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Protective effects in radiation modification of elastomers

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HIGHLIGHTS

- We described the processes of radiation/peroxide crosslinking of the elastomer.
- Aromatic peroxides have a protective effect in the radiolysis of elastomers.
- Aromatic additives have a significant impact on crosslinking and oxidation.
- It is possible synergy of radiation and peroxide crosslinking.
- To study the aging process elastomers used the method of DRS.

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ABSTRACT

Saturated character of ethylene/octene thermoplastic elastomers demands an application of nonconventional methods of crosslinking connections between chains of molecules. These are organic peroxides, usually in the presence of coagents or an application of ionizing radiation. Several approaches (radiation, peroxide, peroxide/plus radiation and radiation/plus peroxide) were applied in crosslinking of elastomere Engage 8200. Attention was directed to the protection effects by aromatic peroxides and by photo- and thermostabilizers on radiolysis of elastomers. Role of dose of radiation, dose rate of radiation as well as the role of composition of elastomere on the radiation yield of hydrogen and absorbtion of oxygen was investigated. DRS method was used to follow postirradiation degradation. Influence of crosslinking methods on properties of elastomers is described. Results were interpreted from the point of view of protective actions of aromatic compounds.

1. Introduction

Thermoplastic elastomers, as saturated polymers with a low number of double bonds are characterized by high resistance to ozone and thermal aging, but exhibit unsatisfactory mechanical properties. It is believed that the peroxide–radiation crosslinked thermoplastic elastomers achieve better properties than those crosslinked by conventional methods. The undeniable advantages of radiation techniques include the possibility of crosslinking of the elastomer at ambient temperature and are relatively easy to control by the size of the absorbed dose of radiation (Bik et al., 2003; Zagórski et al., 2011; Zagórski and Kornacka, 2013).

Unique for radiation chemistry are primary phenomena. Absorption of ionizing radiation causes the detachment of electrons which travel to places of energetically preferential sites, e.g. positive holes from previous ionizations or places where two chains are close to one another. The positive holes are also wandering along the chains, also to energetically preferable sites, other than those for electrons. Formation of excited states (as a result of electron capture by the hole) also takes place. All these phenomena, precedes the creation of a macroradical. Translation of reactive species takes important role in protective phenomena, if aromatic compounds are present (Głuszewski and Zagórski, 2008).

In the case of elastomers, aromatics are both standard stabilizers (antioxidizers and photostabilizers) as well peroxidizers added for chemical crosslinking. Thermal treatment and radiation processing lower the amount of aromatics by degradation. Combined processes of radiation and chemical crosslinking can substantially influence the yield of the number of crosslinks and processes of oxidegradation of elastomere (Głuszewski et al., 2014).

Under investigation was ethylene–octen thermoplastic elastomer of Engage type, crosslinked by peroxide and subsequently irradiated in the range of doses 20–300 kGy (Perraud et al., 2003; Mishra et al., 2008; Poongavalappil et al., 2013).

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2. Materials and methods

Following sheets were prepared from elastomere Engage 8200 (Table 1), used for determination of the radiation yield of hydrogen and absorption of oxygen. Influence of thermal processes of formation and of the vulcanization and addition of peroxide on phenomena of oxidation in process of ageing were investigated Figs. 1–4.

Properties of Engege 8200: Melt Index, 190 °C/2.16 kg, dg/min – (5.0), Density, g/cm^3 – (0.870), Mooney Viscosity, ML 1+4 @ 121 °C – (8), Ultimate Tensile Strength, MPa – (5.7), Ultimate Tensile Elongation – (1140), 100% Modulus, MPa – (2.3), Hardness, Shore A (1 s) – (66), Shore D (1 s) – (17), Tear Strength, Type C, kN/m – (37.1), Vicat Softening Point, °C – (37), DSC Melting Point, 10 °C/min rate, °C, Dow Method – (59), Glass Transition Temperature, °C, Dow Method – (53), Tc Peak, °C, Dow Method – (4).

Table 1
Elastomeric materials used in the study.

Engage 8200 (ethylene–octane copolymer (the DOW Chemical Company))	Marking
Granules	**G**
Sheet without addition of peroxide	**A**
Sheet with the addition of small amount of peroxide	**B**
Sheet with higher (double in comparison to B) content of peroxide	**C**
Vulcanized sheet without addition of peroxide	**AV**
Vulcanized sheet with peroxide	**BC**
Vulcanized sheet with double amount of peroxide	**CV**

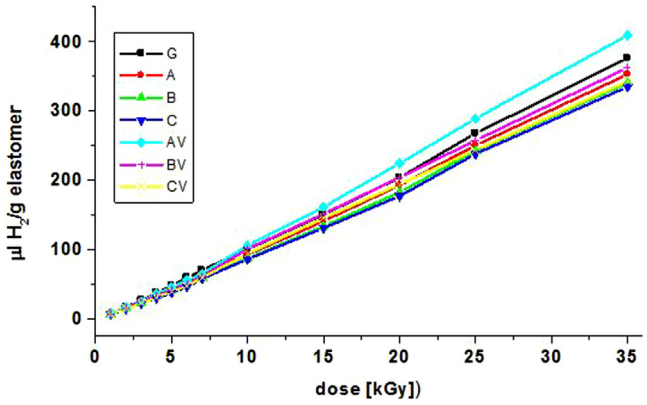

Fig. 1. Volume of hydrogen formed in the result of irradiation of granulate and sheets of elastomers.

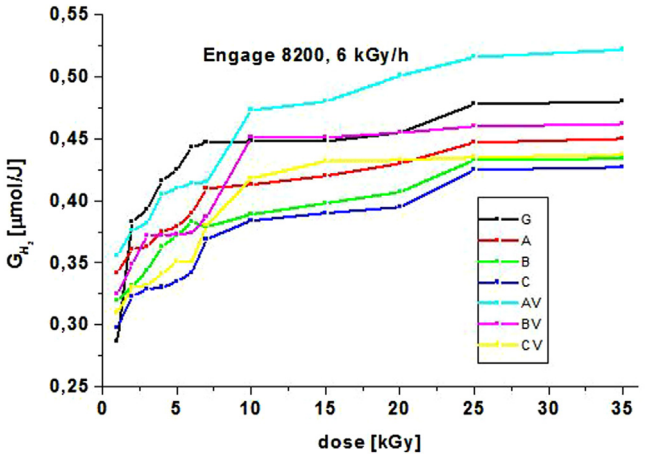

Fig. 2. The yield of hydrogen and the yield of absorbed oxygen vs absorbed dose.

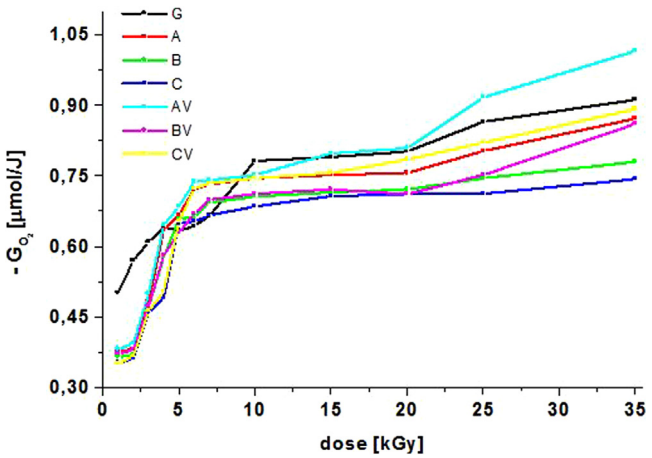

Fig. 3. The yield of hydrogen and the yield of absorbed oxygen vs absorbed dose.

Peroxides used: dicumul peroxide (Perkadox BC409, Akzo Nobel Polymer Chemicals) and Taic 50 (Kettlitz Chemie GmbH & C). Two types of samples were tested: 1% Perkadox BC409 and 0.9% Taic 50 and 2% Perkadox BC409 and 1.8% Taic 50. Samples were formed in a standard way by rolling and then forming (temperature, pressure) Tables 2–5.

2.1. Gas chromatography (GC)

Gas chromatograph Shimadzu (thermal conductivity detector, molecular sieves 5A) was used for the determination of radiation yield of hydrogen evolution (GH_2) and absorption of oxygen (GO_2) from the dose of radiation in the range of 1–35 kGy. Samples were irradiated in air, in closed vessels with gas phase subjected to gas chromatographic analysis, at room temperature. 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 μl. 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. Radiation efficiency was calculated in μmol/J.

2.2. Irradiation

The samples were irradiated in air, at room temperature, at the source of gamma radiation, GC 5000, the Indian production of the dose rate was 7.0 kGy/h. Gamma radiation dose rate was measured with a Fricke dosimeter and alanine dosimeter. Dose distribution was measured with PVC foil. Samples were irradiated in air, in closed vessels with gas phase subjected to gas chromatographic analysis, at room temperature.

2.3. Diffuse reflection spectroscopy (DRS)

One of advantages of diffuse reflection spectroscopy (DRS) is the possibility to investigate polymers in any shape. The principle of measurement 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 then inside reflections leave the sample with spectral information about compounds formed as 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 absorbtion were identified. The band around 210 nm is acquired to peroxide groups. Bands at