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Highly aligned polyacrylonitrile-based nano-scale carbon fibres with homogeneous structure and desirable properties

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ABSTRACT

Continuous polyacrylonitrile-based nano-fibres are produced by an electrospinning approach and then converted to nano-scale carbon fibres (n-CFs) with a homogeneous structure by introducing multi-step hot-stretching in this paper. The processed n-CFs are highly aligned and partially graphitic, yet obtained at a temperature range normally associated with carbonization, and show remarkably uniform structures and a quite smooth surface with a mean roughness of 0.249 nm. The electrical conductivity of the n-CFs reaches 15.5 S/cm along the fibre direction. Tensile tests demonstrate an enhancement of 21% and 60% in tensile strength and Young's modulus, respectively, of polyetherimide composite membranes containing 1 wt% n-CFs treated with multi-step hot-stretching, which is more remarkable reinforcing effect compared to the multi-walled carbon nanotubes. It is believed that the developed approach, electrospinning and multi-step hot-stretching technique, can be a practicable means for the fabrication of continuous n-CF reinforcement with high structural integrity and desirable properties.

1. Introduction

Many advanced technologies, such as are found in aerospace and renewable energy (e.g. windmill blade structures) have been relying on high performance fibres and their resulting composite materials. But growing concerns regarding energy efficiency and environmental threats are resulting in strong appeals from these industries for a new generation of carbon fibres (CFs), exhibiting ultra-light weight and higher mechanical properties. Polyacrylonitrile (PAN)-based CFs have been commercialized for several decades. They possess the highest specific strength and specific modulus among all commercially available advanced reinforcing fibres [1,2]. However, the strongest CFs that can be produced today have a tensile strength of only 7.02 GPa (e.g. Toray T1000®, PAN-based CF), merely 4% of the theoretical value of over 180 GPa [2,3]. The low degree of structural perfection of CFs, which is highly related to the sheath/core structures and surface defects, are the most crucial barriers to significantly improving the mechanical strength and modulus of the CFs. The amount, size, and distribution of structural imperfections, such as nicks, cracks, small holes and pores, most of which are inside the core of the fibres, and the sheath/core structure itself, reduces the strength of the whole CFs due to the weak interaction between the sheath and core. All of these directly lower the mechanical strength of CFs [4–6]. Therefore, to develop a new generation of PAN-based CFs with enhanced strength, the fundamental approach has been to reduce the structural imperfections, in particular, replacing the sheath/core structure by uniform (isotropic) structures that may lead to advanced CFs with dramatically enhanced strength. Development of high quality CFs with homogeneous structure may be a revolutionary in the materials science and engineering.

The most effective way to minimize the imperfections is to reduce the fibre diameter. If the fibre diameter decreased to one tenth of the original, in the same length, the surface area and volume would reduce to one tenth and one hundredth of the original. This can greatly reduce the appearance opportunity of the fibre flaws. To further reduce the diameter of the fibres, even to obtain nano-scale carbon fibres (n-CFs), conventional spinning methods cannot work well. Various researches have demonstrated that electrospinning is an ideal method to produce continuous ultrafine polymer filaments, with diameters being in the sub-micrometer down to nanometer range [7,8]. During electrospinning, the fibres will undergo huge elongation and thinning with a strain rate of 1000 s^{-1} and the drawing ratio is often as high as 10^4 [9]. More than 50 different types of polymer-based nano-fibres (including engineering plastics, biopolymers, and those with electrical, optical or electro-optical activity) have been successfully produced by electrospining [10]. All of these nano-fibres are of great importance for applications in texturing, composite reinforcement, membrane-based separation, sensing, tissue engineering, and fabrication of super capacitors.

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Though Liu et al. proposed a concept that n-CFs with a significantly higher strength can be produced by electrospinning, this type of continuous n-CFs are unlikely to be achieved through ordinary electrospinning approaches owing to the incomplete orientation and structural imperfections [11]. Therefore, further treatment is necessary for improving the structural perfection and fibre orientation of electrospun nano-fibres. It was found that post-spinning in the vicinity of the glass transition temperature was an effective method for improving the mechanical performance of micron-scale fibres, because it not only improved the degree of the fibre alignment, but also reduced the flaw density of the fibres. A post-spinning straining treatment was proposed by Wagner et al. as a way of improving the mechanical performance of nano-fibres [12]. In some of previous investigations, n-CFs have been produced by electrospinning with no further stretching prior stabilization [13–15]. Our previous studies showed that a hot-stretching led to over 300% improvements for electrospun pure PAN and 260% improvement for nanotube modified PAN nano-fibre sheets (containing 2 wt% grafted multi-walled carbon nanotubes) in tensile strength [16]. Moon et al. applied stretching and twisting prior to the stabilization of their electrospun PAN yarns, and stabilization and carbonization of the nano-fibres were conducted by holding yarns at constant length [17]. The highest ultimate strength was about 1.0 GPa obtained owing to the existence of pervasive fibre breakage and low fibre alignment in the resulting fibres, as reported in their study. Most of the n-CFs obtained in the previous studies have obvious sheath/core structural imperfections, rough surfaces, or low fibre alignment. Therefore, there is a lack of necessary breakthroughs in developing high performance continuous CFs.

In this work, a multi-step hot-stretching approach was applied to produce high aligned electrospun continuous n-CFs with uniform structures and avoid the fibre breakage. The resulting n-CFs showed smooth surfaces, and no sheath/core structure was found across the fibre section, which indicated extremely high quality n-CFs were obtained compared to the reported work [13–15,17]. The electrical conductivity of the n-CFs reached 15.5 S/cm along the fibre direction, much higher than that reported in the literature [18]. With the multi-walled carbon nanotube (MWCNT)-reinforced samples as contrast, the tensile properties, storage modulus and AC resistivity of polyetherimide (PEI) composite membranes containing 1 wt% ball-milled n-CFs with and without multi-step hot-stretching treatment were analyzed. The experimental results indicated that the combination of multi-step hot-stretching and electrospinning process was a practicable approach to produce continuous n-CFs with high structural integrity and desirable properties.

2. Experimental

2.1. Materials

PAN terpolymer (precursor fibres, 93.0 wt% acrylonitrile, 5.3 wt% methyl acrylate, and 1.7 wt% itaconic acid, with an average molecular weight of 10^5 g/mol, density of 1.18 g/cm^3, and several micrometers in diameter) was supplied by Courtaulds Co., Nottingham, Nottinghamshire, UK. MWCNTs (purity, ⩾95%; diameter, 15–20 nm) were supplied by Nanotech Port Co. Ltd., Shenzhen, China, and dried at 80 °C prior to use. The PEI used in this study (ULTEM 1000) in a granular form was supplied by General Electric Co., USA. ULTEM 1000 is an amorphous, transparent and amber high performance thermoplastic with density of 1.35 g/cm^3. N,N′-dimethylformamide (DMF) and dichloromethane were purchased from Beijing Chemicals Co., China, to prepare the PAN and PEI solution, respectively.

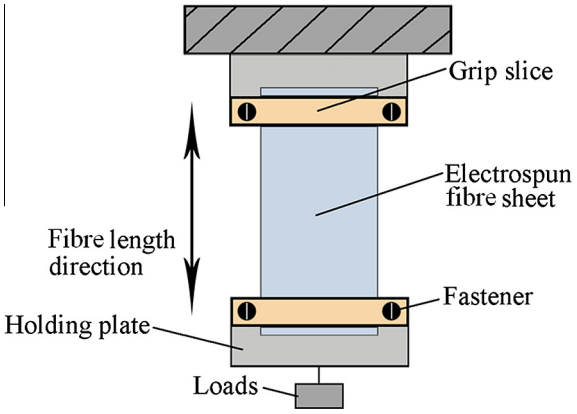

Fig. 1. Schematic of the chamber employed for hot-stretching and stabilization of nano-fibre sheets.

2.2. Sample preparation

2.2.1. Electrospinning

The PAN terpolymer was dried and dissolved in DMF to prepare a 14 wt% solution. After completely dissolving the PAN, the solution was put into an ultrasonic bath for 4 h. Subsequently, the solution was electrospun at room temperature (23 °C), with an applied voltage of 18 kV and a distance of 140 mm between the spinneret and the fibre collector [16]. The electrospun nano-fibres were collected in the form of a sheet on a 16-cm-diameter aluminium foiled rotating drum at a rotation speed of 10.0 m/s for 4 h.

2.2.2. Hot-stretching

In order to increase the orientation of macromolecules, and decrease the voids in the electrospun nano-fibres, the nano-fibres were drawn in three steps with different tensions from 120 to 140 °C. As shown in Fig. 1, the electrospun sheets (100 mm in length, 50 mm in width) were peeled from the aluminium foil and hot-stretched along the nano-fibre direction in air at 120 °C/12 MPa, 130 °C/13.5 MPa, and 140 °C/15 MPa in a chamber. The temperature of the chamber was controlled by the circulation of hot air, and the tensile forces were controlled by the use of different loads of appropriate weights. The tensile forces imposed during hot-stretching and stabilization were determined from the measured nano-fibre sheet weights, lengths, widths and the densities of PAN terpolymer (1.18 g/cm^3) and stabilized fibres (1.4 g/cm^3).

2.2.3. Stabilization

The stabilization was conducted in the same setup as hot-stretching from 180 °C to 280 °C with a constant flow of air through the chamber. The heating rate was 1 °C/min and finally stayed at 280 °C for 2 h to complete the stabilization. During the stabilization, a tensile force of 7 MPa was imposed.

2.2.4. Carbonization

The apparatus used for carbonization is shown in Fig. 2. The stabilized nano-fibre sheets were held at constant length and a form of ladder-type heating and a constant flow of high-purity nitrogen were applied in this step. 2 °C/min from the room temperature to 300 °C and stayed at 300 °C for a half hour, then 5 °C/min from 300 to 1200 °C and stayed at the last temperature for 10 min. After pyrolysis, the temperature was allowed to cool down to room temperature before the sample was exposed to ambient air.

2.2.5. Preparation of n-CF/PEI composite membranes

To grind the carbonized nano-fibre sheets into powders with a certain length, the carbonized nano-fibre sheets were milled for