3D Printable Graphene Composites-supplementary information

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1. Supplementary methods

1.1 Materials

Graphite flakes (~10 mesh) were obtained from Alfa Aesar. $\text{H}_2\text{SO}_4$ (95-98%, AR) and $\text{HCl}$ (36%, AR) were purchased from Suzhou Zhitang Chemicals Co., Ltd., China. $\text{H}_3\text{PO}_4$ (≥85%, AR) and $\text{H}_2\text{O}_2$ (30%, AR) were purchased from Jiangsu Tongsheng Chemical Reagent Co., Ltd., China. $\text{KMnO}_4$ was purchased from Shanghai Chemical Reagent Co., Ltd. Hydrazine hydrate (50%, AR), N-Methyl pyrrolidone (NMP) and ethanol (95%, AR) were all purchased from Sinopharm Chemical Reagent Co., Ltd., China. Acrylonitrile-butadiene-styrene (ABS, Mw=120000-140000 g/mol) was
purchased from Zhenjiang Chimei Chemical Co., Ltd. China. Polylactic acid (PLA, Mw≈51000 g/mol) was purchased from Nature works chemicals Inc, USA.

1.2 Preparation of GO

Briefly, a mixture of H$_2$SO$_4$/H$_3$PO$_4$ (120:13.3 ml) was introduced to a mixture of 1 g graphite flakes and 6 g KMnO$_4$. The reaction was carried out at 50±2 °C and stirred for 12 h with speed of 180 r.p.m. Then the reaction was poured onto ~400 ml ice followed by addition of 1.5 ml H$_2$O$_2$ (30%). The mixture was left overnight, the supernatant was decanted and the bottom solids were washed with deionized water. The solid material was collected via centrifugation (4000 r.p.m., 30 min). The obtained material was further centrifuged in succession with 200 ml water, 200 ml 30% HCl, and 200 ml ethanol (2×) to decant away the impurities. GO/NMP solution was obtained by exchanging water in GO aqueous solution with NMP. GO aqueous solution was exchanged and centrifuged with NMP at 8000 rpm for 20 min per time. To insure NMP fully exchanged water, the procedure was repeated 10 times. GO was redispersed in N-Methyl-2-pyrrolidone (NMP), forming a 5 mg/ml GO-NMP solution. 

*Note we started from GO-NMP solution instead of dried rGO to get a homogenous GO-ABS mixture.*

To assess the rGO weight percentage, same amount of GO aqueous solution (made from 1 g graphite flake) was dried at 110 °C for 24 h, obtaining 1.5 g of product. Afterwards, 0.324 g dried GO was mixed in 200 NMP at 15000 r.p.m. with the homogenizer, followed by addition of 1 ml hydrazine. The reaction was performed at 95 °C for 2 h. Through centrifuging at 8000 r.p.m., washed ethanol (2×) and water(3×)
and dried in a 120 °C oven for 24 h, 0.257 g rGO \( (W_{rGO} = 0.79 \ W_{GO}) \) was obtained, where \( W_{GO} \) was weight of GO and \( W_{rGO} \) was weight of rGO. The GO loading were 0.5, 1.0, 2.0, 3.0, 4.8, 7.0 and 9.1 wt%, calculated from the starting material GO’s weight. Correspondingly, The rGO weight percentage in the composite was calculated as follows: wt % = \( 0.79W_{GO} / (0.79W_{GO} + W_{polymer}) \), where \( W_{polymer} \) was weight of polymer. The rGO loading were 0.4, 0.8, 1.6, 2.3, 3.8, 5.6 and 7.4 wt%, respectively.

1.3 Characterizations

SEM. SEM images were taken from freeze-fractured cross sections of the 4 mm×10 mm×0.5 mm G-ABS composites on Nova Nano SEM 450 at an acceleration voltage of 3 kV. Among these G-ABS composites, the 0.8 wt% and 2.3 wt% G-ABS composites were decorated with a thin layer of gold to minimize charging before imaging. Electrical conductivity. The polymer composites were hot pressed (XLB-D, Shanghai Rubber Machinery Works No.1 Co. Ltd, China) into 4 mm×10 mm×0.5 mm at 10 MPa with a temperature of 210 °C. A 4 mm×10 mm×0.5 mm composite sample was cut into 2 mm wide and 10 mm long strips. The conductivity was measured on a 2mm×10 mm×0.5 mm strip. The d.c. resistance of the composites was recorded using a probe (ST 2558B-F01) and picoammeter (Keithley 4200), the electrical conductivity was then calculated, details of calculation were displayed in Figure S11. Raman analysis. Raman spectroscopy (Renishaw, 785 nm) was used to characterize the samples. For Roman analysis of reduced GO (rGO), rGO sample was prepared as follows. GO solution was chemically reduced to graphene by hydrazine. 3 ml GO water solution (5 mg/ml) was added in 50 ml water, the solution was heated to 95 °C
with stirring speed of 2000 r.p.m., followed by addition of 0.5 ml 50 % hydrazine hydrate. The reaction was kept for 1 h, then the product was collected via centrifugation (8000 r.p.m., 5 min). The black precipitates was washed with 100 ml water and 100 ml ethanol twice, respectively. Finally, the product was dried at 120 ºC for 24 h. **UV-vis analysis.** UV-vis spectra (UV-3600, Shimazu, Japan) were obtained by a diluted aqueous solution of the samples. **TGA.** TGA (Pyris-1 TGA, Perkin Elmer) was performed from 50 to 800 ºC at a heating rate of 10 ºC/min under nitrogen. **DSC.**

\[ T_g \]

was determined using DSC (Q2000, TA Inst. Co.). Samples with 6 mm×6 mm×2 mm were performed in a two-step procedure: in first run, the composites were heated from 20 ºC to 120 ºC at a heating rate of 10 ºC/min, then cool down to room temperature at a cooling rate of 10 ºC/min; in second run, the samples were heated to 160 ºC at a heating rate of 3 ºC/min. **TMA, DMA.** For TMA and DMA analysis, the polymer composites were hot pressed into 6 mm×6 mm×2 mm and 4 mm×10 mm×0.5 mm in a compression moulding machine at 10 MPa with a temperature of 210 ºC. TMA measurements were performed to record the deformation of the sample in the direction of the thickness using a penetration probe under a constant load of 0.01 N. CTE was determined by a thermomechanical analyzer (TMA/SDTA841e, Mettler Toledo, Inc., Switzerland). The samples with 6 mm×6 mm×2 mm were performed in a two-step procedure: in first run, the samples were heated to 120 ºC with a heating rate of 10 ºC/min then cooled down to 25 ºC with a cooling rate of 10 ºC/min to eliminate the influence of enthalpy relaxation; in second run, the samples were heated to 160 ºC with a heating rate of 5 ºC/min. The CTE curves shown in this manuscript are traces
collected in second run. For DMA measurements, a dynamic mechanical analyzer (DMA/SDTA861e, Mettler Toledo, Inc., Switzerland) was used to characterize the mechanical property of the composite samples. The measurement of sample with 4 mm×10 mm×0.5 mm size was carried out in air from room temperature to 150 ºC with a heating rate of 3 ºC/min at a constant frequency of 1 Hz.

2. Figures and tables

![Figure S1](image)

**Figure S1.** (a) A Picture of the homogenizer (Shanghai Specimen and Model factory). (b) A picture of the dispersing rotor and (c) its schematic illustration.
Figure S2. Photographs of 3D printed models using (a) 0.8 wt%, (b) 2.3 wt%, (c) 3.8 wt% and (d) 5.6 wt% G-ABS composite filaments.
Figure S3. Optical images of the 3D printer (a) and nozzle (b). 3D printing nozzle moved back and forth at rate $\sim 20$ mm/s. Scheme illustration of layer by layer manufacturing technique (c) and HBC (d).
**Figure S4.** Photographs of (a) 0.8 wt% G-PLA filament and (b) corresponding 3D printed models.

**Figure S5.** SEM images taken from the surfaces of (a) 2.3 wt%, (b) 3.8 wt% and (c) 7.4 wt% G-ABS composites, GS stands for graphene sheet. (d) Illustration of graphene dispersions in polymer. The composite material is insulating until graphene sheets form an infinite network of connected pathway to conduct electricity.
Figure S6. SEM images taken from cross-section of (a, b, c) 0.8 wt%, (d, e, f) 2.3 wt%, (g, h, i) 3.8 wt%, (j, k, l) 5.6 wt% and (m, n, o) 7.4 wt% G-ABS composites.
Figure S7. Arrangement of four probe measurement on G-ABS samples.

The electrical conductivity of the composites was calculated by a reported method for resistivity measurement. The related equations are displayed below:

\[
\rho = C \cdot \frac{V}{I} \cdot G\left(\frac{w}{s}\right) \cdot D\left(\frac{d}{s}\right)
\]

\[
C = 2\pi s
\]

\[
G\left(\frac{w}{s}\right) = 0.18 , D\left(\frac{d}{s}\right)=0.2205
\]

\[
\sigma = \frac{1}{\rho}
\]

where

\(I\) ---- current
\(V\) ---- voltage
\(\rho\) ---- resistivity

\(G\left(\frac{w}{s}\right), D\left(\frac{d}{s}\right)\) are correction factors determined by: sheet thick (w), probe distance (s), length (d), and width (a) of sheet sample. Here s = 2 mm, a = 10 mm, and d = 2 mm, and w = 0.5 mm
Figure S8. A 3D printed rectangular model by 3.8 wt% G/ABS composite.

According to the formula, \( \rho = \sigma \cdot \frac{V}{I} \cdot G \left( \frac{w}{s} \right) \cdot D \left( \frac{d}{a} \right) \)

\[ C = 2 \pi s \]

\[ G \left( \frac{w}{s} \right) = 0.429, \quad D \left( \frac{d}{a} \right) = 0.2205 \]

\[ \sigma = \frac{1}{\rho} \]

where

- \( I \) ---- current
- \( V \) ---- voltage
- \( \rho \) ---- resistivity

\( G \left( \frac{w}{s} \right), \quad D \left( \frac{d}{a} \right) \) are correction factors\(^2\) determined by: sheet thick (w), probe distance (s), length (d), and width (a) of sheet sample. Here \( s = 2 \text{ mm}, \quad a = 10 \text{ mm}, \quad \text{and} \quad d = 10 \text{ mm}, \quad \text{and} \quad w = 1.2 \text{ mm}. \)

The conductivity reduced from \( 6.4 \times 10^{-5} \text{ S/m} \) to \( 2.5 \times 10^{-7} \text{ S/m} \), ascribing to the formation of vacancies in 3D printing.
Figure S9. Illustration of internal voids formation in 3D printing process.

Figure S10. Plot of the logarithm of dc conductivity ($\sigma_c$) vs the volume fraction ($\phi$) of graphene for the G-ABS composite system. The plot shows an open S curve or “sigmoid” curve$^3$. According to the percolation theory, the conductivity ($\sigma_c$) of G-ABS composites is treated with the law: $\sigma_c = \sigma_f \left( (\phi - \phi_c)/(1 - \phi_c) \right)^t$ $^{30,31}$ when above the percolation threshold, where $\sigma_f$ is the conductivity of graphene, $\phi$ is the graphene volume fraction, $\phi_c$ is the percolation threshold (chosen at the onset of the transition$^{30,35}$, ~ 0.9 vol%), and $t$ is the “universal critical exponent”. Inset is the log-log plot of conductivity against ($\phi - \phi_c$) of graphene in ABS system.
Figure S11. Zoomed in Raman spectra of 2D peaks. GO (black), rGO (red), and G-ABS composite (blue).

Figure S12. (a) Raman spectra of ABS and G-ABS composites. (b) Zoomed-in spectra around 2240 cm$^{-1}$ region.
Table S1. Characteristic Raman spectra bands for GO, rGO, ABS and G-ABS composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Raman Shift (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>1357 1596</td>
<td>D peak</td>
</tr>
<tr>
<td></td>
<td>1596 113</td>
<td>G peak</td>
</tr>
<tr>
<td>rGO</td>
<td>1324 1602</td>
<td>D peak</td>
</tr>
<tr>
<td></td>
<td>1602 69</td>
<td>G peak</td>
</tr>
<tr>
<td>ABS⁷</td>
<td>2236</td>
<td>C≡N stretch (acrylonitrile)</td>
</tr>
<tr>
<td>G-ABS</td>
<td>~1320 ~1600 ~2240</td>
<td>D peak</td>
</tr>
<tr>
<td></td>
<td>~106 ~69 ~59</td>
<td>G peak</td>
</tr>
<tr>
<td></td>
<td>~1600 ~2651</td>
<td>C≡N stretch (acrylonitrile)</td>
</tr>
</tbody>
</table>

Table S2. Characteristic D, G and 2D bands for GO, rGO and G-ABS composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D peak (cm⁻¹)</th>
<th>FWHM of D (cm⁻¹)</th>
<th>G peak (cm⁻¹)</th>
<th>FWHM of G (cm⁻¹)</th>
<th>2D peak (cm⁻¹)</th>
<th>FWHM of 2D (cm⁻¹)</th>
<th>I_D/I_G</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>1357</td>
<td>175</td>
<td>1596</td>
<td>113</td>
<td>2642</td>
<td>--</td>
<td>0.81</td>
</tr>
<tr>
<td>rGO</td>
<td>1324</td>
<td>106</td>
<td>1602</td>
<td>69</td>
<td>2651</td>
<td>115</td>
<td>1.40</td>
</tr>
<tr>
<td>G-ABS</td>
<td>1320</td>
<td>116</td>
<td>1600</td>
<td>59</td>
<td>2618</td>
<td>138</td>
<td>1.43</td>
</tr>
</tbody>
</table>

D peak is related to the breathing modes of sp2 atoms in hexagon rings activated by the defects such as vacancies or grain boundaries, while G peak is due to the bond stretching of all sp2 pairs in both rings and chains⁴. The ratio of D and G peak intensity, denoted as I_D/I_G, combined with their G peak’s FWHM, are used to evaluate the structural disorders/perturbations⁴⁻⁶. As reported, the FWHM of G peak always increase with disorder, while I_D/I_G reaches to its maximum as the distance between defects, L_D, gets close to ~3 nm⁵. In our case as shown in Table S2, the I_D/I_G ratio of rGO and G-ABS were 1.40 and 1.43, respectively, higher than that of GO (I_D/I_G =0.81). Their FWHMs of G peak are 69 and 59 cm⁻¹, which are much smaller than GO’s 113 cm⁻¹, indicating an increase of L_D upon reduction of GO by hydrazine⁵.

Besides D and G peaks, 2D peak is the second order of the D peak which does not require any defect to be activated⁵. Its FWHM and dispersion are also important.
indicators for graphene structure’s disorders. In Figure S11, there was only a broad feature for GO from \(\sim2300\) to \(\sim3000\) cm\(^{-1}\), where the 2D, D+D' and 2D' peaks were convoluted ambiguously, suggesting a highly disordered structure\(^5\). After the hydrazine reduction, both rGO and G-ABS showed a more distinctive 2D peaks with FWHMs around 115 and 138 cm\(^{-1}\), respectively, suggesting the restoration of graphene structures\(^5\).

**Table S3.** \(T_g\) and \(T_{\text{onset}}\) obtained from DMA, DSC and TGA on ABS and G-ABS composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_g) (^\circ)C</th>
<th>(T_g) DSC (^\circ)C</th>
<th>(T_g) DMA (^\circ)C</th>
<th>(T_{\text{onset}}) (^\circ)C</th>
<th>Residue (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>106.81</td>
<td>104.89</td>
<td>398.76</td>
<td></td>
<td>1.4</td>
</tr>
<tr>
<td>rGO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>72.1</td>
</tr>
<tr>
<td>0.4 wt% G-ABS</td>
<td>106.93</td>
<td>103.19</td>
<td>339.17</td>
<td></td>
<td>6.1</td>
</tr>
<tr>
<td>0.8 wt% G-ABS</td>
<td>108.51</td>
<td>105.34</td>
<td>349.74</td>
<td></td>
<td>10.0</td>
</tr>
<tr>
<td>1.6 wt% G-ABS</td>
<td>107.08</td>
<td>110.07</td>
<td>363.79</td>
<td></td>
<td>4.9</td>
</tr>
<tr>
<td>2.3 wt% G-ABS</td>
<td>107.72</td>
<td>104.55</td>
<td>357.05</td>
<td></td>
<td>7.4</td>
</tr>
<tr>
<td>3.8 wt% G-ABS</td>
<td>108.13</td>
<td>106.45</td>
<td>362.56</td>
<td></td>
<td>8.3</td>
</tr>
<tr>
<td>5.6 wt% G-ABS</td>
<td>108.46</td>
<td>106.36</td>
<td>359.2</td>
<td></td>
<td>8.4</td>
</tr>
<tr>
<td>7.4 wt% G-ABS</td>
<td>109.22</td>
<td>110.78</td>
<td>365.62</td>
<td></td>
<td>7.8</td>
</tr>
</tbody>
</table>

\(a\) \(T_g\) data is derived from DSC. \(b\) \(T_g\) data is measured by DMA. \(c\) The onset temperature of thermal degradation (\(T_{\text{onset}}\)) is designated as the temperature with 3.8 wt\% weight loss. \(d\) TGA residue after being heated to 800 °C

As displayed in Table S2, discrepancy is discovered between the \(T_g\) values obtained from DMA analysis and DSC measurements, attributing to the fact that DMA is
highly dependent on the frequency of strain oscillation whereas DSC measures a heat quantity in a temperature change between the target sample and the reference sample, and variations are inevitable. Although the ABS and its composites $T_g$ results obtained from these two means are not exactly identical, both show a tendency that the $T_g$ value slightly increased as the graphene loading in composites increased.

**Figure S13.** UV-vis spectra of rGO (pink) and G-ABS composites (blue) in zoomed-in region from Figure 2d.
Figure S14. Storage moduli ($E'$) as a function of temperature for G-ABS composites with different graphene loadings.

DMA was performed at various temperature to determine the storage moduli ($E'$). It is observed that $E'$ of G-ABS composites are higher than pure ABS polymer in the glass regime between 102 ºC and 113 ºC. Also the $E'$ values increase with an increasing graphene content in polymer composites although the increase is not in proportion to the amount of graphene fillers.
The pure ABS had a loss weight of 98.4% after being heated to 800 °C under a nitrogen flow. For ABS and G-ABS samples, a mass weight loss occurred at 400 °C to 480 °C. The mass residue ranged from 6.1 wt% to 10.0 wt% for G-ABS samples after being heated to 800 °C (Table S3), ascribing to the removal of ABS in the composite. For rGO sample, the total weight loss was 28.9 wt% at 800 °C. This major loss could be attributed to the presence of functional groups on the rGO.
Figure S16. Illustration of thermal warping occurred in 3D printing.

During layer by layer process in 3D printing, a layer is ejected from hot chamber, it soon cools and shrinks. Subsequently, another hot layer is paved up and adhered onto the layer which is relatively cold, a steeper temperature gradient between these two layers leads to contraction of hot layer and compression of cold layer until these two layers reach thermal equilibrium, as illustrated in Figure S16. Therefore, thermal stresses are generated in this solidification process, inducing thermal warping in 3D printing. However, thermal stress can be suppressed by utilization of HBP. We set the HBP temperature at 80 º C, approaching $T_g$ of ABS at 106.81 º C. In this case, this is an optimal temperature that ABS layer can be adhered on stiff plate without occurring thermal warping. In assistance with HBP (80 º C), the stresses in plate itself compensate for the thermal stresses inside the ABS layer during 3D printing process.

Thermal stresses are vital to the quality of 3D printed prototypes because huge thermal stresses contribute to thermal warping. It is known that thermal stress ($\sigma_t$) is
proportional to CTE ($\alpha$), temperature change below $T_g$ ($\Delta T$), and Young’s modulus ($E$). The relationship is displayed following: $\sigma_t=\alpha\cdot E\Delta T^8$. Thus, to minimize the thermal contraction, it is feasible and practical to acquire relatively smaller constants of $\alpha$ and $\Delta T$. The dimensional change from TMA measurements shows little variation at a temperature interval from room temperature to $T_g$. DMA and DSC results show that $T_g$ values of all G-ABS composites are close to the pure ABS, so $\Delta T$ (here $\Delta T=T_g-80$) is regarded as a constant.

Supplementary references


**Video S1** shows the 3D printing process in printing 3.8 wt% G-ABS composite filament.