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Compression resistance and hysteresis of carbon fibre tows with grown carbon nanotubes/nanofibres

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ABSTRACT

Growth of carbon nanotubes (CNT) or carbon nano-fibres (CNF) on fibrous substrates is a way to increase the fracture toughness of fibre reinforced composites (FRC), with encouraging results reported in the recent years. The issues for these materials related to manufacturing of these composites are, however, less investigated. Following the study of compressibility of woven carbon fibre preforms with CNT/CNFs grown on the fibres using the CVD method [Compos Sci Technol 2011; 71(3): 315–325], this paper describes compression tests on the carbon tows used in these fabrics. The results of the measurements include pressure vs. thickness diagrams in consecutive compression cycles and hysteresis of the compression. The results confirm a drastic change of compressibility of fibrous assemblies in the presence of CNT/CNF grafting.

1. Introduction

Growth of carbon nanotubes (CNT) or carbon nanofibres (CNF) on fibrous substrates is a widely investigated method for introduction of nano-reinforcements in fibre reinforced composites (FRC), with creation of a hierarchical mixture of nano- and micro-reinforcements. The reader is referred to comprehensive reviews on the subject in Refs. [1,2]. The successful developments of tough nano-engineered FRC (nFRC) have drawn attention to manufacturability of these composites, with such issues as behaviour of nano-engineered fibrous preforms in different types of Liquid Composite Moulding (LCM) processes [3,4], and more specifically their permeability [5,6], formability [7] and, finally, compressibility [4,8]. We discovered [8,9] that the random "forests" of CNT/CNFs on carbon fibres are not easily compressible, in spite of the seemingly flexible and deformable thin and long CNT/CNFs, which, when in contact, have very low friction between them. This observation is in concordance with experimental studies of compression of other types of random assemblies of CNTs – "buckydisks" and "buckycolumns" [10,11]. The high compression resistance is due to the extremely high number of contacts in the assembly (several thousands per 1 μm^3 for a volume fraction of CNTs of about 20% [8,12]). It was found [9] that the compressibility of carbon woven reinforcements is seriously affected by the growth of CNT/CNFs on the surface of the fibres. The fibre volume fraction, achievable by compaction under pressure of 0.1 MPa (1 bar), is decreased by a factor of 1.3–1.5 for the studied fabrics with 6 wt.% of CNT/CNF growth. It is concluded that the change of the compaction behaviour of a CNT/CNF-grown-on preform should be taken into account during manufacturing of nFRC.

The present paper continues the study [9], reporting results of compression tests on the yarns (carbon tows) taken from the same woven fabrics. The results of the measurements include load-thickness diagrams in consecutive compression cycles and hysteresis of the compression. The results extend the observations of [9] to a new, intra-yarn, inter-fibre hierarchical level of the nano-engineered textile preforms. They also provide benchmarking data for future extension of models of compression of random CNT/CNF assemblies [8] to hierarchical assemblies consisting both of fibres and CNT/CNF grown on them.

2. Materials

The reader is referred to [9] for details of the catalyst deposition and the CNT/CNF growth process on the fabrics. To repeat here in short the procedure, CNT/CNF was grown on the fabrics using the following steps:

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Table 1
Parameters of the carbon tow samples.

Fabric type	A	B
Processed in	University of Twente	Nanocyl
Producer	TenCate	Porcher industries
Yarn type	3 K Torayca® ← T300 J	3 K HS
Fibre count	3000	3000
Fibre diameter, μm	7	7
Presence of sizing	No, de-sized at manufacturer prior to delivery	Yes
Yarn width[a], mm	1.57 ± 0.08[b]	1.49 ± 0.07[b]
Samples' ID:		
Virgin	A	B
Catalyst treated only	AC	BC
With CNT/CNF growth (relative mass of the growth)	AG (6.5%)	BG1 (5.9%)
		BG2 (10.6%)

[a] Yarn width measured on the surface of the fabric.
[b] Standard deviation in 10 measurements.

1. Deposition of the catalyst precursor: the fabric is immersed in a solvent containing the catalyst precursor and is dried afterwards at room temperature in open air.
2. The sample is then heated up to the temperature used in the growth process in an inert atmosphere.
3. For fabric A the metal salts on the fabric are reduced into pure catalytic metal particles (hydrogenation of nickel nitrate to elementary nickel); for fabric B this step is omitted.
4. CNT/CNF growth: the fabric is processed in the gas chamber with N_2:C_2H_4:H_2 (proportion 50:40:10) for the time chosen to achieve the desired yield of the growth.

Table 1 shows parameters of these carbon tows (the words "tow" and "yarn" are used in this paper as synonyms), extracted from the woven carbon fabrics; Fig. 1 shows images of typical yarn specimens. The latter were carefully extracted from the fabric strips of 25 mm width. Because of this handling, one cannot exclude certain loss of the grown CNT/CNF from the surface of the fibres. An important feature of the tow specimens is the crimp, preserved after extraction from the fabric (Fig. 1b). No tension was applied to the tow specimens during compression test, hence the crimp affects the compression resistance at least in the first compression cycle.

Table 1 shows also characteristics and nomenclature of the yarn sample types tested in compression, which are the same as used for the fabric samples in [9]. Fabric A was processed to have one level of growth (sample AG), fabric B had lower and higher growth loading (samples BG1 and BG2). The yarns, that were only subjected to catalyst deposition and thermal treatment at the temperature of the growth step, without N_2:C_2H_4:H_2 gas flow, were also tested (these samples are referred to as AC and BC).

Fig. 2 shows SEM images of a virgin tow and the tows after grafting. In summary, the grown CNT/CNF assemblies can be described as follows. On fabric A the nano-assembly consists of CNFs, probably with cup-stacked morphology, of different diameters: thin ones, with diameter in the range 20–50 nm, and very thick CNFs with diameter about 200 nm. The CNFs are organised in a dendrite-like structure covering the carbon fibres. On fabric B two populations of CNT/CNF are present: CNTs with diameter about 20 nm and cup-stacked CNFs with diameter 50–100 nm.

It is highly desirable to know more details of the morphology of the grafting: thickness of the grafted material, length of the CNTs/CNFs, their orientation distribution. There are no established methods of measurement of these details; development and application of such methods would be a subject of full scale research work and separate publication(s). For estimations now we have only SEM images of Fig. 2 and rough values of CNTs/CNFs length based on the time of reaction. These sources allow estimations of the CNT/CNF diameters, given above. The thickness of the grafting and the length of CNTs/CNFs can be estimated as lying in the range of few micrometers. The CNTs/CNFs are definitely non-aligned, and even no prevailing orientation can be seen on SEM images.

SEM observations of the yarns after the loading were also done, but no visible change in the morphology of the grafting was noticed.

3. Experimental technique

A Deben microtest system (Fig. 3a) was used to measure the compression resistance. The load cell was 5 N, test speed 0.15 mm/min. The Deben apparatus was equipped with a specially designed compression head with a cylindrical pivot (Fig. 3a), which allows parallel adjustment of the compression surfaces during a compression test without a specimen. After that, three tests are performed without a specimen to establish the calibration curves (Fig. 3b) for calculating the thickness of the specimen under a given compression force. The force is measured by the load cell, and the compliance and hysteresis of the machine are accounted for by subtracting the calibration curves from the compression diagrams. Different calibration curves are used for the loading and for the unloading phase. The calibration curves are re-registered after few hours of testing. The standard deviation of the calibration curves is in the range of 0.0015–0.0020 mm, which constitutes an error of about 1.5–2% of a typical measured thickness of 0.1 mm. This error is also well below the carbon fibre diameter (7 μm), which is a natural measure of uncertainty of thickness measurement of a fibrous assembly.

Three successive compression cycles (loading–unloading) were performed for each specimen. Because of the crimped shape of the yarns (Fig. 1), the first cycle is not representative and should be considered as pre-conditioning of the specimen. This phenomenon is referred to as "set" or "conditioning" in textile mechanics [13–16]. It involves reordering of the fibres in yarns, or fibre bundles in fabrics, which is irreversible because of friction between the fibres. The difference between the second and the third cycle and the hysteresis of the compression diagram of one full cycle characterise the resilience of the carbon fibre/growth system.

The maximum load level was set at 3 N. The force was recalculated into pressure using (specimen length x nominal yarn width) as a presented area. The specimen length under force corresponds

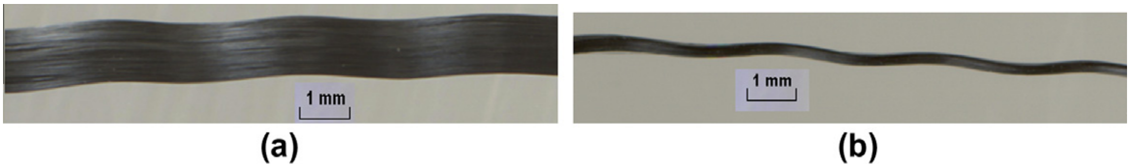

Fig. 1. Carbon tows (type A) taken out of woven fabrics: (a) surface view; (b) side view.