



ELSEVIER

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

On row-structures in sheared polypropylene and a propylene–ethylene copolymer

 Robert H. Olley^{a,*}, Geoffrey R. Mitchell^{a,b}, Yasmin Moghaddam^a
^a Department of Physics, University of Reading, Whiteknights, Reading RG6 6AF, UK

^b Centre for Rapid and Sustainable Product Development, Polytechnic Institute of Leiria, Rua de Portugal – Zona Industrial, 2430-028 Marinha Grande, Portugal

ARTICLE INFO

Article history:

Received 5 August 2013

Received in revised form 20 December 2013

Accepted 14 January 2014

Available online 20 January 2014

Keywords:

Polypropylene

Copolymer

Nucleation

SEM (scanning electron microscopy)

WAXS (wide-angle X-ray scattering)

SAXS (small-angle X-ray scattering)

ABSTRACT

The crystallisation of polymers such as polyethylene or polypropylene from the melt is greatly influenced by the flow-thermal history prior to the crystallisation. We explore the influence of the chemical configuration of polypropylene based chains on the formation of row structures on crystallisation. We use a combination of in situ time resolved small-angle X-ray scattering, ex situ wide angle X-ray scattering with optical and scanning electron microscopy to show that row nuclei are formed in random copolymers of propylene with a limited amount of ethylene subjected to modest shear flow fields. We contrast observations performed using two homopolymers of isotactic polypropylene and one random copolymer of propylene and ethylene. We propose that it is not strictly necessary to argue that the row nuclei are already crystalline nor to invoke epitaxial crystallisation as the mechanism for the nucleation of lamellae, as similar structures can be formed on carbon nanotubes and fibrils of dibenzylidene sorbitol. The combination of microscopy and scattering provides a powerful approach to investigating these phenomena, especially as compared to either technique used in isolation.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The crystallisation of polymers from stressed melts is of widespread interest both from a science viewpoint and from a technological processing perspective. The subject of crystallisation from stressed melts has been reviewed by Kumaraswamy [1] and more recently by Janeschitz-Kriegl [2], and one frequent occurrence in the time sequence of crystallisation from a stressed melt is the formation of row nuclei which give rise to structures known as “shish-kebabs”. In polypropylene such oriented structures may also grow on heterogeneous linear nuclei such as fibres by transcrystallisation [3], for example in the case of in situ grown nanofibrils [4] or through the addition of nanoparticles such as carbon nanotubes [5], whereas the presence of

materials such as graphene nanosheets [6] may enhance the development of homogeneous row nuclei.

Polypropylene is the polymer best known for its remarkable propensity for forming row structures, but they are also found in polyethylene [7–9] as well as isotactic polystyrene [10], poly(phenylene sulfide) [11] and polylactide [12].

In polyethylene [7–9] and in polypropylene [13] the nuclei may be formed from a particular fraction of the polymer melt and in such cases it is well established that the generation of row nuclei is very dependent on the presence of a high molecular weight fraction or ‘tail’ in the polymers. Various models have been proposed, some depending on the coil-stretch transition [14,15], though alternative models exist such as [16]. Seki et al. have argued that row nuclei occur when there is sufficient of this HMW fraction to allow long-chain overlap [17]. Regardless of the mechanism of formation of the shish, it is understood that the kebab formation is a case of lamellar crystallisation on pre-crystallised fibres (shish) that serve as nucleation sites for the kebabs [18].

* Corresponding author. Address: Electron Microscopy Laboratory, J.J. Thomson Building, University of Reading, Whiteknights, Reading RG6 6AF, UK. Tel.: +44 (0)118 378 4616; fax: +44 (0) 118 378 4606.

E-mail address: R.H.Olley@reading.ac.uk (R.H. Olley).

Isotactic polypropylene, like most semi-crystalline polymers, crystallises from a quiescent melt in the form of spherulites but it readily assumes other geometries, crystallising from homogeneous row nuclei to form row structures or cylindrites, or from heterogeneous surfaces to give transcrystalline layers [19]. Row structures or cylindrites are easily generated by first shearing the melt, and can form in a range of number densities, ranging from isolated ones whose development can be followed easily under the optical microscope to very dense parallel arrays where the individual structures cannot be discerned optically. In polypropylene, a high tacticity index has been found favourable to the development of shish-kebabs [17]. This raises questions as to the polymer attributes required to form row nuclei. Some work has been performed on blends of medium molecular weight branched polyethylene with a minority component of high or ultra-high molecular weight linear polyethylene (ethylene homopolymer). There the high molecular weight linear component has been observed to template the growth of the branched polyethylene [8,15]. However, we are not aware of any work where a copolymer by itself has been shown to form row structures, whether this be a majority ethylene or a majority propylene copolymer. This work compares the behaviour of two propylene homopolymers with that of a propylene–ethylene copolymer to explore the effects of the copolymerisation on the formation of row nuclei and subsequent templated lamellar growth.

2. Materials

Three polypropylene based materials were employed in this study, all supplied by Borealis, Finland and the characteristics are detailed in Table 1. As a ‘reference’ material we used a high-crystallinity homopolymer polypropylene HCPP with high tacticity. We compared this reference material with a second homo-polymer (ZNPP) prepared using Ziegler–Natta technology and which exhibits a lower tacticity and weight average molecular weight. The third material is a random copolymer (RACO) based on propylene with 5.1 wt% ethylene as comonomer. In terms of the melt flow index HCPP and RACO are very similar whilst the ZNPP system is substantially higher.

3. Experimental methods

3.1. Small-angle X-ray scattering

Time-resolving small-angle X-ray scattering (SAXS) measurements were made using the intense flux available

Table 1
Properties of the polypropylene based polymers used in this work.

	HCPP	ZNPP	RACO
Comonomer ethene wt%	0	0	5.1
MFR 2.16 kg; g/10 min	6.5	19	7.9
Tacticity; mmmm tetrads	97.8	93.0	–
T_m °C	165.8	164.3	137.2
M_n Daltons	65,650	75,100	77,650
M_w Daltons	310,000	208,000	266,500
M_w/M_n	4.7	2.8	3.4

on the fixed wavelength beamline 16.1 at the Daresbury Synchrotron Radiation source. Scattering data were collected using the Rapid Area Detector System with a time-cycle of 10 s. The scattering geometry was calibrated using a wet collagen fibre. The in situ small-angle X-ray scattering measurements employed a parallel plate shear cell equipped with mica windows, specially designed to facilitate in situ time-resolving X-ray scattering measurements [20]. A schematic of the shear cell and scattering geometry is shown in Fig. 1. The rotating plate consists of a stainless steel tri-spoke arrangement covered with a thin mica disc (0.03 mm in thickness), which allows the incident beam to pass unhindered for 85% of each revolution. An upstream synchronised rotating mask, fabricated from lead, minimised the background intensity for the period of a revolution when a spoke would have intercepted the incident beam. The fixed plate consists of a stainless steel plate with a single chamfered hole covered with a thin mica disc. The shear cell was equipped with electrical heating and cryogenic gas cooling system which allowed the sample temperature to be controlled and varied at set rates. The geometry of the cell was such that the incident beam was normal to the flow direction and parallel to the velocity gradient.

In this work, each sample was subjected to a defined temperature/shear flow cycle and an example is shown in Fig. 2. The design of the shear cell enabled X-ray scattering data to be obtained throughout the cycle. The specific cycle shown here contained the following stages: (a) heating from room temperature to 192.4 °C at a rate of 20°/min; (b) held at 192.4 °C for 5 min; (c) cooled to room temperature at a rate of 10 °C/min. When the sample reached a selected temperature, T_s , a shear rate of 20 s⁻¹ was applied for 25 s, giving a total of 500 shear units. During the shearing period, the sample continued to cool and over the shearing period the temperature dropped by 4.2 °C. After cessation of shear, cooling continued to below room temperature, after which the sample was removed from the shear cell. The 10 s data accumulation cycle used throughout the heating cycle gave a temperature variation of ~1.7 °C for each recorded scattering pattern. Samples for use in the shear cell were pre-moulded into discs 1 mm in thickness and 19 mm in diameter in the melt using a simple metal mould and hydraulic press.

3.2. Ex situ wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) data were obtained for processed samples at room temperature using two different approaches. The first used a flat plate Rigaku/MS Saturn 92 CCD camera with a Rigaku FR-D rotating anode generator.

In the second method, intensity data were recorded as a function of α at a fixed value of $|Q|$ range using a symmetrical transmission diffractometer equipped with a graphite monochromator and pinhole collimation and a Cu K α X-ray source where α is the angle between the symmetry axis of the sample and the scattering vector Q and $|Q| = 4\pi\sin\theta/\lambda$, where λ is the incident wavelength and 2θ is the scattering angle. This instrument allowed a map of the undistorted reciprocal space in contrast to the limitations of a flat

Download English Version:

<https://daneshyari.com/en/article/7806401>

Download Persian Version:

<https://daneshyari.com/article/7806401>

[Daneshyari.com](https://daneshyari.com)