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Processing and characterization of polyethersulfone wet-spun nanocomposite fibres containing multiwalled carbon nanotubes

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ABSTRACT

Novel semi-conductive fibres from multiwalled carbon nanotubes (MWCNT) based-polyethersulfone (PES) have been produced by wet spinning insight of incorporation in composite matrix. *N*-methyl-2-pyrrolidone (NMP) was chosen as dispersing medium for MWCNT by sonication and as solvent for PES. MWCNT reinforced-PES fibres were spun into water coagulation bath with an observed instantaneous liquid-liquid demixing. After washing and drying steps, fibres are either directly characterized or annealed at 250 °C during 15 min and 24 h prior to characterization. Scanning electron microscope (SEM) micrographs performed in each configuration disclose presence of macrovoids, pores and empty spaces inside fibres before thermal annealing whereas after thermal annealing, fibres display a cohesive and continuous morphology. A significant mechanical properties improvement of the wet-spun fibres is noticed by rising annealing time. Transmission electron microscope (TEM) investigations have also been carried out and reveal a two phases microstructure in unannealed fibres with a separation between a PES-rich continuous phase and NMP-rich nodules containing exclusively MWCNT. TEM images suggest also thermal annealing process allows solvent evaporation, MWCNT aggregation and a conductive nanofillers network formation in PES nanocomposite fibres. Electrical measurement in unannealed fibres indicate a deficiency of conductive character between 0.25 and 2 wt.% MWCNT whereas a lowering electrical percolation threshold is achieved in fibres by increasing annealing time, around 1.5 and 1 wt.% MWCNT for respectively a 15 min and 24 h thermal annealing. Influence of MWCNT sonication duration on electrical conductivity is also examined showing a gradually reduction of fibres' electrical conductivity by dispersion time increasing until losing their semi-conductive state. A dispersion analysis let suppose that a whole MWCNT agglomerates network is split in smaller but denser clusters which are dispersed and taken away from each other during sonication, which causes the conductive path rupture.

1. Introduction

Nowadays, the whole aerospace industry is dealing with major challenges such as cost savings, weight reduction and improved durability. The mutation from metallic to composite parts is an important key for reducing costs and the environmental imprint caused by transport. However, this turn to composites causes technical issues such as for lightning strike protection or electromagnetic interference (EMI) shielding due to low electrical conductivity, low toughness, and poor transverse and interlaminar properties of the composites [1]. Solutions have been found, such as the presence of metallic mesh on the surface for the electrical conductivity issue, but this is to the detriment of weight-saving requirements. The development and incorporation of new material combinations in composite through innovative synergies appear to be an adequate solution. Thus, there is growing demand from the aerospace industry to develop carbon nanotube (CNT)-based materials. These novel materials have to be produced in the form of film, yarn or even fibre based on high-performance engineering thermoplastics for CNT pre-orientation and alignment [2] with a view to their insertion in composite matrices.

Since their identification by Iijima [3], CNT have continued to draw the attention of industry and science owing to their exceptional mechanical and electrical properties [4]. Their extraordinarily high aspect ratio allows the material properties to be enhanced with a low percentage of incorporated nanofillers compared to other carbon fillers, such as carbon black [5]. To form CNT-based fibres, the nanofillers are often incorporated in

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conventional polymer matrices, such as polypropylene [6], polyamide [7], polylactic acid [8] or even polymethylmethacrylate [9] mainly by electrospinning or melt spinning. These CNT-based fibres can be used as sensors due to the percolating network formed inside [10]. However, the processing of polymeric CNT-based fibres still faces some challenges, particularly regarding CNT dispersion and viscosity issues. Firstly, CNT tends to agglomerate creating weak area and centres of stress concentration in the fibres, leading to a significant decrease of mechanical properties. Secondly, the CNT incorporation in polymer matrix causes a rise of viscosity which could affect the fibre formation [2,11]. The use of dissolvable thermoplastic fibres, films or veils as reinforcement to improve fracture toughness and thermo-mechanical properties of thermosetting composites is fast-growing. In particular, systems with polyetherimide (PEI) [12,13], polysulfone (PSF) [14], phenoxy [15], polyamide [16,17] and polyester [18] have been investigated. High performance polymers such as polyethersulfone (PES) are also well known for their miscibility and compatibility with epoxy resins, allowing an improved toughness of the resin [19,20]. In this way, the combination of CNT and PES could enable electrical and mechanical properties of the composites to be improved through the incorporation in thermoset resin. At the moment, PES is particularly implemented in the form of hollow fibre membranes for gas and liquid filtration by using the dry/wet inversion process [21] or in some cases by electrospinning [22]. The processing of PES-based fibre tackles the problem of technical issue arising from the high viscosity of PES especially in the melt mixing process. The wet spinning process has therefore been chosen as an alternative way for implementing this thermostable polymer in fibre form. The first step of this process is based on the standard phase-inversion technique by coagulation, as used for membrane formation [23,24]. The phase inversion involves the mixing and demixing of a three-component system: solvent/polymer/non-solvent [25]. The polymer is firstly solubilised in a solvent to form a homogeneous solution in a stable thermodynamic state. A change in thermodynamic state is then induced by contact with the polymer solution with a coagulation solution composed of a non-solvent of the polymer which is also miscible with the polymer solvent. This change creates equilibrium between two phases: a polymer-poor liquid phase and a polymer-rich liquid phase allowing different possibilities of morphology (porous, dense or mixed) which will also depend on a diffusional exchange of solvent and non-solvent and their demixing kinetics during material formation [26,27]. Then drawing, washing, drying, finishing and winding steps often complete this first step to give added values to the fibres.

In view of the new challenge to spin high-performance polymers, such as PES and its CNT-based nanocomposites, this paper aims at suggesting an alternative method based on the wet-spinning process to form novel semi-conductive fibres for composite materials. A lab scale wet spinning prototype has been developed to form PES/MWCNT fibres and will be explained in the following part. The influence of different spinning conditions and thermal annealing on the fibre morphology and mechanical properties will be investigated and discussed. Finally, this study will focus on the electrical conductivity of the fibres according to MWCNT content before and after the annealing treatment in correlation with morphology and dispersion analysis.

2. Experimental methods

2.1. Fibre preparation

2.1.1. Materials

The polyethersulfone (PES) used in this study is PES 4100 G (Mw = 37,500) supplied by Sumitomo Chemicals (Japan). This thermostable polymer is a high-performance amorphous polymer with a glass transition at around 226 °C and a density evaluated as d = 1.37 g/cm^3.

Multiwalled carbon nanotubes (MWCNT) are produced using the catalytic vapour deposition (CVD) system and were supplied by Nanocyl (Belgium) under the reference NC7000® with a degree of purity equal to 90%. Their average diameter and length are respectively 9.5 nm and 1.5 μm with a surface area of 300 m^2/g. *N*-methyl-2-pyrrolidinone (NMP) from Sigma Aldrich is employed as a solvent to disperse MWCNT and to dissolve PES. Water will be used as the coagulation bath solution.

2.1.2. Spinning solution preparation

A MWCNT dispersion was prepared in NMP (*N*-methyl-2-pyrrolidone) from 0 to 2 wt.% MWCNT content with a sonication system in a continuous cycle at 8.4 kHz. This NMP/MWCNT solution is sonicated between 5 min and 4 h to study the influence of the dispersion time on the morphology and properties. At room temperature, PES is dissolved into NMP-MWCNT solution during several hours on a stage rotating at around 400 rpm. The NMP-MWCNT/PES solution is in a 90/10 wt.% proportion to minimize the viscosity issue during the wet-spinning process and to facilitate injection through the syringe needle.

2.1.3. Wet-spinning process and post treatment

The wet-spun nanocomposite fibres are produced by using a lab scale wet spinning prototype (cf. Fig. 1). Once complete solubilization is obtained, NMP-MWCNT-PES solution is passed through a 10 ml syringe and a syringe pump is used to inject the spinning solution through a single hole spinneret with a diameter of 500 μm at 100 ml/h into a coagulation bath. Due to the boundary pressure of the syringe pump and the high viscosity of spinning solution, the flow appears discontinuous but regular. The coagulation bath contains 100% water at room temperature. The nanocomposite fibre is formed according to the phase inversion process in the coagulation bath and is held during 24 h in another bath containing water to reduce the solvent content. The fibre is then dried in ambient air and annealed at 250 °C between 15 min to 24 h prior to characterizations. Fibres are annealed under a low constraint (unquantifiable) between two clips to allow pre-drawing and maintaining the fibres in the oven. The influence of thermal annealing on fibre properties will be discussed later.

2.2. Fibre characterization

2.2.1. Morphology analysis by SEM

Scanning electron microscopy (SEM Hitachi S4700) was performed by UMET laboratory from University Lille I (France) to gain information on the morphology of wet-spun fibres. The cryofracture surfaces were analysed using an SEM Hitachi S4700 operating at 6 kV and 15 mA. The specimens were immersed into liquid nitrogen for 2 min before breaking. The fracture surface was carbon-coated prior to observation.

2.2.2. Dispersion analysis by TEM

Transmission electron microscopy analyses of the wet-spun PES fibres were performed with a PHILIPS CM 120 device in order to study the influence of thermal annealing and time of dispersion of the MWCNT distribution. Ultramicrotomy has been used to prepare TEM samples with a thickness of 70 nm. The wet-spun fibres were embedded in the polyester/styrene resin M01510 from CCP composites with 1 wt.% of initiator MEKP (Sigma-Aldrich) and 0.2 wt.% of accelerator NL 51 P (AksoNobel). Then, the samples polymerized during 24 h at room temperature.