Marmara Journal of Pure and Applied Sciences 2015, Special Issue-1: 19-22
DOI:10.7240/mufbed.62638

Simulation Model for Stabilization of Carbon Fibres

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ABSTRACT

Due to their outstanding physical properties carbon fibres bear huge potential for light-weight applications. Carbon fibres are mainly produced from precursor fibres made from wet-spun polyacrylonitrile (PAN). In the production process of carbon fibres the most time consuming and thus most expensive step is the stabilization of the precursor. During the stabilization the precursor changes its color from white to black and becomes infusible. Currently, there is no model for describing the stabilization model mathematically. First steps of analysis have been done by Dunham and Eddy in 1992 to describe the stabilization method with a differential equation. In this project a numerical approach based on their work is followed. However, there are still some challenges to cope with until it is possible to fully understand and describe the stabilization process.

Keywords: Carbon fibre, precursor, stabilization, simulation, mathematical modelling.

I. INTRODUCTION

Carbon fibres possess excellent mechanical properties as well as low density. Therefore, they are very suitable for the use in lightweight constructions. Until now, carbon fibres are not well established in market sectors like automotive industry or renewable energy industry. Limiting factors for the development of the market are the complicated and expensive manufacturing and the associated high price for carbon fibres. The production of carbon fibres is divided into two individual steps. The polyacrylonitrile (PAN) fibres are first stabilized and afterwards carbonized. Especially the stabilization process requires a long processing time and is thus very energy and cost-intensive. To get the best performance every precursor material needs a particular temperature profile. Currently these temperature profiles have to be determined with the trial-and-error method by laborious test runs. These tests can be reduced significantly by the usage of a simulation model which can predict the resulting stabilization of a carbon fibre.

II. METHODOLOGY

The stabilization of a carbon fibre is divided into three main reactions: the dehydrogenization, the oxidation and the cyclization. Based on the work of M.G. Dunham and D. D. Edie [1] these reactions can be described by the following differential equations.

$$\frac{\partial y_{CN}}{\partial t} = -k_1\left(1-e^{k_i t}\right)y_{CN} \tag{1}$$

$$\frac{\partial y_{C=C}}{\partial t} = k_2 C^0_{o_2,x} y_{o_2}\left(1-y_{C=C}\right) \tag{2}$$

$$\frac{\partial y_{bo}}{\partial t} = k_3 C^0_{o_2,x} y_{o_2}\left(1-y_{bo}+y^0_{bo}\right) \tag{3}$$

Furthermore, the free oxygen and the current temperature in the fibre bundle are modelled with these differential equations.

$$\frac{\partial y_{o_2}}{\partial t} = \frac{D_e}{R_b^2}\frac{\partial\left(\zeta\frac{\partial y_{o_2}}{\partial\zeta}\right)}{\zeta\partial\zeta} - \frac{1}{2}k_2 C^0_{rep,x} y_{o_2}\left(1-y_{C=C}\right) - \frac{1}{2}k_3 C^0_{rep,x} y_{o_2}\left(1-y_{bo}+y^0_{bo}\right) \tag{4}$$

$$\frac{\partial\theta}{\partial t} = \frac{\alpha_e}{R_b^2}\frac{\partial\left(\zeta\frac{\partial\theta}{\partial\zeta}\right)}{\zeta\partial\zeta} + \frac{(-\Delta H_1)}{T^0_x\rho c_p}k_1 C^0_{rep}\left(1-e^{kt}\right)y_{CN} + \frac{(-\Delta H_2)}{T^0_x\rho c_p}k_2 C^0_{o_2,x} C^0_{rep} y_{o_2}\left(1-y_{C=C}\right) + \frac{(-\Delta H_3)}{T^0_x\rho c_p}k_3 C^0_{o_2,x} C^0_{rep} y_{o_2}\left(1-y_{bo}+y^0_{bo}\right) \tag{5}$$

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Submitted: 15 October 2014, **Revised:** 04 March 2015, **Accepted:** 01 July 2015

With

- $y_{CN}y_{CN}$: concentration of nitrile group
- $y_{C=C}y_{C=C}$: concentration of carbon double bounds
- $y_{bo}y_{bo}$: concentration of bounded oxygen
- k_i : constant rate of cyclization
- k_j : constant for reaction
- $C^0_{o2,x}C^0_{o2,x}$: initial concentration of free oxygen in air
- $y_{o_2}y_{o_2}$: free oxygen concentration
- $\Theta\Theta$: current Temperature
- $C^0_{rep}C^0_{rep}$: initial concentration of acrylonitrile repetition unit
- D_eD_e : diffusion coefficient of oxygen through fibre
- R_bR_b : radius of fibre bundle
- $\alpha_e\alpha_e$: heat transfer coefficient
- $\Delta H_j\Delta H_j$: reaction enthalpy of reaction j
- $T^0_xT^0_x$: initial temperature
- $\rho\rho$: fibre density
- $\zeta\zeta$: normalized coordinate for radius

With the equations (1) – (5) the concentrations of the bounded oxygen and carbon double bounds in a fibre bundle can be described. Using the normalized coordinate a 1-dimensional model of the cross section can be built (Figure 1-2).

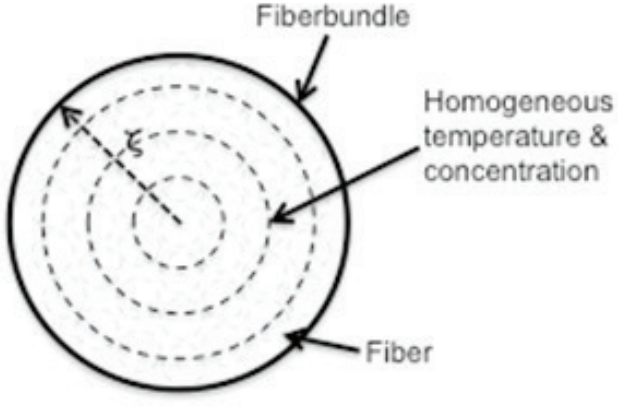

Figure 1. Acceptance for the fibre bundle

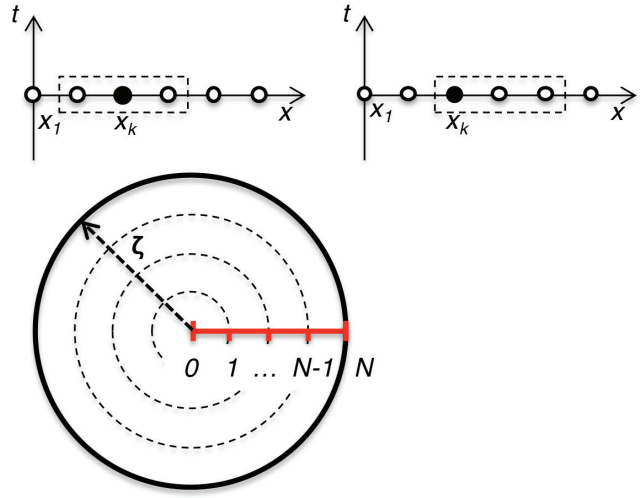

Figure 2. Central differences and forward differences on equidistant nodes 0 to N [2]

The time derivations are discretized with the implicit Euler method (Figure 3).

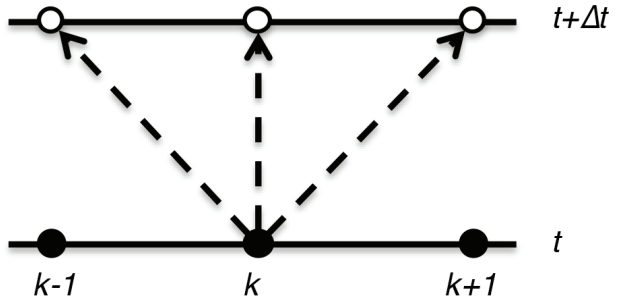

Figure 3. Implicit Euler method [3]

As a result of this approach a linear equation system is gained.

$$\frac{y_{CN_i}^{m+1}-y_{CN_i}^{m}}{\Delta t} = -k_{1_i}^{m+1}\left(1-e^{kt}\right)y_{CN_i}^{m+1} \quad (6)$$

$$\frac{y_{C=C_i}^{m+1}-y_{C=C_i}^{m}}{\Delta t} = k_{2_i}^{m+1}C^0_{o2x}y_{o2_i}^{m+1}\left(1-y_{C=C_i}^{m+1}\right) \quad (7)$$

$$\frac{y_{bo_i}^{m+1}-y_{bo_i}^{m}}{\Delta t} = k_{3_i}^{m+1}C^0_{o2x}y_{o2_i}^{m+1}\left(1-y_{bo_i}^{m+1}+y^0_{bo}\right) \quad (8)$$

$$\frac{y_{o2_i}^{m+1}-y_{o2_i}^{m}}{\Delta t}=\frac{D_e}{R_b^2}\frac{1}{\zeta}\left(\frac{y_{o2_{i+1}}^{m+1}-y_{o2_i}^{m+1}}{\Delta\zeta}-\zeta\frac{y_{o2_{i+1}}^{m+1}-2y_{o2_i}^{m+1}+y_{o2_{i-1}}^{m+1}}{\Delta\zeta}\right)-\frac{1}{2}k_{2_i}^{m+1}C_{rep,x}^{0}y_{o2_i}^{m+1}\left(1-y_{C=C_i}^{m+1}\right)$$

$$-\frac{1}{2}k_{3_i}^{m+1}C_{rep,x}^{0}y_{o2_i}^{m+1}\left(1-y_{bo_i}^{m+1}+y_{bo}^{0}\right) \quad (9)$$

$$\frac{\theta_i^{m+1}-\theta_i^{m}}{\Delta t}=\frac{\alpha_e}{R_b^2}\frac{1}{\zeta}\left(\frac{\theta_{i+1}^{m+1}-\theta_i^{m+1}}{\Delta\zeta}-\zeta\frac{\theta_{i+1}^{m+1}-2\theta_i^{m+1}+\theta_{i-1}^{m+1}}{\Delta\zeta}\right)$$

$$+\frac{(-\Delta H_1)}{T_x^0\rho c_p}k_{1_i}^{m+1}C_{rep}^{0}\left(1-e^{k_i t}\right)y_{CN_i}^{m+1}$$

$$\frac{(-\Delta H_2)}{T_x^0\rho c_p}k_{2_i}^{m+1}C_{o2,x}^{0}C_{rep}^{0}y_{o2_i}^{m+1}\left(1-y_{C=C_i}^{m+}\right) \quad (10)$$

$$+\frac{(-\Delta H_3)}{T_x^0\rho c_p}k_{3_i}^{m+1}C_{o2,x}^{0}C_{rep}^{0}y_{o2_i}^{m+1}\left(1-y_{bo_i}^{m+1}+y_{bo}^{0}\right)$$

The obtained equation system can be solved with known numerical means. Most of the required parameters are already recorded in the relevant literature. Only a few parameters like the reaction enthalpy, the Arrhenius pre-exponential factor and the activation energy of stabilization have to be gained experimentally. Therefore the Differential Scanning Calometry (DSC) is especially suited (Figure 4). The DSC is a technique to measure emitted and absorbed heat for a heating sample.

The DSC can be operated under different atmospheres. Figure 5 shows the heat output for a PAN-Precursor in an oxygen atmosphere. In an oxygen atmosphere all three basic reaction (dehydrogenization, oxidation and cyclization) take place. From the DSC results the following graphs (Figure 5-8) for the heat output over the time is gained. In the graph are two peaks, which stand out. These peaks are associated with the cyclization and the oxidation reaction.

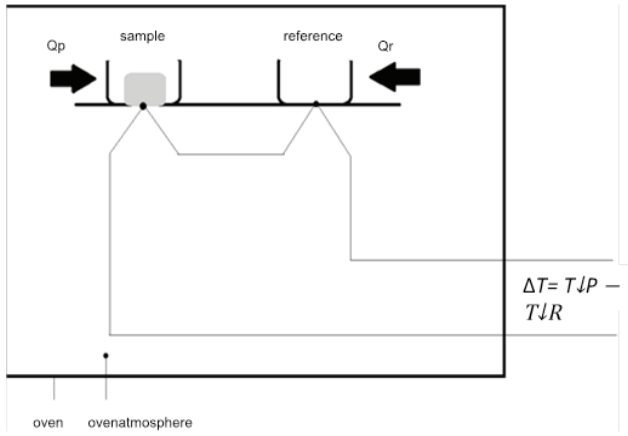

Figure 4. Structure of a Differential Scanning Calometry

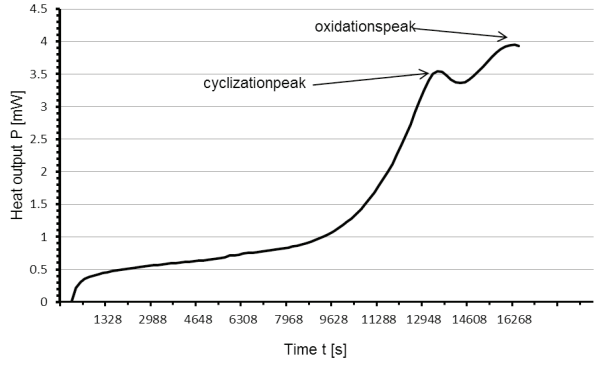

Figure 5. DSC in oxygen atmosphere

The dehydrationpeak is not directly recognizable. The method of Fitzer and Müller predicts that this peak is included in the cyclizationpeak (Figure 6) [2]. To make this peak visible the heat output in a nitrogen atmosphere has to be measured. In this atmosphere neither dehydration nor oxidation can take place. Only the influence of the cyclization reaction on the heat output can be seen.

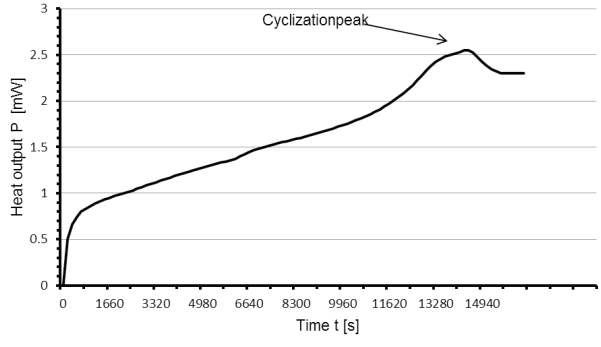

Figure 6. DSC in nitrogen atmosphere

Deduction the first from the second graph produces a graph that only depends from oxidation and cyclization, shown in Figure 7.

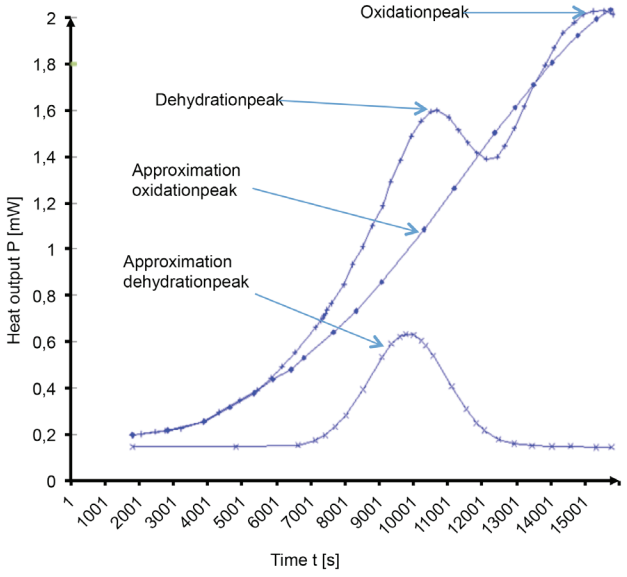

Figure 7. Deducted graph

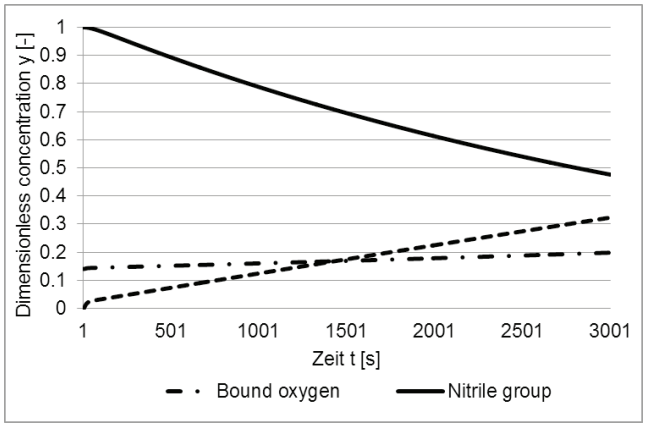

Figure 8. Reactions during stabilization in a fibre bundle

This graph directly shows the dehydrationpeak and the oxidationpeak. The Gauß-Newton method separates both reaction, to get an approximation for the oxidation- and the dehydrationpeak. With these data the needed parameter are calculable by the method of Borchardt and Daniels [4].

III. RESULTS

Currently the solution of the differential equations over a section of a fibre bundle offers a good approximation of the stabilization process under the assumption of a constant temperature profile and homogenous fibre distribution, as shown in Figure 8. In future projects the influence of the heat transfer and the distribution of the fibres will be analysed. Afterwards this both parts are connected into a coupled simulation with can predict the stabilization rate under given process parameters

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