PROPERTIES AND USE OF CHEMICAL FIBRES

MECHANISMS OF TRANSFORMATION OF ACRYLIC FIBRES DURING THERMOOXIDATIVE STABILIZATION

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The shrinkage of polycrylonitrile fibres comprising 93% acrylonitrile, 5.7% methyl acrylate, and 1.3% itaconic acid was investigated by a thermomechanical method in heating them from room temperature to 300°C. It was shown that the irreversible shrinkage of the fibres during their first heating is due to a decrease in the stresses accumulated during spinning. The shrinkage observed in repeated heating of the fibres is caused by two processes: 1) by unfolding of segments of PAN macromolecules in the amorphous constituent of the structure of the polymer with an increase in the temperature (thermoelastic effect); this part of the shrinkage is reversible in heating-cooling cycles; 2) by cyclization of the polymer units due to polymerization of CN groups; this is the irreversible part of the shrinkage. In the 200-300°C temperature region, relaxation processes caused by irreversible unfolding of the macromolecules of the “melted” ordered structure of the fibre also contribute to the shrinkage. Mechanisms of the shrinkage processes in a wide range of temperatures are proposed. Shrinkage caused by physical processes of transformation of the structure of the fibre and chemical processes of formation of heterocycles is distinguished. It was shown that the kinetics of cyclization of PAN fibres can be investigated during their thermooxidative stabilization as one of the stages of fabrication of carbon fibres from PAN based on thermomechanical data.

Thermooxidative stabilization is an important stage in the conversion of polyacrylonitrile (PAN) fibres into carbon fibres. The essence of this stage is transforming the PAN fibres into nonmelting structures. It is primarily conducted in air medium, where oxygen acts as the agent that causes the conversion reactions. Various aspects of the mechanism of the reactions that take place in the stage of stabilization of PAN fibres have been widely studied by many investigators. Rings are formed according to the mechanism of polymerization of nitrile groups, and heterocycles undergo changes during heating in oxidizing medium, changing from conjugated structures at the beginning of the process to totally aromatic structures formed as a result of a ring dehydrogenation reaction [12]. It is assumed that intermolecular cross-linking reactions also take place together with the cyclization reactions [6].

During oxidative stabilization, the PAN fibre shrinks, which consists of two processes, as considered in [6, 13-17]: so-called physical, or primary, shrinkage and shrinkage that takes place after it, chemical or secondary, shrinkage. The shrinkage processes in the stage of oxidative stabilization of PAN have a large effect on the mechanical properties of the carbon fibre obtained in the next stage, since the orientation of the macromolecules of the polymer and some other properties of the fibres change during shrinkage [6, 15]. For this reason, elucidating the nature and mechanisms of the shrinkage processes in fabrication of carbon fibres from PAN is a very important problem. The magnitude of the shrinkage and rate of its evolution are a function of the structural state of the PAN fibres, degree of the stress level of the structure fixed in orientational drawing of the fibres, residual moisture and solvent content in the fibre, and other factors. In addition, cyclization of PAN can also affect shrinkage processes [16]. The results of studying shrinkage of PAN fibres during thermooxidative stabilization are discussed, the nature of the shrinkage and its dependence on the structural state of the polymer and other factors are elucidated in the present article.

Acrylic fibres comprised of 93% acrylonitrile, 5.7% methyl acrylate, and 1.3% itaconic acid with an elementary fibre linear density of 0.17 tex were used in the study. The experiments were conducted on a highly sensitive Ulvac Sinku Riko TM-
Fig. 1. PAN fibre shrinkage curve.

Fig. 2. Shrinkage curves for PAN fibres in successive heating of the sample: a) 1) first heating to 160°C; 2) second heating to 240°C; 1) 108°C; II 182°C; b) 1) first heating to 145°C; 2) second heating to 145°C; 3) third heating to 175°C; 4) fourth heating to 175°C; vertical mark on the curve: 102°C (beginning of shrinkage).

7000 thermomechanical instrument (Japan), which allows measuring the coefficients of thermal expansion of substances. All of the measurements were performed in air with a heating rate of 10°C/min and at a constant temperature with a 0.02 cN/tex load. The sample clamping length was 15 mm.

A typical thermomechanical curve is shown in Fig. 1. It consists of four characteristic zones. The first zone, up to the glass transition temperature (Tg), is characterized by the absence of deformation or slight shrinkage. Primary shrinkage takes place in the second zone, in the 100-170°C temperature region. The degree of the shrinkage is a function of the history of the sample and varies within the limits of 5 to 10%. In the third zone, the shrinkage slows, while the fourth zone, which is the region of secondary shrinkage, occurs at a temperature of 200 to 280°C and is due to chemical and physical processes of transformation of the structure of the fibre. The most intensive shrinkage, which usually comprises 50-80% of the total shrinkage, takes place in this zone.

The curve of the deformation behavior of PAN fibres changed if the sample was heated repeatedly. This can be seen in Fig. 2a, where the shrinkage curves were obtained as a result of a temperature effect on the sample in two successive heating cycles. Curve 1 corresponds to the first heating cycle, to 160°C, and curve 2 corresponds to the second cycle, where the sample was again heated to 240°C after cooling to room temperature. The character and causes of the change in the shrinkage curves are discussed below; we will now consider the shrinkage curves shown in Fig. 2b, which were obtained in heating—cooling cycles of the same fibre sample. Curve 1 describes the behavior of the sample in the first heating to 145°C at the rate of 10°C/min. The shrinkage attained 3.3%. When this temperature was reached, the furnace was removed and the sample was left to freely cool almost to room temperature. As Fig. 2 shows, the sample became longer. The elongation was 0.53%, or approximately one-sixth of the total shrinkage. When the sample was repeatedly heated, the character of the shrinkage processes changed (curves 2-4). The second heating, like the first, was to 145°C (curve 2). Slight elongation was observed on the initial segment of the curve. After reaching a temperature of ~102°C, it was replaced by much less intense shrinkage than on the first heating, 0.55%. In this case, the sample also lengthened in the cooling cycle, and the elongation was almost equal to the shrinkage, i.e., 357