



Tensile strength of glass fibres with carbon nanotube–epoxy nanocomposite coating

Naveed A. Siddiqui^a, Man-Lung Sham^a, Ben Zhong Tang^b, Arshad Munir^c, Jang-Kyo Kim^{a,*}

^a Department of Mechanical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong

^b Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong

^c National Engineering and Scientific Commission, P.O. Box 280, Islamabad, Pakistan

ARTICLE INFO

Article history:

Received 7 February 2009

Received in revised form 22 May 2009

Accepted 4 July 2009

Keywords:

A. Glass fibre
A. Particle-reinforcement
B. Strength
B. Fibre/matrix bond
Carbon nanotubes

ABSTRACT

A study has been made of a concept of ‘healing’ coatings applied onto the brittle fibre surface to reduce the stress concentrations and thus to improve the reinforcing efficiency in a composite. Coatings made from neat epoxy and carbon nanotube (CNT) reinforced epoxy nanocomposite were applied onto the individual glass fibres as well as rovings. It is shown that the 0.3 wt.% CNT–epoxy nanocomposite coating gave rise to a significant increase in tensile strength of the single fibre for all gauge lengths, better than the neat epoxy coating. The results on glass fibre roving also indicated a clear beneficial effect of nanocomposite impregnation on tensile strength. The rovings impregnated with the CNT nanocomposite exhibited a more uniform strength distribution and higher strengths than those impregnated with the neat epoxy. The changes in prevailing failure mechanisms influenced by the epoxy and nanocomposite coatings have been identified.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Brittle fibres made from glass, graphite, alumina and silicon carbide are widely used as reinforcements for plastic, ceramics and metal matrices to produce high performance composite materials with attractive mechanical and structural properties. One of the major issues concerning these fibres is that the measured strengths are significantly lower than their theoretical values. The strengths of the materials are influenced by the presence of surface and internal defects that are created during manufacturing and handling. Therefore, a thin film of sizings consisting of coupling agents, a film former and other constituents is normally applied to glass fibres immediately after being drawn from molten glass [1]. The sizings aim to promote the fibre–matrix adhesion through the coupling effect, as well as to avoid damage during handling. It can also effectively reduce the stress concentration at the surface flaws by blunting the crack tips [2,3], providing a useful healing effect; thereby enhancing the strength of the fibres. Applications of various polymeric coatings as sizing or part of sizing have been reported [4]. When an epoxy-based sizing was used, the distribution of the defects on the fibre surface became narrower than fibres without coating [5]. In recent studies, the idea of nano-material reinforced polymer coatings on glass fibres has been explored

[6,7]. When a polymer sizing containing 0.2 wt.% carbon nanotube (CNT) was applied on the surface of alkali resistance glass fibre, a significant improvement in tensile strength of glass fibres was noted [7]. The improvement in fibre tensile strength was attributed to the CNTs in polymer coating acting as the “bridges” at the defect tips on the fibre surface, which in turn delay the crack opening. The schematic illustration shown in Fig. 1 shed insight into the crack healing effect of CNT reinforcements in the coating.

The failure of fibres, however, is a complex statistical process involving scattered failure of fibres at flaw sites. The fracture is often initiated from the microscale flaws having the highest stress concentrations based on the weakest link concept where a long fibre consists of a series of short-length fibres and their failure strengths are different at various gauge lengths. The fibres exhibit lower tensile strengths with increasing the gauge length because the chances of presence of a “weakest link” become larger, hence, the notch sensitivity of a fibre is greater with a longer gauge length [8]. An effective way of evaluating the healing effect provided by the coating is through the measurement of changes in strength at various gauge lengths.

This paper studies the effects of different fibre coatings and gauge lengths on tensile strengths of individual fibres as well as of bundle fibres. Three types of coatings, namely fibres without coating, fibres with epoxy coating and fibres with CNT–epoxy coating were employed. The results were treated using the two-parameter Weibull statistics to evaluate the healing effect provided by the nanocomposite coatings.

* Corresponding author. Tel.: +852 23587207; fax: +852 23581543.
E-mail address: mejkkim@ust.hk (J.-K. Kim).

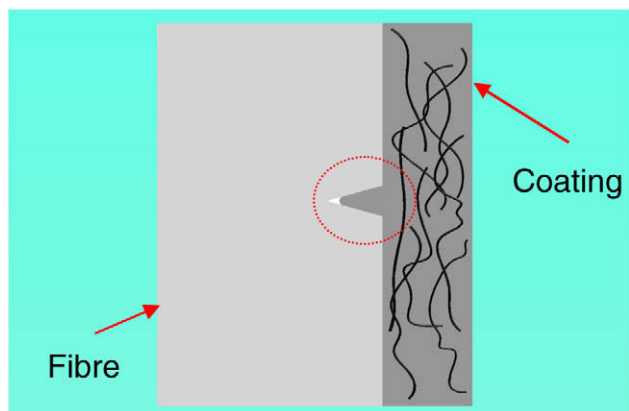


Fig. 1. Schematic illustration of a fibre with CNT-epoxy nanocomposite coating.

2. Experimental

2.1. Materials and preparation of nanocomposite coating

E-glass roving ER 2400 with an average diameter of $24 \pm 2 \mu\text{m}$ (supplied by Hankuk Fibres) was employed in this study. A silane coupling agent was applied during manufacturing according to the supplier's specification. The matrix system consisted of an epoxy, diglycidyl ether of bisphenol A (DGEBA, Epon 828 supplied by Shell) and *m*-phenylenediamine (*m*-PDA, Aldrich) as the curing agent. Multi-walled CNT reinforcements, the same material as those employed previously [9–11], were prepared through a chemical vapour deposition method, and had diameters and lengths ranging between 10–20 nm and 10–50 μm , respectively. Typical transmission electron microscope (TEM) images of the CNTs are presented in Fig. 2. The CNT surface was oxidized and functionalized similarly to the previous report [9]. A desired amount of CNT was dispersed in acetone in a sonication bath (Branson 150) for 30 min, which was then filtered and dried in a vacuum oven. The dispersed CNTs were subjected to oxidation for 1 h in a UV/O₃ chamber (Jelight 144AX-220), which were further functionalized using triethylenetetramine (TETA, Aldrich) to enhance the adhesion with epoxy resin. The CNTs were mixed with an excess amount of TETA solution and the mixture was sonicated at 60 °C for 30 min, which was filtered through a micro-filter and washed with acetone to remove the unreacted amine.

For the preparation of the nanocomposite coating, the functionalized CNTs were added into a preheated epoxy resin with CNT

contents of 0, 0.3 and 0.5 wt.%, and the mixture was sonicated for 1 h, followed by degassing in a vacuum oven at 70 °C. The stoichiometric amount of the curing agent, 14.5 part per hundred of epoxy, was added into the CNT-epoxy mixture to prepare the CNT nanocomposite coating.

2.2. Impregnation of individual fibres and fibre bundles

The single glass fibres were carefully separated from the roving. These fibres were pulled through a coating system comprising a small impregnation bath (Fig. 3a) and a coating through the ceramic rollers. The extraction speed was maintained slow enough to achieve good wetting of the fibres and to allow the excess resin to be removed. All necessary precautions were taken to prevent any damage during handling of the fibres. The rovings, consisting of nominal 4000 individual glass fibres, were impregnated using a system prepared according to the specification, ASTM Standard D2343-03, as illustrated in Fig. 3b. The system consisted of an impregnation device, a set of eight rollers, made of stainless steel and Teflon (upper consolidation roller), and a winder. After impregnation, the rovings were pulled through a series of rollers to remove excess resin and to achieve good wetting as well as uniform spreading of the fibres. The rectangular winder with rods placed at the four corners, was specifically designed to obtain straight segments of impregnated glass fibre bundles with a uniform width of $5 \pm 0.5 \text{ mm}$ and thickness of $0.5 \pm 0.1 \text{ mm}$. Both the individual and bundle fibres were cured in an oven at 80 °C for 2 h, followed by post curing at 150 °C for 3 h. The fibre volume fractions of bundle glass fibres were maintained at approximately 50% after cure.

2.3. Tensile testing and characterization

The individual glass fibres were mounted on specially prepared cardboard frames according to the specification, ASTM Standard D3822-1, using a cyanocrylate adhesive. To study the effects of fibre length on tensile strength, specimens were prepared with 25, 50, 100 and 150 mm gauge lengths, and the central cut out was made in each cardboard tab accordingly. The cardboard, with a single fibre mounted on, was gripped for tensile loading while ensuring straight and vertical fibre alignment. The impregnated bundle fibre specimens of 250 mm long, $5 \pm 0.5 \text{ mm}$ wide and $0.5 \pm 0.1 \text{ mm}$ thick were mounted with tabs made of sand paper and 50 mm long and 25 mm wide (shown in Fig. 4), using the above specification. Single fibre and fibre bundle specimens were tested on universal testing machines (MTS Alliance RT/5 and MTS

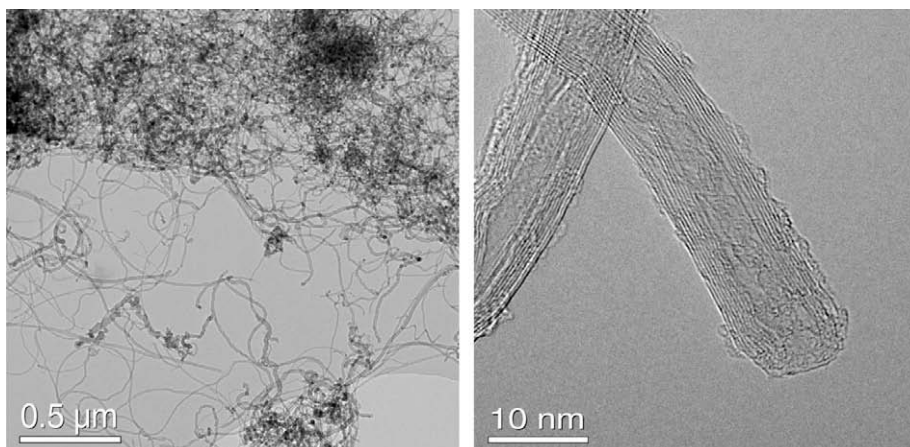


Fig. 2. TEM micrographs showing morphologies of CNTs used in this study.

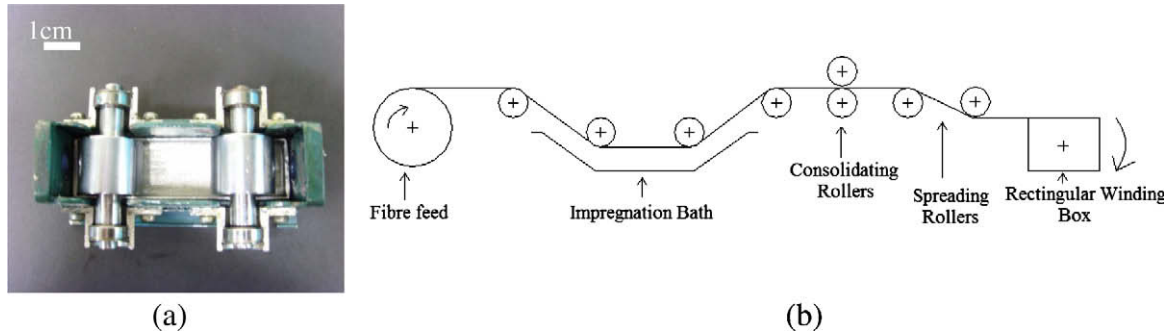


Fig. 3. (a) Photograph of the impregnation device for single fibre coating system; (b) schematic of the coating system for fibre bundles.

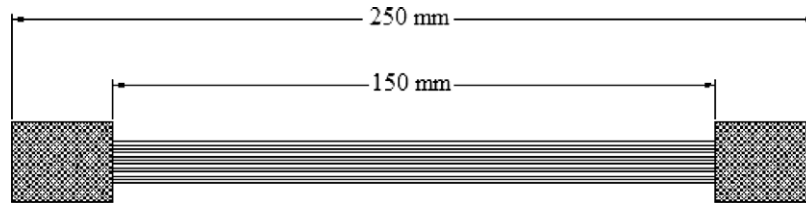


Fig. 4. Geometry and dimensions of test specimen for measuring tensile strength of fibre bundles.

Alliance RT/10 Material Test Systems) with cross head speeds of 0.5 mm/min and 10 mm/min, respectively. At least 20 specimens were tested for each set of conditions. The coating thicknesses on the single glass fibres were determined on a scanning electronic microscope (SEM, Jeol 6700). The dispersion state of CNTs within the nanocomposite coatings and the fracture surface morphologies of the impregnated bundle glass fibres were also examined using the SEM.

3. Results and discussion

3.1. Tensile strengths of single glass fibres

3.1.1. Effect of gauge length on the strength of fibres without coating

It is well known that the as-produced glass fibres show scattering in diameter which may affect the strength of fibres [12]. To reduce the potential variation of tensile strengths arising from the variation in fibre diameter, glass fibres having similar diameter of 24 μm were selected with the aid of an optical microscope for testing. Even so, the tensile strengths exhibited significant scattering. Therefore, two-parameter Weibull model was adopted for the evaluation of strength distribution, in which the probability of failure P , of a fibre with length L failed at a stress σ , can be predicted by:

$$P = 1 - \exp \left[-\frac{L}{L_0} \left(\frac{\sigma}{\sigma_0} \right)^m \right] \quad (1)$$

where m is the Weibull modulus, σ_0 is the characteristic fibre strength (scale factor) at a gauge length L_0 . For simplicity, L_0 is generally taken as unity. By taking the natural logarithms of Eq. (1) and further rearrangement:

$$\ln \left(\ln \left(\frac{1}{1-p} \right) \right) = m \ln(\sigma) - m \ln(\sigma_0) + \ln(L) \quad (2)$$

where m , regarded as the measure of data scatter, can be obtained from the line, $\ln(\sigma)$ against $\ln \left(\ln \left(\frac{1}{1-p} \right) \right)$. The characteristic strength σ_0 , can be obtained from the y-intercept of this line. The probability of fibre failures was estimated by:

$$P = i/n + 1 \quad (3)$$

P gives the probability of failure corresponding to the i th strength value and n is the total number of fibres tested for a given group. Numerous studies have validated the analysis of fibre strength using the similar Weibull statistics. A recent study [13] indicated that both the two and three-parameter Weibull equations could successfully evaluate the influence of gauge length and other factors on the fibre strength.

Fig. 5 shows the Weibull plots for uncoated individual fibres at various gauge lengths. The large variation of fibre strength at a given gauge length and the dependence of fibre strength on gauge length are evident. It is well established that the brittle fibres like glass have internal and surface defects, which influence the strength. The surface flaws, which are more detrimental than the internal flaws, vary in severity and characteristic population. As a consequence, the strengths of brittle fibres become lower at longer gauge lengths, indicating higher notch sensitivity at longer gauge lengths. The Weibull distribution parameters calculated by the linear regression method are listed in Table 1. It can be seen that the regression coefficients R^2 , were all close to unity for all conditions studied, indicating the validity of the method used. The shape

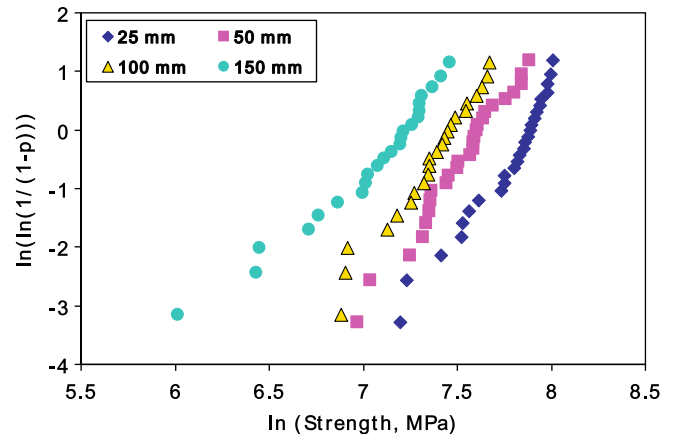


Fig. 5. Weibull plots of tensile strength for uncoated glass fibres of different gauge lengths.

Table 1

Weibull parameters determined from tensile tests of uncoated fibres.

Gauge length (mm)	Weibull modulus, m	Scale parameter, σ_0 (MPa)	Regression coefficient, R^2	Tensile strength (MPa) (mean \pm one std deviation)
25	4.77	5143	0.952	2405 \pm 275
50	4.77	4676	0.978	1890 \pm 264
100	4.72	4666	0.971	1604 \pm 165
150	3.01	7223	0.951	1205 \pm 205

parameter, m , a reflection of defect distribution along the fibre length, was much lower for the gauge length of 150 mm than the shorter gauge lengths. This clearly indicates a higher break sensitivity of fibres at the longer gauge length [14,15].

3.1.2. Effects of fibre coating

The thickness of the coating layer applied onto the glass fibre surface was verified by observing the cross section of fibres using the SEM, as shown in Fig. 6. It appears that the coating procedure described in Section 2 was effective in uniformly coating the glass fibres with a thin layer of neat epoxy or CNT nanocomposite, whose thickness was less than 1 μm . The image taken at a higher magnification, Fig. 6c, revealed that the CNTs were uniformly dispersed within the coating layer. The interfacial adhesion between the fibre and coating was excellent without any evidence of debonding.

Fig. 7 shows the Weibull plots of tensile strengths of the fibres with and without coating, and the corresponding Weibull parameters are given in Table 2. It is noted that the strength of fibres with epoxy coating were higher for all gauge lengths studied and the difference in strength was more pronounced at higher gauge lengths, which is a clear indication of reduction in notch sensitivity due to a fibre coating. It is thought that the epoxy coating filled the

surface cracks, effectively increasing the crack tip radius and thus reducing the stress concentration at the defects [2,3]. The smaller was the effective crack length, and the higher was the fibre tensile strength. The tensile strengths of the fibres with a 0.3 wt.% CNT-epoxy nanocomposite coating was even higher than those with the neat epoxy coating, indicating significant synergy was provided by CNTs in the coating. This observation was common for all gauge lengths. For example, the fibres tested at a gauge length of 150 mm resulted in an improvement of 25% and 7% at 50% probability of failure, compared to fibres without coating and with an epoxy coating, respectively. It appears that the randomly-dispersed CNTs within the nanocomposite coating offer a strengthening mechanism by bridging the surface micro-cracks, as proposed previously [6,7]. The “crack-tip bridging” effect promoted redistribution of the stresses around the surface cracks as far as the coating is intact with the glass fibre, thereby delaying the crack opening. The Weibull moduli were in general higher in the ascending order of no coating, the epoxy coating and the nanocomposite coating with 0.3 wt.% CNTs, confirming the increasingly narrowing data scatter. The result also indicates that the Weibull modulus was somehow less sensitive to the gauge length than to the coating material, whereas the mean tensile strength was more sensitive to the gauge length than the Weibull modulus. The large drop in Weibull

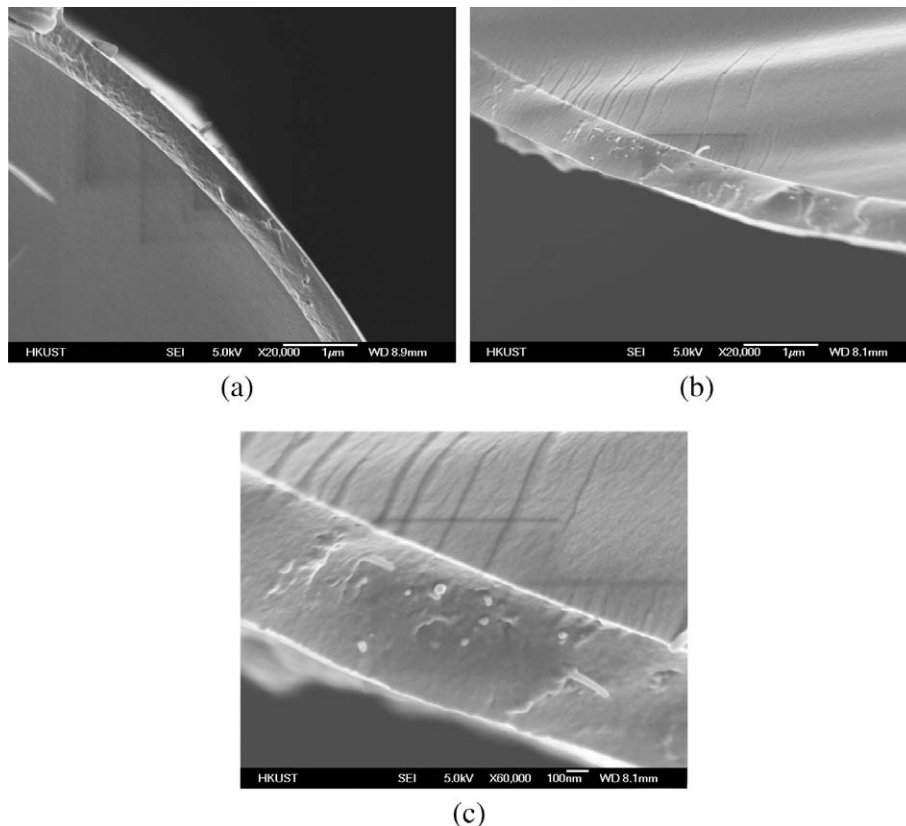


Fig. 6. SEM photographs of cross sections for fibres; (a) with epoxy coating (b, c) with 0.3 wt.% CNT-epoxy nanocomposite coating.

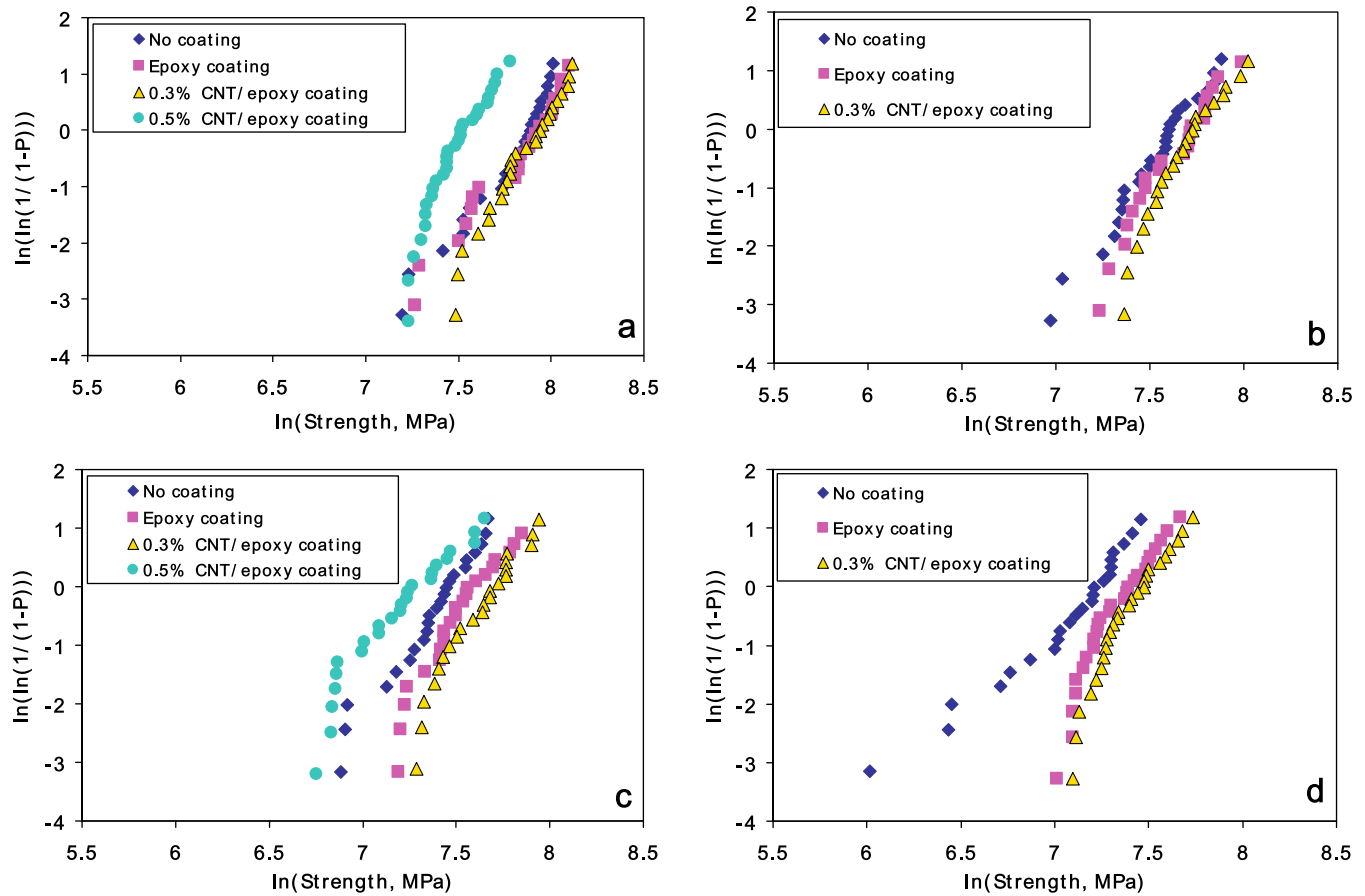


Fig. 7. Weibull plots of tensile strength for the fibres measured at (a) 25 mm (b) 50 mm (c) 100 mm and (d) 150 mm gauge length.

Table 2
Weibull Parameters for fibres with and without coatings measured at different gauge lengths.

Gauge length (mm)	Type of coating	Weibull modulus, <i>m</i>	Scale parameter, σ_0 (MPa)	Tensile strength (MPa) (mean \pm one std deviation)
25	No coating	4.77	5143	2405 \pm 275
	Epoxy coating	4.37	5724	2498 \pm 280
	0.3% CNT–epoxy coating	5.81	4834	2577 \pm 215
	0.5% CNT–epoxy coating	6.81	3053	2000 \pm 285
50	No coating	4.77	4676	1890 \pm 264
	Epoxy coating	5.18	4793	2077 \pm 260
	0.3% CNT–epoxy coating	5.80	4591	2172 \pm 207
100	No coating	4.72	4666	1604 \pm 165
	Epoxy coating	5.23	4923	1853 \pm 190
	0.3% CNT–epoxy coating	5.33	5285	2057 \pm 295
	0.5% CNT–epoxy coating	4.05	4668	1364 \pm 200
150	No coating	3.01	4311	1205 \pm 205
	Epoxy coating	5.90	3866	1536 \pm 160
	0.3% CNT–epoxy coating	6.00	4105	1643 \pm 155

Table 3
Tensile strengths of bundle glass fibres with different coatings (at a gauge length of 150 mm).

Coating material	Tensile strength of coating material (MPa)	Tensile strength (MPa) (mean \pm one std deviation)	Weibull modulus, <i>m</i>
Epoxy	71 \pm 4	844 \pm 70	14.4
0.3 wt.% CNT–epoxy coating	83 \pm 2	914 \pm 56	19.2
0.5 wt.% CNT–epoxy coating	75 \pm 7	960 \pm 53	21.0

modulus at the gauge length of 150 mm represents the typical of exponential behaviour.

However, a further increase in CNT content in the coating to 0.5 wt.% was not beneficial, due probably to CNT agglomeration in the coating [10,16], which may have acted as a different type of stress concentration. The CNTs tended to agglomerate in the resin when the content was above the optimal value, reducing the strength of CNT–polymer nanocomposites [10,11]. The tensile strengths of the coating materials given in Table 3 further support this claim. The morphologies taken from the fracture surfaces of the same CNT–epoxy nanocomposites are shown in Fig. 8. Prominent CNT agglomerates were identified from the specimen

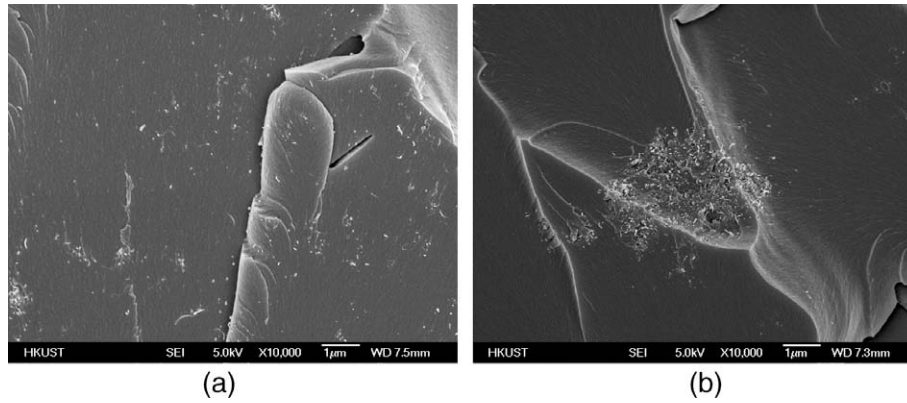


Fig. 8. SEM images of fractured surfaces of (a) 0.3 wt.% CNT-epoxy (b) 0.5 wt.% CNT-epoxy nanocomposites showing dispersion state of CNTs in epoxy.

containing 0.5 wt.% CNTs, whereas the CNTs were relatively well dispersed in the specimens containing 0.3 wt.% CNTs.

Further evaluation was made of the effects of coating material by plotting the mean tensile strengths as a function of gauge length, as shown in Fig. 9. The mean strengths exhibited typical parabolic decreases with increasing gauge length for all coating materials studied. For a given gauge length, the mean strength was higher in the order of the nanocomposite coating with 0.3 wt.% CNTs, the epoxy coating, without coating and the nanocomposite coating with 0.5 wt.% CNTs, which is consistent with the observations noted previously.

3.2. Fracture mechanics analysis of the crack healing effects of coating

As discussed above, the coating made from the 0.3 wt.% CNT-epoxy nanocomposite provided a substantial healing effect on glass fibre. It is of particular interest to further understand the role of different coatings in improving the fibre strength from the fracture mechanics viewpoint. Assuming that a glass fibre contains surface flaws of varying sizes and orientations and the fracture of the fibre in tension is triggered by the longest crack. According to the linear elastic fracture mechanics, the critical stress intensity factor, K_{IC} , for a circumferential crack of effective length, a_c , in the middle of a fibre is given by [17]:

$$K_{IC} = F\sigma_c\sqrt{\pi a_c} \tag{4}$$

where F is a dimensionless function related to the geometry and the ratio of the crack length to geometric dimension; σ_c is the critical stress applied at remote fibre ends for fracture of the fibre with

an effective crack length, a_c . K_{IC} can be approximated to $1 \text{ MPa}\sqrt{\text{m}}$ [18], assuming F is given by [17]:

$$F = \frac{1}{2\beta^{1.5}} \left[1 + \frac{1}{2}\beta + \frac{3}{8}\beta^2 - 0.363\beta^3 + 0.731\beta^4 \right] \\ = 0.5\beta^{-1.5} + 0.25\beta^{-0.5} + 0.1875\beta^{0.5} - 0.1815\beta^{1.5} + 0.3655\beta^{2.5} \tag{5}$$

where $\beta = 1 - \alpha$, and $\alpha = a/b$, a and b are the crack length and half the fibre diameter, respectively. By applying binomial series, Eq. (5) is simplified:

$$F = 1.1215 + 0.13975\alpha \tag{6}$$

Because $a \ll b$, α approaches to zero; and F can be simplified to 1.12.

A two-parameter model was successfully used [19,20] to predict the residual strengths of composite laminates with different damage sizes, knowing the original strength of the laminate containing intrinsic flaws of a certain size. The same approach is used here to correlate the strengths of the glass fibres with and without a coating, i.e.

$$\frac{\sigma_c}{\sigma_u} = \left(\frac{a_u}{a_c} \right)^n \tag{7}$$

where σ and a are the tensile strength and the surface crack length of fibres, respectively; and the subscripts u and c refer to the uncoated and coated fibres, respectively. n is an exponent, equal to 0.5 when the fibre material is linearly elastic up to fracture, and smaller than 0.5 when the fibre material shows pseudo-plastic zone at the crack tip before fracture [21]. In this analysis, $n = 0.5$ was taken as the stress-strain curves of the glass fibres were linear elastic up to fracture for all cases. Eq. (7) implies that the fibres with smaller intrinsic defect sizes or shorter effective crack lengths would have higher tensile strengths, which is also equally reflected by Eq. (4).

Therefore, the effective crack lengths a_c were estimated using Eqs. (4) and (7) from the known mean tensile strengths of uncoated and coated fibres, and are plotted against gauge length for three different fibre surface conditions, as shown in Fig. 10a. As expected, the intrinsic crack lengths of all glass fibres increased with gauge length as a result of increasingly decremental strength as Eq. (8) indicates. More importantly, the nanocomposite coating containing 0.3 wt.% CNTs presented an obvious advantage of a shorter crack length for a given gauge length than the epoxy coating or the fibre without coating. A further analysis is made with reference to the logarithmic plot shown in Fig. 10b, indicating approximately a linear relationship between $\text{Ln}(a_c)$ and the gauge length. The slopes of the lines were 0.0065, 0.007 and 0.01 for the fibres with CNT-epoxy nanocomposite coating, epoxy coating and the fibre without coating, respectively. These values can be regarded as the “effective crack length coefficients”: the smaller is the coeffi-

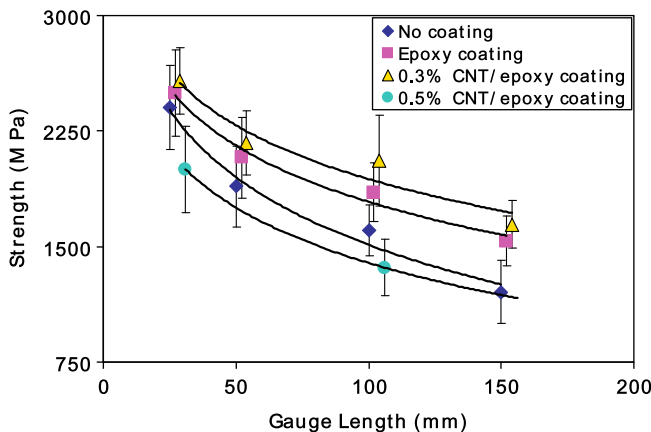


Fig. 9. Variation of tensile strengths of single glass fibres as a function of gauge length (mean value ± one std deviation) for different coatings.

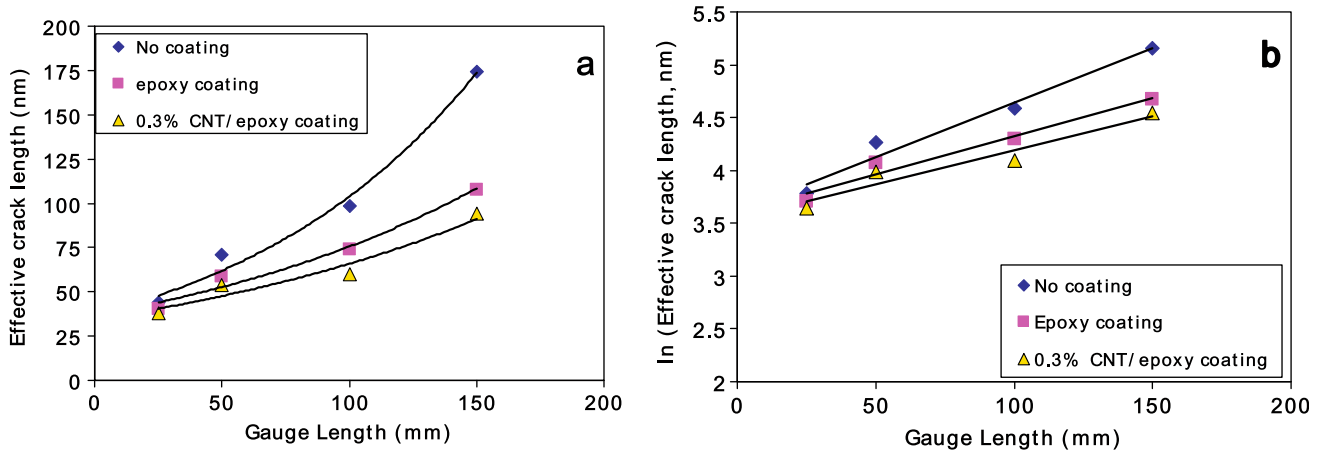


Fig. 10. Plots of (a) effective crack length vs gauge lengths and (b) Ln (effective crack length) vs gauge length for different fibre coatings.

cient, the more uniform distribution is the damage size or effective crack length. This indicates that the surface defects have an even distribution after coating with CNT–epoxy nanocomposite. As a summary, the tensile strengths of the fibres with different coatings are plotted against effective crack length in Fig. 11. It should be noted that all data points fell on a curve represented by Eq. (4). The implication is that for a fibre with known fracture toughness, the strength can be improved by reducing the defect size or effective crack length present on the surface. The gauge length is an important parameter that affects the effective crack length and thus the fibre tensile strength as the data points indicate.

3.3. Effect on CNT–epoxy nanocomposite coating of fibre bundles

The tensile strengths of glass fibre bundles with different coating materials were measured at a fixed gauge length of 150 mm. Fig. 12 shows the Weibull plots of tensile strengths of fibre bundles, and Table 3 summarizes the data obtained for fibre bundles as well as coating materials. The mean tensile strengths of coating materials increased after addition of 0.3 wt.% CNT. However, further increase in CNT content to 0.5 wt.% marginally reduced the strength of the coating due to the possible agglomeration of CNTs, as discussed in Section 3.2. For the coated bundle fibres, both the mean tensile strength and the Weibull modulus were higher for the samples with 0.5 wt.% CNT–epoxy nanocomposite coating. It

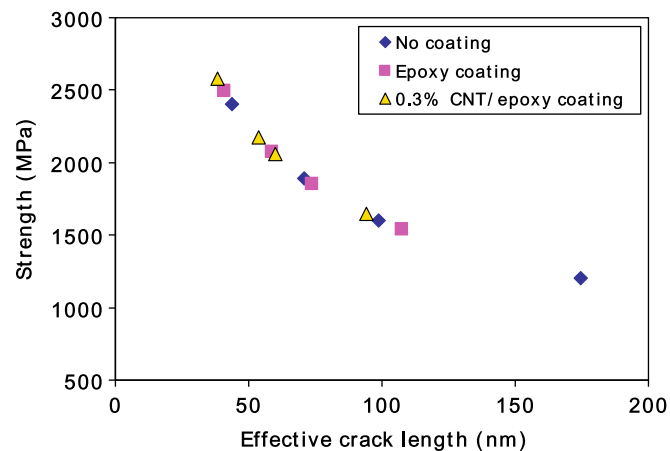


Fig. 11. Variation of tensile strengths of single glass fibres with effective crack length for different fibre coating.

is obvious that the incorporation of CNTs in the epoxy further enhanced the effects of fibre coating on crack healing. The higher effectiveness at 0.5% CNT than at 0.3% CNT indicates that the potential agglomeration of CNTs in the coating of fibre bundle was not as serious as in the single fibre coating because the coating was generally much thinner on single fibres. Alternatively, the negative effect of CNT agglomeration on the strength of fibre bundle was not as detrimental to the strength of single fibres.

The SEM photographs of the fracture surfaces shown in Fig. 13 suggest that there was a transition in fracture mode between the samples with different coatings. The fibre bundles coated with neat epoxy failed predominantly by progressive fibre debonding and fibre pullout, namely ‘longitudinal splitting’, followed by breakage of fibres at multi-levels along the fibre direction (Fig. 13a and b). The extensively pulled-out fibres of different lengths on the fracture surface indicate that the damage initiated from various locations along the interface. In sharp contrast, the fibre bundles coated with a CNT–epoxy nanocomposite failed transversely and flat across the specimen width with relatively few debonding and fibre pullout, namely ‘transverse fracture’ (Fig. 13c and d). In the latter samples, the interfaces between the fibre and the resin were intact even after failure, indicating that fibres were strongly bonded to the coating material. The failure was rather catastrophic compared to the former samples with the neat epoxy coating.

Judging from the significant change in interfacial fracture morphology which is schematically presented in Fig. 14, it appears that the change in interfacial adhesion due to the presence of CNTs in the epoxy coating was mainly responsible for the transition in failure mode from longitudinal splitting to transverse fracture [22–24]. It is well known [1] that the interfacial adhesion in polymer composites is very sensitive to the wettability of the fibres with the matrix. It is suspected that the inclusion of amino-functionalized CNTs enhanced the wettability by reducing the surface energy of the epoxy matrix. Similar results have been reported in a study based on the epoxy matrix composites reinforced with ultrahigh molecular weight polyethylene [25,26]: addition of a small amount of graphitic nanofibres (with reactive amino functional groups) led to significant improvement in wetting property of an epoxy and interfacial adhesion.

4. Concluding remarks

The effects of different fibre coatings and gauge lengths on tensile strengths of individual glass fibres well as of bundle fibres were studied. Fibres with three types of surface conditions, including fibres without coating, fibres with epoxy coating and fibres

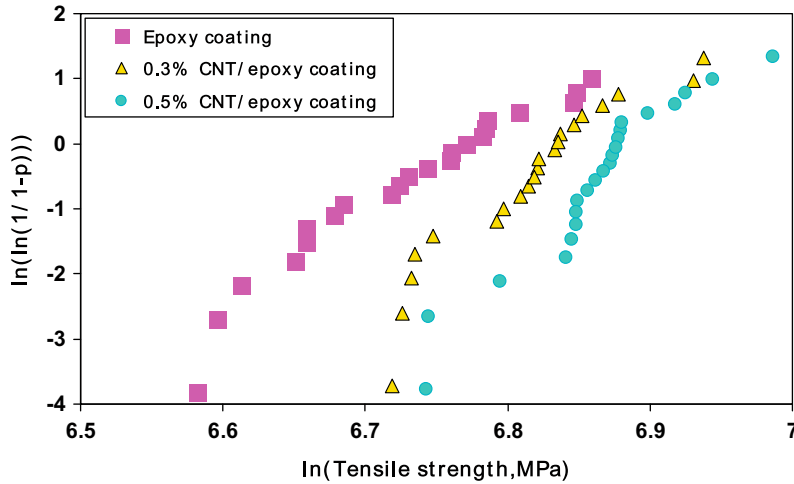


Fig. 12. Weibull plots of tensile strength for fibre bundles with neat and CNT-modified epoxy coatings.

with CNT-epoxy coating were employed. The following can be highlighted from the study:

- (i) The single fibres coated with the 0.3 wt.% CNT-epoxy nanocomposite exhibited larger strength improvement than fibres with a neat epoxy coating, compared to fibres without coating. This suggests that the CNTs added into the epoxy coating further enhanced the crack healing effect.
- (ii) The crack healing effect of fibre coating was explained in terms of the 'effective crack length coefficient' which was obtained from the crack length vs gauge length curves. The

results indicate that the smaller is the coefficient, the more uniform distribution is the damage size or effective crack length.

- (iii) The dispersion of CNTs in the polymer coating is an important factor affecting healing effect. A poor dispersion may have a detrimental effect on tensile strength as observed for the 0.5% CNT-epoxy coating.
- (iv) The glass fibre bundles impregnated with CNT-epoxy nanocomposite led to much higher tensile strength than those with neat epoxy coating, with accompanied change in failure mode. The enhancement of interfacial adhesion arising from

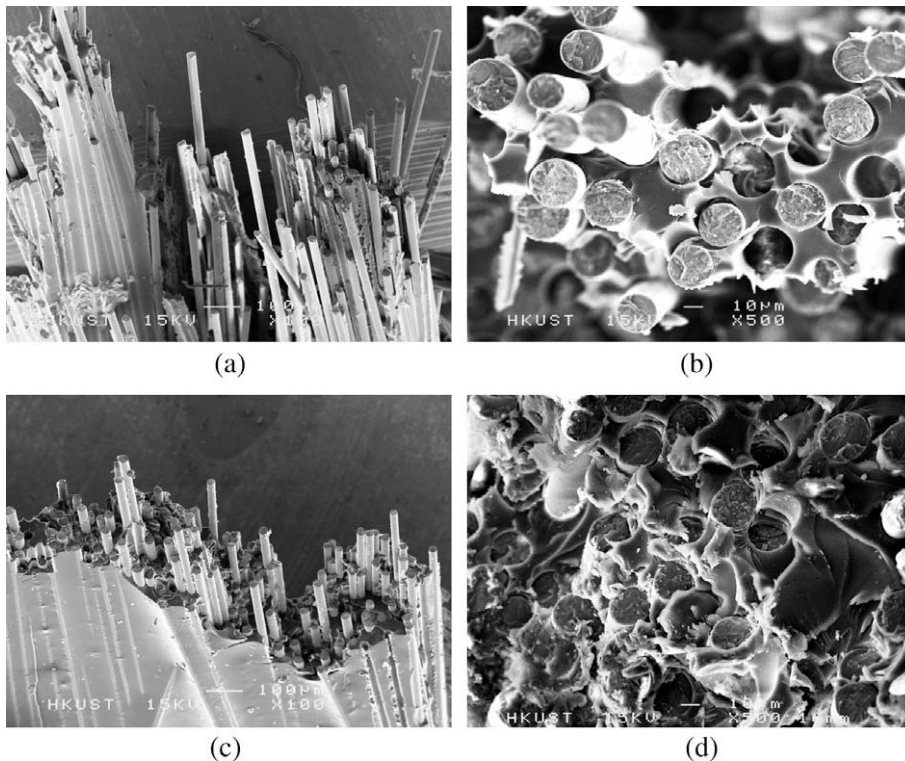


Fig. 13. SEM images of fractured surfaces of fibre bundles: (a, b) with neat epoxy coating and (c, d) with 0.3% CNT-epoxy nanocomposite coating.

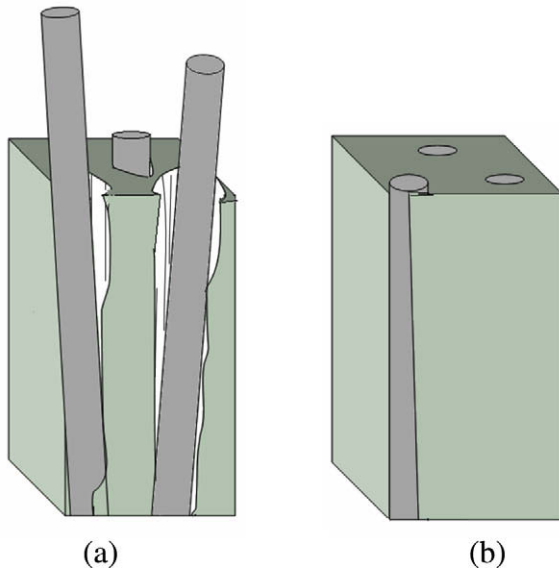


Fig. 14. Schematics of failure modes in (a) fibre bundles with neat epoxy coating and (b) fibre bundles with 0.3 wt% CNT-epoxy nanocomposite coating.

the amino-functionalized CNTs was partly responsible for the beneficial effect of the nanocomposite on tensile strength of bundle fibres.

Acknowledgements

This project was supported by the Research Grant Council of Hong Kong SAR (Project No. 614607). Technical supports from the Materials Characterization and Preparation Facilities (MCPF) are much appreciated.

References

- [1] Kim JK, Mai YW. Engineered interfaces in fibre reinforced composites. Oxford (UK): Elsevier Publishers; 1998.
- [2] Dibenedetto AT, Lex PJ. Evaluation of surface treatments for glass fibres in composite materials. *Polym Eng Sci* 1989;29:543–55.
- [3] Zinck P, Pays MF, Rezakhanlou R, Gerard JF. Mechanical characterization of glass fibres as an indirect analysis of the effect of surface treatment. *J Mater Sci* 1999;34:2121–33.
- [4] Loewenstein KL. The manufacturing technology of continuous glass fibres. Amsterdam, New York: Elsevier; 1983.
- [5] Ahlstrom C, Gerard JF. The adhesion of elastomer-coated glass fibres to an epoxy matrix. Part 1: The effect of the surface treatments on the tensile strength of the glass fibres. *Polym Compos* 1995;16(4):305–12.
- [6] Gao SL, Mader E, Plonka R. Nanostructured coatings of glass fibres: improvement of alkali resistance and mechanical properties. *Acta Mater* 2007;55:1043–52.
- [7] Gao SL, Mader E, Plonka R. Nanocomposite coatings for healing surface defects of glass fibres and improving interfacial adhesion. *Compos Sci Technol* 2008;68:2892–901.
- [8] Pierce FTS. The tensile strength for the cotton yarns – the weakest link. Theorems on the strength of long and of composite specimens. *J Text Inst* 1926;17:355–68.
- [9] Sham ML, Kim JK. Surface functionalities of multi-wall carbon nanotubes after UV/Ozone and TETA treatments. *Carbon* 2006;44:768–77.
- [10] Ma PC, Kim JK, Tang BZ. Effects of silane functionalization on the properties of carbon nanotube/epoxy nanocomposites. *Compos Sci Technol* 2007;67:2965–72.
- [11] Li J, Ma PC, Sze CW, Kai TC, Tang BZ, Kim JK. Correlations between percolation threshold, dispersion state and aspect ratio of carbon nanotubes. *Adv Funct Mater* 2007;17:3207–15.
- [12] Davies IJ. Effect of radius variation on the mean strength of brittle fibres. *J Mater Sci Lett* 2001;20:1103–5.
- [13] Zafeiropoulos NE, Baillie CA. A study of the effect of surface treatments on the tensile strength of flax fibres: Part II application of Weibull statistics. *Composites Part A* 2007;38:629–38.
- [14] Andersons J, Joffe R, Hojo M, Ochiai S. Glass fibre strength distribution determined by common experimental methods. *Compos Sci Technol* 2002;62:131–45.
- [15] Wu HF, Netravali AN. Weibull analysis of strength-length relationships in single Nicalon SiC fibres. *Mater Sci* 1992;27:3318–24.
- [16] Coleman JN, Khan U, Gun'ko YK. Mechanical reinforcement of polymers using carbon nanotubes. *Adv Mater* 2006;18:689–706.
- [17] Tada H, Paris PC, Irwin GR. The stress analysis of cracks handbook. 2nd ed. Paris Productions, Inc.; 1985.
- [18] Gao SL, Mader E, Plonka R. Coatings for glass fibers in a cementitious matrix. *Acta Mater* 2004;52:4745–55.
- [19] Hirai Y, Hamada H, Kim JK. Impact response of glass woven fabric laminates: Part 1. Effect of silane coupling agents. *Compos Sci Technol* 1998;58:91–104.
- [20] Hirai Y, Hamada H, Kim JK. Impact response of glass woven fabric laminates: Part 2. Effect of temperature. *Compos Sci Technol* 1998;58:119–28.
- [21] Caprino G. On the prediction of residual strength for notched laminates. *J Mater Sci* 1983;18:2269–73.
- [22] Kim JK, Mai YW. Fracture of CFRP containing impregnated fibre bundles. *Compos Sci Technol* 1993;49:51–60.
- [23] Qiu J, Zhang C, Wang B, Liang. Carbon nanotubes integrated multifunctional multiscale composites. *Nanotechnology* 2007;18:275708.
- [24] Zhao FM, Takeda N. Effect of interfacial adhesion and the statistical fibre strength on the tensile strength of the unidirectional glass fibre/epoxy composites. Part 1: Experimental results. *Composites Part A* 2000;31:1203–14.
- [25] Neema S, Salehi-Khojin A, Zhamu A, Zhong WH, Jana S, Gan YX. Wettability of nanoepoxies to UHMWPE fibres. *J Colloid Interf Sci* 2006;229:332–41.
- [26] Zhamu A, Zhong WH, Sone JJ. Experimental study on adhesion property of UHMWPE fibre/nano-epoxy by the fibre pull-out. *Compos Sci Technol* 2007;66:2736–42.