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Application of Electron Beam Radiation to Modify Crosslink Structure in Rubber Vulcanizates and Its Tribological Consequences

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The aim of this work was the modification of crosslink density and structure of rubber vulcanizates in order to control surface energy, mechanical strength under static as well as dynamic conditions and in consequence, tribological properties of the materials. Sulphur vulcanizates of styrene-butadiene rubber, filled with carbon black, were subjected to electron beam radiation in the range from 150 to 200 kGy. Changes in crosslink density and structure were determined applying the method of selective swelling of rubber in "hard" and "soft" solvents. The modification influences the ability of material of energy dissipation and its surface wettability. The changes are discussed from the friction and abrasion of rubber point of view.

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1. Introduction

According to the mechanistic theory of friction proposed by Moore, friction force is considered as a superposition of adhesional and hysteretical components [1]. This approach seems to be oversimplified, especially for rubber vulcanizates — the materials for which crosslink density and structure decide of their engineering and functional properties. The higher the crosslink density, the harder and stiffer the material. Short C–C and monosulphide crosslinks make rubber vulcanizates more elastic, whereas long polysulphide ones, due to their lability, improve their damping properties. The higher the crosslink sulphidity, the higher the surface energy of rubber vulcanizates, especially its polar component [2]. By modifying crosslink density and structure one can control engineering and functional properties of the materials, e.g. mechanical strength, friction, abrasion, adhesion or wettability. It is well known that ionizing radiation, e.g. electron beam (EB), applied to rubber produce macroradicals, which depending on its macromolecular structure, result in material crosslinking or degradation [3]. It seems likely that action of EB radiation can also result in modification of crosslink structure of rubber vulcanizates [4, 5]. The paper presents the influence of treatment applied to sulphur vulcanizates of styrene-butadiene rubber (SBR) on their tribological properties.

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2. Experimental

2.1. Materials

Rubber mixes of SBR (Ker 1500, Synthos, Poland), filled with 40 phr of high abrasion furnace carbon black — HAF (N 330), were prepared with a laboratory two-roll mill. The samples crosslinked to similar crosslink density with various sulphur systems (Table I) were vulcanized at 160 °C during time $\tau_{0.2}$, determined rheometrically according to ISO 3417.

The conventional SBR vulcanizates were compared to the rubber samples subjected to EB irradiation. The rubber mixes after moulding at 160 °C, during the time selected experimentally in order to get shaped, were modified by EB radiation of a dose 150 kGy and 200 kGy. The e-beam irradiation of studied materials has been carried out in the Elektronika 10/10 linear accelerator located at the Institute of Nuclear Chemistry and Technology, Warsaw, Poland. The samples have been placed in the horizontal position in the front of the pulsed, scanned beam and the total doses were obtained by multipass exposure (25 kGy per pass). The irradiation conditions were as follows: energy 10 MeV, pulse current 470 mA, pulse frequency 400 Hz. Maximum electron range in the vulcanizates was *ca.* 4.5 cm, the used range 2.5 cm. Dosimetry of electron beam was performed using graphite calorimeter; the measuring error ±4%.

TABLE I

Rubber samples before modification.

No.	Sample	Crosslink structure [%]			$\nu \times 10^{-5}$
		C–C and C–S–C	C–S_2–C	C–S_n–C	[mol/cm^3]
1.	TMTD	88.0	5.6	6.4	21.2
2.	S_8 + MBTS	0.0	81.2	18.8	34.1
3.	S_8 + DPG	40.2	16.3	43.5	24.5

TMTD — SBR crosslinked with tetramethylthiuram disulphide;
S_8 + MBTS — SBR crosslinked with sulphur and mercaptobenzothiazol sulphenamide;
S_8 + DPG — SBR crosslinked with sulphur and diphenylguanidine

TABLE II

Rubber samples after EB irradiation.

No.	Sample	Crosslink structure [%]			$\nu \times 10^{-5}$
		C–C and C–S–C	C–S_2–C	C–S_n–C	[mol/cm^3]
1.	TMTD				
	150 kGy	83.0	7.6	9.4	25.2
	200 kGy	83.0	8.9	8.1	27.5
2.	S_8 + MBTS				
	150 kGy	56.2	11.7	32.1	35.5
	200 kGy	51.5	16.0	32.5	39.7
3.	S_8 + DPG				
	150 kGy	59.9	9.4	30.7	38.3
	200 kGy	58.5	7.8	33.7	39.5

TMTD — SBR crosslinked with tetramethylthiuram disulphide;
S_8 + MBTS — SBR crosslinked with sulphur and mercaptobenzothiazol sulphenamide;
S_8 + DPG — SBR crosslinked with sulphur and diphenylguanidine

2.2. Techniques

2.2.1. Crosslink density and structure

Crosslink density of rubber samples was calculated from the equilibrium swelling in toluene data, applying the Flory–Rehner equation [6]. Structural composition of crosslinks was evaluated according to the procedure described by Saville and Watson [7], based on selective dissolving of crosslinks in thiol — amine solvents (OTAM/OTAT).

2.2.2. Mechanical properties

Mechanical modulus of rubber samples at 100% elongation (S_{100}) was determined according to ISO 37. Hardness (H, °Sh A) of the vulcanizates was measured according to PN-80/C-04234.

2.2.3. Surface energy

Surface energy of rubber samples was calculated from values of contact angle for water and diiodomethane, determined with a K 100 tensiometer (Krüss, Germany). Its polar and dispersive components were calculated based on the approach proposed by Owens and Wendt [8].

2.2.4. Friction characteristics

Experiments were run with a T-11 ball-on-plate tribometer (ITeE — PIB, Poland). 6.35 mm stainless steel ball was pressed with normal load of 5 N to rubber plate, rotated with 35 rpm. Friction parameters were derived from friction characteristics, registered for 15 min, according to the procedure described earlier [9]. Wear of the rubber samples was determined gravimetrically and analyzed with an optical microscope BX-40 (Olympus) under magnification of 50–100×.

3. Results and discussion

Ionizing radiation makes maturing of crosslinks, reducing the amount of poly- and disulphide crosslinks in favour to monosulphide and C–C ones (Table II).

Decreasing crosslink sulphidity of rubber S, calculated as

$$S = \frac{n_1 + 2n_2 + 3n_3}{100},$$

where n_1, n_2 and n_3 — the amounts of the types of crosslinks [%], mono-, di- and polysulphide, respectively, which results in lower polarity of rubber surface (Fig. 1).

The changes to crosslink density correlate to those of mechanical modulus (S_{100}) and hardness (H) of rubber. Higher crosslink density makes rubber more elastic and harder (Fig. 2).

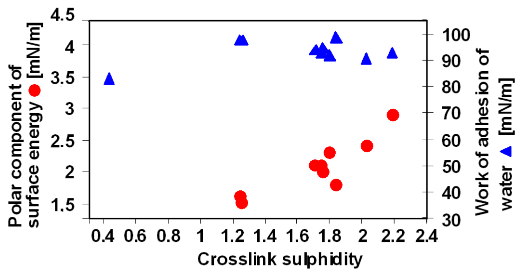

Fig. 1. Influence of crosslink sulphidity on the polar component of surface energy of rubber.

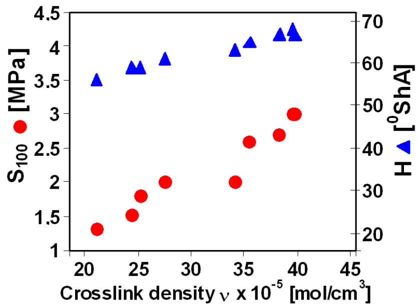

Fig. 2. Influence of crosslink density on mechanical properties of rubber.

Lower polarity of rubber surface, together with its higher stiffness and resulting lower damping, produced by EB radiation, make friction force (T) and abrasion wear of the material decreasing (Fig. 3a–c).

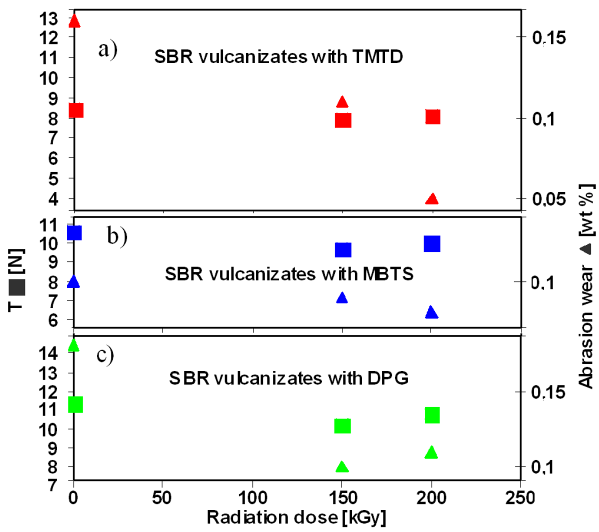

Fig. 3. Influence of EB irradiation on friction force (T) and abrasion wear of rubber SBR vulcanizates with (a) TMTD, (b) MBTS, and (c) DPG.

Increase of crosslink density and the modification of crosslink structure are decisive factors for friction characteristic of rubber working according to the mechanism proposed by Bowden and Tabor [10]. The modification changes mechanism of rubber wear from fatigue originated to abrasion, which results in increase of material durability on service.

4. Conclusions

1. EB radiation of sulphur vulcanizates makes the content of weak di- and polysulphide crosslinks of the lowest energy reduced in favour to monosulphide and C–C ones, lowering crosslink sulphidity.

2. Increase of crosslink density, associated with the modification, correlates with changes to mechanical moduli and hardness of rubber. The effect is mainly related to the additional C–C crosslink being created.

3. Polar component of the surface energy of rubber decreases due to EB radiation of SBR. Together with the increase of mechanical modulus and simultaneous decrease of material damping, due to the increase of crosslink density and the modification of crosslink structure, they result in lower friction and wear of rubber.

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