Carbon Nanotube- and Nanofibre-reinforced Polymer Fibres

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ABSTRACT

A range of multi-wall carbon nanotubes and carbon nanofibres were mixed with a polyamide-12 matrix using a twin-screw microextruder, and the resulting blends used to produce a series of reinforced polymer fibres. The aim was to compare the dispersion and mechanical properties achieved for nanofillers produced by different techniques. A high quality of dispersion was achieved for all the catalytically-grown materials and the greatest improvements in stiffness were observed using aligned, substrate-grown, carbon nano tubes. The use of entangled multi-wall carbon nanotubes led to the most pronounced increase in yield stress. The degrees of polymer and nanofiller alignment and the morphology of the polymer matrix were assessed using X-ray diffraction and calorimetry.

Keywords: nanotubes, nanocomposites, polymer fibres, mechanical properties

1 INTRODUCTION

Although carbon nanotubes were observed at least as early as 1976, it was only more recently that their importance was recognised. Since then, enormous attention has been paid to their fundamental properties and related applications [1], including considerable efforts to exploit the remarkable mechanical properties of individual nanotubes in macroscopic composites [2]. Whilst some encouraging results have been obtained, significant improvements over conventional fillers have generally proved elusive, for a number of reasons. Therefore, it is particularly interesting to consider the use of nanotubes to reinforce structures in which conventional fillers cannot physically be accommodated, such as within micro-components, or fibre composite matrices. As an example, this study focuses on the fabrication and properties of carbon nanofibre and nanotube reinforced polymer fibres. This approach necessitates the use of only small quantities of materials, readily enabling comparisons of different types of nanotube. The development of such nanocomposite fibres will involve the detailed study of dispersion, alignment, and matrix interactions, that will be fundamental for exploiting the full potential of bulk nanotube composites, whilst, at the same time, generating property enhancements that may be applied immediately.

Earlier work, focusing on carbon nanofibre (CNF) reinforced PEEK fibres [3], showed promise, demonstrating that high quality fibres with excellent surface finish and filler dispersion could be obtained using simple thermoplastic processing. The resulting fibres had significant improvements in yield strength and stiffness that could not otherwise be readily achieved. In addition, the presence of nanotubes is not damaging to the key properties of the PEEK matrix, namely, high temperature, chemical, and abrasion resistance; indeed, there is evidence that the wear performance of the blend is substantially improved [4]. A final benefit is that, because PEEK is a high performance material, the nanofibres are no more expensive than the matrix. However, the system has some complications; the degree of crystallinity is affected by the presence of the nanofiller and must be taken into account when assessing the composite properties. This paper describes a series of experiments comparing the CNF used in the PEEK study with three types of carbon nanotube, in an attempt to establish the potential for improvement. In order to simplify processing, and to study a matrix already used commercially for nanotube composites, we decided to focus on a polyamide-12 (PA12).

2 EXPERIMENTAL

The arc-grown nanotubes (AGNT) [5], aligned catalytically-grown nanotubes (aCGNT) [6], and entangled catalytically-grown nanotubes (eCGNT) [7] were produced using previously reported techniques. The catalytically-grown nanofibres (CNF) were purchased from Applied Sciences Inc., USA, grade PR-19-PS. The average outer diameters of these multi-walled nanomaterials were 15, 43, 10, and 155 nm respectively. All of the catalytically-grown materials were essentially pure except for the presence of the catalytic transition metal. The AGNT sample contained significant graphitic and nanoparticulate impurities, with a total nanotube weight content around 40 % [5]. Pellets of PA-12 (VESTAMID L1700, from Degussa) and as-produced carbon powders were weighed, dried, and blended in a DSM twin-screw microextruder, operating at 220 °C at
80 rpm. The extrudate was roughly chopped and fed into a Rheometrics Scientific capillary rheometer at 220 °C and a single strand was spun from a 1 mm diameter die to produce fibre diameters in the range 100 - 200 μm. Nanocomposites with loading fractions up to 15 wt% were produced, depending on the availability of the nanofillers. Composite samples were fractured under liquid nitrogen and examined in a JEOL 6430F FEG SEM, operating at 10 kV after chromium coating. 2D X-ray fibre diffraction patterns were collected using Ni-filtered CuKα radiation on a Photonics CCD system, calibrated using silicon powder. Individual fibre tensile testing was performed on a TA Instruments 2980 Dynamic Mechanical Analyzer applying a constant force ramp of 0.1 N/min, at 30 °C, with a gauge length of 5.5 mm. At least 3 fibres were tested for each sample. Differential scanning calorimetry (DSC) was performed using a TA Instruments DSC 2920 operating at 10 °C/min.

3 RESULTS

Macroscopically, all of the nanocomposite fibres appeared to be of generally good quality, with a reasonable surface finish and uniform diameter, regardless of catalytic nanotube filler type and loading fraction. The entangled multi-wall carbon nanotubes led to a slightly rougher fibre surface compared to the carbon nanofibres and aligned multi-wall carbon nanotubes. Only the PA12 nanocomposite fibres containing the arc-grown multi-wall carbon nanotubes showed non-uniformity in diameter which was independent of filler weight content. All nanocomposite fibres were coloured uniformly black. Typical SEM images of the composite fibres are shown in Figure 1; similarly high levels of dispersion were observed for all of the catalytically-grown materials. However, the unpurified AGNTs showed a poor overall level of dispersion in all cases, with aggregates leading to the formation of voids within the fibres. Maximum pull-out lengths appeared to be around 400 - 500 nm for both CNF and eCGNT but reached several microns for the straighter, more crystalline aCGNT samples.

An example of the two-dimensional X-ray fibre diffraction patterns of the extruded fibres is presented in Figure 2. The main features of the 2D X-ray patterns are an amorphous polymer halo and relatively low intensity crystalline reflections, typical of the γ-phase. The results were confirmed by detailed equatorial diffraction studies. In neither case is there evidence of a change in crystal structure on the addition of nanotubes, as has been observed previously in polypropylene and polyvinylidene fluoride composites [8]. Nor is there the variation in the degree of crystallinity observed with the PEEK samples [3]. The graphitic (002) reflections of the aCNGT and CNF indicate a considerable degree of alignment parallel to the fibre axis due to the shear flow during processing. The AGNT samples showed a random distribution, consistent with the presence of equiaxed nanoparticles and aggregated nanotubes. Equatorial X-ray diffraction patterns of the nanocomposite fibres, show similar diffraction features. By comparing the areas under the peaks, it can be established that the overall degree of crystallinity across all of the as-processed PA12 samples was constant, estimated at around 10 %; this figure is a slight overestimate due to the modest orientation of the polymer crystallites parallel to the axis.

Figure 1. SEM images of the nanocomposite fibres, containing 5 wt% aCGNT, showing the fibre surface as produced (top) and a fracture surface (bottom).

Figure 2. 2D X-ray fibre diffraction pattern for sample containing 5 wt% aCGNT. The pattern shows a strong amorphous halo overlayed by a crystalline peak, and, at larger angles, the (002) graphitic spacing of the nanotubes.
Figure 3 shows DSC thermograms obtained on heating as-spun nanocomposite fibres; as a function of aCGNT content; similar curves were obtained for all the nanocomposites. There is a clear glass transition at around 50 °C, followed by an endothermic melting peak above 170 °C. No significant variations were observed in either shape or onset of the glass transition and melting features. Nevertheless, there appeared to be a change in the heat capacity of all as-spun fibres between 100 °C and the onset to melting at around 170 °C, indicated by small deviations in the gradient. Detailed DSC studies, under different heating rates and cycled conditions, provided further evidence for a broad, underlying exotherm. Such a broad crystallisation above Tg during a DSC experiment is common for polyamides and reflects the relaxation of processing stresses [9]. In an attempt to establish a comparative degree of crystallinity of all nanocomposite fibres the total melting peak area was evaluated, normalised to the fraction of polymer present. This approach led to a roughly constant degree of crystallinity for all the samples between 23 to 27 % (based on an enthalpy of melting of 209.34 J/g for 100% crystalline material [10]). These results are an overestimation of the true, initial, degree of crystallinity of the as-spun fibres due to the recrystallisation process; hence, the X-ray based estimate is more reliable. However, we can conclude that the nanofillers do not affect the maximum crystallinity that can be obtained in this system, although more detailed analysis does indicate a nucleation effect and an associated change in crystal size [11].

A typical set of tensile stress-strain curves of nanocomposite fibres is shown in Figure 4. The pure polymer and many of the nanocomposites revealed a two-stage yielding behaviour between about 3 and 30 % of strain, followed by a stress plateau up to about 190 % strain corresponding to drawing. This particular yielding behaviour is due to the experimental set-up (load control) and the occurrence of strain-induced crystallisation after initial fibre necking. The occurrence of the characteristic two-stage yielding behaviour could be seen for all nanocomposites up to a filler concentration of about 5 wt% (about 10 wt% in case of the carbon nanofibres). At higher filler loading fractions the tensile behaviour changed to a simple yielding, followed by a steady stress increase.

As shown in Figure 5, the nanocomposite fibre stiffness and yield strength increase linearly with filler content in all cases. As can be seen, the aCGNTs show the steepest increase in composite stiffness, closely followed by the eCGNTs. These results are in agreement with the trend in nanotube crystallinity observed in Raman data. The AGNTs present the worst increase in nanocomposite stiffness; a result that can be attributed to their poor dispersion and alignment. The yield stress data showed similar trends with both the eCGNTs and aCGNTs revealing the most prominent increases as a function of filler weight content, although the eCGNT come out top most likely as result of increased constraint of the polymer matrix due to their relatively high surface area. The results are qualitatively consistent with earlier studies on single filler types (in some case single loading fractions) but a detailed comparison is beyond the scope of these proceedings.

4 CONCLUSIONS

Nanofilms provide interesting opportunities to reinforce polymer fibres. Carbon nanofibres have already been shown usefully to improve the strength, stiffness, and wear properties of PEEK fibres, as well as a range of other thermoplastic matrices. This study has successfully explored the potential of various multi-wall carbon nanotubes and nanofibres as mechanical reinforcements in polyamide-12 composite fibres. Linear improvements in yield strength and stiffness were observed that were greater for well-dispersed nanotubes than for nanofibres. Further improvements might be achieved using nanotubes of greater intrinsic quality and straightness. Many questions remain as to the characteristics of the optimal nanotube.
reinforcement that will only be answered by continued comparative studies.

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