Active polymeric reducing agent for self-healing asphalt concrete

Sergey Inozemtcev and Evgeniy Korolev
Moscow State University of Civil Engineering, Yaroslavskoe shosse, 26, Moscow, 129337, Russia

E-mail: inozemtsevss@mail.ru

Abstract. The possibility of using an active polymer component as a reducing agent for the implementation of the self-healing of asphalt concrete technology is considered in the paper. It was found that the thiol-containing urethane AR-polymer is an effective reducing agent capable of replacing traditional reducing agents based on hydrocarbon oils. AR-polymer is a reducing agent that can be encapsulated using alginate technology. The volume of the reducing agent in the capsule is limited to a maximum allowable value of 83±1%, which can be achieved using the alginate technology. It has been proven that the type and properties of the reducing agent does not affect the change in the mechanical properties of the capsules. The strength of the capsules decreases by 2...6% for different ratios of RA/A when the content of sodium alginate decreases from 3.33% to 2.08%. The greatest efficiency of capsules with the maximum content of AR-polymer as a reducing agent and higher strength is achieved when using emulsions containing 2.50% sodium alginate at RA/A = 5.0 ± 0.2.

1. Introduction
The development of "smart" materials that can controllably change properties under the influence of artificial influences or natural operating factors during operation is a promising solution in the field of materials science aimed at increasing the durability of structures [1, 2].
Self-healing technologies have become more widespread in this direction. The formation of a new operational property of the material is achieved by using encapsulated reducing agents [3 ... 6], which are added to asphalt concrete in the form of capsules with a reducing agent [7 ... 10].
For the production of capsules with a reducing agent for asphalt concrete, there are various technologies that differ in the used starting components, the complexity of the technological process and the properties of the product.
Rejuvenators in the form of organic oils of various molecular weights, including vegetable oils, are mainly used as an encapsulated reducing agent for self-healing asphalt concrete. However, the mechanism of action of such a reducing agent in asphalt concrete consists in the dissolution of bitumen components aged in the process of operation and a local decrease in fragility. It is quite problematic to achieve a significant restoring effect with this approach, since the transformation of existing defects does not occur, but only the development and formation of new cracks slows down.
The use of active functional modifiers, including those based on polymer, which, after physical and mechanical transformations, are capable of forming new physical and chemical bonds between defect planes (cracks) during the restoration process, is a promising direction.

2. Materials and methods

The traditional reducing agent based on sunflower oil and the reducing agent based on thiol-containing urethane "AR-polymer" are considered as a reducing agent. The main properties of sunflower oil are presented in table 1.

Table 1. Properties of sunflower oil

| Parameter                        | Unit  | Value          | Method                  |
|----------------------------------|-------|----------------|-------------------------|
| Dynamic viscosity at 25°C        | Pa·s  | 0.05           | section 2.1             |
| Density at 25 °C                 | g/cm³ | 0.918 ± 0.05   | National standard 3900  |
| Acid number                      | mg KOH/g | 0.025 ± 0.01  | National standard 31933 |
| Fractional composition:          |       |                |                         |
| palmitic acid                    | %     | 6.61           |                         |
| stearic acid                     | %     | 3.61           |                         |
| oleic acid                       | %     | 30.91          | National standard 31663 |
| linoleic acid                    | %     | 57.13          |                         |
| others                           | %     | 1.74           |                         |

"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. The hardener used for the polymer is tetramethylthiuram disulfide C₆H₁₂N₂S₄. The main properties of the polymer are presented in table 2.

Table 2. Properties of "AR-polymer"

| Parameter                        | Unit  | Value          |
|----------------------------------|-------|----------------|
| Dynamic viscosity at 25°C        | Pa·s  | 9.7            |
| SH-group content                 | %     | 1.5-2.5        |
| Tensile strength after curing    | MPa   | 1.0            |
| Elongation at break              | %     | 100            |
| Permanent deformations           | %     | until 6        |

The encapsulation of the reducing agent was carried out using alginate technology [7], in accordance with which calcium alginate capsules are formed. An aqueous solution based on sodium alginate (C₆H₇O₆Na), which is a sodium salt of alginic acid extracted from brown algae, is used for encapsulation. The reducing agent is added to the alginate solution with high-intensity mixing, the alginate emulsion is formed, which is divided into separate drops with the help of a separating funnel through a solution of calcium chloride. Separate capsule containers containing the reducing agent are formed after excess moisture has been removed from the droplets by drying.

Aqueous solutions containing 3.33%; 2.50% and 2.08% sodium alginate by weight of water were investigated as a basis for alginate emulsions. The concentration of the reducing agent in the emulsion was varied to 35% by weight of water. A calcium chloride solution for the production of capsules was prepared at a CaCl₂·H₂O ratio of 1:50.

An overhead stirrer with a maximum rotation speed of 2000 rpm was used to prepare the alginate solution and emulsion.
2.1. Technological properties of alginate emulsions
Emulsion separation rate was evaluated by the number of drops per minute during the separation of the emulsion using a funnel.
The dynamic viscosity of the investigated liquid media was determined using a rotary viscometer with a coaxial cylinder measuring cell at a temperature of 25 °C at a constant shear rate of 50 s⁻¹. To determine the yield stress of alginate emulsions, the shear stress was measured under conditions of a linear change in the shear rate from 10 to 3500 s⁻¹ at a temperature of 25 °C.

2.2. Physical and mechanical properties of capsules
The capsule size was measured using a calibrated scale of a Nikon Eclipse MA200 optical microscope. The maximum load on the capsules was measured on a mechanical Uniframe press using a dynamometer with a maximum measuring limit of 1 kN (Figure 1).

![Figure 1. Device for determining the maximum load on the capsules: 1 - dynamometer; 2, 3 - fixed Uniframe press plates; 4 - hinge plate of the dynamometer; 5 - capsule](image)

2.3. Recovery efficiency
The effectiveness of the investigated reducing agents was assessed based on the results of physical and mechanical tests, which included a study of the ability of the reducing agent to recreate bonds in the composite after the formation of defects.
The study of the ability of the reducing agent to recreate bonds after the formation of defects was carried out on samples of organomineral composites which contain on bitumen and mineral fillers of various grain sizes.
Bitumen BND 50/70, granite aggregates and carbonate mineral filler with a CaCO₃·MgCO₃ content of at least 91 % were used to make bitumen-mineral mixtures.

| Parameter                      | Unit | Value | Method               |
|--------------------------------|------|-------|----------------------|
| Softening point                | °C   | 51    | National standard 33142 |
| Brittleness temperature        | °C   | -20   | National standard 33143 |
| Penetration at 25 °C           | 0.1 mm | 67    | National standard 33136 |
| Penetration at 0 °C            | 0.1 mm | 36    | National standard 33136 |
| Change in softening point after aging | °C | 5     | National standard 18180 |
Table 4. Grading of mineral materials

| Material | Fraction content, %, less than the sieve mesh size |
|----------|--------------------------------------------------|
|          | 10.0  5.0  2.5  1.25  0.63  0.315  0.16  0.071 |
| Aggregate| 100.0 29.0 17.7 12.2  8.7   8.2   5.5   2.0   |
| Filler  | –       –      –     –     –     –     100.0 100.0 98.5 |

The ability of the reducing agent to restore bonds after the formation of defects was evaluated on half-cylinder samples from organic-mineral mixtures with different component ratios. The samples were tested for bending strength after thermostating at a temperature of 0±2 °C for 2 hours according to the scheme shown in Figure 2. The load was applied to the samples until fracture in two parts. Then, the fracture surfaces were uniformly treated with a reducing agent, and the two parts of the sample were aligned with the help of bundles so that the fracture surfaces were in contact with each other (Figure 3).

![Figure 2. Bending test scheme](image1)

![Figure 3. Healed samples](image2)

After incubation for 7 days at a temperature of 20±2 °C, the samples were re-cooled in a climatic chamber at a temperature of 0±2 °C for 2 hours and tested for bending strength. The calculation of the ability of the reducing agent to recreate bonds after the formation of defects was carried out using the healing index of the bending strength:

\[ k = \frac{R_{bh}}{R_b} \times 100\% \]

where \( R_b \) and \( R_{bh} \) – bending strength before and after recovery, respectively, MPa. Bending strength was calculated using the formula:

\[ R_b = \frac{P}{2RT} \]

where \( P \) – maximum breaking load, N; \( T \) – half-cylinder sample width, cm, \( R \) – half-cylinder sample radius, cm.

3. Results and discussion
The self-healing technology of organomineral composites involves the use of an encapsulated reducing agent, which is added in the form of capsules to the mixture at the preparation stage. The efficiency of the applied self-healing technology is determined both by the ability of the reducing agent to eliminate the consequences of the formation of defects in the composite [11], and by the complex of physical and mechanical properties of capsules and technological properties of the emulsion, which used for their production (Figure 4).
The main criterion for the efficiency of the self-healing technology is the efficiency of the applied reducing agent and its effect on defects in the material structure.

Sunflower oil, used as a reducing agent, wets cracks in the surface of a defect (cracks) after the destruction of the capsule, diffuses into the matrix, has a rejuvenating effect due to the restoration of the composition of the light fractions of the binder [12 ... 14]. The mechanism of action of such a reducing agent consists in increasing the binder's own potential for recovery [15] and decreasing the rate of further formation of defects by reducing the brittleness.

The use of a polymer as a reducing agent will allow, after wetting the crack surfaces and starting the polymerization process, due to the hardener and vulcanizer present in the matrix, to form an interlayer that glues the defect.

The effectiveness of the encapsulation technology, the reducing agents used, is determined by the relative volume that they occupy in the capsule. Capsules with a higher content of the reducing agent will have a greater effect on recovery.

Taking this into account, capsules with a smaller diameter have an advantage, since the use of large capsules makes it difficult to evenly distribute them in the volume of the material.

The strength of the capsules is a key physical and mechanical property that determines the implementation of the self-healing technology. Optimum strength should ensure the integrity of the capsules during the compaction of the asphalt concrete mixture and not prevent their destruction during the formation of defects in the asphalt concrete. The maximum load that the capsule can withstand until the moment of destruction in compression is an indicator that reflects the ability to resist mechanical stress. The results of determining the breaking load during compression of capsules are shown in Figure 5.
An increase in the content of the reducing agent in the composition of the alginate emulsion leads to a decrease in the breaking load during compression, which is explained by a change in the geometric parameters of the capsules (Figure 6). At the same time, the change in the content of sodium alginate in the studied range does not significantly affect the change in the mechanical properties of the capsules. A decrease in the content of sodium alginate from 3.33 to 2.08 % leads to a decrease in strength by 2...6 % at different ratios RA/A. It should be noted that the type and properties of the reducing agent do not affect the change in the mechanical properties of the capsules. The change in the breaking load upon compression of the capsules on the ratio of the reducing agent and sodium alginate is described by the general linear relationship 

\[ F = -3.6207 \cdot RA/A + 35.524. \]

Figure 5. Dependence of the breaking load during compression of capsules on the ratio of the reducing agent and sodium alginate (RA/A): white markers – capsules with AR-polymer; black markers – capsules with sunflower oil

Figure 6. The dependence of the change in the geometric parameters of the capsules on the ratio of the reducing agent and sodium alginate (RA/A): a) the diameter of the capsules; b) the volume of the reducing agent in the capsule; white markers – capsules with AR-polymer; black markers – capsules with sunflower oil

With an increase in the content of the reducing agent in the alginate emulsion, the capsule diameter and the volume of the reducing agent in the capsule change exponentially. The size of the capsule

\[ D = 1.423 \cdot (1 + 0.985e^{-0.508 \cdot RA/A}). \]

\[ V = 1.665 \cdot (1 + 0.985e^{-0.508 \cdot RA/A}). \]
increases due to the increase in its volume of the reducing agent that it can accommodate. At the same time, it can be seen in Figure 6b that the volume of the reducing agent in the capsule is limited by the maximum allowable value that can be provided by the alginate technology. The graph shows a plateau at 83%, after reaching which, an increase in the content of the reducing agent in the alginate emulsion has no significant effect. Alginate emulsion formulations that provide to produce capsules with maximum reducing agent content are optimal. Considering the dependence of the change in the volume of the reducing agent in the capsule:

\[ V = 80.12 \left( \frac{2}{1 + e^{-1.207 \cdot RA/A}} - 1 \right) + 0.753 \cdot RA/A \]

the value of the RA/A ratio, ensuring the production of capsules with a volume of the reducing agent of at least 83±1 %, should not be less than 4.8±0.2.

The effectiveness of capsules with the same volume of the reducing agent and strength characteristics is determined by their diameter. A more uniform distribution of the required volume of the reducing agent in the volume of the composite is achieved by using capsules with a smaller diameter. Thus, taking into account the dependence of the change in the diameter of the capsules:

\[ D = \frac{1.42}{1 + 0.986 e^{-0.508 \cdot RA/A}} \]

the size of the capsules providing the highest efficiency of the self-healing technology should correspond to the value of 1.35±0.5 mm.

Since the dynamics of changes in the physical and mechanical properties of capsules is the same, it is advisable to optimize the compositions of alginate emulsions in terms of their technological properties. The implementation of the self-healing technology includes the selection of the optimal ratio of the components of the emulsion for encapsulation with the required fluidity and resistance to delamination, which will ensure the maximum speed of the capsule production process.

It has been established [7, 16] that the reducing agent in the composition of alginate emulsions has a structuring effect and the production of emulsions with maximum viscosity at various concentrations of sodium alginate is achieved along a certain recipe limit (Figure 7a).

This effect of maximum structuring is also observed for alginate emulsions with AR-polymer and causes maximum resistance to flow, which affects the rate of separation of the emulsion into individual granules (drops) (Figure 7b). The dependences of the change in the rate of separation of the emulsion on the recipe factors (Figure 7) are described by quadratic dependencies with the regression coefficients shown in Table 5.

\[ Y = a \cdot RA/A + b \cdot RA/A + c \]
Table 5. Coefficients of equations for the change in the rate of separation of emulsions

| Sodium alginate content, % | a      | b            | c          |
|---------------------------|--------|--------------|------------|
| 3.33                      | 0.3045 | -2.6123      | 38.392     |
| 2.50                      | 1.9947 | -8.0441      | 26.314     |
| 2.08                      | 0.8389 | -2.1794      | 6.140      |

The optimal composition of the alginate emulsion is determined by the efficiency criterion, taking into account both the mechanical requirements for the capsules and the manufacturability of the emulsions, which can be represented as a function:

$$k_f = \sqrt[4]{k_F k_D k_V V},$$

where $V$ is the separation rate of the alginate emulsion, drops/min; $k_F = F_{RA}/F_0$ is the criterion of capsule strength; $F_{RA}$ is maximum load for capsules containing AR-polymer, N; $F_0$ is maximum load for particles without a reducing agent, N; $k_D = D_{RA}/D_0$ is geometric criterion for capsules; $D_{RA}$ - diameter of capsules containing AR-polymer, mm; $D_0$ is particle diameter without a reducing agent, mm; $k_V = V_{RA}/V_{max}$ is capsule volumetric criterion; $V_{RA}$ is the volume of the reducing agent in the capsule, %; $V_{max}$ is the maximum volume of the reducing agent in the capsule, taken 99%.

The results of calculating the efficiency criterion of the considered alginate emulsions are shown in Figure 8.

![Figure 8. Dependence of the capsule efficiency criterion on the ratio of the reducing agent and sodium alginate](image)

The calculation results show that the highest efficiency of capsules with the maximum content of AR-polymer as a reducing agent (more than 83 %) and higher strength is achieved for emulsions containing 2.50 % sodium alginate at RA/A=5.0±0.2.

It has been proved that obtaining capsules with a reducing agent content of at least 83% when using AR-polymer as a reducing agent is achieved with the help of alginate emulsions, the optimization of which is carried out by regulating the recipe and technological parameters. AR-polymer is a thiol-containing urethane polymer, which, unlike the traditional reducing agent, is an adhesive, which will allow the composite to be restored by gluing the crack surfaces. The effectiveness of gluing the surfaces of the defect is determined by the strength of their adhesion to each other due to the formation of adhesive bonds by reducing agent. Determination of the degree of recovery using AR-polymer and sunflower oil was carried out on half-cylinder samples of bitumen-mineral mixtures of various compositions according to the degree of strength retention after repeated bending tests at a temperature of 0 °C. In the first bending test, half-
cylinder samples were destroyed along the main crack until two halves were formed, then a reducing agent was applied to each fracture surface, and the halves of the samples were re-combined together. The repeated bending test was carried out after 7 days of recovery at a temperature of 25 °C. The results of determining the degree of recovery using various reducing agents are presented in table 6.

| Parameter                               | Reducing agent | Value          |
|-----------------------------------------|----------------|----------------|
| Bitumen content, %                      | –              | 17.4 16.1 8.8 8.0 16.7 7.1 |
| Filler content, %                       | –              | 82.0 83.3 21.8 22.0 83.3 21.2 |
| Aggregates content, %                   | –              | 69.1 69.7 – 71.7 |
| Complex additive content, %             | –              | 0.6 0.6 0.3 0.3 – – |
| Healing index $k$, %                    | Sunflower oil  | 0.0 0.0 0.0 0.0 0.0 0.0 |
|                                         | AR-polymer     | 14.0 8.3 20.1 12.3 0.3 0.2 |

The use of sunflower oil as a reducing agent does not lead to the restoration of bonds between the surfaces of the resulting defects - the healing index for bending strength is 0. The use of AR-polymer as a reducing agent for bitumen-mineral mixtures allows to restore up to 20% of strength after destruction of the composite integrity. Recovering is achieved when using a complex additive containing a hardener and a polymer vulcanizer. The recovery process using AR-polymer includes wetting the crack surface, diffusion into the surface layers through the pores, interaction with the hardener and vulcanizer in the bitumen binder, polymerization and the formation of an elastic layer which glues the defect (Figure 9). The use of a thiol-containing urethane AR-polymer with terminal mercaptan groups as a reducing agent is a reasonable technical solution. This makes it possible to implement the technology of encapsulation using alginate emulsions [16] and to provide a regenerating effect during its polymerization in an organic-mineral composite due to the formation of adhesive bonds.
4. Conclusion
According to the research results, it was found that the thiol-containing urethane AR-polymer is an effective reducing agent that can replace traditional reducing agents based on hydrocarbon oils. It has been established that the thiol-containing urethane AR-polymer is a reducing agent, the encapsulation of which is possible using alginate technology. The volume of the reducing agent in the capsule is limited to a maximum allowable value of 83 ± 1%, which can be achieved using the alginate technology. It has been proven that the type and properties of the reducing agent does not affect the change in the mechanical properties of the capsules. A decrease in the content of sodium alginate from 3.33 % to 2.08 % leads to a decrease in strength by 2...6 % at different ratios RA/A. The highest efficiency of capsules with the maximum content of AR-polymer as a reducing agent (more than 83 %) and higher strength is achieved for emulsions containing 2.50 % sodium alginate at RA/A=5.0±0.2.

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