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Evolution of radial heterogeneity in polyacrylonitrile fibres during thermal stabilization: An overview

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ABSTRACT

Thermal stabilization of polyacrylonitrile (PAN) fibres is an essential step in the carbon fibre manufacturing process. The formation of radial heterogeneity in polyacrylonitrile precursor fibres in the thermal stabilization process is an important issue that is not well understood and needs to be addressed as it affects the quality of the resultant carbon fibres. Hence, in this review we put forward the recent developments on the evolution of radial heterogeneity in the PAN fibres during the thermal stabilization process.

Contents

1. Introduction

It is well known that carbon fibre is cruising through the current material world and established as a material of the 21st century because of its unique properties such as high specific strength, high specific stiffness, low thermal expansion coefficient and low density [1]. Carbon fibres find applications in the manufacturing of automobiles, aircrafts, sports goods, energy and biomedical fields [2]. Carbon fibres can be manufactured from various precursors including polyacrylonitrile (PAN), rayon and pitch [3,4]. However, majority of the commercial carbon fibres are manufactured from PAN precursor because of its ability to produce high performance

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carbon fibres with a good carbon yield at a faster rate of pyrolysis [2,5–8]. During the manufacturing process the precursor fibres experience substantial physical and chemical changes [9,10]. The manufacture of carbon fibres involves various steps 1. Dope formulation and spinning of precursor fibres [11,12] 2. Thermal stabilization of PAN precursor fibres in the air atmosphere at a temperature range of 200–300 °C in air atmosphere [5,7,13] 3. Low temperature carbonization in inert atmosphere up to 700–1000 °C [4,14–17] 3. High temperature carbonization up to 1600 °C [4,5]. Out of the three stages of manufacturing, the thermal stabilization of PAN precursor fibres is considered to be critical and the most time consuming step in the manufacturing process [18,19].

The thermal stabilization is an exothermic process that involves reactions such as cyclization, dehydrogenation and oxidation [20,21]. Cyclization reaction leads to the formation of cyclized structures with the conversion of C≡N to C=N in the polymer structure. Dehydrogenation reaction is associated with the elimination of hydrogen in the form of H_2O and further helps in the development of double bonds between carbon atoms. The formation of carbonyl groups takes place after oxidation reaction [18,20,22–25]. After thermal stabilization, the fibres will be infusible and heat resistant because of the evolution of the stable structure [26]. During the conversion process, the linear structure of the PAN precursor will be converted to ladder polymer structure at the end of thermal stabilization, which further transforms to turbostratic graphitic structure in the resultant carbon fibres [5,8,9]. The final properties of the carbon fibres significantly depend on the structure of the thermally stabilized PAN fibres [18]. The overview of the manufacturing process and the structural changes in the fibres are shown in Fig. 1.

Despite research work conducted over the last 60 years, the strongest carbon fibres commercially available in the market possess a tensile strength of ~7 GPa and a tensile modulus of ~290 GPa, however based on the C-C bond strength calculations the theoretical tensile strength of the carbon fibres is ~180 GPa [6,18,27]. The enormous gap between theoretical and practically evaluated strength of the carbon fibres is due to the presence of structural flaws that arise during the manufacture of carbon fibres [28]. The structural imperfections consist of 1. Bulk defects like pores, cracks and flaws occurred by internal stress 2. Surface defects such as nicks and punctures 3. Radial structure heterogeneity known as skin-core effect [28].

In the current review, focus is on the evolution of radial heterogeneity in PAN precursor fibres during the thermal stabilization process and its effect on the properties, morphological aspects of the fibres. Moreover, approaches to avoid the formation of radial heterogeneity in the fibres that are available in the literature are discussed.

2. Various concepts on the evolution of radial heterogeneity

Radial heterogeneity or skin-core effect is the variation in the structure (physical and chemical) along the cross section of the fibres. An optical microscopy image of the fibre cross section is shown in Fig. 2 [29] with the skin of the fibres in light colour and core in dark colour. Various studies [29–36] were conducted on PAN fibres during the thermal stabilization process to elucidate this effect. Mainly three theories related to the development of skin-core structure are available in the literature. According to the first theory the heterogeneous distribution of oxygen content along the cross section of the fibres leads to this radial structure heterogeneity. The second theory says that the higher extent of cyclization reactions in the core of the fibres compared to skin leads to the skin-core effect. The third theory believes that the skin-core structural difference already exists in the precursor, created in the spinning process and carried forward during the thermal stabilization process.

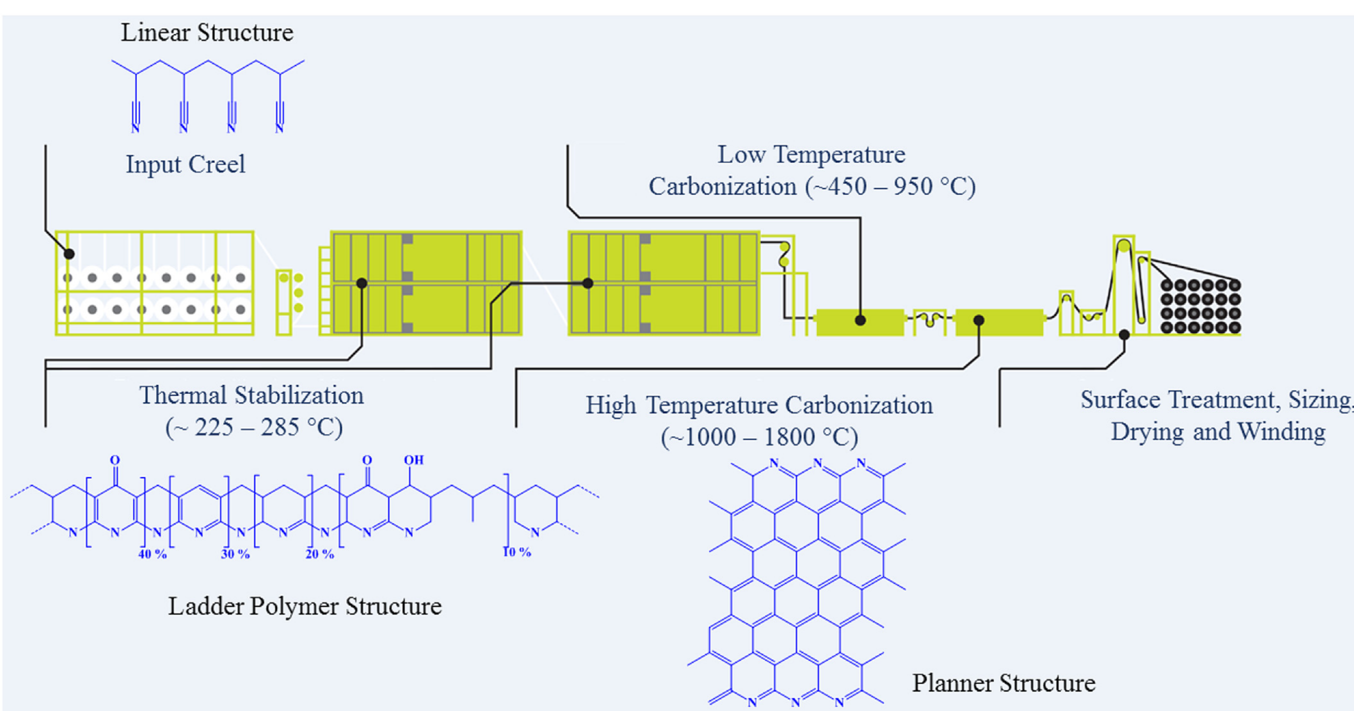

Fig. 1. A schematic of the conversion of PAN fibre to Carbon fibre taken from Carbon Nexus manufacturing unit, Australia and corresponding proposed chemical structures at each stage of carbon fibre manufacturing process [5].