Method for assessing the effect of self-healing of asphalt concrete with encapsulated modifier

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Abstract. A unified methodology for assessing the ability of a material to heal itself does not exist at present. It is due to the absence of criteria characterizing the ability of a material to independently respond to conditions in a controlled manner and to take measures to eliminate an adverse effect on the properties or structure of the material. Usually, the self-healing ability is assessed using the coefficient of relative change of a measured indicator (for example, strength), which does not allow for two parameters: residual strength, which depends on the number of not broken bonds after the test, and the binder's own potential for recovery. The paper proposes a method for calculating the healing efficiency, taking into account the relative difference in the loss of strength, material with the use of an encapsulated modifier and without it. The proposed recovery factor reflects the effect of the encapsulated modifier on the change in the strength of the composite under study; therefore, to assess the efficiency of a self-healing material, it is also necessary to take into account the properties in the initial period of time and their stability under operating conditions. The problem of choosing the optimal indicator of material properties for assessing the recovery effect and improving the calculation method taking into account the duration of the recovery period is not solved and requires additional large-scale studies.

1. Introduction

Durability, as the ability of a material to resist structural changes caused by operating conditions, is not suitable for determining the service life of a material - the period of time until the material reaches its limit state (failure) [1, 2]. At the same time, it is obvious that these two characteristics of the material change symbatically, that is, the higher the durability, the longer the service life. Durability is very useful in assessing the ability of a material to heal itself. At the same time, it is important to describe the process of structure formation in terms of destruction. For this we use the classical definition of destruction - the process of dividing a whole material into parts in the process of exposure to external forces [3]. It occurs due to the formation and development of cracks, the appearance of which is energetically favorable near defects, as well as during their development and integration into larger associates. Hence, it follows that during the operational period, the process of structure formation consists in the transformation of the parameters of the material structure, the formation and development of defects with their transformation
into a system of cracks of various lengths not exceeding the critical size. The latter refinement is very important, since the critical crack length will determine the spontaneous process of material destruction (brittle fracture; Griffiths theory [4]) or the size of the crack will be comparable to the size of the product (sample), depending on the nature of the fracture of the material (brittle, brittle-plastic or plastic). In this case, material recovery is a change in the concentration of defects, as well as the concentration and length of the crack system. Research in this area is an important theoretical substantiation of the theory of material recovery, requiring additional experimental research, which is necessary to develop a model that is most adequate to real materials.

Bitumen-based materials belong to a separate group of materials, for example, asphalt concrete, which are classical representatives of composite materials, but have a very important feature: at positive temperatures (above the glass transition temperature), bitumen is a viscous liquid. Strength in asphalt concrete occurs when bitumen is converted into a thin-film state. The multicomponent composition of bitumen is another feature, since it changes under the influence of climatic factors (thermo-oxidative destruction, segregation of light components by mineral components, evaporation, etc.). As a rule, this leads to a significant increase in viscosity and a discrepancy between the existing (initial) thickness of the bitumen layer and external influences. It follows from this that the growing discrepancy between the thickness of the bitumen film and external loads due to a change in the component composition of bitumen is the main source of destruction of asphalt concrete; the initial increase in the thickness of the bitumen film is irrational, since the rutting process proceeds much more intensively than the process of changing the component composition of bitumen. In this case, the achievement of the limiting state by the asphalt concrete pavement will be much faster. It can be assumed that rutting resistance can be described by a function close to the classical form for such regularities:

\[ K \propto \frac{\mu(t)}{h_b^n}, \]

where \( \mu(t) \) is the viscosity of bitumen, which increases during operation; \( h_b \) is average film thickness of bitumen; \( n \) is exponent (\( n>1 \)).

From the presented dependence it can be seen that, while maintaining \( \mu(t) \), an increase in the bitumen film thickness will affect the rutting of the coating the stronger, the more significant the effect of the bitumen film thickness on this property (the greater the value of \( n \)):

\[ \frac{dK}{dh_b} \approx n \frac{\mu(t)}{h_b^{n+1}}. \]

Thus, initially increasing the thickness of the bitumen layer to improve durability is a waste of time.

The traditional solution for extending the service life of asphalt concrete pavement is the use of various types of impregnations (sealers), which are used at the operation stage in order to prevent the development of primary defects [5...9]. Impregnating compositions (asphalt sealers) after processing the surface of the asphalt concrete pavement diffuse into the material, restoring the molecular composition of the bituminous binder, which leads to a decrease in rigidity [10, 11].

Rejuvenators – low molecular weight organic compounds, are the main component of such impregnating compositions (sealers), which dissolve in bitumen, compensate for the loss of maltenic fractions during aging during operation [12...19]. The result of self-healing is the restoration of the integrity of the physicochemical bonds in the composite by means of: wetting of the crack surfaces, diffusion of molecules between the surfaces, and arbitrary scattering of molecules, which provides hardening [20].
The quality of the self-healing technology consists of the technological properties of the capsules and the restorative properties of the encapsulated agent. A unified methodology for assessing the ability of a material to heal itself does not exist at present. It is due to the absence of general theory of self-healing and criteria characterizing the ability of a material to independently respond to conditions in a controlled manner and to take measures to eliminate an adverse effect on the properties or structure of the material.

2. Materials and methods

The main components for obtaining asphalt concrete with a self-healing ability were: a bituminous binder, mineral aggregates, functional additives and an encapsulated modifier consisting of a reducing agent and an encapsulating agent.

Mineral aggregates were mixed in the following ratio to ensure the required grain size composition: coarse aggregate – 67 %; fine aggregate – 21 %; filler – 12 %. The sieve gradation of aggregates for the developed composite is presented in Table 1.

| Parameter       | Value  |
|-----------------|--------|
| Sieve size, mm  |        |
| 15              | 92.3   |
| 10              | 58.8   |
| 5               | 33.0   |
| 2.5             | 21.7   |
| 1.25            | 18.4   |
| 0.63            | 16.5   |
| 0.315           | 14.7   |
| 0.16            | 12.7   |
| 0.071           | 10.6   |

Table 1. Sieve gradation of asphalt mix.

Cellulose fibers "Viatop-66" (state standard 31015-2002) were used as a stabilizing additive to prevent segregation and runoff of the bituminous binder.

Sunflower oil and AR-polymer [17], in a calcium alginate shell in the form of containers with a radius of 1.3 mm and a breaking load of 19 N [18, 19] were used as an encapsulated modifier. AR-polymer is a thiol-containing urethane polymer with terminal mercaptan groups (SH-), produced by PolyMix Kazan LLC in accordance with TU 2226-001-90014974-11 [20]. The content of capsules in the composition of the composite was 1.5 %, 3.0 %, 4.5 %, 9.0 %, and 13.5 % of the bitumen mass.

Bitumen BND 60/90 (state standard 22245-90) with a softening temperature of 51 °C and a brittleness temperature according to Fraas - minus 20 °C was used as a binder for asphalt with encapsulate sunflower oil. Bitumen BND 60/90, modified with tetramethylthiuram disulfide – 0.33%, manganese dioxide – 1.22% and sulfur – 2.0%, was used as a complex binder for asphalt concrete with encapsulated AR-polymer. The binder content in the asphalt concrete (SMA-15) was 7 %.

The asphalt concrete mixture was used to make cylinder-samples with a height and diameter of 71.4 mm. For this, the mixture of the required mass was placed in a cylindrical form and compacted in two stages: with the help of vibration and a weight providing a load of 30 ± 5 kN for 3 minutes and subsequent compaction with a hydraulic press providing a pressure of 20.0 ± 0.5 MPa for 3 minutes. Then the sample was removed from the mold.

For calculating the healing factor, the values of compression strength at a temperature of 20 °C, obtained during cyclic fracture and recovery, were used. Asphalt concrete samples were thermostated in a climatic chamber at a temperature of 20 °C for at least 2 hours, after which they were tested under compression at a loading rate of 3 mm/min and the maximum load at failure was determined (Figure 1). After that, the samples were stored at a temperature of 20 °C for 7 days and then they were re-thermostated and tested. The test plan included 4 compression tests and three recovery periods of 7 days. The test plan for asphalt concrete samples is shown in Figure 2.
The average density and residual porosity of the studied samples on bitumen and complex binder were 2.43 g/cm³ and 3.0 %, respectively.

The values of the ultimate compressive strength at a temperature of 20 °C obtained during cyclic fracture and recovery were used to calculate the healing factor.

3. Results and discussions

The results of determining the ultimate strength at 4 consecutive cycles of compression tests and periods of recovery of asphalt concrete with different contents of the encapsulated modifier are shown in Figure 3.

An increase in the content of capsules with sunflower oil and AR-polymer in asphalt concrete leads to a decrease in compressive strength. This is due to an increase in the proportion of structural elements in the bulk of the material, which are less able to resist mechanical stress than the matrix or aggregates. In addition, capsules can be considered as additional structural defects (prior to the implementation of their functional use), which is identical to a decrease in the concentration of structural bonds in the material. According to the Rebinder equation, the decrease in structural bonds $N_{st}$ with an increase in the number of defects $v_p$ ($v_p$ is the volume fraction of defects) will be equal to:

$$N_{st} = B_0 \Delta v_p,$$

where $B_0 = \sqrt{R_0 / \gamma f_c}$; $R_0$ is strength of a defect-free material (material constant); $\gamma$ is a constant; $f_c$ is the strength of a single bond.
Hence, with the equality \( \Delta \nu_p = \nu_k \) (\( \nu_k \) is the volume fraction of the capsules), the negative effect of the capsules on the strength of the material is obvious.

At the same time, the effect of the content of capsules on the strength of asphalt concrete on bitumen and on a complex binder is different. Thus, the decrease in the strength of asphalt concrete on a complex binder at the maximum concentration of the encapsulated modifier is 1.9 times less than for asphalt concrete based on bitumen. This is due to the formation of stronger structural bonds in the composite with the modified bitumen binder than with bitumen, and the initial strength \( (R_0) \) is 36% higher.

The total loss of strength after 4 compression tests for asphalt-concrete on bitumen was 47%, and for a complex binder - 38%, which indicates a higher resistance of the structure to repeated mechanical stress. It should be noted that after each compression test, the asphalt concrete samples have residual strength. This is due to the fact that, prior to testing, the set of bonds ensures the resistance of the asphalt concrete to critical loads, which are ultimate and are fixed during the compression test. In this case, during loading, part of the structural bonds is destroyed, and part after removal of the load ensures the state of the structure, which is characterized by residual strength.

Quality criteria for calculating the efficiency of a self-healing material were proposed in [25]: the degree of restoration of the state of the structure; the rate of restoration of the state of the structure; the durability of the restored structure and the timelines of the initiation of the regenerating process. However, a large amount of empirical research is needed to select the property indicators that would characterize each of the quality criteria.

Methods for assessing the self-healing ability of materials proposed in various works, which were described in [26], consist in calculating the coefficient of relative change in the measured indicator (healing index):

\[
HI = \frac{X_h}{X_0},
\]

where \( X_0 \) and \( X_h \) – an indicator of the properties (for example, strength) of a material before and after self-healing, respectively.

This coefficient, in accordance with [25], can be referred to the category of indicators reflecting the degree of restoration of the state of the structure, which is insufficient for an objective assessment of the technology of self-healing. The results of calculating the healing index for asphalt concrete with different contents of the encapsulated modifier are shown in Figure 4.

![Figure 4. Change in healing index (HI) after repeated compression test of asphalt concrete with capsules with: sunflower oil (a); AR-polymer (b).](image)

Healing index for asphalt concrete with encapsulated sunflower oil after the fourth compression test varies from 0.68 to 0.64 with a capsule content of 1.5 to 13.5 %. Healing index for asphalt concrete with
encapsulated sunflower oil after the fourth compression test varies from 0.68 to 0.64 with a capsule content of 1.5% to 13.5%. Healing index for or asphalt concrete with encapsulated AR-polymer is 0.79; 0.85; 0.82; 0.70; 0.68 with a capsule content of 1.5%; 3.0%; 4.5%; 9.0%; 13.5%, respectively. This index shows a high level of healing both when using encapsulated sunflower oil and AR-polymer. However, the healing index does not take into account two indicators: residual strength, which depends on the number of not broken bonds after the test, and the binder’s own potential for recovery.

A more accurate approach to assessing the healing effect is to take into account the change in the loss of strength of the material when using the encapsulated modifier. The strength loss index is the reciprocal of the healing index, which will be calculated as the fracture index \( IR = 1 - \frac{X_h}{X_0} \), the calculation results of which are shown in Figure 5.

**Figure 5.** Change in strength loss index (IR) after repeated compression test of asphalt concrete with capsules with: sunflower oil (a); AR-polymer (b).

Index IR shows that the strength loss decreases to varying degrees with different contents of capsules. The strength loss index for asphalt concrete with encapsulated AR-polymer is lower than that with encapsulated sunflower oil. Taking into account the relative difference in the strength loss of asphalt concrete with and without an encapsulated modifier, the recovery factor is calculated using the following formula:

\[
k_h = \frac{IR'}{IR}
\]

where \( IR' = 1 - R_h/R_0 \) is the strength loss index of asphalt concrete without capsules; \( IR = 1 - R_0/R_0 \) is the strength loss index of asphalt concrete with an encapsulated modifier; \( R_0 \) and \( R_h \) is compressive strength of asphalt concrete before recovery without capsules and with encapsulated modifier, respectively, MPa; \( R_h \) and \( R_h \) is compressive strength of asphalt concrete after restoration without capsules and with encapsulated modifier, respectively, MPa.

The results of calculating the coefficient of healing, taking into account the relative difference in the loss of strength of asphalt concrete with the encapsulated modifier and without it, are shown in Figure 6.

a)
Figure 6. Change in coefficient of healing ($k_h$) after repeated compression test of composite with capsules with: sunflower oil (a); AR-polymer (b).

Analysis of Figure 6 shows that at a content of 3% of capsules, the degree of recovery is maximum, which may be due to the optimal content in the structure of the composite, at which the negative effect of their presence in the bulk of the material is minimal, and the recovery effect by the encapsulated modifier is maximal.

4. Summary
The coefficient of healing for asphalt concrete with encapsulated sunflower oil shows that, upon repeated compression, the total loss of strength, taking into account the effect of the modifier, is 28% less. For asphalt concrete with an optimal content of encapsulated AR-polymer, the healing coefficient shows that the total loss of strength, taking into account the effect of the modifier, is 46% less. At the same time, the healing efficiency with the use of encapsulated AR-polymer is 1.87 times higher than with the use of encapsulated sunflower oil.

A greater restorative effect is observed after the second period of healing, which may be due to the achievement of the opening of the maximum number of capsules and the participation of the modifier in the healing process, the result of which is the formation of new structural bonds. The decrease in the recovery effect after the third period of healing is due to the exhaustion of the recovery potential of the encapsulated modifier, and as a result of the fourth compression test, more bonds are destroyed than was restored during healing.

It should be noted that the proposed coefficient of healing allows one to assess the effect of the encapsulated modifier on the change in the strength of the composite under study, therefore, to fully assess the effectiveness of a self-healing material, it is necessary to take into account both the properties in the initial period of time and their rate of change under operating conditions [25…28].

The problem of choosing the optimal indicator of material properties for assessing the recovery effect and improving the calculation method taking into account the duration of the recovery period is not solved and requires additional large-scale studies.

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Acknowledgments
This work was financially supported by the Grants Council of the President of the Russian Federation (SP-5069.2021.1)