Production of Corrosion-Resistant Polymer Concrete Reinforced with Various Fibers

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Abstract. Polymer concretes (PC) unlike common concrete (produced based on cement, as cohesive material) are notable for the high durability on compression – 50…90 MPa, and especially, on tension – 6…10 MPa, with unique corrosion resistance. However, they are also associated with such negative properties, such as high deformability, creep. Because PC works well on tension, their application is perspective for production of shock resistant construction material, but for this, it is necessary their strengthening by additional reinforcing mechanisms. In addition, because of the differences in the durability and deformability on compression, as well as on tension, is important that stipulates the necessity of reinforcement of PC tensile and bent elements. This work presents and discussed the reinforcement of PC by hybrid fibers. The major goal of this work is the production of such hybrid fiber-reinforced polymer concrete (HFRPC) with high durability on tension and high shock resistance that preserves these properties in conditions of aggressive environments. The primary cohesive methods are unsaturated polyester resins, as polymers. The fiber reinforcements (course and fine) are primarily basalt and steel fibers, andesite selected for their chemical resistance and durability the technological parameters for the production and processing of nano and ultrafine dispersive powders from the rock using vibration and planetary mills, and the physical and mechanical properties of these concretes are presented and discussed. The data on the corrosion resistance coefficient of these processed PC (corrosion resistance coefficient - $K_{cr}$, diffusion coefficient of aggressive liquids - $K_d$) is also presented and discussed.

1. Introduction

For the recent period, more and more publications are appearing related to PC, in particular, to specific concretes based on polyester resins. Various fillers are proposed for the production of such concretes, including fillers from industrial wastes [1, 2, 3]. It is considered that various fibers, both artificial and natural, enhance PC [4, 5]. The properties of a new type of concrete are compared with ordinary (cement) concrete [6]. The chemical resistance of PC on the polyester resin is studied [7]. The acquaintance with these and other literary sources allows to state that the effect of dispersed reinforcement of PC by hybrid fibers (e.g., basalt and steel) has not been thoroughly studied so far.

The possibility of such a three-dimensional reinforcement of polyester resins can be judged from the figure below (Figure 1).
A specific issue is to study the chemical resistance of the obtained HFRPC in concrete corrosive medium - in groundwater sulfate waters and in the air in the presence of hydrogen sulfide. Such aggressive environments are often encountered in the construction and operation of buildings.

To date, there is insufficient data on a behavior of PC under a tensile strained state in aggressive media. The data available in the literature refer to a testing of PC on compression and bending. The purpose of real work was to prove the advantage of PC working on tension over cement concrete and to determine the coefficient of resistance in two environments - 5% $Na_2SO_4$ and 1.5% $H_2SO_4$ to change the strength of the material on tension. The choice of the type of aggressive media and the purpose of their concentrations are based on the following considerations: as an experience of construction and exploitation of underground structures show, the most common and dangerous corrosive environments are sulfate and hydrogen sulfide corrosion. In groundwater, the concentration of sulfate - ions can reach 20 000 ... 25 000 mg / l, and the content of hydrogen sulfide in the air can be $> 0.03$ mg/m$^3$.

Such concentration of sulfate - ions causes intense corrosion of high density concrete, even not mentioning the resistance of low density concrete. As to the above mentioned concentration of hydrogen sulfide in the air, such concentration, at the relative humidity of air $\geq 95\%$, causes an appearance of thionic bacteria, namely, Th thioparus and Th thiooxidans, which promote a formation of sulfuric acid from hydrogen sulfide. Sulfuric acid of low concentration is very dangerous for concrete. Under these conditions, at both – sulfate and acid corrosion, concrete structures are quickly out of order, big material resources are spent for their repair and the restoration work carried out is practically unsuccessful. Therefore, based on the preliminary mining-geological and hydro-geological study of the construction site, it is necessary to develop compositions of PC capable to resist to destructive effects of the aggressive media on a structure.

Thus, the goal of this work was to obtain PC with hybrid discrete reinforcement, to study its physical, mechanical properties, chemical resistance in sulfate and hydrogen sulfide media, and to study the diffusion process occurring at the material contact with these liquid media.

**Figure 1.** Three-dimensional discrete reinforcement of polyester resin
2. Materials and methods

A) The components of HFRPC

To produce HFRPC, the following substances were used: a) low reactivity unsaturated polyester resin on orthophthalic acid with a low peak exotherm and low volume shrinkage. Akcobalt 6% (cobalt 2-ethylhexanoate mixture) and Akperox A1 (Methyl Ethyl Ketone Peroxide-MEK) were the curing agents of resin. The polyester resin was modified with a gel-like polysulfide; b) resin filler - andesite in the form of a mixture of coarse (0.15-2 mm) and fine-grained (<0.15 mm) fractions; c) aggregate in the form of granite crushed stone with a size of 10-12 mm; d) basalt and steel fibers, as the means for discrete reinforcement (basalt fiber - 2.1 cm long, linear density 525 tex., the diameter of an elementary fiber - 15.1 µ, the length of steel fiber with hook end - 3.5 cm, diameter - 0.63 mm (Figure 2).

![Steel (a) and basalt (b) fibers](image)

B) Production and testing the samples

From the above listed HFRPC components, most are precursors. A coarse-grained fraction of andesite powder was obtained by processing andesite sulfur in Retsch crusher BB 200 jow. The fine-grained fraction was produced at first on Vibratory Disc Mill RS 200, and then in a PULVERISETTE 7 premium Line planetary mill. In this fraction, a portion of grains with sizes 100...200 nm was 5%. Figure 3 shows a principle of an action of the micro-mill: the material is grinded by grinding balls in a grinding bowl. Centrifugal forces arose from a rotation of the bowl around its axis and a rotation of a backing plate, effect on the material. A bowl and a backing plate rotate in opposite directions. Therefore, the centrifugal forces act alternately in one direction, then in the opposite direction. As a result, the balls moving along the inner wall of the bowl show a frictional effect, and striking against the opposite wall – show a shock effect on the grinded material. The method of dry grinding was used. A bowl and balls made of zirconium oxide were selected as a grinding bowl and grinding balls. The grinding bowl had a capacity of 80 ml. The diameter of the grinding balls is 3 mm. The number of balls per bowl is 230-250. Mass ratio of balls to the pieces of andesite is 10:1.
The specific weight of the produced powder is 2.78 gr/cm³, powder density – 1.55 g/cm³.

The composition of HFRPC (in mass parts): broken granite of a fraction 10-12 mm - 54-56; andesite powder - 34-35; polyester resin modified by polysulfide - 10-12; resin hardenable system and plasticizer 1.4-2.0. The consumption of basalt and steel fibers was, accordingly, 3 kg and 15 kg, respectively, per 1 m³ of HFRPC.

To cast the samples, the mixtures in small amounts were prepared using a laboratory mixer. The modified polyester resin was firstly loaded into the mixer, and then, at the continuous operation of the mixer, the filler was added to the resin hardener. After that, the aggregate was loaded into the mixer with basalt and steel fibers. Such a separate scheme proved to be convenient for the preparation of HFRPC because the polyester resin, compared to other resins (e.g. furan), is a binder with less and regulated exothermicity.

All types of the test samples were cast into silicone molds obtained from the models made of polylactide (PLA) or acrylonitrile-butadiene-styrene (ABS) plastics. The models were prepared on a 3D printer.

The test samples of HFRPC were: a) cylinders with a diameter of 15 cm and a length of 15 cm to determine the ultimate strength for axial tension; b) cylinders with a diameter of 10 cm and a length of 10 cm - to determine the resistance to impact; c) disks with a diameter of 5 cm and a thickness of 3 mm - to study the diffusion characteristics of HFRPC (Figure 4).
While testing the cylinder samples for tension, a compressive load was applied along the diametrical plane. The test was carried out using a press to determine the strength of materials on compression. The samples were installed on the press so that the plates of the press adjoined two mutually opposite generators (Figure 5). The direction of the compressive force coincided with the diametric plane of the sample, and the sample axis passed through the center of the hinge of the press plate. The load was continuously increasing and uniformly at a rate of 1.5 kgf/cm² in 1 second until the sample was destroyed. The value of the tensile strength on the axial tension was calculated by the formula \[ \sigma_t = \frac{2P_{max}}{\pi dl} \], where \( P_{max} \) - the breaking load, kgf; \( d \) - the diameter of the cylinder, cm; \( l \) - the length of the cylinder, cm.

![Figure 5. The test setup for axial tension](image)

The resistance to HFRPC shock was determined on a special device - copra (Figure 6). The sample was installed at the guides of the copra plane. The weight suspended on a certain height from the surface of the sample was repeatedly dumped onto it until the first crack appeared. The mass of the weight is 2 kg, the maximum dropping height - 90 cm. The total work spent on a breaking the sample, per unit volume, characterizes the impact resistance of the material (kgf.cm/cm³). This method does not have a claim on to determine the stresses occurred during the impact of the load on the material. It was used to obtain the comparative data on the resistance of the materials (in our case, cement concrete and HFRPC) to a shock.

![Figure 6. Impact resistance test coper](image)
As the criteria for evaluation of suitability of HFRPC in aggressive environments, the $K_{cr}$ of the material and the $K_d$ of liquid media in PC were adopted. $K_{cr}$ is the ratio of the retained short-term strength of the material after an effect of aggressive media on its initial short-term strength. Unlike the available literature data on $K_{cr}$ obtained by testing of the samples on compression and bending, in this work, the corrosion resistance was evaluated by tensile strained state of the material. $K_d$ was determined by the sorption method, the essence of which is in the registration of the velocity of liquid absorption in plane samples - disks placed in an aggressive medium. Fick’s differential equation of diffusion determines an accumulation of substance by a sample at a certain point as a function of time. $K_d$ in cm²/sec was determined by the formula $K_d = 0.0494 \frac{\sigma^2}{\tau_0}$, where $\sigma$ is the thickness of the sample, cm; $\tau_0$ - the time for which the sample mass increases to 0.5 $M_{max}$, sec ($M_{max}$ is the mass of the testing sample at steady sorption balance, g).

3. Results and discussion

The petrographic study of andesite showed that it is formed by minerals amphibole, pyroxene, feldspar, quartz and volcanic glass (Figure 7). In the samples of andesite sulfur, pyroxene and amphibole predominate determining the high quality of andesite, as a filler of HFRPC. The average chemical composition of andesite, in %: $SiO_2$ - 59; $Al_2O_3$ - 17; $CaO$ - 6; ($FeO + Fe_2O_3$) - 7; ($Na_2O + K_2O$) - 5; $MgO$ - 3; ($TiO_2 + MnO + P_2O_5$) - 1; $H_2O$ - 1.

Figure 7. Microscopic study of rock-forming minerals, x40

As the preliminary experiments showed, andesite powder breaks the homogeneity of the resin, and therefore, its mechanical strength decreases. At further filling of the resin, the strength increases and, at a certain content of the solid phase, reaches a maximum exceeding the strength of pure resin. This optimum amount of andesite corresponds to the conversion of the resin into a state of thin oriented films. The strength of such a material is determined by the forces of sticking the resin to the surface of the filler to a greater extent than the cohesive forces of adhesion of the resin itself. With an excessive amount of andesite in the mixture, the resin becomes insufficient for wetting and binding of individual solid particles and the mechanical parameters are sharply reduced. As it turned out, unlike the PC on furan resins, for HFRPC on polyester resin, the chemical interaction of andesite with the resin does not play a decisive role in the strength of the material. The results of studying the effect of the quantitative content of a polyester binder on the compressive and tensile strengths are given in Figure 8.
The initial short-term strength of HFRPC on tension is approximately 2 times higher (14...17 MPa) than the initial short-term strength of PC on the base polyester. The value of strength on compressing (75...95 MPa) is also high. It turns out that $H_2SO_4$ is more aggressive than sodium sulfate. $K_{cr}$ of the material in both media under compression is always significantly higher than at stretching tension (Figure 9).

Dependence between the decrease of the short-term strength of HFRPC and its release time in aggressive media (Figure 10) can be expressed by the following function: $K_{cr} = a \tau^b$, where $a$ and $b$ are constant coefficients, depending on the composition of HFRPC and aggressive medium, $\tau$ is the time. Processing of experimental data gives the values $\ell_{ga}$ and $b$ presented in Table 1.
Figure 10. Dependence between $K_{cr}$ of HFRPC and its release time in 5% $Na_2SO_4$ and 1.5% $H_2SO_4$

Table 1. The values of coefficients $\ell ga$, and $b$

| Medium          | $\ell ga$ | $b$  |
|-----------------|-----------|------|
| 5% $Na_2SO_4$   | -0.023    | -0.033 |
| 1.5% $H_2SO_4$  | -0.051    | -0.036 |

The equations of the time dependence of the strength of HFRPC operated in these media, accordingly, are $\ell gK_{cr} = -0.023-0.033\ell g\tau$; $\ell gK_{cr} = -0.051-0.036\ell g\tau$. Here, a testing time $\tau$ is shown in months. The calculated values (Table 2) $K_{cr}$ at $\tau$ equal to 12 months ($K_{cr}^{12}$) and 200 months ($K_{cr}^{200}$, supposed time of exploitation) are the following:

Table 2. The values $K_{cr}$ depending on the operating time.

| Medium          | $K_{cr}^{12}$ | $K_{cr}^{200}$ |
|-----------------|---------------|---------------|
| 5% $Na_2SO_4$   | 0.87          | 0.73          |
| 1.5% $H_2SO_4$  | 0.81          | 0.72          |

Diffusion testing of HFRPC in aggressive media (Table 3) shows that $K_d$ of the proposed HFRPC is of the same order ($10^{-8}$ cm$^2$/sec), as in modern nano-structured PC [8, 9]. These results open the way to determine the transit time due to the diffusion of the aggressive liquid through the HFRPC for the timing of the penetration of the liquid through the polymer films. But the duration of penetration of the liquid through the protective layer of HFRPC does not characterize the time of the beginning of corrosion of steel fibers. To excite the corrosion process, it is necessary to have an electrolyte film on the surface of the reinforcing element. If the conditions for starting and development of corrosive processes occur, as experiments have shown, basalt fibers are more stable in the liquid media than the steel fibers.

Table 3. The values $K_d$ of aggressive media in HFRPC

| Medium          | $K_d$, cm$^2$/sec after holding, month |
|-----------------|---------------------------------------|
|                 | 6          | 12          | 18          |
| 5% $Na_2SO_4$   | 0.11 $\cdot 10^{-8}$ | 1.19 $\cdot 10^{-8}$ | 1.66 $\cdot 10^{-8}$ |
| 1.5% $H_2SO_4$  | 0.41 $\cdot 10^{-8}$ | 2.02 $\cdot 10^{-8}$ | 2.31 $\cdot 10^{-8}$ |

The results of studying the shock resistance of cement concrete and HFRPC – the object of the study show that reinforcement of concrete with hybrid fibers (basalt, steel) is an effective way to produce a material with high shock resistance. The test results for shock resistance are as follows: common (cement) concrete - 3.8 kgf.cm/cm$^3$; HFRPC - 38.4 kgf.cm/cm$^3$. The proposed material showed approximately 10 times more resistance to shock loads.

Table 1. The values of coefficients $\ell ga$, and $b$
Table 4 shows the effect of aggressive media on the shock resistance of HFRPC after its curing in aggressive media for one year.

Table 4. Shock resistance of materials after the impact of aggressive media

| Medium        | Shock resistance, kgf.cm/cm$^3$ |
|---------------|---------------------------------|
|               | Cement concrete | HFRPC             |
| 5% Na$_2$SO$_4$ | 0.05              | 31.2              |
| 1.5% H$_2$SO$_4$ | 0.01              | 28.3              |

4. Conclusion

HFRPC on the base of unsaturated polyester, andesite filler with micro-,nano sized, basalt and steel fibers grains are obtained. As a result of 1.5 - year exposure of the HFRPC samples in 5% sodium sulfate and 1.5% sulfuric acid, the chemical resistance coefficient of the material versus time has been found with a form of a power function. It has been determined that HFRPC of a given composition is more sensitive to the influence of aggressive media under the tensile strain state. The revealed dependence $K_{cr} = f(t)$ allows conditionally predicting the resistance of HFRPC for a long period. It is assumed that after approximately 17 - year operation of the material in the sulfate medium, $K_{cr}$ will be 0.79, and in the sulfuric acid medium - 0.71. $K_d$ of the proposed HFRPC is of the same order ($10^{-8}$ cm$^2$/sec), as in the modern nano-structured HFRPC. The values $K_d$ of the liquid media in HFRPC are necessary for the correct choice of continuous or discrete armature in order to produce shockproof HFRPC. In this regard, it should be noted that in these aggressive media, basalt fiber is less susceptible to corrosion than the steel fiber.

Acknowledgments

This work was supported by the Shota Rustaveli National Science Foundation (SRNSF) [Grant #217292, Title: “Hybrid fiber-reinforced polymeric composites with matrix strengthened nano,-ultra powders”].

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