LOW-TEMPERATURE THERMOCHEMICAL TRANSFORMATIONS OF THE COAL TAR PITCH BY THE CHEMICAL ADDITIVES

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Coal tar pitch is the main product of the processing of coal tar, which is formed during the production of coke from coal. Taking into account the fact that hundreds of millions tons of coal charge are processed in the world, the production of coal tar pitch is large-scale (1.5-2 % of coal charge) and its basic amount is used for the production of electrode products and pitch coke.

Due to the fact that pitch is a product of high-temperature pyrolysis of coal - a non-renewable natural resource, the search for new ways of rational use of the chemical potential of coal tar pitch is becoming relevant. The features of the structure and properties of the coal tar pitch indicate that on its basis can be created fundamentally new materials with the most diverse characteristics, which will significantly expand the field of its application.

Coal tar pitch is a complex heterogeneous system of highly condensed carbon and heterocyclic compounds and products of their compaction, differing in aromatics degree, composition, properties, molecular structure and ratio to solvents. Coal tar pitch, due to the features of its composition, is an extremely reactive material. The thermal action on the pitch promotes the thermochemical reactions, which lead to changes in the molecular mass and structure of the pitch.

Various chemical additives can be used to change the pitch properties. It will depend on the purpose and the field of application of the materials that will be obtained. The ability of the pitch to actively interact with various chemical additives allows to be carried out the process at relatively low temperatures - up to 200 ^{0}C.

In order to enhance the polymeric properties of the pitch the low temperature modification is used by polymeric additives, in particular polyvinyl chloride (PVC) and maleated ethylene vinyl acetate (MEVA). Modification of a coal tar pitch allows to change its polymeric properties in a given direction and use it as a polymer matrix for obtaining pitch-based composites. The advantages of the modification is that this process is carried out at relatively low temperatures (< 200 °C), that is, in conditions in which there is no the pitch significant carbonization.

The purpose of most domestic and foreign researchers in the field of thermochemical transformations of coal tar pitch is the determination of the effect of the pitch thermal oxidation on its ability to carbonization and graphitization. Therefore, the vast amount of works in this direction was carried out at temperatures of 250-340 °C and above. As a result, it was found that a transformation successive process of low molecular weight hydrocarbons into high molecular weight hydrocarbons occurs according to the scheme:

$$\gamma \rightarrow \beta \rightarrow \alpha_2 \rightarrow \alpha_1$$

The use of a coal pitch as a composite materials matrix requires low temperatures compared to the thermal and thermo-oxidative modification of the pitch. Thermochemical transformations of the pitch at low temperatures (less than 200 °C) are studied little.

Some authors point out that, at temperatures up to 200 °C, mainly distillation of volatile substances is observed, that is the main reason for changing the pitch rheological properties. However, the investigations carried out at low temperatures in the range of 150-170 °C allowed to change the slightly simplified view of the processes mechanism occurring under these conditions.

As shown in the research (Table 1), thermochemical transformations of the pitch at 150-170 ^{0}C lead to the formation of low molecular weight hydrocarbons due to the destruction of mainly condensed aromatic compounds of the β-fraction and, to a lesser extent, of high molecular weight oligomers of the α-fraction. Thus, at low temperatures 150-170 °C the topological scheme of chemical transformations of the pitch components changes:

$$\alpha \rightarrow \beta \rightarrow \gamma$$

At modification of coal tar pitch by polyvinylchloride, there is an intensive chemical interaction between components of a reaction mixture. The research results of the PVC influence on the thermochemical transformation of coal tar pitch at t = 170 °C and τ = 2 h are shown in Table 1. The change in the group composition compared with the calculated one by additivity law showed that the addition of PVC to the coal tar pitch initiates the β-fraction synthesis from the γ-fraction, which is accompanied by an increase of vicat softening point of the pitch. Also, an increasing the modifier amount intensifies these processes. Adding of 5% of PVC leads to a sharp increase in the α-fraction proportion.

Table 1

An influence of PVC on the change of group composition and the softening point of coal tar pitch

Modifier, % of pitch weight	Δα, %	Δβ, %	Δγ, %	t_v, °C
PVC, 0	-0,2	-1,2	1,4	60
PVC, 1	-0,4	1,0	-0,6	61
PVC, 3	0,7	4,5	-5,2	69
PVC, 5	3,2	6,4	-9,6	70

Thermogravimetric analysis was carried out on a combined thermal analyzer STA PT1600 (Linseis, Germany) with a dynamic heating mode up to 900 °C in argon medium, a temperature rise rate of 10 °C/min. Results of the thermogravimetric analysis of the system pitch : PVC (3% to pitch) before and after modification showed the presence of additional peaks on the DTG curve of the modified pitch (Fig. 1, curve 3) in comparison with the thermogram of the initial mixture (Fig. 1, curve 2), that indicates on the formation of new compounds during the modification. The bifurcation of the melting endothermic peak (75-175 °C) confirms the presence of new structural units, and exothermic peak (223 °C) indicates that the interaction between PVC and pitch continues.

Investigation of thermochemical transformations of coal tar pitch at modification with MEVA showed a chemical interaction of the components, which leads to the growth of the least condensed γ-fraction of the pitch (Table 2).

Table 2

An influence of MEVA on the change of group composition and the softening point of coal tar pitch

Modifier, % of pitch weight	Δα, %	Δβ, %	Δγ, %	t_v, °C
MEVA, 0	-0,2	-1,2	1,4	60
MEVA, 3	-0,9	-0,9	1,8	59
MEVA, 5	-0,8	-2,1	2,9	60

The obtained thermogram for the pitch, modified by the MEVA-PVC complex modifier (Fig. 2, curve 4), is very different from the pitch thermograms, modified individually by each modifier. On the DTG curve many peaks of different intensity are allocated. This means that they characterize the destruction of many new molecular entities that are the result of the complex interaction of pitch, PVC and MEVA. The DTA curve of the pitch, modified by PVC-MEVA

complex modifier (Fig. 2, curve 4'), also has a different shape from the corresponding curves of other experiments. Thus, the thermal analysis results show that the combination of modifiers of PVC and MEVA leads to additional chemical interaction in the system and the formation of new molecular entities.

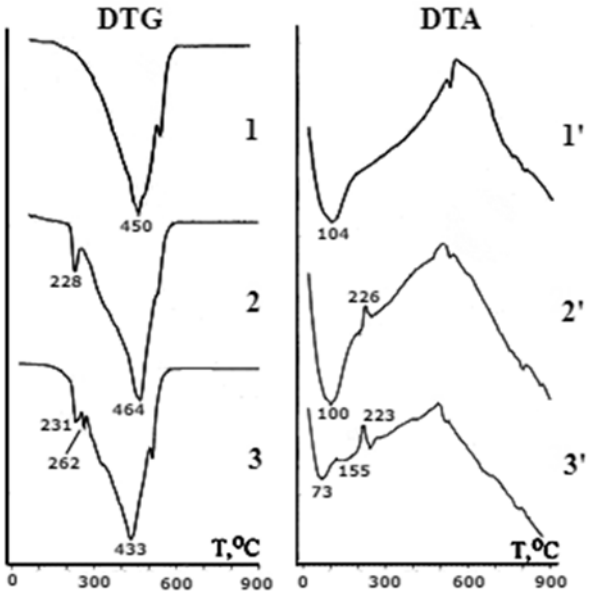

Fig. 1. Thermogravimetric curves of the base coal pitch (1, 1'); system pitch : PVC 3% before modification (2, 2'); system pitch : PVC 3% after modification (3, 3').

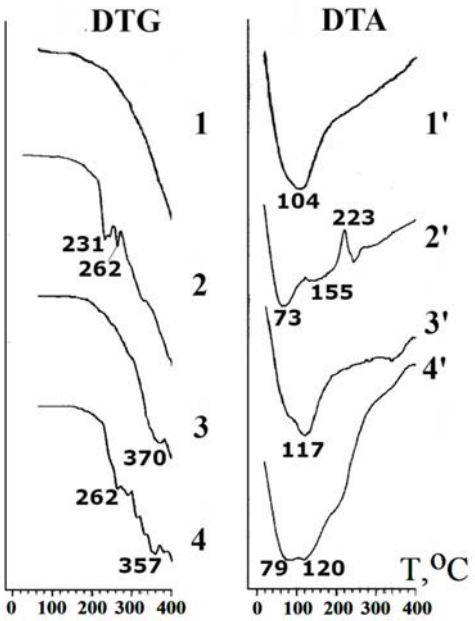

Fig. 2. Thermogravimetric curves of base pitch (1, 1') and pitch after modification: pitch : PVC 3% (2, 2'); pitch : MEVA 5% (3, 3'); pitch : PVC 3% : MEVA 5% (4, 4').

The changes that occurred at low temperature modification of the coal tar pitch under the active additives influence were studied using the method of IR spectroscopy (Nicolet iZ10 FTIR spectrometer). The research results by the method of IR spectroscopy showed (Fig. 3) that during the heat treatment of the coal tar pitch its condensation degree increases (increasing the intensity of the band 3040 cm^{-1}). IR spectra confirmed that PVC and MEVA interact with the pitch at T = 170 ^{0}C.

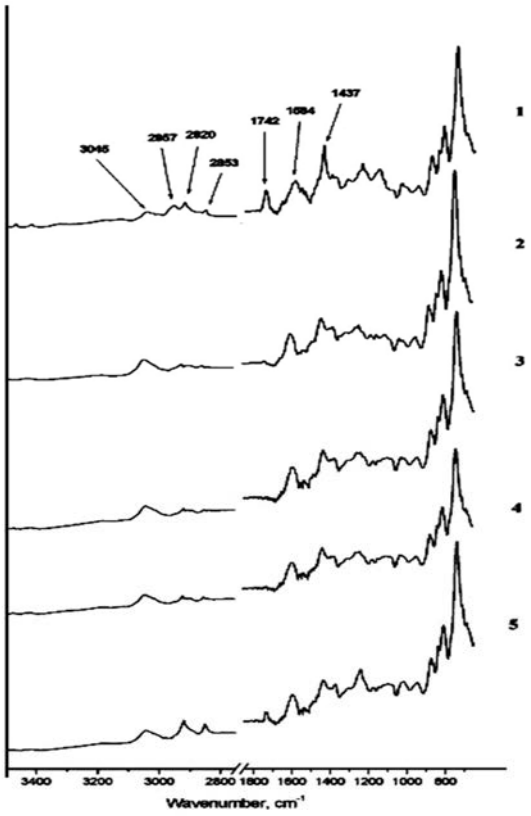

Fig. 3 IR spectra: 1 - base pitch; 2 - heat-treated pitch without additives; 3 - system pitch : PVC (3%) after modification; 4 - system pitch : MEVA (5%) after modification; 5 - system pitch : PVC (3%) : MEVA (5%) after modification.

One of the key steps in the low-temperature modification of the pitch to obtain the pitch-composite is its basic stabilization. Therefore, the study of the thermochemical processes of the pitch interaction with stabilizers is an important task. The analysis of obtained data showed that in all mixtures with the stabilizer, the pitch loses weight when heated in the presence of oxygen, that is, there are destructive processes with the formation of low molecular weight volatile compounds. Calculation according to the additivity law showed that stabilizing additives in the amount of 2% interact with the pitch, as indicated by the difference in actual weight loss from the calculated one. Melamine, calcium stearate and zinc stearate in the amount of 2% slow down the destructive processes in the pitch (in contrast to the irganox), that confirms the decrease in weight loss and the deviation from the additivity law.

Using the IR spectral analysis, it was established that at T = 150 °C an increase in the aromatic degree of the coal tar pitch (increase in the intensity of the band 3045 cm^{-1}) occurs, both in the presence of stabilizers and without them. Zinc stearate and calcium stearate, interacting with the components of the pitch, reduce the condensation of the system, forming methylene bridges between the aromatic rings (increasing the stretching vibrations of 2920 and 2850 cm^{-1} of the aliphatic group CH_2). Due to the reduction of the condensation of the pitch aromatic systems, the processes of different substitutes separation and the formation of low molecular weight volatile compounds are inhibited.

Thus, studies have shown that coal tar pitch undergoes thermochemical transformations at low temperatures of 150-170 °C, in the presence of various chemical additives and without them. This is developed in the change of the group and chemical composition, as well as the structure of the pitch. Adding various chemical additives to coal tar pitch can change its properties in a given direction, that in the future can significantly expand the field of its application.