Bitumen chemical modification by a thermoplastic polymer

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Abstract. Oil road bitumen was modified by a copolymer of ethylene with vinyl acetate (EVA) and 3-glycidyloxypropyltrimethoxysilane (epoxysilane). These modifiers were simultaneously introduced into the BND 90/130 oil bitumen at a temperature of 165 °C. The components were mixed up during two hours with further isothermal holding at the same temperature during the required period. Epoxysilane crosslinks bitumen with EVA making it possible to obtain an immiscible bitumen polymer binder. The optimal content of EVA is 12 mph, epoxysilane - 3 mph with a mixing time of 4 hours. The optimal bitumen polymer binder is characterized by the following properties: softening point of 66 °C, penetration at 25 °C = 50, penetration index of 2.15, brittleness temperature of -22 °C. Separation is significantly reduced. NMR spectroscopy has revealed that the introduction of the binding agent to the bitumen-polymer binder does not create low-mobile structures. It allows forecasting the high binder stability during storage and transportation.

Keywords: bitumen modification, polymer-bitumen binder, polymer-bitumen binder stability, bitumen chemical modification, bitumen-epoxy.

1 Introduction

Bitumen-polymer binders (BPB) were introduced in road construction instead of conventional bitumen in 2000, not a very long time ago [1]. The advantages of bitumen-polymer binders [2, 3, 4] and mastic fillers [5, 6] over the non-modified bitumen are well-known: wide ductile temperature range, high elasticity and resistance to atmospheric aging. Despite of this, BPBs have not been often used in road construction until recently due to their high price [7]. However, the unsatisfactory quality of the existing pavement surfacings has led to the scope of application of BPBs having multiplied recently [8-10]. It was found out that the major technological challenge associated with bitumen-polymer binders is their tendency toward delamination during storage and transportation. The Russian State Standard GOST 52056-2003 “Polymer-bitumen binders for roads on the basis of block copolymers of styrene-butadiene-styrene type. Specifications” regulates the storage and transportation conditions of such binders, thus entailing serious technological inconveniences for manufacturers. Nevertheless, the Russian regulations do not provide any stability requirements for binders as opposed to bitumen emulsions [11-13]. The literature has been lately increasingly focusing on this issue [14-19]. However, the importance of the BPB compositional stability and BPB properties during storage and transportation were a topic up for investigation much earlier as it was believed that the abovementioned factors were indispensable for ensuring that bitumen-concrete mixes and asphalt-concrete based on modified bitumen were prepared in a quality manner [20-21].

One of the popular thermoplastic modifiers is the copolymer of ethylene with vinyl acetate (EVA) [22-23], capable of forming a deformation-resistant net inside bitumen thus improving the elasticity, cohesion and adhesive properties. Thermoplastics are more often used in the southern Russian regions where the deficiencies generally pertaining to the thermoplastic-based BPB, such as insufficient elasticity and cracking resistance at low freezing temperatures [24, 25], do not occur.
2 Materials and methods
To obtain the immiscible BPB with the use of EVA, we used the chemically reactive additive binding the bitumen matrix with polymer modifier in our work. It is considered that the chemical interaction of the components in bitumen-polymer compositions ensures their homogeneity and stability. They reduce the likelihood of the composition delaminating due to the different densities of the bitumen and the modifiers [26-27].

The technology behind the binder was as follows: the 11708-210 brand EVA containing 26-28 % vinyl acetate and the binding agent, 3-glycidyloxypropyltrimethoxysilane (epoxysilane, ES), the heterofunctional telechelic substance the epoxy group of which is capable of chemical interaction with the carboxy group of bitumen asphaltens [28], with the methoxy silane groups reacting with acetylic fragments of ethylene and vinyl acetate copolymer [29-31], were simultaneously introduced into the BND 90/130 oil bitumen at a temperature of 165 °C. The components were mixed up during two hours with further isothermal holding at the same temperature during the required period.

3 Results and Discussion
3.1 Optimization
In order to optimize the concentrations of epoxysilane and ethylene and vinyl acetate copolymer, as well as the alignment time of the components, the three-factor rotatable experimental plan was implemented, where the factors were the optimizable parameters, and the optimization criteria were the main properties of the bitumen binder: the softening temperature Ts, penetration at 25 °C P25, the ductility at 25 °C D25, the brittleness temperature Tbr, the storage stability, the penetration index IPe, the elasticity at 25°C E25 and the change in the softening temperature after warm-up ΔTs.

The three-factor experiment results cannot be illustrated in the graphical representation in the form of one three-dimensional graph. That is why to illustrate the results for each binder characteristic taken as the input, each of the factors was alternately considered as constant and taken as being equal to its value in the center of the plan. Therefore, three three-dimensional graphs were plotted for each BPB characteristic that made it possible to find out the optimal values of the experiment factors.

Figure 1 shows the dependence of the bitumen softening temperature and ES and ethylene and vinyl acetate copolymer concentration and the time of reaction.
As it can be seen, the surface has its maximum in all three graphs. It should be noted that this maximum coincided with the center of the plan. The increase in the epoxysilane concentration entails the increase on the softening temperature but only as long as the ES participates in reactions. Its excess amount in the composition acts as the plasticizer reducing the binder heat-resistance. The increase in the polymer content in the BPB first entails an intense rise in the softening temperature. However, the increase in the polymer concentration by more than 12% does not lead to a rise in the heat-resistance, and thus, it is not effective. The dependence of the heat-resistance on the time alignment of components is of extreme nature. At first, the time of alignment is directly related to the behavior of the chemical reaction, however, once the component binding process is completed, the isothermal holding at high temperatures produces only a destructive effect on the composition.

Similar figures were obtained for other properties. The analysis of these figures showed that the effect of epoxysilane and ethylene and vinyl acetate copolymer on the binder hardness correlates with the heat-resistance data: the heat-resistant binders are harder. The increased delamination of the composition leads to increased penetration due to the floating of the loose swollen polymer. This effect was observed in the works [20, 21].
The excess ES not involved in the reaction has a negative impact on the binder brittleness temperature while the polymer improves this indicator even in the free form. The increased alignment time also has a positive impact on the brittleness temperature of the composition.

The stability procedure of the modified bitumen is regulated by the intergovernmental state standard GOST EN 13399-2013 “Bitumens and bituminous binders. Determination of storage stability of modified bitumens”. This procedure consists in isothermal holding of the binder-column 100-120 mm high in a vertical tube of 25-40 mm in diameter and 160 mm high at 180 °C for three days with a further evaluation of properties in the upper and lower thirds of the cylinder.

Figure 2 shows the dependence of the binder delamination on the ES and ethylene and vinyl acetate copolymer concentrations and time of reaction. The y-axis shows the difference in densities of the upper and lower parts of the delaminated binder.
c) **Figure 2.** The dependence of the bitumen delamination on: a) ES and ethylene and vinyl acetate copolymer content; b) ethylene and vinyl acetate copolymer content and time of reaction; c) ES content and time of reaction.

It is obvious that the excess of components increases the delamination of the composition while the alignment duration has an extreme impact on this indicator. During the initial period, time has a positive impact on the binder stability, as the chemical reactions occur during this period, and the further settling of the binder only serves to facilitate the delamination process. It should be noted that the epoxysilane-free binders are characterized by much higher delamination.

The graphs given above and the other plotted graphs show that the center of the plan was selected correctly. The optimal content of ethylene and vinyl acetate copolymer - 12 phr, epoxysilane - 3 phr, alignment time - 4 h. The properties of the developed binder as compared to the pure bitumen are given in Table 1.

| BINDER | \( T_{55}, ^\circ C \) | \( P_{25}, 0.1 \) | \( D_{25}, CM \) | \( E_{25}, % \) | \( T_{inf}, ^\circ C \) | DELAMINATION, \( G/CM^2 \) | PI | \( \Delta T_{55}, ^\circ C \) |
|--------|----------------|----------------|----------------|----------|----------------|----------------|------|----------------|
| BND 90/130 – 100 PHR | 44 | 109 | 71 | 13 | -17 | 0 | -0.8 | 4 |
| BND 90/130 – 100 PHR + EVA - 12 PHR | 63 | 61 | 10 | 58 | -21 | 0.012 | 2.1 | 3 |
| BND 90/130 – 100 PHR + EVA - 12 PHR + ES – 3 PHR | 66 | 50 | 11 | 55 | -22 | 0.002 | 2.15 | 3 |

3.2 **Molecular mobility assessment**

Therefore, the developed binder truly possesses a high range of properties and low delamination. However, the interaction of binder components as well as the mechanistic potential of producing the lattice pattern in the composition always requires a syneresis risk assessment as one of the main factors of the stability of the binder [32-33]. For this purpose, we assessed the molecular mobility of the bitumen compositions by measuring the nuclear magnetic relaxation on the NMR analyzer “Chromatech-Proton 20 M”. The low molecular mobility of the bitumen components will be indicative of the formation of dense lattice or high-molecular components in the composition that induce crystallization, syneresis and delamination in the binder.
The working frequency for the protons was 20 MHz. The measurement results of the lateral nuclear magnetic relaxation for three samples are given in Figure 3 in the coordinates of the free induction decay (FID) signal - the time.

![Figure 3](image-url)

**Figure 3.** The dependence of free induction decay on the time:
1 - pure bitumen;
2 - bitumen - 100 phr, ethylene and vinyl acetate copolymer - 12 phr;
3 - bitumen - 100 phr, ethylene and vinyl acetate copolymer - 12 phr, ES - 3 phr.

In simple cases (liquids), the FID depends on the time exponentially and such coordinates produce a line the slope of which is used to determine the lateral relaxation time $T_2$. The longer the $T_2$ time the smaller the slope. These lateral relaxation time values determined in this method by the motion of the hydrogen atoms contained in the compositions are inversely proportional to the correlation time values $\tau_C$ characterizing the molecular mobility.

The initial value of the FID signal is proportional to the number of the hydrogen centers (protons) in the sample. As their number was different in the test samples, normalization to the same initial value was performed prior to plotting the dependences. Figure 3 shows that the dependences of the FID and time are typical for all samples and are different from the straight line. It follows that the NMR and molecular mobility data correlation can be of qualitative nature only.

In order to facilitate the comparison of the nuclear magnetic relaxation of the samples between each other, the dependences were approximated by the Eq. (1)

$$A(t) = A(0) \cdot [p_c \exp\left(-\frac{t}{T_{2c}}\right) + p_b \exp\left(-\frac{t}{T_{2b}}\right) + p_a \exp\left(-\frac{t}{T_{2a}}\right)]$$

where $p_a$, $p_b$, $p_c$ – parts $T_{2a}$, $T_{2b}$, $T_{2c}$ – times of relaxation of component decomposition. Therefore, all the molecules were distributed by some “phases” differing by molecular mobility. The quotations show that in our case the notion of “phase” is not related to the existing physical phases.

**Table 2.** NMR-spectroscopy results.

| Sample Nos. | $p_c$ | $T_{2c}$, $\mu$s | $p_b$ | $T_{2b}$, $\mu$s | $p_a$ | $T_{2a}$, $\mu$s |
|-------------|-------|-----------------|-------|-----------------|-------|-----------------|
| 1           | 0.52  | 12.6            | 0.23  | 80.6            | 0.25  | 319             |
| 2           | 0.45  | 12.7            | 0.25  | 91              | 0.30  | 401             |
| 3           | 0.51  | 12.3            | 0.25  | 87              | 0.31  | 376             |
“Phase” “C” characterizes the least mobile molecules primarily belonging to the asphaltene molecules. “Phases” “A” and “B” belong to maltenes and the other, more mobile molecules of the prepared mix.

The addition of the ethylene and vinyl acetate copolymer to the bitumen according to the NMR data (Table 2) slightly reduces the microviscosity of the mix (the molecular mobility and share increase in phase “A”). This may be due to the higher mobility of the ethylene and vinyl acetate copolymer and its impact on the maltene component of the bitumen. The addition of the binding reagent according to the NMR data (Table 2) does not practically change the microviscosity of the mix.

Therefore, the introduction of the NMR method to the bitumen-polymer binder does not create low-mobile structures that allow forecasting the high binder stability during storage and transportation.

4 Conclusions

1. The conducted studies have shown that in order to produce the immiscible bitumen-polymer composition with the use of ethylene and vinyl acetate copolymer, it is reasonable to use the heterofunctional telechelic substance the epoxy group of which is capable of chemical interaction with carboxy group of bitumen asphaltenes with the methoxy silane groups reacting with acetyllic fragments of ethylene and vinyl acetate copolymer.

2. The factors for producing the immiscible bitumen-polymer binder with the use of ethylene and vinyl acetate copolymer have been optimized. The optimal content of ethylene and vinyl acetate copolymer - 12 phr, epoxysilane - 3 phr, alignment time - 4 h.

3. The NMR method has shown that the introduction of the binding agent to the bitumen-polymer binder does not create low-mobile structures which makes it possible to forecast the high binder stability.

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