EFFECT OF A THERMOMECHANICAL ACTION ON
MESOPHASE FORMATION IN AN ISOTROPIC
PITCH MELT

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Structure formation in an isotropic pitch melt affects the temperature and force field and the duration and conditions of pauses between testing cycles. Under the effect of shearing forces, formation of the mesophase in an isotropic pitch melt takes place at a lower temperature than in the absence of a force field.

Isotropic and liquid-crystalline pitches are a promising type of raw material for fabrication of carbon fibres. They make it possible to obtain higher values of the strength, modulus of elasticity, thermal and electrical conductivity, and other valuable properties of fibres. Mesophase pitches are usually obtained by heat treatment of isotropic pitches [1-3]. Dehydrogenation polycondensation takes place in these conditions, accompanied by an increase in the size of polycyclic aromatic mesogenic molecules capable of forming an independent phase — a liquid crystal. The characteristics of the mechanism of this process are examined in detail in [3]. At the same time, we know that liquid crystals can be formed in saturated or supersaturated isotropic solutions of polymers with stiff molecular chains. The mutual orientation of these molecules in flow with a certain velocity gradient initiates formation of a liquid-crystalline phase [4]. In this case, the isotropic solution is metastable, and a mechanical field causes its transition to a state with lower free energy.

From this point of view, it was expedient to investigate the degree of stability of the structure of a melt of petroleum isotropic fibre-forming pitches obtained by heat polycondensation of the heavy resin from pyrolysis of hydrocarbons with the technology developed at the Bashkir Scientific-Research Institute of Petroleum Processing [5, 6]. An isotropic, glassy structure is basically characteristic of such pitches, but formation of associates with a relatively ordered structure is also possible, confirmed by electron microscopic and rheological studies [7].

In particular, an anomalously sharp increase in the viscosity of the pitch melt, especially marked with an increase in the time the sample rests between testing cycles, was detected during rheological tests at temperatures much lower than the temperatures of obtaining the pitch (250 and 350°C, respectively). It was also found that the effectiveness of melt flow on its viscosity is a function of the composition of the pitch, primarily the concentration of the \( \alpha \) fraction in it, characterized by a molecular structure with the highest number of condensed aromatic rings. At the same time, the possible formation of an optically anisotropic phase was not investigated in these conditions [7], and the contribution of heat and mechanical (shear) effects on cross-linking in the melt was also not investigated separately. These questions are examined in the present article. The rheological studies were conducted on a PIRSP-03 rheogoniometer at 325°C in argon medium in the velocity gradient range of \( 10^{-1} \) to \( 10^{-3} \) sec\(^{-1} \); the shear stress \( \tau \) was varied in the range of \( 10^{3} \) to \( 10^{6} \) Pa. The formation of an optically anisotropic phase was evaluated with a MIN-8 polarization microscope.

To exclude the effect of the force field, the first series of experiments was conducted with the following method. Curve 1 in Fig. 1 was obtained by the standard method: thermostating of the sample in the working unit of the rheogoniometer for 30 min, determination of points for 30 min. Curve 2 was obtained for a fresh sample of pitch which was held in the working unit for 1.5 h until the rheological experiment began. Curve 3 was obtained after holding the melt in the working unit for 2.5 h, the instrument was switched off, and the flow curve was taken with the standard method after 24 h. Curve 4 was obtained for a sample successively tested in regimes 1, 2, and 3, i.e., exposed to shear three times with total thermostating for 90 min. A comparison of the data obtained with the results in [7] shows that not only the temperature and duration of heating, but also the force factor affect the structure of the pitch melt. This is especially graphically seen in comparing curves 3 and 4.
An increase in the initial viscosity with a temperature-time effect is another feature of the change in the rheological properties of pitch. This change could be due to formation of a mesophase in the pitch in which the concentration of the mesogenic component is higher than the critical value. Increasing the temperature to 325°C significantly decreases the viscosity of the system, which causes the beginning of a spinodal process of separation of the mesophase, increasing the overall viscosity of the melt. An additional shear effect accelerates the shift to phase equilibrium.