

Resource-saving polymer compositions for construction purposes

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Abstracts. The results of the use of building materials based on thermoplastic (polyvinyl chloride) and thermosetting (urea-formaldehyde) polymers of industrial waste as fillers instead of traditional ones that allow solving resource saving issues are presented in the compositions. Polyvinyl chloride materials of profile molded products with increased strength by 1.5–2 times were obtained by replacing 50% of the traditional “chemically precipitated chalk” filler with waste from water treatment of thermal power plants. The strength of heat-insulating foams based on urea-formaldehyde resin is increased 3 times by introducing only 0.2 m.p. carbonate water treatment waste per 100 m.p. resins in the binder. The effect is achieved through the implementation of the principle of "condensation" filling of polymer matrices. In polymers of different chemical nature, during filling, the mechanisms of matrix reinforcement associated with the activity of the surface of the filler particles are realized. They are proposed for the practical implementation of the formulation and production technology of profile and sheet materials, as well as heat-insulating foam plastic.

Key words: polyvinyl chloride, urea-formaldehyde foam, carbonate fillers, industrial waste.

1. Introduction

All polymer building products are based on a very small number of industrial polymers. At the present stage of economic development, Russia is experiencing a steady tendency of the advanced use of polymers in construction, due to their high technical and economic efficiency. Of course, it should be noted right away that polymer building materials are composite materials and therefore always multi-component systems, including a variety of different functional additives, depending primarily on the chemical nature of the polymers, as well as processing conditions and their operating conditions as part of building structures. Therefore, the polymer to create a composite material is selected taking into account all these factors, putting the properties of the polymer at the forefront [1].

By the degree of use of polymers as building materials, the most important of thermoplastic and thermosetting polymers can be distinguished. Among thermoplastic ones - it is polyvinyl chloride and polystyrene, and among thermosetting ones - epoxy polymers, polyurethanes and some others.

To reduce the contribution to the cost of products of the main component of polymeric materials, in particular polyvinyl chloride, as functional additives, it is promising to use various types of fillers, both natural and industrial waste, but without causing damage to the processing and operation conditions [2–4]. In our research, the task is to choose multifunctional fillers, leading to the growth of such problematic properties of PVC compositions as reducing the viscosity of melts, increasing thermal

stability, and increasing mechanical properties, in particular impact resistance [5-8]. We have developed general principles for the selection of fillers, given their dispersion, chemical nature and material composition [8], this is especially true of fillers from industrial waste. Mineral fillers in most cases reduce residual stresses and increase mechanical properties, such as impact strength, hardness. Some of them can reduce fire resistance, especially in plasticized PVC compositions, and heat resistance. [9-11]. Each of the fillers has its own characteristics, one of the most common mineral fillers is hydrophobized chalk.

The most basic requirement for particulate fillers is good compatibility with the polymer, including the polymer melt. Active fillers are most effective. In PVC compositions, the activity is determined by the conditions of the physicochemical interaction of the surface of the fillers and the polymer binder.

In compositions based on urea-formaldehyde resins [12], which is the subject of our studies with thermosetting polymers, the activity of the filler is understood as their chemical activity associated with the possibility of chemical reactions of the filler with the components of the polymer composition. It is a reaction of a carbonate filler with acidic resin curing catalysts. This reaction is accompanied by the release of carbon dioxide, so this method can be implemented in the production of gas-filled plastics based on urea-formaldehyde polymers. A modern thermal insulation material made of urea-formaldehyde resin is penoizol. In addition to urea-formaldehyde resin, it contains alkylbenzene sulfonic acid (foaming agent), phosphoric acid (curing catalyst) and water [13]. We suggest [14] the use of chemically active fillers to combine traditional air-mechanical foaming of foams with chemical gas formation. This allows us to

improve to some extent the low mechanical strength inherent in such foams, to reduce sorption moisture due to the open porosity of the structure of the foam and also provides an additional resource for increasing the foaming coefficient.

Thus, in the work as a filler of both PVC compositions and urea-formaldehyde resin during foaming, finely dispersed waste of chemical treatment of thermal power plants was used as a filler, the chemical basis of which is made up of calcium and magnesium carbonates to the maximum extent. In this case, the task is to assess the change in the technological and operational properties of the materials being developed taking into account the different chemical nature and conditions of the formation of the structure with the used polymer matrices.

2. EXPERIMENTAL PART

Since PVC compositions and urea-formaldehyde polystyrene have different functional purposes for use as part of building structures, various evaluation methods have been chosen to evaluate the effectiveness of their filling.

2.1 Rating of the properties of PVC composites

Filled PVC compositions are intended for the production of rigid PVC products; in this regard, the following methods for evaluating technological and operational properties are adopted: determining the melt flow index on a plastometer at 190 ° C and a load of 21.6 κ g, extruded for 10 minutes; determination of thermal stability by the time of the induction until the color of the indicator changes during the evolution of hydrogen

chloride during dehydrochlorination of PVC samples at 180 ° C; determination of tensile stress for extruded specimens on a tensile testing machine at a specimen strain rate of 100 mm / min.

2.2 Rating of the properties of urea-formaldehyde foams

To assess the quality of the foams, the following test methods were selected: determination of compressive force at 10% deformation of the samples; accelerated determination of sorption moisture within 24 hours at a temperature of (22 ± 5) C; measuring the coefficient of thermal conductivity of the foam; determination of the amount of carbon dioxide released as a result of the interaction of 1 g. filler with an excess of phosphoric acid.

3. Discussion

Experimental studies are devoted to the results of filling a polyvinyl chloride matrix and urea-formaldehyde resin. In the work, dehydrated carbonate waste (CW) was used as a filler. The effectiveness of this type of industrial waste is due to its chemical nature and high particle size. Dehydrated waste consists of 92% of magnesium and calcium carbonates (CaCO_3 и MgCO_3), in addition, it contains up to 2% silicon dioxide SiO_2 and up to 5% iron oxide Fe_2O_3 . It is a fine powder. Two samples were prepared from dehydrated carbonate sludge, namely immediately after drying and grinding, as well as after hydrophobization of 1% stearic acid. Their chemical composition is identical. It is known that the greater the dispersion of the chalk filler, the greater the degree of filling of the polymer, however, a tendency to

aggregation of particles may occur, especially if they have sizes less than 1 micrometer [15-18]. The results for determining the average particle size and the calculation of the specific surface are presented in table 1. The measurements were carried out on a laser analyzer in different environments: hydrophobized filler in ethanol, and the initial chemically deposited filler-waste in distilled water. From the presented data it follows that hydrophobization practically does not affect the dispersion of carbonate filler particles. The specific surface area of the filler particles is commensurate with the specific surface area of a conventional filler of hydrophobized chemically deposited chalk (4395 cm²/g).

Table 1. The size and specific surface of the carbonate filler particles

Indicator	Original CW		Hydrophobized CW	
	original	1 min. US	original	1 min. US
The average particle size, microns	15,80	13,65	15,05	14,60
Specific surface area, cm ² /g	2730	3162	2868	2956

In order to fill the basic PVC compositions of rigid shaped and molded products, instead of the traditional chalk, it was partially replaced by a hydrophobized dehydrated carbonate filler. The total amount of filler in the basic formulation of PVC compositions is 10 m.p. per 100 m.p. of PVC. The results of the change in the main indicators of PVC samples are presented in Table 2.

Table 2. The size and specific surface of the carbonate filler particles

Ratio chalk/ CW	Tensile strength, MPa	Melt flow rate, g / 10 min	Thermostability, min
100 мєЛ	43	2,6	114
70:30	41	2,0	111
50:50	48	1,8	106
30:70	44	2,0	109
100 KO	43	2,2	108

From these data it follows that the most optimal ratio of the components of chalk/CW by changing the complex of properties is in the range from 50:50 to 30:70. A significant increase in strength is observed, the thermal stability remains almost at the level, with a slight tendency to decrease. And the melt flow index completely satisfies the conditions for the extrusion of melts of PVC compositions. The observed increase in the viscosity of the melts (a decrease in the melt flow index) positively affects the reduction of technological shrinkage and increases the dimensional stability of the finished products. The marked decrease in thermal stability is due to the presence of iron oxide in the carbonate filler, which can stimulate the dehydrochlorination of PVC macromolecules upon exposure to high temperatures. This fact may lead to changes in the thermomechanical properties due to an increase in the number of mechanical links of structures of a fluctuation nature, which was discovered during the modification of PVC [19]. The increase in tensile strength by more than 20% compared with compositions filled with traditional calcium carbonate is explained, obviously, by the fact that solid highly dispersed, but not compatible with the polymer

substances in the range up to 10% vol., form bulk structures with hardened interfacial layer. The morphology of PVC particles specified in the synthesis is not completely destroyed during processing [20], but forms joint structures with a finely divided filler.

Thus, in PVC-based building materials, dehydrated carbonate filler may well be an effective substitute for traditional natural expensive fillers. To fill the urea-formaldehyde resin when creating the foamed material, a non-hydrophobized version of carbonate waste was selected, since the foaming technology is associated with aqueous colloidal dispersions.

Usually, in the technology for producing urea-formaldehyde foams, in particular, penoizol, a three-stage technology for producing samples is used: preparing a foaming solution with a curing catalyst (phosphoric acid), preparing a filler suspension in a urea-formaldehyde resin, and then combining the two reaction mixtures. However, in the technology of polycondensation filling adopted in this work, air-mechanical foaming is supplemented by the process of chemical gas formation as a result of the interaction of carbonate waste water treatment with a curing catalyst with the release of carbon dioxide.

The reactions responsible for gas formation are as follows:

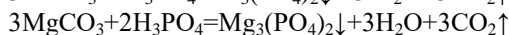
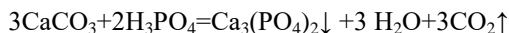


Table 3 presents the data on the analysis of gas formation during the interaction of 1 gram of carbonate fillers with a solution of phosphoric acid.

Table.3. Parameters of the chemical interaction of carbonates with phosphoric acid

Carbonate filler	Amount (CaCO ₃ +	Amount CO ₂ , ml	Amount t H ₃ PO ₄ , ml	Reaction time,

	MgCO ₃)			min
Chalk	99 %	10,2	0,45	1,8
CW	92 %	7,6	0,19	3,6

From these data it follows that both the rate and yield of carbon dioxide are higher when using chalk.

In this case, the formed insoluble phosphates of calcium and magnesium are finely dispersed fillers of the matrix of inter-pore septa from the urea-formaldehyde polymer, changing the morphology of the pore structure and the average pore size. First of all, mechanical properties are affected by both cellular structure of samples and the structure of the polymer matrix itself [21]. During filling, the density of the foams increases slightly, however, in the case of chemical filling, the increase is not critical and does not adversely affect the thermal conductivity of the foams. If unfilled penoizol has a density of about 8-10 kg/m³, then in the presence of fillers, the density increases (Table 4).

Table 4. Operational properties of urea-formaldehyde foam

Type and amount of filler in the foam per 100 m.p. of fesin	Density kg/m ³	Compressive strength, MPa	Coefficient of thermal conductivity W/(m·K)	Sorption moisture in 24 hours, %
Penoizol (without filler)	8	0,007	0,033	18
0,2 m.p. chemically precipitated	13	0,007	0,033	16

chalk				
0,2 m.p. dehydrated waste water treatment	22	0,016	0,032	9

The most high-density foams are obtained when using waste water treatment. In the case of the use of chalk, a rapidly proceeding reaction with the formation of CO₂ will lead to the fact that even before the gel formation of the foam mass, the released CO₂ manages to leave the composition of the reaction mass into the atmosphere, therefore, matrix strengthening is not observed and the strength remains at the level of unfilled polystyrene. Due to the intense chemical reaction in the medium of the formed cellular structure, residual shrink stresses appear, which lead to crack formation of the foam. When carbonate waste is used, favorable conditions are created both for the formation of a denser and stronger structure of the matrix of partitions, and for the formation of a cellular structure, in which, along with the open porosity characteristic of foams obtained by foaming, there are also closed pores due to the gas generation mechanism. Therefore, even an increase in density does not lead to an increase in the coefficient of thermal conductivity, that is, the heat-shielding properties are maintained at a high level. And the presence of closed pores and higher strength of the filled polymer explain an increase in strength by almost 3 times and a decrease in sorption moisture by 2 times.

4. Conclusion

The technological and operational-technical properties of building materials based on polyvinyl chloride and urea-formaldehyde resins filled with dehydrated fine-dispersed waste from chemical treatment of thermal power plants are studied. The possibility of using them to replace

traditional natural fillers, in particular chemically precipitated hydrophobized chalk is shown. Thus, taking into account the chemical nature and conditions of formation of the polymer structure, it was established:

1. In PVC compositions, it is advisable to partially replace the chalk with the waste in question in a hydrophobized form, which allows to increase the strength characteristics of hard materials.
2. In the composition of urea-formaldehyde foams, the use of carbonate waste without hydrophobization is effective, realizing the combination of two types of pore formation, namely, foam and gas formation in aqueous polymer systems. An increase in the strength of foams was revealed while maintaining their heat-shielding properties, which expands the possibilities of using this cheap polystyrene as thermal insulation in building structures.

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