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Assessing the structure of recycled polyethylene-modified bitumen using the calorimetry method

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Abstract

The bitumens, having different compositions, and recycled polyethylene, consisting of low- and high-melting point crystallites, were used for the preparation of bitumen/polymer blends. The structure of bitumen/polymer blends is studied using methods of calorimetry, optical microscopy and oscillatory shear test. The different thermal and viscoelastic behaviors are found at low and high contents of the recycled polyethylene in bitumen/polymer blends. A study of the concentration dependences of thermal characteristics shows that an abrupt increase in the melting enthalpy of bitumen/polymer blends with a monotonous increase in the concentration of polyethylene is due to the formation of a co-continuous structure in the blend. It is revealed that the thermal behavior of bitumen/polymer blends can be used for evaluation of the degree of compatibility of polycrystalline recycled polyethylene and bitumens. The assumption is made that the absence of the low-temperature effects on the heat flow curves of bitumen/polymer blends can testify the good compatibility of bitumen and polycrystalline recycled polyethylene.

Keywords Bitumen/polymer blends · Recycled polyethylene · Thermal behavior · Compatibility

Introduction

Bitumen and polymer-modified bitumen (PMB) are widely used in road construction and in production of roofing and waterproof materials [1, 2]. An important factor which determines the application of PMBs is their structure. It is known [1, 3] that the polymer introduced into bitumen is swollen in light bituminous components and forms a polymer-rich phase. This phenomenon is followed by enrichment of bituminous phase with asphaltenes and asphaltene-rich phase formation. This process is called "physical distillation process." When the polymer-rich phase is dispersed in bitumen, PMBs are used mainly as road construction materials, and when the polymer phase is continuous, PMBs are used as roofing materials [4].

There are large publications about the use of recycled polymers for the bitumen modification [4, 5]. In conditions of shortage and high cost of virgin polymers, the usage of recycled polymers is a good way to reduce the anthropogenic load on the environment. The recycled polymers have poor mechanical, optical and surface properties compared to virgin polymer. The change in their properties occurs due to environmental and thermo-mechanical degradation during service and recycling process [6]. Thus, the study of the compatibility of bitumen with recycled polymer is a topical task.

The method of calorimetry is widely used for the analysis of bitumens [7, 8], polymers [9–11] and bitumen/polymer blends [12–14]. The bitumen's DSC curves show effects of vitrification, cold crystallization and a wide endothermic melting effect in the temperature range from − 30 to 70 °C [7, 8]. The calorimetry method is used to estimate the fraction of the crystalline phase in the material [15, 16], as well as the degree of aging of PMBs [17, 18]. It was offered [5] to evaluate the compatibility of bitumen

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with polyethylene by the analysis of endothermic effects at − 60 and − 13 °C on the heat flow curves.

The thermal behavior of bitumen/polymer blends depends on the type of polymer used. When semi-crystalline polymers (such as SBS) are used, the glass transition temperature of the bitumen is shifted, and the value of thermal effects decreases [19]. The DSC curves of blends of bitumen and crystalline polymers, in particular polyolefins, show the endothermic effect of the melting of the crystallized polymer in the high temperature range (above 100 °C) [3, 20, 21]. It is shown that the peak of polymer melting in bitumen/polymer blend is shifted to lower temperatures [3, 5], in comparison with the melting peak of a neat polymer. This effect is due to the swelling of the polymer in the bitumen components.

This paper presents the results of experimental studies of the change of the thermal and viscoelastic behaviors and structure of bitumen/polymer blends when the content of the polymer increases. An important task of the study is to find the concentration at which the formation of co-continuous structure occurs. Based on the obtained results, new approach to assessing the structure of bitumen/polymer blends is developed.

Experimental

The bitumens BNK 40/180 (corresponding to the 180/200 penetration grade) of the JSC "Kirishinefteorgsintez" (Russia) (bitumen 1) and the JSC "Ryazan Oil Refinery Company" (Russia) (bitumen 2) were used for the preparation of PMBs. Technological properties and composition of these bitumens are given in Table 1.

Recycled polyethylene (PE) was used as a bitumen-modifying agent. Melt flow rate of the PE was defined by ASTM D1238-04. The heat flow curve of the PE is shown in Fig. 1 and thermal characteristics in Table 2.

The bitumen/PE blends were prepared in a Corvette 42 disperser using a 2-blade Z-stirrer. The content of the recycled PE in the bitumen/polymer blends ranged from 1 to 13% mass with a step of 1–2%.

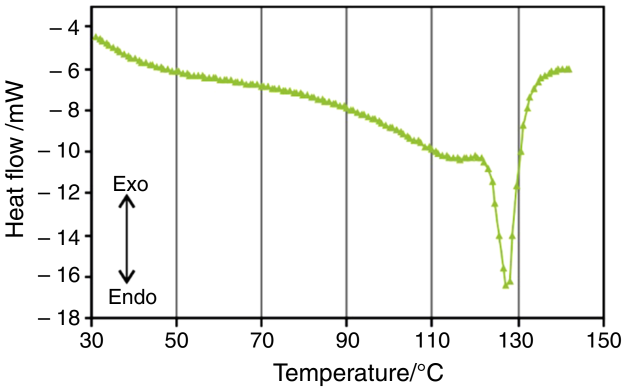

Fig. 1 The heat flow curve of the recycled polyethylene

Calorimetry tests were carried out with C80 calorimeter (Setaram, France) using 200 mg samples. In order to delete any thermal history effects, two heating/cooling cycles were employed, so that crystallization and melting properties were obtained from the second cycle. A heating rate of 1 °C min^{-1} was selected. Temperature ranged from 20 to 200 °C. The temperature calibration was performed using indium. The energy calibration was performed using the Joule effect method in the factory and checked by measuring the heat of fusion of naphthalene. The experimental uncertainties in the measurements of temperatures and enthalpies were ± 0.5 °C and ± 0.01 J g^{-1}, respectively.

Optical microscopy was used to study the morphology of bitumen/polymer blends. A drop of molten sample was placed on microscope slide and then was kept at room temperature for 24 h. Photomicrographs of PMB were obtained on a fluorescent microscope a Mikmed-6 in the light of a mercury lamp at room temperature.

Dynamic temperature sweep test, in linear viscoelastic range, was carried out in the RheoStress6000 rotational rheometer, using parallel plate geometry at a frequency of 1 Hz and a constant amplitude of 0.01 rad. Temperature ranged from 5 to 150 °C.

In order to determine the composition of bitumens, the SARA method was used. Asphaltenes (As) were

Table 1 Technological properties and composition of the bitumens

	Bitumen 1	Bitumen 2	Standard
Ring & ball softening point/°C	42	39	ASTM D36-95
Fraas break point/°C	− 25	− 12	GOST 11507-78
Penetration at 25 °C/0,1 mm	154	172	ASTM D5-05
SARA composition/mass%			
Saturates	26.3	13.2	
Aromatics	23.2	29.0	
Resins	33.0	48.5	
Asphaltenes	17.6	9.3	

Table 2 Melt flow rate (MFR), temperature of start of melting (T_{onset}), temperature of the summit of melting peak (T_{m}), the width of the melting peak ($\Delta T = T_{\mathrm{min}} - T_{\mathrm{onset}}$) and the melting enthalpy (ΔH) of the recycled polyethylene

	MFR/g 10 min^{-1}	T_{onset}/°C	T_{m}/°C	ΔT/°C	$\Delta H_{\mathrm{polymer}}$/J g^{-1}
PE	1.84	92.0	127.5	35.5	82.6

precipitated by a 40-fold excess dilution of the bitumen with n-heptane. The precipitated asphaltenes were washed in a Soxhlet apparatus with n-heptane until the filtrate was colorless. Then the asphaltenes with a filter were washed out with benzene, which was then evaporated. The separation of the maltene was carried out by liquid adsorption chromatography using two columns. In the first column, saturates + aromatics (S + A) and resins were separated using hexane and a mixture (1:1) of benzene with isopropyl alcohol, respectively. In the second column, the separation into saturates (S) and aromatics (A) was carried out with a mixture of hexane and benzene in different ratios. The purity of obtained fractions was controlled by the refractive index. Silica gel ASKG was used as adsorbent in both columns.

Results and discussion

The thermal behavior of the polymer and bitumen/polymer blends

On the heat flow curve of the recycled PE, wide endothermic effect with a low-temperature shoulder (in the temperature range 92–123 °C) and a high-temperature peak (in the temperature range 123–135 °C) was registered (Fig. 1). It is known that the melting point of high-density polyethylene (HDPE), consisting of large linear molecules, is 125–130 °C, that of linear low-density polyethylene (LLDPE) is 116–118 °C, and that of low-density polyethylene (LDPE) with highly branched macromolecules is 103–110 °C [6]. From a microstructural point of view, the thermal behavior of the recycled PE results from the existence of crystals, formed by normal and branched macromolecules of polymer. In the recycled PE, the structures similar to HDPE with a melting point close to 127.5 °C prevail. There are also the structures similar to LDPE or LLDPE with a melting temperature about 110–115 °C. The melting enthalpy (ΔH) of the recycled PE in the temperature range 90–130 °C is given in Table 2.

Despite the same penetration grade, the bitumens used for the preparation of bitumen/polymer blends differ significantly in SARA composition. Bitumen 1 has a higher content of saturates and asphaltenes and a lower content of aromatics and resins (Table 1).

The heat flow curves of bitumen/polymer blends show the endothermic effect of the PE melting in the temperature range of 113–128 °C (Fig. 2). This endothermic peak, in contrast to the wide melting peak of the neat PE, has two pronounced minima. The appearance of two melting peaks on heat flow curves of PMBs confirms the presence of two separate crystalline phases in PE [5].

The melting peak of PE's crystalline phase in the bitumen, in comparison with the melting peak of neat PE, shifts to lower temperatures on 7–13 °C. This fact can be attributed to the formation of crystallites with smaller size and/or the polymer swelling in bitumen's components [4, 16].

The difference in thermal behavior of bitumen/PE blends with bitumens of different compositions was established (Fig. 2). The heat flow curves of blends with bitumen 1 (with a high content of saturates and asphaltenes) in addition to endothermic peak at 113–128 °C have the low-temperature endothermic effect at 90–112 °C. As described above, the neat PE has this low-temperature

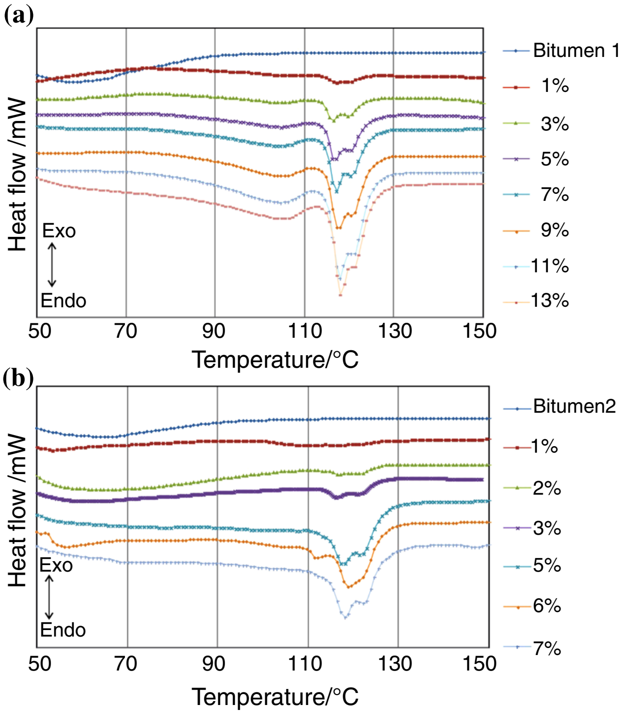

Fig. 2 The heat flow curves of blends of bitumen 1 (**a**) and bitumen 2 (**b**) with recycled polyethylene

effect as well. When the content of the PE in the blend increases, the size of the low-temperature effect increases proportionally. There is no low-temperature effect on the heat flow curves of blends with bitumen 2 (with a high content of aromatics and resins and a low content of asphaltenes) even at high content of the PE. In this regard, it can be assumed that the low-temperature crystallites of the recycled PE swell well in bitumen with a high content of aromatics and low content of asphaltenes [1] and do not form separate phase.

The melting enthalpy of polyethylene in bitumen/polymer blends (ΔH_{blend}) is defined as an area of endothermic effect in the temperature interval of 90–130 °C. Also the calculated melting enthalpy ($\Delta H_{\text{calc.}}$) is calculated based on the content of polymer in blend and the polyethylene melting enthalpy as $\Delta H_{\text{calc.}} = (\Delta H_{\text{polymer}} \times \%\ \text{PE})/100\%$ (Table 3). (The values $\Delta H_{\text{polymer}}$ are taken from Table 1.)

The melting enthalpies of bitumen/polymer blends with different bitumens are similar at low PE content (up to 3% mass). The melting enthalpies of bitumen/polymer blends with bitumen 2 (with a high content of aromatics) are higher than the ones of bitumen/polymer blends with bitumen 1 at polymer content 5–7% mass. It is also noticed that the melting enthalpies of bitumen/polymer blends change abruptly when the PE content increases from 5 to 7% mass for bitumen 1 and from 3 to 5% mass for bitumen 2. At the same time, the melting enthalpies of bitumen/polymer blends are significantly lower than calculated melting enthalpy at low PE concentrations (1–5% for bitumen 1 and 1–3% for bitumen 2) and equal or higher than calculated melting enthalpy at high concentrations of the PE (7% and above for bitumen 1; 5% and above for bitumen 2).

In accordance with the "physical distillation process" [1], the thermal behavior of bitumen/polymer blends at low and high concentrations of PE can be explained as follows. The recycled PE, especially low-temperature crystallites, swells significantly in the bitumen components at low concentrations. When the content of the polymer increases, the proportion of the PE with original thermal characteristics increases in blends. The higher melting enthalpy of blends (ΔH_{blend}) in comparison with the calculated one ($\Delta H_{\text{calc.}}$) may indicate either the uneven mixing [21] or, most likely, the increase of the portion of the non-interacting (neat) polymer due to its incomplete compatibility [1].

Rheological characterizations: linear viscoelastic behavior

In order to analyze the viscoelastic behavior of bitumen/polymer blends, the temperature sweep test in oscillatory shear, at constant frequency, was carried out. It is shown that when PE content increases, the values of both viscoelastic moduli increase (Figs. 3 and 4). Neat bitumen and bitumen/PE blends with a low PE content (1–5% by mass for bitumen 1 and 1–3% for bitumen 2) show a similar viscoelastic behavior (Figs. 3 and 4), namely a continuous decrease in the elastic and losses moduli with increasing temperature. Thus, a smooth transition from the glassy to the Newtonian behavior occurs. At the higher PE content, the change in both viscoelastic moduli is less dependent on the temperature in the temperature region of 20–110 °C. At higher temperature, significant reduction in both moduli occurs. This temperature shifts to the higher value when the PE content increases. The similar behavior of bitumen/polymer blends shows that as the PE content increases, the thermal susceptibility and, consequently, in-service performance of the blends increase [5].

For the bitumen 2/PE blends with a content of PE 5 and 7% mass, a rubber plateau is noticed on the "elastic modulus versus temperature" curves in the temperature range of 60–110 °C (Fig. 4). Due to the high compatibility of the bitumen 2 and PE, the viscoelastic behavior of these blends is similar to viscoelastic behavior of a polymer. Consequently, the different thermal behaviors of bitumen 1/PE and bitumen 2/PE blends are a result of their different compatibility with the PE. A high compatibility of bitumen having high content of aromatics and low content of

Table 3 The melting enthalpy of bitumen/polymer blends (ΔH_{blend}) and the calculated melting enthalpy of blends ($\Delta H_{\text{calc.}} = (\Delta H_{\text{polymer}} \times \%\ \text{PE})/100\%$)

Parameter	1%PE	3%PE	5%PE	7%PE	9%PE	11%PE	13%PE
Bitumen 1/polymer blends							
ΔH_{blend}/J g^{-1}	0.6	1.8	3.2	7.7	8.0	12.9	11.9
$\Delta H_{\text{calc.}}$/J g^{-1}	0.8	2.5	4.1	5.8	7.4	9.1	10.7

	1%PE	2%PE	3%PE	5%PE	6%PE	7%PE
Bitumen 2/polymer blends						
ΔH_{blend}/J g^{-1}	0.5	0.7	1.8	7.8	8.3	8.9
$\Delta H_{\text{calc.}}$/J g^{-1}	0.8	1.7	2.5	4.1	5.0	5.8

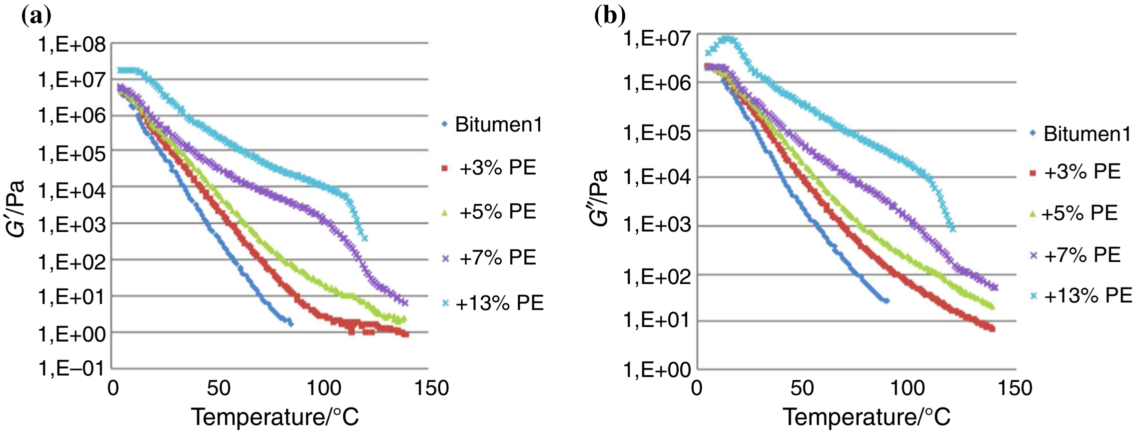

Fig. 3 Evolution of the elastic (G') and loss (G'') moduli with temperature for bitumen 1/PE blends with different PE contents

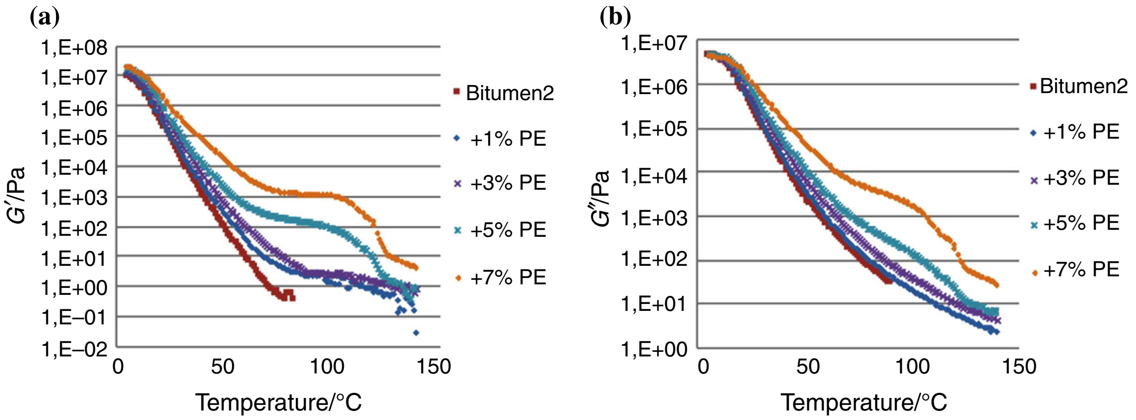

Fig. 4 Evolution of the elastic (G') and loss (G'') moduli with temperature for bitumen 2/PE blends with different PE contents

asphaltenes with PE (especially its low-temperature crystallites) is reflected in the absence of the low-temperature effects (90–112 °C) on the heat flow curves. Apparently, the crystallites of the recycled PE with low melting temperature swell well in bitumen's components and form an amorphous rubber-like phase. The crystallites with high melting temperature retain their structure.

Microstructural characterizations of the PMBs by optical microscopy

The structure of bitumen/polymer blends was studied by optical microscopy. This method allows to visually assess the distribution of the polymer- and asphalt-rich phases in bitumen/polymer blends and to calculate their proportions. Photomicrographs of the bitumen/polymer blends are shown in Fig. 5.

The microphotographs of the blends with low content of PE [5% for bitumen 1 (Fig. 5a) and 3% for bitumen 2 (Fig. 5c)] show separate particles of polymer-rich phase (light colored areas) dispersed in a continuous bitumen phase (dark area). It is impossible to distinguish separate particles of polymer- and asphaltene-rich phases on the microphotographs of the blends with high content of PE [7% for bitumen 1 (Fig. 5b) and 5% for bitumen 2 (Fig. 5d)]. These concentrations of PE are critical concentrations of the formation of the co-continuous structure in bitumen/polymer blends.

Interestingly, these critical concentrations, in which co-continuous structures in bitumen/PE blends form, are similar to concentrations in which the sharp increase in the melting enthalpy of polymer phase by calorimetry and a changes in viscoelastic behavior by oscillatory shear test occur.

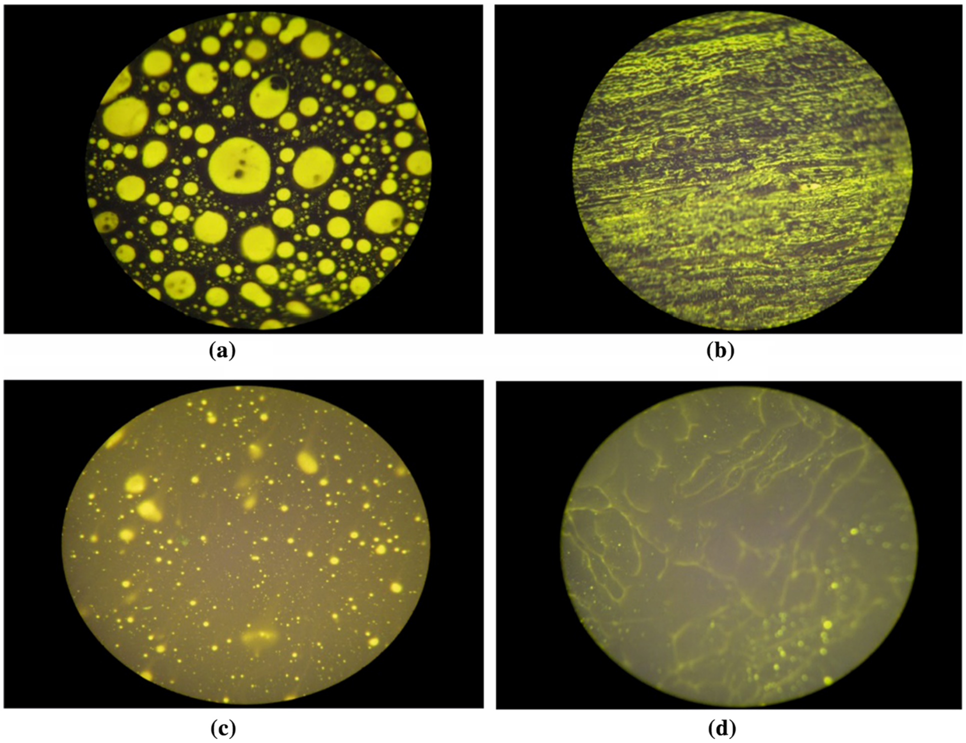

Fig. 5 Optical micrographs of bitumen/PE blends: **a** bitumen 1, 5% mass PE; **b** bitumen 1, 7% mass PE; **c** bitumen 2, 3% mass PE; **d** bitumen 2, 5% mass PE

Conclusions

The bitumens, having different SARA composition, and recycled PE, consisting of low- and high-melting point crystallites, were used for the preparation of bitumen/polymer blends. The compatibility of bitumens with polycrystalline recycled PE was studied using methods of the calorimetry, oscillatory shear test and optical microscopy. The concentrations, at which the formation of co-continuous structure of bitumen/polymer blends occurred, were revealed. It was found that the abrupt increase in the melting enthalpy of bitumen/polymer blends with a monotonous increase in the concentration of polyethylene is a result of a co-continuous structure formation. It is revealed that the thermal behavior of bitumen/polymer blends can be used for evaluation of the degree of compatibility of bitumens with polycrystalline recycled PE. The assumption is made that the absence of the low-temperature effects (90–112 °C) on the heat flow curves of bitumen/polymer blends can testify the good compatibility of bitumen and polycrystalline recycled PE. The crystallites of the recycled PE with low melting temperature swell well in bitumen's components and form an amorphous rubber-like phase. The crystallites with high melting temperature retain their structure in bitumen.

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