

# THE KINETIC STUDY OF DEHYDROGENATION REACTION FOR PAN-BASED CARBON FIBER PRECURSOR DURING THERMAL STABILIZATION

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## Introduction

PAN-based precursor fibers are often employed to product high quality carbon fibers, with undergoing a series of temperature and atmosphere controlled process, thermal stabilization, carbonization and graphitization [1]. Thermal stabilization is one of the most significant and time-expended steps in the production of carbon fibers [2]. Generally, PAN-based precursor fibers are stabilized for one to two hours in air furnaces with a temperature range of 180 to 280°C approximately. During this process, a series of gas-solid phase chemical reactions take place, which can be attributed to three major reactions: cyclization, dehydrogenation and oxidation. Dehydrogenation is the formation of double bonds (-C=C-) which stabilizes carbon chains in order to form the ladder structure making the fibers heat-resistant and infusible [3]. The dehydrogenation reactions proceed with oxidation and removal of water. In this work, the kinetics of dehydrogenation reaction and structural evolution for polyacrylonitrile (PAN) copolymer fiber during thermal stabilization in air were studied by Fourier transform infrared (FTIR) spectroscopy. Reaction order (n), reaction rate constants (k) at different temperatures, activation energy (Ea) and pre-exponential (A) were calculated through the variation of absorbance for double bonds (-C=C-) with the increasing of reaction time.

## Experimental

PAN copolymer fibers used in the work were obtained from "SAF" 3K (3,000 filaments per tow) carbon fiber precursor of Courtaulds containing 1.2% itaconic acid (IA) and 6% methyl acrylate (MA). Precursor bundles were cut to a number of filament tows with an average length of 60 cm, and then fixed on a stainless steel shelf to keep length and restrain shrinkage during stabilization. The shelf on which filament tows were fixed was put in air furnace with a flowing air atmosphere. The furnace worked at 210, 225, 240, 255 and 270°C respectively and from 10 to 100 min with an interval of 10 min for every temperature point. Therefore, we can prepare 10 Oxidized fiber samples at each temperature point.

The FTIR analyzer with a type of Tensor 27, Bruker Optic, Germany, was utilized to record the IR spectrum of the samples. A resolution of 0.482 cm<sup>-1</sup> and mirror velocity of 0.059cm/s were used for the measurement. And the spectral scan range began from 400 to 4000 cm<sup>-1</sup>. Oxidized fiber

samples were cut to powder and then weighed 5 mg per sample to mix uniformly with 300mg KBr powder. Ultimately, for each sample 100mg mixture was weighed to analyze FTIR.

## Results and Discussion

With the development of reaction, the concentration of carbon-carbon single bonds (-C-C-) decreased, on the contrary, double bonds (-C=C-) increased, but the overall concentration remained constant. Coming down to FTIR, it turned out to be the absorbance of functional group which has a linear relation with concentration according to Lambert-Beer's law. In the IR spectrum, the double bonds group usually absorb at 1660 cm<sup>-1</sup> and the single bonds group at 1060 cm<sup>-1</sup>. Assuming C(C=C) to express the double bonds concentration and C(C-C) to express the single bonds concentration, and the total concentration is C. So the fraction of double bonds concentration can be written as

$$x_{C=C} = \frac{C(C=C)}{C(C=C) + C(C-C)} = \frac{C(C=C)}{C} \quad (1)$$

In terms of Lambert-Beer's law, the relation of absorbance (A) and concentration is

$$A = E \cdot L \cdot C \quad (2)$$

in which E stands for the absorptivity constant and L expresses the path length.

Then the fraction of double bonds concentration can be written as [4]

$$\begin{aligned} x_{C=C} &= \frac{A(C=C)/E(C=C) \cdot L}{A(C=C)/E(C=C) \cdot L + A(C-C)/E(C-C) \cdot L} \\ &= \frac{A(C=C)}{A(C=C) + r \cdot A(C-C)} \end{aligned} \quad (3)$$

$$r = \frac{E(C=C)}{E(C-C)} = \frac{2A(C=C)(t=\infty)}{A(C-C)(t=0)} \quad (4)$$

The ratio of absorptivity constant "r" can be calculated by FTIR data and listed in Table 1.

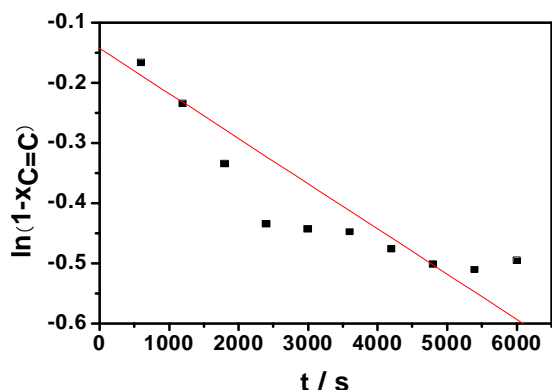
**Table 1. The Ratio of Absorptivity Constant at Different Temperature**

Temperature/°C	210	225	240	255	270
r	0.37	0.43	0.48	0.48	0.45

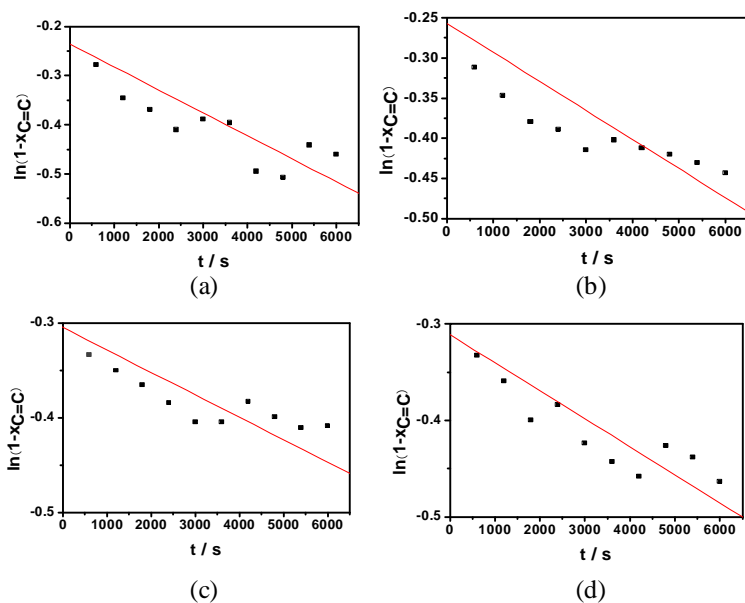
According to the FTIR data, at different temperatures, the relationships between ln(1-x<sub>C=C</sub>) and time basically tend to be linear, which indicates the first-order kinetic relationship.

As seen in Fig. 1, the linear transformation of first-order kinetics is fit for the experimental data. By the chemical

kinetic analysis, the negative value of the slope of the line fitting to the data evaluates the reaction rate constant.



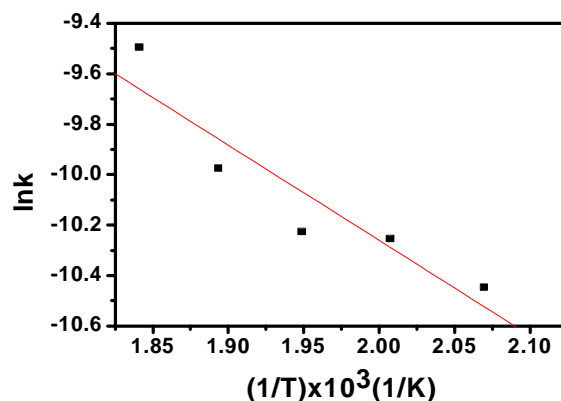
**Fig. 1** first-order kinetic relationship for PAN fiber in air at 210°C, slope =  $-2.90612 \times 10^{-5}$ ,  $k = 2.90612 \times 10^{-5} \text{s}^{-1}$ ; —, fitted, ■, experimental.



**Fig. 2** first-order kinetic relationship for PAN fiber in air (—, fitted, ■, experimental):

- (a) at 225°C, slope =  $-3.51859 \times 10^{-5}$ ,  $k = 3.51859 \times 10^{-5} \text{s}^{-1}$ ;
- (b) at 240°C, slope =  $-3.62098 \times 10^{-5}$ ,  $k = 3.62098 \times 10^{-5} \text{s}^{-1}$ ;
- (c) at 255°C, slope =  $-4.65566 \times 10^{-5}$ ,  $k = 4.65566 \times 10^{-5} \text{s}^{-1}$ ;
- (d) at 270°C, slope =  $-7.51098 \times 10^{-5}$ ,  $k = 7.51098 \times 10^{-5} \text{s}^{-1}$ ;

In Fig. 2 (a) ~ (d), rate constants at different temperatures can be evaluated. Referring to Arrhenius equation,  $\ln k$  and  $1/T$  have linear relation, as seen in Fig. 3. The slope of the line equals to  $-E_a/R$  and the intercept is  $\ln A$ . ( $E_a$ , activation energy;  $R$ , ideal gas constant,  $8.314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ;  $A$ , pre-exponential)



**Fig. 3** Activation energy ( $E_a$ ) analysis: the linear transformation of  $\ln k$  and  $1/T$ ; slope =  $-3769.66801$ ,  $E_a = 31.34102 \text{ kJ/mol}$ ,  $A = 0.06581 \text{s}^{-1}$ .

### Conclusions

Based on Lambert-Beer's law, the kinetics of dehydrogenation for PAN copolymer fibers during thermal stabilization in air were studied by FTIR. By first-order kinetic and Arrhenius equation, we can conclude that dehydrogenation is a pseudo first order reaction, the Activation energy,  $E_a = 31.34102 \text{ kJ/mol}$ , and pre-exponential,  $A = 0.06581 \text{s}^{-1}$ . The rate constant of this reaction can be expressed as:

$$k = 0.06581 e^{\frac{31341.02}{RT}} (\text{s}^{-1}) \quad (5)$$

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