

Fracture and fatigue behaviour of carbon fibre composites with nanoparticle-sized fibres

Shang-Nan Tsai^{a,*}, Declan Carolan^a, Stephan Sprenger^b, Ambrose C. Taylor^a

^a*Department of Mechanical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom*

^b*Evonik Nutrition & Care GmbH, Charlottenburger Strasse 9, 21502 Geesthacht, Germany*

Abstract

Fibre composites with thermoset polymer matrices are widely used. However, thermosets are very brittle, which can limit the applications of fibre composites. In this work, silica nanoparticles (SNPs) were used to modify two fibre sizings to improve the toughness of carbon fibre composites. Mode I interlaminar fracture and fatigue crack growth tests were conducted on the composites made using the silica nanoparticle-sized fibres. There was no significant change in the fatigue crack growth rate with the addition of SNPs. However, the addition of SNPs to either sizing increased the composite toughness. The fracture energy was significantly increased from 166 J/m² to 220 J/m² (increased by 33%) with only 0.89 wt% on fibre weight of SNPs. This is significantly more efficient than adding SNPs into the matrix, which can require addition of up to 20 wt% of SNPs [1], to achieve the same improvement in toughness.

Keywords: Carbon fibres, Adhesion, Fracture toughness, Sizings

1. Introduction

Fibre composites are widely used because of their light weight and high mechanical strength and stiffness. Composites can be found in daily lives in structural applications, such as the frames of bicycles, car bodies, ship hulls and aircraft fuselages. Such fibre composites typically comprise continuous fibres embedded in a thermoset polymer matrix. Although

*Corresponding author

Email address: s.tsai15@imperial.ac.uk (Shang-Nan Tsai)

14 these thermoset polymers have many beneficial properties such as a high glass transition tem-
15 perature and low creep, they have a major disadvantage of being very brittle since they are
16 highly crosslinked. This brittleness can limit the applications of fibre composite parts since
17 they require not only high strength, but also good resistance against impact, fracture and
18 fatigue to prevent premature and catastrophic failure.

19 To overcome this brittleness for engineering applications, fibre composites are tough-
20 ened by adding second-phase modifiers into the thermoset matrix. There are many potential
21 modifiers that have been used to improve the toughness of thermoset polymers. These in-
22 clude pre-formed particles such as core-shell rubber [2–5], thermoplastic polymer [6, 7],
23 aluminium [8], ceramic [8–12] and carbon (e.g. carbon nanotubes and graphene [13–15])
24 particles. Phase-separable modifiers such as thermoplastics [16–19], rubbers [20–22] and
25 block copolymers [23] have also been used. For example, when silica nanoparticles (SNPs)
26 are added to epoxy polymers, the toughness increases as the concentration is increased (see
27 Figure 1) [24].

28 Increasing the fracture energy of fibre composites is more difficult than for bulk ther-
29 moset polymers, as the size of the plastic zone at the crack tip is constrained by the stiff
30 fibres, therefore less energy is absorbed during crack growth. This can result in a poor trans-
31 fer of toughness from the bulk polymer to the composite, and a limiting fracture energy can
32 be reached where further increases in the matrix toughness do not increase the toughness
33 of the composite [25]. Moreover, many of the modifiers discussed above increase signif-
34 icantly the viscosity of the resin and thus manufacturing fibre composites using infusion
35 processes with these modified resins can become impossible. One modification that has been
36 particularly successful is the addition of silica nanoparticles. These particles are typically
37 20 nm in diameter and are surface-treated to prevent agglomeration. Thus the increase in
38 resin viscosity is very small, and they can readily flow between the fibres during infusion.
39 Silica nanoparticle-modified epoxy resins have resulted in improvements of fibre composite
40 toughness and fatigue behaviour [1, 26–31]. For example, adding 10 wt% of SNPs into the
41 matrix epoxy increased the fracture energy of a unidirectional (UD) glass fibre reinforced
42 polymer (GFRP) by 200% [27], and also extended the tensile fatigue life by 3 to 4 times [29].

However, directly adding modifiers into the matrices of fibre composites requires significant addition of modifiers, e.g. up to 20 wt% of the matrix resin [1], which leads to an increased cost in materials and manufacturing for practical applications.

The present work investigates the addition of silica nanoparticles into fibre sizings. Sizings are the agents applied to raw fibres during fibre manufacturing, they protect the fibres during processing and control the adhesion between the fibres and the matrix. Since the fibres take most of the load when fibre composites are in service, good adhesion between the fibres and the matrix means that stress is transferred effectively to the fibres, which contributes to better mechanical properties. Research has showed that adding silica nanoparticles into fibre sizings can increase the interlaminar shear strength (ILSS) of carbon fibre composites [32]. The aim of the present work is to reduce the addition levels of silica nanoparticles required to improve fracture toughness and fatigue life of fibre composites, with no increase in resin viscosity, by introducing the silica nanoparticles into sizings.

2. Experimental Methods

2.1. Materials

Carbon fibre composites were manufactured using carbon fibres with unmodified and silica nanoparticle (SNP) modified sizings. The sizing formulations used in this work are listed in Table 1. The carbon fibre (HF10-12k), diglycidyl ether of bis-phenol A (DGEBA) epoxy resin (E54), methyl tetrahydrobenzoic anhydride hardener (HK021) and one of the fibre sizings (HS-1) were obtained from Hengshen, China. A second sizing, Neoxil 965, was obtained from Aliancys, Switzerland. Nanopox FW 404, an aqueous emulsion of epoxy and silica nanoparticles, was obtained from Evonik, Germany. The concentration of SNPs in FW 404 emulsion is 22.4 wt% (as the emulsion contains 44 wt% water and 56 wt% Nanopox F400 [33]). Nanopox F400 contains 40 wt% of SNPs [33]. Therefore the concentration of SNPs in dried FW 404 is 40 wt% on solid (since the water is removed). The sizing and SNP contents of the fibres is shown in Table 1. The average diameter of the silica nanoparticles is 20 nm [33]. The modified sizings containing SNPs were applied to the fibres by Hengshen, who also manufactured the unidirectional (UD) laminates by vacuum assisted resin infusion (VARI),

71 a standard procedure used to manufacture fibre composites. The produced UD composite
72 panels had a thickness of 3 mm.

73 2.2. Double Cantilever Beam Specimen Preparation

74 Mode I interlaminar fracture tests and fatigue crack growth (FCG) tests were conducted
75 using double cantilever beam (DCB) specimens machined from the UD composite panels by
76 waterjet cutting. Each specimen had a size of 150 mm $\times$ 20 mm $\times$ 3 mm with a 30- μ m-thick
77 release film insert of 45 mm in length at the midplane of one end to provide a starter crack.

78 Each side of the insert film end was grit-blasted, cleaned with acetone and then adhered
79 with two aluminium load blocks using Araldite 2014-1 two component epoxy adhesive from
80 Huntsman. The blocks were clamped to the specimens in a jig and cured in an oven at 50
81 °C for two hours. After bonding the load blocks, the side of each specimen was painted with
82 white ink and the crack length was marked, from the end of the inserted film, every millimetre
83 for the first 25 millimetres and then every 5 millimetres.

84 2.3. Mode I Interlaminar Fracture Test

85 Interlaminar fracture tests were carried out to determine the mode I fracture energy at
86 crack initiation, $G_{IC,init}$, and during crack propagation, $G_{IC,prop}$. The DCB specimens were
87 tested using an Instron 5584 universal testing machine at room temperature and a displace-
88 ment rate of 1 mm/min. The testing procedure used was according to the BS ISO 15024 [34]
89 and ASTM D5528 [35] standards. A travelling microscope was used to measure the crack
90 growth.

91 The specimens were first precracked by loading until the crack grew up to 5 mm from the
92 end of the insert film, which generated a sharp natural crack. The specimens were unloaded,
93 and then reloaded until the crack propagated to 110 mm (65 mm from the insert film). The
94 displacement and load were recorded when the crack grew to each mark. The values of
95 fracture energy at crack initiation, $G_{IC,init}$, were calculated using the Max/5% increase in
96 compliance method; the fracture energies during crack propagation, $G_{IC,prop}$, were calculated
97 using the modified compliance calibration (MCC) method [34]. Five specimens were tested
98 for each sizing formulation.

2.4. Fatigue Crack Growth Test

Fatigue crack growth (FCG) tests were conducted using the DCB specimens at room temperature, taking reference to the BS ISO 13003 [36] and ASTM E647 [37] standards. The DCB specimens were first pre-cracked as mentioned above to determine the maximum displacement, $\delta_{\max}$, for the FCG test. The fatigue tests were carried out using an Instron 8872 servohydraulic universal testing machine, in displacement control. The displacement ratio ($R = \delta_{\min}/\delta_{\max}$) used was 0.1, at a cyclic loading frequency of 10 Hz using a sinusoidal waveform.

To measure the crack length during the fatigue tests, the machine was briefly paused and held at $\delta_{\max}$ after a prescribed number of cycles had completed. The load and crack length (measured using a microscope) were recorded and the tests were continued. Three specimens were tested for each formulation. The relationship between the crack propagation rate per cycle, da/dN , and the maximum energy release rate, $G_{\max}$, was calculated using the 7-point incremental polynomial method [37]; the FCG curve of $\log(da/dN)$ against $\log(G_{\max})$ was also plotted.

2.5. Fractographic Studies

Images of the fracture surfaces of the tested specimens were taken using a scanning electron microscope (SEM), Hitachi S-3400N (for the FCG specimens), or a field emission SEM (FE-SEM), Zeiss Ultra Plus Field Emission SEM (for the DCB fracture specimens). The samples were sputter-coated with a gold or gold-palladium layer before taking images to prevent charging. The thickness of the sputter-coated layer had a thickness about 5 to 10 nm. These images were used to identify the failure and toughening mechanisms.

3. Results and Discussion

3.1. Introduction

The mode I interlaminar fracture energies and fatigue crack growth rates of the fibre composites using unmodified and SNP-modified sizings were measured. Two different sizings were used, each sizing had three formulations: unmodified (no SNPs), 0.53 wt% SNPs

126 and 0.89 wt% SNPs based on fibre mass, as shown in Table 1. The effect of the addition of
127 SNPs to the sizings is discussed and compared to that of the addition of SNPs to the matrix.
128 The images of the fracture surfaces were also studied to identify the toughening mechanisms.

129 3.2. Interlaminar Fracture Energy

130 The calculated values of the mode I interlaminar fracture energy at crack initiation, $G_{IC,init}$,
131 and propagation, $G_{IC,prop}$, for the carbon fibre composites with the unmodified and SNP-
132 modified sizings are shown in Table 2. For the composites using the unmodified sizings, N0
133 and H0, the fracture energies at crack initiation are 85 J/m² and 108 J/m² respectively, this
134 difference results from using different sizing agents. On the other hand, for the composites
135 using SNP-modified sizings, although the fracture energy at crack initiation only shows a
136 small increase of 15% when the main sizing agent is Neoxil 965 with the addition of 2.22 wt%
137 of Nanopox FW 404 (sizing N2), the fracture energy at crack initiation increases significantly
138 by 101% when the main sizing agent is HS-1 with the addition of 2.22 wt% of FW 404 (sizing
139 H2), see Table 2. It is also noted that the $G_{IC,init}$ values of each formulation have large standard
140 deviations, which indicates that crack initiation is an unstable process.

141 For crack propagation, the fracture energy shows no significant change (there is only an
142 increase of 7% for sizing N1) when SNPs are added to the Neoxil 965 sizing agent. However,
143 $G_{IC,prop}$ increases from 166 J/m² to 220 J/m² (an increase of 33%) with the addition of 2.22
144 wt% of FW 404 to the HS-1 sizing agent (sizing H2).

145 Comparing the fracture energies at crack initiation and propagation, it is noted that for the
146 higher addition level of SNPS (sizings N2 and H2 compared to unmodified sizings N0 and
147 H0, see Figure 2), the difference between the fracture energies at crack initiation and propa-
148 gation decreases. This decrease of the difference means that there is a reduction of the size
149 of the crack resistance curve (R-curve), which is a sign of a more stable crack propagation.
150 For sizing H2, the difference between the crack initiation and propagation fracture energies
151 is only 3 J/m² (Table 2).

3.3. Comparison with SNP-modified matrices

Table 3 shows the relative $G_{IC,prop}$ values compared with published values for which SNPs are added into the matrices of UD carbon fibre/epoxy composites [1, 30]. The epoxy system used for the SNP-modified matrices in the literature was DGEBA epoxy (Araldite-F) and piperidine hardener [1, 30]. The manufacturing processes of the carbon fibre composites using the modified matrices were vacuum assisted resin infusion moulding (VARIM) [1] or using the prepreg impregnated with the modified epoxy matrices and then fabricated by vacuum bagging [30].

According to Table 3, it is clear that the method of adopting a modified sizing can achieve the same level of improvement using significantly fewer SNPs compared with adding the SNPs into the matrix. The increase of the fracture energy of the composite using an SNP-modified matrix, containing up to 20 wt% SNPs in the matrix, is 21%. However, sizing H2 achieves a higher increase of 33% while only adding 0.89 wt% (on fibre mass) to the sizing agent.

3.4. Fatigue Crack Growth

Figure 3 shows a typical FCG curve (on log-log axes) of a UD carbon fibre composite. The right-hand region I is where the crack grows rapidly at the beginning of the cyclic loading and $G_{I,max}$ approaches $G_{IC,prop}$. Region II is where the crack grows steadily, and the relationship typically follows a linear Paris-Erdogan law relationship. The left-hand region III is where the crack grows very slowly or stops growing and the energy release rate reaches the threshold value, G_{th} , below which crack growth does not occur.

The gradient of region II, m_G , reflects the sensitivity of the crack growth rate to the change of cyclic load, as shown in Table 4. In Table 4, the value of m_G was calculated according to the energy release rate while m_K is the related gradient when the mode I stress intensity factor (K_I) is used as the horizontal axis of the FCG curve (using $G_I = K_I^2(1 - \nu^2)/E$, where E is the Young's modulus and ν is the Poisson's ratio). The gradient m_G values of the composites using the unmodified sizings (N0 and H0) are 2.02 and 3.98. For the composites using modified sizings (N2 and H2), the m_G values are 5.90 and 3.00, and the related m_K values

are 11.80 and 6.00. Although in this work no significant change of the gradient was found within experimental variation for the various sizings used, the gradients are generally larger than metals whose m_K are usually taken as 3 to 4 [38, 39], see Table 4. This confirms that the fibre composites are more sensitive to fatigue crack growth than metals.

3.5. Fractographic Studies

The FE-SEM images from the tested samples of mode I interlaminar fracture tests were studied. The fibre surfaces of the composite using unmodified sizing (H0) are clean and adhered with little epoxy (see Figure 4a), an obvious debonding of a fibre can also be seen, which indicates a relatively poor adhesion between the fibre and matrix. On the other hand, silica nanoparticles can be found on the fibre surfaces in the SNP-modified sizing samples (see Figure 4b&c). It is noted that a greater addition of SNPs results in a better SNP dispersion; SNPs were spread more evenly across the fibre surfaces. As can be seen in Figure 4b&c, both sizing H1 and H2 contain SNPs, however, the fibre surfaces in Figure 4c are adhered with more SNPs than in Figure 4b. Better SNP dispersion results in a better adhesion between the fibres and the matrix, since the surfaces of the fibres are adhered with more epoxy and SNPs after testing; the fibre surfaces shown in Figure 4b&c are rougher than the surfaces in Figure 4a.

A strong adhesion between the fibres and the matrix results in more fragmentation of the fibres when the crack grows, since the fibres cannot be pulled out so easily and are more likely to break due to the tensile force caused by the crack growing. As can be seen in Figure 5b&d, there are more fragmented fibres since the adhesion is better. However, if the adhesion is weak, the fibres are easier to pull out and can bridge between the crack faces (see Figure 5a&c). The improvement of adhesion can also be seen in the SEM images from the FCG-tested samples (see Figure 6), as more epoxy can be found adhered to the fibres in Figure 6b than in Figure 6a; there is debonding in Figure 6a, which also indicates poor adhesion.

The fibres absorb energy and then break as the crack grows. The presence of more fragmented fibres resulting from good adhesion means that more energy is absorbed by the fibres, which results in an increased difficulty of crack growth and hence an improvement of the

toughness. However, if the adhesion is improved too much, there would be a negative effect such that fewer fibres break because few fibres pull out, which leads to a reduction of $G_{IC,prop}$ [7]. This effect was observed in sizing N2, where in comparison with sizing N1, the adhesion is stronger but fewer fragmented fibres and so a smaller reduction of $G_{IC,prop}$ was observed.

A good adhesion also contributes to the increase of $G_{IC,init}$ (sizings N2 and H2 compared with the unmodified sizings N0 and H0). Since the increases of $G_{IC,init}$ are more significant than $G_{IC,prop}$, the magnitudes of the R-curves reduce, which results in more stable crack propagation.

4. Conclusions

Fibre composites are widely used in aerospace and transport applications, however, the brittleness of thermoset polymers used as the matrices can limit their applications. Research has shown that adding silica nanoparticles (SNPs) to the matrices can improve the toughness of fibre composites, however, this requires significant additions of SNPs, which can be up to 20 wt% of the matrices and increase the cost of materials and manufacturing. In this research, instead of modifying the matrices, the sizings of the fibres were modified using SNPs, allowing much lower volumes of SNPs to be used. Two sizing agents for carbon fibres have been modified by the addition of SNPs at two concentrations. Mode I interlaminar fracture tests and fatigue crack growth (FCG) tests have been conducted on the composites made using the sizing-modified fibres.

Although the modified sizings had no significant effect on the fatigue behaviour, they improved the mode I fracture energy of the composites. Maximum improvements of 101% in the fracture energy for crack initiation and 33% for crack propagation have been found when the sizing agent composed of 1.78 wt% HS-1 and 2.22 wt% Nanopox FW 404 (sizing H2) was used. The level of improvement for the modified sizings is the same compared with the literature adding SNPs to the matrices, while the modified sizings use significantly fewer SNPs. On the other hand, with the higher addition level of SNPs to the sizings, the magnitudes of the R-curves are smaller, this indicates a more stable crack propagation.

The toughening mechanisms of the SNPs on the composites have also been investigated.

236 When the concentration of SNPs is higher, the particles were dispersed better across the
237 fibre surfaces, which resulted in better adhesion between the fibres and the matrix epoxy. A
238 better adhesion contributes to more fragmentation of the fibres and more energy absorption.
239 Therefore, the toughness can be improved. It is also noted that good adhesion contributes to
240 the reduction of the magnitudes of the R-curves. However, if the adhesion is improved too
241 much, few fibres pull out and less fibres break, which leads to a reverse effect that the fracture
242 energy decreases.

243 Directly modifying fibre sizings with silica nanoparticles has great potential for the appli-
244 cation of fibre composites, especially for situations where high toughness is required, since
245 it can improve the fracture energies more efficiently than directly adding modifiers into ma-
246 trices. The same level of improvement can be achieved by using significantly fewer silica
247 nanoparticles.

248 **Acknowledgements**

249 The authors would like to thank the Ministry of Education, Republic of China (Taiwan),
250 for a PhD studentship for Shang-Nan Tsai. They would also like to acknowledge the finan-
251 cial support of the Irish Research Council and Marie Curie Actions under the ELEVATE
252 fellowship scheme for Dr. Declan Carolan. Some of the equipment used was provided by Dr.
253 Ambrose Taylor's Royal Society Mercer Award for Innovation.

254 **Data Availability**

255 The raw and processed data required to reproduce these findings cannot be shared at this
256 time as the data also forms part of an ongoing study.

257 **References**

- 258 [1] Tang Y, Ye L, Zhang D, Deng S. Characterization of transverse tensile, interlaminar
259 shear and interlaminar fracture in CF/EP laminates with 10 wt% and 20 wt% silica
260 nanoparticles in matrix resins. *Composites Part A: Applied Science and Manufacturing*
261 2011;42(12):1943–50.

- 262 [2] Kim DS, Cho K, Kim JK, Park CE. Effects of particle size and rubber content
263 on fracture toughness in rubber-modified epoxies. *Polymer Engineering & Science*
264 1996;36(6):755–68.
- 265 [3] Lin K, Shieh Y. Core-shell particles designed for toughening the epoxy resins.
266 II. Core-shell-particle-toughened epoxy resins. *Journal of Applied Polymer Science*
267 1998;70(12):2313–22.
- 268 [4] Quan D, Ivankovic A. Effect of core-shell rubber (CSR) nano-particles on mechanical
269 properties and fracture toughness of an epoxy polymer. *Polymer* 2015;66:16–28.
- 270 [5] Thitsartarn W, Fan X, Sun Y, Yeo JCC, Yuan D, He C. Simultaneous enhancement of
271 strength and toughness of epoxy using POSS-rubber core-shell nanoparticles. *Compos-
272 ites Science and Technology* 2015;118:63–71.
- 273 [6] Dixon DG, Harris SJ, Dempster M, Nicholls P. The effect of PEEK fibres and powder
274 on joints made with a high temperature adhesive. *The Journal of Adhesion* 1998;65(1-
275 4):131–62.
- 276 [7] Kinloch AJ, Taylor AC. The toughening of cyanate-ester polymers. Part I: Physi-
277 cal modification using particles, fibres and woven-mats. *Journal of Materials Science*
278 2002;37(3):433–60.
- 279 [8] Griffiths R, Holloway DG. The fracture energy of some epoxy resin materials. *Journal*
280 *of Materials Science* 1970;5(4):302–7.
- 281 [9] McGrath LM, Parnas RS, King SH, Schroeder JL, Fischer DA, Lenhart JL. Investiga-
282 tion of the thermal, mechanical, and fracture properties of alumina-epoxy composites.
283 *Polymer* 2008;49(4):999–1014.
- 284 [10] Broutman LJ, Sahu S. The effect of interfacial bonding on the toughness of glass filled
285 polymers. *Materials Science and Engineering* 1971;8(2):98–107.

- 286 [11] Spanoudakis J, Young RJ. Crack propagation in a glass particle-filled epoxy resin.
287 Journal of Materials Science 1984;19(2):473–86.
- 288 [12] Masania K. Toughening mechanisms of silica nanoparticle-modified epoxy polymers.
289 Phd thesis; Imperial College London; London, UK; 2010.
- 290 [13] Gojny F, Wichmann M, Fiedler B, Schulte K. Influence of different carbon nanotubes
291 on the mechanical properties of epoxy matrix composites - a comparative study. Com-
292 posites Science and Technology 2005;65(15-16):2300–13.
- 293 [14] Chong HM, Taylor AC. The effect of graphene nanoplatelets on the fracture toughness
294 of epoxy polymers. In: Proceedings of 37th Annual Meeting of the Adhesion Society.
295 San Diego, USA: Curran Associates; 2014.
- 296 [15] Yeh MK, Tai NH, Liu JH. Mechanical behavior of phenolic-based composites rein-
297 forced with multi-walled carbon nanotubes. Carbon 2006;44(1):1–9.
- 298 [16] Bucknall CB, Gilbert AH. Toughening tetrafunctional epoxy resins using polyetherim-
299 ide. Polymer 1989;30(2):213–7.
- 300 [17] Bucknall CB, Partridge IK. Phase separation in epoxy resins containing polyethersul-
301 phone. Polymer 1983;24(5):639–44.
- 302 [18] Kinloch AJ, Yuen ML, Jenkins SD. Thermoplastic-toughened epoxy polymers. Journal
303 of Materials Science 1994;29(14):3781–90.
- 304 [19] Johnsen BB, Kinloch AJ, Taylor AC. Toughness of syndiotactic polystyrene/epoxy
305 polymer blends: microstructure and toughening mechanisms. Polymer
306 2005;46(18):7352–69.
- 307 [20] Yee AF, Pearson RA. Toughening mechanisms in elastomer-modified epoxies. Journal
308 of Materials Science 1986;21(7):2462–74.

- 309 [21] Kinloch AJ, Shaw SJ, Tod DA, Hunston DL. Deformation and fracture behaviour
310 of a rubber-toughened epoxy: 1. Microstructure and fracture studies. *Polymer*
311 1983;24(10):1341–54.
- 312 [22] Wang F, Drzal LT, Qin Y, Huang Z. Enhancement of fracture toughness, mechani-
313 cal and thermal properties of rubber/epoxy composites by incorporation of graphene
314 nanoplatelets. *Composites Part A: Applied Science and Manufacturing* 2016;87:10–22.
- 315 [23] Chen J, Taylor AC. Epoxy modified with triblock copolymers: morphology, mechanical
316 properties and fracture mechanisms. *Journal of Materials Science* 2012;47(11):4546–
317 60.
- 318 [24] Bray DJ, Dittanet P, Guild FJ, Kinloch AJ, Masania K, Pearson RA, et al. The modelling
319 of the toughening of epoxy polymers via silica nanoparticles: The effects of volume
320 fraction and particle size. *Polymer* 2013;54(26):7022–32.
- 321 [25] Hunston DL. Composite interlaminar fracture: effect of matrix fracture energy. *Journal*
322 *of Composites, Technology and Research* 1984;6(4):176–80.
- 323 [26] Kinloch AJ, Mohammed RD, Taylor AC, Sprenger S, Egan D. The interlaminar tough-
324 ness of carbon-fibre reinforced plastic composites using hybrid-toughened matrices.
325 *Journal of Materials Science* 2006;41(15):5043–6.
- 326 [27] Hsieh TH, Kinloch AJ, Masania K, Sohn Lee J, Taylor AC, Sprenger S. The toughness
327 of epoxy polymers and fibre composites modified with rubber microparticles and silica
328 nanoparticles. *Journal of Materials Science* 2010;45(5):1193–210.
- 329 [28] Awang Ngah S, Taylor AC. Toughening performance of glass fibre composites with
330 core-shell rubber and silica nanoparticle modified matrices. *Composites Part A: Applied*
331 *Science and Manufacturing* 2016;80:292–303.
- 332 [29] Manjunatha CM, Taylor AC, Kinloch AJ, Sprenger S. The tensile fatigue behaviour
333 of a silica nanoparticle-modified glass fibre reinforced epoxy composite. *Composites*
334 *Science and Technology* 2010;70(1):193–9.

- 335 [30] Deng SQ, Rosso P, Ye L, Friedrich K. Interlaminar fracture of CF/EP composites mod-
336 ified with nano-silica. *Solid State Phenomena* 2007;121-123:1403–6.
- 337 [31] Sprenger S. Fiber-reinforced composites based on epoxy resins modified with
338 elastomers and surface-modified silica nanoparticles. *Journal of Materials Science*
339 2014;49(6):2391–402.
- 340 [32] Sprenger S. Improved performance of glass and carbon fibre-reinforced composites by
341 using nanosilica in the fibre sizing. In: *Proceedings of SAMPE China 2017*. Beijing,
342 China; 2017.
- 343 [33] NANOPOX F Products. Material datasheet; Evonik; Geesthacht, Germany; 2008.
- 344 [34] BS ISO 15024. Fibre-reinforced plastic composites - Determination of mode I inter-
345 laminar fracture toughness, G_{IC} , for unidirectionally reinforced materials. BSI; London,
346 UK; 2001.
- 347 [35] ASTM D5528-13. Standard Test Method for Mode I Interlaminar Fracture Toughness
348 of Unidirectional Fiber-Reinforced Polymer Matrix Composites. ASTM International;
349 West Conshohocken, USA; 2013.
- 350 [36] BS ISO 13003. Fibre-reinforced plastics - Determination of fatigue properties under
351 cyclic loading conditions. BSI; London, UK; 2003.
- 352 [37] ASTM E647-15. Standard Test Method for Measurement of Fatigue Crack Growth
353 Rates. ASTM International; West Conshohocken, USA; 2015.
- 354 [38] Bolotin VV. Mechanics of fatigue; vol. 11 of *Mechanical Engineering*. Boca Raton:
355 CRC Press; 1999.
- 356 [39] Roylance D. Fatigue. MIT OpenCourseWare, Massachusetts Institute of Tech-
357 nology, Massachusetts, USA. Available from: [https://ocw.mit.edu/courses/
358 materials-science-and-engineering/3-11-mechanics-of-materials-
359 fall-1999/modules/MIT3_11F99_fatigue.pdf](https://ocw.mit.edu/courses/materials-science-and-engineering/3-11-mechanics-of-materials-fall-1999/modules/MIT3_11F99_fatigue.pdf); 2001. [Accessed: 11-July-2018].

Table 1: Sizing formulations

Neoxil 965		Nanopox FW404	SNP content	HS-1		Nanopox FW404	SNP content
N0	4	0	0	H0	4	0	0
N1	2.67	1.33	0.53	H1	2.67	1.33	0.53
N2	1.78	2.22	0.89	H2	1.78	2.22	0.89

* wt% based on fibre mass

Table 2: Fracture energies of the modified-sizing composites

Sizing formulation	$G_{IC,init}$ (SD) (J/m ²)	Change	$G_{IC,prop}$ (SD) (J/m ²)	Change	$G_{IC,prop} - G_{IC,init}$ (J/m ²)
N0	85 (81)	-	175 (24)	-	90
N1	57 (70)	-33%	187 (18)	+7%	130
N2	98 (54)	+15%	175 (23)	0%	77
H0	108 (62)	-	166 (20)	-	58
H1	103 (42)	-5%	181 (11)	+9%	78
H2	217 (30)	+101%	220 (32)	+33%	3

Table 3: Improvement of $G_{IC,prop}$ compared with literature

Formulation	SNP content (wt%)	Relative $G_{IC,prop}$	Reference
Sizing N0	0	1.00	
Sizing N1	0.53 ^a	1.07	
Sizing N2	0.89 ^a	1.00	
Sizing H0	0	1.00	
Sizing H1	0.53 ^a	1.09	
Sizing H2	0.89 ^a	1.33	
SNP modified matrix	0	1.00	[1, 30]
	2 ^b	1.23	[30]
	4 ^b	1.54	[30]
	10 ^b	1.01	[1]
	20 ^b	1.21	[1]

a: wt% on the fibre mass

b: wt% of the matrix

Table 4: Fatigue gradient of the sizing-modified composites and comparison with metals

Formulation	Gradient m_G	Gradient m_K
Sizing N0	2.02	4.05
Sizing N1	1.17	2.34
Sizing N2	5.90	11.80
Sizing H0	3.98	7.97
Sizing H1	0.52	1.04
Sizing H2	3.00	6.00
Steel	-	3 [39]
Aluminium	-	3 [39]
Nickel	-	3.3 [39]

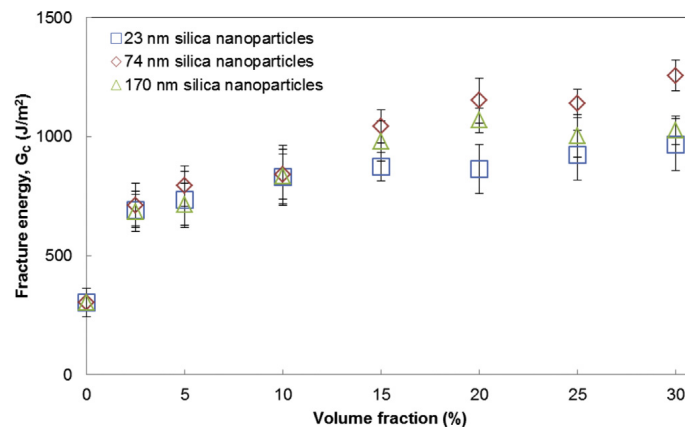
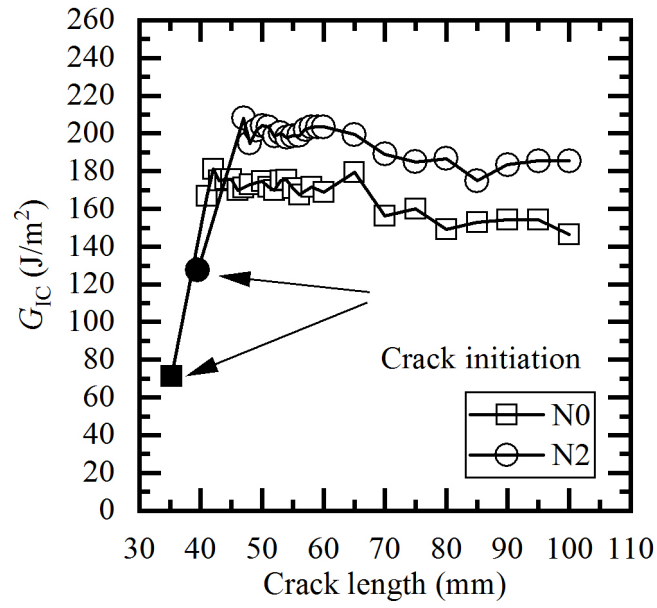
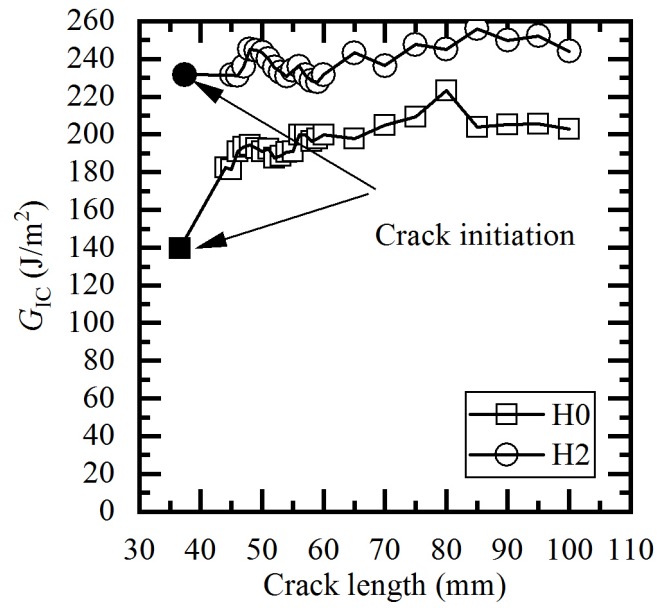


Figure 1: Fracture energy of bulk epoxy modified with silica nanoparticles with different particle size [24]



(a) sizing N0 & N2



(b) sizing H0 & H2

Figure 2: R-curve (resistance curve) comparison of unmodified and SNP-modified UD carbon fibre composites

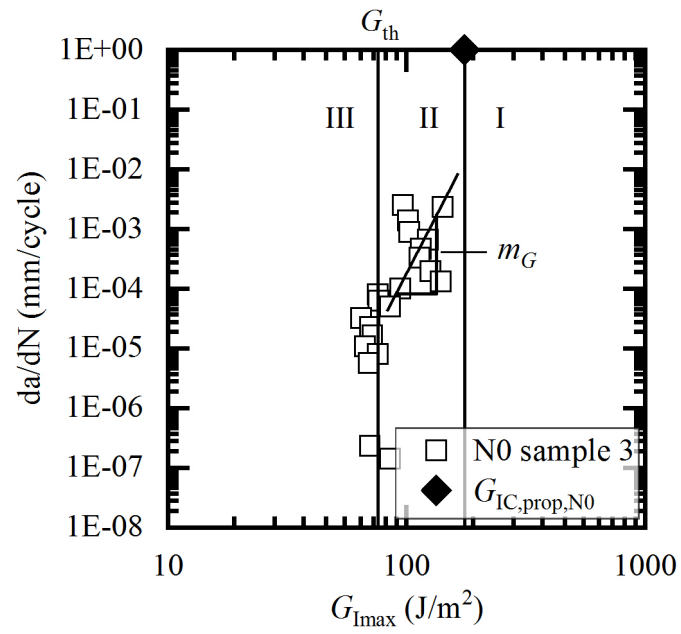
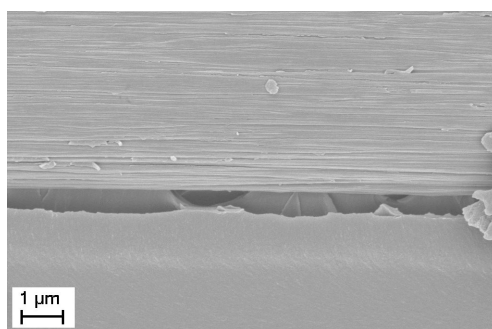
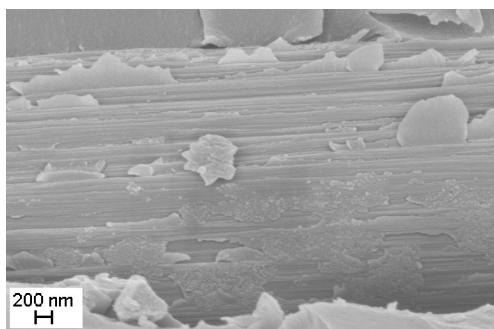


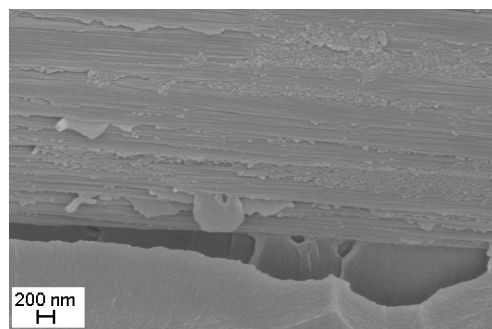
Figure 3: Fatigue crack growth (FCG) curve of UD carbon fibre composite using sizing N0



(a) sizing H0 (unmodified)

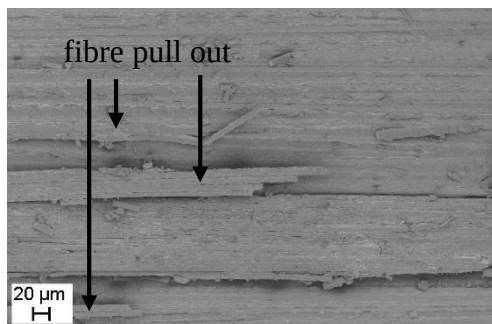


(b) sizing H1 (1.33 wt% FW404)

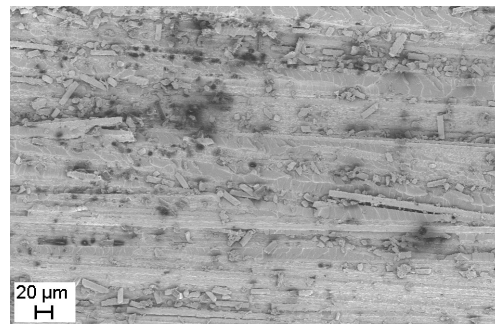


(c) sizing H2 (2.22 wt% FW404)

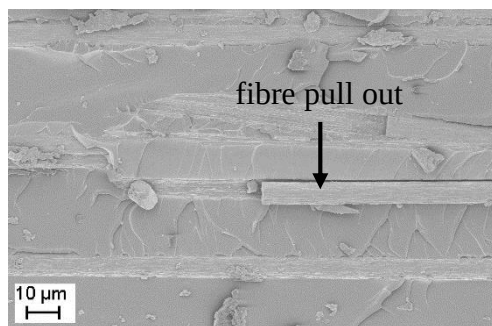
Figure 4: Silica nanoparticle dispersion and fibre/matrix adhesion (DCB fracture surfaces)



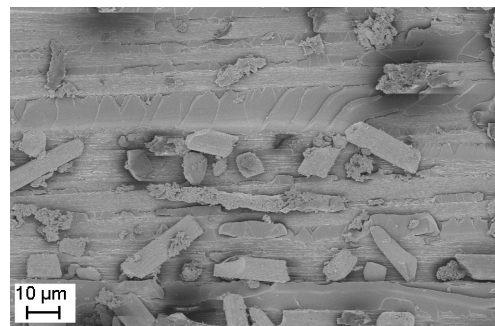
(a) sizing N0 - fibre pull out



(b) sizing N1 - fibre fragmentation

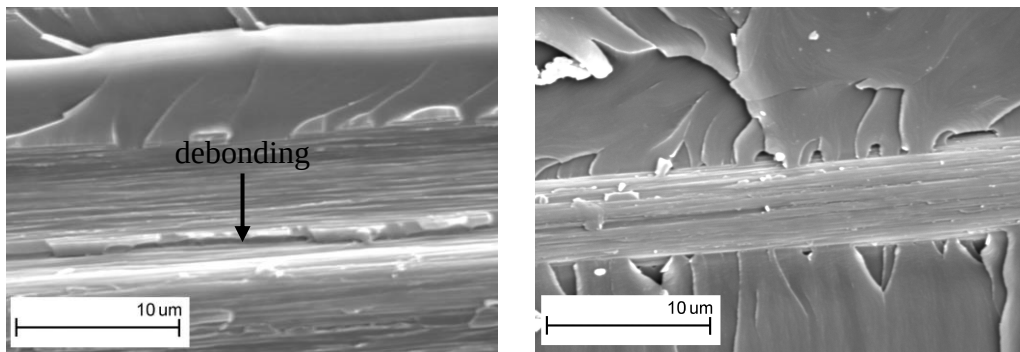


(c) sizing H0 - fibre pull out



(d) sizing H1 - fibre fragmentation

Figure 5: Fibre pull out and fragmentation (DCB fracture surfaces)



(a) sizing N0 - poor adhesion (debonding indicated) **(b)** sizing N1 - better adhesion

Figure 6: Fibre/matrix adhesion (fracture surfaces from FCG)