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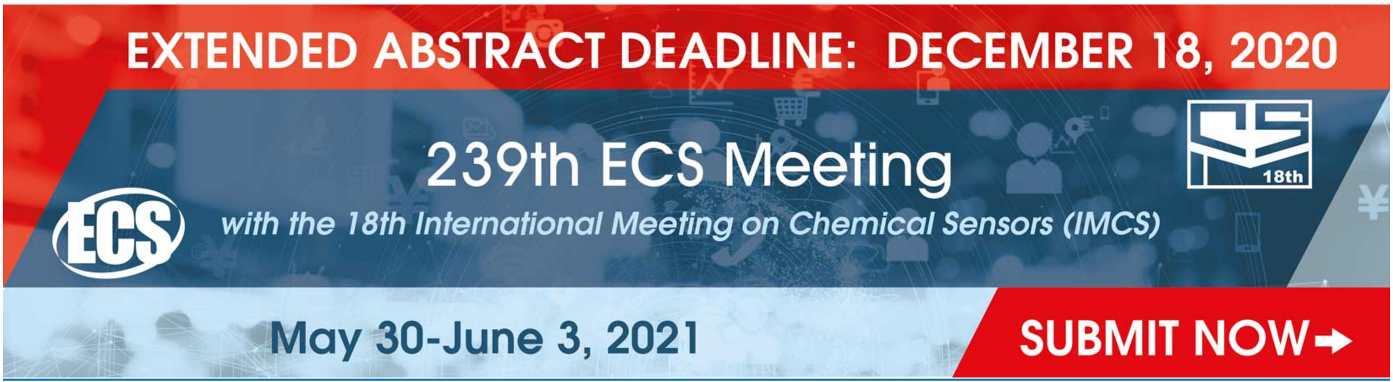

Elastomer modification by means of ionizing radiation

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Abstract. One of the priorities for improving the performance characteristics of elastomer compositions is their physical modification, which allows to obtain materials with a new set of performance properties. Among the known methods of modifying products based on elastomers, one of the actual methods is radiation modification. It allows you to control the physico-mechanical and elastic-strength characteristics of products. In connection with the foregoing, the development of a technology for the radiation modification of elastomers with the aim of increasing their operational characteristics is relevant. In this work, the effect of ionizing radiation on the thermo-physical and operational properties of elastomeric compositions for the tread of career tires was investigated. It was established that the level of the maximum temperature developed in the samples depends on the degree of vulcanization of the elastomeric compositions. In samples of tread rubber, heat generation is reduced by 2–4 % after treatment with accelerated electrons. In the process of exposure to ionizing radiation, the formation of free radicals and their subsequent recombination occurs. Revealed an increase in crosslinking density in modified specimens. The correlation dependences between the thermophysical properties of elastomeric compositions and the intensity of heat generation in them are established. It was determined that the best thermo-physical properties of polymers with a degree of crosslinking *t80*. The wear resistance of the modified elastomeric compositions is increased up to 3.5 times.

1. Introduction

Radiation is a powerful energy source for chemical processing applications in several industries. Nuclear radiation is ionizing; radiation induced materials give positive ions, free electrons, free radicals, and excited molecules. A wide range of reactive species become available; they can be used as an origin for radiation-initiated reactions such as modification, cross linking, or degrading materials [1, 2].

Polymer materials are exposed to high-energy radiation in order to change their properties. As a result, it is necessary to understand how radiation modifies the structure and properties of the polymer. As will be discussed below, radiation has a profound effect on the physical properties of polymers due to their long chain structure. When an electron beam or X-ray radiation source interacts with a polymer material, its energy is absorbed by the material and active particles are formed, such as radicals, which initiate various chemical reactions. These reactions include crosslinking, degradation, grafting and curing. These radiation-induced reactions are the cause of many useful applications in rubber materials. Important properties of polymeric materials, such as mechanical properties, thermal stability, chemical resistance, processability and surface properties, can be significantly improved by radiation treatment. A very large amount of literature allows us to predict the sensitivity to radiation of certain types of polymers [3–23]. This article discusses the basic principles of radiation processing, the types of radiation used, radiation chemistry, as well as the industrial use of X-rays and electron beams to modify and improve the properties of the polymer.

1.1. Types of radiation sources

Various ionizing radiation, such as X-rays and accelerated electrons, are widely used for radiation processing of material. These emissions affect the molecular structure and macroscopic properties of polymeric materials. The energy ranges of various emissions are given in table 1. In radiation technologies, the main sources of radiation are X-rays and electron beams.

Table 1. Frequency and wavelength of various radiation sources.

Radiation	Frequency (Hz)	Wavelength (μm)	Energy
Gamma rays	10^{24}–10^{19}	10^{-7}–10^{-6}	124 MeV to 124 keV
X-rays	10^{19}–10^{17}	10^{-6}–10^{-3}	124 keV to 1.24 keV
UV	10^{17}–10^{15}	10^{-2}–1	1.24 keV to 12.4 eV
IR	10^{15}–10^{12}	1– 10^{2}	12.4 eV to 124 meV
Electron beam	10^{21}–10^{18}	10^{-7}–10^{-4}	12.4 MeV to 12.4 keV
Microwave	10^{12}–10^{10}	10^{3}–10^{5}	124 meV to 1.24 meV

High-energy electrons are formed in electron beam accelerators. Electron beams reach high kinetic energies in the range from keV to several MeV in accelerators. The electron beams generated by accelerators have a monoenergetic character. Such rays are unidirectional and can be directed directly at the material and move from one end to the other. The required dose is delivered to the product by transporting the product under the beam at certain speeds.

To create electron beams using electron guns with a heated cathode of tungsten or its alloys. The resulting electron beams are accelerated in a tube in which a high vacuum is maintained. It is possible to control the diameter, density, direction and other characteristics of the beam. Currently, accelerators with a relatively low cost and good biological protection have been developed. Accelerated electrons are considered the safest and most promising ionization type of radiation.

Characteristic X-ray radiation – electromagnetic radiation emitted during transitions of electrons from the outer electron shells of the atom to the internal ones (characteristic spectrum). The characteristic spectrum is a linear X-ray spectrum that arises during the transitions of the electrons of the upper shells of an atom to the K-, L-, M-, N-shells located closer to the nucleus. The frequencies of the lines of the characteristic spectrum of chemical elements obey the Moseley law.

X-ray radiation can also be obtained at charged particle accelerators. Those synchrotron radiation occurs when a particle beam is deflected in a magnetic field, as a result of which they experience acceleration in a direction perpendicular to their movement. Synchrotron radiation has a continuous spectrum with an upper boundary. With correctly selected parameters (magnetic field and particle energy), X-rays can also be obtained in the synchrotron radiation spectrum.

Under the influence of X-ray radiation, polymers undergo profound chemical and structural changes, leading to a change in physicochemical and physico-mechanical properties. By adjusting the irradiation intensity, it is possible to change the properties of the polymers in a given direction. The nature of the processes occurring under the action of X-ray radiation, strongly depends on the type of polymer.

1.2. Absorbed dose

The degree of change in material properties caused by radiation depends on the absorbed dose, which corresponds to the energy released by radiation per unit mass of material. The unit of measure is gray, Gy, and 1 Gy corresponds to 1 J of energy, which is stored in 1 kg of material.

Most industrial radiation applications require that the absorbed dose be evenly distributed throughout the material. The uneven distribution of radiation may be due to the limited penetration range compared to the thickness of the sample, for charged particles, or due to a change in the electronic equilibrium between the surface and the bulk, for gamma rays. The presence in the material of substances with very different chemical compositions or densities can also cause dose inhomogeneities. Therefore, it is recommended to use Monte Carlo codes [16] to calculate the required dose.

1.3. Ionization

With the passage of ionizing radiation through a substance, ionization and excitation of the molecules of this substance occur. When using flows of charged particles (electrons, protons, α-particles, fragments at the time of fission), ionization and excitation occurs directly as a result of collisions.

When molecules are excited, their vibrational energy increases (thermal activation of the substance); dissociation of matter into radicals is also possible.

In the process of ionization of molecules, a secondary electron with high energy is formed: $B \rightarrow B^{*} + e$. This electron quickly (in 10^{-16} s) loses its energy, causing ionization and excitation of several molecules of the substance. He also participates in a number of other processes leading to a decrease in his energy.

The information obtained on the primary radiolysis of ionization and excitation was taken from experimental works [18]. In addition to breaking the bond, depending on the level of excitation or its stability, an excited molecule can also transfer its excitation to a neighboring molecule through various mechanisms [11–13].

Thus, when ionization radiation passes through a substance, a large number of active particles of various nature (free radicals, ions, solvated electrons, photons, etc.) appear in it, and their concentration can far exceed the concentration characteristic of thermodynamic equilibrium. Therefore, radiation-chemical processes usually occur at high speeds and at very low temperatures.

1.4. Modified polymer changes

Molecular changes caused by ionizing radiation in a polymer can be of several types [14]:

- emission of volatile compounds (hydrogen H_2, carbon oxides CO and CO_2, hydrocarbon molecules);
- the creation of unsaturated bonds and other molecular bonds – crosslinking and breaking of the measuring chain.

New bonds created by ionizing radiation cannot be predicted in advance. They depend on the chemical structure of the polymer [15], the nature of the generated excited states, the composition of the polymer (impurities, fillers) and on the radiation parameters. The presence of oxygen during irradiation will also change the mechanism of degradation, because oxygen reacts with radicals resulting from radiolysis.

1.5. Radiation crosslinking

Radiation crosslinking has been used since the 1970s to crosslink polyethylene in cases of cables, pipes, heat shrink tubes, and film, but also to crosslink rubber in tires. Reconditioned rubber compounds for tires are also crosslinked to improve their compatibility [20–22].

Polymer crosslinking is the largest commercial application of radiation treatment. The required doses are usually in the range between 50 and 200 kGy and include one-step reactions or reactions with a short kinetic chain length. As a result, covalent bridges are formed between the polymer chains at a certain temperature (spatial network formation).

As a rule, crosslinked materials exhibit not only the best physico-mechanical and chemical properties, but also thermal and fire resistance. Radiation crosslinking gives polymers such properties as insolubility, infusion, a significant improvement in their dimensional stability in chemically aggressive and high-temperature conditions, improved abrasion resistance, and increased strength.

2. Materials and methods

The object of the study is a rubber mixture based on natural rubber used for the production of the tread-running part of an oversized tire part. An approximate recipe for this mixture is presented in table 2.

Table 2. Test compound formulation.

Name of rubbers and ingredients	Content (phr)[a]	Mass (%)
Natural rubber	100	56.55
Silica	10	5.65
Carbon black N234	45	25.45
Sulfur	1.3	0.73
Others components	20.55	11.62
Total	176.85	100

The density of the rubber compound 1.136 g cm^{-3}

[a] Parts per hundred parts of rubber

When testing on a vibration rheometer, the material undergoes constant alternating shear deformations, which allows us to record a continuous curve of changes in the properties of the material during the testing of one sample, reflecting not only the change in the plastoelastic characteristics of the rubber mixture, but also its vulcanization characteristics. The vulcanization characteristics of rubber compounds were determined using an ODR 2000 vibroreometer.

Table 3 presents the data on the kinetics of vulcanization of the investigated rubber compounds – the tread-running part of the tire (Pb) obtained on the ODR 2000 rheometer.

Table 3. Kinetic parameters of vulcanization of the investigated rubber compounds.

Name rubber compound	ML (dN m)	MH (dN m)	t_{s2} (min)	t_{50} (min)	t_{90} (min)	The difference MH - ML (dN m)
Pb	5.94	39.61	4.77	6.92	9.19	33.67

2.1. Irradiation

The samples were irradiated in air at room temperature, the radiation source was UELR-10-10C, the dose rate varied from 5 kGy to 50 kGy with an interval of 5 kGy. The applied acceleration energy and beam current were 1.8 MeV and 1 mA, respectively. The dynamic irradiation technique was used [21].

2.2. Mechanical test

Mechanical properties, such as tensile strength, modulus, elongation at break, etc., were measured at room temperature (25 ± 2) °C and active traction speed (500 ± 50) mm min^{-1}. A test method using a sample in the form of a blade that was cut from a molded sheet [19].

The mechanical properties of rubber samples irradiated after vulcanization with different doses are shown in figures 1 and 2.

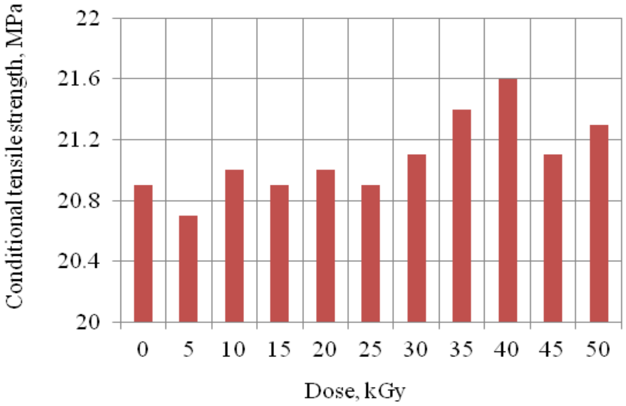

Figure 1. Graph of conditional tensile strength versus sample irradiation dose.

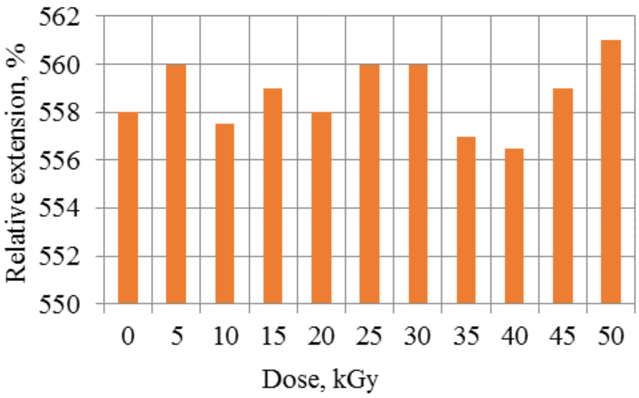

Figure 2. Graph of the relative elongation at break from the dose of the sample.

2.3. Resistance to abrasion

The tests were carried out at room temperature (23 ± 2) °C, on the MI-2 installation, the samples corresponded to GOST 263. As a result of the abrasion tests, we obtained the values of abrasion resistance, as well as the values of the coefficients of friction and abrasion. The data are given in table 4.

2.4. Cross-linking density by equilibrium swelling

The equilibrium swelling method is most often used in determining the crosslink density of vulcanizates. For the study, rectangular samples of vulcanizates with a size of (20 × 10 × 2 ± 0.2) mm, cut from the central part of the rubber plate, are used.

As a result of the experiment, the values of the number of cross-links in 1 cm^3 of the vulcanizate (n), as well as the cross-linking density (v), were obtained. The data obtained are summarized in table 5.

2.5. Resistance of rubber to crack growth during repeated bending

Samples were tested on a De Mattia Flex Testing machine according to GOST 9983-74 (method B) at a temperature of +22 °C. After the test time, the crack parameters for each rubber sample of different ciphers were determined, table 6.

Table 4. Abrasion test results.

Dose (kGy)	Abrasion resistance (-)	Coefficient (-)	Coefficient of friction μ (-)
Source sample	63.15	0.019	1.31233
5	63.39	0.015	1.16846
10	67.88	0.015	1.18992
15	61.38	0.016	1.27418
20	65.04	0.016	1.23762
25	67.98	0.015	1.26464
30	65.93	0.016	1.29962
35	80.30	0.015	1.21854
40	68.24	0.014	1.22569
45	67.23	0.013	1.43077
50	75.78	0.013	1.37274

Table 5. The spatial grid of the studied rubber.

Dose (kGy)	Spatial Grid Index		
	Mc (kg mol^{-1})	$n\cdot10^{-18}$ (cm^3)	$v\cdot10^4$ (mol cm^{-3})
Source sample	6779.0	0.75	1.60
5	6742.0	0.75	1.62
10	6786.0	0.75	1.61
15	6756.0	0.76	1.61
20	6691.0	0.76	1.62
25	6697.0	0.77	1.64
30	6649.0	0.76	1.64
35	6667.0	0.77	1.65
40	6675.0	0.77	1.67
45	6680.0	0.79	1.66
50	6684.0	0.80	1.67

Table 6. Test results of rubber samples for resistance to crack propagation during repeated bending.

Dose, kGy	Crack size (mm) / Number of cycles (thousand)				
	100	150	200	250	300
Source sample	8.0	10.0	×	×	×
5	8.5	×	×	×	×
10	8.5	9.0	×	×	×
15	9.0	10.0	×	×	×
20	7.5	8.0	11.0	×	×
25	6.5	10.0	×	×	×
30	8.0	8.0	×	×	×
35	8.0	9.0	11.0	×	×
40	5.0	7.0	9.5	10.0	11.0
45	6.0	7.0	9.5	11.0	×
50	7.0	8.0	9.0	10.0	×

3. Conclusion

In this article, we presented the first basic phenomena arising from the interaction of ionizing radiation and a polymer, and the application of the effects of ionizing radiation to create new materials.

Thus, in the course of the studies it was found that the dose of 40 kGy is optimal for the modification of tread rubber by ionizing radiation, which allows:

- improve the resistance of rubber to abrasion by 1.3–1.5 times;
- adjust the density of cross-linking;
- reduce heat generation by 5 %;
- increase the resistance of tread rubber to the formation and growth of cracks in conditions of repeated bending by more than 2 times.

The effects of ionizing radiation on polymers have been studied and used in industry for decades. From a fundamental point of view, the researchers identified features depending on the polymer (chemical structure, conformation, etc.) and on the irradiation conditions (nature of radiation and energy, temperature, atmosphere, etc.). These effects of ionizing radiation on polymers were used by manufacturers to produce new materials with specific and desired properties. Despite the fact that the process of exposure of polymers to ionizing radiation has been used for decades, comprehensive research and innovation is still needed to develop new technological and industrial applications.

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