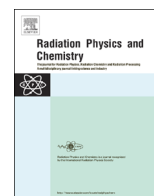




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## Synergistic effects in the processes of crosslinking of elastomers

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## HIGHLIGHTS

- Aromatic peroxides play a role in radiation crosslinked elastomers.
- Chromatographic determination of oxygen can be helpful in the description of the oxidation of polymers.
- DRS is a good way of describing the process of aging of polymers.

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## ABSTRACT

Radiation crosslinking of elastomers is an example of the modification of polymers by ionizing radiation. In practice, often parallel both traditional crosslinking (with peroxide) and radiation treatment is applied (Bik et al., 2003, 2004). Elastomers can be irradiated both before and/or after vulcanization products. The aim of this study was to investigate the system of the mixed radiation/peroxide and peroxide/radiation crosslinking of selected elastomers (Engage 8200, HNBR). In particular, attention was directed to the influence of the protective effects of aromatic additives in elastomers (peroxides, thermal- and light stabilizers) on the phenomenon of crosslinking and postradiation oxidation. Aromatic peroxides may undergo modifications during the preirradiation, which affect the subsequent processes of vulcanization. In this way the method of gas chromatography (GC) was applied for determination of hydrogen and oxidation effects, never described before for Engage 8200. Using that approach, radiation efficiency of hydrogen evolution and oxygen absorption efficiency of the polymers has been identified. To describe the phenomena of postradiation oxidation of elastomers, the method of Diffuse Reflection Spectrophotometry (DRS) was also applied.

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## 1. Introduction

Radiation induced crosslinking is an alternative to traditional methods of crosslinking of elastomers. Radiation methods may be more convenient, because materials can be processed at ambient temperature, whereas traditional methods, e.g. of vulcanization of rubber demand not only an addition of crosslinking agent but also heating of the elastomers. The control of the radiative process is easy by adjusting the power and dose of applied radiation. Combination of methods, radiation induced and traditional one is also possible, e.g. by preemptive crosslinking by radiation and thermal finishing. Reversed approach is also possible; both realize synergy phenomenon. The purpose of the present paper is to investigate named processes by application of two techniques, one after another, seldom applied in radiation chemistry of polymers.

The starting point of radiation induced ageing of elastomers is detachment of hydrogen atom. If it is not connected with crosslinking (see above) it leaves free radical center attaching oxygen molecule if available in the polymer physically. The peroxide thus formed starts post-irradiation reactions, leading to disruption of chains and formation of lower molecular weight of products of degradation. In the contrary to photochemical ageing, radiation induced ageing starts from all constituents of elastomer, present in the material and absorbing energy proportional to their participation and their electron density.

In processes of radiation induced crosslinking and postradiation oxidation, the presence of aromatic compounds plays an important role (Seguchi et al. 2012). These compounds exert protection effect by energy and charge transfer in irradiated polymer matrix (Głuszewski and Zagórski 2008). It can be modified by the mode of presence of additive in the mixture or composite. Aromatic compounds, of increased resistance to ionizing radiation, can dissipate energy by radiative or radiationless processes.

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In the case of elastomers of the ENGAGE type, aromatic compounds are represented by both standard antioxidants and photostabilizers and also by peroxides added for chemical crosslinking. In spite of increased resistance to radiation, aromatic compounds eventually are degraded. In the case of double action crosslinking, these effects influence the final result.

Using previous experience in the application of gas chromatography to radiation chemistry of polymers (Sugimoto et al. 2013), as well as application of the DRS method to the investigation of radiation chemistry of polymers (Zagórski 2003), the present investigation was expected to be also fruitful in the case of elastomers, never investigated in that direction. Elastomer ENGAGE 8200 seems to be the proper representative of such materials. There is no information in the literature about the radiation induced oxidation of irradiated elastomers, in particular of mentioned type.

The purpose of the present investigation is exploration of the role of aromatic additives on the process of radiation induced and mixed radiation catalytic/thermal crosslinking. The new approach in the investigation consists in the determination of both hydrogen and oxygen in one operation of irradiation and gas chromatographic analysis. The investigation is combined with DRS determination (below), giving full picture of results.

## 2. Experimental

### 2.1. Investigated elastomers

Polymer Engage 8200 (ethylene–octane copolymer, the DOW Chemical Company) was investigated in the shape of granules (with symbol Z), foils (A), foils with the addition of small amount of peroxide (B) and higher (double in comparison to B) content of benzoyl peroxide (C), vulcanized foil (AV) and foils vulcanized with peroxides (BV) and vulcanized with double amount of peroxide (CV). Other elastomers, like NBR (copolymer of butadiene and acrylonitrile, Chemical Plant S.A. DWORY, Poland) and HNBR (hydrogenated nitrile butadiene rubbers, commercial name Therban) were also used.

### 2.2. Irradiations

Irradiations were done by electron beam and by gamma radiation, for the purpose of comparison. Different dose rates and doses were applied. Two gamma radiation sources were used, one of the dose rate of 0.62 kGy/h, the second of 7.0 kGy/h power. The electron beam accelerator Elektronika 10/10 was used, producing scanned beam of electrons of energy of 10 MeV and of 9 kW power with the possibility of changing the dose rate by controlling the speed of the conveyor. The dose rates in accelerator irradiations were 18,000 kGy/h. Samples were irradiated in air, in closed vessels with gas phase subjected to gas chromatographic analysis, at room temperature. The use of different dose rates allowed to describe the impact of diffusion of oxygen on degradation processes and consequently on the properties of processed of polymers.

In some experiments irradiated samples were subjected to ageing, before investigation, see Section 2.4.

### 2.3. Gas chromatography

Yields of hydrogen and absorption of oxygen were determined by gas chromatography Fig. 1. Gas chromatograph type GC 2014 by Shimadzu, with thermal conductivity detector, column packed with molecular sieves 5A was applied for analyses of gaseous products formed in samples submitted to the electron irradiation

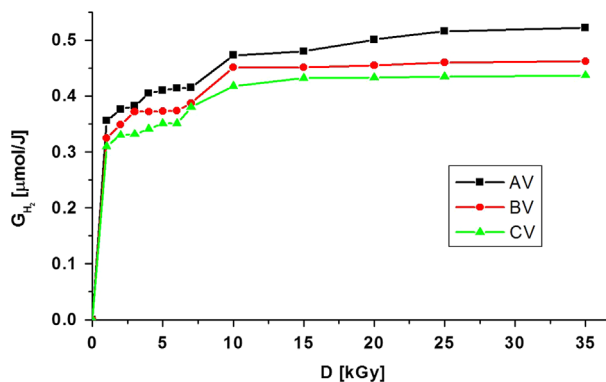


Fig. 1. The yield of hydrogen vs. absorbed dose of vulcanized foils.

Table 1

Radiation yields of hydrogen formation and oxygen consumption, immediately after the irradiation and 24 h after. Symbols of samples are explained in text.

	$G_{H_2}$	$G_{O_2}$ [ $\mu\text{mol/J}$ ]					
		EB	7 kG/h	0.7 kGy/h	After 24 h		
Z	0.480	0.444	0.467	1.082	0.458	0.646	1.632
A	0.450	0.429	0.445	1.025	0.451	0.530	1.400
B	0.434	0.307	0.311	0.789	0.385	0.481	1.216
BV	0.522	0.343	0.334	0.987	0.379	0.528	1.137

(hydrogen and carbon monoxide) as well as for the loss of oxygen in the atmosphere surrounding the sample in the irradiation vessel. The gas chromatograph was attached by interface to the PC computer where the data were acquired by program CHROMAX. The carrier gas was argon (99.99%), calibration gases were hydrogen 99.99% and oxygen 99.99%. Operations were done with syringes of volume 10, 25 and 500 ml. The chromatographic system was working at 220 °C, the column was kept at 40 °C and the detector at 100 °C. The rate of flow of carrier gas was 10 ml/min.

### 2.4. Diffuse reflection spectroscopy

One of the advantages of diffuse reflection spectroscopy (DRS) is the possibility to investigate polymers in any shape. The principle of measurement (Soebiantiano et al., 1995) consists in directing the beam of analyzing light on the surface of the sample. Part of light is reflected back unchanged, but another is bent into the sample and after inside reflections are leaving the sample with spectral information about compounds formed in the result of irradiation and/or compounds present before and destroyed. In our investigations the spectrophotometer JASCO V-670 equipped with reflection device was used. Several bands of absorption were identified. The band around 210 nm is ascribed to peroxide groups. Bands at 295–320 nm are ascribed to CO groups at the end of chains (products of degradation) and peaks in the range of 245 to carboxyl groups in the middle of polymer chains.

The efficiency of DRS investigation has been tried in the case of irradiated HNBR elastomers (Fig. 3).

The case of present elastomers is shown in Figs. 4 and 5.

## 3. Results and discussion

The protection effect of aromatic peroxide in the radiolysis of elastomer ENGAGE 8200 is shown on the example of three kinds of samples (A, B, and BV), Table 1.

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