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Gamma irradiation effect on polystyrene + SBR blends: morphology and microhardness

Summary — Blends with 0, 5, 10 and 13 weight % of styrene/butadiene (SBR) copolymer embedded in a rigid polystyrene matrix were prepared. Microhardness was determined and morphology evaluated by scanning electron microscopy (SEM) before and after gamma irradiation. We relate the morphology to chemical structure and to composition of the SBRs as well as to irradiation dosages. We also connect the microhardness to the impact strength determined previously.

Key words: polymer blends, polystyrene, SBR, microhardness, impact behavior, gamma irradiation, SEM, surface morphology.

High impact polystyrene (HIPS, another abbreviation term PS-HI) contains an elastomeric phase. Typically, there are small islands of the elastomer in PS. In turn, each such island contains PS inside. One can manipulate HIPS properties by varying: a) the size distribution and the morphology of the elastomer particles [1]; b) the content of the elastomeric phase; c) the chemical structures of the elastomeric phase and the matrix; d) the molecular weight distributions, and e) the adhesion between the matrix and the rubber particles.

A wide variety of natural or synthetic elastomers had been employed in making HIPS material. One uses often a synthetic styrene/butadiene rubber (SBR) with different structures (star, linear, block or random), configurations (1,4-*trans*-, 1,4-*cis*- or 1,2-vinyl) and particle sizes in the range from 0.4 to 10 μm [1—5].

Conventional scanning electron microscopy (SEM) of HIPS provides only 2D pictures. More sophisticated tools such as digital image processing [6], nuclear magnetic resonance (NMR) and ultrasonic degradation have been employed. These techniques provide valuable data on particles morphology, particle size distribution and concentration of the elastomeric phase [1].

At the same time SEM micrographs provide information on craze propagation, stress bands formation, as well as void formation, factors that can enhance or deteriorate the performance [7—9]. If voids are present, SEM results do not provide the depth. We have decided to apply a microhardness test as an indirect way to evaluate the 3D structure of HIPS in conjunction with SEM.

Transmission electron microscopy (TEM) of HIPS morphology shows „salami" structures, consisting of polystyrene domains surrounded by polybutadiene membranes [10, 11]. To a certain extent, good mechanical properties can be attributed to crazing mechanisms: a) craze formation of the matrix-rubber particles interface [4, 8, 5], b) shear band yielding [1] and c) cavitation [1].

In principle it should be possible to control the craze fracture but unfortunately our understanding of the processes involved is insufficient. The craze formation depends on the applied stress and the quantity and diameter of the particles [9, 12]. There has been a controversy on increasing the rubber particle diameter because the impact resistance can go either way [13]. Apparently, this is a consequence of difficulties in achieving simultaneous control of the size and internal structure of the two-phase islands. Piorkowska and her colleagues [14] as well as Loch and coworkers [15] concluded that increased island size is advantageous for craze initiation — thus providing an energy dissipation mechanism.

Some results obtained for nylon blends have been used as guidance to evaluate the particle size effects in HIPS [13, 16]; applying the results for polymers with shear yield to those with crazing should be done with great caution. Apparently particles with diameter below 2 μm are not effective in the improvement of the polystyrene impact resistance [17]. Nevertheless, these kinds of particles are effective for polymers with shear yield [13].

The importance of the content of SBR as well as the chemical structure results in some degree of control of the impact characteristics of blends, even when there is a

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limited reduction in the stiffness, yield stress and creep resistance [5, 7, 18—20]. Permanent adhesion of the SBR to the brittle matrix can be enhanced by ionizing radiation, which often causes amorphization of polymeric materials [19].

One can also manipulate mechanical properties of materials by irradiation. This has been done for instance by Żenkiewicz [21] so as to affect tensile properties of polypropylene films by EB (electron beam) radiation.

In the preceding paper [5] we have determined the Izod impact strength of polystyrene (PS) + SBR systems, performing also thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of non-irradiated and γ-irradiated samples with varying SBR concentration. In the present paper we report SEM and microhardness testing results before and after gamma irradiation. We would like to connect the present results with those obtained earlier, for a better understanding of relations of mechanic performance with morphology of these materials.

EXPERIMENTAL

Blend preparation

Blends with 0.5, 10 or 13 weight % of SBR in a PS matrix have been prepared exactly as before [5]. To avoid repetition, we refer the reader to the preceding paper for all the details, reminding only the characteristics of used SBR samples (table 1).

Table 1. Characteristics of SBRs

SBR type	Styrene content, wt. %	Butadiene content, wt. %	Structure of SBRs	Isomers, wt. %			Molecular weights	
				1,4-*trans*	1,4-*cis*	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

Microhardness testing

Indentations were performed by using a Matsuzawa model MHT2 microhardmeter, under the constant load of 10 g over 15 seconds. The indentation produces an area of pyramidal shape with 136° between the opposite faces.

Morphological characterization

The materials were submerged in OsO_4 for 48 hours and cooled in liquid nitrogen for 0.5 hours. They were cut into pyramidal shapes with a RMC model MT 6000-XL micrometer that produces very thin and uniform cuts with diamond knives and then vacuum-coated with carbon (shells between 3 to 10 nm) in a vacuum pump (E. F. Fullam) at 50 militorrs (6.66 Pa). Finally the surfaces were analyzed by SEM in a JEOL model JSM-5200 machine, in the secondary-electron mode at 25 keV.

Irradiation procedure

The blends were subjected to gamma radiation in air at the room temperature applying dosages of 10, 50, 100, 150, 200 and 250 kGy at the dose rate of 0.11 kGy/h. The irradiation was provided by a 651 PT Gamma Beam Irradiator 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.

BEHAVIOR OF NON-IRRADIATED SAMPLES

The results concerning microhardness test are presented in a block diagram as Fig. 1. In general, with the increasing of the SBR content, the microhardness values decrease. This is in contrast to Izod impact energy values reported before [5]. The highest microhardness values are obtained for PS + SBR-3 blends which exhibit an ease of shear yielding and low elastic modulae (both in tension and in bending), as well as intermediate values of impact resistance [5]. On the other hand, the PS + SBR-4 blends exhibit the lowest microhardness values but they have the highest impact resistance [5]. A tentative conclusion is that the capability to absorb energy on impact is associated with low microhardness.

As for chemical structures of SBR, blends containing linear SBRs (SBR-5, SBR-4 and SBR-3), the microhardness decreases, passes through a minimum (Fig. 2), and increases again as a function of the butadiene content.

Effects of increasing the butadiene content can be seen in the surface morphologies. An increase from 60 % (SBR-5) to 70 % (SBR-4) makes the surfaces less homogeneous with semi-spherical rubber particles that act as *in-situ* reinforcing agents. Particles with diameter below

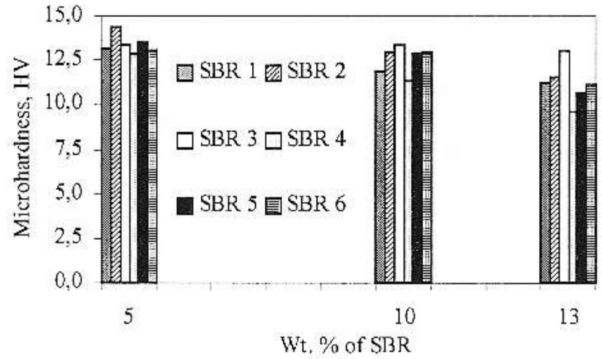


Fig. 1. Microhardness (in HV = Vickers Hardness) vs wt. % of SBR

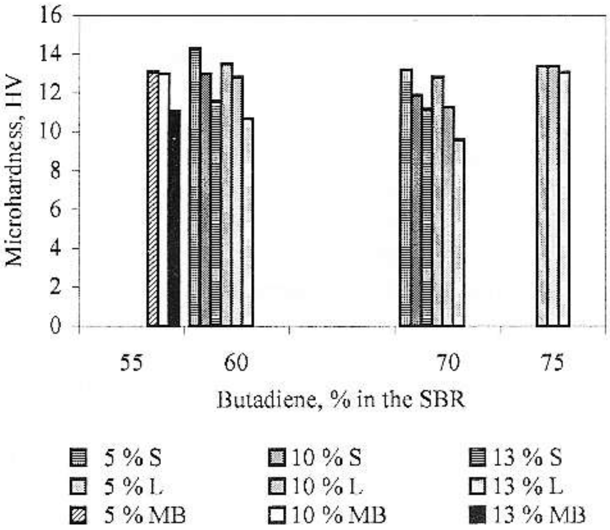


Fig. 2. Microhardness (in HV = Vickers Hardness) vs wt. % of butadiene in the SBRs of different structures (S = star, L = linear, MB = multiblock)

5 µm (Fig. 3a and 3b) show poor mechanical properties in microhardness, tension and flexion, but excellent impact performance [1]. The highest impact values are due to regular distribution and homogeneity of the rubber particles (Fig. 3b). Increases in the rubber particle sizes are seen for a higher content of butadiene (75 %, SBR-3, Fig. 3c). We know the result is an increment in the microhardness but lower impact values (Fig. 3c).

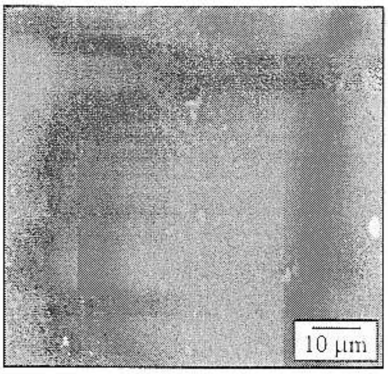
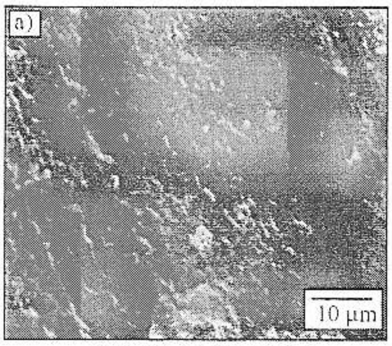
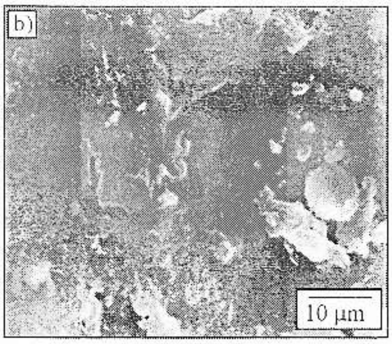


Fig. 4. Polystyrene matrix



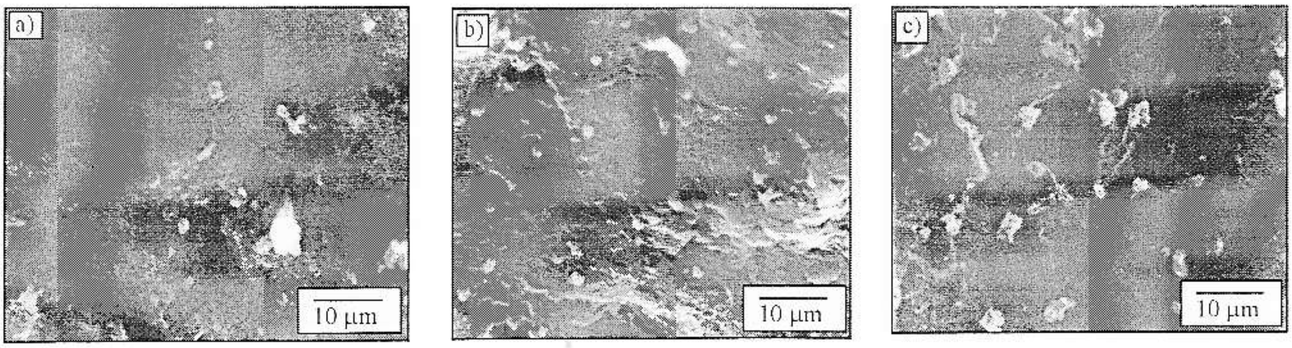
87 % PS + 13 % SBR-1



87 % PS + 13 % SBR-2

Fig. 5. Blends containing star SBRs

Consider now the polystyrene matrix as the reference material for blends (0 % SBR, Fig. 4). The morphologies reveal that the reinforcing agents are distributed in poly-



87 % PS + 13 % SBR-5 87 % PS + 13 % SBR-4 87 % PS + 13 % SBR-3

Fig. 3. Blends containing linear SBRs

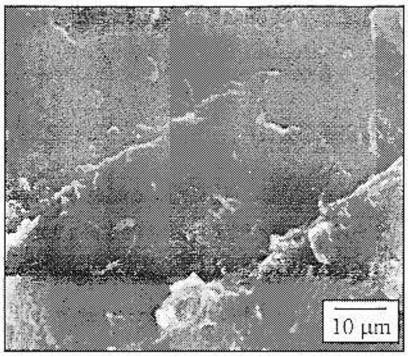


Fig. 6. Blend containing multiblock SBR-6: 87 % PS + 13 % SBR-6

styrene matrix and provide regular homogeneity. It seems that linear macrostructure SBRs allow deeper indentations.

A different behavior is observed for blends using star-SBRs (SBR-2 and SBR-1), for which increasing the butadiene content diminishes the microhardness (Fig. 2). We see here rubber particles with irregular shapes and larger sizes, with dark zones corresponding to some voids (Fig. 5a and 5b). It is important to mention that the sample surfaces prior to loading were mirror-polished.

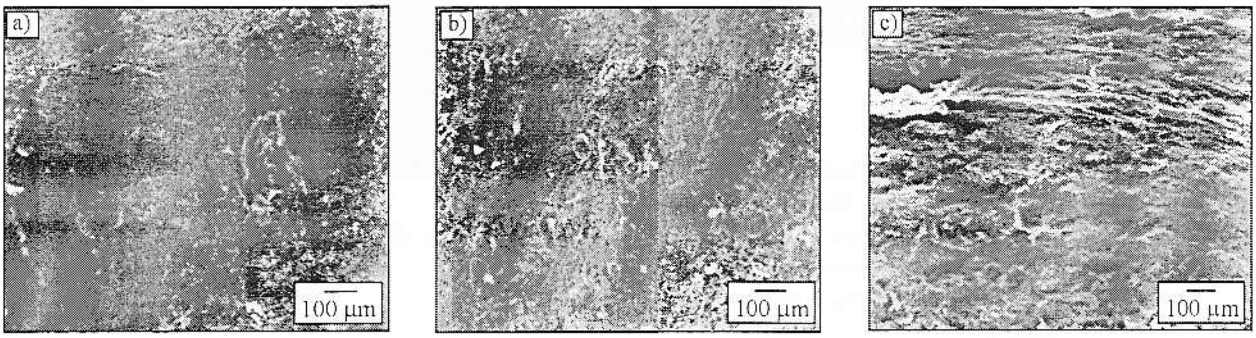
Consider now the sizes of the rubber particles (from 0.4 to 10 μm) in relation to the indentation values (from 36.0 to 43.8 μm). Apparently the voids depths are approximately four times the rubber particle diameters. We can also connect non-homogeneity with the microhardness; high butadiene contents produce a high number of voids on the surfaces, allowing deeper indentation to the detriment of microhardness. Finally, when using multiblock-SBRs (SBR-6), poor homogeneous surfaces with particles of diameters less than 15 μm and a variety of structures can be seen (Fig. 6).

IRRADIATED SPECIMEN BEHAVIOR

After irradiation with dosages between 10 kGy and 250 kGy several changes in blends morphology are seen. For blends containing star SBR-1 we observe particles of various size and shapes dependent on the dosages (Fig. 7). Moreover, different behaviors are seen at different dosages: 1) the surfaces are homogeneous with particles of several sizes when reaching 50 kGy, 2) the matrix begins to disrupt at 150 kGy and, 3) well-defined crazes appear, with several fractured particles, at 250 kGy.

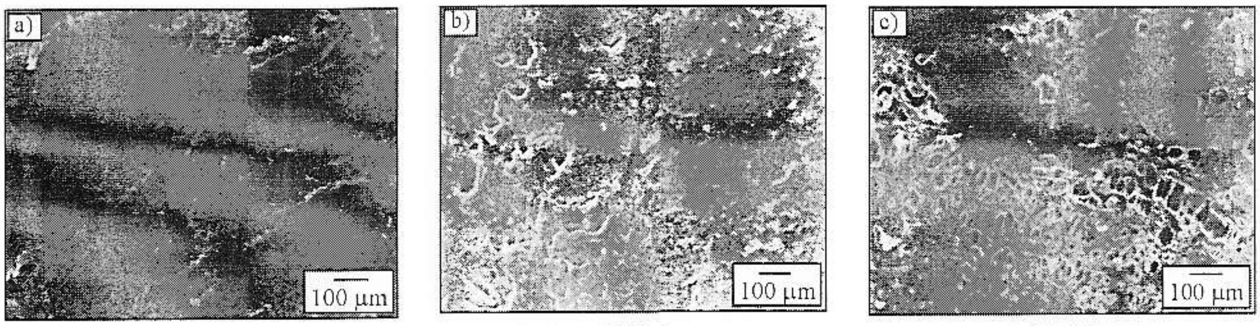
The morphologies are different for blends using star SBR-2 (Fig. 8): in general, they are less homogeneous than in blends with SBR-1 and there is more disintegration, with large number of particles of different shapes. The particle diameters increase until 100 microns or so. As blends with star SBR-1, the matrix begins to break at 150 kGy; at 250 kGy voids of more than 100 μm are formed.

For irradiated blends containing linear SBR-3, the surfaces drastically change, because multiple well-de-



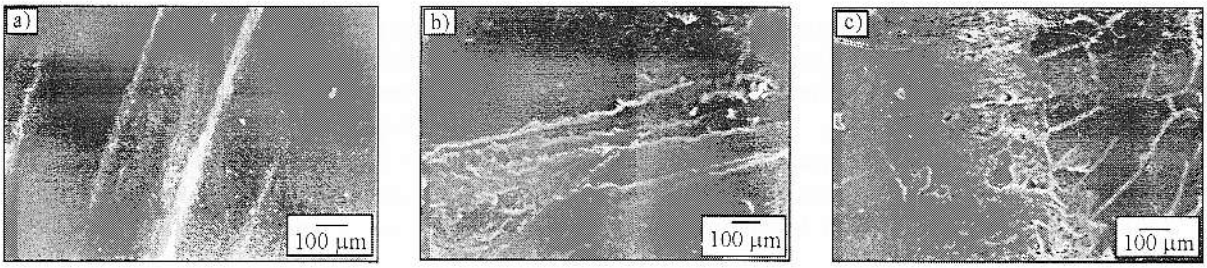
50 kGy 150 kGy 250 kGy

Fig. 7. Irradiated blends containing star SBR-1



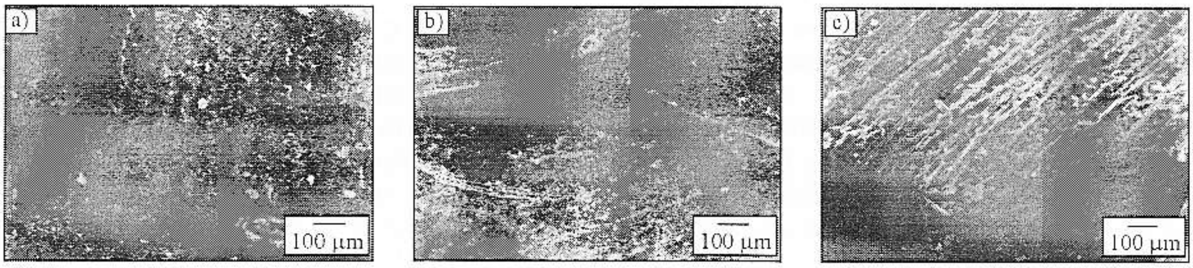
50 kGy 150 kGy 250 kGy

Fig. 8. Irradiated blends containing star SBR-2



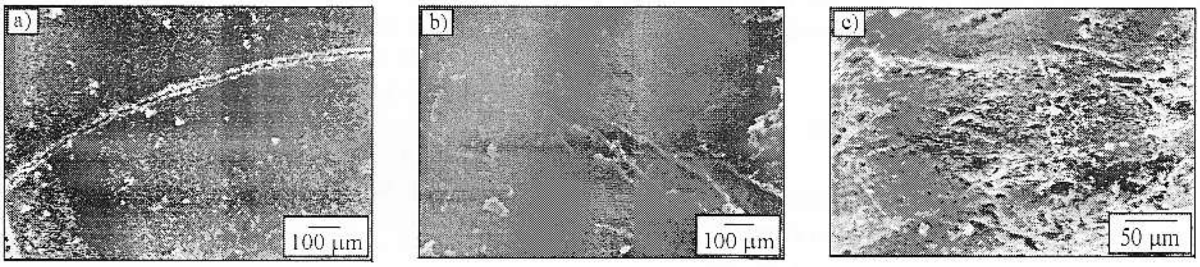
50 kGy 150 kGy 250 kGy

Fig. 9. Irradiated blends containing linear SBR-3



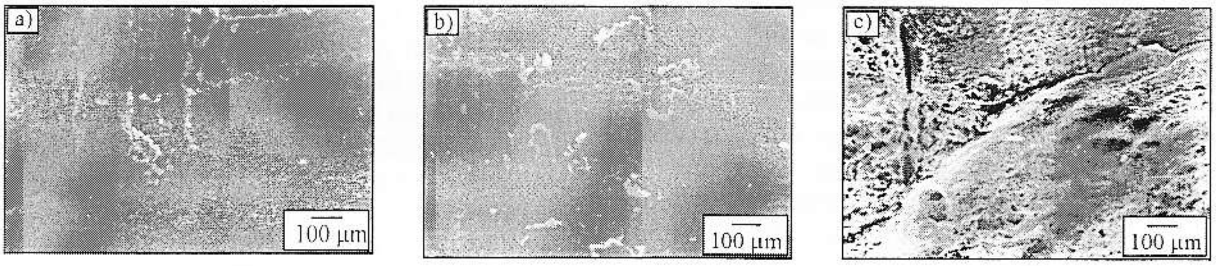
50 kGy 150 kGy 250 kGy

Fig. 10. Irradiated blends containing linear SBR-4



50 kGy 150 kGy 250 kGy

Fig. 11. Irradiated blends containing linear SBR-5



50 kGy 150 kGy 250 kGy

Fig. 12. Irradiated blends containing multiblock SBR-6

fined crazes with different lengths appear. Such behavior is observed since 50 kGy, where the crazes follow a preferential way and are 50 µm wide with a constant separation between them (Fig. 9a). The number of crazes is increasing when the dose increases to 150 kGy; they show branching on one hand and a large number of particles on the other (Fig. 9b). Finally, at 250 kGy poor surfaces are formed with branching crazes and several voids surrounded by particles clusters (Fig. 9c).

For linear SBR-4 with only 5 % of difference in butadiene content with respect to linear SBR-3, the blend morphologies are very different. We recall here that blends with SBR-4 show the highest impact values before and after irradiation [5]. At 50 kGy we see homogeneous surfaces with several particles but no crazes (Fig. 10a). This situation changes for 150 kGy (where the highest impact was obtained), because well-defined crazes are 20 µm wide on the average, and we see a large number of particles with similar diameters (Fig. 10b). In blends containing linear SBR-3 poor surfaces are found for 250 kGy; a considerable number of crazes following preferential ways are present (Fig. 10c).

In contrast to blends containing linear SBR-4, when linear SBR-5 is used, the surfaces are less homogeneous. At 50 kGy the crazes appear, with their length reaching 100 μm; they follow curved trajectories. Moreover, there are rubber particles of various sizes and shapes (Fig. 11a). Nevertheless, at 150 kGy these surfaces change, because multiple oriented crazes appear with different lengths (Fig. 11b) and a large number of rubber particles. At 250 kGy we find a detrimental effect of gamma-radiation that makes possible larger visible cracks; this is due to considerable number of particles with different shapes and sizes and mainly to the massive formation of voids with sizes larger than 100 μm (Fig. 11c).

Finally, when using multiblock SBR-6, the surfaces after irradiation are quite different from star and linear SBRs. For example, at 50 kGy some, but not well defined crazes appear. There are no rubber particles with large diameters (Fig. 12a). At 150 kGy particles with sizes larger than 150 μm are seen (Fig. 12b). The situation changes drastically at 250 kGy (as for star or linear SBRs) because of the presence of voids surrounding the crazes and a diversity of dispersed particles.

CONCLUDING REMARKS

The increasing of the butadiene content in SBRs and the gamma radiation improve the impact strength on one hand and deteriorate the microhardness on the other. Moreover, combining SEM and microhardness techniques, it was possible to evaluate and correlate both the morphological surfaces and the mechanical properties.

We find that not-irradiated and irradiated blends using linear SBRs, which turned our to be the best structures from the point of view of high impact resistance [5], show lowest microhardness values. Both characteristics are due to the morphological structures, which include an even spatial distribution of particles, homogeneous particle sizes and the absence of void formation. By contrast, star and multiblock structures in which a large number of crazes are present provide sites for craze propagation. We reiterate that crazes in our materials are largely caused by irradiation. This is in contrast to the much more frequent craze formation by impact or by other mechanical means. On the base of our results one can choose the best SBRs composition and structure as well as preferable radiation dosages for manufacturing high impact materials.

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REFERENCES

1. Bucknall C. B.: *„Toughened Plastics"*, Applied Sciences Publishers, London 1977, p. 187.
2. Rivera-Gastelum M. J., Robles-Vazquez O., Puig J. E., García Garduño M. J., Castaño V. M., Monroy V. M.: *Mater. Letters* 1993, **17**, 84.
3. Keskkula H.: *Adv. Chem. Series* 1989, **222**, 289.
4. Park I., Keskkula H., Paul D. R.: *J. Appl. Polym. Sci.* 1992, **45**, 1313.
5. Brostow W., Castaño V. M., Horta J., Martínez-Barrera G.: *Polimery* 2004, 49, 9.
6. Okamoto Y., Miyagi H., Kago M., Takahashi K.: *Macromolecules* 1991, **24**, 5639.
7. Martínez-Barrera G., Rojas J. M., Herrera R., Castaño V. M.: *Internat. J. Polymer. Mater.* 1997, **38**, 7.
8. Kramer E. J., Berger L. L.: *Adv. Polym. Sci.* 1990, **91/92**, 1.
9. Donald A. M: „Crazing" in „Performance of Plastics" (Ed. Brostow W.), Hanser, Munich-Cincinnati 2000, chapter 13.
10. Castaño V. M., Oliva E., del-Real A., Mexía P., Viquez S., Rivera E., Martínez E.: *Polym. Bull.* 1994, **32**, 693.
11. Young R. J., Lovell P. A.: *„Introduction to Polymers"*, Second Edition, Chapman & Hall, London, 1991, p. 234.
12. Goodier J. N.: *J. Appl. Mech.* 1998, **55**, 39.
13. Grocela T. A., Nauman E. B.: *Polym. Mater. Sci. & Eng.* 1990, **63**, 488.
14. Piorkowska E., Argon A. S., Cohen R. E.: *Macromolecules* 1990, **23**, 3838.
15. Loch F. C. e.a.: *Polymer* 1995, **36**, 2173.
16. Narisawa I., Kuriyama T., Ojima K.: *Makromol. Chem. Symp.* 1991, **41**, 87.
17. Cook D. G., Rudin A., Plumtree A.: *J. Appl. Polym. Sci.* 1993, **48**, 75.
18. Martínez-Barrera G., Vázquez F., Alvarez-Castillo A., López-Castañares R., Castaño V. M.: *Internat. J. Polym. Mater.* 2000, **46**, 27.
19. Martínez-Barrera G., Castaño V. M., Rodríguez R.: *Radn. Phys. & Chem.* 2004, **69**, 155.
20. Martinez-Barrera G., Menchaca C., Pietkiewicz D., Brostow W.: *Mater. Sci. Medziagotyra* 2004, **10**, 166.
21. Żenkiewicz M.: *Polimery* 2003, **48**, 66.

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