Polymer Bulletin 56, 47–52 (2006)
DOI 10.1007/s00289-005-0461-7

Polymer Bulletin

Dynamic Mechanical Properties of Compatibilized PET with Radiation Oxidized HDPE

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Received: 4 May 2005 / Revised version: 7 October 2005 / Accepted: 17 October 2005

Summary

Binary blends of HDPE/PET exhibit poor mechanical properties because of their non compatibility. In this work, HDPE was oxidized by gamma-ray preirradiation in air, subsequently heated to destroy peroxides formed by this irradiation and to form polar groups in the HDPE, and then extruded with PET as a compatibilizing method of the blend. The dynamic mechanical properties were studied, and an improvement was observed when the PET content was increased while the HDPE used was irradiated. The largest increase in the mechanical properties was observed for PET contents between 10 and 20% (w/w). The improvement in the dynamic mechanical properties is believed to occur because of a percolation effect of the PET in the HDPE matrix and the radiation-improved compatibility by means of polar groups formed in the polyethylene.

Keywords:

Irradiation, Polymer blends, Percolation, Dynamic Mechanical Properties

Introduction

Blends of polyethylene terephtalate (PET) and high density polyethylene (HDPE) have been investigated by several authors because of the large availability and relative low cost of PET, especially, that obtained from recycling [1, 7-10]. In general, their studies have been centered on improving their compatibility and thereby improving their mechanical properties. They have shown that miscibility of PET and HDPE is limited to certain ranges of composition, temperature or pressure and their attempts have been aimed at extending these ranges by different methods, i.e. by using radiation to modify one or both of the monomers by cross linking or modifying one of the monomers to obtain a complete miscibility. These binary blends show unfavorable interaction at a molecular level, which can lead to the presence of high interfacial tension in the melt. Studies on the reactive compatibilization of this blend have been reported. The most widely used reactive functional groups for compatibilization of HDPE/PET blends are acid anhydride and epoxy groups that can react with the carbonyl end groups of PET [2, 4-5]. Improved compatibility of this blend by the use of a blocked isocyanide group was studied by Kim et al [6]. High energy radiation is a well known technique for the modification of polymers; however, little work concerning the effects of irradiation on the properties of polymer blends has been done. There have been a few attempts to improve the miscibility by using radiation by modification of one or both polymers [7-11]. Blends of HDPE, which easily cross-link when exposed to irradiation, and PET, which cross-links at higher doses, due to the aromatic group, were irradiated and the effect of formation of the cross-linked copolymer was studied. The main objective of this work was the determination of the dynamic mechanical properties of blends of oxidized HDPE and PET. The HDPE was oxidized by means of irradiation in presence of air, then heated to destroy any peroxide formed by this irradiation and to form polar groups in the HDPE (-OH, -C=O and –COOH).

Experimental

Materials

High-density polyethylene (HDPE), with a density of 0.958 g/cm^3 and a crystallinity of 64.15%, polyethylene terephtalate (PET), with density of 1.404 g/cm^3, molecular weight (Mw) equal to 49,000 and crystallinity of 3.1% from PEMEX Co, México, City, were used for the binary blends. The HDPE and PET were blended in different ratios, and then, extruded using a Brabender 2504 laboratory scale extruder. The mixing stage temperature was set at 180^{o}C, and the extruder conditions were as follows: the temperature was set at 190^{o}C, the screw speed of 32 rpm at atmospheric pressure.

Material irradiation

Pristine HDPE powder was irradiated at absorbed doses of 50, 100 and 200 kGy in the presence of air at room temperature with a dose rate of 9.8 kGy/h, using a Gamma Beam 651 PT (Co-60 gamma ray source), from Nordion Co. Canada. Then, it was heated to 110°C, in order to break the peroxide and hydroperoxide formed and to form polar groups in the HDPE.

Gel fraction and elemental analysis

A blend of 50/50 of pristine PET and unirradiated and irradiated HDPE, was extruded in a Brabender 2504 under the same conditions described before. The gel fraction of the blend samples was determined via soxhlet extraction using xylene at 135ºC, for 30 h, to eliminate any polyethylene that did not cross-linked followed by an extraction in m-cresol to eliminate any fraction of PET that did not cross-linked either. After extraction, the composition of the cross-linked blend was determined by elemental analysis (Desert Analytics).

Mechanical Testing

Dynamic mechanical analysis testing was performed using a Perkin-Elmer Dynamic Mechanical Analyzer (DMA) using the tensile testing mode. A testing temperature range between -140°C and 40°C and a heating rate of 2°C/min were selected. The frequency was held constant at 1 Hz and an initial load of 2.5 x 10^5 Pa was applied to the sample. The thickness of the different laminates tested varied between 0.8 to 0.55 mm. Specimen cutting was performed using a razor blade and a straight edge as a guide. Any imperfections on the edges were eliminated using 100-grit sand paper.

Results and discussion

The gel formation of the irradiated blend of HDPE/PET at different PET fractions is shown in table 1 and the amount of PET present in the cross-linked fraction is shown in Table 2.

Table 1. Gel % in irradiated HDPE/PET samples for different PET contents

HDPE/PET	Dose (kGy)	Gel (%)
50/50	50	12.30
50/50	100	24.60
50/50	200	46.15
60/40	50	29.30
60/40	100	46.15
60/40	200	64.61

Table 2. Percent of PET for the cross-linked HDPE/PET at different irradiation doses

HDPE/PET	Dose (kGy)	PET in gel fraction (%)
50/50	50	7.9
50/50	100	2.8
50/50	200	3.1
60/40	50	3.9
60/40	100	3.5
60/40	200	0.3

Small gel percentage was observed after the extraction of the samples without irradiation. The gel percent increased linearly with the radiation dose for the 50/50 HDPE/PET blend but for the 60/40 blend, such linearity disappeared. Because of the increasing polar groups formed in the pre-irradiated HDPE, a maximum of 7.9 % of PET was found in the 50/50 blend at an irradiation dose of 50 kGy. This percentage decreased for higher irradiation dose, probably because of the degradation of the HDPE due to high oxidized irradiation, with the increase in dose [10, 11].

The behavior of the storage modulus as a function of temperature for the different blends is shown in figure 1. For the 100/0 HDPE/PET blend, figure 1-a, the storage modulus is higher for the irradiated samples at temperatures close to the Tg of HDPE. The effect of the irradiation is not as noticeable for temperatures close to the beta transitions. It should be remembered that even when a high density polyethylene is being used, it still has some degree of ramification. A small change attributable to the radiation is observed between the pristine HDPE and the blend with a 10% PET. It is noticed that at temperatures below the Tg, the storage modulus of both irradiated and non-irradiated are the same. At temperatures above the Tg the storage modulus of the blend subjected to radiation is a little bit higher than that observed for the non-irradiated HDPE sample. However, a 10% PET content, figure 1-b, is considered too small for any interaction at the HDPE and PET interfaces to be reflected noticeably on the elastic modulus of the material. At temperatures below the Tg, the PET content is small and the behavior of the blend is dominated by that of the HDPE. Upon a temperature increase, the HDPE shows a more elastomer-type behavior and the contribution of the PET domains on the elastic modulus is more noticeable.

For the blend with a 20% PET content, figure 1-c, the effect of radiation is more significant for temperatures below and above the Tg and from that observed for the 10% PET content. It should be remembered that because of the incompatibility between the HDPE and PET, isolated PET domains will be formed in a HDPE matrix or vice versa, depending on the blend composition [12]. In general, polymers which reverse phases (depending on the mixing process) show a percolation threshold between a 15 % to a 20 % content of the dispersed phase. Therefore, it can be assumed that, the percolation threshold for PET is also close to a 20 %. The increase in the elastic modulus can be explained considering that upon percolation, the interfacial contact area between both polymers increases significantly. This should result in a better interaction between the two polymers and consequently in a higher elastic modulus. If any cross-linking results, then, a higher elastic modulus will be expected. Finally, for the blend with a 30 % PET content, figure 1-d, an inversion of behavior of the elastic modulus is observed.

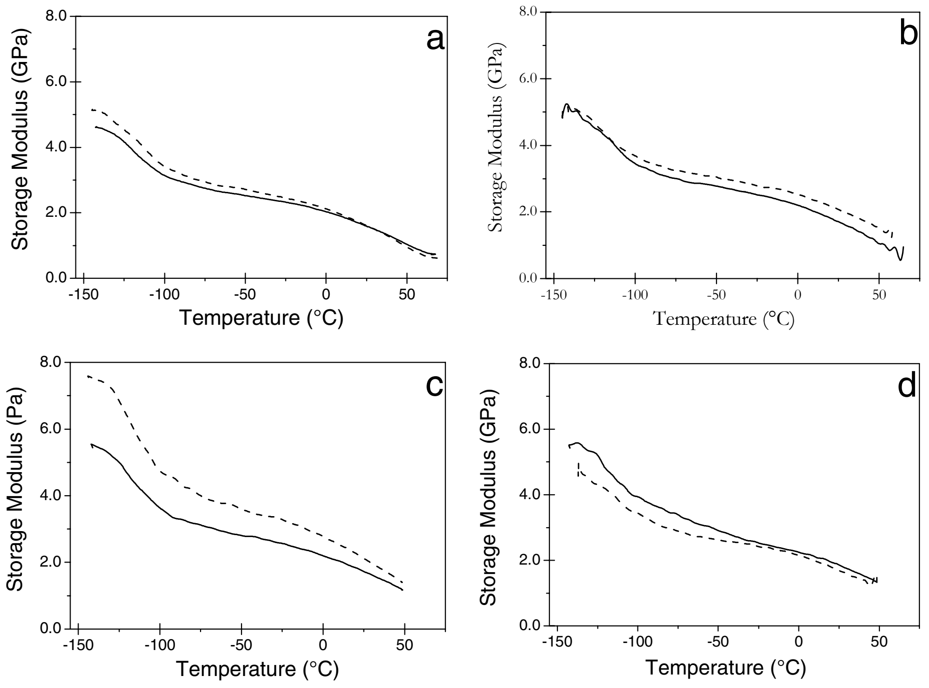

Figure 1. The storage modulus for the non-irradiated (———) and irradiated (– – – –) blends; HDPE/PET: (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30

In figure 2, a linear behavior of the storage modulus for the non irradiated blends (solid line) of HDPE/PET is observed as a function of the composition. The slope of such trend is positive but with a temperature increase, such slope tends to zero. This more noticeable for temperatures above 30ºC where the slope can be considered to be practically equal to zero. It should be remembered that the amorphous phase of a polymer governs the behavior of its elastic modulus and that in this case, for temperatures above 30° C, the amorphous phases of both polymers are the elastomeric phase, and therefore, the elastic modulus of both polymers will be of approximately the same value.

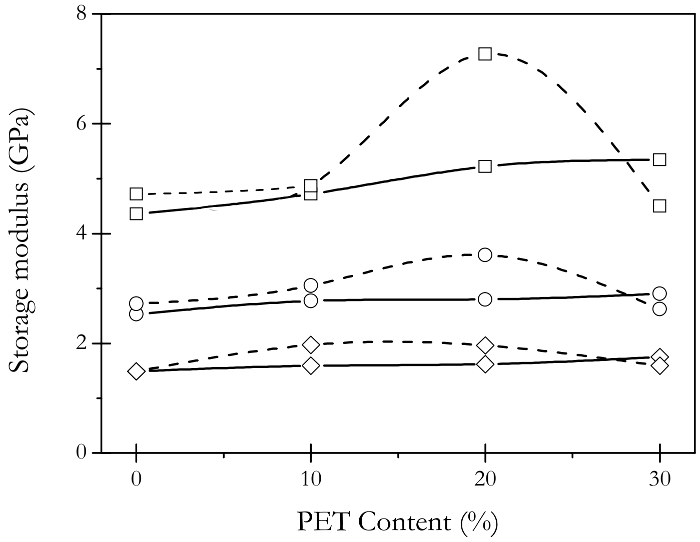

Figure 2 The storage modulus for different temperatures for the non-irradiated (———) and irradiated (– – – –) blends; HDPE/PET at: (□) -130º C, (○) -50º C, (◊) 30º C

In figure 2, a nonlinear behavior of the storage modulus for the irradiated blends (dash line) of HDPE/PET is observed as a function of the composition. In this figure, the change of the elastic modulus for the blend with a 20% is more noticeable. As it has been mentioned, such behavior can be attributed to the percolation of PET in the HDPE. However, the largest increase of the elastic modulus is observed for a temperature of -130º C, and for higher temperatures, such increment is lower. When PET is forming isolated domains in the HDPE, its contribution to the effective modulus of the blend is smaller. In this case, it can be said that the amorphous phase of the HDPE is governing the effective modulus of the blend. When PET has percolated, its amorphous phase has a larger contribution to the elastic modulus of the blend, being such contribution larger when both polymers are in the glassy state, as it would correspond to temperatures close to -130º C.

The maximum increments in rigidity are of approximately 40% for the blend at -130º C and 15 %, also for the 30º C. Evidently, the fact that PET content of approximately a 20 % is close to the percolation threshold, is common to all blends. The increment of the storage modulus can be attributed to the effect of irradiation of the HDPE is evident for all compositions and to the formation of polar groups in the HDPE.

Conclusions

Little gel percentage was observed after the extraction of the samples without irradiation. The gel percent increased with the radiation dose, and with the amount of HDPE in the blend. A maximum of 7.9 % of PET was found in the 50/50 cross-linked blend at an irradiation dose of 50 kGy, because of the predominant polar groups formed by irradiation in air, with further irradiation, degradation of the polar groups formed (-OH, -C=O and –COOH) suffer degradation and compatibilization behavior decrease.

The dynamic mechanical properties were improved when the PET content was increased and when the PET was irradiated. The largest increase in the storage modulus was observed for PET contests between 10 and 20% (w/w). Such improvement in the properties is believed to occur, first, because of the percolation of PET in the HDPE matrix and the radiation-improved compatibility by means of polar groups formed in the polyethylene.

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