Supplementary Information

Collision-induced activation: Towards industrially scalable approach to graphite nanoplatelets functionalization for superior polymer nanocomposites

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Contents:

1. Materials and general experimentations ........................................................................................................ Page S2
2. Measurements .................................................................................................................................................. Page S2
3. Grafting estimation ......................................................................................................................................... Page S5

Fig. S1. TGA thermograms of GNP, m-GNP and f-GNP at heating rate of 10 °C/min under nitrogen atmosphere. ................................................................. Page S5
Table S1. Mechanical properties of epoxy nanocomposites containing various contents of GNP and f-GNP. ........................................................................ Page S6
Table S2. Summary of the effect of different graphene chemical treatments on the tensile, the flexural properties, and glass transition temperature in several nanocomposites containing low loadings of graphene (e.g. 0.5 %wt) as reported in the literature. ........................................................................ Page S7
Fig. S2. SEM images of fracture surfaces of pure epoxy (a) and epoxy/0.5% GNP nanocomposites (b & c). ........................................................................ Page S12
Fig. S3. SEM image of fracture surface of epoxy/5% f-GNP nanocomposites containing high level of agglomerations (red arrow). ........................................................................ Page S12

References ......................................................................................................................................................... Page S13

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1. Materials and general experimentations
Graphite nanoplatelets (grade C, with a surface area of ~518 m²/g as measured by BET) was supplied as bulk dry powder by XG Sciences’ xGnP®, Michigan, USA, which typically consist of aggregates of sub-micron platelets having a particle diameter of <10 μm and a thickness of less than a few nanometers. The received graphite nanoplatelets were refluxed in deionized water/ethanol solution for 72 h and then filtered and well-rinsed. The washed graphite nanoplatelets was then heated for 3 min at 700 °C under argon atmosphere before storing in a vacuum oven at 100 °C to remove any impurities and moisture prior to use. Maleic anhydride (98%) was obtained from Sigma and used as received. An epoxy resin of DER 332 having equivalent weight of 175 g/eq under trademark of The Dow Chemical Company and hardener of tetraethylenepentamine was used as thermosetting epoxy polymer system (Sigma-Aldrich). All solvents used in this study were of analytical grade.

2. Measurements
Brunauer–Emmett–Teller (BET) surface area was measured by a Micromeritics TriStar 3000 using adsorption isotherm of nitrogen at 77 K and Malvern Mastersizer 2000 (UK) was used for determining particle sizes. Deionized water was used as a dispersion media for particle size measurements. The reflective index of 2.42 was used in the calculation of particle size distribution of graphene nanoplatelets. Each experiment was carried out three times and error bars were not determined as the differences were insignificant. Fourier transform infrared (FTIR) analysis was performed by a Bruker Vertex 70 FTIR spectrometer in ATR mode with a resolution of 4 cm⁻¹. Raman measurements were conducted using a Renishaw InVia Raman Microspectrometer (Renishaw, Gloucestershire, UK) with diode laser at 514 nm at room temperature. All carbon-13 nuclear magnetic resonance (¹³C-NMR) measurements were done on a Bruker AVANCE III NMR spectrometer operating at 75.4 MHz. Samples were packed into 4mm zirconia MAS rotors and magic-angle-spinning (MAS) at 10 kHz was used. ¹³C measurements with direct carbon excitation and proton decoupling during acquisition were done to get comparable carbon spectra. For these a ¹³C excitation 90° pulse of 3 microseconds was used, applying a recycle delay of 24 sec for 6k sampled scans, totaling in 51 h measurement time per sample. X-ray photoelectron spectroscopy (XPS) analysis was performed using an AXIS Nova spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al Kα source at a power of 180 W (15 kV × 12 mA) and a hemispherical analyser operating in the fixed analyser transmission mode. The total pressure in the main vacuum chamber during analysis was typically 10⁻⁸ mbar. Survey spectra were acquired at a pass energy of 160 eV. To obtain more detailed
information about chemical structure, oxidation states etc., high resolution spectra were recorded from individual peaks at 20 eV pass energy (yielding a typical peak width for polymers of 0.8 - 1.0 eV). All elements present were identified from survey spectra. The atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity factors supplied by the manufacturer. Binding energies were referenced to the C 1s peak at 284.5 eV for graphitic carbon. Precision (i.e. reproducibility) depends on the signal/noise ratio but is usually much better than 5%. The latter is relevant when comparing similar samples. Water contact angles were measured using a KSV Model CAM101 Contact Angle Meter (KSV Instruments Ltd, Finland) equipped with an Olympus DP70 high resolution microscope. The image of each drop was captured after 0.1 seconds after deposition onto sample surface in ambient conditions. Thermogravimetry analysis (TGA) experiments were carried out using a TA Instruments Q50 TGA, which were conducted in nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 750 °C. Dynamic mechanical properties of the produced materials were measured using a TA Instruments Q800 DMA. The samples were polished to ~30mm×10mm×1 mm before being mounted on a single cantilever clamp. The DMTA tests experimental conditions were: temperature range, 25–250 °C; frequency of 1 Hz; and heating rate 5 °C/min. The tensile properties were measured by using an Instron Universal machine at cross-head speed of 5 mm/min according to ASTM D638. The tensile strengths and Young's moduli of the nanocomposites were measured. In addition, the Halpin–Tsai model as a micromechanical model was employed to predict the tensile modulus of epoxy nanocomposites. This model links the modulus of a nanocomposite to constituent properties, concentrations of each constituent, as well as aspect ratio and orientation of the filler. According to this model, the composite tensile modulus (E_c) can be predicted by the following equations 1-4.

$$E_c = \left[ \frac{0.375 \left( 1 + \frac{\xi \eta_t V_t}{1 - \eta_t V_t} \right) + 0.625 \left( 1 + \frac{2 \eta_t V_t}{1 - \eta_t V_t} \right) }{ \eta_t} \right] E_m$$

2D Randomly oriented filler

(1)

$$E_c = \left[ \frac{0.2 \left( 1 + \frac{\xi \eta_t V_t}{1 - \eta_t V_t} \right) + 0.8 \left( 1 + \frac{2 \eta_t V_t}{1 - \eta_t V_t} \right) }{ \eta_t} \right] E_m$$

3D Randomly oriented filler

(2)

Where the $\eta_t$ and $\eta_l$ parameters can be calculated by following equations:
\[ \eta_T = \left( \frac{E_f}{E_m} \right)^{-1} \quad \eta_L = \left( \frac{E_f}{E_m} \right)^{-1} + \frac{2}{E_f/E_m + \xi} \]

For all the above formulations, \( \xi, V_f, E_m, \) and \( E_f \) are shape factor, volume fraction of filler, tensile modulus of matrix, and tensile modulus of filler, respectively. For the Halpin-Tsai model, the tensile modulus of GNPs, \( E_f \), was equal to the modulus of exfoliation in the graphite c-axis (through-the-plane) in the order of 36.5 GPa and the filler shape factor, \( \xi \), is equal to 0.667 \((L/d)\) for platelets\(^{3-6}\).

In order to study flexural strength and modulus, 3-point bending test also were conducted according to ASTM D790-02 using an Instron universal testing machine. The tests were performed with a 10 kN load cell at a cross-head speed of 2 mm/min and the span-to-depth ratio was maintained at 16:1. The maximum flexural stress at failure on the tension side of a flexural sample, calculated from Eq. 4, was considered as the flexural strength \((S)\) of the material. Moreover, flexural modulus \((E)\) was determined from the slope \((m)\) of the initial straight-line portion of the load-deflection curve according to Eq. 5.

\[ S = \frac{3PL}{2bd^2} \]
\[ E = \frac{L^3m}{4bd^3} \]

Where \( P \) is the applied load at the deflection point, \( b, d \) and \( L \) are the width, depth of the samples and the span length, correspondingly. At least five specimens from each sample were tested and the average data and standard deviation of strengths and moduli were reported.

The morphology of nanocomposites was studied by scanning electron microscopy of mechanical-fractured and freeze-fractured surfaces. For the mechanical-fractured surfaces, the samples were fractured during mechanical test and the freeze-fractured surfaces were manually prepared by cooling in liquid nitrogen. The obtained fracture surfaces were sputter-coated with gold. The SEM observations were obtained with a Philips field emission gun SEM (model: XL30, Netherlands) operated at 25 kV.
3. Grafting estimation

Surface functionalization degree could be approximately quantified using the following equation\textsuperscript{7,8}:

\[
\text{attached amount (mmol/g)} = \frac{1000\Delta W}{(100 - \Delta W)M}
\] (6)

Where \(\Delta W\) is difference of % weight loss for pure GNP with \(m\)-GNP during degradation process at an inert atmosphere, up to 600 °C, which is the temperature, assuming that graphitic structure of graphite nanoplatelets remains untouched and existing weight loss only results from the molecules on the surface. The \(M\) is the molecular weight of maleic anhydride. For our graphene nanoplatelets systems, \(\Delta W\) and \(M\) are ~8.5% and 98.06 g/mol, respectively. Accordingly, ~0.94 mmol maleic anhydride equaled to 92.1 mg was obtained to be attached on per gram of pure GNP.

![TGA thermograms of GNP, m-GNP and f-GNP at heating rate of 10 °C/min under nitrogen atmosphere.](image)

**Fig. S1.** TGA thermograms of GNP, \(m\)-GNP and \(f\)-GNP at heating rate of 10 °C/min under nitrogen atmosphere.
Table S1. Mechanical properties data of epoxy nanocomposites containing various contents of GNP and f-GNP.

| Nanoplatelets (wt %) | Nanoplatelets (vol %) | Tensile Strength (MPa) | Tensile Modulus (GPa) | Tensile Strength (MPa) | Tensile Modulus (GPa) |
|----------------------|-----------------------|------------------------|-----------------------|------------------------|-----------------------|
| 0                    | 0                     | 58.18±1.7              | 2.10±0.011            | 58.18±1.7              | 2.10±0.011            |
| 0.5                  | 0.29                  | 68.1±1.8               | 2.18±0.017            | 89.94±2.1              | 2.28±0.015            |
| 1                    | 0.59                  | 56.73±2.5              | 2.23±0.020            | 74.65±1.6              | 2.39±0.026            |
| 2                    | 1.19                  | 49.60±2.1              | 2.43±0.025            | 67.67±1.9              | 2.63±0.032            |
| 5                    | 3.01                  | 37.84±3.5              | 2.89±0.034            | 56.51±3.4              | 3.27±0.041            |
| 0                    | 0                     | 72.3±2.7               | 2.40±0.023            | 72.3±2.7               | 2.40±0.023            |
| 0.5                  | 0.29                  | 88.18±1.7              | 2.51±0.019            | 119.93±2.1             | 2.78±0.026            |
| 1                    | 0.59                  | 69.02±1.8              | 2.73±0.033            | 99.25±2.2              | 3.11±0.024            |
| 2                    | 1.19                  | 58.54±2.9              | 2.95±0.041            | 88.58±3.6              | 3.29±0.039            |
| 5                    | 3.01                  | 50.18±2.8              | 3.45±0.038            | 75.87±3.4              | 3.95±0.042            |
Table S2. Summary of the effect of different graphene types and chemical treatments on the tensile, flexural properties, and glass transition temperature in nanocomposites containing low loadings of graphene as reported in the literature.

| Graphene type (0.5wt%, unless otherwise mentioned) | Tensile properties Approximate percentage differences (%)<sup>a</sup> | Flexural properties Approximate percentage differences (%)<sup>a</sup> | $T_g$ (%)<sup>b</sup> | Comments | Ref. |
|--------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-----------------|-----------------|-----|
| Modulus | Strength | Modulus | Strength |                | Better wettability and dispersion/ Strong interfacial adhesion/ Crack deviations/Crack bridging/ Graphene pull-out resistance/ Mechanical locking | The present work. |
| GNP with no modification | +3.8 | +17 | +4.6 | +22 | +19.3 | Homogenous dispersion/ Good bonded interface/ Prevention of crack propagation/ Crack barrier effect | 9 |
| Tetraethylenepentamine functionalized GNP | +8.6 | +54.6 | +15.8 | +65.8 | | | |
| GNP with no modification | +3.2 | -4.6 | ----- | ----- | Homogenous dispersion/Strong interfacial interaction | 10 |
| 4,4'-diaminodiphenylsulfone Modified GNP | +53.2 | -1.5 | | | | |
| Graphene | | | | | | |
| A bio-based epoxy monomer (GA-II) functionalized graphene | +36 | +18.2 | +11.5 | +7.8 | | | |
| Ammonia-modified graphene nanosheets | +5.2 | +27.8 | +7.7 | +41.4 | +6<sup>c</sup> | Homogeneous dispersion/ Strong interfacial interactions/ Pull-out resistance/ Crack propagation resistance | 11 |
| GNP with no modification | +14.6 | +14.9 | | | | |
| Polybenzimidazole functionalized GNP | +27.15 | +26.7 | | | +1.9 | Better dispersion/ Crack initiation and propagation resistance/ Efficient stress-transfer/ Crack deflection/ Crack bridging/ Strong interfacial interactions | 12 |
| Synthesized a water-soluble perylene bisimide modified graphene | +81 | +36.6 | +16.3 | +44.2 | | uniform dispersion/ Strong interfacial interactions | 13 |
| 2-(4-aminophenyl) ethanol modified graphene (0.4 wt%)<sup>d</sup> | | | | | | Promoted molecular level of dispersion/ Higher efficiency of load transfer at the interface/ Crack propagation resistance/ Crack deflection | 14 |
| Modification                                      | Δσ (MPa) | Δε (%) | Notes                                                                 |
|--------------------------------------------------|----------|--------|----------------------------------------------------------------------|
| **Polyoxyalkyleneamine (B200 surfactant) modified GNP** | +17.3    | -19.6  | Improved dispersion/ Improved filler-matrix interface                |
| **Brominated GNP**                               | -----    | -14.5  | Improvement of interfacial adhesion                                  |
| **GNP with no modification**                     | +2.10    | +16    | Enhanced dispersion/ Crack deflection/ Crack bridging/ Better GNP’s pull-out resistance |
| **GNP modification**                             | +6.25    | +36    | Uniform dispersion/ Promotion of cross-linking reactions of epoxy and hardener/ Improvement of interfacial binding and the mechanical interactions/ Tilting and twisting of the cracks |
| **GNP (1 wt%)**                                  | -----    | -11.7  | Crack deflection and crack bridging                                  |
| **Imidazole functionalized reduced GO (0.4 wt%)** | +11.5    | +97.2  | Homogeneous dispersion/ Covalent bonding at the interface            |
| **GO with no modification**                      | +6.7     | +22.3  | Improved compatibility and dispersion/ Strong interfacial interaction/ Crack resistance |
| **diglycidyl ether of bisphenol-A functionalized GO** | +16.5    | +61.4  |                                                                       |
| **GO**                                           | +6.6     | +20    |                                                                       |
| Material                                      | GO    | Polyetheramine-functionalized GO$^c$ | GO modification | Microwave exfoliated reduced GO | Thermal exfoliated graphene (0.2 wt%)$^d$ | Poly(amidoamine) modified GO (3D graphene skeleton) (0.2 wt%)$^d$ | Thermally reduced graphene (TRG); (0.1 wt%)$^d$ |
|----------------------------------------------|-------|-------------------------------------|-----------------|---------------------------------|------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| 3-glycidoxypropyltrimethoxysilane functionalized GO | +14   | +37.3                               |                 |                                 |                                         |                                                 |                                                 |
| GO                                          | +6.7  | +22.3                               |                 |                                 |                                         |                                                 |                                                 |
| Polyetheramine-functionalized GO$^c$         | +10.8 | +57.2                               |                 |                                 |                                         |                                                 |                                                 |
| GO modification                             |       |                                     |                 |                                 |                                         |                                                 |                                                 |
| Base-washed                                  | +16   | +7                                  |                 |                                 |                                         |                                                 |                                                 |
| 3-amino propyl trimethoxysilane              | +20   | +13.2                               |                 |                                 |                                         |                                                 |                                                 |
| 3-glycidoxy propyl trimethoxysilane          | +16   | +12.3                               |                 |                                 |                                         |                                                 |                                                 |
| Microwave exfoliated reduced GO             | +10.9 | +5.1                                | +12.8           | +23.4                           |                                         | Good dispersion/ Good interfacial chemical bonding/ Disturbing and resisting the development of crack growth and prevented crack propagation/Enhanced energy absorption/ Crack bridging |
| Thermal exfoliated graphene (0.2 wt%)$^d$    | Not reported | +39                                | +15             | +10                             |                                         | A stable homogeneous structure in the formation of composites/ Good dispersibility and ordered arrangement/ Improved interface adhesion |
| Poly(amidoamine) modified GO (3D graphene skeleton) (0.2 wt%)$^d$ | +141  | +75                                 | +43.2           |                                 |                                         |                                                 |                                                 |
| Thermally reduced graphene (TRG); (0.1 wt%)$^d$ | ----- | +8.7                                | +15             | +1.3                            |                                         | Improved dispersion/ Strong interface/ Mechanical interlocking/ Better Wettability |

Enhanced dispersion level/ Strong sheet-matrix bonding/ Crack tip bifurcation/ Crack pinning/ Crack bridging

Modified dispersion/ Chemical interfacial Bonding/ High Energy dissipation

Uniform dispersion/ Strong filler-matrix interface/ Deflection of propagating crack fronts

Without change
|                          |                  |        |        |                                      |                                                                 |
|--------------------------|------------------|--------|--------|-------------------------------------|------------------------------------------------------------------|
| Carboxylic functionalized TRG, (0.1 wt%)<sup>g</sup> |                  | +18.7  | +22    |          | Well dispersion/ Better load transferring from the matrix to the reinforcements/ Induction of high anisotropy in properties via self-aligned along the in-plane direction |
| GO                      |                  | +6.3   | +32.7  | -        | +3.7    |                                                                 |
| Highly stable reduction of GO (Using hydrazine)     |                  | +15.6  | +46.4  | -        | -2.8<sup>c</sup> | Fiber-filler chemical bonding/ Efficient dispersion and uniform distribution |
| 4-aminobenzoyl-functionalized graphite              |                  | +23    | +8.2   | -        | -17.5<sup>c</sup> | Superior dispersion and exfoliation/ Strong interfacial interactions/ Crack deflection/ Effective phase transfer agent |
| triglycidyl para-aminophenol (TGPAP) treated GO EP20-GO1.0<sup>f</sup> | Not reported      | +91.8  |        | +37.7   | +36.5    |                                                                 |
| reduced GO (0.1 wt%)<sup>d</sup>                   |                  | +31    | +40    | -        | -        | Frictional pull-out/ Improvement of mechanical interlocking-adhesion at the nanofiller-matrix interface/ Crack deflection |
| Thermally reduced graphite oxide                     |                  | -18    | -7     | -        | -        | Mechanical interlocking/ Better adhesion/ Crack deflection |

**Notes:**
- <sup>a</sup> = Increase
- <sup>b</sup> = Decrease
- <sup>c</sup> = Significant
- <sup>d</sup> = Weight percentage
- <sup>e</sup> = Functionalized
- <sup>f</sup> = GO EP20-GO1.0
- <sup>g</sup> = TRG

**References:**
28, 29, 30, 31, 32, 33
| Anisotropic graphene aerogel | ----- | +12.4 | +1.1 | ----- | Reduction of difficulties to uniformly disperse/ Crack tip blunting and deflection/ Obstructing crack propagation |
|----------------------------|-------|-------|------|-------|--------------------------------------------------|
| CVD graphene foam | ----- | +25.5 | +35.1 | +35.8c | Integrated 3D structure of GF can totally eliminate the issues of uniform dispersion/ Interlocking mechanism/ Enhancing the interfacial adhesion/ Inducing local crack tip blunting/ Formation of microcracking bifurcation dilatation fracture process zone |

a) Percentage increase "+" or percentage decrease "+" of mechanical properties compared to neat epoxy.
b) Percentage increase "+" or percentage decrease "+" of glass transition temperature compared to untreated nanoparticle/epoxy nanocomposite.
c) The value states the percentage differences of $T_g$ compared with neat epoxy glass transition temperature.
d) The value in brackets indicates that the content of the graphene-based nanofiller which is either lower or higher than 0.5 wt%.
e) An average amount for mechanical properties data are reported for any length of polyether amine coupling agent which is grafted to GO.
f) The prepared epoxy/GO mixtures or nanocomposites are denoted as EPx-GOy, where x is the TGPAP weight percentage in the epoxy oligomer, and y is the GO content in parts per hundred parts of epoxy resin without a curing agent (phr).
Fig. S2. SEM images of fracture surfaces of pure epoxy (a) and epoxy/0.5% GNP nanocomposites (b & c).

Fig. S3. SEM image of fracture surface of epoxy/5% f-GNP nanocomposites containing high level of agglomerations (red arrow).
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