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Carbonate-containing precipitate of sugar production from sugar beet as filler for polymer concrete

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Abstract. Polymer concrete is widely used in economic activities and construction. They consist of a polymer resin (polyester, phenol-formaldehyde, epoxy, etc.) and various fillers, the content of which can reach 85%. Many industrial wastes according to their physical and chemical properties can be used as substitutes for traditional materials in construction. One of such waste is the carbonate-containing saturation precipitate, which is formed during the production of sugar from sugar beet (CCP). The possibility of using CCP as filler for polymer concrete is investigated in the paper. Experimental samples with different contents of thermally modified precipitate and quartz sand were made. It is shown that when the precipitate is added to the mixture in an amount of up to 20%, the results of the compressive and flexural strength measurements do not differ from those samples which are made on the basis of quartz sand. Then the strength begins to decrease, and after 28% becomes lower than the control samples. Therefore, we came to conclusion that 15-20% of the precipitate to the mixture should be considered a rational amount of the additive.

The density of the experimental samples increases insignificantly with the addition of modified CCP due to the more intensive chemical interaction of the resin with carbon in the CCP composition when using pure quartz sand is used.

1. Introduction

The discovery of polymeric materials and the development of ways of manufacturing products based on them became a breakthrough in science and materials science in its time. They have a lot of valuable qualities: low weight, plasticity, flexibility and ease in using. They also have water resistance and resistance to chemical influences, high heat and sound insulation properties [1, 2]. So, for example, Carbon fiber / epoxy composite materials have a density of 1.45-1.6 g / cm3 with a tensile strength of 1.06–1.5 GPa, while steel has a density of 7.8 g / cm3, with a tensile strength of only 1.03 GPa. The fatigue strength of the most of the metallic materials from 30% to 50% of the tensile strength, while the fatigue strength of the carbon fiber / polyester composite material is 70% to 80% of its tensile strength [3].

Therefore, it is not surprising that products based on polymers are of great variety and are used universally.

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Polymer concrete is widely used in economic activities and construction. They consist of a polymer resin (polyester, phenol-formaldehyde, epoxy, etc.) and various fillers, the content of which can reach 85% [4–6].

Various natural materials are traditionally used as a filler (Table 1) [1, 7, 8].

Chemical Family	Examples				
Inorganic Oxides	Glass, MgO, SiO ₂ , Sb ₂ O ₃				
Hydroxides	$Al(OH)_2, Mg(OH)_2$				
Saltz	CaCO ₃ , BaSO ₄ , CaSO ₄ , Phosphates				
Silicates	Talc, Mica, Kaolin, Wollastonite, Montmorillonite, Nanoclay,				
	Feldspar, Asbestos				
Metals	Boron, Steel				
Carbon-Graphite	Carbon fibers, Graphite fibers and flakes, Carbon nanotubes				
Natural Polymers	Cellulose, Wood flour and fibers, flax, cotton, starch				
Synthetic Polymers	Polyamide, Polyester, Aramid				

Table 1. Chemical Families of Fillers for Polymers

In spite of the fact that such materials as: sand, crushed stone, chalk are not deficient in the environment, their extraction from natural sources harms ecosystems. While extracting any natural resources destruction of natural landscapes takes place inevitably. Disturbance of soil cover, emissions and noise pollution are connected with the use of trucks. Therefore, the search for ways to reduce of the building industry demands in natural materials is an urgent task.

Many industrial wastes according to their physical and chemical properties can be used as substitutes for traditional materials in construction [9–16]. One such waste is the carbonate containing saturation precipitate, which is formed during the production of sugar from sugar beet (CCP). This is a large-tonnage waste, intensively formed in agro industrial regions. A small part of it is used for various types of economic activity; the bulk is traditionally transported to industrial waste landfills.

Many authors have carried out research on its use as fillers in the manufacture of paint and varnish products and building materials [17–19].

We have proposed that CCP can be used as filler in the production of polymer concrete as a substitute for natural quartz sand.

2. Materials and methods

The analysis of peculiarities of the chemical composition and structure of the CCP samples has been carried out by using the scanning electron microscope of high resolution «TESCAN MIRA 3 LMU».

Pilot samples of polymer concrete were manufactured according to the instructions for the technology of preparation of polymer concrete and products made of them [4] and factory instructions for the resin used.

For the manufacture of polymer concrete samples, a polyester resin AROPOL S 280 E and accelerator for the resin curing process Butanox (commercial name) were used.

Compression strength of the experimental samples was determined on a hydraulic laboratory press PSU-10.

The Vertex 70 FTIR spectrometer was used for infrared (IR) researches.

3. Results and discussion

A saturation precipitate, calcined at a temperature of 600° C for 30 minutes was used in the work. During heat treatment cracking of the initial aggregates takes place and the CCP has a particle size of 5–40 µm. The true density of the material is 2720 kg / m3 [17]. The main chemical component of the obtained material is calcium carbonate (up to 98%), there is a small amount of carbon (about 2%).

The elemental composition of CCP and modified material according to the results of energy dispersive analysis is presented in Table 2.

Element	0	Ca	С	Mg	Si	Р	Al	
№ of analyzed section	ССР							
29	41,7	27,2	23,6	2,9	2,2	1,3	1,1	
30	50,4	26,3	18,2	2,4	1,6	0,8	0,3	
31	45,3	33,9	15,4	2,5	1,5	1,1	0,3	
32	43,6	28,6	20,8	3,1	1,7	1,8	0,4	
	modified CCP							
26	42,9	35,1	12,8	4,2	2,4	1,8	0,8	
27	44,4	37,9	7,6	4,3	3,6	1,6	0,6	
28	43,6	40,4	11,4	2,7	1,1	0,8	-	

Table 2. Elemental composition of initial and thermally modified CCP, wt. %

It has been established that thermo-modified CCP is a nanocomposite material, since a nano layer of amorphous carbon creates an inhomogeneous cover whose protrusions and cavities are active centers (Figures 1, 2) [17, 20].



Figure 1. The sizes of the protrusions and scales covering the surface of the modified CCP



Figure 2. The micrograph of the surface of the modified CCP particles

Amorphous carbon, included of the modified CCP, has chains of different lengths in its composition: thus, as a result of X-ray diffraction researches, compounds with C_8 , C_{70} , and C_{80} chains were found, what can suggest the presence of unsaturated compounds. The presence of unsaturated bonds is a positive factor, since such compounds can come into partial interaction with the resin during polymerization.

Researches were carried out using IR spectroscopy to confirm this assumption. It was found that in the carbon included in CCP, there are molecular vibrations at frequencies of 770, 1070 and 1600 cm⁻¹, specific for the following chemical bonds: [= C = C =] (frequency range from 1500 to 1600 cm⁻¹), [C-O] (frequencies from 850 to 1200 cm⁻¹), [CC] (frequencies from 900 to 1100 cm⁻¹, 800–900 cm⁻¹.

To evaluate the possibility of using a modified saturation precipitate during the manufacturing polymer concrete experimental samples were made. The content of resin and hardener in all samples was the same, 21% and 0.5%, respectively, the total mass of the filler was 78.5 wt. %. As the filler quartz sand (module size 2,2) and thermally treated CCP in different ratios were used.

The temperature at which mixing of the samples was 20°C. Further the system was self-heating up to a temperature above 100°C due to the exothermic polymerization reaction. After mixing the components, the mixture was poured into molds and left for hardening in air for a day, after which it was subjected to compressive and flexural strength tests.

Microphotographs of sections of experimental samples presented in Figure 3, allow evaluating the internal structure of polymer concrete. It can be seen that the sample with the addition of CCP in the amount of 20 wt. % (b) has no noticeable differences from the control one (a).





Figure 3. Microphotographs of sections of samples of polymer concrete with different ratio of fillers: a – without CCP, b – sample containing 20 wt.% of modified CCP

Figure 4 shows the results of samples researches on compressive and flexural strength.

It is seen that when the precipitate is added to the mixture up to 20%, the strength in both cases does not differ from samples made on the basis of quartz sand. Then it begins to decrease, and after 28% it becomes lower than the strength of the control samples. Consequently, a rational amount of the additive will be 15–20% of the precipitate to the mixture. Figure 5 shows a graph of dependence of density of experimental samples on the amount of precipitate added. It can be seen that the density of the experimental samples increases insignificantly with the increase in the precipitate additive.



Figure 4. Dependence of compressive (a) and flexural strength (b) on the amount of precipitate added





It is known that micro- and carbon nanostructures have a positive effect on the properties of polymer products [21–23], so the increase of density is presumably due to the more intense chemical interaction of the resin with carbon entering in the composition of CCP than when using pure quartz sand. Growth of the overall strength of products is not observed.

On the basis of the conducted experiments it can be concluded that the saturation precipitate, modified by heat treatment, can be used as filler in the production of polymer concrete so the strength characteristics of the obtained products are not worse than the control samples made with use of quartz sand.

Conclusion

Thermally modified CCP is a nanocomposite material, possessing a number of qualities кальция calcium with micro- and nanoparticles of carbon that make it a valuable secondary raw material for use in construction and the production of polymer products. The conducted researches made it possible to establish that polymer concrete, manufactured with the addition of modified CCP in an amount up to 20%, is not worse in quality according to the of compressive and flexural strength of control samples made on the basis of pure quartz sand. The density of the experimental samples increases insignificantly with the addition of modified CCP due to the more intensive chemical interaction of the resin with carbon included in CCP when using pure quartz sand.

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