Review article
UDC 662.749.33
DOI: 10.52957/2782-1900-2026-7-1-93-113

THE PHYSICO-CHEMICAL ANALYSIS OF THE MOLECULAR STRUCTURE OF BINDING AND ELECTRODE PITCHES

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Keywords:
coal tar pitch, electrode pitch, binder pitch, IR spectroscopy, EPR spectroscopy, NMR spectroscopy, thermal treatment of pitches, mesophase, thermal oxidation.

Abstract. *The paper reviews research on the molecular structure of binder and electrode pitches by physicochemical analytical methods. The research demonstrates the effect of modifications on changes in the molecular structure of binder pitches determined by IR spectroscopy. Additionally, it presents the results of studies on the determination of the polyaromatic composition of the pitches. The author performed a comparative analysis of the results of studies on the determination of the structural and group composition of coal and petroleum pitches. Physicochemical methods for determining the mesophase structure of pitches are described.*

For citation:
Kovalev R. Yu. *The physico-chemical analysis of the molecular structure of binding and electrode pitches* // From Chemistry towards Technology Step-by-Step. 2026. Vol. 7, Iss. 1. P. 93-113. URL: https://chemintech.ru/ru/nauka/issue/7073/view

Introduction

The paper describes physicochemical analytical methods for determining the molecular structure of binding pitches. Electrode pitch grades B1 and B are used as binding agents in the production of anode paste [1]. The studies [2-4] demonstrate the possibility of producing electrode pitch directly from coal by thermally dissolving G and GZh grades of coal in the anthracene fraction (coal-to-solvent ratio = 1:2).

The papers [5-7] experimentally demonstrate the feasibility of using pitches with increased T_p and high-melting-point pitches as binders in the production of carbon materials. For example, in [5] it is shown that a mixture of high-temperature pitch and petroleum coke (in a pitch/coke ratio of 25/75) had a plasticity of over 1000 kg·m and a viscosity of 600 kg·m. It is higher for the electrode pitch in a pitch-coke mixture (25/75) as its the plasticity is 140 kg·m and the viscosity is 40 kg·m.

The paper [8] demonstrates the possibility of using a binder pitch with a T_p of 103 °C and modifications based on it. The pitch containing the α_2 fraction. It is soluble in quinoline but

insoluble in toluene - yielded a high coke yield. Furthermore, the carbon block obtained by carbonising this pitch had a high compressive strength [8]. The carbon materials were prepared from pitch with softening points T_p = 209 °C and 124 °C by mixing them with pitch distillates at 400 °C, followed by carbonisation at T = 900 °C and graphitisation at T = 2700 °C [9].

Infrared (IR) spectroscopy is used to determine the molecular structure of pitch; chromatography is used to determine the composition of polyaromatic pitch compounds (PAPCs); electron paramagnetic resonance (EPR) spectroscopy is used to investigate the electronic structure; nuclear magnetic resonance (NMR) spectroscopy is used for structural and group analysis. The relevance of this study concerns determining the effect of heat treatment or modification of binder pitches on the molecular structure. It also involves determining the effect of modifications to binder pitches on their carcinogenic activity.

Of particular interest is the study of the mesophase structure of pitch. According to Brooks and Taylor [10, 11], a mesophase is observed during the thermal transformation of carbonisable pitch (Fig. 1).

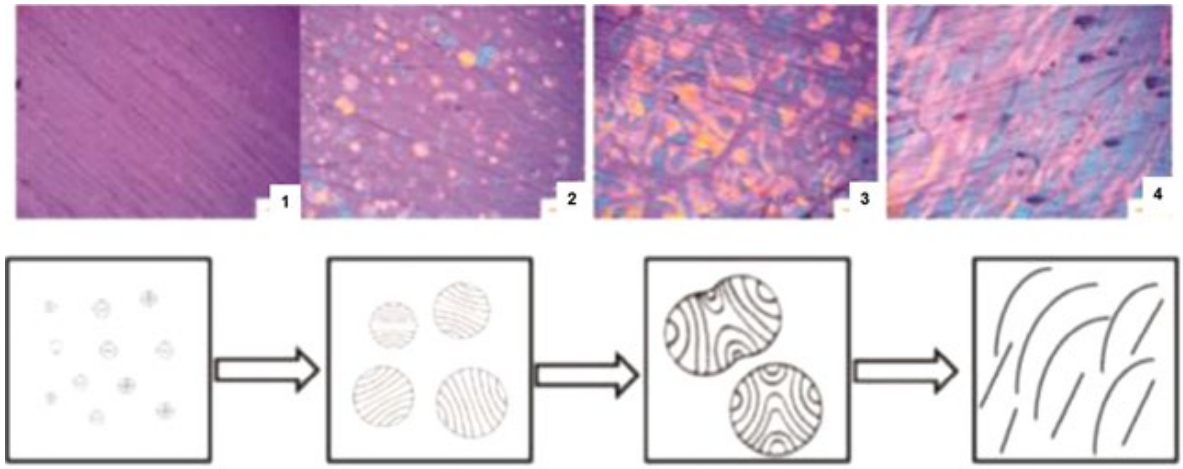

Fig. 1. The formation and development of a bulk liquid-crystalline phase under suitable conditions [10–12]

A model for the formation of a mesophase (Fig. 1) in naphthalene pitch has been proposed: (1) – the generation of optically anisotropic spheres in an isotropic matrix, (2) – growth of anisotropic spheres in an isotropic matrix, (3) – coalescence of anisotropic spheres in an isotropic matrix, (4) – deformation and destruction of the anisotropic coalesced sphere with the formation of a three-dimensional liquid-crystalline structure [10–12]. The carbonaceous mesophase appears to be an intermediate product in the carbonisation process, formed through the polymerisation of the main compounds in coal pitch [13, 14].

To produce new carbon-based materials, it is necessary to determine their microstructure, including mesophase structure.

The purpose of this study is to summarise the results obtained using physicochemical methods to investigate the molecular structure and properties of binding pitches. Therefore, a review of physicochemical methods for determining the carcinogenic activity of binder pitches was made. As a result, a comparative analysis of the molecular structure of mesophase pitches was performed.

Main body

1. The method of IR spectroscopy. IR spectroscopy was used to investigate the molecular structures of alternative pitches from coals [2], the binder pitch, and fractions isolated from it [8], modified pitches in [15, 16], and thermal oxidation products in [21]. The effect of modifications on the intensity of bands in the IR spectrum of pitches was examined [15, 16]. The study considers the effect of thermal oxidation, and the addition of an anthracene fraction on the molecular structure of pitches in [21].

Figure 2 shows the IR spectra of coal tar pitch, petroleum pitch, and pitch obtained by the thermal dissolution of coal.

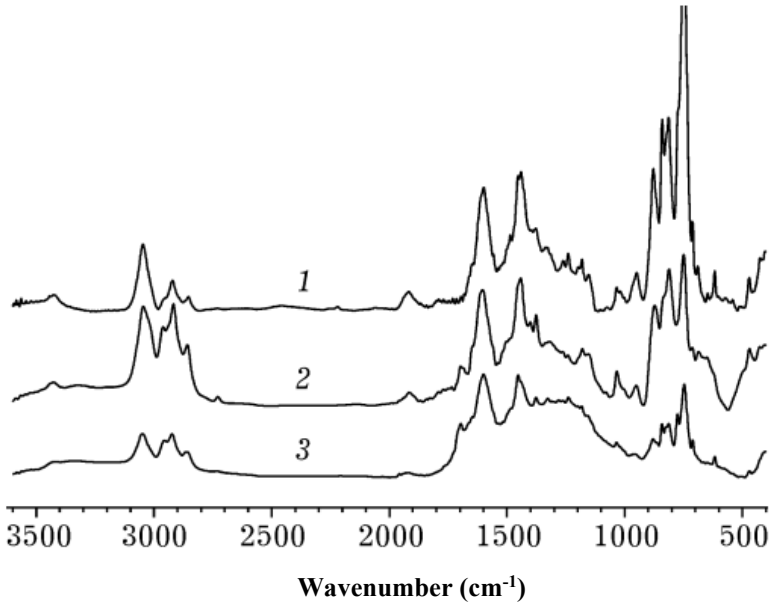

Fig. 2. IR spectra: 1 – coal tar pitch, 2 – petroleum tar pitch, 3 – pitch extracted from coal [2].

The lines at 2854–2923 cm^{-1} and at 1452 cm^{-1} and 1376 cm^{-1} are associated with aliphatic C–H bonds [2]. Low intensity of C–H vibrations (700–900 cm^{-1}) was observed in the aromatic structure of the pitch extracted from coal, compared with that of coal tar pitch [2]. The low intensity of these lines indicates a reduced content of PAHs. It is characteristic of the low carcinogenic activity of the pitch. It defines the potential for extracting pitch from coal as a method of producing a binder with low carcinogenic activity.

In [8], an analysis was conducted of the molecular structure of pitch with a T_p of 103 °C and the fractions isolated from it.

The pitch and the fractions isolated from it consisted mainly of aromatic rings and hydrogen atoms that were not substituted by aliphatic chains. In all pitch fractions, the majority of lines were observed in the range from 1700 to 700 cm^{-1} [8]. For the α_2 fraction, the intensity of the 1600 cm^{-1} line was higher than for the other pitch fractions [8]. High line intensities at 700–900 cm^{-1} are characteristic of the hexane-soluble γ-pitch fraction.

In [15, 16], modifications were made to the raw material to reduce the carcinogenic activity of the pitches. IR spectroscopy was used to investigate changes in the molecular structure of the modified pitches. Figure 4 shows the IR spectra of medium-temperature pitch and its modifications with iodine following heating for 12, 24, and 72 hours [10].

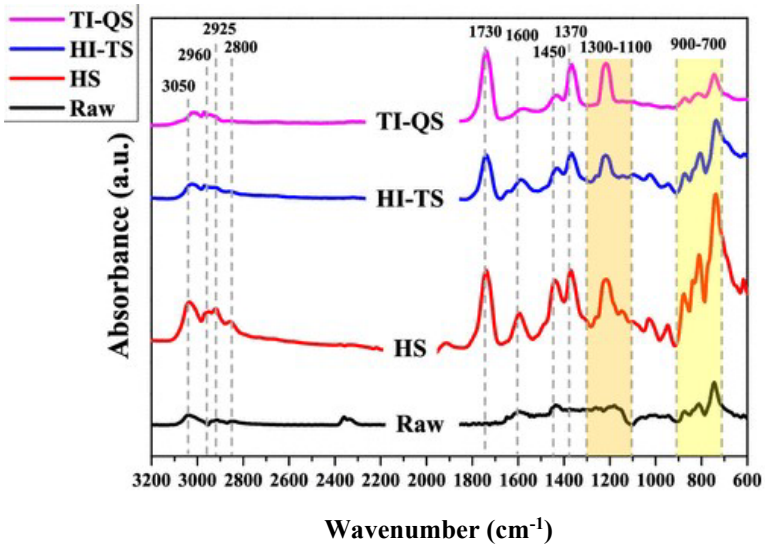

Fig. 3. IR spectra of binder pitch; hexane-soluble fraction (γ); fraction insoluble in hexane but soluble in toluene (β); fraction insoluble in toluene but soluble in quinoline (α_2) [8].

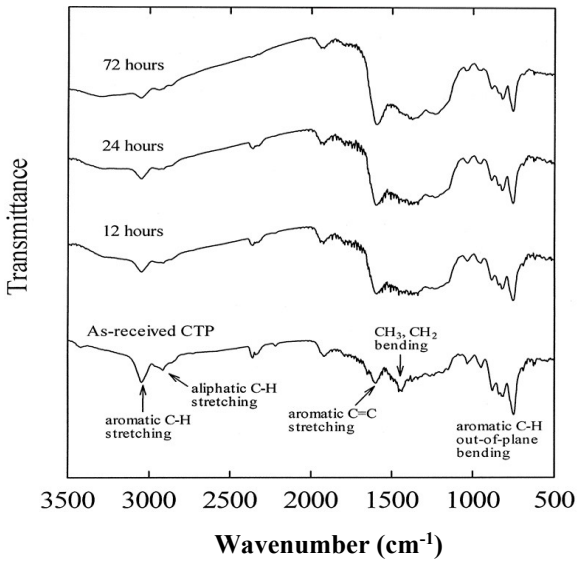

Fig. 4. IR spectra of medium-temperature pitch and its iodine-modified derivatives, which were heat-treated for 12, 24 and 72 hours at 373 °C [15].

Figure 4 shows that the IR spectrum of pitch consists mainly of lines associated with the vibrations of aromatic molecules; a small peak at 2800 cm^{-1} is associated with aliphatic C–H vibrations [15]. Modification of the pitch with iodine did not result in any significant changes to the qualitative composition of the pitch's molecular structure. A decrease in the intensity of the peak at 2800 cm^{-1} and the disappearance of the band at 1470 cm^{-1} associated with the bending of the aliphatic CH_3, and CH_2 fragments were observed [15]. Apparently, these phenomena are not related to the modifying additives. However, they are associated with an increase in the holding time during heat treatment. There was a decrease in the intensity of the lines at 700–900 cm^{-1}. It may indicate a reduction in the intensity of C–H vibrations in the aromatic structure. It is prospective for the application of this modification to reduce the PAH content in the pitch.

For pitches modified with aldehyde, benzaldehyde and furfural, the following IR spectra were observed (Fig. 5).

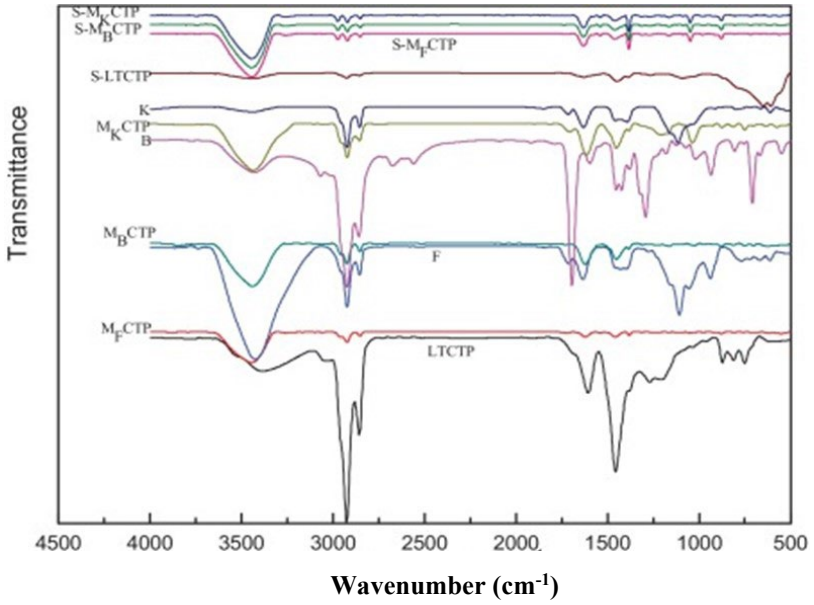

Fig. 5. IR spectra of low-temperature curing pitch (LTCP), its modifications (M_BCTP (benzaldehyde-modified), M_FCTP (furfural-modified), M_KCTP (aldehyde modification)), the modifying additives furfural-F, benzaldehyde-B, aldehyde-K and semi-cokes based on them (S-LTCP, S-M_BCTP, S-M_KCTP, S-M_FCTP) [16].

In the IR spectrum of low-temperature coal tar pitch, CH lines (2790–3000 cm^{-1}) and lines at 1633 cm^{-1} and 1460 cm^{-1} are observed. They are attributed to the aromatic valence vibration of the C=C bond [17–20]. Upon modification of this pitch with furfural, benzaldehyde, and aldehyde, a decrease in the intensity of these bands is observed. However, the bands appear in the 3300–3600 cm^{-1} range, which are attributed to the OH valence vibration [17–20]. A band also appears at 1028 cm^{-1} due to the stretching of C–O–C bonds [17–20]. Following modification, a bridged structure emerged, i.e. carboxyl and hydroxyl groups were attached to the aromatic groups via aliphatic bridges. There was also a decrease in the intensity of the lines at 700–900 cm^{-1}, indicating a reduction in the PAH of the pitches after modification. A noticeable decrease in the intensities of these lines was also observed for the semi-cokes obtained from the modified pitches.

The study of the IR spectra of pitch with the addition of an anthracene fraction and the product of its thermal oxidation is also of great interest.

Figure 6 shows insignificant difference in the spectra in terms of composition. For the initial pitch, lines were detected at 745–1000 cm^{-1}, associated with the C–H bending vibration in the aromatic structure. The line at 3045 cm^{-1} is associated with the C–H vibrational mode in the aromatic structure [21]. The line at ~1630 cm^{-1} is associated with C=C in the aromatic structure of the pitch [21].

An increase in the intensity of the lines at 745, 811 and 877 cm^{-1} is observed in the IR spectrum for the pitch following its thermal oxidation. Furthermore, following thermal oxidation, there was an increase in the intensity of the line at 1630 cm^{-1}, associated with the C=C vibration, and in the intensities of the lines at 3045 and 2924 cm^{-1}, associated with the aromatic structure. At the same time, an increase in the intensities of the line associated with the aliphatic structure of the pitch (1473 cm^{-1}) was observed.

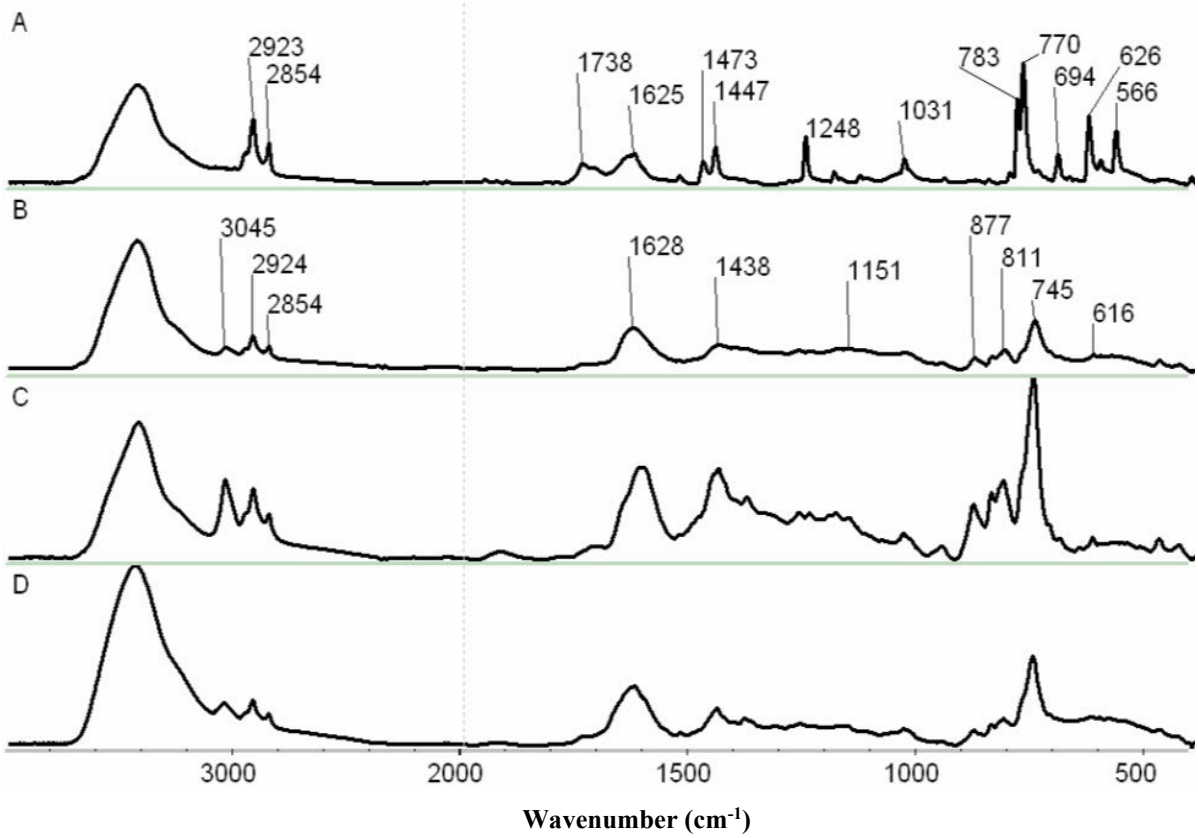

Fig. 6. IR spectra for the following materials: A – anthracene fraction, B – coal tar pitch, C – pitch exposed to air at T = 250 °C for 2 hours, D – pitch with 39.10% anthracene fraction added, thermally oxidised at T = 250 °C [21].

However, despite the high aromaticity of the anthracene fraction compared to the starting pitch, the product obtained had low aromaticity compared to the anthracene fraction [21]. This is presumably due to the part of the anthracene fraction reacts with the light fraction to form naphthenic or aliphatic compounds. It may also be related to the presence of a methyl group associated with the anthracene fraction [21]. For the initial pitch, lines were detected at 745–1000 cm^{-1}, associated with the C–H bending vibration in the aromatic structure. The peak at 3045 cm^{-1} is associated with C–H vibration in the aromatic structure [21]. The peak at ~1630 cm^{-1} is associated with C=C in the aromatic structure of the pitch [21].

2. The method of EPR spectroscopy. EPR spectroscopy is used to determine the number of paramagnetic centres and the electronic structure of the coal tar pitch binder. Of particular interest is the effect of thermal treatment of the pitches on the number of paramagnetic centres. In [22], the concentration of paramagnetic centres for the α- and γ-fractions was determined to be $5 \cdot 10^{17}$ and 10^{16}, respectively. The number of paramagnetic centres increases during thermal oxidation (360 °C) compared to vacuum distillation of the pitch at high temperatures; a sharp increase in paramagnetic centres was observed in the α-fraction from 5 to 8×10^{17} and in the β-fraction from 1 to $2^{*}10^{17}$ [22].

In [15], EPR spectra were obtained as a function of the iodine modification of the initial pitch at a temperature of 373 °C and for different thermal holding times (Fig. 7).

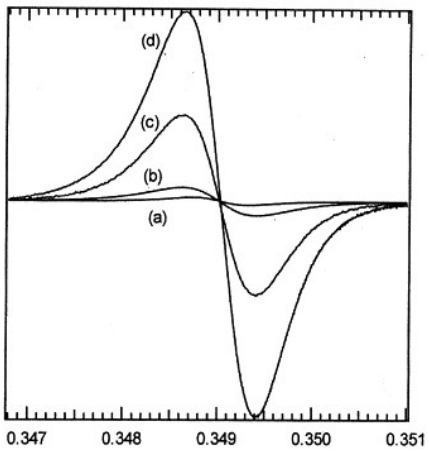

Fig. 7. EPR spectra: (a) – a medium-temperature pitch at room temperature; a pitch modified with iodine (I_2) over 12 hours (b), 24 hours (c) and 72 hours (d) at a temperature of 373 °C [15].

Medium-temperature coal tar pitch produced a weak signal with a width of 0.56 mT at room temperature [15]. As the exposure time of the pitch mixed with iodine I_2 was risen, the width of the EPR spectrum increased to 0.8 mT [15]. The signal intensity rises with increasing holding time. Extending the holding time in the I_2 medium increased the content of unpaired electrons in the pitch. As the heating time of the pitch with I_2 additives increased, the number of paramagnetic centres raises. This may be due to halogens, and in this case I_2, are active electron donors [15].

In [23], a comparative analysis of the EPR spectra of pitch and pitch-based fibres is conducted. For the pitch, a spectrum with a narrower width than that of the PEC fibres was observed. It remained virtually unchanged, with minor variations occurring in the range from 6.0 to 6.15 GHz (0.6 mT) depending on the power supplied to the resonator.

EPR spectroscopy is also used to study electrode pitches containing a mesophase in their microstructure to investigate its growth during heat treatment. In [24], the concentration of free radicals in mesophase pitch was determined to be ~$1.2 \cdot 10^{19}$ g^{-1} using EPR spectroscopy. The molecules consist of relatively small aromatic regions linked by aliphatic and aryl bridges [24]. According to [15, 22, 24, 25], for a medium-temperature pitch, upon its further heat treatment in the temperature range 400–450 °C, with the appearance of mesophases and their subsequent growth, the content of paramagnetic centres remains unchanged compared to the initial medium-temperature pitch. In [26], the authors suggested that the appearance of a mesophase is accompanied by a sharp increase in paramagnetic centres. In the temperature range 420–460 °C, there was a sharp decrease in the spin-lattice relaxation time [26]. From the data obtained, the authors in [22] concluded that the emergence of the mesophase in the pitch is caused by the aggregation of molecular fragments into polycyclic aromatic compounds (a decrease in the number of paramagnetic centers). This process was accompanied by dehydrogenation (an increase in the number of paramagnetic centres). These two processes counterbalanced each other. Therefore, the number of paramagnetic centres remained unchanged [26]. For an electrode pitch containing a mesophase, EPR spectrum measurements were conducted in [27]. EPR measurements yield slightly asymmetric signals with a width of 5–$10 \cdot 10^{-4}$ T; the shape of the lines approximately corresponds to the Lorentzian form [27].

3. The method of ^{1}H and ^{13}NMR spectroscopy. According to [2], NMR spectra based on chemical shifts in coal tar pitch and in the thermal dissolution product revealed the presence of aliphatic groups: 6–7% in the thermal dissolution products; 5–10% in coal tar pitch. Aromatic carbon exceeds 90% according to ^{13}C NMR spectroscopy [2].

In [28], a study was conducted using ^{1}H NMR spectroscopy on petroleum pitch, pitch from heavy pyrolysis resin, and commercial coal tar pitch. For petroleum pitch, the proportion of aliphatic hydrogen (0–5 pmm) is 76.9%, and the proportion of aromatic hydrogen (6–9.5 pmm) is 23.1%. For industrial coal tar pitch, the proportion of aliphatic hydrogen (0–5 pmm) is 14.8%, and the proportion of aromatic hydrogen (6–9.5 pmm) is 85.2% [28]. This finding may indicate a low content of PAHs in petroleum pitch.

4. Chromatographic methods of analysis. A chromatographic method is used to determine the quantitative and qualitative content of polycyclic aromatic hydrocarbons (PAHs) in pitch. In [29, 30], the PAH composition of pitch was analysed using gas chromatography. In [29], chromatograms were determined for pitch obtained by low-temperature thermal oxidation (T = 275 °C) of coal tar over a period of 20 hours (air flow rate 60 L/kg*h).

In the studies under consideration, the following sample heating regimes were selected for the extraction of PAHs: 1. heating was conducted to a temperature of 250 °C with a holding time of 30 min [29]; 2. heating took place from 50 to 260 °C with a holding time of 10 min, heating rate 4 °C/min [30].

Figure 8 shows the chromatograms of the resin and the pitch obtained from it.

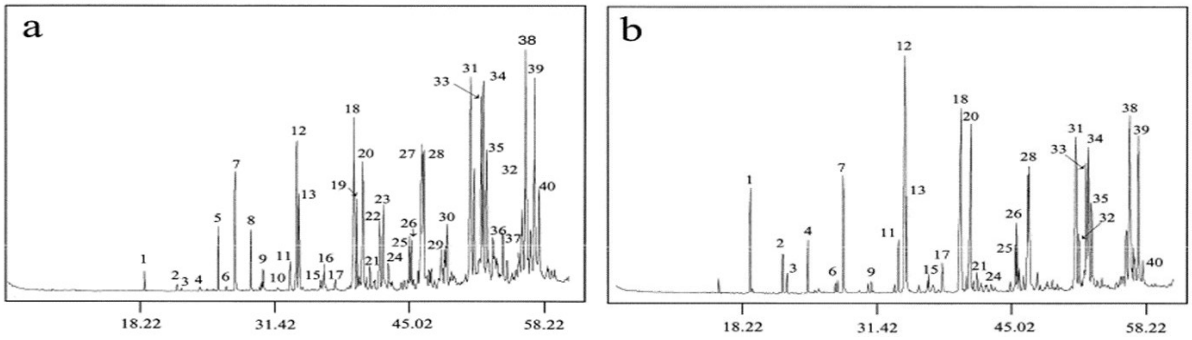

Fig. 8. Chromatograms of the toluene-soluble fraction of the starting resin (1) and the resulting pitch (2) [29].

Figure 8 shows the pitch contained higher levels of naphthalene (1), phenanthrene (12), 1,2-methylnaphthalene (2, 3), biphenyl (4) and 1-phenylnaphthalene (17) compared with the resin [29]. The following compounds were completely absent in the pitch: benzo[a]fluorene, acenaphthylene, dihydroanthracene, benzo[a]anthracene, benzoacenaphthene and perylene. Indeed, they present in coal tar [29]. Compared with the resin, the content of benzo[a]pyrene (by approximately 30%), dibenzofuran, methylfluorenes, benzofluoranthen, indene[1,2,3-*cd*]pyrene and benzo[1,2,3]perylene decreased [29].

Figure 9 shows the chromatograms of the initial pitch and the pitch after low-temperature thermal oxidation for 25 hours.

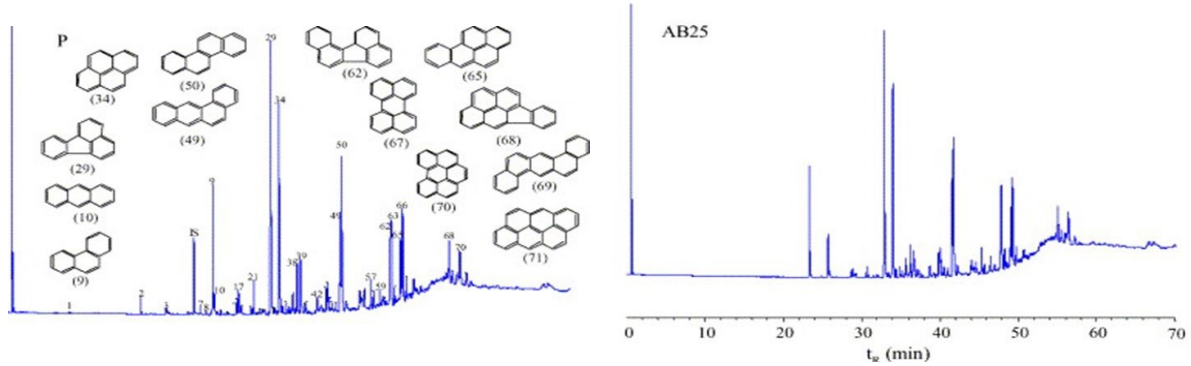

Fig. 9. Chromatograms of the initial pitch (P) and pitch (AB25) following thermal oxidation at 275 °C for 25 hours [30].

Figure 9 shows a decrease in benzo[e]pyrene from 5.9 to 1.47 and a decrease in benzo[a]pyrene from 9.68 to 1.62 [30]. Quinoline, acenaphthene, fluorene, methylenacenaphthene, and tetrahydroanthracene disappeared [30]. There was a decrease in phenanthrene from 9.9 to 4, fluoranthene from 23 to 1.8, and pyrene from 22.0 to 2.0. However, there was an increase in carbazole from 2.66 to 4.0 and methylphenanthrene from 0.8 to 3.0 [30].

The benz[a]pyrene content following low-temperature thermal oxidation of the pitch decreased by 90% compared to the initial pitch. Indeed, the benz[a]pyrene content in the pitch obtained from the thermally oxidised resin decreased by approximately 30%. Therefore, the method of low-temperature thermal oxidation of pitch is effective in reducing its benzo[a]pyrene content.

5. Gravimetric analysis of pitches.

One of the earlier studies [31] demonstrated that both the temperature of the maximum volatilization rate of pitch thermolysis products (T_m) and the temperature range over which the greatest quantity of volatile matter is released from coals (ΔT), can also be used to characterise the thermal stability of coal-based binder pitches.

Based on data [25, 32], it was established by thermogravimetric analysis (TGA) that the percentage of heat loss for medium-temperature pitch in the 200–500 °C range was 65%. In [33], TGA analysis of binder pitches revealed that the yield of pitch coke increased with an increase in the α-fraction of the pitch.

In [9], there is TGA analysis of high-melting-point petroleum binder pitches. Figure 10 presents the thermogravimetric analysis data for binder pitch (BP) with T_p = 124 °C, high-melting-point pitch (HMP) and distillate-modified pitches (MP-1, MP-2, MP-3) [8].

At stage 1 (thermal treatment under atmospheric conditions) (Fig. 10), both SP and VPP lost up to 5% by mass upon reaching a temperature of 200 °C; the modified pitches lost 7–16% by mass within the same temperature range [9]. At stage 2 (isothermal treatment under air atmosphere) (Fig. 10), both SP and the modified pitches underwent rapid mass loss [9]. At stage 3 (thermal treatment in an inert atmosphere), for the VPP pitch, mass loss began at 450 °C and continued upon reaching a temperature of 600 °C; a loss percentage is 35% [9]. For the SP pitch, the percentage loss was 65%; for the distillate-modified pitches; mass loss began at 200 °C [9].

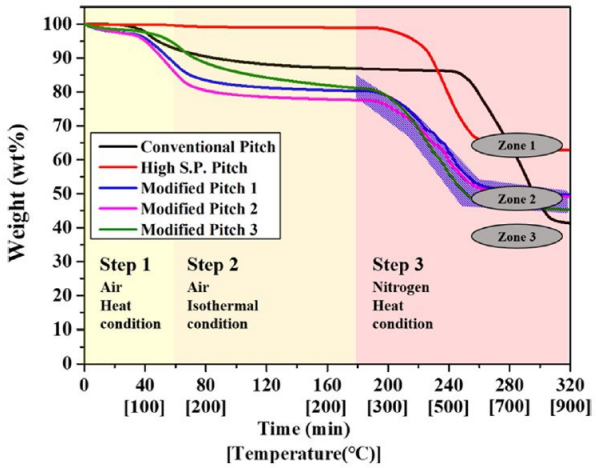

Fig. 10. The extent of the reduction in pitch mass as a function of temperature and time [9].

In [34], TGA was performed on a binder pitch with T_p = 115 °C; a high-melting-point pitch with T_p = 235 °C; petroleum binder pitches with T_p = 118 and 235 °C. Figure 11 shows the thermogravimetric curves of the binder pitches.

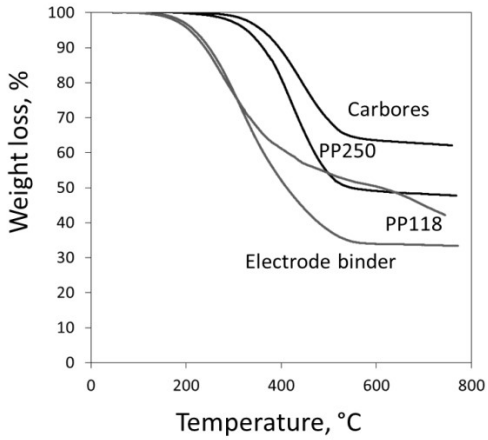

Fig. 11. The dependence of the reduction in binder pitch mass on temperature changes [34]: electrode binder (coal pitch binder with T_p = 115 °C); carbores (high-melting-point coal pitch binder with T_p = 235 °C); petroleum pitch binders PP250 and PP118.

Figure 11 shows that the highest percentage of mass loss (~70%) was observed for the coal tar pitch binder with T_p = 115 °C. The percentage of mass loss for the petroleum pitch binder with T_p = 118 °C was ~60%. For the petroleum pitch binder with T_p = 250 °C, the percentage of loss was ~55%; the lowest percentage of loss (~40%) was observed for the high-melting-point coal pitch binder. These results may be attributed to differences in the α-fraction content of these pitches, as demonstrated in [33].

In [35], TGA analysis showed that the addition of an anthracene fraction to pitch, followed by heat treatment at 300 °C, increases the percentage of mass loss at temperatures of 250–550 °C.

In [36], TGA analysis showed that the percentage of thermal loss at 350–550 °C was ~40% for medium-temperature pitch and ~20% for high-temperature pitch. The α and α_1 fractions of the pitch are thermally stable; the highest percentage of loss was characteristic of the γ fraction [36]. In [37], TGA analysis showed that as the heat treatment temperature of synthetic pitch

from the anthracene fraction increased from 400 to 480 °C (duration 5 h); the rate of thermal loss at T ~ 200–450 °C decreased from 95% to 2%.

6. Microscopic methods for analysing pitches. The mesophase (liquid-crystalline, anisotropic) microstructure of coal-based pitches is of particular interest for research. In [38], an analysis of the microstructure of electrode and medium-temperature pitches using microscopic methods revealed no mesophase spheres in the microstructure. The appearance of mesophase spheres was observed during the heat treatment of pitches under pressure [39]. During the study of the microstructure of high-temperature pitches, a mesophase structure in the form of spheres was observed. The maximum number of mesophase structures had an area of 5 μm^2; the maximum size of the mesophase had an area of 10 μm^2 [39]. The presence of a mesophase microstructure was observed for products of the thermal dissolution of Grade G coal in [40]. Mesophase spheres and their growth were observed during the heat treatment of synthetic mesophase pitch at T > 400 °C; the growth of mesophase spheres was observed as the duration of the pitch's heat treatment at 440 °C was increased from 1 to 6 hours [37]. Fig. 12 shows micrographs of the pitch structure during the initiation of the mesophase.

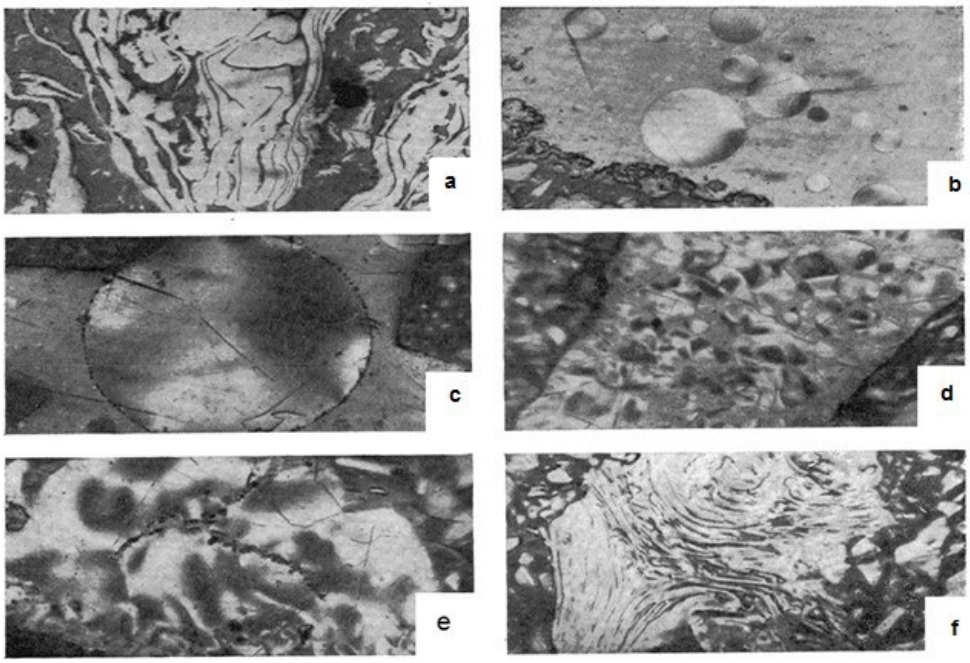

Fig. 12. Formation of the mesophase structure of the pitch [41]: **a** – initial pitch; **b**, **c** – formation of mesophase spheres (d_{max} = 40 μm) and their growth to ~150 μm (at T = 390–420 °C); **d**, **e** – coalescence of mesophase spheres (420–425 °C); **f** – mesophase structure.

Figure 12(a) shows the microstructure of an isotropic pitch. Upon heating from 390 to 420 °C, mesophase spheres appear. As the temperature rises, the spheres coalesce appears to form a three-dimensional mesophase structure (Figure 12(e)).

Fig. 13 shows micrographs of the structure of synthetic naphthalene pitch and the products of its heat treatment at T > 400 °C, as reported in [42].

According to Fig. 13, the initial pitch had an isotropic microstructure (without mesophase content); the pitch obtained by thermal oxidation of the isotropic pitch contained mesophase spheres (5%) in its microstructure. Mesophase pitches were obtained at 420 °C

(for Figure 12c – 30 vol.%) and 430 °C for 4–8 hours (Figures 12d–g from 50 to 100 vol.%). The authors in [42] obtained a continuous isotropic pitch matrix reinforced with pitch mesophases, as shown in Fig. 12b and Fig. 12c. When the pitch mesophase content increases to ~50 vol.% (Fig. 12d), large mesophase spheres and a partially fused texture are present; the isotropic pitch remains a continuous phase [42]. With a further increase in the mesophase content to ~75 vol.%, some isotropic spherical or ellipsoidal mesophases clearly coalesce into an optically anisotropic continuous phase, as shown in Figure 12e [42]. A pitch with a high mesophase content of ~98 vol.% exhibits a strongly oriented fine flow texture, as shown in Figure 12f [42]. A mesophase content of 100 vol.% was also observed, as shown in Figures 12g and h [42]. In [43], mesophase pitches with the structure shown in Fig. 14 were obtained from the $\gamma+\beta$ fraction isolated from the puck by adding polystyrene and heating to 430 °C at atmospheric pressure.

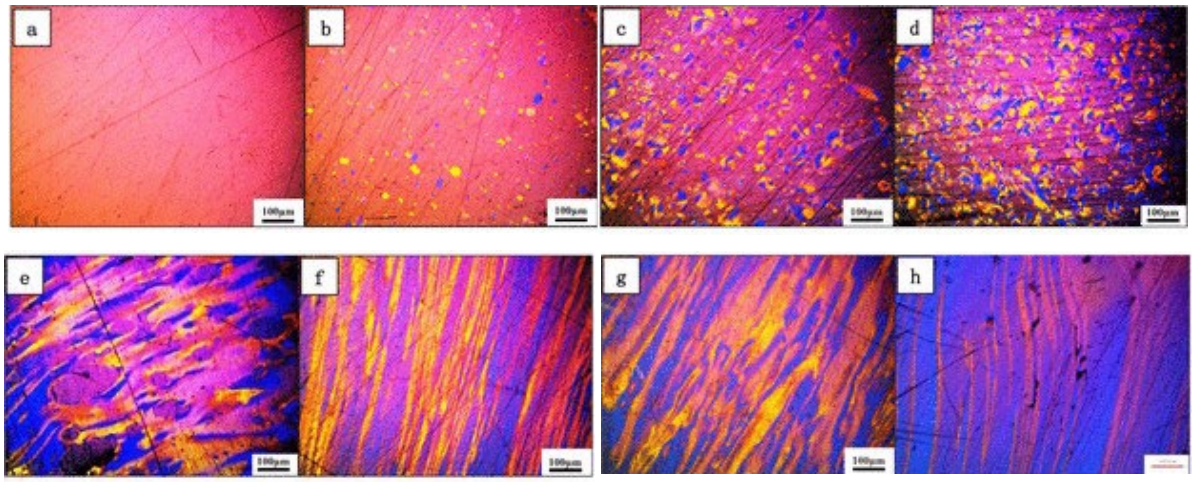

Fig. 13. Microstructure of the initial pitch (**a**), pitch with low mesophase content (5 vol. %) (**b**) – pitch obtained by thermal oxidation of the initial pitch, and microstructures of pitches obtained by heat treatment of the initial pitch, demonstrating typical mesophase contents (**c** – 30; **d** – 50; **e** – 75; **f** – 98 and **g**, **h** – 100 vol. %) [42].

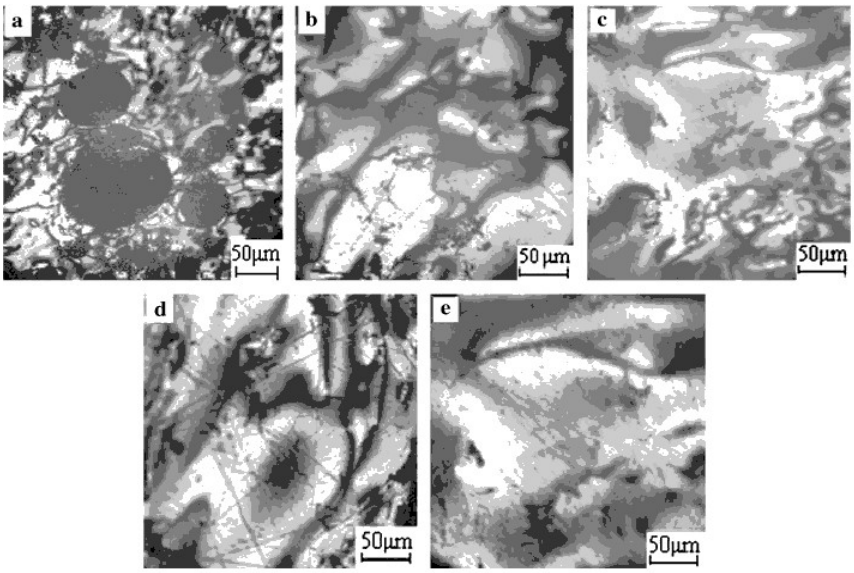

Fig. 14. Microphotographs of pitches prepared from the $\gamma+\beta$ fraction and polystyrene: without polystyrene (**1**); with 5% polystyrene by weight (**2**); with 10% by weight of polystyrene added (**3**); with 15% by weight of polystyrene added (**4**); with 20% by weight of polystyrene added (**5**) [43].

The mesophase content with a coarse-mosaic morphology in the mesophase pitch without additives is approximately 74%; in this case, the mesophase was incomplete. Pitch with a mesophase content of 100% was observed in samples containing 5–20% polystyrene. This shows that mesophase coalescence improves significantly with the addition of polystyrene. Polystyrene additives are highly effective, as the formation of a voluminous mesophase occurs at 5% by weight.

7. X-ray diffraction analysis of pitches.

X-ray diffraction was used to determine the lattice parameters of the mesophase pitch. According to [25], the ability of the medium-temperature pitch to reflect X-rays at the (002) and (100) maxima suggests the presence of aromatic rings in the pitch structure, grouped into so-called clusters. The (002) peak corresponds to the graphite-like phase [25]. In [44], a (002) peak and two-dimensional (10) reflections were observed for a low-temperature pitch. In [45], high-melting-point pitches containing a mesophase were investigated. The X-ray diffraction pattern of the pitch contained (002), (10) and (004) peaks; a line at a scattering angle of 7.5°, associated with the hydrocarbon phase, was also observed [45].

Figure 14 shows X-ray diffraction patterns for mesophase pitch and mesophase pitches obtained by modification with polystyrene [43].

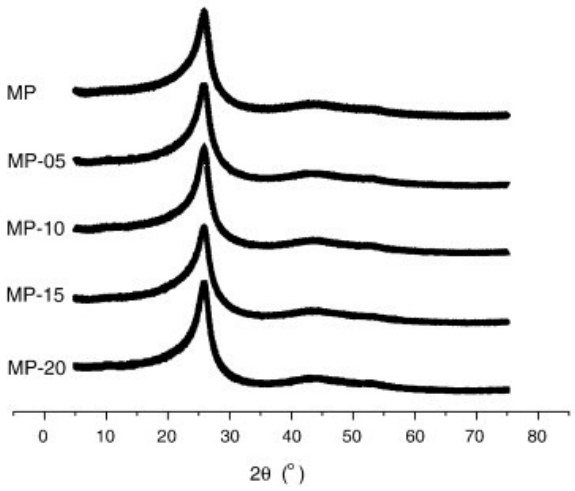

Fig. 15. X-ray diffraction patterns of mesophase pitches obtained from the $\beta+\gamma$ fraction of coal tar pitch and polystyrene by heating to 430 °C [43].

Figure 15 shows that as the mesophase increased, the interplanar spacing d_{002} decreased from 3.45 to 3.43 Å. At the same time, the packing size L_c increased. This may be due to the fact that, as a result of reactions during heat treatment (T > 400 °C) of the modified pitch, the number of alkyl groups attached to the aromatic rings increased from 23 to 36 [43]. An increase in the intensity of the (002) peak was also observed; the (10) and (100) peaks had low intensity [43].

8. Spectral methods for determining the mesophase structure of pitches.

8.1. The method of IR spectroscopy.

Mesophase pitches were investigated using IR spectroscopy in [43, 46].

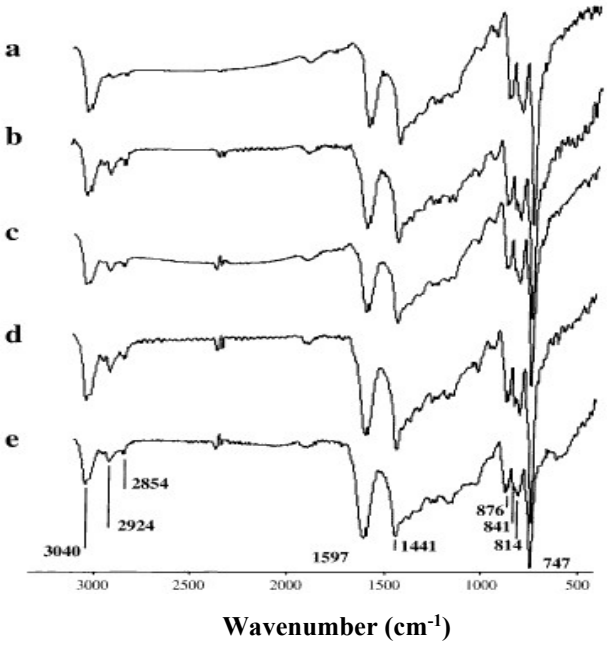

Fig. 16. IR spectra of mesophase pitches based on the $\gamma+\beta$ fraction and polystyrene: 1 – mesophase pitch obtained without additives; 2 – mesophase pitch obtained with a 5% additive; 3 – mesophase pitch obtained with a 10% additive; 4 – mesophase pitch obtained with a 15% additive; 5 – mesophase pitch obtained with a 20% additive by mass [43].

An increase in the mesophase content in the pitch leads to rise in the intensity of the line at 1600 cm^{-1}; an increase in the intensity of the lines associated with aliphatic groups (2920 cm^{-1}, 2850 and 1380 cm^{-1}).

Figure 17 shows the IR spectra of the mesophase granules.

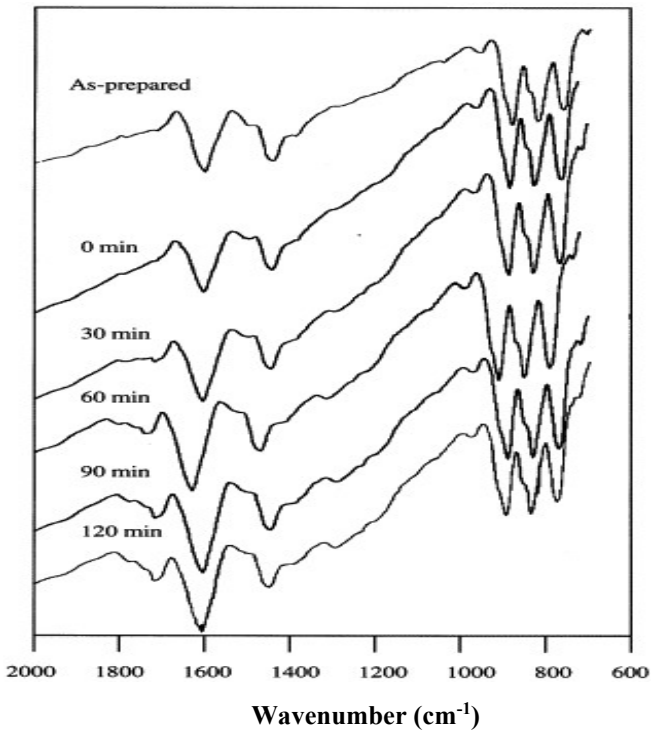

Fig. 17. IR-Fourier spectra of the freshly prepared starting material and the stabilised product in the form of mesophase carbon granules (without carbon black) at 270 °C at various time points [46].

The starting material had lines at 1600, 1440, and 900–700 cm^{-1} (Fig. 17). The first two lines are attributed to aromatic C=C and methylene hydrogen in-plane bending. The line at 900–700 cm^{-1} corresponds to out-of-plane aromatic C–H bending [46, 48]. The intense methylene-hydrogen bending line at 1440 cm^{-1} (Fig. 17) is due to a significant number of naphthenic rings. Stabilisation at 270 °C without holding time evidently did not alter the intensity of these lines. Stabilisation for 30 minutes yielded new lines in the 1730–1650 and 1250 cm^{-1} regions (Fig. 17). They are attributed to C=O, in particular to ketone, aldehyde, carboxylic acid functional groups, and C–O and O–H lines [47]. Lines at approximately 1735 and 1770 cm^{-1} (Fig. 17), attributed to ester and anhydride functional groups [46,47], appeared after a 60-minute stabilisation period, accompanied by a further increase in intensity at 1710 and 1600 cm^{-1} (Fig. 17). This indicates the formation of an ester and anhydride molecular system with deeper oxygenation and oxidative polycondensation [46–48]. Longer stabilisation periods of 90 and 120 minutes steadily increased the intensity of these lines, particularly at 1730–1650 cm^{-1}. It suggests the formation of ketone, aldehyde and carboxylic acid functional groups is predominant [46].

8.2 The ^{1}H NMR spectroscopy method.

In [43], an analysis was conducted of ^{1}H NMR spectra for mesophase pitches obtained by modification with polystyrene. Table 1 shows the NMR spectral data as a function of the component content in the starting material and the growth of the mesophase.

Table 1. Analysis of ^{1}H NMR spectroscopy data for mesophase coals obtained from the γ+β fraction with polystyrene additives; MP-0 is pitch without polystyrene additives; MP-5, MP-10, MP-15, MP-20 – mesophase pitches obtained by adding 5, 10, 15 and 20% polystyrene to the initial raw material [43].

Name	H_{AR}, %	H_α, %	H_β, %	H_γ, %
MP-0	88.0	4.4	6.4	0.9
MP-5	84.0	4.5	10.6	0.9
MP-10	81.4	8.7	9.7	0.8
MP-15	78.9	14.2	6.0	0.4
MP-20	66.7	16.0	16.8	0.5

Using ^{1}H NMR spectroscopy, the molecular compositions were determined based on chemical shifts: 6.5–9.5 ppm – aromatic hydrogen (H_{AR}); 2.1–4.5 ppm – aliphatic hydrogen at the α position (H_α); 1.1–2.1 ppm - aliphatic hydrogen at the β position ($H\beta$), and 0.5–1.1 ppm – aliphatic hydrogen at the $_\gamma$ position (Hγ) respectively [42]. The aromatic hydrogen content decreases as the proportion of polystyrene in the starting material increases and as the mesophase increases. However, this is accompanied by an increase in the H_α and H_β contents. The majority of alkyl groups ranged from α-methylene to aromatic rings [42]. This result is consistent with the IR spectroscopy findings (Fig. 16).

In [42], ^{1}H NMR spectroscopy revealed a decrease in the intensity of aromatic hydrogen as the mesophase content increased from 50% to 98%. At a mesophase content of 98%, there is a decrease in aromatic hydrogen and an increase in the content of aliphatic hydrogen in the β-position compared to the initial isotropic pitch. It may indicate an increase in naphthenic structures for the mesophase naphthalene pitch.

8.3 The method of combination scattering spectroscopy (CS spectroscopy).

An analysis of the molecular structure of mesophase synthetic pecs based on naphthalene was conducted by IR spectroscopy [49]. An intense line at 1580 cm^{-1} (the G band for graphite) and a broad D band (defect) at 1350 cm^{-1} were observed [49]. There were also observed lines at 1609, 1248, 1288 and 1376 cm^{-1}. It can be explained by the specific structure of the mesophase pitch and the characteristics of the raw material from which it was obtained.

In [50], an analysis was performed of the FT-IR spectra of mesophase pitches (MP, MP-10 and MP-20) obtained by heat treatment at T > 400 °C of a product based on pitch from ethylene resin with polystyrene additives. As the amount of additives increased, the percentage of mesophase content in the pitch increased. Figure 18 shows the IR spectra of mesophase pitches.

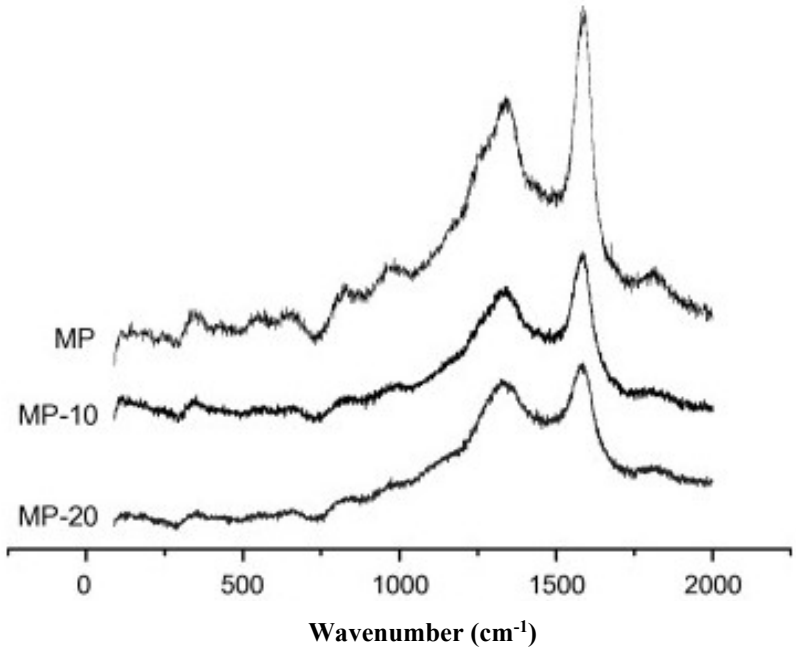

Fig. 18. CR spectra for the mesophase pitches MP (no additives), MP-10 (10% additives) and MP-20 (20% additives) [50].

Figure 18 shows the G band at around 1600 cm^{-1} and a broad, complex band lying between 1150 and 1500 cm^{-1}, the typical wavenumber ranges for the D band [50]. The relative intensities of the D and G bands are 4.136 for MP, 6.417 for MP-10 and 7.272 for MP-20; the width of the 1600 cm^{-1} band (Fig. 18) for MP, MP-10 and MP-20 is approximately 45, 75 and 85 (Fig. 18) respectively. IR spectroscopy results show that there are more alkyl groups in the mesophase pitches of MP-10 and MP-20 than in MP [50].

Discussion

According to IR spectroscopy, the molecular structure of petroleum pitches [2, 8, 15, 16, 21] consists mainly of aromatic compounds with a lower content of aliphatic compounds. The IR spectroscopy data are confirmed by NMR spectroscopy.

According to IR and NMR spectroscopy, petroleum pitch binders have a low PAH content [2, 28]. It correlates with [34], combining mass spectrometry with UV spectroscopy. As a result, petroleum pitches had a low PAH content compared to coal-based binder pitches.

In [16], pitches modified with formaldehyde, benzaldehyde, and furfural reduced proportion of aromatic compounds; the number of hydroxyl and carboxyl groups had increased. According to IR spectroscopy, the molecular structure of the modified pitch had a bridged structure and corresponded to that of a phenolic resin. The phenols and PAHs present in the pitch reacted via polymerisation with the aldehydes, ultimately forming phenolic resins [16]. This modification method can be used to produce a binder with a reduced benz[a]pyrene content.

For the low-temperature pitch (250 °C) of thermal oxidation, IR spectroscopy revealed an increase in the intensities of lines associated with the molecular structure of PAH [21]. A decrease in the intensity of these lines was observed upon modification of the anthracene fraction of the pitch followed by further low-temperature thermal oxidation [21].

To study the composition of PAHs, chromatographic methods of analysis are used. They are effective ones for reducing benz[a]pyrene at the low-temperature oxidation of medium-temperature pitch, where the benz[a]pyrene content can be reduced by 90% [30]. Presumably, at thermal oxidation temperatures up to 300 °C, the benz[a]pyrene molecules were destroyed or separated along with volatile substances and light components of the pitch or resin, thereby reducing its content in the final product.

Coal tar pitches modified with I_2 showed a tendency towards an increase in the amplitude of their EPR spectra (Fig. 7). It is due to I_2 is an electron donor, and as the heating time increased, electrons were transferred to the pitch molecules, yielding various radicals. Their number increased, as evidenced by the growth in the amplitude and width of the EPR spectrum (Fig. 7). As the number of unpaired electrons increased, the relaxation time decreased and the amplitude of the EPR spectrum increased (Fig. 7). Unmodified pitch had a low EPR spectral amplitude, and the spectral width was 0.6 mT [15].

The electrode pitches lack mesophase spheres in their microstructure. Mesophase spheres and their growth are observed during the heat treatment of pitch at T > 400 °C. According to XRF, NMR, IR, and FTIR spectroscopy, the growth of the mesophase in the pitch was accompanied by an increase in the content of aromatic carbon and aliphatic hydrogen. For example, as the addition of polystyrene to the $\gamma+\beta$ fraction of the pitch increased, a fully-fledged three-dimensional mesophase appeared (Fig. 14). This was accompanied by a change in the molecular structure. According to IR spectroscopy, there was an increase in the intensity of lines associated with aliphatic compounds. It correlates with the NMR analysis data. The increase in the number of aliphatic groups, compared to aromatic groups, may be attributed to the influence of modifying additives on the initial pitch product. As a result of pyrolysis, polystyrene molecules (alkyl and other radicals) were released and attached to the pitch product molecules during heat treatment. Most of the detached radicals may range in structure from α-methylene groups to aromatic rings [43]. As the number of additives increased, the content of aliphatic hydrogen raises, as indicated by the NMR spectra. The presence of a greater number of alkyl groups and other radicals forms a closer interaction with the low-molecular-weight components of the mesophase pitch and improves its properties. A mosaic structure in pitches without additives [43] appeared upon heating coal pitch to T = 430°C. In the IR spectrum for pitch with a mosaic structure (Fig. 16), a line at 2920 cm^{-1} is observed, which is attributed to the aliphatic C–H valence band; C=C lines are also present (peak at 1600 cm^{-1}, Fig. 16), and lines

in the range from 700 to 800 cm^{-1} (Fig. 16). They are associated with bending vibrations in the aromatic structure. There is also a line at around 1400 cm^{-1} (Fig. 16). It is associated with bending vibrations of the aliphatic structure. It can be assumed that, when preparing the mesophase pitch without the use of additives, the initiation of the mesophase occurred in an isotropic system during heating of the pitch to 430 °C, without the formation of large spherulites or complete structural 'disorder'. Presumably, under these conditions, mesophase nuclei appear in the isotropic system. It apparently transforms into spherulites of insufficient size and located at a certain distance from one another. As the temperature rises above 400 °C, these spherulites coalesce with one another and form a mosaic structure. When additives are introduced followed by heat treatment, the number of mesogens increases, and the number and size of the spherulites rise. They coalesce, resulting in the formation of a fully developed three-dimensional mesophase structure. At the same time, the molecular structure of the pitch changes, and the number of aliphatic compounds attached to aromatic compounds increases. A similar result was observed during the modification of petroleum pitch with polystyrene followed by heat treatment in [50]. Furthermore, according to [41, 42], the growth of the mesophase was accompanied by an increase in the secondary α_1 fraction.

Due to its maximum α_1 fraction content and maximum T_p, mesophase pitch cannot be used as a binder, but can be used as a raw material for the production of needle coke [50].

Conclusion

Information is presented on the molecular structure of various pitches derived from experimental data obtained previously in studies using IR, NMR, and EPR spectroscopy. Using EPR spectroscopy, it was established that thermal oxidation leads to an increase in the number of paramagnetic centres in the pitch; a particularly large increase in paramagnetic centres occurred in the α-fraction. The chromatographic analysis is an effective method for determining PAH content. An analysis of the literature has identified the possibility of reducing the benz[a]pyrene content in pitch by low-temperature thermal oxidation. Methods for identifying the mesophase structure of pitch and for investigating the molecular structure of mesophase pitches are discussed.

Funding

The study was performed within the framework of the state assignment of 'Federal Research Centre of Coal and Coal Chemistry of the Siberian Branch of the Russian Academy of Sciences' project No. 124041100047-4.

Conflict of interest

The authors declare no conflict of interest in financial or any other sphere.

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Received 07.11.2025
Approved after reviewing 18.02.2026
Accepted 04.03.2026