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Characteristics of carbon nanotube yarn structure unveiled by acoustic wave propagation

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ABSTRACT

The strength transfer efficiency from individual carbon nanotubes (CNTs) to micro-sized yarns is an order of magnitude lower than that for conventional textile yarns. To improve the strength transfer efficiency, a good understanding of the frictional interaction between the nanotubes in the yarn (yarn internal friction, or viscoelasticity) is needed. Here, an acoustic wave propagation method is employed to elucidate the relationship between the structural characteristics and the viscoelastic behaviours of several types of dry-spun CNT yarns. The insertion of a high twist increases the CNT packing density in a yarn but results in a decrease of yarn modulus whilst the internanotube friction peaks at an intermediate twist level. Crosslinking increases the CNT yarn modulus and reduces the internanotube friction. Folding single twisted yarns into a torque-free plied yarn, a common practice in textile processing, leads to reductions in both modulus and internanotube friction. CNTs in densely packed twistless CNT yarns are highly aligned with each other, leading to very high modulus and very low internanotube friction.

1. Introduction

Individual carbon nanotubes (CNTs) have shown very high tensile strength and modulus [1–3]. The discovery of drawable carbon nanotube forests opened up the possibility for constructing pure carbon nanotube macrostructures that sparked interest in developing applications from these structures [4–9]. The web drawn from a carbon nanotube forest had a rather low capability for transferring mechanical load [4]. Insertion of twist can densificate the CNT web into a yarn (called fibre by some researchers) with dramatically increased mechanical strength [10]. Despite intensive research efforts since 2002, CNT yarns still only achieve a small fraction of the strength of their constituent CNTs. The realized strength transfer efficiency from individual CNT to yarn is about an order of magnitude lower than that for conventional textile yarns [5,11]. Unlike conventional textile yarns in which friction provides the cohesion between fibres, in dry-spun carbon nanotube yarns van der Waals attraction is the major mechanism for load transfer between nanotubes, which is evident from the high strength of twistless yarns formed by rub-densification and solvent-shrinking [12,13].

Measured tensile properties of conventional textile fibres and yarns are highly dependent on the strain-rate used in tensile testing [14–16]. Their behaviours at high strain-rate have traditionally been used to elucidate the structure and interaction between molecules, fibrils and fibres in the textile structures. Charch and Moseley [16] reported that orientated polymer fibres such as polyamide, acrylic and polypropylene increased their Young's moduli by up to three fold as the straining rate increased from 1% per minute to 100,000% per minute. Smith et al. [14] showed that the moduli of

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viscoelastic fibres and yarns tested at high straining rate using a projectile impact test at 38–40 m/s were much higher than their moduli obtained from quasi-static test. On the other hand, the modulus of linear-elastic glass fibres tested at such high straining rate was only 4% higher than its quasi-static Young's modulus.

The highest strain rate in a material is achieved at the velocity of acoustic wave propagation (sonic velocity). The sonic velocity (c) and Young's modulus (E) of linear elastic material is related by the well-known wave propagation equation:

$$c = \sqrt{E/\rho} \quad (1)$$

where ρ is the mass density of the material. In the textile industry, specific modulus $E' = E/\rho$ (N/tex) is preferred because the linear density (1 tex = 1 mg/m) of fibres and yarns can be determined more conveniently than the cross-sectional area of these materials. Eq. (1) has been used to determine the elastic modulus of the material from experimentally determined sonic velocity. The elastic modulus determined by the sonic method is known as dynamic modulus or sonic modulus. Throughout this paper, the term sonic modulus is used to avoid confusion with the storage modulus and loss modulus derived from the popular dynamic mechanical analysis (DMA).

Sonic velocity testing has routinely been used in research and development of polymer fibres since the 1950s [15–17]. Amorphous polymers have low mechanical properties. By drawing extruded polymer fibres to a high draw ratio (the ratio between resulting length and initial length of the fibres), the long molecular chains in the fibres are orientated along the fibre axis, resulting in dramatic improvements in fibre strength and modulus. Moseley [15] related Hermans orientation factor α [18] in polymer fibres with the sonic velocity and modulus of the fibres:

$$\alpha = 1 - \frac{c_u^2}{c^2} = 1 - \frac{E'_u}{E'} \quad (2)$$

where c_u and E'_u are respectively the sonic velocity and specific sonic modulus for an undrawn (isotropic) fibre, and c and E' are the sonic velocity and specific sonic modulus of the drawn fibre, respectively. The above relationship is used routinely in determining the degree of molecular orientation in polymer fibres.

Where viscosity (displaying time effects such as stress relaxation and creep) is significant, orientation of molecules in a polymer fibre (or fibres in a yarn) takes place under low strain rate deformation such as in quasi-static loading test. However, when fibres are subjected to high strain rate cyclic stress, there is insufficient time for the flow and orientation of molecules in the fibres (or the rearrangement of fibres in a yarn) before the applied force is reversed in direction. Nolle [19] analysed the strain wave motion in a viscoelastic strip material and derived a relationship between c/c_o and a dimensionless parameter $\tau\omega = \omega\Upsilon/E_{qs}$, where Υ denotes the viscosity coefficient associated with the Young's modulus E_{qs} determined by quasi-static test, ω is the angular frequency of the wave, $c_o = (E_{qs}/\rho)^{1/2}$, and c is the phase velocity of the wave in the material (i.e., sonic velocity). The sonic modulus E_s can be calculated from the relationship $E_s = \rho c^2$ in Eq. (1).

The theoretical relationship between the modulus ratio E_s/E_{qs} and $\tau\omega$ according to Ref. [19] is shown in Fig. 1, which shows the general trend of increase of the modulus ratio with increasing viscosity of the material.

The modulus ratio (E_s/E_{qs}) has also been taken as an indication of the internal friction (fibre–fibre friction) in conventional textile fibres and yarns [20,21]. High ratio of sonic to static modulus was reported to correspond to larger creep for synthetic fibres [20]. The modulus ratio is typically between 1.5 and 3 for conventional staple fibre yarns, such as wool yarns [22], cotton yarns [21] and blended viscose-polyester yarns [23]. Chemical treatments that introduce crosslinking between cotton fibres was found to increase both the sonic modulus, static modulus and the sonic/static modulus ratio of cotton yarns [21].

In this paper, the mechanical properties of CNT yarns at sonic strain-rate and quasi-static strain rate are reported for a number of types of yarn structures, including yarns spun to different twist levels, rub-densificated yarns, plied yarns and yarns undergone crosslinking treatment. The sonic modulus results are used to interpret the structural characteristics of these carbon nanotube yarns.

2. Experimental

2.1. Carbon nanotubes

Vertically aligned carbon nanotube arrays (forests) were grown on silicon wafer substrates bearing a thermal oxide layer (100 nm) and iron catalyst coating (2.5 nm) using chemical vapour deposition (CVD) of acetylene (5%) in helium (700 sccm) at 680 °C for 20 min. The CNTs were multi-walled in nature with 7 ± 2 walls, and an outer diameter of 10 ± 3 nm and an inner diameter of 4 ± 1 nm. The CNTs are approximately 350 μm long. SEM images of the CNT forest and TEM images of individual CNTs were published previously [11].

2.2. Carbon nanotube yarn production

Twisted CNT yarns were produced using the so-called Up-spinner [5]. The CNT forest attached to a spindle rotates at

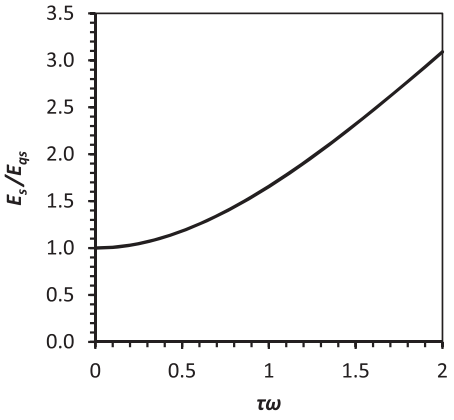

Fig. 1 – Theoretical relationship between modulus ratio and the dimensionless physical parameter $\tau\omega$ of material drawn according to [19].