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The Effect of Polyvinyl Chloride on the Properties of Coal Tar Pitch

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Abstract

Coal tar pitch is a thermoplastic material, which exhibits weak polymer properties. This material is a promising raw material for the production of various carbon materials due to its availability and cheapness. However, its properties often do not meet the requirements for the production of modern carbon materials. This paper presents the results of the studies of the effect of polyvinyl chloride on the properties of coal tar pitch. Experimental studies have shown that polyvinyl chloride actively influences the properties of the modified pitch. The fractional composition of the modified pitch changed: the number of higher molecular α_2- and β-fractions increased, and the amount of low molecular weight γ-fraction decreased. It was found that modified pitch viscosity increased with an increase in the amount of polyvinyl chloride. The X-ray diffraction (XRD) analysis showed, and Scanning Electron Microscopy (SEM) photographs confirmed that the interaction between pitch and polyvinyl chloride is accompanied by molecular-structural transformations, as a result of which the structure of the modified pitch changes. Thus, knowledge of the regularities of interaction processes between the pitch and polyvinyl chloride makes it possible to significantly change its properties. It may be useful for adjusting pitch to use it as a precursor for various carbon materials.

Keywords: *Coal tar pitch; Polyvinyl chloride; Modification; Rheological properties; Thermal behavior; Precursor; Carbon material.*

1. Introduction

Coal tar pitch (CTP) is the most massive chemical product that is formed during the production of coke from coal charge. Therefore, many researchers have a significant scientific interest in the study of its properties for use in various fields [1–5]. Modern research methods [1] have established that CTP is a complex heterogeneous dispersed system of highly condensed aromatic carbo- and heterocyclic compounds, and their compaction products with active functional groups. CTP is a thermoplastic material, which exhibits weak polymer properties. The features of the structure and properties of coal tar pitch indicate that fundamentally new materials with various characteristics can be created on its basis [6–13]. This material is a promising raw material for the production of various carbon materials due to its availability and cheapness. However, the properties of CTP often do not meet the requirements for the production of modern carbon materials: solid carbon foams, fibers, adsorbents, composites. Nevertheless, considering that pitch is by its nature an extremely reactive material, and it can actively interact with various chemical additives, it can be modified to change its properties [2–4, 10, 12]. As is known, CTP contains various functional groups, which can activate and enter into chemical interaction under certain conditions. In addition, the highly condensed aromatic compounds present in the pitch are characterized by a low strength of chemical bonds at the periphery.

This paper presents the results of the studies of the effect of polyvinyl chloride (PVC) as an active polymer additive on the properties of CTP. Choosing PVC as a modifying additive for CTP was primarily due to the possibility of chemical interaction with pitch components [14, 15].

2. Experimental section

2.1. Raw materials

Medium-temperature CTP had the Mettler softening point of 108°C and a coke yield of 56 wt.%. The Quinoline Insolubles (QIs) and Toluene Insolubles (TIs) were 9 and 34.9 wt.% respectively. The CTP had α-fraction of 34.9 %, α_2-fraction of 25.9 %, β-fraction of 34.1 %, γ-fraction of 31.0 %. A viscosity of CTP at 140°C and at 160°C were 9.3 and 1.3 Pa·s respectively.

PVC suspension PVC-S CAS: 9002-86-2, powder with a particle size of 100–200 microns, a density of 1380 kg/m^3. It is a polar polymer with high intermolecular interaction. By the solubility parameter (20.2 MPa$^{1/2}$) PVC refers to a moderately polar polymer. This indicates sufficient simplicity of its combination with other polymers. Therefore, PVC is considered an easily compounded polymer.

2.2. Coal tar pitch modification

To perform experiments the small lab-scale equipment was used: a lab batch reactor equipped with a stirrer and a mill. First, a mixture of the CTP and PVC was prepared by dispersive mixing in a mill for 15 minutes. PVC was added in the amount of 1–20 weight part (wt.p.) per 100 wt.p. of the CTP. The prepared mixture was subjected to heat treatment in a lab batch reactor in which it was mixed for 120 min at 170°C. After cooling, the finished mixture of modified CTP in the form of solid pieces was obtained.

2.3. Methods of samples studying

To determine the molecular structure and supramolecular organization of the CTP due to the complexity of its composition and structure, a complex of physical, physicochemical, and chemical research methods was used.

Fractionation. Due to the complexity of the chemical composition of the CTP, it is characterized by fractional composition, which is determined by the method of sequential extraction with solvents, by which the fractions are isolated: α-fraction insoluble in toluene; α_1-fraction, insoluble in quinoline; α_2-fraction, insoluble in toluene and soluble in quinoline; β-fraction, soluble in toluene and insoluble petroleum ether; γ is the fraction soluble in petroleum ether.

Fractional composition of the CTP was determined by the method of sequential solvent extraction in accordance with the scheme (Figure 1). Petroleum ether, toluene, and quinoline were used as solvents.

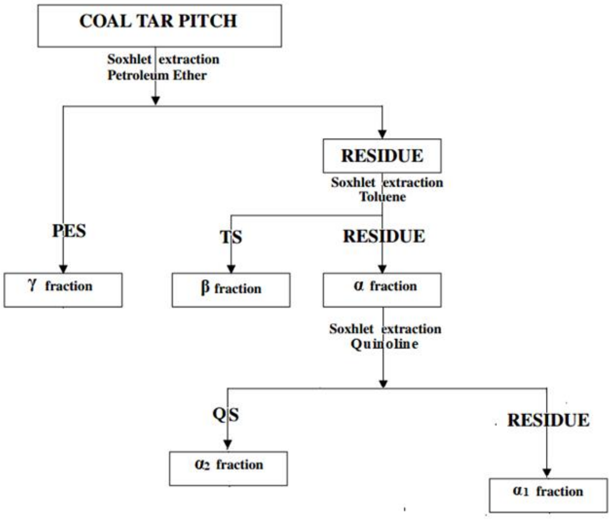

Figure 1. Scheme for the separation of the initial and modified pitches (PE – petroleum ether; T – toluene; Q – quinoline)

Thermogravimetry. The STA PT1600 thermal analyzer (Linseis, Germany) was used for thermogravimetric (TGA) and thermal analysis (DTA). Powder samples (sample weight 10 mg) were placed in open alumina pan and heated from 25 to 900°C at a heating rate of 5°C/min in argon (flow rate 6 L/h).

Spectroscopy. Fourier transform infrared (FTIR) techniques have been used to determine the functional groups involved in intramolecular and intermolecular interactions during thermo-chemical transformations of the CTP. FTIR spectra of the samples were obtained using pitch powders on Nicolet iZ10 model FTIR spectrometer. The spectra were obtained in the range 400–4500 cm^{-1}.

Rheometry. Rheological properties: dynamic viscosity was determined using a rotational cone-and-plate viscometer RHEOTEST-2.1. The viscosity of samples of the modified CTP (MCTP) with a high content of PVC (5 wt.p. or higher) was characterized by the melt flow index, which was determined using the equipment of the brand IIRT-AM (according to ASTM D1238, ASTM D3364, GOST 11645). The essence of the method was to determine the mass of the material in grams extruded from the instrument for 10 min under given conditions of temperature and pressure (with a load of 49, 98 N (5, 10 kgf) and under normal conditions). Temperature range is from 0 to 400°C ± 0.2°C. Diameter of the calibrated capillary is 2.095 ± 0.005 mm, length of the calibrated capillary is 8.000 ± 0.025 mm.

X-ray Diffraction. The X-ray diffraction (XRD) method was used to determine the parameters of the supramolecular structure of the MCTP. XRD of CTP and MCTP were performed in X'Pert Pro MPD diffractometer from PANanalytical (Holland), with a copper ka radiation (1.54Å) generated at 45 kV and 40 mA. The angles from 5 to 90°2Th were scanned at step increment of 0.039°. The interlayer spacing (d_{002}) calculated using the Bragg equation, was used as an indicator for the extent of ordering.

Scanning Electron Microscopy. Scanning Electron Microscopy (SEM) images were obtained using Tescan VEGA3 SB scanning electron microscope. Electron source: tungsten heated thermo-cathode. The resolution in high vacuum mode (SE) is 8 nm at 3 kV. Increase from 3 to 10^5.

3. Results and discussion

3.1. Fractional composition

Fractional composition test (Figure 1) was performed to obtain information for the chemical composition of initial and modified pitches. That is necessary for better understanding of the processes taking place during heat treatments and interaction of the pitch with PVC.

The results of studies on the effect of PVC on the thermochemical transformation of CTP under selected conditions (at 170°C for 120 min) are shown in Figure 2.

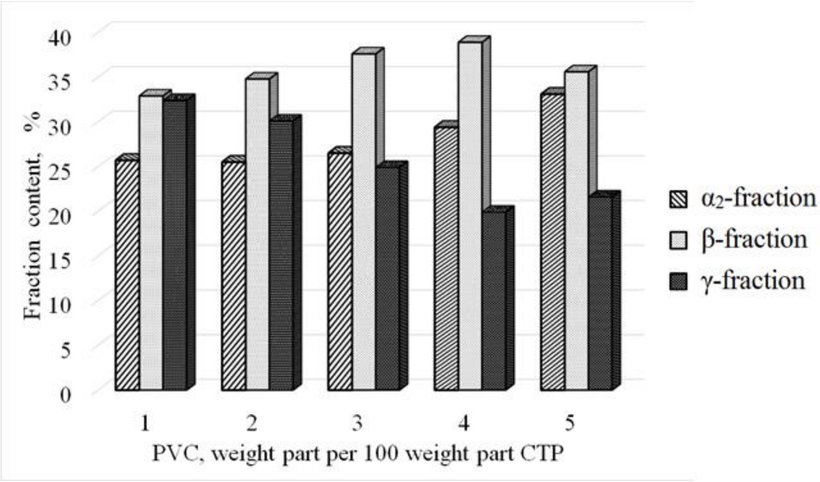

Figure 2. Group composition of the CTP, heat-treated without additives, and CTP modified with PVC (at 170 °C for 120 min)

The β-fraction and α₂-fraction include oligomeric substances, which represent associates of structural units, each of which has several aromatic rings, heteroatoms and aliphatic groups along the periphery. α₂-fraction in contrast to β-fraction contains more condensed systems and less aliphatic groups. The least condensed γ-fraction is a multicomponent mixture of carbo- and heterocyclic compounds.

The analysis of the data obtained (Figure 2) showed that the introduction of PVC into CTP initiates the synthesis of α₂- and β-fractions due to the γ-fraction. The increase in the amount of modifier from 1 to 3 wt.p. mainly intensified the processes of the β-fraction synthesis. The presence of chlorine-containing polymer in the reaction zone initiated the reaction activity of γ-fraction hydrocarbons with low molecular weight. This contributed to the formation of oligomers, thus increasing the content of β-fraction and reducing the γ-fraction content.

Increase in the PVC content from 3 wt.p. up to 5 wt.p. resulted in lower growth of the β-fraction, but at the same time, there was an increase in the amount of higher-molecular α₂-fractions. The reason for this could be the high reactivity of the formed condensed aromatic compounds with alkyl side groups that form the basis of the β-fraction, which partly, as a result of polycondensation processes, formed substances of oligomeric structure entering into the α₂-fraction.

As can be seen from Figure 2, the increase in the amount of PVC up to 10 wt.p. led to the decomposition of the β-fraction, resulting in a rise in the content of α₂-fractions and γ-fractions. It can be assumed that when PVC interacts with CTP, the resulting condensed aromatic compounds with alkyl side groups, at reaching a certain molecular weight, begin to break down. The degradation of β-fraction macromolecules can occur with the elimination of side groups, as a result of weakening of the binding energy at the periphery of molecules, which is typical of polycyclic aromatic hydrocarbons, as well as by cross-links. When macromolecules break down, free radicals of various sizes are formed. As a result of the recombination of large free radicals, more condensed aromatic compounds are formed (α₂-fraction). The recombination of free radicals of small size increases the content of γ-fraction components.

The obtained results indicate that CTP interacts with PVC. The result is an increase of the amount of higher molecular weight α₂- and β-fractions, and a decrease in the low molecular weight γ-fraction content.

3.2. Thermal behavior

Thermal analysis of pitch, modified with 3 and 5 wt.p. of PVC (Figure 3), showed the presence of additional peaks on the derivative thermogravimetry curves (DTG) at 210–260°C compared to the DTG curve of the initial CTP. And the increase in the PVC amount leads to an increase in the peaks intensity. An exothermic peak is formed on the DTA curve of the modified pitch. Thus, there is a process of mass loss with energy release.

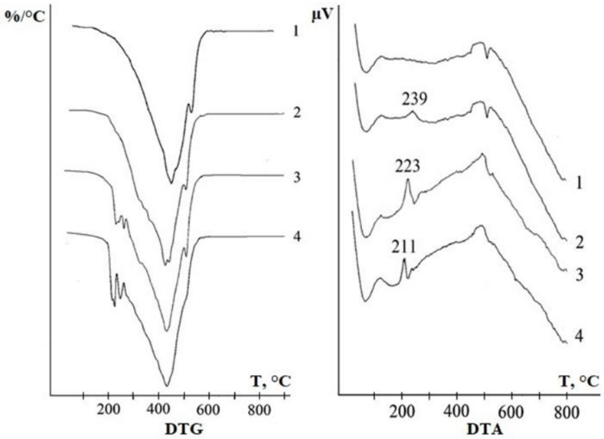

Figure 3. DTG and DTA curves of CTP, modified with PVC at 170 °C for 120 min. PVC amount: 1 – 0 wt.p.; 2 – 1 wt.p.; 3 – 3 wt.p.; 4 – 5 wt.p.

The emergence of new peaks indicates that during the modification, new compounds were formed as a result of the connection of CTP molecules to the active polymeric radicals formed during the destruction of PVC. When heated in an inert medium, an intense destruction of the products of the interaction of PVC and pitch begins at the specified temperature interval, which is accompanied by the release of low molecular weight products (DTG peak). As a result, a significant amount of exothermic radicals (exothermic peak on DTA) that are involved in polycondensation processes are formed. It should be noted that the greater the amount of PVC used for the modification of the CTP, the lower the temperature of destruction of new compounds formed (displacement of the exothermic peak in the area of lower temperatures). This indicates their lower thermal stability.

3.3. Spectroscopic studies

Fourier transform infrared spectroscopy has been used as one of the most effective techniques providing information on functional groups in complex solids. The FTIR spectra made it possible to compare samples of the initial and modified pitch and obtain relevant information on changes in their chemical composition.

To obtain the information about the composition and structure of the functional groups in the organic substance of the initial and modified CTP, their FTIR spectra were obtained (Figure 4).

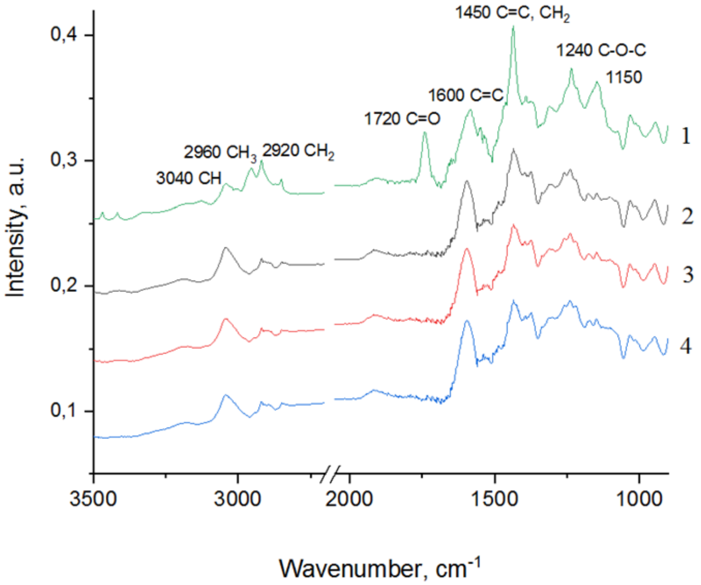

Figure 4. FTIR spectra of CTP (1) and pitch modified with PVC at 170°C for 120 min. Amount of PVC: 2 – 5 wt.p.; 3 – 10 wt.p.; 4 – 20 wt.p.

The presence of 3040 cm^{-1} (stretching vibrations of aromatic bonds $C\text{-}H_{ar}$) and 1600 cm^{-1} (stretching vibrations of $C{=}C_{ar}$) bands showed that aromatic compounds are contained in the analyzed pitches [16]. The absence of the characteristic band of the benzene ring 1500 cm^{-1} (plane vibrations of the benzene ring) indicated system condensation. As the condensation degree increases, the role of conjugation of double bonds C=C becomes dominant, and the intensity of the 1600 cm^{-1} band increases, while the intensity of the 1500 cm^{-1} band decreases.

Modification of CTP with PVC (5–20 wt.p.) increased its condensation degree, as indicated by an increase in the intensity of 3040 and 1600 cm^{-1} bands. In addition, the content of the aromatic hydrogen increased in modified pitches, which confirmed the decrease in the content of aliphatic CH_2 groups (a decrease in the intensity of 2920 and 2820 cm^{-1} stretching vibration bands, as well as deformation vibrations of 1450 cm^{-1} [17]) and the absence of CH_3 groups (the absence of 2960 cm^{-1} band [14]). The FTIR spectra of the modified pitches showed a decrease in the number of oxygen-containing groups, which was confirmed by the disappearance of the 1720 cm^{-1} band (stretching carbonyl C=O vibrations [10]) and the weakening of the 1240 cm^{-1} band (asymmetric stretching vibrations of the $C\text{-}O\text{-}C_{ar}$ aromatic esters). A sharp decrease in the intensity of the 1150 cm^{-1} band (plane vibrations of substituents in the benzene ring) showed that the number of substituents in the benzene ring decreased in the modified pitches.

FTIR spectral analysis showed that when CTP interacts with PVC, the oxygen-containing groups of pitch are actively involved. In addition, due to the detachment of methylene and methyl groups, active radicals are formed, after recombination of which high-molecular condensed aromatic compounds are formed.

3.4. Rheological studies

Rheological studies (Figure 5) confirmed that thermochemical transformations that occurred during the modification of CTP with polyvinyl chloride significantly influenced its structure.

It is known that the viscosity depends on the chemical composition and on the molecular-kinetic characteristics of the system. The interaction of CTP and PVC molecules led to the formation of supramolecular structures, the number and size of which had an effect on viscosity. Thus, the viscosity indirectly characterized intermolecular interaction in the pitch, as in the case of any other condensed system.

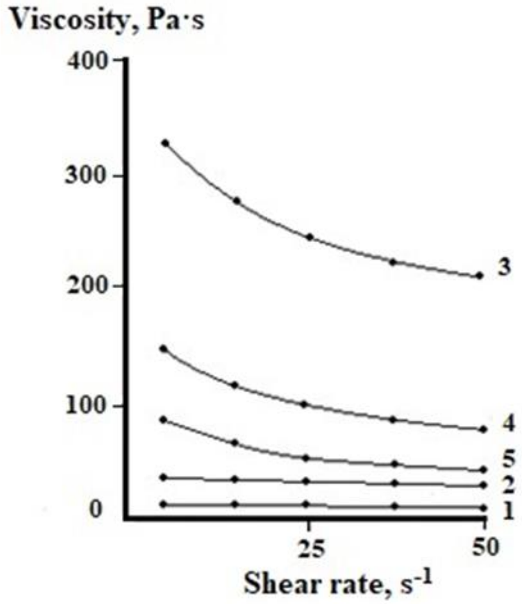

Figure 5. The dependence of viscosity (at 135°C) on the shift speed of CTP and pitches, modified with 3 wt.p. of PVC: 1 – initial pitch; 2 – pitch, heat-treated without additives; 3 – pitch, modified at 135°C; 4 – pitch, modified at 145°C; 5 – pitch, modified at 155°C

As can be seen from Figure 5, at 135°C and above, CTP shows a Newtonian flow (Figure 5, sample 1), i.e. it is a completely destroyed structure. The viscosity of the heat-treated pitch without PVC (Figure 5, sample 2) is approximately 3 times more than CTP viscosity, but under these conditions its flow also corresponds to a completely destroyed structure. Introduction of 3 wt.p. of PVC to the CTP (Figure 5, sample 3) leads to an increase in intermolecular interaction, which is manifested in the sharp increase in viscosity and anomaly of viscosity compared to the CTP and heat-treated CTP. The degree of viscosity anomaly of the modified pitch increases with a decrease of temperature from 155°C (Figure 5, sample 5) to 135°C (Figure 5, sample 3).

Due to the sharp increase in pitch viscosity when adding PVC (more than 3 wt.p.), the change in the rheological properties of the pitch was investigated by determining the melt flow rate (MFR). It is established that the strength of the structure of modified pitches, which is determined by the strength of intermolecular bonds, increases with the increase of the amount of PVC. This is confirmed by a decrease of MFR (Figure 6), that is, an increase of viscosity. At the intermolecular interaction of the pitch with PVC in the range of 10–20 wt.p., the formation of the most durable structures is observed, as evidenced by a sharp decrease in MFR from 23.8 to 1.1 g / 10 min.

Figure 7 shows the dependence of the MFR on the temperature in the range of 130–150°C, which is characteristic for the pitch modified by the PVC. As the temperature increases, the MFR increases, that is, the viscosity decreases.

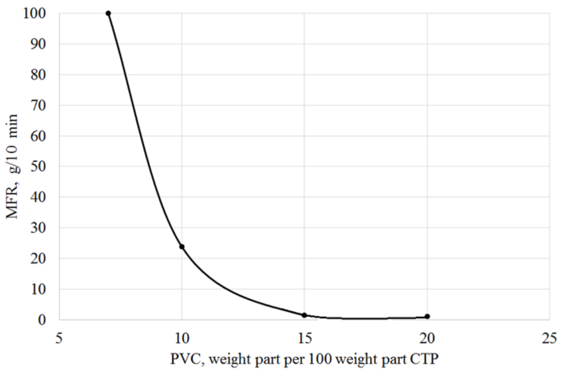

Figure 6**.** Dependence of the MFR of the modified pitch on the amount of PVC (load weight 10 kg at 150°C)

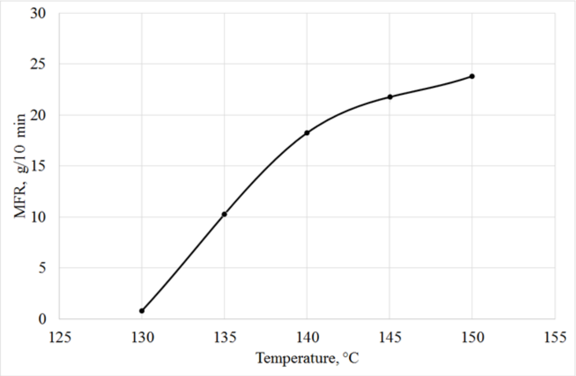

Figure 7. Dependence of the MFR of pitch modified with 10 wt.p. of PVC (load weight 10 kg) on the temperature

Rheological studies have shown that the addition of PVC in the heat treatment (170°C) of CTP contributed to thermochemical transformations, which significantly changed the structure of the modified pitch. Due to the processes of cross-linking and strengthening of intermolecular bonds, the viscosity of the resulting material was increased, the anomaly of viscosity appeared and the strength of the structure increased.

3.5. X-ray Diffraction

XRD analysis allowed to determine the structural parameters of pitch modified with PVC. XRD diffractograms of initial CTP and pitch modified with PVC at 170°C are represented in Figure 8–9.

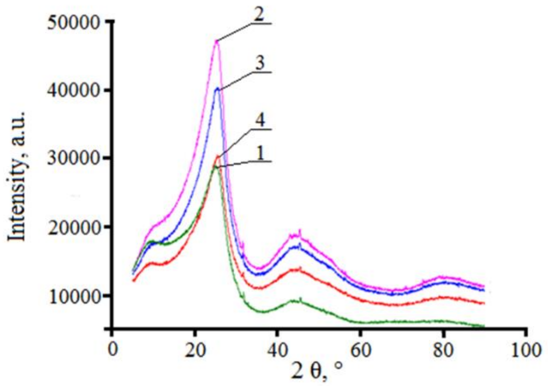

Figure 8. Initial XRD diffractogram of initial and modified pitches. Experimental profiles of diffraction peaks (002), (10) and γ-band of the initial pitch (1) and pitches modified with PVC: 2 – 5 wt.p.; 3 – 10 wt.p.; 4 – 20 wt.p.

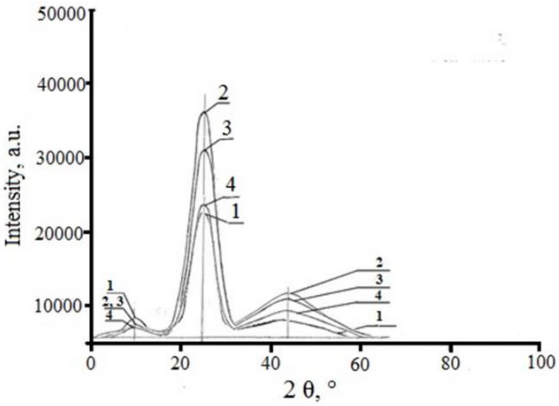

Figure 9. Corrected XRD diffractogram of initial and modified pitches. The corrected profiles of diffraction peaks (002), (10) and γ-band of the initial pitch (1) and pitches modified with PVC: 2 – 5 wt.p.; 3 – 10 wt.p.; 4 – 20 wt.p.

The Table 1 shows the structural parameters determined by diffraction profiles (002), (10) and the γ-band.

The crystallinity degree (n) (the number of carbon layers in the package) was determined by the formula:

$$n = L_c / d_{002} + 1 \quad (1)$$

where L_c is thickness of carbon packs of layers in [nm], d_{002} is the distance between adjacent monolayers in height in packs in [nm].

The aromaticity degree (m) (the number of six-membered cycles in the layer) was determined by the formula:

$$m = L_a / 0.28 \quad (2)$$

where L_a is grid size in a layer in [nm], 0.28 nm is an aromatic ring diameter.

Table 1. Structural parameters of the initial and modified pitches.

No. sample	Sample composition, wt.p. CTP	PVC	d002-spacing nm	Lc (nm)	La (nm)	K (γ)	n	m
1	100	0	0.355	2.71	3.53	0.08	8.6	12.6
2	100	5	0.363	2.73	3.35	0.04	8.5	12.0
3	100	10	0.353	3.26	5.00	0.05	10.2	14.2
4	100	20	0.358	2.97	3.46	0.04	9.3	12.4

Maximums (002) and (10) are responsible for the dimensions of the nuclear part of the pitch molecular structure: band (002) characterizes the degree of order of grid location in space, and band (10) indicates the degree of condensation of the nuclear part, that is, the size of the grids in the plan along the axis (L_a).

Band (002) showed that the average distance between adjacent monolayers (d_{002}) in height in blocks (packs) was 0.353–0.363 nm for pitches modified with 5–20 wt.p. of PVC (Table 1). Maximum (002) is asymmetric for the initial and modified pitches (Figure 8) due to γ-band arising as a result of ordering in the peripheral part of pitch substance structure, caused by the contacts of non-aromatic side hydrocarbon groups. The relative contribution of the γ-band, which characterizes the length and branching of the side chains, to the intensity of the total band is calculated by the formula:

$$K_\gamma = \frac{S_\gamma}{S_\gamma + S_{002}} \qquad (3)$$

where $S\gamma$ and S_{002} are integral band intensities.

This indicator allows comparing the concentration of ordered aliphatic groups in pitches modified with PVC.

Comparison of the γ-band of the initial CTP with the modified pitch (Figure 9 and Table 1) showed that when the pitch interacts with PVC, the proportion of the peripheral (side) irregular part in the elementary structural units of pitch macromolecules decreases by almost 2 times compared to the regular part.

The average size of carbon monolayers in the plane (L_a) of the nuclear part of the modified pitches changed under the action of PVC: for 10 wt.p. – increased to 5 nm, and for 5 and 20 wt.p. – decreased to 3.35–3.46 nm compared with the initial pitch.

The thickness of the carbon packs (blocks) of layers (L_c) of the modified pitches increased to 2.73–3.26 nm compared with the initial pitch. This indicates an increase in the degree of mutual orientation of the layers. Up to 10 wt.p. of PVC the orientation degree increases, and then decreases, remaining higher relative to the pitch without PVC.

Structures consisting of the nuclear part, including 8–10 monolayers of the condensed part (size 3.35–5.0 nm), with a distance of 0.353–0.363 nm between them were found in pitch.

When PVC is added, the modified pitch acquires a more ordered structure (L_c and n increase), K (γ) decreases. At a consumption of 10 wt.p. of PVC the aromaticity degree significantly increases.

Thus, XRD analysis showed that when pitch interacts with PVC, molecular-structural transformations occur in the pitch. This causes a change in the supramolecular structure of the pitch.

3.6. The morphology of the samples

The SEM studies of modified pitch samples made it possible to establish differences in their structure. Figure 10 shows the SEM-micrographs of the studied samples. As can be seen from Figure 10 surface relief of modified pitch particles depends on the amount of PVC.

In the sample of the initial CTP, when milling particles, a chaotic distribution of chips in all directions is observed. The surface of the particles has an uneven angular fracture with elements of stepped surface.

When adding 5 wt.p. of PVC, the layered structure of the particles of the sample powder begins to manifest, surface structure becomes wave-like.

The particles of pitch powder, modified by 10 wt.p. of PVC, have a more clearly defined lamellar surface. When destroyed, particles are formed as plates of various sizes. XRD data indicate that the structure of these samples is the most ordered (Table 1, sample 3).

Sample with 20 wt.p. of PVC has a layered wave-like structure in the form of flakes of various shapes, layered on each other.

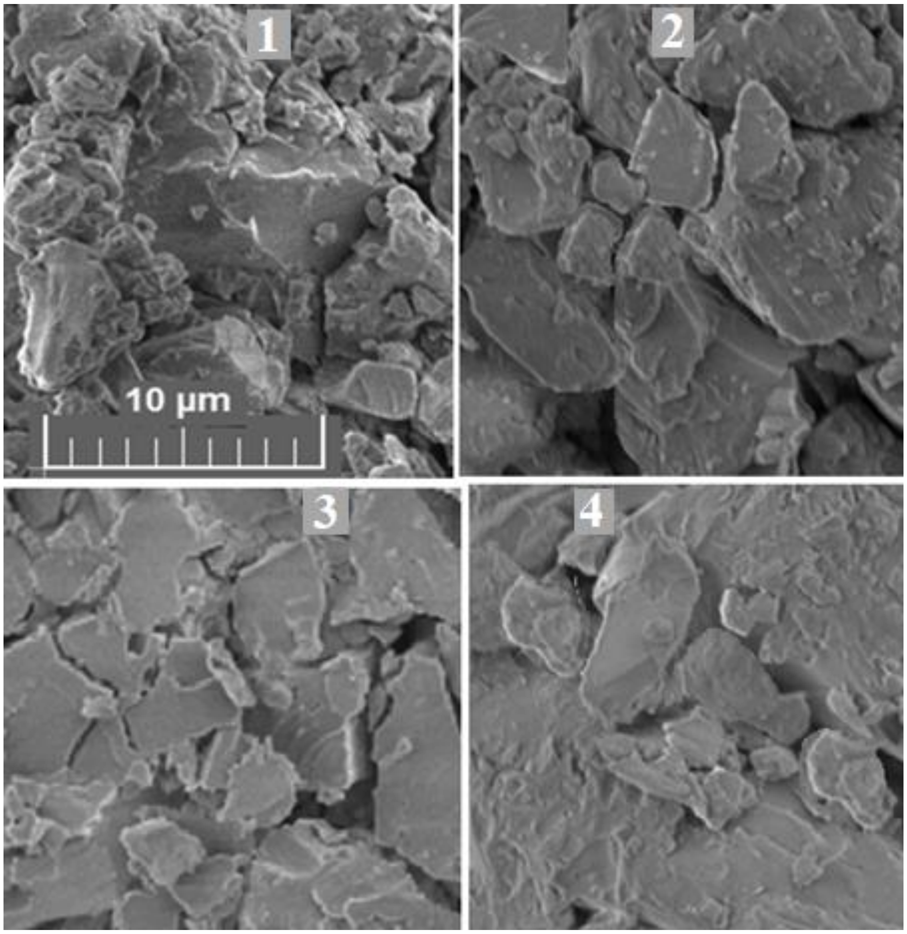

Figure 10. SEM micrographs of samples of the initial (1) and modified pitch. The amount of PVC: 2 – 5 wt.p.; 3 – 10 wt.p.; 4 – 20 wt.p.

4. Conclusions

Experimental studies have shown that PVC actively influences the properties of the modified CTP. The fractional composition changed with the interaction of the CTP with PVC; the number of higher molecular α_2- and β-fractions increased, and the amount of low molecular weight γ-fraction decreased.

The thermal analysis of pitch modified with PVC has shown that in the process of modification, new compounds are formed as a result of the connection of pitch molecules to the active polymeric radicals formed during the degradation of PVC. The more PVC was spent for pitch modification, the lower was the thermal stability of the newly formed compounds.

On the basis of the FTIR spectral analysis, it was found that the modification of CTP with PVC (5–20 wt.p.) increased its condensation degree and aromatic hydrogen content. Also, FTIR spectral analysis showed that oxygen-containing pitch groups are actively involved in the interaction of pitch with PVC. The detachment of methylene and methyl groups contributed to the formation of active radicals, after recombination of which new high molecular condensed aromatic compounds were formed.

As shown by rheological studies, the addition of PVC in CTP heat treatment (170°C) contributes to the thermochemical transformations, which significantly change the structure of the modified pitch. It was found that modified pitch viscosity increased with an increase in the amount of PVC. It indicates an increase in the strength of intermolecular bonds. The most durable structures were observed in the interaction of the pitch with PVC in the range of 10–20 wt.p., which was confirmed by a sharp decrease in MFR from 23.8 to 1.1 g/10 min.

XRD analysis allowed determining the structural parameters of pitch modified with PVC. Structures consisting of the nuclear part, including 8–10 monolayers of the condensed part (size 3.35–5.0 nm), with a distance of 0.353–0.363 nm between them were found in the pitch. When PVC is added, the structure of the modified pitch becomes more ordered. Thus, XRD analysis showed, and SEM photographs confirmed that the interaction between pitch and PVC is accompanied by molecular-structural transformations, as a result of which the structure of the modified pitch changes.

Thus, knowledge of the regularities of interaction processes between the pitch and PVC makes it possible to significantly change its properties. It may be useful for adjusting pitch to use it as a precursor for various carbon materials.

Abbreviations

CTP, coal tar pitch; DTA, thermal analysis; DTG, derivative thermogravimetry; d_{002}*, average distance between adjacent monolayers; FTIR, Fourier transform infrared; K (γ), the relative contribution of the γ-band;* L_a*, the average size of carbon monolayers in the plane of the nuclear part of the modified pitches;* L_c*, the thickness of the carbon packs (blocks) of layers; m, the aromaticity degree (the number of six-membered cycles in the layer); MCTP, modified coal tar pitch; MFR, melt flow rate; n, the crystallinity degree (the number of carbon layers in the package); PE, petroleum ether; PVC, polyvinyl chloride; Q, quinolone; Qis, quinoline insoluble; SEM, scanning electron microscopy; T, toluene; TGA, thermogravimetric; Tis, toluene insolubles; wt.p., weight part; XRD, X-ray diffraction.*

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