



## Review

## Interlaminar fracture toughness and CAI strength of fibre-reinforced composites with nanoparticles – A review

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## ABSTRACT

Some recent developments are reviewed in the use of nanoparticles as additional reinforcing phases in fibre-reinforced polymer (FRP) laminates (especially with brittle thermosetting resins) to enhance interlaminar fracture toughness and compression after impact (CAI) strength. There has been considerable interest in the past decades in using nanoparticles as secondary reinforcement, in addition to the primary reinforcing fibres in FRP laminates, in a “hybrid” approach. This is based on the clear improvement in mode I fracture toughness of nanoparticle-modified resin matrices,  $G_{IC}^m$ , with the aim of increasing interlaminar fracture toughness,  $G_{IC}^c$  and  $G_{IIIC}^c$ , and further enhancing the CAI strength of FRP laminates. With addition of nanoparticles,  $G_{IC}^c$  is effectively increased; however, the transfer efficiency from  $G_{IC}^m$  to  $G_{IC}^c$  is generally similar to that for composites with conventional unmodified matrices, with  $G_{IC}^c/G_{IC}^m > 1$  for brittle matrices but  $G_{IC}^c/G_{IC}^m < 1$  for very tough matrices. Nanoparticles seem to have extended the regime of  $G_{IC}^c/G_{IC}^m > 1$ . However, the positive correlation between  $G_{IC}^m$  and  $G_{IIIC}^c$  or CAI strength is not clear. To advance research in this area, a number of fundamental and technical issues must be resolved in order to fabricate high-performance composites with hybrid reinforcements, including (1) uniform dispersion and alignment of nanoparticles, (2) optimised interface between nanoparticles and matrix; and (3) low viscosity of nanoparticle-modified matrix resins for ease of impregnation of reinforcing fibres with a high volume fraction (>60 vol%).

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## 1. Introduction

Advanced fibre composites, such as carbon fibre (CF)/epoxy (EP) composites, invented over a half century ago, have found broad

applications in the aerospace, maritime, automobile and sport industries in recent years [1]. In particular, the new Boeing 787, claimed to be 20% more fuel-efficient, employs advanced composite materials for almost all its airframes. In competition, the new Airbus A350 has advanced composite materials making up 52% of its structure weight. However, structures made of advanced CF/EP composites run the potential risk of suffering from extension

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of internal defects under impact and fatigue loadings, due to the brittle nature of epoxy resins.

To maximise the specific stiffness (stiffness-to-weight ratio) and the specific strength (strength-to-weight ratio), most advanced composites in practical applications adopt a 2D laminate configuration of multiple reinforcing fibre/epoxy “prepreg” layers. Delamination has been recognised as a fundamental issue in damage resistance for laminated composite structures [2]. Over the past three decades, substantial research efforts in the composite research community have been dedicated to the development of toughened fibre–matrix composites. There are basically two distinct approaches. One approach is based on 3D fibre reinforcement using advanced textile techniques [3], e.g. stitching, z-pinning, waving, braiding, knitting, etc., which has proven to be an effective way to produce 3D composites, but it may not be an effective way to fabricate toughened 2D composite laminates, with the sacrifice of reduction in the in-plane effective fibre volume fraction, leading to decreases in stiffness and strength [4]. Meanwhile, stitching and z-pinning techniques may damage fibres in the 2D plane and induce localised stress concentrations, reducing the in-plane strength and stiffness. The second approach is to develop modified epoxy resins with improved toughness or to introduce a resin-rich layer between individual “prepreg” layers uniformly, or selective “interleaving” [5]. However, interleaving also suffers from reduction in in-plane strength and stiffness in most cases.

Modified thermosetting matrix resins for fibre-reinforced composites have evolved greatly over the past three decades in overcoming the brittle nature of thermosetting polymers by dispersion of the second phase that normally consists of micron-sized soft organic (rubber or thermoplastic) or inorganic rigid particles. These fillers are expected to provide extrinsic toughening mechanisms such as crack pinning, matrix shear yielding or shear banding, micro-cracking, rubber cavitation, crack deflection, and particle tearing (soft particles) or bridging (rigid particles) [6,7]. However, approaches incorporating soft particles suffer from drawbacks such as reduction in the glass transition temperature ( $T_g$ ) and even in stiffness and strength of the composites. Moreover, it is apparent that toughening methods such as introducing micron-sized inorganic fillers into epoxy matrices result in only moderate improvement in the fracture toughness of the high cross-linked epoxies that are used in aerospace applications [8].

As mentioned above, the matrix toughening technique (including interleaving between layers of composite laminates) is a common method for toughening brittle epoxy composites. Strong correlations have been reported between the matrix mode I fracture toughness  $G_{IC}^m$  and the composite mode I interlaminar fracture toughness  $G_{IC}^c$  [2]. An established view is that (i) for matrix  $G_{IC}^m$  low-

er than about  $0.5 \text{ kJ/m}^2$ , the composite  $G_{IC}^c$  is greater than the matrix  $G_{IC}^m$  and there is approximately a linear relation between these toughness values; (ii) as the matrix  $G_{IC}^m$  increases above  $0.5 \text{ kJ/m}^2$ , the incremental increase in the composite  $G_{IC}^c$  is clearly smaller than that in the matrix  $G_{IC}^m$ ; and (iii) for matrix  $G_{IC}^m$  above  $2.0 \text{ kJ/m}^2$ , there is little gain in the composite  $G_{IC}^c$  [9]. As shown in Fig. 1, a large increase in matrix fracture toughness,  $G_{IC}^m$ , does not always lead to a proportionate increase in the interlaminar fracture toughness,  $G_{IC}^c$ , of composite laminates. The composite  $G_{IC}^c$  with brittle matrix resins (e.g. less than  $200 \text{ J/m}^2$ ) ranges from slightly greater to three times greater than the corresponding matrix  $G_{IC}^m$ , where the matrix  $G_{IC}^m$  is directly transferred to the composites accompanied by additional fracture mechanisms such as fibre bridging and breakage, peeling and interfacial debonding. However, for toughened matrices such as modified thermosetting and thermoplastic polymers, the composite  $G_{IC}^c$  is clearly lower than the  $G_{IC}^m$  of the bulk polymers. The poor transfer from  $G_{IC}^m$  to  $G_{IC}^c$  is attributed to fibre constraint effects that limit the ductility of the matrix resin and confine volume of crack-tip plastic deformation zone [2].

Meanwhile, fibre-reinforced composites are notch sensitive and lose much of their structural integrity when damaged. Damage can be caused during service and may be introduced by machining of fastener holes, stress concentrations near designed cutouts, or accidentally dropping tools on the composites. In-service damage of composite airframes may also result from impact by runway debris, hailstones, bird strike, ground service vehicles, ballistics, etc. In many instances, the damage caused by such impact may be invisible or barely visible on the surface but can significantly reduce the strength of the composite component; however, such damage can cause significant reduction in the strength of compression after impact (CAI), which is a typical measure of the damage tolerance of fibre-reinforced composites.

Some mechanistic models relating impact response to the fracture properties of fibre-reinforced composites have been reported. In one work, mode II interlaminar fracture toughness,  $G_{IIc}^c$ , of the composite was directly related to the transverse threshold load that developed internal delamination [10]. Another early work [11] reported that toughened resins significantly reduced the damage caused by impact and substantially improved residual strength. Kim and Sham [12] reported that the mode I opening component was very low compared to the mode II shear component under low-energy transverse impact, and the latter dominated the whole damage growth process. However, Kuboki et al. [13] concluded that a positive relation existed between  $G_{IC}^c$  and the critical incipient impact damage.

Many factors determine the damage resistance and damage tolerance of fibre-reinforced composites. Among these factors, the mechanical properties of fibre and matrix, interface/interphase, as well as fibre configurations, play important roles in determining impact damage resistance and damage tolerance of composites [14]. The development in the last decades of polymer nanocomposites such as epoxy nanocomposites provides new opportunities to explore new fracture behaviour and multi-functionality beyond those found in conventional FRP composites. It has been well demonstrated that the addition of well dispersed nanoparticles in brittle epoxies can simultaneously increase their modulus of elasticity, yielding or tensile strength, ductility and plane strain fracture toughness [15]. The presence of small amounts of nanoparticles in a matrix can improve the impact properties of polymer nanocomposites, with the reduction of subcritical cracks in the matrix [16] or enhanced phase adhesion and constraint to polymer chain movement [17]. All these research efforts clearly indicate that there is a good potential to increase the  $G_{IC}^c$ ,  $G_{IIc}^c$  and CAI strength of fibre-reinforced composites via the incorporation of nanoparticles into the matrix of fibre-reinforced composites, addressing

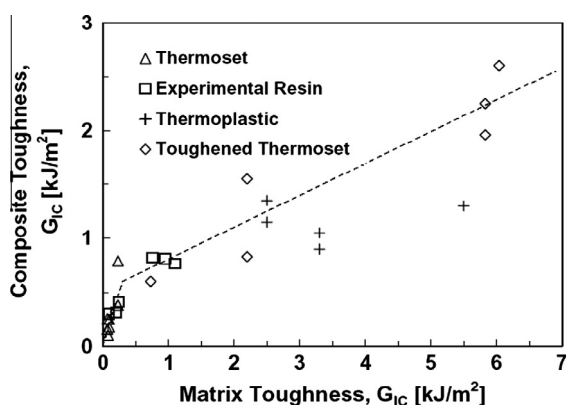


Fig. 1. Mode I interlaminar fracture toughness of composites  $G_{IC}^c$  and mode I matrix toughness  $G_{IC}^m$  [2].

the drawbacks of conventional approaches with organic and inorganic micro-sized particles.

This review aims to consolidate current essential knowledge of the fundamental roles of nanoparticles in fibre-reinforced epoxy matrix composites, addressing the effects of the  $G_{IC}^c$  of modified epoxy matrices on the  $G_{IC}^c$ ,  $G_{IIc}^c$  and CAI strength of fibre-reinforced laminates. The relationships among  $G_{IC}^c$ ,  $G_{IIc}^c$ , and  $G_{IIc}^m$  and CAI strength are discussed, with reference to recent available research data.

## 2. Epoxy nanocomposites

Extensive studies have been devoted to epoxy nanocomposites using nano-sized additives such as nanoparticles (silica,  $TiO_2$ ,  $Al_2O_3$ ), carbon nanotubes and fibres (CNTs/CNFs), and nanoclays, because of their unique mechanical properties in improving the performance of epoxies [18]. Three types of nanoparticles can be distinguished, depending upon the reinforcing dimensions to the fibre–matrix composites:

0-D: Nano-particulate materials, such as spherical silica nanoparticles obtained by *in situ* sol–gel methods or by polymerisation promoted directly from their surfaces [19–21], carbon black [22], fullerene [23],  $TiO_2$  and alumina particles [24,25]. The effects of particulate materials on  $G_{IC}^c$  and  $G_{IIc}^c$  of composite laminates have been studied using nanosilica by Kinloch et al. [26,28], Zeng et al. [27], Wichmann et al. [29], Deng et al. [30], Tsai et al. [31], Hsieh et al. [32], Ye et al. [33] and Tang et al. [34]; carbon black (CB) by Wichmann et al. [29], Ye et al. [33] and Zhang et al. [35,36]; fullerene by Ogasawara et al. [37]; and alumina by Akinyede et al. [38] and Kelkar et al. [39].

1-D: Nano-fibrous materials, in the form of fibres or tubes such as carbon nanotubes (CNTs) [29,40], carbon nanofibres, and tubular clay-halloysite [41,42], which have been studied as reinforcing nanoparticles. The effects of fibrous materials on  $G_{IC}^c$  and  $G_{IIc}^c$  have been studied using cup-stacked carbon nanotube (CSCNT) by Yokozeki et al. [43,44]; CNTs (double-walled CNTs, multi-walled CNTs) by Wichmann et al. [29], Seyhan et al. [45,46], Karapappas et al. [47], Godara et al. [48] and Warriar et al. [49]; vertically-aligned CNT (VACNT) forest grown directly on fibre surface by Veedu et al. [50] and Garcia et al. [51] or on Si substrate and then transfer-printed onto prepreps by Garcia et al. [52] and Wardle et al. [53]; vapour-grown carbon nanofibre (VGCNF) by Sadaghian et al. [54], Kostopoulos et al. [55], Ahir et al. [56] and Quaresimin and Varley [57]; and halloysite nanotube (HNT) by Ye et al. [58].

2-D: Layered materials in the form of single or multiple layers of sheets; fully or partially exfoliated clays and silicates belong to this family. The effects of layered materials on  $G_{IC}^c$  and  $G_{IIc}^c$  composites laminates have been studied mainly with nanoclay by Becker et al. [59], Vlasveld et al. [60], Siddiqui et al. [61], Xu and Hoa [62], Subramaniyan and Sun [63], Quaresimin and Varley [57], Tsai and Wu [64] and Iqbal et al. [65].

The mechanisms for increases in fracture toughness of polymers via incorporation of micro-sized particles have been extensively studied within the past several decades. Several theories have been developed to explain and comprehend the effects of particle-toughening confirmed by experimental observations. The most common micro-mechanical mechanisms leading to an increase in fracture toughness in these systems are (i) localised inelastic matrix deformation and void nucleation/growth, (ii) particle/fibre debonding, (iii) crack deflection, (iv) crack pinning, (v) fibre pull-out, (vi) crack tip blunting (or crack tip deformation) and (vii) particle/fibre deformation or breaking at the crack tip. These mechanisms are influenced by several parameters such as the volume fraction of particles, particle size and shape, interfacial bonding, and are often difficult to distinguish between them [40]. As

nanoparticles are normally so much smaller than the crack-tip opening displacement, it is unlikely that all these mechanisms can simultaneously play significant roles for the toughening, though almost all these mechanisms have been cited for comprehending the values of increased fracture toughness of polymer nanocomposites. In addition, most studies attributed the role of the enormous surface area of nanofillers in general, however, almost all polymer nanocomposites exhibited partly agglomerated dispersion of nanofillers to some extent, and few systems could achieve full dispersion.

The localised inelastic matrix deformation such shear banding between particles, void nucleation and growth as well as crack deflection at agglomerates have frequently been cited as the key mechanisms leading to the increases in fracture toughness. For nano-particulate materials, such as nanosilica, debonding of the nanosilica and subsequent plastic void growth were most likely to be responsible for the increase in fracture toughness [66]. For nano-fibrous materials, such as nanotubes, the bridging mechanism suppresses the growth of nano-pores, as well as the propagation of cracks and contributes positively to the increase in fracture toughness [67]; meanwhile, the extraordinary high interface area of nanotubes may lead to a significant increase in fracture energy due to “nanotube pull-out” [40]. For layered materials, such as nanoclay of intercalated structures, exfoliated platelets were observed to produce nanovoids/cracks promoting shear yielding of matrix at the tip of the propagating crack and in the entire processing zone surrounding it. The formation of massive microvoids/cracks and the increase of the fracture surface area due to crack deflection were identified as the major toughening mechanisms in highly exfoliated epoxy/clay nanocomposites [68].

## 3. $G_{IC}^c$ – $G_{IIc}^m$ relationship

Most of above-mentioned studies have dealt with interlaminar fracture toughness, in particular  $G_{IIc}^c$ , though some also extended to characterise the  $G_{IIc}^c$  and CAI of composite laminates. Based on the data available in the above-mentioned studies on a variety of neat thermosets and nanoparticle-toughened thermosets,  $G_{IIc}^m$  with  $G_{IIc}^c$  of their fibre-reinforced polymer (FRP) laminates is plotted in Fig. 2, without any attempt to systematise fibre type, fibre sizing, and fibre volume fraction. Some other studies did not specify whether the  $G_{IIc}^c$  was for initiation or propagation (normally the plateaued value of a  $G_{IIc}^c$ – $\Delta a$  curve (ASTM D5528)). The dashed line in Fig. 2 indicates that the  $G_{IIc}^c/G_{IIc}^m$  ratio is 1.0.

One clear observation is that nanoparticles have not been able to generate very tough matrices with  $G_{IIc}^m > 2.0$  kJ/m<sup>2</sup>, and most values of  $G_{IIc}^c$  are less than 1.5 kJ/m<sup>2</sup>. However, those results are similar

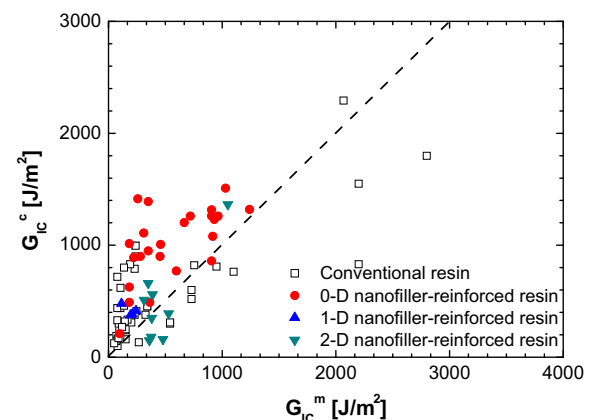


Fig. 2.  $G_{IC}^c$  and  $G_{IIc}^m$  nanoparticles in matrix resins.

**Table 1**Fracture toughness of composites,  $G_{IC}^m$ , and laminates,  $G_{IC}^c$ , and  $G_{IC}^m/G_{IC}^c$  with different kinds of nanoparticles incorporated.

Reference	Filler (wt%)	Fracture toughness (J/m <sup>2</sup> )			
		$G_{IC}^m$	$G_{IC}^c$	$G_{IC}^m/G_{IC}^c$	
<i>Nanoparticles</i>					
Kinloch et al. [26]	Nanosilica (20 nm)	0	103	439	<b>4.26</b>
		11.9	363	489	1.35
		2.3/9 CTBN	964	1260	1.31
		4.5/9 CTBN	917	1080	1.18
		10.5/9 CTBN	1240	1320	1.06
Zeng et al. [27]/Liu et al. [95]	Nanosilica (20 nm)	0	277	500	<b>1.81</b>
		4	390	636	1.63
		6	465	657	1.41
		8	546	643	1.18
		10	690	629	0.91
		12	791	621	0.79
Kinloch et al. [28]	Nanosilica (20 nm)	0 (Anhydride)	83	710	<b>8.55</b>
		10 (Anhydride)	125	610	4.88
		10/9 CTBN (Anhydride)	610	1250	2.05
		0 (Amine)	70	450	6.43
		10 (Amine)	112	225	2.01
		10/9 CTBN (Amine)	575	700	1.22
		0	137	800	<b>5.84</b>
Wichmann et al. [29]/Gojny et al. [96]	Carbon black (35 nm)	0.3	222	890	4.01
		0	137	800	<b>5.84</b>
Wichmann et al. [29]	Fumed silica (7 nm)	0.5 vol%	454	900	1.98
		0.5 (EP-mod.)	597	770	1.29
		0	238	900	<b>3.78</b>
Deng et al. [30]	Nanosilica (20 nm)	2	310	1110	3.58
		4	349	1390	3.98
		0	190	830	<b>4.37</b>
		10	280	900	3.21
Tsai et al. [31]	Nanosilica (20 nm)	20	350	950	2.71
		10/10 CTBN	930	1230	1.32
		10/10 CSR	1030	1510	1.47
		0	77	439	<b>5.70</b>
		12	183	489	2.67
Hsieh et al. [32]	Nanosilica (20 nm)	2.3/9.0 CTBN	720	1261	1.75
		10/9.0 CTBN	906	1316	1.45
		0	77	330	<b>4.29</b>
		10.0	183	1015	5.55
	Nanosilica (20 nm)	10.0/9.0 CTBN	906	860	0.95
		0	77	718	<b>9.32</b>
		10.	183	626	3.42
		10.0/9.0 CTBN	906	1263	1.39
Ye et al. [33]/Zhang et al. [35]	Carbon black (35 nm)	0	238	995	<b>4.18</b>
		3	257	1415	5.51
Tang et al. [34]	Nanosilica (20 nm)	0	238	995	<b>4.18</b>
		10	458	1007	2.20
		20	666	1203	1.81
Ogasawara et al. [37]/Jiang et al. [87]	Fullerene	0	88	170	<b>1.93</b>
		1.0	97	210	2.16
<i>Nanofibres</i>					
Wichmann et al. [29]/Gojny et al. [96]	MWCNT ( $D = 15$ nm), DWCNT $D = 3$ nm)	0	137	460	<b>3.36</b>
		0.3 (DW)	210	385	1.83
		0.3 (DW-NH <sub>2</sub> )	242	415	1.71
		0.3 (MW)	194	375	1.93
Seyhan et al. [45,46]	MWCNT	0	106	620	<b>5.85</b>
		0.1 (MW-mod.)	115	480	4.17
<i>Nanoplatelets</i>					
Becker et al. [59]	Nanoclay	0	267	133	<b>0.498</b>
		2.5	360	150	0.417
		5.0	480	160	0.333
		7.0	375	180	0.480
		0	144	320	<b>2.22</b>
Siddiqui et al. [61]/Iqbal et al. [65]	Organoclay	3	388	560	1.44
		5	313	510	1.63
		7	350	660	1.89
		0	120	270	<b>2.25</b>
Liu et al. [97]/Xu and Hoa [62]	Nanoclay	2	380	350	0.921
		4	530	390	0.736
		0	2067	2292	<b>1.11</b>
Subramaniyan and Sun [63,98]	Nanoclay	5	1051	1364	1.30

to the well-established trend of the  $G_{IC}^c-G_{IC}^m$  relationship, as shown in Fig. 1 [2], where the composite  $G_{IC}^c$  is actually greater than the resin  $G_{IC}^m$  with  $G_{IC}^c/G_{IC}^m > 1$ . Moreover, the nanoparticles seem to have

increased the positive correlation to a  $G_{IC}^m$  value of 1.5 kJ/m<sup>2</sup>, in comparison with composites without nanoparticles [2]. This change may be attributed to the interaction between nanoparticles

and reinforcing fibres, which promotes additional toughening mechanisms. It has been reported in many studies that the presence of nanoparticles can enhance the fibre–matrix interfacial adhesion strength [69,70]. Assuming that the fracture surface may be modelled by a group of fibre cylinders, the fracture surface in a composite usually has the morphology of a corrugated roof, giving actual fracture surface areas that are 57% greater than the flat fracture surface observed in the fracture of brittle resins without fibres. It has been estimated that matrix deformation contributes more than 75% of composite  $G_{IC}^c$  in CF/thermoplastic matrix composites, with other fracture mechanisms contributing the remaining 25% [71]. Stronger interfaces can suppress premature interfacial failure “short-circuits”, thereby increasing fracture energy [72].

It is well appreciated that other factors such as fibre type, fibre size, fibre volume fraction, fabrication method and characterisation conditions also influence the  $G_{IC}^c$  values; however, these factors are not reviewed here individually, the aim being to highlight the effects of nanoparticles. Table 1 shows the ratio of  $G_{IC}^c/G_{IC}^m$  for individual composite laminate systems in current studies.  $G_{IC}^c/G_{IC}^m$  represents fracture toughness transfer efficiency from matrix to composite laminate. With nanoparticles added, thermoset resins have enhanced fracture toughness in terms of  $G_{IC}^m$ . However, as shown in Table 1, as the amount of nanoparticles increases, most of the  $G_{IC}^c/G_{IC}^m$  values decrease, indicating that transfer efficiency decreases.

The low transfer efficiency of resin fracture toughness into delamination fracture toughness for very ductile resins is the result of the constraint on the development of a larger plastic zone in the resin-rich region between plies by the fibres in the adjacent plies

[2]. Assuming that the bulk plastic zone is large compared to the inter-fibrillar spacing, then, when fibres are added into the matrix, a first possible change in the fracture energy is that it is simply reduced by the volume fraction of the fibres. This rather optimistic estimation forms the upper bound on  $G_{IC}^c$  of a composite [73].

However, in the composite systems studies thus far, the  $G_{IC}^c$  achieved is generally far from the upper bound estimated on a volume fraction basis. Nonetheless, it is useful to obtain an estimate of the size of the plastic zone in these composites. By assuming that the plastic zone ahead of the crack tip can be approximated by the Dugdale line zone [74], the thickness of the plastic zone at the crack tip,  $\rho$ , can be approximated by

$$\rho = G_{IC}/\sigma_y \quad (1)$$

where  $G_{IC}$  is the plane strain fracture toughness and  $\sigma_y$  is the tensile yield strength of the matrix. Table 2 shows the calculated thickness of the plastic zone at the crack tip  $\rho$  for different kinds of nanoparticle-reinforced resins. The table illustrates that with nanoparticles incorporated into the base matrix resin, the size of the plastic zone increases compared to that of the neat matrix resin, some of them being even double and triple the original plastic zone in the neat matrix resin in composite laminates. However, compared to conventional matrix resins toughened by organic particles such as rubber [2], which normally exhibit a clear decrease in yielding strength, matrix resins toughened by nanoparticles normally have an increase in yielding strength (Table 2). Therefore, with the same value of  $G_{IC}^m$ , the thickness of the plastic zone at the crack tip,  $\rho_{nano}$  for matrix resins toughened by nanoparticles should be smaller than

**Table 2**  
Calculated thickness of the plastic zone at the crack tip  $\rho$  for different kinds of nanoparticle-reinforced epoxy resins.

Reference	Epoxy/Filler/Curing agent	Filler (wt%)	$\sigma$	$G_{IC}^m$	$\rho$	Increment (%)	
<i>Nanoparticles</i>							
Zeng et al. [27]/Liu et al. [95]	DGEBA/Nanopox F400/Piperidine	0	42.1	277	<b>6.58</b>	0	
		Nanosilica (4)	42.0	390	9.29	41	
		Nanosilica (6)	43.1	465	10.79	64	
		Nanosilica (8)	42.7	546	12.79	94	
		Nanosilica (10)	46.5	690	14.84	126	
		Nanosilica (12)	48.3	791	16.38	149	
Kinloch et al. [28]	DGEBA/Nanopox F400 & Bakelite EPR 486/Albidur HE 600	0	145	83	<b>0.57</b>	0	
		Nanosilica (10)	155	125	0.81	42	
		TGMDA/Albipox 1000 & Albbox XP 23/0206/M-DEA & M-DIPA amine	0	160	70	0.44	0
		Nanosilica (10)	175	112	0.64	45	
Wichmann et al. [29]	DGEBA/Aerosil A380 (7 nm)/NA	0	63.8	137	<b>2.15</b>	0	
		Fumed silica (0.5 vol%)	62.8	454	7.23	236	
		Fumed silica (0.5 vol% (EP-mod.))	64.5	597	9.26	331	
Deng et al. [30]	DGEBA/Nanopox F400/Piperidine	0	64.8	238	<b>3.67</b>	0	
		Nanosilica (2)	74.0	310	4.19	14	
		Nanosilica (4)	69.3	349	5.04	37	
Tang et al. [34]	DGEBA/Nanopox F400/Piperidine	0	64.8	238	<b>3.67</b>	0	
		Nanosilica (10)	69.4	458	6.60	80	
		Nanosilica (20)	72.4	666	9.20	151	
Zhang et al. [35]	DGEBA/CB (35 nm)/Piperidine	0	64.8	238	<b>3.67</b>	0	
		Carbon black (3)	71.6	257	3.59	-2	
Jiang et al. [87]	Bisphenol-A type, novolac type and TGDDM/nanom -mixTM ST/4,4-DDS	0	90.5	88	<b>0.97</b>	0	
Gojny et al. [96]	DGEBA/CB (30 nm)/NA	Fullerene (1)	92.0	97	1.05	8	
		0	63.8	137	<b>2.15</b>	0	
		Carbon black (0.3)	63.1	222	3.52	64	
<i>Nanofibres</i>							
Gojny et al. [96]	DGEBA/Nanocyl MWCNT (D = 15 nm) and DWCNT D = 3 nm)/NA	0	63.80	137	<b>2.15</b>	0	
		DWCNT (0.3)	67.77	210	3.10	44	
		DWCNT-NH <sub>2</sub> (0.3)	67.02	242	3.61	68	
		MWCNT (0.3)	63.17	194	3.07	43	
<i>Nanoplatelets</i>							
Siddiqui et al. [61]	Epon 828 (DFEBA)/I30.P organoclay/ 1,3-phenylenediamine and 4,4-methylenedianiline	0	73.5	144	<b>1.96</b>	0	
		Nanoclay (3)	69.0	388	5.62	187	
		Nanoclay (5)	67.0	313	4.67	138	
Liu et al. [97]	TGDDM/Nanomer I.30E/Aradur 976-1	0	204	120	<b>0.59</b>	0	
		Nanoclay (2)	206	380	1.84	213	
		Nanoclay (4)	208	530	2.55	334	

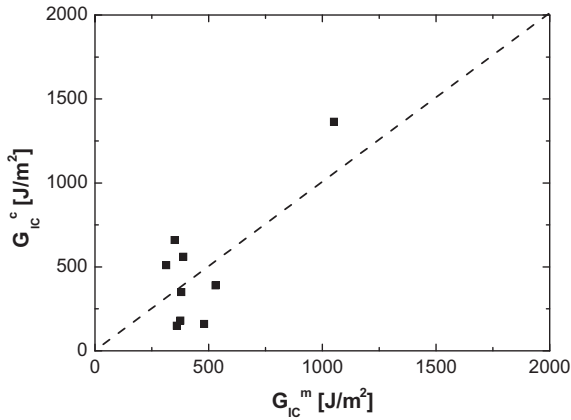


Fig. 3.  $G_{IC}^m$  and  $G_{IC}^c$  with nanoplattlets in matrix resins.

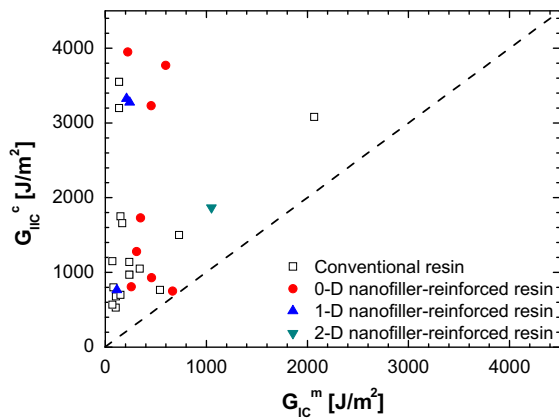


Fig. 4.  $G_{IIc}^m$  and  $G_{IIc}^c$  with nanoparticles in matrix resins.

$\rho_{conventional}$  of conventional matrix resins. This provides another mechanism for the extended regime of  $G_{IC}^c/G_{IC}^m > 1$ .

Fig. 3 shows the relationship of  $G_{IC}^m$  and  $G_{IC}^c$  with nanoplattlet (e.g. nanoclay) modification. Surprisingly, even for brittle epoxies, the increment for the composite  $G_{IC}^c$  is somewhat smaller than that of the resin  $G_{IC}^m$ . The “abnormal” trend of  $G_{IC}^m - G_{IC}^c$  for nanoplattlet-modified epoxies may be attributed to severe nanoclay agglomeration, leading to incomplete matrix infusion [63,64]. These agglomerated nanoclays act as “inert” fillers with a certain volume fraction in the laminates, which do not contribute to the deformation energy in the laminate; thus it is reasonable to expect that the fracture energy will be reduced by the volume fraction of these inert filler materials.

#### 4. $G_{IIc}^c - G_{IIc}^m$ relationship

Mode II interlaminar fracture toughness,  $G_{IIc}^c$ , as a function of neat resin toughness,  $G_{IIc}^m$ , is presented in Fig. 4 and listed in Table 3. The agglomeration of these data in Fig. 4 indicates that  $G_{IIc}^c$  is not very sensitive to  $G_{IIc}^m$ , whether the resins have been modified with nanoparticles or not. However, it seems that nanoparticles may have the capability to increase the  $G_{IIc}^c$  of brittle matrix resins with  $G_{IIc}^m < 0.5$  kJ/m<sup>2</sup>, though the accuracy of data and actual mechanisms involved cannot yet be confirmed. When the individual laminate in Table 3 is carefully analysed, with nanoparticles added,  $G_{IIc}^m$  increases but  $G_{IIc}^c$  may increase or decrease, depending on the particle types. Meanwhile, the same trend as that for  $G_{IC}^c$  can be found, namely that for a particular matrix system, the transfer efficiency of  $G_{IIc}^m$  to  $G_{IIc}^c$  decreased with the amount of nanoparticles in the matrix, as shown in Table 3.

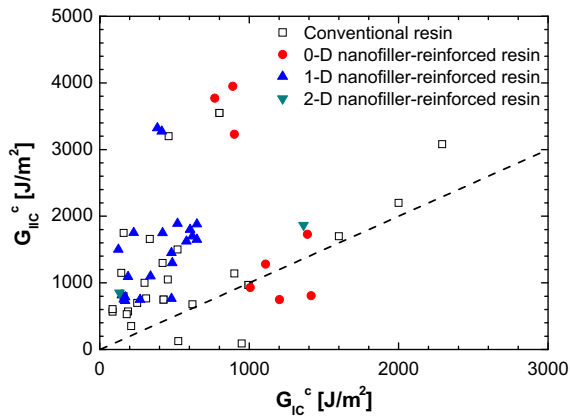
The toughness ratio ( $G_{IIc}/G_{IC}$ ) is a material property. Materials like rocks, concrete, gypsum, etc. have low toughness ratios and hence have been observed to fail more easily by shear. The  $G_{IIc}/G_{IC}$  ratio for composites with brittle resins is usually in the range 3–10. For composites made of very ductile resins, the ratio of  $G_{IIc}/G_{IC}$  is closer to 1.0 [2]. Table 4 and Fig. 5 show the fracture toughness ratio ( $G_{IIc}^c/G_{IIc}^m$ ) of composite laminates with different kinds of nanoparticle-modified epoxies. It can be concluded from Table 4 that with nanoparticles incorporated in matrix resins, the resins became toughened while the toughness ratio decreased; however, if the nanoparticles were modified with good interac-

**Table 3**  
Fracture toughness of composites,  $G_{IIc}^m$ , laminates,  $G_{IIc}^c$ , and  $G_{IIc}^c/G_{IIc}^m$  with different kinds of nanoparticle incorporated.

Reference	Nanoparticle	Filler (wt%)	Fracture toughness (J/m <sup>2</sup> )		
			$G_{IIc}^m$	$G_{IIc}^c$	$G_{IIc}^c/G_{IIc}^m$
<i>Nanoparticles</i>					
Wichmann et al. [29]	Fumed silica (7 nm)	0	137	3550	<b>25.9</b>
		0.5 vol%	454	3230	7.11
		0.5 (EP-mod.)	597	3770	6.31
Deng et al. [30]	Nanosilica (20 nm)	0	238	1140	<b>4.79</b>
		2	310	1280	4.13
		4	349	1730	4.96
Tang et al. [34]	Nanosilica (20 nm)	0	238	968	<b>4.07</b>
		10	458	929	2.03
		20	666	750	1.13
<i>Nanofibres</i>					
Wichmann et al. [29]/Gojny et al. [96]	Carbon nanotube (30 nm)	0	137	3550	<b>25.9</b>
		0.3	222	3950	17.8
Wichmann et al. [29]/Gojny et al. [96]	MWCNT ( <i>D</i> = 15 nm) DWCNT <i>D</i> = 3 nm)	0	137	3200	<b>23.4</b>
		0.3 (DW)	210	3325	15.8
		0.3 (DW-NH <sub>2</sub> )	242	3275	13.5
Zhang et al. [35]	Carbon nanotube (35 nm)	0	238	968	<b>4.07</b>
		3	257	808	3.14
Seyhan et al. [45,46]	MWCNT	0	106	680	<b>6.42</b>
		0.1 (MW-mod.)	115	765	6.65
<i>Nanoplattlets</i>					
Subramaniyan and Sun [63,98]	Nanoclay	0	2067	3082	<b>1.49</b>
		5	1051	1867	1.78

**Table 4**  
Fracture toughness ratio ( $G_{IIc}^c/G_{IIc}^m$ ) of FRP laminates with different kinds of nanoparticle-modified epoxies.

Reference	Filler (wt%)	Fracture toughness (J/m <sup>2</sup> )			$G_{IIc}^c/G_{IIc}^m$
		$G_{IIc}^m$	$G_{IIc}^c$	$G_{IIc}^c$	
<i>Nanoparticles</i>					
Wichmann et al. [29]	0	137	800	3550	<b>4.44</b>
	Fume silica (0.5 vol%)				
	Fume silica (0.5 vol% (EP-mod.))	454	900	3230	3.59
Tang et al. [34]	0	597	770	3770	<b>4.90</b>
	Silica (10)	238	995	968	<b>0.97</b>
	Silica (20)	458	1007	929	0.92
Zhang et al. [35]	0	666	1203	750	0.62
	Carbon black (3)	238	995	968	<b>0.97</b>
		257	1415	808	0.57
<i>Nanofibres</i>					
Wichmann et al. [29]/Gojny et al. [96]	0	137	460	3200	<b>6.96</b>
	DWCNT (0.3)	210	385	3325	8.64
	DWCNT-NH <sub>2</sub> (0.3)	242	415	3275	<b>7.89</b>
Ye et al. [41,58]	0	–	420	1300	<b>3.10</b>
	HNT (1)	–	580	1625	2.80
	HNT (2)	–	605	1800	2.98
	HNT (3)	–	620	1700	2.74
	HNT (5)	–	650	1650	2.54
Yokozeki et al. [43]	0	–	86	605	<b>7.03</b>
	CSCNT (5)	–	170	786	4.62
Seyhan et al. [45,46]	0	106	620	680	<b>1.10</b>
	MWCNT-mod. (0.1)	115	480	765	<b>1.59</b>
Karapappas et al. [47]/Kostopoulos et al. [99]	0	–	300	1000	<b>3.33</b>
	MWCNT (0.1)	–	270	750	2.78
	MWCNT (0.5)	–	420	1750	4.17
	MWCNT (1.0)	–	480	1450	3.02
<i>Nanoplatelets</i>					
Quaresimin and Varley [57]	0	–	427	750	<b>1.76</b>
	Nanoclay (5)	–	133	850	6.39
Subramaniyan and Sun [63,98]	0	2067	2292	3082	<b>1.35</b>
	Nanoclay (5)	1051	1364	1867	1.37



**Fig. 5.** Toughness ratios for conventional and nanoparticle-reinforced resin laminates.

tions with resins or fibres, the presence of nanoparticles would increase the toughness ratio.

## 5. CAI strength

As delamination can be produced by low-velocity impact, large strength reductions in compression can occur. Delamination divides the laminate into sub-laminates which have a lower bending stiffness than the original laminate and are less resistant to buckling loads. Under a compressive load, a delamination can cause buckling in one of three modes: global instability/buckling of the laminate, local instability (buckling of the thinner sub-laminate)

or a combination of the above. The mode of failure generally changes from global, to local, to mixed mode as the length of delamination increases. In this way,  $G_{IIc}^m$ ,  $G_{IIc}^c$ , and  $G_{IIc}^c$  in composites can all have a predominant effect on CAI strength. Table 5 summarises some comprehensive studies with  $G_{IIc}^m$ ,  $G_{IIc}^c$ ,  $G_{IIc}^c$  and CAI strength measured respectively. The CAI strength results were measured after the quasi-isotropic  $[45/0/-45/90]_n$  composite laminates were subjected to transverse impact with energy/thickness ratio in 6.2–6.7 J/m normally. From Table 5, it can be seen that with the addition of nanoparticles, in most cases the CAI strength increases as  $G_{IIc}^m$  or  $G_{IIc}^c$  increases.

Davies and Zhang [75] proposed a simple model based on the Mode II interlaminar fracture toughness of the composite,  $G_{IIc}$ , to predict the critical force to initiate delamination damage during transverse impact.

$$p_{crit}^2 = \frac{8\pi^2 E t^3 G_{IIc}}{9(1-\nu^2)} \quad (2)$$

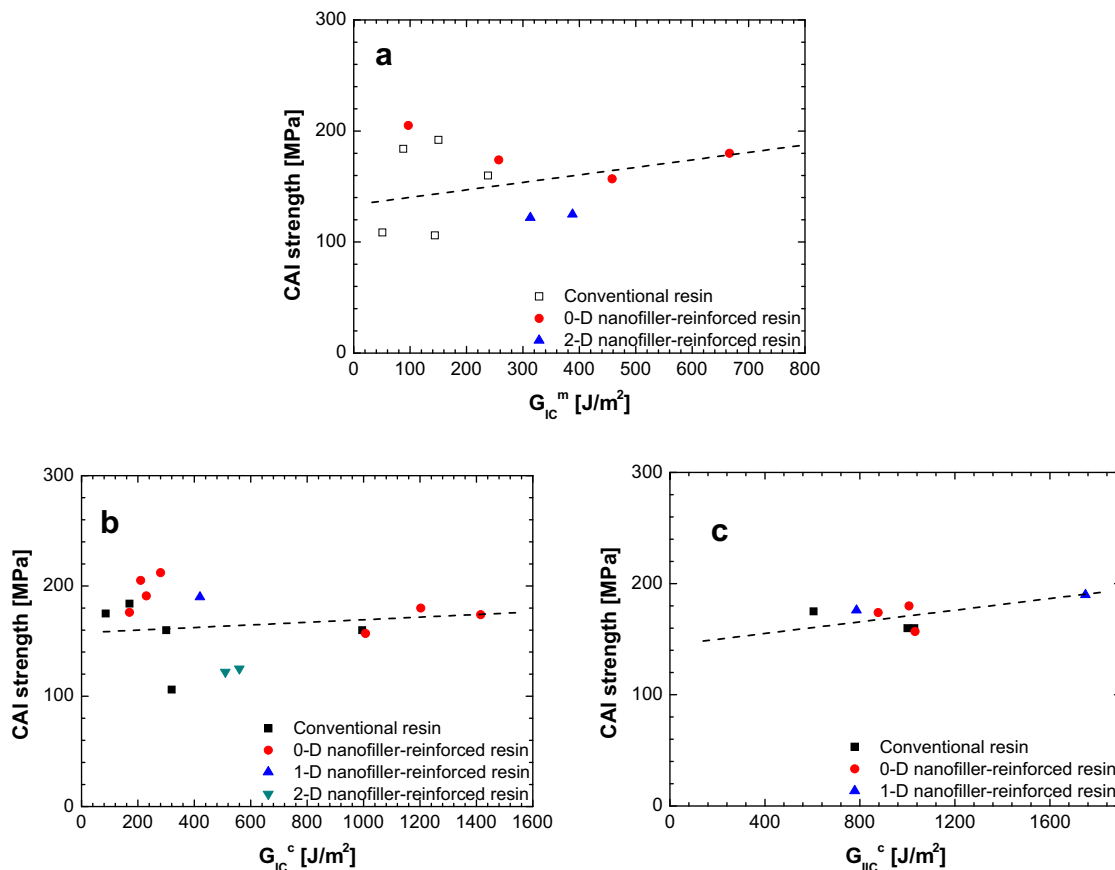
where  $E$  is the equivalent in-plane modulus,  $\nu$  is the Poisson's ratio and  $t$  is the thickness of laminate. The predictions from Eq. (2) for the initiation of delamination agreed well with their experimental data on quasi-isotropic laminates [76]. Eq. (2) supports the common views in the composites research community that a high  $G_{IIc}$  is beneficial to damage resistance under transverse impact.

Fig. 6 shows CAI strength as a function of  $G_{IIc}^m$ ,  $G_{IIc}^c$  and  $G_{IIc}^c$  without consideration of other factors such as fibre type, fibre volume fraction, lay-up configuration, and processing method. To our best knowledge, only a few research teams have tried to characterise the effects of nanoparticles on the CAI strength of FRP laminates. Individual results with certain kinds of nanoparticle indicate improvement in CAI strength, as shown in Table 5; however, once

**Table 5**

Transfer efficiency from fracture toughness of composites,  $G_{IC}^m$ , and interlaminar fracture toughness,  $G_{IC}^c$  and  $G_{IIc}^c$ , to CAI strength of laminates with different kinds of nanoparticle incorporated.

Reference	Filler type	Filler (wt%)	Fracture toughness (J/m <sup>2</sup> )			CAI	CAI/ $G_{IC}^m$	CAI/ $G_{IC}^c$	CAI/ $G_{IIc}^c$
			$G_{IC}^m$	$G_{IC}^c$	$G_{IIc}^c$				
Tang et al. [34]	Nanosilica (20 nm)	0	238	995	968	160	<b>0.67</b>	<b>0.16</b>	<b>0.17</b>
		10	458	1007	929	157	0.34	0.16	0.17
		20	666	1203	750	180	0.27	0.15	0.24
Zhang et al. [35]	Carbon black (35 nm)	0	238	995	968	160	<b>0.67</b>	<b>0.16</b>	<b>0.17</b>
		3	257	1415	808	174	0.68	0.12	0.22
Ogasawara et al. [37]/Jiang et al. [87]	Fullerene	0	88	170	–	184	<b>2.09</b>	<b>1.08</b>	–
		0.1	–	230	–	191	–	0.83	–
		0.5	–	280	–	212	–	0.76	–
		1.0	97	210	–	205	2.11	0.98	–
Yokozeki et al. [43]	CSCNT	0	–	86	605	175	–	<b>2.03</b>	<b>0.29</b>
		5	–	170	786	176	–	1.04	0.22
Karapappas et al. [47]/Kostopoulos et al. [99]	MWCNT ( $D = 10\text{--}15\text{ nm}$ )	0	–	300	1000	160	–	<b>0.53</b>	<b>0.16</b>
		0.5	–	420	1750	190	–	0.45	0.11
Siddiqui et al. [61]/Iqbal et al. [65]	Nanoclay	0	144	320	–	106	<b>0.74</b>	<b>0.33</b>	–
		3	388	560	–	125	0.32	0.22	–
		5	313	510	–	122	0.39	0.24	–



**Fig. 6.** CAI strength with (a)  $G_{IC}^m$ , (b)  $G_{IC}^c$ , (c)  $G_{IIc}^c$  for pristine and nanoparticle-modified resins and their laminates.

we combine all the available data in the literature and plot the CAI strength with  $G_{IC}^m$ ,  $G_{IC}^c$  and  $G_{IIc}^c$ , respectively (Fig. 6), the results show that generally, CAI strength of laminates does not have clear relationship to  $G_{IC}^m$ ,  $G_{IC}^c$  and  $G_{IIc}^c$ . The CAI strength of composite laminates is one of the most important parameters for assessing the damage tolerance of laminated composites, but it is also the least understood property as it is dependent on a variety of other properties [77,78] such as stiffness, strength, ductility and fracture toughness of fibres, matrices, and interfaces/interphases. It has been observed over the years that toughened composites can

clearly increase damage resistance to impact, but damage tolerance as indicated by CAI may not increase accordingly [79–81]. Some recent studies by Uddin and Sun [80] indicate that adding 15 wt% nanoparticles can lead to 81% and 62% increases in the longitudinal compressive strength of unidirectional glass fibre-reinforced composites with fibre volume fractions of 42% and 50%, respectively, extrapolated from off-axis strength data and the elastic-plastic fibre micro-buckling model. Tsai et al. [81] reported a 7.4% increment in longitudinal compressive strength by adding 20 wt% nanoparticles into the epoxy matrix of unidirectional glass



fibre-reinforced composites. The reported enhancements are attributed to the increased confinement associated with the strengthened interface/interphase or increased stiffness of the matrix with nanoparticles, which delays the micro-buckling of individual or bundles of fibres in compression that triggers the compression failure of unidirectional composites.

## 6. Further exploration

Research characterising the effects of nanoparticles on interlaminar fracture toughness and CAI strength of hybrid composite laminates reinforced by traditional continuous fibres and nanoparticles is still immature. Some aspects can be improved to further explore and utilise the potential of nanoparticles in developing the high-performance hybrid composites. There have been several review articles addressing some specific nanoparticles, especially CNTs, for toughening polymers, [40,82,83]. The most straightforward manufacturing process for hybrid fibre-reinforced composites involves dispersing nanoparticles into a matrix system, followed by infusion/impregnation of the nanoparticle-modified matrix into the primary fibre assembly. The combination of nanoparticles with conventional fibre-reinforcements in polymer composites has been achieved predominantly through two different routes [82], (a) dispersing nanoparticles entirely throughout the composite matrix and (b) attaching nanoparticles (e.g., CNT) directly onto primary reinforcing fibres. The former is normally used in practice because of its convenience in processing using traditional equipment.

The main issues in the utilisation of nanoparticle-modified matrices have been the difficulties in obtaining uniform dispersion of nanoparticles and in achieving good adhesion between nanoparticles and matrix. Agglomeration of nanoparticles can lead to filtering effects against the primary fibres, leading to nanoparticle segregation and depletion. Nanoparticle agglomeration can significantly degrade the performance of both nanoparticle-modified matrices and hybrid composites. Several techniques have been used to improve nanoparticle dispersion in polymer matrices, including dry-mixing [84], simple-solution method assisted by high-energy sonication [85], thermal annealing followed by sonication [86], high-speed shear mixing using a shear mixing container [56] and calendaring [67]. Due to its efficiency, shear mixing, involving calendaring with a three-roll mill, is currently favoured as the best means to disentangle and disperse nanoparticles, especially nanotubes, nanofibres and nanoclay in resins. However, most of the studies have also pointed out that completely homogeneous dispersion of nanoparticles was not achieved. Therefore, organic surfactants and compatibilisers may be needed to improve the dispersion of these nanoparticles without weakening the other properties of polymer matrices. As the interfaces may affect the effectiveness of load transfer from the polymer matrix to nanoparticles, surface modification of nanoparticles is needed to promote better dispersion of nanoparticles and to enhance interfacial adhesion between the matrix and nanoparticles. Meanwhile, the studies summarised in Table 5 indicate that if the nanoparticles are modified with good chemical interactions with resins or fibres, the presence of nanoparticles will definitely increase  $G_{IC}^c/C_{IC}^c$ .

One of the most successful examples is nanosilica, with the trademark Nanopox F400, obtained at a concentration of 40 wt% in the diglycidyl ether of bisphenol-A (DGEBA) epoxy resin [20,21,25,26,30–32,34]. The surface-modified silica nanoparticles had an average particle size of about 20 nm with a narrow range of particle size distribution. Silica nanoparticles were synthesized during a sol-gel manufacturing process, whereby they were formed in situ, and the particle size and excellent dispersion re-

mained unchanged during any further mixing and/or blending operations. Furthermore, despite the relatively high silica content of 40 wt%, the nanofilled epoxy resin still had a comparatively low viscosity due to the agglomerate-free colloidal dispersion of the silica particles in the epoxy resin [34]. The recently available fullerene/bisphenol-A epoxy (Epikote 828; Japan Epoxy Resins Co., Ltd.) master batch (fullerene 5 wt%) provided by Frontier Carbon Corp is another example [37,87]. More and more commercial providers of nanoparticle-matrix composites with consistent material properties will appear with the improvements in processing methods and equipment, which will give a greater range of suitable nanoparticle-modified matrices for FRP composites.

For fabricating composite laminates, hand lay-up with dipping, brushing and rolling has the advantages of simplicity, but is limited to relatively low fibre volume fractions and may always include voids and defects within the laminate of poor quality. The interlaminar shear strength and transverse flexural strength of unidirectional fibre composites is roughly inversely proportional to the square of void content in the composites, which highlights the importance of fabrication of high quality composites [88,89]. A high fibre volume fraction (>60 vol%) is essential for fibre-reinforced composites to maintain their superior performance with specified stiffness and strength in comparison with high-performance light metallic alloys [90]. Automated procedures such as resin transfer moulding (RTM) and vacuum-assisted resin infusion (VARI) are typical methods for fabricating fibre-reinforced composites of high quality; both methods, especially the latter, are preferred for the production of large and complex structural composite parts. Preparing composite prepreg using fibre filament impregnation on a drum followed by hand-layup and vacuum bagging for curing in an autoclave is also a good method for fabricating composite laminates of high quality [91]. Most automated manufacturing methods, particularly RTM, require a matrix resin with a low viscosity, in a typical order of 0.5–1 Pa s [92]. However, the viscosity of most nanoparticle-modified matrices increases dramatically with an increase in nanoparticle content, leading to incomplete matrix impregnation and infusion or misplacement of fibre reinforcement. To penetrate into the primary fibre tows and avoid filtration effects low nanoparticle content can be used, but such an approach reduces the potential for significantly enhanced fracture toughness [82,93]. A diluted matrix using an organic solution may help impregnation, but the gradual change in matrix viscosity with evaporation of the solution or complete removal of the solution may also add new problems in controlling the quality of composites.

Meanwhile, studies of hybrid composites using 1-D fibrous and 2-D platelet nanoparticles, such as CNTs, clays and graphene [100–102] dispersed in polymers, have reported only marginal mechanical property enhancement if there is no control of the alignment of the nanoparticles. Attaching nanoparticles directly onto primary reinforcing fibres has been studied, particularly by using VGCNT [50–53]. With this method, CNTs may act as interlaminar nano Z-fibres/Z-pins, termed “interlaminar nanostitches” [82]. However, due to the time-consuming nature and other cost-limiting factors of hybrid laminate fabrication, larger scale and commercial production would be difficult in the current stage.

As stated above, when the size of the plastic deformation zone is roughly comparable to the fibre-fibre spacing between plies, the transfer efficiency of modified matrix fracture toughness to composite interlaminar fracture toughness decreases dramatically. As reported by Kinloch et al. [26,28], Hsieh et al. [32] and Xu et al. [94], a combination of silica nanoparticles and carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber microparticles in a DGEBA epoxy as the matrix for carbon and glass-fibre-reinforced composite can achieve synergetic effects, as shown in Table 1, with clearly enhanced  $G_{IC}^m$  and  $C_{IC}^c$ . The cavitation of rubber particles and

subsequent void growth promoting significant matrix shear deformation are the main toughening mechanisms, and meanwhile, the dissipated energy in the process of debonding of nanosilica particles from the matrix also contributes to the improvement of fracture toughness in such ternary composites [94]. Based on the fracture toughness mechanisms in modified matrices, appropriate selection of different nanoparticles can be a practical way of further exploring and utilising nanoparticle-modified matrices for making hybrid fibre-reinforced composites.

## 7. Concluding remarks

Research in using nanoparticles to enhance interlaminar fracture toughness and CAI strength of hybrid composite laminates reinforced by traditional continuous fibres and nanoparticles is at an immature stage, because in most cases there has been no standardised procedure for the preparation and fabrication of hybrid composites. Different fibre volume fractions have been achieved with diverse fabrication methods from hand-layup with dipping, brushing and rolling to an automated process such as VARI, which produces composites with different qualities in terms of meso-/micro-structures such as fibre alignment and voids in composites. It is still difficult to reach definite conclusions as to the effects of nanoparticles on  $G_{IC}^c$  and CAI strength of composite laminates. With the data available in the literature, we can see that after the addition of nanoparticles,  $G_{IC}^c$  is effectively increased in most cases; however, it generally shows transfer efficiency from  $G_{IC}^m$  to  $G_{IC}^c$  similar to that of composites with conventional unmodified matrices, i.e.,  $G_{IC}^c/G_{IC}^m > 1$  for brittle matrices, but  $G_{IC}^c/G_{IC}^m < 1$  for very tough matrices. Nanoparticles seem to have extended the regime of  $G_{IC}^c/G_{IC}^m > 1$ . However, the positive correlation between  $G_{IC}^m$  and  $G_{IC}^c$  or CAI strength is not clear.

To achieve practical applications of fibre-reinforced composites with hybrid reinforcements, a number of fundamental and technical issues need to be resolved, including uniform dispersion and alignment of nanoparticles, optimal interface between nanoparticles and matrix, and low viscosity of nanoparticle-modified matrix resins for ease of fabrication of fibre-reinforced composites with a high fibre volume fraction (>60 vol%). The use of multiple particles in micro-/nano-scales to achieve synergetic effects in toughening, strengthening or even multi-functionality (e.g. sensing and shielding) is another interesting aspect for further exploration.

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