Research of the petroleum road bitumen modification process with secondary polyethylene terephthalate

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Abstract. Modification of bitumen with polymers is an effective way to improve its properties. Despite the sufficiently widespread use of this method, currently there are practically no appropriate methods of this process calculation. Moreover, there are almost no the models to determine the size of formed polymer particles in modified bitumen of non-traditional polymer modifiers. The paper gives a mathematical description of the secondary polyethylene terephthalate particles formation in bitumen during the process of its modification. In terms of the stochastic approach, we obtained the analytical expressions for the differential distribution function of polymer particles in size, as well as the average size, surface, and volume. According to the research, increasing the rotation speed of the stirring mechanism leads to a decrease of the average particle size of the polymer. We use free software wxMaxima to perform the calculations.

Keywords. bitumen modification, polyethylene terephthalate, size distribution, average size, modelling.

1 Introduction

Actually, during the operation of motorway roads their relatively low reliability is determined by the low quality indicators of the raw materials used, including road bitumen even with full compliance with the technology of asphalt concrete mixtures and the technology of road pavement construction.

This claim proceeds from the Law of Congruence of Properties established by I.A. Rybiev. The law specifies the dependence of binder and conglomerate on its basis [1].

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Whenever, polymer modifiers are gaining popularity for use in road construction, since they are an efficient method of improving the technical and operational characteristics of bituminous binder, and asphalt concrete mix. When the content of polymer additives is in the range of 1 to 3 (5) % of bitumen weight, there are significant changes in the characteristics of their heat resistance, penetration, extensibility, elasticity, and brittleness [2].

Indeed, many studies [3-9] concern with styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) copolymers as bitumen modifiers. They are the most common ones for bitumen binders [4, 6, 7, 8] forming a spatial polymer matrix at certain concentrations in the bitumen system. However, the cost of these modifiers is quite high.

Moreover, many studies concern with the other types of polymer modifiers, partially obtained through the recycling of household waste: thermoplastic rubbers based on ethylene propylene rubber (EPR), and high-density polyethylene (HDPE) [5, 9]. The mechanism of change of bitumen rheological properties during modification can be both similar to the process of modification of SBS and SIS. However, it can also be due to the creation of dispersed phase of modifier in the dispersion medium of bitumen.

Consequently, the most common modifiers of bitumen are thermoplastic elastomers and polyolefins [10].

Although, there are also mentions of secondary polyethylene terephthalate (PET) [11] – a thermoplastic polymer from the class of polyesters, being used as a bitumen modifier. A structuring function of inert fine filler was assigned to the polymer in this study. PET dispersion particles act as centers of physical adsorption, since chemisorption processes between the particles of the dispersed medium and the dispersion phase are unlikely.

The results of [11] provide our further research. Notwithstanding the indicative nature of the empirical data, the process of polyethylene terephthalate dispersion formation has no provable mathematical apparatus to determine particle size, specific reaction surface area, and their average volume.

Hence, obtaining analytical expressions for the determination of the dispersion indices described above in terms of the stochastic approach is the aim of this research.

**Materials and Methods**

The bitumen modification process proposed in this paper involves thermomechanical dispersion of polyethylene terephthalate in bitumen medium and occurs in several stages.

At the first preliminary stage, PET particles are obtained (in the form of plates or flexes) by grinding recyclables to the size of 5-15 mm (thick-walled substandard sections of raw materials must be removed).

The second stage involves the introduction of the obtained PET particles (10 % by mass of bitumen) into BND 60/90 bitumen heated to a temperature of 255 ºC according to GOST 22245-90. The metal reactor was heated by an AIRHOT IP5000 induction furnace. The homogenization of the modified binder was performed with a laboratory stirrer RW 20 DIGITAL, with a shaft rotation frequency \( v = 60 \) Hz. Temperature control was performed by a non-contact laser pyrometer AMO P400.

The homogenization time of the modified binder in a 20-liter container is 10-12 minutes, subject to temperature stability.

During the process of the modified binder homogenization flexa plates are pulled into microfilaments; their subsequent destruction is provided under the influence of temperature and mechanical action of the stirrer blades.

The homogenisation process results in the formation of an emulsion of polyethylene terephthalate, which is in a structurally liquid state of the bitumen system.

Further, cooling of the formed mass in air to the crystallisation temperature of PET is conducted. The process is performed with the stirring device switched on. When the
temperature is reduced to 160-180 °C, new PET particles in the form of dispersion are formed in the bitumen throughout its volume.

Results

According to preliminary experimental studies, the formed PET particles have a polydisperse composition, and a shape close to spherical one. The size distribution of the formed PET particles in bitumen has a significant impact on the resulting asphalt concrete. Hence, it is relevant to develop a mathematical description to evaluate the above distribution and identify the modes providing the most favourable option.

Since the process of particle formation in the PET bitumen melt is probabilistic in nature, for its description we will use the probabilistic approach, which is effectively used in modelling disperse flows, including those with liquid phases [12].

Using the probabilistic approach [13-17], we first describe a set of elements of the phase space \( d\Omega \), which in this case will be a combination of the random velocity of the PET particle and its random size \( D \). It corresponds to the mechanism of formation of PET particles from the melt in the process of temperature reduction [13,15]:

\[
d\Omega = dv dD.
\]

For the convenience of calculations and presentation of the results, we introduce non-dimensional nomenclature for random variables:

\[
D_B = \frac{D}{D_0}, w = \frac{v}{v_0},
\]

Here \( D_0 \) is an average size (diameter) of the mineral powder particles that are part of the asphalt concrete being formed; the \( v_0 \) is maximum linear velocity of the edge of the stirring mechanism.

According to [13, 17], the distribution of the number of formed particles \( dN \) in the phase volume element \( d\Omega \) is described by the expression:

\[
dN = A \exp(-E_{E_0}^{-1}) d\Omega.
\]

The energy of the stochastic motion of the particles \( E \) in this case can be represented as the sum of the kinetic energy imparted to the particles during the motion of the stirring mechanism and the surface energy [13]:

\[
E = E_k + E_p.
\]

The kinetic energy transmitted to the particles by the stirring mechanism is represented as two components:

\[
E_k = \frac{m v^2}{2} + \frac{I_x \omega^2}{2}.
\]

Where \( I_x = \frac{2}{5} mR^2 \) is the moment of inertia of the PET particle, \( \omega \) is the angular velocity of its rotation, which can be considered proportional to the velocity \( v \), or \( \omega = 2v_0 w D_0 D_B^{-1} \).

The surface energy of the particles is determined by the formula [13, 14]:

\[
E_p = \pi D^2 \sigma,
\]
where \( \sigma \) is the surface tension coefficient [N/m].

Then the expression for the energy of stochastic motion is as follows:

\[
E = \frac{mv^2}{2} + \frac{I\omega^2}{2} + \pi D^2 \sigma,
\]

(7)

And the same in a non-dimensional nomenclature is:

\[
E = \frac{11\pi p D_b^3 D_0^3 \sigma^2}{120} + \pi D_b^2 \sigma.
\]

(8)

The expression for the differential particle size distribution function \( f(P) \) according to [12-14] will be formed for the reduced elementary phase volume \( d\Omega' = dw \):

\[
f(P) = \frac{1}{N} \frac{dN}{dD_b} = \frac{1}{N} \int_{w_{min}}^{w_{max}} \text{Aexp}(-EE_0^{-1})dw.
\]

(9)

Here \( w_{min}, w_{max} \) are the smallest and largest values, respectively, of the non-dimensional parameter \( w \).

After calculating a certain integral in (9), the probability density function of material particles in accordance with the non-dimensional nomenclature \( D_b \) is as follows:

\[
f(P) = \frac{A}{N} \left( \frac{x_1[\text{erf}(x_2 v_{max}) - \text{erf}(x_2 v_{min})]}{x_2} \right).
\]

(10)

Here the values \( x_1 \) and \( x_2 \) are derived from the following expressions:

\[
x_1 = \sqrt{30} \exp(-\pi \sigma D_0^2 D_b^2 E_0^{-1}), \quad x_2 = \sqrt{11\pi p D_b D_0 v_0} \sqrt{\rho D_b D_0 E_0^{-1}}.
\]

(11)

Mathematical transformations were performed with the free software product wxMaxima.

The parameters of the probability density function in accordance with particle size distribution \( f(P) = \frac{1}{N} \frac{dN}{dD_b} \) are constants \( A \) and \( E_0 \).

To determine the constant \( A \), we will make a normalization requirement:

\[
N = \int_{\Omega} dN.
\]

(12)

Solving equation (12) we have:

\[
A = \frac{u_0}{u_1 \text{erf}(u_3 v_0 w_{min}) + u_2 \text{erf}(u_3 v_0 w_{max})}.
\]

(13)

In this expression, the values \( u_0-u_3 \) are determined by the formulas:

\[
u_0 = \sqrt{11\pi p D_b D_0 v_0} \sqrt{\rho D_b D_0 E_0^{-1}}, \quad u_1 = \sqrt{30} (D_{b_{max}} - D_{b_{min}}), \quad u_2 = \sqrt{30} (D_{b_{max}} - D_{b_{min}}), \quad u_3 = \sqrt{11\pi p D_b D_0 v_0}.
\]

(14)
Here \( \text{erf}(x) \) is the error function [18].

The energy constant \( E_0 \) is determined from the energy balance compiled for the moment of the dispersed flow formation of PET particles:

\[
E_0 = E_p. \tag{15}
\]

Here \( N \) is the number of particles in the flow; \( E_0 \) is the energy of the particles moving together with mixing paddle before the transition to a disperse state.

The expression for the energies \( E_0 \) and \( E_p \) included in (15) is represented as:

\[
E_0 = \sum_1^N m_v E_p = \int \Omega E dN. \tag{16}
\]

Solving equation (15) we have:

\[
E_0 = \frac{k_1}{k_2}. \tag{17}
\]

Where the values \( k_1 \) and \( k_2 \) are taken from the expressions:

\[
k_1 = \pi^2 (AD_0^6 \rho^2 k_3 + AD_0^5 \rho k_4 + AD_0^4 k_5) k_0, k_2 = \pi (AD_0^6 \rho k_6 + AD_0^5 k_7) k_0 - 9600 E_p. \tag{18}
\]

The values \( k_0, k_3-k_8 \) are determined in accordance with the formulas:

\[
k_0 = \exp\left( \frac{-11 \pi D_0^3 v_0^2 v_2 + 120 \pi \sigma D_0^2}{120 E_0} \right), k_3
\]
\[
= 121(-D_{b_{\min}}^2 v_0^4 w^4 + 2D_{b_{\min}} v_0^4 w^4 + D_{b_{\max}}^2 v_0^4 w^4 - 2D_{b_{\max}} v_0^4 w^4), k_4
\]
\[
= 2200(-D_{b_{\min}}^2 k_8 + 2D_{b_{\min}} k_8 + D_{b_{\max}}^2 k_8 - 2D_{b_{\max}} k_8), k_5
\]
\[
= 9600(-D_{b_{\min}}^2 + 2D_{b_{\min}} + D_{b_{\max}}^2 - 2D_{b_{\max}}), k_6
\]
\[
= -1320D_{b_{\min}} k_8 + 1760D_{b_{\min}} k_8 + 1320D_{b_{\max}} k_8 - 1760D_{b_{\max}} k_8, k_7
\]
\[
= 9600(-D_{b_{\min}}^2 + D_{b_{\min}} + D_{b_{\max}}^2 - D_{b_{\max}}), k_8 = v_0^2 w^2. \tag{19}
\]

The graph of the probability density function of the number of PET particles over a non-dimensional parameter \( D_b \) is shown in Figure 1.
Fig. 1. Graph of the probability density function of the number of PET particles over a non-dimensional parameter $D_b$ at $E_0 = 2.11 \cdot 10^2$, $A = 3.02 \cdot 10^6$.

The main average characteristics of the process (non-dimensional diameter $D_b$, particle surface $S$, and volume $V$) of the formation of PET particles according to [13, 14] are taken from the expressions:

$$D_{b \text{avg}} = N^{-1} \int_D D_b D_0 dN, S^{\text{cp}} = \pi N^{-1} \int_D D_b^2 D_0^2 dN, V^{\text{avg}} = (6N)^{-1} \int_D D_b^3 D_0^3 dN. \quad (20)$$

After integrating expressions (20) we have:

$$D_{b \text{avg}} = \frac{A}{N b_1} (D_{b_{\text{max}}} - D_{b_{\text{min}}}) b_2, \quad (21)$$

where

$$b_0 = \sqrt{30} \sqrt{\pi} \exp(-\pi \sigma D_0^2 E_0^{-1}), \quad b_1 = \sqrt{11 \rho D_0 E_0^{-1} v_0 D_0}, \quad b_2$$

$$= b_0 \text{erf} \left( \frac{\sqrt{\pi} b_1 w_{\text{max}}}{2 \sqrt{30}} \right) - b_0 \text{erf} \left( \frac{\sqrt{\pi} b_1 w_{\text{min}}}{2 \sqrt{30}} \right). \quad (22)$$

The average value of the particle surface is found in accordance with the formulas:

$$S^{\text{avg}} = \frac{\pi A D_0^2}{N b_1} (D_{b_{\text{max}}} - D_{b_{\text{min}}}) b_2. \quad (23)$$

The average value of the particle volume is found in accordance with the formulas:
\[ V_{avg} = \frac{\pi D_0^3}{6 N b_1} (D_{b_{max}} - D_{b_{min}}) b_2. \] 
\[ (24) \]

Meanwhile, the most interesting of these values is \( D_{b_{avg}} \).

The theoretical dependence of \( D_{b_{avg}} \) on \( v_0 \) is constructed using expression (21), it is shown in Figure 2.

Fig. 2. Theoretical dependence of \( D_{b_{avg}} \) on \( v_0 \)

**Discussion**

The probability density function of the polymer particles number in bitumen by size (Fig. 1) allows us to determine the composition of particles after modification. It enables the selection of the process necessary modes. According to this graph, as the particle size increases, their number decreases. This theoretical dependence allows us to estimate particle sizes from \( 10^{-6} \) m to 0.0002 m. The comparative experimental studies conducted in the laboratory of Yaroslavl State Technical University show the adequacy of the developed mathematical description to experimental data.

Therefore, taking into account the dependence in Figure 2, there is the growth of \( v_0 \), and the decrease in the value of \( D_{b_{avg}} \). Indeed, at values of \( v_0 \) from 0 to 1, the decrease in \( D_{b_{avg}} \) occurs most intensively. Then there is a slowdown in the rate of decline \( D_{b_{avg}} \).

**Conclusions**

Modification of road bitumen with polymers is one of the most effective methods to improve the quality specifications of asphalt concrete mixtures. Application of an apparatus equipped with an stirrer with a relatively simple constructional design as a mixing device will provide effective distribution of polymer in liquid bitumen. The developed mathematical description allows us to assess the influence of the mixer operating and design parameters on the size
and distribution of the formed elements in the modified bitumen. It provides the selection of the asphalt concrete mixture rational composition ensuring the required reliability and durability indicators.

Acknowledgements

The authors express their gratitude to the Yaroslavl State Technical University (Yaroslavl, The Russian Federation) administration for the equipment and material base provided. We also express our gratitude and deep appreciation to Igor V. Golikov, Doctor of Chemical Sciences, Valery M. Gotovtsev, Doctor of Engineering Sciences, and Anatoly I. Zaitsev, Doctor of Engineering Sciences for their invaluable assistance.

This paper was prepared within the framework of the dissertation research of Denis V. Gerasimov "Development of the composition and principle of production of composite material for road construction using phosphogypsum and secondary polyethylene terephthalate".

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