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# Prediction of the Properties of Modified Phenol-Formaldehyde Composites Using Mathematical Modeling of the Composition of the Polymer Mixture

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**ABSTRACT**

The paper presents the results of studies of adhesive strength under shearing, thermal stability, and the content of the gel fraction of adhesive materials and enamels based on modified phenol-formaldehyde resins. Epoxy resin and polyvinylpyrrolidone were used to modify the phenol-formaldehyde resin. The influence of the content of components in the phenol-formaldehyde composition and the curing conditions on the properties of the obtained adhesive materials and coatings is analyzed. The effect of polyvinylpyrrolidone on internal stresses in adhesive joints has been established. By mathematical planning, the isolines of the characteristics of composite materials based on modified phenol-formaldehyde resin depending on their component's compositions are plotted, and the regression coefficients are found, enabling one to get materials with predicted properties. From a technical and economic point of view, the following content of additives in modified phenol-formaldehyde resin is most optimal: epoxy resin from 25 to 50 wt%, polyvinylpyrrolidone from 0.5 to 1.0 wt%, curing catalyst from 1 to 2.5 wt%.

**Keywords:** phenol-formaldehyde resins, epoxy resin, polyvinylpyrrolidone, adhesion strength, regression equation, Scheffe's method.

## INTRODUCTION

Phenol-formaldehyde resins (PFR) are used in various industrial applications requiring a durable, smooth, and flawless coating. The phenolic coating provides long-lasting, high-quality protection against corrosion, scratches, and cracks [1, 2]. Heat-treated phenolic coatings can be used in a wide range of acidic environments, even highly acidic environments, as they have excellent acid chemical resistance even at high temperatures [3, 4]. Thus, phenolic coatings are optimal for various industrial applications such as fume hoods, pumps, pipes, and tank linings. These coatings have an optimal balance between flexibility, elasticity, strength, wear resistance, chemical resistance, film stiffness, and impact resistance [5].

Other applications for PFR include foamed phenol-formaldehyde resin for insulation and various applications in the rubber industry, including tires. Phenolic resins are a safer alternative to resorcinol when used as crosslinkers in rubber products such as tires. Phenolic resins

help reinforce rubber structures and improve adhesion [6, 7].

Therefore, at the moment, the primary heat-resistant coatings will continue to be coatings based on phenol-formaldehyde or epoxy resins (ER) [8]. Thus, developing new types of enamels based on PFR is an urgent task.

Studies [9] on the effects of nano-$SiO_2$ particles on the tensile properties and tensile fracture face morphology of the phenolic amine/epoxy resin system show that the uniform dispersion of $SiO_2$ nanoparticles plays an important role in promoting the tensile performance of nanocomposites. Additionally, increases of 184.1% and 217.2% were achieved by adding 1.5% weight parts of nano-$SiO_2$ in composites for the tensile strength and tensile modulus, respectively.

In work [10] found that the thermal conductivity was increased by 6.5% in the phenolic resin by adding 0.45 wt% graphene and 0.15 wt% single-wall carbon nanotubes (maintain the mass ratio 3:1). It is shown that if graphene and carbon nanotubes are added in proportion, the thermal conductivity of phenolic resin will be improved significantly, which is better than only carbon nanotubes or graphene. Graphene oxide/phenolic formaldehyde resin composites show good mechanical, electrical, thermal, and frictional properties, as well as dielectric and flame retardant properties [11].

In work [12] showed that adding phenolic into epoxy could improve the mechanical performances of epoxy resins and epoxy-based composites at room temperature, and the phenolic influenced epoxy-based plain-woven laminated composites more than epoxy matrix at room temperature. However, at high temperatures, the addition of phenolic decreased the mechanical performances of epoxy resins and epoxy-based composites, and the adverse effect of phenolic became more severe with the increase of phenolic content at high temperatures. In addition, the thermogravimetric analyses were also conducted from 30°C to 800°C on phenolic modified epoxy resins. The results showed that the phenolic modified epoxy resin had an earlier loss in weight than unmodified epoxy resin. The earlier loss in weight meant that the addition of phenolic into epoxy resin led to the formation of unstable molecules at high temperatures.

In work [13], phenolic resins were modified with functionalized silica sols, and materials with high resistance to ablation in an acetylene-oxygen flame were obtained. Ethylenediamine was used as a hardener for epoxy-functionalized sols.

In work [14], cardanol-based epoxidized resole resins were synthesized by reacting resole type phenolic resin and epichlorohydrin in an alkaline environment at 120°C. Resole-type phenolic resins were synthesized by reacting cardanol and formaldehyde in the presence of sodium hydroxide as a catalyst. These prepared samples were hardening using 15% polyamide as a curing agent at 120 ± 2°C for 1 h. Mechanical and chemical resistance characteristics of prepared samples were evaluated to assess the possibility of using such thermosetting resins as a new eco-friendly material for engineering applications. It was found that the prepared resin systems exhibit better properties compared to commercial epoxy resin in terms of increase in tensile strength, elongation-at-break, impact strength, castings and gloss, scratch hardness, adhesion, and flexibility of the films. The anticorrosive properties of the prepared resin systems' chemical resistance are superior to unmodified epoxy resins.

The development of a technology for obtaining a new material consists in creating an optimal technological process for molding products with controlled properties based on the use of data on the technical properties of the feedstock [15]. The composition of the initial mixture has a versatile effect on the properties of polymers, which makes it challenging to choose the ratio of components for its synthesis [16]. In this regard, the composition of the initial mixture to obtain compositions with optimal properties for a particular case was found using the method of mathematical planning of the experiment, which significantly reduces the proportion of experimental costs. In this case, the result of the research is a multifactorial mathematical model in the form of a polynomial of a given degree – a regression equation [17].

The previous work [18] developed a method of obtaining non-toxic composite materials based on modified phenol-formaldehyde resin with improved adhesive properties and heat resistance. Epoxy resin and polyvinylpyrrolidone (PVP) were used to modify PFR and N,N-dimethylaniline (DMA) as a curing catalyst. It is shown that the main properties of the obtained composites significantly depend on the ratio of the components of the polymer mixture and the hardening parameters. Therefore, this work aimed to optimize the composition of the developed phenol-formaldehyde composites using mathematical

planning of the experiment, to determine the values of the regression coefficients, and to plot isolines of their essential characteristics. This will make it possible to choose the optimal composition of the mixture to obtain material for a specific purpose.

### Research methods

The compositions were prepared by the previously described method [18].

To study the process of structuring compositions, prepared the specimens of compositions in the form of films in molds of polytetrafluoroethylene with 55 mm in diameter. Samples were hardening at 150–160°C for 25–30 min. The content of gel fraction was found by the extraction method of preliminarily crushed films with ethanol in a Soxhlet device.

The adhesion strength of metal-glass glued joints at uniform shearing was performed on a TiraTest 2200 tensile-testing machine (Germany) with an extension rate of 50 mm/min. Samples were hardening at 150–160°C for 25–30 min.

Internal mechanical stresses in adhesive joints were determined by the cantilever method, which is based on measuring the bending height of the cantilever plate with the polymer composition applied to it concerning the base plate. Due to internal stresses in the film, the substrate bends, and the free end of the console deviates from its initial state.

Internal mechanical stresses σ (MPa) were calculated using the formula [19]:

$$\sigma = \frac{E \cdot t^3 \cdot h}{30 \cdot l^2 \cdot \Delta\delta \cdot (\delta + \Delta\delta)} \quad (1)$$

where: $E$ – modulus of elasticity of the substrate plate, MPa;
$\delta$ – the thickness of the substrate plate, m;
$h$ – deviation of the console from the initial position, m;
$l$ – the length of the plate with a polymer composition, m;
$\Delta\delta$ – the thickness of the polymer film, m.

Thermal stability of composites was determined by the Vicat method according to the ASTM D1525 [20]. Samples were made in Teflon molds and hardened at 85–90°C for 2 hours.

Five samples of each composition were prepared to test the characteristics mentioned above of the modified PFR. Conducted at least three parallel measurements and determined the marginal deviations of the results.

To plot the isolines of the main technical characteristics of the modified PFR and promptly select the optimal composition of adhesives and enamels based on them, mathematical planning of the experiment was carried out using the Scheffe complex lattice plan method [17].

## RESULTS AND DISCUSSION

The developed composite materials based on PFR can be used as heat-resistant adhesive materials and enamels for various purposes, as well as a binder for obtaining press powders. Therefore, one of the main properties of such materials is adhesive strength and thermal stability, which significantly depend on the degree of hardening of the compositions (gel fraction content). The results of studies of these three properties of composites depending on the ratio of components are presented in Table 1.

Composite samples were tested for adhesive strength of metal-glass glue joints under uniform shear. An increase in the amount of ER and the hardening catalyst in the compositions increases the adhesive strength of the glue joint as a result of the complete hardening of the compositions (Table 1).

The increase in the adhesion of the adhesive joint based on the modified PFR can be explained, according to the molecular (adsorption) theory of polymer adhesion [21], by the presence of highly polar NCO groups in the PVP molecule [22], which can form hydrogen bonds with the metal. Epoxy and hydroxyl groups of the modified oligomer and the appearance of new polar groups during the hardening of the compositions also contribute to the formation of additional chemisorption bonds with the surfaces to be glued, as a result of which the adhesion of glue joints increases. The strength of the adhesive seam also increases due to the formation of a dense combined network (interpolymer complex) during the interaction of PFR with ER and PVP in the presence of DMA, as well as PFR with PVP [18].

However, the effect of the amount of PVP on adhesion is limited – adhesion increases noticeably when the PVP content increases to 1.0 wt% and then decreases. Therefore, the optimal PVP content in the composition is 0.5–1.0 wt%.

It is known [23] that internal stresses significantly affect glue joints' adhesive strength. In the formation or operation of glue joints, significant internal stresses cause their spontaneous destruction. Glue joints based on PFR modified with ER are characterized by an adhesive protection mechanism [24]. Therefore, determining these connections' adhesive strength and internal stresses is extremely important when evaluating their protective capacity.

In this regard, the effect of PVP content in modified compositions on internal stresses in adhesive joints was studied (Fig. 1). The values of the internal stresses agree well with the results of the adhesive strength measurement. PVP-containing compositions have significantly lower internal stresses. Compositions with PVP content of 0.5–1 wt% have the lowest internal stresses.

The thermal stability of the modified compositions (Table 1) also increases with increasing EC and DMA content. The effect of PVP on thermal stability is extreme, with a maximum at PVP content of 1 wt%. An increase in the PVP content in the composition above one wt% leads to a decrease in thermal stability. This is explained by the fact that the addition of PVP in small quantities is accompanied by the formation of chemical cross-linking nodes in the resin hardening process. With a further increase in the PVP content, the orderliness in the packing of the chains is destroyed, and a more defective structure with physical bonds is formed.

To facilitate the search for compositions of glue materials and coatings with predetermined properties, mathematical planning using the method of Scheffe's simplex lattice plans was carried out.

Influence the ratio of the components of the polymer mixture (PFR, ER, PVP) to the properties of the compositions were studied. The ratio of other components of the system was assumed to be constant. In particular, the content of the hardening catalyst DMA was one wt%.

When studying the properties of a mixture that depends only on three components, the factor space is a regular two-dimensional simplex – an equilateral triangle (Fig. 2). For the system, the ratio is:

$$X_1 + X_2 + X_3 = 1 \qquad (2)$$

where: $X_i \geq 0$ – the concentration of the $i$-th component in the mixture, wt%;
$X_1$ – PFR content, wt%;
$X_2$ – ER content, wt%;
$X_3$ – PVP content, wt%.

The triangle's vertices correspond to pure substances, the sides to dual systems. The optimization was carried out for the most important properties of the compositions – shear adhesive strength (MPa), Vicat thermal stability (°C), and gel fraction content (%). Not the entire concentration triangle was studied, but only its local part, which is a simplex with vertices $A_1$(100 wt% PFR); $A_2$(50 wt% PFR; 50 wt% ER); $A_3$(95 wt% PFR; 5 wt% PVP) (Fig. 2).

The upper limit of PVP content is 5 wt% caused by technological complications – with a higher content of PVP, the duration of preparation

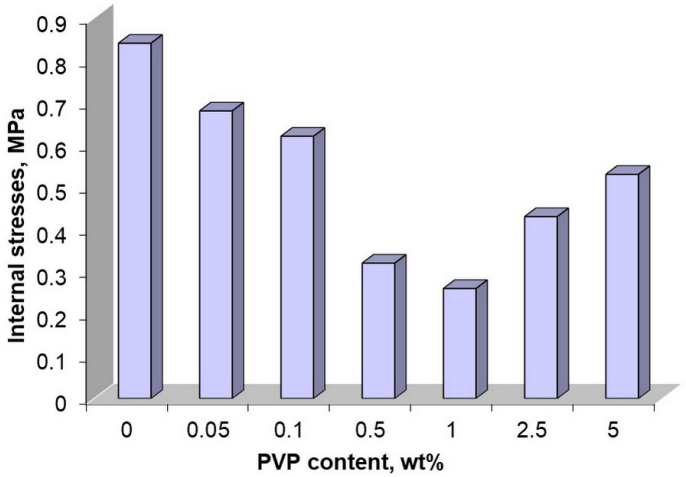


**Fig. 1**. Dependence of internal stresses in PFR-based glue joints on PVP content. Hardening conditions – 150–160°C for 25–30 min

**Table 1**. Technological and operational characteristics of the composites based on PFR*

| Composition, wt%. | | | | Adhesion shearing strength, MPa | Gel-fraction content, % | Vicat thermal stability, °C |
|---|---|---|---|---|---|---|
| PFR | ER | PVP | DMA | | | |
| 74.25 | 25 | 0.5 | 0.25 | 1.9±0.2 | 74.28 | 80±2 |
| 74 | 25 | 0.5 | 0.5 | 3.8±0.3 | 83.38 | 88±2 |
| 73.5 | 25 | 0.5 | 1.0 | 5.7±0.3 | 99.4 | 120±2 |
| 72 | 25 | 0.5 | 2.5 | 6.6±0.3 | 99.8 | 130±2 |
| 74 | 25 | 0 | 1 | 4.8±0.3 | 98.4 | 115±2 |
| 73.5 | 25 | 0.5 | 1 | 5.7±0.3 | 99.4 | 120±2 |
| 73 | 25 | 1.0 | 1 | 6.4±0.3 | 99.6 | 125±2 |
| 71.5 | 25 | 2.5 | 1 | 4.8±0.3 | 98.5 | 110±2 |
| 69 | 25 | 5.0 | 1 | 3.1±0.3 | 95.2 | 100±2 |
| 97.5 | 1 | 0.5 | 1 | 0.9±0.2 | 2.05 | 86±2 |
| 93.5 | 5 | 0.5 | 1 | 1.6±0.2 | 17.73 | 82±2 |
| 88.5 | 10 | 0.5 | 1 | 2.8±0.2 | 69.93 | 100±2 |
| 73.5 | 25 | 0.5 | 1 | 5.7±0.3 | 99.4 | 120±2 |
| 48.5 | 50 | 0.5 | 1 | 7.5±0.3 | 99.9 | 130±2 |

**Note:** *Adhesion strength and gel-fraction content – samples were hardening at 150-160 °C for 25-30 min; Vicat thermal stability – samples were hardening at 85–90°C for 2 hour

and the cost of the composition increase significantly, and its viscosity increases.

The ER content is more than 50 wt% increases the composition cost without improving its properties.

To use in this case, the plans used for the study of complete diagrams renumbered and accepted the compositions at the vertices of $A_i(X_1^{(i)}, X_2^{(i)}, X_3^{(i)})$, where $i$ = 1, 2, 3, by independent pseudo-components of $Z_i$. At the same time, the condition must be fulfilled:

$$Z_1 + Z_2 + Z_3 = 1 \quad (3)$$

The planning of the experiment was carried out in the coordinate system of pseudo-components relative to the new variables $Z_1$, $Z_2$, $Z_3$.

The value of $Z_k^{(i)}$ ($k$, $i$ = 1, 2, 3) was found by solving two systems of equations:

$$\begin{aligned}
&X_1^{(1)} \cdot Z_1^{(1)} + X_2^{(1)} \cdot Z_1^{(2)} + X_3^{(1)} \cdot Z_1^{(3)} = 1;\\
&X_1^{(2)} \cdot Z_1^{(1)} + X_2^{(2)} \cdot Z_1^{(2)} + X_3^{(2)} \cdot Z_1^{(3)} = 0;\\
&X_1^{(3)} \cdot Z_1^{(1)} + X_2^{(3)} \cdot Z_1^{(2)} + X_3^{(3)} \cdot Z_1^{(3)} = 0;\\
&X_1^{(1)} \cdot Z_2^{(1)} + X_2^{(1)} \cdot Z_2^{(2)} + X_3^{(1)} \cdot Z_2^{(3)} = 0;\\
&X_1^{(2)} \cdot Z_2^{(1)} + X_2^{(2)} \cdot Z_2^{(2)} + X_3^{(2)} \cdot Z_2^{(3)} = 1;\\
&X_1^{(3)} \cdot Z_2^{(1)} + X_2^{(3)} \cdot Z_2^{(2)} + X_3^{(3)} \cdot Z_2^{(3)} = 0,
\end{aligned} \quad (4)$$

where: $Z_k^{(i)}$ – the content of the pseudo-component $Z_k$ in the vertices of the original simplex;

$X_k^{(i)}$ – the content of the $k$-th component in the vertices of $Z_i(A_i)$:

$$\begin{aligned}
&X_1^{(1)} = 1; \quad X_2^{(1)} = 0; \quad X_3^{(1)} = 0;\\
&X_1^{(2)} = 0.5; \quad X_2^{(2)} = 0.5; \quad X_3^{(2)} = 0;\\
&X_1^{(3)} = 0.95; \quad X_2^{(3)} = 0; \quad X_3^{(3)} = 0.05.
\end{aligned}$$

The following values were obtained:

$$\begin{aligned}
&Z_1^{(1)} = 1; \quad Z_2^{(1)} = 0;\\
&Z_1^{(2)} = -1; \quad Z_2^{(2)} = 2;\\
&Z_1^{(3)} = -19; \quad Z_2^{(3)} = 0.
\end{aligned}$$

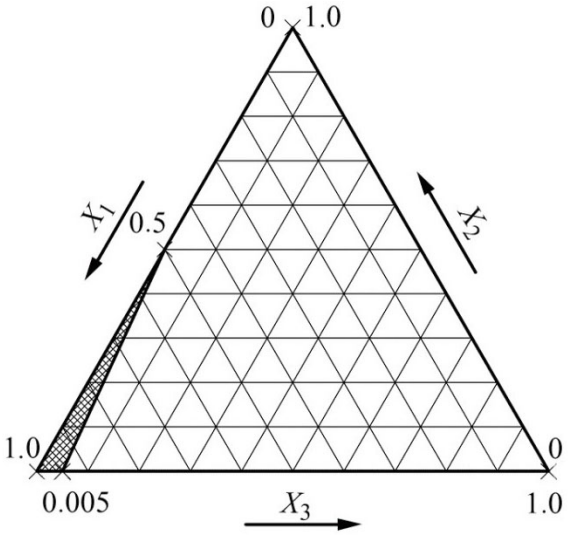


**Fig. 2**. The field of PFR-compositions properties research

We also received formulas for transferring coordinates from one system to another:

$$\begin{aligned} Z_1 &= Z_1^{(1)} + X_2 \cdot \left(Z_1^{(2)} - Z_1^{(1)}\right) + X_3 \cdot \left(Z_1^{(3)} - Z_1^{(1)}\right); \\ Z_2 &= Z_2^{(1)} + X_2 \cdot \left(Z_2^{(2)} - Z_2^{(1)}\right) + X_3 \cdot \left(Z_2^{(3)} - Z_2^{(1)}\right); \\ Z_3 &= 1 - (Z_1 + Z_2). \end{aligned} \quad (5)$$

Next, formulas (6) for the transition from pseudo-components to real concentrations were determined. For this, the obtained values of $Z_k^{(i)}$ were substituted into relation (5).

$$\begin{aligned} Z_1 &= 1 - 2X_2 - 20X_3; \\ Z_2 &= 2X_2; \\ Z_3 &= 20X_3. \end{aligned} \quad (6)$$

To obtain the regression equations, a Scheffe's simplex lattice plan was drawn up concerning the pseudo-components $Z_1$, $Z_2$, $Z_3$. We used the reduced polynomial of the second order for the ternary system:

$$\begin{aligned} y' = \beta_1 Z_1 + \beta_2 Z_2 + \beta_3 Z_3 + \\ + \beta_{12} Z_1 Z_2 + \beta_{13} Z_1 Z_{32} + \beta_{23} Z_2 Z_3 \end{aligned} \quad (7)$$

The minimum number of experimental points for determining the coefficients of this polynomial is 6 ($C_{3+2-1}^2 = C_4^2 = 6$).

Three levels of each factor (0; 1/2; 1) influencing the experiment were used to create the planning matrix. After registering the coordinates of the simplex grid points, we will obtain a planning matrix (Table 2).

The coordinates of all six points (Table 2) of the planning matrix were successively substituted into equation 7 to obtain the coefficients of the polynomial:

$$\begin{aligned} &y_1 = \beta_1;\ y_2 = \beta_2;\ y_3 = \beta_3; \\ &\beta_{13} = 4y_{13} - 2(y_1 + y_3); \\ &\beta_{12} = 4y_{12} - 2(y_1 + y_2); \\ &\beta_{23} = 4y_{23} - 2(y_2 + y_3). \end{aligned} \quad (8)$$

**Table 2**. Experiment planning matrix

| Experiment number | $Z_1$ | $Z_2$ | $Z_3$ | $y_{exp}$ |
|---|---|---|---|---|
| 1 | 1 | 0 | 0 | $y_1$ |
| 2 | 0 | 1 | 0 | $y_2$ |
| 3 | 0 | 0 | 1 | $y_3$ |
| 4 | 1/2 | 1/2 | 0 | $y_{12}$ |
| 5 | 1/2 | 0 | 1/2 | $y_{23}$ |
| 6 | 0 | 1/2 | 1/2 | $y_{13}$ |

In our case, $y'_1$ (MPa) is the regression equation of adhesive strength of the composition, $y'_2$ (°C) is the regression equation of Vicat thermal stability, and $y'_3$ (%) is the regression equation of the gel fraction content.

Table 3 presents the conditions and results of experiments in pseudo-components and on a natural scale. The average results of adhesive strength, thermal stability, and gel fraction content were obtained from 3 parallel experiments. Experiments 7, 8, and 9 were used as control points.

Next, the coefficients of the regression equations were calculated according to formulas (8), and the regression equations in pseudo-components were obtained:

for $y'_1$:

$$\begin{aligned} &\beta_1 = 0.69;\ \beta_2 = 7.53;\ \beta_3 = 0.78; \\ &\beta_{12} = 3.08;\ \beta_{13} = 0.78;\ \beta_{23} = 2.74, \\ &y'_1 = 0.69Z_1 + 7.53Z_2 + 0.78Z_3 + \\ &+ 3.08Z_1Z_2 + 0.78Z_1Z_3 + 2.74Z_2Z_3; \end{aligned} \quad (9)$$

for $y'_2$:

$$\begin{aligned} &b_1 = 75;\ b_2 = 130;\ b_3 = 80; \\ &b_{12} = 50;\ b_{13} = 30;\ b_{23} = 20, \\ &y'_2 = 75Z_1 + 130Z_2 + 80Z_3 + \\ &+ 50Z_1Z_2 + 30Z_1Z_3 + 20Z_2Z_3; \end{aligned} \quad (10)$$

for $y'_3$:

$$\begin{aligned} &b_1 = 1.65;\ b_2 = 99.9;\ b_3 = 1.80; \\ &b_{12} = 190.5;\ b_{13} = 1.3;\ b_{23} = 190.6, \\ &y'_3 = 1.65Z_1 + 99.9Z_2 + 1.80Z_3 + \\ &+ 1.80Z_3 + 190.5Z_1Z_2 + 1.3Z_1Z_3 + 190.6Z_2Z_3. \end{aligned} \quad (11)$$

To obtain the regression equation in the initial variables, dependencies (6) were used:

$$\begin{aligned} y_1 = 0.69 + 19.84X_2 + 17.4X_3 - \\ - 44.8X_2X_3 - 12.32X_2^2 - 312X_3^2; \end{aligned} \quad (12)$$

$$\begin{aligned} y_2 = 75 + 210X_2 + 700X_3 - \\ - 2400X_2X_3 - 200X_2^2 - 12000X_3^2; \end{aligned} \quad (13)$$

$$\begin{aligned} y_3 = 1.65 + 577.5X_2 + 29X_3 - \\ - 48X_2X_3 - 762X_2^2 - 520X_3^2. \end{aligned} \quad (14)$$

**Table 3**. Conditions and results of experiments

| No | Pseudo-components | | | Real variables | | | $y'_{1\,exp}$ | $y'_{2\,exp}$ | $y'_{3\,exp}$ |
|---|---|---|---|---|---|---|---|---|---|
| | $Z_1$ | $Z_2$ | $Z_3$ | $X_1$ | $X_2$ | $X_3$ | | | |
| 1 | 1 | 0 | 0 | 1 | 0 | 0 | 0.69 | 75 | 1.65 |
| 2 | 0 | 1 | 0 | 0.5 | 0.5 | 0 | 7.53 | 130 | 99.9 |
| 3 | 0 | 0 | 1 | 0.95 | 0 | 0,05 | 0.78 | 80 | 1.80 |
| 4 | 1/2 | 1/2 | 0 | 0.75 | 0.25 | 0 | 4.88 | 115 | 98.4 |
| 5 | 1/2 | 0 | 1/2 | 0.975 | 0 | 0,025 | 0.93 | 85 | 2.05 |
| 6 | 0 | 1/2 | 1/2 | 0.725 | 0.25 | 0,025 | 4.84 | 110 | 98.5 |
| 7 | 2/3 | 0 | 1/3 | 0.983 | 0 | 0,017 | 0.97 | 83 | 2.28 |
| 8 | 2/3 | 1/3 | 0 | 0.833 | 0.167 | 0 | 3.18 | 105 | 78.2 |
| 9 | 0 | 2/3 | 1/3 | 0.8 | 0.167 | 0.033 | 2.95 | 100 | 75.6 |

Three points were used to check the adequacy of the obtained equations (Table 3, experiments 7–9). The *t*-ratio was found for each control point:

$$t = \frac{\Delta y\sqrt{n}}{s_y^2\sqrt{1+\xi}} \tag{15}$$

where: $\Delta y = \left|\overline{y}_{exp} - y_{calc}\right|$;
$n$ – the number of testings at each point ($n$ = 3);
$s_y^2$ – variance of reproducibility.

$$\xi = \sum_{i=1}^{3} a_i^2 + \sum_{1\langle=i\langle=3} a_{ij}^2 \tag{16}$$

$$a_i = x_i(2x_i - 1); \qquad a_{ij} = 4x_i x_j. \tag{17}$$

$$S_y^2 = \frac{\sum_{u=1}^{m}(y_u - \overline{y})}{m-1} \tag{18}$$

$$\overline{y} = \frac{\sum_{u=1}^{m} y_u}{m} \tag{19}$$

where: $m$ – the number of testings at each point ($m$ = 3).

The obtained results are presented in Table 4. At the level of significance $p = 1 - \beta = 1 - 0.95 = 0.05$ (where $\beta$ is the confidence probability, $\beta = 0.95$) and the number of degrees of fluency $f = 6$: $t_{table} = 2.45$, i.e., $t_{calc.} < t_{table}$. Therefore, all regression equations are adequate for the experiment.

The obtained regression equations make it possible to determine such properties of the composition as shear adhesive strength, Vicat thermal stability, and yield of the gel fraction for any composition of the initial mixture. MathCad Prime

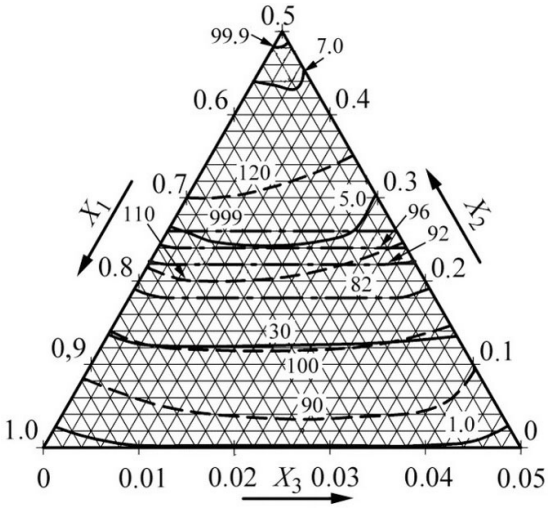


**Fig. 3**. Lines with equal composite materials property values. Solid line – adhesion strength in shear, MPa; dashed line – Vicat thermal stability, °C; dash-dotted line – content of the gel-fraction, %

**Table 4**. Checking the model for adequacy

| No | $y_{exp}^{(1)}$ | $y_1$ | $\Delta y_1$ | $s_{y^{(1)}}$ | $y_{exp}^{(2)}$ | $y_2$ | $\Delta y_2$ | $s_{y^{(2)}}$ | $y_{exp}^{(3)}$ | $y_3$ | $\Delta y_3$ | $s_{y^{(3)}}$ | $\xi$ | $t^{(1)}$ | $t^{(2)}$ | $t^{(3)}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 7 | 0.97 | 0.90 | 0.07 | 0.12 | 83 | 83.43 | 0.43 | 1.08 | 2.28 | 1.99 | 0.29 | 0.64 | 0.83 | 0.64 | 1.02 | 0.35 |
| 8 | 3.18 | 3.66 | 0.48 | 1.18 | 105 | 104.49 | 0.51 | 1.16 | 78.2 | 76.84 | 1.36 | 1.48 | 0.83 | 0.95 | 1.48 | 0.81 |
| 9 | 2.95 | 3.64 | 0.69 | 1.22 | 100 | 101.30 | 1.30 | 1.40 | 75.6 | 76.97 | 1.37 | 1.49 | 0.83 | 1.22 | 1.33 | 0.98 |

6.0 PC program was used to calculate the properties mentioned above at various concentrations of components. Based on the calculations, lines of equal values of the properties of the modified PFR were plotted (Fig. 3). This will significantly reduce the experimental search for the ratio of components to obtain adhesive materials and enamels with predetermined properties.

## CONCLUSIONS

By mathematical planning, the isolines of the characteristics of composite materials based on modified PFR depending on their component's compositions are plotted, and the regression coefficients are found, enabling one to get materials with predicted properties.

The effect of the ratio of the components of the modified phenol-formaldehyde composition on the adhesive strength, Vicat thermal stability, and the yield of the gel fraction of the hardened materials was studied. The adhesive strength of the joints increases with an increase in ER content up to 50 wt% and PVP content – up to 1 wt%. According to the PVP content in the modified PFR from 0.5 to 1.0 wt%, glue joints based on it have the lowest internal stresses.

The developed material's thermal stability depends mainly on its hardening degree. Therefore, with an increase in the content of DMA, it increases.

From a technical and economic point of view, the following content of additives in modified PFR is most optimal: ER from 25 to 50 wt%, PVP from 0.5 to 1.0 wt%, DMA from 1 to 2.5 wt%. The conditions of hardening of glue joints or coatings based on such materials can be varied in a wide range by adjusting the content of the hardening catalyst, as well as the temperature and duration of the process.

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