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Gamma irradiation effects on impact strength and thermal properties of SBR-toughened polystyrene

Summary — Effects of chemical structure, composition, thermal stability and molecular weights of the rubber phase in amorphous polystyrene + styrene/butadiene rubber (SBR) blends on impact behavior were investigated. Blends with 5, 10 and 13 wt. % of SBR embedded into a rigid polystyrene matrix were prepared as well as the samples without SBR. For all blends the Izod impact tests were performed and those with the best impact strength values were submitted to gamma irradiation. The Izod impact tests of the irradiated samples were then performed. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) runs were made for both irradiated and not-irradiated blends. Blends compositions with the highest impact energies have been defined. Gamma irradiation initially enhances the impact energies but then reaches a maximum around 150 kGy above which the impact strength eventually becomes lower than in the samples not subjected to irradiation.

Key words: polystyrene, SBR, polymer blends, gamma irradiation, impact strength, thermal properties.

Development of polymer blends with improved impact properties is an object of both pure and applied research [1–4]. An important example in this category is so-called high-impact polystyrene (HIPS) in which the embedded soft rubber phase improves the impact strength of the brittle polystyrene matrix. The resulting materials have a fairly wide range of applications including automotive bumpers and helmets [5].

Both block or graft copolymers obtained by a variety of processes have been used to enhance the impact energy. In general, block copolymers have been more extensively used as compatibilizers than the graft copolymers. A wide variety of materials have been used as the rubber phase, including the styrene/butadiene rubber (SBR) manufactured by anionic or free radical poly-

merization [6] as one of the preferred choices. The reason for the preference is the flexibility of molecular structures since linear, block, multiblock, star, random, *etc.* options are all possible — what in turn allows the creation of materials with the performance adapted to a specific application [7]. Most SBRs used for blending had as *trans-* as *cis-* configuration of bound butadiene units as well as a vinyl part in the copolymers.

It is possible in principle to control a number of parameters, which determine the impact properties such as: rubber phase content, particle size distribution and rubber phase morphology, the chemical structure and interfacial adhesion between the rubber and the matrix. The discrete phase is formed by particles with fairly complicated structures, generally solid particles with sizes in the range from 0.4 to 5 μm , in amount between 3 and 9 wt. % of the total material [5]. Scanning Electron Microscopy (SEM) shows the morphology of the surfaces as being formed by different structures (spherical, elongated, *etc.*) due to the partial miscibility of the components of the blend as well as the voids that influence the impact behavior [8].

The importance of the content of SBR as well as the chemical structure results in some degree of control of the impact characteristics of the blends, even when there is a limited reduction in the stiffness, yield stress and creep resistance. Permanent adhesion of SBR to the brittle matrix can be enhanced by ionizing radiation, which

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often causes an amorphization of polymeric materials [9]. The gamma radiation penetration the materials is a function of its energy, as well as the "witness" material density. The gamma radiation (1.17–1.33 MeV) shows deeper penetration than protons or electrons. However, these kinds of radiation have also their uses, as for instance in a recent study of Żenkiewicz [10] of tensile properties of polypropylene films subjected to EB (electron beam) radiation. For protons one can achieve penetration depths down to 7.5 cm, for 100 MeV electrons 32.5 cm and for gamma radiation the average 40 cm [11].

Polystyrene (PS) does not undergo crosslinking easily when gamma-irradiated in air but it does in vacuum. We have on one hand a protective effect of the benzene rings and reactive C=C bonds on the other. The molecular weight and the sample age also affect the behavior of PS. Gel formation has been known for a long time to occur at 270 kGy but the crosslinking yield is only 0.03 [12].

Thermophysical characteristics is an integral part of evaluation of polymeric materials [13] and includes thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). We note that the glass transition temperature T_g of polystyrene is in the range from 92 to 98 °C [14] while the respective melting temperature T_m = 242 °C for isotactic and 287 °C for syndiotactic PS [15].

We have studied polystyrene + SBR blends of varying composition and the SBRs of different chemical structures. Izod impact testing was carried out and the thermal behavior was investigated by TGA and DSC. The best impact materials were submitted to varying gamma radiation doses to establish the changes in the impact performance, thermal and structural stability of the rubber reinforcement and to evaluate the polymer adhesion.

EXPERIMENTAL

Blend preparation

19 blends with 0, 3, 5 and 10 wt. % of SBR from Industrias Negromex S.A., Lerma, Mexico, were prepared in matrices of polystyrene (PS). PS was obtained from Resirene S.A., Tlaxcala, Mexico. The SBRs had different chemical compositions and structures, also different values of the weight-average molecular weight M_w and number-average molecular weight M_n , as presented in Table 1.

Each blend was first prepared in a Haake-Büchler Model 600 co-rotating twin screw extruder. The processing conditions were 75 rpm and the temperature sections: zone 1 — solids transport (190 °C), zone 2 — melt (200 °C), zone 3 — pumping (200 °C) and zone 4 — die (200 °C). Afterwards, the blends were injected in a Negri-Bossi Model NB-90 injector with the following specifications: injection pressure — 0.9 MPa, planar profile of temperature — 200 °C and the cycle time 70 s.

The additives used for all blends were:

— antioxidants: BHT (2,6-di-*tert*-butyl-*p*-cresol) and Irganox 1076 (octadecyl-3,5-di-*tert*-butyl-4-hydroxyhydro cinnamate) from Ciba Specialty Chemicals, Tarrytown, NY, USA;

— lubricants: Loxamide (*cis*-13-decosonic amide) from Fisher Scientific Ltd., Ottawa, Ontario, Canada and magnesium stearate.

Mechanical testing

Izod notched impact testing was performed in a Model 66 Impactometer from Tinius-Olsen, Shakopee, MN, USA. The specimen dimensions were 25.4 × 12.7 × 12.7 mm. The ASTM D256 procedure was followed. The Izod method allowed to obtain the values of the energy necessary to cause the fracture of the specimen; the technique was explained in [16]. The resulting values will be referred as Izod impact strength or impact strength. Averages from five samples of each composition are reported.

Thermal characterization

A Dupont 910 Thermobalance, connected with the 2100 system (Thermal Analysis Instruments, Wilmington, DE, USA) was used to study the samples of 20 mg weight, under N₂ atmosphere (100 mL/min) and the heating rate of 10 deg/min at the temperature range from 20 to 500 °C ± 0.1 °C. Melting temperatures and the enthalpies of fusion were determined with a Dupont 910 Differential Scanning Calorimeter (DSC), under the N₂ atmosphere and the heating rate of 10 deg/min at the same temperature range.

Irradiation procedure

The blends were subjected to gamma radiation in air at the room temperature with doses of 10, 50, 100, 150, 200 and 250 kGy. The dose rate (0.11 kGy/h) was provided by a 651 PT gamma source manufactured by the Atomic Energy of Canada Limited (AECL, Chalk River, Ontario) and located at the Institute of Nuclear Sciences of the National Autonomous University of Mexico.

RESULTS AND DISCUSSION

Impact behavior

The Izod impact strength values are presented as a bar diagram in Fig. 1 as a function of the type and concentration of SBR in the specimens. The data show that the 87 % PS + 13 % SBR-4 blend is the best impact-resistant material. We recall that SBR-4 has a linear structure and contains 30 wt. % of styrene and 70 wt. % of butadiene (Table 1). At the opposite end of the impact behavior spectrum, the lowest impact strength is seen for the 95 % PS + 5 % SBR-5 blend, in which SBR-5 is also

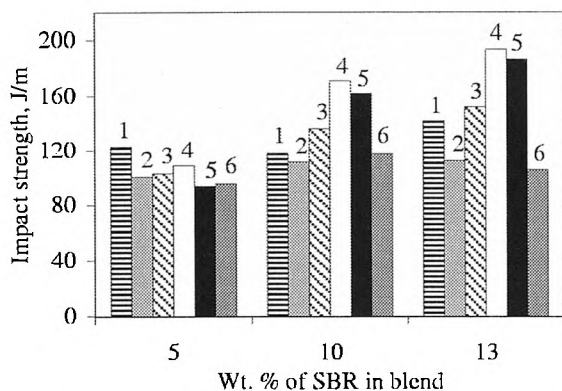


Fig. 1. Effects of the type and content of SBR on the impact strength of the non-irradiated PS + SBR blends: 1 — SBR-1, 2 — SBR-2, 3 — SBR-3, 4 — SBR-4, 5 — SBR-5, 6 — SBR-6 (symbols of SBRs see Table 1)

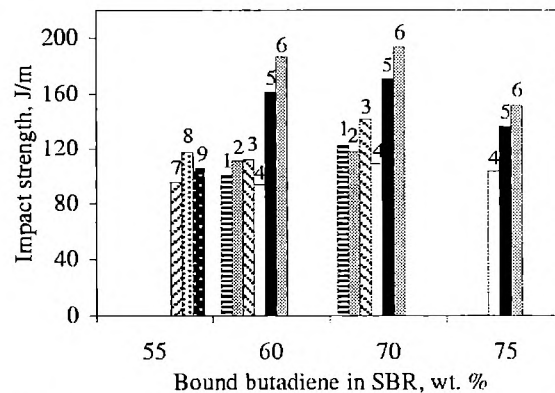


Fig. 2. Impact strength vs. part of bound butadiene as well as the structure and content of SBR in non-irradiated PS + SBR blends. Structure of SBR: 1, 2, 3, — star-like; 4, 5, 6 — linear; 7, 8, 9 — multiblock. SBR content: 1, 4, 7 — 5 wt. %; 2, 5, 8 — 10 wt. %; 3, 6, 9 — 13 wt. %

linear and of 60/40 butadiene/styrene ratio. To put these results into proper perspective, we note the result for the pure PS matrix, namely Izod impact strength $U_I = 72.64$ J/m. Thus, addition of SBR of various structures and in varying concentrations results in the impact strength improvement ranging from 28.8 % to 166.3 %.

More generally, the impact strength goes symbatically with the SBR contents. As for the chemical structures of the SBRs, the two best impact materials have 53 % of 1,4-*trans*-, 38 % of 1,4-*cis*- and 9 % of 1,2-butadiene monomer units contents but different molecular weights: $M_w = 220\ 000$ for SBR-4 and $M_w = 330\ 000$ for SBR-5.

Figure 2 is also a bar diagram, this one showing the impact strength as a function of the butadiene contents in SBRs, as well as the content and structure of SBR. The highest values are seen for SBR containing 70 wt. % of

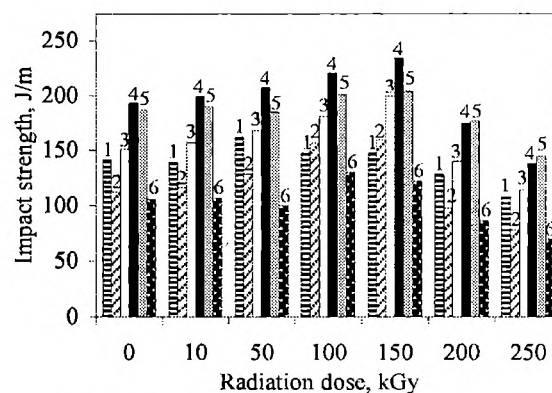


Fig. 3. Effects of radiation dose and the type of SBR on the impact strength of the irradiated PS + SBR blends. SBR content 13 wt. %, description of bars as in Fig. 1

Table 1. Characteristic of SBRs

SBR type	Styrene content, wt. %	Butadiene content, wt. %	Structure of SBRs	Isomers, wt. %			Molecular weight	
				1,4- <i>trans</i>	1,4- <i>cis</i>	1,2-vinyl	M_w	M_n
SBR-1	30	70	Star	53	34	13	210 000	183 000
SBR-2	40	60	Star	53	32	15	330 000	287 000
SBR-3	25	75	Linear	53	37	10	110 000	98 000
SBR-4	30	70	Linear	53	38	9	220 000	207 000
SBR-5	40	60	Linear	53	38	9	330 000	313 000
SBR-6	43	57	Multiblock	53	34	13	180 000	162 000

bound butadiene, that is for linear structure. The data for SBR containing 60 and 70 wt. % of bound butadiene are almost the same.

The effects of irradiation and the type of SBR on the impact strength of blends containing 13 wt. % of SBR are represented in Fig. 3. The highest values once again are obtained for the blends containing SBR-4. The respective improvement at 150 kGy amounts to 21.2 % in comparison with the same blend non-irradiated and 222.8 % in comparison with the polystyrene matrix.

The blends containing SBR-2 or SBR-3 show a similar behavior as those with SBR-4. That is, with increasing irradiation dose, the impact strength values first increase, pass through a maximum at 150 kGy and then decrease. The final values are lower than the initial ones, so that at high doses the objective of the irradiation is defeated. We recall the results of Żenkiewicz on EB-radiation of polypropylene (PP) showing maxima on the curves of rupture strength and ultimate elongation as a function of the irradiation dose [10]. We also note the

results of Sek and coworkers [17] who have applied UV irradiation or heating to modify polynaphthalimides. The result was additional ring formation of the pyrrole type and an increase in glass transition temperature. Thus, irradiation can be made to improve the mechanical behavior — provided the dose is optimized. The optimum dose is material dependent. For our blends containing SBR-1 the maximum is around 50 kGy rather than 150 kGy. Of course, other options exist also; calcium carbonate gives good results for PP toughening — as reported by Goldman and Copsey [18].

The blends containing SBR-5 or SBR-6 do not show the same type of behavior. We see first the minima of impact strength at 50 kGy, then maxima (at 150 kGy for SBR5 and at 100 kGy for SBR-6) and finally descending curves.

The crosslinking of our thermoplastics by irradiation is vastly different from crosslinking leading to thermoset formation — such as curing of epoxy resins. In the latter case the curing is accompanied by significant shrinkage and appropriate steps need to be taken to eliminate void formation [19].

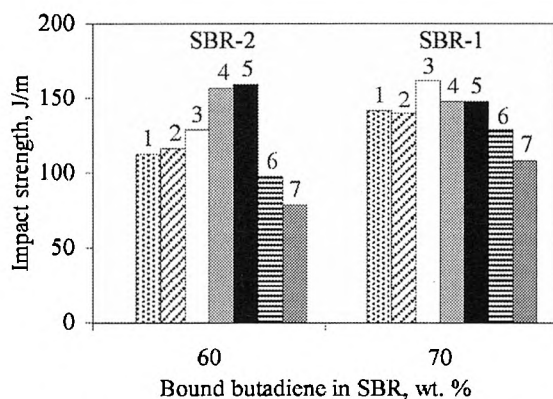


Fig. 4. Impact strength vs. part (in wt. %) of bound butadiene for PS + SBR blends containing star SBR at different irradiation doses (in kGy): 1 — 0, 2 — 10, 3 — 50, 4 — 100, 5 — 150, 6 — 200, 7 — 250. SBR content 13 wt. %

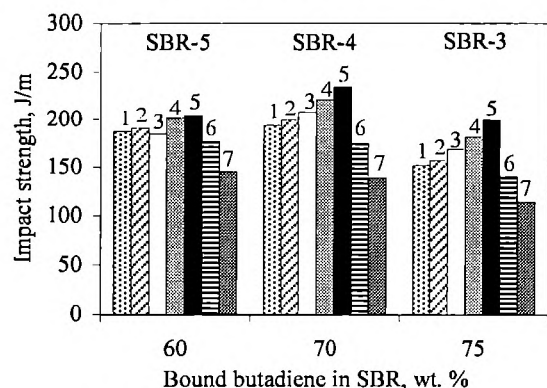


Fig. 5. Impact strength vs. part (in wt. %) of bound butadiene for the PS + SBR blends containing linear SBR at different irradiation doses. SBR content 13 wt. %, description of bars as in Fig. 4

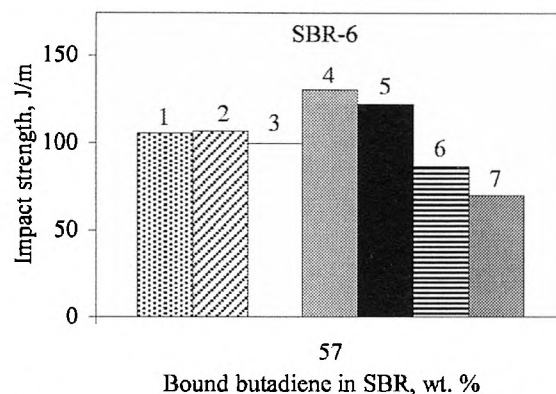


Fig. 6. Impact strength vs. wt. % of bound butadiene for the PS + SBR blends containing multiblock SBR at different irradiation doses. SBR content 13 wt. %, description of bars as in Fig. 4

We can also consider the impact strength values of the irradiated blends in terms of other factors:

- linear or star structures are preferred;
- butadiene concentration between 60 and 70 wt. % gives optimal results;
- the molecular weight $M_w = 2.2 \cdot 10^5$ is better;
- 53 wt. % of 1,4-*trans*-, 38 wt. % of 1,4-*cis*- and 9 wt. % of 1,2-butadiene component is preferred.

These statements are supported by the results presented in Figs. 4—6 respectively for star, linear and multiblock SBR.

Thermophysical properties

Consider first the thermal stability of the non-irradiated samples. The TGA results are reported in Table 2. For the pure polystyrene matrix 97.9 % of the initial weight remains until 382 °C — an adequate thermal stability. The irradiated samples show even better thermal stability, but only insignificantly so. The last column in Table 2 lists the temperature of the maximum peak of the TGA derivative curve at which rapid thermal decomposition leading to the remaining weight decreasing to zero occurs.

Table 2. TGA data of PS matrix and PS + SBR blends with different SBR-4 contents

	Weight loss at $T_{max}^*)$, %	T_{max} , °C
PS	2.1	382.2
95 % PS + 5 % SBR-4	4.1	385.4
90 % PS + 10 % SBR-4	2.7	393.1
87 % PS + 13 % SBR-4	2.4	389.4

^{*)} T_{max} — temperature of the maximum peak of TGA derivative curve

DSC results of non-irradiated samples are reported in Table 3. Our result concerning pure PS, namely $T_g = 97.3$ °C agrees perfectly with the value of 97.5 °C listed

Table 3. DSC data of PS matrix and PS + SBR blends with different SBR-4 contents

	$\Delta T, ^\circ\text{C}$	$T_g, ^\circ\text{C}$	Heat flow, W/g
PS	91.9—104.2	97.3	-0.184
95 % PS + 5 % SBR-4	94.4—103.7	99.1	-0.026
90 % PS + 10 % SBR-4	94.3—103.9	101.0	-0.033
87 % PS + 13 % SBR-4	97.6—105.7	101.2	-0.023

by Plazek and Ngai [14] for amorphous PS. Since the glass transition constitutes a region rather than a single point, we list the respective temperature ranges (column 2) as well as the single T_g temperature values (column 3). One can recall here the Fourier-transform infra-red (FT-IR) and FT-Raman spectroscopies results for PS [20]: the glass transition weakens the bands at 689 cm^{-1} (corresponding to C-H bonds with γ_w -vibration modes, visible in FT-IR), and also bands at 616 cm^{-1} (corresponding to the rings with δ -vibration modes, visible in FT-Raman spectra). We observe the T_g increase with the increasing SBR contents.

The DSC diagrams do not show the melting transition — a result consistent with the apparently fully atactic and thus amorphous material.

In Table 4 we report TGA results after irradiation for the sample which showed the highest impact strength (87 % PS + 13 % SBR-4) as a function of the radiation dose. The first weight loss increases somewhat as a consequence of irradiation, but not in a significant way.

Table 4. TGA data of the highest impact 87 % PS + 13 % SBR blends, non-irradiated and irradiated with 100 kGy to 250 kGy doses

Doses, kGy	Weight loss at $T_{max}^*)$, %	$T_{max}, ^\circ\text{C}$
0	2.4	389.4
100	2.1	384.6
150	5.0	392.9
200	5.1	381.1
250	5.0	379.3

^{*)} T_{max} — see Table 2.

Table 5. DSC data of the highest impact 87 % PS + 13 % SBR blend, non-irradiated and irradiated with 100 kGy to 250 kGy gamma irradiation doses

Doses, kGy	$\Delta T, ^\circ\text{C}$	$T_g, ^\circ\text{C}$	Heat flow, W/g
0	97.6—105.7	101.2	-0.023
100	96.1—101.0	100.5	-0.023
150	96.3—102.9	100.0	-0.056
200	95.4—101.9	99.7	-0.038
250	95.0—102.1	99.1	-0.047

Table 5 summarizes the DSC results for the same samples as studied by TGA in Table 4. With increasing

irradiation dose the T_g value decreases from $101.2\text{ }^\circ\text{C}$ (0 kGy) to $99.1\text{ }^\circ\text{C}$ (250 kGy) *i.e.* by about 2 deg.

CONCLUDING REMARKS

Both addition of SBR and irradiation improves the impact strength of polystyrene. The results depend on the ratios of bound styrene/butadiene in SBR, and on the content of SBR in the blend as well as on the shapes of SBR molecules (star, linear, multiblock). The reasons might be improved compatibility and/or crosslinking effects. The irradiation first creates crosslinking structures, hence higher impact strength. Further irradiation, however, results in chain scission -which causes the observed impact strength lowering. Our results allows to define the optimized styrene/butadiene ratios, as well as the best chemical structure for manufacturing of good impact materials. All materials we have investigated show good thermal stability at elevated temperatures.

Other surface treatments aimed to improve the properties are also in use and have been described for instance by Garbassi and Occhiello [21]. Some of them can be quite useful for commercial applications while "plasma polymerization is very complex and not fully understood" [21].

A paper on morphology of the same blends studied by scanning electron microscopy and their microhardness is in preparation.

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