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EVALUATION OF THE EFFECT OF TENSION DURING CARBON FIBRE PROCESSING

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ABSTRACT

This study investigates the development of carbon fibre structure from precursor to carbon fibre for different tensions applied during the stabilisation process. Fibres were extracted from various stages along the production process and the fraction of unreacted nitrile groups as a measure of the extent of reaction examined. The results of DSC and FTIR analysis showed more progress in stabilisation with lower tow tension applied. Although a lower fraction of unreacted nitrile groups under less tension is an indicator for a more developed molecular structure, the analysis of the subsequent carbon fibre revealed that the application of higher tension favours the development of fibres with higher strength and modulus.

1 INTRODUCTION

The manufacture of carbon fibre from polyacrylonitrile (PAN) precursor fibres consists of two stages, stabilisation followed by carbonisation. During stabilisation, by formation of cyclised structures, the fibre becomes thermally stable to withstand the high temperatures applied during carbonisation. In this stabilisation stage of the manufacturing process, the fibre undergoes a large amount of physical and chemical structural transformations. The extent of reactions, such as cyclisation, dehydrogenation, oxidation reactions and crosslinking of molecular chains greatly affect the final structure of the subsequent carbon fibre.

The conversion process of PAN into carbon fibre very much depends on a large number of processing parameters. Temperature, dwell time and tension are considered to be the most critical process parameters in the stabilisation process [1]. As the final properties of the carbon fibres significantly depend on the structure of thermally stabilised PAN fibres [2, 3], the control of the stabilisation process, and structure development during stabilisation is essential [4]. While researchers have been studying the influence of processing parameters in the carbon fibre manufacturing process [1, 5, 6], only a few studies have been dedicated to the effect of tension in the stabilisation process on the carbon fibre structure. The reason for this might be the lack of access to industrial equipment that is capable of varying tension and confidential nature of carbon fibre manufacturing process. The open-access Carbon Nexus carbon fibre research line at Deakin University, Australia provides new opportunities to analyse the process systematically in regards to different processing parameters and study their effects on the quality of carbon fibre.

The focus of this research is to develop a deeper understanding of the effect of tension on the formation of chemical and physical structure during the stabilisation process. For this purpose, the changes of properties and evolution of structure throughout the stabilisation process and subsequent carbon fibre were studied for fibres produced at various tensions.

2 EXPERIMENTAL

2.1 Materials and processing

Fibres used in this study were manufactured from Bluestar PAN-based precursor on the Carbon Fibre Research Line at Carbon Nexus, Deakin University (Australia). The PAN fibre is copolymerized with 6% methyl acrylate (MA) and 1% itaconic acid (IA).

Carbon fibres were produced at three different tension settings, low, medium and high. As both high tension and low tension conditions can cause fibre damage, it is vital to understand the process ability over the wide range of possible stretching ratios. The fibres were processed at a speed of 120m/h, at temperatures between 230 and 260°C and further carbonised in an inert atmosphere at approximately 900°C in the low temperature furnace and 1400 °C in the high temperature furnace.

Figure 1: Carbon Fibre Research Line at Carbon Nexus, Deakin University (Australia)

2.2 Fibre characterization

Samples were taken at different stages of the oxidation process (Zone 1 to Zone 4) and after carbonisation (carbon fibre). The fibre strength was then characterised using a FAVIMAT single fibre tensile tester. The properties of the precursor used for this study are listed in Table 1.

Table 1: Properties of the precursor fibres.

Sample	Linear density (cN/dTex)	Diameter (µm)	Tensile strength (GPa)	Tensile modulus (GPa)	Elongation (%)	Density (g/cc)
Precursor AN/MA/IA	1.63 ± 0.27	13.25 ± 1.02	0.52 ± 0.04	10.37 ± 0.96	16.96 ± 1.14	1.18 ± 0.005

The extent of reaction and fraction of reacted nitriles with respect to different tensions applied during stabilisation were assessed using differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR).

The FTIR spectroscopy was performed on a Vertex 70 FTIR Spectrometer (Bruker) using KBr discs (1mg sample in 100mg KBr). The spectra were recorded between wavenumber 400 and 4000cm^{-1}. Absorbance spectra were obtained with a resolution of 4 cm^{-1} and 32 scans for each sample. After baseline correction, the spectra were deconvoluted using a method reported by Nguyen-Thai and Hong [7], where the 2240 cm^{-1}, 1620 cm^{-1} and 1590 cm^{-1} are assigned to the vibrations of C≡N, C=C and C=N respectively. The fraction of unreacted nitriles was then calculated using Equation (1).

$$f = \frac{I_{2240}}{I_{2240} + \frac{I_{1620}+I_{1590}}{I_{2240}} I_{1590}} = \frac{I_{C\equiv N}}{I_{C\equiv N} + \frac{I_{C=C}+I_{C=N}}{I_{C\equiv N}} I_{C=N}} \qquad (1)$$

DSC Analysis was performed using a DSC Q200 (TA Instruments, New Castle (USA)). Fibre samples with a weight of 6 - 7mg were prepared for DSC analysis. The fibres were placed in an aluminium pan and heated with a heating rate of 10°C/min from 20 - 450°C under air atmosphere. Samples were weighed on a XS105 Dual Range Analytic Balance of Mettler Toledo (USA). The exothermic heat [J/g] under each curve was determined to calculate the extent of reaction (EoR) of each sample according to Equation (2), where H_{Pre} is the exothermic heat of virgin PAN fibre, and H_{Stab} is the exothermic heat of each sample.

$$\mathrm{EoR}\ (\%) = \frac{H_{Pre} - H_{Stab}}{H_{Pre}} \cdot 100 \qquad (2)$$

3 RESULTS AND DISCUSSIONS

Fibre samples were taken after each zone of the stabilisation process to investigate differences in the progress of stabilisation along the production line and as a result of varying tension settings using DSC and FTIR analysis. After further processing in the low-temperature (LT) and high (HT) furnace, carbon fibres were collected and the results of the mechanical tests are discussed in this section.

3.1 Progress of stabilisation

Figure 2 depicts the DSC traces of the PAN precursor fibres produced under medium tension, after each stabilisation zone. The initial precursor trace (black) contains two peaks, one related to cyclisation at approximately ~290°C, and another peak associated with oxidation and dehydrogenation reactions at approximately ~340°C [8]. It can be observed that the peak related to cyclisation reaction reduces as the fibre is processed through each stabilisation zone, while the oxidation process takes only part to a small degree and most evidently in Zone 4. With a stabilisation temperature of 230-260°C only the high temperature region facilitates the oxidation as this reaction is known to have the higher activation energy [9].

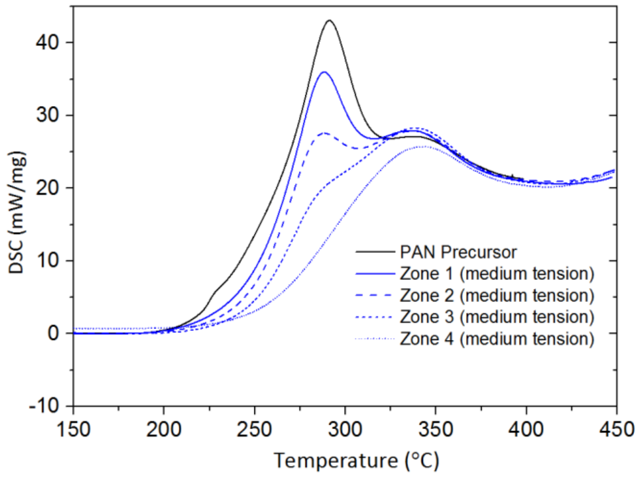

Figure 2: DSC traces of PAN precursor fibres and oxidised PAN fibres produced under medium tension

The DSC results of oxidised PAN fibres (Zone 4) are presented in Table 2. Interestingly, the fibres with the lowest tension applied revealed the highest extent of reaction. One explanation might be the wider tow width observed with lower tension and associated higher exposure to oxygen than the tight samples. The other reason for a less developed chemical structure with higher draw applied to the fibres can be a restricted ability to form cyclised polymer arrangements.

Table 2: DSC results of PAN precursor fibres and oxidised PAN fibres

Fibre	ΔH (J/g)	Extent of Reaction (%)
Precursor	2073	/
OPF (Low tension)	1059	61.81
OPF (Medium Tension)	1180	57.45
OPF (High Tension)	1363	50.85

The fraction of unreacted nitriles after the stabilisation process, determined using FTIR analysis, are shown in Figure 3, where a low amount of unreacted nitriles refers to higher extent in cyclisation. Overall, about 40% of the nitrile groups are consumed in the first zone of the stabilisation process, approximately 25% in the second zone and gradually less in the following two zones suggesting that a substantial part of the cyclisation reaction occurs at the very beginning of the process. When comparing the results between different tension settings, the least amount of unreacted nitriles was found with fibres produced under low tension, which agrees with the higher extent of reaction observed using DSC.

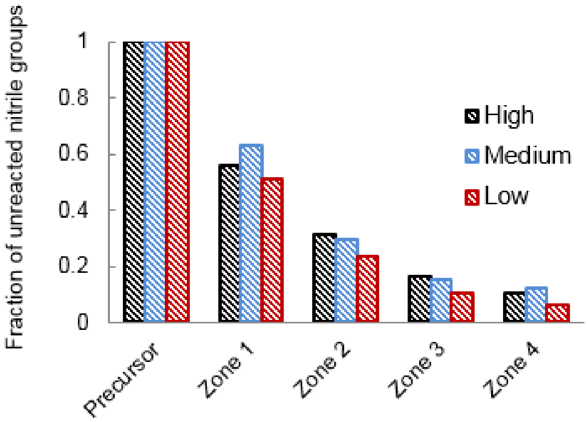

Figure 3: Fraction of unreacted nitrile groups throughout the stabilisation process for different tensions applied (low, medium, high).

3.2 Properties of carbonised fibres

The final properties of carbon fibres are heavily driven by its microstructure, which is believed to be a result of the thermal stabilisation history. During carbonisation of oxidised fibres at high temperature, further rearrangement of the remaining polymer structure into turbostratic carbon and following formation of layered graphitic structure take place, accompanied with densification.

The tensile strength and modulus of the carbon fibres manufactured under different tensions during the stabilisation process are shown in Figure 4. The results reveal that higher mechanical properties can be achieved with the application of higher tension during stabilisation. Although the progress of reaction was more advanced with oxidised PAN fibres produced under lower tension, the molecular structure might have been more oriented which produces higher tensile properties. To make more conclusive interpretations about the link of tension dependent microstructure and carbon fibre properties, future investigations will include wide-angle x-ray scattering (WAXS) and Raman spectroscopy.

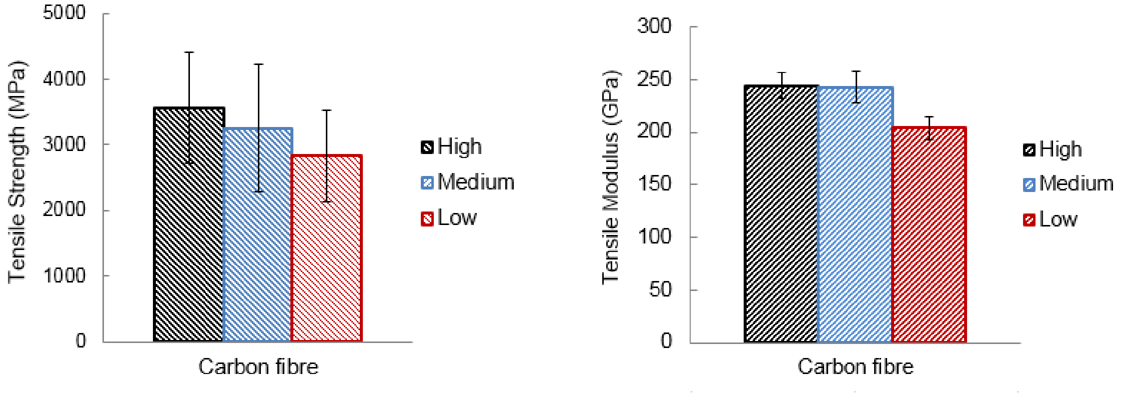

Figure 4: Tensile strength and modulus of carbon fibres produced under different tensions (low, medium, high).

9 CONCLUSIONS

The changes of properties and evolution of structure during the stabilisation process and subsequent carbon fibre were studied for fibres produced at various drawing ratios. The results from DSC and FTIR analysis show a general trend of more progress in conversion of PAN into stabilised fibres with less tension applied to the tow. These observations might be due to a combination of the wider tow width and associated higher exposure to oxygen, as well as less restricted ability to form cyclised polymer arrangements compared to high tension samples.

Although the lower fraction of unreacted nitrile groups with less tension is an indicator for a more developed molecular structure, the tensile strength results of the resultant carbon fibres show that the application of higher tension favours the development of high-strength fibre. This suggests that the tensile strength is driven by the molecular orientation, the origin of the subsequent aligned graphitic structure formed during the carbonisation process.

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