RADIOACTIVE STRUCTURING HIGH SATURATED BUTADIENE-NITRILE COPOLYMER

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Abstract

Radioactive cross-linking of hydrogenised butadiene-nitrile rubber (BNR-40) was investigated during radiation effects with the presence of triallyl ether of cyanuric acid (TAECA), 2,6-diamino-phenyl-simm triazine (DAPhST), zinc oxide and carbon black in systems: BNR-40+TAECA, BNR-40+DAPhST, BNR-40+TAECA+DAPhST and BNR-40+TAECA +DAPhST+ZnO+P514. By the help of physical-chemical and spectral method the change of molecular structure of hydrogenized BNR-40 was determined with the presence of TAECA and DAPhST. Values of radioactive-chemical yield (RCY), number of cross-linked molecules ($1/M_{n\tau}$) and quantity of effective cross bonds in hydrogenised BNR-40 were defined for each researched systems depending on absorbed dose.

It is evident, that radioactive-chemical yield of cross-linking and formation of effective cross chemical bonds in hydrogenized butadiene-nitrile rubbers (HBNR) depends on both capacity of dose and absorbed dose, and on condition of irradiation [1]. For increasing yield of cross-linking and acceleration of radioactive-chemical reactions, proceeding in elastomers, different organic sensitizers were suggested [2]. More effective data for elastomer mixture on base of high-saturated butadiene-nitrile rubbers (HSBNR) are peroxide and radioactive vulcanization [3,4].

It was established, that in the presence of chlorine containing and amino containing aromatic compounds the radioactive-chemical yield of cross bonds increase by the rise of concentration of low-molecular monomers and absorbed doses. Polyfunctional monomers of triallyl ether of cyanuric acid, aromatic diamines have been widely used as cross-linking and sensitizing agents for hydrogenized elastomers [6]. Formed elastomers can contain set of cross bonds of various energies. Besides, amino containing substances are often put into the composition of elastomer as a sensitizer, which allows getting optimum properties of elastic materials at less doses of irradiation. However, the role of TAECA and 2,4-diamino-6-phenyl-simm-triazine as cross-linking agents and sensitizers in radioactive-chemical processes hasn't been researched yet.

In the present work research results of radioactive-structuring of hydrogenized BNR-40 were given by low molecular polyfunctional monomers of triallyl ether of cyanuric acid and 2,4-diamino-6-phenyl-simm-triazine by the use of sol-gel analysis method, based on static theory of network structure.

Experimental

As a research object synthetic butadiene-nitrile rubber BNR-40 was used. HSBNR was synthesized by hydrogenising BNR-40 with the use of hydrogen in organic solvent by homogeneous catalyst-palladium acetate.

Hydrogenation reaction was carried out within 5 hours. Use of palladium acetate as homogeneous catalyst in hydrogenation of BNR-40 allows obtaining of HSBNR with hydrogenising degree till 95%.

While selecting low molecular polyfunctional monomers of triallyl ether of cyanuric acid and 2,4-diamino-6-phenyl-simm triazine as cross-linking agents during irradiation it was basically taken into account by means of introducing reactive functional groups into polymer chains for identification of structural parameters of elastomer network.

Low molecular viscous monomer TAECA was dissolved in toluene. The powdered hydrogenised BNR-40 was treated by the obtained solvent. Then BNR-40 powder was dried and the polymer was pressed from it at 120^0C. By this way the samples containing low molecular monomer from 1,0 to 3,0 mass/hour were prepared.

For estimation of effectiveness of zinc oxide (ZnO) and carbon black (P 324) as activating and filling agents in structuring process, the following indications were brought to notice: structure, elementary composition, sizes of particles, oil value, and specific surface area.

In laboratorial roll mills polymer mixture (mass/hour for 100 mass/hour polymer), containing 5,0 mass/hour zinc oxide and 60 mass/hour carbon black, was prepared after close mixing hydrogenized BNR-40 within 5 min. with f=12 friction. Mixtures, which don't contain zinc oxide and carbon black, have also been prepared.

Structure and individuality of TAECA and DAPhST were confirmed by IR-, UV, and H´-NMR-spectroscopy, temperature melting and element analysis.

Radiolysis of hydrogenised BNR-40 and mixtures on their base was carried out by gamma rays Co^{60} at capacity of 4,9 Gr/s at room temperature. Hydrogenised BNR-40 was irradiated in vacuum. 5 gr of samples were put into ampules and vacuumed till residual pressure $1{,}3\cdot10^{-1}$ MPa. Sizes of particles in final mixture were 1-3mkm. Dosimetry of γ-quantum Co^{60} source was carried out by chemical method–ferrosulphate [7].

Characteristic viscosity of irradiated hydrogenized BNR-40 in toluene was determined at 293 K by known method on viscosimeter “Ubellode”. Calculation was carried out according to Marc Hauvnik equation at values of constants $K=1,16\cdot10^5$ and X= 0,73 (for toluene).

Radioactive-chemical yield of concentration of cross bonds (N_c) number of cross-linked chains ($1/M_{n\tau}$) and cross bonds (N_c) were determined by sol-gel method [8]. Parameters of space network of cross-linked polymer were calculated according to Flory-Rener formula [9].

Change of molecular structure of hydrogenized BNR-40 was estimated by IR-spectroscopy. Spectra were recorded in zone of 700-2400 sm^{-1} by use of prism NaCl and LiF [9]. Spectra of samples were recorded before and after irradiation.

Interpretation of spectra was carried out in accordance with correlation tables and indications. Rheological properties of radioactive vulcanizates were determined according to reference materials [10].

Results and discussion

Interaction character of polymer chains of elastomer with low molecular monomer plays great role in the radioactive cross-linking process of elastomer. This interaction was caused by formation of physical and chemical bonds, quantity and ratio of which can change depending on properties of interacting components.

Above-mentioned experimental data allow making some essential conclusions about interaction character of hydrogenized BNR-40 under effect of ionizing rays.

In table 1 the change of characteristic viscosity of irradiated hydrogenized BNR-40 and mixture in irradiation process was shown, and figures of its viscosity were given at radioactive cross-linking, obtained on viscosimeter “Ubellode”.

Data analysis show that during irradiation of hydrogenized BNR-40 with 300 kGr dose its characteristic viscosity falls more than 1,5 times (table 1). Decrease of viscosity can be the result of two factors: 1) destruction of main chain; 2) formation of cyclic structure. In consequence of intermolecular cross-linking, space network is formed at 50 kGr dose, the difference in content of characteristic viscosity increases by rise of dose as compared without TAECA and DAPhST. Molecular mass grows in both systems (2,3) due to the increase of gel density in polymer.

Table 1. Influence of irradiation dose on change of characteristic viscosity [ήchar.] of hydrogenized BNR-40 and mixture by TAECA and DAPhST (solvent toluene, 20^0C).

Sample	Irradiation dose of, kGr					
	50	100	150	200	250	300
	Characteristic viscosity [$ή_{char.}$]					
Hydrogenized BNR-40	0,3	0,6	0,7	0,9	1,2	1,5
BNR-40+ TAECA	0,7	1,1	1,7	2,1	2,5	2,7
BNR-40+ DAPhST	0,5	0,9	1,4	1,8	2,2	2,4
BNR-40+TAECA+ DAPhST	1,1	1,6	2,2	2,6	2,9	3,2

However in quasi binary systems HBNR-40 by adding TAECA and DAPhST (4) the difference in content of characteristic viscosity in comparison with additives TAECA (2) and DAPhST (3), viscosity increases by the rise of dose, but at 300kGr it provides higher content of viscosity.

Structural changes in system HBNR-40 +TAECA, irradiated in vacuum till 150-300 kGr dose (fig.1), show that irradiation causes essential changes in it. According to changes of spectra of absorption it is obvious that bands in zone 930 and 995 sm^{-1} decrease, which is typical for oscillations of C-H bonds in vinyl double bonds, as well as the bands of –C=C- bonds disappear in zone 1650 sm^{-1}, which corresponds to valence oscillations of –C=N- triazine ring. Small increase of intensiveness of bonds 1720 sm^{-1} were observed, in case of using DAPhST, during the irradiation in vacuum (fig.2) intensiveness of bonds 820 sm-1 (out-of-plane deformation vibrations of C-H bond in compounds $R_1R_2C=CHR_3$), 940 and 1645 sm^{-1} decreases considerably (corresponding to deformation vibrations C-H and valence vibrations C=C in vinylden group $C=CH_2$).

Comparison of IR-spectra of absorbed in binary systems of hydrogenized BNR-40 with low molecular monomers in initial position and absorbed till 150 and 300 kGr dose, as well as spectra of the lowest molecular compounds, irradiated under such conditions show that not depending on individual structure of these compounds, the concentration of double bonds decrease in functional groups, caused both as polymerization of monomers and interaction of them with polymer (joining by double bonds to macro radicals). Besides, the isomerization of TAECA takes place together with polymerization in ether of cyanuric acid by double bonds [11]. Diminution of intensiveness of absorption zones, which is specific for investigated low molecular polyfunctional monomer, simply indicates to expenditure of them in irradiation process, as the dose increases.

Comparison of data by content change of characteristic viscosity (table 1) and by IR-spectra (fig.1) show that, the role of LPFM as cross-linking agents of radioactive cross-linking process of hydrogenized BNR-40 is brought to the increase of general non-saturation in system and increase of susceptibility to irradiation effect. LPFM acts mainly in zone of dose till 400-500 kGr, so far as the general part of functional groups reacts, and then the process proceeds like in pure hydrogenized BNR-40.

For selection of more rational ways of radioactive cross-linking of hydrogenized BNR-40 by LPFM, the researches were carried out on the establishment of general regularities of LPFM effect on space network parameter of polymers.

Structural changes of binary mixtures (2-4) were estimated after irradiation according to number of cross-linked molecules ($1/M_{n\tau}$) and number of cross bonds (N_c).

The structural parameters of polymer networks were determined for estimation of cross-linking process and destruction of elastomers, while swelling radioactive samples in solvents of toluene and acetone, which were extracted within 50 hours by cold acetone at argon atmosphere. Change of radioactive-chemical yield of linkages ($1/M_{n\tau}$) and cross bonds ($N_c \cdot 10^{-19}$, bonds/sm^3) was estimated on 100 eV absorbed energy. Obtained results were given in fig.2 and 3.

As it is seen from curves fig. 2 the curve 1 is formed approximately 4 times less than cross bonds, during the irradiation of hydrogenized BNR-40 till 500 kGr dose. The small value of radioactive-chemical yield of cross bonds in hydrogenized BNR-40 is related to high radiation resistance [6]. Introduction of DAPhST to the content of hydrogenized BNR-40 leads to monotone increase of yield of cross bonds. It is natural, that formation of cross bonds takes place with small rates at 50kGr dose. Further this rate both as in BNR-40+DAPhST, and in BNR-40+TAECA at 500 kGR dose the radioactive yield of cross bonds, formed in system BNR-40+DAPhST makes $3{,}5 \cdot 10^{-19}$, bonds/sm^3, but in BNR-40+TAECA at 300 kGr the yield of cross bonds makes $5{,}5 \cdot 10^{-19}$, bonds/sm^3 for 100 eV (fig. 2 curve 3). It must be noted, that polymer chain is destructed by the increase of dose in system BNR-40 + TAECA. The nature of TAECA, DAPhST and their molecular structures has influence on the value of radioactive-chemical yield. With the combined presence of TAECA and DAPhST in system BNR-40+TAECA+DAPhST of hydrogenized BNR-40 the yield of cross bonds makes $8{,}1 \cdot 10^{-19}$, bonds/sm^3 (fig. 2 curve 4).

Researches of changes in radioactive-chemical yield of cross bonds (G_{Nc}) and mixture samples on base of hydrogenized BNR-40 with low molecular monomers (TAECA and DAPhST) showed the presence of their structuring, that is formation three dimensional structure due to interaction of polymer radicals, formed during the irradiation of hydrogenized BNR-40 [5].

As it is seen from the fig.3 hydrogenized BNR-40, irradiated at 400 kGr dose, radioactive-chemical yield of cross-linking makes 1,5 linkages for 100 eV. Introduction of NFM of TAECA and DAPhST type to hydrogenized BNR-40 leads to some increase of cross-linking rate, more intensive structuring is observed during irradiation of hydrogenized BNR-40 and its mixture. In irradiated system BNR-40+TAECA cross-linking rate is higher than in BNR-40+DAPhST. According to its structure and effect of active lateral functional groups TAECA is more reactive at the same dose. At 400 kGr the yield of linkages' number in system BNR-40+DAPhST makes 3,5 linkages, but in systems BNR-40+TAECA and BNR-40+TAECA+ DAPhST it makes 5,1 and 6,0 linkages for 100 eV (fig. 3). Differences of data, obtained for each NFM at the same concentrations show, that TAECA possesses more effectiveness as cross-linking agent for radioactive structuring process of hydrogenized BNR-40. Such high effectiveness of TAECA is related with the presence of allyl groups in molecule of this compound.

By this way generalization of investigation results of influence peculiarities of low molecular polyfunctional monomers on structure and property of hydrogenized BNR-40 allows suggesting approach to the selection of structuring agents, providing improvement of properties of radioactive vulcanizates.

Activation and acceleration of inter phase interaction in systems on base of hydrogenized BNR-40 defines improvement of such important characteristics like rheological properties of radioactive vulcanizates.

5,0 mass/hr. zinc oxide and 60 mass/hr. carbon black P514 were added as an activation and acceleration of system BNR-40+TAECA+ DAPhST Concentrations of cross bonds were determined in system at different doses (table 2). The data, given in table 2, show, that viscosity increases according to Moony in system as the dose rises, but rigidity and plasticity of vulcanizates are reduced. Elasticity also increases. This testifies that with the presence of metal oxide and carbon black due to additional structuring BNR-40 in irradiation process and dispersing of them in polymer matrix due to formation of chemical bonds (C-C) cause less diffusion in aromatic hydrocarbon.

Table 2. Change of rheological (plasto-elastic) indications of filled mixtures of hydrogenized BNR-40 with low molecular monomers.

Radiated system	Dose, kGr	Concentration of cross bonds $N_c \cdot 10^{-19}$, sm^3	Viscosity on Moony st. unit	Rigidity st. unit	Plasticity, st. unit	Elasticity, %	Swelling in benzine-benzene (3:1)
BNR-40+TAECA+DAPhST+ +ZnO+P514	150	9,4	48	1750	0,42	30	38
	300	11,8	64	1340	0,33	38	31

By this way introducing active low molecular polyfunctional monomers (TAECA, DAPhST) into molecular chain of polymer of different chemical nature and their interaction with polymer provides radioactive structuring of hydrogenized BNR-40. The carried out investigations provided to reveal the influence of TAECA and DAPhST on effectiveness of radioactive cross-linking of hydrogenized BNR-40 and to establish structuring action of NFM. Activity of metal oxide and carbon black was established in radioactive-chemical processes. Introduction of 5,0 mass/hr. zinc oxide and 60 mass/hr. carbon black (P514) activates additional cross-linking and output of cross bonds in polymer molecule.

The achieved positive results lead to change of plasto-elastic properties of radioactive vulcanizate on base of hydrogenised BNR-40 during irradiation with 150-300 kGr dose and diminution of swelling of radioactive vulcanizates in aromatic hydrocarbons, which has practical meaning and confirms the expansion possibility of application field of NFM.

However, mechanism of radioactive-chemical processes, which cause the changes of properties, is to be investigated.

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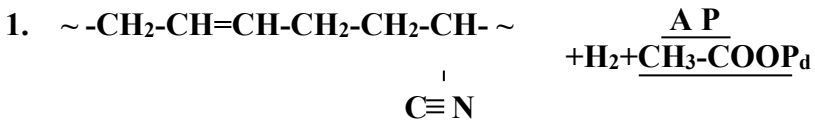
Синтез ВБНК

Орг. раствор.

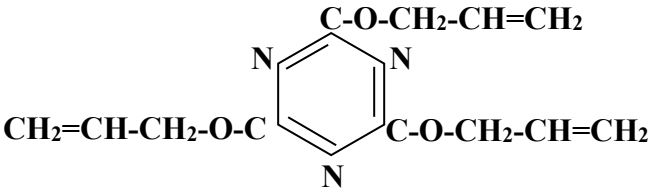
1. 

~ -CH₂-CH=CH-CH₂-CH₂-CH- ~
C≡ N

A P
+H₂+CH₃-COOP_d

~ -CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH- ~ 95%
C≡N

2. Триалиловый эфир циануровой кислоты



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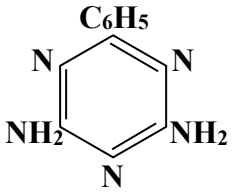

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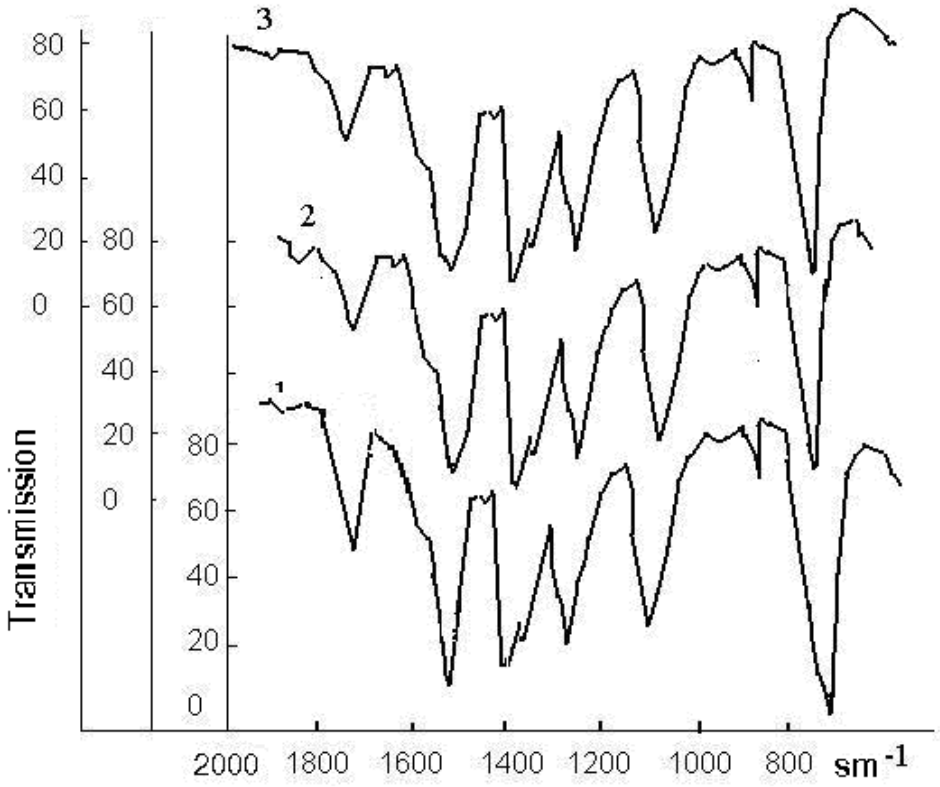

Fig.1 IR-spectra of absorption of samples of hydrogenised BNR-40 by adding TAECA (3,0 mass/hour) 1-non-irradiated; 2-150 kGr; 3-300 kGr.

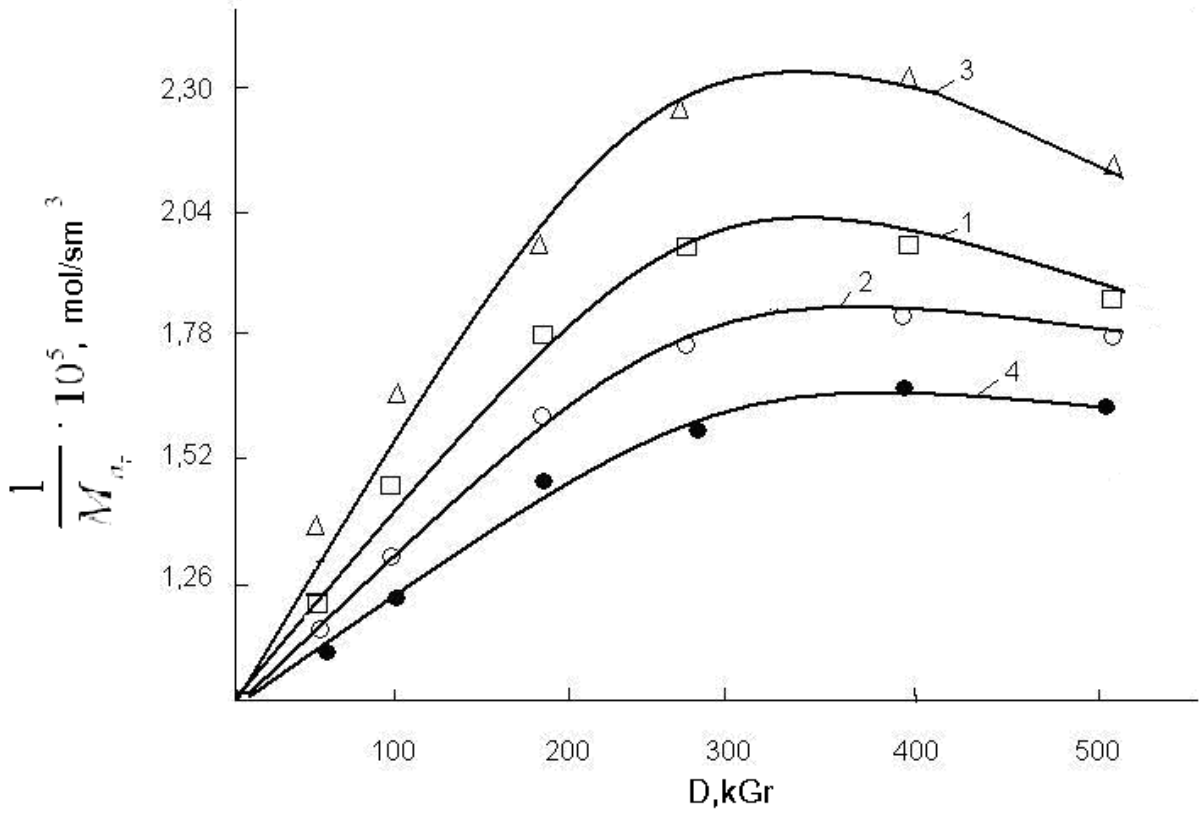

Fig.2. Dependence on absorption dose of concentration output of linkages in hydrogenised BNR-40 in systems: BNR-40+TAECA (1); BNR-40+DAPhST (2); BNR-40+TAECA + DAPhST (3); BNR-40 (4).

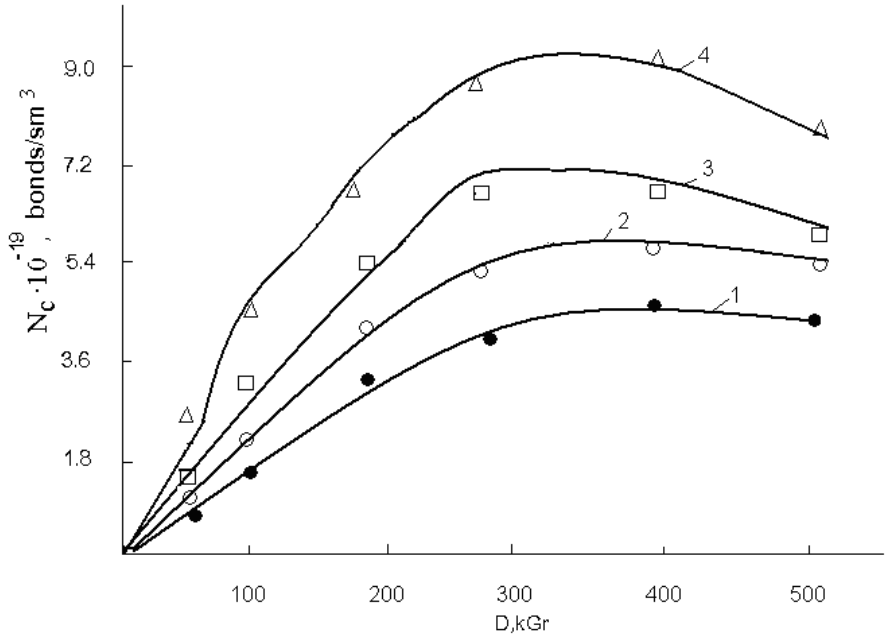

Fig. 3. Dependence on dose of yield concentration of cross bonds of hydrogenized BNR-40 in systems: BNR-40+TAECA (3); BNR-40+DAPhST (2); BNR-40+TAECA + DAPhST (4); BNR-40 (1).