Supporting information

Approaching the theoretical limit for reinforcing polymers with graphene

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Relationship between strength and volume fraction

For a composite that fails by filler pullout, it is relatively straightforward to model the composite strength. We assume that individual flakes only pullout if they intersect the final fracture surface. In addition, the side of the fracture surface where pullout occurs is that which results in more than half the flake remaining embedded in the polymer. Thus, assuming the flakes are rectangular with side a, with sides parallel to the sample and assuming the fracture surface is perpendicular to the applied stress, the length of flake exposed after pullout will vary from 0 to a/2 with a mean of a/4.

We assume the force to fracture the sample is the sum of the force to fracture the polymer-only part of the fracture surface and the shear force required to break the polymer-flake interface. Then the force required to break the sample is:

$$F_B = \sigma_P\left(A - N_F ta\right) + \tau N_F 2a \times \frac{a}{4}$$

Where σ_P is the polymer strength, A is the sample cross sectional area, N_F is the number of flakes intersecting the final fracture surface, t is the flake thickness, a is the flake length and τ is the interfacial shear strength. The bracketed term is the area of polymer which undergoes tensile fracture, while the factor of 2 in the second term accounts for the fact that the interfacial fracture occurs on both top and bottom of each flake.

We can calculate N_F, realising that only flakes whose centres are within a/2 of the final fracture surface will be involved in pullout. This means that N_F is just

$$N_F = \frac{N}{V} Aa$$

Where N/V is the total number of flakes per volume of composite, and A is the sample cross sectional area. The total number of flakes per volume of composite (N/V) is given by

$$\frac{N}{V} = \frac{V_f}{a^2 t}$$

This means that

$$N_F = \frac{AV_f}{at}$$

Substituting this into the first equation and diving through by A to give the strength results in

$$\sigma_B \approx \left(\tau \frac{a}{2t} - \sigma_P \right) V_f + \sigma_P$$

For pseudo rectangular flakes with long axis, L and short axis, w, we can approximate

$$a \approx \frac{L + w}{2}$$

giving

$$\sigma_B \approx \left(\tau \frac{L + w}{4t} - \sigma_P \right) V_f + \sigma_P$$

When a flake size distribution is present, this can be modified to

$$\sigma_B \approx \left(\tau \frac{\langle L \rangle + \langle w \rangle}{4 \langle t \rangle} - \sigma_P \right) V_f + \sigma_P$$

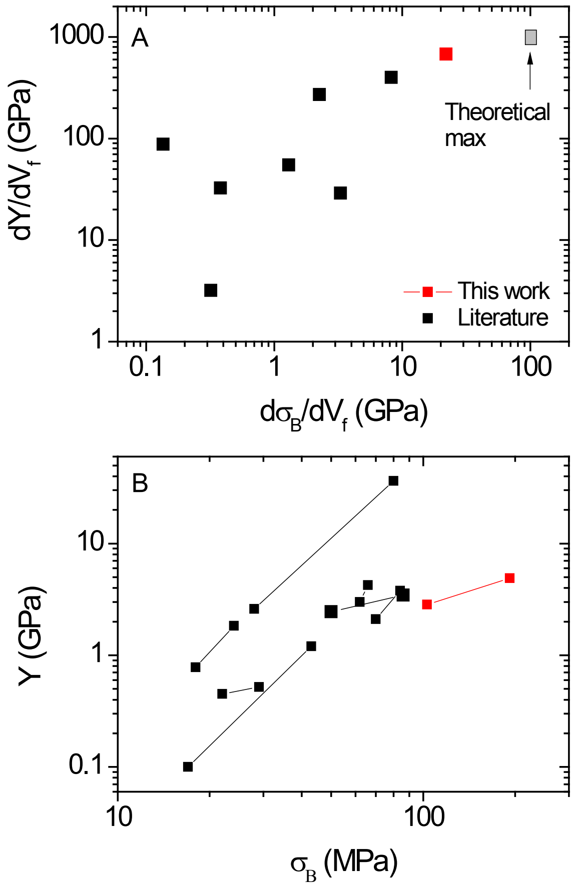

Figure S1: A) Data for dY/dV_f plotted as a function of $d\sigma_B/dV_f$ for polymer/graphene composites from the literature. This data is limited to composites studied by tensile testing. In addition, in most cases, the rates of increase had to be estimated from the presented data. The theoretical maximum reinforcement is shown by the gray square. B) Summery of increase in mechanical properties for graphene/polymer composites from the literature. The data consists of sets of two points joined by a line. In each case the lower data point represents the neat polymer. The upper data point represents the maximum reinforcement achieved. Note that one data set shows extremely good reinforcement. In this case the graphene volume fraction was 38% while for all other cases it was <6%. In each panel, the data presented in this work is shown in red. See table S1 for details of literature data.

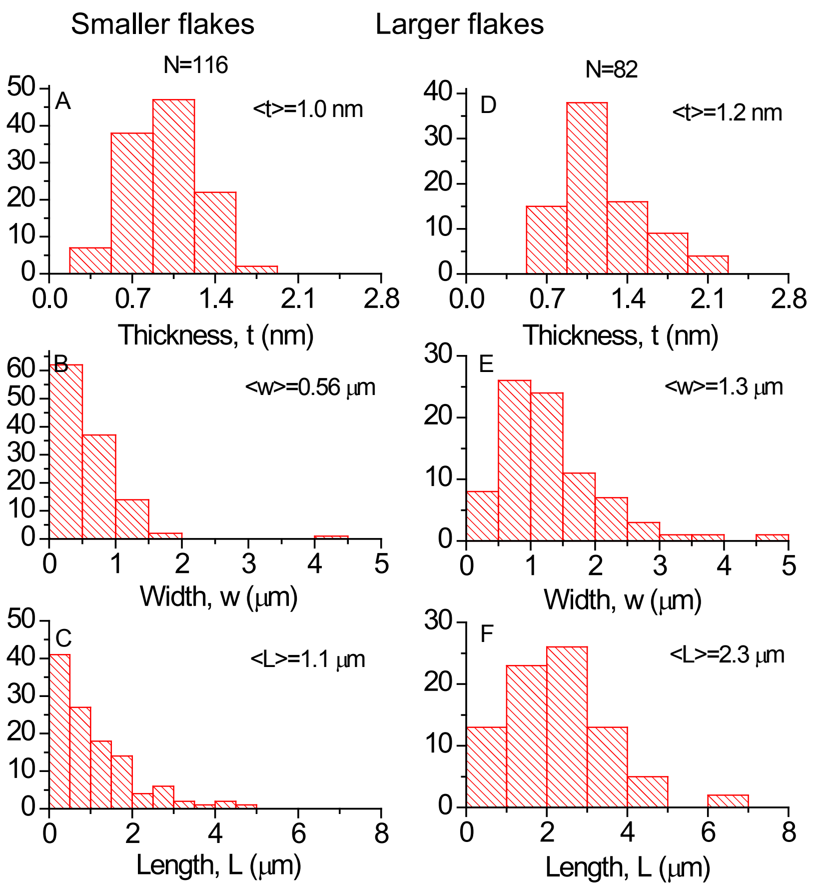

Figure S2: Statistical data as measured by TEM for flake dimension for both larger and smaller flakes. NB flake thicknesses were measured by the edge counting method as described in Khan et al, Small, 6, 864, 2010.

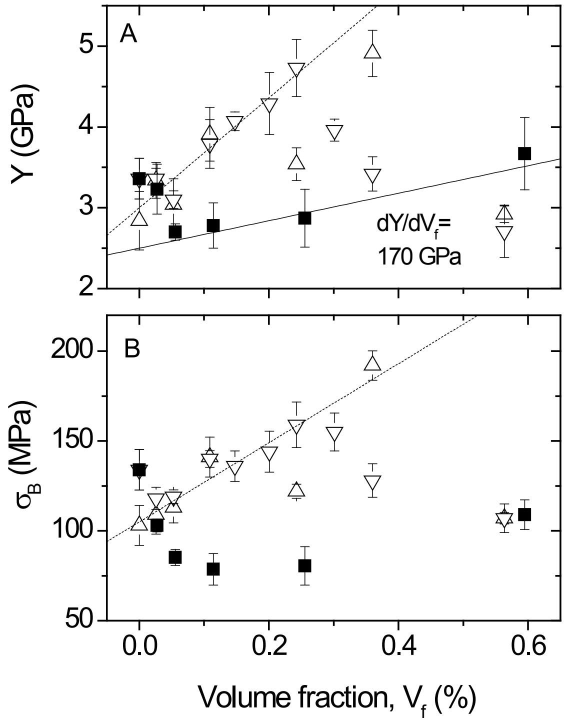

Figure S3: Comparison of mechanical properties of composites prepared with size selected (large) flakes (open triangles) with as-exfoliated (smaller) flakes (closed squares). The dashed lines are linear fits to the large-flake data while the solid line is a linear fit to the small-flake data.

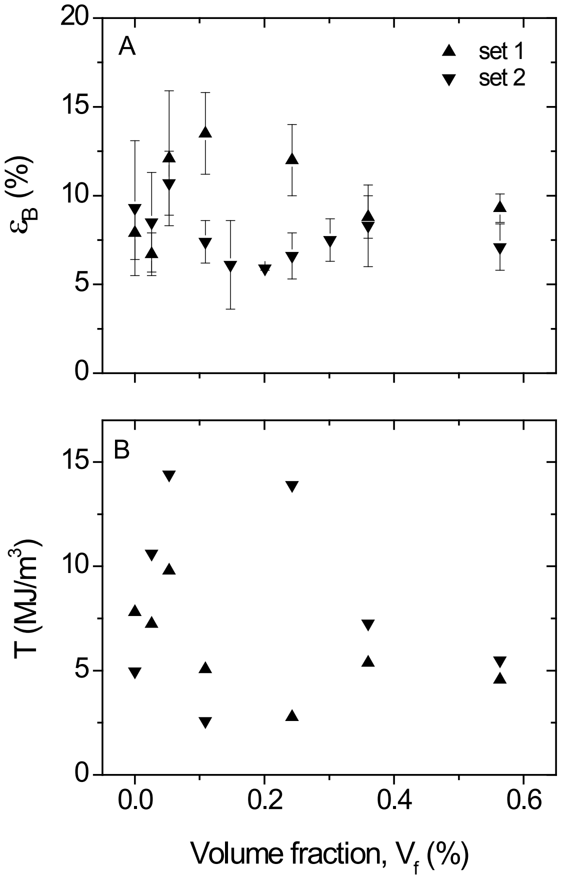

Figure S4: Strain at break (A) and toughness (B) as a function of graphene volume fraction for the size selected (large) flake composites. Note that slightly different strain at break results were found for the two independent sets of composites measured. Note that the variations in toughness are caused by the variations in the strain at break. The reasons for these variations are unclear.

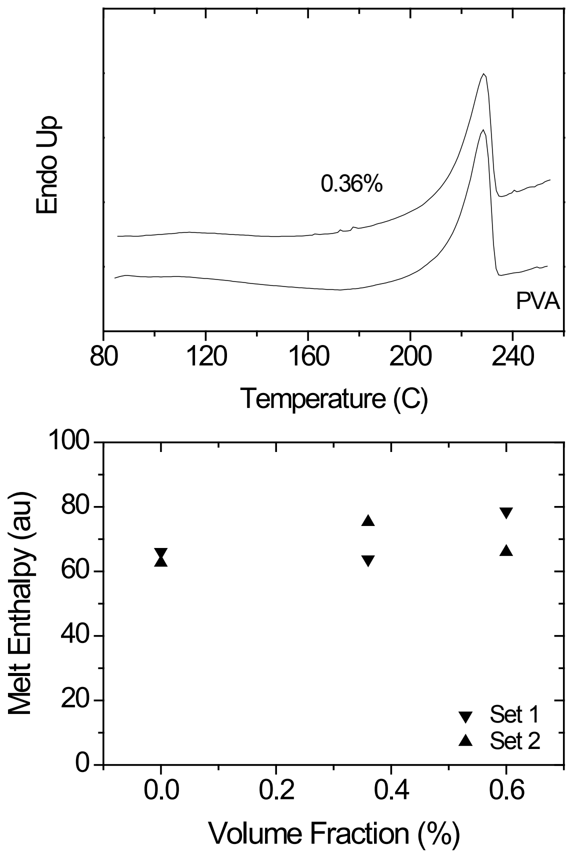

Figure S5: Differential scanning calorimetry (DSC) data for some of the size selected (large) flake composites studied here. A) The DSC scans for the PVA and the 0.36vol% sample (i.e. that with the highest mechanical properties). The peak at ~220C^{o} represents melting of PVA crystallites. B) Melting enthalpy as a function of graphene content. This shows that the crystallinity is constant with graphene content.

Reference	**Filler Material**	**Polymer Matrix (max V_f)**	**dY/dV_f (GPa)**	**$d\sigma_B/dV_f$ (MPa)**	**Poly Y, Y_{max} (GPa)**	**Poly σ_B $\sigma_{B\ max}$ (MPa)**
Macromolecules, 2010, 43, 2357	RGO	PVA (0.02)	55	1300	0.1 1.2	17 43
Nature Nanotechnology, 2008, 3, 327	Functionalized Graphene Sheets (FGS)	PMMA (0.0062)	271	2258	2.1 3.8	70 84
Advanced Functional Materials, 2009, 19, 2297	GO	PVA (0.0025)	400	8180	2.45 3.45	50 86
Advanced Functional Materials, 2010, **20,** 3322	GO	PVA (0.383) PMMA (0.65)	88 11	136 209	2.6 36.4 0.67 7.5	28 80 12.2 148
Journal of Applied Polymer Science, 2010, 118, 275	RGO	PVA (0.003)	NA	8833	NA	23 49.5
Polymer, 2010, **51**, 3431	RGO	PVA (0.022)	3.2	318	0.45 0.52	22 29
Composites Science and Technology, 2010, **70**, 1120	Expanded Graphite (EG)	Epoxy (0.016)	22	381	0.78 1.83	17.7 23.8
Journal of Polymer Science B, 2010, **48,** 850	Exfoliated Graphite	p-lactide (0.043)	29	2666	3.0 4.25	62 70
Macromolecular Rapid Communications, 2009, **30,** 316	GO	PC (0.06)	5.3	NA	2.35 2.67	NA

Table S1: Here the max V_f refers to the volume fraction where the mechanical properties display a maximum. Y_{max} and $\sigma_{B\ max}$ refer to those maximal values.