TEMPERING OF ACRYLIC TWISTS IN OXIDATIVE THERMAL STABILIZATION

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Oxidative thermal stabilization of acrylic twists has a relatively high rate at a temperature close to the temperature of autocatalytic heating (250-260°C). To conduct the process at this temperature, it is necessary to temper the twists, not allowing the temperature in the core of the twist to increase by more than 5-6°C. In this case, conductive tempering is the most appropriate method. It was shown that in conductive tempering of acrylic tape 2 mm thick between two metal plates with the maximum possible exothermic effect of 60 cal/(g·sec), the change in the temperature in the core of the twist does not exceed 2°C, while in convective heat transfer, heating of the twist can attain 10°C for a tempering air flow rate of 5 m/sec. It was hypothesized that the more intensive heat transfer in conductive tempering in comparison to convective tempering is due to the high thermal conductivity of the contacting material and the absence of a boundary layer of air through which heat transfer takes place slowly with the convective method due to the low thermal conductivity of air. It was experimentally shown that in conductive tempering of twists, the duration of oxidative thermal stabilization can be reduced to 30 min.

Oxidative thermal stabilization is one of the most important process stages in production of high-strength carbon fibres. It is conducted with the twists under tension in air medium at a temperature of 180-300°C for 1-3 h. In comparison to carbonization, which lasts for 5-10 min, thermal stabilization is a slow stage which makes it difficult to group the oxidation and carbonization furnaces in one highly efficient production line. To increase the productivity of the equipment, the thermal stabilization process is conducted at the maximum possible temperature, where the slightest overheating will cause autocatalytic spontaneous combustion of the material. For this reason, correctly selecting the method of tempering acrylic twists during their heat treatment is very important.

In oxidative thermal stabilization of polyacrylonitrile or copolymers of acrylonitrile at the indicated temperatures, in addition to oxidative processes accompanied by addition of 8-12% oxygen, cross-linking of the macromolecules by formation of intermolecular cross links, partial pyrolysis of the polymer with liberation of acrylonitrile, ammonia, and hydrogen cyanide, and polymerization of nitrile groups with formation of cyclic ladder oligomers take place [1]. Some of these processes take place with release of a large amount of heat, characterized by steep elevation of the exothermic peak on the differential scanning calorimetry (DSC) curve. The beginning of the peak is observed at 180-210°C as a function of the composition of the copolymer, supermolecular structure of the fibre, and heating rate, and the peak maximum falls in the region of 260-290°C. The exothermic effect is 70-150 cal/g. At the high heating rate of 2-15°C/sec, the heat flux can attain 16-160 cal/(g·sec), which can result in autocatalytic overheating and destruction of the fibre with insufficient heat transfer.

The situation is complicated by the fact that to guarantee high efficiency of the equipment, the process must be conducted at the highest possible temperature (240-260°C), which is close to the maximum of the exothermic effect and makes the process difficult to control. The reaction of polymerization of CN groups probably makes the greatest contribution to the exothermic effect. The kinetics of this reaction is usually characterized by the decrease in the intensity of the 2240 cm⁻¹ absorption band corresponding to stretching vibrations of CN groups. The high activation energy of the polymerization reaction, 43 kcal/mole [2], indicates its important dependence on the temperature. The reaction rate constant increases sharply beginning at 220°C —

Fig. 1. Models of heat transfer: a) convective; b) mixed convective and conductive; c) conductive; $\delta$: thickness of an acrylic tape made of twists; $l$ and $h$: linear dimensions; $v_h$ and $v_i$: blowing rate; $R$: roller radius; $\delta_i$: roller thickness; $\delta_c$: plate thickness.

Fig. 2. Diagram for calculating temperatures in elementary volumes for convective and contact boundaries.

by approximately 2.8 times every 10°C. As a consequence, even slight heating of the twist can sharply accelerate the reaction due to the exothermic heat and when heat transfer is insufficient, control of the process can be lost.

There is also another important reason why more attention must be focused on maintaining the temperature during thermal stabilization. This concerns the necessity of respecting the defined temperature regime with narrow limits of deviation of the temperature from the assigned temperature in time. A process regime with gradual or step-wise temperature elevation is recommended [3]. This is probably related to the creation of the most favorable conditions for the occurrence of reactions leading to formation of a ladder polymer and suppression of cross-linking reactions and pyrolysis [4]. The accurate regulation of the temperature regime of processing acrylic twists with low thermal conductivity is only possible after a careful study of the conditions of heat transfer in the twist—heat carrier system. It was important to comparatively analyze the possibility of using convective and conductive (contact) heat transfer for tempering acrylic twists to search for ways to intensify thermal stabilization and control the chemical reactions that take place.