

Construction compositions based on integrated binding of thermoplastic waste

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Abstract. The paper suggests a solution of the actual problem of processing polymeric municipal waste in building materials with a high complex of decorative and operational properties. The work is aimed at studying the processes of structure formation and hardening in the system "multicomponent thermoplastic binder - mineral filler" in the manufacture of polymer concrete products for construction purposes. During the research methods of infrared spectroscopy, differential thermal analysis, standard methods for determining the structure and properties of building products were used. As a result of the research, compositions of a complex thermoplastic binder including polymeric consumption waste (PET, PP) are proposed taking into account the volumes of their sampling at the waste sorting stations. An additive - a compatibilizer based on an ethylene-vinyl acetate copolymer with grafted reactive polar acrylate and epoxy groups, is also included. It was found that the introduction of a compatibilizer promotes the activation of the physicochemical interaction between the components of the polymer binder and between the polymer matrix and the mineral surface of the fillers. There was also an increase in the density and strength of the resulting artificial stone. The optimal content of the additive in an amount of 5% of the total mass of the complex binder was experimentally determined. With the introduction of a compatibilizer in smaller amounts, the effect of strengthening the flexural strength decreases, and when more compatibilizers are introduced, the strength of the products remains the same at bending, and the compressive strength decreases. Mechanisms of interphase interactions are proposed, taking into account the chemical-mineralogical composition of mineral fillers (based on carbonates and aluminosilicates). The possibility of participation of epoxide and acrylate functional groups in the formation of intramolecular and intermolecular hydrogen bonds with the formation of polyassociates was established. The revealed patterns of interaction make it possible to ensure the compatibility of weakly polar PET with other multitonnage thermoplastics, as well as compatibility of the complex polymer binder with mineral fillers. The management of the processes of structure formation in the studied systems makes it possible to obtain high decorative and operational parameters of the construction products.



1. Introduction

Waste treatment is one of the basic principles of the waste management hierarchy (in accordance with "Directive 2008/98 / EC on waste"). According to the normative reference book of ITS 15-2016, with an annual volume of waste production and consumption in the Russian Federation of more than 5 billion tons, polymer waste accounts for 1.07 million tons. In addition, 4.6-6% of polymers are selected from the total volume of solid municipal waste, which is about 0.6 million tons per year. Statistical data are given for 2015, the volume of waste grows annually, the best available technologies for recycling polymer waste, according to ITS 15-2016, have not been identified. The data cited point to the urgency of the problem of recycling polymer waste. The solution can be technologies for processing such wastes in material-intensive industries, including in the production of building materials, where polymers, due to their manufacturability, reduced density, high tensile strength and other valuable qualities, allow to obtain durable construction products with a high complex of decorative and operational properties.

2. The Goal

In the structure of polymer waste, according to ITS 15-2016, about 40% are polyolefins - polyethylene (HDPE, LDPE) and polypropylene (PP), and about 20% - polyethylene terephthalate (PET). PET waste is easily identified during sorting, and the amount of PET recovered from municipal waste often exceeds the amount of recovered polyolefins by two or more times (according to the data of Waste Management JSC). Although the remaining types of polymers (polystyrene, polyvinylchloride, etc.) are present in the total volume of polymer waste generated, it is much more difficult to extract today, mostly coming from inappropriate disposal of waste for disposal.

Therefore, the aim of the research presented in this paper was to prepare a binder for building compositions from polymer waste (a mixture of PET and PP thermoplastics) with the justification of the processes of structure formation and hardening in the "thermoplastic binder-mineral filler" system in the manufacture of polymer concrete composites for construction purposes (such as paving, facing, tactile tiles, curbstone, etc.).

3. Methods

PET and PP wastes were used as the main components of the polymer binder. Also, the compatibilizer "Etatilen EVA-g-GMA" (EVA) manufactured by "New Polymer Technologies" LLC was introduced into the binder. It is a modified copolymer of ethylene and vinyl acetate (content of vinyl acetate groups 22%) with grafted reactive polar acrylate and epoxy groups (degree inoculations of 2,3-epoxypropyl methacrylate 3%).

Mineral fillers of various chemical and mineralogical composition and specific surface S' , controlled by a computerized device PSH-12, were introduced into the polymeric binder. Among the carbonate fillers used: limestone flour (content of CaCO_3 not less than 90%, $S' = 1000 \text{ cm}^2/\text{g}$), chalk (content of CaCO_3 at least 95%, $S' = 6000 \text{ cm}^2/\text{g}$), microcalcite (CaCO_3 content not less than 98%, $S' = 8000 \text{ cm}^2/\text{g}$). In order to identify the optimum filling parameters, the degree of filling of the compositions was varied from 50 to 85% by weight, the content of the complex binder was suitably from 15 to 50% of the total weight of the composition.

Samples were made from polymer-mineral compositions: polymer waste was crushed and loaded into a melting-mixing unit, the mass melted at a temperature of 270°C . The compatibilizer was introduced into the composition by charging polymers into the melt with continuous stirring; further, a filler was added to the composition. The finished mixture was dosed and loaded into a mold. The rod samples were pressed at a specific pressure of 25 MPa for 2 minutes, with cooling by natural aging for 3 hours.

To study the composition and the presence of functional groups in the polymer binder, infrared spectroscopy was used. The spectra were recorded on the "Infralum FT-801" instrument. To monitor temperature transitions and thermal effects, a differential thermal analysis was performed on the

"Derivatograph Q-1500D" instrument. The physical and mechanical properties of the samples (tensile strength at flexure R_{tb} , compressive strength R , average density) were determined by standard methods.

4. Results

Modern research in the field of processing of polymeric waste [1-8] reveals many problematic points that require additional experimental and analytical work.

It is known that immiscibility is the key rule for polymer mixtures, while miscibility is an exception, but in recent decades, ways have been found to improve the compatibility of polymers with each other and with other components of the compositions [9-10]. Due to the study of the role of block copolymers in the interphase interaction of polymer mixtures, a concept of compatibilization has been developed. The compatibilizer changes the nature of the interfaces between phases, reducing the interfacial tension and contributing to the steric stabilization of the mixture [9]. An important problem for structural polymeric composites is their resistance to fracture, especially when impacted [9], which is enhanced by the combination of rigid (such as PET) and "soft" (such as polyolefins) thermoplastics.

In the present work, the binder for the building composition was a mixture of polymer waste (PET, PP), firstly, in order to simulate a real situation that takes into account the sample sizes of the polymers at the waste sorting stations, and secondly, in order to obtain structural strength (which PET provides) and increasing the resistance of construction products to shock loads (which provides PP). In order to activate the physico-chemical interaction between the components of the polymer binder and between the polymer matrix and the mineral surface of the fillers, the EVA compatibilizer was added to the composition of the building composition.

The obtained experimental dependences of the strength (Figures 1-4) of the samples on the filling parameters for compositions with and without a compatibilizer indicate the following regularities:

The presence of a compatibilizer in the compositions leads to a certain decrease in the compressive strength of the samples, but the bending strength is higher throughout the range of filling degrees, probably due to homogeneous plastic deformation of the phase of the compatibilizer [11]. This effect is realized when the content of the compatibilizer is 5% of the total mass of the complex binder (in the replacement of the PP part), and when the compatibilizer is introduced in smaller amounts, the effect of strengthening the bending strength decreases; With the introduction of more compatibilizers, the strength of the samples remains the same when bending, and the compressive strength is reduced.

The IR spectrum of the individual EVA compatibilizer confirms the presence of reactive epoxy groups in it, a strong epoxy and ether bond absorption band at $1240-1250\text{ cm}^{-1}$, and a weak absorption band of the epoxy group at 870 cm^{-1} [12]. It is known that epoxide cycles at a temperature of the order of $150-180\text{ }^{\circ}\text{C}$ are able to open and participate in chain extension reactions. In addition, both epoxy and acrylate functional groups are active in the formation of intramolecular and intermolecular hydrogen bonds with the formation of polyassociates. The formation of polyassociates through hydrogen bonding, as well as intramolecular hydrogen bonds, is confirmed by the appearance on IR spectra of compositions containing EVA, a strong broad absorption band at $3420-3590\text{ cm}^{-1}$.

It was found that the average density of the samples naturally increases with the degree of filling of the compositions, however, when the binder content in the composition is less than 20%, decompaction is observed, indicating a lack of a binder. The dependences of the strength characteristics (Figures 1-2) of the samples on the binder content in the composition are extreme, in general, the highest values of strength parameters are recorded in the range of the filling degrees of 60-70% by weight of the composition, regardless of the type and specific surface of the filler.

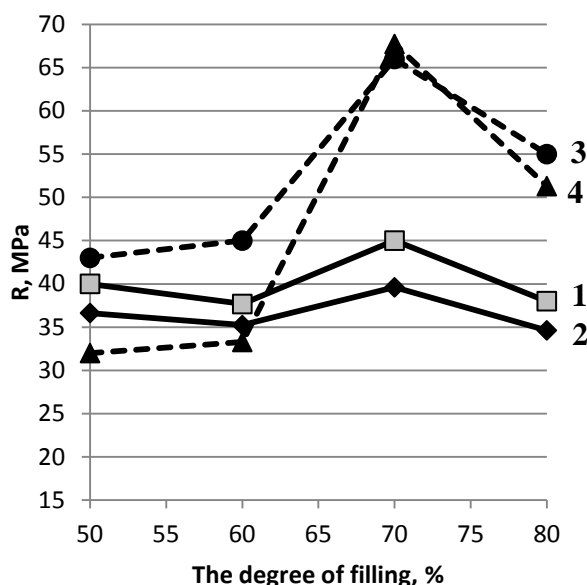


Figure 1. Dependence of compressive strength of samples of the filling degree of the composition.

The compositions include as a binder: 1, 3 - PET, PP in a ratio of 70 : 30 by weight; 2, 4 - PET, PP, EVA in the ratio 70 : 25 : 5 by weight; as a filler: 1, 2 - limestone flour; 3, 4 - clay with $S' = 1000 \text{ cm}^2/\text{g}$.

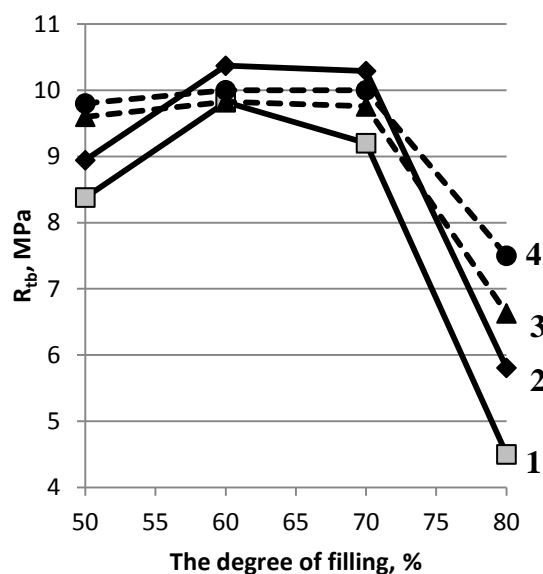


Figure 2. Dependence of the ultimate strength at bending of samples on the degree of filling of the composition.

The dependences of the strength characteristics of the samples on the specific surface of the filler (Figures 3-4) are ambiguous. With an increase in the degree of dispersion of carbonates, strength parameters increase, and for aluminosilicates, an inverse relationship is observed. It should be noted that the polarity and high reactivity of calcium carbonate causes a number of its disadvantages when using polymeric composites as filler, including embrittlement of polyethylene during filling [13-14], as well as a weak strengthening effect compared to other excipients due to the trigonal crystal structure [14]. At the same time, carbonate fillers are common and available, so it is advisable to develop ways to improve their compatibility with thermoplastics, which is solved by the use of elastic copolymers of ethylene, which in the test compositions is an EVA compatibilizer. In the case of filling with aluminosilicates, it is likely that the excess surface energy of clay particles of nanoscale level leads to their aggregation and loss of their unique properties at high degrees of filling, which can be solved by their preliminary organomodification to produce partially exfoliated and intercalated structures [15-16].

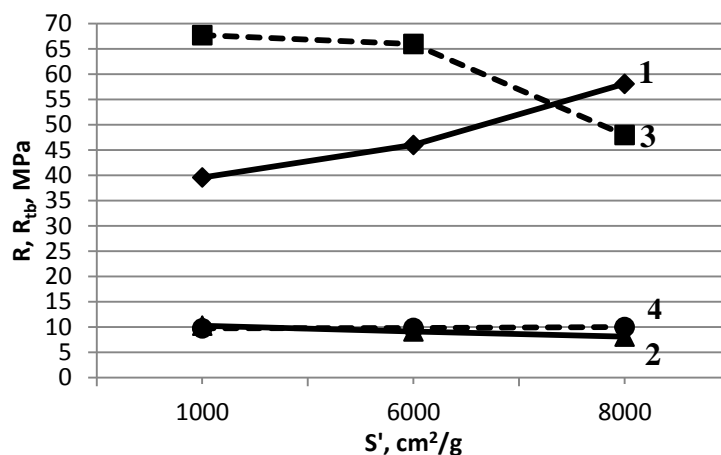


Fig. 3. Dependence of the compressive strength (1, 3), the ultimate strength (2, 4) of specimens on the specific surface of the filler. The compositions include as a binder PET, PP, EVA in the ratio 70 : 25 : 5 by weight; as a filler 1 - carbonates; 2 - aluminosilicates.

Thermal analysis of the studied compositions revealed the following patterns. On the derivatograms of individual polymers, the endoeffects of melting are recorded: for PET in the range 235-265 oC with a maximum at 255 oC, for PP in the range of 130-170 oC with a maximum at 165 oC, for EVA in the range of 40-110 oC with a maximum at 75 oC. On the derivatogram of the complex binder, the endoeffect of melting is not expressed, probably due to the "blurring" of the melting region. In all cases, melting is accompanied by a horizontal course of thermograms.

Insignificant losses in mass begin for all investigated compositions, including filled, with 230 oC. Sharp kinks on thermograms, indicating intensive losses of mass, which is accompanied by exothermic effects of thermo-oxidative destruction of polymers on derivatograms, are recorded with maxima at 370 °C for unfilled and 380 °C for filled compositions without a compatibilizer. In compositions containing the EVA compatibilizer, the maximum effect of the thermal oxidative destruction is shifted to a temperature range of 400 °C for unfilled and 415 °C filled with carbonates, and in compositions filled with aluminosilicates - by 440 °C. These dependencies indicate a greater thermal stability of EVA-containing formulations.

5. Conclusions

1. The presence of a compatibilizer in the composition of a binder on the basis of waste polyethylene terephthalate and polypropylene promotes the growth of the strength of polymer composites in bending. The activation of interphase interaction in compositions containing a compatibilizer, through the possible formation of polyassociates through a hydrogen bond, as well as intramolecular hydrogen bonds is shown. The presence of the compatibilizer in the composition contributes to an increase in the thermal stability of the composites.
2. An increase in the strength of building composites with an increase in the specific surface area of carbonate fillers was established, provided that a compatibilizer is present in the composition. Excess surface energy leads to aggregation of the filler particles and a certain decrease in the strength characteristics of the composites as the specific surface area of the filler is increased, in the case of aluminosilicate fillers.
3. It was found that the highest values of density and strength parameters of composites are recorded with a binder content in the range of 30-40% by weight of the composition, regardless of the kind and specific surface of the filler.

4. The involvement of polymer waste in the production of building materials can significantly reduce the environmental impact of man-made environment in the conditions of continuing irreversible reduction of natural resources.

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