

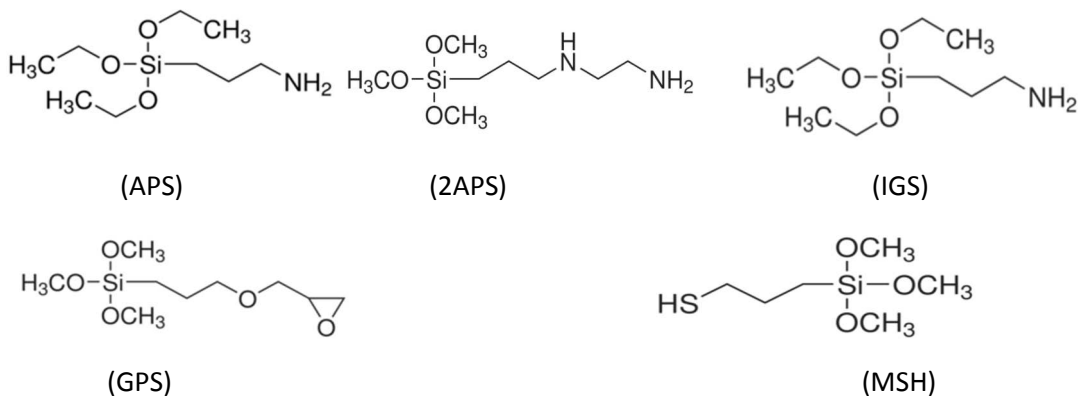
Manipulating Dispersion and Distribution of Graphene in PLA through Novel Interface Engineering for Improved Conductive Properties

Yu Fu,¹ Linshu Liu,² Jinwen Zhang^{1*}

¹School of Mechanical and Materials Engineering, Composite Materials and Engineering Center, Washington State University, Pullman, Washington 99164, United States

E-mail: jwzhang@wsu.edu Fax: +11-509-335-5077 Tel: +11-509- 335-8723

²Eastern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, 600 East Mermaid Lane, Wyndmoor, Pennsylvania 19038, United States



Scheme 1 Chemical structures of silane agents used.

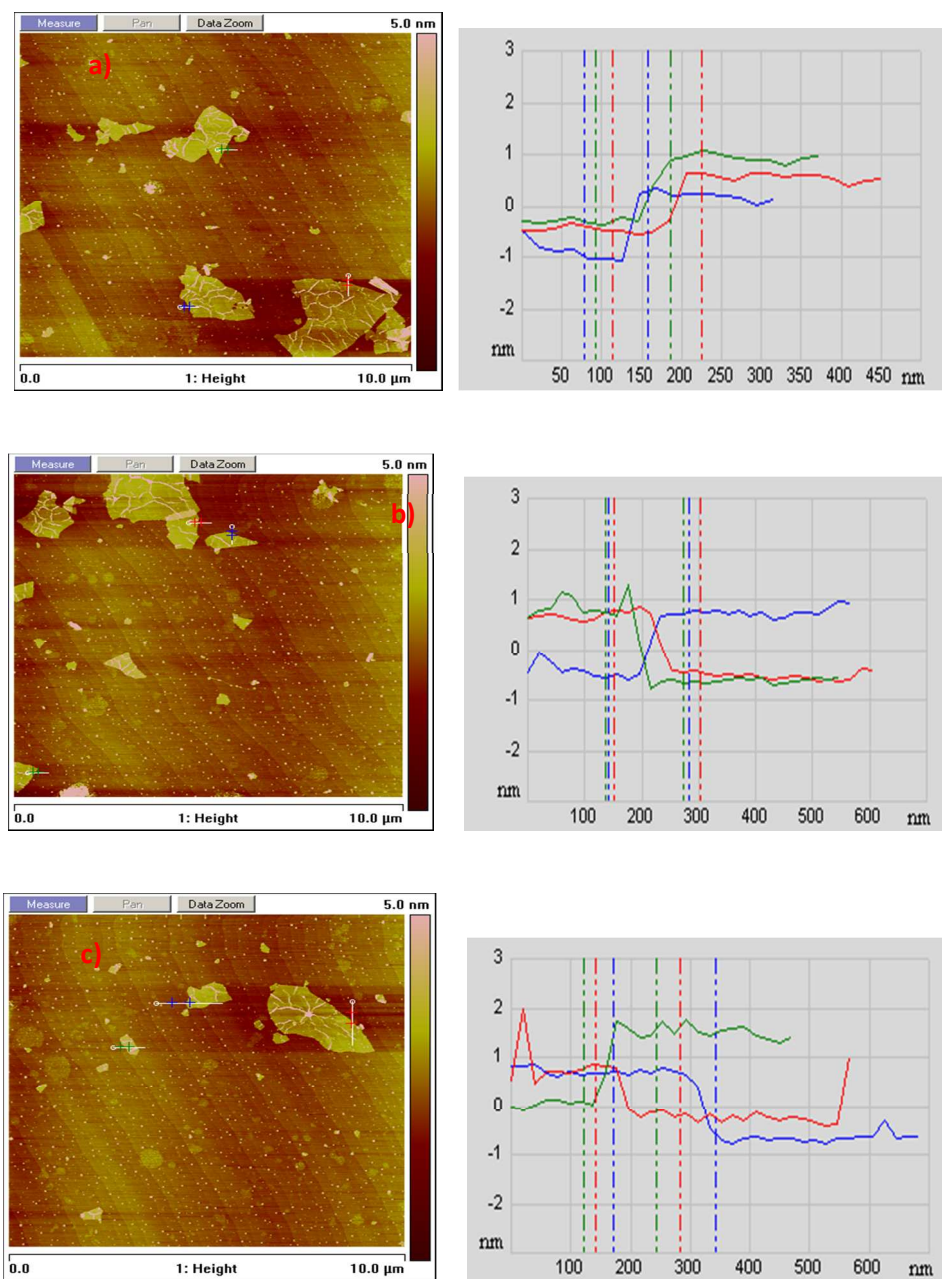


Fig. 1 AFM morphology of GO a), GO-APS b), and GO-MSH c) and their corresponding height profiles.

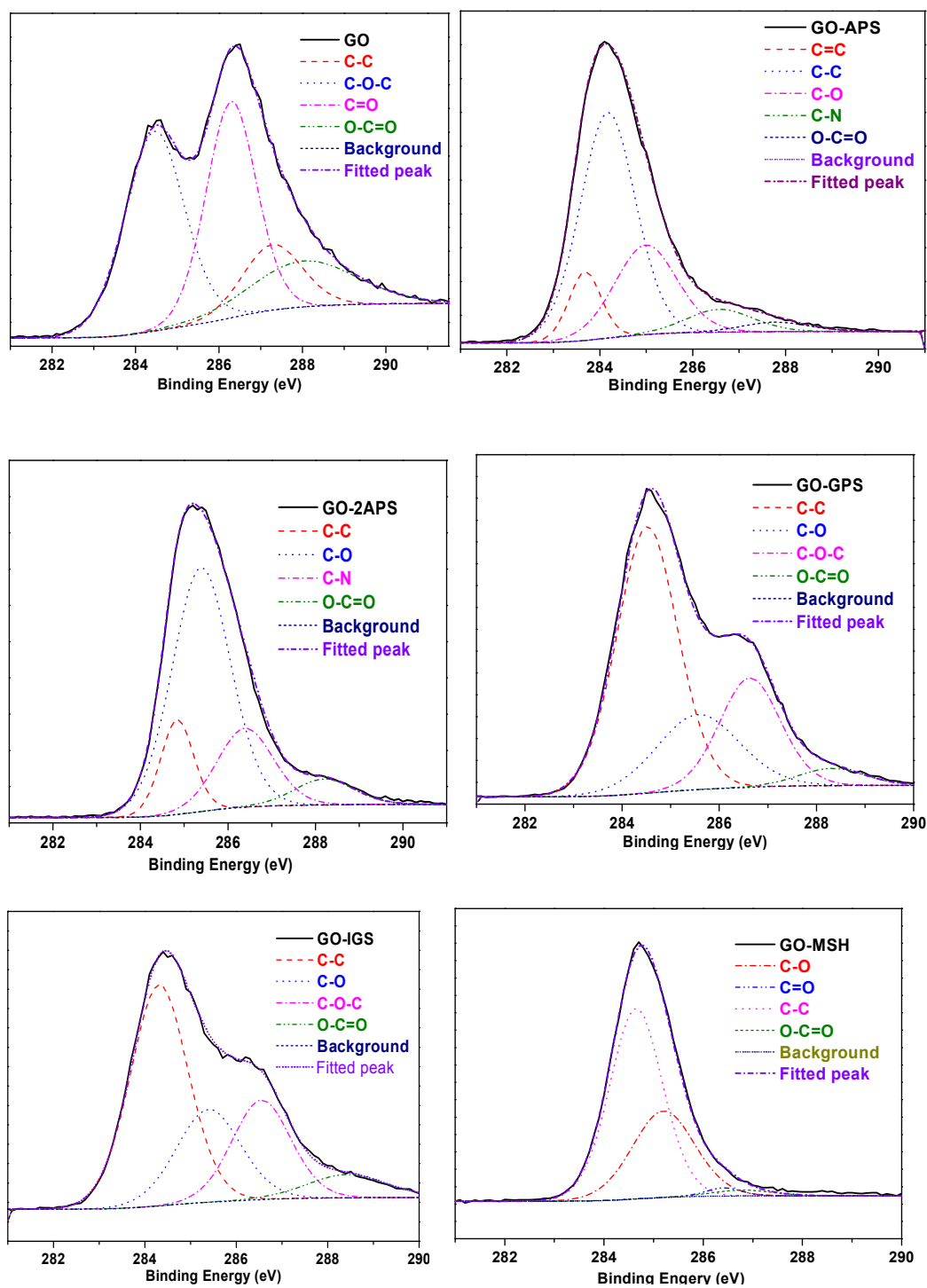


Fig. 2 Deconvolution of the C1s peak of the XPS spectra of GO and f-GO.

The location and dispersion state of the nanofillers at the thermodynamic equilibrium can first be predicted by the value of the wetting parameter (ω), which is defined as follows:¹

$$\omega = \frac{\gamma_{fGO-PLA} - \gamma_{fGO-Rubber}}{\gamma_{PLA-Rubber}} \quad (1)$$

where $\gamma_{PLA-Rubber}$ is the interfacial energy between the PLA and rubber (EBA-GMA) phases, and γ_{fGO-p} is the interfacial energy between *f*-GO and the polymer component - PLA or rubber. If $\omega > 1$, *f*-GO will mainly reside in the rubber phase; if $\omega < -1$, *f*-GO will be dispersed in the PLA phase; and if $-1 < \omega < 1$, *f*-GO will be concentrated at the interface. Because it is not easy to obtain the interfacial energy between different components directly, the Girifalco-Good (geometric mean method) equation is usually used:¹

$$\gamma_{ij} = \gamma_i + \gamma_j - 2\sqrt{\gamma_i \gamma_j} \quad (2)$$

where γ_i and γ_j are the surface energies of the *i* and *j* components.^{2,3,4} Thus, by applying the Owens and Wendt equation the surface energies of PLA and rubber can be first determined:

$$\gamma_L (1 + \cos \theta) = 2\sqrt{\gamma_i^d \gamma_L^d} + 2\sqrt{\gamma_i^p \gamma_L^p} \quad (3)$$

where γ_L is the surface tension of the probe liquids used (**Table 1**), θ the average static contact angles, γ_i^d and γ_i^p the nonpolar and polar parts of γ_i , respectively, and $\gamma_i = \gamma_i^d + \gamma_i^p$ the total surface energy of the polymers (**Table 2**).⁵

The total surface energy values of PLA and rubber at room temperature were found to be 31.74 and 22.35 mJ/m², respectively. These values are close to those reported in literature.^{6,7} The surface energy values of the *f*-GO were also determined using the same method. To achieve the surface energies of PLA and rubber at the processing temperature (180°C), the relation $\frac{d\gamma}{dT} = -0.06$ mJ/K was applied as an approximation.^{8,9} **Table 2** gives the surface energy values of the corresponding components.

According to Eq. (1), the wetting parameters can be calculated and then the location of the *f*-GO at thermodynamic equilibrium can also be predicted in the blend matrix. The results are presented in **Table 3**. It predicted that the *f*-GO would mainly reside in the PLA phase. This is theoretically reasonable because the nanofillers prefer to disperse in the melt phase with lower viscosity. Actually, other factors such as kinetic effect of processing might also play certain roles in determining the selective location of the nanofillers.

Table 1 Probe liquids used in the experiment

Probe liquids	γ^T (mJ/m ²)	γ^d (mJ/m ²)	γ^p (mJ/m ²)
Diiodomethane	50.8	50.8	0
Formamide	58.0	39.0	19.0

Where superscript *T*, *d*, and *p* refer to total, dispersive part, polar part of surface energy.

Table 2 Contact angles and surface energies of the corresponding components in the resulting nanocomposites

Contact angles (o)	PLA	EBAGMA	GO	GO-APS	GO-MSH
γ^T					
Diiodomethane	55.2 (1.2)	72.5 (1.8)	35.0 (0.6)	61.9 (1.9)	36.7 (0.3)

Formamide	72.3 (1.5)	82.1 (1.3)	20.1 (0.8)	65.2 (0.4)	40.1 (1.2)
γ^T (mJ/m ²)	31.74	22.35	55.08	31.22	47.7
γ^T at 180 °C (mJ/m ²)	22.44	13.05			

Where superscript T , d , and p refer to total, dispersive part, polar part of surface energy.

Table 3 Calculation of interfacial energy and ω

γ_{ij}^T	EBAGMA	GO	GO-APS	GO-MSH
PLA	1.27	7.21	0.72	4.71
EBAGMA		14.51	3.9	10.85
ω		-5.75	-2.50	-4.84
Predicted location		PLA	PLA	PLA

Where superscript T , d , and p refer to total, dispersive part, polar part of surface energy.

Water contact angle is used to further investigate wettability of the resulting nanocomposites. If a water droplet rests on a solid surface and spreads to form a small contact angle, it indicates that the solid substrate is wetted by water and has a hydrophilic characteristic. **Fig. 3** shows the water droplet easily rested on the GO nanocomposite surface with a smaller contact angle compared with the f -GO nanocomposite surfaces. The static aqueous contact angle of 53° suggested that the GO nanocomposite had a hydrophilic surface. In contrast, GO-APS and GO-MSH were less hydrophilic, showing static aqueous contact angles of 83° and 66°, respectively. The higher hydrophilicity of GO was due to the presence of more polar oxygen-containing groups in GO. The contact angles from the organic solvent also gave the same tendency as those of water contact angles.

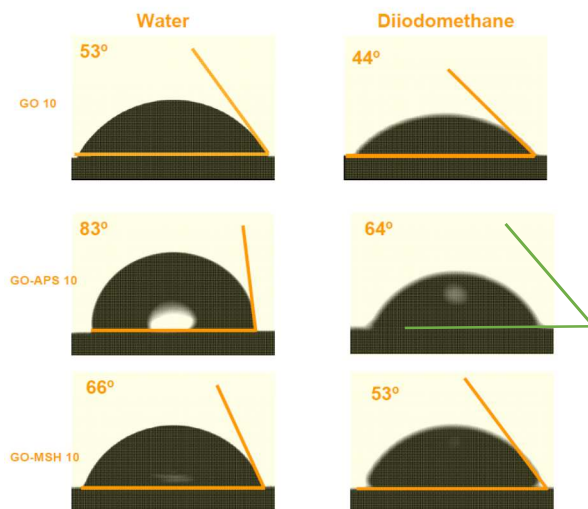


Fig. 3 The static contact angles of water and diiodomethane on the *f*-GO nanocomposite sheet surfaces.

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