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Composite Materials Based on Elastomer, Co-oligomer and Bitumen

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Abstract

Chemical modification of phenyl-formaldehyde oligomers (PFO) was carried out, and compositions based on elastomer, co-oligomer and bitumen were developed in order to achieve significant improvement of characteristics and expand the areas of PFO application. The phenol-formaldehyde oligomer was modified with carbamide by co-polycondensation in an alkaline medium. The basic physicochemical, physical-mechanical and performance characteristics of the co-oligomer were studied. The co-oligomer of the new composition, obtained at the first stage of the investigation, was used as a binder. At the second stage of investigation, a three-component composition was developed on the basis of elastomer, co-oligomer and bitumen, and a composite material was prepared. This material was shown to exhibit good protective properties, and it may be recommended to provide anticorrosive protection of the equipment and installations in oil and gas mining industry. The effect of the amounts of introduced components on the major characteristics of the resulting composition was studied. It is shown that the introduction of a nitrogen-containing modifier (carbamide) into PFO causes a decrease in the content of free phenol and formaldehyde, which is important both from the environmental viewpoint and in relation to the hazardous action of these components on the human organism.

Keywords: elastomer, co-oligomer, bitumen, modification, composition, anticorrosion coating

INTRODUCTION

Many works published during the recent years deal with modification of phenol-formaldehyde oligomers (PFO), in particular using various organic compounds containing nitrogen, chlorine, bromine, sulphur and other elements, for the purpose of improving their properties and expanding the areas of their application [1–8]. Modification of existing oligomers with compounds containing functional groups opens broad possibilities to prepare composite materials for various purposes.

Phenol-formaldehyde oligomers are the products of phenol polycondensation with formaldehyde, with linear or branched structure, able to form three-dimensional structures during solidification. These oligomers are applied in many branches of industry due to the relative availability of initial raw materials and a number of valuable properties (relatively high thermal stability and chemical inertness). Introduction of various functional groups into oligomer composition allows us to vary its reactivity and physical-mechanical properties, which provides broad targeted use. For this reason, PFO production is permanently growing. At present, the amount of PFO production is about 5 % of the entire amount of industrial plastics manufactured in the world. The reasons of rapid growth of PFO production and consumption

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are related to the impressive achievements of the chemistry of these materials and to expansion of their application areas. Finally, a sharp increase in the production of PFO was promoted also by substantial achievements in decreasing the toxicity of these materials. For instance, PFO species with decreased content of free phenol and formaldehyde have already been developed.

Modification of oil residues (bitumen) with co-oligomers allows obtaining compositions characterised by broad ranges of physical-mechanical and performance parameters. The characteristics of oil extracted in Azerbaijan from sea and on land exhibit substantial variations, in particular in paraffin content. At the Baku petroleum refining plant, bitumen is mainly produced from offshore oil in which paraffin content sometimes reaches 8 %, in comparison with normative concentration 2–3 %. For this reason, the quality of bitumen manufactured from this oil sometimes does not meet standard requirements in a number of parameters (stretchability, softening, fragility, etc.). One of the components used to improve the performance characteristics of the composite based on bitumen and co-oligomer is butadiene-nitrile elastomer.

It is known that for the formation of corrosion-proof coatings, the functional groups that are present both in elastomer and in co-oligomer affect the improvement of the performance characteristics of the resulting composite. Improvement of physical-mechanical properties (strength and chemical stability of the coating) is also positively affected by the filler – bauxite sludge, which includes metal oxides [9, 10]. Introduction of the filler into compositions causes acceleration of solidification of the coatings based on elastomer, co-oligomer and bitumen, and renders durability to coatings [11–15].

The goal of the work at the first stage was to carry out chemical modification of PFO to improve its characteristics, and at the second stage – to develop a three-component composition based on elastomer, modified co-oligomer and bitumen, and to make a composite material on this basis.

EXPERIMENTAL

Initial reagents for the development of compositions were elastomer (SKN-40), co-oligomer (modified PFO), bitumen (85/25 grade), filler (bauxite sludge) and solvent (acetone).

A feature of SKN-40 elastomer is the presence of polar nitrile groups rendering specific properties to it.

Phenol-formaldehyde oligomer modified with carbamide (CPFO) is a viscous liquid of light yellow colour, well soluble in acetone, ethanol, dioxane and tetrahydrofuran.

The content of free phenol and formaldehyde in CPFO is lower than in non-modified oligomer (PFO). The reason is that modification with carbamide containing active amide and hydroxyl groups causes an increase in the degree of phenol, formaldehyde and carbamide co-polycondensation. Physicochemical and physical-mechanical properties of PFO and CPFO have been determined [16, 17]. The physicochemical and physical-mechanical characteristics of carbamide-modified and non-modified PFO are presented in Table 1.

Nitrogen content was determined using Kjeldahl's method, the concentration of free phenol was measured with Koppeschaar method. The latter method is based on the transformation of phenol after steam distillation into tribromophenol using a 0.1 M solution of potassium bromide-bromate as the brominating agent. Excessive bromine reacts with potassium iodide, and iodine released in this process is titrated with sodium thiosulphate. The content of free formaldehyde is determined according to GOST 16704-2017, molecular mass is measured using the cryoscopic method, the viscosity of 50 % solution in ethanol is determined with a VZ-4 viscosimeter at a temperature of 20 °C according to GOST 8420-2022, the drop point is measured with Ubbelohde instrument according to GOST 16388-2017, sample density is determined according to GOST 18995.1-73, adhesion characteristics of samples are measured according to GOST 15140-78, the degree of cure is assessed using extraction method, and Brinell hardness is determined according to GOST 4670-91. Penetration (indentation) and stretchability (ductility) of bitumen were determined using the known procedures according to the State Standards. Thermomechanical tests of samples were carried out with a PTB-1-2Zh instrument, with a cylindrical indenter (the cross section of the indenter is 1 mm^2).

Bitumen species (85/25 grade) are resinous substances (natural and artificial), composed of the mixtures of asphaltites, hydrocarbon resins, the products of their oxidation and polymerisation. The widest application for making protec-

TABLE 1

Physicochemical and physical-mechanical characteristics of non-modified and carbamide-modified phenol-formaldehyde oligomer (PFO and CPFO, respectively)

Parameter	PFO	CPFO
Nitrogen content, wt%	–	8.6
Free phenol content, wt%	13–15	0.5–2.0
Free formaldehyde content, wt%	8.2–9.7	3.4–4.6
Molecular mass (cryoscopic method)	400–450	760–820
Softening temperature according to Ubbelohde, °C	60–65	75–80
Viscosity of 50 % solution measured using VZ-4, s	40–42	54–58
Density, kg/m^3	1120–1125	1250–1280
Cure at 140 °C, 5 h, % (based on results of sol-fraction extraction from the samples with boiling solvent for 6 h)	92–94	97.6–98.0
Adhesion strength, MPa	2.2–2.4	3.8–4.2
Brinell hardness, MPa	220–230	275–280

Note. PFO and CPFO are non-modified and carbamide-modified phenol-formaldehyde oligomers, respectively.

TABLE 2

Physical-mechanical parameters of 85/25 grade bitumen

Показатель	Measuring units	Value
Penetration at 25 °C (the depth of needle penetration by 0.1 mm is accepted as penetration unit) (GOST 11501-78)	mm/10	20–30
Softening temperature (ring/ball) (GOST 11506-73)	°C	80–90
Stretchability at 25 °C (GOST 11505-75)	cm	2.5
Flash point (GOST 4333-87)	°C	246

tive coatings has been won by oxidised bitumen characterised by increased softening temperature and good compatibility with other film-forming coatings. The positive properties of bitumen include relatively high softening temperature, stability against the action of climatic factors, water and chemical reagents. The main parameters of 85/25 grade bitumen are presented in Table 2.

Modification of oil residues with co-oligomers allows obtaining compositions with a broad range of physical-mechanical and performance characteristics. Carbamide-phenol-formaldehyde co-oligomer was applied as a modifier to improve the characteristics of bitumen. The quality of modified bitumen was tested according to GOST 12801-84.

The filler was bauxite sludge, high-tonnage waste from the Gyanja alumina plant. Since alumina (aluminium oxide) is the major raw material to produce aluminium and is widely used in the national economy, it is an important task to broad the areas of bauxite sludge application. The composition of bauxite sludge is, %: SiO_2 4.98, Al_2O_3 25.56, Fe_2O_3 48.75, CaO 1.32, MgO 5.02, SO_3 1.61, a sum $Na_2O + K_2O$ 1.04, volatile compounds 11.72. Bauxite sludge is dark-red dispersed powder with the density of 3700 kg/m^3 [18].

Acetone (GOST 2768-84) was used as a solvent. Three-component composition was prepared using bitumen (85/25 grade, GOST 22245-90) 40–60 wt%, butadiene-nitrile elastomer (SKN-40) 3–5 wt%, CPFO (co-oligomer) 5–25 wt%, bauxite sludge 5–7 wt%. The components were thoroughly mixed in a laboratory reactor at 50–60 °C for 30 min. The data on the composition of components and physicochemical characteristics of the resulting compositions are shown in Table 3.

The use of CPFO allowed us to expand the raw material basis for the composition and to improve its quality characteristics.

During the formation of corrosion-proof coating based on the three-component composition, a mixture of elastomer, co-oligomer and bitumen manifests itself as the disperse phase. Dispersion takes place when co-oligomer phase accounts for less than 20 %. However, in the case when the fraction of elastomer exceeds 4 %, a matrix is

TABLE 3

Composition of the components and physicochemical characteristics of resulting compositions

Bitumen of 85/25 grade, wt%	Co-oligomer, wt%	Butadiene-nitrile elastomer, wt%	Filler, wt%	T_{soft}, °C	Penetration, 0.1 mm	Stretchability, cm
40	5.0	3.0	5.0	60.0	16	22
45	10	3.5	5.5	64.5	15	25
50	15	4.0	6.0	64.8	20	28
55	20	4.5	6.5	64.6	18	30
60	25	5.0	7.0	64.5	18	32

formed, which results in co-oligomer separation from the system in the form of spherical particles.

Corrosion-resistant coating was manufactured using the resulting composition as follows. At the first stage, a solution of elastomer, co-oligomer and bitumen was prepared, then this solution was charged into the laboratory reactor, and sieved filler was added in the portions of 0.5 g with uninterrupted mixing. After the introduction of the whole necessary amount of the filler, mixing was continued for 30 min more.

The ready composition was applied on the sample surface purified from corrosion products. The composition was applied with a brush or a spraying gun, in two layers, each of them was 50–60 μm thick. Then the samples with coatings were exposed in a thermostat for solidification.

Solidification was carried out in the following temperature mode: at 80 °C for 0.5 h, at 100 °C for 0.5 h, at 120 °C for 1.0 h, and at 140 °C for 4.0 h.

RESULTS AND DISCUSSION

Compositions based on elastomer, co-oligomer and bitumen can be considered as composites in which bitumen acts as a matrix, while co-oligomer is the dispersed phase. In the case of low co-oligomer concentrations, the compositions may be considered as dispersion-reinforced. Reinforcement in this situation is due to the fact that fine dispersed particles prevent the propagation of cracks in the matrix. This effect is observed for dispersed phase content 2–4 vol%. For the higher co-oligomer concentration with respect to bitumen, the compositions may be considered as fibrous or resinous. These compositions are characterised by increased strength, elasticity and resistance to fatigue destruction, which is especially important to provide the performance reliability of the material. Combination of bitumen with co-oligomers is not accompanied by chemical reaction, because co-oligomers are mostly inert to bitumen. At high temperatures, co-oligomer is in dissolved or softened state, which simplifies its uniform dispersion in bitumen [19–22].

The use of co-oligomer allows obtaining new composite materials based on bitumen, with improved qualitative characteristics of the latter, such as stretchability and adhesive ability. The developed compositions based on elastomer, co-oligomer and bitumen were tested under laboratory conditions as a corrosion-proof coating on steel samples. After solidification of compositions, the major physical-mechanical and performance characteristics of the resulting coatings were determined. Two coatings with different co-oligomers PFO and CPFO were tested (Table 4).

One can see in the data shown in Table 4 that solidified compositions with three-dimensional reticulate structure possess good physical-mechanical and protective characteristics. The introduction of modified co-oligomer into three-dimensional composition affects all physical-mechanical characteristics of the resulting coatings: strength, elasticity, fragility, hardness, etc.

Thermal oxidative degradation of PFO, CPFO and the compositions based on elastomer, co-oligomer and bitumen was investigated using the methods of thermogravimetric and differential thermal analysis.

Investigation was carried out using a Q-1500D derivatograph of Paulic–Paulic–Erdey system (MOM, Hungary) with programmed control providing uniform furnace heating at a rate of 0.5–20 °C/min.

During the formation of compositions involving thermosetting plastics, gas products are removed with simultaneous (sometimes acute) increase in the viscosity of the system. This has a substantial effect on chemical structuring processes and on the removal of volatile products from the material, which, in turn, affects the performance characteristics of solidified material. The temperature of PFO destruction onset was determined to be much higher in comparison with CPFO and compositions prepared on the basis of elastomer, co-oligomer and bitumen.

TABLE 4

Physical-mechanical and performance characteristics of the obtained corrosion-proof coatings

Parameter	Coating based on	
	SKN-40 + PFO + bitumen	SKN-40 + CPFO + bitumen
Impact strength of the film (using U-1 instrument), kgf · cm (GOST 4765-73)	30	38
Bending strength of the film (using ShG-1 instrument), mm (GOST 6806-73)	3.0	5.0
Adhesion of coating , cross-hatch test , score (GOST 31149-2014)	1.0	1.0
Adhesion to metal, MPa (GOST 15140-78)	18–20	24–28
Relative viscosity (using VZ-4 viscosimeter), at 20 °C, s (GOST 8420-74)	48	54
Swelling for 30 days, at 20 °C, % (GOST 12248.6-2020)	5–6	–
Stability in aggressive medium (GOST 12020-72):		
Reservoir water, 30 days at 20 °C, %	0.306	0.389
10% NaOH solution, 30 days at 20 °C, %	0.094	0.124
Oil- and petrol-resistance, 30 days at 20 °C, %	0.148	0.192

TABLE 5

Parameters of thermooxidative destruction of PFO, CPFO and composition

Sample	Mass loss at 200–300 °C, %	Half-decomposition temperature (50 % destruction), °C	Coke number at 600 °C, %	$E^{a}_{(400-600\ °C)}$, kJ/mol
PFO	11–21	500	42	57
CPFO	4–22	550	46	63
Composition	5–28	565	50	67

Note. 1. PFO, CPFO – non-modified and carbamide-modified phenol-formaldehyde oligomers, respectively. 2. Coke number is the ratio of the mass of non-volatile solid residue, formed during heating the carbon-containing material under standard conditions to the mass of sample under investigation. 3. E^{a} is activation energy of processes that take place within temperature range 400–600 °C

Mass loss at the initial stage of thermooxidative destruction is low and varies within the range of 2–12 % for PFO, 2–3 % for CPFO and 0.1–3 % for compositions.

Starting from 200–300 °C, intense evolution of destruction products takes place, and mass loss becomes substantially larger: it is 11–21 % for PFO, 4–12 % for CPFO, and 5–28 % for the compositions.

The rate of destruction product evolution decreases at the third stage in comparison with the second one. Some parameters of thermooxidative destruction of PFO, CPFO and compositions are presented in Table 5.

One can see that the temperature of 50 % destruction is higher than 500 °C for the studied samples, however, the temperature of destruction onset for PFO is much lower than for CPFO and compositions based on these oligomers. All samples under study are characterised by different destruction intensities: the highest coke number at 600 °C was determined for the composition based on elastomer, co-oligomer and bitumen. The activation energy of processes taking place within temperature range 400–600 °C increases and equals 57 kJ/mol for FPO, 63 kJ/mol for CPFO and 67 kJ/mol for the compositions.

According to the obtained data, the studied samples differ from each other in all parameters, which points to different mechanisms of destructive processes at the second and third stages of thermooxidative destruction.

The obtained results allow us to conclude that the composite materials developed on the basis of elastomer, co-oligomer and bitumen exhibit high corrosion-proof characteristics and are recommended for use as protective corrosion-proof coatings for steel equipment operated in petroleum and chemical industry.

CONCLUSION

1. The methods of directed modification of PFO with carbamide are developed for the purpose of improving the characteristics of oligomers and broadening the areas of their application. Since PFO modification with carbamide is a chemical reaction, an increase in the amount of function-

al groups in CPFO caused improvement of the major characteristics of co-oligomer. This allows broader ranges of application of the functional co-oligomer.

2. The introduction of nitrogen-containing modifier (carbamide) into PFO leads to a decrease in the content of free phenol and formaldehyde, which is important both from the environmental point of view and in relation to the hazardous effect of these compounds on human organism.

3. Compositions based on elastomer, co-oligomer and bitumen are developed. The main characteristics of the coating obtained on the basis of composition involving co-oligomer modified with carbamide were better than the characteristics of the coating prepared from non-modified oligomer.

4. Thermooxidative destruction of PFO, CPFO and the composition based on elastomer, co-oligomer and bitumen was investigated. The temperature of PFO destruction onset was determined to be much lower than that for CPFO. Different values of mass loss and activation energies point to destructive processes differing from each other in chemical nature at the second and third stages of thermooxidative destruction of these samples.

5. Taking into account adhesion ability, stability against water, aggressive media and thermal stability, the developed composite materials are recommended for use as protective coatings against corrosion of equipment and installations operated in oil and gas industry.

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