Journal of Carbon Research

Article

Fabrication of Graphene-Reinforced Nanocomposites with Improved Fracture Toughness in Net Shape for Complex 3D Structures via Digital Light Processing

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Figures

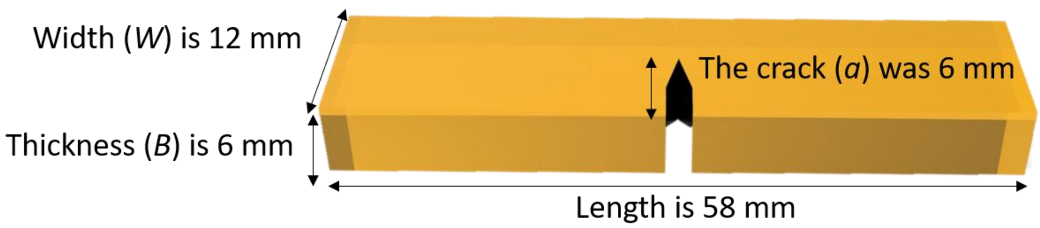

Figure S1. Schematic of the KIC specimen.

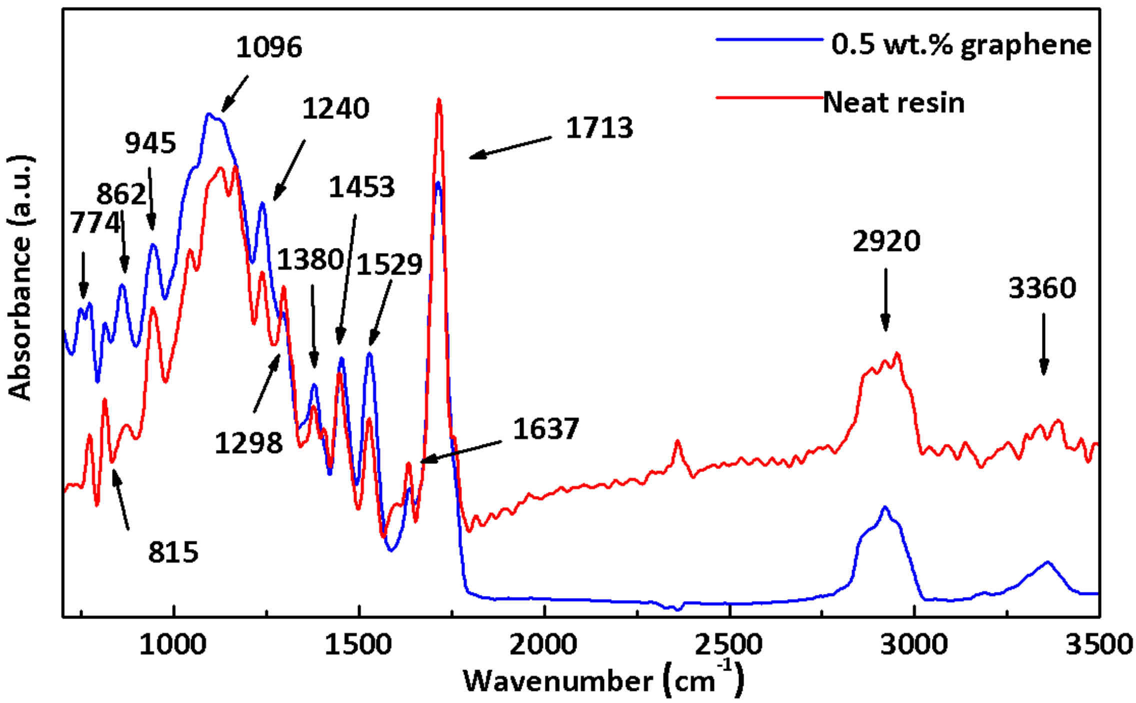

Figure S2. FTIR spectra of UV-cured reference resin and 0.5 wt. % graphene-reinforced nanocomposites.

In the high-wave-number spectral region, a broad peak at 3360 cm^{-1} was observed, which corresponded to the O–H stretching vibration. The peaks at 1380, 1453, and 2920 cm^{-1} were assigned to the symmetric C–H bending vibration and the asymmetric C–H bending and stretching vibrations, respectively. The stretching vibrations of C=O at 1713 cm^{-1} can be found from the spectrum as well. The peaks at 1529 cm^{-1} were assigned to the stretching vibrations of C–C corresponding to the aromatics group. The external bending signals of C–H bonds were confirmed at 862 and 774 cm^{-1}. The peaks of oxygen functionalities were detected at 1240 and 1096 cm^{-1}, which were ascribed to the C–O–C stretching vibration. Further, relevant bonds corresponding to N–H wagging, C–N stretching, and N–H bending at 815, 1298, and 1637 cm^{-1}, respectively, could be noticed.

Halpin–Tsai Model

The Halpin–Tsai model is a mathematical model for the prediction of elasticity of composite materials based on the geometry and orientation of the filler and the elastic properties of the filler and matrix. The model is a function of the aspect ratio of the nanofiller, along with constituent properties and the volume fractions of the two phases (matrix and reinforcement). The Halpin–Tsai equation can be written as

$$\frac{E_c}{E_m} = \frac{1+\zeta\eta\varphi_f}{1-\eta\varphi_f} \tag{1}$$

With

$$\eta = \frac{(\frac{E_f}{E_m} - 1)}{(\frac{E_f}{E_m} + \zeta)} \quad (2)$$

where E_c, E_f, and E_m are, respectively, the composite, filler, and matrix elastic modulus; φ_f is the volume fraction of the filler, and ζ is a Mori–Tanaka modified shape factor, which was corrected for platelet graphene reinforcement by comparing the Halpin–Tsai equation with Mori–Tanaka's theory. The shape factors corresponding to plates were chosen in accordance with [1].

For uniaxial oriented plates, it can be stated that

$$E = E_{(\parallel)} = E_{(11)} \quad (3)$$

$$E_{(\perp)} = E_{(33)} \quad (4)$$

The calculation of the moduli of a composite with randomly oriented fillers can be solved by an approximated solution inspired by laminate plate theory. For 2D in-plane random materials, the modulus of the composite can be writen as

$$E_{2D\ random} \cong 0.625\ E_{(\perp)} + 0.375\ E_{(\mathrm{II})} \quad (5)$$

For a fully random 3D platelet material, according to the shape of the filler, the storage modulus of graphene-reinforced composites with randomly oriented graphene nanoflakes is calculated with a simplified equation for randomly oriented of flakes:

$$E_{3D\ random\ platelet} \cong 0.49\ E_{(\parallel)} + 0.51\ E_{(\perp)} \quad (6)$$

where $E_{(\parallel)}$ and $E_{(\perp)}$ correspond to the elastic modulus of the composite in the longitudinal and transverse directions, respectively, which coincides with upper and lower bound rule of mixtures values. $E_{(\parallel)}$ and $E_{(\perp)}$ are calculated with the Halpin–Tsai equation by using $\zeta_{//} = \frac{2}{3} * \mathrm{W/\,t}, \zeta_{\perp} = 2$ for $E_{(\parallel)}$ and $E_{(\perp)}$.

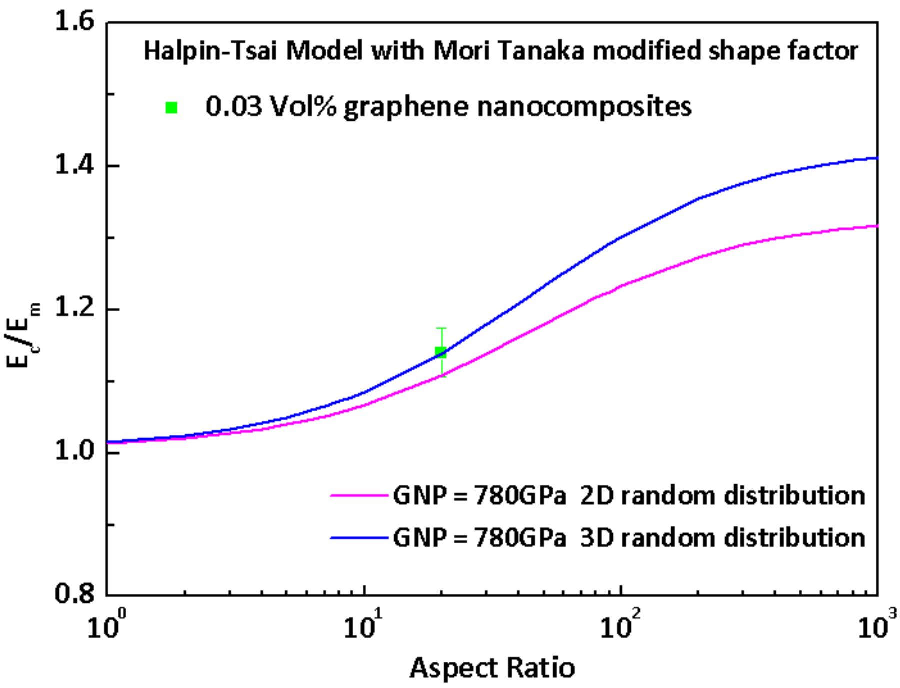

Figure S3. Halpin–Tsai models with Mori–Tanaka modified shape factor of composite modulus ratio *E*c/*E*m as a function of the filler aspect ratio together with experimental data of 0.03 vol % graphene nanocomposites. Model predictions assumed for platelet moduli of 780 GPa with a 2D planar or 3D random orientation.

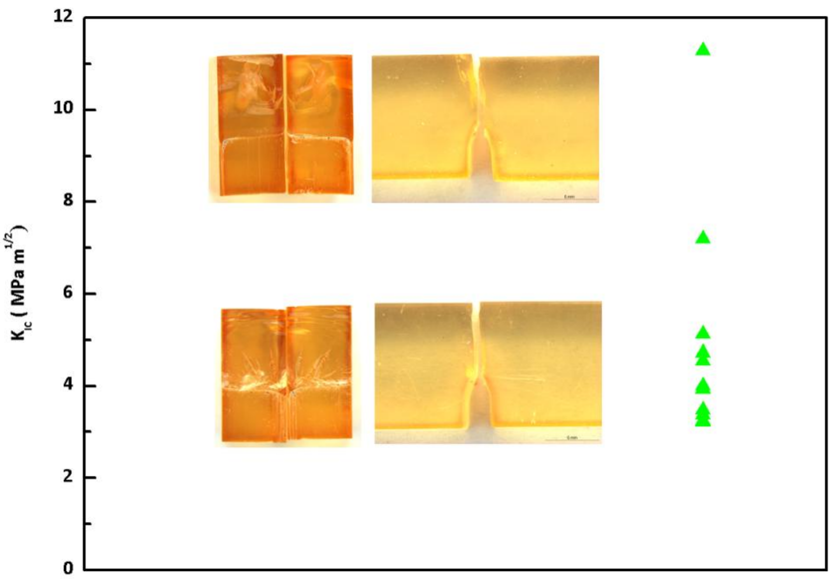

Figure S4. The K_{IC} value and optical images of failed fracture toughness test specimens for the neat resin with 30° sharp notch tips.

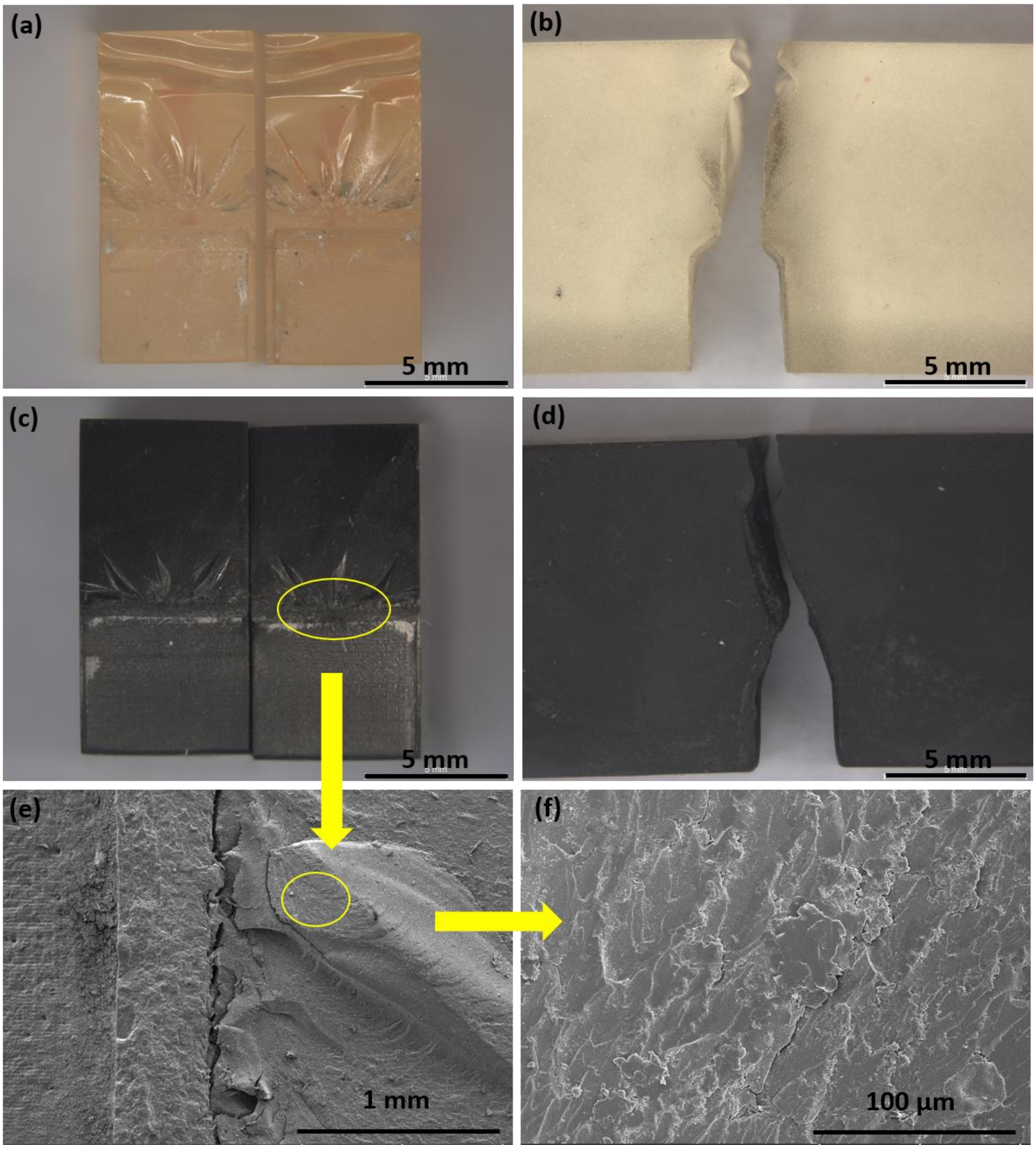

Figure S5. Optical microscopy images of fracture surface and fractured lateral view of graphene/resin composites after a failed fracture toughness test: (**a**,**b**) the neat resin specimens; (**c**,**d**) 0.5 wt. % nanocomposite specimens. SEM images of the fracture surfaces of: 0.5 wt. % nanocomposites specimens; (**e**) magnification of the circled domain in (**c**); and (**f**) magnification of the circled domain in (**e**).

Reference

1. Van Es MA. Polymer-clay nanocomposites: the importance of particle dimensions: TU Delft, Delft University of Technology; 2001.