Article

Development of Mineral Fillers for Acid-Resistant Filling Composites

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Abstract: This article presents the results of research on the development of chemically resistant polymer–mineral casting composites based on industrial waste. The aim of this work is to develop a technological basis for obtaining effective inorganic fillers and highly filled composites for use in chlorine-containing environments. On the basis of theoretical data, mineral fillers and a polymer binder for filling composites were selected, optimal quantities of input hardeners and an appropriate thermal curing mode were determined, and the influence of the filling degree on the properties of composites was studied. The influence of various factors on the properties of the obtained composites was also studied, and the possibility of using local raw materials to obtain special-purpose composites was investigated. Ash from a thermal power plant (TPP) was used as an acid-resistant filler in composites. Two components were chosen as binders: phenol formaldehyde resin and mineral filler (TPP ash). As the third component, hydrolytically active fillers—anhydrite, phosphogypsum and phosphate slag—were used. The degree of filling has a significant influence on the properties of composites, including the compressive strength, chemical resistance and degree of curing, the values of which were elucidated across a wide range of composite variations based on the degree of filling. The conducted research allowed us to establish the limit of admissible anhydrite content, which should not exceed 15 mas.%. To optimize the chemical resistance and durability of the composites of the investigated substances, the method of mathematical planning was used. According to the results of this study, the optimal compositions of composites, in terms of anhydrite, phosphogypsum and phosphorus slag contents, were selected. At the maximum possible degree of filling, these composites exhibit high target characteristics.

Keywords: composite material; mineral filler; phenol formaldehyde; anhydrite; phosphogypsum; phosphate slag

1. Introduction

The creation and production of effective structural materials based on local natural and technogenic raw materials remains an urgent problem for Kazakhstan. This is especially true for multifunctional materials combining high chemical resistance, strength and electrophysical properties [1].

Composite materials based on polymer binders have been widely used recently. This is promoted by their high chemical resistance, comparative simplicity of application, manufacturability and other positive properties. However, as experience shows, in conditions of strong, aggressive impact, polymeric materials often cannot provide a reliable long-term protection of building structures and equipment under increased pressure and temperature conditions [2,3]. The search for ways to increase the strength, density, chemical resistance and durability of protective coatings has led to the creation of a wide array of

polymer composite materials (PCMs) incorporating polymer additives or polymer concretes (P-concretes), the nomenclature of which has often been arbitrary and without proper justification [4–6].

The production of polymer products from polypropylene (PP) has recently increased. PP has a good combination of physical and mechanical, thermophysical and electrical properties, as well as good processability compared to other thermoplastics, which creates a strong competitive position in the world market [7,8]. However, the large market demand puts forward new requirements for general and technical products obtained from polymers: increased hardness, impact resilience and heat resistance. The use of mineral fillers allows the technological parameters and thermal deformation and strength properties of the materials to be adjusted, reducing the cost, etc. The modification of PP is usually achieved in the process of polymer processing by introducing filler into the polymer melt, which allows the process of obtaining products with desired performance properties to be optimized. Widely used mineral fillers for PP include talc, chalk, asbestos, and mica, with their total content ranging from 20 to 40%.

Mineral fillers are primarily used to reduce shrinkage, residual stresses and the tendency to crack and to increase the strength characteristics of composites [9,10].

Powdered polymers, such as polyvinyl chloride, polyethylene, polyformaldehyde and polytetrafluoroethylene, can also be used as dispersed fillers [11,12]. They increase chemical resistance and, together with other dispersed and fibrous fillers, improve wear resistance, friction coefficient and dielectric characteristics of composites. Their efficiency increases if, during the process of obtaining and processing PCMs, they do not melt but are stored as particles of an independent phase [13–16].

In studies [17] on the effect of fillers on synthesis reactions and the structure of three-dimensional polymers, the formation of a more three-dimensional structural mesh in the presence of fillers was noted. This is due to the influence of the interface on the rates of growth and breakage reactions, as well as the adsorption decrease in the mobility of growing polymer chains. The filler surface also affects the effective density of the three-dimensional mesh; additional nodes appear as a result of mutual interaction with the surface. It was also found that the chemical nature of fillers affects the rate and depth of oligomer curing [18–20].

There are data on the study of epoxy resin curing by amines in the presence of glass fiber, dispersed quartz and other silicate fillers [21–23]. It was found that with the increase in filler concentration, the thermal and elastic properties of the filled polymer change, and the glass transition temperature increases. This is explained by the fact that the binder molecules in the adsorption layer do not participate in the curing reaction, as a result of which the density of this layer is lower than that of the cured resin, and its properties change more sharply with temperature. Consequently, the changes in the elastic modulus and thermal expansion coefficient are due to differences in the interaction between the mesh links in the binder in the presence of filler.

It is known that the curing system is a mixture of components, and the selective sorption of one of them on the filler surface is possible [24]. In cases of adsorbed water on the filler surface, there is a possibility of binder hydrolysis, which also affects the curing reaction. Dehydrated, highly dispersed filler can absorb water, the presence of which reduces the degree of curing [25].

Carbon-fiber-reinforced composites are mainly used for heat-resistant products. They are characterized by high tensile compression, bending, and impact strength [26]; have high chemical resistance; are practically wear-free in dry friction; and are used in pump parts operating in aggressive media. An obstacle to the wide application of these materials is the high price of carbon fiber.

Currently, the issue of obtaining hydrochloric acid is acute due to its high demand in chemical, metallurgical, mining, light and other industries.

One of the modern methods is electrolysis of a table salt solution, which produces hydrochloric acid and alkali. The hardware design of this process requires the use of chemically resistant materials with high strength and dielectric characteristics.

Highly filled plastic masses on polyester, epoxy, phenol formaldehyde and other resins can be singled out among the materials possessing a complex of these properties.

Currently, such materials are imported from Germany, France and other countries and are expensive and short-lived. They are produced via cold molding.

Resol phenol formaldehyde resins (RPFRs) are widely used in the production technology of composite materials for various purposes [27–29]. These resins, along with the availability, cheapness and simplicity of the technology for preparing composites, have a number of disadvantages [30–33].

In this regard, the development and creation of new effective chemical-resistant composite materials using mainly locally available raw materials appears to be highly relevant.

In this work, the initial prerequisite for the choice of fillers was the introduction of a number of substances into their composition that can systematically change the binding rate of the water released in the polycondensation process, thereby directly affecting the rate and depth of the polymerization of the binder and curing process.

The scientific novelty of this work lies in the investigation of the possibility of using local non-deficient technogenic mineral fillers to obtain polymer–mineral casting chemically composite materials. This study demonstrates the significant influence of the nature of the mineral filler composition on the chemical stability and strength characteristics of the resulting composites.

2. Materials and Methods

2.1. Materials

Ash from Almaty TPP was used as an aluminosilicate acid-resistant filler [34]. As a binder in polymer–mineral filling composites, resol-type phenol formaldehyde resin, specifically an "arzamite solution" of various grades, was used [35].

Phosphorus production slags are characterized by a rather stable chemical composition, primarily comprising the following components by mass percentage: SiO_2 at 41.0–43.0%; CaO at 45.4–47.2%. Phosphogypsum contains the following: CaO at 30.0–33.0%; SO_3 at 42.0–45.0%. The chemical compositions of the raw materials used are presented in Table 1.

Table 1. Chemical compositions of raw materials.

The Name of Material	Composition, Mass%								
	SiO_2	Al_2O_3	CaO	MgO	Fe_{total}	SO_3	P_2O_5	$C_{org.}$	$\sum$
Phosphogypsum	11.0	7.5	32.4	-	-	42.5	6.0	-	99.4
Phosphoric slag	43.4	1.2	47.6	3.7	0.3	0.6	1.5	-	98.3
Anhydrite	-	-	41.2	-	-	58.0	-	-	99.2
TPP ash	61.3	29.3	0.9	0.7	3.2	-	-	3.6	99.0

2.2. Methods

Before introduction into the filling composite, it is necessary to perform preliminary operations associated with the removal of hygroscopic moisture from the filler and grinding and sifting it. To determine the optimum dehydration temperature, a differential thermal analysis of all starting materials and their mixtures was carried out.

The process of preparing powdered fillers included the following operations: drying at a temperature of 200 °C, grinding in a ball mill, and sifting through a No. 008 sieve. TPP ash was pre-calcined at a temperature of 900 °C to remove unburned particles and activate the surface. Fillers are mixtures of various substances, with the exception of anhydrite, which is a monomineral slow-setting gypsum binder ($CaSO_4$) [36]. The use of anhydrite

with phosphogypsum, as well as phosphoric slag and ash from TPP, expands the ability to control the rate and depth of curing of the binder [37].

Based on the indicated mineral fillers, composites with 50% filling were prepared, containing, in addition to the filler, a polymer binder (Arzamit-5 phenol formaldehyde resole resin) and hardener (benzenesulfonic acid dissolved in ethylene glycol—BSA + EG).

Filling composites were prepared as follows. Bulk components and an arzamite solution were weighed out. The mixture was thoroughly mixed until a homogeneous mass was added, to which the hardener was added. The resulting mixture was re-mixed for another 10–15 min. A homogeneous mass was poured into a vibroform without lubricating it. Vibration was carried out for 10–30 min at a vibration frequency of 100 Hz. The cured samples were removed from the vibroforms and adjusted via mechanical processing to the specified sizes, and their properties were studied using various methods.

Further research was devoted to the search for new compositions of mineral fillers and filling composites based on them, with the aim of improving both the strength properties of composite materials and corrosion resistance [38].

Previously, the chemical resistance of a number of mineral fillers was determined because, despite the polymer enveloping the filler grains, they may come into direct contact with an aggressive environment.

The chemical resistance of the obtained samples of materials in chlorine-containing media was determined using an accelerated powder method considering the ratio of the weight of the milled product after exposure to aggressive media to the weight of the same product before exposure, expressed as a percentage. A measure of 1 kg of crushed sample grains weighed with an accuracy of 0.002 g was placed in a flask with an aggressive medium and boiled in a water bath for 1–3 h. The temperature of the aggressive medium during the tests was approximately 100 °C. At the end of the specified time, the grain sample was filtered, washed and dried to constant weight. After cooling in the desiccator, the sample was weighed with an accuracy of 0.0002 g. The chemical resistance of the sample was expressed as a percentage by calculating the ratio of the weight of the sample after the test to its initial weight according to the following formula:

$$ChR = \frac{G}{G_1} * 100\%$$

where G and G_1 represent the mass of material grains before and after the test, respectively.

The final result was taken as the arithmetic mean of the results of at least two parallel determinations, the discrepancy between which should not exceed 0.5%.

Compressive strength was determined on cubic samples with a rib length ranging from 30 to 100 mm, with parallel ground surfaces on a press providing pressure up to 20 tons. The compressive strength limit, defined as the pressure at which mechanical destruction occurs relative to the area of the cube face (MPa), was determined based on the arithmetic mean of compressive strength indicators from at least 5–10 samples of the same material.

The bending strength was determined using samples shaped like parallelepipeds with a cross-section of 30 × 30 mm and length ranging from 150 to 230 mm, with parallel ground surfaces. The ratio of the bending moment to the moment of resistance (MPa) was taken as the bending strength. The arithmetic mean of the bending strength results of at least three samples of the same material was taken as the test result.

3. Results and Discussion

Materials with high resistance to hydrochloric acid include graphite and quartz sand. Good resistance is characterized by the TPP ash, which was used as an acid-resistant filler in the composites. To determine the areas of composites with the best characteristics and establish optimal ratios of the components of the casting composites, we used the simplex lattice planning experiment design method. In the content of the composites, the two components remained constant—a binder phenol formaldehyde resin (PFR) and a

mineral filler (ash from TPP). Hydrolytic active fillers—anhydrite, phosphogypsum and phosphoric slag—were used as the third component [39]. For each series of composites, 15 compositions were prepared with different ratios of components.
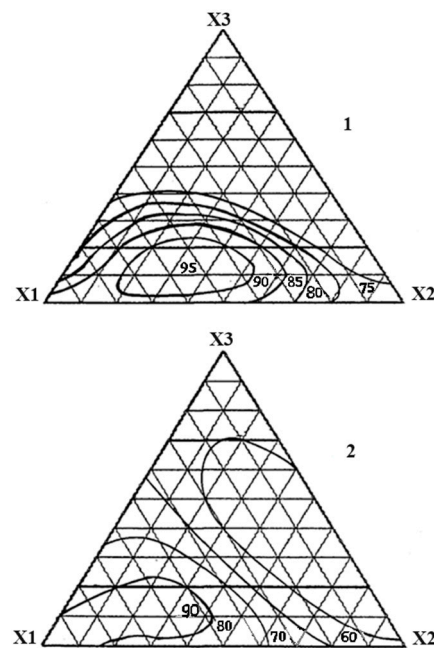
Table 2 presents the planning matrix, including the ratio of components and the measured properties for the arzamite (X_1)–ash (X_2)–anhydrite (X_3) composite. The optimization of the compositions of the casting composites was carried out according to two main target characteristics: the chemical resistance of the cured composites in 30% HCl and strength (breaking stress under compression). To obtain initial data for mathematical processing, experimental determinations of the indicated properties were carried out using 15 compositions.

Table 2. Planning matrix and results of measurements of chemical resistance and strength of arzamite (PFR)–ash–anhydrite composite at 20 °C.

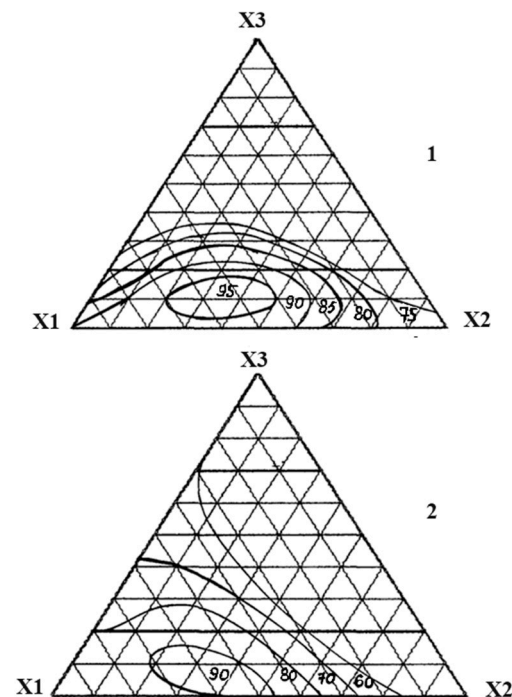| No.	Component, Fraction of Units			Chemical Persistence in 30% HCl, %	Compressive Strength under Compression, MPa
	X_1	X_2	X_3		
1	1	0	0	98.0	95.0
2	0	1	0	85.4	50.2
3	0	0	1	52.2	42.4
4	1/2	1/2	0	90.6	75.1
5	1/2	0	1/2	71.0	54.8
6	0	1/2	1/2	48.8	40.5
7	3/4	1/4	0	93.2	68.8
8	1/4	3/4	0	80.3	60.1
9	3/4	0	1/4	75.1	75.4
10	1/4	0	3/4	52.4	54.9
11	0	3/4	1/4	60.7	45.1
12	0	1/4	3/4	50.1	50.5
13	1/2	1/4	1/4	95.3	70.6
14	1/4	1/2	1/4	84.6	55.4
15	1/4	1/4	1/2	65.0	50.2

Similar experiments were carried out for the remaining composites. A composite composition–property diagram for the three studied composites is shown in Figure 1. Chemical resistance contours of 30% HCl at 95% for the three composites are indicated by solid lines, and the strength contours (30, 40, 50, 60 MPa) for the arzamite (PFR)–ash–anhydrite composite are indicated by a dotted line. Comparing the data for various composite compositions with satisfactory properties reveals that satisfactory properties are limited to the areas located at the bottom of the diagram. This indicates that the content of component X_3 should be minimal (no more than 20%). The optimal compositions for the arzamite–ash–anhydrite composite occupy a wider area of the chart compared to other composites. Moreover, the composites with maximum strength and chemical resistance overlap well in the region of a rather high total filler content (40–60%).

The region with the highest compressive strength values of the cured composites (60 MPa) is located near the X1 angle (PFR). The regions of the compositions with maximum strength (60 MPa) and chemical resistance (95%) overlap well within a rather high aggregate filler content range (40–60%). Thus, regions of optimal composites of the PFR–ash–anhydrite system were determined. These compositions include the following components in the specified proportions by mass percentage: PFR at 40–60%; ash at 20–40%; anhydrite at 10–25%.

Figure 1. Diagrams of the "composition–property" of the filling composite. PFR (Xl)–TPP ash (X2)–anhydrite (X3); (1) Composition and chemical resistance in HCl, %; (2) composition and strength, MPa.

Similar studies have been carried out on composite material in the arzamite–ash–phosphogypsum system. The composition–property diagrams for the composites of the arzamite–ash–phosphogypsum system are shown in Figure 2. Isolines are built on composition–property diagrams with equal values of chemical resistance (75, 80, 85, 90, 95%) in 30% HCl and strength (30, 40, 50, 60 MPa) corresponding to destructive stress at the compression of cured composites.
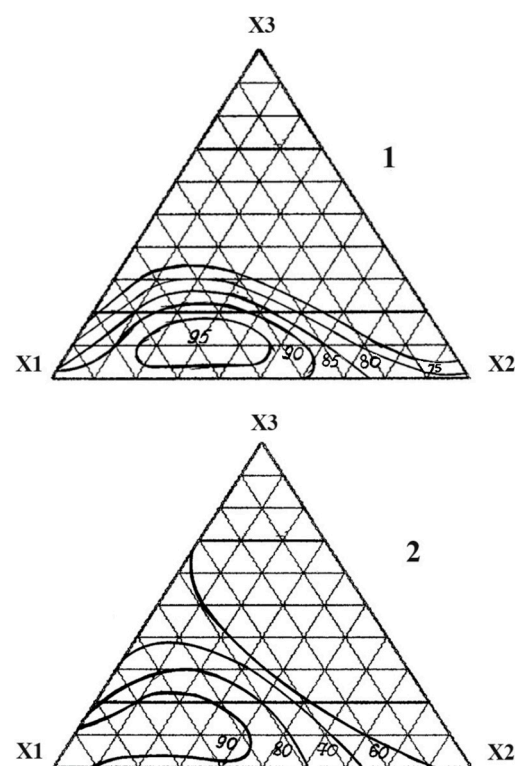

Figure 2. Composition–property diagrams of the filling composite. PFR (Xl)–TPP ash (X2)–phosphogypsum (X3); (1) Composition–chemical resistance in HCl, %; (2) composition–strength, MPa.

The range of phosphogypsum filling composites having high chemical resistance (not less than 95%) to hydrochloric acid is more limited than that for anhydrite compositions.

The isothermal section at 20 °C (Figure 2) also showed a clear pattern of a decrease in the chemical resistance of cured filling composites as the content of hydrolytically active filler phosphogypsum increased. Thus, as the phosphogypsum content increases from 20 to 40%, the chemical resistance of the composites in 30% hydrochloric acid decreases from 95 to 75%; i.e., the addition of 1% by mass of phosphogypsum to the composite causes (as with anhydrite) a 1% reduction in the chemical resistance of the material.

In the case of using phosphorus slag as an active filler (Figure 3), there is also a noticeable shift in the areas of compositions with high chemical resistance towards the angle Xl (PFR). The content of phosphorus slag in the area of the highest chemical resistance values (95%) is limited to 10–15 mas.%. The amount of aluminosilicate filler added—TPP ash—can also be varied in a narrower range: from 25 to 40 mas.%. The amount of binder (PFR) ranges from 45 to 60% by weight.

Figure 3. Composition–property diagrams of the filling composite. PFR (Xl)–TPP ash (X2)–phosphoric slag (X3). (1) Composition–chemical resistance in HCl, %; (2) composition–strength, MPa.

The dependence of strength on the qualitative and quantitative composition of cured composites has a similar character. When phosphorus slag is added to the casting composite in amounts ranging from 15 to 40%, there is a monotonic decrease in the strength of the cured composite material from 60 to 30 MPa. There is a shift in isolines with high strength values (40, 50, 60 MPa) towards increasing concentrations of the binder (PFR) in composites.

The region with the highest strength values (60 MPa) is located near the angle Xl (PFR).

When combining the composition–chemical resistance and composition–strength diagrams for composites of the arzamite–ash–phosphorus slag system, the areas of compositions with maximum strength (60 MPa) and chemical resistance (at the level of 95%) overlap within the limits of the total content of hydrolytically active and acid-resistant fillers ranging from 35 to 45%. Thus, the areas with optimal compositions of composites of the PFR–ash–phosphorus slag system were determined. These compositions include the specified components in the following ratios by mass percentage: 40–60% PFR; 20–40% ash; and 10–15% phosphorus slag.

Thus, using the method of mathematical planning of the experiment, the areas of optimal compositions for three composite systems were determined, including mineral hydrolytically active fillers (anhydrite, phosphogypsum and phosphorus slag), acid-resistant filler (TPP ash) and polymer phenol formaldehyde binder (PFR—arzamite-5 resin).

The analysis of the diagrams showed that the areas of compositions with optimal properties for all studied composites occupy small areas on the concentration triangle and are concentrated at the bottom of the diagrams. There is an increase in properties for all composites as the content of hydrolytically active fillers in the casting composites decreases, as well as a shift in isolines with high properties towards the angle of the binder Xl (PFR).

The permissible limits of the content of each of these components in chemically resistant casting composites has been indicated, at which the target characteristics of the cured test composites are at a fairly high level: their chemical resistance in 30% hydrochloric acid is no less than 95%, and the compressive strength is no less than 60 MPa.

The conducted studies allowed us to determine the areas of composite compositions with optimal properties (Table 3).

Table 3. Components and properties of optimal composites.

Components	Contents of the Composites, Mass%				
	1	2	3	4	5
Phosphogypsum	15.0				
Phosphorus slag		15.0			
Anhydrite			15.0	15.0	15.0
TPP ash	20.0	20.0	20.0	25.0	30.0
PFR + BSA	65.0	65.0	65.0	60.0	55.0
Cure conditions					
Temperature, °C	120	120	100	110	120
Time, min	240	200	120	160	180
Chemical resistance, %					
30% H_2SO_4	96.6	98.8	97.0	98.5	99.3
30% HCl	96.2	97.4	96.0	97.5	98.0
20% NaOH	96.0	96.7	96.0	97.1	97.5
Tensile strength, MPa					
At compression	45.3	53.0	50.2	57.0	60.2
At bending	18.7	23.4	21.1	25.3	28.0

The most limited range of compositions with optimal property values covers those with phosphoric slag. Compositions using phosphogypsum in this respect occupy an intermediate position. Thus, the areas of composite compositions with satisfactory target properties—chemical resistance and strength—were determined.
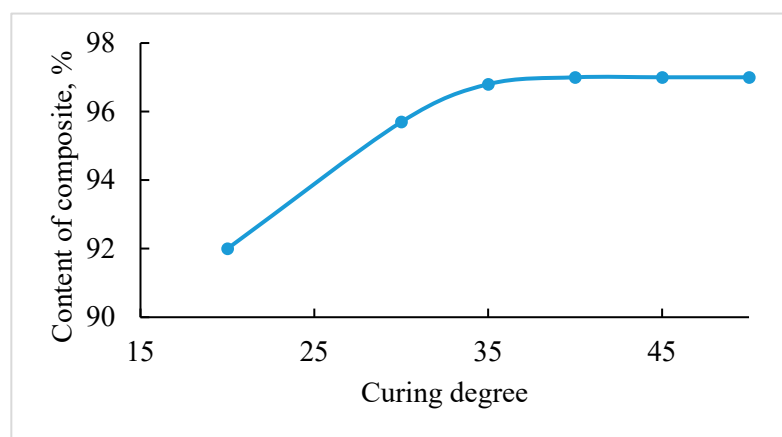
The nature of the interaction of mineral fillers with a polymer binder was studied, and it was shown that during the curing of the composite at the binder–filler interface, the chemical interaction of the hydroxyl groups of the filler takes place. The chemical interaction of the hydroxyl groups of the filler and the methyl groups of the polymer leads to the formation of Si–O–R and Ca–O–R bonds. The method of simplex–lattice planning was used to optimize the chemical resistance and strength of the composites of polymer–mineral casting compositions to determine the areas with an optimal composite composition using ash from TPP, anhydrite, phosphogypsum and phosphoric slag.

The next step was the study of various factors that influence the properties of the composites and the determination of the most promising composite compositions within certain optimal areas.

The properties of PFR and composites based on them are directly dependent on the degree of curing. The higher the degree of resin curing, the better its heat resistance, as well as its physical, mechanical and dielectric properties. However, the maximum degree of cure is not always the best option for composite materials based on PFR of the resole type. On the contrary, it is not recommended to achieve very hardened curing, as this can lead to shrinkage of the material with the appearance of external and internal cracks. In this regard, a more objective assessment of the composites can be obtained by comparing their properties, especially strength characteristics and chemical resistance.

One of the products of the polycondensation process, as is known, is water, the presence of which adversely affects the properties of the composite. The introduction of hydrolytically active substances that bind water should lead, according to Le Chatelier's principle, to a shift in the polycondensation reaction equilibrium to the right, i.e., to an increase in the degree of curing [40–42]. Indeed, as follows from Figure 4, when the contents of anhydrite, phosphogypsum and phosphorus slag in the composites increase, the degree of curing of phenol formaldehyde resin increases to a certain limit, after which the degree of curing remains almost unchanged with an increase in the content of fillers.

Figure 4. The effect of the content of anhydride, phosphogypsum and phosphorus slags on the degree of cure of phenol formaldehyde resins.
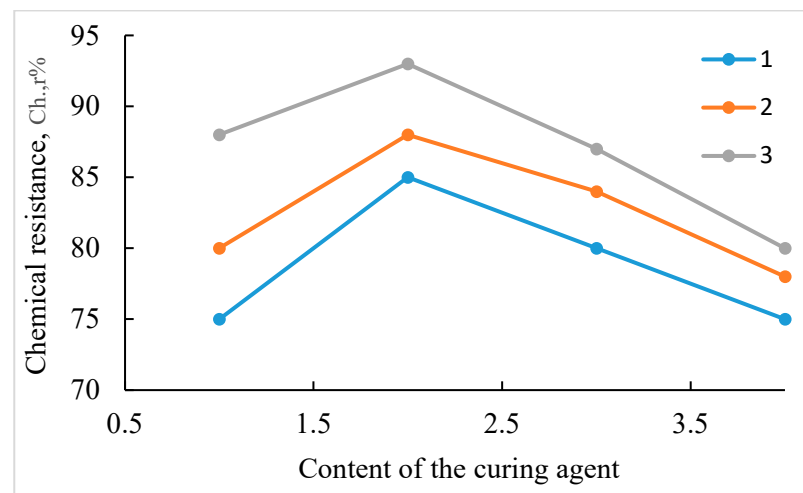
For all studied fillers, the effective content of hydrolytically active components in the composites is 15–20% with a total degree of filling at the level of 40–45%.

Figure 5 shows the dependence of the chemical resistance of the resin–ash composite with anhydrite, phosphogypsum and phosphoric slags with 50% filling on the content of the introduced hardener. As the amount of hardener introduced increases up to a certain limit, the chemical resistance of the composites also increases, after which the value of the properties decreases. The optimum for compositions with anhydrite is a hardener content of 2.5–3.0% of the total weight of the composite.
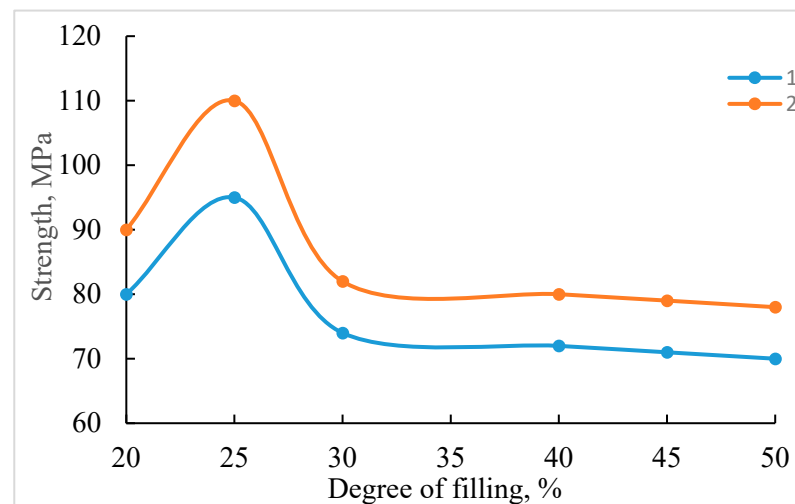
For composites with phosphoric slags and phosphogypsum, the optimum norms of the hardener are 2.8% and 3.3%, respectively.

This is likely due to the different hydrolytic activity of the introduced fillers, which take part in the polycondensation of PFR. A decrease in chemical resistance for all samples can be explained by the fact that the excess hardener present in the composite mass disturbs the macrostructure of the composite. Moreover, a high degree of binder curing causes internal stresses in the sample, the formation of microcracks, the violation of encapsulation and other structural defects of the composites.

The dependence of the strength and chemical resistance on the degree of filling is shown in Figure 6. At first, there is a slight increase in both the corrosion resistance and compressive strength; then, with an increase in the filler content above 50%, the abovementioned indicators decrease.

Figure 5. The dependence of the chemical resistance of the composites on the content of the introduced hardener. (1) Resin–ash composite with anhydrite; (2) resin–ash composite with phosphogypsum; (3) resin–ash composite with phosphoric slags.

Figure 6. Dependence of the strength and chemical resistance of composites on the degree of filling.
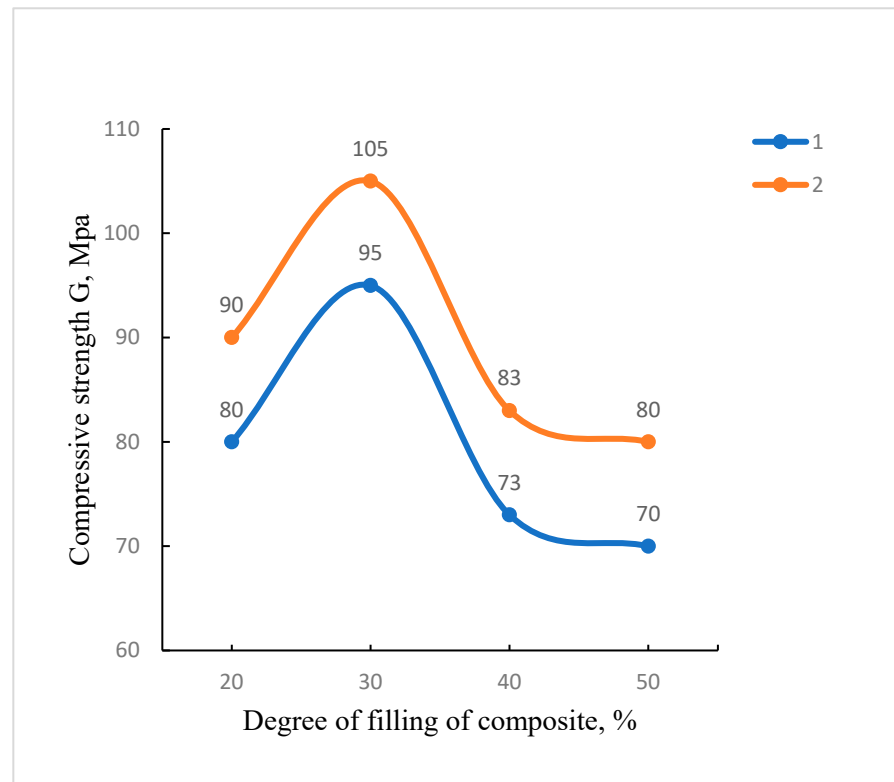
According to the results of the studies, it can be concluded that the content of chemically unstable hydrolytically active fillers in the composites should be limited, and the content of chemically stable minerals should be at its maximum.

It is known that the filler content in the composite has a great influence on its strength and deformation properties. In this case, the optimal degree of filling substantially depends on the nature and dispersion of the filler and the method of its introduction into the composite.
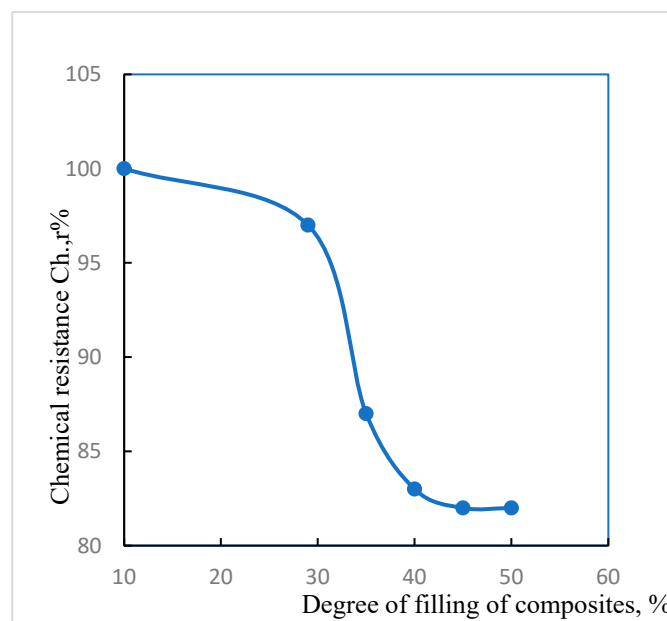
To study the influence of the degree of filling on the properties of the composites, ash and hydrolytically active fillers were selected. The content of hydrolytically active fillers in all composites was 15%. The total degree of filling varied from 15 to 60 mas. %.

Changes in the structure of the PFR (degree of its hardeners) and the content of residual moisture cannot affect properties of the compositions such as compressive strength and chemical resistance (Figures 7 and 8). The nature of the dependence of these properties on the degree of filling is approximately the same and partly correlates with the change in the degree of hardeners of the composites. Initially, there is some growth in both corrosion resistance and compressive strength; then, with an increase in the content of anhydrite, these indicators decrease. The chemical resistance of samples containing more than 10 ppm

of anhydrite (28%—the total degree of filling) is especially noticeable, which is due to the low value of this property in the filler itself.

Figure 7. Dependence of compressive strength (G) on degree of filling of composites. (1) Composite with anhydrite; (2) composite with phosphogypsum.

Figure 8. Dependence of chemical resistance of samples on the degree of composite filling.

It should also be noted that the use of phosphogypsum instead of anhydrite as a filler in the test samples leads to the deterioration of the strength characteristics of the composites over the entire range of compositions (Figure 7).

The results of experiments show that with an increase in the curing temperature to 120 °C, the chemical resistance and strength of the composites increase, and curing of samples at higher temperatures leads to the deterioration of these properties. This is due to the fact that when the liquid composites are heated, their viscosity decreases; additionally, gas and vapor emission, the compaction of the structure and a porosity decrease are facilitated.

Above 120 °C, a sharp acceleration of the curing reaction, internal heating of the sample, and expansion and deformation of the mass occur, leading to numerous defects that reduce the properties. At temperatures above 150 °C, the polymer matrix is degraded. Thus, the optimum temperature range of curing for the studied compositions is 100–120 °C.

The optimal compositions of these composites were subjected to long-term tests of chemical resistance in acidic and alkaline environments. The test duration was up to 30 days at room temperature. The nature of the dependencies of chemical resistance on the exposure time for all samples is similar. Weight loss of the samples is observed in the initial period of exposure to an aggressive environment, and then the mass stabilizes. No visible changes in the surface state of the samples were observed.

For the composites obtained during testing, some basic physical and mechanical characteristics were determined, the indicators of which are given in Table 4.

Table 4. Characteristics of experimental casting composites.

No.	Indicator Name	Number of Composites				
		1	2	3	4	5
1	Density, g/cm^3	1.37	1.38	1.38	1.37	1.39
2	Heat resistance according to Martens, °C	159	142	156	151	164
3	Linear expansion coefficient 10^7	40.0	44.1	48.0	50.7	48.0
4	Temperature of destruction, °C	250	255	250	260	250
5	Water absorption, mg	37	-	34	39	38
6	Shrinkage, %	0.47	0.46	0.41	0.47	0.42
7	Beats volumetric electron resistance, Om	3.6	7.4	8.8	9.1	1.3
8	Beats on top Electron resist, Om/cm	7.4	9.5	6.2	8.7	7.6
9	Electric strength, MV/m	20	17.7	17.8	18.3	18.3

The degree of filling has a significant influence on the properties of composites, in connection with which the values of compressive strength, chemical resistance and degree of curing were obtained within a wide range of composition variation (by degree of filling). The conducted research allowed us to establish the limit of admissible anhydrite content, which should not exceed 15%. The introduction of filler above these limits is not expedient because the depth of the polycondensation reaction and the content of residual moisture no longer depend on the amount of anhydrite introduced. The determining influence of inorganic fillers (anhydrite, phosphogypsum, phosphorus slag and TPP ash) on the chemical resistance and physical–mechanical properties of composites has been revealed; the limits of component contents providing high chemical resistance (95%) to 30% hydrochloric acid and compressive strength (not less than 60 MPa) have been established. The optimal content of active fillers in composites (10–20%), which form crystalline hydrates in the process of curing of compositions, has been experimentally determined and statistically confirmed, which organizes the structure of the material and increases its chemical resistance and strength properties.

Since one of the main requirements for the composite material under development is its corrosion resistance, the data on the statistics in the medium of 30% HCl of both separate fillers and compositions based on them were obtained.

To eliminate the porosity of products and reduce shrinkage phenomena, composites containing a mixed polymer binder (phenol formaldehyde resin) were tested, which displayed close to the specified values of flexural strength and chemical resistance to 30% HCl.

When obtaining casting composites and products based on them in production conditions, a positive point was the absence of visible cracks, sinks, and defects; satisfactory removal from the mold; and workability in finishing to the specified dimensions.

Pilot production tests of the developed technology carried out at the scientific research institute Stromproekt JSC confirmed the correct choice of composites and technological parameters, as well as the prospects for the production of polymer–mineral casting composites.

4. Conclusions

In this study, based on optimal composites, casting compounds were synthesized and their physical and chemical, physical and mechanical, thermal, electrical and other operational characteristics were determined. Based on the presented data, the materials produced using the developed fillers and casting compositions have good strength, thermal and electrophysical properties, meeting the requirements for such materials.

This study revealed the influence of inorganic fillers on the chemical resistance and physical and mechanical properties of composites. It also established the content limits of components that provide high chemical resistance (95%) and strength (not less than 60 MPa):

- For the first time, the effect of hydrated calcium compounds on the curing process of filled phenol formaldehyde pouring compositions was established, which consists in binding of polycondensation water and increases the degree of binder curing.
- Using mathematical planning methods, the optimal content of active fillers (10–20 wt.%) was experimentally determined for compositions. These fillers form crystalline hydrates during curing, organizing the structure of the sample and enhancing its chemical resistance and strength properties.

This study examined the effect of hydrolytically active mineral substances on the process of the polycondensation of the polymer matrix, as well as the properties and degree of cure of composite materials. It is established that the process of binding of polycondensation water with a hydrolytically active filler enhances the properties of the cured composite, likely due to an increased adhesion of mineral fillers to the binder.

The research results may be used in the development and production of chemically resistant composite polymer–mineral materials using industrial waste as a base.

Author Contributions: Conceptualization, L.M.K. and S.O.A. (Saule O. Akhmetova); methodology, S.O.A. (Saule O. Akhmetova); software, S.O.A. (Sandugash O. Abilkasova); validation, L.M.K., S.O.A. (Sandugash O. Abilkasova), S.O.A. (Saule O. Akhmetova), M.S.S. and Z.E.S.; formal analysis, S.O.A. (Saule O. Akhmetova); investigation, L.M.K., S.O.A. (Sandugash O. Abilkasova), S.O.A. (Saule O. Akhmetova), M.S.S. and Z.E.S.; resources, L.M.K. and S.O.A. (Sandugash O. Abilkasova); data curation, L.M.K. and S.O.A. (Saule O. Akhmetova); writing—original draft preparation, L.M.K., S.O.A. (Saule O. Akhmetova) and S.O.A. (Sandugash O. Abilkasova); writing—review and editing, S.O.A. (Saule O. Akhmetova) and M.S.S.; visualization, Z.E.S.; supervision, L.M.K. and S.O.A. (Saule O. Akhmetova); project administration, L.M.K. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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