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AMMONIA-FREE, LOW-TOXIC PRESS-MATERIALS WITH IMPROVED ELECTROINSULATING PROPERTIES BASED ON MODIFIED NOVOLAK PHENOL-FORMALDEHYDE RESIN

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Abstract. The technological and operational properties of press-materials based on novolak composition modified jointly by epoxydianic resin and polyvinylpyrrolidone depending upon filler nature and pressing conditions have been determined. The reactivity of obtained press-powders has been investigated depending upon filler type, as well as curing conditions of composites under which ammonia and formaldehyde are not emitted. It has been shown that developed press-materials have the same technological and operational properties compared with known phenoplasts but their heat resistance, impact strength and electroinsulating properties are better.

Keywords: press-materials, phenoplast, novolak phenol-formaldehyde resin, gel-fraction, filler.

1. Introduction

In connection with the wide use of phenol-formaldehyde resins (PFR) in industry and everyday life the necessity of production of new phenoplasts originates. These phenoplasts should have high physico-mechanical indexes and universal complex of properties to operate under different conditions. The versatility of PFR application is conditioned by a wide temperature range of their curing and operation as well as their possibility to produce various operational characteristics depending upon the material purpose.

Developing the reactive compositions with prognostic properties it is necessary to determine the effect of components ratio and forming conditions on the rate and degree of compositions cross-linking. In order to predict the properties of obtained composites it is important to know chemism of the reactions which may proceed in the system depending upon components nature and curing conditions of the compositions of oligomeric type during material formation, namely – the composite based on mineral fillers with such specific characteristics as high adhesion, plasticity, *etc*.

Phenol-formaldehyde press-materials are characterized by high heat resistance and physico-mechanical indexes [1], resistance to the action of organic solvents, acids and weak alkalis [2]. The imperfection of such press-materials is the dependence of dielectric properties upon temperature and current frequency. At the same time brittleness of the wares based on phenol-formaldehyde resins may be considerably decreased in the case of exchange of powder fillers for fibrous ones [3, 4].

Novolak press-powders contain hardeners, for example hexamethylenetetramine. As a result they harden with the emission of toxic volatile products (ammonia, formaldehyde) and press cycle duration is within 2–5 min [5].

Press-powders on the basis of developed by us phenol-formaldehyde compositions modified by polyvinylpyrrolidone (PVP) and epoxy-dianic resin (EDR) were obtained under joint heating in alcoholic solution [6]. They do not emit the above-mentioned volatile products because binder curing takes place using mechanism of intermacromolecular cross-linking with the formation of combined structure “penetrating network” [7]. To force the curing process N,N-dimethylaniline (DMA) was used. Thus, the main task of the work was to investigate the reactivity of press-materials, as well as their operational and physico-mechanical properties.

2. Experimental

To obtain press-powders on the basis of phenol-formaldehyde novolak composition modified by epoxy-dianic resin ED-20 and PVP (PFR:EDR:PVP:DMA = 73.5:25:0.5:1) the following fillers were used:

- mineral fillers – kaolin, quartz flour, marble aggregate;
- organic filler – wood flour.

Press-materials were obtained by laked method from alcoholic solution in accordance with the procedure described in [8, 9].

The grinded filler was added to the alcoholic solution of the mixture. The mixing was carried out at 307–317 K for 2–3 h. Then the reactive mass with moisture content of 50 % was dried in vacuum oven at 323–333 K till the moisture content became 3.5–4 %. The obtained product was grinded in ball mill and sifted using a sieve with a grid No. 0335K. Coarser fraction was returned back to the mill for additional grinding.

The polymeric compositions were prepared in the following way. Phenol-formaldehyde lacquer (PHL) was obtained *via* dilution at 313–323 K of a given mass of novolak phenol-formaldehyde resin in isopropyl alcohol. PVP was dried for 4 h at 333 K in an oven. The corresponding ass of PVP was dissolved in isopropyl alcohol and thoroughly mixed with PHL and epoxy resin. Then a catalyst for DMA hardening was added.

To establish the optimum temperature, a compacting pressure and curing time we investigated the effect of a filler nature on the gel-fraction yield. The gel-fraction content was determined using the extraction of preliminary grinded samples in Soxhlet apparatus by ethanolamine. The extraction was carried out for 18 h. After the extraction the films were dried for 8–10 h in the oven till the mass became constant and weighted.

To determine the physico-mechanical properties of developed press-materials we used samples in the form of rods with the size of 10× 15×60 mm pressed by means of P 474A press-machine.

The surface hardness of polymeric material was determined using Heppler consistometer by indentation of steel cone with 53°08’ in the sample at loading of 50 N for 60 s. The static flexural strength was determined in accordance with standards. Impact elasticity was determined in accordance with standards using pendulum hammer of 2083KM-0.4 type. Specific electrical resistivity of pressed samples was measured in accordance with standards. The experiments were carried out using teraohmeter of E6-13A type in accordance with standards by means of rectangular copper electrodes. Water absorbing of the samples was determined in cold water accordingly to standards.

3. Results and Discussion

By the value of gel-fraction yield (G) and press-powder properties the rational content of the filler (C_f) is determined (Fig. 1). This value is 60–80 mas %. Moreover, under the similar curing conditions the filler nature slightly affects the curing degree of press-powders. But the most rapid cross-linking to the deep curing degree takes place for the compositions filled with organic filler – wood flour (60 mas %). The compositions with mineral fillers achieve maximum curing degree at their content of 70–90 mas %. Regardless of curing conditions and filler nature the curing time (t) of press-powders is within 0.8–0.1 min per 1 mm of ware’s thickness.

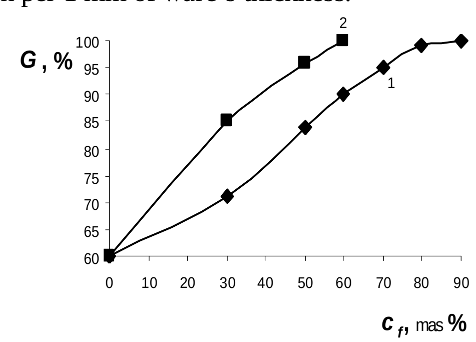

Fig. 1. Effect of filler nature and content on the gel-fraction yield of the composites: mineral filler (1) and organic filler (2). T = 433 K; P = 30 MPa; t = 10 min (d = 10 mm)

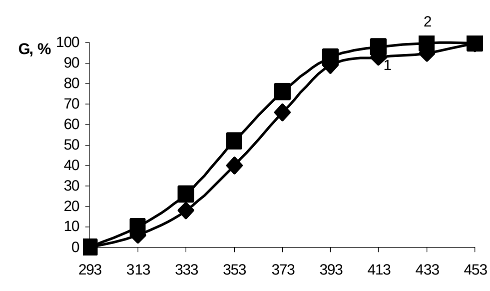

Fig. 2. Effect of the temperature on the cross-linking degree of the composites: mineral filler (1) and organic filler (2). t = 10 min (d = 10 mm); P = 30 MPa; C_f = 70 mas %

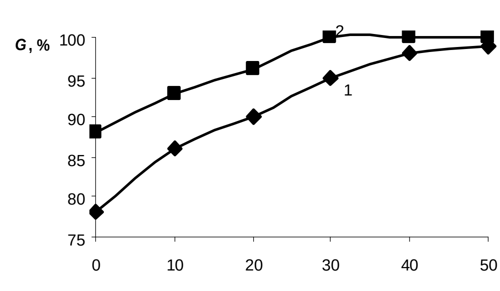

Fig. 3. Effect of the compacting pressure on the cross-linking degree of the composites: mineral filler (1) and organic filler (2). t = 10 min (d = 10 mm); T = 433 K; C_f = 70 mas %

One can see from Figs. 2 and 3 that the increase in temperature and compacting pressure considerably accelerates the press-powder curing and increases the cross-linking degree independent of the filler nature. At the same time we may assert that the compositions are already reactive at 393 K.

Under all curing conditions the rate and degree of cross-linking are the highest for the press-powder with wood flour. This fact may be explained by additional interaction between the functional group of combined binder and hydroxyl groups of cellulose in the curing process. The higher reactivity of filled phenol-formaldegyde compositions compared with unfilled ones is explained by allocation of functional groups over the filler surface as a result of the binder adsorption.

On the basis of obtained results the rational technological parameters of developed press-materials were determined (Table 1). The developed press-materials are transformed into goods using the method of direct pressing and regimes typical of those for commercial phenoplasts processing. The new materials are characterized by the same contraction at pressing but have the higher curing rate in the press-form that may considerably increase the productivity of large-tonnage productions.

Using given regimes the samples for determination of physico-mechanical properties depending upon the filler type were pressed. Physico-mechanical properties of pressed materials are represented in Table 2.

Table 1

Technological properties of press-materials based on modified PFR

Property	Kaolin	Quarts	Marble aggregate	Wood flour
Shrinkage, %	0.35-0.65	0.40-0.70	0.40-0.70	0.55-0.85
T, K	443±5	443±5	448±5	418±5
P, MPa	30±2	30±2	35±2	30±5
Curing time per 1 mm of ware's thickness, min	0.9-1.4 / 1.0-1.5	0.9-1.4 / 1.0-1.5	0.9-1.4 / 1.0-1.5	0.6-0.9 / 0.6-1.0

Note: developed press-powders / industrial press-powders [10]

Table 2

Physico-mechanical properties of press-materials based on modified PFR

Property	Kaolin	Quarts	Marble aggregate	Wood flour
Bending stress, MPa	68.0	51.0	56.0	75.0
Impact strength, kJ/m^2	12.4	9.8	10.3	13.0
Surface hardness, MPa	1160	985	900	930
Water absorption, %	0.16	0.09	0.13	0.24
Heat resistance by Vike, K	148	152	145	130
Volume resistivity, Om·m	$8\cdot10^{10}$ / $2\cdot10^{9}$	$3\cdot10^{11}$ / $7\cdot10^{9}$	$5\cdot10^{10}$ / $2\cdot10^{9}$	$6\cdot10^{11}$ / 10^{10}

Note: developed press-powders / industrial press-powders [10]

The materials filled by wood flour are characterized by the highest mechanical and electroinsulating properties but have a low heat resistance and high water absorption that may be explained by peculiarities of a cellulose chemical structure [11]. The lowest value of water absorption and high values of heat resistance, surface hardness and electroinsulating properties have the compositions filled with a quarts flour. Therefore they may be recommended for the production of electro-technical goods. The compositions with kaolin have the highest values of surface hardness. Goods on the basis of developed press-powders are characterized by values of a specific electric resistivity which are higher by the order than those of commercial phenoplasts independently of the filler type.

4. Conclusions

Thus, the press-materials based on PFR of novolak type and modified by PVP and ED-20 epoxy-dianic resin are characterized by the high reactivity and the same operational characteristics as known phenoplasts have. At the same time they are better in relation to heat resistance, impact strength and electroinsulating properties.

Moreover, in contrast to the known industrial phenoplasts, the developed press-powders do not emit volatile products during their processing that increases the production standards and ecological compatibility. Press-materials with quarts flour have unique combination of operational properties – high heat- and water-resistance, excellent electroinsulating properties and satisfactory mechanical characteristics. Such combination allows to recommend them for the production of general-duty and electro-technical goods.

Acknowledgments

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БЕЗАМІАЧНІ, МАЛОТОКСИЧНІ ПРЕС-МАТЕРІАЛИ З ПІДВИЩЕНИМИ ЕЛЕКТРОІЗОЛЯЦІЙНИМИ ВЛАСТИВОСТЯМИ НА ОСНОВІ МОДИФІКОВАНОЇ НОВОЛАКОВОЇ ФЕНОЛО-ФОРМАЛЬДЕГІДНОЇ СМОЛИ

Анотація. *Встановлено залежності технологічних і експлуатаційних характеристик прес-матеріалів на основі сумісно модифікованої епоксидіановою смолою і полівінілпіролідоном новолакової композиції в залежності від природи наповнювача та умов пресування. Досліджено реакційну здатність одержаних прес-порошків в залежності від типу наповнювача, а також умов затвердження композитів, при якому не виділяється амоніак і формальдегід. Показано, що розроблені прес-матеріали відзначаються аналогічними технологічними та експлуатаційними характеристиками в порівнянні з відомими фенопластами, а за теплостійкістю, ударною в'язкістю і електроізоляційними властивостями перевищують їх.*

Ключові слова: *прес-матеріали, фенопласти, новолакова феноло-формальдегідна смола, гель-фракція, наповнювач.*