism of PET/ST2000 blends at the presence of TMPTA under γ-ray radiation.
radiation at a high absorbed dose (>100 kGy), the integrated mechanical properties could be enhanced significantly. The irradiated sample at a dose of 100 kGy even could not be broken under the impact test load, and at the same time, has nearly no loss of tensile strength. But when the sample was irradiated at an excess dose (>150 kGy), the mechanical properties would be also weaken due to the excess crosslinking of the polymer chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated chains. Compared with the impact-fractured surface morphologies of PET, the irradiated and un-irradiated

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.51173175), the Foshan Scientific and Technological Innovation Team Project (No.2013ST100041), and the Foshan University-City Cooperation Project (Scientific and Technological Innovation Project, No.2014HK100291).

We thank Prof. Yuan Hu and Dr. Bi-bo Wang of the University of Science and Technology of China for their helpful advice and assistance.