American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN : 2320-0936
Volume-12, Issue-3, pp-17-24
www.ajer.org
Research Paper Open Access

Preparation of Polyconjugated Cooligomers of 4-Aminophenol with Resorcin and Their Electrically Conductive Compositions

G.A.Mansurova, R.A.Akhmedova, D.N.Aliyeva,
Ch.O.Ismailova, B.A.Mamedov
Institute of Polymer Materials of the Ministry of Science and Education of the Republic of Azerbaijan, Sumgait

ABSTRACT:
By the oxidative copolycondensation reaction of 4-aminophenol with resorcin, the polyfunctional polyconjugated meltable and soluble cooligomers, including aminohydroxyphenylene and dihydroxyphenylene links and exhibiting thermal-stable, semiconductor and paramagnetic properties, as well as high reactivity in the reactions characteristic for aromatic amine and hydroxyl groups have been obtained.

The synthesized cooligomers have been used as active additives in preparation of electrically conductive compositions on the basis of thermoplasts and rubbers. The antistatic polymer-oligomer compositions of LDPE, PP and PS with cooligomers of 4-aminophenol and resorcin have been obtained. It has been shown that the rubbers obtained by partial substitution of carbon black by cooligomers of 4-aminophenol with resorcin in the composition of vulcanizate from BR show high heat-physical, physical-mechanical and electrical properties.

Keywords: *aminophenol, resorcin, cooligomer, electrically conductive polymer compositions*

Date of Submission: 18-02-2023 Date of acceptance: 02-03-2023

I. INTRODUCTION

It was known that various types of electro-active thermoplastic polymer materials and rubbers are widely used in various fields of engineering and industry, where it is required to remove electrostatic charges arising from friction and deformation of products [1]. Such materials are obtained by introduction of electrically conductive additives into the composition of the corresponding polymer materials, since thermoplasts, thermoelastoplasts and elastomers are good electrical isolators. The powdered graphite, various marks of carbon black and metal powders are usually used as such additives [2, 3]. Under certain conditions, the particles of such additives form continuous electrically conductive structures. However, the polymer composition materials developed with the use of metal powders do not have the necessary elastic properties, and also the initial polymers are incompatible with metal particles, which naturally lead to rapid destruction of current-conductive structures as a result of deformation of products during exploitation. The use of electrically conductive additives of organic nature (for example, various types of structured carbon blacks) allows to obtain electrically conductive composite materials with good physical-mechanical properties due to the good compatibility of the components [4-8].

It should be also noted that the polyfunctional aromatic polyconjugated oligomers possess thermal stability and radiation resistance, paramagnetism, semiconductivity, stabilizing and antistatic activity [6-11]. Besides these, they exhibit solubility, meltability and high reactivity in various chemical conversions [5-15].

Considering this circumstance, we have synthesized the oligoaminophenols, including reactive functional groups, by the oxidative polycondensation reaction of aminophenols in the presence of hydrogen peroxide or sodium hypochlorite, and by oxidation of these oligomers with molecular oxygen in an alkaline medium, the macroradicals of aminophenoxyl type with various concentrations of paramagnetic centers have been obtained [8].

II. EXPERIMENTAL PART

The synthesis of cooligomers of 4-aminophenol (4-APh) and resorcin (Rc) was carried out in 500 ml three-neck flask equipped with thermometer, mechanical stirrer and reflux condenser. 1.09 g (0.01 mol) of 4-APh, 1.10 g (0.01 mol) of resorcin, 17 g of 30% solution of hydrogen peroxide (0.06 mol H_2O_2) and 140 ml of distilled water were placed in the flask. The oxidative polycondensation reaction was carried out at 363 K for 8 h at intensive mixing of the reaction mixture. In other experiments, the temperature and the reaction carrying out time, and also the molar content of comonomers and oxidizer were changed. The synthesized samples of cooligomers were purified from monomer residues by washing with hot distilled water and dried at 373 K in a vacuum box (13.3 Pa) to constant mass.

The oxidation of the synthesized cooligomers of 4-APh and Rc (COAPhR) was carried out in a glass reactor equipped with a magnetic stirrer, a thermometer and a bubbler. 16.5 g (0.15 mol) of COAPhR, 110 ml of C_2H_5OH were loaded into the reactor and after reaching the given temperature, the dry and purified oxygen was passed through the system at rate of 5.6 l/h. After the reaction completion, the reaction mixture was filtered, the obtained precipitate was washed with ethanol and dried in a vacuum (13.3 Pa) at 313-323 K to a constant mass. The kinetics of oxidation of COAPhR samples was studied volumetrically by measuring the volume absorbed by the reaction mixture of oxygen at its constant pressure (98.066 kPa), according to the methodology described in [9-11].

The IR spectra of COAPhR were taken for thin films of oligomers deposited on NaCl monocrystals (for those COAPhR samples, which did not form high-quality films, the tablets were obtained from a fine-grained mixture of oligomer and KBr by pressing under pressure) on spectrometer Agilent Cary-630, the UV spectra of COAPhR samples were taken in ethanol using the spectrometer Agilent -60 M-80. The EPR spectra of COAPhR samples were taken on the spectrometer RE-1806. DPhPH and 2,2,6,6-tetramethyl-4-oxypiperidine-1-oxyl were used as standards [9].

The molecular weights (MW) and molecular weight distribution (MWD) of the cooligomers were determined on gel chromatograph “Waters” (refractometric detector) [8]. Three styrogel columns with porosity 200, 500 and 1000Å were used. Eluent – tetrahydrofuran. Eluent feed rate – 1.0-1.1 ml/min. The trial was introduced for one minute as 0.2% solution of the sample of cooligomers in tetrahydrofuran. For calculation, it was used the calibration dependence, which is described by the equation $V_R = 30.8–4.0·\lg M$, where V_R – retention volume, ml; M – molecular weight. The average molecular weights were calculated on formulas

$$\overline{M}_w = \Sigma W_i M_i \text{ and } \overline{M}_n = \frac{1}{\Sigma W_i / M_i},$$

where W_1 – mass part of fractions with molecular M_i(it was defined as the ratio of the area of *i*-th part of the chromatogram to all area).

The electrical measurements have been carried out according to the generally accepted methodology on direct current by means of an amplifier in 3-16, and on alternating current by means of the bridge R-571 – in low frequencies and cubmeter – in the field of high frequencies ($5·10^4 – 3·10^7$ Hz).

The rubber mixture on the basis of butyl rubber (BR) and the sample of the synthesized cooligomers was made using laboratory rollers. The rubber was firstly plasticized on the rollers, and then the necessary components, including an oligomer compound were added in a certain sequence and mixed. Depending on the peculiarities of the mixture components, the temperature of the rollers was adjusted in the front roller in the range of 303-313 K, in the final roller in the range of 343- -348 K.

Observing the sequence of introduction of the components, the preparation of the rubber mixture was carried out as follows: 1) BR – 0; stearin tech. – 3 min; captax – 5 min, tiuram – 7 min, zinc oxide+cooligomer – 10 min; sulphur – 15 min, total mixing time – 20 min, vulcanization temperature – 313-323 K. 2). Further, by means of PG-63 hydraulic press, the obtained mixtures were pressed in special press-molds as the plates with thickness of 1.5-2.0 mm. Using standard knives, the samples of the need forms and sizes were cut from the obtained plates for determination of physical-mechanical (tensile strength, specific elongation, residual deformation), electrical and other properties.

The strength and deformation properties of the samples were determined by means of RM-250 breaking machine.

The electrical resistance (R) of the sample area in Ohm was calculated on the formula:

$$R = \frac{V}{I}$$

where: V – the voltage value in the sample area between the voltage electrodes, measured by an electrometer (B), I – Current passing through the sample (A).

From all the measurements of R on one sample, the arithmetic mean of the resistance of the sample was calculated (R_{av}).

The specific volumetric electrical resistance – ρ_v (Ohm·cм) was calculated on the formula:

$$\rho_v = \frac{R_{av} \cdot h \cdot b}{l}$$

where: R_{av} – average arithmetical value of electrical resistance of the sample (Ohm), h – sample thickness (cm), b – sample width (cm) and *l* – distance between voltage electrodes (cm).

The specific volumetric electrical conductivity (σ_v), $Ohm^{-1} \cdot cm^{-1}$, was calculated on the formula:

$$\sigma_v = \frac{1}{\rho_v}$$

III. RESULTS AND DISCUSSION

The synthesis of cooligomers of 4-aminophenol with resorcin was carried out by the oxidative polycondensation reaction of comonomers in the presence of hydrogen peroxide, and macroaminophenoxyl radicals with various concentrations of paramagnetic centers (PMCs) by oxidation of COAPhR with molecular oxygen in an alcohol-alkaline medium.

The synthesized samples of COAPhR are powders of dark-brown or black color, well soluble in polar organic solvents and melting under load at 380–413K, depending on the synthesis conditions. Their composition and structure has been established by the methods of elemental, chemical and IR-spectral analyses, and molecular-weight indices – by a method of gel-permeating chromatography (Table 1, 2).

Table 1. Synthesis conditions and some indices of cooligomers of 4-aminophenol with resorcin in the presence of H_2O_2

№	Rc, mol	APh, mol	H_2O_2, mol	T, K	τ, h	Yield of COAPhR,%
1	0.02	0.01	0.05	363	8	39
2	0.01	0.02	0.05	363	8	50
3	0.01	0.01	0.04	363	8	63
4	0.01	0.03	0.06	363	8	73
5	0.02	0.02	0.06	363	8	65
6	0.01	0.01	0.05	363	8	43
7	0.02	0.02	0.12	368	8	87
8	0.02	0.02	0.12	353	8	58
9	0.02	0.02	0.12	343	8	42
10	0.02	0.02	0.12	368	4	57
11	0.02	0.02	0.12	368	6	72
12	0.02	0.02	0.12	368	10	90

Table 2. Synthesis conditions and some indices of cooligomers of 4-aminophenol with resorcin in the presence of H_2O_2

APh+Rc, mol	H_2O_2,mol	T, K	yield, %	Elemental nitrogen, %	OH group, %	MW indices		
						$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
0.04	0.12	343	42	6.55	21.0	830	700	1.19
0.04	0.12	353	58	6.34	21.4	860	740	1.16
0.04	0.12	363	65	6.20	21.6	950	770	1.23
0.04	0.12	368	87	5.95	21.7	1130	850	1.33
0.06	0.06	368	89	6.02	21.6	1220	930	1.31
0.06	0.12	368	92	6.13	21.5	1340	1050	1.28
0.06	0,18	368	93	6.15	21.4	1510	1160	1.30

The results of elemental analysis and determination of the content of hydroxyl groups indicate that during the cooligomerization of 4-aminophenol with resorcin, the dehydration reaction with the formation of ether bonds and the isolation of ammonia does not occur. Indeed, in the IR spectra of oligomers, the absorption band of C–O–C-group at 1230 cm^{-1} is not detected. At the same time, in the spectra the wide intensive absorption band characteristic for the associated hydroxyl (3201.6 cm^{-1}) and amine groups (3078.7 cm^{-1} and 2981.4 cm^{-1}) is fixed at 2800-3600 cm^{-1} (Figure 1 and 2). In addition, in the IR spectra, the absorption bands of benzene rings of aminophenol and dihydroxybenzene fragments (1170, 1610, 1512 and 1439 cm^{-1}) and unplanar deformation vibrations of aromatic –CH groups of benzene rings at 709 cm^{-1} (for two neighboring CH-groups) and 833cm^{-1} (for isolated – CH groups) are appeared.

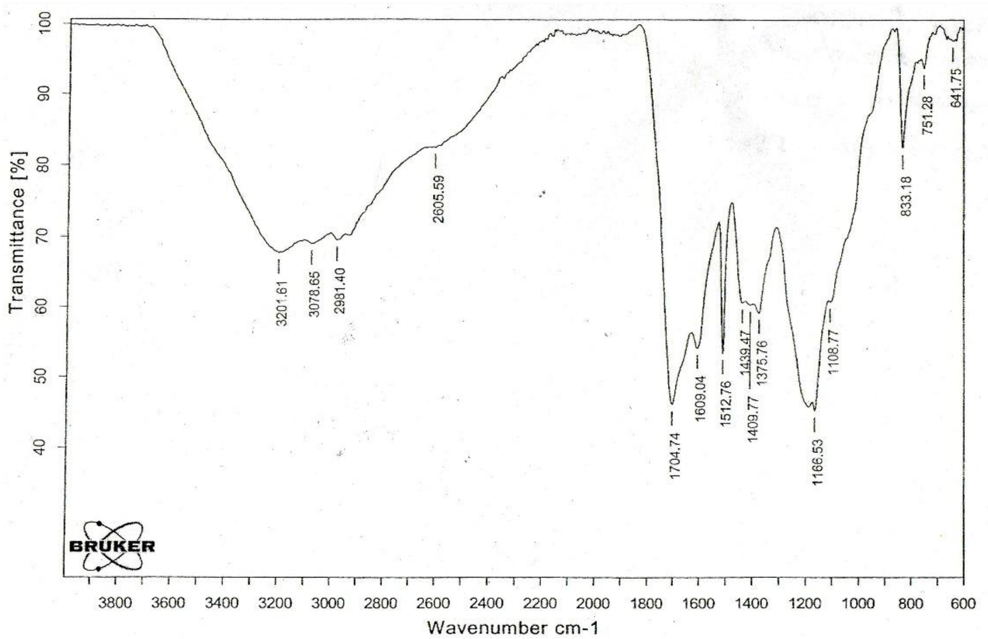

Figure 1:IR spectra of COAPhR obtained under the conditions: $[APh]_0$ = 0.018 mol/l, $[Rc]_0$ = 0.027 mol/l, $[H_2O_2]_0$ = 0.135 mol/l, T=348 K, τ=6 h

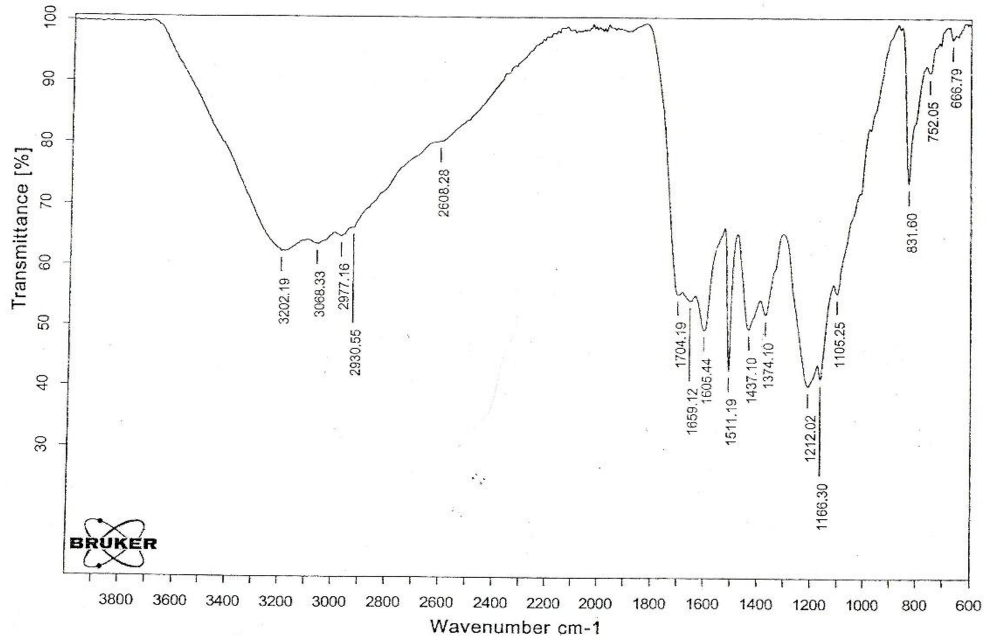

Figure 2: IR spectra of COAPhR obtained under the conditions: $[APh]_0$ = 0.027 mol/l, $[Rc]_0$ = 0.018 mol/l, $[H_2O_2]_0$ = 0.135 mol/l, T=348 K, τ=6 h

In the UV spectra of the synthesized samples of COAPhR, the wide intensive peak with maximum at 225 nm, and also less intensive absorption bands with maxima at 280 and 325 nm have been fixed. The first of them is E-band ($\pi\rightarrow\pi^*$ excitation, and the second characterizes $n\rightarrow\pi^*$ transitions of unshared electrons of nitrogen and oxygen atoms. The last peak indicates the presence of a system of polyconjugated bonds.

Thus, it can be concluded that the macromolecules of the synthesized COAPhR consist of the following structural units:

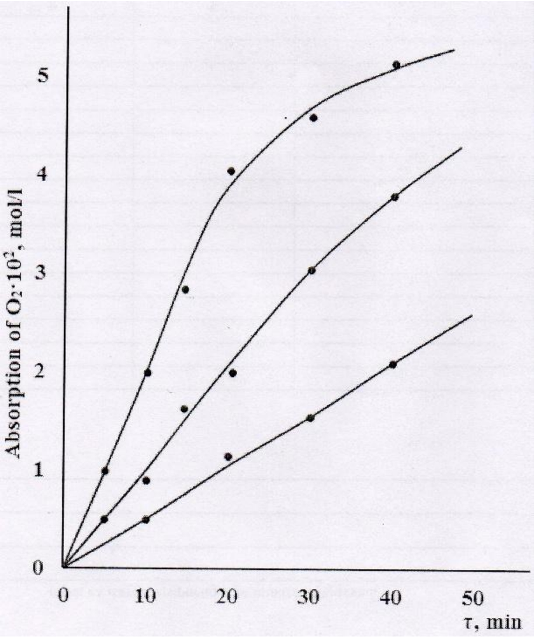

Figure 3: Kinetic curves of oxygen absorption by an alkaline solution of COAPhR in methanol. $[COAPhR]_0$ mol/l =0.092 (1), 0.046 (2), 0.024 (3), $[KOH]_0$ = 0.18 mol/l (1-3), T = 313 (1-3).

The obtained samples of COAPhR have electron exchange activity; their aqueous and alcoholic solutions intensively absorb the molecular oxygen (Figure 3). The oxidation rate constant values of COAPhR are sufficiently high (k=0.042-0.24 min^{-1} at 313-333 K, solvent-methanol), and the activation energy value is 83.4 kJ/mol. The stable macroradicals of phenoxyl type can be obtained by oxidation, i.e, the obtained and oxidized COAPhR samples show the paramagnetic concentrations of PMCs $\sim 5.6 \cdot 10^{17} \div 2.75 \cdot 10^{19}$ spin/g) and semiconductor (E = 1.3÷1.67 eV, $\sigma_0 \sim 10^{-14} \div 10^{-8}$ $Ohm^{-1} \cdot cm^{-1}$ at 298 K) properties. Moreover, the concentration growth of PMCs in the composition of COAPhR samples by 1-2 orders leads to a noticeable growth of their electrical conductivity (Table 3 and 4). Consequently, these cooligomers can execute the function of an antioxidant in the composition of composites and thereby increase their heat- and thermal resistance, and also the effective exploitation life.

Table 3. Preparation of COAPhR samples with various concentration of PMC

N	$[KOH]_0$, mol/l	$[COAPhR]_0$*, mol/l	T, K	τ, h	$[PMC] \cdot 10^{-19}$, spin/g
1	1.5	2.0	308	0.25	1.20
2	1.5	1.5	308	0.25	1.58
3	1.5	0.75	308	0.25	0.85
4	0.35	0.75	308	0.25	0.92
5	0.70	0.75	308	0.25	0.97
7	0.70	0.75	303	0.25	1.18
8	0.70	0.75	313	0.25	1.72
9	1.5	1.5	308	0.50	1.89
10	1.5	1.5	308	0.75	2.75

*concentration of PMC for the initial COAPhR samples was $0.56 \cdot 10^{18}$ spin/g.

Table 4. Some electrical indices of the samples containing various concentrations of PMC – COAPhR

$[PMC] \cdot 10^{-18}$, cm^{-3}	σ(0), $Ohm^{-1} \cdot cm^{-1}$	σ(ω) at 10^6 Hz, $Ohm^{-1} \cdot cm^{-1}$	$N(E_r) \cdot 10^{20}$, $cm^{-3} \cdot eV^{-1}$	$N_0(E_F) \cdot 10^{-18}$, cm^{-3}
1.2	$1.29 \cdot 10^{-14}$	$1.2 \cdot 10^{-9}$	0.51	1.31
8.5	$1.83 \cdot 10^{-10}$	$2.5 \cdot 10^{-8}$	2.95	8.32

11.8	$6.0 \cdot 10^{-10}$	$6.5 \cdot 10^{-8}$	4.82	12.3
18.9	$1.0 \cdot 10^{-9}$	$2.3 \cdot 10^{-7}$	7.21	19.1

The possibility of increase of the electrical conductivity of COAPhR with an increase of the concentration of PMC in its composition was used for preparation of the antistatic polymer compositions on the basis of thermoplastics by introduction of 5÷15% of COAPhR into their composition by subsequent treatment of the material surface with an alcoholic or aqueous alkali solution. It is seen from Table 5 that ρ_v after the introduction of COAPhR into the composition of thermoplastics is essentially decreased.

Table 5. ρ_v values of composition materials on the basis of thermoplasts and COAPhR

COAPhR ,%	Thermoplast, %	ρ_v x10^{-8} (Ohm·см), on the basis of		
		LDPE	PP	PS
5	95	7.1 (9.2)	6.5 (8.9)	5.6 (6.8)
10	90	3.6 6.4	2.3 (4.0)	1.2 (2.7)
15	85	0.84 (1.9)	0.67 (1.2)	0.49 (0.91)

The synthesized samples have been used as an active additive for the preparation of the rubber mixtures of COAPhR on the basis of rubbers, for example, butyl rubber (BR). In this case, the rubber mixtures on the basis of BC have been prepared according to the standard formulation of ingredients with the only difference that instead of carbon black (partially) the COAPhR samples (from 20.0 to 45 mass p. per 100 mass p. of rubber) have been used (Table 6).

It has been revealed that the introduction of COAPhR into the composition of the rubber mixtures, instead of black carbon, leads to an increase in the tensile strength and specific elongation, and also to a decrease in the elastic modulus of the obtained rubbers. For example, for rubbers obtained by vulcanization of the mixture on the basis of BR, including 20mass. h. of COAPhR instead of carbon black, the tensile strength is increased to 22.4÷25.2 MPa, the specific elongation reaches 623÷6890 %, and the modulus at elongation is decreased by 200% from 9.4-9.8 to 8.4÷8.5MPa. Along with this, the thermal stability and service life of the obtained rubbers are increased, which has been evidently connected with the structural peculiarity of COAPhR – the availability of aromatic polyconjugated bonds stipulates the high thermal stability of cooligomer, and the participation of hydroxyl and amine groups in benzene rings – its antioxidant activity.

Since COAPhR samples with various PMC content show the high electrical conductivity, their joint use with electrically conductive carbon black allows to obtain the rubbers with a specific volumetric conductivity 10^{-8}-10^{-6}Ohm^{-1}·cm^{-1}. Moreover, the content growth of COAPhR from 20 to 45.0 mass p. (from the mass of rubber) instead of carbon black, and also an increase in concentration of PMC

Table 6. Compositions of rubber mixtures, physical-mechanical and electrical indices of the obtained vulcanizates on the basis of butyl rubber and COAPhR

№	Ingredients			Mixtures (mass, g)			
				1	2	3	4
1	Butyl rubber			100	100	100	100
2	Technical stearin			3.0	3.0	3.0	3.0
3	Captax			0.65	0.65	0.65	0.65
4	DPhPH			1.3	1.3	1.3	1.3
5	Zinc oxide			5.0	5.0	5.0	5.0
6	Carbon black			50	30	15	5
7	COAPhR			0	20	35	45
8	Sulphur			2.0	2.0	2.0	2.0
Properties							
Mixtures	Vulcanization time, min.	Tensile strength, MPa	Specific elongation, %	Residual deforma-tion, %	Modulus at elongation, MPa		$\sigma \cdot 10^7$, Ohm^{-1}·см$^{-1}$
					200%	300%	
1	2	3	4	5	6	7	8
Before aging							
1	40	19.8	700	4.5	9.8	14.3	
	60	18.9	690	4.8	9.5	13.8	
	80	19.4	673	4.4	9.6	14.1	
2	40	22.4	680	7.2	8.5	12.4	0.11
	60	23.8	672	7.0	8.3	12.9	0.27
	80	25.2	623	6.7	8.4	13.3	0.25

1	2	3	4	5	6	7	8
3	40	22.9	675	10.0	6.9	11.0	3.8
	60	22.5	663	12.2	7.4	11.6	5.9
	80	23.0	610	13.6	7.8	12.5	6.4
4	40	24.3	670	12.4	6.5	9.5	26
	60	26.4	657	13.8	6.9	10.6	31
	80	28.7	605	13.5	7.4	11.3	35
After storage at 373 K for 24 h.							
1	40	15.5	395	2.9	7.2	17.5	
	60	16.3	423	1.7	5.4	15.1	
	80	16.9	428	1.4	4.9	17.1	
2	40	20.1	570	4.5	7.0	11.9	0.15
	60	21.3	524	3.6	6.8	12.4	0.31
	80	22.4	510	3.4	7.2	12.8	0.45
3	40	21.8	574	5.2	5.4	9.8	4.9
	60	22.5	516	6.3	5.9	10.3	6.7
	80	22.9	478	7.4	6.5	11.1	7.8
4	40	23.6	550	5.9	5.2	8.7	68
	60	24.9	523	7.0	5.8	9.2	82
	80	26.1	485	7.8	6.2	9.6	83

in the composition of COAPhR leads to an increase of the specific electrical conductivity of the obtained rubbers. The percolation effect is achieved at content ~22.9 mass p. of COAPhR for rubbers obtained from BC (Figure 4).

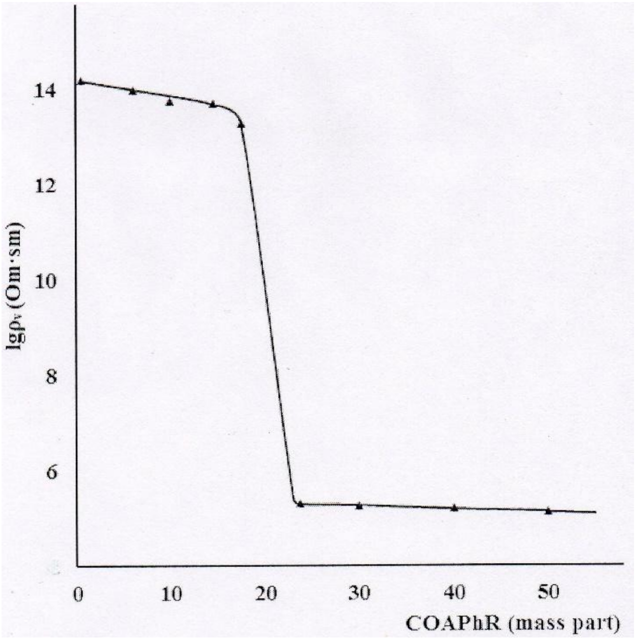

Figure 4: Change of the specific volume resistance of vulcanizates from COAPhR content in the composition of vulcanizate obtained on the basis of BR.

The reinforcing properties of COAPhR in the composition of the rubber composition have been probably stipulated by the optimal combination of such indices as small particle size, low density, good compatibility of components and the participation of amine and hydroxyl groups in the formation of the spatial net. Indeed, the specific volume resistance of the obtained rubbers depends on the mixing time at various contents of COAPhR. The main reasons for the change of the specific resistance value of made rubbers are the structuring or destruction of the rubber macromolecules. As a result of vulcanization, a mesh is formed and occurs higher internal stress in the rubber. With the increase of the rolling duration, the probability of mechanical destruction of spatially cross-linked macromolecules grows also, the consequence of which is the formation of defective zones in the vulcanizate matrix (Table 7).

Table 7. ρ_V values of vulcanizates obtained at various mixing times and COAPhR content (vulcanization time – 40 min.)

N	COAPhR content per 100 m.p. of BR, m.p.	Mixing time, min		$\sigma\cdot10^7$, $Ohm^{-1}\cdot cm^{-1}$
		Total	with COAPhR	
1	20.5	41	2	0.35
2	20.5	44	5	1.9
3	20.5	46.5	7.5	4.3
4	35.0	41	2	5.3
5	35.0	44	5	8.9
6	35.0	46.5	7.5	12.1
7	45.0	41	2	71
8	45.0	44	5	84
9	45.0	46.5	7.5	98

Thus, the probability of accumulation of the static electric charges on the surface of rubber products during their exploitation with use of the developed rubbers is minimized.

IV. CONCLUSIONS

By the oxidative copolycondensation reaction of 4-aminophenol with resorcin, the polyfunctional polyconjugated soluble and meltable cooligomers, including aminohydroxyphenylene and dihydroxyphenylene links with high reactivity in the reactions characteristic for aromatic amine and hydroxyl groups have been obtained

The stable macroradicals of phenoxyl type can be obtained by oxidation of COAPhR. The obtained and oxidized COAPhR samples exhibit paramagnetic (PMCs concentration ~$5.6\cdot10^{17}\div2.75\cdot10^{19}$ spin/g) and semiconductor ($E = 1.3\div1.67$ eV, σ_0 ~$10^{-14}\div10^{-8}$ $Ohm^{-1}\cdot cm^{-1}$ at 298 K) properties.

COAPhR samples have been used as active fillers in the preparation of electrically conductive compositions on the basis of thermoplasts and rubbers. The antistatic polymer-oligomer compositions of LDPE, PP and PS with COAPhR have been obtained.

It has been shown that at the partial substitution of carbon black of COAPhR in the composition of vulcanizate from BR, the obtained rubbers show high heat-physical, physical-mechanical and electrically conductive properties.

REFERENCES

[1]. Herbert Naarmann, “Polymers, Electrically Conducting” in Ullman’s Encyclopedia of Industrial Chemistry, Wiley-VCH, 2002.
[2]. Kaverinskiy, V.S., Smekhov, F.M.,Electrical properties of paint- and lacquer materials and coatings, Khimiya, Moscow, 1990.
[3]. Pud, A., Ogurtsov, N., Korzhenko, A., Shapoval, Q.: Some aspects of preparation methods and properties of polyaniline blends and composites with organic polymers.Prog. Polym. Sci.28, 1701–1758 (**2003**).
[4]. Valipour, A.Ya., Modhaddam, P.N., Mamedov, B.A.:Some aspects of chemical procedures & application trends of polyaniline as an intrinsically conductive polymer.Life Sci. J.9, 409–421 (**2012**).
[5]. Valipour, A.Ya., Modhaddam, P.N., Mamedov, B.A.: Synthesis of hydrophilic template as a matrix polymer for preparation of soluble conductive polyaniline composites.Archives de Science Journal65, 14–20 (**2012**).
[6]. Ragimov, A.V., Mamedov, B.A., Gasanova, S.G.:New Efficient Dielectric and Antistatic Materials Based on Oligoaminophenols.Polymer International43, 343–348 (**1997**).
[7]. Valipour, A.Y., Moghaddam, P.N., Mammedov, B.A.: Resent advances in hybridorganic-inorganic conductive polyaniline nanocomposites. Jokull journal 2013, 211–251 (**2013**).
[8]. Mammadov,B.A., Ahmadova,R.A., Mashayeva,S.S.etall.: Preparation of polyfunctional polyconjugated oligomers of 4-aminophenol and their use in making of heat-resistant electro-conducting rubbers.Industrial production and use of elastomers1,34–39 (**2014**).
[9]. Tefera, M., Geto, A., Tessema, M., Admassie, S. et all.: Voltammetric determination of uric acid using multiwall carbon nanotubes coated-poly(4-amino-3-hydroxy naphthalene sulfonic acid) modified glassy carbon electrode.FoodChemistry210, 156–162 (**2016**).
[10]. Bhandari, H., Srivastav, R., Choudhary, V., Dhawan, S.K.: Enhancement of corrosion protection efficiency of iron by poly(aniline-co-amino-naphthol-sulphonic acid) nanowires coating in highly acidic medium.J.Thin Solid Films519,1031–1039 (**2010**).
[11]. Doğan, F., Şirin, K., Kolcu, F., Kaya, İ.: Conducting polymer composites based on LDPE doped with poly(aminonaphthol sulfonic acid).Journal of Electrostatics94, 85–93 (**2018**).
[12]. Lingappan, N, Cho, B, Jang, M, Choi, BC, Gal, YS, Lim, KT.:Fabrication and Characterization of Graphene/Poly(p-Phenylenediamine) Hybrids. J Nanosci Nanotechnol 13, 3719–3722 (**2013**).
[13]. Ma, H.L., Zhang, H.B., Hu, Q.H. et al.: Functionalization and Reduction of Graphene Oxide with p-Phenylene Diamine for Electrically Conductive and Thermally Stable Polystyrene Composites.Appl. Mater.&Interfaces4, 1948–1953 (**2012**).
[14]. Fernández Naiara; Sanchez-Fontecoba Paula; Castillo-Martínez Elizabeth; et al.: Polymeric Redox-Active Electrodes for Sodium-Ion Batteries.ChemSusChem. (**2017**),10.1002/cssc.201701471
[15]. Muench, S., Wild, A., Friebe, C., Häupler, B., Janoschka, T., and Schubert, Ulrich S.: Polymer-Based Organic Batteries. Chem. Rev. 116, 9438−9484 (**2016**).