

# FUNCTIONAL OLIGOMERS BASED ON PHENOL-FORMALDEHYDE RESINS

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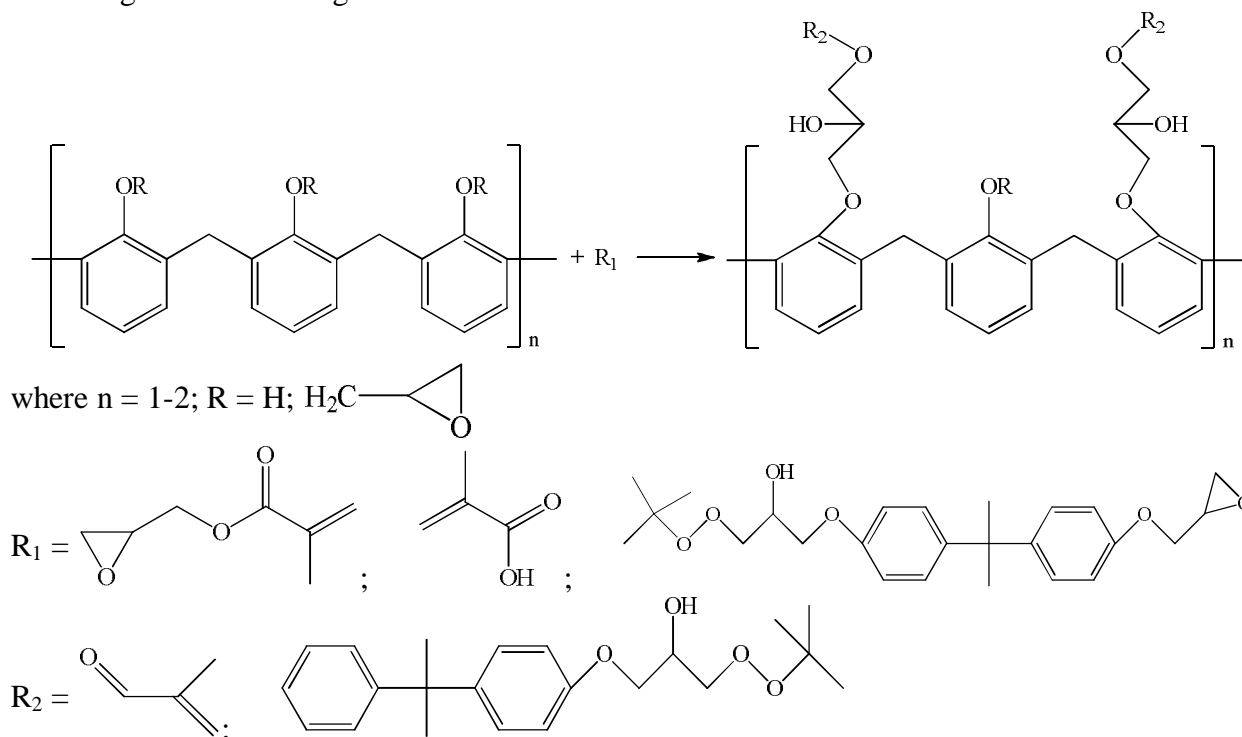
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Phenol-formaldehyde resins (PhFRs) are the most known products applied for the production of casting compounds, protective coatings, glues, etc. [1-3]. The advantages of these resins are high thermal stability, heat insulation and aggressive media resistance of the wares based on them [3].

To improve the operational characteristics of PhFRs, as well as to combine them with other polymer materials, PhFRs are modified with various low- and high-molecular compounds [3]. The resins may be modified at the stage of chemical reaction with low-molecular compounds, as well as at the stage of ware formation.

In this work on the basis of known PhFRs we created new oligomers with unsaturated double bonds or labile peroxy groups in the side chains.

The initial compounds for the synthesis were novolac phenol-formaldehyde resin (NPhFR) and polyglycidyl phenol-formaldehyde resin (PGPhFR). The oligomers were synthesized according to the following scheme:



Glycidyl methacrylate (GMA), methacrylic acid (MA) and peroxy derivative of ED-24 epoxy resin were used as the low-molecular compounds.

### *Synthesis of phenol-formaldehyde oligomers with methacrylic fragments*

The new compounds were synthesized by two ways:

- (i) NPhFR was used as an initial compound. GMA, which contains methacrylic fragment in its structure, was a modifier (1.5 mol/phenolic group). A catalyst was KOH in amount of 0.6 mol per one phenolic group of the initial resin [4]. The reaction temperature was 333 K, reaction time – 6 h. The reaction was carried out in the medium of inert gas using isopropyl

alcohol as the reaction medium. The resulting product (Oligomer I) has the molecular weight of 640 g/mol and bromine number 22.9 g Br<sub>2</sub>/100 g product.

- (ii) PGPhFR was the initial resin and MA (1.0 mol/g-eq epoxy group) was a modifier. Benzyl triethylammonium chloride (BTEAC) in amount of 0.2 mol/g-eq epoxy group, 60% aqueous solution, was used as a catalyst [5]. The reaction temperature was 353 K, reaction time – 6 h. To prevent polymerization by double bonds, inert gas was used and toluene was a reaction medium. The resulting product (Oligomer II) has the molecular weight of 590 g/mol and bromine number 28.1 g Br<sub>2</sub>/100 g product.

#### ***Synthesis of phenol-formaldehyde oligomers with peroxy groups***

To obtain phenol-formaldehyde resins with peroxy groups (PhFOP) novolac phenol-formaldehyde resin was used [6]. Peroxy derivative of ED-24 epoxy resin (PO) was used as a modifier. The catalyst was KOH in amount of 0.4 mol/phenolic group. The reaction was carried out at 323 K for 6 h in the medium of isopropyl alcohol. PO amount was 0.5 mol/phenolic group. The synthesized oligomer (Oligomer III) has the molecular weight of 750 g/mol and active oxygen content of 1.6 %.

#### ***Phenol-formaldehyde oligomers with functional groups as additives for epoxy-oligomeric mixtures***

The synthesized oligomers contain methacrylic fragments and residual phenolic (Oligomer I) or epoxy (Oligomer II) groups or residual phenolic and peroxy groups (Oligomer III) and may be used as active additives for epoxy-oligomeric mixtures [7]. The mixtures composed of ED-20 dianic epoxy resin and TGM-3 oligoesteracrylate were used as epoxy-oligomeric ones. Polyethylenepolyamine was a hardener. When we used Oligomer I and II as the additives, the mixture additionally contained PO. The amount of phenol-formaldehyde oligomer with functional groups in the mixtures was 8.3–26.7 wt%.

The protective films were formed stepwise: first at room temperature for 24 h and then at heating to 383, 403 or 433 K for 15, 30, 45, 60 and 75 min. The optimum process conditions have been determined. The process chemistry was established and confirmed using IR-spectroscopy.

#### ***Bitumen-polymeric mixtures***

Bitumen-polymeric mixtures were investigated using road bitumen BND 60/90 with the following characteristics: penetration 44·0.1 mm, ductility 89 cm, softening temperature 319 K and adhesion 40.5 %. Oligomers I and III were used as polymeric components in amount of 1, 3, 5 or 7 wt% per 100 mass parts of bitumen [6]. Bitumen-polymeric mixtures were studied at 443, 463 and 483 K for 0.5, 1.0 or 2.0 hours. To determine the reasons for the changes in operational characteristics the structural-group composition of the formed mixtures was studied.

The conducted investigations allowed to assert that PhFR-based functional oligomers may be used as the additives for epoxy-oligomeric mixtures to produce protective coatings with improved performance. On the other side, the introduction of the synthesized oligomers into bitumen allows to improve the properties of commercial bitumen.

#### **References**

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