CHANGE IN PROPERTIES OF POLYCAPROAMIDE DURING A HEAT-TREATMENT PROCESS

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It is well known that the thermo-oxidative processes which accompany the preparation and processing of polyamides exert an unfavorable action on the technological process of preparing fibres from them and lead to a drop in their quality [1]. A large number of studies of the mechanism of this process and of methods for evaluating the extent of thermo-oxidation [2-6] have been devoted to this problem. However, up till now there have been no direct methods which are suitable practically for characterizing the change in polycaproamide (PCA) quality upon thermo-oxidative degradation.

In the present article, we give experimental data which make it possible to establish the connection between changes in some characteristics of PCA during the process of heat treatment.

The objects of study were PCA specimens in the form of flakes having a low-molecular compound content of 0.75% by wt. and a moisture content of 0.5%. The specimens were heated in still air at 160°C for periods of 5 to 100 min. Molecular characteristics such as relative viscosity, intrinsic viscosity, viscosity mean molecular weight, and content of N-groups were determined by well-known methods [7]. The degree of oxidation of the PCA during the heat-treatment process was determined from the content of carbonyl compounds [7], the Huggins constant [8], from the integral UV-absorption of a 3% solution of the PCA in sulfuric acid in the 240-260 nm region [6], and from the relative degree of chemical nonuniformity $d_c$ determined by the formula

$$d_c = \frac{K_H - 0.25}{MDP}$$

where $K_H$ is the Huggins constant; and $MDP$ is the mean degree of polymerization.

The collection of data on change in mean viscosity molecular weight, relative viscosity, and intrinsic viscosity indicates a rise in these figures with the course of heat treatment time (Fig. 1). However, the kinetics of change in these is not the same. The greatest rate of increase in the molecular characteristics of PCA is observed in the first 30 min of heat treatment, after which it decreases markedly. Such a course of the curves cannot be explained unequivocally by an increase in molecular weight of the polymer only. It is well known that the thermo-oxidative degradation of PCA which takes place by a radical-chain mechanism leads mainly to the formation of cross-links and branched structures as a result of recombination of radicals which have been formed. It was to be expected that this process would be intensified as the duration of heat treatment was increased. The sharp rise in relative and intrinsic viscosity of PCA in the first 30 min of an experiment can probably be explained by the fact that, along with a structure formation process, additional polycondensation is taking place as a result of displacement of the reversible polycondensation reaction in the direction of an increase in polymer molecular weight because of the small water content.

The decrease in slope of the viscosity and molecular weight curves on longer duration of the action of temperature and atmospheric oxygen indicates that, along with additional polycondensation and cross-linking, processes of degradation begin to play a significant role; these lead to a change in chemical structure as a result of deamination and decarboxylation, aminolysis, acidolysis, and depolymerization, and also homolytic breakdown of C—N and C—C bonds. In confirmation of this are the data on N-group content (Fig. 1, curves 4, 5), which show a continuous decrease in these, this being more significant in the initial stage of treatment. We note that the curve which depicts the change in carboxyl group content is more strongly curved than that for the change in amino group content. This is an indication that during the degradation process, reactions of decarboxylation or other chemical reactions involving carboxyl groups predominate. With the course of heat-treatment time, a change in color of the polymer was observed, which indicates the formation of colored degradation products as a result of reaction of amino groups with oxidation products of the PCA.
As is evident from the foregoing, molecular characteristics give definite information about changes in PCA as a result of heat treatment but it is not possible from these characteristics to obtain sufficiently clear ideas about the features of the processes which take place thereupon. In this connection, it was of interest, simultaneously with investigation of the molecular characteristics, to follow the change in such characteristics as the Huggins constant, the relative degree of chemical nonuniformity, the UV-absorption of the PCA solution, and the content of carboxyl groups, which make it possible to obtain more complete information about the products of thermo-oxidative degradation.

The results of our studies showed (Fig. 2) that the increase in Huggins constant and in relative degree of chemical nonuniformity takes place with almost a constant rate. Since these figures indicate the presence of branching and cross-links in the polymer, from the data of these studies it follows that the breakdown in linear form of the macromolecules takes place over the course of the entire thermo-oxidation process and is in a proportional dependence on the duration of heat treatment.

The change in integral UV-absorption of the PCA solution in the initial stage of the treatment is slight, but after a 20-min action of temperature and air, it takes place similarly to the change in Huggins constant (Fig. 2). As is known, UV-absorption has a more general character and cannot serve as a direct measure of chemical nonuniformity. However, in the present case, a good correlation between the results of studies of UV-absorption and the Huggins constant exists in polymer which has been heat-treated for a longer time, where the Huggins constant exceeds 0.28 and the relative degree of nonuniformity is greater than $2.2 \times 10^{-4}$.