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Confirmation of a nanohybrid shish-kebab (NHSK) structure in composites of PET and MWCNTs

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Additional Supporting Information may be found in the online version of this article.

ABSTRACT

Here, the confirmation of an oriented nanohybrid shish-kebab (NHSK) crystalline structure in a series of composites of poly(ethylene terephthalate) (PET) and multiwall carbon nanotubes (MWCNTs) is reported. The combined use of small- and wide-angle X-ray scattering (SAXS/WAXS) and thermal analysis has been used to investigate the morphology development in PET-MWCNT nanocomposites under hot isothermal crystallization conditions. The MWCNTs act as both heterogeneous nucleating agents and surfaces (oriented shish structures) for the epitaxial growth of PET crystallites (kebabs) giving an oriented crystalline morphology. In contrast, the PET homopolymer does not show any residual oriented crystalline morphology during isothermal crystallization but gave a sporadic nucleation of a classic unoriented lamellar structure with slower crystallization kinetics. The results provide a valuable insight into the role of MWCNTs as nano-particulate fillers in the morphology development and subsequent modification of physical properties in engineering polymers.

KEYWORDS: polymer-MWCNT nanocomposites, crystalline morphology, kinetics, small- and wide-angle X-ray scattering (SAXS/WAXS)

Composites incorporating multiwall and/or single walled carbon nanotube (MWCNT/SWCNT) fillers and a polymer matrix, offer exciting potential for industrial applications. This is due to modification of many properties, e.g. mechanical and electrical compared with the neat homopolymer.¹⁻⁵ The CNT filler provides not only direct reinforcement due to their outstanding physical properties, but also secondary reinforcement

via modification through their influence on the final polymer crystal morphology. Our recent work has shown the value of MWCNTs as a functional nanofiller in poly(ethylene terephthalate) (PET); improvements in mechanical properties were linked to the direct MWCNT reinforcement and its dramatic nucleating effects on the polymer matrix.^{6,7} Whilst it has been shown that CNTs act as nucleating agents in polymer crystallization

during processing, what is not understood is their influence on the evolution and final macrostructure.

It has been proposed that polymer-CNT composites form either a trans-crystalline (TCL) structure,⁸⁻¹⁰ or a modified version of the classic shish-kebab structure.^{8,11} A TCL structure has been observed in model systems during the solution crystallization of polyolefins on CNT fibers,^{9,10} where the polymer crystallites grow to the CNT fibre axis giving a compact layer on the fiber surface. However, a 'nanohybrid shish-kebab' (NHSK) morphology is also possible, where individual CNTs act as heterogeneous nucleation sites (or shish) where polymer chains wrap around them and crystallites (kebabs) grow epitaxially outwards during crystallization.¹²⁻¹⁴ Recently, a hierarchal NHSK has been reported for electrospun poly(ϵ -caprolactone) MWCNT composites; here a secondary level of structure termed 'nanofiber shish-kebab' (NFSK) evolved after incubation of the NHSK nanofibers in solution.¹⁵

The development of a NHSK morphology is thought to be depended on several parameters e.g., CNT diameter, periodicity of the kebabs, lamellar thickness as well as the preparation conditions of the polymer-CNT composite.⁸ The evolution of TCL and NHSK morphologies mentioned, have mainly been seen in polyolefin systems during solution crystallization on CNTs but there are almost no studies with regard the structure evolution of engineering polymer systems such as polyesters prepared via melt mixing with low concentrations of CNTs.

The development of a NHSK morphology with different crystalline growth scenarios has been suggested; firstly, crystalline growth only occurs via nucleation on the CNT surface; secondly, nucleation occurs exclusively in the polymer matrix; thirdly a combination of both.¹⁶ Several crystallization models are plausible for polymer-CNT composites, although scarce data exists to fully support any particular hypothesis in melt composite systems. We report here compelling evidence of the evolution of a NHSK structure in

PET-MWCNT nanocomposites during hot isothermal crystallization from the melt. For the first time, we present data to clarify the role of the MWCNTs which not only act as nucleation points for NHSK-type crystallization, but due to residual orientation from the initial processing method any crystalline structure that evolves from the melt has a predisposed orientation. This is compared with the PET homopolymer which shows a classic randomly oriented lamellar structure. The combined use of small- and wide-angle X-ray scattering (SAXS/WAXS) and thermal techniques have been employed in this study allowing the time resolved morphology and crystallization kinetics of the materials to be studied. In these results the use of X-ray scattering, in particular SAXS, allows the differentiation of a polymer shish-kebab morphology as opposed to a regular lamellar morphology to be made, giving the periodicity of the shish-kebab morphology and orientation during the hot isothermal crystallization processing.

Figure 1, shows the 2D SAXS and WAXS patterns obtained for the neat PET and PET-MWCNT composites. The second and third columns, show WAXS/SAXS data of the neat PET sample at 30 °C; here no residual crystalline structure from the cast extrusion process is observed. In contrast, WAXS for the PET-MWCNT samples (at 30 °C), shows the emergence and increased sharpening of the PET triclinic unit cell reflections (010) and (0-11).¹⁷ In the PET4% sample, these reflections begin to concentrate as arcs perpendicular to the extrusion direction, indicating some preferred orientation. In the SAXS, increased scattering (concentrated red intensity around the central beamstop) is observed, indicating some residual crystalline content from the extrusion process. For the PET2% and PET4% composites, some preferred orientation is seen in the scattering pattern around the beamstop (arc-like intensity).

Column four shows the SAXS patterns of the melted samples at 270 °C. Samples were held at this temperature to erase any residual

crystalline structure from the extrusion process, whereby

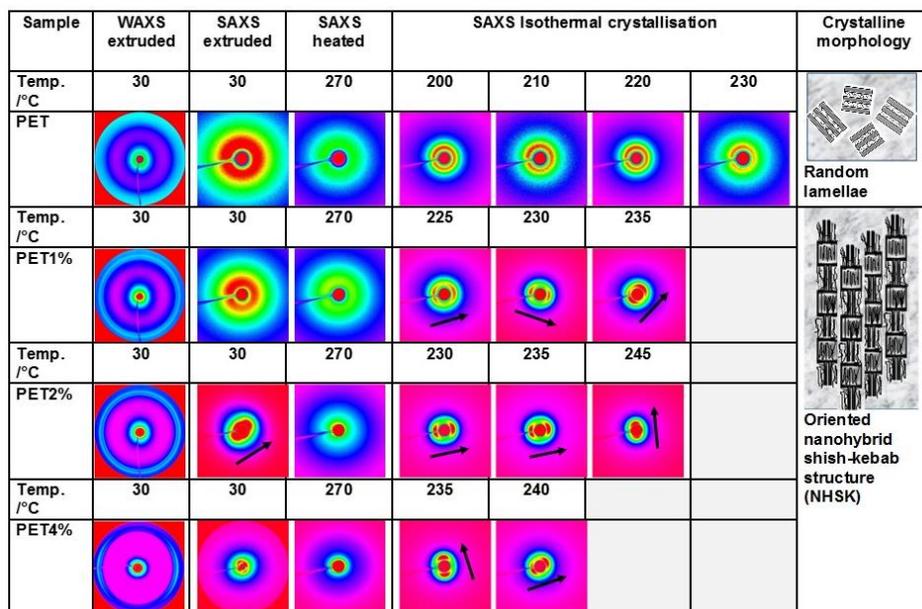


FIGURE 1 2D SAXS and WAXS patterns from the extruded cast samples at 30 °C; SAXS in the melt at 270 °C and at various isothermal hot crystallization temperatures. Neat PET shows a random lamellar structure whereas PET-MWCNT nanocomposites show oriented NHSK structures once crystallized. SAXS: high intensity red; low intensity pink. Black arrows indicate the extrusion direction.

the diffuse scattering indicates any residual crystalline structure and/or orientation is destroyed.

The following four columns in Figure 1, show the final SAXS patterns from the hot isothermal crystallization process at various temperatures. SAXS patterns for the neat PET (at each temperature), show a random crystalline lamellar structure revealed by an intense red scattering ring around the beamstop. This is in sharp contrast to all the PET-MWCNT composites, where at high temperatures, the crystalline structure evolves with preferred orientation; evidenced by the intense red scattering arcs formed around the beamstop. As the crystallization temperature is lowered there is a tendency for a weaker scattering ring to

develop around the beamstop alongside the arc-shaped scattering. It should be noted that the change in tilt in the SAXS peaks is due the orientation of the samples in the DSC pan and instrument and is not an artifact of the crystallization process – the extrusion direction is indicated in the oriented SAXS patters by a black arrow. The final column in Figure 1, shows schematics of the crystalline morphology attributed to the SAXS patterns.^{7,18,19} Neat PET has a random lamellar structure, whereas the PET-MWCNT composites show a different oriented crystalline morphology. We attribute this morphology to a nano-hybrid shish-kebab structure (NHSK), where the MWCNTs act as the nano-shish and the PET crystallites (kebabs) grow epitaxially out from nucleation sites on

the surface of these nano-shish. The oriented nature and evolution of the NHSK structure in

the composites can be further confirmed by

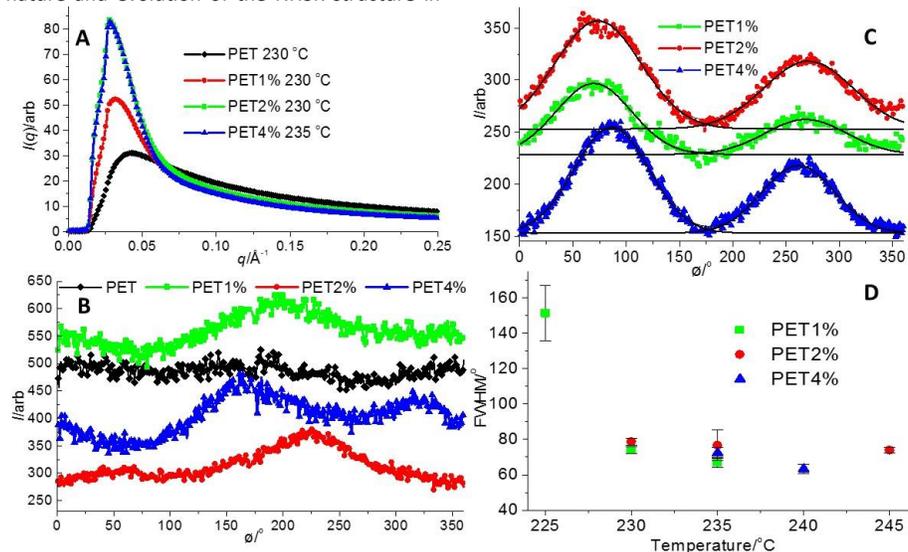


FIGURE 2 (A) Example 1D scattering profiles from 2D SAXS data (sector integrations). Azimuthal profiles for: (B) all extruded samples at 30 °C; (C) PET-MWCNT composites isothermally crystallized at 235 °C (Gaussian fits shown by black lines); (D) change in the FWHM for PET-MWCNT samples with increasing isothermal crystallization temperature.

comparing the 1D intensity plots, $I(q, q)$ and azimuthal profiles $I(q, \varphi)$, from the SAXS patterns and crystallization kinetics.

Figure 2A, shows examples of 1D SAXS profiles $I(q, q)$ obtained from the 2D SAXS patterns for PET, PET1%, PET2% 230 °C and PET4% 235 °C. The SAXS maxima shifts to lower q in the composites compared with the neat PET. (Correlation function analysis of these profiles is given in Figure 3.)

Figure 2B and 2C, show the azimuthal profiles for the extruded samples at 30 °C and isothermally crystallized PET-MWCNT composites at 235 °C, respectively, allowing the comparison of relative orientation between samples. The crystallized samples show the development of two peaks in the azimuthal intensity indicating significant orientation

compared with the same extruded samples at 30 °C. However, at 30 °C, peaks develop in the profiles for the PET-MWCNTs composites as the wt% MWCNTs increases, but no peaks are observed for neat PET at 30 °C, signifying no preferred orientation once extruded (Figure 2B). Quantitative analysis of the relative orientation using the average full-width half maximum (FWHM) of the peaks (using a Gaussian fitting profile) with increasing crystallization temperature is shown in Figure 2D. The reduction in FWHM indicates an increase in orientation. There is a slight decrease in orientation as the isothermal crystallization temperature decreases down to ~230 °C. However, a significant drop in orientation is observed for PET1% when crystallized at 225 °C. This suggests that a change in morphology from a well oriented NHSK crystalline structure to a less well

oriented crystalline structure occurs as the crystallization temperature is reduced.

To investigate the morphology that emerges during isothermal crystallization and associated crystallization kinetics, 1D meridional SAXS

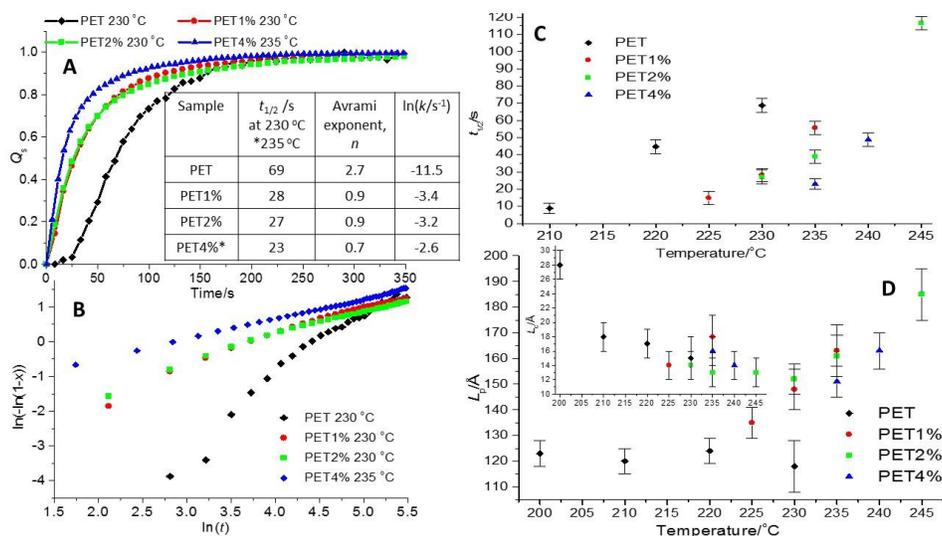


FIGURE 3 Isothermal crystallization data obtained from 1D meridional SAXS profiles. (A) Selected normalized crystallization curves at 230 °C for neat PET, PET1% and PET2% and PET4% at 235 °C – inset table details the crystallization half-life, Avrami exponent n , and rate constant k , for the selected data. (B) Avrami plots for the crystallization curves in (A). (C) Crystallization half-lives ($t_{1/2}$), for all samples with increasing isothermal crystallization temperature. (D) Final long period L_p , for all samples with increasing isothermal crystallization temperature – inset shows the estimated crystallite dimensions, L_c .

profiles $I(q, q)$ (see Figure 2A), were computed from the 2D time-resolved SAXS data throughout the crystallization process. From the 1D meridional profiles the normalized scattering invariant, Q_s , was obtained allowing the development of the isothermal crystallization process to be followed. From this data the crystallization half-time, $t_{1/2}$, was determined. Avrami plots,²⁰ were generated for the isothermal crystallizations process, allowing the rate constant, k , and Avrami exponent, n , to be extracted. Finally, correlation function analysis,^{7,21} was performed on the 1D meridional SAXS profiles where the SAXS long period (L_p), and crystallite size (L_c), at the end of

the isothermal crystallization process was calculated. Figure 3A and 3B, give examples of the isothermal crystallization curves, Avrami plots and extracted data for neat PET, PET1% and PET2% samples crystallized at 230 °C and at 235 °C for PET4%. The crystallization kinetics of the neat PET is significantly increased ($t_{1/2}$ values half) on the addition of MWCNTs. The Avrami analysis gives detail on the dimensionality of the crystalline growth unit n , and rate constant k , which is seen to increase for the PET-MWCNT samples. The exponent n , is markedly different for neat PET at 2.7 compared to that for the composites at almost unity. A value of 2.7 indicates a 2D type of

growth unit (disk shaped) via sporadic nucleation, for neat PET.²² This correlates with the SAXS data showing a randomly oriented lamellar structure emerges. However, a value of

n tending to unity, indicates instantaneous nucleation with a fiber or rod type of crystal growth, which further confirms the emergence of a NBSK structure from

heterogeneous MWCNT nucleation sites. Figure 3C, shows $t_{1/2}$ for the isothermal crystallizations of all samples. The PET-MWCNT composites show increased crystallization kinetics clarifying the MWCNTs act as nucleating agents. It is worth noting that neat PET would not crystallize at temperatures above 230 °C (within experimental time limits). However, on addition of MWCNTs crystallization at high temperatures was rapid verifying the nucleation effect of the MWCNTs.

Finally, Figure 3D, shows the change in long period L_p , for the samples with increasing isothermal crystallization temperature. The long period represents the average length-scale of the thickness of the crystal and amorphous regions in the sample morphology. For neat PET this is reasonably constant as the temperature increases. However, for the PET-MWCNT samples, L_p significantly increases with temperature. This is not mirrored though by the increase in the crystallite size, L_c (inset plot in Figure 3D), which remains relatively constant with increasing temperature. The crystallization process at lower temperatures will encourage the nucleation, insertion and growth of lamellae in the amorphous regions of the polymer matrix, reducing the value of L_p but the crystallite size does not tend to increase (little perfection and growth occurs) at these temperatures.

The data presented here gives a detailed insight into the role of MWCNT fillers during the isothermal crystallization of PET. It is evident that the MWCNTs drastically influence the crystalline morphology of the PET, in addition to acting as nucleating agents increasing the crystallization kinetics. The data presented reveals that the pre-orientation of the MWCNTs from the extrusion process on melting of the

polymer matrix is not lost, that is, the MWCNTs do not relax into a random network in the viscous polymer melt. Hence, they act as pre-aligned nucleating agents increasing the hot crystallization kinetics of the polymer (confirmed by the decrease in $t_{1/2}$). Further to this, the type of growth unit is also changed (Avrami analysis), from disk-like in neat PET (which is indicative of an initial spherulitic-lamellar type of crystalline structure) to rod-like, which refers to an oriented fibril or shish-kebab crystalline structure.

With the differing crystalline morphologies arising in the neat and PET-MWCNT composites during hot isothermal crystallization we propose a model which describes the unique role of the MWCNTs. This is shown pictorially in Figure 4. In this model, the pre-oriented MWCNTs act as the heterogeneous nucleating sites for the epitaxial growth of PET crystallites, hence the oriented NBSK structure prevails at high crystallization temperatures (Figure 4A). As the isothermal crystallization temperature reduces, the MWCNTs produce a NBSK structure, however the average orientation tends to decrease. This is because random crystalline lamellae start to sporadically nucleate and grow in the PET matrix (Figure 4B). In contrast, neat PET will crystallize in a random lamellar structure at lower crystallization temperatures (Figure 4C).

The combined use of SAXS/WAXS and thermal techniques have allowed us to unequivocally show the contrasting morphology in a set of PET-MWCNT nanocomposites compared with neat PET. The data revealed that a NBSK structure predominates in the PET-MWCNT composites, with crystallization being controlled by the residual orientation of the MWCNT matrix. Whereas, an unoriented lamellar

structure is observed in the neat PET. This was verified by examining the crystallization kinetics and growth geometry in the samples under hot isothermal crystallization conditions. This is in contrast to observations that a shish-kebab structure will only prevail after an external shear field is applied to the polymer composite (e.g. uniaxial deformation^{6,7} or fiber spinning¹⁵).

The results here provide a valuable insight into the role of MWCNTs not only in their reinforcing properties, but also in the distinctive modification of the crystalline morphology of a polymer matrix. This ~~having~~ ~~has~~ significant impact ~~in~~ ~~on~~ the use of such fillers in the processing and

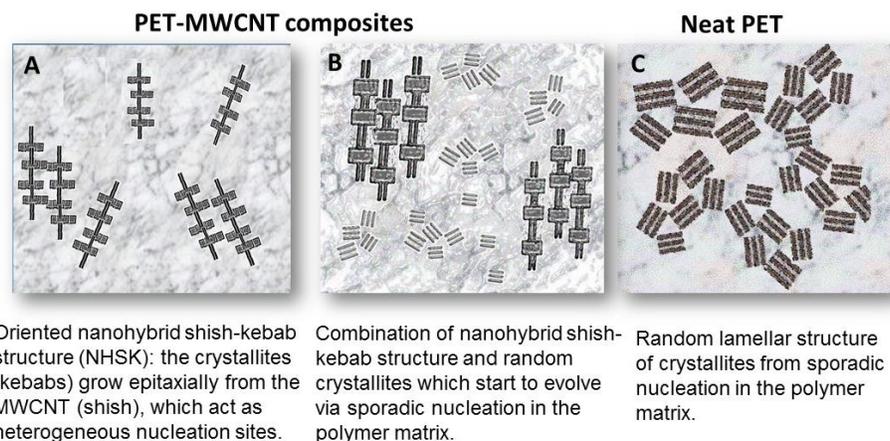


FIGURE 4 Proposed model of morphology evolution in polymer and polymer-MWCNT composites during isothermal crystallization. (A): Oriented nanohybrid shish-kebab (NHSK) morphology formed at high crystallization temperatures; (B) A mixture of a NHSK and random lamellae morphology as the crystallization temperature is dropped; (C): Randomly oriented lamellar morphology which is seen to develop in neat polymer melt isothermal crystallization.

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modification of ~~the~~ physical properties ~~in~~ ~~of~~ engineering polymers.

EXPERIMENTAL The PET-MWCNT composites were prepared via a cast extrusion process (as previously reported,^{6,7} 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 SEM⁶) 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 (as previously reported).^{6,7} 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 . Static SAXS/WAXS patterns were obtained for the samples at 30 °C and SAXS at 270 °C. SAXS data was also obtained throughout the isothermal crystallization process for subsequent kinetic analysis. Further details of the composite

preparation, experimental set-up and data analysis is given in the Supporting Information.

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E. L. Heeley, D. J. Hughes, E. M. Crabb, J. Bowen, O. Bikondo, B. Mayoral, T. McNally

Confirmation of a nanohybrid shish-kebab (NHSK) structure in composites of PET and MWCNTs

The development of an oriented nanohybrid shish-kebab morphology (NHSK) in a series of PET-MWCNT nanocomposites was followed during hot isothermal crystallization. The MWCNTs act as heterogeneous nucleation sites for the soft epitaxial growth of PET crystallites which increased the crystallization kinetics compared to neat PET. This providing valuable information on the morphology development during processing in engineering polymers.

GRAPHICAL ABSTRACT FIGURE

