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Non-isothermal kinetic analysis of oxidative stabilization processes in PAN fibers

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ABSTRACT

Non-isothermal kinetic analysis of oxidative stabilization processes in polyacrylonitrile (PAN) fibers was studied with the use of the differential scanning calorimetry (DSC) data. PAN terpolymer fibers consisting of acrylonitrile, methyl acrylate and itaconic acid were studied. Kinetic parameters and kinetic models of nitrile cyclization and oxidative destruction of chain fragments and functional groups were obtained. On the basis of these kinetic models constant heat flow temperature programs with maximum heat flow of 0.11 mW/mg for PAN fiber and 0.09 mW/mg for pre-oxidized PAN fiber were calculated. It was shown that simulated degree of conversion coincides within errors with cyclization index (CD) for stabilized fiber. CD can be used as an estimation of degree of conversion in research and practical applications. Technique of kinetic analysis, that was used, allows optimization of conditions for thermal stabilization for any required cyclization index and degree of conversion for the oxidative stabilization process in PAN fibers.

1. 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 of PAN fibers in air followed by carbonization of stabilized fibers in inert atmosphere at 1000–1800 °C [2].

Parameters of thermo-oxidative stabilization step have a 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 include formation of cyclic structures by initiation of primary cycles formation in the presence of carboxyl structure fragments (initiating step), followed by nitrile groups polymerization reaction [3–5]. Secondary chemical processes include oxidation of the functional groups and polymer chain links (CH_3–, –CH_2–, HO–, etc.), thermal destruction and related removal of low-molecular (H_2O, CO, CO_2, HCN, etc.) and high-molecular (polyenes, alkyl nitriles, differential polymer chain fragments with nitrile groups) products. Main physicochemical processes are the following: atmosphere air diffusion into the fibers, reaction products diffusion from fiber volume, fiber shrinkage and heat capacity change. The scheme of oxidative stabilization was described in details in papers [3,6].

Thus oxidative stabilization process is quite complicated and strongly depend on composition and structure of initial copolymer. Nowadays this is the least understood step of carbon fiber production though this process is studied almost for 50 years. That is why new approaches and methods to solve this problem are required.

Recently the research focus has shifted towards kinetic analysis as an alternative research technique for stabilization investigation. Kinetic analysis of the processes allows to describe the whole process and also to simulate the processes according to various temperature programs without time-consuming experiments. In numerous papers [3,7–9] kinetics of oxidative stabilization of PAN was investigated by isothermal methods. However, these methods are unable to accurately describe the processes taking place in PAN by the following reasons:

- with fiber heating the significant part of the process occurs before reaching the fixed temperature and as a result we observe only the final part of the process;
- as PAN stabilization is a strongly exothermic process the released reaction heat leads to self-heating of the specimen. Therefore the specimen at DSC instrument never reaches fixed temperature according to the temperature program.

The approach of non-isothermal kinetics which is discussed in the present paper is close to real process of carbon fiber production.

The optimization of PAN thermal treatment conditions is an important factor in technology of high strength carbon fibers. That

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is why one of the main purposes of our kinetic analysis is optimization of oxidative stabilization conditions. DSC measurements were used as the input data as it is the most accurate and informative physicochemical method of analysis.

2. Experimental

2.1. Fibers

A special PAN fiber made by SNV Ltd. (Saratov, Russian Federation) was used in experiments. Commercial acrylic fiber "Nitron" was made of terpolymer (acrylonitrile, methyl acrylate and itaconic acid). The main characteristics of the fiber were: 1K tow, linear mass density 360 tex. More details can be found in technical documents.

2.2. DSC measurement

DSC measurements were carried out using DSC 204 Phoenix calorimeter (Netzsch Geratebau GmbH).

The special sample holders in the form of a coil were used for DSC measurements of PAN fibers thermal stabilization. PAN fiber pieces with the mass of 4–6 mg were wound around the coil. For this purpose the bundle of fibers with liner mass density of about 30 tex was taken from the original tow. The same empty coil was used as a reference.The coils were made of an aluminum-base alloy DT-16. The coils were 5 mm in height, 6 mm in diameter, 0.5 mm in crimps height for upper base, 1 mm in crimps height for lower base. 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.

2.3. Specimen preparation

Thermal oxidative stabilization of PAN fibers is a quite complicated process that includes chemical processes, heat and mass transfer phenomena (physical processes). In order to perform kinetic analysis of chemical processes it is necessary to adjust measuring conditions so that reaction rate is limited by chemical processes.

In the literature kinetics of stabilization process is studied by thermal analysis, most commonly by DSC. Standard technique of thermal analysis includes the use of aluminum pans with pierced lid as sample holder. Although in majority of papers samples were made of homopolymer (PAN), its copolymers, films made from polymer solution in a solvent or chopped fibers [3,8,10].

Standard technique cannot be used in the present paper. When standard pans are used gaseous reaction products stay in the pans and oxygen concentration decreases. As a result oxidative stabilization occurs under non-standard changing conditions. Besides, oxidative stabilization is limited by diffusion because of the lack of oxygen and the results obtained are distorted. PAN cyclization is a highly exothermal reaction so with the use of standard pans the fiber overheats during thermal stabilization that also distort the experimental results. Intensive shrinkage of chopped PAN fibers during oxidative stabilization leads to pseudo-thermal effects caused by the change of fiber geometry. Therefore standard sample preparation can distort the observed phenomena.

For these reasons we suggested to use special aluminum coils as PAN fiber holders. This specimen preparation allows to avoid limitations described above. When PAN fiber is wound around the coil in a single-layer mode free access of oxidizer to fiber surface and removal of the reaction products is provided. As no mechanical treatment is applied to the fiber it keeps fiber structure features and normalizes fiber shrinkage because fiber ends are fixed at coil.

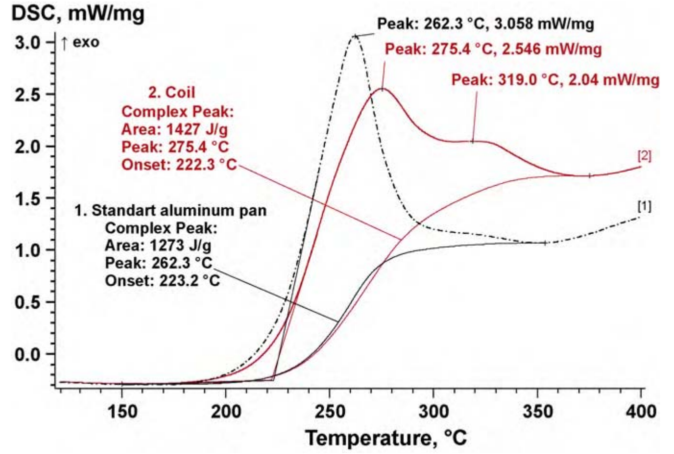

Fig. 1. DSC curves of PAN fiber stabilization in aluminum pan (curve 1) and at coil (curve 2). Heating rate was 5 K/min, atmosphere air, gas flow was 50 ml/min.

It should also be mentioned that large coil mass compared to specimen mass allows to realize quasi-stationary thermal file that is necessary for reproducible and reliable results.

Fig. 1 shows DSC curves of PAN thermal stabilization process. Curve 1 corresponds to stabilization of chopped fiber in standard aluminum pan with pierced lid, curve 2 presents the process for the fiber wounded around the coil. Experimental conditions such as heating rate, atmosphere and its dynamics were identical. Fig. 1 demonstrates the difference between stabilization processes in these two cases. DSC curve of the sample at the coil (curve 2) has two maxima while curve 1 demonstrates one clear peak. The heats of the processes are quite different. Oxidation process in pan has lower heat because of the lack of oxygen. Curves shapes and temperatures of characteristic points are also different. Therefore kinetics of the processes corresponds to different mechanisms. Based on the above said all DSC measurements were made with the use of coils as sample holders.

3. Results and discussion

3.1. DSC analysis

DSC curves for PAN fiber stabilization with different heating rates of 2.5, 5, 7.5 and 10 K/min are shown in Fig. 2. Table 1 presents parameters of the curves.

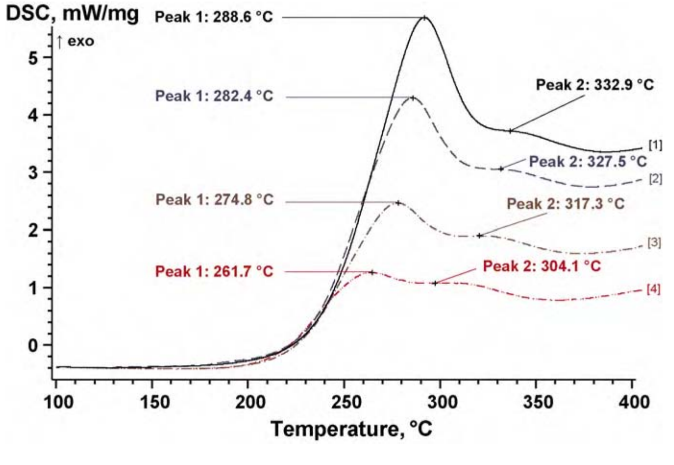

Fig. 2. DSC curves of PAN fiber stabilization with different heating rates: (1) 10 K/min, (2) 7.5 K/min, (3) 5 K/min and (4) 2.5 K/min.

Table 1
Parameters of DSC curves for different heating rates.

Heating rate, K/min	Temperature of maximum P1, °C	Temperature of maximum P2, °C	Max heat flow P1, mW/mg	Max heat flow P2, mW/mg	Process enthalpy ΔH, J/g
2.5	262	304	1.48	1.30	1776
5	275	317	2.60	2.06	1319
7.5	282	328	3.94	2.75	1304
10	289	333	5.47	3.58	1271

The data presented in Fig. 2 indicate that DSC curve of PAN oxidative stabilization process has two maxima named P1 ($T_{P1} \sim 260–290\,^\circ C$) and P2 ($T_{P2} \sim 300–335\,^\circ C$). The lower temperature peak is usually referred to cyclization process, the higher temperature peak is usually referred to oxidative destruction [11]. Temperatures of maxima of both peaks shift to higher temperatures with increase of heating rate. This effect corresponds to changes of heat-exchange conditions and can be used for activation energy calculations [12].

3.2. Kinetic analysis of oxidative stabilization process

Kinetic analysis of any process allows to determine the direction of the process, its rate, temperature and concentration dependence of the process rate. However kinetic description is suitable only for single-step reactions. If these models are used for complicated multi-step processes such as oxidative stabilization the obtained results have some limitations. Reaction order values corresponding to molar concentrations of reactants at mass action law are treated as apparent ones. Activation energy of the process at Arrhenius equation is considered as a temperature coefficient of the reaction rate only.

DSC curves (Fig. 2) 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 [13] and was successfully used by our group earlier [14]. Model-free methods and model-fitting methods are implemented in the software. Model-free methods are used to calculate Arrhenius parameters of process such as apparent activation energy E_a/R and pre-exponential factor A (Eq. (1)). Arrhenius parameters are estimated using Ozawa–Flynn–Wall [15] isoconversional method. The obtained values are used as initial values for non-linear regression procedure.

$$\frac{d\alpha}{dT} = Ae^{(-E_a/RT)}f(\alpha) \tag{1}$$

where A is pre-exponential factor, E_a/R is temperature coefficient of the reaction rate, $f(\alpha)$: conversional function corresponding to process mechanism, α: degree of conversion.

Model-fitting operates through multivariate non-linear regression with Marqardt–Levenberg hybrid algorithm. If type of conversion function could not be determined *a priory* 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.

Oxidative stabilization of PAN fibers is a multi-step process with consecutive and parallel stages in different temperature ranges. 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) (Fig. 3).

Such deconvolution procedure was made for all DSC curves with different heating rates. Correlation coefficient was $r = 0.995$ in all cases.

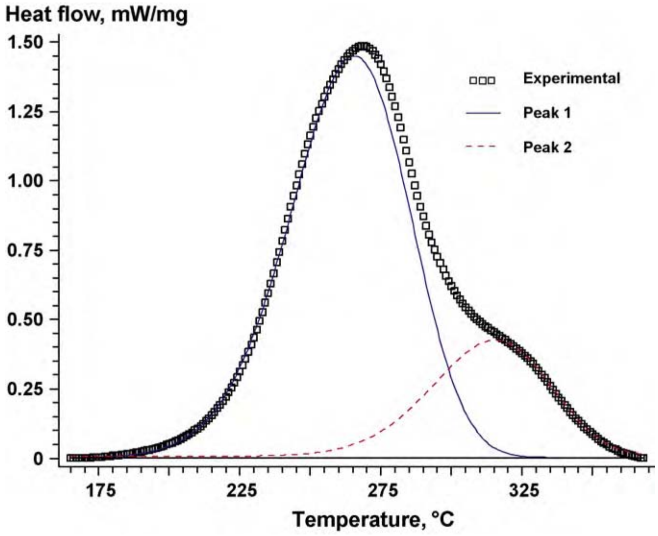

Fig. 3. DSC peaks deconvolution. Heating rate was 5 K/min.

Kinetic parameters were calculated for each stage with non-linear regression (see Figs. 4 and 5).

According to the literature [11] the first DSC peak corresponds to the cyclization process of carbon-chain polymer. The mechanism of the process is responsible for structure and rate of production of polyconjugated system.

Kinetic models were obtained for the first and the second peaks. The best curve fit for the first stage was obtained using Prout–Tompkins n-th order (Eq. (2); Fig. 4), the best curve fit for the second stage was obtained using n-th order reaction equation

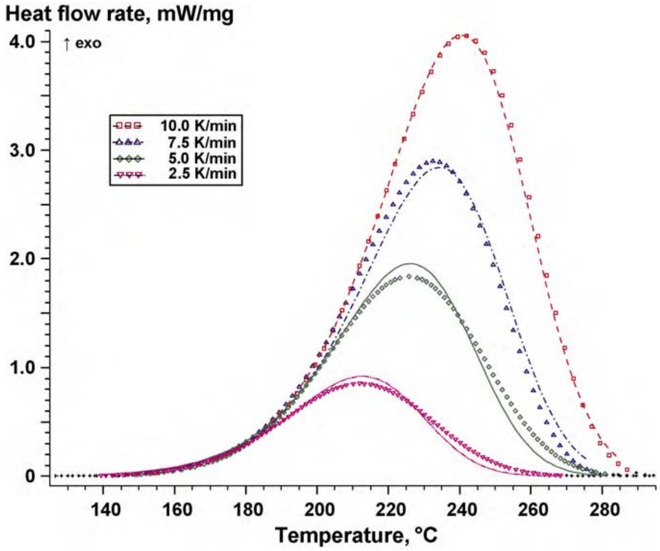

Fig. 4. Prout–Tompkins approximation of the first peak (P1) of DSC curve of PAN fiber stabilization ($r = 0.99$).

Table 2
Kinetic analysis results of oxidative stabilization process of PAN fiber. Kinetic parameters for first and second processes obtained for deconvolved peaks (P1 and P2), kinetic parameters for first and second processes obtained for the whole DSC curve (P1 total and P2 total).

Peaks PAN	E_a/R, 10^3 K	lgA	n	m	Model type
P1	11.5 ± 0.5	7.7 ± 0.5	1.1	0.14	Prout–Tompkins *n*-th order
P2	19.9 ± 0.5	12.3 ± 0.5	1.3	–	*n*-th order
P1 (total)	13.5 ± 0.5	8.5 ± 0.5	0.9	0.01	Prout–Tompkins *n*-th order
P2 (total)	18.3 ± 0.5	11.9 ± 0.5	2.0	–	*n*-th order

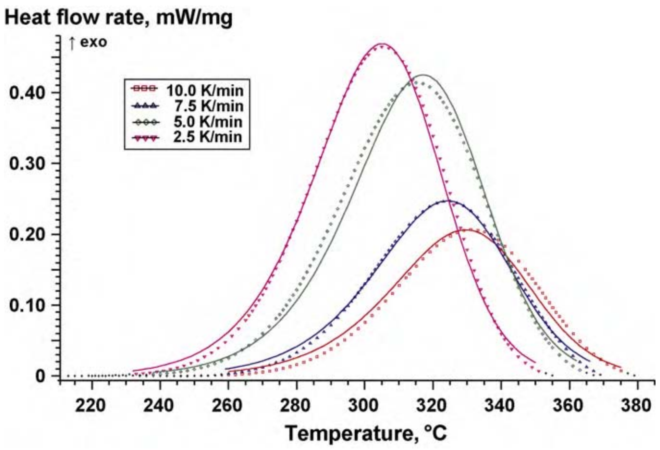

Fig. 5. *n*-th order reaction equation approximation of the second peak (P2) of DSC curve of PAN fiber stabilization ($r = 0.99$).

(Eq. (3); Fig. 5).

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

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

Kinetic parameters calculated for each stage were used as initial parameters for non-linear regression optimization of the whole DSC curve (Fig. 6; Table 2).

Statistical analysis showed that the best fit for cyclization process was Prout–Tompkins equation. So cyclization process can be described as nucleation of cyclic fragments on the fiber surface.

Nucleation is a random process at surface defects. So the mechanism of the process is strongly dependent on sample history and structure. In order to avoid this limitative stage an additional step was used. The concentration of nucleation centers is increased to several percent at the same conditions for each sample. Thermal treatment is carried out after this procedure. This process is often used in technical process of PAN fiber stabilization and is called pre-oxidation.

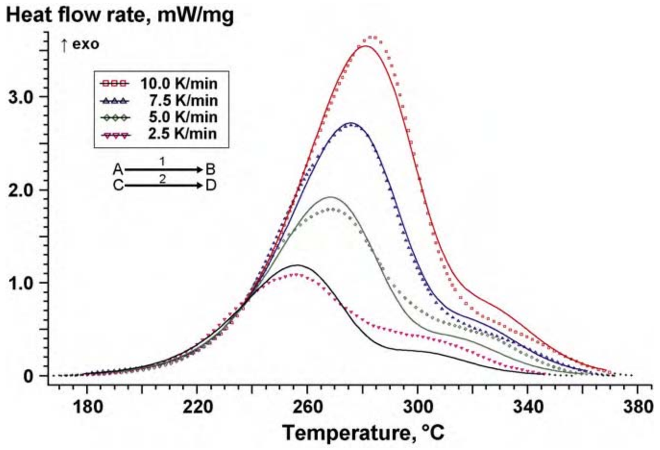

Fig. 6. Approximation of the DSC curve of the oxidation process of PAN fiber with two parallel independent reactions model ($r = 0.95$).

In present work pre-oxidation was carried out by PAN fiber heating at $T = 160\,^{\circ}\mathrm{C}$ during 1 min under constant stretching at draw ratio of 5%. PAN fiber color changes from white to golden yellow. In order to confirm that nucleation process takes place we carried out a series of DSC measurements in inert atmosphere and calculated cyclization index CD [16] (Eq. (4)). Cyclization index was of ~5%.

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

where ΔH_{ox} is heat of the processes in oxidized or partially oxidized sample (in inert atmosphere), ΔH_{o} is heat of the processes in initial PAN sample (in inert atmosphere).

Although DSC curves (Fig. 2) do not demonstrate any process at temperature range of pre-oxidation process, it is known [17] that molecular and supramolecular structure of polymers changes at the pre-oxidation step.

Thus pre-oxidation can be considered as natural nucleation process under standard conditions and affects kinetics of oxidation process. Kinetic analysis was made for oxidative stabilization of pre-oxidized fiber. The calculation procedure was described before. The first process (cyclization) was described with first order reaction equation (Fig. 7).

$$f(\alpha) = 1 - \alpha \quad (5)$$

The second process (oxidation) was fitted with *n*-th order as well as for initial PAN fiber. Kinetic analysis results are shown in Table 3.

The obtained results demonstrate that cyclization process is a heterogenetic topochemical process with nucleation stage. Reaction interface forms and radially propagates into the fiber.

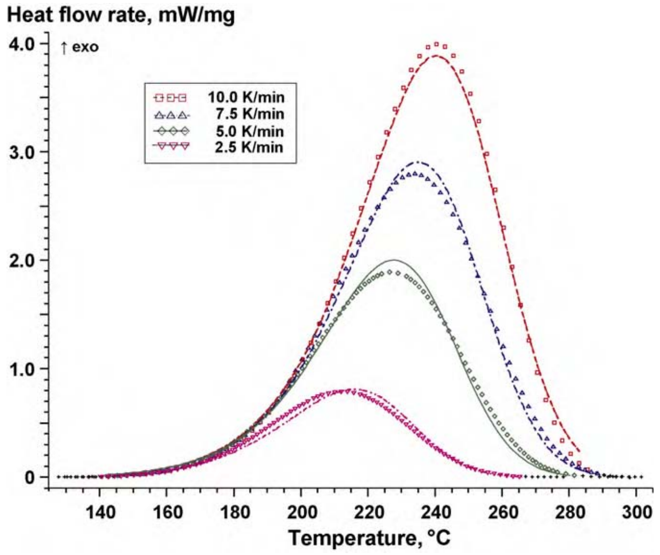

Fig. 7. First order reaction equation approximation of the first peak (P1a) of DSC curve of pre-oxidized PAN fiber oxidation ($r = 0.99$).

Table 3
Kinetic analysis results of oxidative stabilization process of pre-oxidized PAN fiber. Kinetic parameters for first and second processes obtained for deconvolved peaks (P1a and P2a), kinetic parameters for first and second processes obtained for the whole DSC curve (P1a total and P2a total).

Peaks activated PAN	E_a/R, 10^3 K	lgA	n	Model type
P1a	13.2 ± 0.5	9.1 ±0.5	1.1	1st order
P2a	20.0 ± 0.5	12.3 ± 0.5	1.3	n-th order
P1a (total)	15.4 ± 0.5	10.0 ± 0.5	1.0	1st order
P2a (total)	21.5 ± 0.5	13.1 ± 0.5	2.0	n-th order

3.3. Oxidative conditions optimization

Nitrile groups cyclization makes the main contribution to the whole heat flow of the process. It was shown above that the cyclization is a highly exothermic and autocatalytic processes. These two factors can cause local overheating and thus cause microscopic (structural) and macroscopic (mainly surface) defects.

On the other hand it is known from the literature [16] that base units of PAN fibers are interlacing oriented parts (crystallites) and amorphous parts which have different behaviors during stabilization. Amorphous parts are more exposed to oxidative processes and destruction in comparison to crystalline areas. If heating regime is not optimal cleavage of polymer chain is the most probable because of intensive heat flow during cyclization. This forms structural defects and causes macroscopic defects formation in material. That is why we suppose that in order to minimize such defects formation and to increase the homogeneity of stabilized fiber the process should be stationary with constant heat flow rate and/or constant mass loss rate. Mass loss rate is strongly depended on destructive processes and removal of gaseous products during fiber stabilization.

Temperature program (Fig. 8) for constant heat flow rate was calculated using kinetic analysis results. The program was calculated with the use of the following conditions: 30–270 °C temperature range, duration ~240 min. Under these conditions degree of conversion is constant and is 0.4%/min, the maximum heat flow rate is not more than 0.11 mW/mg for PAN fiber and 0.09 mW/mg for pre-oxidized PAN fiber.

In order to confirm our calculations and conclusions TG and DSC experiments were carried out with the calculated temperature program (Fig. 9). The experiments revealed some features of kinetic analysis and of PAN fiber behavior during stabilization under such conditions. Fig. 9 shows good agreement between experimental and calculated curves (Fig. 8) in temperature range below 210 °C (200 min) and the maximum heat flow rate is not more than 0.11 mW/mg. With the following linear heating DSC signal increases synchronically that does not agree with kinetic calculations. This can be easily explained because kinetic software does not take into account changes of thermo-physical characteristics of a material, first of all Cp, during stabilization. It can be seen (see Fig. 2) that heat capacity of fibers changes significantly during stabilization process and the difference between baselines before and after the experiment is 1.5 mW/mg even for the lowest heating rate of 2.5 K/min. Thus significant increase of DSC signal with heating from 210 to 270 °C concerns with changes of fiber heat capacity, because transition from carbon-chain structures to cyclic ones is attended by sharp increase of Cp value [18].

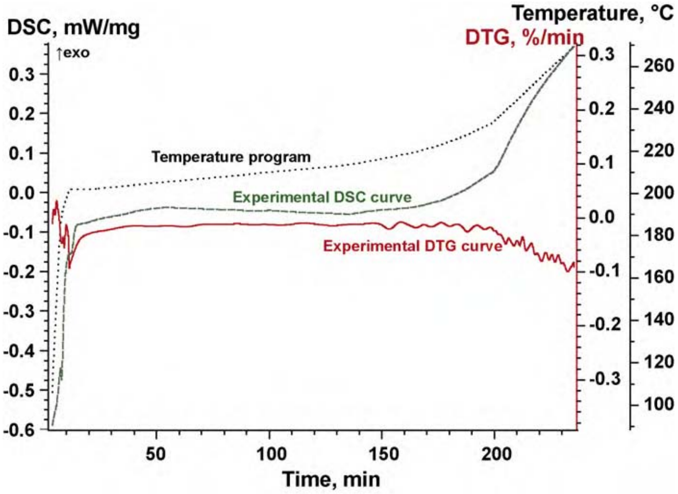

Fig. 9. TG and DSC experiments according to the calculated temperature program for PAN fiber.

DTG and DSC curves (Fig. 9) demonstrate that mass and heat transfer processes are symbate, so they probably correlate to the same structural changes. That is why the calculated program allows to control not only heat flow but also removal of gaseous products from fiber during stabilization. It is of great importance for homoge-

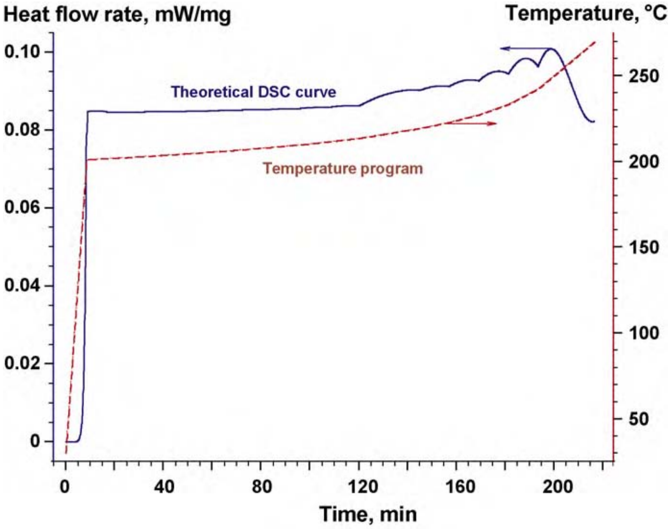

Fig. 8. Calculated DSC curve with constant heat flow rate of PAN fiber stabilization process.

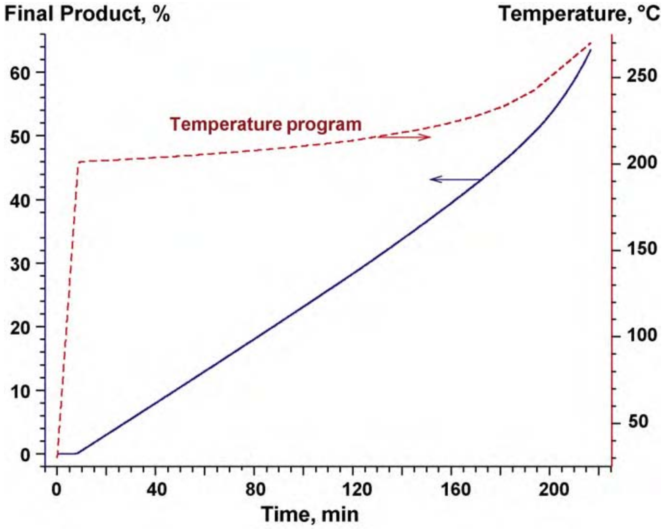

Fig. 10. Time dependence of "final product" (sum of calculated reaction products concentrations).

nous structure formation and minimization of surface defects of stabilized fiber.

Simulated degree of conversion for oxidative stabilization according to this temperature program was 65% for PAN fiber (Fig. 10) and 68% for pre-oxidized PAN fiber. Results of calculations were compared with experimental data. Two DSC measurements were made. PAN fiber and pre-oxidized PAN fiber were stabilized in DSC instrument according to the calculated temperature program (Fig. 9). Then cyclization index CD (Eq. (4)) of the stabilized fiber was measured in inert atmosphere. CD was of $65 \pm 1\%$ for PAN fiber and $68 \pm 1\%$ for pre-oxidized PAN fiber. Good agreement of experimental data and calculated results confirm accuracy of kinetic analysis of processes in PAN fiber and validity of obtained kinetic parameters.

4. Conclusions

Kinetics of oxidative stabilization of PAN fiber was studied.

Technique for thermal analysis of PAN fiber was offered with the use of coil as sample holder. Advantages over standard procedure of PAN fiber study in aluminum pans were discussed.

DSC measurements of PAN fiber were carried out in air atmosphere. Non-isothermal kinetic analysis was carried out for these data. Kinetic parameters and kinetic models of oxidative stabilization were obtained: nitrile cyclization was fitted with Prout–Tompkins *n*-th order model, and oxidative destruction of chain fragments and functional groups were fitted with second order reaction 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. The maximum heat flow rate is not more than 0.11 and 0.09 mW/mg for PAN and pre-oxidized PAN fiber, correspondingly.

It was shown that simulated degree of conversion coincides within errors with cyclization index CD for stabilized fiber. Therefore CD can be used as an estimation of degree of conversion in research and practical applications.

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.

It was shown that heat flow and removal of gaseous products correspond to the same processes in fibers during stabilization, that provides an additional flexibility in experimental conditions simulation for high quality stabilized fiber production.

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