Optimization of the epoxy resin water dispersion for modification of the RAP cold recycled mixes

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Abstract: This article presents the results of studies to optimize the composition of water dispersion of epoxy resin for the modification of RAP cold recycled mixes. The resulting water dispersion is easily combined with the bitumen emulsion and can be easily applied in the preparation of cold mixes. This kind of modification will significantly improve their reliability and durability and to closer in magnitude to the properties of hot asphalt concrete widely used for the construct of road pavements. In order to improve the efficiency of the modification process, the process of emulsification of epoxy oligomers in the presence of nonionic surfactants and further application of the obtained dispersions as a component of bitumen emulsions used for the preparation of RAP cold recycled mixes is justified. This kind of integrated approach to the selection of the composition of water dispersion of epoxy resin provided a higher level of its interaction in the formation of elastic and viscous bonds of increased strength in the formation of the structure of composites based on asphalt, bitumen emulsions and cement.

1. Introduction
Asphalt pavements, even when the absence of an intensive traffic flow, are destroyed over the time. Constant exposure to solar radiation, air oxygen, water and chemical anti-icing agents dissolved in it, alternate freezing and thawing lead to negative changes in the asphalt structure and reduce its strength. This is primarily due to the change in the properties of bitumen, its ageing under the influence of these factors. The content of bitumen in asphalt is usually in the range of 5 to 8 wt.%, Therefore at least 90% of the old asphalt mass is a complete road construction material.

The most acceptable technology for recycling an old asphalt is cold recycling, which eliminates the heating of asphalt with accelerated ageing of bitumen residues, reduces transport costs for moving materials, and provides good environmental performance in the work area. All the technological operations are performed directly on the road. To restore the properties of the asphalt, bitumen emulsions
and cement are commonly used. This makes it possible to obtain a monolithic material with corresponding to traditional hot asphalt properties up to 30–40% [1]. Thus, the most challenging issue in this technology is to ensure the quality of the asphalt restored.

Today epoxy resins are widely used for modification of bitumen and bitumen emulsions for preparation of hot, warm and cold bitumen-mineral mixtures [2-8]. However, many research results show different efficiency of this kind of modification, which is due to the insufficiently developed methodology for designing the compositions of modified binders (modified emulsions).

2. Experiments

The most common epoxy oligomers (EO) with different physical and chemical characteristics were selected for the research: epoxy diane resins with different amounts of epoxy groups NPEL 127, NPEL 128 (manufactured by NanYa Corporation, China) and novolacinated resin NPPN 631 (manufactured by NanYa Corporation, China), epoxy aliphatic resin, PPPN 631 (manufactured by NanYa Corporation, China), epoxy aliphatic resin, China NPPN 631 (manufactured by NanYa Corporation, China), epoxy aliphatic resin, China, epoxy aliphatic resin NPPN 631 (manufactured by NanYa Corporation, China), epoxy aliphatic resin DEG-1 (manufactured by Epital, Russia). Table 1 shows the main physical chemical properties of the resins.

| Resin     | Equivalent weight of epoxy groups (g/eq) | Mass fraction of epoxy groups (%) | Surface tension σ (mN/m) a | Density (g/cm³) |
|-----------|------------------------------------------|----------------------------------|----------------------------|----------------|
| NPPN 631  | 174.0                                    | 24.71                            | 50.0                       | 1.210          |
| NPEL 127  | 183.9                                    | 23.38                            | 46.4                       | 1.167          |
| NPEL 128  | 186.5                                    | 23.06                            | 46.5                       | 1.169          |
| DEG-1     | 167.3                                    | 25.70                            | 38.6                       | 1.177          |

a - the measurement of the surface tension value was carried out on an automatic device “Processor Tensiometer K-100 MK 2” (KRUSS, Germany) using the ring break method. The calculations used correction factors taken from Harkins and Jordan tables.

To assess possibility and effectiveness of combining epoxy resin with bitumen, rheological parameters of resins were carefully studied. Rheological studies were carried out at 20°C using an automatic Physica MCR 101 rheometer (Munzing Chemie, Austria) with the Rheoplus/32 v2.81 computer control program (where the shear strain rate in the stationary mode varied from 1 to 300 s⁻¹). A plate-plate system with a gap of 0.5 mm was used as the measuring system.

Figure 1 shows the rheological curves of individual EO, from which it follows that they behave like Newtonian fluids, since their flow maintains a constant of viscosity (η) for different shear deformations (γ), and a linear dependence of shear stress (τ) on γ value. Here Novolac type NPPN 631 has the highest viscosity. The epoxy aliphatic resin DEG-1 is the least viscous, so that it is usually not used in its pure form but serves as a plasticizer composition for other resins.

From the data presented here, it follows that NPEL-127 resin has a low dynamic viscosity at high shear rates typical for production-type dispersing units. Consequently, the energy consumption when obtaining dispersions of this resin will be the lowest.

In order to identify the best emulsifier, nonionic surfactants of various chemical nature never before used for emulsifying epoxy oligomers by the method chosen were studied. Physical and chemical properties of surfactants, as well as their mixtures, are presented in Table 2. The specificity of non-ionic surfactants in contrast to ionic surfactants is that the low polarity of single functional groups is compensated by their number in long hydrophilic chain, what considers to be an additional advantage in protective films formation around epoxy oligomer particles.

Under laboratory conditions, to obtain aqueous dispersions of EO, a phase inversion method from highly concentrated dispersions was used [9], that provided stable dispersions with predictable properties.
In order to select the most appropriate emulsifier for resin NPEL-127 an emulsifier solution was prepared in water, where amount of EO was calculated then introduced and dispersed on an LDU-3 MPR unit (manufactured by LLC Labotex, Russia) at a rotor speed of 5000 rpm. The dispersion time in all cases was 10 minutes. The concentrated epoxy dispersion obtained was diluted to a concentration of bitumen emulsion of 65 wt. %.

Fig. 1. Dependence of shear stress and dynamic viscosity on shear rate for NPEL 127 (1, 1'); NPEL 128 (2, 2'); NPPN 631 (3, 3') and DEG-1 (4, 4') resins

Table 2. Physical and chemical properties of some surfactants

| №   | Surfactant compound title                          | State of aggregation | Active ingredients content (mass %) | Density at 25 °С (g/ml) | pH  | Surface tension σ, (mN/m)* |
|-----|---------------------------------------------------|----------------------|-------------------------------------|-------------------------|-----|-----------------------------|
| 1   | Polycarboxylic acid salt (M-5)                    | liquid               | 34.0                                | 1.31                    | 9.5 | 29.60                       |
| 2   | Alkyl polyethylene glycol ether of ethylene oxide (N-7) | liquid               | 70.0                                | 1.00                    | 10.0| 38.72                       |
| 3   | Acrylic polymer in butyldiglycol (E-7)            | liquid               | 50.0                                | 1.04                    | 2.0 | 41.57                       |
| 4   | High molecular block copolymer in butyldiglycol (E-9) | liquid               | 40.0                                | 1.00                    | 8.0 | 44.25                       |
| 5   | Non-ionic polyurethane in water (T-6)             | liquid               | 40.0                                | 1.07                    | 6.5 | -                           |

* - the measurement of the surface tension value was carried out on an automatic device “Processor Tensiometer K-100 MK 2” (KRUSS, Germany) using the ring break method. The calculations used correction factors taken from Harkins and Jordan tables. For surfactants in paragraph 5 of this table to measure σ is not possible because of the value being outside the measuring range.

Dispersion stability was chosen as a criterion for assessing its quality, where the stability was characterized by the time of the first signs of delaminating appearance. The particle size distribution of dispersions was investigated at the automatic photometric sedimentometer FSH-4 (manufactured by Scientific Production Association, Russia), which allowed to judge about the reasons for their high or low stability. The data obtained are presented in Table 3.
Table 3. Stability and types of ES dispersions when using surfactants of various nature, as well as their mixtures

| Sample No | Emulsifiers | Dispersion stability (days) | Fraction mass content in the range of 0.1 – 5.0 microns |
|-----------|-------------|-----------------------------|--------------------------------------------------------|
| 1         | N-7         | 27                          | 22.4                                                   |
| 2         | E-7         | 30                          | 78.5                                                   |
| 3         | E-9         | More than 30                | 99.2                                                   |
| 4         | M-5         | 3                           | 50.1                                                   |
| 5         | E-7 + N-7   | 30                          | 95.3                                                   |
| 6         | E-9 + N-7   | More than 30                | 73.7                                                   |
| 7         | M-5 + N-7   | 7                           | 53.1                                                   |
| 8         | E-9 + T-6   | More than 30                | 96.6                                                   |

From the data given in Table 4 it follows that the most stable dispersions are obtained using high-molecular polymer in butyl diglycol No. 3 (E-9) as an emulsifier, as well as its mixture with a solution of non-ionic polyurethane in water No. 8 (T-6). In such dispersion’s fractions in the range of 0.1 – 5.0 μm predominate (see Fig. 2).

Fig. 2. Chart of particle size distribution depending on their mass in dispersion

To assess the effectiveness of the emulsifier E-9 and confirm the correctness of the NPEL-127 resin choosing, we studied the aggregative stability of dispersions on different resins by the method [10]. Thus, the dispersions obtained were placed in 25 ml graduated cylinders, and then to study the change in their particle size distribution during storage an automatic photo-drift meter FSH-4 (Russia) was used. The results of the experiment on the study of aggregative stability are shown in Table 5.

Table 4. Stability of epoxy resin dispersions

| Type of resin | Emulsifier Content (%) |
|---------------|------------------------|
|               | Dispersion stability when phases ratio is resin:water/hour |
|               | 3:1 | 3:2 | 1:1 | 1:4 | 1:9 |
| DEG-1         | 2   | 744 | 744 | 0.5 | 0.5 | 744 |
| DEG-1         | 4   | 744 | 744 | 0.5 | 24  | 24  |
| DEG-1         | 6   | 744 | 744 | 24  | 24  | 744 |
| NPEL 128      | 2   | 282 | 282 | 282 | 282 | 0.3 |
| NPEL 128      | 4   | 600 | 600 | 600 | 67  | 67  |
| NPEL 128      | 6   | 556 | 556 | 556 | 4.2 | 0.3 |
| NPEL 127      | 2   | 744 | 528 | 528 | 341 | 144 |
| NPEL 127      | 4   | 744 | 744 | 744 | 1.6 | 1.3 |
| NPEL 127      | 6   | 744 | 744 | 744 | 22  | 19  |
Table 4. Dispersion stability when phases ratio is resin:water/hour

| Type of resin | Emulsifier Content (%) | Dispersion stability |
|---------------|------------------------|----------------------|
|               |                        | 3:1 | 3:2 | 1:1 | 1:4 | 1:9 |
| NPPN 631      | 2                      | 472 | 216 | 217 | 143 | 195 |
| NPPN 631      | 4                      | 671 | 259 | 288 | 336 | 119 |
| NPPN 631      | 6                      | 744 | 217 | 217 | 139 | 139 |

From the Table 4 it follows that stability of ES aqueous dispersions depends on the type of resin, its quantity, and the content of emulsifier. For NPEL 128 and NPEL 127 resins, dispersion stability to delaminating increases, reaching its maximum at a resin: water ratio = 1:1 and hold it at 3:2 and 3:1 ratio. For NPPN 631 resin, the dispersion resistance to delaminating increases, reaching a maximum at a ratio of 3:1 and an emulsifier content of 6%. DEG-1 resin has shown the best indicators of dispersion stability; however, in practice, this resin is used only as a co-emulsifier or thinning compound for more viscous resins; therefore, in its pure form it is not very promising for obtaining rigid bonds in asphalt. NPEL-127 resin showed the greatest stability of dispersions in the range of emulsifier content of 2–6 wt%, with a resin: water phase ratio from 1:1 to 3:1. In the dispersion, the content of particles with a size of 0.1–5 μm is 99.9–100.0% of their total number, being a sign of its high quality. It should be noted that in this case the emulsifier concentration in the solution 4.5 times exceeds the critical concentration of micelle formation (CCMF), conforming to Antonov's rule [11].

As a result of the research, it was found that for practical use the dispersion of the NPEL 127 resin is most suitable when resin: water ratio is 3:1 with an emulsifier content of 2% of resin weight.

Using the developed optimal water dispersion of NPEL-127 resin together with the bitumen cationic emulsion, RAP cold recycled mixes with increased reliability and durability characteristics can be prepared. As a hardener of epoxy resin can be used a water solution of amine adduct, or any other waterborne hardener of epoxy resins.

To study the effects of modification of the RAP cold recycled mixes with epoxy resins, supplied in the step of preparation in the form of water dispersions, is a direction for future research.

3. Conclusions
As a result of the studies, a stable dispersion of epoxy resin NPEL-127 was obtained using a high-molecular block copolymer in butyldiglicol as an emulsifier, which allows to store the dispersion for a long time and mix it with bitumen emulsions to obtain binders in RAP recycling technologies.

The proposed algorithm for optimizing the composition of water dispersion of epoxy resin can be used for further research aimed at selecting the most effective oligomers containing epoxy groups for modification of RAP cold recycled mixes.

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