SUPPORTING INFORMATION

The "superlubricity state" of carbonaceous fillers on polyethylene-based composites in a molten state

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Graphite, Graphite Oxide, and multilayer graphene oxide characterisation

The graphite (Gr) consists of carbon layers with covalent and metallic bonding within each layer which are stacked in an AB sequence and are linked by van der Walls interactions produced by a delocalised π orbital. The carbon layers in graphite are known as graphene layers ¹. After Hummer's method, the graphite is oxidised and can be called graphite oxide (GrO). The structure of GrO contains regions with functional groups between the layers at the basal plane (hydroxyl and epoxy groups) and the edges (carboxyl groups) and also un-oxidised regions. The interactions between GrO layers include electrostatic, hydrogen bonds, and π orbital van der Waals interactions due to inserted functional groups².

Successfully obtaining GrO using Hummer's method can be confirmed by the results presented in Figures 1-4S. Figure 1S shows the diffractograms of Gr and GrO. At approximately 26° a peak is observed, referring to the plane (002) of the graphite structure with an interlayer spacing of 0.3156 nm. After the oxidation process, the plane (002) shifted to $\sim 11.6^\circ$. This indicates enlarged interlayer spacing to values close to 0.8140 nm due to the insertion of functional groups in the graphite structure. The Raman spectroscopy in

Figure 2S shows the increase in the D-band intensity ($\sim 1350 \text{ cm}^{-1}$) for oxidised graphite. The intensity of this band increases due to the presence of incomplete bonds and functional groups linked to the structure of the material caused by the oxidation. Both phenomena lead to a loss of the sp² hybridisation present on the graphite structure³.



Figure1S. X-ray diffractograms of graphite and graphite oxide.



Figure 2S. Raman spectra of graphite and graphite oxide.

The thermogravimetric analysis presented in Figure 3S shows an initial weight loss up to 140 °C due to the elimination of water followed by a loss weight between 140 and 330 °C (~ 28.13%) that can be attributed to the volatilisation of oxygenated groups present due to the graphite oxidation process ⁴. This can also express that GrO is thermally reduced at this temperature range. Meanwhile, the graphite does not show any loss of mass during the test. The FTIR spectrum (Figure 4S) shows the presence of functional groups generated in GrO by the graphite oxidation process. The GrO spectrum presents a broad peak at approximately 3427 cm⁻¹, attributed to the stretching vibration of O-H that can be from the water absorbed by the GrO. The 1730 cm⁻¹ peak on the GrO spectrum is related to the stretching vibration of C=O in the carboxyl and carbonyl groups. The peak around 1619 cm⁻¹ is attributed to C=C stretches. The presence of this peak in both samples (Gr and GrO) indicates that not every region of the graphite was oxidised. The peak at 1371 and 1224 cm⁻¹ is a result of the –OH vibration in the carboxyl group (edge plane) and alcohol group (basal plane), respectively. The presence of the C-O-C epoxide group can also be confirmed by the presence of a peak around 1054 cm⁻¹ ^{5,6,7,8,9}.



Figure 3S. Thermogravimetric curves of graphite and graphite oxide.



Figure 4S. Infrared spectra of graphite and graphite oxide.

The fragmentation degree after graphite oxidation

To verify the fragmentation degree after graphite oxidation, the sizes of the crystal were calculated. It is known that the ratio between the intensities of the D and G bands (ID/IG) is inversely proportional to the in-plane crystallite sizes (La) (Equation 1) ¹⁰. In Raman spectroscopy (Figure 2S), a clear rise in the D intensity (ID) with oxidation can be observed, which leads to a significant increase in relation to ID/IG ¹⁰. According to Equation 1 (λ is the laser line wavelength), the in-plane crystallite sizes (La) of graphite reduced from 21.61 nm to 19.4 nm after the oxidation process (reduction of 8.77%). In XRD (Figure 1S), using the Scherrer equation (Equation 2)¹⁰ where the radiation wavelength λ_{XRD} , θ , the position of the (200) peaks, and B(2 θ) is the half-height width of the (200) peaks, the crystallite size along the c axis (Lc) was calculated for graphite and GrO. Lc was reduced from 19.5 nm to 17.9 nm for the domain at 26.47° when B changes from 0.7884 to 0.8565° due to oxidation (reduction of 8.2%). When the (200) plane was changed to 11.7°, the Lc is 11.20 nm showing a reduction of 42.56% when compared to graphite.

$$La(nm) = (2.4 x 10^{-10}) \lambda_{laser}^4 \left(\frac{I_D}{I_G}\right)^{-1}$$
(1) $Lc(nm) = \frac{1.84\lambda_{XRD}}{B(2\theta)\cos(\theta)}$ (2)

The drastic reduction of the calculated grain size gives a strong indication that the flake fragmentation occurred during the graphite oxidation. An increase in the number of flakes means an increase in the number of incommensurable interfaces (flake-flake contact and boundary grain) in the material^{11,12}. Despite a misorientation of the boundary grain, the random crystallographic orientations of various grain contents in the flake can restrict the slipping at this interface. Each boundary grain has a preferential slipping direction; as a consequence, multiple slipping directions will be constrained by the boundary's grains. This observation agrees with Hall-Petch in relation to the polycrystalline materials, which shows that the "slipping" stress is inversely proportionally to grain size¹³. However, flake-flake contact has a higher ability to slip than the grain boundary regions.

Rheological Tests of Composites (HMWPE-fillers and HDPE-fillers)

Figure 5S shows the loss modulus (G") of HMWPE-Fillers (0.1% wt.) composites obtained from the oscillatory test.



Figure 5S. Loss Modulus (G") of pure HMWPE and its composites with 0.1 wt.% of mGO, GrO,

and Gr.

Figure 6S and Table 1 show data from molecular weight and molecular distribution of the pure HMWPE and HMWPE-Filler(0.1% wt.) samples tested using an oscillatory test.



Figure 6S. Molecular weight distribution of pure HMWPE and its composites containing 0.1 wt.% of mGO, GrO, and Gr.

Table 1S. Number-average molecular weight ($\overline{M}n$), weight-average molecular weight ($\overline{M}w$) and

| | \overline{M} n (g/mol) | \overline{M} w (g/mol) | PD |
|--------------------|--------------------------|--------------------------|-------|
| HMWPE | 172,000 | 248,300 | 1.446 |
| HMWPE/mGO (0.1wt%) | 189,000 | 253,300 | 1.339 |
| HMWPE/GrO (0.1wt%) | 164,000 | 271,400 | 1.654 |
| HMWPE/Gr (0.1wt%) | 175,000 | 267,700 | 1.529 |

polydispersity index (PD) of pure HMWPE and its composites containing 0.1 wt.% of mGO, GrO, and Gr.

Figure 7S shows the loss modulus (G") of pure HMWPE and HMWPE-Fillers (5% wt.) composites obtained from the oscillatory test.



Figure 7S. Loss Modulus (G") of pure HMWPE and its composites with 5.0 wt.% of mGO, GrO, and

Gr.

Figure 8S shows the loss modulus (G'') of pure HDPE and HDPE-Fillers (5% wt.) composites obtained from the oscillatory test.



Figure 8S. Loss Modulus (G") of pure HDPE and its composites with 5.0 wt.% of mGO, GrO, and

Gr.

In Figure 9S the transferred shear stress (τ) from HDPE and HMWPE during the steady shear flow test can be observed.



Figure 9S. Shear Stress of polymers (HDPE and HMWPE) measured from steady-state.

Estimation of relaxation time (λ)

Equation 3 described by the Carreau-Yasuda model:

$$\eta(\dot{\gamma}) = [\eta(0) - \eta(\infty)][1 + (\lambda \gamma)^{a}]^{\frac{n-1}{a}} + \eta(\infty)$$
⁽³⁾

where η is the flow-curve measurements of viscosity, $\eta(0)$ the low-shear limiting viscosity, $\eta(\infty)$ high-shear limiting viscosity, λ the relaxation time, n the power-law index, and a a parameter that describes the transition from Newtonian to shear-thinning behaviour.

Table 2S shows the relaxation time (λ) of the HMWPE, HDPE, and their respective composites obtained from Anton Paar RheoCompassTM Software and calculated using the Carreau-Yasuda model.

Table 2S. Relaxation Time (λ) of the HMWPE and HDPE and respective composites obtained using the

| Composites | Relaxation Time-λ (s) |
|----------------------|-----------------------|
| HMWPE | 205.5 |
| HMWPE-mGO (0.1 wt.%) | 123.26 |
| HMWPE-GrO (0.1 wt.%) | 83.83 |
| HMWPE-Gr (0.1 wt.%) | 157.77 |
| HMWPE-mGO (5 wt.%) | 104.05 |
| HMWPE-GrO (5 wt.%) | 113.73 |
| HMWPE-Gr (5 wt.%) | 163.03 |
| HDPE | 25.85 |
| HDPE-mGO (5 wt.%) | 36.65 |
| HDPE-GrO (5 wt.%) | 43.92 |
| HDPE-Gr (5 wt.%) | 30.18 |

Carreau-Yasuda equation

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