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Obtaining of Resins Based on Model Mixtures with Indene, Coumarone and Styrene and their Usage as Bitumen Modifiers

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Abstract

Coumarone-indene resins (CIR) with epoxy groups have been synthesized via radical co-oligomerization on the basis of model mixtures with indene, coumarone and styrene. The synthesized resins are proposed to be used as a modifier of commercial petroleum bitumen (adhesive additive). The influence of the composition of raw materials on the CIR yield and their modifying properties has been determined.

Keywords: *Indene; Coumarone; Resin; Bitumen; Modification.*

1. Introduction

Currently, about 90 % of bitumen in the world is used by the road industry. However, when using the commercial road bitumen, a number of problems arise, the main of which is imperfect performance properties, first of all, of the oxidized bitumen. One way to solve this problem is to modify commercial road bitumen. However, the use of modifiers is limited due to their considerable cost. Therefore, it is important to look for low-cost substances that would improve the performance of bitumen, first of all, its adhesive characteristics.

To date coumarone-indene resins (CIR), as a high-quality and cheap modifier of road bitumen, may be produced from coal coking volatile products [1-5]. CIR significantly improves the adhesion properties of road bitumen, including those at low temperatures and increases the softening temperature. Bitumen emulsions based on bitumen modified with coumarone-indene resin have significantly better performance than emulsions obtained using unmodified road bitumen [1-10].

CIR were obtained in its "pure" form and with additional functional groups from the following types of raw materials selected at coke-chemical plants of Ukraine:

- fraction 140-190°C and 150-190°C, distilled under laboratory conditions from "heavy" benzene. "Heavy" benzene is the residual fraction obtained after distillation of the gasoline fraction, also called as "crude" benzene, during coal coking;
- light coal tar fraction (LCF). This is the first fraction obtained due to the distillation of liquid coking products which are condensed from volatile products under normal conditions;
- coumarone-indene fraction. A narrow fraction obtained at the coke plant due to the distillation of "crude" benzene.

CIR obtained from different types of raw materials, by different methods and under different conditions, significantly differed by their modifying properties [1-4, 9-10]. Thus, it was necessary to study how the composition of raw materials (the ratio of indene, coumarone, and styrene) influences the yield and modifying quality of CIR. For this purpose, a modifier with functional

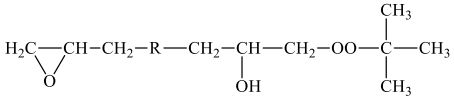
epoxy groups for the oxidized road petroleum bitumen was synthesized via radical co-oligomerization method on the basis of model mixtures. We used functional epoxy groups because they proved to be the most effective adhesive additives [7, 9].

2. Experimental

2.1. Initial materials

The following individual (pure) substances were used to create resins based on model mixtures:
- indene produced by LLC "NVP" UKRORGSYNTEZ" (Ukraine), with n_D^{20}1.5765, d_4^{20}0.9966;
- coumarone produced by LLC "NVP" UKRORGSYNTEZ" (Ukraine), with n_D^{20}1.5648, d_4^{20}1.0776;
- styrene, which was dried with solid alkali before use and purified by distillation at 50°C and a residual pressure of 300-400 Pa. Characteristics of styrene: n_D^{20}1.5471, d_4^{20}0.906;
- glycidyl methacrylate (GMA) produced by Aldrich, USA, with n_D^{20}1.449, d_4^{20}1.9042 was used as a monomer in the process of radical co-oligomerization to introduce epoxy groups into the structure of coumarone-indene resin;

Monoperoxide derivative of Bisphenol A diglycidyl ether (PO) was used as an initiator of the reaction for obtaining coumarone-indene resins with epoxy groups:



where R= $-OC_6H_4C(CH_3)_2C_6H_4O-$.

BND 60/90 bitumen produced by PJSC "Ukrtatnafta" (Kremenchuk, Ukraine) was used. The characteristics of pure bitumen are given in Table 1.

Table 1. Physico-mechanical properties of pure bitumen

Bitumen	Parameters			
	Softening point (T_s), °C	Penetration at 25°C (P_{25}), 10^{-4} m	Ductility at 25°C (D_{25}), m·10^{-2}	Adhesion to glass, %
BND 60/90	46	70	63	33

2.2. Resins synthesis

Radical co-oligomerization of unsaturated compounds was performed according to the synthesis procedure described in [9].

Co-oligomerization was carried out in metal ampoules by the capacity of 1.0 L. The ampoules were loaded by the corresponding mixture, blown with an inert gas, closed and placed into a thermostat. Radical co-oligomerization proceeded at 120°C for 6 h. After co-oligomerization, the ampoule was cooled to room temperature, the reaction mixture was transferred to a distillation flask and unreacted raw material was distilled under vacuum. The resulting product was dried in a vacuum-dryer at 40°C to a constant weight.

Via radical co-oligomerization of unsaturated compounds, new polymers with free epoxy groups have been obtained [9]. The composition of the reaction mixture and the characteristics of the resulting products are given in Table 2.

Table 2. Composition of the model systems and characteristics of the synthesized resins

Mixture number	Initial monomers /quantity, g[1]	Resins characteristics		
		Yield, %	Epoxy number (e.n.), %	M_n, g/mol
I	Indene/50.0	74.9	15.6	550
II	Coumarone 50.0	37.2	17.6	640
III	Styrene/50.0	99.0	12.4	n. d.[2]
IV	Indene/17.0 Coumarone/17.0 Styrene/17.0	84.8	14.4	790

[1]The quantity of GMA in the mixtures was 50.0 g, PO – 25.0 g. Toluene (400 g) was the reaction medium. Mixture II apart from the resin dissolved in toluene contained the residue in the amount of 15.7 % with e.n. of 19.0 %.
[2]The resin based on mixture III was poorly soluble in organic solvents, so its molecular weight was not determined.

The structures of the synthesized resins were confirmed by IR spectroscopy (Figures 1-3).

The presence of epoxy groups in the synthesized resins is confirmed by stretching vibrations at 908 and 2936 cm^{-1}. The presence of hydroxy groups introduced by PO initiator is confirmed by stretching vibrations at 3472 cm^{-1} (System I, Figure 1), 3478 cm^{-1} (System II, Figure 2) and 3504 cm^{-1} (System IV, Figure 3). The presence of GMA fragments is confirmed by the stretching vibrations of the carbonyl group at 1724 cm^{-1} (system I, Figure 1) and 1728 cm^{-1} (systems II and IV, Figures 2 and 3). The stretching vibrations at 756 cm^{-1} corresponding to the 1,2-disubstituted benzene ring in the indene molecule confirm the introduction of the indene fragment into the resin structure (system I, Figure 1).

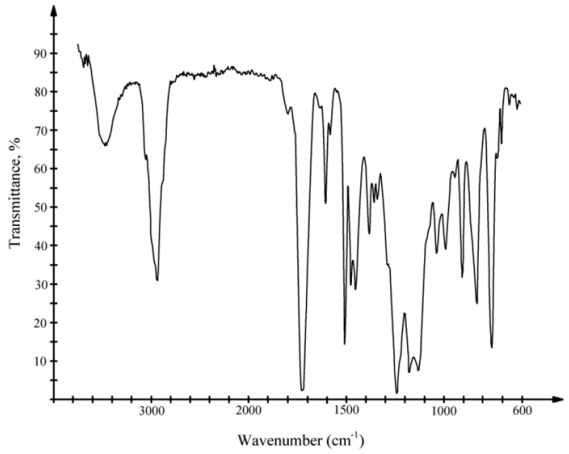


Figure 1. IR spectrum of the resins based on mixture I

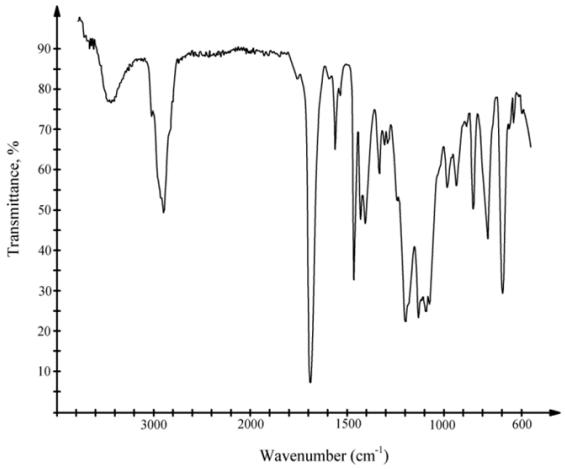


Figure 2. IR spectrum of the resins based on mixture II

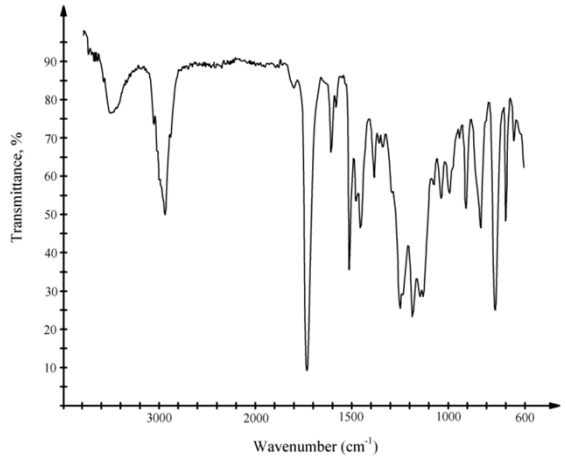


Figure 3. IR spectrum of the resins based on mixture IV

In the IR spectrum of system II (Figure 2), the band at 756 cm^{-1}, corresponding to the stretching vibrations of 1,2-disubstituted benzene ring and the band at 1056 cm^{-1}, corresponding to the C–O–C ether bond in coumarone confirm the presence of cou-marone fragment in the resin structure.

The indene fragment in the resin based on system IV is confirmed by the absorption band at 756 cm^{-1}; stretching vibrations at 756 and 1056 cm^{-1} indicate the presence of coumarone (Figure 3).

2.3. Analytical determination

The number-average molecular weights (Mn) of the synthesized resins weredetermined using cryoscopy in benzene. The content of epoxy groups (epoxy number, e.n.) was determined according to the procedure described in [11].

The infrared spectra of the obtained substances were taken on a Nicolet IR 200 (Thermo Electron Co., USA) equipped with a GoldenGate ATR diamond crystal. Each spectrum was recorded with a resolution of 4 cm^{-1}. Samples were prepared as powder or they were dissolved in acetone.

2.4. Preparation of PMB and its analysis

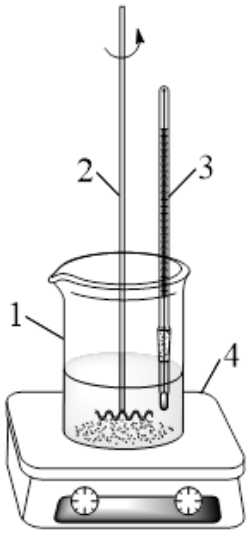


Figure 4. Laboratory installation for producing modified bitumen
1–cylindrical capacity; 2–mixing device;
3–thermometer; 5 –electric heater

The laboratory installation for the obtaining of polymer modified bitumen (PMB) is shown in Figure 4. PMB was prepared in the following way. A necessary amount of bitumen was heated to 190 °C. Then the modifier and plasticizer were added in a required amount and stirred for 1 h at Re=1200.

The analysis of physico-technological properties of bitumen and polymer modified bitumen were carried out according to standardized methods:

- softening point - by "ring and ball" method in accordance with [12];
- penetration (depth of needle penetration) - according to [13];
- bitumen ductility - according to [14];
- index of "adhesion to glass" (adhesion) - according to [15].

3. Results and discussion

The highest yield of resins is obtained when using pure styrene. In this case, it is possible to introduce the least amount of functional groups into the resin and it is difficult to determine the molecular weight of the resin, since the resin obtained is insoluble or slightly soluble in organic solvents.

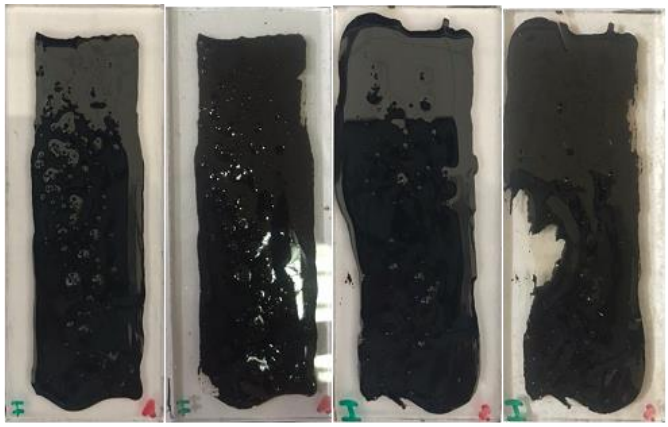
The results of experimental studies on the modification of road petroleum bitumen with coumarone-indene resins obtained on the basis of model mixtures are given in Table 3 and Figures 5-8.

Table 3. Characteristics of PMB obtained with coumarone-indene resin based on model mixtures

PMB number	Characteristics of PMB				
	Softening point according to the "ring and ball" method, °C	Ductility, $m \cdot 10^{-2}$ (cm)	Penetration at 25^0C, $m \cdot 10^{-4}$ (0.1 mm)	Adhesion to glass, %	Homogeneity
Pure bitumen (BND 60/90)	46	70	63	33	+
I	49.5	77	70	97	+
II	50.5	>100	69	95	+
III	49.5	30	50	82	±
IV	51.5	36.1	51	86	+

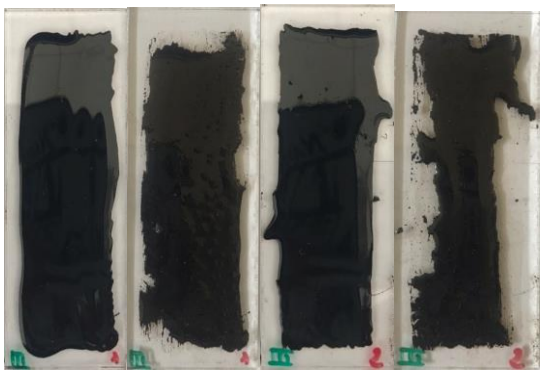
Mixing conditions: T=190^{0}C, time is 60 minutes, modifier amount is 1 %.

As can be seen from the results obtained, the best bitumen modifier can be considered as a resin with epoxy groups based on coumarone. The styrene as a component of raw material leads to a deterioration of the resin modifying ability: the bitumen plasticity (ductility and penetration) decreases, and the positive effect on the adhesion properties is less compared to indene- and coumarone-based resins.



98.42% 94.63%
Figure 5. Adhesion of PMB-I

94.58%
Figure 6. Adhesion of PMB-II



88.18% 76.75%
Figure 7. Adhesion of PMB-III

72.89% 98.13%
Figure 8. Adhesion of PMB-IV

4. Conclusion

The resins were synthesized via radical co-oligomerization on the basis of model raw materials, which consisted of glycidyl methacrylate and the diglycidyl ether monoperoxide derivative, as well as indene, coumarone or styrene, or their mixture. The synthesized product was used as adhesive additives to the road petroleum bitumen.

It has been established that the presence of the investigated monomers (indene, coumarone or styrene) in the raw materials has different effect on the yield and quality of the obtained resin in terms of the effectiveness of its further use as a modifier of petroleum road bitumen, in particular:

- when using styrene as the main component of the raw materials, the highest resin yield is observed. The resin is poorly soluble in organic solvents and poorly mixed with bitumen even in the amount of 1 wt.% relative to the mixture. Its presence in road bitumen significantly degrades the plastic properties (penetration and ductility);
- when coumarone and/or indene are used as a major component of the raw materials, the yield of obtained CIS is lower, but the resin has a better effect on the qualitative characteristics of the modified petroleum road bitumen (it significantly improves ductility, penetration and adhesion; increases the softening temperature).

Addition of resin of all types to road bitumen in the amount of 1 wt.% relative to the mixture considerably improves the adhesive properties of the resulting bitumen: resin I (obtained using indene) - by 194 %; resins II (obtained using coumarone) – 188 %; resins III (obtained using styrene) - by 148 %; IV resins (obtained using a mixture of indene, coumarone and styrene) – by 161 %.

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