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Polyaniline fibres containing single walled carbon nanotubes: Enhanced performance artificial muscles

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Abstract

Organic conducting fibres based on either inherently conducting polymers (polyaniline) or carbon nanotubes (CNTs) have previously been produced. In this work the integration of CNTs into polyaniline fibres has been achieved using wet spinning techniques. It is shown that addition of small amounts of CNTs significantly improves the mechanical, electronic and electrochemical properties of the polyaniline fibre. These improved properties result in increased electromechanical actuation when used as artificial muscle fibres.

Keywords: Polyaniline; Single wall carbon nanotubes; Composite fibres; Wet spinning; Artificial muscles

1. Introduction

Polyaniline (PANi) may exist in six different forms, ranging from fully reduced (luecoemeraldine) or the fully oxidized (pernigraniline). The most conductive form is emeraldine salt as highlighted in Scheme 1.

Wet spinning processes have been developed to produce high tenacity, conductive, electroactive fibres [1–3]. The initial requirement for wet spinning is the formation of high concentration solutions of appropriate viscosity and stability. Polyaniline solutions are known to undergo gelation upon standing such that they become unstable for fiber spinning [4]. Recent studies [5,6] have demonstrated that polyaniline emeraldine base (EB) is more soluble in *N*,*N′*-dimethyl propylene urea (DMPU) than *N*-methyl-2-pyrrolidinone (NMP), and that the onset of gelation is delayed in the DMPU solvent. To delay gelation, further gel inhibitors such as 2-methyl azaridine have been added [4]. Alternatively, the use of a reducing agent such as phenyl hydrazine to produce luecoemeraldine (LEB) can overcome the problem of gelation [7]. The fibres produced from EB and LEB can be acid doped to produce the conductive emeraldine salt (ES) form. Doping raises conductivity considerably but is detrimental to the mechanical properties [8].

In attempts to improve mechanical properties, blends of PANi with other polymers such as poly(*p*-phenylene tercphthalamide) [9] and poly-ω-aminoundecanole [10] have been produced. Unfortunately, the addition of high tenacity insulator polymers to the PANi matrix significantly decreases the conductivity. There is, therefore, a need to introduce reinforcing fillers that enhances mechanical properties of PANi fibre while having a positive impact on electronic properties. In this regard the use of carbon nanotubes (CNTs) as conductive reinforcement for PANi has been investigated and reported here.

The discovery of carbon nanotubes by Iijima in 1991 [11] captured the attention of researchers in a wide range of areas. CNTs have high tensile strength (100 GPa), high Young's modulus (0.6 TPa) [12] and exceptional electrical conductivity (5000 S/cm) [13]. CNTs have been used as a reinforcement filler in polyvinyl alcohol [14], epoxy [15] and poly(propionylethylenimine-*co*-ethylenimine) [16] host matrices. The addition of CNTs has also been found to increase the strength and conductivity of polypyrrole (PPy) [17]. The addition of CNTs to polyoctylthiophene (POT) has been shown to enhance the conductivity by five orders of magnitude with an 11% (w/w) percolation threshold [18]. The synthesis and characterization of PANi–CNT composites has also been inves-

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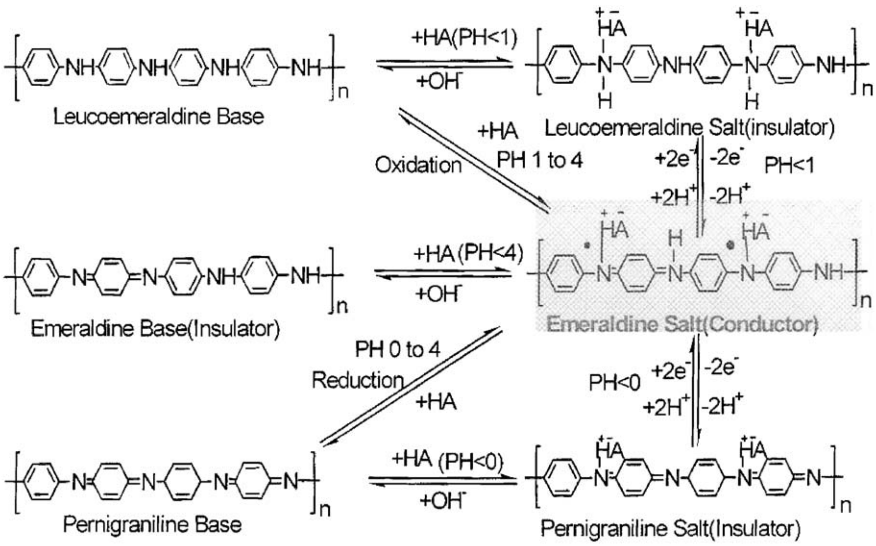

Scheme 1. The different forms of polyaniline.

tigated [19–22]. Direct dissolution of pristine CNTs (without chemical functionalization) in aniline can occur via formation of donor acceptor charge complexes [23]. Using this approach, PANi–CNT composite films have been fabricated by chemical [24] or electrochemical [22] polymerization of aniline containing dissolved CNTs. The electrochemical deposition of polyaniline on CNT substrates [25] has also been investigated. Alternatively, CNTs have been blended with polyaniline in solvents such as NMP or DMPU [26,27]. The enhanced electroactivity and conductivity of the PANi–CNT composite films has been attributed to the strong interaction between CNTs and PANi, which enhances the effective degree of electron delocalization. It was also shown that PANi containing 1% CNT is more mechanically stable than neat PSNi [27].

The present work describes wet spinning of PANi–CNTs composite fibers. Protocols that enable a stable feed solution containing 10% (w/w) PANi and 2% (w/w) CNTs in DMPU have been developed. The resultant composite fibers show significant improvement in conductivity, electroactivity, mechanical strength and performance as electromechanical actuators (artificial muscles).

2. Experimental

Free standing bucky paper was obtained from purified single wall carbon nanotubes (Hipco@CNI) using a previously reported procedure [28]. The CNTs were dispersed at 0.1 mg/ml in a 0.5 wt% aqueous solution of Triton X-100 using 30 min sonication. The bucky paper was obtained after filtration of dispersed solution on a 0.02 μm. Whatman anodisc followed by washing with methanol and water and drying at 130 °C for 30 min. The appropriate amount (10, 20, 40 mg) of the CNT bucky paper was sonicated in 20 g DMPU (98%, Sigma–Aldrich) for 2 h at 60 °C to drive the CNTs into solution. 50 mg of EB powder (Santa Fe Science and Technology) (MW = 280,000) was then added to the CNT dispersion while sonicating for a few seconds. Then 2 g of polyaniline (EB) and 0.65 g phenyl hydrazine were added gradually over a 2 h period to the PANi–CNT–DMPU dispersion at 5 °C. The spinning solution was stirred another 2 h (40 rpm) at 0 °C. Finally, a further 2 h stirring under a dynamic vacuum ensured a bubble free solution ready for fibre spinning.

Prior to spinning, the solution was passed through a 400 μm filter then transferred to a nitrogen (N_2) pressure vessel. Nitrogen pressure was used to drive the spinning solution through a second filter (200 μm, Millipore) then through a single hole spinneret with $L/D = 4$ and $D = 250$ μm and finally to the coagulation bath. The lengths of the first and second bath were 2 and 1 m, respectively. Both baths contained 10% (w/w) NMP in water at 20 °C. The N_2 pressure was adjusted to between 20 and 80 psi to control the injection rate for the spinning dope. In the first coagulation bath the solution solidified and the emerging fibre was taken up on the first bobbin ($D = 2.5$ cm) at a linear velocity of 2 m/min. The semi-solid fibre was then passed through the second bath and collected using a linear velocity of 4 m/min on the second bobbin ($D = 5$ cm). The fibre was then kept for 2 h in a water bath to reduce the solvent content, and then for 12 h in air at room temperature in preparation for the hot drawing process.

The drawing process involved hand stretching of the as-spun fiber across a soldering iron wrapped with Teflon tape and heated to 100 °C. This process was used to stretch the fibers to approximately twice their original length.

The complete removal of residual solvent was carried out firstly by extraction in a water bath for 24 h followed by drying in a vacuum dryer at 50 °C for 12 h. The fibres were then doped in methane sulfonic acid (1 M) for the required time followed by air-drying.

A Shimadzu 1601 and a Gary 5000 were employed for UV–vis and NIR spectroscopy, respectively. Mechanical tests were carried out using a dynamic mechanical analysis (DMA) instrument Q-800 (TA series) in strain rate mode to record the force–displacement data generated at constant temperature (10 mm gauge length, 0.5 mm/min).