Journal of Engineering Science | | *Vol. 2, no. 1 (2018), pp. 76 - 80*
Fascicle *Architecture, Civil and Environmental Engineering* *ISSN 2587-3490*
Topic *Civil Engineering* *eISSN 2587-3504*

OPERATING PROPERTIES OF EPOXY COMPOSITIONS UNDER THE INFLUENCE OF ABSORPTION-ACTIVE ENVIRONMENT

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Received: February, 10, 2018
Accepted: May, 29, 2018

Abstract. It was researched the influence of the multifraction mineral frame, that includes zeolite and furfural on the properties of different filled compositions. Such compositions are intended for the use under the influence of water and oil products and other agents (in the elements of structures connected with the maintenance of transport). Whereas it is practically impossible to conduct long-term testing in such inhomogeneous environments, the properties of the compositions were measured after exposure separately in water and two kinds of oil.

Keywords: *polymer composite materials, zeolite, furfural, water and light oil absorption*

1. Problem formulation

The high resistance materials are necessary for protection of concrete constructions, that work in contact with water, oil products and other agents. Such materials were used for repair of many hydrotechnical constructions operated in Ukraine for many decades. Polymer solutions based on epoxy resins have the necessary set of properties for performing the works listed above. Despite the high primary cost of epoxy binders their application is justified on the total costs of the life cycle of structures due to the reduction of costs for repair and replacement of structures, elimination of consequences of failures, environmental and other measures. Given the ability to regulate properties, improve durability and durability, and reduce the cost of these materials, using various modifiers and fillers (from their huge diversity), development of filled modified epoxy compositions designed for specific operating conditions is relevant.

2. Research methodology

As a basic component of compositions for repair and protection of concrete structures, it is advisable to use the epoxy-rubber resin "Macro" produced in Ukraine. Improving the operational properties of solutions on this resin can be facilitated by the introduction of certain dosages of furfural and zeolite (patent of Ukraine No. 5408). In particular, the positive role of zeolite in reducing water absorption has been estimated [1]. It is known [2] that aluminosilicate (the crystal structure of which is formed by tetrahedral fragments [SiO4] 4- and [AlO4] 5-, united by common vertices into a three-dimensional framework) has molecular sieve properties. However, the reasons and conditions for its positive effect on the structure of furfural modified epoxy compositions (in particular, on the criteria of adsorption and resistance in water and oil products) are not clear.

In epoxy resin furfural is introduced as an organic modifier that is capable of increasing water and chemical resistance, adhesion and strength properties of the material, and also serves as a polymerization accelerator and, to a certain extent, plasticizes the compositions.

In the experiment to determine the physico-mechanical and operational properties [3], a 27-point D-optimal plan was used. The levels of the five parameters of the disperse system varied. To determine the effect of the components of the dispersed phase on properties of system, they are represented among the variable factors by a hierarchy of relationships-the fractions of the components of the embedded subsystems (rather than individual mass parts in the dispersion medium, taking into account the experience of analyzing the role of the zeolite in [4]): мineral frame - 280 ± 100 mass parts; share in the frame of the filler – 0,6 ± 0,3 mass parts, the proportion of zeolite in the filler - 0,16 ± 0,10 mass parts, the proportion of large zeolite - 0,25 ± 0,25 mass parts, furfrol - 7 ± 5 mass parts.

3. Results and discussion

Long-term operation of polymer composite materials, with constant or periodic contact with an aggressive environment (water), usually leads to changes in their properties. Adsorption-active environment penetrating the composite due to diffusion and molecular transport along the structure defects promote the mobility of structural elements, reduce the strength of intermolecular bonds and thereby facilitate the "slippage" of molecular chains and molecular formations relative to each other, which is manifested in a decrease in energy, necessary for the destruction of material [5].

Among the characteristics determined for 27 compositions, there was water absorption W (%) after 1, 3 and 6 months (τ = 30, 90, 180 days) of stay in water. From these data, for each composition, it was possible to obtain (with an acceptable error) the analytical dependences of W on the time τ of the same exponential type (1) and the corresponding equations of water absorption rate (2). In Figure 1, such dependences are shown for the composition at the center of the experimental region (xi = 0, i = 1-5).

$$W = a\cdot(1-\exp[-b\cdot\tau]) \quad (1)$$

$$dW/d\tau = a\cdot b\cdot\exp[-b\cdot\tau] \quad (2)$$

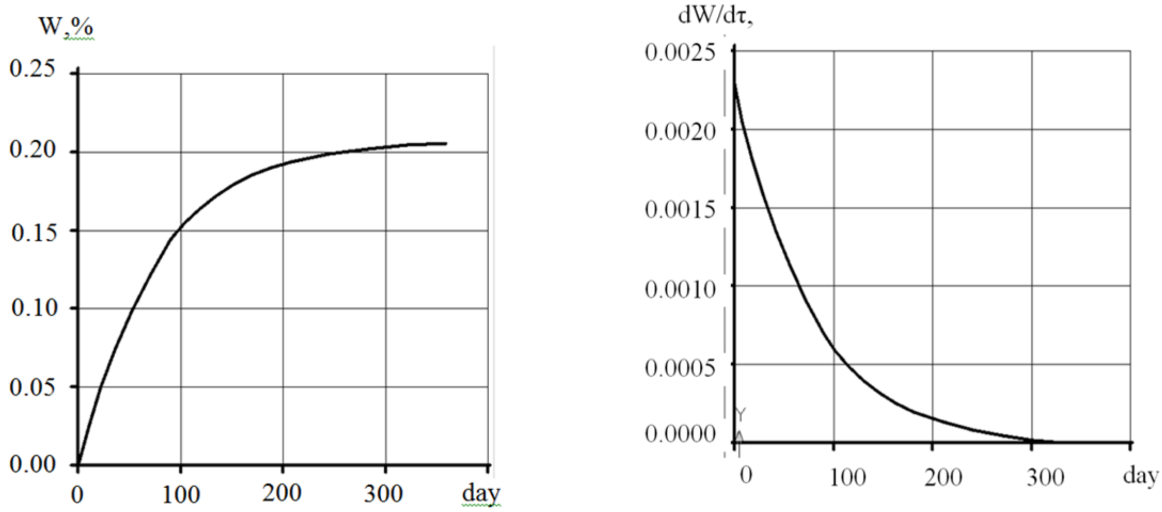
The parameter a in the models (1 - 2) corresponds to the maximum amount of water absorbed by the polymer solution, b – the rate indicator of water recruitment.

The obtained models (27 pairs of curves) make it possible to estimate the water absorption and its velocity for 27 compounds at any time. In particular, one can predict W after a year in water.

According to such estimates, by the levels of parameter a, rate b and other generalizing parameters of the water absorption kinetics, it is possible to compare compositions in the analysis and design of material quality.

All 27 curves of water absorption fit into the range of values shown in Figure 2a (at the maximum absorption a in the range from 0.2 to 0.6%). A picture of the decrease in the intensity of water absorption as the water is collected is represented by the zone in Figure

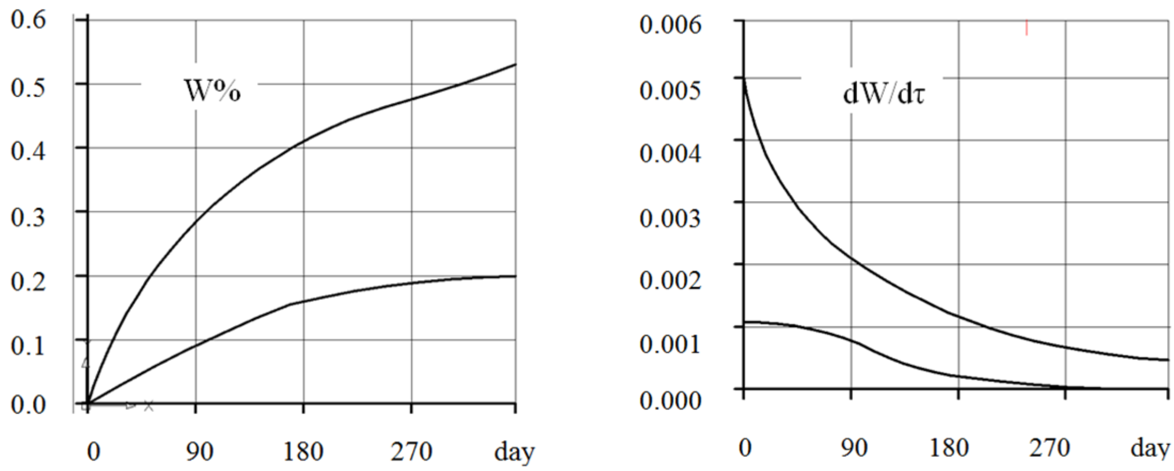
2b, covering the velocity curves for all compositions (maximum, initial velocities in the range 0.001-0.005).



a) b)

Figure 1. The water absorption curves (a) and the absorption rate (b) for the central composition (xi = 0, i = 1-5)

A comparative analysis of the water absorption curves of different compositions shows that the most noticeable effect on this process is exerted by the furfural content. Moreover, a lower water absorption level at any exposure time corresponds to the average dosage.



a) b)

Figure 2. Changes in the quantity (a) and rate indicator of water recruitment (b) in the field of experimental data

It should be noted that these data showed a weak correlation between W_6 and density (r = 0.48).

In the analysis of the ES model, describing the total field [6] of water absorption in the coordinates of all five composition parameters, it is established that the minimum level of this field is $W_{6.min}$ = 0.009%, at x1 = + 1 (maximum filling with the mineral framework), x2 = x3 = -1 (the minimum filler and the minimum part of the zeolite in it), x4 = 1 (the maximum amount in the zeolite of coarse grains), x5 = -0.07 (average dosage of furfural). The maximum is $W_{6.max}$ = 0.045% at x1 = -1 (low filling), x2 = +1 (maximum filler content,

little sand), x3 = 0.16, x4 = 0.60 (medium level of zeolite modification with increased content of coarse grains) and x5 = +1 (much furfural).

Among other characteristics, the oil absorption of P modified epoxy solutions was determined after a 6-month exposure in "light" and "heavy" oil (PL and PH), according to the plan of the five-factor natural experiment. Sufficiently low values of PL and PH are obtained with a faster average absorption of light oil by 30%. The absence of a linear static coupling between the levels PL, PH and the corresponding water absorption levels is revealed.

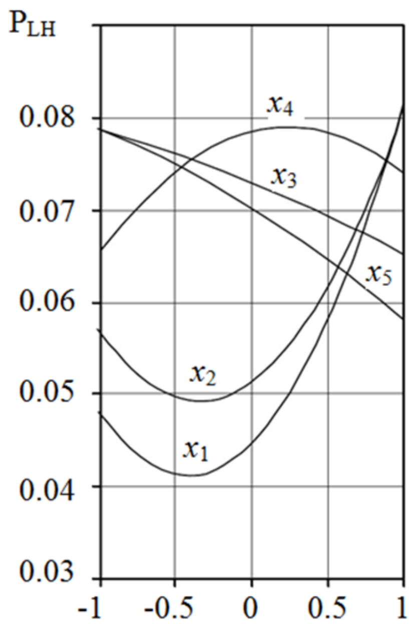


Figure 3. One-factor dependence of oil absorption PLH depending on the composition factors in the zone of maximum values

A significant negative correlation was found between the absorption of water and light oil in maximally filled compositions, $r\{P_L,W\}$ = 0.58). The ones shown in Figure 3, the oil absorption curves PLH, depending on each of the normalized factors in the PLH maximum zone, were obtained using a second-order ES model constructed from the data of the planned experiment using the k-transformation [7] (because the minimu m P levels are close to zero) for

$$kP_{LN} = \ln[p/(1-p)],$$

$$p = (P_{LH} - p_{LH\,\min})/(P_{LH.\max} - P_{LH.\min}).$$

The graphs generally reflect the positive effect of the zeolite, especially for hard solutions (with a reduced tar consumption). In such compositions, with an increased filling of the mineral framework, furfural significantly reduces the absorption of oil.

Conclusions

1. It is obvious that an increase in the share of the mineral skeleton leads to a decrease in water absorption. The effectiveness of the organic modifier - the average dosage of furfural - is confirmed. With increased filling, an additional positive effect can be given by a mixture of large and small zeolite grains.

2. In all the investigated range of compositions of epoxy composites, water absorption (up to 0.6%) does not exceed the values characteristic for this class of materials.

3. The absence of a linear static connection between the corresponding levels of water and oil absorption indicates that the same material structures differently prevent the mass transfer of three different liquids.

4. The positive role of organic (furfural) and mineral (zeolite) matrix modifiers in highly-filled epoxy compositions has been revealed.

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