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EFFECT OF POLYVINYL BUTYRAL AND METAL OXYCHLORIDES ON THERMOPHYSICAL PROPERTIES OF PHENOLIC RESINS

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The effect of polyvinyl butyral, magnesium-zinc oxychloride, and viscose fibers on the thermophysical properties of phenol-formaldehyde composites is investigated.

Thermosetting plastics modified by linear polymers dispersed at the molecular level form, upon solidification, a spatial net structure of the semi-interpenetrating type (SIN) [1]. Materials with an SIN structure of the polymer matrix are more elastic and more resistant to friction-contact fatigue than are individual thermosetting plastics. An increase in the thermal conductivity and a decrease in the thermal wear of these materials can be achieved by additional modification of the polymer matrix by structure-forming mineral substances, e.g., magnesium-zinc oxychloride (MZO). However, the mutual effect of linear polymers dispersed at the molecular level and mineral structure-forming substances on the thermophysical properties of phenolic resins has not been studied so far.

In the present work we investigate the effect of polyvinyl butyral (GOST 9439-73), magnesium-zinc oxychloride, and hexamethylenetetramine (TU 6-09-36-70) on the thermophysical properties of phenol-formaldehyde polymers. The magnesium-zinc oxychloride was produced by reacting magnesium chloride (GOST 4340-76) with zinc oxide (GOST 10262-74). Waste viscose fibers (TU 6-06-442-79) were used as a filler. Samples were produced by compression pressing at a temperature of 160-170°C under a pressure of 40 MPa for 1 min per 1 mm of item thickness. The characteristics of the phenol-formaldehyde composites necessary for calculation of their heat capacity and thermal conductivity were estimated on an IP-400 device in the temperature range of 25–225°C.

Inasmuch as the choice of an optimum component composition in the binder for producing composites with a high thermal conductivity is not straightforward, we studied by the method of mathematical experiment design [2] the effect of the concentration of the ingredients on the thermophysical properties of the material. The thermal conductivity coefficient λ and specific heat capacity C_p of the phenol-formaldehyde composite were chosen as optimization parameters, and the contents of polyvinyl butyral (X_1), magnesium-zinc oxychloride (X_2), and hexamethylenetetramine (X_3) were chosen as factors. The composition corresponding to the basic level of variation of independent variables contained $C_1 = 6 \pm 2$ wt.pt. polyvinyl butyral, $C_2 = 10 \pm 4$ wt.pt. magnesium-zinc oxychloride, and $C_3 = 10 \pm 4$ wt.pt. hexamethylenetetramine.

As a result of realization of the experiment plan and statistical processing of the experimental data on an ASVTM 40-30 computer, equations reflecting the effect of component concentration on the thermophysical properties of phenyl-formaldehyde composites at different test temperatures were obtained.

1. Thermal conductivity coefficient of composites:

1.1. $T_t = 25°C$,

$$\lambda_1 \cdot 10^4 = 1162 + 6.06X_1 - 11.96X_2 - 29.7X_3 +$$

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$$+ 4X_1X_2 + 13.17X_1X_3 + 29.33X_2X_3 - 21.63X_1^2 - 25.16X_2^2 + 33.23X_3^2; \quad (1)$$

1.2. $T_t = 50°C$,

$$\lambda_2 \cdot 10^4 = 1956 - 11.59X_1 - 63X_2 - 54.12X_3 -$$

$$- 16.62X_1X_2 - 62.04X_1X_3 + 78.62X_2X_3 - 17.59X_1^2 - 50.59X_2^2 + 42.57X_3^2; \quad (2)$$

1.3. $T_t = 75°C$,

$$\lambda_3 \cdot 10^4 = 1672 + 40.64X_1 - 27.7X_2 - 107.9X_3 +$$

$$+ 12.75X_1X_2 - 25.58X_1X_3 + 43.08X_2X_3 + 36.17X_1^2 + 16.72X_2^2 + 87.67X_3^2; \quad (3)$$

1.4. $T_t = 100°C$,

$$\lambda_4 \cdot 10^4 = 3636 - 60.69X_1 + 35.04X_2 - 126.6X_3 +$$

$$+ 10.04X_1X_2 - 16.29X_1X_3 + 60.12X_2X_3 - 27.34X_1^2 - 170.2X_2^2 + 23.63X_3^2; \quad (4)$$

1.5. $T_t = 125°C$,

$$\lambda_5 \cdot 10^4 = 4290 - 212.4X_1 - 25.63X_2 - 22.66X_3 -$$

$$- 137.2X_1X_2 + 52.46X_1X_3 - 11.62X_2X_3 - 79.81X_1^2 + 45.58X_2^2 - 23.95X_3^2; \quad (5)$$

1.6. $T_t = 150°C$,

$$\lambda_6 \cdot 10^4 = 4510 - 31.24X_1 - 140.7X_2 + 45.7X_3 -$$

$$- 4.542X_1X_2 - 139.8X_1X_3 + 147X_2X_3 - 119.4X_1^2 + 163.2X_2^2 - 77.35X_3^2; \quad (6)$$

1.7. $T_t = 175°C$,

$$\lambda_7 \cdot 10^4 = 4592 - 63.76X_1 - 96.66X_2 - 14.59X_3 +$$

$$+ 77.58X_1X_2 - 152.4X_1X_3 + 223.3X_2X_3 - 166.3X_1^2 + 165.1X_2^2 - 65.4X_3^2; \quad (7)$$

1.8. $T_t = 200°C$,

$$\lambda_8 \cdot 10^4 = 4902 - 22.04X_1 - 55.13X_2 + 8.034X_3 +$$

$$+ 69.71X_1X_2 - 225.5X_1X_3 + 177.7X_2X_3 - 178.1X_1^2 + 107.8X_2^2 - 121.5X_3^2; \quad (8)$$

1.9. $T_t = 225°C$,

$$\lambda_9 \cdot 10^4 = 5297 + 73.74X_1 - 2.32X_2 - 52.02X_3 +$$

$$+ 45.67X_1X_2 - 278.1X_1X_3 + 193.6X_2X_3 - 188.1X_1^2 + 40.35X_2^2 - 229.4X_3^2. \quad (9)$$

2. Specific heat capacity of composites:

2.1. $T_t = 25^oC$,

$$C_{1p} = 818.7 + 36.12X_1 + 62.81X_2 + 40.67X_3 +$$

$$+ 90.12X_1X_2 + 33.04X_1X_3 + 7.625\,X_2X_3 + 63.38X_1^2 + 56.01X_2^2 - 4.741X_3^2; \tag{10}$$

2.2 $T_t = 50^oC$,

$$C_{2p} = 1420 + 33.63X_1 - 36.78X_2 - 9.368X_3 -$$

$$- 1.625X_1X_2 - 16.87X_1X_3 - 16.54X_2X_3 + 41.9X_1^2 + 14.32X_2^2 - 10.54X_3^2; \tag{11}$$

2.3. $T_t = 75^oC$,

$$C_{3p} = 1683 + 23.12X_1 - 5.459X_2 - 0.045X_3 +$$

$$+ 38.37X_1X_2 - 3.208X_1X_3 + 4.458X_2X_3 - 2.337X_1^2 + 10.27X_2^2 - 4.576X_3^2; \tag{12}$$

2.4. $T_t = 100^oC$,

$$C_{4p} = 1767 + 40.57X_1 - 20.75X_2 + 24.35X_3 +$$

$$+ 34.29X_1X_2 - 3.792X_1X_3 + 19.37X_2X_3 + 30.32X_1^2 + 50.83X_2^2 + 9.695X_3^2; \tag{13}$$

2.5. $T_t = 125^oC$,

$$C_{5p} = 1891 + 77.24X_1 - 58.45X_2 + 18.05X_3 -$$

$$- 3.083X_1X_2 - 0.167X_1X_3 - 9.5X_2X_3 + 79.24X_1^2 + 38.7X_2^2 - 11.8X_3^2; \tag{14}$$

2.6. $T_t = 150^oC$,

$$C_{6p} = 2058 + 79.18X_1 - 28.48X_2 + 29.24X_3 +$$

$$+ 20.62X_1X_2 + 16.71X_1X_3 + 40.79X_2X_3 + 104.3X_1^2 + 28.93X_2^2 - 0.884X_3^2; \tag{15}$$

2.7. $T_t = 175^oC$,

$$C_{7p} = 2263 + 82.36X_1 + 36.33X_2 + 103.7X_3 +$$

$$+ 69.79X_1X_2 - 22.96X_1X_3 + 44.46\,X_2X_3 + 65.64X_1^2 - 30.88X_2^2 - 49.2X_3^2; \tag{16}$$

2.8. $T_t = 200^oC$,

$$C_{8p} = 2203 + 156.5X_1 + 85.18X_2 + 165.7X_3 -$$

$$- 39.42X_1X_2 + 39.42X_1X_3 + 17.83X_2X_3 + 139.8X_1^2 - 30.78X_2^2 - 90.23X_3^2; \tag{17}$$

2.9. $T_t = 225^oC$,

$$C_{9p} = 1979 + 174.3X_1 + 152.7X_2 + 204.4X_3 -$$

$$- 10.08X_1X_2 - 102.4X_1X_3 + 78.67X_2X_3 + 78.62X_1^2 + 77.38X_2^2 + 20.46X_3^2. \tag{18}$$

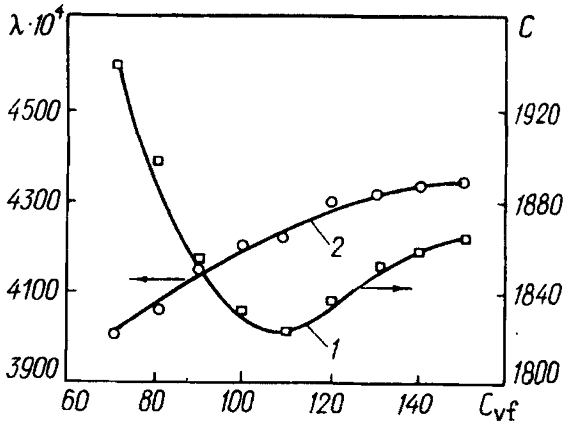

Fig. 1. Dependences of the specific heat capacity (1) and thermal conductivity coefficient (2) of phenol-formaldehyde polymer containing 4.34 wt.pt. polyvinyl butyral, 9.608 wt.pt. magnesium-zinc oxychloride, and 6 wt.pt. hexamethylenetetramine on the concentration of viscose fiber ($T_t = 100°C$; λ, W/m·K; C, J/kg·K; C_{vf}, wt.pt.).

The Fisher criterion ($F_{theor} = 5.05$) was used to verify the adequacy of the equations obtained [2]. Experimental values of the Fisher criterion and the confidence intervals of the coefficients of the regression equations are, respectively (numbers 1 to 18 correspond to numbering of equations):

1) $F_{exper} = 4.22$; $\Delta b_i = 3.7812$; $\Delta b_{ii} = 3.6809$; $\Delta b_{ij} = 4.9403$;
2) $F_{exper} = 0.96$; $\Delta b_i = 3.6921$; $\Delta b_{ii} = 3.5942$; $\Delta b_{ij} = 4.824$;
3) $F_{exper} = 7.12$; $\Delta b_i = 3.5444$; $\Delta b_{ii} = 3.4503$; $\Delta b_{ij} = 4.6309$;
4) $F_{exper} = 2.49$; $\Delta b_i = 3.4762$; $\Delta b_{ii} = 3.384$; $\Delta b_{ij} = 4.5419$;
5) $F_{exper} = 1.21$; $\Delta b_i = 3.5612$; $\Delta b_{ii} = 3.4667$; $\Delta b_{ij} = 4.6529$;
6) $F_{exper} = 0.71$; $\Delta b_i = 4.5231$; $\Delta b_{ii} = 4.4032$; $\Delta b_{ij} = 5.9098$;
7) $F_{exper} = 1.75$; $\Delta b_i = 3.7093$; $\Delta b_{ii} = 3.6109$; $\Delta b_{ij} = 4.8464$;
8) $F_{exper} = 1.84$; $\Delta b_i = 10.1613$; $\Delta b_{ii} = 9.8917$; $\Delta b_{ij} = 13.2763$;
9) $F_{exper} = 1.02$; $\Delta b_i = 29.6037$; $\Delta b_{ii} = 28.8184$; $\Delta b_{ij} = 38.6791$;
10) $F_{exper} = 5.17$; $\Delta b_i = 3.7424$; $\Delta b_{ii} = 3.6431$; $\Delta b_{ij} = 4.8897$;
11) $F_{exper} = 0.32$; $\Delta b_i = 4.2337$; $\Delta b_{ii} = 4.1214$; $\Delta b_{ij} = 5.5315$;
12) $F_{exper} = 0.28$; $\Delta b_i = 3.6174$; $\Delta b_{ii} = 3.5215$; $\Delta b_{ij} = 4.7264$;
13) $F_{exper} = 0.36$; $\Delta b_i = 3.6381$; $\Delta b_{ii} = 3.5415$; $\Delta b_{ij} = 4.7533$;
14) $F_{exper} = 1.72$; $\Delta b_i = 3.4405$; $\Delta b_{ii} = 3.3492$; $\Delta b_{ij} = 4.4952$;
15) $F_{exper} = 1.13$; $\Delta b_i = 3.2597$; $\Delta b_{ii} = 3.1732$; $\Delta b_{ij} = 4.2590$;
16) $F_{exper} = 1.21$; $\Delta b_i = 3.5444$; $\Delta b_{ii} = 3.4503$; $\Delta b_{ij} = 4.6309$;
17) $F_{exper} = 4.26$; $\Delta b_i = 3.6143$; $\Delta b_{ii} = 3.5185$; $\Delta b_{ij} = 4.7224$;
18) $F_{exper} = 3.45$; $\Delta b_i = 3.4340$; $\Delta b_{ii} = 3.3429$; $\Delta b_{ij} = 4.4867$.

It is evident from a comparison of the experimental and tabulated values of the Fisher criterion that Eqs. (1), (2), (4-9), and (11)-(18) are adequate and Eqs. (3) and (10) are nearly adequate models of the thermophysical properties of the composite material.

Inasmuch as polyvinyl butyral-modified phenol-formaldehyde polymers at temperatures higher than 125°C have low strength, which reduces their load-carrying capacity, the optimum content of modifiers in the composition was determined from the coordinates of the maximum of function (4), describing the thermal conductivity of the material at a test temperature of 100°C. It was found by analysis of Eq. (4) that the phenol-formaldehyde composite possesses the maximum calculated value of the thermal conductivity coefficient $\lambda = 0.3806$ W/m·K.

Since the composite material with the optimum composition is not wear-resistant and has a low impact strength, in order to improve its resistance to stresses, the polymer matrix was reinforced with chopped viscose fiber. Figure 1 presents data on the effect of the concetration of viscose fiber on the thermophysical properties of the phenol-formaldehyde composite. It is evident that the curve of the thermal conductivity coefficient grows continuously with an increasing content of viscose fiber. This can be explained by the transition of the binder into the boundary-layer state on the surface of the fiber filler and by the higher thermal conductivity of viscose fibers compared to the phenol-formaldehyde polymer [3, 4]. In contrast to the thermal conductivity coefficient, the curve of the specific heat capacity of the phenol-formaldehyde composite has a minimum at a content of 110 wt.pt. of viscose fiber in the binder.

Thus, modification of the phenol-formaldehyde polymer by polyvinyl butyral, magnesium-zinc oxychloride, and viscose fiber makes it possible to improve the thermophysical characteristics of composite materials and recommend their use in friction units of machines and mechanisms.

REFERENCES

1. Yu. S. Lipatov and L. I. Sergeeva, Interpenetrating Polymer Nets [in Russian], Kiev (1979).
2. V. V. Tikhomirov, Mathematical Methods of Experiment Design in Investigations of Nonwoven Materials [in Russian], Moscow (1969).
3. V. V. Kharitonov, Thermophysics of Polymers and Polymer Compositions [in Russian], Minsk (1983).
4. A. F. Nikolaev, M. S. Trizno, Kh. A. Mamin, and E. V. Moskalev, Plasticheskie Massy, No. 11, 40-42 (1975).