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Structure of Coal Tar Pitch Asphaltenes

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Abstract

Lately, side products of oil processing and coal liquefaction, *i.e.*, asphaltenes, have been extensively investigated. The data regarding the macromolecular structure and morphological characteristics of asphaltene aggregates were mainly acquired in the area of petrochemical technologies. It is known that the concentration of asphaltenes in solution and the presence of additives of various chemical nature have an effect on the structure of asphaltene associates. The data about the formation of planar asphaltene associates and condensed graphite-like structures are of particular interest. In connection with the optimizing of conditions for anodic mass graphitization, coal tar pitch asphaltenes (β -fraction) were investigated. Coal tars with high contents of β -fraction proved themselves in the best way as efficient binders upon thermal treatment of the anodic mass. The present work investigated structural characteristics of macromolecules of medium-temperature coal tar pitch (CTP) using a set of physicochemical methods. The method of selectively soluble groups was used to isolate β -fraction asphaltenes; toluene and hexane were utilised as selective solvents. In order to form asphaltene films, a 0.01 % solution of asphaltenes in toluene was selected. It was demonstrated that structural fragments of CTP asphaltene molecules contained mainly condensed compounds with a number of rings of 3–7. These species contained C11 alkyl substituents and larger the content of which could not be practically determined. Therefore the structure of CTP asphaltene molecules could be described by the Speight model. The coke residue of CTP asphaltenes is characterised by the presence of crystallites from naphthenoaromatic layers. These structures are comprised of subunits of 7–8 layers, with a size of 20–25 Å, graphite-like; an interlayer distance of 3.42 Å.

Key words: coal tar pitch, asphaltenes, coke residue, structural fragments, films

INTRODUCTION

The synthesis of carbon materials and research on their properties are relevant objectives of modern material science. Particular academic research interest towards materials of this type is linked to a great number of varieties of allotropic modification of carbon, based on which materials with diverse and even unique physicochemical properties may be obtained.

Lately, there is an urgent problem of producing dimeric graphite nanolayers with a large area all the way to single-layered nanocrystalline graphene [1]. As a rule, the known methods for the preparation of graphene are based on the me-

chanical or chemical cleavage of natural gas or pyrolytic graphite [2–4], and also on the epitaxial growth of graphene films [5]. It was possible to achieve the most practical success when making graphene films with a large area by chemical methods for the deposition of graphene from the gas phase over silicon and nickel substrates. These films were demonstrated to be comprised of domains of mono- or bilayer graphene with lateral sizes of just 5 μm [6]. Recently, the authors of [7] have reported the synthesis of electrically conductive carbon nanolayers with an area between 13 nm and 41 nm using carbon precursors obtained by the self-assembly of asphaltene molecules. Hence, it may be suggested that the se-

lected research area is not only of scientific but also of practical interest.

Asphaltenes are high-molecular-mass compounds, components of oil and coal, prone to forming colloidal ordered structures [8, 9, 16] formed after macromolecular self-assembling and stacking. These compounds pass into a modification insoluble in traditional solvents under exposure to light, whereas the former are transformed into carbenes and carboids when exposed to concentrated sulphuric acid [9].

The structure of asphaltene molecules has been investigated already during a long time [10–15]. Asphaltenes may be isolated from both subsoil resources and their processing products, to which considerable differences in structure and chemical composition are linked to. Comparative research on asphaltenes isolated from coal and oil revealed differences in their structure [17, 18]. The average molecular mass of coal asphaltene molecules is by twice higher than that of oil asphaltenes as demonstrated. Coal asphaltene molecules have shorter alkyl chains than their analogues obtained using oil with the same molecular mass [19]. Nevertheless, typical oil and coal asphaltenes have on average the same number of aromatic rings in polycondensed nuclei of molecules (about 8 rings) and are different according to the length of alkyl side chains: it is five times greater in oil asphaltenes.

Asphaltenes isolated from secondary products of oil and coal processing, i.e. coal and oil tar pitches, are underexplored. Research on the structure of coal tar pitch asphaltenes (β -fraction) is almost not carried out, though their practical value has been widely described in the literature. Their role upon the preparation of carbon and graphite materials using coal tar pitch (CTP) as a binder is known [4, 19–22].

For the purposes of successful graphitization, coal tar with the optimum composition should be notable for a high fraction of β -fraction. Research works on exploring self-assembly trends of oil asphaltene molecules in solutions are of separate interest. As demonstrated by the investigation of aggregating processes, they may be controlled by inhibitors. Surfactants and organic solvents are usually used as the latter [8, 9]. For example, the behaviour of molecular associates of oil asphaltenes in toluene was investigated in [8, 23, 24]. It is worth noting that the nature and the regularities of the formation of oil asphaltene associates with different shapes have been extensively explored lately in theoretical works [25, 26].

This research work is devoted to the characterisation of the macromolecular structure of hexane-

insoluble CTP asphaltenes [27–29] relying on thermogravimetric analysis (TGA) data, and also research information on thermal destruction of asphaltenes by gas-liquid chromatography–mass spectrometry (GLC-MS), X-ray phase analysis (XPA), scanning (SEM) and transmission electron microscopy (TEM), infrared (IR) spectroscopy, and elemental analysis. The data acquired on the structure of structural groups of asphaltene macromolecules and the chemical composition of products of thermal destruction of asphaltenes would be used to comprehend self-assembly and stacking processes of asphaltene macromolecules and to generate new approaches for producing (2D) layers of graphite with a high area.

EXPERIMENTAL

Asphaltenes were isolated from granulated medium-temperature CTP (melting point 87 °C) manufactured by the JSC “Altai-Koks” according to the method of selectively soluble groups [28]. Toluene and hexane were used as selective solvents. In order to extract a fraction of asphaltenes most prone to the association reaction, treatment with solvents was carried out at room temperature. Hexane-insoluble asphaltenes from toluene extract were isolated by extract dilution with hexane.

After the dilution, the solution was aged for 24 h; the precipitate was filtered off, washed with hexane, and dried at 80 °C to remove C6 residues. The resulting samples were analysed by thermal analysis and IR spectroscopy (Fourier Transform Infrared spectrometer InfraLUM FT-81).

The films were obtained using a 0.01 % solution of hexane-insoluble asphaltenes in toluene by applying onto glass plates that were later exposed to thermal treatment in an EKPS-10B furnace. Selecting the solution concentration was made relying on the data of [10].

Research on the thermal decomposition process of the samples was carried out by TGA using a NETZSCH STA 409 PG/PG derivatograph under an inert atmosphere in a temperature range between 40 and 650 °C with a heating rate of 5 °C/min. Volatile products generated during asphaltene thermolysis were condensed in a trap at –10 °C, then extracted with hexane and analysed by GLC-MS using the Agilent 6890N GC with the Agilent 5973 detector. The coke residue after thermal destruction of asphaltenes was investigated by XPA (Bruker D8 X-ray powder diffractometer, SEM (JEOL, JCM-6390), TEM (JEOL, JEM 2100), and elemental analysis (ICP-OES iCAP 6000 Duo).

RESULTS AND DISCUSSION

Figure 1 presents TGA data. As demonstrated by changing the sample mass during temperature rise, CTP asphaltenes begin losing mass at a relatively low temperature; the first minimum is located at a temperature of around 100 °C. There is a more vigorous decomposition in the 200–500 °C temperature range. Upon completion of the process at a temperature of 650 °C, the residual mass of the sample is 44–75 %. Decomposition of CTP asphaltenes over a wide temperature range points out their non-homogeneous composition, whereas approximation of a broad peak indicates the presence of three extrema at temperatures of 322, 435, and 498 °C. The maximum rate of thermal destruction of asphaltenes is noted in the DTG curve at 321 °C. This decomposition process of CTP asphaltenes may be due to a wide distribution range along MM or to peculiarities of the structural arrangement of separate polyfunctional components of molecules with different thermal stability.

As demonstrated by analysis of chromatography and mass-spectroscopy data for asphaltene decomposition products, the latter contain condensed aromatic compounds, molecules of which are comprised only of an even number of carbon atoms between C14 and C24 (around 94 %), and also oxygen- and sulphur-containing heteroaromatic compounds (about 6 %). The number of aromatic nuclei in molecules varies between 3 and 7. The distribution of aromatic compounds

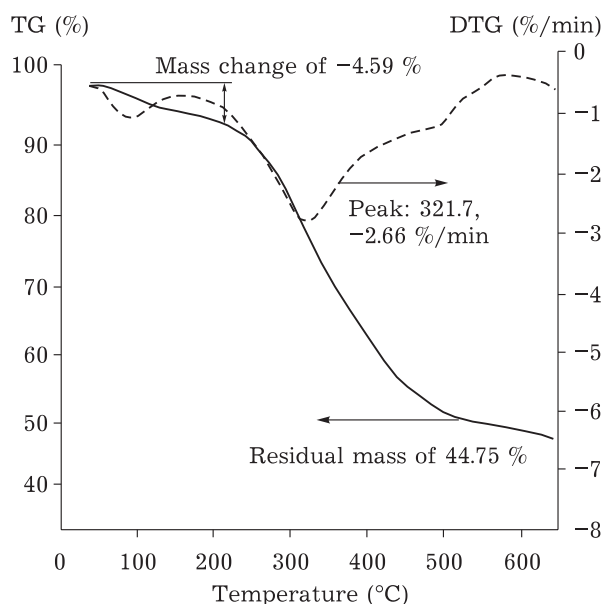


Fig. 1. TG-DTG curves of CTP asphaltenes.

according to the content of carbon atoms is characterised by a maximum at C20 (25.48 %), whereas 18.72 % for these species is identified as benz(a)pyrene and its isomers.

The solid residue of CTP asphaltenes is notable for typical shining. According to SEM data (Fig 2), coke residue particles have the form of twisted fibres.

The XPA investigation of coke residue particles has detected the presence of graphite-like structures therein. As ascertained, asphaltene molecules under scrutiny are comprised of 7–8 layers of naphthoaromatic hydrocarbons. The inter-layer distance is 3.42 Å, and the thickness of subunits formed by them is 20–25 Å.

Asphaltene molecules are likely to consist of aliphatic and heteroatom-bridged condensed aromatic rings.

According to IR spectroscopy data, asphaltene macromolecules have aromatic and aliphatic moieties in their structure (Fig. 3, a). The absorption bands (AB) at 3069, 1444, and 1601 cm^{-1} are related to stretching vibrations of the C–H bond and the aromatic ring, respectively; the intense band at 715 cm^{-1} points to the presence of $(\text{CH}_2)_n$ groups, and the AB at 2946 and 2875 cm^{-1} correspond to vibrations of CH_3 and CH_2 moieties in alkanes. Heating in the air atmosphere to 500 °C resulted in changing the structural-group composition of the compound: the absorption bands of aromatic ring vibrations vanished. At the same time, a new set of bands referred to vibrations of C=C and C=O double bonds appeared in the IR

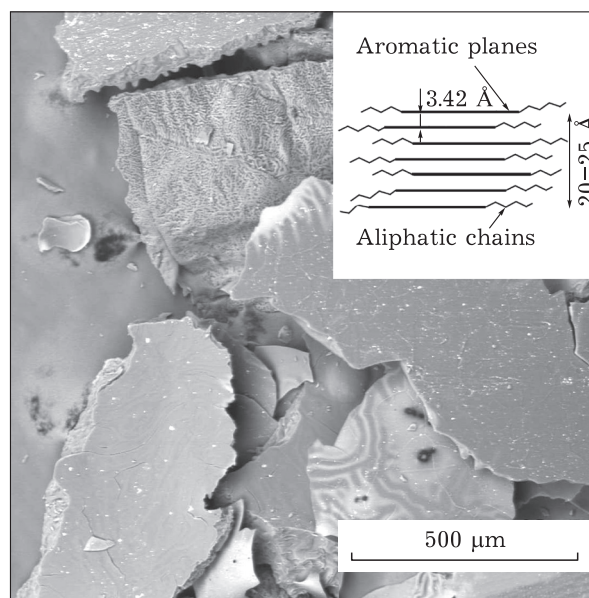


Fig. 2. Micrographs of coke residue particles of CTP asphaltenes. The sample was heated to 650 °C.

spectrum, which is typical for oxidized condensed aromatic structures (see Fig. 3, b). Heating in an inert medium to a temperature of 800 °C resulted in a reduction of the intensity of absorption bands of condensed structures, which indicates substance carbonization without oxidation.

According to the results of elemental analysis by ICP-OES, samples of residues of coke asphaltene produced upon heating in an inert medium to 800 °C contain sulphur (around 2 mass %), iron (0.006 mass %), and also silicon (traces).

The data about the formation of CTP asphaltene associates were acquired in the course of the research on the film morphology and structure. Figure 4, a represents fragments of asphaltene films acquired through SEM and TEM. According to TEM, asphaltene films contain inclusions with loose agglomerates with sizes about 1 nm, of spherical shape. The latter consist of 5 nm particles (see Fig. 4, b).

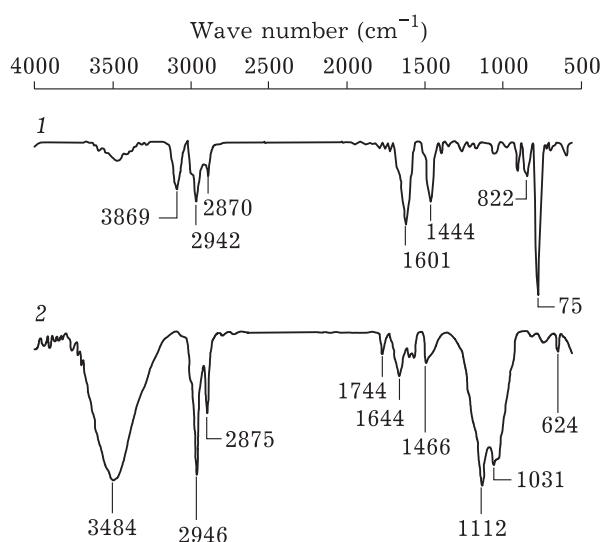


Fig. 3. IR spectra of CTP asphaltene film obtained using a 0.1 % toluene solution (1), the solid residue of the film after heating to 500 °C (2).

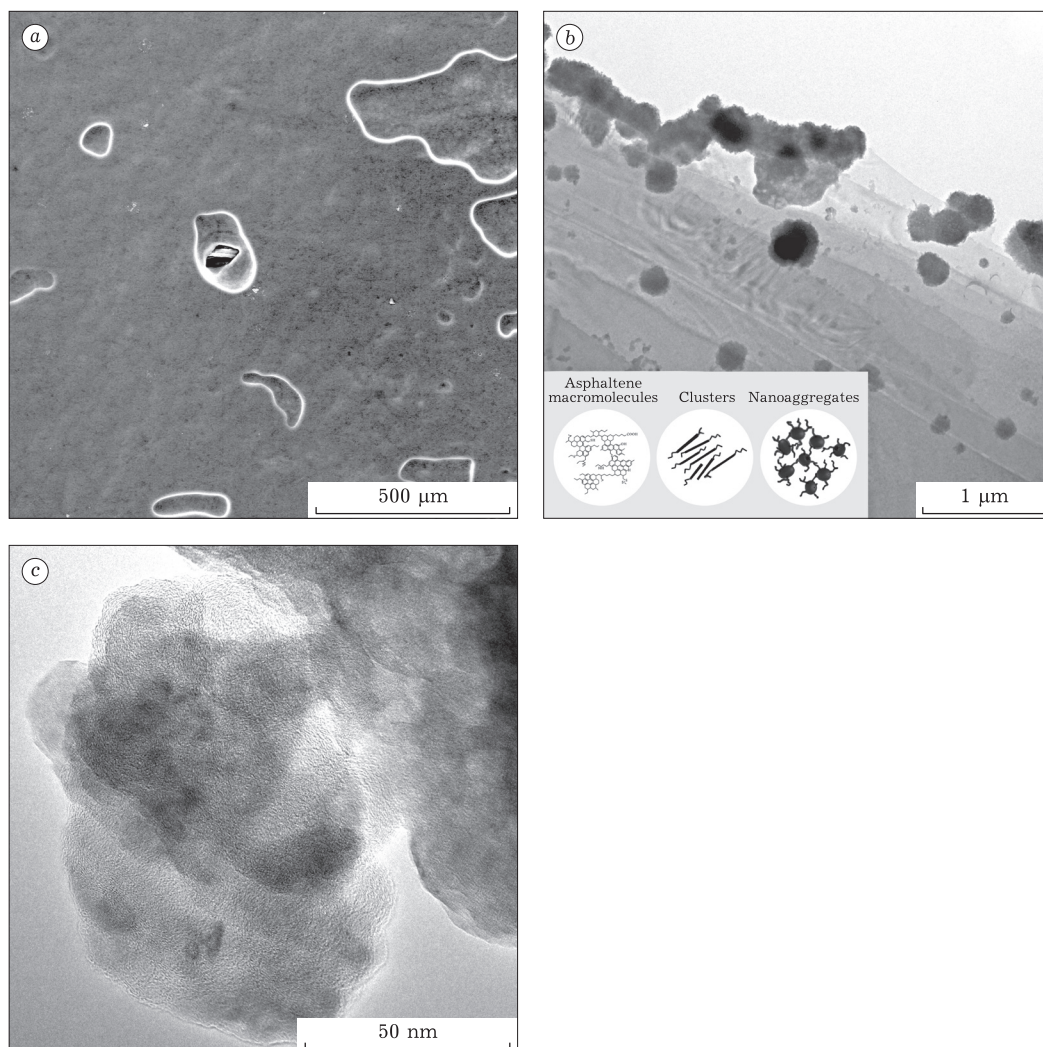


Fig. 4. SEM (a) and TEM (b, c) images of asphaltene film sections.

According to XPA data, asphaltene films are amorphous prior to thermal treatment. However, there are regions with ordered (oriented) layers in addition to typical separate layers (see Fig. 4, a). Nevertheless, in accordance with TEM data, there are regions with ordered (oriented) layers in addition to typical separate layers (see Fig. 4, c).

The presence of films made of graphite-like particles formed by condensed asphaltene structures (their existence is shown in [30, 31]) indicates that elongated (2D) layers with the graphite-like structure may be formed on the substrate surface during film pyrolysis after the ordering of such species. Thus, in order to obtain nanostructured layers, it is required to determine formation conditions for such planar CTP asphaltene associates in the solution and address the challenge of the topographic position of planar associates on the substrate surface.

CONCLUSION

As demonstrated by the acquired results, all structural fragments of CTP asphaltene molecules mainly contain condensed aromatic structures with a number of rings between 3 and 7 that contain aromatic substituents with C11 and larger the content of which could not be practically determined. Therefore the structure of CTP asphaltene molecules may be described by the Speight model [32]. According to XPA data, the coke residue of CTP asphaltenes is characterised by the presence of crystallites made of naphthoaromatic layers. These structures consist of subunits of 7–8 layers with a thickness of 20–25 Å and are graphite-like, with an interlayer distance of 3.42 Å.

The research on self-assembly and stacking trends of asphaltene macromolecules upon generating asphaltene structures on the substrate surface may open up a new prospect to address the challenge of obtaining (2D) layers of graphite with a large area.

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