



Structural transformation of polyacrylonitrile fibers during stabilization and low temperature carbonization



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ABSTRACT

The effect of oxidative stabilization and carbonization processes on the structure, mass and mechanical properties of polyacrylonitrile (PAN) precursor fibers was analyzed. A gradual densification of the fibers occurring from mass loss, decrease in fiber diameter and increase in density were observed after stabilization at a maximum temperature of 255 °C and carbonization at a maximum temperature of 800 °C. The tensile strength and modulus of the fibers were found to decrease after stabilization but then increased after low temperature carbonization. The thermal processing of the precursor fibers affected their mode of failure after tensile loading, changing from a ductile type of failure to a brittle type. The type of failure correlated well with the crystal structure changes in the fibers. Whilst the PAN precursor fiber started to exotherm above 225 °C in air, no prominent exothermic reaction was measured in the carbonized fibers in air up to 430 °C. The aromatization index of stabilized fiber was calculated to be ~66%, and that of carbonized fiber was ~99%. FTIR studies indicated that the variation in the chemical structure of the fibers with the stabilization of the fibers. Radial heterogeneity in the stabilized fibers was observed however it was not promoted to the carbonized fibers. Finally, a method to calculate mass retention of PAN precursor fiber after heat treatment was developed, and the calculated percentage mass retained of the precursor fiber after oxidation and carbonization were found to be 81% and 51%, respectively. This study proposes an effective method to calculate the percentage of mass retained by precursor fibers after stabilization and low temperature carbonization to provide a model for evaluating carbon fiber yield from a given amount of fibers.

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1. Introduction

Carbon fiber is commonly utilized as a reinforcing material in composite materials because of its relatively high strength and lightweight characteristics [1]. Commercial carbon fibers are produced by heat treatment of polyacrylonitrile (PAN) precursor fibers due to its potential for the manufacturing carbon fibers with high strength and stiffness [2]. Since its inception, improvements on the mechanical properties and effective manufacturing costs have constantly been sought [3–6]. In order to develop cost forecasting of the carbon fiber it is imperative to

understand the mass and energy changes in precursor fiber when processed in a manufacturing environment. The manufacture of carbon fiber involves the stages of stabilization and carbonization [2]. The PAN precursor fibers are stabilized to withstand high temperature during carbonization process. During stabilization transformation of linear macromolecular structure into aromatic ladder structure takes place [7]. This occurs via cyclization reaction around 280 °C, followed by dehydrogenation and oxidation reactions [8] leading to the stabilization of the fiber for high temperature carbonization [2]. Once stabilized, it is referred to as oxidized PAN fiber (OPF). Carbonization removes most non-carbon elements from the fiber by heating to extreme temperatures, violently shaking them off and reducing the fiber mass. This further compacts the aromatic ring structure, transforming it into turbostratic graphite structure to form carbon fibers [9]. At

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this point typically up to 95% or more of the atomic composition consists of carbon atoms [10].

Many scientific studies and reports have focused on improving mechanical properties of carbon fiber, namely modulus and strength by optimizing the process parameters [1]. Also many literature have been written based on understanding the chemical transitions of PAN precursor fiber and changes in fiber structure when converted into carbon fiber [3,9,11]. Thus a large knowledge bank already exists on how PAN precursor fiber changes mechanically and chemically during heat treatment and variation of process factors. One of the most important parameters in the process of carbonization is temperatures which has been shown to significantly affect the mechanical properties of the fibers [12]. However, little research focuses on low temperature carbonization and its effects on the structure property relationships of the fibers. Moreover little work has been undertaken to analyze linear mass transition specifically, but the other effects of pyrolysis have been heavily analyzed [1,2,4–7,10].

The goal of this study is to gain knowledge of the chemical and physical transformations and the level of mass retained after PAN precursor fiber is stabilized and carbonized. This will provide insights into the approximation of carbon fiber yield after low temperature treatment, as the fiber changes chemically and physically at each stage. Here the whole process of stabilization and carbonization was carefully performed on a pilot scale carbon fiber manufacturing line. This enables a better understanding of the process parameters as well as the material properties that can be beneficial for the industrial scale production of carbon fibers.

2. Materials and methods

PAN precursor fibers provided from Bluestar Fibres Co. Ltd were stabilized and then carbonized using Carbon Nexus multi-tow carbon fiber production line at Deakin University (Fig. 1). Thirty tows were processed under same operating conditions. Each tow consists of 24000 filaments (24K). The composition of the precursor is 93% acrylonitrile, 6% Methyl acrylate and 1% Itaconic acid. The details of the properties of the precursor are shown in Table 1.

The line possesses four stabilization ovens (zones 1, 2, 3, and 4) and low temperature and high temperature furnaces with four temperature zones as shown in Fig. 1.

2.1. Fiber heat treatment

The process parameters used for stabilization and carbonization

of precursor fibers are shown in Table 2. The precursor fibers were stabilized in air at 225 °C, 235 °C, 245 °C and 255 °C in each oven respectively. Ovens 1 and 2 operated under a 4.7% draw, while ovens 3 and 4 operated under 0.9% at drive three. They were then carbonized in the low temperature furnace in nitrogen atmosphere at 487 °C, 650 °C, 750 °C and 800 °C in each zone respectively under a 2.2% draw. Nitrogen flow levels were set to 75L/min at either end of the furnace. The speed of the line was set to 120 m/h at the unwinding site. The resident time of fiber at this speed in the heated zones 1 and 3 was twenty-four minutes each, and in zones 2 and 4 was twenty minutes respectively. Residence time in the low temperature furnace was approximately four minutes. Draw is the pull experienced by the fibers by maintaining slightly higher speed at the output roller compared to input roller of an oven.

2.2. Density testing

The density of fibers was measured with an Ultrapycometer (ultrapyc 1200e Quantachrome instruments) under Helium environment. The stabilized and carbonized fibers were dried in an oven prior to density measurement in order to reduce the effect of moisture. Density of the fiber samples was obtained by performing several iterations on each samples until the standard deviation between the values <0.005. The average density of the iterations was reported.

2.3. Single fiber tensile testing

The tensile properties were measured using the FAVIMAT tensile testing machine equipped with a vibroscope and a load cell of 210 cN. A gauge length of 25 mm was considered. A set of 25 filaments were tested for each sample. A test speed of 12.5 mm/min was used for PAN and OPF samples were as 2 mm/min was used for carbon fibers. A grip force of 40 cN was considered for this testing. Each tensile test was conducted with an application of initial pre-tension of 0.5 cN. Initially, linear density of each filament was determined by the vibroscope before proceeding with the tensile testing. Moreover, the obtained linear density was used to calculate the percentage mass retained by the treated samples using the following equation (1).

$$\text{Percentage mass retained} = 100 - \left(\frac{Ld_p - Ld_t}{Ld_p} \times 100 \right) \quad (1)$$

Where Ld_p represents linear density of the precursor and Ld_t represents linear density of the treated fiber.

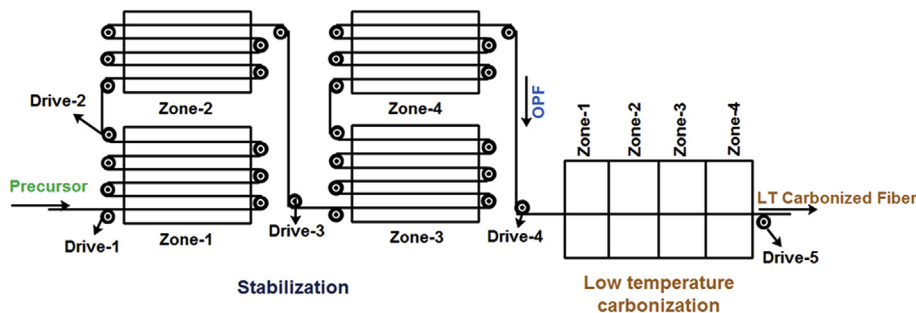


Fig. 1. Schematic representation of the Carbon Nexus carbon fiber manufacturing line.

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