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## <sup>1</sup> Development of a predictive model for study of skin-core phenomenon in stabilization process of PAN precursor

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### A R T I C L E I N F O

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### A B S T R A C T

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 Q3 concentration (in air at atmospheric pressure) governing the skin-core formation.

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### <sup>8</sup> Introduction

9  $Q4$  Over the past several years, carbon fibers (CF), due to being a bigh strength and bigh performance material, have been broadly  $10$  high-strength and high-performance material, have been broadly<br> $11$  used in many industries including acrospase and automotive [1] <sup>11</sup> used in many industries including aerospace and automotive  $[1]$ .<br><sup>12</sup> The utilizations application of arrhan flow stams from its <sup>12</sup> The ubiquitous application of carbon fiber stems from its  $\frac{13}{2}$  externe ding approaching such as high together tensor the light weight. <sup>13</sup> outstanding properties such as high tensile strength, light weight,<br> $\frac{14}{14}$  high *Neung modulus* [2], high teuchness and stiffness [2], law <sup>14</sup> high Young modulus [\[2\]](#page--1-0), high toughness and stiffness [\[3\]](#page--1-0), low<br><sup>15</sup> density [2,4], and bigh thermal stability [5,5], Almast 00% of <sup>15</sup> density [\[2,4\],](#page--1-0) and high thermal stability [\[5,6\]](#page--1-0). Almost 90% of<br><sup>16</sup> needuced explore fibers are made from polyger limitails (DAN) fiber <sup>16</sup> produced carbon fibers are made from polyacrylonitrile (PAN) fiber<br>17 programs [7] Three store are involved in the conversion of PAN 17 precursor [\[7\]](#page--1-0). Three steps are involved in the conversion of PAN precursor into carbo fibers: oxidative stabilization carbonization  $18$  precursor into carbon fibers: oxidative stabilization, carbonization<br> $19$  and graphitization. The stabilization step is the most intricate  $19$  and graphitization. The stabilization step is the most intricate,  $20$  and determining and time consuming step in the production of 20 rate-determining and time-consuming step in the production of  $21$  carbon fiber Stabilization step also has the largest impact on the carbon fiber. Stabilization step also has the largest impact on the

quality of the final fibers. In this step, the PAN precursor goes 22<br>through an ovidation oven with different isothermal zones with 23 through an oxidation oven with different isothermal zones with  $^{23}$ <br>an increasing temperature gradient from 180, 200 °C [8,0] to form  $^{24}$ an increasing temperature gradient from  $180-300 \degree C [8,9]$  $180-300 \degree C [8,9]$  to form  $^{24}$ a heat resistant structure. Various physical and chemical changes  $\frac{25}{26}$ happen at this stage including the uptake and penetration of  $\frac{26}{27}$ 0xygen (physical changes) and fiber shrinkage and coloration due  $\frac{27}{10}$ <br>to chamical changes, such as suclization, debudressention  $\frac{28}{10}$ to chemical changes, such as cyclization, dehydrogenation,  $^{28}$ <br>suidation and appellation apartime Fig. 1 shows the sympated oxidation and crosslinking reactions. [Fig.](#page-1-0) 1 shows the suggested  $^{29}$ <br>stage of shamical geographics in stabilization geographical The  $^{30}$ steps of chemical reactions in stabilization process  $[10]$ . The  $30$ <br>result of these reactions is a ladder like melocular structure. result of these reactions is a ladder-like molecular structure,  $31$ <br>which makes the ovidined DAN fiber (OPE) best resistant and  $32$ which makes the oxidized PAN fiber (OPF) heat-resistant and  $32 \tanh 19.11$ unmeltable  $[9-12]$ . 33<br>These properties are essential for fiber carbonization at higher  $34$ 

These properties are essential for fiber carbonization at higher  $34$ <br>nperatures (1000, 2000 °C) [11.12]. As many parameters (at least temperatures (1000–2000 °C) [\[11,12\]](#page--1-0). As many parameters (at least  $35$ <br>14 parameters) [13] are involved in the stabilization process the 14 parameters) [\[13\]](#page--1-0) are involved in the stabilization process, the  $36$ <br>process is evaluated as a poplinear complex chemical-physical process is evaluated as a nonlinear complex chemical–physical  $37 \text{ systems}$  The key controlling parameters in the stabilization process system. The key controlling parameters in the stabilization process  $38$ <br>are Temperature. Time and Tension (bereafter refer to as TTT) [10] are Temperature, Time and Tension (hereafter refer to as TTT) [\[10\]](#page--1-0).  $39$ <br>The clin care offect is a structural flaw inherited from the 40 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 [\[10\].](#page--1-0)

41 stabilized fibers. It is one of the most important factors affecting  $\frac{42}{100}$  the most inpursion of the most input carbon. Show as it  $\frac{42}{13}$  the mechanical properties of the resultant carbon fiber as it<br> $\frac{43}{13}$  reduces the homogeneity of the fiber and cause structural defects  $^{43}$  reduces the homogeneity of the fiber and cause structural defects  $^{44}$   $^{112,141}$  Three parameters including filameter diameters exused  $\frac{44}{12,14}$ . Three parameters, including filament diameters, oxygen<br> $\frac{45}{12}$  explicit from the clup to the care of filament, and temperature  $^{45}$  gradient from the skin to the core of filament, and temperature<br> $^{46}$  gradient are significant factors in the formation of a skin core  $^{46}$  gradient, are significant factors in the formation of a skin-core<br> $^{47}$  structure [712.15]. Oxygen and temperature are operational <sup>47</sup> structure [\[7,12,15\].](#page--1-0) Oxygen and temperature are operational  $^{48}$  parameters (and can be altered) while diameter is a specification <sup>48</sup> parameters (and can be altered) while diameter is a specification  $49$  $^{49}$  of the fiber.

 $^{50}$  During cyclization and dehydrogenation, the linear PAN  $^{51}$  macromolecules are changed into a ladder aromatic polymer At  $51$  macromolecules are changed into a ladder aromatic polymer. At  $52$  the same time, the fibers take up over molecules through  $52$  the same time, the fibers take up oxygen molecules through oxidation reactions. The oxygen penetrates from the surface to the  $53$  oxidation reactions. The oxygen penetrates from the surface to the  $54$  inside of the fibers. During these reactions a ladder shaped dense  $^{54}$  inside of the fibers. During these reactions, a ladder-shaped dense<br> $^{55}$  layer is first formed on the surface of the fiber proventing the  $^{55}$  layer is first formed on the surface of the fiber preventing the  $^{56}$  $56$  oxygen from penetrating inside the fiber. As the reaction continues,<br> $57$  the surface reacts with oursen and become fully stabilized while  $57$  the surface reacts with oxygen and become fully stabilized while<br> $58$  the inside is only partially stabilized due to insufficient oxygen  $58$  the inside is only partially stabilized due to insufficient oxygen.<br> $59$  This loads to the skip some structure [15,16]. The structure of both <sup>59</sup> This leads to the skin-core structure [\[15,16\].](#page--1-0) The structure of both the skin and the core of the fiber is shoot like with the structure of  $60$  the skin and the core of the fiber is sheet-like with the structure of  $61$  the skin being more sompact and uniform with good orientation <sup>61</sup> the skin being more compact and uniform with good orientation  $\frac{62}{100}$  with grass the structure of the gas heing losse and last orientated  $\frac{62}{63}$  whereas the structure of the core being loose and less orientated  $\frac{63}{63}$  [12] According to Ju at al. [12] the survey content in the slip of <sup>63</sup> [\[12\]](#page--1-0). According to Lv et al. [12], the oxygen content in the skin of  $64$  the stabilized PAN is greater than that in the sexe which squees <sup>64</sup> the stabilized PAN is greater than that in the core, which causes<br> $\frac{65}{2}$  non-uniformity in the stabilized fiber structure. Yu et al. [17]  $^{65}$  non-uniformity in the stabilized fiber structure. Yu et al. [\[17\]](#page--1-0)  $^{66}$  observed that the skip sero merphology is due to fact exugan  $^{66}$  observed that the skin-core morphology is due to fast oxygen untake and consequent intense aromatization  $^{67}$  uptake and consequent intense aromatization.<br> $^{68}$  Various techniques including Nano Dyn

<sup>68</sup> Various techniques, including Nano Dynamic Mechanical<br><sup>69</sup> Analyzer (NanoDMA) Energy Dispersive X-ray (EDX) and Trans-<sup>69</sup> Analyzer (NanoDMA), Energy Dispersive X-ray (EDX), and Trans-<br><sup>70</sup> mission Electron Microscopy (TEM), have been used to investigate <sup>70</sup> mission Electron Microscopy (TEM), have been used to investigate<br><sup>71</sup> the radial beterogeneity in stabilized fibers [12.14.18–20]. Nunna <sup>71</sup> the radial heterogeneity in stabilized fibers [\[12,14,18](#page--1-0)–20]. Nunna<br><sup>72</sup> et al. [18] has investigated the relationship between the annear-<sup>72</sup> et al. [\[18\]](#page--1-0) has investigated the relationship between the appear-<br> $^{73}$  ance of radial beterogeneity and the process parameters (TT)  $^{73}$  ance of radial heterogeneity and the process parameters (TIT)<br> $^{74}$  during the stabilization process. According to their study the  $^{74}$  during the stabilization process. According to their study, the  $^{75}$  extent of the progress of stabilization improved with rise in <sup>75</sup> extent of the progress of stabilization improved with rise in<br><sup>76</sup> temperature (from 225 to 235 °C) and time (from 12 to 24 min): <sup>76</sup> temperature (from 225 to 235 °C) and time (from 12 to 24 min);<br><sup>77</sup> however it decreased with increase in tension on the fibers (from <sup>77</sup> however, it decreased with increase in tension on the fibers (from<br> $\frac{78}{2500}$  1600, 2550 cM). The radial beters represents use absented at 225 °C in <sup>78</sup> 1600–2550 cN). The radial heterogeneity was observed at 235 °C in<br><sup>79</sup> the fibers. Although they shound that the presess improved with <sup>79</sup> the fibers. Although they showed that the process improved with  $\frac{80}{2}$  in gauges in terms apply through the nodial between single  $80$  increase in temperature and time, the radial heterogeneity also  $81$  increased with these narrentians  $81$  increased with these parameters.

rate at which oxygen reacts with the fiber is more than its diffusion  $\frac{84}{100}$ rate from the skin to the inner parts of the filament  $[8,21]$ . As such,<br>the core proportion of the ckin care defect can be reduced by the core proportion of the skin-core defect can be reduced by  $86$ <br>changing the temperature and thermal time treatment as these  $87$ changing the temperature and thermal time treatment, as those  $87$ <br>two are the effective parameters in formation of skin sere  $88$ two are the effective parameters in formation of skin-core  $^{88}$ <br>89 <sup>89</sup><br>In order to investigate the skip, some effect on other phenomena. <sup>89</sup>

In order to investigate the skin-core effect on other phenomena,  $\frac{90}{2}$ <br>leakin-core would need to be quantified first. The core ratio  $\frac{05}{2}$ the skin-core would need to be quantified first. The core ratio  $\frac{Q5}{5}$  <sup>91</sup> (Eq. (1)) has been used in this study to quantify and measure the  $\frac{92}{93}$ progress of this defect [\[7\]](#page--1-0).

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

As the tows being processed contains a large number of  $\frac{94}{25}$ filaments (6000, 12,000 or 24,000 filaments), the quantification of  $^{95}$ <br>clin care, structure, involves, uncertainty, and, can marghy be  $^{96}$ skin-core structure involves uncertainty and can merely be  $^{96}$ <br>expressed using probabilities methods such as probability density expressed using probabilistic methods, such as probability density  $\frac{97}{100}$ <br>functions. The density functions falls in two categories: parametric  $\frac{98}{100}$ <sup>98</sup> functions. The density functions falls in two categories: parametric and non-parametric  $[22]$ . 99<br>These methods have been utilized in different applications and  $100$ 

These methods have been utilized in different applications and  $100$ <br>applicable to quantify the ckin core structure [22, 25]. To the are applicable to quantify the skin-core structure  $[23-25]$ . To the  $101$ <br>hest of our knowledge, the non-uniformity in the structure of best of our knowledge, the non-uniformity in the structure of  $102$ <br>stabilized fiber has not yet been fully statistically analyzed or stabilized fiber has not yet been fully statistically analyzed or  $103$ <br>quantitatively characterized [1112.17.18]. This research fulfille quantitatively characterized  $[11,12,17,18]$ . This research fulfills  $104$ <br>this gan by quantifying ckin care defect using probability density this gap by quantifying skin-core defect using probability density<br>functions to prodict the probability of skip sore oscurrence functions to predict the probability of skin-core occurrence.<br><sup>105</sup> functions the gases sectional non uniformity of suidinal

In this paper, the cross sectional non-uniformity of oxidized  $107$ <br>N fibers has been investigated by analysis of ortical misro.  $108$ PAN fibers has been investigated by analysis of optical micro-<br>scopic images of their cross sections. In an attempt to obtain a manufold of their scopic images of their cross-sections. In an attempt to obtain a  $109$ <br>chamical understanding of the skip care observations and  $110$ chemical understanding of the skin-core observations and confirm the results, the same samples were analyzed by Fourier  $111$ transform infrared attenuated total reflectance mapping (FTIR- $^{112}$ ATR mapping) and the results have been compared with that of  $113$ <br>contigal migroscopic images. The probabilistic method has then  $114$ optical microscopic images. The probabilistic method has then  $114$ <br>been used to analyzes the claim serie defect based on OM as it is a  $115$ been used to analyses the skin-core defect based on OM as it is a  $115$ <br>simpler mathed to quantify this defect and predict the probability.  $116$ simpler method to quantify this defect and predict the probability  $116$ <br>of its equivance in relation to the operational parameters (TTT) of  $117$ of its occurrence in relation to the operational parameters (TTT) of  $117$ <br>the stabilization process the stabilization process.

The main contributions of this paper are as follows: 119

• Structural study of OPF filaments by IR-Mapping ATR system and  $120$ <br>comparison with optical migroscopy images comparison with optical microscopy images.

<sup>82</sup> As it was explained, the high temperature gradient introduces a<br> $^{83}$  clip care defect. When the treatment temperature is high the skin-core defect. When the treatment temperature is high, the

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