RADIATIVE VULCANIZATION OF HIGH SATURATED BUTADIEN-NITRILE RUBBER WITH THE PRESENCE OF POLYFUNCTIONAL MONOMERS

Sh.M.Mammadly, A.A.Garibov, A.Kh.Salehov, D. Sh. Mammadov, U.A.Ibrahimova

Institute of Radiation Problems of NAS of Azerbaijan, Baku AZ 1143, F.Agayev 9

Siraz_mm55@mail.ru

Hydrogenized butadiene-nitrile rubber (HBNR) possesses full complex of such properties as heat, oil and benzene resistance, providing the use of its different branches of industry. Many research works have been devoted to this polymer due to its unique properties [1-7]. Structure of HBNR essentially differs from the other types of BNR in view of saturated character of its molecule. That's why it's cross-linking proceeds on absolutely other mechanism, than other saturated BNR. Peroxide and radiative vulcanization are more effective for elastomer mixtures on base of high saturated BNR [1, 8, 9].

Earlier [10] we have examined structural transformation of HBNR-40 during the effect of ionizing radiation on them.

For achieving higher degree of cross-linking the authors [1] worked out the receptor of resin mixture on base of high saturated BNR, in which dien containing product was used as coagent of peroxide vulcanization.

It is also known, that peroxide with increased temperature is used for vulcanization of HBNR [11]. For obtaining vulcanizates with high physical-mechanical characteristics authors [11] recommend to use much dosages 40%-bis-tret (butyl-peroxyisopropyl) peroxide 8-10 mass/hr. for 100 mass/hr. elastomer [2].

Introduction of polar functional groups (aromatic chlorine, nitrogen, amines, amides and oth.) into polymer chains in the cross-linking process prevails over destruction, herewith structuring of elastomer reaches at comparative small absorption doses [13].

Process of radiative effect on high saturated peroxide BNR hasn't been widely researched. Only the data of radiative vulcanization of non-saturated butadiene-nitrile rubbers exist [2, 12].

In connection with the above mentioned it was expedient for hydrogenized BNR to use radiative vulcanization method by introducing (tabl. 1) hexachlorineparaxylol (HCHPX) and 2-amino-4,6-bis (trichlorinemethyl)-simm triazine (ABTST) into receptor at 120-200^{0}C.

For selection of more rational ways of radiative vulcanization the investigations were carried out for establishing general regularities of γ-rays effect on worked out peroxide

receptor on base of hydrogenized rubber (Terban 2202 and BNR-40) structure and properties of resin.

Herewith we have taken into consideration the effect of structure and composition of hydrogenized rubbers on radiative-chemical yield of general number of chains ($1/M_c$) and number of cross linked molecules ($1/M_c$), which takes place as a result of interaction between low molecular components with elastomer, defining at final properties of vulcanizates.

Epoxide dian resins (ED-5), carbon black P324 and zinc oxide (tabl.1) were put into content of elastomer for providing high elasticity of vulcanizates, as well as for diminution rigidity of radiative vulcanizates.

Table 1. Basic ingredients and their content (mass/hr) in elastomer mixtures on base of hydrogenized BNR-40 and Terban 2207 by vulcanized peroxide (1), radiative (2,3) and thermoradiative effects (4).

Ingredients	Density, %	Numbers of mixtures			
		1	2	3	4
HBNR-40 (Russia)	98	-	-	100	100
Terban 2207 (FRG)	99,5	100	100	-	-
HChPX (hexachlorineparaxylol)		-	3,0	2,0	2,0
ABTST (2-amino-4,6-bis-trichlorinemethyl simm triazine)		-	5,0	5,0	5,0
Sulphur		-	-	0,2	0,2
Zinc oxide			6,0	5,0	5,0
Magnesium oxide			-	-	-
Epoxide resin		-	6,0	6,0	6,0
Stearine acid			-	-	-
TAC (triallylcyanurite)			-	-	-
BTBPIP (bis-tetrabytil peroxyisopropyl benzene)			-	-	-
Carbon black HA			-	-	-
Carbon black P-324		-	60	60	60

Experimental

In laboratorial rolls after close mixing hydrogenized rubbers Terban 2202 and BNR-40 within 7 min., with friction f=1:2 elastomer mixture (mass/hr to 100 mass/hr rubber) (tabl.1), then samples were formed in press like plate shape 0,2 mm at 80^0C. Filled and unfilled raw plates

were put into container and ampules. Radiative vulcanization was carried out on γ-radiation source Co^{60} [14] at room temperature. Radiative-thermal vulcanizates were obtained by preliminary heating in press at 180^0C within 5-7 min. and following irradiation on air at 25^0C at dose interval from 100 to 500 kGr at irradiation dosage 6,9 Gr/s. In the investigated samples absorbed dose was calculated by comparing electron densities of investigated and dosimetric systems [15].

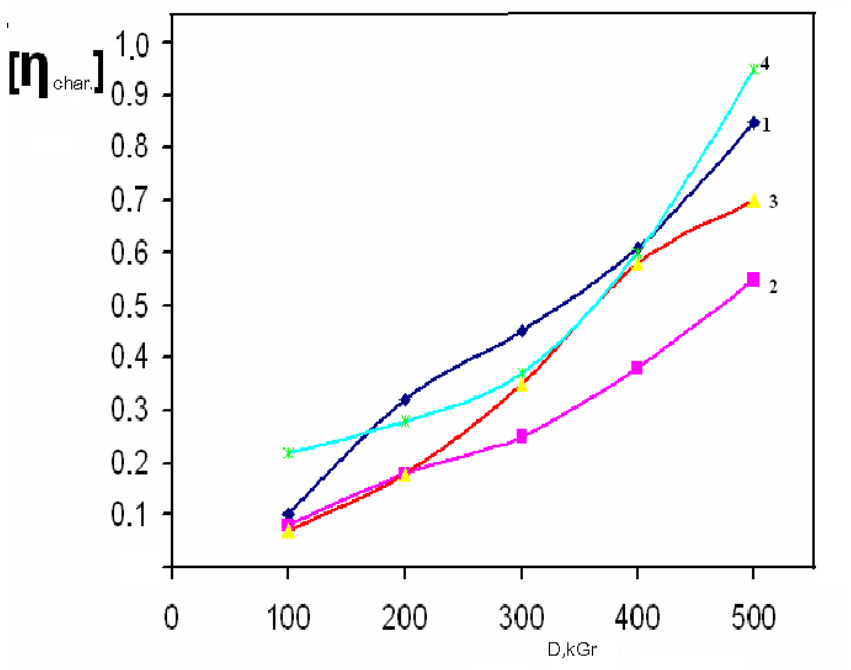
Sol-gel analysis was carried out by known method [16]. Samples were extracted by hot acetone within 24 hr. It was dried till constant mass, but then it was extracted again by cold benzene within 30 hr.

Physical-mechanical and deforming properties of filled resins were determined on samples at high doses of irradiation and combined thermoradiative way adding small doses of sulphur [17]. Standard peroxide resin on base of hydrogenized rubber Terban 2202, which is used in resin industry, has been tested for comparison.

Results and discussion

Interaction of elastomers with low molecular compounds is important matter in vulcanization by action of γ-quantum. Radiative vulcanizates don't possess necessary complex of properties without low molecular additives.

Data, given in fig. 1, show, that by increase of irradiation dose from 100 to 500 kGr, the structuring rate rises simultaneously, which leads to increase of molecular mass of unfilled vulcanizates. Great rate of changes were observed for mixtures 3 and 4 during vulcanization with the presence of 0,2 mass/hr sulphur, since radiative vulcanization process of hydrogenized BNR-40 leads to additional structuring. Obtained resins contain bonds of two types C-C and C-S-C, that provides higher molecular mass than for radiative vulcanizates on base of hydrogenized elastomer Terban 2207 (fig. 1 curve 2). On base of given values of characteristic viscosity of radiative unfilled vulcanizates, the value of molecular mass from 320 thousand till 500 thousand units were determined. Further increase of irradiation dose, which leads to diminution of structuring, is followed by decrease of molecular mass of radiative vulcanizates, which appears from value of characteristic viscosity of polymer solvents, obtained higher than 500 kGr irradiation dose.



Fiq.1. Changes of characteristic viscosity of unfilled samples on base of hydrogenized BNR-40 and Terban 2207 in dependence on irradiation dose.
1-peroxide; 2-mixture-2; 3-mixture-3; 4-mixture-4.

Raw elastomer mixtures on base of hydrogenized rubber Terban 2207 with additives peroxide (5,0 mass/hr) and triallyl cyanurate (TAC 3,0 mass/hr), have been vulcanized (γ-rays, Co^{60}). As it is seen from fig.1 (curve 2) additions BTBPIP and TAC increase degree of radiative structuring of mixtures on base of hydrogenized rubber Terban 2207 at 99,5% saturation. From comparative data (fig.1) it is seen, that molecular masses of obtained peroxide is second to radiative vulcanizates in molecular masses, which contain low molecular vulcanizing agents of hexachlorineparaxylol (HChPX) and 2-amino-4,6-bis-trichlorinemethylsimm tirazine (ABTChT) and small quantity of sulphur (0,2 mass/hr). It is important to mark, that absence of double links in hydrogenized BNR-40 and terban 2207 is the reason of low effectiveness of formation processes of space network, in consequence of which high irradiation doses are required for achieving optimum properties. Determination results of some structural parameters of vulcanizing network, formed under effect of γ-irradiation by sol-gel method, allow fully characterizing the obtained vulcanizing agent HChPX and ABTST.

Data, given in table 2, which describe change of general number of chains and number of cross linked molecules, indicate that as judged by vulcanization rate more active structurizing systems for hydrogenized BNR-40 is the composition : sulphur + HChPX +

ABTST+zinc oxide+ED-5. As it was expected, content of general number of chains and cross linked molecules noticeably increases, when absorption dose rises. Maximum content of yield in model and in peroxide unfilled vulcanizate is close and confirms that investigated HChPX, ABTST and ES act in structuring process. Concentration of general number of network chains ($1/M_c$) and number of cross-linked molecules ($1/M_{n_\tau}$) in vulcanizates with investigated systems increases (tabl.1) in accordance with their activity. Higher radiative-chemical yield of cross linked molecules ($1/M_{n_\tau}$), network chains ($1/M_c$) in thermoradiative vulcanizates with investigated low molecular compounds (HChPX + ABTST+S+ES+ZnO) in comparison with peroxide vulcanizates testifies, that structuring under action of ionizing irradiations proceeds effectively. Inversion takes place in radiative vulcanizates on base of hyrogenized rubber Terban 2202 (mixture 2). Density is formed in space network lower than in peroxide and other investigated resins.

Table 2. Change of structural parameters of networks of unfilled peroxide, radiative and thermoradiative vulcanizates during swelling in toluene solvents.

Type of vulcanization	Vulcanizing systems	General number of chains $\frac{1}{M_c}\cdot 10^5$, mol/sm^3	Number of cross linked molecules $\frac{1}{M_{\pi\tau}}\cdot 10^5$, mol/sm^3
Peroxide	BTBPIP+TAC+ZnO+stearin	8,6	2,1
Radiative	HChPX+ABTST+ED-5+ZnO	6,3	1,3
Thermoradiative	HChPX+ABTST+S+ED-5+ZnO	10,2	3,2

During determination of physical-mechanical properties of unfilled resins (table 3) on base of hydrogenized rubber Terban 2207 and BNR-40 it was established, that vulcanizates are not high stable and it is important to include filler and herewith physical-mechanical properties of obtained vulcanizates increase by growth of dosages (40-60) of carbon black and irradiation dose.

The data, given in table 3, show, that stability of vulcanizates rises by increasing irradiation dose and value of relative lengthening decreases. Optimum physical-mechanical properties of vulcanizates reach at 400-500 kGr doses.

Table 3. Comparative properties of filled vulcanizates of hydrogenized BNR-40 and Terban 2207

Indications	Vulcanization			
	Peroxide	Radiative		Thermoradiative
	1	2	3	4
Stretching stability (R, MPa)	25	14	16	23
Relative lengthening (ε_p) %	300	750	580	470
Rebound elasticity, %	40	55	48	37
Solidity by TM-2, st.unit	72	60	63	70
Residual deformation at compression (20%, 150^0 C, 72 hr.)	68	52	59	70
Coefficient of heat ageing (150^0C, 150 hr.)				
By f_p	0,57	0,66	0,71	0,80
By ε_p	0,37	0,57	0,61	0,62
By N	0,51	0,61	0,68	0,77
Changes of mass during swelling in methylethyl cetone (24 hr., % mass)	87	68	74	85

Further rise of physical-mechanical indications can be achieved by including sulphur, optimum dose remains as it was before, but stability increases in radiative (Terban 2207) and BNR-40 till 14-16 Mpa, but in thermoradiative up to 23 Mpa. Concentration of sulphur doesn't influence on stability. Optimum content of sulphur in vulcanizate makes at interval 0,2-0,4 mass/hr for 100 mass/ hr rubber.

By heat ageing the radiative vulcanizates don't surpass peroxide (mixture 1). During ageing of resins at tense condition, the best results were obtained on radiative resins, which contain HChPX, ABTST, ES and furnace carbon black. However resins don't possess advantages over peroxide by accumulation rate of residual deformation. Essential advantages are radiative by resistance against effect of solvents. As it is seen from table 3 radiative vulcanizates, not depending on receptor, change all during swelling in benzine-benzene (3:1), than peroxide.

It is known, that elastomers on base of BNR-40 are widely used in atomic techniques as condensing materials [2]. That's why the study of radiative ageing regularities of these elastomers at a wide interval of absorbed doses in dependence on chemical nature of elastomers is of great interest. Elastomer ageing by effect of absorbed doses can be

characterized according to the change of residual deformation (ε) during accumulation, equilibrium module ($E\infty$) and relaxation rate of tension (σ_t / σ_0) at continuous compression.

According to GOST-9.701-70 radiation properties of elastomer materials at compressed position is valued by absorbed dose, at which E_{ost}= 80 %, but σ_t / σ_0 =0,2.

From the obtained data (table 4) it is obvious, that in those cases, when sudden growth of equilibrium module was observed, the structuring prevails over, which differs by considerable accumulation of residual deformation, relaxation of tension changes insignificantly and, vice versa, at less growth of equilibrium module the accumulation of residual deformation changes insignificantly, but tension relaxes with great rate. Correlation is absent in comparison with heat ageing of elastomer at radiative ageing between accumulation rate of residual deformation and relaxation rate of tension. Residual deformation of elastomer increases at 2000-3000 kGr doses and makes 40-45 %, that is, in this case elastomers practically mustn't work as condenser. Tension falls not more than 20-30 % at 3000 kGr doses.

Table 4. Changes of deformation properties of filled resins on base of hydrogenized rubber Terban 2207 (2) and BNR-40 (3,4) at radiative ageing.

Absorbed dose, kGr	Numbers of mixtures	Value of network chains $1/M_c$, Mol/sm^3	Indications		
			Residual deformation at the compression $\varepsilon_{resi.}$, 20%, 24 hr.	Equilibrium module, MPa	Relaxation of tension σ_t / σ_0, MPa
2000	2 (Terban 2207)	2,7	62	80	0,9
2250		4,3	65	100	0,8
2500		6,1	71	120	0,7
3000		8,7	73	130	0,6
2000	3 (BNR-40)	4,6	58	95	0,7
2250		7,9	64	125	0,5
2500		9,7	66	150	0,4
3000		11,1	69	130	0,3
2000	4 (BNR-40)	10,3	55	120	0,5
2250		14,7	59	140	0,3
2500		16,0	66	-	0,2
3000		-	71	-	0,2

It is interesting to note behavior of hydrogenized rubber Terban 2207 with the presence of peroxide compounds after additional irradiation. As it is seen from the data given in fig. 2, rate of structural changes in peroxide resins at radiative ageing is considerably higher than in corresponding radiative vulcanizates.

Radiative resistance of hydrogenized rubber Terban 2207 was valued both by lengthening equilibrium module, relaxation of tension and by accumulation of residual deformation. Peroxide resins, obtained by radiative way of vulcanization at ageing of absorbed doses up to 3000 kGr, possess lower properties in comparison with radiative resins at tense position. Equilibrium module in peroxide resins changes 20-25 % at irradiation up to 3000 kGr dose during the whole ageing cycle, but relaxation rate of tension changes in peroxide resins approximately 1,5 times more.

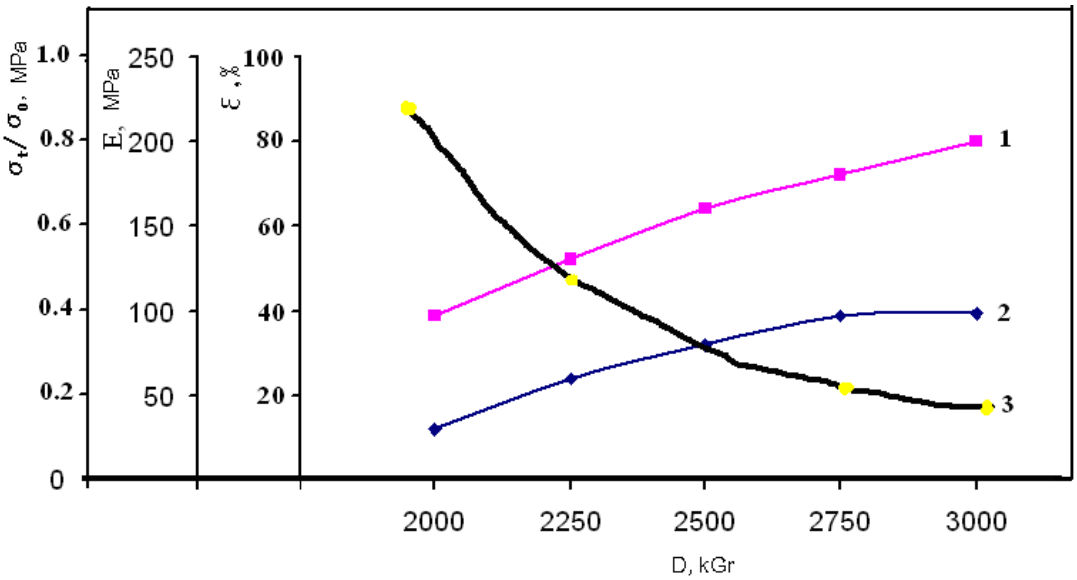


Fig. 2. Changes of deformation properties of filled irradiated resins on base of hydrogenized rubber Terban 2207 at radiative ageing. 1-residual deformation at the compression; 2-equilibrium module; 3-relaxation of tension.

By this way, analysis of results allows making a conclusion, that by radiative vulcanization it is possible to obtain resins on base of hydrogenized rubber Terban 2207 and BNR-40. C-C and C-S-C chemical bonds, which are formed in molecule of polymer, lead to change of space network of vulcanizates. This position shows that yield of network of chain and cross-linked molecules increases in elastomer, which by basic physical-mechanical characteristics doesn't yield to corresponding peroxide resins.

The obtained vulcanizates keep resistance against heat and radiative ageing at tense condition with the presence of chlorine, amino and epoxide compounds.

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Sulphur		-	-	0,2	0,2
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Magnesium oxide			-	-	-
Epoxide resin		-	6,0	6,0	6,0
Stearine acid			-	-	-
TAC (triallylcyanurite)			-	-	-
BTBPIP (bis-tetrabytil peroxyisopropyl benzene)			-	-	-
Carbon black HA			-	-	-
Carbon black P-324		-	60	60	60

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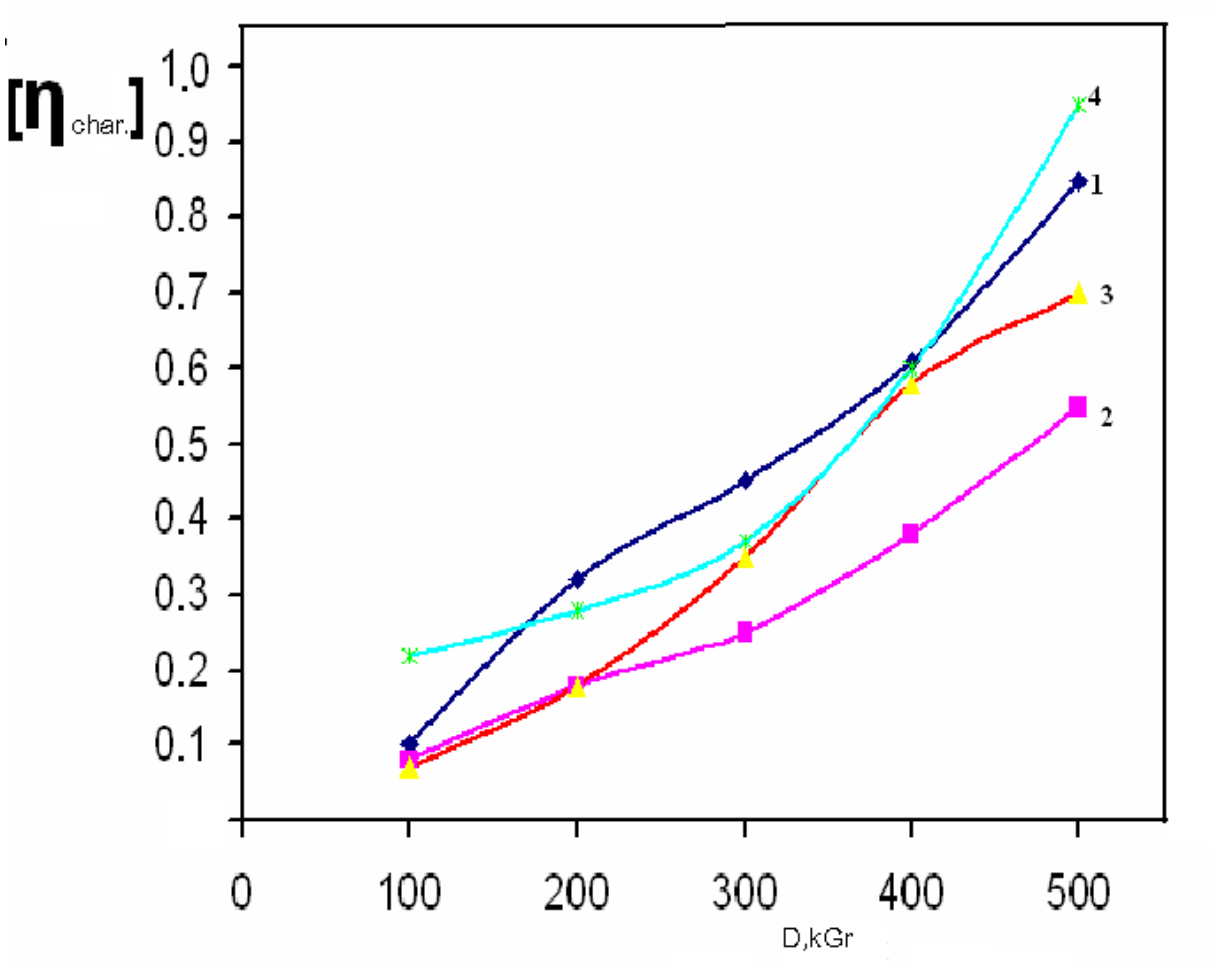
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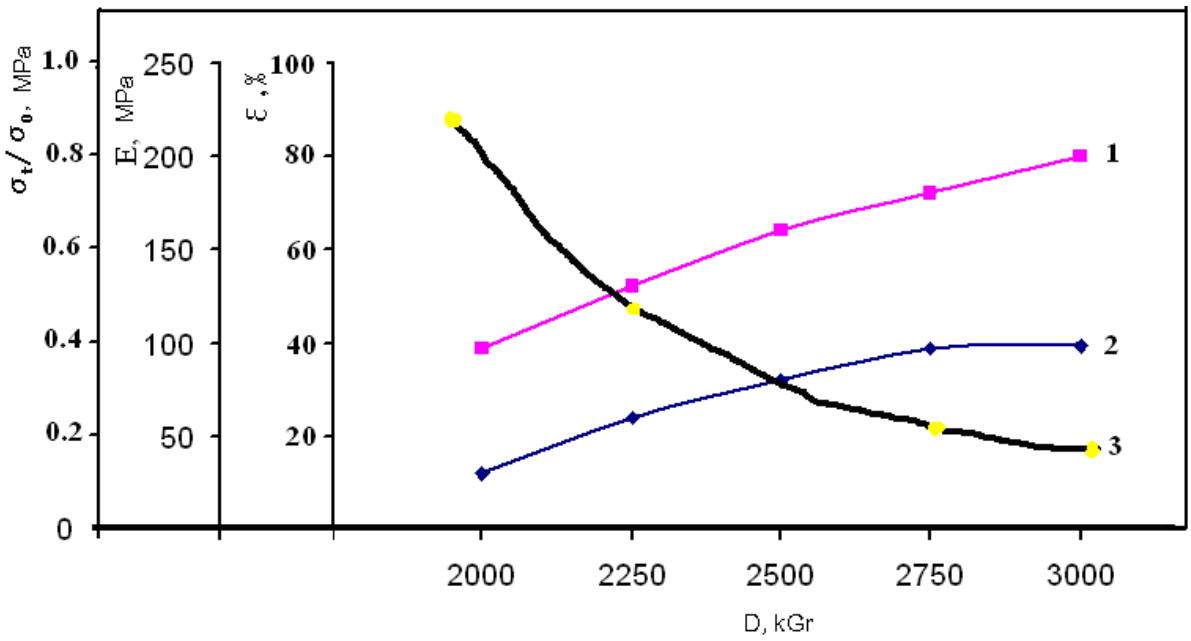
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	Peroxide	Radiative		Thermoradiative
	1	2	3	4
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Relative lengthening (ε_p) %	300	750	580	470
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Solidity by TM-2, st.unit	72	60	63	70
Residual deformation at compression (20%, 150^0 C, 72 hr.)	68	52	59	70
Coefficient of heat ageing (150^0C, 150 hr.)				
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Table 4. Changes of deformation properties of filled resins on base of hydrogenized rubber Terban 2207 (2) and BNR-40 (3,4) at radiative ageing.

Absorbed dose, kGr	Numbers of mixtures	Value of network chains $1/M_c$, Mol/sm^3	Indications		
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2500		9,7	66	150	0,4
3000		11,1	69	130	0,3
2000	4 (BNR-40)	10,3	55	120	0,5
2250		14,7	59	140	0,3
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Fiq.1. Changes of characteristic viscosity of unfilled samples on base of hydrogenized BNR-40 and Terban 2207 in dependence on irradiation dose. 1-peroxide; 2-mixture-2; 3-mixture-3; 4-mixture-4.



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3-relaxation of tension.