Paint-and-varnish and adhesive composites based on phenolic oligomers

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SUMMARY

A review is given of research conducted in recent years in the field of the development of composite coatings and adhesive compositions based on phenol formaldehyde oligomers. Film-forming materials of different composition, the properties of coatings based on them, and also the fields of their application are described. Adhesive composites for the gluing of different materials – metals, wood – also used as binders are presented. The practical importance of the conducted research is substantiated.

As unmodified PRs form very brittle coatings, they are modified for the purpose of plasticisation and to give them a combination of valuable properties, or alternatively composite materials based on a blend of PR with more plastic and hydrophobic resins, for example epoxy, alkyd, or natural resins, are produced [4].

In the literature, special attention is paid to the creation of new epoxy phenol varnish composites [5–15]. For example, the US company VCV Speciality Chemicals has placed on the market a new epoxy phenol novolac resin [5] for application in PVMs with a high dry residue for coatings with a high crosslink density and accordingly increased heat and corrosion resistance. The resin can be used either as an independent film-forming material or in combination with other resins of the bisphenol A or novolac types. Epoxy phenol varnish composites with different β-alkylated oligomers have been examined [6], and the influence of the type of β-alkylating agent and the degree of β-alkylation on processes occurring during preparation, storage, and curing of epoxy phenol composites based on them has been investigated. The stability of new epoxy phenol varnish composites based on β-alkylated resols has been studied during their preparation and storage [7]. The composites are designed to protect food cans. A detailed investigation has been made [8] of the influence of the prehistory of epoxy phenol varnishes and the regime for forming coatings of similar designation on their structure. In the same study [8], the preferential characteristics of varnishes recommended for curing under conditions of the highest temperatures (>300°C) were also determined.

In a patent [9], the composition for a fire-resistant, heat-shielding coating was developed, including a polymer binder (phenol furfural formaldehyde resin, epoxy...
resin, a copolymer of vinyl chloride with acrylonitrile), a plasticiser (perlite, talc, mica), and a curing agent (hexamethylenetetramine in aliphatic alcohol). The obtained coating possesses high adhesion, working life, and heat-shielding properties (heating to 175°C). Bilym et al. [10] give the results of investigating the thermal modification of epoxy phenol film and block matrix systems of composites.

Russian scientists [11] conducted a complex investigation into the combination of epoxy and phenol formaldehyde oligomers (PFOs) by electromagnetic dispersion. Methods for controlling the structure of epoxy phenol composites and its influence on the characteristics of coatings based on them were investigated.

Hybrid oligomers have been synthesised [12] by the polycondensation of resol and novolac PFOs in the solvent dioxane. By their esterification in n-butyl alcohol, oligomers have been produced that are of interest as components of epoxy phenol composite coatings and adhesives.

A composite [13] based on butanolised hybrid PFOs with epoxy resin of grade ED-20 is not inferior in its physicomechanical properties (drying time 1–2 days, adhesion 1 rating, impact strength 40 cm, elasticity 1 mm, M-3 hardness 0.25 nominal units) and adhesive properties to known analogues, and in petrol resistance is even superior to them. Possessing the combination of properties described above, the proposed composite can be recommended as a protective coating for the inner walls of petrol tanks and other vessels for the storage of petroleum products.

An improvement in the physicomechanical properties of PFOs is promoted by the use of unsaturated chlorine (bromine)-containing epoxy compounds as modifiers, thereby expanding the range of epoxy modifiers [14].

In order to select the optimum ratio of components, and to select the temperature and time conditions of formation of the wear-resistant working layer of hard discs, an investigation was made [15] of the relationships governing processes of structure formation in dilute and concentrated solutions of blends of epoxy novolac and phenol formaldehyde resins (PFRs) in different solvents and in films.

Protective paint systems based on PRs with polyesters are known [16–18]. Composites for the protection of metals contain, as a film-forming component, a blend of 50–90% PFR and 10–50% carboxylated polyester with an acid number of 15–200 and an OH number of 20–200 [16, 17]. In another study [18], developed water-based paint systems contain 1–40 parts resol PFR per 100 parts acrylated polyester (PES). Acrylated PES is produced by the grafting of acrylic monomers onto the matrix PES with a number-average molecular weight of 2000–100 000 and an OH number of 10–20, and a blend of vinyl monomers containing methacrylic acid.

In a patent application [19], the development of varnish coatings for metal surfaces that is based on resorcinol-modified PR is described. US scientists have proposed [20] a composite for coating manufacture. It contains two components, one of which is a quasi-prepolymer of isocyanate and a compound with active hydrogen, and the other a mixture of polyester polyol containing terminal amino groups and having a molecular weight of >1500 and a chain elongator with terminal amino groups and PFR. Gelation of the composite after mixing of the components begins after <13 s.

Studies are known [21, 22] in which, to produce film-forming components, PR is modified with different compounds. Low-migration, low-odour, and low-swelling sheet offset printing ink [21] contains rosin-modified PR and a plasticiser from a group of water-insoluble fatty acid esters and sterically hindered polyhydric alcohols and/or ethanol. A study was made [22] of the surface-active properties of ethoxylated adducts of resol and novolac PFRs and polyethylene glycols (PEGs) with molecular weights of 1000, 1500, and 4000. Increase in the molecular weight of PEG, along with improvement in the surface-active properties, ensures the production of coatings with high technological properties during painting and with elasticity.

The adhesive properties of composite materials based on PRs enable them to be used not only as paint-and-varnish coatings but also as adhesives for different materials, to which a fairly large number of studies in the literature have been devoted. Possessing a comparatively shorter curing time and high adhesion to steel, to different polymer substrates, and to wood, composites of this kind are of practical importance as adhesives.

Phenol urea formaldehyde resins with adhesive properties were produced [23] by the polycondensation of phenol and urea separately with formaldehyde, with repeated polycondensation of condensates at 90°C in the presence of a heterogeneous catalyst.

The governing relationships were established [24], the production conditions were substantiated, and the optimum ratios of PRs and epoxy oligomers with polyvinylpyrrolidone (and also the amount of catalyst) producing the maximum strength of the adhesive material were determined, as well as the dependence of the adhesion strength of the adhesive on its composition were determined.

PRs of the resol type in a quantity of 0–30% effectively increase [25] the adhesion of epoxy amine adhesives. Good adhesive properties are possessed by composites [26] also containing phenolic and epoxy resins, nitrile rubbers, polyvinyl acetals, traditional polyamines and polyanimes based on vegetable oils with acid groups and on polyanimes, polycrylates, neoprene, or reactive polyurethanes. The modification of a phenol formaldehyde oligomer (PFO) [27] with
aminophenylmonomaleinamide in alkaline medium has a positive effect on the physicomechanical and service properties of adhesive composites based on it. In patents [28, 29], adhesive composites are proposed that contain: 100 parts Nairit polychloroprene rubber, 90 parts [28] and 100 parts [29] butyl phenol formaldehyde resin, 2 parts tetramethylthiuram disulphide [28], 5 parts zinc oxide, 12 parts magnesium oxide, 800 parts [28] and 850 parts [29] solvent (a mixture of ethyl acetate and xylene), 12 parts magnesium oxide, 800 parts [28] and 2.5–20.2 parts [28] and 2.7–21.4 parts [29] aniline resin with an aniline content of <15%.

Sedliacik and Sedliacik [30] report an increase, by adding PRs, in the heat stability of cured adhesive materials based on polyvinyl acetics, as the latter decompose at <100°C. Here, a PR content greater than 30% is undesirable, as this leads to a reduction in the resistance to direct pull of adhesive mixtures used for the gluing of metals in the production of aircraft. The obtained adhesive materials are durable. The positive effect of PFR additions on the strength and ageing of glued joints when an adhesive based on polyvinyl acetate or a copolymer of vinyl acetate and N-methylolacrylamide is used has also been examined by Lopez-Sueroz and Frazier [31].

An adhesive composite [32] containing bisphenol A epoxy resin ED-20, an oligourethane based on hexamethylene diisocyanate and ethylenediamine with terminal isocyanate groups, and curing agent polyethylenepolyamine modified with an oligomer produced by three-component condensation of p-tert-octylphenol, formaldehyde, and 2-chloro-3-phenylamine-propene-1 under mild conditions has been reported. A PO-modified adhesive composite, in terms of its physicomechanical properties (tensile strength 34 MPa, elongation at break 90–92%, resistance to uniform direct pull 40.8 MPa, gluing shear strength for steel 44.7 MPa, for glass-fibre-reinforced plastic 39.0 MPa, for rubber 9.3 MPa, for PVC 5.5 MPa, for high-impact polystyrene 0.4 MPa, for polyurethane 0.81 MPa, and so on), can be recommended for application in engineering, instrument making, and footwear production.

Studies are known [33–35] in which, in order to improve certain properties of PF adhesives, use is made of components of animal and also vegetable origin. An example is the possibility of using the hydrolysis products of carotene as additives to PF-based adhesives to improve their ecological and hygienic properties [33], without adversely affecting their physicomechanical properties. Fractions of sodium salt of wheat straw lignin (WSL) are used [34] to fill PFRs in the manufacture of adhesive composites, where the reduced molecular weight of WSL is accompanied with an improvement in the adhesive properties and a reduction in the formaldehyde content and viscosity.

Use is also made [35] of cashew nut shell oil along with other components (nanocomponents, melamine, formaldehyde) with the aim of modifying methylphenol resin and producing an adhesive for different materials in block brakes. The catalytic process of modification is carried out for 0.5 h at a temperature of 70–140°C, as a result of which a composite is produced with good rupture strength, strength, and high heat stability.

Adhesive composites [36–38] containing boron, silicon, titanium, and also their compounds are cured at room temperature and have a high heat stability. Titanium- and silicon-containing adhesive based on novolac resin of grade SF-294 is suitable [36] for the assembly and repair of articles operating at temperatures of up to 1600°C. An adhesive composite developed by the same authors [37], comprising a furfural solution of novolac PFR modified with heteroorganic compounds and filled with finely disperse powders of amorphous boron and crystalline silicon, is suitable for materials working at temperatures of up to 400°C both in a protective atmosphere and in air. The strength of adhesion of the adhesive layer of composites based on PFR, boron carbide, and silicon dioxide in the gluing of graphite amounts to 17.1 MPa [38]. Furthermore, when heat treated up to 1500°C, the formation of borosilicates occurs, which gives the adhesive joints high heat stability and low shrinkage during heat treatment.

Materials based on wood and phenolic binders in the form of wood particle board (WPB) [39, 40], plywood [41, 42], fibre board (FB) [43–45], and adhesive wood structural elements are widely used in construction. They can be used in particular for outer facing in regions with high humidity owing to their high moisture [46] and weather resistance.

Investigations were conducted [41] into developing the composition of a PFR adhesive for the manufacture of plywood from coniferous wood. The gelation time of adhesive based on PFR of grade SFZh-3014 with the use of a modifier at 950°C amounts to 5 min, i.e. its reactivity is more than 8 times that of the base. For similar purposes, an adhesive composition [42] based on lignosulphonate-powder-modified PFRs of grades SFZh-3013M and SFZh-3014M is suitable. The physicomechanical properties and also the technological effectiveness of WPB semiproducts formed by rapid pressing are influenced favourably [47] by the use as the binder of PFRs modified with ethylene, propylene, and butylene glycols and glycerin, and in the case of the latter two the pressing time can be shortened by 20% with retention of the physicomechanical properties of the WPB.

To coat wood materials, use is also made of a composite [48] consisting of a mixture of urea formaldehyde resin and phenol resorcinol formaldehyde resin taken in a mass ratio of 1:1–15, where the curing agents are mono-, tri-, or polycarboxylic acids. Adhesive composites or binders for wood and polymeric materials of similar
component composition [49] differ in that they contain glyoxal monoaacetals and glyoxylic acid, possibly in the form of water-soluble salts.

An adhesive composition based on PFR with a bromine content of 10 wt% has been developed [50]. Plywood panels obtained with its application have high shear strength between the layers, fire resistance, and resistance to cold and hot water. In another work [51] an investigation is made of the effect of additions of NaOH, lime milk, and Na2SiO3 on the mechanical properties of plywood coated with a mixture of soy (1 part) and PF adhesives (3 parts), where the soy adhesive reduces the cost without adversely affecting the properties of the plywood. By different methods of analysis, studies have been made of the effect of PF [52] and PF tannin [53] adhesives on the structure of wood, and the positive influence of fillers on the properties of PFRs used for the production of WPB and adhesives based on similar resins for the gluing of wood has been established [54].

As can be seen from this review of the literature published in recent years, paint-and-varnish and adhesive materials based on PFRs are of great practical importance. PFRs are used chiefly for the creation of ground coats for motor vehicles, coatings for metal containers, anticorrosion paints for marine vessels, and printing inks, and here the use of phenolic coatings in containers, anticorrosion paints for marine vessels, and offset printing ink.

Phenolic/polyurea coating copolymer compositions and process.

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