American Journal of Polymer Science 2016, 6(1): 12-17
DOI: 10.5923/j.ajps.20160601.02

Structural Parameters and Dynamical Properties of the Radiative and Peroxide Vulcanizates Based on EPM Participation

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Abstract It is shown that irradiation of ethylene-propylene rubber (EPM) does not form a spatial network of small doses (150-300 kGy) that becomes fully soluble, indicating degradation of the molecular chains. It was found that irradiation of unfilled elastomer a low molecular weight radiation-chemical yield (RCY) cross-linking is 0,127 crosslinks on 100 eV absorbed energy. The introduction of the sensitizer DTBFM increases the speed of crosslinking, radiation-chemical yield of crosslinking (G_c) increased approximately 1.5-fold and 3.6-linking at 100 eV. By selecting the filler, and the dosage of sulfur, able to obtain vulcanizates of EPM, which are the source of physical and mechanical properties are not inferior peroxide vulcanizates. Structural changes in the aging process, was evaluated by the change in stress relaxation and conditional equilibrium modulus (ε, %).

Keywords Ethylene-propylene, Radiation, Peroxide crosslinking, Vulcanization, Relaxation, Modulus, Aging, Vacuum, Oligomer, Rubber

1. Introduction

It is known that the elastomeric material (EM) on the basis of ethylene-propylene rubber (EPM) have a high ozone, oxygen, weather resistance and heat resistance number of aggressive media (alcohols, glycols, ketones, hydraulic fluids, bases). [1-6] The copolymers It is also characterized by high dielectric performance, relatively high strength, elasticity, high abrasion resistance. As dynamic properties and permeability EPM similar to natural rubber. Due to the absence of unsaturation in the side chains (EPM) curing it causes difficulties.

Ethylene-propylene rubber (EPM) is one of the most promising general purpose elastomers [7-10]. Currently widely used of these copolymers vulcanization with peroxides in the presence of small amounts of sulfur [5, 11]. For vulcanizates with high physical and mechanical properties necessary to use large dosages of dicumyl peroxide (5.0 wt.h. per 100 wt.h. of elastomer), which is highly undesirable in a production environment because of the hazards of the product and decomposition of peroxides. [12-13] In addition, the presence of peroxides, as is known, adversely affected by the thermal aging of the elastomeric material. [14-16]

It is known that crosslinking saturated low molecular weight organic compounds elastomers can improve the technological and dynamic performance vulcanizates. [5, 4]

In particular, the high flexibility of chains and polar groups on the oligomers wasps basis maleimides leads to changes in the structure and properties of materials. [15]

The lack of double bonds in the EPM is the reason for the low efficiency of the formation of the spatial grid, so that in order to achieve optimum properties requires more integral dose. [2, 13]

Since radiation unfilled vulcanizates based on EPM does not have high strength. The introduction of the filler into the elastomer radiation-chemical yield (RCY) linking with increasing dosages of carbon should result in changes in the properties of vulcanizates [17-21].

In this regard, of particular interest are the choice of carbon and low molecular weight organic sensitizers, containing functional groups of different nature [1, 22, 23]. The presence of functional groups as part of their offers additional possibilities for modifying the properties of the elastomer to reduce the radiation dose without impairing the basic properties of the vulcanizates. In addition, the introduction of carbon black (filler) of the EPM, is less

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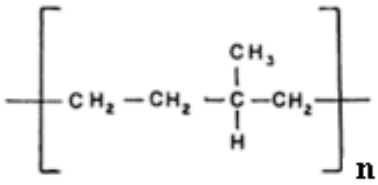
Published online at http://journal.sapub.org/ajps

affected by a decrease in the strength characteristics of vulcanizates temperature aging.

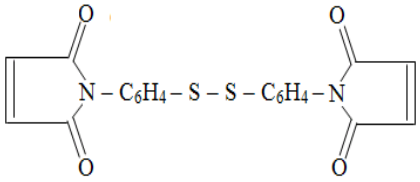
The aim of this study was to investigate the possibility of holding for ethylene elastomer (EPM) method of radiation curing, which allows to exclude from the formulation curing agents, such as dicumyl peroxide. Development of methods for the study of cross-linking and curing process, as well as determine the effect of the sensitizer and the carbon black in the mechanical and dynamic properties of elastomeric materials.

2. Experimental

The object of the study served as technical ethylene-propylene elastomer (EPM, Russia) catalyst prepared by copolymerization of ethylene and propylene in the presence of complexing catalysts. EPM molecules composed of alternating units of ethylene and propylene having the structural formula:



Propylene content was 50 mol/(%). Action fillers (furnace 324 and n-channel K354) under the action of mechanical and chemical properties of the composites was evaluated by the particle size (28-36 nm), bulk density (340 kg / m^2) and surface area (84-106 m^2 / kg). To reduce the irradiation dose and protect against radiation damage using a reactive low molecular weight compounds (LWC) as a sensitizing agent, 4,4'-dithiobis (N-phenyl maleimide DTBFM) of general formula:



Bifunctional sensitizing agent 4,4'-dithiobis (N-phenyl maleimide) has a high binding energy of the atoms connecting malemidnye group which is active in the reactions of maleimides accelerates release radicals and crosslinking elastomers. Selecting zinc oxide activation process for crosslinking accounted for at a rate of vulcanization of elastomers degree.

Composition investigated elastomeric compositions given in Table 1.

The reaction mixture of rubber and vulcanizing system was performed in micromixer "Brabender" while simultaneously loading into the chamber of the mixer corresponding ingredients. The concentration of the rubber in the mixture was 100 wt. h.

Table 1. Composition of the systems

Components	wt/h in 100 wt/h. of elastomer		
	1	2	3
EPM ……	100	100	100
Dicumyl Peroxide (DP)…	-	-	5,0
Sulfur ……..	0,2	0,2	0,5
DTBFM ……	6,0	6,0	6,0
ZnO ……	5,0	5,0	5,0
Black Carbon			
F324……	50	-	50
C354……	-	50	-

Offset elastomer blends (Table 1) were performed at 313K for 15 min. on rolls. Then, samples were formed in a thickness of band plates of 0.3 mm in a press at 358-363K. Irradiation of the samples placed in the vials, and the mold containers carried Co^{60} γ-rays at a power of 6.9 Gy / sec in air at 293K. The absorbed dose in the samples was calculated by comparing the density of the electronic and dosimetry systems [2, 13]. Radiation-chemical yield (RCY), the number of cross-linked molecules ($1/Mn_\tau$) is defined by Flory Renera. [24]

Mesh thickness and irradiated peroxide vulcanizates was determined by equilibrium swelling in benzene at room temperature. Samples were heated in benzene vulcanizates during the day. The degree of equilibrium swelling Q (%) was calculated by the equation:

$$Q = \frac{m_{swel} - m_{dry}}{m_{dry}} \cdot 100$$

m_{swel} −the mass of the swollen sample ob - mg;

m_{dry} - weight of the dried sample mg.

Tensile strength elongation was measured on a test tensile testing machine (RMI-500 company Tinius Olsen) with a load of 500 kgs. The dynamic properties of the samples was set to relaxometer axial compression VN 5305.

Increasing the amount of force in the samples (equilibrium modulus) to the instrument PURM-1 (Russia).

3. Results and Discussion

Irradiation of elastomer without the addition of small doses does not form a spatial grid (Figure 1). When dissolved in toluene raw elastomer not subjected to irradiation, it has a gel fraction after the irradiation doses of 150-300 kGy elastomer becomes fully soluble, indicating degradation of the molecular chains. When high doses of irradiation, crosslinking increases output, until the formation of a continuous spatial grid. As expected, the irradiation of a polymer with a high molecular weight gel formation starts at a lower dose (Figure 1).

Upon irradiation elastomer without carbon black with a low molecular weight (hardness 340 gauss) radiation-chemical yield (RCY) crosslinking is 0.7 crosslinks per 100 eV of absorbed energy (Fig. 1, curve 1), by irradiation at the plasticity elastomer (hardness 1100 gauss) radiation-chemical yield increases and amounts to 2.6

crosslinks per 100 eV (Fig. 1, curve 3). Thus, for radiation curing EPM advisable to use a higher molecular weight. Moreover, the laboratory data on known that a copolymer of hardness 1000-3000Gs relatively easily processed on the rollers, is well mixed with carbon black, the vulcanization is easily formed into a monolithic mixture.

Introducing elastomer sensitizer 4,4'-dithiobis-N-phenylmaleimide (DTBFM) leads to a certain increase in the rate of crosslinking. RCY crosslinking increases by about 1.5-fold (Fig. 1, curve 4) and is 3.4 crosslinks per 100 eV. However, this effect becomes lower when moving to compounding.

It is known that unfilled vulcanizates based on EPM have very low strength. [1-4] As a result, their use in the art is of no interest. In this regard, we have carried out studies of the influence of active filler on the kinetics of radiation crosslinking and the properties of the vulcanizates.

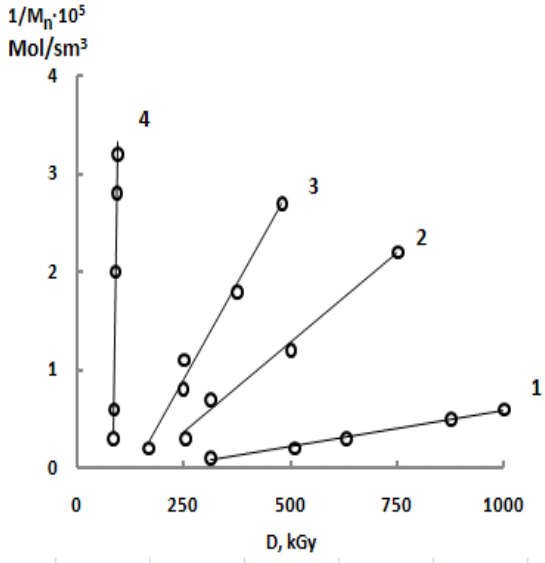


Figure 1. Dependence of crosslinked molecules ($1/Mn_{\tau}$) in the EPM on the radiation dose: 1-low molecular weight polymer (340 gauss cruelty); 2-the low molecular weight polymer with carbon black F324; 3-low molecular weight polymer (1100 gauss stiffness); 4-the low molecular weight polymer with a sensitizer

Introduction into a mixture of carbon black (furnace and channel) leads to a sharp increase crosslinking speed, due to the formation of network structures in the presence of a macromolecule polymer with carbon black [4]. Radiation-chemical yield (RCY) crosslinking (G_c) increases in 5-6 times with the introduction of 60 wt.h. of furnace carbon black (Fig. 1, curve 2) and crosslinking of 2.2 to 100 eV. This dramatically increases the strength characteristics of the vulcanizate. The dependence of the physical and mechanical properties of vulcanizates of the radiation dose is presented in the table. 2. As can be seen from Table. 2, the effect of the dose of irradiation on the properties of vulcanizates filled with carbon black, is 250-350 kGy.

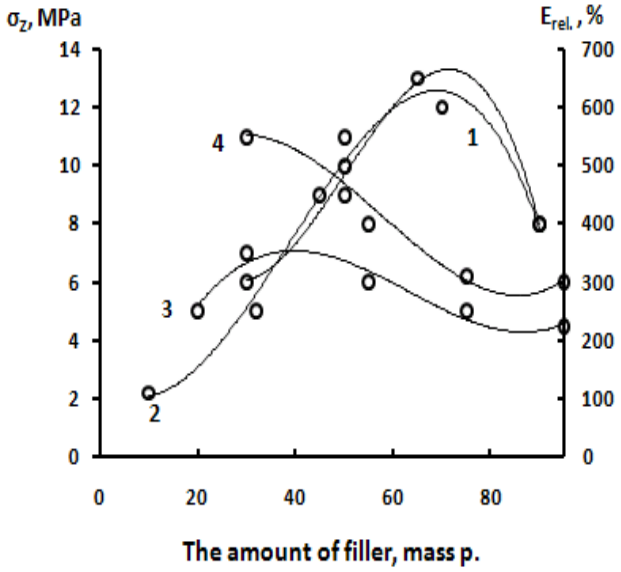


Figure 2. Dependence of the physical and mechanical properties of vulcanizates of radiation on the degree of filling and the type of filler: 1-resistance to tearing (σz), F324; 2-elongation (ε, %), F324; 3-resistance to tearing (σz), C354; 4-elongation (ε, %), C354

Fig. 2 shows the dependence of the physical and mechanical properties of radiation EPM vulcanizates by filling degree and type of filler. As follows from the data presented on the strength of both types of fillers there pronounced optimum content corresponding to 50-60 wt. h. of the filling 100 h. elastomer. At the optimum filling soot P324 radiation vulcanizates have a strength 20-30% greater than the filling channel black. The optimal dose of rubber filled the channel and furnace blacks is the same.

Table 2. Physical and mechanical properties of the radiation curing of EPM containing carbon black

Absorbed dose, D kGy	Maximum swelling in toluene,%	Resistance at break σ, MPa	Elongation, E,%	The residual elongation,%	The equilibrium modulus, MPa
50	-	-	900	104	-
70	-	0,9	940	116	-
90	-	1,2	950	110	-
130	380	2,4	950	171	1,21
170	300	4,0	880	118	1,2
250	196	15,7	405	0	2,1
350	191	15,9	400	11,2	2,4
500	-	10,0	340	15	-

The introduction of 0.2 wt.h. of the sulfur increases the strength by approximately 30-40%, with a further increase in the dosage of sulfur and 0.5 wt.h. of strength remains practically the same level (see. Fig. 3, Curve 1).

Introduction of sulfur in the investigated dose range does not alter the dose required to obtain optimum properties of vulcanizates. Increasing the strength of the case, obviously, it is possible to explain the formation of C-C bonds and, together additional C-S-C linkages sulfide.

Thus, by adjusting the filler, managed to get the radiational vulcanizates of EPM, according to the initial physical and mechanical ticks, the characteristic is not inferior to known peroxide vulcanizates.

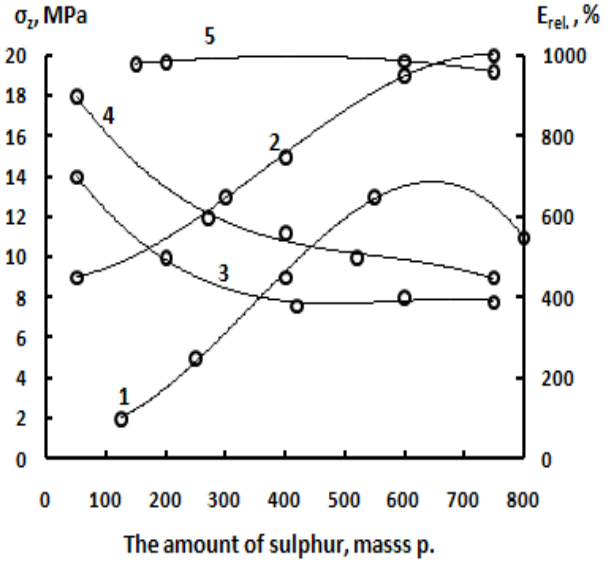


Figure 3. Dependence of tensile strength (1,2,3) and elongation (4.5) vulcanizate sulfur content (1) and the irradiation dose (2.4) vulcanizate with 0.5 wt. h sulfur; (3-5) vulcanizate without sulfur

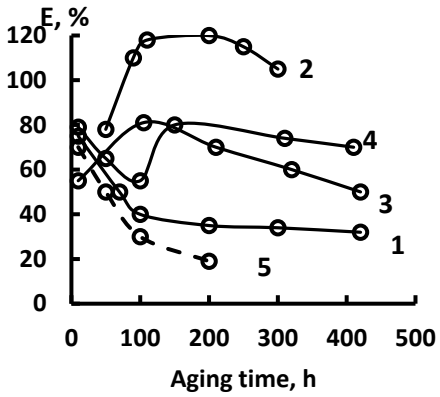


Figure 4. Dependence of the equilibrium radiation module and peroxide vulcanizates of the duration of EPM heat aging (473 K) in a vacuum: 1-radiation vulcanizate; 2-peroxide vulcanizate; 3-radiation vulcanizate with sulfur; Aging at 473K in air: 4-radiation vulcanizate; 5-peroxide vulcanizate

In order to identify the advantages of peroxide vulcanizates to conduct a comparative study of the properties during thermal aging in a free and statically deformed state (Figure 4).

Structural changes in the vulcanizates in the aging process, was evaluated by the change in the conditional-equilibrium modulus (ε, MPa) (Fig. 4).

As follows from the data presented in Figure 4, the rate of structural changes in peroxide vulcanizate aging in air is much higher than the corresponding radiation vulcanizates. Basic physical and mechanical properties of the radiation-curable rubber save 2-3 times more than the corresponding peroxide rubber. Radiation and peroxide rubber differ not only in the rate of aging, but also by the nature of the structural changes. In peroxidic vulcanizates when heated in the air has no crosslinking. Radiation vulcanizates when subjected to heating in vacuo minor degradation. Ravnovestny module throughout the entire cycle of aging varies by only 15-20%.

Structuring peroxide vulcanizates obviously can not be explained by the presence of sulfur bonds have been radiation cured elastomers prepared from the addition of sulfur, a tendency of degradation under heating in vacuum (Fig. 4).

With aging in air like the peroxide and radiation from the dominant process is vulcanizates crosslinking, structuring of the rate of peroxide in rubber are significantly higher than those of the radiation (Figure 5). The upper temperature limit at which both radiation and peroxide rubber can maintain a long time the elastic properties of air at 423K and 473K in vacuo. However, the save of the properties of peroxide rubber 2-3 times less than the radiation.

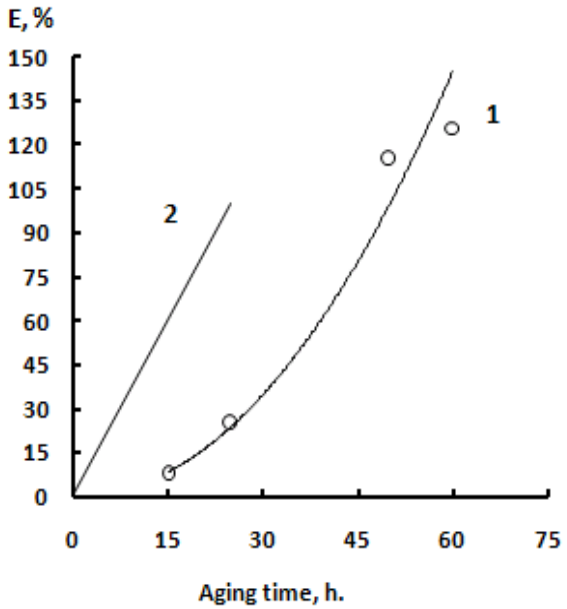


Figure 5. Changes in the equilibrium of the module the duration of aging and peroxide radiation at vulcanizates (423K) on air; 1-radiation vulcanizate; 2-peroxide vulcanizate

Elastomers obtained by radiation curing, have a significant advantage over the corresponding peroxide rubbers aging statically - deformed state. With aging, the air

velocity of chemical stress relaxation rubbers in radiation is about 2 times less (Figure 6). Thus, by radiation crosslinking of rubber can be obtained on the basis of EPM, on basic physical and mechanical characteristics, not conceding a peroxide elastomer. Radiation vulcanizates have an advantage over peroxide by heat aging resistance, as in free; and in a statically deformed state.

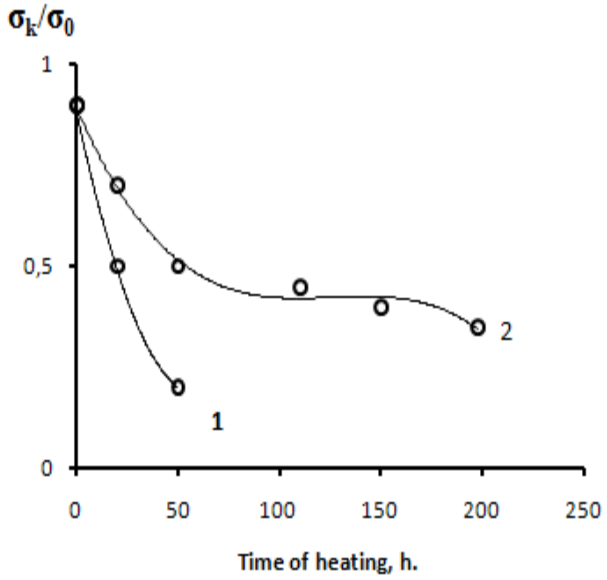


Figure 6. Relaxation and stress radiation peroxide rubber in the air at 423 K.1- radiation vulcanizate; 2- peroxide vulcanizate

4. Conclusions

The paper discusses methods of structuring by radiation curing of unsaturated ethylene-propylene elastomers (EPM). For durable elastic material which is introduced into the low-molecular compounds of carbon different brands (furnace and channel) and sensitizer 4,4'-dithiobis-N-phenyl maleimide (DTBFM) the nature and dosage of which are selected according to strict and individual characteristics of the polymer. Reported an increase in download speed in the presence of the filler, the sensitizing effect DTBFM depends on the nature of the filler and which make it possible to obtain a variety of elastomeric materials with improved set of both technological and operational properties.

Physical and mechanical properties of radiation and peroxide vulcanizates based EPM is influenced sensitizer (DTBFM), carbon black and irradiation conditions on the structural parameters of the grid vulcanizates, which causes long ethylene content in EPM.

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