Effects of Radiation on Mechanical Properties of Polybutadiene/Polystyrene Blends

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SYNOPSIS

Blends containing 3 wt % low molecular weight polybutadiene (PB) in a polystyrene (PS) matrix were prepared via a precipitation technique that yielded spherical, submicron pools of PB. Tensile specimens made from these blends were then irradiated with high energy electrons in air at dose levels from 0 to 70 Mrads. The blends, which previously showed high levels of toughness approaching that of high impact PS, lost all enhanced toughness when irradiated above 10 Mrads. Analysis of pure PS specimens irradiated over the dose range from 0 to 45 Mrads showed no appreciable dependence of mechanical behavior on dose level. Molecular weight studies of the polybutadiene demonstrated only a very modest increase in molecular weight in the dose range studied here; therefore, reduced mobility of the PB in the blends was not the reason for the dramatic drop in toughness with radiation dose. It was concluded that radiation-induced scission of the PS near the surface of the blends resulted in a significant local reduction in molecular weight. This degraded layer led to premature craze failure and hence a low level of toughness. It was demonstrated that the absence of oxygen during the irradiation process or the removal of the scissioned surface layer via mechanical abrasion resulted in a recovery of toughness. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The ability to toughen normally brittle thermoplastics such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) without sacrificing strength and rigidity has been the subject of research for many years.¹⁻³ It has recently been discovered⁴ that the addition of a few weight percent of low molecular weight polybutadiene (PB) can significantly toughen PS, with negligible reduction in modulus, through the enhancement of crazing. The PB, which phase separates in the form of submicron pools, locally plasticizes the PS of the craze matter in a complex and interactive manner. This plasticization allows easier craze tuft drawing and hence substantially higher craze velocities.⁵ Thus the addition of 5 wt % PB results in craze velocities three orders of magnitude higher than those found in pure PS.⁶ The higher craze velocities allow the specimen to match the imposed strain rate at reduced levels of craze flow stress, thus avoiding premature fracture from extrinsic flaws and achieving a higher strain to fracture and a higher level of toughness.

A key requirement for the localized plasticization phenomenon is adequate diluent mobility. Craze velocities measured at -20° C on PB/PS blends were two orders of magnitude lower than those obtained at room temperature, a direct result of increased PB viscosity at low temperature.⁷ These blends exhibited a total loss of enhanced toughness as a consequence of this reduced PB mobility. Qin et al.8 demonstrated the effects of both the molecular weight and the vinyl content of the PB diluent on tensile toughness of blends containing low molecular weight PB dispersed in PS; both of these molecular-level parameters are reflected in the level of the PB bulk viscosity. Qin et al.⁸ found that an increase in PB viscosity of one order of magnitude (accomplished either with increased molecular weight or increased vinyl content) resulted in a decrease in the tensile

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toughness by a factor of 2. It was unclear, however, whether the change in the toughness resulted from the reduced mobility of the PB or from a subtle change in blend morphology. Although it was fairly evident that the tensile toughness change arose from the former effect, it was desirable to change the PB viscosity *after* the blending procedure in order to conclusively establish if any changes in mechanical properties arise from changes in the properties of the diluent and not from the preparation procedure.

With this consideration in mind, blends were exposed to radiation in an effort to crosslink the PB component. Previous work⁹⁻¹¹ has shown that PB is easily crosslinked with electron irradiation while PS is fairly resistant to radiation due to the presence of the aromatic ring.¹²⁻¹⁵ It was anticipated that irradiation would decrease the mobility of the PB without disturbing the morphology of the blend or the mechanical properties of the matrix PS. In this article we report the effects of electron irradiation did cause the expected reduction in the tensile toughness of these blends, although not for the reasons suggested above.

EXPERIMENTAL

Sample Preparation

PS of molecular weight 350,000 g/mol and a polydispersity of 2.3 was obtained from Polysar in Springfield, MA. The PB, purchased from Scientific Polymer Products, had a molecular weight of 2,600 g/mol and a (1, 2) vinyl content of 29%. Blends containing 3 wt % PB in PS were prepared by a precipitation technique as discussed elsewhere.⁶⁻⁸ The resulting powder was compression molded at 200°C for 5 min into films 0.5-mm thick. "Dogbones" with a 2.5-mm width and a gauge length of 6.35 mm were then milled from the films, sanded, and polished.⁶

Irradiation Procedure

Both PB/PS and pure PS dogbones were irradiated with 2.5-MeV electrons supplied by the Van de Graaf generator at the High Voltage Laboratory at MIT. Samples were irradiated both in air and *in vacuo*. To prepare the latter samples, dogbone specimens were placed in glass tubes equipped with ground glass joints that were sealed with ground glass stopcocks. The tubes were connected to a high vacuum line and were pumped down to 10^{-4} torr for 24 h, after which the tubes were isolated and irradiated. A blower directed a stream of air on the samples to minimize temperature increases that are known to change the radiation chemistry of a system.^{13,16} Overlays were placed on the air-irradiated samples to ensure equal ionization throughout the sample.

Specimens were irradiated from 1 to 70 Mrads. Yellowing was observed in many of the samples after irradiation.¹⁷ Following irradiation, the samples were washed with a dilute Ivory soap solution, rinsed with distilled water, and dried in a vacuum oven for 24 h at 80°C. In addition to the tensile samples, pure PS films and powder were irradiated, along with troughs of liquid PB, to determine the effects of radiation dose on the individual components.

Tensile Testing

Samples were tested in an Instron 4201 load frame at 23°C and a strain rate of 2.6×10^{-4} s⁻¹.

Molecular Weight Determination

Molecular weights of both the irradiated PS and the PB were determined with gel permeation chromatography (GPC). The system was calibrated with both PB and PS standards. Toluene was used for the PS samples, and tetrahydrofuran for the PB samples. The GPC system consisted of a series of Waters UltrastyrogelTM columns (10^3-10^5 Å) and a differential refractometer. The 0.6 wt % solutions were filtered with a 0.5- μ m LC filter (Millipore) prior to injection.

Dilute solution viscometry was performed on the PB samples with a Ubbelohde Viscometer (size OC) at 25°C with toluene as the solvent. The system was calibrated with acetone and toluene. A minimum of five concentrations were tested for each sample, with concentrations varying from 8% down to 1% by weight. All samples were filtered with a 0.5- μ m LC filter. Viscosity-average molecular weights were calculated from the determined value of the intrinsic viscosity with Mark-Houwink parameters¹⁸ of K = 0.051 mL/g and a = 0.76. These interpolated values were determined with the assumption of a linear dependence of the parameters on PB vinyl content.

Viscometry measurements were also made on the pure PB samples. A Rheometrics RMS-800 Mechanical Spectrometer equipped with a cone-andplate fixture was operated at 25° C in a steady shearing mode over a shear rate range of $0.1-100 \text{ s}^{-1}$. A cone angle of 0.04 rad and a radial dimension of 3.00 cm was used for all tests. Samples were allowed to stabilize thermally for a minimum of 10 min. Three separate determinations were made for each decade of shear rate, with each test lasting 30 s. Fluid samples were allowed to thermally stabilize in the fixture before each run. The temperature was monitored with a thermocouple mounted on the bottom surface of the plate.

RESULTS AND DISCUSSION

Figure 1 shows a typical transmission electron micrograph for a 3% blend. The PB phase, stained with osmium tetroxide for enhanced electron contrast,¹ separates into small pools $\leq 0.1 \ \mu$ m. No evidence of craze initiation from these pools was found in crazed samples examined with transmission electron microscopy.

The effect of radiation on mechanical behavior was ascertained with tensile measurements made on the 3% blend. The stress-strain results for the blend system irradiated in air are shown in Figure 2. These results are similar to those observed by Qin et al.⁸ who examined the mechanical properties of PB/PS blends as a function of PB molecular weight. Both those results and the results presented here demonstrate a gradual increase in fracture stress accompanied by a decrease in strain to fracture.

For comparison, pure PS samples were irradiated in air over the same dose range, then tensile tested. The results from these stress-strain measurements are shown in Figure 3. The 10-Mrad sample showed a slight enhancement in strain to fracture, but other samples irradiated to higher dose levels displayed the same value as the unirradiated specimen. Little evidence of crazing was visually observed in samples irradiated to dose levels higher than 45 Mrads. These results suggest that there was little change in the mechanical behavior of PS with irradiation for these modest radiation doses, which is consistent with previous research.^{12,13,15}

The fracture stresses determined from Figures 2 and 3 are plotted as a function of radiation dose in Figure 4. The 3% blend demonstrated an increasing trend of fracture stress with radiation dose that leveled off at a constant value of 36 MPa at around 45 Mrads. The fracture stress for PS, on the other hand, decreased slightly with radiation dose from 43 to 41 MPa over the radiation dose range from 0 to 70 Mrads. This result is in agreement with that of Bowmer et al.¹⁹ who observed a modest decrease in the tensile strength of PS at doses greater than 80 Mrads. This decrease was attributed to chain scission at the surfaces of the sample, an observation that will be substantiated and discussed below.

The values of strain to fracture, also determined from Figures 2 and 3, are shown in Figure 5 as a function of radiation dose. From an initial value of 0.2, the strain to fracture decreased quickly after a dose of 1–5 Mrads, and finally leveled off to a constant low value of 0.05 at 45 Mrads. The pure PS showed very little change in strain to fracture as a function of radiation dose and remained somewhat constant around the value of 0.05. Sisman and Bopp²⁰ observed a similar invariance of fracture strain with radiation dose, and noted that a dose of 500 Mrads was necessary to cause a 10% decrease in strain to fracture for PS homopolymer.

The tensile toughness is directly proportional to the strain to fracture. In Figure 6, the toughness drops from an initial value of 4.8 MJ/m^3 to less than 2 MJ/m^3 after a radiation dose of 10 Mrads. The data for the blends intersected the results for PS around 40 Mrads, at which point the two sets of data converged onto roughly the same line.

These results superficially supported the contention that the radiation treatment was affecting only the PB and not the PS; therefore it appeared that the hypothesis that the loss in toughness was due solely to the increase in molecular weight of the PB might be valid. Additional samples were prepared and tested, however, that cast some doubt on this explanation.

Bulk PS and PB were irradiated in air to 10 Mrads. These samples, designated PB_r and PS_r, were then blended with their unirradiated counterparts in an attempt to isolate the component that caused the decrease in toughness observed in Figure 6. Two blends were prepared, one containing 3% PB_r in unirradiated PS, and one containing 3% unirradiated PB in PS_r. The blends were prepared via the precipitation technique described previously, then molded and cut into tensile specimens.

The mechanical behavior of these blends is shown in Figure 7, along with the results for the unirradiated blend (PB/PS) and for a sample irradiated after blending (PB/PS)_r. The blend PB/ PS_r containing irradiated PS had approximately the same fracture strain as the unirradiated blend and showed a slightly higher flow stress. What was surprising, however, was the fact that the blend PB_r/PS, containing 10 Mrad-irradiated PB, also showed the same fracture strain. The craze flow stress of PB_r/PS was the same as the blend (PB/ PS)_r, which was irradiated to 10 Mrads after blending, yet the PB_r/PS did not show the loss in toughness exhibited by the (PB/PS)_r sample.



Figure 1 Transmission electron micrograph of 3% PB/PS blend. PB pools are stained with osmium tetroxide to provide electron contrast.

These results indicated that radiation-induced crosslinking of the PB phase may not have been responsible for the decreased toughness in the irradiated blends, and that radiation effects in the PS phase may have contributed in some way.

The effects of radiation dose on the molecular weight of the PB and PS were assessed with a variety of techniques as previously described. The results for the weight-average (GPC) and viscosity-average (dilute solution viscometry) molecular weights are plotted in Figure 8 as a function of radiation dose. The GPC results show an increase in molecular weight by a factor of roughly 2.5 for a dose level of 60 Mrads. Very little change in molecular weight was observed for dose levels around 10 Mrads, where the tensile toughness dropped off dramatically (Fig. 6). Shear viscometry experiments were also conducted on the irradiated PB in bulk. The results from these experiments are shown in Figure 9 as a function of radiation dose. The viscosity was tested over a range of shear rates from 0.1 to 100 s^{-1} . Each sample exhibited an almost constant viscosity for the range of rates investigated. The trend of the viscosity was almost identical to the results found from



Figure 2 Stress-strain behavior of 3% PB/PS blend as a function of radiation dose. Specimens were irradiated in air. Strain rate = 2.6×10^{-4} s⁻¹.

GPC: the viscosity doubled for a dose level of 60 Mrads, but showed little change for dose levels between 1 and 10 Mrads.

These results are consistent with the data shown in Figure 7 in that the PB is not affected to any important degree at low dose levels. It was possible to compute the dose necessary to produce a PB gel based on the G(X) value²¹ and the initial molecular weight of 2600 g/mol. [Note that G(event) indicates the number of events that occur for 100 eV of absorbed radiation, i.e. G(X) describes the number of crosslinks formed per 100 eV, G(S) the number of scissions, etc.] Although PB has a G(X) on the order of 3.6, Witt¹⁵ demonstrated that physical blends of PB and PS have a linear dependence of G(X) on PS content. Witt points out that PS merely serves as a diluent to irradiation in blends, rather than absorbing radiation from the PB chains, as is observed in PB/PS copolymers.^{14,15} He concedes, as do Basheer and Dole,²² that in blends containing spheres of one phase in a continuous matrix of another, the smaller the spheres, the greater the



Figure 3 Stress-strain behavior of pure PS as a function of radiation dose. Specimens were irradiated in air. Strain rate = $2.6 \times 10^{-4} \text{ s}^{-1}$.

amount of energy transfer from the smaller domain chains to the matrix due to greater interfacial contact. As this is presumably the case for our blends,



Figure 4 Craze flow stress of (\bigcirc) 3% PB/PS blend and (\Box) pure PS as a function of radiation dose. The filled data points indicate the samples where no crazing was observed. Specimens were irradiated in air.



Figure 5 Strain to fracture of (\Box) 3% PB/PS blends and (\bullet) PS as a function of radiation dose. Specimens were irradiated in air.

which contain PB pools less than 0.1 μ m in diameter, a G(X) value of 0.04 (that of pure PS) would be appropriate. This value would give an approximate gel point of 9,300 Mrads based on an initial molecular weight of 2,600 g/mol. Therefore, little change would be realized in the PB phase for the dose levels used in this study.

Given the results discussed above, it was reasonable to suspect that the observed loss in toughness was somehow associated with the PS component of the blends. Molecular weights were determined for pure PS irradiated in air and *in vacuo* with GPC. The samples were irradiated in both powder form and film form. Weight-average molecular weights for the various PS systems are plotted in Figure 10



Figure 6 Tensile toughness of (\Box) 3% PB/PS blends and (\bullet) PS as a function of radiation dose. Specimens were irradiated in air.



Figure 7 Mechanical behavior of 3% PB/PS blends with varying components irradiated to 10 Mrads (signified by X_r). (a) PB/PS, (b) PB/PS_r, (c) PB_r/PS, and (d) (PB/ PS)_r. $T = 23^{\circ}$ C, strain rate = 2.6×10^{-4} s⁻¹.

as a function of radiation dose. The results for the air-irradiated powder are noteworthy; M_w for this system increased to 5.6×10^5 g/mol at a dose of 10 Mrads, then leveled off at this value for doses up to 45 Mrads. The approach of the limiting value in the air-irradiated sample is consistent with the results of Alexander and Toms²³ who suggested that this behavior indicates that oxygen is not inhibiting crosslinking but rather enhancing chain scission. The molecular weight of the PS powder irradiated *in vacuo* increased up to 1×10^6 g/mol for a dose of 45 Mrads. The absence of oxygen prevented extensive scission; thus a larger increase in molecular weight was realized. The data for the air-irradiated



Figure 8 Effect of radiation dose on molecular weight of PB irradiated in air. (O) Viscosity-average MW and (Δ) weight-average MW.



Figure 9 Effect of radiation dose on the bulk viscosity of PB irradiated in air. Viscosity was determined with a cone-and-plate configuration for a rate sweep over three orders of magnitude $(0.1-100 \text{ s}^{-1})$; reported values are an average of each sample over the rates. $T = 25^{\circ}$ C. Values are normalized with the viscosity of the unirradiated PB.

film lay between the former two systems, having less surface area than the air-irradiated powder but more oxidative degradation than the *in vacuo* irradiated powder. As discussed by several researchers, ^{19,23} an increase in specific surface area will increase the amount of surface scission in air-irradiated samples.

These results suggested that the PS used in this study was susceptible to radiation-induced degradation, particularly near the sample surface. Given the relatively small strain to fracture found in unirradiated PS homopolymer, any radiationinduced embrittlement would be difficult to ascertain, as seen in Figure 5. The effects of the PS embrittlement would be magnified, however, in the blends toughened by the inclusion of the low molecular weight PB.

Sears and Parkinson²⁴ observed extensive oxidation of PS irradiated in air, evidenced through IR spectroscopy by the presence of carbonyl and hydroxyl groups normally not present in PS. Gröllmann and Schnabel²⁵ suggested that the rate limiting step in main chain scission is the diffusion rate of oxygen, an observation also supported by Franks.²⁶ Alexander and Toms²³ demonstrated that the absorbed oxygen in PS is not enough to cause chain scission (tightly stacked thin films showed no evidence of oxidative effects, while isolated films did), and that a steady supply of fresh oxygen to the sample surface is necessary. G values for both PS and PB irradiated in air and in vacuo are shown in Table I. No information was available for PB irradiated in air. Note that PS undergoes little scission



Figure 10 Molecular weight dependence of PS on radiation dose. (\bigcirc) Film in air, (\bigcirc) powder *in vacuo*, and (\Box) powder in air.

in vacuo, evidenced by a small value of G(S), but PS irradiated in air experiences extensive scission.

A reduction in the molecular weight of the PS at the surface of a tensile specimen could lead to the embrittlement observed in the air-irradiated blends in the following way: the molecular weight of the PS decreases to the chain entanglement limit near the surface, and the PS chains can no longer draw into stable craze matter. Surface-nucleated crazes would thus quickly transform into cracks, which leads to premature sample failure. This sequence of events is shown schematically in Figure 11.

To test this hypothesis, two additional sets of tensile experiments were conducted. In the first of these tests, PB/PS blend tensile specimens were irradiated *in vacuo* to a dose level of 10 Mrads where the radiation effects on the pure PB were negligible. The stress-strain results for these tests, along with the air-irradiated specimen and the unirradiated blend are shown in Figure 12. The air-irradiated specimen displayed a marked decrease in strain to

Table IProduct Yields of Irradiation ofPolybutadiene (PB) and Polystyrene (PS)

Polymer	G(X)	G(S)	G(S)/G(X)
PB (air, 30% vinyl) ^a	1.8	_	
PB (in vacuo, 1,4) ^b	5.3	0.5	0.1
PS (air) ^c	0.02	0.10	4.5
PS (in vacuo) ^b	0.03	0.02	0.7

^a Adapted from Pearson et al.¹⁰

^b Adapted from Dole.³³

^c Adapted from Bowmer et al.¹⁹



Figure 11 Proposed schematic for loss in toughness in irradiated PB/PS blends. (a) Craze growth without presence of scissioned layer and (b) craze growth with scissioned layer. The magnified regions show the polymer chains that compose the craze tufts. Shorter polymer chains in the scissioned layer results in chain pullout and subsequent void formation.

fracture; the strain to fracture for the sample irradiated *in vacuo* was identical to the unirradiated sample. These results suggest that oxygen does indeed play a role in the reduced toughness observed in the air-irradiated samples.

In the second set of tests, the surface-scissioned layers of irradiated PB/PS blends were mechanically removed through polishing techniques in an attempt to recover some toughness. Bowmer et al.¹⁹ and Brown and O'Donnell¹⁶ demonstrated that successive layers could be removed from irradiated PS samples with a lapping wheel to allow analysis of the molecular weight as a function of depth. Their work suggested that 0.3 mm had to be removed from an initial 3-mm thick bar irradiated to 50 Mrads with γ radiation in air in order to remove the scissioned layers. The molecular weights of the grindings were determined with both dilute solution viscometry and GPC in their studies.

A similar procedure was tried on the blend samples used in this work. Tensile samples with 3% PB/ PS were prepared, but were not polished as before.



Figure 12 Mechanical behavior of 3% PB/PS blend at 10-Mrad radiation dose for various systems. (a) 0 Mrads, (b) in air, and (c) *in vacuo*. T = 23°C, strain rate = 2.6 $\times 10^{-4}$ s⁻¹.

They were irradiated in air to a dose level of 45 Mrads. Following this, 0.05 mm was removed from each side of the samples with 600 grit wet-dry sandpaper, after which the samples were polished with aluminum oxide slurry. The samples were subsequently tested in the Instron tensile tester. In Figure 13 the (c) results for these tests are compared with (b) the unpolished irradiated sample and (a) the unirradiated sample. The mechanical removal of the oxidized surface layer clearly resulted in a partial recovery of toughened behavior.



Figure 13 Mechanical behavior of 3% PB/PS blend at 45-Mrad radiation dose for various systems. (a) 0 Mrads, (b) in air, and (c) in air, surface layer removed. $T = 23^{\circ}$ C, strain rate = 2.6×10^{-4} s⁻¹.

As shown schematically in Figure 11, the loss of toughness arises from a brittle surface layer created by radiation-induced degradation of the PS. The samples studied in this work rely on surface-initiated crazes to generate high levels of toughness. A craze forms by the repeated drawing of polymer chains to form ordered tufts. If the molecular weight falls below the chain entanglement limit in the region of a craze, the chains will continue to draw until a critical flaw forms and leads to craze failure. Yang et al.²⁷ examined the craze fibril stability in PSs with molecular weights varying from 37,000-20,000,000 g/ mol and found that fibril stability decreased significantly as the molecular weight dropped from 200,000 to 50,000 g/mol, and that fibrils failed by random chain disentanglement at the craze-bulk interface. Gent and Thomas²⁸ observed a sharp decrease in tensile strength with decreasing molecular weight in a series of PS samples with varying molecular weights (50,000-200,000 g/mol). For molecular weights near the entanglement limit (30,000-35,000 for PS), there was insufficient chain entanglement to prevent chain pull-out as the sample is strained. The earlier results of Bowmer et al.¹⁹ support these observations: they demonstrated a decrease in the tensile and flexural fracture strength of PS irradiated in air as well as a molecular weight change as a function of depth for an irradiated PS bar. Similar results were shown for polysulfones by Brown and O'Donnell¹⁶ and by Hill et al.²⁹

Rolland³⁰ demonstrated that a very tough polymer such as polycarbonate or acrylonitrile butadiene/ styrene (ABS) could be made brittle by the application of a brittle coating. He explained that after a sharp crack is initiated in the surface layer, the bulk material is unable to arrest this fast-moving crack, and the entire material has the characteristics of a brittle material. As shown in Figure 11, we are suggesting that irradiating the PS/PB blends in air essentially results in specimens covered with a brittle coating. Birkinshaw et al.³¹ found that high-impact PS (HIPS) irradiated in air to relatively low dose levels demonstrated a reduction in impact strength, which the authors attributed to crosslinking of the PB phase. The experimental results found by Birkinshaw et al.³¹ can also be explained by consideration of the fact that PS surface scission would also take place in their sample preparation. Mlinac-Misak et al.³² also observed a decrease in impact strength of HIPS irradiated in air with UV irradiation, but attributed this to scission in the linkage between the PB and the PS as evidenced by IR studies on the carbonyl groups that they assumed were attached to the PB. It is possible, however,

that the carbonyls were on the PS chains, which would also be a warning flag of the presence of chain scission, and that reduced toughness was due to the surface embrittlement effect.

CONCLUSIONS

The results from the various tests conducted in this study, along with the observations of other researchers, all point to the fact that irradiation caused oxidative degradation in the surface PS, and that it was this reduction in molecular weight that led to the observed loss in toughness. Crosslinking of the PB was not responsible for the radiation-induced embrittlement as was initially postulated. The absence of air during irradiation or the removal of the degraded skin layer minimized the loss of toughness in the irradiated blends. Additionally, redissolution of the irradiated PS will remove the skin layer, as observed in the PB/PS_r blends shown in Figure 7. Thus, while the results of the present study did not provide evidence for the presumed effects of PB mobility on toughness, they did clearly show the deleterious effects of radiation on the surfaces of PS when irradiated in the presence of oxygen. This damaged PS surface can have serious consequences in regard to the toughness of these blends if surfaceinitiated crazes are central to the toughening mechanism.

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