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Epitaxial crystallization of precisely fluorine substituted polyethylene induced by carbon nanotube and reduced graphene oxide

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Crystallization of well-defined precision polyethylene with fluorine substituent on every 21st backbone carbon (PE21F) induced by low-dimensional carbonaceous nanofillers (carbon nanotube (CNT) and reduced graphene oxide (RGO)) via solution crystallization and supercritical CO_2 assisted solution crystallization were investigated. Transmission electron microscopy was used to investigate the morphology of carbonaceous nanofiller-induced PE21F crystals. The kebab-like and rod-like crystals formed on the CNT and RGO, respectively. Selected area electron diffraction (SAED) pattern revealed that the c-axis of polymer chain is parallel to the surface of the RGO. Differential scanning calorimetry (DSC) revealed the melting temperatures (T_m) of PE21F lamellae nanocomposites increased with crystallization temperature increasing. The X-ray diffraction (XRD) results showed that the incorporation of nanofillers did not influence the crystal structure of PE21F. The chemical composition of the PE21F nanocomposites measured by X-ray photoelectron spectra (XPS) confirmed substituent F as a defect of chain was accommodated into the crystal lattice.

1. Introduction

Low-dimensional carbonaceous nanofillers, 1-dimensional carbon nanotube (CNT) and 2-dimensional graphene, has obtained great interest in both basic and applied research in the past ten years due to their unique mechanical, thermal and electrical properties [1–6]. Extensive research has been reported that the incorporation of nanofillers into polymers can significantly improve the thermal stability and mechanical properties of polymer matrix [7–20], which is important for their practical application. Carbonaceous nanofillers also are effective nucleating agents for a variety of semi-crystalline polymers which can accelerate polymers crystallization [21–30] and promote the phase structure transformation [31–34]. Simulation study also shows that heterogeneous nucleation agent as a substrate for epitaxial growth decrease the surface free energy barrier, which is a practical method to enhance polymer nucleation [35].

Carbonaceous nanofillers-induced polymers crystallization give us the opportunities to reveal the interface between carbonaceous nanofillers and polymer crystals. The carbon nanotube (CNT) can induce polymers to form “nanohybrid shish kebab” (NHSK) structures [36–39]. The mechanism of nucleation is described as “soft epitaxy” [36–38]: CNT can be considered as rigid macromolecules, the polymer chains prefer to align along the tube axis regardless of the lattice matching between the polymer chain and the graphitic sheet. For 2-dimensional graphene, lattice matching should play the dominant role in surface-induced polymer epitaxial crystallization. The space lattice matching of PCL and RGO results in thicker edge-on lamellae and improves the interaction between RGO and PCL matrix [40]. Crystalline lattices matching of PE and HOPG results in formation of lamellae much thicker than in the bulk but also generates stable monoclinic form at the interface [41]. It is now generally accepted that the occurrence of polymer epitaxy is based on some certain crystallographic matches and a 15% mismatching is assumed to be the upper limit for the occurrence of the epitaxial growth on the basis of lots of investigation results [42]. But little study has been done on the polymer epitaxial crystallization with periodically changed crystallographic matches.

It is well known that the most accepted modeled polymer for

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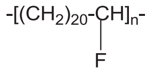
the polymer epitaxial crystallization is the simplest polymer, polyethylene (PE). Substituent different with hydrogen has a significant impact on the crystallization behavior of polyethylene since it as a defect of chain disturbs length of continuous methylene sequences. But common polyethylene with random substituent different with hydrogen possesses intra- or intermolecular heterogeneity, even both exist, make the study complex. Therefore polyethylene with periodical substituent can be a suitable model polymer on the study of epitaxial crystallization. Acyclic diene metathesis polymerization (ADMET) offers an alternative synthetic route to such well-defined PE derivatives, which contain substituent place at a precise distance along the PE backbone. ADMET polymers have a general repeating unit, $-[(CH2)_m\text{-}CHX]_n-$, where m is 8–74 and X is groups of various types, such as halogen, alkyl group, other functional groups [43–51]. The well-defined primary structure makes ADMET polymers suitable model systems to study the effect of precise placement of substituent on the crystallization of polyethylene.

In the present paper, the precision ADMET polyethylene with F atoms placed on each every 21st backbone carbons was chosen as model to study the influence of low-dimension carbonaceous nanofillers on the chain packing and the crystal lattice structure of semicrystalline polymers with substituent. Compared to the unsubstituted polyethylene chain, the orthorhombic lattice expand due to an increase in both, van der Waals radius and bond length of C–F, which in turn alter the melting temperature [48]. As increasing the volume of substituent to Cl and Br, accommodation of the larger atoms distort the all-trans ordering of vicinal intra- and intermolecular carbons resulting in a more defective structure and, as a consequence, in significantly decrease the melting temperatures and degrees of crystallinity. These thus give evidence for the impact of substituent as a defect on both melting and crystallization. In this paper, the morphology of polyethylene substituted by F lamellae was clearly revealed by transmission electron microscopy (TEM), and the orientation of the polymer chain induced by nanofillers was determined by selected area electron diffraction (SAED). The crystal structures of nanocomposites were described on the basis of X-ray diffraction, Melting temperatures (T_m) values shown by differential scanning calorimetry (DSC) reflecting the evolution of crystallizable sequence length. This study will establish better understanding of the influence of low-dimension carbonaceous nanofillers on the chain packing and the crystal lattice structure of semicrystalline polymers with substituent, and so as to achieve the aim of providing guidance to fabricate polymer-carbonaceous nanocomposites with expected physical properties as well as other functionalities.

2. Experimental section

2.1. Materials

Purified HiPco single-walled CNTs (SWNTs, average diameter range is 6 nm) were purchased from Times Nanotechnologies Inc. Pristine MWCNTs (95% purity; MWNT-10, average diameter range is 8 ~ 10 nm; length range is 5 ~ 20 μm; Alfa Aesar, MWCNT-20, average diameter is 20 nm; length range is 5 ~ 20 μm; Alfa Aesar) were used without any additional treatment to preserve the integrity of CNT sidewall structure. GO was exfoliated by ultrasonication from graphite oxide which was produced by modified Hummers' method [52]. RGO was prepared by thermal exfoliation and reduction of GO [53]. P-xylene were purchased from Sigma–Aldrich and used as received. The precision ADMET polyethylene with F atoms placed on each every 21st backbone carbons has been studied, labeled as PE21F, where the number corresponds to the precise location of the side group in the PE backbone. The synthesis of these polymers required the preparation of α-ω diene monomers, followed by ADMET polymerization and subsequent exhaustive hydrogenation [48]. Their repeated structural unit is the following:



$$-[(CH_2)_{20}\text{-}\underset{\displaystyle F}{\underset{|}{C}}H]_n-$$

The molecular weight was determined by GPC using a Agilent PL-GPC 220 instrument with HPLC grade chloroform as the mobile phase at a flow rate of 1.0 mL/min and a calibration with polystyrene standards ($M_w = 22400$ g/mol, $M_w/M_n = 2.1$).

2.2. Sample preparation

PE21F nanocomposites were obtained as follows. Nanofillers were firstly put into p-xylene and the mixture was stirred in the disintegrator for 30 min at a rotation speed of 1200 $r \cdot min^{-1}$ and then sonicated for 2–3 h at 45 °C to make nanofillers-p -xylene suspension with the nanofillers mass concentration controlled at 0.1 wt%. PE21F-p-xylene solution was prepared by dissolving PE21F into p-xylene at 120 °C with stirring at 1200 $r \cdot min^{-1}$ for 2h, where the mass concentration of PE21F was controlled at 0.1 wt%. Then, 10 g nanofillers-p-xylene solution was mixed with 10 g PE21F - p-xylene solution at 120 °C for 5 min. The mixture was then quenched to the preset crystallization temperature T_c within 1 min and then stirred at 1200 $r \cdot min^{-1}$ for another 15 min. After that, the stirring rate was decreased to 400 $r \cdot min^{-1}$ to avoid destroying the PE21F kebabs deposited on nanofillers. The crystallization time was controlled to be 3 h and the stirring was stopped. Sample was isothermally filtered after crystallization to remove the uncrystallized materials. Subsequently, nanocomposites were transferred into ethanol (25 °C). After washed by ethanol carefully for 3 times, nanocomposites were freeze dried at 50 °C at vacuum for 36–48 h.

The Qunxus' method [54] of preparing PE nanocomposites by Supercritical CO_2 (SC CO_2)was employed. The detailed experimental procedure is as following. Nanofillers were firstly put into p-xylene and the mixture was stirred for 30 min at a rotation speed of 1200 $r \cdot min^{-1}$ and then sonicated for 2–3 h at 45 °C to make nanofillers-p-xylene suspension with the nanofillers mass concentration controlled at 0.1 wt%. PE21F -p-xylene solutions were prepared by dissolving PE21F into p-xylene at 120 °C with stirring at 1200 $r \cdot min^{-1}$ for 2h, where the mass concentration of PE21F was controlled at 0.1 wt%. Then, 10 g CNT-p-xylene solution was mixed with 10 g PE21F-p-xylene solution at 120 °C for 5 min. The mixture was fast transferred into a stainless steel autoclave at the preset crystallization temperature T_c within 1 min. Supercritical CO_2 was then charged into the autoclave up to the desired pressure within a short time. After keeping the supercritical fluid condition for 2h, the system was slowly depressurized and the sample was collected and labelled.

2.3. Characterization

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images was conducted by a JEOL JEM2100 transmission electron microscope with an accelerating voltage of 200 kV, Nanocomposites suspensions were collected on a carbon-coated TEM grid. Differential scanning calorimetry (DSC) experiments were carried out using a Perkin–Elmer DSC8000. The samples with an average weight of 2–4 mg were heated from 30 to 160 °C at a scanning rate of 10 °C/min under a nitrogen atmosphere and were cooled and reheated using the same rate. The X-ray diffraction (XRD) patterns were recorded on a Bruker D8