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INFLUENCE OF BUTADIENE/STYRENE COPOLYMERS ON THE MODIFICATION OF POLYPROPYLENE IN ELECTRON BEAM IRRADIATION

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Radiation chemistry of the system: styrene/butadiene/styrene (SBS) copolymer with polypropylene, has been investigated in the full range of proportions from 0% SBS–100% PP to 100% SBS–0% PP. Ionizing energy deposition is distributed to absorbing moieties according to their contribution to the electron pool in the material. The participation of primary ionization acts in constituents of low concentration is negligible, but these compounds take part in secondary reactions. These are detected by specific techniques for determination of transients, e.g., by electron paramagnetic resonance (EPR). Radiation generates alkyl radicals in the pure PP, which change subsequently into peroxide radicals in the presence of oxygen. At high concentration of SBS the transfer of paramagnetic centers $SBS^{\bullet} \rightarrow PP^{\bullet}$ is observed. Important product analysis methods, i.e., UV-Vis absorption spectrophotometry, can be applied in polymer chemistry only as diffuse reflected light spectrophotometry (DRS), described in the preceding paper, as a new approach to the radiolysis recognition. The presence of stable unsaturations formed by radiation are observed by DRS. These effects are drastically reduced already by the presence of 10% of SBS, what indicates intensive protection action and the transfer of single ionization spur sites.

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INTRODUCTION

In the last decades radiation processing of polymers has been developed on a large scale and commercially implemented, due to the availability of large gamma and electron beam sources of low LET (linear energy transfer) ionizing radiation. Many basic questions are not answered yet and also the number of possible combinations of polymers and blends remains far from being exhausted. Radiation chemistry of polymers shows that in spite of identical starting point of reactions, *i.e.*, the single ionization spurs (80% of deposited energy, almost independently of the kind of polymer), a diversity of subsequent chemical reactions occurs, specific for particular types of polymers. These reactions are influenced by additives present for the purpose of conventional processing and by uncontrolled reagents like the oxygen in surrounding atmosphere which is extremely reactive with free radicals formed by the interaction of ionizing radiation in the polymer. Although the primary products induced by radiation are formed randomly in particular moieties of the material, in the proportion resulting from their electron participation in the mixture or blend, the transfer of energy in the initial stage or transfer of intermediates occurs in subsequent stages of the development of reactions. As a result, a variety of final products is formed, identified in the course of product analysis. The latter involves stable products as well as intermediates of different stability.

Radiation processing of polymers, applied for the purpose of modification of properties, is connected with radiolytic changes in molecules of components and additives. Ionizing energy deposition is distributed to absorbing moieties according to their contribution to the electron pool in the material. The participation of primary ionization acts in components of low concentration is negligible, but these compounds take part in secondary reactions described by mechanisms of energy transfer. These are detected by product analysis and specific techniques for determination of transients, *e.g.*, by electron paramagnetic resonance (EPR). Important product analysis methods, *i.e.*, UV-Vis absorption spectrophotometry can be applied in polymer chemistry only as diffuse reflected light spectrophotometry (DRS), applied to irradiated polypropylene [1,2].

The remaining 20% of the energy deposited in the polymer appears in multi-ionization spurs with products different from these which are produced in the dominating single-ionization spurs. That phenomenon is common for all irradiated media, liquid and solid [3] and has to be taken into account also in the field of radiation chemistry of polymers. Accumulation of substantial amount of energy in a narrow region of the chain causes its scission, followed by formation of new terminals. Single ionization spurs usually do not cause chain scissions.

The basic radiation induced reaction, originating mainly from single ionization spurs is dehydrogenation (abstraction of hydrogen), causing eventually the formation of unsaturated moieties in the polymer, and very different secondary consequences, from crosslinking to degradation. Both types of reactions are running simultaneously, but in polyethylene the final crosslinking is dominating, being the base of production of heat-shrinkable polymers, whereas in polypropylene radiation leads the degradation. The latter phenomenon spoils the application of polypropylene, undergoing radiation processing, if proper additives are not applied. Ethylene-polypropylene copolymers have a comparatively good radiation resistance because negative effects of polypropylene degradation are counterbalanced by the crosslinking of polyethylene.

Aromatic compounds are more resistant towards ionizing radiation because of mechanisms directing the dissipation of energy straightforward into heat. That property of aromatics, also of polymers with aromatic moieties, is responsible for protection against radiolysis of aliphatic blocks present in the material. Therefore butadiene-styrene elastomer is more resistant towards the ionizing radiation than polybutadiene rubber expressed *e.g.*, by radiation yield of hydrogen. In our previous paper [4], effects of radiation on PE-linear SBS have been described. In another investigation, the elongation at break of PE-SBS blend (50–50) increased two times after the dose of 100 kGy [5,6] as the result of crosslinking (gel content in the blend after irradiation was 73%). The conclusion was supported by results of EPR experiments. Processes in PE-SBS blends with 25, 50 and 75% of SBS were not the simple sum of processes observed in neat PE and neat SBS polymer, what indicates interactions between the two components of the blend. Previous papers show, that irradiation of PP causes 10 fold increase of the MFI (melt flow index), influences the mechanical properties: elongation at break is lowered. Irradiation of PP-SBS blends show improvement of properties.

The aim of the present study is the investigation of the absorption of ionizing energy in PP-butadiene/styrene block copolymer blends in a

full range of proportions, which helps to explain the mechanisms of energy transfer. The investigation on microscopic and mechanical properties, as well as of radiation chemistry of PP/SEBS (hydrogenated SBS triblock copolymer-styrene-ethylene/butylene-styrene block copolymer, [Kraton G1652], styrene content 30%) blends will be described in subsequent papers.

EXPERIMENTAL

The polymers used were styrene-butadiene-styrene triblock copolymer, SBS of linear structure (Cariflex 1102), styrene content 29%; styrene-butadiene-styrene triblock copolymer (SB)_x, of radial structure (Cariflex 1184), styrene content 30%; isotactic polypropylene, iPP for injection molding (Malen J400). Polypropylene-SBS copolymer blends (0–100%) were obtained by double melt mixing in a single-screw extruder. Samples for mechanical tests, as well as for diffuse reflectance spectrophotometry (DRS) and electron paramagnetic resonance (EPR) were prepared by compression molding at 180°C.

Irradiation was effected with the scanned beam of 10 MeV (high monochromacity) electrons from the linac LAE 13/9 in the Institute of Nuclear Chemistry and Technology in Warsaw (INCT). Samples were irradiated with doses of 30, 60 and 100 kGy, whereas only the 30 kGy dose was applied in one irradiation act, resulting in a tolerable adiabatic increase of temperature [7]. Higher doses were applied by split dose technique, with the separation of irradiations by periods of cooling, at room temperature.

Gel content was determined by extraction with boiling xylene, melt flow index was determined in Zwick Plastometer; crystallinity of polypropylene was determined by differential scanning calorimeter (DSC), from Polymer Laboratories, in nitrogen atmosphere, at a heating rate of 10 deg/min, assuming enthalpy of fully crystalline polymer $\Delta H_m^0 = 290 \text{ J/g}$. The EPR measurements were performed with a Bruker ESP 300 Spectrometer (INCT) at room temperature under the following conditions: modulation amplitude of 0.35 mT, microwave power of 2 mW and sweep width of 20 mT. A reference sample of $0.5 \times 10^{-4} \text{ M}$ DPPH solution in benzene was applied for quantitative analysis. As the area under experimental spectrum is proportional to the number of unpaired spins, the result of double integration of the first derivative EPR signals were compared with those of the standard (DPPH) and the number of free radicals per gram was determined for some samples. Spectra were recorded 3 hours after irradiation and those irradiated with the dose of 60 kGy were investigated additionally 3 days and 3 weeks after the irradiation, as well as 7 months later.

Diffuse reflectance absorption spectra (DRS) were recorded on Perkin-Elmer Lambda 9 spectrophotometer with light integration sphere.

RESULTS AND DISCUSSION

SBS copolymers, both linear and radial, show identical EPR spectra after doses of 30 and 60 kGy. As was proved earlier [4], the EPR signals can be ascribed to one type of paramagnetic product. Spectra recorded at wide range of microwave power (0.02–20 mW) as well as those taken after few weeks from irradiation do not change shape. It seems that this type of signal can originate from anisotropic interactions of two equivalent protons of hyperfine splitting equal $A_{\text{iso}} = 1.10$ mT and $g_{\parallel} = 2.0006$ and $g_{\perp} = 2.0065$. It will be shown in the next paper that in hydrogenated SBS, the number of radicals decreases sharply in comparison to the SBS polymer containing double bonds. Although the hyperfine splitting in that case is also ca. 1.10 mT, the number of lines is reduced to two.

The EPR spectrum of polypropylene is composed of 7% from the peroxide radical signal and 93% from the spectrum of the alkyl radical. The conversion of alkyl radicals into peroxide radicals is explained by the ease with which oxygen molecules can penetrate intermolecular spaces in polypropylene. In the PP-SBS (50:50) mixtures, the rate of this process increases dramatically, because as is seen from the analysis of EPR spectra, 80% of primary products after the dose of 30 kGy and 61% after the dose of 60 kGy are oxidized to peroxide radicals; the rest of the composed spectra are alkyl radicals from PP. It is remarkable that in irradiated copolymers composed of chains of PS and PB, the paramagnetic product decays slowly, without conversion to peroxide radical, visible in the EPR spectrum. The presence of SBS in the mixture with PP creates conditions which allow an easier access of oxidizing agent to alkyl radicals in polypropylene. The relative participation of peroxide radicals in mixtures irradiated to 30 kGy is higher, indicating the increasing effect of influence of elastomere on the radiolysis of PP with the diminishing dose of radiation.

The concentration of radicals in all investigated polymers and their mixtures, after 7 months of storage at room temperature is on the limits of detection by EPR: their concentration is not higher than 1–2% of the initial concentration. In this case, for the samples in which PP is present (PP, PP-SBS), the shape of the signal indicates the trace amount of peroxide radical, but signal of paramagnetic products in copolymer SBS preserve the character of the spectra recorded immediately after the irradiation. Changes of peroxide radicals concentrations observed by EPR correspond with changes in the

crystalline structure in the investigated mixtures. The presence of 50% of SBS copolymer causes the increase of concentration of the crystalline phase in the PP matrix, which may suggest that the presence of copolymer increases the concentration of crystalline nucleation. That view is supported by the fact of lower melting temperature of crystallites, in the case of homo-polypropylene as well as in polypropylene mixed with elastomere. After a dose of 60 kGy, the concentration of crystalline phase in the PP and in the PP matrix in the mixtures PP-SBS is similar to that before irradiation—there is no reason to assume otherwise.

Figure 1a, b, c shows the experimental EPR spectra of PP-SBS blends as function of time elapsed after 60 kGy irradiation at room temperature and the storage at the same temperature. Figure 2 shows the decay of radicals expressed as concentration of spins. The yield of all radicals is close to 0.53 per 100 eV of absorbed energy (or 0.055 $\mu\text{moles per J}$ in the SI system). The precision of the measurement of yields of spin, by comparison with the concentration of spins in DPPH (a standard practice in the EPR method), measured in the same conditions, is 25%, but even taking the upper confidence limit, the yield is equivalent to the 20% energy-yield of multi-ionization spurs. It is an open question if that coincidence is meaningful. Discussion of EPR results in comparison to investigations on crystallinity of blends and results of mechanical investigation on irradiated material will be described in the next paper.

The spectroscopic investigations (diffuse reflectance spectrophotometry, DRS, [8]), were performed on samples of the same composition. The method allows to record optical absorption spectra in polymer blends of poor transparency. Figure 3 shows the spectra of products absorbing in UV, in irradiated blends of polypropylene containing no SBS, 10, 25 and 75% of SBS and the SBS alone. The products exhibit absorption band at 312 nm and are more stable than free radical products (except peroxides) observed by the EPR method. Although a precise identification of these semi-stable products is not possible at present, the most probable explanation of the UV absorption is that it is due to unsaturated moieties (UM) in the polypropylene chain. However, there is a striking difference between the dependence of the concentration of unsaturated species on the aliphatic-aromatic proportion. In our case, the fact of dramatic reduction of formation of UM already by 10% addition of SBS is a remainder of the classic concave curve of radiolysis of a aliphatic-aromatic mixture in radiation chemistry. The radiolysis of aromatic component is not only less extensive in comparison to the aliphatic participant, but also a protection effect is exhibited by the aromatic participant.

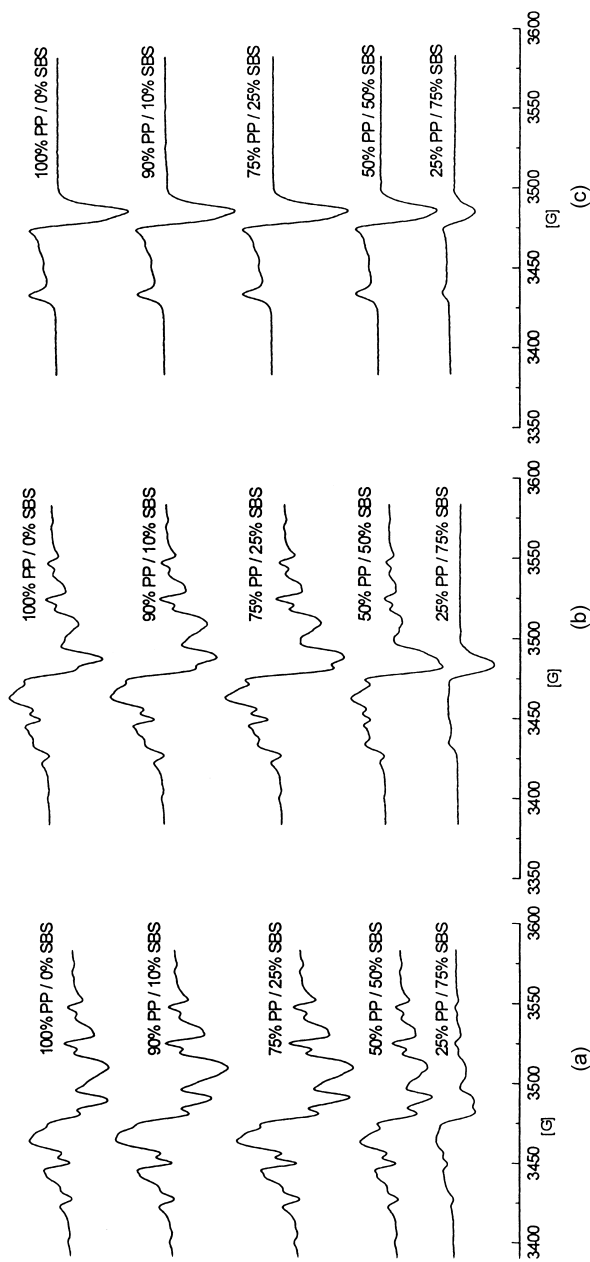


FIGURE 1 EPR spectra of PP and PP-SBS blends after 60 kGy dose of 10 MeV electron beam irradiation, in the function of time elapsed after irradiation. (a) Immediately after irradiation, (b) 3 hours after irradiation, (c) 3 days after irradiation.

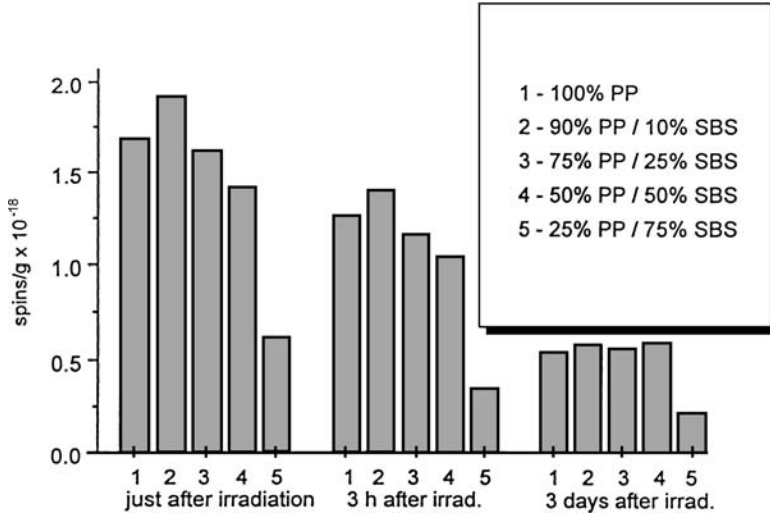


FIGURE 2 Concentration of spins in PP and PP-SBS blends, after 60 kGy dose of 10 MeV electrons in the function of elapsed time.

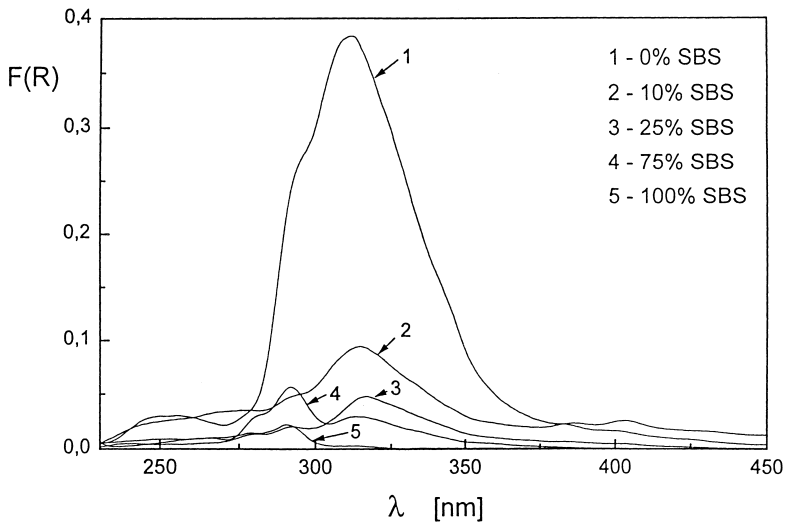


FIGURE 3 Diffuse reflectance absorption spectra of PP, PP-SBS blends, and SBS after the 60 kGy dose of 10 MeV electrons. All spectra are measured against unirradiated sample, therefore they show only absorption of species formed in the result of radiolysis.

The phenomenon is explained by energy transfer of single-ionization spurs to the energy dissipating constituent. Such transfers can happen only with single ionizations and excitations, which are able to move inside the macromolecule and to and from the neighbor molecule. The best argument for that is the fact that 10% of SBS in the blend is absorbing only 10% of energy but the secondary effect exceeds much that 10% participation.

The same PP-SBS systems show opposite picture in the EPR investigation: In Figure 2, which shows the yield of spins in irradiated samples, there is no significant diminution of radical concentration in the blend containing 10–50% of SBS immediately after irradiation, and 3 hours after irradiation. This strange difference can be explained only by discussion of early stages of radiolysis in polymers, possibly in terms of single- and multi-ionization spurs. As it is known in general radiation chemistry, the products of both kinds of spurs are more or less different, depending on the chemistry of the irradiated system. In the case of low linear transfer of energy (LET) radiations, *i.e.*, γ and high energy electrons, ca. 80% of energy is deposited in single-ionization spurs, responsible for free radicals, and the rest is located in multi-ionization spurs, which produce mainly the debris of a region of the molecule and in the case of polymers cause the irreparable scission of the chain. Therefore two loose ends of a chain are formed, with terminals different from those formed by single ionizations. The location of multi-ionization spurs is completely random and is not a subject to any energy transfer, or modification, as it is in the case of single ionization spurs.

CONCLUSIONS

Ionizing radiation generates in pure polypropylene alkyl radicals $-\text{CH}_2\text{C}^*(\text{CH}_3)\text{CH}_2-$, which change subsequently into peroxide radicals in the presence of oxygen. In compositions with SBS, the rate of peroxide radicals formation increases, but even at an SBS content of 75% the EPR spectra do not show signals characteristic for that copolymer. After three days all samples show the presence of peroxide forms exclusively. Experiments do not show signs of formation of one phase by the PP and SBS, but comparatively high “surplus” of PP radicals seems to indicate the transfer of paramagnetic centers $\text{SBS}^* \rightarrow \text{PP}^*$. There is no correlation of DRS results in the PP-SBS mixtures, with EPR results. Optical results do show rather the presence of stable unsaturations formed by interaction of radiation energy. These effects are drastically reduced by a mere 10% addition of

SBS, indicating an intensive protection action and the transfer of single ionization spur sites.

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