Analysis of thermal stabilization process for organomorphic preforms made of oxidized polyacrylonitrile

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Abstract. Simulation and analysis of thermophysical processes in PAN-fiber-based pressed samples that occurs during thermal stabilization were carried out. It is significant fact from the heat transfer point of view that the heat stabilization process proceeds with a definite exothermic effect. Herewith a strongly pronounced coupling between both the intensity of heat generation and the temperature level and heating rate at each point of the sample was observed. The influence of the main factors that effects on the sample temperature state, such as the density and thermal conductivity of the preform material, also the rate constants of the thermal stabilization process, was studied. The experimental data of the sample temperature state in the thermal stabilization process is presented and was compared with the analysis results.

1. Introduction
In the manufacturing of reinforced carbon-carbon (RCC) and ceramic matrix composites (CMC) [1-5], polyacrylonitrile (PAN) as a feedstock in the form of tows of monofilaments or organomorphic frames consisting of carbonized pressed PAN is used [6-9]. The first stage of the RCC and CMC manufacturing is to conduct thermal stabilization (oxidation) of the PAN feedstock. During the thermal stabilization process, cyclization and oxidation of the PAN preform occur. It is significant fact from the manufacturing point of view that the thermal stabilization process proceeds with a definite exothermic effect, therefore, too rapid heating of the PAN preform can lead to the excessive heat generation and thermal burning of the preform. In the manufacturing of the continuous carbon filaments, this heat is removed by fibers blow-off with large volume of air that allows to achieve the temperature difference in the fiber along the length of no more than 2 degrees to guarantee exclusion of burning which drastically reduces the filaments strength. Obviously, this approach cannot be used for heat treatment of pressed organomorphic preforms.

Experimental selection of the time-temperature regime of thermal stabilization may require a large time and material consumption and does not guarantee the achievement of an optimal result. Therefore, one should rely on the results of mathematical simulation that should determine effects of the main factors on the sample temperature state in the thermal stabilization process and allow selection of a rational regime.
2. Model of thermal stabilization process

The object of the study was organomorphic frame of non-woven fabric Oxypan®, consisting of partially oxidized PAN staple fibers Pyron®.

The complexity of the thermal stabilization process simulation was that several processes were simultaneous and interconnected in the sample – heat transfer by thermal conductivity and volumetric heat generation during an exothermic reaction. In this case, at each point of the sample the heat generation intensity (the power of internal heat sources) was dependent both on the temperature at this point and on the heating rate. It was assumed that physicochemical transformations in the organomorphic frame sample occur with the heat generation in the thermal stabilization process. Also the changes in the thermal stabilization process completion degree of the material was determined by Arrhenius equation. To simulate this process, the rate constants of the process were required.

In study [10], the thermal stabilization process of the PAN tow was investigated. Herewith it was considered that the multiple Arrhenius equation could be used to describe the oxidation reactions and heat generation in the tow. To determine the rate constants of the thermal stabilization process, two experimental dependences obtained using a DSC-calorimeter at different heating rates of the tow, were used. Based on the analysis of the number of heat-generation curve maxima, it was found that two reactions proceeded in the thermal stabilization process. The following rate constants were obtained for the PAN tows with filaments of 0.17 tex: $E_1 = 146.5 \cdot 10^6$ J/kmol; $k_1 = 7.3 \cdot 10^{11}$; $Q_1 = 1.2 \cdot 10^6$ J/kg; $E_2 = 83.7 \cdot 10^6$ J/kmol; $k_2 = 5.6 \cdot 10^4$; $Q_2 = 2 \cdot 10^8$ J/kg.

Similar studies for tows with filaments from 0.08 to 0.12 tex were presented in [11]. The mathematical model of the thermal stabilization process was corresponding to [10], but it was assumed that the reaction proceeded in one step. It was shown that the activation energy for different heating rates and filaments linear density was in the range from 185.27 to 351.15 J/kmol. Also the pre-exponential factor was from $1.6 \cdot 10^{13}$ to $1.24 \cdot 10^{13}$ s$^{-1}$. The total thermal effect of the reaction was set as $9.7 \cdot 10^5$ J/kg. Apparently, accounting only one reaction led to a significant dependence of the rate constants on the heating rate and a big difference of the results from the data obtained in [10].

Significantly more complex models of the thermal stabilization process were used in [12]. The temperature dependences of the pre-exponential factor and fiber density were taken into account and various kinetics and nucleation models were applied. In this case, as well as in [10], a conclusion about the behavior of two chemical processes: autocatalytic and first order, was drawn. Such a different mathematical description of the process made it difficult to directly compare it with the data of [10] and [11].

In general, it can be stated that, at present, the rate constants of the thermal stabilization process with respect to the processing of tows and fabrics based on PAN feedstock were determined with various degrees of reliability. However, the thermal stabilization parameters for nonwoven materials that differ in fiber diameter from tows, linear density of filaments and the degree of initial oxidation are completely absent. Unfortunately, the value of initial oxidation is not disclosed by the material manufacturer.

Therefore, to determine parameters of the thermal stabilization process the special study was carried out. As the result, it was found that two successive stages were occurred in the thermal stabilization process. Its rate constants are presented in Table 1.

| Parameter                        | Stage 1       | Stage 2       |
|----------------------------------|---------------|---------------|
| The initial mass fraction $\Gamma$ | 0.0472        | 0.205         |
| Activation energy $E$, J/kmol    | $37.38 \cdot 10^6$ | $39.42 \cdot 10^6$ |
| Pre-exponential factor $k$, s$^{-1}$ | 12241         | 1.186         |
| Thermal effect $Q$, J/kg         | $96.34 \cdot 10^3$ | $122.53 \cdot 10^3$ |
It is apparent that the thermal effect absolute value was much less compared with other researchers [8, 9] that was natural result as the Pyron® fiber was already partially oxidized in the delivery condition.

3. Heat transfer model in the thermal stabilization furnace
A geometric model of the thermal stabilization furnace with a sample box mounted in it is shown in Figure 1 and 2. Heaters made of nichrome wire wound on ceramic tubes were heating source. A steel box with a sample was mounted on ceramic and steel plates placed on the furnace hearth. A sample of the organomorph frame in the form of a pressed PAN flat plate with dimensions of 95 × 95 × 40 mm was clamped between two steel plates. To create pressure a massive steel load was placed on the sample upper surface. The uniformity of sample heating was increased by filling the box with furnace coke to a height of approximately two-thirds of the overall size. The top of the box remained free.

Physical and mathematical models of heat transfer in the thermal stabilization furnace were developed. A three-dimensional steady-state process of combined radiation-conductive heat transfer was considered. In the simulation, the experimentally measured dependence of the nichrome heaters power on time was used (Figure 3). Herewith it was assumed that power was uniformly released in the entire volume of the heaters. The gas medium in the furnace volume was taken diathermic radiation-transparent. Conductive heat transfer in all solid bodies was also simulated in furnace insulation, ceramic tubes and plate, box frame, filling and load. The analysis was carried out in the COMSOL Multiphysics.

To evaluate the influence of the exothermic effect in the pressed array of the organomorph frame, an experimental temperature measurement was performed at various points of the sample. The hot junction of one thermocouple was placed in the sample central part in a previously prepared recess. The second junction was located on the sample edge.

Comparison of the experiment and numerical simulation showed that the calculated and experimental temperature values were in complete good agreement, and the maximum difference between them does not exceed 10 °C (Figure 4).

4. The process effect analysis on the sample temperature state
As criterion for estimating the sample temperature state, the temperature difference between its center and edge was chosen. That particular criterion is most simultaneously dependent on both the rate constants of thermal stabilization process and the materials thermophysical characteristics and the furnace operating regime. A series of parametric studies was carried out in order to identify the influence of the material thermophysical characteristics (Figures 5 and 6), rate constants (Figures 7-9) and the heaters power (Figure 10). It is apparent that the sample density, the thermal effect of the exothermic reaction and the pre-exponential factor were of the greatest influence.

Figure 1. Thermal stabilization furnace model
1 – alundum tubes; 2 – nichrome heaters; 3 – steel box; 4 – furnace coke filling; 5 – sample of the organomorphic frame; 6-8 – steel plates; 9 – steel load; 10 – ceramic plate

**Figure 2.** Organomorphic frame sample box

**Figure 3.** The dependence of the furnace heaters total power on time, W

**Figure 4.** Experimentally measured (1) and calculated (2) temperature difference between the center and the edge of the sample (3), K
Figure 5. The effect of sample density on the temperature difference between its center and edge
1 – experimental data; 2-6 – the density of the sample 300; 600; 900; 1200; 1500; 1800 kg/m³

Figure 6. The effect of thermal conductivity of the sample on the temperature difference between its center and edge
1 – experimental data; 2-7 – thermal conductivity of the sample is 0.012; 0.0036; 0.060; 0.084; 0.108 W/(m-K)

Figure 7. Effect of activation energy on the temperature difference in the sample
1 - experimental data; 2-4 - activation energy ×10⁻⁶ – 31.53; 39.42; 47.30 J/mol

Figure 8. The effect of the pre-exponential factor on the temperature difference in the sample
1 - experimental data; 2-4 – pre-exponential factor ×10⁻⁶ – 0.711; 1,186; 1,660 s⁻¹
Figure 9. Influence of thermal effect on the temperature difference in the sample
1 – experimental data; 2-6 thermal effect ×10⁻³
1 – 61, 122, 183, 244, 366 J/kg

Figure 10. Effect of heater power on the temperature difference in the sample
1 – experimental data; 2-6 heater power as a percentage of the nominal – 96; 100; 104; 108; 112%

5. Conclusion
The model of organomorphic preforms thermal stabilization made of oxidized PAN is presented. The analysis of the main process parameters significance on the sample temperature state was conducted. It was shown that the sample density, the heat effect of the exothermic reaction and the pre-exponential factor are of the greatest influence. The comparison of the experimental and calculated temperature values are in a good agreement.

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