A novel method for determination of occurrence order of stabilization reactions in carbon fiber precursor

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Abstract. Thermal stabilization is an important step in production of carbon fiber from polyacrylonitrile (PAN) precursors. During thermal stabilization step different thermochemical reactions take place almost simultaneously. Understanding the onset and temperature range of the stabilization reactions is a key for adjusting processing parameters such as tension, stretching, etc. However, stabilization reactions are very complex and overlap with each other. In order to separate the stabilization reactions, we combined the results of different thermal analysis techniques, namely Differential Scanning Calorimetry (DSC), Thermogravimetry (TGA) and Thermomechanical Analysis (TMA), to study behaviour of PAN precursors during stabilization. By means of combining the results of these techniques, we were able to determine the temperature range and occurrence order of each of stabilization reactions regardless of the composition of initial PAN fibers and history of fiber formation.

1. Introduction
Carbon fibers are good candidates for high performance applications requiring both great mechanical properties and light weight [1,2]. Among different production steps, thermal stabilization is an important step in production of carbon fibers from PAN precursors, during which different reactions including cyclization, dehydrogenation and oxidation take place [3]. Thermal stabilization converts the linear structure of PAN fibers to an intermediate cyclic structure. This structure has a critical role in subsequent processing steps such as carbonization and graphitization [4,5].

Thermal stabilization reactions are very complex and depend on the chemical composition of the initial PAN fibers and stabilization conditions such as atmosphere and heating rate. In different atmospheres different reactions occur. Changing the heating rate causes a shift in initiation temperature of chemical reactions. With an increase in the heating rate, initiation temperature of chemical reactions shifts to higher values. Increasing heating rate has also been shown to enhance weight loss in the form of chain fragmentation [6,7].

Understanding the onset and temperature range of the stabilization reactions is a key for adjusting processing parameters. Despite numerous studies, still there is not a certain agreement on the occurrence-order and temperature range of each of stabilization reactions. Using different analysis methods, researchers have presented different interpretations regarding the occurrence order of reactions. The discrepancy originates mainly from the differences in the chemical composition of the studied fibers, which is one of the main factors determining the mechanism of reactions [8].
Due to concurrent occurrence of stabilization reactions and the effect of structure and chemical composition of precursor fiber on these reactions, a clear approach for their separation, independent from chemical and physical structure of precursor fibers, is not proposed. In this paper we apply different characterization techniques, namely DSC, TGA and TMA, in order to shed some light on the stabilization reactions.

2. Experimental
PAN fibers containing Itaconic acid (IA) and Methyl acrylate (MA) comonomers were used. Exothermic reactions of PAN precursor were studied in a DSC 2010, TA Instrument (both in air and nitrogen atmospheres) at a heating rate of 2 °C/min in temperature range of 40 to 400 °C. Weight loss of fibers during stabilization process was measured in a TGA, Perkin-Elmer. Heating rate of 2 °C/min was employed and fibers were heated from room temperature to 450 °C. Thermomechanical analysis (TMA) of PAN fibers was done in a Mettler Toledo TMA SDTA 840. The samples were scanned during the heating process from 30 to 400 °C at heating rates of 2 °C/min under air atmosphere. 0.022 CN/tex tension was applied to the fibers.

3. Results and Discussion
The main changes occurring during thermal stabilization of PAN fibers include intramolecular cyclization of linear structure which leads to formation of ladder polymer and development of intermolecular cross-links of nitrile groups, dehydrogenation and chain fragmentation and oxygen uptake [8,9]. The occurrence order of stabilization reactions is determined by studying and coupling the results of DSC, TGA and TMA curves.

Since oxidation reactions do not occur in neutral atmosphere, we compared thermal behaviour of fibers in both neutral and oxidative atmosphere as an approach to separate oxidation from other stabilization reactions. DSC thermograms in both air and nitrogen atmospheres and TGA graph in air atmosphere are shown in figure 1. According to DSC thermograms, onset of exothermic peak in air and nitrogen is at 175 °C and 210 °C, respectively (Table 1). Since oxidation reactions do not occur in nitrogen atmosphere during heating process, primary reactions from 175 to 210 °C are considered to be oxidation and probably dehydrogenation resulting from oxidation. The first peak temperature (T_{pk1}) in air atmosphere is 250 °C. T_{pk1} shifts to 258 °C in nitrogen atmosphere due to the absence of oxidation reactions. Second exothermic peak at 302 °C which is eliminated in nitrogen atmosphere is due to oxidation reactions in this temperature range.

Weight loss of PAN fibers at different temperatures is a multi-stage process due to elimination of Hydrogen, HCN, NH₃, H₂O and so forth. Chain fragmentation is another possible source of weight loss. Limited weight gain during heating is due to the oxidation reactions which introduce carbonyl (C=O) and hydroxyl (OH) groups into the polymer backbone. However, hydroxyl groups may undergo dehydrogenation reactions at higher temperatures, which finally contribute to total weight-loss. Cyclization reactions do not contribute in weight loss of fibers [8].
Figure 1. DSC in air (a) and nitrogen atmospheres (b) and TGA thermograms of PAN fibers in air (c)

TGA was performed to realize the temperature range of dehydrogenation reactions. TGA graph shows a limited weight loss at 175 °C (0.2%), which can be attributed to moisture evaporation and decomposition of sizing. There is not any significant weight-loss in the range of 175 - 210 °C (T_i of DSC peak in air and nitrogen atmospheres, respectively), which indicates absence of reactions that cause weight loss, namely dehydrogenation. According to DSC results in both air and nitrogen atmospheres, it is approved that oxidation reactions are dominant in this temperature range (175 - 210 °C). Weight-loss of fibers shows 1.5% increase from 210 to 258 °C (T_{pk} in nitrogen atmosphere). 1% of this weight loss has occurred in a wide range of 210 - 250 °C, while 0.5% has occurred in the narrow range between 250 and 258 °C. Since the temperature range of 210 - 258 °C is the range that DSC curves exist in both atmospheres, it can be concluded that dominant reaction in this temperature range is cyclization, which is intensified in the air atmosphere. Given the more intense weight loss in the range of 250 - 258 °C, it seems that dehydrogenation reactions also occur in this range and overlap with cyclization reactions. Weight loss increases to 4.8% at 302 °C. This indicates that dehydrogenation reactions along with limited chain fragmentation are present in this range. However, the presence of second exothermic peak in DSC thermogram in air atmosphere shows the presence of oxidation reactions in final region of the curve. After 274 °C (T_f of first exothermic peak in air atmosphere) the weight loss becomes less steep due to oxygen uptake.

TMA curves of PAN fibers and their first derivative (DTMA) are shown in Figure 2. During Thermal stabilization of PAN fibers, two steps of shrinkage occur, namely physical shrinkage (due to physical relaxation of stressed molecules) and chemical shrinkage (due to chemical reactions) [6,10]. TMA is also used for determination of temperature range of cyclization reactions and its results are coupled with DSC and TGA. Physical shrinkage (10.4%) in this type of PAN fibers occurs below 210 °C and chemical shrinkage (17.6%) occurs in the range of 210 - 264 °C. Onset of chemical shrinkage at 210 °C is ascribed to initiation of cyclization reactions, which confirms the results of DSC and TGA.
Therefore, it can be concluded that in this type of PAN fibers stabilization reactions occur in the following order: 1- Oxidation (above 175 °C), 2- Cyclization (above 210 °C), 3- Dehydrogenation (above 250 °C). It should be noted that chemical reactions are dominant in the mentioned ranges, but overlap with each other in the other ranges. Furthermore, it should be mentioned that this determined order can be altered by a change in chemical composition and spinning conditions of PAN. In addition, the change in heating rate during stabilization would shift the mentioned temperature to higher or lower values.

Table 1. DSC data of PAN fibers in air and nitrogen atmosphere

|          | Air            | Nitrogen       |
|----------|----------------|----------------|
| Ti a     | 175 (°C)       | 250 (°C)       |
| Tpk1 b   | 250 (°C)       | 302 (°C)       |
| Tpk2 c   | 302 (°C)       | 302 (°C)       |
| ΔT = Tr d − Ti | 181 (°C) | 210 (°C) |
| Ti d     | 210 (°C)       | 258 (°C)       |
| ΔT = Tr − Ti | 258 (°C) | 92 (°C) |

a Ti: Initiation Temperature of Exothermic Peak  
b Tpk1: First Peak Temperature  
c Tpk2: Second Peak Temperature  
d Tr: Finish Temperature of Exothermic Peak

4. Conclusion
By designing a series of experiments using DSC, TGA and TMA analysis, the occurrence order of chemical reactions during thermal stabilization of PAN fibers was investigated. According to the results obtained from comparison of DSC graphs in air and nitrogen atmosphere and coupling the results with TGA, reactions starting after 175 °C in PAN fibers containing itaconic acid and methyl acrylate comonomers, were oxidation. TMA results showed the shrinkage of fibers due to cyclization reactions, which started above 210 °C. Comparison of DSC graphs in air and nitrogen atmospheres and TGA results also showed that cyclization reactions of PAN fibers started above 210 °C. TGA results showed the presence of dehydrogenation reactions above 250 °C. It should be noted that chemical reactions are dominant in the mentioned ranges, but overlap with each other in the other
ranges. Using the method explained here, it is possible to determine the occurrence order of stabilization reactions of different types of PAN fibers independent from structure and history of spinning. This approach can be used to design the heat treatment temperature and stress during stabilization process accurately and efficiently.

5. References
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