CARBON NANOTUBE NANOCOMPOSITE FIBERS: PROCESSING AND MILLIFLUIDIC CHARACTERISATIONS

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Keywords: nanocomposites, fibers, millifluidic, nanotubes.

Abstract

In nanocomposite materials, the final properties are strongly related to the distribution of the carbon nanotubes (CNTs) inside the polymer matrix, adding new performances to the material. To a certain extent, the composite structure can be tuned during processing, through the control of the dispersion or interactions between the nanotubes and the polymer, and the spatial re-arrangement of the structure. This paper is dedicated to the synthesis of carbon nanotube fibers via wet-spinning. The method has been scaled-up and a new pilot for continuous production has recently been set-up. Moreover, an original millifluidic method has been developed in order to characterize the strength of the fiber during the process. This millifluidic in-situ characterization method can be extended to various fiber processes, as many synthetic or natural polymer fibers are produced via the transformation of a liquid solution into a solid filament. In particular, electrospun nanofibers could be characterized by this method.

1 Introduction

Many fiber production technologies are based on “wet spinning” processes [1, 2]. These processes can be subdivided in various methods depending on the used materials. Natural or synthetic polymer solidification can indeed result from various phenomena including dehydration, injection in poor solvents, pH variations, temperature variations, etc. [2-9]. The kinetics of solidification is primarily limited by the diffusion of the solvent, additives and polymer molecules. Such mechanisms can be quite complex and differ from a system to another depending on the specific chemical, physical and structural features of the used materials. Most of the time, the experimental accessible knowledge on the kinetics of fiber formation is essentially based on observations of the initial and final fiber materials [2]. The intermediate stages of solidification remain elusive in spite of their critical importance. A reason for our lack of knowledge is due to the technical difficulty of probing the mechanical strength of a material that is continuously moving and solidifying in a very short time. We propose in this work to use the circulation of fibers in extensional flows to overcome this difficulty and assess the in-situ solidification of wet-spun fibers. Extensional flows have already been shown to be efficient at inducing the scission of polymer chains at a molecular scale [9-13]. Even though the scission of a chain in an extensional flow has not yet been directly visualized, this phenomenon has been the topic of several previous studies. Extensional flows are also used for example to apply mechanical stress on living cells [14] or

pressure variations around emulsion droplets [15]. A similar approach is explored in this work at a macroscopic scale using filaments of several tens of microns in diameter and indefinite length. These are the typical dimensions of actual synthetic textile and natural fibers. The fibers experience a tensile stress due to viscous drag forces arising from velocity gradients of the surrounding fluid along the fiber axis. The fibers break when the stress exceeds the fiber tensile strength, thus allowing the visualization of the scission of a chain in an extensional flow. This approach is validated with the example of the solidification of polyvinyl alcohol (PVA)-carbon nanotube composite fibers [16, 17]. Nanoparticles based wet-spun fibers are currently being developed to achieve fibers with novel or enhanced properties and functionalities [3, 16-23]. Moreover, the method is also successfully used and validated to characterize the mechanical properties of nanofibers, made by electrospinning.

2 Materials and testing methods

Single walled nanotubes provided by Thomas Swan are used. The nanotubes are dispersed at a weight fraction of 0.3wt% in an aqueous solution of sodium dodecyl sulphate (SDS). The dispersions are homogenized by a sonication treatment during 90 min using a Branson S-450D tip sonicator operating at 40 W. Sonication induces the scission of the nanotubes leading to an average length of the nanotubes of about 500nm. The PVA was obtained from Seppic-France. Different molecular weights are tested, from 27kg.mol^{-1} to 195kg.mol^{-1}. The hydrolysis ratio of all the investigated polymers is 99%. The PVA is dissolved in water at 90°C. The concentration of the PVA is adjusted so that all the solutions exhibit a viscosity of 125 cPs at room temperature. The following concentrations are used: PVA 195kg.mol^{-1} at 5.0wt%, PVA 145kg.mol^{-1} at 6.5wt%, PVA 61kg.mol^{-1} at 10wt% and PVA 27kg.mol^{-1} at 15wt%. The solutions are Newtonian in the experimental conditions of the work. The fibers obtained by the coagulation of the nanotube dispersion into the co-flowing stream of the PVA solution [11] exhibit a composite structure with a large fraction of nanotubes (>15 wt%) embedded in a PVA matrix. The nanotube dispersion is injected through a syringe needle with a conical tip that has a 300µm internal diameter. The injection rate of the dope is 50µL.min^{-1}. The glass pipes have an internal diameter of 2.4mm. The total length of the line is 2 meters. The PVA solution is injected with a pump (Labotron LDP-4) in the pipe and circulates along the line at a controlled flow rate of 150mL.h^{-1}.
Nanocomposite PMMA-nanotubes fibers have been produced by electrospinning, following an already described method [24].

3 Results and discussion

As already described in reference [16], the fibers are produced by injecting an aqueous dispersion of nanotubes in the co-flowing stream of an aqueous PVA solution. This is achieved by using co-axial pipes (Figure 1). A coagulation of the nanotubes occurs, resulting from the adsorption of polymer chains at the interfaces of the nanotubes [26]. After some time, the fiber becomes “solid” and can be extracted from the coagulating liquid. It can then be treated by classical methods of fiber technologies [1].

Figure 1: experimental set-up used to induce an extensional flow around a fiber. As shown in the upper drawing, the fiber is translated by the surrounding fluid at the centre of the pipe at a controlled velocity. The extensional flow is achieved with a diameter constriction of the pipe. The constriction can be located at different distances *L* from the spinneret. This allows estimating the fiber strength at different residence times.

The extensional flow used to probe the fiber solidification is achieved in a pipe with a diameter constriction. The constriction can be put at various places along the pipe. This allows the progressive solidification to be probed at different stages of the process. When the constriction is close to the spinneret from which the liquid dope is injected in the coagulation medium the fiber is still weak and breaks easily. When the constriction is placed further down along the line, after the fiber has spent a longer residence time in the coagulating fluid, the fiber can sustain a much greater stress. This reveals a more advanced stage of solidification. The practical and basic interests of this approach have been validated by testing the efficiency of different polymers at inducing the coagulation of carbon nanotube fibers [17].

The nanotubes and the polymer form a gel like solidifying structure which is transported along a line by the surrounding PVA solution. The system is deformed in extension and the deformations involve forces on the physical bonds. The latter arise from the adsorption of polymer chains onto the nanotubes. An experimental device to probe the deformation and failure of the present fibers should therefore have the capability to induce stresses up to a few kPa. Such a device is made of a line of transparent glass pipes connected with joints. The mean velocity of the PVA solution is of $0.5 m.min^{-1}$ at the centre of the pipe. In the above conditions, the coagulating fibers have a diameter of approximately 130µm. The geometrical parameters of the constrictions entirely determine the extensional strain rates, which vary from approximately 1.0 sec^{-1} to 4.3 sec^{-1}. But stronger or weaker extensional flow fields can simply be achieved by using different diameter constrictions. The location of the constriction along the spinning line is changed by placing the diameter reduction in between different joints of the line. This allows the behaviour of the fiber to be probed at different times after the nanotube dispersion has been injected in the PVA solution.

The fluid accelerates along the axis of the pipe at the entrance of the constriction. This induces the development of an extensional flow field. The gel-fiber transported by the fluid is stretched in response to the acceleration of the supporting fluid. As a result, parts of the fiber upstream of the constriction are drawn and circulate faster than the supporting liquid. As sketched in Figure 1, the velocity difference results in a drag force F_l pointing upstream. By contrast, parts of the fiber downstream of the constriction circulate more slowly than the surrounding fluid because they are still bound to the rest of the fiber. The velocity difference on this side leads to a drag force F_r pointing downstream. The combination of these viscous forces result in a tensile stress with a maximum at a well defined point where $F_l = F_r$. The fiber breaks at this point if the maximum stress exceeds the tensile strength of the fiber. The strength of the fiber evolves rapidly as the nanotubes remain in contact with the coagulating polymer solution. Indeed the polymer chains diffuse throughout the fiber and bind the nanotubes together. Assessing the kinetics of this solidification becomes possible by using different extensional flow geometries and by placing the constriction at different locations along the spinning line.

Several important features can be deduced from these experiments. If the fiber does not spend a sufficient time in the coagulating medium before experiencing the constriction, it is cut into small fragments of remarkably regular size. This confirms that the fiber breaks for a well defined maximum of stress that we could quantitatively estimate by measuring the length of the cut fragments [17]. As shown in Figure 2, it is also observed that the length of the fragments increases when the fiber stays longer in the coagulating medium in the pipe. This quantitatively reflects the increased solidification of the fiber with its residence time.

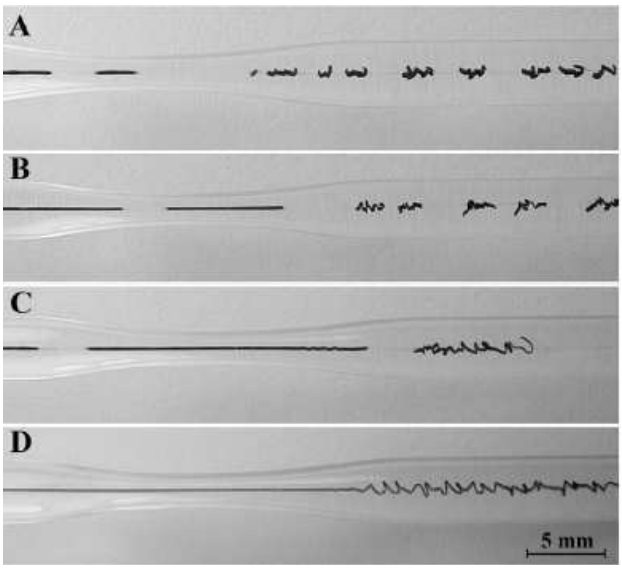

Figure 2: Experimental realization of fiber scission in an extensional flow. From picture (A) to (D), the residence time of the fiber in the PVA solution is increasing. The molecular weight of the PVA is Mw = 195kg.mol^{-1}. When the fiber is still too weak to sustain tensile forces induced by the extensional flow in the diameter constriction of the glass pipe, it is cut into small fragments of uniform length. The longer the residence time is, the longer the fragments are. In the lower picture (D), the constriction is placed even further from the spinneret. The fiber is stronger and can pass through the constriction without breaking.

The molecular weight of the coagulating polymer is one of the main factors in the spinning process since it is expected to strongly affect the strength of the fiber and the coagulation kinetics. Using the above method, we observed than in spite of an expected slower diffusion the longer polymer chains induced a faster and more effective solidification. This solidification was probed in the present conditions up to a typical stress of about 20kPa. Only fibers that exhibited a tensile strength greater than this value could pass through the constriction without being cut.

The constriction has also been successfully used to characterize the tensile strength of electrospun nanofibers. The nanofibers, suspended in a carrier fluid, experienced the constriction and were cut into fragments which were then collected and analyzed with optical microscopy. A statistical measurement of the fragment lengths was done and the average strength of the fibers could be extracted from the experiments. The obtained values were in good agreement with those obtained on the same fibers by pull-out experiments with an AFM cantilever [19]. This proves that the constriction method can be transposed to the study of various types of pure and composite fibers.

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