Supplementary Material (ESI) for Soft Matter
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Polymers under Extreme Two-dimensional Confinement: Poly(ethylene oxide) in Graphite Oxide

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1. Determination of the amount of PEO in the PEO/GO sample

Thermogravimetric analysis coupled to mass spectrometry (TGA/MS) was used to determine the amount of PEO in the PEO/GO sample. These results were also confirmed by inelastic neutron spectroscopy (INS). TGA and differential thermal analysis (DTA) profiles of PEO, GO and PEO/GO are compared in Fig. 1a. Whereas neat PEO decomposes in only one step characterized by a maximum temperature peak (T_p) of 360 ºC, the confined polymer showed a clear reduction of its decomposition temperature and presented two distinct weight-loss features at T_p = 214 ºC and 295 ºC. Mass spectroscopy was very helpful in identifying the origin of these weight losses.

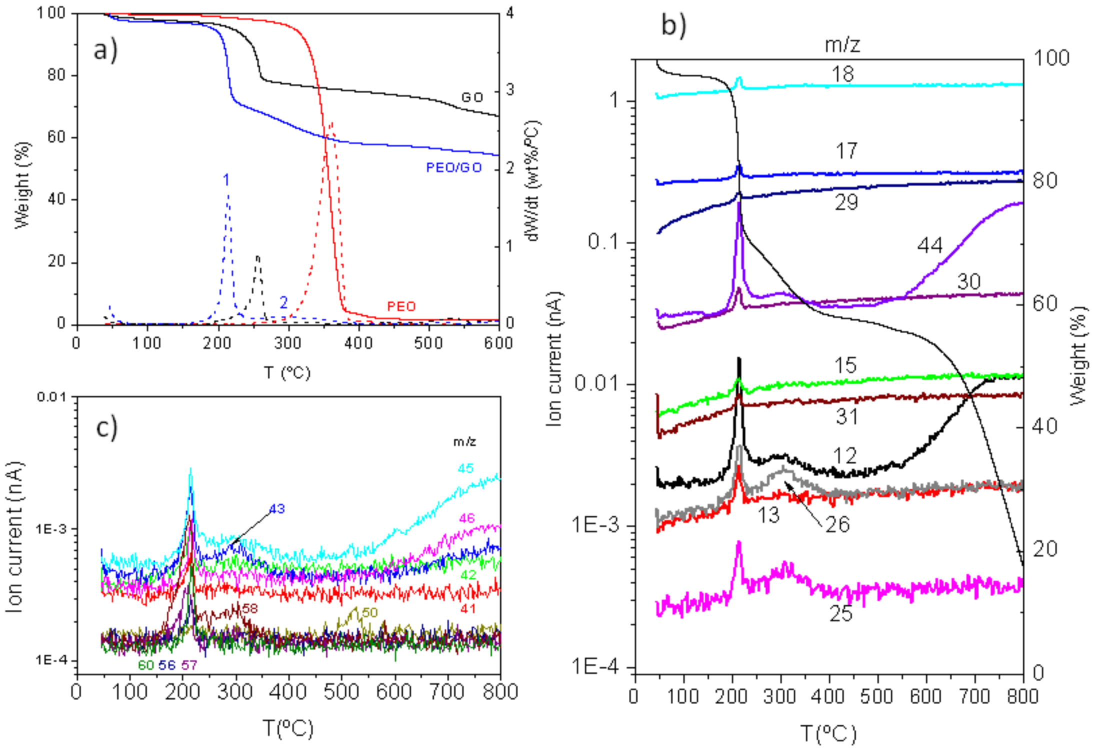

Fig. 1. a) TGA and DTA profiles of PEO, GO and PEO/GO recorded at 1 ºC/min in helium flow. b) and c) Combined TGA/MS results of PEO/GO.

The evolved gas in the PEO sample (graph not shown) revealed the existence of a wide range of ion fragments: m/z ion peaks appear at 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60. The degradation mechanism of PEO proceeds via random-chain scission of C-O bonds and C-C bond cleavage,[1-3] leading to the formation of a series of molecules such as mono and diether oligomers, ethylene glycol, diethylene glycol, 1,3 dioxolane, 2-methoxy-1,3 dioxolane, methyl vinyl ether, ethyl vinyl ether, 2-butenal[4,5] and also furan, oxalic acid, ethylene oxide, and oxymethylene species.[1] The fragment ions observed in the MS profiles correspond to these species and to their fragmented products.

The decomposition products of PEO in the PEO/GO sample were identified by the m/z signals arising from the polymer. The following m/z signals were found in PEO/GO (Fig. 1b and c): 12, 13, 15, 17, 18, 20, 22, 24, 25, 26, 29, 30, 31, 41, 42, 43, 44, 45, 46, 50, 56, 57, 58, 60. Signals with m/z = 12, 18, 43, 44, 45, 46 and 50 are common to both GO and PEO/GO. Ion signals with m/z = 18 have been ascribed to H_2O (H_2O^+) and those with m/z = 12, 44, 45 and 46 to CO_2 [12 (C^+), 44 (CO_2^+), 45 ($^{13}CO_2^+$), 46 ($C^{18}O^{16}O^+$)].[6] The low intensity signal with m/z = 43 could arise from $C_2H_3O^+$ fragments and that with m/z = 50 from stable fragments in GO.[6] The remaining signals with m/z = 13, 15, 17, 20, 22, 24, 25, 26, 29, 30, 31, 41, 42, 56, 57, 58, 60 in PEO/GO are characteristic of PEO decomposition. Therefore, the presence of all these ions at 214 ºC and ions with m/z = 26 and 58 at 295 ºC implies that PEO in PEO/GO decomposes in two stages. By evaluating the weight loss of PEO/GO and the weight loss of GO at 450 ºC, we obtain a composition of 20 wt% of PEO in the PEO/GO sample. These results are corroborated by the PEO/GO INS data shown in Fig. 4 of the manuscript. Normalization of these data on the basis of a 20 wt% PEO in PEO/GO and subsequent subtraction of the GO background resulted in identical spectral features to those of bulk PEO in the C-H stretch region ca. 3000 cm^{-1}. This result firmly confirms the above-determined value of 20wt% of PEO in the PEO/GO sample.

2. Estimates of adsorbed PEO on the outermost GO surfaces

Polymer adsorption on the outermost surfaces of the GO substrate can occur, even when PEO/GO samples are thoroughly washed with water and filtered. An estimate of the amount of PEO that could eventually remain adsorbed on the outermost GO surfaces can be performed by comparing liquid-nitrogen Brunauer-Emmett-Teller (BET) surface areas for pristine (2.5 m^2/g) versus exfoliated GO (630 m^2/g). Such a comparison provides a direct measure of external interfacial areas, as N_2 is incapable of entering the GO galleries at ambient pressure. On the basis of these data, we obtain a ratio of 250/1 in favor of the intercalated phase. This ratio gives an upper (conservative) bound of 1% polymer adsorbed on the external surfaces of the final PEO/GO intercalate. Therefore, any effects arising from the presence of externally adsorbed polymer are negligible. Moreover, XRD, dielectric, and INS data provide firm evidence for the existence of a distinct PEO phase very different from the bulk (neat PEO).

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