DEVELOPMENT OF A POST-PROCESSING METHOD TO TAILOR THE MECHANICAL PROPERTIES OF CARBON NANOTUBE/NYLON FIBRES

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Abstract

In this work, a methodology to improve the mechanical properties of nanocomposite fibres was developed. Multi-walled nanotubes (MWNT) were first combined into a polyamide 12 (PA12, nylon 12) matrix through twin-screw extrusion. Pellets were subsequently melt spun with a capillary rheometer. To further improve the fibres' mechanical properties, three post-drawing parameters were systematically investigated: temperature, drawing speed and elongation. Elastic modulus and tensile stress values were increased by at least 300% and exhibited the best improvements under the following post-drawing conditions: 140°C and 500% elongation, regardless of drawing speed.

1 Introduction

Over the past decades, there have been significant advancements towards the development and manufacturing of high performance fibres with exceptional mechanical properties. These exceptional properties are obtained through the alignment and stretching of the polymer chains which was perfected through specific manufacturing techniques developed over the years [1]. Further improvement now lies in the reinforcement of the fibres themselves by using micro and nano particles. In the past two decades, carbon nanotubes (CNT) have been studied as reinforcing materials and have showed to improve mechanical, thermal and electrical properties [2, 3].

As stated previously, one of the main methods to improve the mechanical properties of thermoplastic fibres consists of enhancing the alignment of the polymer chains by post-drawing. This process has been extensively studied for conventional thermoplastic fibres, especially for melt spinning [4-6]. In the past 10 years, a certain number of studies were published regarding the effect of post-drawing on various thermoplastic fibres reinforced with single-walled and multi-walled nanotubes (SWNT and MWNT). Haggenmueller *et al.* found that the draw ratio (*DR*) increased tensile stress, but did not have a significant effect on the elastic modulus or the alignment of the CNTs for MWNT/polymethyl methacrylate (PMMA) fibres [7]. Houphouet-Boigny studied these properties in more details with melt spun polypropylene (PP) fibres containing MWNTs [8]. Fibres were post-drawn at room temperature according to three different winding speeds and results were similar to Haggenmueller *et al*. The modulus of elasticity data did not show any particular trend, but a maximum increase of 600% in tensile stress was measured for the highest *DR* values and CNT contents. Based on TEM and two-dimensional X-ray diffraction patterns, a preferential alignment of the CNTs was qualitatively observed along the fibres axis. More recently, studies published by Mazinani *et al.* and Sulong *et al.* reported data on cold-drawn MWNT/polyethylene (PE) and MWNT/polyethylene terephthalate (PET) fibres, showing that mechanical drawing did not significantly influence the properties, regardless of CNT content [9, 10].

It is expected that post-drawing at high temperature would however lead to better results as it would allow the polymer chains and nanotubes to move and rearrange themselves more easily. A certain number of studies reported such a trend for MWNT/nylon 12 and SWNT/PET fibres [11, 12]. Perrot *et al.* measured modulus and yield strength values as high as double those of unreinforced fibres with a maximum draw ratio of 7. Moore *et al.* however published contradicting results for CNT/PP fibres [13]. The addition of CNTs mostly led to worse elastic modulus and tensile strength values, before and after hot drawing.

In this paper, a systematic investigation of the effects of post-drawing parameters of MWNT/PA12 fibres on their tensile properties and morphology will be presented. This work aims to evaluate: a) the possibility to further improve the mechanical properties of melt spun MWNT/PA12 fibres produced from masterbatches commercially available by applying a post-drawing step, and b) the most important post-drawing parameters in terms of speed, temperature and elongation. The results will be compared to commercially available high performance fibres and their expected ballistic performance.

2 Materials and testing methods

2.1. Materials

Rilsan® polyamide 12 and Graphistrength C M1-20 masterbatch provided by Arkema Inc. were used in this study. The masterbatch was diluted and mixed with PA12 through a twin-screw extruder to create nanocomposite samples with lower CNT contents of 0.5 wt%, 1.0 wt%, 2.0 wt% and 5.0 wt%. A masterbatch of neat PA12 was also prepared under the same thermal conditions for comparison. Prior to each processing step and experiment, the material was dried at 80°C under regulated pressure for at least 48 hours.

2.2. Melt spinning and post-drawing

Nanocomposite pellets containing 0 wt%, 0.5 wt%, 1.0 wt%, 2.0 wt% and 5.0 wt% MWNT were extruded with a Rosand capillary rheometer. A quantity of 50 g to 60 g of material was spun for each masterbatch through a die with a 1 mm diameter hole. The speed of the piston was set at 10 mm/min and the fibres were collected on a roller at a speed of 152 m/min. The fibres' diameters varied between 110 and 200 μm, with corresponding draw ratios from 83 to 25. Post-drawing was performed with a Brückner biaxial stretching machine. Fibre samples of 115 mm in length were cut and individually clamped in the machine at room temperature. The effects of drawing temperature (100°C, 120°C, 140°C), speed (1 m/min, 3 m/min, 5 m/min) and elongation (300%, 500%) were investigated. A total of 128 fibres were stretched, but drawing speeds of 5 m/min and final elongations of 500% were not always successfully achieved for all samples as fibres had the tendency to break under these conditions.

2.3. Testing methods

Tensile tests were performed with an Instron 5548 Microtester machine with a load cell of 5N. A gauge length of 25 cm and a cross-head speed of 5 mm/min were used. Fibre samples of approximately 50 cm in length were glued to a paper frame, according to the ASTM standard D3379-75. The fibres diameter was measured with a Nikon Eclipse L150 optical microscope at a magnification of 10X. The dispersion of the nanotubes within the filaments was assessed through TEM (Philips CM200 200kV). Fibres were cut transversally at an angle of approximately 30^{o} and 80 nm thick slices were cut by cryo-microtomy (-100^{o}C) using a Leica Ultracut UCT microtome.

3 Results and discussion

3.1. Mechanical properties

The elastic modulus, *E*, was calculated as the slope of the stress-strain curves between 1.0% and 4.0% strain. In order to adequately compare the results and eliminate dimensions effects, the average *E* values were plotted as a function of draw ratio on Figure 1 a) to c) for all elongations and drawing speeds. The results were divided in 3 sections:

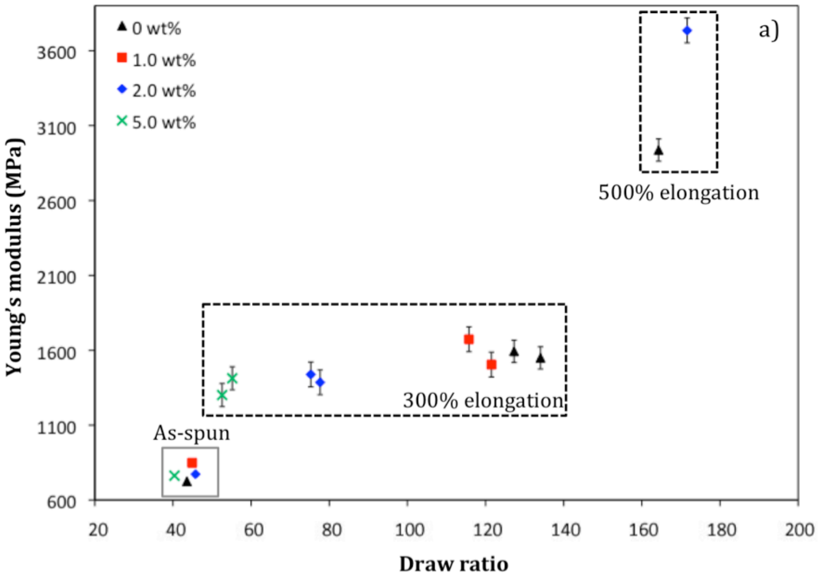
1) As-spun fibres (grey square in lower left corner);
2) Fibres post-drawn until 300% elongation, at all drawing speeds (centered dashed rectangle);
3) Fibres post-drawn until 500% elongation, at all drawing speeds (dashed rectangle in upper right corner).

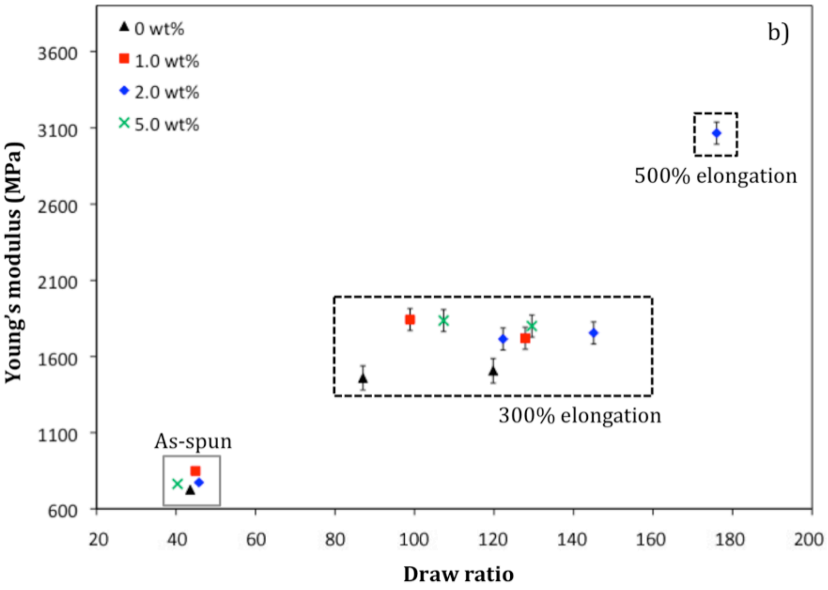
Drawing speeds of 5 m/min could only be reached at 140^{o}C. Moreover, the drawing speed, within the range investigated, did not influence significantly the elastic modulus. The values are therefore not identified on Figure 1. Figure 1 a) shows results for fibres post-drawn at 100^{o}C. After 300% elongation, the measured elastic modulus ranged between 1.2 GPa and 1.7 GPa. Highest values were obtained for pure PA12 fibres and samples containing 1.0 wt% MWNT. The draw ratio and drawing speed did not have a significant effect on the results. At 100^{o}C, it was only possible to stretch fibres containing 0 wt% and 2.0 wt% MWNT to a 500% elongation at 1 m/min. For these conditions, nanocomposite fibres exhibited the best elastic modulus, 3.7 GPa.

Figure 1 b) shows the average *E* for fibres post-drawn at 120^{o}C. After 300% elongation, the elastic modulus values obtained at 120^{o}C are slightly higher than those obtained at 100^{o}C. *E* values vary between 1.4 GPa and 1.8 GPa. Fibres containing 2.0 wt% and 5.0 wt% MWNT possess a higher elastic modulus than pure PA12 filaments. However, there was no clear influence of the nanotubes weight fraction as all points were distributed horizontally. Highest *E* value was obtained at 500% elongation, 3.1 GPa, which was only possible to reach with samples containing 2.0 wt% MWNT, at 1 m/min.

Finally, Figure 1 c) shows the average *E* for fibres post-drawn at 140^{o}C. After 300% elongation, data points are more scattered. In addition, for similar *DR*, a clear increase in modulus is obtained with MWNT content, from 1.0 wt% to 5.0 wt%. The drawing speed did not have a significant effect on the results. Finally, highest elastic moduli were obtained after 500% elongation for filaments containing 5.0 wt% MNNT (3.8 GPa), followed by 2.0 wt% MWNT (3.5 GPa) and 1.0 wt% MWNT (3.4 GPa).

The elongation at break ranged between 300% and 350% for as-spun fibres containing 0 to 5.0 wt% MWNT. After post-drawing, the draw ratio had the most significant impact on the reduction of the strain at break. After 300% elongation, all samples broke below 150% and after 500% elongation, all fibres broke below 130%. In both cases, strain at break decreased with an increase of CNT content. The tensile strength was reported to increase by at least 300% after post-drawing of as-spun fibres. Temperature and drawing speed did not have a significant effect on the values, but it was observed to generally increase with MWNT content for the same post-drawing conditions. Compared to post-drawn PA12 fibres, tensile strength improved by up to 62% at 300% elongation and 41% at 500% elongation.





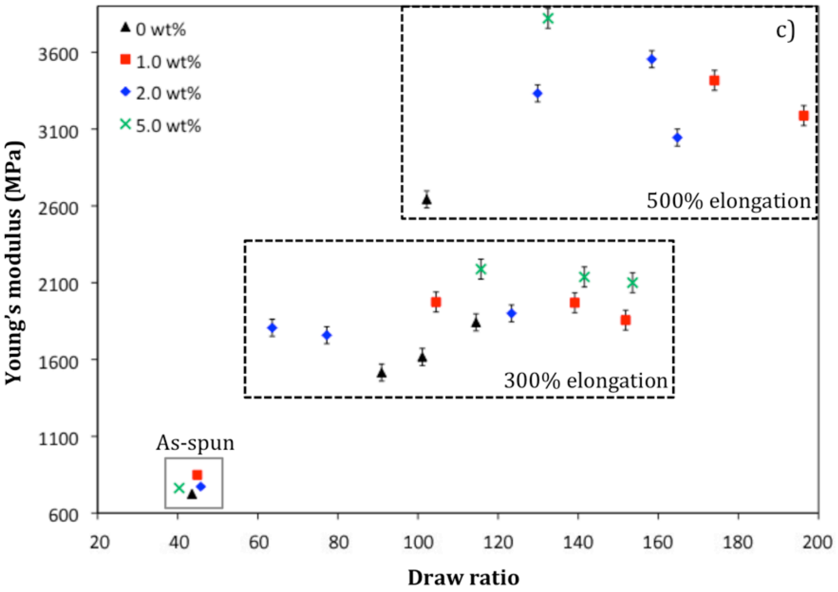


Figure 1. Average Young's modulus for MWNT/PA12 fibres post-drawn at 1 m/min at a) 100°C, b) 120°C, and c) 140°C

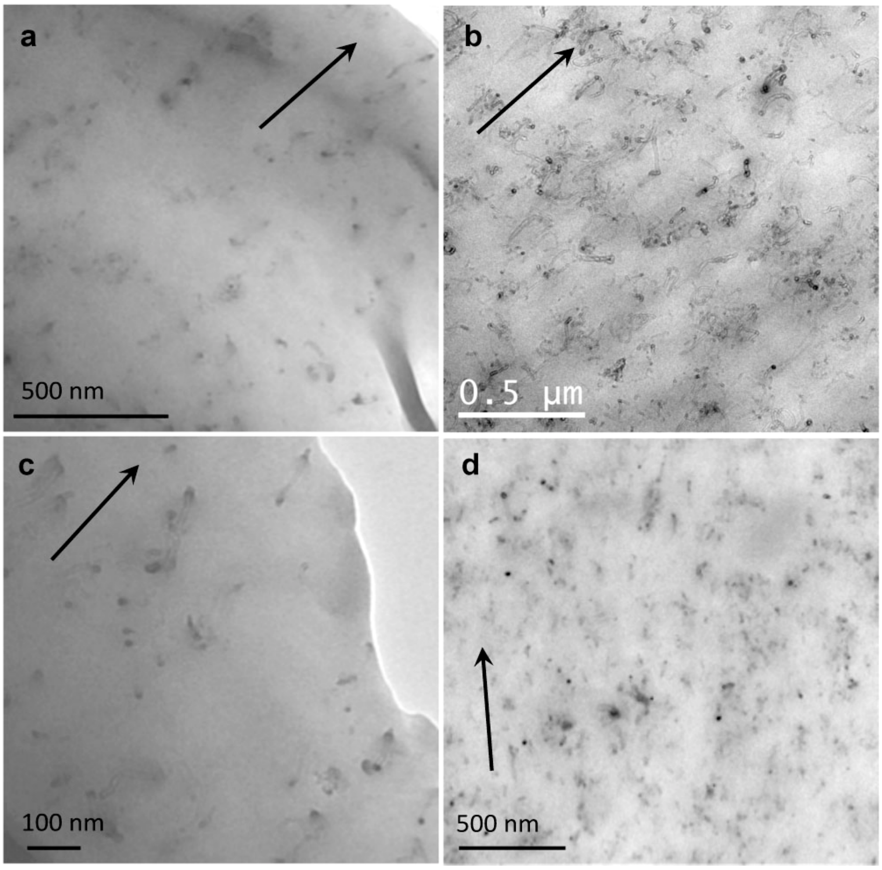


Figure 2. TEM images of PA12 fibres containing 1.0 wt% MWNT, post-drawn until 300% (a) and 500% (c) elongation and fibres containing 5.0 wt% MWNT, post-drawn until 300% (b) and 500% (d) elongation, at 140°C. The black arrows show the direction of the fibres' axis.

TEM images of post-drawn fibres at 300% and 500% elongation are presented in Figure 2 for 1.0 wt% and 5.0 wt% MWNT. After 300% elongation (Figure 2 a and b), the nanotubes distribution was relatively uniform, but they did not appear to be specifically aligned along the fibre's axis. After 500% elongation (Figure 2 c and d), the nanotubes were more dispersed and the presence of clusters was considerably reduced, compared to as-spun fibres and fibres post-drawn until 300%. As for the alignment of the MWNTs, the pictures revealed the presence of nanotubes aligned along the fibres' axis, but their alignment remained modest, even at the highest elongation value.

3.2. Predicted ballistic performance

Following the mechanical characterization of nanocomposite fibres, it is of great interest to relate their properties to tangible applications. A significant field of application for CNT/thermoplastic fibres lies in the improvement of personnel protection gear. It is expected that the addition of carbon nanotubes could improve the properties while reducing the overall mass of the equipment. This section will briefly discuss the expected performance of MWNT/PA12 fibres for ballistic impact compared to materials commercially available.

According to a model developpped by Cunniff [14-16], the main fibre properties to take into consideration when designing textile-based protective gear are: tensile strength (σ_m), tensile strain at break (ε_m), fibre density (ρ_f) and elastic modulus (E). In terms of personnel armour, the ballistic impact potential can be evaluated through a parameter, noted U^*, and described by Equation (1):

$$U^* = \frac{\sigma_m \varepsilon_m}{2\rho_f}\sqrt{\frac{E}{\rho_f}} \tag{1}$$

U^* corresponds to the fibre specific toughness multiplied by the fibre strain wave velocity and is usually expressed as $(U^*)^{1/3}$ in m/s. The specific toughness of MWNT/PA12 fibres presented in this work was estimated based on the area under their respective stress-strain curves.

Figure 3 shows the U^* parameter of a few common high performance fibres: Kevlar®, carbon, nylon 6,6 and polypropylene (PP, Curv™). Those values were compared to MWNT/PA12 fibres. For as-spun filaments, U^* increases with nanotube content, up to 5.0 wt%, where it reaches a plateau at $(U^*)^{1/3} = 500$. This is mostly caused by the increase of tensile strength while the elongation at break remained constant. The performance of MWNT/PA12 fibres is lower than carbon fibres and Kevlar®, but well above PP. For post-drawn fibres at 300% elongation, U^* of pure PA12 filaments is above that of carbon fibres and low performance aramid fibres, but it decreases with MWNT weight fraction. Fibres post-drawn at 500% elongation, while producing the most promising results in terms of elastic modulus and tensile strength, exhibit the worst performance as MWNT content increases. This behaviour is caused by a significant decrease in the strain at break of nanocomposite fibres stretched until 500%, consequently producing fibres of lower toughness. However, the performance of MWNT/PA12 is better than Curv™ for all post-drawing conditions.

In theory, fibres post-drawn at 300% elongation show the most promising results in terms of protective gear applications for MWNT contents below 5.0 wt%. Even though these results suggest that MWNT/PA12 fibres would be comparable, in the best case, to carbon fibres, they highlight two important aspects of the post-drawing method presented in this paper:

1) This post-drawing technique allows tailoring of the properties of the fibres, depending on the expected applications.
2) If applied to high performance fibres, such as nylon 6,6, PP or UHMWPE, this method could lead to significant improvements with the inclusion of carbon nanotubes as it is possible to reach higher draw ratio, tensile strength and Young's modulus values with the appropriate post-drawing conditions.

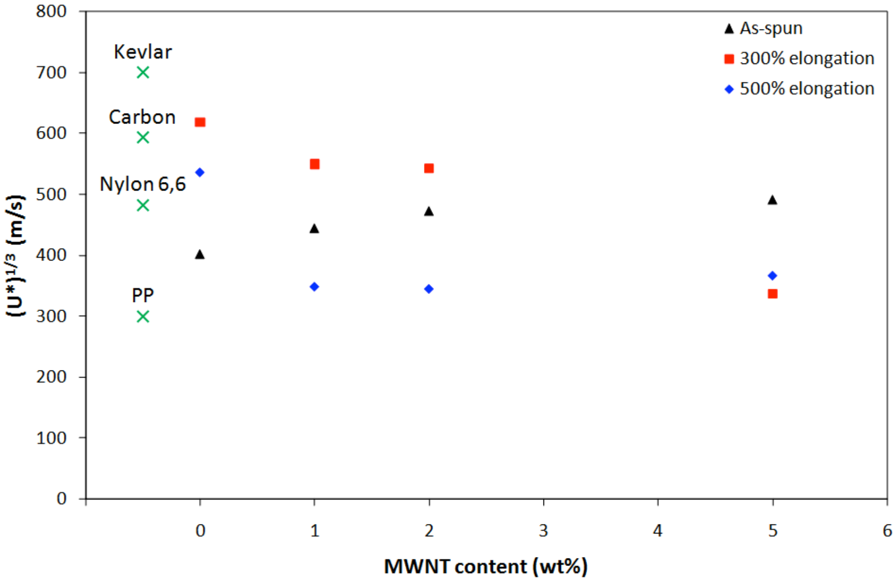


Figure 3. Comparison of ballistic impact potential (U^*) of high performance fibres and post-drawn MWNT/PA12 fibres.

4 Conclusions

In this work, a post-processing method to identify key parameters to improve mechanical properties of CNT/thermoplastic fibres was presented. Melt spun MWNT/nylon 12 fibres were post-drawn under specific conditions to further enhance their mechanical properties. A systematic investigation of the effects of drawing speed, temperature and elongation on the mechanical properties was carried out. It was observed that higher temperature and elongation values had the greatest impact on the Young's modulus and tensile strength. The elastic modulus increased by at least 300% compared to as-spun fibres and the tensile strength was improved by up to 62% for fibres containing 5.0 wt% MWNT. The drawing speed, within the values investigated, did not have a significant effect on the mechanical properties. These improvements were explained by the alignment of the polymer chains and better nanotubes dispersion at higher post-drawing temperatures (140°C) and elongation (500%).

This post-processing technique showed that the properties of CNT/thermoplastic fibres can be tailored according to specific parameters, depending on the requirements of the goal applications. For instance, according to Cunniff's model for ballistic performance, fibres post-drawn until 300%, at 140°C, would be best suited for such applications. It is expected, however, that greater improvements could be obtained if this post-drawing method were to be applied to other material systems and spinning techniques for the production of high performance fibres.

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