Filling of Epoxy Polymers as a Factor of Obtaining a Multi-component Composition with Improved Strength Properties

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Abstract. The article investigates a filled two-component polymer system (FTPS). Being production wastes, dispersed abrasive particles (AP) (formulation I) and discrete carbon fibers (CF) (formulation II) were used as the filling and strengthening phase. The reasonability of the choice of the FTPS fillers was evaluated by the availability of the ingredients of secondary material resources in the region and their market value. An increase in the strength due to the dispersion of another phase (AP and CF), which is more stiff and durable than the main polymer, in the polymer matrix was understood as the strengthening of the FTPS polymer composition. The set of the indices of the FTPS mechanical properties varied depending on the shape of the filler particles. The mixing of the FTPS dry components of the formulations I and II was carried out under normal conditions at the laboratory of the Department of Construction Materials and Special Technologies. The obtained results indicate a positive effect of the FTPS modification. The introduction of the fillers and chemical additives results in an increase in the strength characteristics of the composition, which makes it possible to consider the developed FTPS formulation not only as waterproofing but also as strengthening, thereby expanding the area of its use.

Keywords: Filled two-component polymer system (FTPS) · Modified concrete · Abrasive particles · Carbon fibers · Tensile strength · Bending strength

1 Introduction

In order to improve the strength characteristics of the filled two-component polymer system (FTPS), it can be reinforced with a dispersed material of mineral and organic nature, which is followed by the formation of a new set of properties of the composition due to interfacial interactions at the polymer-solid interface. They primarily include adsorption or molecular interactions. They are responsible for adhesion at the interphase boundary, as well as for the physical, mechanical and other properties of filled systems. The interfacial interactions determine the specific features of the boundary layer structure, the nature of molecular packing, molecular mobility, morphology and other properties [1–3].

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Particular attention is paid to the reinforcement of polymers contributing to the strengthening of structures. Combining the FTPS and fillers is an essential way to create advanced composite materials with a tailored set of properties differing from the properties of the initial components, which makes it possible to obtain materials with completely new technological or operational characteristics. For composite polymer materials, two types of strengthening are distinguished:

- highly filled systems in which the polymer serves to envelop the reinforcing elements (long fibers) and occupies a smaller volume in the composition (20–50%);
- low filled systems in which the properties of the composition are closer to those of the polymer base, and small amounts of fibers or dispersed particles (5–25%) are introduced as the strengthening phase.

In accordance with the generally accepted classification of fillers, the following types are most often used in heterophase polymer formulations: spherical elements; crystalline fillers; fibrous fillers; synthetic polymers forming a filamentary network structure [4–9].

The investigations of low filled FTPS systems are of scientific and practical interest. There, dispersed abrasive particles (AP) (formulation I) and discrete carbon fibers (CF) (formulation II), being production wastes, are used as the filling and strengthening phase.

2 Research Methods

The reasonability of the choice of the fillers for multi-component polymer system was evaluated by the availability of the ingredients of secondary material resources in the region and their market value.

Strengthening of polymers is determined by the presence of a filler and the emergence of certain structures in the filled polymers, which cause a change in the properties of the polymer. An increase in the strength due to the dispersion of another phase (AP and CF), which is more stiff and durable than the main polymer, in the polymer matrix was understood as the strengthening of the FTPS polymer composition. Thus, the strengthening is carried out through combining the polymer system and the filler system in a free state, which leads to the "averaging" of their properties. The set of indices of the FTPS mechanical properties can vary depending on the shape of the filler particles. For fibrous carbon fillers, the index of the ultimate tensile stress at break is the most important one since fibers in a composite polymer material work mainly in tension. Compression, bending and shear are critical for grained abrasive fillers, which work primarily in compression, but can also work in tension and shear.

The conducted investigations pursued the goal of choosing the optimal formulations of FTPS taking into account their filling with discrete carbon fibers (CF) and abrasive particles (AP). Secondary epoxy resin modified with phenol–formaldehyde resin was used as a polymer binder. Polymer coatings were applied to the specimens made of cement-sand mortar (W/C = 0.55). The mixing of the FTPS dry components of the formulations I and II was carried out under normal conditions at the laboratory of the Department of Construction Materials and Special Technologies. The polymerization reaction of the filled FTPS with curing proceeds within 10–16 h. The viability of the

FTPS at the temperature of 20–23 °C is 4 h, the viability of the mixtures decreases with an increase in the air temperature. It is recommended to use the composition at positive temperatures. The dry polymer mixture can be stored for up to 3 years if it is packed to be moisture-proof.

The best diluents for epoxy resins are glycidyl ethers: cresyl glycidyl ether, butyl glycidyl ether, phenyl glycidyl ether, furyl glycidyl ether and glycidyl ethers of α-branched synthetic fatty acids. However, their high toxic potential does not allow us to recommend these ethers for widespread use. In the course of the conducted investigations, ketone diluents were used since they are considered to be the best solvents for epoxy resins and epoxy-resin-based compositions; they are capable of dissolving large amounts of a copolymer. The solutions have low viscosity, they are stable during storage and do not degrade when large volumes of diluents are added. Ketones are non-corrosive and relatively non-toxic [10–12].

3 Results and Discussion

The test results of the strength characteristics of the filled FTPS compositions are presented in Table 1.

Table 1 Test results of the strength of the filled compositions of FTPS

Strength of specimens	Reference specimen	Formulations of the filled composition					
		Names of the fillers and their introduction % of the polymer base mass					
		AP (I)		CF (II)		AP + CF (1:1)	
		5	15	5	15	5	15
σ_{break}, MPa	2,3	2,4	2,3	3,6	4,1	4,3	5,3
σ_{comp}, MPa	36,3	40,0	40,3	37,8	38,8	52,8	58,8
σ_{bend}. MPa	13,3	14,1	14,8	24,1	25,4	27,8	29,9

An analysis of the test results (Table 1) demonstrated that an increase in the strength characteristics of the specimens with a polymer coating is typical of the FTPS filling with both abrasive particles and carbon fibers. The diagrams of changes in the strength characteristics of the filled polymer systems depending on the type of the filler are given in Figs. 1 and 2.

The formulations combining both fillers in the ratio of 1:1 exhibit the highest indices of strength characteristics. An increase in the amount of the fillers from 5 to 15% gives an average 5% increase in strength. In comparison with the reference filler-free specimen, the tensile strength at break increased by 60%, the compressive strength increased by 50%, and the bending strength increased by 30%.

One of the most common physicochemical phenomena occurring at the “filler–polymer” interface is wetting. Good wetting of the substrate surface is one of the necessary

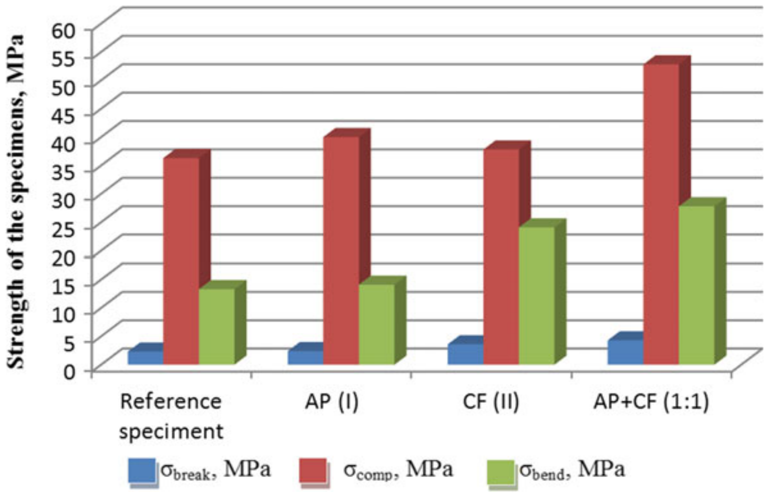

Fig. 1 Change in the strength characteristics of the specimens with FTPS coating depending on the type of the filler, at the filler content of 5%

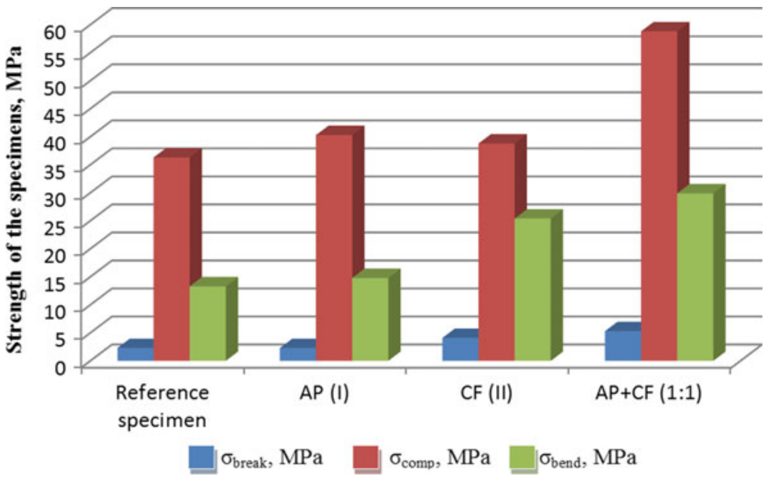

Fig. 2 Change in the strength characteristics of the specimens with FTPS coating depending on the type of the filler, at the filler content of 15%

conditions for obtaining a polymer composite material of a defect-free structure with high physico-mechanical properties.

Polyhydrosiloxanes (KOZh 136–41) were used as a chemical additive to enhance the adhesion characteristics of the FTPS, which were added in the process of the preparation of the polymer composition. The investigation of the effect of the additives on the adhesion of the FTPS polymer base to the substrate surface when applying the FTPS compositions to concrete with the aim of waterproofing and additional strengthening is of scientific and practical interest. From a theoretical point of view, the improved wetting of the surfaces of the fillers and the substrate with the modified FTPS mixture can be explained as follows.

The surface-active agents introduced into the filled FTPS solution are adsorbed at the phase boundary, forming a monomolecular layer oriented in a strictly defined manner. These adsorbed layers change the balance of forces in the system and contribute to the reduction in the surface energy of the binder, which is a necessary condition for wetting [10–16].

In addition, the applied additive helps to reduce the viscosity of FTPS as a result of its interaction with particular chains and units of macromolecules. Through changing the conformation of the chains of the polymer base, the additive facilitates the formation of a dense oriented layer of them at the interface. This effect of the organic additives makes it possible to increase the number of contacts of macromolecules with the surface of the solid and enhance the adsorption interaction both in the system of polymer–substrate and in the system of filled polymer–substrate. This, in turn, improves the wetting of the contacting surfaces and contributes to the growth of adhesion. The results of the experiment are presented in Table 2 and in Figs. 3 and 4.

Table 2 Adhesion characteristics of the modified FTPS composition

Name of additive	Concentration c (%)	Contact angle of wetting σ, grad	Interfacial tension σ_l (mJ/m^2)	Work of adhesion W_a, (mJ/m^2)	Work of cohesion W_c, (mJ/m^2)	Spreading coefficient S	Relative work of adhesion Z_a
FTPS	–	23,64	41,58	80,90	85,70	3,70	0,9629
KOZh 136–41	0,1	23,39	40,87	79,37	84,18	−3,54	0,9648
	0,5	22,75	38,84	75,53	80,00	−3,24	0,9663
	1,0	22,73	38,21	74,31	78,66	−3,17	0,9668
	3,0	22,70	38,11	73,44	77,76	−3,13	0,9689

When introduced into the formulation of the FTPS, the organosilicon fluid 136–41 significantly reduces the interfacial tension of the polymer mixture, being a surface-active agent (SAA) for it. With an increase in the SAA concentration, a regular decrease in the interfacial tension occurs. Thus, at the maximum concentration of KOZh 136–41 (3%), the interfacial tension decreases by 8.7%.

The processes taking place at the polymer-substrate interface are explained in terms of the adsorption theory of adhesion, which considers the adhesion to be a result of the activity of the forces of molecular interaction between the molecules of the adhesive substance and the substrate [17–22].

Being adsorbed at the phase boundary, the organosilicon fluid KOZh 136–41 helps to reduce the interfacial tension of the FTPS. The contact angle decreases, the wettability increases with a decrease in the work of adhesion (Table 2). The value of the relative work of adhesion of the composition is 0.9629–0.9689, which is close to unity. Consequently,

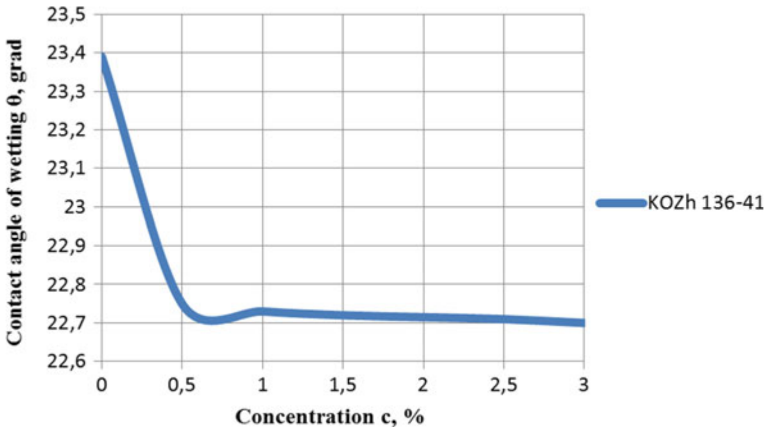

Fig. 3 Change in the contact angle of wetting of FTPS depending on the concentration of KOZh 136–41 modifier

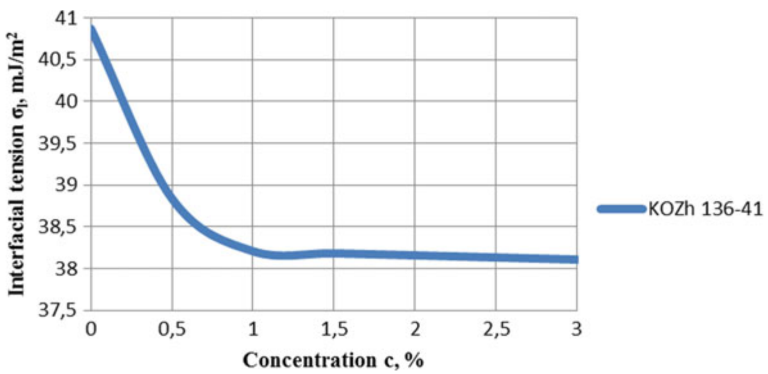

Fig. 4 Change in the interfacial tension of the FTPS depending on the concentration of KOZh 136–41 modifier

the values of the adhesion forces between the molecules of the polymer and the substrate approach to the values of the cohesion forces of the molecules of the polymer itself. This contributes to the formation of a material with a homogeneous, defect-free structure [23, 24].

However, the introduction of surface-active chemical additives affects not only the adhesion of the polymer coating to the base of a construction product or metal. The effect of the chemical additives on the change in the strength characteristics of the filled composition of the FTPS (AP + CF) was evaluated depending on the sequence of their introduction into the composition. Pretreatment of the surface of AP and CF with KOZh 136–41 and GKZh-10 additives significantly adds to the growth of strength characteristics. The surface of the fillers was treated with the 3% additive at the filler mixture content (AP + CF) of 5 and 15%. The results are presented in Table 3. The experimental results demonstrate (Table 3, Figs. 5 and 6) a change in the strength characteristics of the coated specimens tending to grow due to the pretreatment of the surface of the fillers. The strength indices of the specimens increased (the values below the line, Table 3) by 10–15%, on average, in comparison with the specimens with non-modified surface of abrasive particles and carbon fibers.

Table 3 Test results of the strength of the filled compositions of FTPS

Strength of specimens	Formulations of the filled composition of FTPS			
	AP + CF (1:1)		AP + CF (1:1)	
	5	15	5	15
	KOZh 136–41 (3%)		GKZh-10 (3%)	
σ_{break}, MPa	4,5/5,2	5,5/6,1	4,5/4,9	5,5/5,8
σ_{comp}, MPa	53/61,2	59/65,3	53/60,7	59/63,9
σ_{bend}, MPa	28/32,8	30/33,6	28/30,8	30/32,6

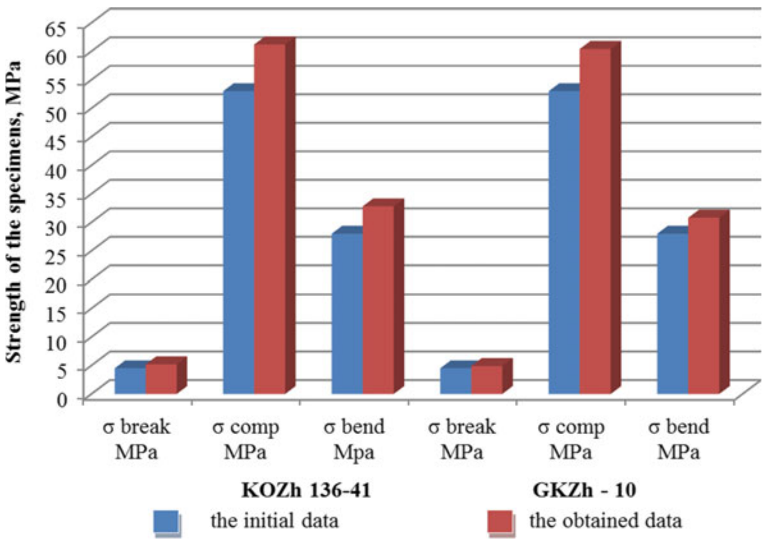

Fig. 5 Change in the strength characteristics of the specimens with the FTPS coating (formulation III, 5%), and in the type of the chemical additive (3%)

The effect of the surface modification of AP and CF fillers due to their pretreatment was assessed through the change in the indices of water permeability and water absorption. Several series of specimens with filled FTPS (AP + CF) and with unfilled polymer coating on all sides were manufactured. The water permeability was characterized as an ability of the coating to pass water or aqueous solutions. The essence of the method of the test without pressure was to determine the change in the mass of the coated specimen placed into an aqueous medium or solution and kept there for a selected period of time.

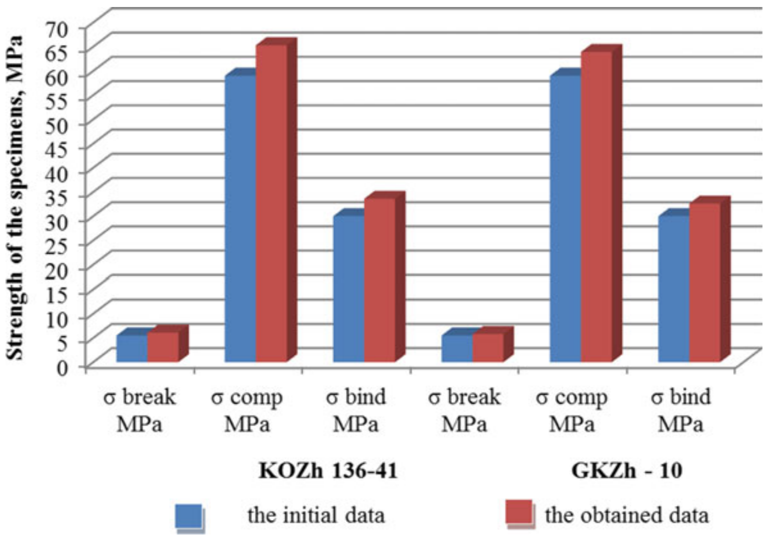

Fig. 6 Change in the strength characteristics of the specimens with the FTPS coating (formulation III, 15%), and in the type of the chemical additive (3%)

The specimens for the test are shown in Fig. 7a, b. The thickness of the coating was 300–350 μm.

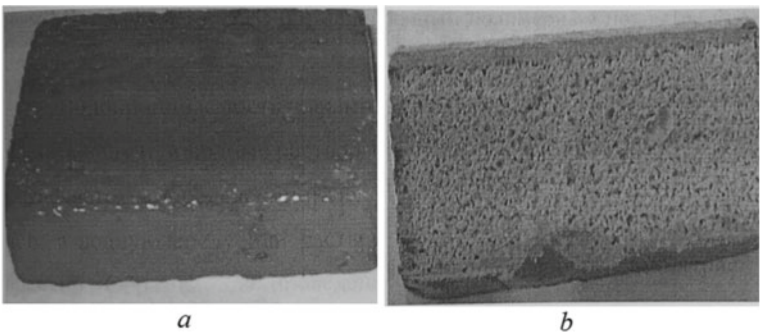

Fig. 7 Specimen with the FTPS coating for the tests. **a** General view of the specimen; **b** section view of the specimen

The authors carried out the quantitative assessment of the water permeability according to the average test indices calculated for each of the specimens according to the formula (1):

$$W = \frac{\Delta m}{F \cdot \tau}, \frac{\text{g}}{\text{cm}^2 \cdot \text{days}}, \quad (1)$$

where $W\gamma$—water permeability of the coating; Δm—change in the mass of the coated specimen (g) over time—τ; F—area of the specimen, cm^2.

The test results are presented in Table 4. The application of the polymer composition to the surface of the specimens resulted in the twofold decrease in the water permeability. In the case of further exposure of the polymer-coated specimens to water, a decrease in the water permeability index and its stabilization were observed. The treatment of the filler surface with the chemical additive led to an additional decrease in the water permeability by 40% due to the formation of a denser structure of the filled composition and additional adhesion of the cement matrix to the modified surface of the fillers. The values of the water absorption indices of the specimens with the polymer coating without filler treatment (6.4%) and with the FTPS polymer coating with filler surface treatment (1.6%) were compared with the reference specimen without a coating (11.7%). The decrease in the index was from 2 to 7 times, respectively.

Table 4 Change in the water permeability ($\times 10^{-5}$) of the specimens depending on the time of exposure to water

Cement-sand specimen	Time of exposure to water, days			
	30	60	90	180
Without a coating	6,93	13,07	18,13	18,13
With a coating without filler treatment	3,30	2,67	2,53	2,21
With a coating with the filler treatment	2,35	2,23	1,82	1,79

4 Conclusions

Thus, the obtained results indicate a positive effect of the modification of the FTPS and the filler mixture surface with organosilicon fluids, which determines the sequence of the technological operations in the process of manufacturing of the filled polymer composition of FTPS. The introduction of the fillers and chemical additives leads to an increase in the strength characteristics of the composition, which makes it possible to consider the developed formulation of the FTPS not only as waterproofing but also strengthening, thereby expanding the area of its use. Low filled systems in which the properties of the composition are closer to those of the polymer base allow revealing and using the properties of the modified epoxy base to the fullest degree. The strengthening phases are introduced in small amounts in the form of short carbon fibers or dispersed abrasive particles (5–25%). For fibrous carbon fillers, the index of the ultimate tensile stress at break is the most important since fibers in a composite polymer material work mainly in tension. Compression, bending and shear are critical for grained abrasive fillers, which work primarily in compression, but can also work in tension and shear. In this regard, a necessity arises for a practical investigation of the effect of concrete base characteristics on the conditions of its joint work with the protective polymer coating. In this case, the performability and chemical resistance of concrete with polymer coatings depend on numerous factors.

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