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PII: S0167-577X(16)31301-5
DOI: <http://dx.doi.org/10.1016/j.matlet.2016.08.024>
Reference: MLBLUE21308

To appear in: *Materials Letters*

Received date: 24 April 2016
Revised date: 29 July 2016
Accepted date: 6 August 2016

Cite this article as: Yuan Wang, Binling Chen, Ken E. Evans and Oana Ghita, Novel Fibre-like Crystals in Thin Films of Poly Ether Ether Ketone (PEEK) *Materials Letters*, <http://dx.doi.org/10.1016/j.matlet.2016.08.024>

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Novel Fibre-like Crystals in Thin Films of Poly Ether Ether Ketone (PEEK)

Yuan Wang*, Binling Chen, Ken E. Evans, Oana Ghita

College of Engineering, Mathematics and Physical Sciences, University of Exeter,

North Park Road, EX4 4QF, UK

*Correspondence to: Yuan Wang (E-mail: y.wang@exeter.ac.uk)

Abstract

This paper highlights the fabrication and characterization of a new type of crystal in quenched, cooled and annealed PEEK films. Following this process, a “fibre-like” crystal structure has been identified. Across the film surface, these fibres cross each other and form a random network of interconnected fibres.

Keywords: PEEK, Thin-films, Fibre-like crystal, AFM, Electron microscopy

Introduction

Shortly after their invention in the 1960s, Poly Ether Ether Ketone (PEEK) polymers underwent a great deal of research into understanding their fundamental properties and crystal structure [1,2,3]. The current literature on the crystal structure of PEEKs established the presence of a spherulitic morphology, with an on-going debate on the origin and type of lamellae present in these spherulites. Several studies [4,5,6,7] hint to the presence of two populations of lamellae with two different thicknesses, which potentially link to the double melting behavior of PEEK. Other studies [8,9] do not agree with the dual crystal morphology and explain the dual melting point through a simple melting-recrystallization effect. A recent study by Wang et al.[10], identified the presence of two crystal morphologies assembled into a hierarchical structure. This study shows further the unique self-assembly ability of PEEKs and the

fabrication of a novel fibre-like crystal structure in thin films. The preparation method and the characterization of these crystals are reported here.

Experimental method

Film preparation

Thin PEEK films of approximately 250 μ m thickness were manufactured by melting and crystallization using two different methods.

Method 1: Firstly, the PEEK 150PF powder (Victrex,UK) was spread evenly on a glass slide (Fisherbrand microscope slides, 0.8-1mm thickness), the layer of powder was heated up on a hotplate (V14160 Bibby HC500 hotplate) at 400 $^{\circ}$ C for 5mins. Its thickness was controlled using an in-house built doctor blade rig. No glass cover was applied on top of the PEEK powder. The molten film on the glass slides was quickly transferred to another hot plate and isothermal crystallized at 300 $^{\circ}$ C.

Method 2: Molten PEEK film was prepared in the same method as Method 1. This time, the molten film on the glass slide was immediately quenched in deionized water, which allows the formation of transparent PEEK film. The transparent PEEK film was air dried at room temperature, followed by annealing on a hotplate at the temperature of 300 $^{\circ}$ C for various times (5, 10, 30, 60, 120min).

Scanning Electron Microscopy

The surface of the thin PEEK films was examined by SEM (Hitachi S-3200N, Japan). The specimens were sputter coated with gold with a thickness of 5nm. The acceleration voltage was 20kV.

Wide Angle X-Ray Diffractometry (WAXD)

The measurements were performed with a Bruker D8 Advance WAXD with copper anode at room temperature. XRD data were collected in the angular range where $2\theta=10^{\circ}$ - 40° . The step size of 2θ was 0.02° . The crystal size was calculated from equations (1):

$$L = K\lambda/FW_{(s)}\cos\theta \quad (1)$$

where λ is the wavelength of the copper anode (0.154 nm), K is constant ($K = 1$) and $FW_{(s)}$ is the specimen peak broadening at half the maximum intensity (FWHM) in radians.

Atomic Force Microscope (AFM)

AFM imaging was carried out on the films prepared with method 2, using a Bruker Innova AFM, mounted with standard tapping mode silicon probes (RTESPA-CP, Bruker) and using nominal resonant frequency of 300 kHz, with nominal spring constant of 40 Nm^{-1} . Areas were scanned in tapping mode with a resolution of 512×512 pixels at 0.5 lines s^{-1} .

Results and Discussion

Figure 1 presents the SEM images of the top surface of the PEEK films prepared by both crystallization methods. Figure 1(a) shows the typical spherulitic structure developed in the isothermal crystallized PEEK film. Figure 1 (b)-(f) shows the SEM images of annealed PEEK film after quenching. The presence of fibre-like crystals is present in all the quenched films. The crystals have a width between 0.3 to 3.2 microns depending on the annealing time. Figure 2 shows the effect of annealing time on the width of fibre-like crystals. To take a number of measurements for quantitative

analysis, a number of low magnification images, as those in Figure 1, were taken from various positions along the film. The width of fibre-like crystals in each image was measured using the Oxford Instruments' INCA software. Then, the average value and standard deviation of crystal width was calculated and presented on Figure 1. There is a clear increase in crystal width up to 60mins annealing time.

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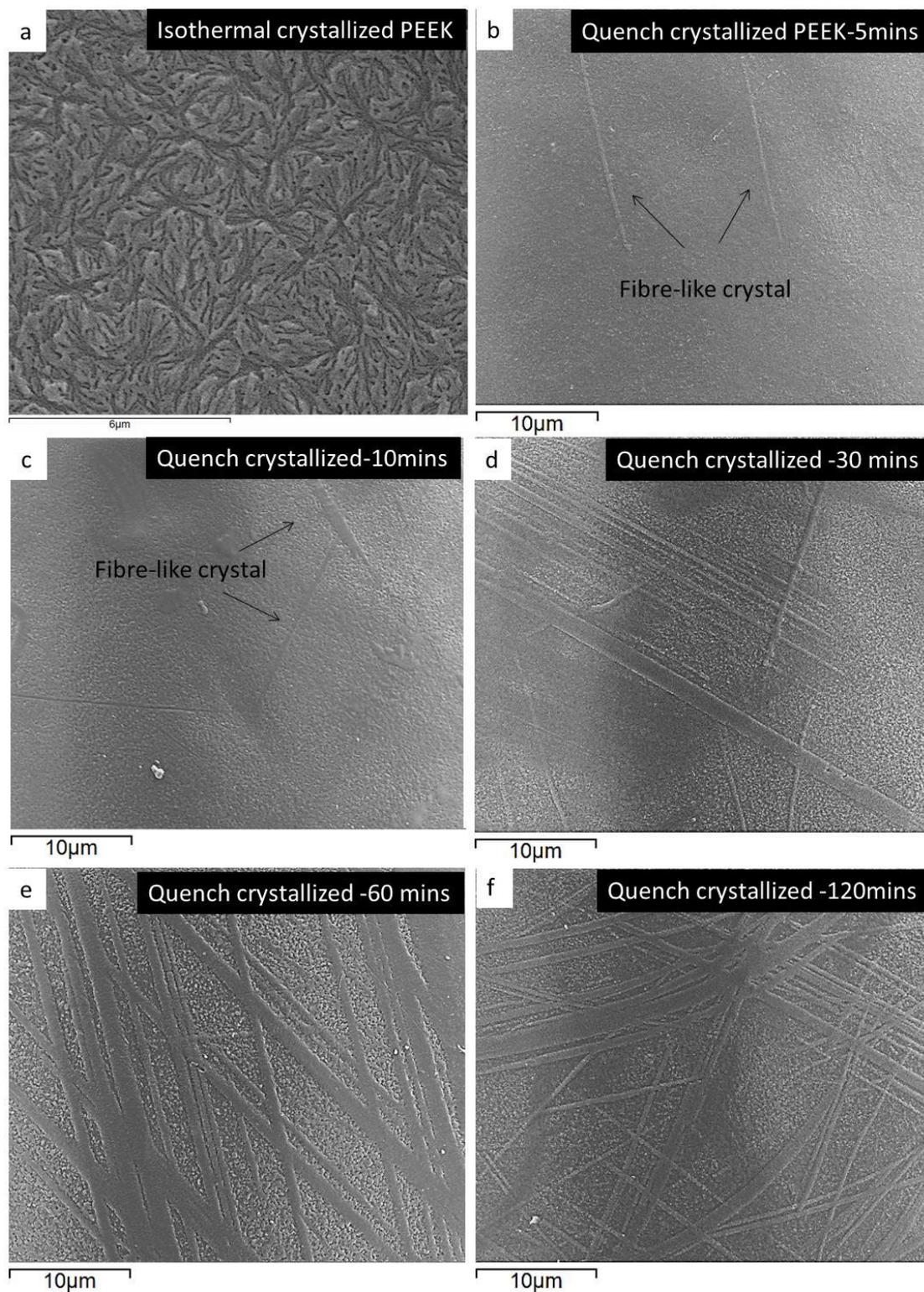


Figure 1. SEM images of spherulitic crystal and fibre-like crystals.(a) typical spherulitic crystal found in isothermally crystallised PEEK film. (b),(c),(d),(e),(f) show the fibre like crystals identified in the quenched and annealed PEEK film prepared at 300°C for 5mins, 10mins, 30mins, 60mins, 120mins, respectively.

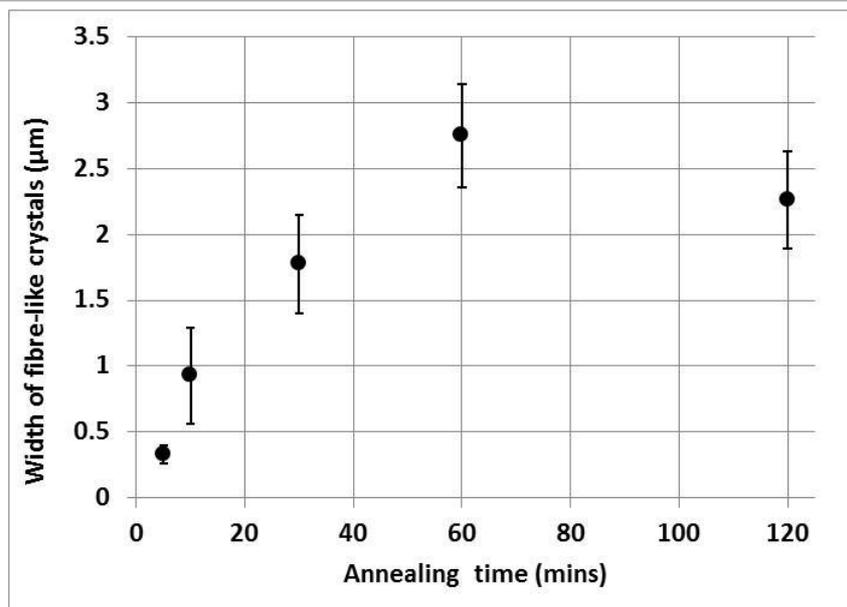


Figure 2. The change of crystal width with the annealing time

The higher magnification SEM images in Figure 3 show the distribution of the crystals on the surface of quenched/annealed PEEK film. Figure 3(b) and (d) shows that the “fibres” are composed of aligned granular crystals. Randomly distributed granular crystals amongst the aligned “fibres” were also present on the top surface of the film. Figure 3 (e) shows the interaction between these fibre-like crystals, how the aligned granular crystals crossover each other.

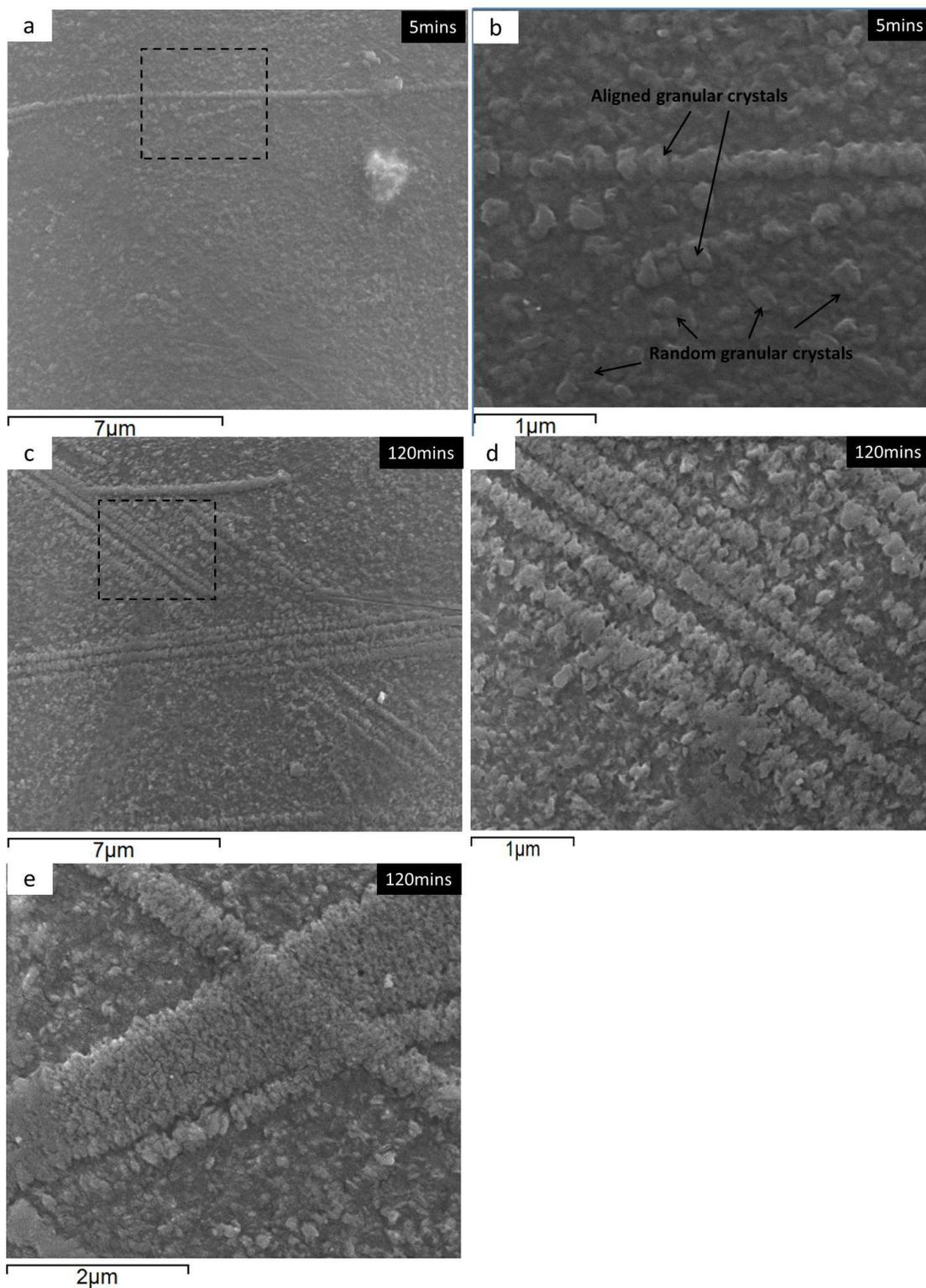
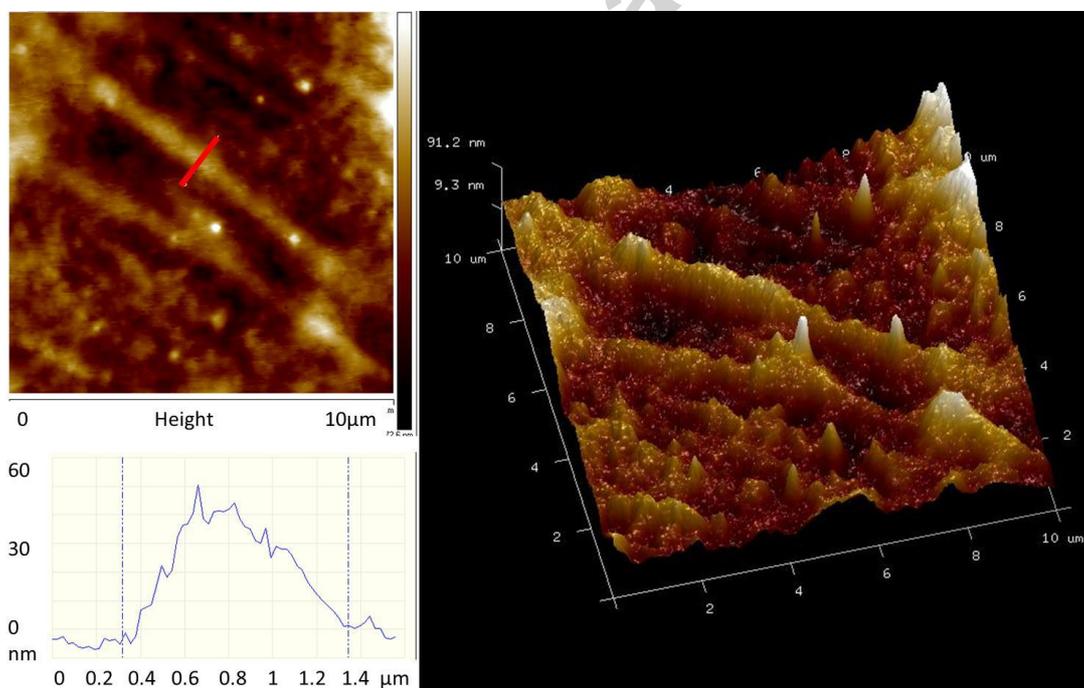
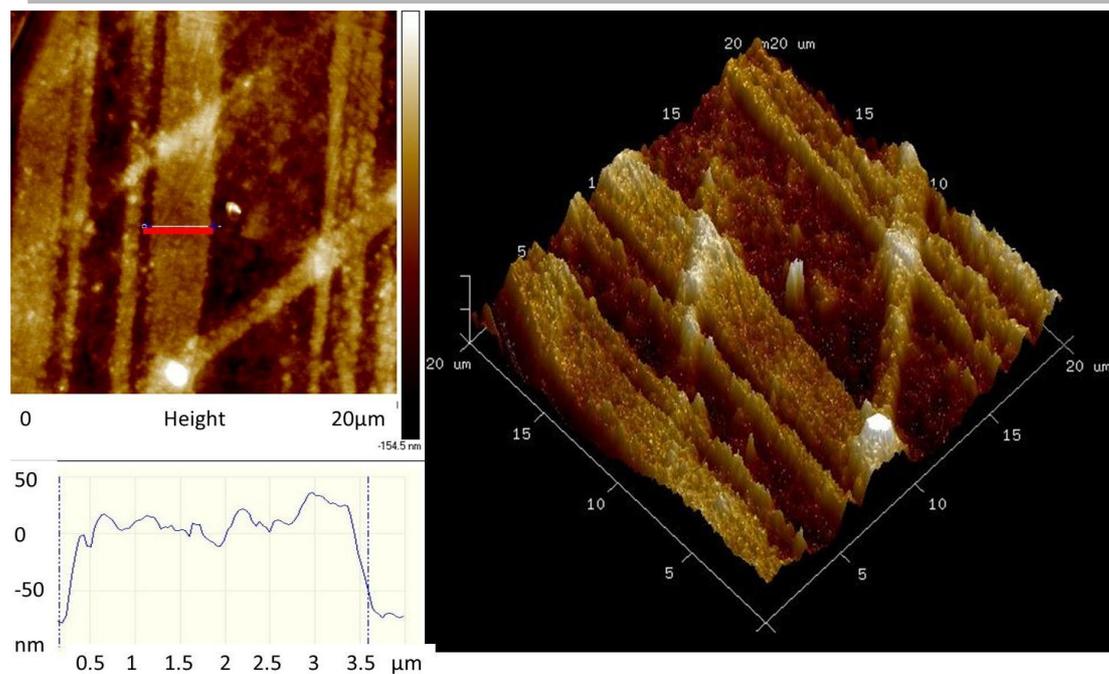


Figure 3. SEM images show the details of fibre-like crystal structure at high magnification.(a)-(c) shows the granular crystals aligned in one direction to form fibre-like crystal.(d) represents a zoomed in image of (c)- area examined is highlighted by the square box. (e) Crossover between fibre-like crystals

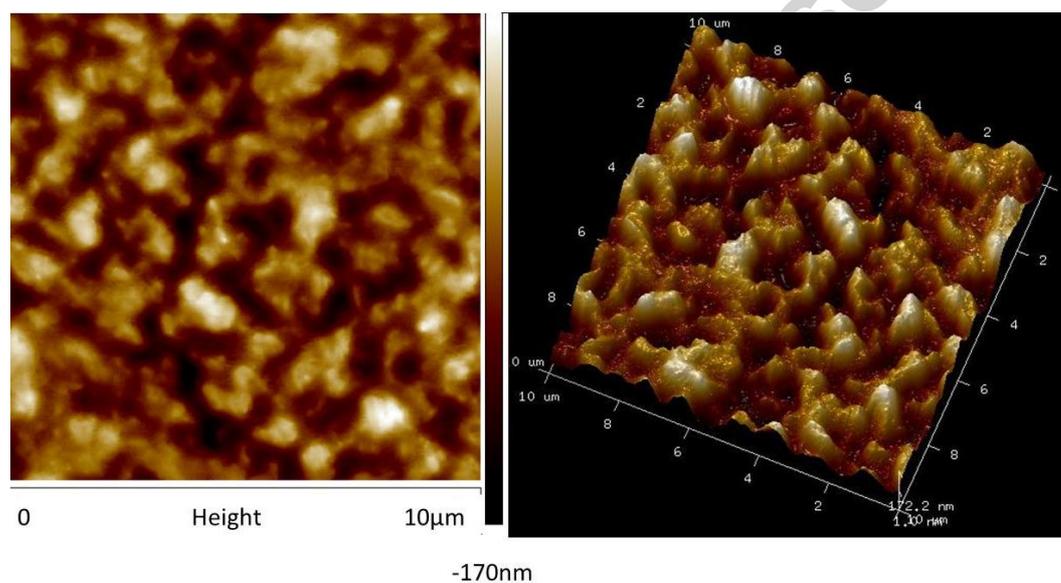
Another interesting finding from the SEM investigation is that the fibre-like crystals and the random distributed granular crystals seem to be protruding from the surface of the film. AFM was used to study their protrusion heights. Figure 4 (a) and (b) shows the AFM scanning images of fibre like crystals on the surface of PEEK films which were quenched and annealed for 10 mins and 60 mins, respectively. Figure 4 (c) shows the randomly distributed crystals on the surface of PEEK films quenched and annealed for 60 mins. In Figure 4 (a) and (b), the surface profile of the fibre-like crystals measured approximately 1 μm width and 60nm height for the films created over 10 mins annealing time, and 3 μm width and 100nm height for the films fabricated over 60 mins annealing time. The AFM 3D surface reconstruction in Figure 4 (b) shows also how the fibre-like structures cross over each other. It seems that the height of the fibre-like crystals increased with the annealing time although further AFM imaging is required for a final conclusion.



(a)



(b)



(c)

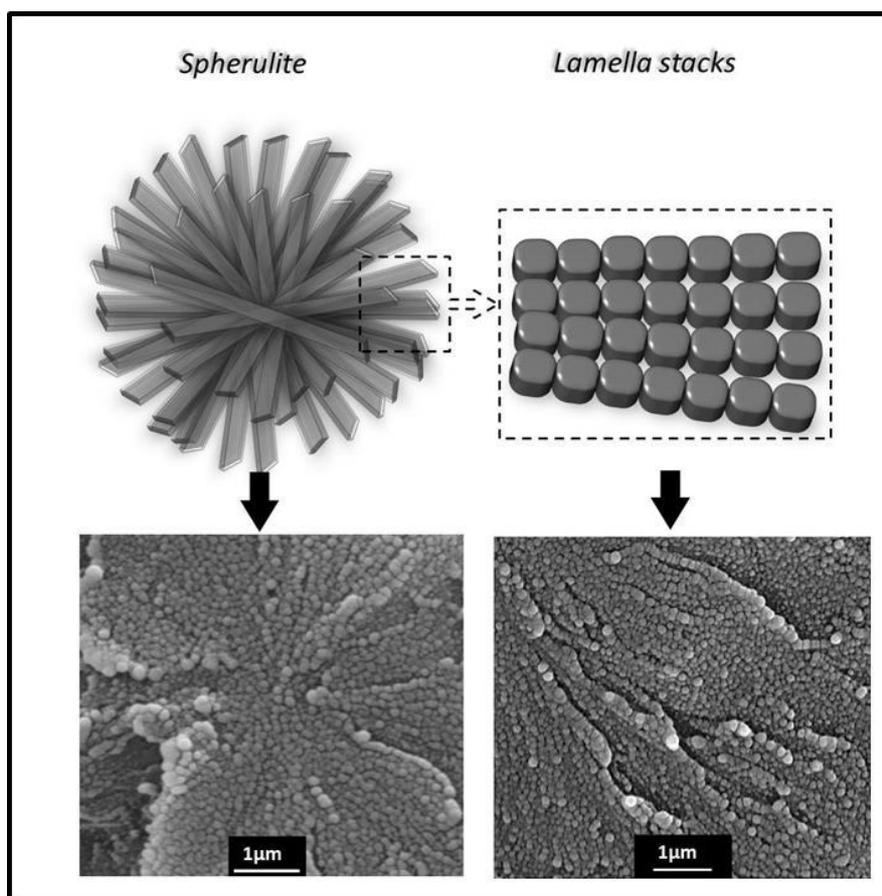
Figure 4. AFM height image and 3D image of (a) fibre like crystals on the surface of the PEEK film after quenching and annealing for 10 mins, (b) fibre like crystals on the surface of PEEK films after quenching and annealing for 60 mins, and (c) the random distributed crystals on the surface of PEEK films after quenching and annealing for 60 mins.

Table 1. Measured lamellar thickness and peak width at half maximum intensity for all XRD peaks at 5, 30 and 60mins annealing times

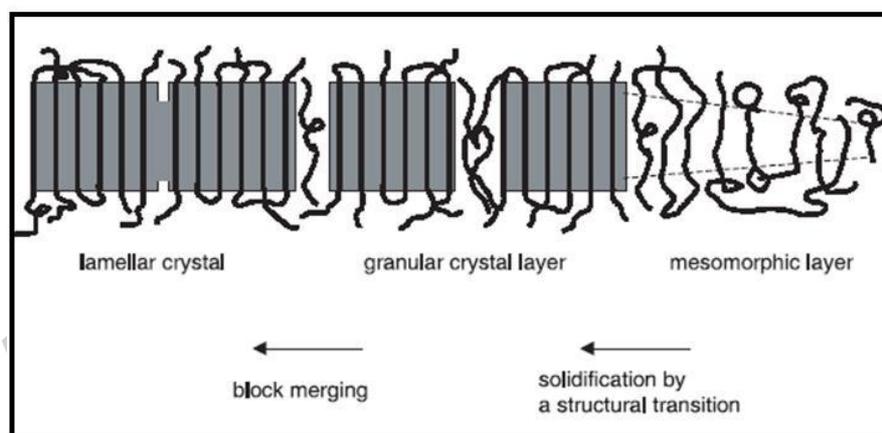
| | 5mins | | | 30mins | | | 60mins | | |
|-------|------------|-------|--------------------|------------|-------|--------------------|------------|-------|--------------------|
| | 2 θ | FHWM | lamellar thickness | 2 θ | FHWM | lamellar thickness | 2 θ | FHWM | lamellar thickness |
| [110] | 18.8 | 0.65 | 13.8 | 19.1 | 0.61 | 14.9 | 18.9 | 0.638 | 13.8 |
| [111] | 20.7 | 0.98 | 9.2 | 20.9 | 1.105 | 8.0 | 20.8 | 0.894 | 9.7 |
| [200] | 22.5 | 0.961 | 9.2 | 23 | 1.039 | 8.6 | 22.8 | 0.87 | 10.3 |
| [211] | 28.8 | 1.131 | 8.0 | 29 | 0.937 | 9.7 | 28.7 | 0.964 | 9.2 |

The XRD results presented in Table 1 show that there is no correlation between the lamellar thickness and the width of the fibre-like structures as a function of the annealing time. It could be argued that the fibre-like arrangement presented here is a shish-kebab structure. Although not able to definitively confirm this hypothesis at this stage, there are few distinct differences between the two methods of fabrication of these structures. Generally, the shish kebab structure is formed by crystallization from a polymer solution or polymer melt under shear stress [13, 14]. It was noticed that the shish kebab structures have the same dimensions (length and width) in the very first stages of crystallization as well as those formed during the later stages [13]. The method used here for creation of the fibril-like structures did not employ any shear stresses and the width of the fibrils increases with annealing time. However, it is possible that a certain degree of stress was created during the quenching from melt and the differences in thermal contraction of the substrate and polymer film. In our previous publication [10], PEEK samples obtained through melt crystallization had hierarchical spherulitic crystal structure which was composed of self-assembling granular crystals, as shown in Figure 5. Strobl et al.[11] observed a similar granular crystal blocks in polyolefin and proposed that the granular mesosphere-domain is the building block of the spherulitic structure (Figure 5). In comparison with the melt-crystallized structures, SEM investigation suggests that the self-assembling blocks in

the quenched crystallized PEEK orientated along the fibre axis of fibre-like crystal.



Wang's Model



Strobl's Model

Figure 5. Crystallization mechanism by self-assembling of granular crystals [10, 11].

In order to understand the origin of the nucleation process for the formation of these “fibre” like crystal structures, the substrate (glass slide) has been closely examined. It

is well known that the substrate surface plays an important role in the heterogeneous nucleation of polymer crystallization [12]. Therefore, it was suspected that the fibre like crystals might have originated from scratches on the glass substrate. However, as can be seen in the supplementary material, Figure 1s (a), the glass substrate was scratch free. Furthermore, the glass slide surface was purposely scratched to understand the influence of the surface scratch on the fibre-like crystal formation. Figure 1s (b) in the supplementary material shows the scratch made on the glass slide. The film formed on the purposely scratched glass slide was examined on the top and backside. Figure 1s (c) and (d) in the supplementary material show the SEM images taken from top and backside surfaces of the film. The backside of the film had a clear imprint of the pre-defined scratch and the scratch seems not to impact on the crystal formation. The fibre-like crystals were observed in the same manner on the surface of the film.

The detailed crystallization mechanism of these fibre-like crystals is not yet clear at this stage and will be the subject of further investigation, as they may represent an interesting opportunity for anisotropic property enhancement.

Acknowledgement

The authors would like to thank for the support of the UK Engineering and Physical Science Research Council (EPSRC grant no EP/L017318/1).

Reference

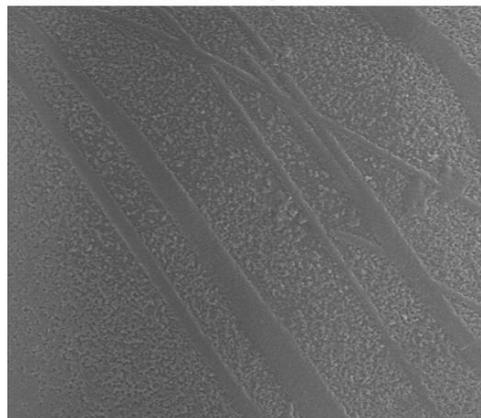
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Highlights

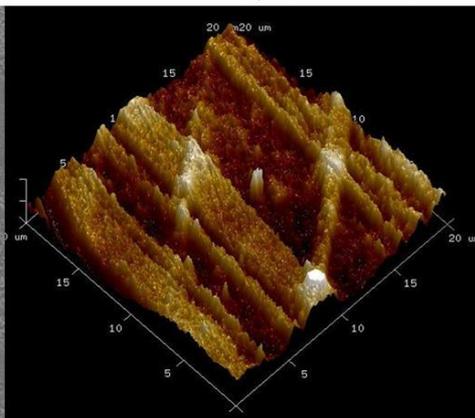
- An unusual fibre-like crystal was found in PEEK thin film through quench cooling followed by annealing.
- The fibre-like crystals grow in width with annealing time according to SEM and AFM studies.
- The fibre-like crystals are present amongst normal spherulitic crystals.

Fibre-like Crystals-SEM



10μm

Fibre-like Crystals-AFM



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