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Possibility Improvement Technology of Modification Road Bitumen by the Green Epoxy Rapeseed Oil on the Basis of Renewable Raw Material

Yurii Hrynchuk[1], Iurii Sidun[2], Volodymyr Gunka[1], Volodymyr Reutskyy[1], Iryna Koval[1], Pavlo Matcipura[1], Mykola Mosiuk[3]

[1] Institute of Chemistry and Chemical Technology, Lviv Polytechnic National University, 12 Bandera street, Lviv, Ukraine
[2] Institute of Building and Environmental Engineering, Lviv Polytechnic National University, 12 Bandera street, Lviv, Ukraine
[3] Institute of Tourism and Geosciences Ivano-Frankivsk National Technical University of Oil and Gas, 15 Karpatska Street Ivano-Frankivsk Ukraine

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Abstract

Epoxy modification of bituminous binders is recognized as an effective technology for changing the physical and mechanical properties of asphalt concrete. It allows you to design durable road structures. However, the physical and mechanical properties of epoxy asphalt systems are still insufficiently studied. In this work, attention is paid to the study of physical and mechanical properties of bituminous binders in the process of modification of their ecological (green) epoxy compounds on the basis of cheap and available renewable raw materials in the presence of initiators (hardeners). For this purpose, a model of modification of road bitumens bio based epoxy rape oil is proposed. Various organic hardeners (adipic acid, formic acid, polyethylene polyamine and maleic anhydride) were used to intensify the process. It is established that such model allows to obtain bitumen with improved properties.

Keywords: *Bitumen; Epoxide; Rapeseed oil; Modification; Green epoxy rape oil.*

1. Introduction

Today in the world the most widespread coverings for highways are asphalt concretes. But despite high demand, these coatings are not perfect. The problem lies in the binder - bitumen, the quality of which mostly leaves much to be desired. Various modifiers are used to improve the properties of bitumen [1-10]. Which are usually divided into the following groups: polymers, adhesion promoters, waxes, fibers, natural bitumen, rubber crumb, various chemical reagents (polyphosphoric acid, ferric chloride, organometallic complexes). The most commonly used modifiers are polymers, which are also divided into certain groups: thermoplastics, thermo-elastoplasts, terpolymers (reactoplasts or thermosetting polymers), latexes.

Among these polymer modifiers, thermosetting polymers, in particular epoxy resins and their hardeners, have been little studied. However, studies to date indicate that epoxy-containing additives can radically change the properties of bitumen and asphalt concrete and the effect of their use can be much higher than other modifiers. Asphalt concrete mixtures of different types, which include epoxy resins, are called epoxy asphalt concrete.

Studies [12-16] have shown that epoxy asphalt concrete has high strength and track resistance at elevated temperatures; high resistance to the formation of cracks from prolonged transport and low temperatures; resistance to fuels and lubricants; increase in (2 - 4) times the service life of road surfaces.

Epoxy asphalt concrete should be used for the installation of asphalt pavements on congested sections of roads, concrete and reinforced concrete foundations of bridges [17-18].

In [19] it is claimed that during the hardening of asphalt concrete there are some polymerization reactions between the epoxy resin and the hardener and their crosslinking with bitumen, which can change the properties of the final product. Polymerization reactions are the interaction between a carboxyl group and an epoxy group, through which an ether carbonyl group is formed, due to which carbonyl acid molecules and epoxy molecules are connected to each other, forming a crosslinked network [20]. Commodity amine and amide hardeners for petroleum epoxy resins, as well as dibasic carboxylic acid can act as initiators.

Studies [21-23] also confirm that epoxy resin can significantly improve the properties of asphalt binder. However, the reviewed studies indicate that modern epoxy resins made from crude oil are quite expensive and not environmentally friendly. In view of the above, the use of epoxy compounds based on vegetable origin, in particular rapeseed oil, for the modification of road bitumens is promising. Which are cheap to produce, affordable, environmentally friendly and made from renewable raw materials, which, moreover, is produced in sufficient quantities by Ukraine. Based on previous studies [8-9], which indicate the feasibility of using rapeseed epoxide to modify road bitumen and asphalt concrete, the authors propose to modify the bitumen so-called bio based epoxy rape oil. By bio based epoxy rape oil we mean the use as a modifier of epoxy rapeseed oil (EPO) obtained from renewable and environmentally friendly raw materials, rapeseed oil. Special initiators (hardeners) were used to intensify the modification.

Therefore, our research was aimed at developing a new model capable of predicting the behavior of modified epoxy rape oil bitumens in different conditions and ways to intensify this process using initiators. It is important for us to understand the mechanism of modification and curing and how it affects the physical and mechanical properties of epoxy bitumen systems.

2. Background

Bitumen is a compound based on various molecular structures: asphaltenes, resins and oils. Epoxy compounds are monomers or short-chain copolymers having an epoxy group at either end, and they are polymerized using hardeners. In bitumen binder epoxy systems, polymer chains are formed by the reaction of an epoxy modifier with initiators with reaction functional groups in a solid matrix. This phenomenon is called polymerization, which involves the formation, branching and crosslinking of epoxy polymer chains. During polymerization, the molecular weight increases and a higher molecular weight is achieved when all the chains are interconnected in a network [24].

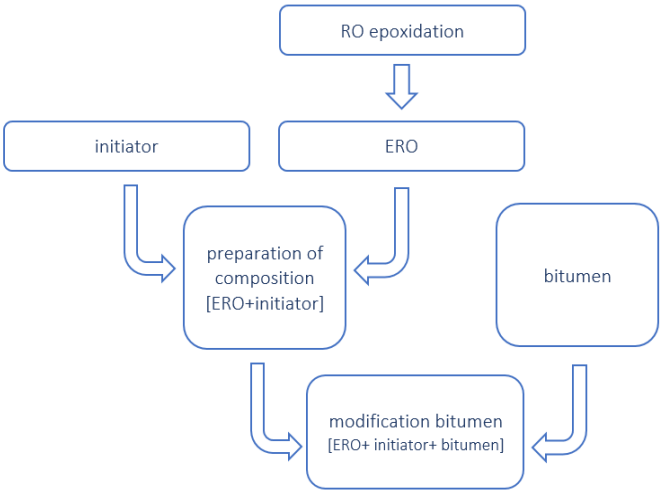

Figure 1. Scheme of bitumen modification by green epoxy rape oil

In previous works [8-9], a study was conducted on the modification of bitumen and asphalt concrete with rapeseed oil epoxide (EPO) on the basis of cheap and renewable raw materials, rapeseed oil (PO). The results show that the nature of the change in the qualitative properties of bitumens of different brands of modified EPO is the same. The obtained results allow to characterize EPO as an effective modifier for petroleum road bitumens and asphalt concretes based on them.

All the obtained results of the qualitative characteristics of the modified bitumens were achieved at high temperatures of 180-190ºC and a long duration of modification, more

than 5 hours. Such technological parameters are quite expensive and impractical. From the analysis of literature sources [25] and the idea of epoxy compounds, we proposed to optimize this technology by adding initiators according to the following scheme (Figure 1), which will accelerate the polymerization of the epoxy component in bitumen at lower temperatures.

3. Experimental

3.1. Initial materials and methods

The first step was to determine the effect of the composition [ERO: initiator] on the process of modification of bitumen70 / 100 PJSC "Ukrtatnafta", Ukraine (Table 1).

Table 1. Characteristics of road bitumen 70/100

Index	Value
Penetration at 25°C, m·10^{-4} (0,1 mm)	70
Softening point, °C	46
Ductility at 25°C, m*10^{-2} (sm)	100
Adhesion to glass, %	33
Index of penetration	-1,5
Plasticity interval	64

EPO was used by epoxidation of RO according to the method [8], EN = 6.52%. Based on previous studies [8], the content of the modifier composition (EPO) with hardener (initiator) - 3%, process temperature - 180°C, process time - 5 hours.

According to Fig.1 combined EPO with initiators (ratio 1: 0.1 [ERO: initiator]). As initiators used: polyethylene polyamine (PEPA), maleic anhydride (MA), formic acid (FA) and adipic acid (AA) and used this composition to modify bitumen.

All bitumen modification experiments were performed in a thermostatic reactor with a paddle stirrer. To heated to 180°C bitumen was added 3% of the mass. a mixture of EPO with the initiator. The temperature remained constant throughout the experiment. Samples of modified bitumen were taken at intervals of 1 h for 5 h of modification. Tests of modified bitumen samples were evaluated by the following parameters: temperature of softening, penetration at a temperature of 25°C, ductility at a temperature of 25°C, adhesion to glass [26-29].

The research results showed that the sufficient modification time is 2 hours, during which time the values of the physical and mechanical properties of the modified bitumen reached constant values and did not change after that time. The results of the modification are given in Table. 2.

Table 2. Physical and mechanical characteristics of bitumen

Bitumen 70/100	Softening point, °C	Penetration at 25°C, m·10^{-4} (0,1 mm)	Ductility at 25°C, м·10^{-2} (sm)	Adhesion to glass, %
-	46	70	>100	33
+3% [ERO]	51	68	>100	38
+3% [ERO + AdA]	48	66	>100	65
+3% [ERO + MC]	47	75	>100	35
+3% [ERO + MA]	49	63	>100	55
+3% [ERO+PEPA]	47	58	>100	95

The results obtained indicate that the addition of the initiator to the composition of the EPO has a positive effect on the physical and mechanical properties of the modified bitumen and generally allows to influence the conditions of the modification. However, this effect also depends on other factors, such as temperature, type of initiator and its content in the composition with EPO. Thus, during the first hour of modification, the adhesion of the modified bitumen increases from 33% to 95% when added to the EPO amine initiator - polyethylene polyamine, when added to the modifier adipic acid, the adhesion of bitumen increases to 65%. and is virtually unchanged when using other initiators. The use of the modifying composition ERO

with the initiator also allows you to influence the softening point and penetration, and the modified bitumen becomes harder.

A good result is the modification time, because you can see the achievement of maximum values of quality bitumen in these conditions for the first 2 hours of the process. Without the use of initiators, this time was> 5 h [9].

Tests of modified bitumen composition [ERO + AdA] were repeated 30 days after modification. Interestingly, the values of physical and mechanical properties (softening point + 3°C, penetration - 5 m·10^{-4}) changed in comparison with the indicators of modified bitumen tested immediately after modification. In general, bitumen has become harder, this can be explained by the fact that epoxy compounds have a gelatinization time of 1-5 h and fully polymerize not earlier than 24 h after the start of the reaction [24], indicating crosslinking and polymerization reactions in bitumen with epoxy rape oil after modification.

In the second stage of the study, the composition [EPO: initiator] was combined with bitumen to establish the optimal content of the modifying composition in road bitumen. The influence of the molar ratio [EPO + initiator): bitumen] on the physical and mechanical properties of modified bitumen was studied (Fig.2 - Fig.4). The composition of the epoxy of rapeseed oil with the initiator was introduced into the bitumen in the amount of 0.5-3% of the mass. The content of the initiator in the EPO - 5% of the mass. Modification of bitumen was carried out at a temperature of 160°C for 2 hours.

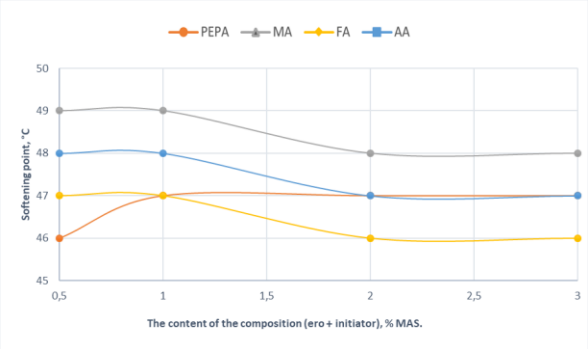

Figure 2. Dependence of softening temperature of modified bitumen on the content of the composition [EPO: initiator]

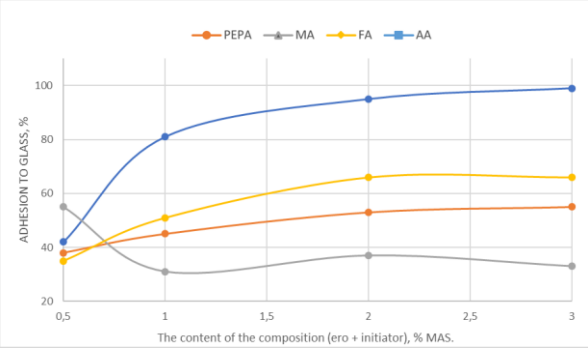

Figure 3. The dependence of the adhesion of the modified bitumen on the content of the composition [EPO: initiator]

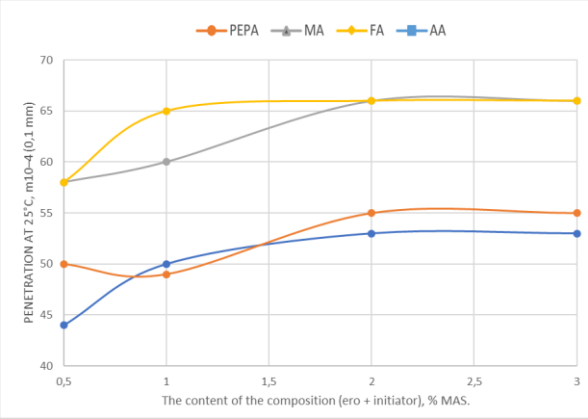

Figure 4. Dependence of penetration of modified bitumen on the content of the composition [EPO: initiator]

The results show that increasing the content of the composition [EPO: initiator] in bitumen from 0.5 to 3% wt., Can increase adhesion from 33% to 95%. There are also slight changes in penetration and softening temperature when using initiators in the process of bitumen modification. Moreover, the duration of the process was reduced from 5 h to 2 h, and the temperature dropped to 160°C.

It is necessary to thoroughly study the effect of the composition (EPO: initiator)] on bitumens of other brands. Also, additional research is needed to study the effect of this modifying system on asphalt mixtures.

4. Conclusion

Improvement of technology of modification of high-quality road bitumens by rapeseed epoxy by use of organic initiators (hardeners) is offered. The influence of adipic acid, formic acid, polyethylene polyamine and maleic anhydride as initiators in the modifying system with EPO on the physical and mechanical properties of modified bitumens was studied.

It is shown how the properties of modified road bitumen depend on the content in the composition of the ERO initiator. The use of initiators in the composition with EPO has a positive effect on the physical and mechanical characteristics of the modified bitumen and in general allows to influence the conditions of the modification. In particular, the modification time was reduced by 3 hours to 1-2 hours. The process temperature dropped to 160°C

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To whom correspondence should be addressed: Dr. Volodymyr Gunka, Institute of Chemistry and Chemical Technology, Lviv Polytechnic National University, 12 Bandera street, Lviv, Ukraine,
E-mail: vgunka@gmail.com