

KINETIC ANALYSIS OF OXIDATIVE STABILIZATION PROCESSES IN PAN FIBERS

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Introduction

Carbon fibers are widely used for manufacturing of carbon fiber reinforced composites with improved mechanical properties [1]. The most common technological process to obtain high strength carbon fibers is the thermal treatment of polyacrylonitrile (PAN) fibers. The process consists of stretching and oxidative stabilization (OxS) of PAN fibers in air followed by carbonization of stabilized fibers in inert atmosphere at temperature more than 1000°C.

Parameters of thermo-oxidative stabilization step have strong influence on high strength and high modulus of final carbon fibers. At this step significant chemical and physical changes in carbon-chain polymers structure occur. The main chemical processes are oxidation of functional groups and chain fragments, nitrile fragments cyclization, condensation of carbonyl fragments, thermal destruction. The main physical processes are atmosphere air diffusion into the fibers, reaction products diffusion from fiber volume, fiber shrinkage and heat capacity change [2].

Thus oxidative stabilization process is quite complicated and strongly depended on composition and structure of initial copolymer. Nowadays this is the least understood step of carbon fiber. That's why new approaches and methods to solve this problem required.

Investigation of carbon-chain polymer conversion into cyclic structures at molecular level is practically impossible. Therefore phenomenological method based on formal kinetics study is used.

In majority of papers classical (isothermal) kinetics technique was used [3,4] that cannot exactly match real processes in PAN fiber. Therefore non-isothermal kinetics of oxidative stabilization of PAN fibers using differential scanning calorimetry (DSC) was used in present paper.

Experimental

A special commercial PAN fibers "Nitron" (SNV Ltd, Russian Federation) were used for investigation. The fibers were made of terpolymer (acrylonitrile, methylacrylate and itaconic acid). The main characteristics of the fiber were: 1K tow, linear mass density of 360 tex.

DSC measurements were carried out using DSC 204 Phoenix calorimeter (Netzsch Geratebau GmbH). Special sample holders in the form of a coil were used for DSC measurements of PAN fibers thermal stabilization. PAN fibers pieces with the mass of 4-6 mg were wound around the coil. The same empty coil was used as a reference.

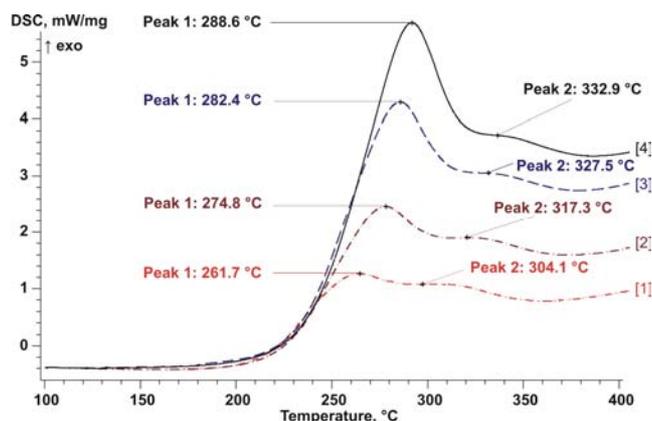


Fig. 1 DSC curves of PAN fiber oxidative stabilization with different heating rates: (1) – 10 K/min, (2) – 7.5 K/min, (3) – 5 K/min, (4) – 2.5 K/min.

The specimen was heated in the instrument with the heating rates of 2.5, 5, 7.5 and 10 K/min in the temperature range of 30–450 °C in dry air atmosphere with a constant flow of 50 ml/min (fig. 1).

Results and Discussion

The data presented at Fig. 1 clearly indicate that PAN OxS process has at least two steps. The lower temperature peak corresponds to cyclization process, the higher temperature peak corresponds to oxidative destruction [5].

DSC curves (Fig. 1) were used to calculate kinetic parameters of stabilization process in PAN fibers. Netzsch Thermokinetics 3 software was used for kinetic calculations. The software was described by Opfermann [6].

PAN OxS process is a multi-step one with individual steps at different temperature ranges (see Fig.1). In such cases possible errors in estimation of initial values of kinetic parameters are certainly large. The whole DSC curves were represented as superposition of single-stage processes. DSC curves for each stage were obtained by means of the peak deconvolution software (Netzsch Peak Separation). Model-free methods are used to calculate Arrhenius parameters of process such as apparent activation energy E_a/R and pre-exponential factor lgA (eq. 1). The parameters are estimated using Ozawa–Flynn–Wall [7] isoconversional method. The obtained values are used as initial values for non-regression procedure. Model-fitting operates through multivariate non-linear regression with Marquardt–Levenberg hybrid algorithm. If type of conversion function couldn't be determined *a priori* then non-linear regression procedure is used for each type of conversion function available in Thermokinetics software and statistical comparison of fit qualities is performed. Statistical analysis allows to choose $f(\alpha)$ function with minimal sum of least squares of deviations between calculated DSC curves and experimental ones.

$$\frac{d\alpha}{dt} = A \cdot e^{\left(\frac{-E_a}{RT}\right)} \cdot f(\alpha) \quad (1)$$

where $f(\alpha)$ – conversional function corresponding to process mechanism, α – degree of conversion.

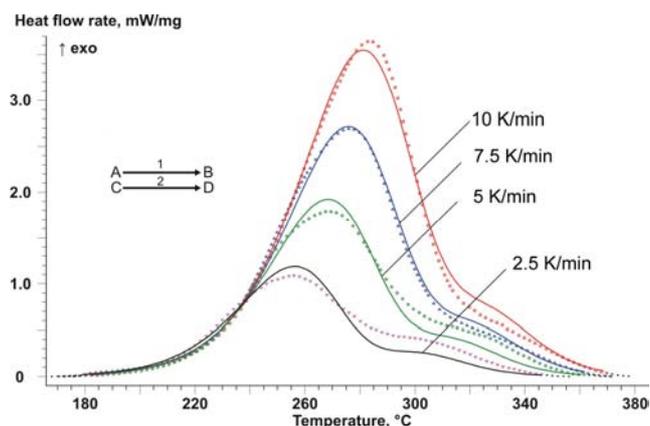


Fig. 2 Approximation of the DSC curve of the of PAN fiber oxidative stabilization with two parallel independent reactions model ($r = 0.95$).

The kinetic analysis demonstrated that PAN OxS can be described as two parallel independent reactions. Kinetic models of these two processes were obtained. The first process (nitrile cyclization) was fitted with Prout-Tompkins n -th order model (1,2), the second one (oxidative destruction of chain fragments and functional groups) was fitted with second order equation (1,3) (fig. 2). Kinetic parameters of PAN OxS are shown in table 1.

$$f(\alpha) = (1 - \alpha)^n \alpha^m \quad (2)$$

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

Table 1. Calculated kinetic parameters of PAN OxS processes.

Peaks	$E_a/R, 10^3 \cdot K$	$lg A$	n	m
Peak1	13.5 ± 0.5	8.5 ± 0.5	0.9	0.01
Peak2	18.3 ± 0.5	11.9 ± 0.5	2.0	—

Practical importance of the present work is that temperature program for PAN stabilization with constant heat flow rate can be calculated on the base of kinetic analysis (fig. 3). This allows minimizing defects in fibers caused by local overheating and low thermal conductivity of the material.

With the use of various temperatures, processes rates and other parameters a temperature program can be calculated appropriate for given instrument for PAN fiber stabilization.

To estimate the degree of conversion cyclization index (CD) was used (eq. 4) [3].

$$CD\% = \left(1 - \frac{\Delta H_{ox}}{\Delta H_o}\right) \cdot 100\% \quad (4)$$

where ΔH_{ox} is heat of the processes in oxidized sample (in inert atmosphere); ΔH_o is heat of the processes in initial PAN sample (in inert atmosphere).

The series of experiments demonstrated that simulated degree of conversion calculated with the use of "Thermokinetics" Software coincides within errors with cyclization index CD for stabilized fiber. For the given temperature program (fig. 3) CD was 62%.

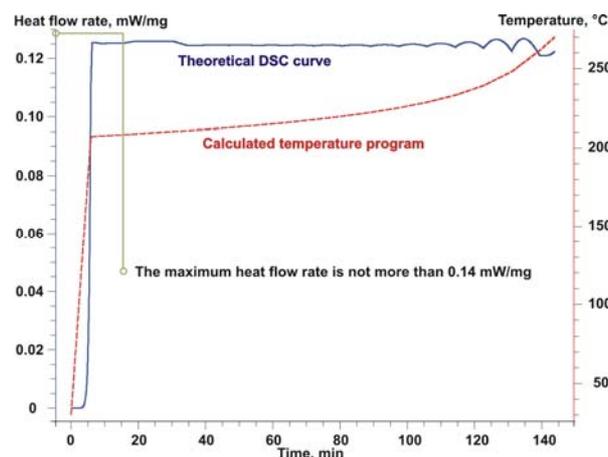


Fig. 3 Calculated temperature program and heat flow of PAN fiber OxS process.

Conclusions

The present paper demonstrated that non-isothermal kinetics can be effectively applied to describe complicated multi-step processes such as PAN OxS. With the use of DSC curves at different heating rates kinetic parameters of PAN OxS were obtained. Kinetic models were obtained for the first and second processes: nitrile cyclization was described with Prout-Tompkins equation, oxidative destruction of chain fragments and functional groups was described with second order equation. It was shown that cyclization and oxidative destruction can be described as parallel independent processes.

Temperature program for constant heat flow rate was calculated on the basis of obtained kinetic analysis results. It was shown that simulated degree of conversion coincides with cyclization index CD for stabilized fiber. The used technique of kinetic analysis allows planning of conditions for thermal stabilization for any required cyclization index and degree of conversion for the oxidative stabilization process in PAN fibers.

References

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