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Development of a predictive model for study of skin-core phenomenon in stabilization process of PAN precursor

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ABSTRACT

Studying the presence and progress of fiber defects, such as skin-core structure, is an important tool for analysis of a chemical process. In this article, the skin core morphology has been analyzed by optical microscopic (OM) images and Fourier transform infrared attenuated total reflectance mapping (FTIR-ATR mapping). The results of FTIR-ATR mapping showed that the fiber is almost uniform in the core area while OM images are accurate enough to be used for skin-core analysis. Using OM images, the core ratio of samples were measured to quantify the skin-core structure. Non-parametric kernel density estimation methods have then been compared with conventional parametric distribution models using these data. The results reveal that the parametric methods cannot adequately describe the skin-core phenomenon and that the non-parametric distributions are more appropriate for the quantification of skin-core morphology. By applying the non-parametric distributions, a model has been developed, which describes the relationship between the skin-core defect and the operation parameters of the fiber production. This approach can be used to predict the probability of skin-core occurrence and can be used to decrease the presence of this phenomenon in the carbon fibers production industry. Our results show that temperature is one of the most significant operational parameter at a typical oxygen concentration (in air at atmospheric pressure) governing the skin-core formation.

Introduction

Over the past several years, carbon fibers (CF), due to being a high-strength and high-performance material, have been broadly used in many industries including aerospace and automotive [1]. The ubiquitous application of carbon fiber stems from its outstanding properties such as high tensile strength, light weight, high Young modulus [2], high toughness and stiffness [3], low density [2,4], and high thermal stability [5,6]. Almost 90% of produced carbon fibers are made from polyacrylonitrile (PAN) fiber precursor [7]. Three steps are involved in the conversion of PAN precursor into carbon fibers: oxidative stabilization, carbonization and graphitization. The stabilization step is the most intricate, rate-determining and time-consuming step in the production of carbon fiber. Stabilization step also has the largest impact on the quality of the final fibers. In this step, the PAN precursor goes through an oxidation oven with different isothermal zones with an increasing temperature gradient from 180–300 °C [8,9] to form a heat resistant structure. Various physical and chemical changes happen at this stage including the uptake and penetration of oxygen (physical changes) and fiber shrinkage and coloration due to chemical changes, such as cyclization, dehydrogenation, oxidation and crosslinking reactions. Fig. 1 shows the suggested steps of chemical reactions in stabilization process [10]. The result of these reactions is a ladder-like molecular structure, which makes the oxidized PAN fiber (OPF) heat-resistant and unmeltable [9–12].

These properties are essential for fiber carbonization at higher temperatures (1000–2000 °C) [11,12]. As many parameters (at least 14 parameters) [13] are involved in the stabilization process, the process is evaluated as a nonlinear complex chemical–physical system. The key controlling parameters in the stabilization process are Temperature, Time and Tension (hereafter refer to as TTT) [10]. The skin core effect is a structural flaw inherited from the

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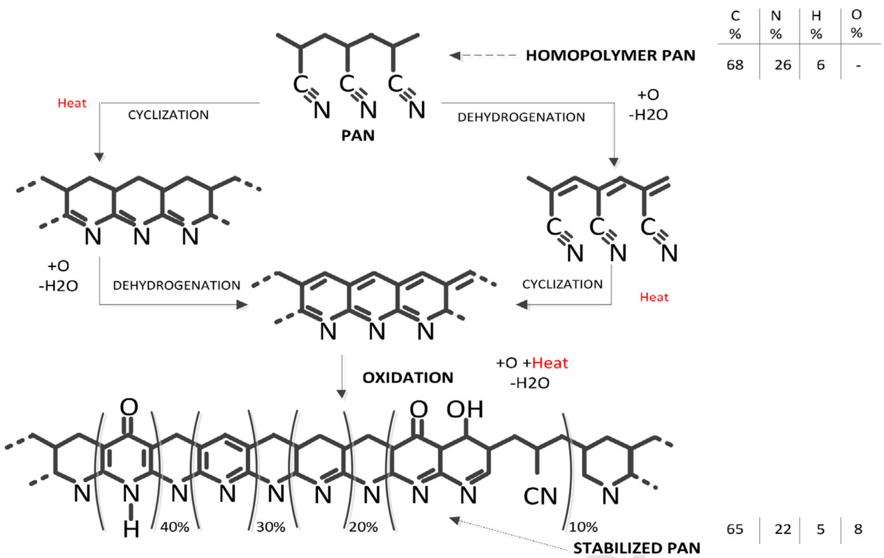

Fig. 1. Suggested steps for the stabilization process of PAN [10].

stabilized fibers. It is one of the most important factors affecting the mechanical properties of the resultant carbon fiber as it reduces the homogeneity of the fiber and cause structural defects [12,14]. Three parameters, including filament diameters, oxygen gradient from the skin to the core of filament, and temperature gradient, are significant factors in the formation of a skin-core structure [7,12,15]. Oxygen and temperature are operational parameters (and can be altered) while diameter is a specification of the fiber.

During cyclization and dehydrogenation, the linear PAN macromolecules are changed into a ladder aromatic polymer. At the same time, the fibers take up oxygen molecules through oxidation reactions. The oxygen penetrates from the surface to the inside of the fibers. During these reactions, a ladder-shaped dense layer is first formed on the surface of the fiber preventing the oxygen from penetrating inside the fiber. As the reaction continues, the surface reacts with oxygen and become fully stabilized while the inside is only partially stabilized due to insufficient oxygen. This leads to the skin-core structure [15,16]. The structure of both the skin and the core of the fiber is sheet-like with the structure of the skin being more compact and uniform with good orientation whereas the structure of the core being loose and less orientated [12]. According to Lv et al. [12], the oxygen content in the skin of the stabilized PAN is greater than that in the core, which causes non-uniformity in the stabilized fiber structure. Yu et al. [17] observed that the skin-core morphology is due to fast oxygen uptake and consequent intense aromatization.

Various techniques, including Nano Dynamic Mechanical Analyzer (NanoDMA), Energy Dispersive X-ray (EDX), and Transmission Electron Microscopy (TEM), have been used to investigate the radial heterogeneity in stabilized fibers [12,14,18–20]. Nunna et al. [18] has investigated the relationship between the appearance of radial heterogeneity and the process parameters (TTT) during the stabilization process. According to their study, the extent of the progress of stabilization improved with rise in temperature (from 225 to 235 °C) and time (from 12 to 24 min); however, it decreased with increase in tension on the fibers (from 1600–2550 cN). The radial heterogeneity was observed at 235 °C in the fibers. Although they showed that the process improved with increase in temperature and time, the radial heterogeneity also increased with these parameters.

As it was explained, the high temperature gradient introduces a skin-core defect. When the treatment temperature is high, the rate at which oxygen reacts with the fiber is more than its diffusion rate from the skin to the inner parts of the filament [8,21]. As such, the core proportion of the skin-core defect can be reduced by changing the temperature and thermal time treatment, as those two are the effective parameters in formation of skin-core morphology.

In order to investigate the skin-core effect on other phenomena, the skin-core would need to be quantified first. The core ratio (Eq. (1)) has been used in this study to quantify and measure the progress of this defect [7].

$$Core\ ratio\% = 100 \times \frac{Area\ of\ core\ (ROI2)}{Total\ area\ of\ filament\ cross\ section\ (ROI1)} \quad (1)$$

As the tows being processed contains a large number of filaments (6000, 12,000 or 24,000 filaments), the quantification of skin-core structure involves uncertainty and can merely be expressed using probabilistic methods, such as probability density functions. The density functions falls in two categories: parametric and non-parametric [22].

These methods have been utilized in different applications and are applicable to quantify the skin-core structure [23–25]. To the best of our knowledge, the non-uniformity in the structure of stabilized fiber has not yet been fully statistically analyzed or quantitatively characterized [11,12,17,18]. This research fulfills this gap by quantifying skin-core defect using probability density functions to predict the probability of skin-core occurrence.

In this paper, the cross sectional non-uniformity of oxidized PAN fibers has been investigated by analysis of optical microscopic images of their cross-sections. In an attempt to obtain a chemical understanding of the skin-core observations and confirm the results, the same samples were analyzed by Fourier transform infrared attenuated total reflectance mapping (FTIR-ATR mapping) and the results have been compared with that of optical microscopic images. The probabilistic method has then been used to analyses the skin-core defect based on OM as it is a simpler method to quantify this defect and predict the probability of its occurrence in relation to the operational parameters (TTT) of the stabilization process.

The main contributions of this paper are as follows:

- Structural study of OPF filaments by IR-Mapping ATR system and comparison with optical microscopy images.

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