Beamline: BM28

Proposal number: 28-01 -1127 **Date of experiment:** 17/9/15 – 21/9/15

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Investigating the crystallization kinetics, morphology and orientation development of processed PET/MWCNTs polymer composite blended films.

INTRODUCTION Polyethylene terephthalate (PET) multi-walled carbon nanotube (MWCNT) composites exhibit excellent electrical, mechanical and thermal properties. The key to understanding the improvements in physical properties of the polymer is to be able to follow the structure development of these composites during processing. This allowing the influence of the MWCNTs on the nucleation and crystallization process of the PET to be determined. However, the complex role that MWCNTs play in the crystalline morphology development in polymer composites during processing is still poorly understood. Here, we show the development of a nanohybrid shish-kebab (NHSK) structure in PET-MWCNT composites during hot isothermal crystallization. The results indicate that MWCNTs act as nucleation points for NHSK-type crystallization and the crystalline morphology that evolves has a predisposed orientation induced from the initial processing method [1-3].

EXPERIMENTAL Two-dimensional (2D) Small and Wide-Angle X-ray Scattering (SAXS/WAXS) measurements were performed on the XMaS (BM28) beamline. The PET-MWCNT composites were originally prepared via a cast extrusion process (as previously reported, [4,5]), being referred to by the MWCNT wt% loading PET; PET1%, PET2% and PET4% herein. The MWCNTs were well dispersed in the PET matrix (confirmed by optical microscopy and SEM [1,5]) with a small fraction aligned in the extrusion flow direction due to the design of the die used in the extrusion process. The melting temperature T_m, of all samples was ~254 °C, but the crystallization temperatures T_c, for the PET-MWCNT composites were higher at ~220 °C (compared to 194 °C for neat PET), owing to the nucleating effects of the MWCNTs. The samples were heated in a Linkam DSC, to 270 °C, held for 10 minutes, then quenched at a rate of 50 °C min^{-1} to the crystallization temperature; at undercoolings just below T_m. SAXS and WAXS data was collected on a MAR-CCD detector. Both SAXS and WAXS data were obtained for the samples at 30 °C. SAXS data was then obtained at 270 °C and throughout the isothermal crystallization process for subsequent kinetic analysis.

RESULT AND DISCUSSION On XMaS (BM28), combined small- and wide-angle X-ray scattering (SAXS/WAXS) and thermal techniques were used to follow the time resolved morphology development and crystallization kinetics of the PET-MWCNT composites. SAXS, reveals the crystalline morphology (shish-kebab or regular lamellar) and orientation during the hot isothermal crystallization process from the melt. WAXS gives information on the polymer crystal lattice. Figure 1, shows 2D SAXS and WAXS of the composite samples (extruded at 30 °C). No residual crystalline structure for neat PET is observed in either SAXS or WAXS. In contrast, the PET-MWCNT composites show increased scattering around the beamstop, indicating some residual crystalline content from the extrusion process is present. PET2% and PET4% composites, also show some preferred

orientation (arc-like intensity around the beamstop). WAXS for the PET-MWCNT samples, shows the crystalline PET triclinic unit cell reflections (010) and (0-11). Final SAXS patterns from the hot isothermal crystallization process show for neat PET, a random crystalline lamellar structure prevails.

Figure 2A, shows the change in orientation (FWHM), with increasing crystallization temperature. Significant orientation is seen in the composites whereas no orientation is seen in neat PET. Figure 2B, shows the hot crystallization curves giving the crystallization half-times, $t_{1/2}$. The PET-MWCNT composites show increased crystallization kinetics (reduction in $t_{1/2}$), compared to neat PET, during crystallization from the melt.

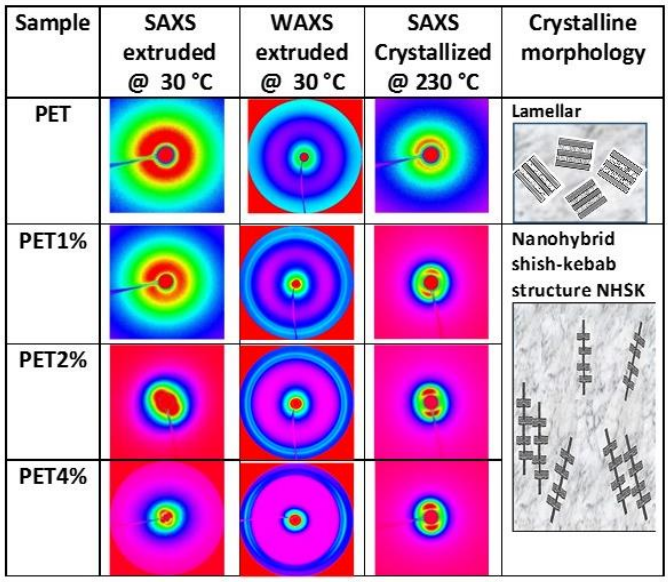

Fig. 1. 2D SAXS and WAXS patterns from extruded samples at 30 °C and SAXS when crystallized at 230 °C. Neat PET shows a random lamellar morphology whereas PET-MWCNT composites show an oriented NHSK morphology.

CONCLUSIONS MWCNTs are seen to drastically influence the crystalline morphology of PET, by acting as pre-aligned nucleating agents increasing the crystallization kinetics of the polymer. This has significant impact on the use of such fillers in the processing and modification of the physical properties of engineering polymers.

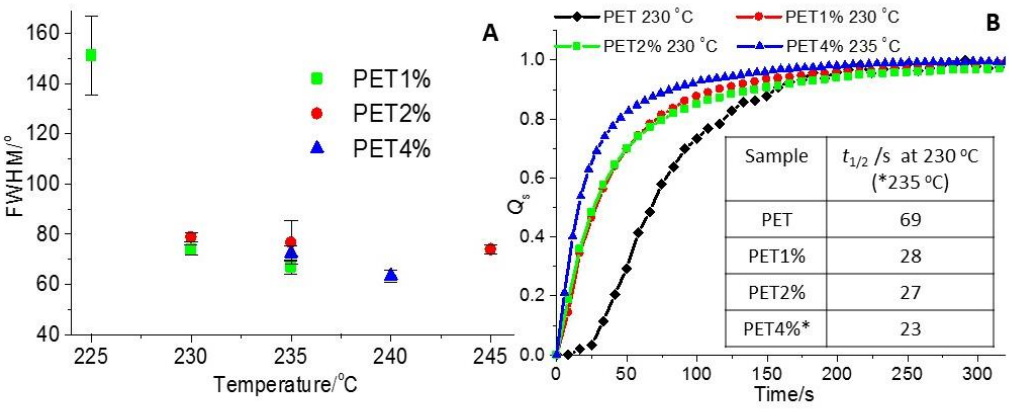

Fig. 2. A: the change in orientation full-width half max (FWHM), for PET-MWCNT samples with increasing crystallization temperature. **B**: selected crystallization curves – inset table details the crystallization half-time ($t_{1/2}$).

1. *E.L. Heeley, D.J. Hughes, E.M. Crabb, J. Bowen, O. Bikondoa, B. Mayoral,* S. Leung *T. McNally*. "*The formation of a nanohybrid shish-kebab (NHSK) structure in melt-processed composites of poly (ethylene terephthalate) (PET) and multi-walled carbon nanotubes (MWCNTs)*" submitted, *Polymer*, **2017**.

2. E. L. Heeley, D.J. Hughes, E.M. Crabb, J. Bowen, O. Bikondoa, B. Mayoral, T. McNally, Confirmation of a nanohybrid shish-kebab (NHSK) structure in composites of PET and MWCNTs, *J. Polym. Sci., Part B: Polym. Phys*. 55, **2017**, 132.

3. *E.L. Heeley, D.J. Hughes, E.M. Crabb, J. Bowen, O. Bikondoa, B. Mayoral, T. McNally. "A nanohybrid shish-kebab (NHSK) structure in composites of PET and MWCNTs*" XMaS Newsletter, **2016**, pg. 12.

4. E. L. Heeley, D. J. Hughes, E. Crabb, M. Kershaw, O. Shebanova, S. Leung, B. Mayoral, T. McNally, "*Structure evolution in polyethylene terephthalate (PET) - multi-walled carbon nanotube (MWCNT) composite films during in-situ uniaxial deformation*" *Polymer* **2016,** *92*, 239.

5. B. Mayoral, P. R. Hornsby, T. McNally, T. L. Schiller, K. Jack, D. J. Martin. "*Quasi-solid state uniaxial and biaxial deformation of PET/MWCNT composites: structural evolution, electrical and mechanical properties*" *RSC Adv*. **2013**, *3*, 5162.