Effect of electron beam irradiation on structure and properties of styrene-butadiene rubber

Katarzyna S. Bandzierz[a],[*], Louis A.E.M. Reuvekamp[b], Grażyna Przybytniak[c], Wilma K. Dierkes[b], Anke Blume[b], Dariusz M. Bieliński[a]

[a] Institute of Polymer and Dye Technology, Lodz University of Technology, Stefanowskiego 12/16, Lodz 90-924, Poland
[b] Elastomer Technology & Engineering, University of Twente, Drienerlolaan 5, Enschede 7500 AE, The Netherlands
[c] Centre of Radiation Research and Technology, Institute of Nuclear Chemistry and Technology, Dorodna 16, Warsaw 03-195, Poland

ARTICLE INFO

ABSTRACT

Crosslinking and chain scission occur simultaneously during irradiation of polymers and influence their properties in an opposite way. To characterize the radiation-induced changes and evaluate how they influence the performance of the polymer, quantification of these reactions is crucial. In this work, the effect of styrene-butadiene rubber (SBR) radiation curing with doses ranging from 25 kGy to 200 kGy, at room temperature and air atmosphere was investigated. The Charlesby-Pinner and Charlesby-Rosiak equations were used to characterize the curing process. Only the Charlesby-Rosiak equation gave good linear representation of the data and allowed to obtain the parameters, which characterize the irradiated SBR system: (i) gel dose, (ii) ratio between chain scission and crosslinking, and (iii) radiation yields of crosslinking and chain scission. These parameters showed that SBR is quite resistant to ionizing radiation, where crosslinking predominates over chain scission. The effect of irradiation on in-rubber properties is discussed. An increase in radiation dose resulted in change of tensile strength, elongation at break, mechanical modules, hardness, glass transition temperature and thermo-oxidative stability. Freezing point depression experiments were also conducted. The depression of the solvent freezing temperature in swollen polymer gels provided information on polymer network and mesh size, staying in agreement with the crosslink density values.

1. Introduction

The action of ionizing radiation on polymers causes changes in their structure, which results in their modification and alteration of performance. The degree of change of a particular property per unit of absorbed energy is characterized by radiation resistance (Klinshpont et al., 1994). This parameter provides information to what extent the polymer can be modified by ionizing radiation. The radiation resistance, and predominant reactions, which occur in the polymer during its irradiation, are dependent on several factors: (i) chemical structure of the macromolecules; (ii) physical nature of the polymer; (iii) type and amount of additives present in the irradiated system; and (iv) conditions of the irradiation process.

Due to the fact that ionizing radiation carries very high energy, it affects all components of the material, proportionally to their electron participations (Głuszewski and Zagórski, 2003). In other words, it is non-selective and interacts with the whole bulk of the material. When ionizing radiation is absorbed, radicals are generated in the system.

Since radicals are very reactive and usually short-living, they react very fast. The occurring reactions are very complex, and can lead to: crosslinking, chains scission, change in number and character of double bonds, cyclization, isomerization, oxidation, emission of low-molecular gas products (e.g. H_2 and CH_4), and the like (Gehman and Gregson, 1960; Böhm and Tveekrem, 1982). Many of these reactions occur simultaneously and to different extent, causing changes in the molecular structure of the polymers.

Basically, in a radiation-induced modification of polymers, the largest influence on properties have commonly two types of reactions: crosslinking and chains scission. Crosslinking is a chemical reaction that results in the formation of a chemical bond between the polymer chains. Chain scission is a reaction, which causes the breaking of a main-chain bond of a polymer macromolecule. According to the mechanism of the first reaction, the generated macroradical finds in its vicinity a partner chain to recombine. As a result a chemical bond – a carbon-carbon (C-C) crosslink – is formed between the recombining chains. The crosslinks increase the molecular weight of the polymer.

Subsequently, due to these crosslinking reactions the curing process is taking place, i.e. a chemical process of converting polymer chains into a uniform, permanent and durable three-dimensional network. In radiation curing, addition of curatives is not required. Due to that, the radiation cured rubber consists only of the polymer chains connected via crosslinks. Consequently, the "isolated effect of crosslinks" can be obtained (Fox and Loshaek, 1955). In the second type of reaction – chain scission, the macroradical does not find a partner to recombine. As a result, a structural rearrangement occurs, leading to breakage of the polymer backbone chain and formation of new dangling ends. Chains scission is therefore counterproductive to crosslinking and brings opposite changes: it causes lowering of the crosslinking effectiveness and deterioration of the properties of the material. However, the chain scission, which is an undesirable reaction, always accompanies crosslinking and cannot be eliminated. Commonly, one of the reactions predominates over the other and has a strong influence on the modification of the structure and resulting properties.

Nowadays, the most commonly used type of radiation-induced modification of polymers is crosslinking (Clough, 2001). Among polymers prone to crosslink, there is a large group of rubbers, including hydrogenated acrylonitrile-butadiene rubber (HNBR) (Bik et al., 2004; Zagórski, 2004; Das et al., 2005), acrylonitrile-butadiene rubber (NBR) (Hill et al., 1996; Yasin et al., 2002; Stephan et al., 2007; Vijayabaskar et al., 2008), styrene-butadiene rubber (SBR) (Witt, 1959; Anderson, 1960; Shaltout, 2009; Wang et al., 2009; Ali et al., 2013; Wang et al., 2016; Moustafa et al., 2011), natural rubber (NR) (Moustafa et al., 2011; Charlesby and von Arnim, 1957; Bauman, 1960; Mullins and Turner, 1960; Minoura and Asao, 1961; Manaila et al., 2014), ethylene-propylene copolymer (EPM) and ethylene-propylene-diene terpolymer (EPDM) (Geissler et al., 1978; Vroomen et al., 1991; Zaharescu and Podină, 2001; Chowdhury and Banerji, 2005), polybutadiene (BR) (Parkinson and Sears, 1967; Kozlov et al., 1969; Hayashi et al., 1980; Shen et al., 1995), chloroprene rubber (CR) (Hill et al., 1993), silicone rubber (Frounchi et al., 2006). The properties of rubbers, such as hardness, tensile strength and elongation at break, are strongly dependent on the presence of crosslinks (Coran, 2013), therefore irradiation of rubbers has a profound effect on their performance.

Incipient polymer network spanning the entire system is formed at a gel point, i.e. when statistically one crosslink is formed per one initially existing polymer chain in the irradiated system. To reach the gel point, the absorption of a particular amount of energy in a form of ionizing radiation is required. Hence, this energy is named gel dose (D_g). The existence of the gel point is probably related to the presence of antioxidants and photostabilizers (mainly derivatives of amines or phenols) which are added to commercially available rubbers, residues of polymerization regulators and other non-rubberous compounds (Bik et al., 2004). They act as energy traps (Ferry et al., 2012), also referred to as antirads (Anderson, 1960; Bauman, 1960; Clough et al., 1991), energy sponges (Manion and Burton, 1952; Burton and Patrick, 1954; Burton and Lipsky, 1957) and energy sinks (Witt, 1959). When the material is irradiated, mostly affected is its main component: the polymer matrix (Głuszewski and Zagórski, 2003). Part of the energy of ionizing radiation, as well as the radical centers formed on the polymer chains, are transferred from the polymer to these substances. They absorb the excitation energy and dissipate it. Furthermore, these substances trap the radicals and form inactive end products. Accordingly, the number of formed radicals is reduced at this stage. The polymer matrix is therefore stabilized, and this hinders to some extent crosslinking and degradation. During the irradiation process these substances "sacrifice" themselves (Ferry et al., 2012) and are progressively consumed (Davenas et al., 2002). Finally, when they are used up, more pronounced changes in the polymer structure begin. It is also possible that some oxygen, which can be present in the irradiated material, can react with formed radicals and produce slow-reacting peroxy radicals. This could contribute to inhibition of radiation-induced initial reactions.

During irradiation, the formation of the polymer network and its

degradation occur simultaneously. Since both have considerable influence on the resulting properties of the polymer, it is important to investigate these reactions. Charlesby and Pinner (1959) were the first to quantify the number of reactions of chain scission versus crosslinking in 1959. They proposed a straightforward formula, relating the sol fraction to the radiation dose:

$$s + \sqrt{s} = \frac{p_0}{q_0} + \frac{2}{q_0 u_{w,0} D} \tag{1}$$

where:

s – sol fraction (mass fraction of the dissolved material that is constituted of molecules of finite relative molecular masses (Alemán et al., 2007)); [–]; p_0 – degradation density, average chain scission per unit radiation dose [kGy^{-1}]; q_0 – crosslinking density, average crosslinking per unit radiation dose [kGy^{-1}]; $u_{w,0}$ – weight-average degree of polymerization of the primary polymer chains [–]; D – radiation dose [kGy].

This expression is based on several assumptions:

– Chain scission and crosslinking occur at random spatial distribution and proportionally to the radiation dose;
– Ratio between chain scission and crosslinking is constant over the whole range of doses;
– Initial molecular weight distribution is random: $\overline{M}_w/\overline{M}_n = 2$ (where: $\overline{M}_w$ is weight-average molecular weight and $\overline{M}_n$ is number-average molecular weight);
– Crosslinking leads to formation of tetra-functional crosslinks X, not tri-functional endlinks Y;
– Other unidentified factors do not contribute to the process.

Plotting $s + \sqrt{s}$ as a function of $1/D$ leads to a linear relation. After its extrapolation, the p_0/q_0 value is obtained as the intercept of the function with ordinates, thus at $D \rightarrow \infty$. The gel dose D_g can be obtained as a value in which $s + \sqrt{s} = 2$. Since the Charlesby-Pinner model was developed, it has been commonly used to characterize various radiation-modified polymer systems (Bik et al., 2004; Stephan et al., 2007; Liu et al., 2012; Hearon et al., 2013; Svoboda, 2015; Morshedian et al., 2015). However, deviations in the $s + \sqrt{s}$ vs $1/D$ curves are common (Lawton et al., 1958; Wippler, 1958; Turner, 1963; Kitamaru et al., 1964; Kang et al., 1967; Saito et al., 1967; Zhang et al., 1985; Olejniczak et al., 1991; Rosiak, 1998; Shyichuk and Tokaryk, 2005). The graphic representation is often not a straight-line relation, but a concave upward ($\overline{M}_w/\overline{M}_n < 2$) or concave downward ($\overline{M}_w/\overline{M}_n > 2$) (Fig. 1).

The main reason of these deviations is ascribed to an initial molecular weight distribution which is not random, i.e. $\overline{M}_w/\overline{M}_n \neq 2$. In such a case, the Charlesby-Pinner equation is not valid and the plotted experimental data do not fit to the theoretical model. As a result, the parameters characterizing radiation-induced changes are difficult to
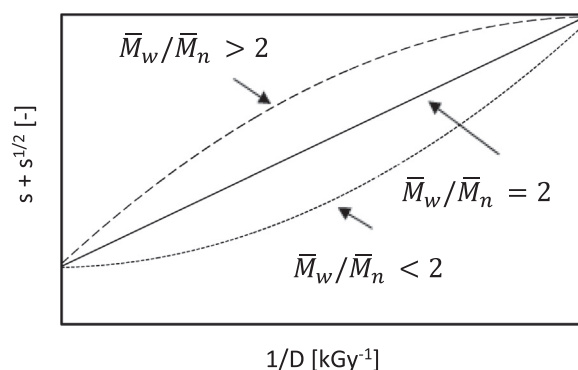

Fig. 1. Graphical representation of data for polymers with various initial molecular weight distributions, according to the Charlesby-Pinner equation.

evaluate.

To overcome this limitation and evolve a versatile approach, the Charlesby-Pinner model was extended by Olejniczak et al. (1991) resulting in the Charlesby-Rosiak equation. The authors introduced a concept of "virtual dose" D_v which is a correction for non-random molecular mass distribution. According to them, the dose D_g required for the real polymer to reach the gel point, for the virtual system is $D_g + D_v$. The modified Charlesby-Pinner equation by Olejniczak and Rosiak has the following form (Olejniczak et al., 1991):

$$s + \sqrt{s} = \frac{p_0}{q_0} + \left(2 - \frac{p_0}{q_0}\right)\left(\frac{D_v + D_g}{D_v + D}\right) \tag{2}$$

To obtain the values of p_0/q_0 and D_g, the intercepts at $D \to \infty$ and $s + \sqrt{s} = 2$ need to be determined in the coordinates $s + \sqrt{s}$ vs $1/D$, respectively. The value of D_v can be evaluated from the slope of the plot $(s + \sqrt{s} - p_0/q_0)$.

Another parameter characterizing the changes induced by ionizing radiation in the polymer, is G_x, the radiation yield of the crosslinking. This value provides information on the amount of new bonds formed per unit of absorbed energy. Accordingly, G_s, the radiation yield of chain scission, informs on the amount of broken bonds in the backbone of the polymer per unit of absorbed ionizing radiation. The G_x and G_s [mol/J] values can be calculated from the Eqs. (3) and (4), which use the dependence between the gel dose, chain scission to crosslinking ratio, and the weight-average molecular weight (Charlesby, 1960; Schnabel, 1981; O'Donnell, 1991):

$$4G_x - G_s = \frac{2}{D_g \overline{M}_{W0}} \tag{3}$$

$$\frac{G_s}{2G_x} = \frac{p_0}{q_0} \tag{4}$$

where:

$\overline{M}_{w0}$ – initial weight average molecular weight [g/mol].

The values of radiation yields G_x and G_s are connected with the radiation resistance. They reflect the radiation stability of polymers, by providing information to what extent the reactions occur in the irradiated system. As a result, the serviceability of a particular polymer under the influence of ionizing radiation can be evaluated.

SBR is commonly used in the tire industry. One of the key components of a tire that contains SBR is the tread of a passenger car tire. Before building a tire, the extruded tread can be irradiated with an electron beam. Such a radiation pre-treatment serves to improve green strength of the compound, to stabilize its shape and thickness and to reduce the thermal curing time of the tire. However, still little is known about the fundamental reactions occurring as a result of SBR irradiation. The aim of the current work was to extend the knowledge on the principal reactions and structural changes, which have a strong effect on the modification of the properties, and entire performance of the SBR material. To describe the radiation curing process, two approaches were adopted and compared to investigate the gelation process and the radiation-induced reactions: (i) the Charlesby-Pinner and (ii) the Charlesby-Rosiak equations. On the basis of these two models, parameters describing the radiation curing process were calculated. To evaluate the dose required to form the incipient network spanning through the system studied, the gel dose was determined. To indicate the type of prevailing reaction occurring during irradiation of SBR-rubber, the ratio between the crosslinking and chain scission reactions was calculated. Furthermore, radiation yields of crosslinking and chain scission were investigated to check the radiation resistance of SBR. The basic parameter describing polymer network – crosslink density – was determined by equilibrium swelling and calculated on the basis of the Flory-Rehner equation (Flory and Rehner, 1943). The polymer network was also studied by freezing point depression experiments, and correlated with crosslink density. It was investigated to what degree the changes in the SBR structure influence the performance of the polymer.

For this purpose, the effect of irradiation on the glass transition temperature was investigated by using Differential Scanning Calorimetry (DSC). Furthermore, static mechanical properties were checked by tensile tests and thermo-oxidative stability by thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

The polymer used in this study was a cold emulsion styrene-butadiene rubber (E-SBR) KER 1500, with 23.5% of bound styrene, produced by Synthos (Poland). The ratio of styrene to butadiene units is therefore one to six or seven. The chemical structure of butadiene consists of 15% 1,2-vinyl, 10% 1,4-cis, and 75% 1,4-trans double bonds. The molecular weight of the E-SBR was $\overline{M}_n = 151000$ g/mol, $\overline{M}_w = 425000$ g/mol, and the dispersity 2.8, as reported by the producer. The Mooney viscosity was $ML(1+4)100\,°C = 50$.

Acetone was used for extraction, toluene for the determination of the crosslink density and tetrahydrofuran (THF) for the sol-gel analyses. All solvents were of analytical grade, obtained from Assink Chemie (The Netherlands). Cyclohexane ($\geq 99\%$) which was used for freezing point depression experiments was provided by Sigma-Aldrich (USA).

2.2. Preparation of samples

The E-SBR was used in its commercial form, without prior purification by extraction. It was masticated on a laboratory two-roll open mixing mill David Bridge (UK) for 3 min. During this process, the temperature of the E-SBR did not exceed 40 °C. Immediately after that, $100 \times 100 \times 2$ mm^3 rubber sheets were compression molded in an electrically heated press Wickert WLP 1600/5*4/3 (Germany) at a temperature of 160 °C under pressure of 100 bar for 10 min, to make the material ready for irradiation. Molding was necessary to prepare the samples for all analyses and mechanical properties tests.

2.3. Irradiation with accelerated electrons

The molded rubber sheets were subjected to electron beam (EB) irradiation at an Elektronika 10/10 linear electron accelerator (Russia), located at the Institute of Nuclear Chemistry and Technology (Poland). The beam of electrons characterized itself with energy of 10 MeV and an average beam power of 10 kW. The absorbed doses were: 25, 50, 75, 100, 150 and 200 kGy. Irradiation process was carried out in air atmosphere at room temperature. The rubber sheets were placed horizontally under the window of the pulsed, scanned beam. The total doses were obtained by multi-pass exposure (approx. 25 kGy per pass). Temperature of

2.4. Extraction with acetone

Irradiated samples were extracted with acetone in a Soxhlet apparatus for 72 h. This was followed by drying them to a constant weight at 55 °C in a Heraeus (Germany) oven with an air circulation system. The acetone-extracted samples were used for crosslink density analysis, DSC glass transition and TGA thermo-oxidative stability studies.

2.5. Sol-gel analysis

To analyze the insoluble (gel) and soluble (sol) fractions, samples of approx. 0.2 g were extracted with tetrahydrofuran (THF) in a Soxhlet apparatus. The total extraction time was 30 days to reach a constant gel fraction. Extraction was followed by drying the samples in a vacuum oven Gallenkamp (UK) for 7 days at 60 °C to a constant weight. The gel content was calculated as:

$$g = \frac{W_2}{W_1} \tag{5}$$

$$s = 1 - g \tag{6}$$

where:

g – gel fraction [–]; s – sol fraction [–]; W_1 – weight of a sample before extraction [g]; W_2 – weight of a dried sample after extraction [g].

2.6. Effect of ionizing radiation on the SBR structure

On the basis of the sol-gel data, the relation of $s + \sqrt{s}$ vs $1/D$ was plotted. According to Charlesby and Pinner, the gel dose was determined as the intercept of the function at $s + \sqrt{s} = 2$. The ratio between chain scission and crosslinking was determined as the intercept of the function with ordinates.

To analyze the data according to the Charlesby-Rosiak equation, a numerical analysis of the sol-gel curves was carried out with use of GelSol95 software (Division of Applied Radiation Chemistry at the Lodz University of Technology) (Numerical Analysis of Gel/Dose Curves – GelSol95 for Windows), providing the closest approximation to a straight line relation for a plot with modified coordinates: $s + \sqrt{s}$ vs $(D_g + D_v)/(D + D_v)$. This served to obtain the best fitting of the experimental data to the Charlesby-Rosiak equation. The values of the gel dose, and the ratio between the chain scission and crosslinking, were calculated based on this fitting curve.

2.7. Crosslink density analysis

To analyze the crosslink density, previously acetone-extracted samples of approx. 0.05 g were swollen to equilibrium in toluene for 4 days at room temperature (23 °C ± 1 °C). This was followed by drying the samples to a constant weight for 4 days at 60 °C in a Heraeus (Germany) oven with an air circulation system. The crosslink density was calculated based on the Flory-Rehner equation (Flory and Rehner, 1943):

$$\nu = -\frac{ln(1-V_r) + V_r + \chi V_r^2}{V_0 \left(V_r^{\frac{1}{3}} - \frac{2V_r}{f} \right)} \tag{7}$$

where:

ν – crosslink density per unit volume [mol/cm^3]; V_r - volume fraction of rubber in a swollen sample [-]; V_0 – solvent molar volume (for toluene: $V_0 = 106.9 \, cm^3/mol$); f – functionality of crosslinks ($f = 4$ assuming the formation of tetra-functional crosslinks); χ – Flory-Huggins rubber-solvent interaction parameter (for the SBR-toluene system: $\chi = 0.378$ (George et al., 1999)).

The calculated crosslink density values are the average of five specimens per system irradiated with a particular dose. The relative standard deviation is approx. 3.0% on average.

2.8. Freezing point depression

The freezing point depression measurements were carried out with use of a DSC Polyma 214 calorimeter from Netzsch-Gerätebau (Germany). The samples for this experiment were first acetone extracted, and then swollen in toluene for crosslink density analysis. The prior equilibrium swelling in toluene served to obtain such kind of network, in which the polymer chains were interconnected by crosslinks, and the non-bonded polymer chains were removed. The samples of approx. 0.001 g were swollen to equilibrium in cyclohexane during 4 days at a temperature of 23 ± 1 °C. The swollen samples were transferred into standard aluminium pans. They were completely submerged in excess of cyclohexane, to make sure that the solvent is trapped inside the polymer network. The pans were sealed with the lid. Various cooling/heating rates (1 °C/min, 2.5 °C/min, 5 °C/min, 10 °C/min,

20 °C/min) were tested. The 5 °C/min rate was chosen, as it provided the best compromise between good resolution, accuracy, good thermal equilibrium inside the DSC cell, and noises. The freezing point depression data points were taken as the values of the peak maxima during the cooling stage. Cyclohexane was used as a solvent, because it is a good swelling agent for SBR (Brandrup and Immergut, 1989) and shows a clear, sharp peak of crystallization.

2.9. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) measurements were performed with use of a DSC Polyma 214 calorimeter from Netzsch-Gerätebau (Germany). The samples of approx. 10 mg were placed in standard aluminum pans with pierced lids. The measurements were carried out in nitrogen atmosphere as follows: (i) cooled at a rate of 10 °C/min from 30 °C to − 110 °C; (ii) stabilized at − 110 °C for 3 min; and (iii) heated at a rate of 10 °C/min from − 110 °C to 30 °C. A prior extraction of the samples with acetone served to obtain smoother thermograms, without influencing the T_g values. A thermal history effect was checked by recording three measurement cycles for a representative set of samples. The same T_g values were obtained, which showed that the measurements were not sensitive to the thermal history. The data for the present study were therefore collected during the first heating scan. The values of the glass transition temperature were taken as the inflection points of the heat capacity change during the heating step. The error bars of the T_g are expressed as the maximum standard deviation of the measurements, i.e. 0.2 °C.

2.10. Mechanical properties

Tensile tests were carried out with use of Zwick Roell type BZ1.0/TH1S universal tensile testing machine from Zwick Roell (Germany). The test specimens were dumbbells type 3 (ISO 37), tested at a constant crosshead speed of 500 mm/min at a temperature of 23 ± 1 °C. Seven dumbbell specimens were tested for each sample and the average was calculated. The error bars of the tensile strength (TS) and elongation at break (E_b) values are expressed as the standard deviation of the measurement.

2.11. Hardness

The hardness of the samples was measured with a Shore A Zwick hardness tester, type 7206 (Zwick, Germany), according to ASTM D2240-02.

2.12. Thermogravimetric Analysis (TGA)

Thermogravimetric analyses were carried out with a TGA 4000 analyzer from Perkin Elmer (USA). Samples of approx. 8 mg, placed in ceramic pans, were heated from 30 °C to 700 °C with a rate of 10 °C/min. The analysis was conducted in synthetic air atmosphere. Prior extraction with acetone served to remove soluble substances, not attached to the polymer network, which could have an effect on the thermal analysis (Chan et al., 1974). The thermo-oxidative stability of the samples was characterized in terms of the onset of degradation temperature (T_0), the temperature of 50% of mass loss ($T_{50\%}$), and the temperature of the highest degradation rate (T_h). The T_0 values were obtained as the intersection point of tangents to two branches of the TG curve. The $T_{50\%}$ values were taken as 50% of the weight loss of the sample, and the T_h as the values corresponding to the maximum of the derivative thermogravimetric (DTG) curve.
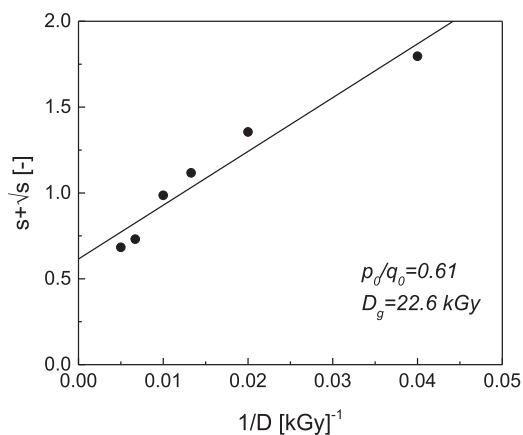
Fig. 2. Experimental data of the sol-gel analysis for the studied SBR, shown in the classical Charlesby-Pinner coordinates.

3. Results and discussion

3.1. Effect of ionizing radiation on the gel formation

To check the validity of the Charlesby-Pinner equation for the investigated radiation-cured SBR, the experimental data obtained from the sol-gel analysis were plotted in the coordinates $s + \sqrt{s}$ vs $1/D$ (Fig. 2). As the graph illustrates, the relation is not a straight line, but a concave downward. This indicates that the initial molecular weight distribution is $\overline{M}_w/\overline{M}_n > 2$. This fits to the molecular weight distribution of the investigated SBR, which is $\overline{M}_w/\overline{M}_n = 2.8$. The deviation of the curve indicates that the plotted data does not fit to the theoretical model of Charlesby and Pinner. As a result, the parameters characterizing radiation-induced changes, such as gel dose and the chain scission to crosslinking ratio, are difficult to evaluate.

To overcome this limitation, the experimental data were plotted according to the Charlesby-Rosiak equation in the coordinates $s + \sqrt{s}$ vs $(D_g + D_v)/(D + D_v)$, giving a straight-line relation (Fig. 3).

D_v that is obtained as the best fit for linearization of the experimental data points was calculated as 39.1 kGy. This is in agreement with the theoretical predictions (Olejniczak et al., 1991). According to these predictions, for polymers with an initial molecular weight distribution broader than 2, D_v that is required to change the random molecular weight distribution to the distribution of the real investigated polymer is of positive value.

The ratio between chain scission and crosslinking p_0/q_0 is 0.24. The value of this parameter indicates that the reactions of intermolecular bond formation prevail over those leading to polymer chain scission.
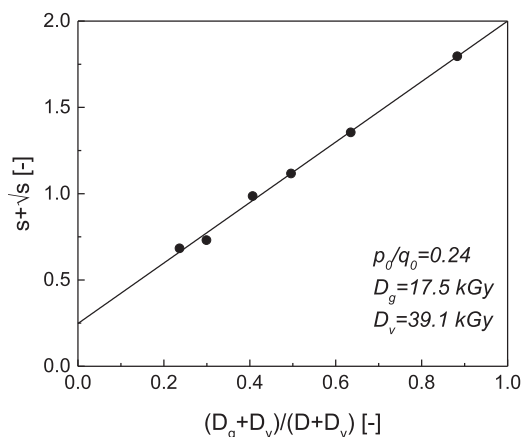

Fig. 3. Experimental data of the sol-gel analysis for the studied SBR, shown in the Charlesby-Rosiak coordinates.
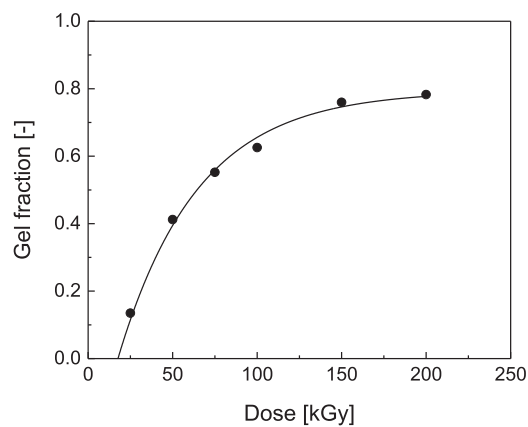

Fig. 4. Gel fraction as a function of radiation dose for the studied SBR.

However, crosslinking is accompanied by chain scission reactions – the determined p_0/q_0 value corresponds to 19% of chain scission, as calculated for all reactions of crosslinking and chain scission in the irradiated system (van Bevervoorde-Meilof, 1998). This leads to partial degradation of the polymer chains.

The calculated gel dose for the SBR under study is 17.5 kGy. For the dose of 25 kGy, which is only slightly higher than D_g, the gel content is very low (Fig. 4). Continuous irradiation with higher doses results in further increase in insoluble polymer fraction. As the graph shows, the largest changes in gel formation occur between the D_g and approx. 125 kGy. After this pronounced increase, at higher doses the gel content starts to level off. This course of changes is typical for polymers, which are prone to crosslinking. A similar tendency in the gel formation in the irradiated SBR corresponds to findings of other researchers (Moustafa et al., 2011; Manshaie et al., 2011).

3.2. Effect of ionizing radiation on SBR structure

3.2.1. Yield of crosslinking and chain scission

To evaluate the efficiency of conversion of absorbed radiation energy to the corresponding chemical reactions in the material, values of radiation yield of crosslinking G_x and chain scission G_s were calculated (Table 1). Since the Eqs. (3) and (4) consider random initial molecular weight distribution, the obtained result is only an approximation.

The basic requirement for gel formation in the irradiated polymer is that G_s/G_x has to be less than 4 (Charlesby, 1960; O'Donnell, 1991; Schnabel, 1990). In the investigated system this value is 0.49, which is another proof that the prevailing reactions induced in SBR by ionizing radiation lead to crosslinking. Additionally, owing to the fact that SBR is amorphous, the reactions of crosslinking and chain scission occur with random spatial distribution, being most probably uniform in the whole bulk of the material.

The values of both radiation yield of crosslinking and radiation yield of chain scission are low. This indicates that the degree of the overall radiation-induced changes in SBR is low. As listed in Table 2, the corresponding values of G_x and G_s for different rubbers (known from literature) are larger than for the SBR investigated in this study. Therefore, it can be concluded that SBR requires higher doses to change its microstructure than many other commonly used, non-aromatic rubbers.

One of the main reasons for such a low degree of structural changes is the presence of aromatic rings in the SBR structure (Głuszewski and

Table 1
Radiation yields of crosslinking G_x and chains scission G_s.

G_x [μmol/J]	G_s [μmol/J]	G_s/G_x [–]
0.076	0.037	0.49

Table 2

Experimental data of radiation yield of crosslinking and chain scission for various rubbers.[a]

	G_x [µmol/J]	G_s [µmol/J]	G_s/G_x [–]
Natural rubber (NR) (Charlesby and von Arnim, 1957)	0.109	–	–
Nitrile rubber (NBR) (30% of acrylonitrile) (Hill et al., 1996)	2.176	–	–
Polybutadiene rubber (cis-1, 4) (BR) (Kozlov et al., 1969)	0.549	0.055	0.10
Ethylene-propylene-diene rubber (EPDM) (Geissler et al., 1978)	0.226	0.059	0.26
Polychloroprene (CR) (Hill et al., 1993)	0.332–0.497	–	–

[a] The original literature data were given as the number of reactions per 100 eV of absorbed energy. To convert the data into SI notation µmol/J, it was multiplied by 0.1036.

Zagórski, 2003; Witt, 1959; Anderson, 1960; Ferry et al., 2012; Clough et al., 1991; Manion and Burton, 1952; Burton and Patrick, 1954; Burton and Lipsky, 1957). The styrene rings, due to the π electron-based resonant structure, exhibit a wide range of energy levels and thus scatter over the energy of ionizing radiation. This phenomenon prevents more pronounced changes in the microstructure of SBR and can be explained in two ways. The first possibility is that the styrene rings directly absorb the energy of ionizing radiation and dissipate it. The second possibility is that the butadiene units, due to a larger participation in the bulk (76.5%), absorb more radiation energy than the styrene rings. This energy or radical centers formed on the polymer chains are then transferred towards the styrene rings, after that scattered by the rings. Therefore, the protective effect is not only limited to the immediate vicinity of the styrene rings, but expands over the further parts of chains. The styrene units provide high radiation resistance by stabilization of the polymer matrix. It is further possible that in this process the styrene rings also sacrifice themselves to some extent, in a similar manner to the anti-aging substances. However, the amount of styrene is appreciably higher than of the anti-aging substances. To understand the changes of the SBR macromolecular structure induced by high-energy radiation even better, an additional investigation was carried out with infrared spectroscopy (ATR-FTIR). However, due to the high radiation resistance of SBR, it was modified by ionizing radiation only to a low extent. As a result, the quantitative changes in the intensity of particular bands are insufficient to follow the mechanism of the reactions occurring (data not shown). Consequently, it could not be checked if the styrene rings sacrifice itself.

There is another possibility to explain the required higher doses for irradiation of E-SBR: the styrene blocks present in the SBR structure make the polymer chains stiffer and decrease their flexibility. Accordingly, the mobility of the macroradicals generated during the irradiation is constrained. This lowers the probability of finding a partner to recombine (Zhen, 2001). As a result, the number of the chain scission reactions is increased. Furthermore, SBR was irradiated in the present study in air atmosphere, and the presence of oxygen and possible oxidation reactions could also have an effect on the number of chain scission reactions. The oxidation could possibly contribute to the number of chain scission reactions, beside the effect of high stiffness of the polymer chains. This can be due to a moderate permeability of oxygen into the bulk of the SBR (George et al., 2001; McKeen, 2012).

3.2.2. Crosslink density

Besides the already discussed values such as the gel dose, chain scission to crosslinking ratio, radiation yields of crosslinking and chain scission, the crosslink density was evaluated as well. It is a basic structural parameter, which characterizes crosslinked polymers by quantifying the number of crosslinks per unit volume in a polymer network. As Fig. 5 shows, crosslinks are successively formed when the
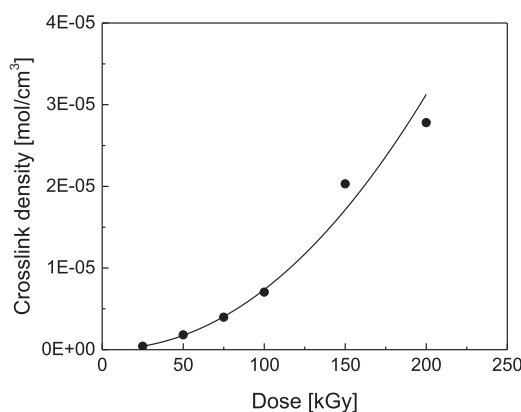
Fig. 5. Crosslink density as a function of radiation dose for the studied SBR.

dose of absorbed radiation increases. Up to the dose of 100 kGy, the increase in crosslink density is low, whereas above this dose, the development of bonds between polymer chains progresses faster. Overall, the formed crosslink density remains low, due to the high radiation resistance of the SBR rubber.

Fig. 6 depicts the relation between gel fraction and crosslink density of the studied SBR. As already discussed, the increase in the gel fraction considerably diminishes from a particularly high dose (approx. 125 kGy). This can be ascribed to the fact that new chemical bonds are formed mainly between already crosslinked polymer chains. It would lead to a further increase in crosslink density, but at the same time an only modest growth of the gel fraction (Mateev and Karageorgiev, 1997).

These data were compared with Wang's findings (Wang et al., 2009; Wang et al., 2016). He investigated the crosslink density of radiation cured SBR with a magnetic resonance crosslink density spectrometer (MRCDS). The two compared sets of data show different tendencies. According to Wang's investigations, in the irradiated SBR, crosslinking reactions prevail to the dose of 150 kGy. A further increase in the dose leads to a decrease in the crosslink density at the dose of approx. 200 kGy. This is followed by another increase in crosslink density with higher doses. This behavior was explained by complex changes of the predominating reaction during the course of irradiation. The results of the present study show that crosslinking is the prevailing reaction during SBR irradiation up to the dose of 200 kGy. The discrepancy between the results of this study and Wang's research can be due to different methods used to analyze crosslinking density.

3.2.3. Freezing point depression

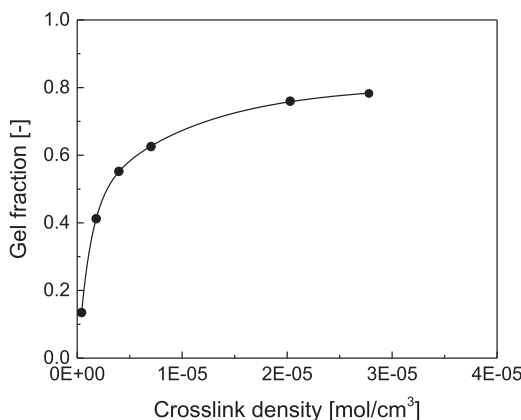Polymer networks can be studied by their analysis in a form of

Fig. 6. Relation between the gel fraction and crosslink density for the studied SBR.

swollen gels. This method is based on the difference in the behavior of a solvent confined in a polymer network and the free solvent outside the gel. In this way, freezing point depression and melting point depression of the confined solvent can be determined, during cooling and heating cycle, respectively. These changes are investigated with a DSC. In the present work, the changes in freezing temperature are considered.

Polymer networks swollen in a solvent are complex systems and possibly multiple factors can influence the freezing behavior of the solvent. However, the lowering of the freezing temperature of the confined solvent is considered to have two main contributions (Jackson and McKenna, 1991). Firstly, the molecules of the solvent entrapped in a polymer network have a lowered thermodynamic potential comparing to the molecules of the free solvent. This is due to the fact that in the polymer network, the solvent molecules are in a chemically different environment. Secondly, physical restrictions of the polymer network, caused by the size of the mesh, constrain the solvent crystals to small size or hinder the crystals nucleation. At the same time, there are no restrictions on solvent crystallization in a free solvent.

It follows that the freezing point depression temperature (ΔT_f) depends also on the crosslink density. Therefore, an analysis of the swollen gels can be used to study the polymer networks (Jackson and McKenna, 1991; Kuhn et al., 1955, 1960; Boonstra et al., 1968; Oikawa and Murakami, 1984; Oikawa and Murakami, 1989; Baba et al., 1999a, 1999b, 2003a, 2003b, 2003c). In the present work, freezing point depression measurements of cyclohexane-swollen radiation cured SBR samples were carried out. The aim was to estimate the network structure on basis of polymer-solvent interactions. The thermograms of pure cyclohexane and swollen radiation cured samples are shown in Fig. 7.

For pure cyclohexane, one intensive peak of freezing solvent appears. For the sample irradiated with the lowest dose, i.e. 25 kGy, also only one peak was recorded, which is slightly broader than the peak of the free solvent. The peak corresponds to the freezing of both the free solvent, as well as the solvent trapped in the polymer network. This is due to the very low crosslink density and large mesh size of the 25 kGy sample. Such network structure allows unconstrained crystallization of the cyclohexane in the polymer network to occur. In case of the sample irradiated with 50 kGy, two overlapping peaks can be observed in the thermogram: the peak of the free solvent and of the solvent trapped in the polymer network. The depression of freezing temperature of the solvent trapped in the gel is clearly visible. For a sample irradiated with 75 kGy, the peak of the solvent entrapped in the polymer network is already well-shaped and separated from the peak of the free solvent. In case of samples irradiated with higher doses also two peaks are distinguished. The peaks corresponding to crystallization of the solvent trapped in the polymer network shift to lower temperatures with an increase in the irradiation dose. Therefore, the freezing point depression is larger. At the same time, the intensity of these peaks decreases, due to a smaller amount of solvent entrapped in the samples with higher crosslink density. It is also accompanied by a broadening of the peaks, which can indicate a broadening of the distribution of the mesh size. The determined ΔT_f values, correlated with crosslink density, are shown in Fig. 8.

The dependence between the ΔT_f and the crosslink density is linear. The values of these two parameters correlate well and provide information on the increase in the crosslink density. The mesh size is smaller at larger crosslink density, which results in a more pronounced freezing point depression. The freezing point depression studies provide information on the degree of crosslinking – the trapped solvent acts as a sensitive probe.
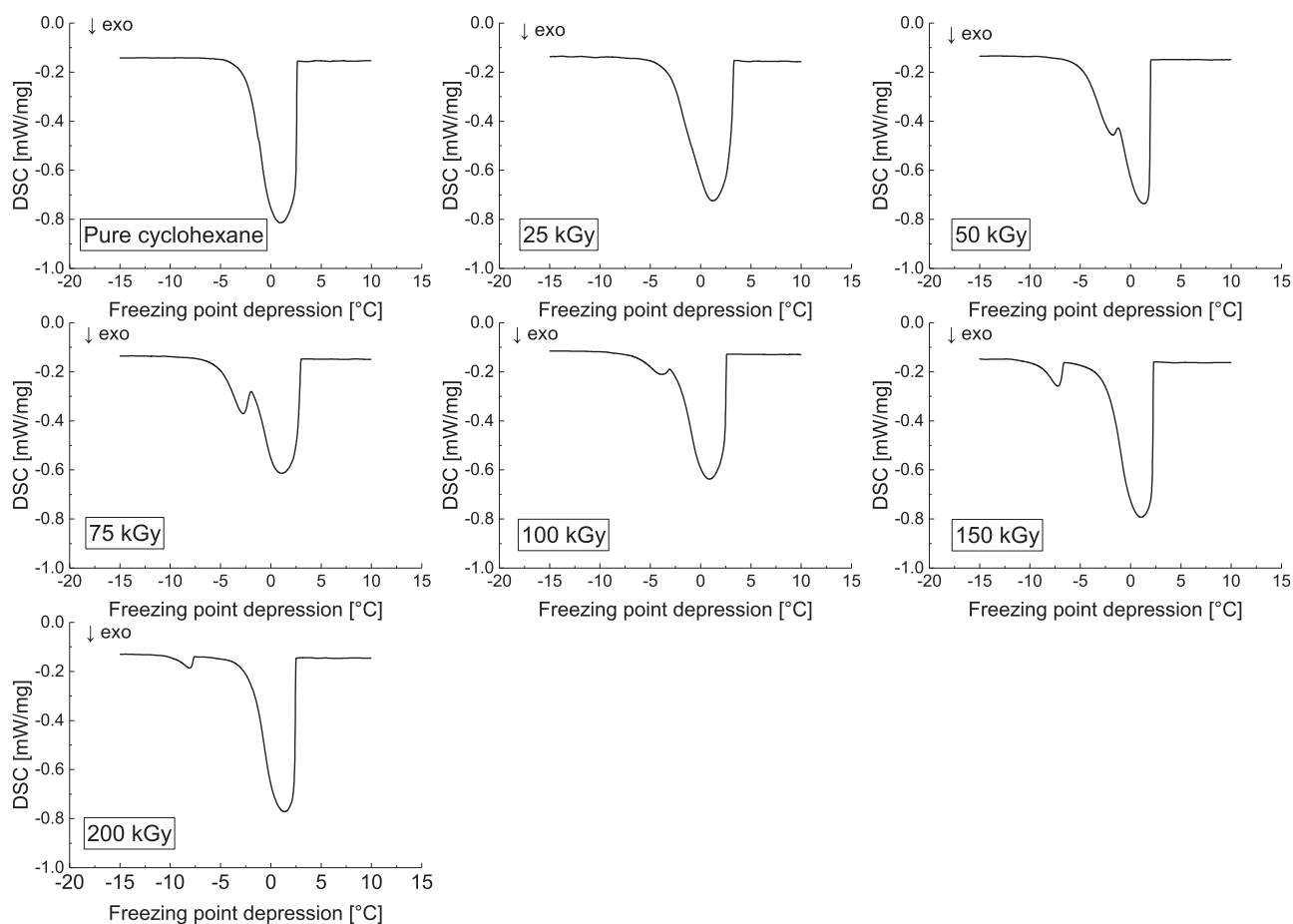

Fig. 7. Freezing point depression of free solvent and solvent trapped in the swollen SBR polymer network.
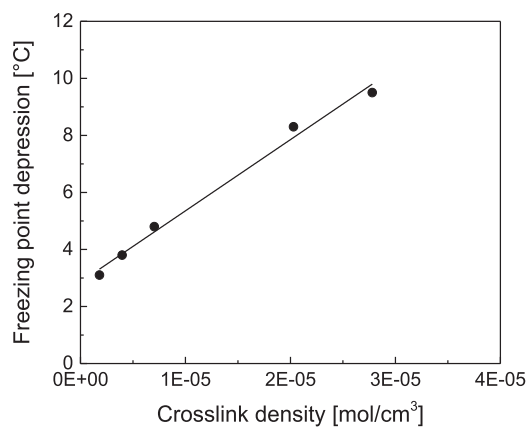
Fig. 8. Freezing point depression as a function of crosslink density for the irradiated SBR (samples irradiated with 50, 75, 100, 150 and 200 kGy).

3.3. Effect of ionizing radiation on the SBR properties

3.3.1. Glass transition temperature

The effect of radiation curing on the glass transition temperature (T_g), investigated by changes in heat capacity with use of DSC, is illustrated in Fig. 9.

The T_g of the uncrosslinked reference is approx. − 52.8 °C. As a result of the initial irradiation, the T_g values are slightly decreased. This decline can be possibly caused by chain scission reactions, which accompanied crosslinking, and caused partial degradation of the polymer chains. Fragments of ruptured chains, exhibiting lowered molecular weight, could contribute to a decrease in the T_g. For samples further irradiated with higher doses, the T_g is slightly increased. However, this change is minor. As already mentioned above, the range of crosslink density formed as a result of SBR irradiation is narrow, which implies that the increase in the T_g is small.

3.3.2. Mechanical properties

To investigate in which way the irradiation of SBR altered the mechanical properties of the material, static room-temperature tensile tests were carried out. Changes in tensile strength (TS) as a function of crosslink density are shown in Fig. 10. The TS of the uncrosslinked reference is very low – approx. 0.5 MPa, which is a typical value for a non-crystallizing, unfilled and uncured rubber. Compared to the reference, the radiation modification serves to improve the TS.

The crosslink density produced by irradiation with 25–100 kGy doses results in an increasing TS. The maximum of TS occurs at the crosslink density produced by 100 kGy. The upward trend of the TS
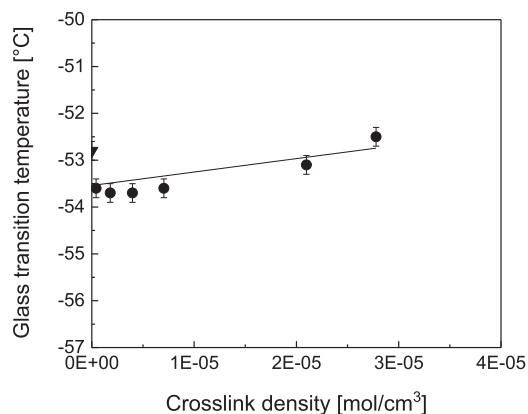

Fig. 10. Tensile strength as a function of crosslink density for the studied SBR (▼ – uncrosslinked reference; • – radiation cured samples). The line in the graph was added to guide the eye, and the position of the maximum is only suggested (explanation in the text below).

improvement is assumed to span as well higher crosslink densities, corresponding to doses between 100 kGy and 150 kGy. However, this range of doses was not employed in the present research. Still, the maximum occurs at very low crosslink density, which is typical for amorphous polymers (Taylor and Darin, 1955). For the crosslink density, obtained by irradiation with a dose of 150 kGy, the TS is already in decline. A further increase in the absorbed dose produced a more crosslinked network structure, which caused deterioration of the tensile properties. This dependence between the TS tensile and crosslink density is typical (Gee, 1947): in the range of low crosslink densities the TS values increase, reaching an optimum, which is followed by a decline.

Fig. 11 shows that an increase in the crosslink density is also reflected as a decrease in the elongation at break (E_b). For the uncrosslinked reference, due to the unconstrained deformability of the polymer chains, the value of E_b is as high as approx. 1970%. Compared to the reference, already the lowest dose of irradiation, i.e. 25 kGy, leads to a considerable decrease in E_b. This decline is caused by the introduction of crosslinks, which hold the polymer chains together and restrain their deformability. However, chain scission reactions most probably also contribute to this large decrease in the E_b. With further irradiation and a rise in the crosslink density, the E_b values are continuously decreased. Irradiation with 200 kGy resulted in a reduction of the E_b value over 2.5 times compared to the uncrosslinked reference.

Irradiation also causes an increase in the hardness and stress at 500% elongation ($SE\ 500$). Changes of these properties are presented in Fig. 12. These dependences are characteristic for polymers, which curing leads to crosslinking.

Fig. 9. Glass transition temperature as a function of crosslink density for the studied SBR (▼ – uncrosslinked reference; • – radiation cured samples). The correlation for radiation cured samples is assumed to be linear.
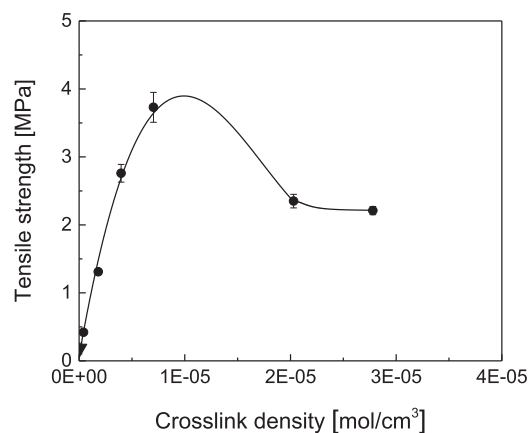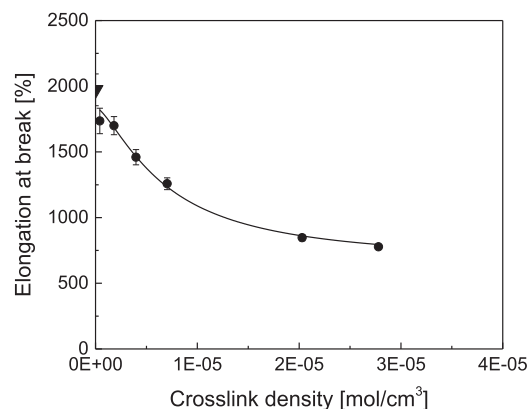

Fig. 11. Elongation at break as a function of crosslink density for the studied SBR (▼ – uncrosslinked reference; • – radiation cured samples).
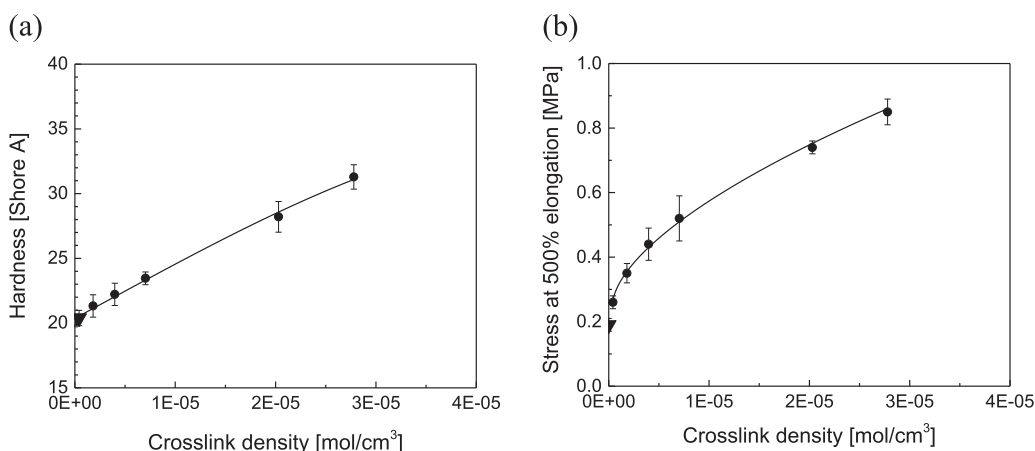
Fig. 12. Properties of the SBR studied: (a) hardness as a function of crosslink density; (b) stress at 500% elongation as a function of crosslink density for the studied SBR (▼ – uncrosslinked reference; • – radiation cured samples).

3.3.3. Thermo-oxidative properties

The thermal stability of polymer materials is an important property with respect to their performance at elevated temperatures. It is postulated that thermal degradation of SBR proceeds via a mechanism of random scission of the polymer chains (Hacaloglu et al., 1997; Castrovinci et al., 2005). During the SBR oxygen-free process of pyrolysis, an evolution of various products of chains decomposition occurs, such as aliphatic and aromatic hydrocarbons (Castrovinci et al., 2005). The major pyrolysis products of SBR are identified as butadiene, 4-vinylcyclohexene, styrene, methylbenzene, ethylbenzene and α-methylstyrene (Ghebremeskel et al., 1996; Choi, 2002). In the present work, the thermogravimetric analysis (TGA) was carried out under synthetic air, to mimic the most common conditions of rubber products use. Since the destructive changes were induced by combined heat and oxygen treatment, the degradation products formed were more complex than in case of oxygen-free pyrolysis studies. The thermo-oxidative stability of the uncrosslinked reference and irradiated samples are characterized in terms of the onset of degradation temperature (T_0), temperature at 50% of mass loss ($T_{50\%}$), and temperature of the highest degradation rate (T_h). Graphs illustrating the changes in these parameters, correlated with the crosslink density, are shown in Fig. 13.

Due to the presence of anti-aging substances, polymerization aids, and other low-molecular substances in the E-SBR used, the TGA analysis was preceded by the extraction with acetone of all samples. In this step, the substances which were not attached to the polymer chains should be removed (Chan et al., 1974). The anti-aging substances were most probably extracted from the non-irradiated reference. Hence, they did not protect the polymer chains against the thermo-oxidative degradation. In case of the cured samples, as a result of initial irradiation, the anti-aging substances most probably "sacrificed" themselves and were consumed. Still, after the irradiation the extraction with acetone was carried out. Accordingly, the anti-aging substances should not influence the thermo-oxidative stability and they will not be further considered.

The uncrosslinked reference shows the highest T_0, $T_{50\%}$ and T_h values of all the investigated samples. Compared to the reference, the irradiation results in a general deterioration of the thermo-oxidative stability in the whole range of crosslink density. Furthermore, for the irradiated samples, the values of the thermo-oxidative parameters are dependent on the irradiation dose. To explain the difference between the uncrosslinked reference and irradiated samples, the degradation process should be followed. During heating of the polymer, at adequately high temperature, the macromolecules degrade in a process of chain scission. As a result, fragments of chains are formed, with progressively shorter length. These fragmented parts can further react with each other or depolymerize. When their size is small enough, these low-molecular products liberate from the bulk. As a result, the weight of the polymer decreases, which is measured during the TGA analysis.

The reference sample was not irradiated. Neither crosslinks nor chain scission fragments were present in this sample, so it consisted only of long polymer chains. To cause thermo-oxidative degradation and release of its products, the combined action of thermal energy and oxygen was needed to cause the breakage of the polymer chains. This occurred at a relatively high temperature.

Compared to the non-irradiated reference, already the initial irradiation with the dose of 25 kGy leads to a considerable decrease in the thermo-oxidative stability. This is due to the fact that in the 25 kGy sample a low number of crosslinks was formed, and at the same time chain scission reactions occurred to some extent. Therefore, a part of the polymer chains were already fragmented, and unconnected to other fragments of the bulk. Consequently, the degradation products could liberate faster, and the destructive changes induced by combined heat and oxygen occurred at a lower temperature than in the reference. In case of the samples irradiated with a higher doses than 25 kGy, the thermo-oxidative stability is improved. In these samples as a result of irradiation, beside chain scission products, more crosslinks were formed. Consequently, some of the fragmented parts are bonded to other chains. Additionally, since crosslinks unite the polymer chains, stabilize them and restrict the molecular mobility, it is possible that more thermal energy is required to cause destructive changes. Therefore, the degradation has to be more advanced to enable the emission of the degradation products from the bulk. Also, as a result of irradiation, the total number of chemical bonds in the polymer is increased, compared to the non-irradiated reference and the 25 kGy sample. At a certain crosslink density, the T_0, $T_{50\%}$ and T_h parameters reach an optimum. It occurs for the samples irradiated with doses between approx. 50 kGy and 75 kGy. With a further increase in dose, the thermo-oxidative stability begin to decline. All curves of the thermo-oxidative stability as a function of crosslink density have a characteristic shape, with first an increase, optimum and finally a decrease. Moreover, the above discussed curves of the thermo-oxidative stability display a similar tendency to the dependence between tensile strength and crosslink density (Fig. 10). In the TS vs crosslink density curve, the optimum occurs at the irradiation dose of approx. 100–150 kGy. Therefore, a crosslink density that provides the maximal tensile strength is very similar to the crosslink density which ensures the highest thermo-oxidative stability. It can be concluded that there is an optimal structure of network, accounting for these properties. Such a relationship was already noticed by Shaltout (2009).

4. Conclusions

The process of electron beam irradiation of SBR leads to changes in its structure. The parameters characterizing the radiation curing process were successfully determined on the basis of the Charlesby-Rosiak equation. The crosslinking predominates over chain scission, and constitute approx. 81% of the reactions. An increase in the radiation dose
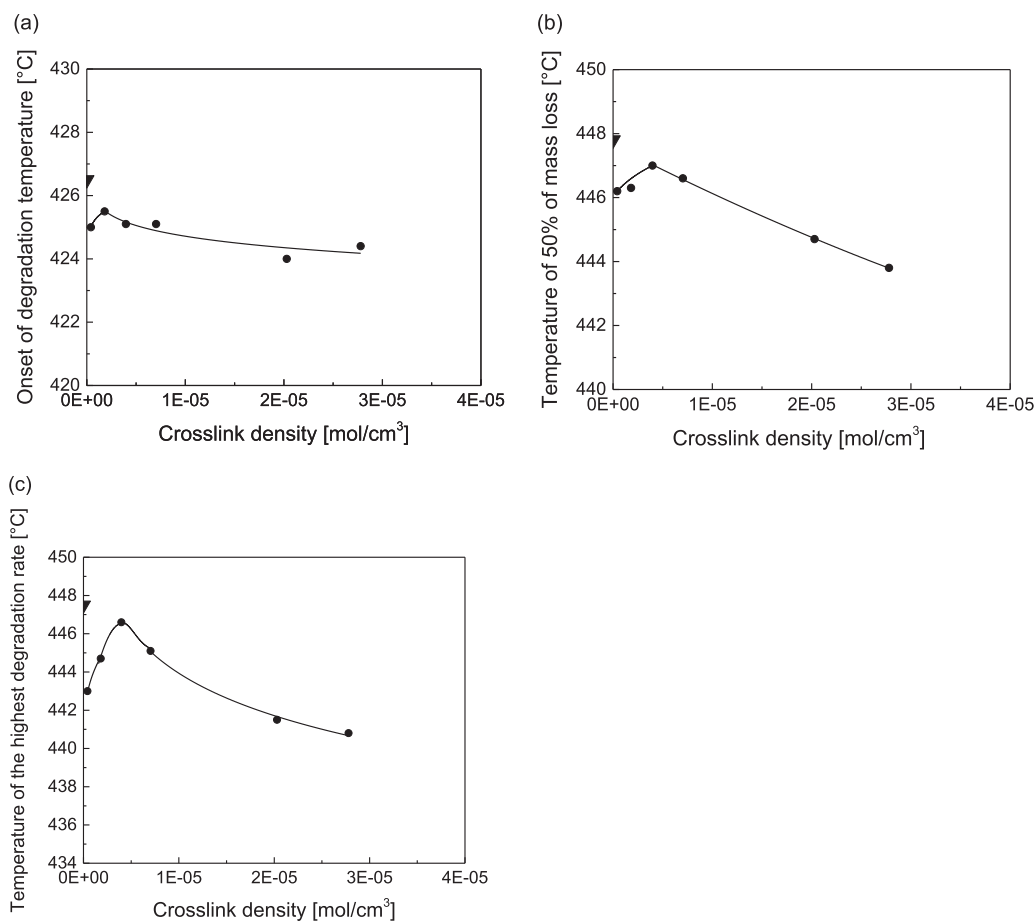
(a)

(b)

(c)

Fig. 13. Dependence between: (a) onset of degradation temperature; (b) temperature at 50% of mass loss; (c) temperature of the highest degradation rate, as a function of crosslink density for the studied SBR (▼ – uncrosslinked reference; • – radiation cured samples).

results in an increase in the crosslink density. This change in the network structure was confirmed by freezing point depression studies, and is in a very good agreement with the crosslink density and freezing point depression values. This proves that the radiation cured SBR can be investigated in a form of swollen gels. Still, as shown by very low radiation yields of crosslinking and chain scission, the degree of changes in the molecular structure of SBR induced by ionizing radiation is low. This is due to the high radiation resistance of the SBR. Both chain scission reactions and high radiation resistance are probably caused by the presence of styrene rings. Additionally, the presence of oxygen could possibly contribute to chain scission. The changes in the SBR structure are reflected by an alteration of the in-rubber properties. The T_g values of the radiation cured samples change only slightly with increasing irradiation dose. At the same time, the static mechanical properties, such as TS, E_b, mechanical modules, and hardness, were influenced to a larger extent. The irradiation caused a change of the thermo-oxidative stability of the polymer. Compared to other commonly used rubbers, the doses required to modify the SBR structure are relatively high.

References

Alemán, J., Chadwick, A.V., He, J., Hess, M., Horie, K., Jones, R.G., Kratochvíl, P., Meisel, I., Mita, I., Moad, G., Penczek, S., Stepto, R.F.T., 2007. Definitions of terms relating to the structure and processing of sols, gels, networks, and inorganic-organic hybrid materials (IUPAC Recommendations 2007). Pure Appl. Chem. 79, 1801–1829. http://dx.doi.org/10.1351/pac200779101801.

Ali, Z., El-Nemr, K., Youssef, H., Bekhit, M., 2013. Mechanical and physicochemical properties of electron beam irradiated rubber/clay nanocomposites. Polym. Compos. 34, 1600–1610. http://dx.doi.org/10.1002/pc.22560.

Anderson, H.R., 1960. Compounding rubber for radiation resistance. J. Appl. Polym. Sci. 3, 316–330. http://dx.doi.org/10.1002/app.1960.070030909.

Baba, M., Gardette, J.-L., Lacoste, J., 1999a. Crosslinking on ageing of elastomers: I. Photoageing of EPDM monitored by gel, swelling and DSC measurements. Polym. Degrad. Stabil. 63, 121–126. http://dx.doi.org/10.1016/S0141-3910(98)00080-9.

Baba, M., Gardette, J.-L., Lacoste, J., 1999b. Crosslinking on ageing of elastomers II. Comparison of solvent freezing point depression and conventional crosslinking evaluation. Polym. Degrad. Stabil. 65, 415–420. http://dx.doi.org/10.1016/S0141-3910(99)00030-0.

Baba, M., Nedelec, J.-M., Lacoste, J., 2003a. Porous volume of inorganic materials and degree of swelling of elastomers monitored by dsc measurements. J. Phys. Chem. B 107, 12884–12890. http://dx.doi.org/10.1021/jp027450t.

Baba, M., Nedelec, J.-M., Lacoste, J., Gardette, J.-L., 2003b. Calibration of cyclohexane solid–solid phase transition thermoporosimetry and application to the study of crosslinking of elastomers upon aging. J. Non-Cryst. Solids 315, 228–238. http://dx.doi.org/10.1016/S0022-3093(02)01610-1.

Baba, M., Nedelec, J.-M., Lacoste, J., Gardette, J.-L., Morel, M., 2003c. Crosslinking of elastomers resulting from ageing: use of thermoporosimetry to characterise the polymeric network with n-heptane as condensate. Polym. Degrad. Stabil. 80, 305–313. http://dx.doi.org/10.1016/S0141-3910(03)00014-4.

Bauman, R.G., 1960. The mechanism of radiation damage to elastomers. II. Crosslinking and antirad action. Rubber Chem. Technol. 33, 483–489. http://dx.doi.org/10.5254/1.3542167.

Bik, J.M., Rzymski, W.M., Głuszewski, W., Zagórski, Z.P., 2004. Electron beam crosslinking of hydrogenated acrylonitrile-butadiene rubber. Kaut Gummi Kunstst. 57, 651–655.

Böhm, G.G.A., Tveekrem, J.O., 1982. The radiation chemistry of elastomers and its industrial applications. Rubber Chem. Technol. 55, 575–668. http://dx.doi.org/10.5254/1.3535898.

Boonstra, B.B., Heckman, F.A., Taylor, G.L., 1968. Anomalous freezing point depression of swollen gels. J. Appl. Polym. Sci. 12, 223–247. http://dx.doi.org/10.1002/app.1968.070120201.

Brandrup, J., Immergut, E.H., 1989. Polymer Handbook, 3rd ed. Wiley-Interscience, Chichester.

Burton, M., Lipsky, S., 1957. Mechanisms of protection in radiolysis of organic systems. J. Phys. Chem. 61, 1461–1465. http://dx.doi.org/10.1021/j150557a003.

Burton, M., Patrick, W.N., 1954. Radiation chemistry of mixtures. Cyclohexane and benzene. J. Phys. Chem. 58, 421–423 (DOI: 1021/j150515a010).

Castrovinci, A., Camino, G., Drevelle, C., Duquesne, S., Magniez, C., Vouters, M., 2005. Ammonium polyphosphate–aluminum trihydroxide antagonism in fire retarded butadiene–styrene block copolymer. Eur. Polym. J. 41, 2023–2033. http://dx.doi.org/10.1016/j.eurpolymj.2005.03.010.

Chan, B.L., Elliott, D.J., Holley, M., Smith, J.F., 1974. The influence of curing systems on the properties of natural rubber. J. Polym. Sci. Pol. Symp. 48, 61–86. http://dx.doi.org/10.1002/polc.5070480108.

Charlesby, A., 1960. Atomic Radiation and Polymers. Pergamon Press, London.

Charlesby, A., von Arnim, E., 1957. Crosslinking of oriented rubber. J. Polym. Sci. A1 25, 151–158. http://dx.doi.org/10.1002/pol.1957.1202510903.

Charlesby, A., Pinner, S.H., 1959. Analysis of the solubility behaviour of irradiated polyethylene and other polymers. Proc. R. Soc. Lond. Ser. A 249, 367–386.

Choi, S.-S., 2002. Characteristics of the pyrolysis patterns of styrene-butadiene rubbers with differing microstructures. J. Anal. Appl. Pyrol. 62, 319–330. http://dx.doi.org/10.1016/S0165-2370(01)00128-0.

Chowdhury, R., Banerji, M.S., 2005. Electron beam irradiation of ethylene-propylene terpolymer: evaluation of trimethylol propane trimethacrylate as a crosslink promoter. J. Appl. Polym. Sci. 97, 968–975. http://dx.doi.org/10.1002/app.21795.

Clough, R.L., 2001. High-energy radiation and polymers: a review of commercial processes and emerging applications. Nucl. Instrum. Methods B 185, 8–33. http://dx.doi.org/10.1016/S0168-583X(01)00966-1.

Clough, R.L., Gillen, K.T., Dole, M., 1991. Radiation resistance of polymers and composites. In: Clegg, D.W., Collyer, A.A. (Eds.), Irradiation Effects on Polymers. Elsevier, London, pp. 79–156.

Coran, A.Y., 2013. Vulcanization. In: Mark, J.E., Erman, B., Roland, M. (Eds.), The Science and Technology of Rubber, 4th ed. Academic Press, Waltham, pp. 337–381. http://dx.doi.org/10.1016/B978-0-12-394584-6.00007-8.

Das, P.K., Ganguly, A., Banerji, M., 2005. Electron-beam curing of hydrogenated acrylonitrile–butadiene rubber. J. Appl. Polym. Sci. 97, 648–651. http://dx.doi.org/10.1002/app.21806.

Davenas, J., Stevenson, I., Celette, N., Cambon, S., Gardette, J.L., Rivaton, A., Vignoud, L., 2002. Stability of polymers under ionising radiation: the many faces of radiation interactions with polymers. Nucl. Instrum. Methods B 191, 653–661. http://dx.doi.org/10.1016/S0168-583X(02)00628-6.

Ferry, M., Bessy, E., Harris, H., Lutz, P.J., Ramillon, J.-M., Ngono-Ravache, Y., Balanzat, E., 2012. Irradiation of ethylene/styrene copolymers: evidence of sensitization of the aromatic moiety as counterpart of the radiation protection effect. J. Phys. Chem. B 116, 1772–1776. http://dx.doi.org/10.1021/jp209535p.

Flory, P.J., Rehner, J., 1943. Statistical mechanics of crosslinked polymer networks II. Swelling. J. Chem. Phys. 11, 521–526. http://dx.doi.org/10.1063/1.1723792.

Fox, T.G., Loshaek, S., 1955. Influence of molecular weight and degree of crosslinking on the specific volume and glass temperature of polymers. J. Polym. Sci. 15, 371–390. http://dx.doi.org/10.1002/pol.1955.120158006.

Frounchi, M., Dadbin, S., Panahinia, F., 2006. Comparison between electron-beam and chemical crosslinking of silicone rubber. Nucl. Instrum. Methods B 243, 354–358. http://dx.doi.org/10.1016/j.nimb.2005.09.013.

Gee, G., 1947. Tensile strength of pure gum natural rubber compounds. J. Polym. Sci. 2, 451–462. http://dx.doi.org/10.1002/pol.1947.120020501.

Gehman, S.D., Gregson, T.C., 1960. Ionizing radiation and elastomers. Rubber Chem. Technol. 33, 1375–1437. http://dx.doi.org/10.5254/1.3542249.

Geissler, W., Zott, H., Heusinger, H., 1978. Investigations on the mechanism of radiation induced crosslinking in ethylene-propylene-diene terpolymers. Macromol. Chem. Phys. 179, 697–705. http://dx.doi.org/10.1002/macp.1978.021790312.

George, S.C., Ninan, K.N., Thomas, S., 1999. Effect of degree of crosslinking on swelling and mechanical behaviour of conventionally vulcanised styrene-butadiene rubber membranes. Polym. Polym. Compos. 7, 343–353.

George, S.C., Ninan, K.N., Thomas, S., 2001. Permeation of nitrogen and oxygen gases through styrene-butadiene rubber, natural rubber and styrene-butadiene rubber/natural rubber blend membranes. Eur. Polym. J. 37, 183–191. http://dx.doi.org/10.1016/S0014-3057(00)00083-5.

Ghebremeskel, G.N., Sekinger, J.K., Hoffpauir, J.L., Hendrix, C., 1996. A study of the thermal degradation products of styrene-butadiene type rubber by Pyrolysis/GC/MS. Rubber Chem. Technol. 69, 874–884. http://dx.doi.org/10.5254/1.3538409.

Głuszewski, W., Zagórski, Z.P., 2003. Radiation sterilization of healthcare products. Contemp. Oncol. 7, 787–790.

Hacaloglu, J., Ersen, T., Ertugrul, N., Fares, M.M., Suze, S., 1997. Pyrolysis mass spectrometric analysis of styrene-butadiene block and random copolymers. Eur. Polym. J. 33, 199–203. http://dx.doi.org/10.1016/S0014-3057(96)00068-7.

Hayashi, K., Tachibana, M., Okamura, S., 1980. Cyclization and crosslinking of polybutadiene in solution by electron beam irradiation. J. Polym. Sci. A1 18, 2785–2791. http://dx.doi.org/10.1002/pol.1980.170180903.

Hearon, K., Smith, S.E., Maher, C.A., Wilson, T.S., Maitland, D.J., 2013. The effect of free radical inhibitor on the sensitized radiation crosslinking and thermal processing stabilization of polyurethane shape memory polymers. Radiat. Phys. Chem. 83, 111–121. http://dx.doi.org/10.1016/j.radphyschem.2012.10.007.

Hill, D.J.T., O'Donnell, J.H., Perera, M.C.S., Pomery, P.J., 1993. Radiation-induced structural changes in polychloroprene. In: Reichmanis, E., Frank, C.W., O'Donnell, J.H. (Eds.), Irradiation of Polymeric Materials. American Chemical Society, Washington, pp. 74–94. http://dx.doi.org/10.1021/bk-1993-0527.ch006.

Hill, D.J.T., O'Donnell, J.H., Perera, M.C.S., Pomery, P.J., 1996. An investigation of radiation-induced structural changes in nitrile rubber. J. Polym. Sci. A1 34, 2439–2454. http://dx.doi.org/10.1002/(SICI)1099-0518(19960915)34:12<2439::AID-POLA18>3.0.CO;2-9.

Jackson, C.L., McKenna, G.B., 1991. On the anomalous freezing and melting of solvent

crystals in swollen gels of natural rubber. Rubber Chem. Technol. 64, 760–768. http://dx.doi.org/10.5254/1.3538588.

Kang, H.Y., Saito, O., Dole, M., 1967. The radiation chemistry of polyethylene. IX. Temperature coefficient of cross-linking and other effects. J. Am. Chem. Soc. 89, 1980–1986. http://dx.doi.org/10.1021/ja00985a002.

Kitamaru, R., Mandelkern, L., Fatou, J., 1964. Irradiation crosslinking of polyethylene: relative efficiency in crystalline and amorphous states. J. Polym. Sci. Polym. Lett. 2, 511–517. http://dx.doi.org/10.1002/pol.1964.110020508.

Klinshpont, É.R., Milinchuk, V.K., Tupikov, V.I., 1994. Radiation resistance of polymer materials. At. Energy 76, 384–389. http://dx.doi.org/10.1007/BF02407450.

Kozlov, V.T., Evseev, A.G., Zubov, P.I., 1969. Effect of temperature on radiolysis of some elastomers. Vysokomol. Soedin. Ser. A 11, 2230–2237.

Kuhn, W., Peterli, E., Majer, H., 1955. Freezing point depression of gels produced by high polymer network. J. Polym. Sci. 16, 539–548. http://dx.doi.org/10.1002/pol.1955.120168238.

Kuhn, W., Peterli, E., Majer, H., 1960. Relation between the anomalous freezing point depression and the mechanical-elastic behavior of gels. Rubber Chem. Technol. 33, 245–253. http://dx.doi.org/10.5254/1.3542140.

Lawton, E.J., Balwit, J.S., Powell, R.S., 1958. Effect of physical state during the electron irradiation of hydrocarbon polymers. Part I. The influence of physical state on reactions occurring in polyethylene during and following the irradiation. J. Polym. Sci. A1 32, 257–275. http://dx.doi.org/10.1002/pol.1958.1203212501.

Liu, W., Wang, M., Xing, Z., Qi, Y., Wu, G., 2012. Radiation-induced crosslinking of polyacrylonitrile fibers and the subsequent regulative effect on the preoxidation process. Radiat. Phys. Chem. 81, 622–627. http://dx.doi.org/10.1016/j.radphyschem.2012.02.029.

Manaila, E., Craciun, G., Stelescu, M.-D., Ighigeanu, D., Fica, M., 2014. Radiation vulcanization of natural rubber with polyfunctional monomers. Polym. Bull. 71, 57–82. http://dx.doi.org/10.1007/s00289-013-1045-6.

Manion, J.P., Burton, M., 1952. Radiolysis of hydrocarbon mixtures. J. Phys. Chem. 56, 560–569. http://dx.doi.org/10.1021/j150497a005.

Manshaie, R., Khorasani, S.N., Veshare, S.J., Abadchi, M.R., 2011. Effect of electron beam irradiation on the properties of natural rubber (NR)/styrene–butadiene rubber (SBR) blend. Radiat. Phys. Chem. 80, 100–106. http://dx.doi.org/10.1016/j.radphyschem.2010.08.015.

Mateev, M., Karageorgiev, S., 1997. The effect of electron beam irradiation and content of EVA upon the gel-forming processes in LDPE-EVA films. Radiat. Phys. Chem. 51, 205–206. http://dx.doi.org/10.1016/S0969-806X(97)00124-2.

McKeen, L.W., 2012. Elastomers and rubbers. In: McKeen, L.W. (Ed.), Permeability Properties of Plastics and Elastomers, 3rd ed. William Andrew, Oxford, pp. 251–285. http://dx.doi.org/10.1016/B978-1-4377-3469-0.10012-8.

Minoura, Y., Asao, M., 1961. Studies on the γ-irradiation of natural rubber latex. J. Appl. Polym. Sci. 5, 233–239. http://dx.doi.org/10.1002/app.1961.070051416.

Morshedian, J., Jahani, Y., Sharbafian, F., Zarei, F.S., 2015. The effect of high-energy electron beam on drawn and undrawn high density polyethylene fibers. Polyolefins J. 2, 109–119. http://dx.doi.org/10.22063/poj.2015.1166.

Moustafa, A.B., Mounir, R., El Miligy, A.A., Mohamed, M.A., 2011. Effect of gamma irradiation on the properties of natural rubber/styrene butadiene rubber blends. Arab. J. Chem. http://dx.doi.org/10.1016/j.arabjc.2011.02.020.

Mullins, L., Turner, D.T., 1960. Radiation crosslinking of rubber. III. Chain fracture. J. Polym. Sci. A1 43, 35–47. http://dx.doi.org/10.1002/pol.1960.1204314104.

Numerical Analysis of Gel/Dose Curves – GelSol95 for Windows. ⟨http://mitr.p.lodz.pl/biomat/old_site/gelsol.html⟩ (Accessed 20 Feb 2016).

O'Donnell, J.H., 1991. Chemistry of radiation degradation of polymers. In: Clough, R.L., Shalaby, S.W. (Eds.), Radiation Effects of Polymers. American Chemical Society, Washington, pp. 402–413. http://dx.doi.org/10.1021/bk-1991-0475.ch024.

Oikawa, H., Murakami, K., 1984. Studies of the network structure of rubber vulcanizates by a cryoscopic method: 1. Polymer 25, 225–229. http://dx.doi.org/10.1016/0032-3861(84)90329-X.

Oikawa, H., Murakami, K., 1989. Relationship between swollen network structure of rubber vulcanizates and mechanism of freezing point depression of swelling solvent. J. Macromol. Sci. B 28, 187–216. http://dx.doi.org/10.1080/00222348908215219.

Olejniczak, J., Rosiak, J., Charlesby, A., 1991. Gel/dose curves for polymers undergoing simultaneous cross-linking and scission. Int. J. Radiat. Appl. Instrum. C Radiat. Phys. Chem. 38, 113–118. http://dx.doi.org/10.1016/1359-0197(91)90052-4.

Parkinson, W.W., Sears, W.C., 1967. Effects of radiation on the olefinic groups in polybutadiene. In: Gould, R.F. (Ed.), Irradiation of Polymers. American Chemical Society, Washingon, pp. 57–70. http://dx.doi.org/10.1021/ba-1967-0066.ch005.

Rosiak, J.M., 1998. Gel/sol analysis of irradiated polymers. Radiat. Phys. Chem. 51, 13–17. http://dx.doi.org/10.1016/S0969-806X(97)00254-5.

Saito, O., Kang, H.Y., Dole, M., 1967. Theory of gel—dose curves for polymers undergoing simultaneous crosslinking and scission. J. Chem. Phys. 46, 3607–3616. http://dx.doi.org/10.1063/1.1841265.

Schnabel, W., 1981. Polymer Degradation: Principles and Practical Applications. Hanser, Munich.

Schnabel, W., 1990. High energy radiation- and UV light-induced crosslinking and chain scission. In: Güven, O. (Ed.), Crosslinking and Scission in Polymers, 1st ed. Kluwer Academic Publishers, Dordrecht, pp. 15–36. http://dx.doi.org/10.1007/978-94-009-1924-2_2.

Shaltout, N.A., 2009. Effect of electron beam irradiation and degree of boric acid loading on the properties of styrene–butadiene rubber. React. Funct. Polym. 69, 229–233. http://dx.doi.org/10.1016/j.reactfunctpolym.2008.12.025.

Shen, Y., Fei, L., Zhao, X., 1995. Study of γ-irradiation crosslinking of cis-l,4-polybutadiene by NMR Microscopy. Appl. Magn. Reson 8, 181–186. http://dx.doi.org/10.1007/BF03162785.

Shyichuk, A., Tokaryk, G., 2005. A comparison of methods to determination of

macromolecule crosslinking yield from gel fraction data. Polimery-W 50, 219–222.

Stephan, M., Vijayabaskar, V., Kalaivani, S., Volke, S., Heinrich, G., Dorschner, H., Wagenknecht, U., Bhowmick, A.K., 2007. Crosslinking of nitrile rubber by electron beam irradiation at elevated temperatures. Kaut Gummi Kunstst. 60, 542–547.

Svoboda, P., 2015. Influence of branching density in ethylene-octene copolymers on electron beam crosslinkability. Polymers 7, 2522–2534. http://dx.doi.org/10.3390/polym7121530.

Taylor, G.R., Darin, S.R., 1955. The tensile strength of elastomers. J. Polym. Sci. 17, 511–525. http://dx.doi.org/10.1002/pol.1955.120178604.

Turner, D.T., 1963. The influence of molecular weight distribution on the solubility analysis of irradiated rubber. J. Polym. Sci. Polym. Lett. 1, 93–95. http://dx.doi.org/10.1002/pol.1963.110010208.

van Bevervoorde-Meilof, E.W.E., 1998. Improving Mechanical Properties of EPDM Rubber by Mixed Vulcanisation. Universiteit Twente, Enschede.

Vijayabaskar, V., Stephan, M., Kalaivani, S., Volke, S., Heinrich, G., Dorschner, H., Bhowmick, A.K., Wagenknecht, U., 2008. Influence of radiation temperature on the crosslinking of nitrile rubber by electron beam irradiation. Radiat. Phys. Chem. 77, 511–521. http://dx.doi.org/10.1016/j.radphyschem.2007.09.011.

Vroomen, G.L.M., Visser, G.W., Gehring, J., 1991. Electron beam curing of EPDM. Rubber World 205 (23), 26–32.

Wang, Q., Wang, F., Cheng, K., 2009. Effect of crosslink density on some properties of electron beam-irradiated styrene–butadiene rubber. Radiat. Phys. Chem. 78, 1001–1005. http://dx.doi.org/10.1016/j.radphyschem.2009.06.001.

Wang, Q., Zeng, J., Zhou, X., Yan, J., 2016. Irradiation vulcanized styrene-butadiene rubber/nanoscale silica composites. J. Polym. Res. 23, 1–6. http://dx.doi.org/10.1007/s10965-015-0899-8.

Wippler, C., 1958. Reticulation du chlorure de polyvinyle sous l'action des radiations ionisantes. J. Polym. Sci. A1 29, 585–594. http://dx.doi.org/10.1002/pol.1958.1202912024.

Witt, E., 1959. The effect of polymer composition on radiation-induced crosslinking. J. Polym. Sci. 41, 507–518. http://dx.doi.org/10.1002/pol.1959.1204113844.

Yasin, T., Ahmed, S., Yoshii, F., Makuuchi, K., 2002. Radiation vulcanization of acrylonitrile–butadiene rubber with polyfunctional monomers. React. Funct. Polym. 53, 173–181. http://dx.doi.org/10.1016/S1381-5148(02)00171-2.

Zagórski, Z.P., 2004. EB—crosslinking of elastomers, how does it compare with radiation crosslinking of other polymers? Radiat. Phys. Chem. 71, 263–267. http://dx.doi.org/10.1016/j.radphyschem.2004.03.083.

Zaharescu, T., Podină, C., 2001. Radiochemical stability of EPDM. Polym. Test 20, 141–149. http://dx.doi.org/10.1016/S0142-9418(00)00015-5.

Zhang, W., Sun, J., Qian, B., 1985. Structure effects on the sol fraction-dose relationship in radiation crosslinking of polymers. Polym. Commun. 59, 17–25.

Zhen, S.J., 2001. The effect of chain flexibility and chain mobility on radiation crosslinking of polymers. Radiat. Phys. Chem. 60, 445–451. http://dx.doi.org/10.1016/S0969-806X(00)00419-9.