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Investigation of modified bitumen binders via Fourier-transform infrared spectroscopy

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Objectives. *This study evaluates the effect of the modification process on the group composition of bitumen and bitumen binders containing rubber powder and hybrid modifier that is based on styrene–butadiene thermoplastic elastomer and rubber crumb. The aim of the study was to determine the presence or absence of functional groups that reflect the direction of physicochemical processes during the preparation of a hybrid modifier in rotary dispersers and during the modification of bitumen binders.*

Methods. *Rubber powder and hybrid modifier were obtained by high-temperature shear grinding using a rotary disperser. Bitumen and modified bitumen binders were investigated via Fourier-transform infrared spectroscopy. Using the method of spectral subtraction, it was determined that during the process of manufacturing modified bitumen binders, structural changes occur in both bitumen and modifiers. During this study, the extraction of modifiers (rubber powder and hybrid modifier) in toluene was performed.*

Results. *The quantitative analysis of changes in the group composition of modifiers before and after the modification procedure was carried out. The active polymer and structural indices were determined. The general trend of the change in the active polymer and structural indices was noted for the initial spectra of the rubber powder and hybrid modifier, and their spectra were obtained after the procedure of subtraction from the spectra of bitumen binders.*

Conclusions. *The interdiffusion of aromatic compounds between the bitumen component and modifier particles was confirmed. On the basis of the results of the extraction of modifiers in toluene, and by taking into account the infrared spectroscopy data, it was determined that during the production of hybrid modifier during the simultaneous grinding of rubber crumb and styrene–butadiene thermoplastic elastomer, there was a chemical interaction between them.*

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Keywords: *bitumen, rubber-polymer composites, rubber powders, IR spectroscopy, bituminous binders, hybrid modifier, high-temperature shear grinding, structural index, spectrum subtraction method.*

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Исследование влияния процесса модификации на групповой состав битума и модификаторов методом Фурье-ИК-спектроскопии

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Цели. *В статье проанализировано влияние процесса модификации на групповой состав битума и битумных вяжущих, содержащих резиновый порошок и гибридный модификатор на основе бутадиен-стирольного термоэластопласта и резиновой крошки. Целью исследования было определение наличия или отсутствия функциональных групп, отражающих направленность физико-химических процессов при получении гибридного модификатора в роторных диспергаторах и при модификации битумных вяжущих.*
Методы. *Резиновый порошок и гибридный модификатор получены методом высокотемпературного сдвигового измельчения на роторном диспергаторе. Битумы и модифицированные битумные вяжущие исследованы методом инфракрасной спектроскопии с Фурье преобразованием. С помощью метода вычитания спектров установлено, что в процессе изготовления модифицированных битумных вяжущих происходят структурные изменения как в битуме, так и в модификаторах. В работе также проведена экстракция модификаторов (резинового порошка и гибридного модификатора) в толуоле.*
Результаты. *Проведен количественный анализ изменений, происходящих в групповом составе модификаторов до и после процедуры модификации. Определены активный полимерный и структурный индексы. Отмечена общая тенденция в изменении активного полимерного и структурного индексов для исходных спектров резинового порошка и гибридного модификатора и их спектров, полученных после процедуры вычитания из спектров битумных вяжущих спектра битума.*
Выводы. *Подтверждена взаимодиффузия ароматических соединений между битумной составляющей и частицами модификаторов. На основании результатов экстракции модификаторов в толуоле и с учетом данных ИК-спектроскопии найдено, что в процессе производства гибридного модификатора совместным соизмельчением резиновой крошки и бутадиен-стирольного термоэластопласта между ними происходит химическое взаимодействие.*

Ключевые слова: *битум, резино-полимерные композиты, резиновые порошки, ИК-спектроскопия, битумные вяжущие, гибридный модификатор, высокотемпературное сдвиговое измельчение, структурный индекс, метод вычитания спектров.*

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INTRODUCTION

In recent years, both in Russia and around the world, traffic has considerably increased. Therefore, the quality of binder for pavements remains relevant because the contribution of binder to the formation of main coating defects is between 40 and 90% [1]. Moreover, numerous studies [2–5], which have been conducted in different countries, show that unmodified bitumen does not provide the proper quality of road surfaces under the conditions of modern heavy traffic. A prerequisite for creating a high-quality asphalt concrete pavement is to modify bitumen binder [6–8].

Thermoplastic elastomers (TPEs) and rubber powders (RPs) are mainly used as bitumen modifiers; in addition, attempts have been made to create hybrid modifiers (HM) [9–13].

Modifiers, depending on the technology of their addition into bitumen, are divided into two groups:

1) Modifiers that are designed to improve bitumen properties prior to the preparation of the asphalt mix by “wet” modification, which involves the stage of continuous cooking of bitumen at high temperatures (usually higher than 180°C). The modification efficiency in this case is achieved by increasing the degree of dispersion of modifiers in bitumen using high-speed mixers.

2) Modifiers that are designed to improve the performance of the asphalt mix by “dry” modification. In this case, the need for long and energy-intensive stages of obtaining modified bitumen binders is eliminated. Modifiers are introduced into the asphalt mix at the time of its preparation in the asphalt mixer. Such modifiers include RP and HM, which are obtained by high-temperature shear grinding. The modification efficiency is achieved by the fast deagglomeration of RP particles or a hybrid modifier upon contact with hot bitumen [6, 14–16].

The first group includes almost all known modifiers. Hybrid binders are mainly obtained by the “wet” method. However, the Federal Research Center of Chemical Physics of the Russian Academy of Sciences has developed a unique hybrid modifier that can be introduced by the “dry” approach, which is similar to the introduction of RP (2nd group modifiers). This approach became possible owing to the joint co-grinding of rubber crumb (RC) and styrene–butadiene thermoplastic elastomer (SBTPE) by high-temperature shear grinding (HTSG).

In this study, infrared (IR) spectroscopy was used to study bitumen, modifiers, and modified bitumen binders. This method allows you to record changes in the group composition and structure of bitumen materials in the process of their modification [17–19]. The aim of the study was to determine the functional groups, the presence or absence of which reflects the physicochemical processes occurring upon receipt of hybrid modifier in rotary dispersants and upon the modification of bituminous binders. To achieve this goal, we used the OMNIC software, with which we performed the procedure of subtracting the spectra of bitumen and modifiers from the spectra of modified bitumen binders. RP and hybrid modifier were extracted with toluene to establish the presence of chemical interaction between rubber and thermoplastic elastomer in the process of obtaining the hybrid modifier by the HTSG method.

MATERIALS AND METHODS

As initial bitumen, BND 60/90 was used, which is recommended for use in road climatic zones II–V. The actual values of the physicochemical parameters of initial bitumen BND 60/90 (*Slavneft-Yaroslavnefteorgsintez*, Yaroslavl, Russia) are presented in Table 1.

The bitumen modifiers used in this study are rubber powder, which is based on used tires STO 11101543-006-2015 (RP studied), and a hybrid modifier obtained by co-grinding RC (cascade production method) and styrene–butadiene thermoplastic elastomer STO 11101543-008-2015 (GM studied). The main characteristics of dispersed elastomeric modifiers are given in Table 2. These modifiers were obtained by the HTSG method on modern installations in rotary dispersants (patent 2612637 Russian Federation, B29B13/00). The raw material for producing dispersed modifiers was RC with a particle size of >1 mm TU 2511-002-56465277-14 (*Oris Prom*, Dzerzhinsk, Moscow oblast, Russia). To obtain GM, we used a mixture of initial RK and SBTPE of the SBS 30-01 L brand (*Voronezhsintezkauchuk*, Voronezh, Russia).

The composition of bitumen binders studied in this study by IR spectroscopy is presented in Table 3.

The samples of RBB and HBB were obtained by mixing bitumen and modifiers obtained by the HTSG method at 160°C for 10 min at the rotation speed of the mixer blades of 600 rpm.

The effect of the modification process on the group composition of bitumen was studied using a Nicolet™ iS5 FT-IR Spectrometer from *Thermo Scientific*™ (USA) with an iD3 ATR Plate.

RESULTS AND DISCUSSION

Using IR spectroscopy, we obtained the spectra of initial unmodified bitumen BND 60/90, rubber-bitumen, and bitumen binders containing HM, as well as the spectra of modifiers (i.e., RP and hybrid modifier obtained by the HTSG method).

Table 1. Physicochemical characteristics of BND 60/90

Parameters	Norm according to GOST 22245-90	Actual value
Penetration grade of unaged binders, 0.1 mm:		
at 25°C	61–90	74
at 0°C	>20	22
Softening point of unaged binders, °C	>47	49
Ductility, cm:		
at 25°C	>55	88
at 0°C	>3.5	3.7
Fraass breaking point, °C	<–15	–22
Flash point, °C	>230	276
Changing the softening point after hardening, °C	<5	5
Penetration index	–1.0 ÷ +1.0	–0.4

Table 2. Characteristics of disperse modifiers

Parameters	Units	RP studied	HM studied
Average particle size	µm	270	250
Specific surface	m^2/g	0.237	0.312
Bulk density	g/cm^3	0.36 ± 0.5	0.32 ± 0.5
Humidity	% by weight, no more than	4	3.2
Residue on the 0.63-mm sieve	%, no more than	2	2
Agglomeration index	no less than	8	8

Table 3. Compounding composition of the investigated bituminous binders

Sample cipher	Sample	Modifier type	Ratio BND/modifier, mass %
1	Bitumen (BND)	–	100/0
2	Rubber-bituminous binder (RBB)	Rubber powder obtained by high-temperature shear grinding (HTSG)	90/10
3	Hybrid bituminous binder (HBB)	Hybrid modifier obtained by HTSG	

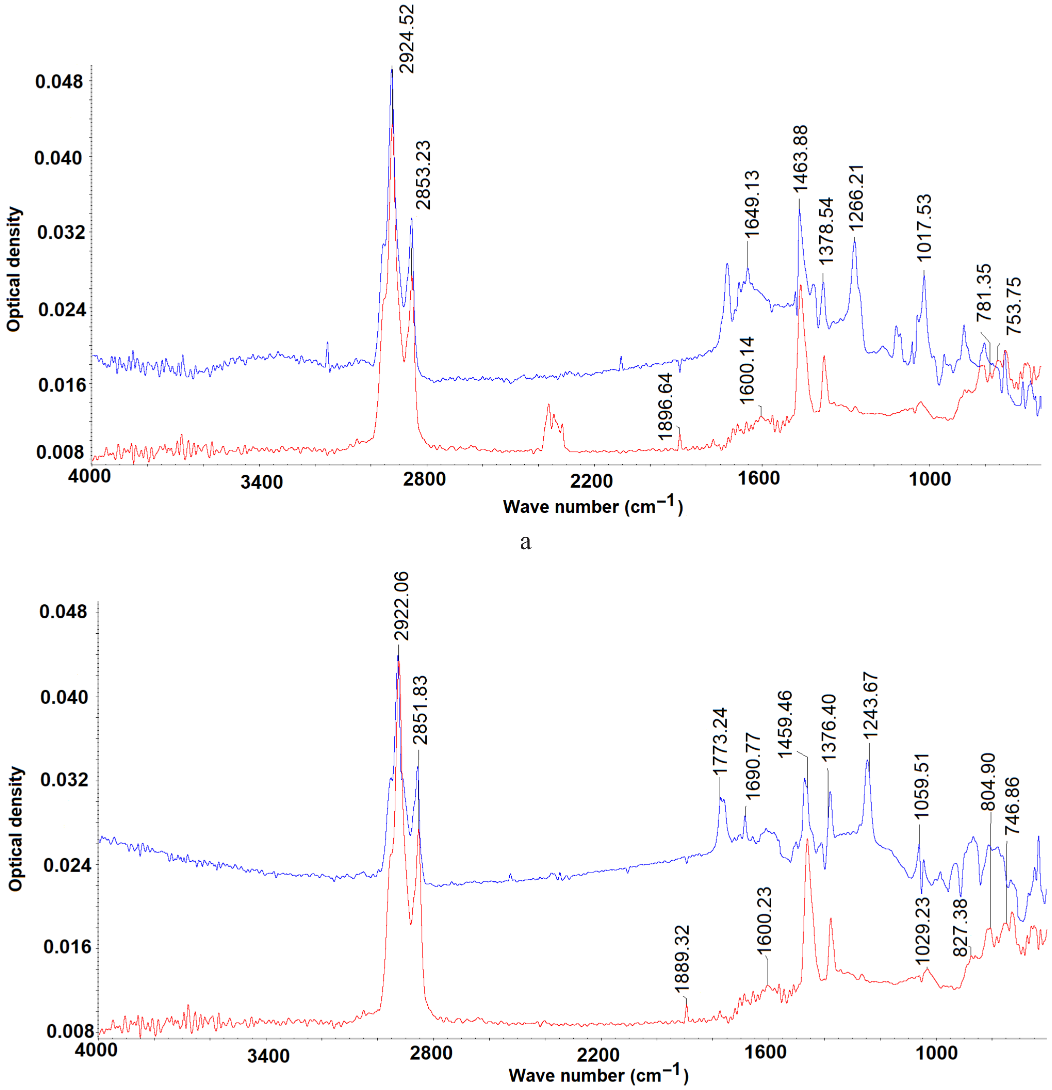
A comparative analysis of the modifying action of the RP and hybrid modifier was carried out by comparing the spectra of bitumen and its modifiers before and after the modification of bitumen. Thus, the spectra of bitumen or the spectra of RP and HM were subtracted from the spectra of modified binders, and the results were compared with the spectra of the initial components of modified bitumen binders.

During the first stage, a change in the composition of bitumen after its modification with RP and hybrid modifier was evaluated. The resulting spectra obtained by subtracting the spectra of the original modifiers from the spectra of modified bitumen binders (samples No. 2 and 3) are shown in Fig. 1.

The qualitative analysis of the spectra is shown in Fig. 1, which demonstrates that the structure of the bitumen component changes during the formation of binders. A considerable change in the group composition of aromatic compounds in bitumen is observed. After bitumen modification with RP (Fig. 1a), the absorption bands of *m*-xylene (753 cm^{-1}) and *p*-xylene (781 cm^{-1}) degenerate, and the bands of aromatic compounds at 1600 cm^{-1} and the band of aromatic triplet of bitumen (746 cm^{-1}) disappear.

The absorption spectrum related to the paraffin–naphthenic fraction (e.g., at 1030 cm^{-1}) is not observed in the spectrum of the bitumen component obtained by subtracting the spectrum of RP from the RBB spectrum. The presence of six-membered aromatic cycles can be detected in bitumen only after modification (peak at 1892 cm^{-1} [20]).

The presence of active radicals on the surface of RP leads to a change in the group composition of oxygen-containing compounds. Thus, the absorption bands of anhydrides and esters degenerate (1771 cm^{-1} and 1752 cm^{-1}, respectively); however, a band appears, which corresponds to the stretching vibrations of the CO group (1243 cm^{-1}, acetates).



a

b

Fig. 1. Spectra of original BND bitumen (red line) and bituminous component (blue line) obtained by subtracting the spectrum of rubber powder (RP) (a) and hybrid modifier HM (b) from the spectrum of the modified bituminous binder.

The nature of changes in the structure of bitumen after modification with a hybrid modifier (Fig. 1b) is similar to the changes caused by the introduction of RP. The group composition of paraffin–naphthenic hydrocarbons changes at 1030 cm^{-1}, when the absorption band present on the spectrum of initial bitumen degenerates in the spectrum of the bitumen component after modification [21].

When using a hybrid modifier, changes are observed at 900–600 cm^{-1}, which are related to aromatic compounds. The degeneration of bands of individual aromatic compounds (746, 753, and 804 cm^{-1}) as well as bands at 1600 cm^{-1} and 1892 cm^{-1}, which characterize five- and six-membered cycles of aromatic compounds [21–23], takes place. Modification with a hybrid modifier leads to the appearance of an absorption band at 1243 cm^{-1} (acetates, phenols).

In the bitumen component of modified binders, both in the case of RP and HM, a band at 1043 cm^{-1} is observed, which corresponds to compounds containing the S=O group (R–SO^{3-}-type compounds).

A distinctive feature characteristic of spectra obtained using only HM is the presence of an absorption band at 700 cm^{-1}, which corresponds to the δ(CH) group of the aromatic ring (polystyrene) and to the absence of a band at 1016 cm^{-1}, which indicates the presence in the sample of sulfur compounds in the form of R–SO–R structures.

A similar procedure for comparing the spectra of initial modifiers with the spectra obtained by subtracting the spectrum of bitumen from the spectrum of modified bitumen binders showed that the changes in the set of functional groups according to their assortment and peak intensities are insignificant. The main feature of the spectra of modifiers, both for RP and HM, after contact with bitumen is the appearance of peaks in the low-frequency region corresponding to aromatic compounds (645, 680, 773, 798, 841, 881, 946 cm^{-1}), which confirms the diffusion of aromatic hydrocarbons from the bitumen component into the volume of modifiers [23].

On the basis of the obtained data, the second stage of this study was dedicated to studying the effect of bitumen modification on the physicochemical processes occurring between RC and TPE upon the receipt of a hybrid modifier. To solve this problem, a comparative analysis of the resulting spectra was obtained by subtracting the spectrum of the RP from the spectrum of the hybrid modifier before and after bitumen modification (Fig. 2).

In the spectrum before modification (blue line), shown in Fig. 2, the absorption band of the δ(CH) group of the aromatic ring (styrene) at 700 cm^{-1} and the band characterizing the presence of C=C double bonds (965 cm^{-1}) are observed [22, 23]. After the bitumen modification procedure, the intensity of these peaks considerably decreases, which is associated with the occurrence of diffusion processes during the transition of unsaturated compounds to bitumen.

For the quantitative analysis of the spectra of modified bitumen binders, the method described in [24] was applied. This approach is based on the fact that during modification, the intensity and nature of the peak at 965 cm^{-1}, which is related to *trans*-alkanes, noticeably changes. It was also established that the absorption band at 810 cm^{-1}, which characterizes C–H bonds in aromatic compounds, remains almost unchanged; therefore, it is considered to be a constant value (Fig. 3). The parameter that describes the quantitative changes that occur in the modified bitumen binder and in HM during the modification

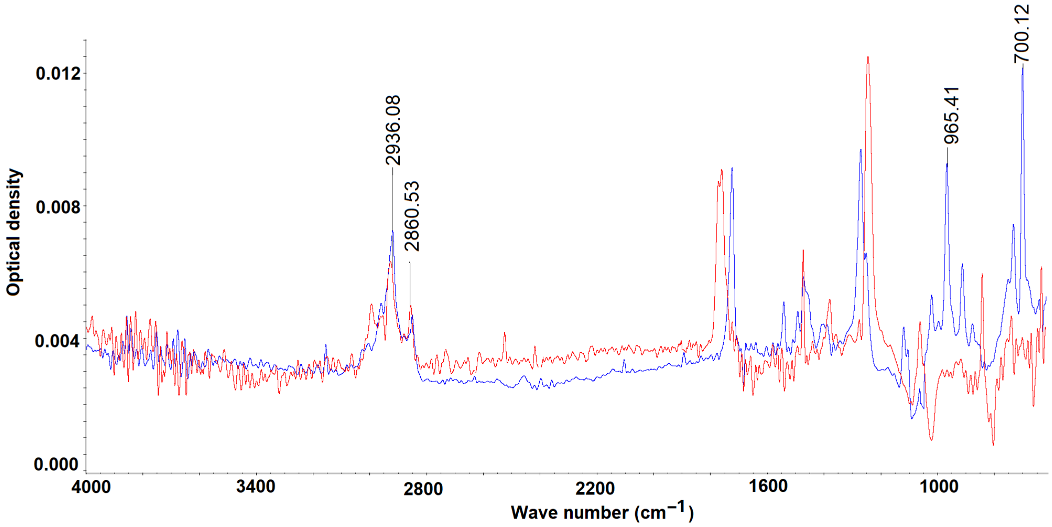


Fig. 2. Spectra obtained by subtracting the RP spectrum from the HM spectrum (blue line for the original modifiers, red line for modifiers after the bitumen modification procedure).

process is the active polymer index (API), which is calculated by the following equation:

$$\mathrm{API} = \frac{S_{965}}{S_{810}},$$

where S_{965} is the peak area at 965 cm^{-1}, and S_{810} is the peak area at 810 cm^{-1}.

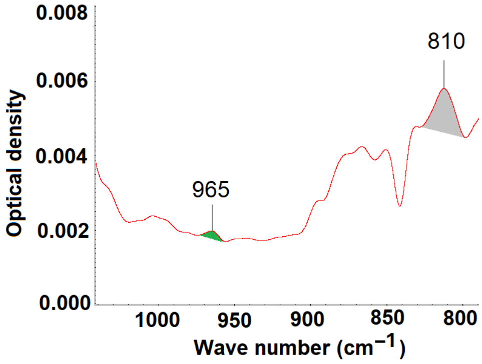


Fig. 3. Determination of peaks for calculating API using HBB as an example.

In [25], for the quantitative analysis of MBB, the structural index (relative optical density) $I_{\mathrm{CH=CH}}$ is used, which equals to the ratio of the peak area at 965 cm^{-1} to the total area of the region between 2000 cm^{-1} and 600 cm^{-1}:

$$I_{\mathrm{CH=CH}} = \frac{S_{965}}{\sum S_{2000-600}}$$

The results of the quantitative analysis of the spectra of modified bitumen binders are presented in Table 4.

The analysis of the data shown in Table 4 allows us to note the general trends in the change in API and $I_{\mathrm{CH=CH}}$ in the initial spectra of RP and hybrid modifier and their spectra obtained after the procedure of subtraction of the spectrum of bitumen from the spectra of bituminous binders. The higher values of these indicators for a hybrid modifier compared to RP are natural and are associated with the presence of the polybutadiene component of SBTPE.

The reverse picture observed in the analysis of the RP and HM spectra after obtaining bituminous binders, which allows us to make an assumption about the possible chemical interactions between RC and TPE during their grinding. When analyzing the spectra of modified bitumen binders, considerably lower numerical values of API and $I_{\mathrm{CH=CH}}$ were obtained. This can occur due to the lower concentrations of modifiers in the binder (bitumen/modifier is 90/10 mass %) and the incorporation of part of the free low molecular weight polymer component of the modifiers into the formed structure of the bitumen binder. A decrease in the structural index $I_{\mathrm{CH=CH}}$ of the hybrid modifier after modification confirms the data from the qualitative analysis shown in Fig. 2. This means that during the manufacturing process of the hybrid modifier, a noticeable physicochemical interaction occurs between the starting components.

To identify the presence of a chemical interaction between RC and TPE during the process of obtaining a hybrid bitumen modifier by the HTSG method, styrene–butadiene thermoplastic elastomer was extracted from the HM sample. The initial RP and hybrid modifier obtained by the HTSG method were placed in toluene and kept there for 14 days. After filtration, the samples were dried and weighed. Samples were dried at constant temperature and humidity. The drying time was determined by achieving a constant mass value of the extracted samples with an accuracy of ±0.001 g. The test results are shown in Table 5.

Table 5 shows that most TPE (>75% for GM 5/95 and >85% for HM 20/80) that are dissolved in toluene are added to hybrid modifier, which confirms the presence of interaction between the polymer and RC during their co-grinding in a rotary disperser.

Table 4. Quantitative analysis of the spectra of MBB and modifiers

Sample	Active polymer index (API)	Structural index $I_{\mathrm{CH=CH}}$
Before modification		
RP	1.466	0.0277
HM	3.245	0.0443
After modification		
RP	0.2400	0.0086
HM	0.2110	0.0052

Table 5. Results of the extraction of RP and thermoplastic with toluene

Parameters	Modifiers/styrene–butadiene thermoplastic elastomer (TPE) content, mass %		
	RP	HM	
	0	5	20
Sample mass, g	0.1207	0.1915	0.1984
Mass of the sample after extraction, g	0.1128	0.1723	0.1543
Mass of substances extracted with toluene, g	0.0079	0.0192	0.0441
Mass fraction of substances extracted with toluene, %	6.54	10.02	22.23
Mass fraction of TPE extracted with toluene, %	–	3.81	17.0

CONCLUSIONS

The use of the method of subtraction of spectra made it possible to evaluate the structural changes occurring in bitumen and its modifiers during the manufacturing of modified bitumen binders. It was determined that using such modification, aromatic hydrocarbons diffuse from the bitumen component to modifier particles. During the modification process, six-membered cyclic aromatic compounds are formed in the bitumen part; the composition of paraffin–naphthenic hydrocarbons is changed, and sulfur compounds are formed and “transferred” from the particles of modifiers to bitumen. Thus, in this study, the phenomenon of interdiffusion between bitumen and modifiers (RP and HM) was confirmed by IR spectroscopy.

The analysis of the results of the extraction of hybrid modifiers in toluene and the IR spectroscopy data allows us to conclude that chemical interaction occurs between RC and thermoplastic elastomer when they are co-milled on a rotary disperser by the HTSG method.

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The authors declare no conflicts of interest.

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