Carbon Fibres with Modulated Properties and Shape along the Fibre Length

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Keywords: Carbon Fibres, Laser Treatment, Fibre Properties

ABSTRACT

The ability to introduce weak regions into carbon fibres at predetermined points should allow failure to occur in a controlled manner, and potentially mitigate the storing of elastic energy leading to sudden catastrophic failure associated with current high performance polymer matrix composites. Here we introduced damage - at the single carbon fibre level - to unsized fibres using a nanosecond pulsed laser source. Various laser treatment parameters were employed to create predefined weak/break points as well as local shape (fibre swelling) modification at the treatment site. The shape and morphology of all individual fibres tested was assessed before and after single fibre tensile tests using SEM to correlate the mechanical properties to fibre shape modification. The laser treatment resulted in swollen fibre regions at the treatment site. In some cases swollen fibres were observed to have a neck region in the centre of the affected region, probably due to simultaneous laser ablation. The tensile mechanical properties of the treated fibres were reduced significantly in comparison to the control fibres; with reductions in strength, strain and modulus of 62%, 55% and 17%, respectively. We demonstrate that the fibre failure occurred in the laser treated region producing two fibre ends with outwardly tapered ends.

1 INTRODUCTION

Lasers are being used to drill holes and shapes into high performance unidirectional carbon fibre composites [1-5], as well as to perforate laminates, breaking the fibres at predefined points to produce highly aligned discontinuous composites with the aim to improving manufacturing ductility and hence increase flexibility in manufacturing [4,5]. These materials can be formed into double curvature parts [4,5]. The fibre length may also be varied throughout the structure, for example from 20 mm to 100 mm, or indeed any length depending on the limitations of the laser/control system [4,5].

Laser drilling/perforation in high performance thermoplastic carbon fibre composites has been reported to result in heat affected damage zones of anisotropic shape, being markedly larger in fibre direction [1]. This is due to the polymer matrix degradation temperature and thermal conductivity being ca. 1-2 orders of magnitude lower than that of carbon fibres [1]. The presence of the carbon fibres causes anisotropic thermal conductivity, leading to easier heat flow parallel to the fibre axis than in the transverse directions. Furthermore, carbon fibre swelling was observed around laser-drilled/machined holes in such composites [2-5]. Carbon fibres have been reported to swell up to 50%

in diameter in the heat affected zone in the vicinity of the hole [1,3]. This swelling behaviour has been attributed to irreversible changes in the arrangements of the basal planes, caused by large and rapid thermal expansion, accentuated by the rapid pressurisation of fine pores within the structure of the fibres [1]. To account for the significant swelling of 50%, two further possibilities have been hypothesised: i) gas entrapment produced by oxidation of carbon, with CO and CO_2 being unable to escape, and ii) intercalation of species between the basal planes when the fibres were at high temperature, leading to extensive exfoliation [1]. In another paper, the effect of carbon fibre type (low and high modulus) on laser-induced swelling was investigated [2]. The authors established that swelling (up to 60% in diameter) only occurred when exposing low modulus, PAN-based fibres to laser treatment [2]. Romoli at el. [3] laser-drilled carbon fibre (T300, Torayca Ltd.)/polyether ether ketone (PEEK) laminates using a Nd-YAG laser emitting at 355 nm, with fast scan rates of up to 4 ms^{-1} in an effort to suppress heat affected zones and consequently detachment of fibres from the matrix. They proposed a removal technique based on the ablation of superimposed layers to mitigate this anisotropic heat affected damage zone [3].

This swelling of carbon fibres via laser treatment presents us with an interesting opportunity to control fibre shape at predefined points, introducing tapered or unduloid regions along the length of the fibre. There is a growing body of evidence both from nature [6] and synthetic composite materials [7-12] to show that suitably bulbous/taperd ends and unduloid fibres [13] can act to increase the work of pull-out, delocalised inelastic deformation and induce strain-hardening. Therefore, laser treatment is a potential tool for the controlled introduction of damage to carbon fibres at predefined points, as well as to locally modifying fibre shape (swelling/tapering). This ability to i) introduce predetermined break/weak points and ii) create outwardly tapering fibre ends could allow for toughening mechanisms observed in high performance natural material, such as nacre [6] to be mimicked. The ability to introduce weak regions to carbon fibres at predetermined points should allow failure to occur in a controlled manner.

2. MATERIALS AND METHODS
2.1 Material, fibre mounting and preparation for ablation and analyses
Unsized, PAN based, AS4 carbon fibres were kindly supplied from Hexcel Ltd. (Cambridge, UK) and according to the manufacturer have a tensile modulus of 231 GPa, tensile strength 4433 MPa, and elongation at break of 1.8%. These fibres were individually mounted on white paper frames. These frames allowed to position and handle the fibres, facilitated laser ablation in groups of 10 fibres (perpendicular to the long axis of the fibres) as well as to characterize them using scanning electron microscopy (SEM), Raman spectroscopy, single fibre tensile testing and post-failure SEM analysis. The paper grid of 3x10 frames used to support the fibres. Single carbon fibres were extracted from a ~30 cm length of cut tow. These fibres were carefully aligned and glued to paper frames. The frames were then cut and tabbed with paper to enable single fibre tensile testing to be performed on both ablated and control fibres. The gauge length measures 20 mm in length and was cut using a sharp scalpel blade ahead of fibre placement. The grid itself was taped all around its perimeter, using thin strips of 3M magic tape (overlapping by circa 3 mm) to prevent substrate (grid) movement.

2.2 Laser ablation
Grids with the fibres mounted on frames were then adhered, using thin strips of tape around their perimeter to anodised aluminium plates, which served as a substrate to hold and maintain the fibres flat. The plate was positioned underneath the laser beam, such that the laser guide path would run vertically through the length of a single column, to irradiate through the mid section of the fibres. Fibres were ablated in groups of 10, one column at a time. A nanosecond (8 ns) pulsed Nd: YVO$_4$ laser with a maximum average power of 17.5 W at $\lambda = 1064$ nm was operated with parameters in the range of 1.1 - 17.5 W of average power, a repetition rate in the range of 50 - 100 kHz and beam scanning speeds in the range of 50 - 200 mm s^{-1}. The laser beam was focused to a spot of ~ 70 μm in diameter on the target. The focal point of the laser beam was set to the height of the aluminium plate (on which the fibres were mounted) to ablate all fibres equally. Laser parameters 1.1 W of average output power, frequency 100 kHz, and speed 100 mms^{-1} resulted in ~20% of fibres being cut through; at 17.5 W, frequency 50 kHz and speed 50 mms^{-1} all fibres were cut. At 1.1 W power, frequency 100 kHz and speed 200 mms^{-1} consistently resulted in intact fibres. The laser operated at 1.1 W power

gives an energy fluence of 0.3 Jcm⁻² (energy per pulse 11 μJ). The laser fired 35 pules per spot, since the laser was run at 100 kHz.

2.3 Scanning electron microscope (SEM) observation of ablated and control fibres, and image analysis

Individual control and ablated fibres mounted in paper frames were used. The same ablated fibres were imaged i) prior to tensile testing for assessment of the ablated region and swelling. Image J was used to quantify swelling and the diameter of the fibre measured well away (~8 mm) from the ablation site, and ii) post tensile testing to determine the failure region. The diameter and length of the ablated region were recorded. Note that no sputter coating/conductive coating was used to aid visualisation. Fibres were imaged using an SEM, JEOL 5160 LV, Jeol Ltd., Japan. The swelling percentage was calculated based on the maximum diameter at the swollen region, relative to the diameter of the same individual fibre int an unaffected region. The affected length is defined here as the region with a diameter in excess of the unaffected region. The apparent taper angle, θ, of the swollen fibres was determined using:

$$\theta = \tan^{-1}\frac{(d_{max} - d_0)}{2L}$$

where d_{max} is the maximum swollen diameter, d_0 is the diameter of the fibre at an unaffected region, and L, the affected length. For fibres exhibiting a neck region in the middle of the swollen or affected length, the neck length is defined here as the length between the two swollen regions at their maximum diameters, and the taper angle defined as the average of the two sides of the swollen regions in the direction of the unaffected region.

2.4 Single fibre tensile testing

Single carbon fibres were tensile tested at 21°C with a crosshead speed of 15 μm s⁻¹, according to BS ISO 11566:1996 using a TST 350 tensile testing rig (Linkam Scientific Instrument Ltd.) equipped with a 20 N load cell. The gauge length was 20 mm. The paper end tabs were gripped in the machine and then the lateral parts of the frames cut through using fine scissors allowing the fibre to be loaded. The displacement and load recorded, and later converted to stress and strain, based on fibre diameters from SEM measurements, the former, and crosshead displacement, the latter. Individual stress-strain plots were corrected such that stress and strain were zeroed at the origin correctly. The strain to failure, maximum stress and elastic modulus were then calculated.

3. RESULTS AND DISCUSSION

3.1 Effect of laser treatment on fibre morphology and shape

The majority of ablated fibres exhibited swelling at the ablation site, causing the fibres to have an unduloid shape (Figure 1), with circa 20% of the ablated fibres exhibiting necking in the middle of the swollen regions (shown in Figures 3a,b). The fibres consistently exhibited one affected region along their length, consistent with a single pass of the laser. These changes in fibre diameter, the affected length and effective tapering angle (defined as running from the diameter of the unaffected region to the maximum swollen diameter on one side of the fibre) are summarised in Table 1.

Table 1. The changes to swollen (number of fibres measured, (n) = 21) and swollen/necked fibres (n = 5). Note that the average minimum neck diameter of the swollen/necked fibres was 8.1 ± 0.7 μm. The length over which the necked fibres tapered from unaffected region to maximum swollen diameter was 72.7 ± 30 μm, and the length of the neck region was 48.2 ± 55 μm.

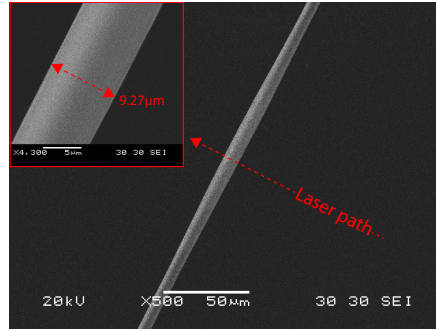| Type designated	Swollen dia. (max) [μm]	Affected length [μm]	Swelling rel. to control dia. [%]	Angle formed due to swelling (one side) [°]
Swollen	9.50 ± 0.7	138 ± 32	37.3 ± 10.0	0.77 ± 0.17
Swollen/ Necked	9.30 ± 0.4	194 ± 111	34.4 ± 7.1	1.55 ± 0.60

Figure 2. Representative SEM image of a swollen fibre, showing, inset the diameter that was directly in the laser path. Note the normal diameter of these fibres, as measured here is 6.93 ± 0.3 μm.
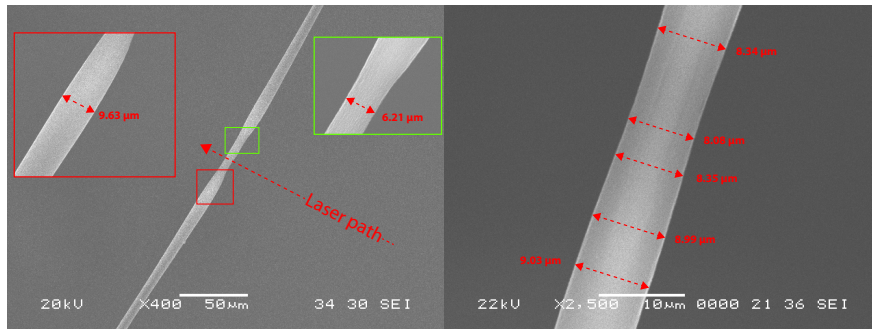

Figure 3. a (left) Representative SEM image of an ablated fibre, showing two swollen regions with a necked region in the centre. Inset, the diameters of the swollen and necked regions. b (right) SEM image of an ablated fibre, exhibiting a necked region with a diameter intermediate to the control fibre diameter and maximum swollen diameter.

For those fibres exhibiting necked regions, the smallest neck diameters varied between 6.2 μm to 9.2 μm, a range smaller and larger than the normal fibre diameter, measured to be 6.9 ± 0.3 μm, suggesting that this necking is due to localised sublimation of the carbon fibre (which may have previously been swollen). Striations due to the ablation can be seen in the necked regions, running along the length of the fibre. The swollen fibres exhibited an affected length of 138 μm $\pm$ 32 μm, with a maximum swollen diameter of 9.5 μm $\pm$ 0.7 μm, a swelling relative to the control fibres of 37.3%, with a taper angle of $0.77° \pm 0.17°$ (on one side). For these swollen fibres, there is a clear trend towards increasing affected length with increased maximum swollen diameters. The swollen/necked fibres exited greater affected lengths, of 196 μm $\pm$ 111 μm, with a maximum swollen diameter of 9.3 μm $\pm$ 0.4 μm. These fibres exhibit a swelling relative to the control fibres of 34.4%, as well as a larger taper angle of $1.55° \pm 0.6°$ due to the necking region acting to reduce the affected length to maximum swollen diameter on each side of the laser treated area. Fibres that were completely cut through using conditions 100% power, frequency 50 kHz and speed 50 mms^{-1} exhibit cotton-bud end shapes (as shown in Figure 4).
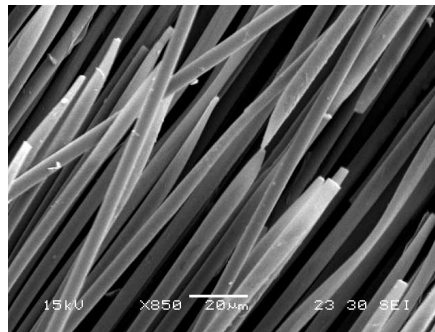

Figure 4. SEM image of a laser treated tow of IM7 fibres (using 50% power, frequency of 100 kHz and beam velocity of 100 mm s^{-1}). Some of the fibres exhibit swelling from their control size of 5.34 SD 0.37 μm to 6.39 SD 0.29 (a swelling of 19.6%), as well as necked fibres to 3.44 μm diameter.

AS4 carbon fibres were chosen over IM7 fibres in this work as they are easier to handle and mount to perform single fibre tests as opposed to thinner IM7 fibres (which have diameters of ~ 5.34 μm). However, for comparison, IM7 fibres were laser treated in the form of a tow (Figure 4). These fibres displayed a similar swelling/necking behaviour as compared to the AS4 fibres. The swelling mechanism align the explanation given by [1,2] that the rapid heating and high thermal gradients generated by laser treatment will volatise non-carbon impurities, creating high gas pressures, with simultaneous structural rearrangement, leaving behind the swollen/tapered structure after impurities have been driven off and the material returns to ambient conditions.

3.2 Effect of laser ablation on fibre tensile properties

The tensile properties of control and laser treated fibres are summarised in Table 3. The laser treated fibres have been designated into two types: swollen and swollen/necked fibres. Both the strength and modulus are reported, the calculation of which was based on the diameter of the fibres in their unaffected region. All fibres exhibited linear elastic behaviour with brittle failure. The control carbon fibres failed explosively, breaking into fragments, whereas the laser treated fibres broke into two, at their pre-defined weak point (swollen or necked regions), resulting in outwardly tapered fibre ends.

Table 3. Tensile mechanical properties of control carbon fibres (number of fibres measured, (n) = 29), and laser treated carbon fibres: swollen (n = 21), and swollen/necked fibres (n = 5).

Type designated	Strength [MPa]	Strain to failure [%]	Modulus [GPa]	Maximum force to failure [mN]
Control	4601 ± 678	1.77 ± 0.2	254.0 ± 14	175.0 ± 26
Swollen	1872 ± 927	0.88 ± 0.5	210.8 ± 29	70.8 ± 36
Swollen/ Necked	1167 ± 853	0.51 ± 0.3	212.7 ± 39	46.0 ± 35

Laser treated fibres failed in tension were then examined post-failure by SEM for determination of their break point and to assess the morphology of the fibre in the failure region. The values of force at failure (maximum) are also given in Table 3, as these values are not affected by area or porosity artefacts, and serve for a further direct comparison with the control fibre values. A significant knockdown in mechanical properties is evident for the laser treated fibres, the swollen fibre maximum force, ultimate tensile strength being reduced by ~60%, with strain and modulus being reduced by ~50% and 17%, respectively, in comparison with control fibres. The swollen/necked fibres exhibited even more of a reduction in maximum force and ultimate tensile strength to ~74%, with strain and modulus being reduced by ~71% and 16%, respectively, in comparison with control fibres. In order to ensure that any damage due to exposure of the electron beam of the SEM was not affecting the test results, control fibres were split into two groups, one tested by tensile testing without pre-testing exposure to the SEM e-beam and the remainder exposed pre-testing. Control fibres, exposed to the beam, with diameters measured individually (number of fibres, n = 16) had a tensile strength 4506 MPa ±756 MPa, Young's modulus of 254 GPa ± 17 GPa and strain to failure of 1.74% ± 0.3 %, in comparison to those with diameters of 6.9 μm ± 0.2 μm (taken from the average of the 16 control fibres measured), n = 13, exhibited a tensile strength 4719 MPa ± 569 MPa, Young's modulus of 256 GPa ± 9 GPa and strain to failure of 1.8% ± 0.2 %. There is no significant difference between these groups, and the results are reported together for all control fibres in Table 3.

4. CONCLUSIONS

The most effective laser parameters that result in laser treated carbon fibres remaining continuous, yet with predefined break/weak points were: 1.1 W power, 100 kHz frequency, with a beam velocity of 200 mm s^{-1} for this particular 1064 nm nanosecond laser. Some fibres were observed to have swollen affected lengths with a necked region in the centre, likely due to localised ablation of the fibre. The laser treated fibres exhibited with maximum diameters of ~9.5 μm, from their control fibre size of 6.9

µm (an increase of ~37%). The average affected length of the carbon fibres from a single laser pass was ~140 µm, over which the swollen diameter tapered back to the control diameter on either side, forming angles of up to 1.55°. The tensile mechanical properties of the treated fibres were reduced significantly in comparison to the control fibres; with reductions in strength, strain and modulus are 62%, 55% and 17%, respectively. More aggressive laser treatment conditions led to the simultaneous swelling and ablation of the carbon fibres, cutting them, whilst rendering their ends outwardly tapered. The laser treated fibres consistently failed in their treated region, resulting in two outwardly tapered ended fibres.

5. ACKNOWLEDGEMENTS

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