

On Technological Properties of Modified Epoxy Composites

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Abstract. The technological properties of epoxy composite materials based on constructional and chemical waste have been reviewed. The viscosity and component wettability of modified epoxy composites have been researched. The use of plasticizing additives to improve mixtures forming has been justified.

One of the primary tasks in selecting the compositions of polymer materials is to improve the plastic-viscous properties of polymer binders by various means of modification [1-5]. This task proves to be even more important for epoxy composites with high degree of filling, since ED-20 epoxy resin is a low-viscosity Newtonian fluid with a dynamic viscosity value equals 12-25 Pa·s at a temperature of 20° C. Dynamic viscosity of the binder with a high degree of filling creates certain difficulties during preparation and forming of mixtures. Thus, an attempt was made to modify epoxy resin with silica-organic KO-922 fluid in the presence of asbestos-containing fibrous nanomodifiers. Such fibrous modifiers used include fine fillers of construction industry waste (FFCI), which are presented as fine-dispersed asbestos fibers in combination with fine-dispersed Portland cement particles; fibrous waste of the chemical industry (FWCI) and natural material of Serpentinite. KO-922 represents itself as a heat-resistant lacquer used for thermal isolation of connector wires in high-temperature environments. The experimental dependencies are represented in Figure 1.

Analysis of the experimental data showed that KO-922 renders plasticizing effect upon polymer composite material. The dependencies are clearly pronounced. The decrease in the dynamic viscosity of the formulations at maximum concentration of the additive ranges from 48 to 61%. The results obtained in Fig. 1 regularities are explained on the basis of the current understanding of polymer structure. Epoxy polymers have a static coil-shaped conformation with a strong intertwining of chains at the molecular level. When a small amount of KO-922 is added to the resin, the frictional forces between congregations and certain molecules of the epoxy oligomer are decreased, which in turn leads to a sharp decrease in dynamic viscosity. With a further increase in concentration of KO-922, aggregates are formed from epoxy oligomers and additives. At the same time, the plasticity of the epoxy resin slows down. Further increase in the concentration of additive content in the binder leads to effective inter-aggregate plasticization, which is accompanied by a further decrease in the dynamic viscosity of the system. It should be noted that, given the equality of the degree of filling for all compositions (in this case ratio is equal to Polymer/Filler = 1/10), the specific surface of the filler has a determining effect on the mobility of the mixture, which is: for FFCI – 4.39 m²/kg, for FWCI – 10.31 m²/kg, for serpentinite – 7.62 m²/kg.



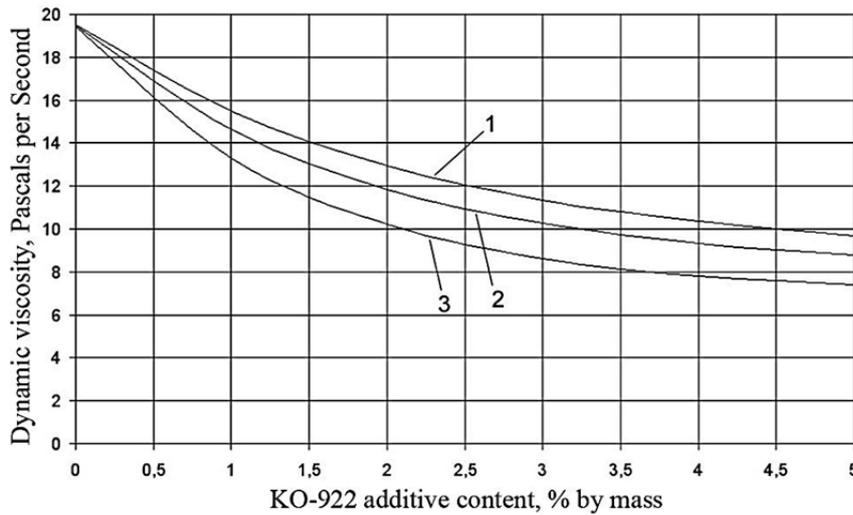


Figure 1. Dynamic viscosity dependency upon additive content: 1–FWCI-based composition; 2–FFCI-based composition; 3–serpentine-based composition.

The optimum concentration of KO-922 [5] provides the formation of additional cross-links in polymer matrix. At the same time, the addition of KO-922 contributes to the physical and mechanical interaction at particle interphase border, which ultimately leads to sped-up curing of the binder and the improvement of the physical and mechanical properties. The plasticizing effect of introduction of KO-922 in maximum concentrations is explained by the fact that they have a destructive effect on large supramolecular formations in epoxy matrix, which in turn leads to formation of smaller clusters by reducing the energy potential on its surface [5]. In addition, the modification of the epoxy resin by KO-922 allows either to reduce the consumption of an expensive polymer binder, or to increase the degree of filling of composites. The latter is a prerequisite for creating materials with increased resistance to chemical corrosion.

A prerequisite for production of a monolithic material with high physical and mechanical properties is a good wettability of filler surface with a polymeric binder.

Mineral materials used as fillers in polymer composite materials have high surface energies and are well-wetted by almost all liquids, including low-viscosity Newtonian ones, to which epoxy resins belong.

The surface of the filler is well wetted by binder if forces of interaction at the interface between the phases prevail over the forces of intermolecular interaction in the polymer matrix [3, 4]. In order to improve the wetting conditions, the introduction into the binding surfactant is carried out or the surface of the filler is treated with special substances.

The measure of substantial wettability by a liquid is the borderline contact angle, which is determined from the equation based on Young's [5]:

$$\cos \Theta = \frac{\sigma_{sg} - \sigma_{sl}}{\sigma_{lg}} \tag{1}$$

where σ_{sg} is surface tension value at «substance – gas» border; σ_{lg} is surface tension value at "liquid – gas" border; σ_{sl} is surface tension value at «substance – liquid» border; Θ – borderline contact angle of wettability.

It follows from formula (1) that if $\sigma_{sg} < \sigma_{sl}$, then $\cos \Theta < 0$ and the liquid does not wet the surface of the substance, i.e. $\Theta > 90^\circ$. If $\sigma_{sg} > \sigma_{sl}$, then the wetting angle is $\Theta < 90^\circ$, then partial wetting occurs. The complete wetting of the solid surface by the liquid will occur at $\Theta = 0$, in this case the borderline contact angle will not be formed.

In addition, wetting will depend on the microrelief of the surface of the body. The borderline contact angle of wettability on a natural solid surface Θ_0 will be determined from the Wenzel-Deryagin relation:

$$\cos \Theta_0 = K_r \cdot \cos \Theta \quad (2)$$

where K_r is the surface roughness coefficient equal to the ratio of the natural surface area to the apparent surface area, almost always above 1.

The decrease in the free surface energy for spreading, as follows from Young's equation, obeys the equation [2]:

$$\Delta\sigma = \sigma_{lg} (\cos \Theta - 1) \quad (3)$$

Considering the equation (2), equation forms as follows:

$$\Delta\sigma = \sigma_{lg} (K_r \cos \Theta - 1) \quad (4)$$

As can be seen from equation (4), as the surface roughness of the wetted surfaces increases (the borderline contact angle Θ of which is slightly less than 90°), it is possible to achieve a equal spreading of the liquid along the surface of the solid body.

For lyophobic surfaces ($\Theta > 90^\circ$) an increase in roughness leads to the reverse effect, since the absolute value of the negative value in expression (4) increases.

The establishment of the equilibrium value of the borderline contact angle is slowed by the phenomenon of hysteresis, which is expressed in the difference in the values of the edge angle for the inflow and the outflow of the liquid.

It is noted in [2, 5] that the hysteresis of wetting is affected by roughness, contamination of the body surface, the adsorption interaction between the body and the wetting liquid, the presence of air bubbles and other inclusions in the liquid.

The task was to investigate the processes of wettability by polymeric binder of various filler types, such as wastes from chemical and construction industries, and natural asbestos-containing material. Binder – epoxy resin grade ED-20, belonging to the class of diene resins, is a product of the condensation of epichlorohydrin with diphenylolpropane in an alkaline medium. It contains in its chain a reactive epoxy group that reacts with amines, acid anhydrides, forming non-meltable and insoluble three-dimensional compounds of the network structure. Epoxy resin brand ED-20 is a viscous liquid of yellow color with a density of $1160 - 1170 \text{ kg/m}^3$, soluble in toluene, xylene, ketones; resistant to water, solutions of salts, acids and alkalis.

Wetting of the surface of fillers with polymeric binders is also hampered by the branched nature of the polymer chains. Therefore, to improve the orientation of the polymer molecules at the boundary of the phase separation, and also to reduce the internal energy of the binder, plasticization is carried out by the introduction of a surfactant.

Plastification of epoxy resin ED-20 was carried out due to the introduction of electroinsulating KO-922 lacquer. Polymethyl-phenylsiloxanes retain elastic properties at 1800°C for 2000 hours, and at 2200°C for 150 hours. High thermal resistance of these polymers is combined with adequate cold resistance (up to $-60 - 95^\circ\text{C}$).

The dependence of the borderline contact angle of wettability of the surface of various types of filler upon the type and content of KO-922 is shown in figure 2.

As can be seen from the results of the study, the KO-922 additive, introduced into the epoxy resin, increases the wettability of the filler by 15-20%. The most effective concentration for KO-922 is 0.1-3.0%.

The improvement of wetting of asbestos-containing fillers with epoxy resin modified with organosilicon additive KO-922 is explained by the following reasons. The additive introduced into the epoxy resin reduces the internal energy of the binder, which, according to equation (1), is a necessary

condition for adequate wetting. In addition, KO-922 helps to reduce the viscosity of epoxy due to interaction with individual chains and links of macromolecules.

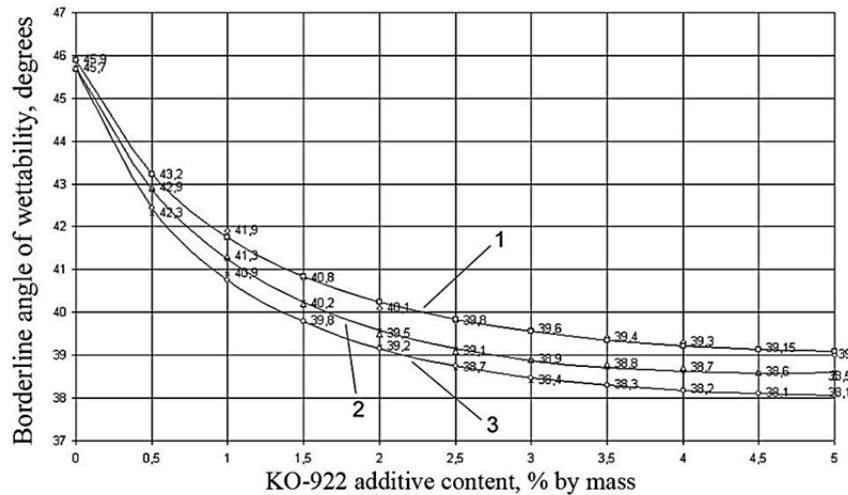


Figure 2. Borderline contact angle dependency upon additive content: 1-FWCI-based composition; 2-FFCI-based composition; 3-serpentine-based composition.

With an increase in the surfactant concentration in the oligomer, this interaction is intensified, which is accompanied by a greater plasticizing effect, and, as a result, an improvement in the wettability of the filler. Due to the introduction of surfactants in ED-20, the adsorption interaction also increases, due to the surface diffusion and migration of the molecules of the modified epoxy oligomer. This increases the number of contacts at the boundary of the epoxy resin filler.

Conclusions

1. The workability of mixtures and forming of products based on a modified polymer binder is facilitated using plasticizers in the form of silica-organic fluids.
2. The nature of the dependence of dynamic viscosity of mixtures on the concentration of the silica-organic plasticizer is established. The optimum content is determined in the range of 2.5 to 3% by mass.
3. The optimum values of the content of the silica-organic plasticizer are determined, at which the wetting of the filler by the binder has the greatest impact on the technological properties of the material. The most effective concentration is the content of the plasticizer in the range of 0.1 to 3% by mass.

References

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