Naphtol Oligomers and their Electroconductive Compositions

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Abstract— *By oxidative polycondensation reaction of 1- and 2-naphthols, the polyfunctional polyconjugated soluble and meltable oligomers showing the thermostable, semiconductive and paramagnetic properties, as well as high reactivity in the reactions characteristic for aromatic hydroxyl groups have been obtained.*

They have been used as active fillers in preparation of electroconductive compositions on the basis of thermoplasts and rubbers. The antistatic polymer-oligomer compositions of LDPE, PP and PS with naphthol oligomers have been obtained. It has been shown that in partial substitution of carbon black by naphthol oligomers in the composition of vulcanizate from BR, the obtained rubbers exhibit high heat-physical, physical-mechanical and electrical properties.

Keywords— electroactive polymers, electroconductive compositions, naphtol, oligonaphtol, oxidation, polycondensation.

I. INTRODUCTION

It was known that the various types of electroactive thermoplastic polymer materials and rubbers are successfully used in the various fields of technique and industry, where it is necessary to remove electrostatic charges arising from friction and deformation of products [1]. Usually these materials are obtained by introduction of electroconductive fillers into the corresponding polymers, since thermoplastics, thermoplastics and rubbers are good electrical isolators. As such fillers, the metal powders, various brands of carbon black and powdered graphite are often used [2, 3]. Under certain conditions, the particles of such fillers form continuous electroconductive structures – in most cases, three-dimensional nets. However, the polymer composition materials developed with use of metal powders do not have the necessary elastic properties and the initial polymers are incompatible with metal particles, which, of course, lead to rapid destruction of current-conductive structures as a result of deformation of products during exploitation. An application of electroconductive additives of the organic nature (for ex., various types of structuring carbon blacks) allow to obtain the electroconductive composition materials with good physical-mechanical properties due to good compatibility of components [4-7].

It should be also noted that the polyfunctional aromatic polyconjugated oligomers possess thermo- and radiation stability, paramagnetism, semiconductivity, stabilizing and antistatic activity. In addition, they show solubility, meltability and high reactivity in various chemical conversions [5-10].

Taking this into account, we have synthesized the oligo(1-naphthol) and oligo(2-naphthol), including reactive hydroxyl groups, oxidative polycondensation of naphthols in the presence of hydrogen peroxide, and by oxidation of these oligomers with molecular oxygen in an alkaline medium there have been obtained the macroradicals of naphthoxyl type with various concentration of paramagnetic centers (PMC).

II. EXPERIMENTAL

The synthesis of naphthol oligomers (NO) was carried out in a 500 ml three-necked flask equipped with thermometer, a mechanical stirrer and reflux condenser. 28.8 g (0.1 mol) of naphthol, 170 g of 30% solution of hydrogen peroxide (0.6 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 4 h in intensive mixing of the reaction. The synthesized samples of NO were purified from residue of monomer with washing of hot distilled water and dried at 373 K in vacuum box (13.3 Pa) to constant mass.

The oxidation of the synthesized naphthol oligomers was carried out in a glass reactor equipped with magnetic stirrer, a thermometer and a bubbler. 21.3 g (0.15 mol) of NO, 110 ml of C_2H_5OH were loaded into a reactor and after achievement of the preset temperature the dry and purified oxygen was passed through the system with rate 5.6 l/h. After reaction completion the reaction system was subjected to the filtration, the obtained precipitate was washed with ethanol and dried in vacuum (13.3 Pa) at 313-323 K to constant mass. The kinetics of the oxidative polycondensation and NO oxidation was studied by volumetric method by measurement of volume, absorbed by reaction mixture of the oxygen at its constant pressure equal to 98.066 kPa according to the method described in [9-10].

The IR spectra of NO were taken for thin films of naphthol oligomers applied on NaCl monocrystals (for those NO samples,

which did not form the high-quality films, tablets were obtained from fine-grained mixture of an oligomer and KBr by pressing under pressure) on spectrometer "Agilent Cary 630 FTIR", of firm "Agilent Technologies". The UV spectra of NO samples were taken in ethanol by means of spectrometer "Agilent Cary 60 spectrophotometer" of firm "Agilent Technologies". EPR spectra of NO samples were taken on spectrometer PE-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 oligomers were determined on gel-chromatograph "Waters" (refractometric detector) [10]. Three styrogel columns with porosity of 200, 500 and 1000Å were used. Eluent – tetrahydrofuran. Eluent feeding rate – 1.0-1.1 ml/min. The sample was introduced for one min. as 0.2% NO solution in tetrahydrofuran. For calculation, it was used a calibration dependence, which is described by the equation V_R = 30.8–4.0·lgM, where V_R is the retention volume, ml; M is the molecular weight. The average molecular weights were calculated on formulas

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

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

The electrical measurements have been carried out according to the standard method on direct current by means of an amplifier B 3-16, and on alternating current by means of a bridge R-571 – in low frequencies and Q-meter – in the field of high frequency ($5\cdot10^4 – 3\cdot10^7$ Hz).

A rubber mixture on the basis on butyl rubber (BR) and the synthesized oligomer compound were made by means of laboratory rollers. On the rollers, the rubber was firstly plasticized, and then the necessary components were added in a certain sequence, including an oligomer compound and mixed. Depending on peculiarities of the mixture components, the temperature of the rolls was adjusted in the front shaft in the range of 303-313 K, in the ending shaft in the range of 343-348 K.

Following the sequence of introduction of components, the preparation of the rubber mixture was carried out as follows: 1) BR – 0; techn.stearin. – 3 min; captax – 5 min, thiuram – 7 min, zinc oxide + oligomer – 10 min; sulphur – 15 min, total time of mixing – 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 in the form of plates with thickness of 1.5-2.0 mm. With use of standard knives, the samples of various shapes and sizes were cut from obtained plates for determination of the 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 breaking machine PM-250.

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

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

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

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

The specific volumetric electrical resistance – ρ_v (Om·cm) was calculated on formula:

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

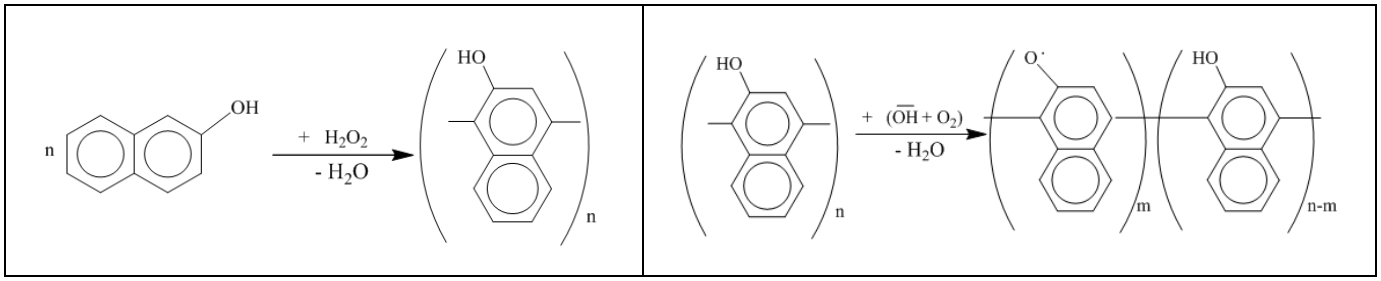
Where: R_{av} – average arithmetic value of electrical resistance of the sample (Om), h –sample thickness (cm), b – sample width (cm) and l – distance between tension electrodes (cm).

The specific volumetric electroconductivity (σ_v), $Om^{-1}\cdot cm^{-1}$, was calculated on formula:

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

III. RESULTS AND DISCUSSION

The synthesis of naphthol oligomers (NO) was carried out by oxidative polycondensation reaction of naphthols in the presence of hydrogen peroxide and the macronaphthoxyl radicals with various concentration of paramagnetic centers (PMC) by NO oxidation with oxygen in alcohol-alkaline medium:



The synthesized NO samples are the powders of dark brown or black color, well soluble in polar organic solvents and melting under load at 380-405 K, depending on synthesis conditions. Their composition and structure has been established by methods of elemental, chemical and IR spectral analyses, and the molecular-weight indices – by a method of gel-permeating chromatography (Table 1).

TABLE 1
SYNTHESIS CONDITIONS AND SOME INDICES OF OLIGOHYDROXYNAPHTHYLENES (T = 4 H)

Naphtol, mol/l	H_2O_2, mol/l	T, K	Yield, %	Elemental composition, %		OH groups, %	MW indices		
				C	H		$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
1.2	1.2	343	29.1	84.16	4.85	10.1	850	730	1.16
1.2	1.2	353	34.5	84.23	4.83	10.3	890	750	1.19
1.2	1.2	363	45.6	83.72	4.72	11.1	960	790	1.22
1.2	1.2	368	51.7	83.84	4.51	11.5	1230	870	1.41
1.6	1.6	368	52.4	84.22	4.59	11.8	1270	960	1.32
1.2	2.4	368	73.5	83.78	4.43	10.6	1370	1030	1.33
1.2	3.6	368	86.9	84.37	4.69	11.9	1560	1180	1.32

The results of elemental analysis and determination of content of hydroxyl groups evidence that they are practically identical for synthesized oligomers and 1-naphthol. This indicates that at naphthol oligomerization the dehydration reaction does not occur and the simple ether bonds are not formed. Indeed, in the IR spectra of oligomers the absorption band of C–O–C-groups at 1230 cm^{-1} are not observed. At the same time, in the spectra at 3400-3580 $cm^{-1}$the wide intensive absorption band characteristic for associated hydroxyl groups is fixed. In addition, in the IR spectra the absorption bands of napthaline ring (1455, 1520 and 1600 cm^{-1}) and nonplanar deformation vibrations of aromatic –CH groups at 770 cm^{-1} (for four neighboring CH-groups) and 875-880 cm^{-1} (for isolated – CH groups) are appeared.

In the UV spectra of the synthesized NO samples, a wide intense peak with maximum at 220 nm, and also less intense absorption bands with maxima at 285 and 330 nm have been fixed. The first of these is E-band ($\pi\rightarrow\pi^*$ excitation, and the second characterizes $n\rightarrow\pi^*$ transitions of the non-divided electrons of the oxygen atom. The last peak indicates the availability of a system of polyconjugated bonds).

The obtained NO samples possess electron-exchange activity, their aqueous and alcohol solutions absorb intensively molecular oxygen (Fig.1). NO oxidation rate constant values are sufficiently high ($k = 3.8\cdot10^{-2} – 24.1\cdot10^{-2}$ min^{-1} at 313-333 K, solvent – methanol), and activation energy value is equal to 84.6 kJ/mol. By NO oxidation one can obtain the stable macroradicals of naphthoxyl type, i.e. the obtained and oxidized NO samples show the paramagnetic (PMC concentration $\sim1.3\cdot10^{17}\div2.75\cdot10^{19}$ spin/g) and semiconducting (σ_0 $\sim10^{-14}\div10^{-9}$ $Om^{-1}\cdot cm^{-1}$ at 298 K, E = 1.3÷1.67 eV) properties. Moreover, an increase of PMC concentration in the composition of NO samples by 1-2 orders of magnitude leads to a noticeable increase of their electroconductivity (Table 2 and 3). Consequently, these oligomers can fulfill the function of an antioxidant in the composition and thus increase the heat- and thermal stability, as well as a period of their effective exploitation.

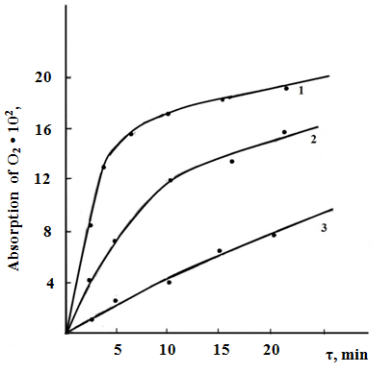


FIGURE 1: Kinetic curves of oxygen absorption by alkaline solution of NO in methanol. $[NO]_0$ = 0.34 mol/l, $[NaOH]_0$ = 0.45 mol/l. T, K: 333 (1), 323 (2) and 313 (3).

TABLE 2
PREPARATION OF NO SAMPLES WITH VARIOUS PMC CONCENTRATION

№	$[OH^-]_0$, mol/l	$[NO]_0$*, mol/l	T, K	τ, min.	$[PMC]\cdot10^{-19}$, spin/g
1	1.5	2.0	308	20	1.30
2	1.5	1.5	308	20	1.47
3	1.5	0.75	308	20	0.75
4	0.35	0.75	308	20	0.87
5	0.72	0.75	308	20	0.95
6	0.72	0.75	308	20	0.79
7	0.72	0.75	303	20	1.18
8	0.72	0.75	313	20	1.72
9	1.5	1.5	308	40	2.25
10	1.5	1.5	308	45	2.75

PMC concentration for initial NO sample was – $0.54\cdot10^{18}$ spin/g.

TABLE 3
SOME ELECTRICAL INDICES OF NO SAMPLES CONTAINING VARIOUS PMC CONCENTRATION

$[PMC]\cdot10^{-18}$, cm^{-3}	σ(0), $Om^{-1}\cdot cm^{-1}$	σ(ω) at 10^6 Hz, $Om^{-1}\cdot cm^{-1}$	$N(E_r)\cdot10^{20}$, $cm^{-3}\cdot eV^{-1}$	$N_0(E_F)\cdot10^{-18}$, cm^{-3}
1.3	$1.25\cdot10^{-14}$	$1.1\cdot10^{-9}$	0.48	1.20
7.5	$1.72\cdot10^{-10}$	$2.3\cdot10^{-8}$	2.90	7.25
11.8	$5.9\cdot10^{-10}$	$6.3\cdot10^{-8}$	4.72	11.9
22.5	$1.2\cdot10^{-9}$	$2.5\cdot10^{-7}$	7.62	19.1

The possibility of increase of the electroconductivity of NO with growth of PMC concentration in its composition has been used for creation of antistatic polymer compositions on the basis of thermoplastics by introduction of 5÷15% of NO into their composition, followed by treatment of the material surface with an aqueous or alcohol solution of alkali. It can be seen from Table 4 that ρ_v after introduction of NO into composition of thermoplasts is essentially decreased.

TABLE 4
ρ_v VALUES OF COMPOSITION MATERIALS ON THE BASIS OF THERMOPLASTS AND NO

NO, %	Thermoplast, %	ρ_v (Om·cm), on the basis		
		LDPE	PP	PS
5	95	$0.81\cdot10^8$ ($7.3\cdot10^8$)	$2.5\cdot10^8$ ($9.1\cdot10^8$)	$4.8\cdot10^8$ ($9.8\cdot10^8$)
10	90	$3.5\cdot10^8$ ($6.4\cdot10^8$)	$8.1\cdot10^8$ ($1.2\cdot10^7$)	$9.5\cdot10^8$ ($2.7\cdot10^7$)
15	85	$8.6\cdot10^8$ ($3.7\cdot10^7$)	$9.8\cdot10^8$ ($6.0\cdot10^7$)	$2.8\cdot10^8$ ($8.5\cdot10^7$)

The synthesized NO samples have been used as active additive for preparation of the rubber mixtures on the basis of rubbers, for ex., butyl rubber (BR). In this case, the rubber mixtures on the basis of BR have been made according to the standard recipe of ingredients with only difference that NO samples have been (partially) used instead of carbon black (from 20.0 to 45 w.p. per 100 w.p. of rubber) (Table 5).

TABLE 5

COMPOSITIONS OF THE RUBBER MIXTURES AND PHYSICAL-MECHANICAL AND ELECTRICAL INDICES OF THE OBTAINED VULCANIZATES ON THE BASIS OF BUTYL RUBBER

№	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	DPhG	1.3	1.3	1.3	1.3
5	Zinc oxide	5.0	5.0	5.0	5.0
6	Black carbon	50	30	15	5
7	NO	0	20	35	45
8	Sulphur	2.0	2.0	2.0	2.0

Mixtures	Vulcanization time, min.	Tensile strength, MPa	Specific elongation, %	Residual deformation, %	Modulus of elongation, MPa		$\sigma \cdot 10^7$, $Om^{-1} \cdot cm^{-1}$
					200%	300%	
1	2	3	4	5	6	7	8
Before aging							
1	40	19.5	710.0	4.2	9.4	14.1	
	60	18.3	700.0	4.5	9.0	13.2	
	80	19.1	663.3	4.3	9.8	14.3	
2	40	21.5	690.0	8.0	8.4	12.1	0.07
	60	23.6	681.5	7.3	8.1	12.5	0.25
	80	24.1	611.4	6.9	8.8	13.0	0.22
3	40	20.9	704.2	10.3	6.5	10.6	3.4
	60	21.6	672.0	12.1	7.0	11.1	5.6
	80	22.6	602.0	13.4	7.3	12.0	4.4
4	40	24.1	695.4	12.0	6.3	9.0	18
	60	26.0	674.0	13.5	6.5	10.1	24
	80	28.5	600.0	15.1	7.1	10.7	32
1	2	3	4	5	6	7	8
After exposure at 373 K for 24 h							
1	40	15.1	382	2.8	7.0	17.6	
	60	15.8	417	1.8	5.2	14.9	
	80	16.3	424	1.3	4.8	17.2	
2	40	20.8	580.7	4.1	7.0	12.8	0.05
	60	22.1	520.2	3.4	6.6	12.2	0.15
	80	22.5	508.4	3.1	7.0	12.9	0.26
3	40	20.3	583.1	4.8	5.1	9.5	4.1
	60	21.2	524.2	6.0	5.5	9.8	5.8
	80	23.5	485.2	7.1	6.4	10.2	6.7
4	40	23.2	575.5	5.7	4.8	8.4	64
	60	24.7	532.4	6.7	5.5	8.9	67
	80	25.8	491.3	7.9	5.9	8.7	73

It has been established that an introduction of NO instead of carbon black into composition of the rubber mixtures leads to an increase of tensile strength, specific elongation and decrease of modulus of elasticity of the obtained rubbers.

For example, a tensile strength for rubbers obtained with mixture vulcanization on the basis of BR including 20 mass p. of NO instead of carbon black is increased to 21.5÷24.1 MPa, a specific elongation reaches 611÷690%, and a modulus in elongation is decreased by 200% from 9.4÷9.8 to 8.1÷8.8 MPa. Along with this, the thermal stability and service life of the obtained rubbers are increased, which is obviously has been connected with structural peculiarity of NO; condensed aromatic structural fragments in the chain of aromatic polyconjugation stipulate high thermal stability, and an availability of hydroxyl groups in naphthalene rings – antioxidant activity. Since NO samples with different contents of PMC exhibit the high electrical conductivity, their joint use with electroconductive carbon black allows to obtain a rubber with a specific volume conductivity 10^{-8}÷10^{-6}Om^{-1}·cm^{-1}. Moreover, a growth of NO content from 20 to 45.0 w.p. (from rubber mass) instead of carbon black and also an increase of PMC concentration in NO composition leads to an increase of specific electroconductivity of the obtained rubbers. An effect of percolation is reached at content ~22.8 mass p. of NO for rubbers obtained from BR (Fig. 2).

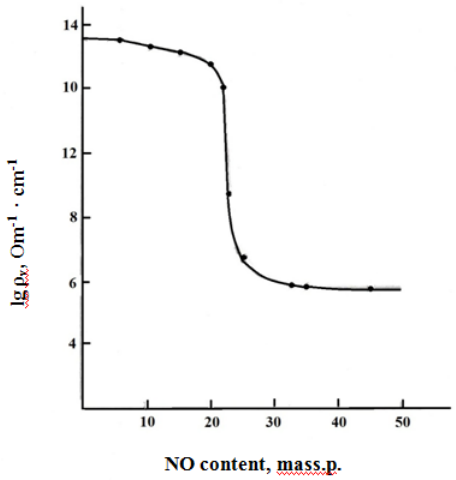


FIGURE 2. Change of specific volume resistance of vulcanizates from content of NO : BR.

The reinforcing properties of NO in the rubber composition have been probably stipulated by optimal combination of such indices as small particle size, low density, good compatibility of components and the participation of hydroxyl groups in the formation of the spatial net. Indeed, the specific volume resistance of the obtained rubbers depends on mixing time at various NO contents. The main reasons of change of specific resistance value of the made rubbers are the structurization or destruction of macromolecules. As a result of vulcanization, it is formed a net and a higher internal tension arises in the rubber. With increase of the rolling duration a probability of mechanical destruction of spatially cross-linked macromolecules is increased, a consequence of which is the formation of defective zones in the vulcanizate matrix (Table 6).

TABLE 6.
P_V VALUES OF VULCANIZATES OBTAINED AT VARIOUS MIXING TIME AND NO CONTENT (VULCANIZATIUON TIME – 40 MIN.)

N	NO content per 100 w.p. BR, w.p.	Mixing time, min.		$\sigma \cdot 10^7$, Om^{-1}·cm^{-1}
		Total	with NO	
1	20.5	41	2	0.28
2	20.5	44	5	1.12
3	20.5	46.5	7.5	3.8
4	35.0	41	2	4.9
5	35.0	44	5	8.3
6	35.0	46.5	7.5	9.8
7	45.0	41	2	65
8	45.0	44	5	82
9	45.0	46.5	7.5	96

Thus, the accumulation of static electric charges on the surface of rubber-technical products during their exploitation with

use of the developed rubbers is minimized.

IV. CONCLUSIONS

1. By oxidative polycondensation reaction of 1- and 2-naphthols, the polyfunctional polyconjugated soluble and meltable oligomers, including the corresponding hydroxynaphthylene links with high reactivity in the reactions characteristic for aromatic hydroxyl groups have been obtained.
2. By oxidation of naphthol oligomers one can obtain the stable macroradicals of naphthoxyl type. The obtained and oxidized NO samples show the paramagnetic (PMC concentration ~$1.3\cdot10^{17}\div2.75\cdot10^{19}$ spin/g) and semiconducting (σ_0 ~$10^{-14}\div10^{-9}$ $Om^{-1}\cdot cm^{-1}$ at 298 K, E = 1.3÷1.67 eV) properties.
3. The naphthol oligomers have been used as active fillers in preparation of electroconductive compositions on the basis of thermoplasts and rubbers. The antistatic polymer-oligomer compositions of LDPE, PP and PS with naphtol oligomers have been obtained.
4. It has been shown that in partial substitution of carbon black by naphthol oligomers on the composition of vulcanizates from BR, the obtained rubbers show the high heat-physical, physical-mechanical and electrical properties.

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