Modeling basalt fibers wetting processes used in the basalt rebar production

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Abstract. The article presents the results of experimental and analytical study of basalt fibers wetting processes with epoxy binders, carried out to improve the quality of basalt rebar. It is revealed that the obtained model of basalt fiber impregnation allows determining the parameters of the binder flow in the porous structure of the monofilament bundle. Numerical results of evaluation of basalt fibers wetting with epoxy binders are presented and their rheological properties are determined.

1. Introduction
Currently, the production volume of basalt rebar for the manufacture of reinforced concrete structures is constantly growing. Basalt rebar has a number of advantages over metal one. They include the absence of corrosion, high tensile strength, low specific gravity, high endurance strength, low creep deformations, and high resistance to aggressive media [1-3].
The successful use of basalt rebar in structures is possible due to the full realization of the basalt fibers load-bearing capacity. The load-bearing capacity of basalt rebar depends not only on the physical and mechanical properties of the reinforcing filler and binder, but also on their interface interaction, i.e. the adhesive strength.

In the literature, there are many works devoted to the study of the adhesive strength of different fibers bonding with polymer matrices [4-10]. The adhesive strength of the polymer-substrate depends on many factors, including the properties of the binder and reinforcing fibers, the parameters of the surface roughness of the fibers, the thickness of the binder layer, the type of lubricant selected, the degree of wettability of the fiber by binders, etc.
The purpose of this paper is to study the parameters of continuous basalt fibers wetting with epoxy binders to improve the physical and mechanical properties of basalt rebar.

2. Modeling of porous medium wetting processes
To describe the wettability process of basalt fibers, imagine that monofilaments are not compressible, have a circular cross-section, and are packed in a roving strictly parallel to each other. This representation of the structure corresponds to the surface morphology of cross-sectional views of basalt rebar (Figure 1). In the model of monofilaments (bundles of monofilaments) packing with a diameter dM, the angle φ determines the packing density of monofilaments bundles, and can vary from 90° to 60°. Figure 2 shows two of the most typical cases of cylindrical monofilaments bundles packing.

Figure 1. Photo of a cross-sectional view of basalt rebar
In order to describe the processes of wettability and flow of the liquid binder in the pores with the cross-section shown in Figure 2, it is advisable to introduce the concept of the hydraulic radius, which has the following formula:

\[ r_c = \frac{S}{\chi}, \]  

(1)

where \( S \) is the cross-sectional area of the pore; \( \chi \) is the wetted perimeter.

Figure 2 shows that the diameter of the monofilament is \( d_m = AB \). Then, taking into account the considered packing scheme of Figure 2a, we get:

\[ S_{\text{mop}} = d_m^2 - \pi \left( \frac{d_m}{2} \right)^2 = d_m^2 \left( 1 - \frac{\pi}{4} \right) = r_m^2 \left( 4 - \pi \right) = 0,215 \cdot d_m^2 \]  

(2)

For the pore section shown in Figure 2b, we get:

\[ r_c = 0,068 \cdot r_m \]  

(4)

Then, for the hydraulic radius of the pore shown in Figure 2a, we have:

\[ r_c = \frac{r_m^2 \left( 4 - \pi \right)}{2 \pi r_m^2} = \frac{r_m^2 \left( \frac{4}{\pi} - 1 \right)}{2} = 0,136 \cdot r_m \]  

(3)

In accordance with the accepted approach to describe the process of impregnation of continuous basalt fibers (Figure 3), replace the pores that have a rather complex shape with capillaries with a circular cross-section having the corresponding hydraulic radius. We assume that the capillary is in contact with a container filled with a liquid binder to the level \( h \), at point A. At point B, it can be open to the atmosphere or have a sealed end. In the first case, the effect of atmospheric pressure will be compensated.

Figure 3. Diagram for the description of the continuous basalt fibers wettability
Let the binder be at point A at time point 0. After some time \( t_0 \), the meniscus will pass the distance \( l_0 \), where its speed in the first moments of time will be high due to low flow resistance. During this time period, the flow rate will be regulated by the laws of hydraulics, where a laminar or turbulent flow will be established. We assume that at some distance from point A, conditions will be created such that the flow of the liquid will correspond to the Poiseuille law. Let's also assume that these conditions will persist throughout the process. This assumption is true for small-diameter capillaries.

Write down the Poiseuille equation:

\[
\frac{dV}{dt} = \frac{4\pi \cdot \Delta p}{8\eta l} (r^2 + 4\varepsilon r^3),
\]

where \( dV/dt \) is the volume of liquid that flows through the capillary cross-section during \( dt \), \( l \) is the length of the liquid column in the capillary during \( t \); \( \eta \) is the liquid viscosity, \( \varepsilon \) is the sliding coefficient, \( \Delta p \) is the total pressure differential along the capillary axis.

For some time \( t \), the liquid will pass the distance \( l \) along the capillary and the meniscus will reach a certain point M, where it will move at a speed \( (dl/dt) \). Let's write the formula for the volume of a liquid column:

\[
dV = \pi r^2 dl
\]

Substitute (6) in (5) and get:

\[
\frac{dl}{dt} = \frac{\Delta p \cdot (r^2 + 4\varepsilon r)}{8\eta l}
\]

The total pressure differential \( \Delta p \) generally includes three independent pressures: atmospheric pressure \( P_a \), hydrostatic pressure \( P_h \), and capillary pressure \( P_s \). We assume that \( P_a = f(t) = \text{const} \). For hydrostatic pressure, in general case we can write:

\[
P_h = h \cdot g \cdot \rho - l \cdot g \cdot \rho \cdot \sin \psi,
\]

where \( l \) is the linear (variable) distance from A to M, \( \rho \) is the liquid density, \( g \) is the gravity acceleration, and \( \psi \) is the angle that determines the position of the point M.

The formula for capillary pressure is as follows:

\[
P_s = \frac{2\sigma}{r} \cos \theta,
\]

where \( \sigma \) is the liquid surface tension, \( \theta \) is the wetting angle.

Add up all the pressures, substitute in (7) and get:

\[
\frac{dl}{dt} = \frac{[P_a + g \rho (h - l \sin \psi) + \frac{2\sigma}{r} \cos \theta](r^2 + 4\varepsilon r)}{8\eta l}
\]

Convert (8) to the following form:

\[
\frac{(r^2 + 4\varepsilon r)}{8\eta} \cdot \frac{dl}{dt} = \frac{l}{P_a + \frac{2\sigma}{r} \cos \theta + \rho gh - g \rho l \sin \psi}
\]

The solution of differential equation (9) is written as follows:

\[
(P_a + \frac{2\sigma}{r} \cos \theta + \rho gh) \cdot \ln[P_a + \frac{2\sigma}{r} \cos \theta + \rho (h - l \sin \psi)] + C
\]

Substitution of the boundary conditions \( t=0, l=0 \) in (10) gives:
Formula (11) allows describing the movement of the column along the capillary in any direction. Next, let's consider a special case where the capillary is located vertically, i.e. \( \psi = 90^\circ \) (Figure 4).

\[
\frac{t + l}{8 \eta} = - \frac{P_t + \frac{2 \sigma}{r} \cos \theta + g \rho h}{g \rho \sin \psi} \cdot \ln \left( 1 - \frac{P_A + \frac{2 \sigma}{r} \cos \theta + g \rho h}{P_A + \frac{2 \sigma}{r} \cos \theta + g \rho h} \right)
\]

(11)

If the capillary is open on both sides, the atmospheric pressure is compensated, then \( P_A = 0 \), and, therefore, (12) is rewritten as:

\[
\frac{t + l}{8 \eta} = - \frac{8 \eta l}{g \rho (r^2 + 4 \varepsilon r)} \cdot \ln \left( 1 - \frac{l}{\Delta h + h} \right)
\]

(13)

\[
\Delta h = \frac{2 \sigma \cos \theta}{r \rho g}
\]

where \( \eta_A \) is the air viscosity.

Expand a logarithm function shown in (13) to two decimal places in a row:

\[
\ln \left( 1 - \frac{l}{\Delta h + h} \right) = \ln \left( 1 - \frac{l}{\Delta h + h} \right)
\]

\[
= \ln \left( 1 - \frac{l}{\Delta h + h} \right)
\]

(14)
After substitution and simplifications in (13), we get:

\[ l^2 = \frac{g \rho r^2 (\Delta h + h)}{8\eta} t \]  \hspace{1cm} (15)

If the capillary is immersed in the liquid for a short distance, then \( h \) can be neglected in comparison with \( \Delta h \), and taking into account the formula for \( \Delta h \), we get:

\[ l^2 = \frac{\sigma \cos \theta}{4\eta} r t \]  \hspace{1cm} (16)

Let's write the formula for the volume of a liquid column passing through a vertical capillary:

\[ V = \pi r^2 l \]

Given that \( m = p \cdot V \)

\[ m = \frac{\pi \rho r^2}{2} \sqrt{\frac{\sigma r t \cos \theta}{\eta}} \]

Hence we get:

\[ m^2 = \frac{k \cdot t \cdot \rho^2 \cdot \sigma \cos \theta}{\eta} \]  \hspace{1cm} (17)

where \( k = \frac{\pi^2 r^5}{4} \), \( k \) is the material constant that characterizes the pore size of the material.

Formula (17) is convenient when it is impossible to register the height of the liquid column rise through time. In this case, the impregnation kinetics is determined by periodical weighing of the samples through time.

Thus, using formulas (15-17), it is possible to describe the kinetics of impregnation of a basalt fibers bundle with binders. However, it is worth noting that these formulas include an unknown equivalent radius of the cylindrical capillary in the roving, which depends on the packing density of the fibers in the roving.

To determine the pore size in roving, a liquid with a known density, viscosity, surface tension and zero wettability (\( \theta = 0^\circ; \cos \theta = 1 \)) is used. The height of the liquid column is measured in the experiment. Further on, the samples are examined for wetting with binders.

3. Experiment and discussion of results

A number of experiments were performed to obtain the source data necessary for calculating the continuous basalt fibers impregnation kinetics.

The research was carried out on rovings based on continuous basalt fibers produced by Kamenny Vek LLC. Linear density of rovings was 1,200, 1,800 and 2,000 g/km. The following binders were used: epoxy resin ED-20 (100 phr) and isomethyltetrahydrophthalic anhydride hardener (i-MTHPhA) (90 phr); epoxy resin ED-20 (100 phr) and triaethanolamintitanate (TEAT) (10 phr); epoxy resin ED-20 (100 phr), active diluent DEG-1 (10 phr) and TEAT (10 phr). Ethyl alcohol was used to determine the pore size in a bundle of continuous basalt fibers.

In experiments on capillary rise, bundles of basalt fibers wound on metal frames with a spacing of 10 mm were used. The frame height was 300 mm. The number of bundles on the frame is at least 10. The frame with bundles was placed in a container with a liquid so that part of the fibers was immersed in the liquid to a depth of 4.5 mm. Impregnation of the bundles was carried out under the action of capillary rising forces at constant hydrostatic pressure. Since the volume of liquid in the container was quite large, its level practically did not change for a long time. To determine the equivalent pore radius, a bundle of basalt fibers was impregnated with ethyl alcohol for 10 minutes. It turned out that the height of the column in the capillary does not depend on the linear density of basalt fibers. The equivalent pore radius was determined by the formula:
To register the height of the capillary rise of the epoxy binder in bundles of continuous basalt fibers, the frames with samples were placed in a heating cabinet and cured after holding in a container with a liquid. After that, the height of the capillary rise was measured; it was considered to be equal to the height of the hardened part of the binder on the fibers.

To determine the surface tension of epoxy binders, the height of the capillary rise was measured using a glass capillary with a radius of 0.4 mm.

The angle of glass wetting with epoxy binders and ethyl alcohol was determined by the sitting drop method at a temperature of 25 °C. In accordance with the method, a drop of the test liquid was applied to the glass plate. Further on, the image, from which the wetting angle was determined graphically, was obtained using a microscope.

The surface tension was determined by the formula:

$$\sigma = \frac{r \cdot \Delta h \cdot \rho \cdot g}{2 \cos \theta}$$

The dynamic viscosity of epoxy binders was determined using an Anton Paar MCR 702 flow meter on a cone-plane measuring system at a temperature of 25 °C. The shear rate was changed from 20 to 420 s\(^{-1}\).

The results of experiments for different binders and ethyl alcohol are shown in tables 1-4.

| Table 1. Properties of ethyl alcohol |
|-------------------------------------|
| Parameter                          | Value       |
| Surface tension, σ, J/m\(^2\)       | 22.8 \(\times\) 10\(^{-3}\) |
| Density (reference value), ρ, kg/m\(^3\) | 789.3      |
| Column rising height, Δh, m         | 129 \(\times\) 10\(^{-3}\) |
| Wetting angle θ, deg                | 0           |

| Table 2. Properties of the studied binders |
|--------------------------------------------|
| Parameter                          | ED-20+i-MTHPhA | ED-20+TEAT | EDT-10 |
| Wetting angle of the glass substrate, θ, deg | 37.8           | 26.6       | 28.4   |
| Capillary rise, Δh, mm               | 10.35         | 8.20       | 10.10  |
| Density, ρ, kg/m\(^3\)              | 1180          | 1180       | 1170   |
| Radius of the glass capillary, r, mm | 0.4            | 0.4        | 0.4    |
| Surface tension, σ, J/m\(^2\)        | 30.3 \(\times\) 10\(^{-3}\) | 21.2 \(\times\) 10\(^{-3}\) | 26.3 \(\times\) 10\(^{-3}\) |
| Dynamic viscosity, η, Pa·s, at t=25°C and a shear rate of 250 s\(^{-1}\) | 0.37           | 12.9       | 5.7    |

| Table 3. Capillary rise height for combinations of binders and continuous basalt fibers (CBF) of various linear densities |
|------------------------------------------------------------|
| Linear density of CBF, tex | 1200 | 1800 | 2000 |
| Δh, mm | ED-20+i-MTHPhA | 91.4  | 79.1  | 88.9  |
|         | ED-20+TEAT     | 78.9  | 79.0  | 80.2  |
|         | EDT-10         | 97.7  | 92.3  | 87.1  |
Table 4. Equivalent pore radius for CBF of different linear densities

| Linear density of CBF, tex | Equivalent pore radius r, µm |
|---------------------------|-----------------------------|
| 1200                      | 45.7                        |
| 1800                      | 45.7                        |
| 2000                      | 45.7                        |

Using the data from tables 1-4, the wetting angle $\theta$ of continuous basalt fibers with base binders was determined using the follow formula:

$$\theta = \arccos\left(\frac{r \cdot \Delta h \cdot \rho \cdot g}{2 \cdot \sigma}\right)$$

Table 5 shows the results of determination of the wetting angle of CBF with epoxy binders using two independent methods: the capillary rise method and the sitting drop method.

Table 5. Wetting angle $\theta$ of basalt fibers with epoxy binders

| Parameter | The wetting angle, deg, according to raise/drop |
|-----------|-----------------------------------------------|
|           | ED-20+i-MTHPhA | ED-20+TEAT | EDT-10 |
| 1200 tex  | 37.1           | 54.0       | 10.5   | 52.0 | 13.3 | 38.6 |
| 1800 tex  | 46.4           | 54.0       | 10.0   | 52.0 | 23.2 | 38.6 |
| 2000 tex  | 39.2           | 54.0       | 10.6   | 52.0 | 29.8 | 38.6 |

It should be noted that in the current experiment, the sitting drop method does not take into account the influence of neighboring fibers in the bundle and the pore size, and is rather crude.

From the experiment on capillary rise, it follows that the smallest wetting angle relative to the CBF has a binder ED-20+TEAT, which means the best wettability of fibers with binders. The greatest wetting angle has a binder ED-20+i-MTHPhA.

Then, using (15), the dependence of the binder meniscus position in the capillary on time was determined:

$$l = r \sqrt{\frac{g \rho (\Delta h + h)}{8\eta}}$$

(20)

$$\Delta h = \frac{2\sigma \cos \theta}{r \rho g}$$

where

Let's transform (20), and after differentiating by $dt$, we get the formula for the speed of the binder meniscus movement, i.e., the impregnation speed:

$$\frac{dl}{dt} = \frac{g \rho (\Delta h + h)}{16\eta l} = r \sqrt{\frac{g \rho (\Delta h + h)}{32\eta t}}$$

(21)

$$\Delta h = \frac{2\sigma \cos \theta}{r \rho g}$$

Thus, it follows from (21) that the speed of the meniscus is directly proportional to the pore radius and the square root of the liquid density, and inversely proportional to the square root of the time and viscosity of the liquid.

Figures 5 and 6 show graphs of the movement $l$ and velocity $v$ of the liquid binder meniscus in the pore of the bundle of CBF of different linear densities with different brands of binders.
Figure 5. Dependence of the liquid meniscus position in the capillary on time for CBF with a linear density of 1200 tex at a temperature of 25°C:
1 – ED20+i-MTHPhA; 2 – ED20+TEAT; 3 – EDT-10.

Figure 6. Dependence of the binders flow rate in the capillary on time for CBF with a linear density of 1200 tex at a temperature of 25°C:
1 – ED20+i-MTHPhA; 2 – ED20+TEAT; 3 – EDT-10.

As can be seen from Figures 5, 6, the curves of the meniscus movement in the capillary of the fibers bundle are identical for all CBF with different linear densities. The impregnation time for the ED20+i-MTHPhA binder is the shortest, and for the ED-20+TEAT binder it is the longest.

As can be seen from Figure 6, the speed of the liquid binder movement in the capillary decreases as the height of the binder column increases. Binders ED20+i-MTHPhA have the highest rate of impregnation, binders ED-20+TEAT - the lowest one.

4. Conclusion
A model is proposed for calculating the packing density of continuous basalt fibers. Using the model of cylindrical fibers impregnation, the parameters of CBF wetting with epoxy binders and the parameters of liquid binder movement in the porous structure were determined. According to the results of experiments, it was found that the equivalent pore size in the CBF roving does not depend on the linear density of the bundle. It was found that the setting drop method for determining the wetting angle of the CBF gives rough results, since it probably does not take into account the pore size and the influence of neighboring fibers in the roving. By the method of capillary rise, it was found that the largest wetting angle of the CBF is found in the ED-20+i-MTHPhA binder, the smallest wetting angle belongs to the ED-20+TEAT binder. The rate of CBF impregnation with the ED-20+i-MTHPhA binder was the highest. The purpose of further research is to determine the effect of the wetting angle on the adhesive strength of the binder-fiber pair.
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