Epitaxial crystallization of precisely chlorine-substituted polyethylene induced by carbon nanotube and graphene

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ABSTRACT

We report morphology, thermal analysis and beam diffraction of polyethylene chlorine-substituted precisely on every 21st backbone carbon, after solution crystallization induced by low-dimensional carbonaceous nano fillers (carbon nanotube and graphene). Kebab-like and rod-like nanofiller-induced crystals were separately observed on the surfaces of carbon nanotube and graphene. Fast-scan differential scanning calorimetry revealed that while the melting point of crystals grown on carbon nanotube remains close to that in the bulk phase, the melting point of crystals grown on graphene is 75°C higher. X-ray diffraction and selected area electron diffraction suggested that graphene induces the formation of orthorhombic form, which is of higher density than the triclinic form in the bulk.

1. Introduction

The study of surface-induced polymer crystallization has obtained particular interest in both basic and applied research in the past ten years due to it provides an efficient way for fabricating special structure with desired property or/and functionality of the polymeric materials [1–8]. It has been well documented that various crystalline polymers can be induced by foreign surface to orient and crystallize, include polyethylene [9–11], polypropylene [12], poly(vinylidene fluoride) [13], polycaprolactone [1], poly(lactic acid) [14], poly(3-hydroxybutyrate) [15], poly(3-hexylthiophene) [17,18], and TA-PPE [19] etc. Even amorphous polymers such as poly(methyl methacrylate) [20] also can be induced to crystallization on the substrates. It is now generally accepted that the occurrence of surface-induced polymer crystallization 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 [11]. One-dimensional or two-dimensional crystallographic matches generate special interactions between the polymer chains and substrate in the contacting interface. Extensive research has been reported that the existence of foreign surface can alter the crystal structure and morphology of polymer, as well as crystallization kinetics. Chang et al. [1].reported that all the PCL chains can form extremely broad lamellae thickness on the PE substrate and the melting temperature of the final epitaxial crystallization of PCL is 15°C higher than that of untreated PCL due to strong interaction between both polymers. The usual orthorhombic form of polyethylene were transformed to the monoclinic form after crystallized at the interface of alkali halide [21], high-density paper [22], and ultra high molecular weight polyethylene (UHMWPE) fiber [23], but the polymer melting temperature did not change a lot.

Low-dimensional carbonaceous nanofillers, include one-dimensional carbon nanotube (CNT) and two-dimensional graphene, can also be used as substrates to induce polymer crystallization. It has been well documented that the topological structure of substrate has great influence on the polymer crystallization behavior [24–31]. For two-dimensional graphene, lattice matching should play the dominant role in surface-induced polymer epitaxial crystallization. The space lattice matching of PE and graphene...
resulted in edge-on lamellae formed on the surface of graphene which is much more thicker than those produced by bulk crystallization [32–34]. The crystalline lattice matching of PE and HOPG generated stable monoclinic form at the interface [35]. The mechanism of carbon nanotube (CNT) inducing polymers to form disk-like crystal lamellae was 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. Li et al. [39,40], found that CNT could induce molecular chain of PLLA to give rise to order conformational during the early period of the over all crystallization, which could be explained in terms of surface-induced conformational order. Though the epitaxial crystallization or soft epitaxy crystallization have been studied by lots of researchers, 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 the polymer epitaxial crystallization is the simplest polymer, namely polyethylene (PE). Substituent different with hydrogen has a significant impact on the crystallization behavior of polyethylene since it acts 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, which makes the study complex. Therefore polyethylene with periodical substituent can be suitable model polymer on the study of epitaxial crystallization. In the present study, the precision Acyclic diene metathesis polymerization (ADMET) polyethylene with chlorine atoms placed on each every 21st backbone carbons was chosen as a model to investigate the structural change of polymer epitaxial crystallization. In this paper, the morphology of polyethylene substituted by Cl 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, and the thermal temperatures (Tm) values were characterized by fast-scan differential scanning calorimetry (DSC). 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, so as to provide 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 (SWCNTs, average diameter range is 6 nm) purchased from Times Nanotechnologies Inc. were used without any additional treatment. GO was exfoliated by ultrasonication from graphite oxide which was produced by modified Hummers’ method [41]. RGO was prepared by thermal exfoliation and reduction of GO [42]. The precision ADMET polyethylene with Cl atoms placed on each every 21st backbone carbons has been studied, labeled as PE21Cl, where the number corresponds to the precise location of the side group in the PE backbone [43]. The repeated structural unit is the following:

\[-\{(CH_2)_{20}\}_n\text{Cl}\]

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 (Mn = 16,624 g/mol, Mw/Mn = 2.43). Structure was characterized by \(^1\)H NMR (Supporting Information Fig. S1).

2.2. Sample preparation

PE21Cl nanocomposites were obtained as follows. Nanofillers were firstly put into p-xylene and the mixture was stirred for 30 min at a rotation speed of 1200 r·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%. PE21Cl-p-xylene solution was prepared by dissolving PE21Cl into p-xylene at 120 °C with stirring at 1200 r·min\(^{-1}\) for 2 h, where the mass concentration of PE21Cl was controlled at 0.1 wt%. Then, 10 g nanofillers-p-xylene solution was mixed with 10 g PE21Cl-p-xylene solution at 120 °C for 5 min. The mixture was then quenched to the preset crystallization temperature Tc. Sample was isothermally after crystallization for 6 h. After washed by ethanol carefully for 3 times, nanocomposites were dried at 40 °C at vacuum for 36–48 h.

The Qunxus’ method [44] 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·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%. PE21Cl-p-xylene solutions were prepared by dissolving PE21Cl into p-xylene at 120 °C with stirring at 1200 r·min\(^{-1}\) for 2 h, where the mass concentration of PE21Cl was controlled at 0.1 wt%. Then, 10 g nanofillers-p-xylene solution was mixed with 10 g PE21Cl-p-xylene solution at 120 °C for 5 min. The mixture was fast transferred into a stainless steel autoclave at the preset crystallization temperature Tc 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 2 h, the system was slowly depressurized and the sample was collected and labeled.

2.3. Characterization

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were 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. The fast-scan differential scanning calorimetry experiments were performed in the commercialized FSC (Flash DSC1, Mettler-Toledo, Switzerland). Before any analysis, the empty chip-sensor experienced the standard procedure for conditioning and calibration. In order to achieve a sufficiently good contact between the sample and the chip-sensor, a small trace of silicon oil was dropped onto both cells of the sample, and of the reference, before the sample was transferred in. The samples were heated from 30 to 240 °C at a scanning rate of 1000 K/s and nitrogen gas was used as the protection atmosphere with the constant flow rate 50 mL/min. The StarE software (Version 10.0) was employed to perform the data treatment. The X-ray diffraction (XRD) patterns were recorded on Bruker D8 diffractometer, using Ni-filtered Cu Kα radiation at 40 kV and 30 mA at room temperature in an angle ranging from 5 to 80° at a rate of 3.5°/min.
3. Results and discussion

3.1. Morphologies of PE21Cl/nanofiller composites

3.1.1. Morphologies of PE21Cl/CNT kebab-like crystals

It can be seen from Fig. 1 that the PE21Cl lamellae decorate SWCNTs periodically and form kebab-like morphologies at all selected experimental temperature. Average sizes of lamellae of PE21Cl formed on SWCNT are listed in Table 1 on the basis of measurement of 200 lamellae. The diameters of the PE21Cl kebab are 16.1 ± 1.2, 26.2 ± 1.0 and 24.6 ± 1.0 nm, respectively, at the crystallization temperature of 60, 70 and 80 °C. The average diameter of the PE21Cl kebab-like crystals first increases then decreases with the increase of crystallization temperature, and the largest diameter of kebab-like crystals forms at the temperature of 70 °C. There are two kinds of crystal nucleation in the solution system of our experiment, heterogeneous nucleation (CNT or RGO induced) and homogeneous nucleation. However, heterogeneous nucleation plays the dominant role at the crystallization condition because of the excellent nucleation ability of CNT or RGO. For the sample crystallized at lower temperature (60 °C), higher undercooling degree is favorable for the nucleation but disadvantageous to the crystal growth. Large densities of crystal nucleus form on the surface of CNT, whereas the supply of polymer chains can not satisfy the growth of so many crystals, which results in kebab-like crystals with small diameter. With the increase of crystallization temperature (70 °C), lower undercooling degree is disadvantageous to the nucleation but favorable for the crystal growth, the diameter of kebab-like crystals increases to maximum. However, as crystallization temperature increases successively (80 °C), crystal nucleus formed on the surface of CNT decrease, and the melt of crystals at higher temperature is intense resulting in the growth of crystals decreases, so the diameter of kebab-like crystals decreases. Therefore, competition of nucleation and crystal growth on the CNT causes the changes of the PE21Cl crystal lamellae, as shown in Fig. 1 and Table 1. On the contrary, the interval of kebab increases monotonically with the increase of crystallization temperature (Table 1), because stable crystal nucleus become less and less with the decrease of undercooling degree. It is known that crystallization ethylene sequence is strongly dependent on crystallization temperature. Consequently, lamellae formed at different temperatures have different thickness. The thickness of kebab-like crystals increases with crystallization temperature increasing, from 5.6 ± 0.6 nm at 60 °C to 6.4 ± 0.5 nm at 80 °C (Table 1). It can be concluded that the crystallization temperature has great influence on the size and periodicity of the kebab-like crystals and the most suitable crystallization temperature for PE21Cl/SWCNT in p-xylene is 70 °C. It should be noted that the diameter of PE21Cl kebab is much smaller than that of HDPE (50–80 nm) [38] and PE21F (54–65 nm) (F has smaller volume (1.52 Å) than Cl (1.75 Å)) [45]. The interval of kebab-like crystals is also much larger than that of PE21F at the same undercooling degree. It suggests that substituent Cl as a defect of chain seriously affects the lateral growth of crystal lamellae. It is worth mentioning that the thickness of PE21Cl kebab-like crystals is smaller than that of PE21F formed at the same undercooling degree (10 °C) [45]. It indicates that the larger substituent Cl disturbs the crystallization of PE more intensely than that of the smaller substituent F.

3.1.2. Morphologies of PE21Cl/RGO rod-like crystals

Although RGO and CNT have the same graphite layer structural unit, RGO has two-dimensional flat area made up of one- or several-atom layers, which is helpful for the strict epitaxial crystallization. Three crystallization temperatures (60, 70 and 80 °C) are selected to that of PE21Cl/SWCNT nanocomposites were chosen to prepare PE21Cl/RGO nanocomposites. It can be seen from the crystals morphologies shown in Fig. 2 that RGO is covered with rod-like crystals. As shown in Table 2, the sizes of PE21Cl crystals are 32 ± 2.0, 57 ± 1.2 and 49 ± 1.0 nm, respectively, at the crystallization temperature of 60, 70 and 80 °C on the basis of measurement of 200 lamellae. Discrete nuclei and small rod-like crystals can be observed on the surface of RGO nanosheets at the crystallization temperature 60 °C. Small nuclei and crystals of PE21Cl grow into largest lamellae when the crystallization temperature increases to 70 °C. As crystallization temperature increases successively, the average size of the PE21Cl lamellae decreases at 80 °C. This phenomenon is similar to the crystallization of PE21Cl on SWCNT. The density of lamellae (number/0.01 µm²) decreases from 35 at 60 °C to 18 at 80 °C, as shown in Table 2. When isothermal crystallization temperature increases, the number of rod-like crystals decreases because less stable crystal nucleus exists at lower undercooling degree. We can also see from Table 2 that the thickness of rod-like crystals increases with crystallization temperature increasing. It also suggests that isothermal crystallization temperature plays a decisive role in thickness and density of lamellae formed on RGO. By contrasting Tables 1 and 2, we can find that the thickness of rod-like crystals formed on RGO is almost same with that of kebab-like crystals formed on SWCNT under the same crystallization conditions, which suggests that the thickness of PE21Cl crystal on CNT and RGO is determined by the crystallization temperature. But the uniformity of the thickness of rod-like crystals induced by RGO is better than that of kebab-like crystals, which may be due to the fact that the two-dimensional RGO is helpful for the strict epitaxial crystallization. Comparing PE21Cl with PE21F [45] and HDPE [46], the maximal thickness and size of PE21Cl lamellae formed on RGO is about 6.5 nm and 57 nm, is smaller than 8.8 nm and 73 nm of PE21F and 13 nm and 100 nm of HDPE. It is also attributed to the influence of substituent Cl.
3.1.3. PE21Cl/nano filler composites prepared with the assistance of supercritical CO2

The supercritical CO2 (SC CO2), as antisolvent, was used to study the effect of crystallization condition on PE21Cl epitaxial crystallization. PE21Cl/nano fillers composites were prepared in p-xylene at 70 °C with the assistance of SC CO2, the experimental pressure of SC CO2 was tuned from 10, 15 to 20 MPa. The crystallization morphologies are shown in Figs. 3 and 4. For these cases, the sizes of the PE21Cl crystal lamellae formed on SWCNT and RGO are listed in Tables 3 and 4. SWCNTs are apt to agglomerate and form small bundles at SC CO2 pressure, and it becomes more and more serious as the SC CO2 pressures rise. Therefore, the diameter of SWCNT is much thicker than that produced without SC CO2. After 3 h isothermal crystallization with the assistance of SC CO2, the diameter of PE21Cl crystals formed on SWCNT at 70 °C and 10 MPa, 49 ± 3.2 nm, is much larger than that of crystals solution crystallized after 6 h isothermal crystallization (Table 1). Similarly, the lamellae size of PE21Cl formed on RGO at 10 MPa, 62 ± 3.3 nm, is also much larger than that of crystals solution crystallized after 6 h isothermal crystallization (Table 2). It suggests that SC CO2 can accelerate the lateral growth of lamellae. The diameter of the PE21Cl kebab-like crystals decreases with the increasing pressure of SC CO2, from 49 ± 3.2 nm at 10 MPa and 62 ± 3.5 nm at 15 MPa to 71 ± 3.1 nm at 20 MPa. This rule also can be observed in PE21Cl/RGO system as indicated in Table 5. The size of the rod-like crystals of PE21Cl/RGO nanocomposites is 62 ± 3.3, 66 ± 2.8, and 40 ± 2.3 nm, respectively, at the CO2 pressure of 10, 15, and 20 MPa. This phenomenon can be attributed to the following reasons. With an increasing pressure of SC CO2, the amount and speed of CO2 dissolved in p-xylene increase and the solvent power of p-xylene decreases. Therefore, more PE21Cl chain can be deposited rapidly and accelerate the lateral growth of lamellae, and the diameter of the lamellae hence first increases. However, if the CO2 pressure is excessively high, both the amount and speed of the PE21Cl chain precipitation are greatly increased and can induce the increase of the nucleation number, which can lead to the formation of more lamellae. The interval of PE21Cl

<table>
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<tr>
<th>Table 1</th>
<th>The size of lamellae of PE21Cl formed on SWCNT based on the TEM images of 200 lamellae.</th>
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<td>Sample (crystallization temperature)</td>
<td>Diameter of kebab (nm)</td>
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<tr>
<td>PE21Cl/SWCNT (60 °C)</td>
<td>16.1 ± 1.2</td>
</tr>
<tr>
<td>PE21Cl/SWCNT (70 °C)</td>
<td>26.2 ± 1.0</td>
</tr>
<tr>
<td>PE21Cl/SWCNT (80 °C)</td>
<td>24.8 ± 1.0</td>
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<th>Table 2</th>
<th>The size of lamellae of PE21Cl formed on RGO based on the TEM images of 200 lamellae.</th>
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<tr>
<td>Sample (crystallization temperature)</td>
<td>Size of lamellae (nm)</td>
</tr>
<tr>
<td>PE21Cl/RGO (60 °C)</td>
<td>32 ± 2.0</td>
</tr>
<tr>
<td>PE21Cl/RGO (70 °C)</td>
<td>57 ± 1.2</td>
</tr>
<tr>
<td>PE21Cl/RGO (80 °C)</td>
<td>49 ± 1.0</td>
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Fig. 2. TEM images of PE21Cl/RGO nanocomposites produced in p-xylene at different temperatures for 6 h. (a) 60 °C, (b) 70 °C, (c) 80 °C. The PE21Cl and RGO concentrations are all 0.05 wt%.

Fig. 3. TEM micrographs of PE21Cl/SWCNT nanocomposites produced at different SC CO2 pressures: (a) 10 MPa, (b) 15 MPa, and (c) 20 MPa in p-xylene at 70 °C for 3 h.
the thickness of the crystal lamellae which is directly related to crystallization temperature. Therefore, the optimum SC CO2 pressure is 15 MPa at which the rod-like crystal lamellae size is the maximum.

3.2. Thermal behavior of PE21Cl/nanofillers composites

Further insight into the unique crystallization mode of PE21Cl/nanofillers composites is given by their melting behaviors as measured by fast-scan differential scanning calorimetry shown in Fig. 5. Fast-scan differential scanning calorimetry is sensitive to detect small mass of samples (as low as 9 ng), which is why we chose this instrument [47]. The melting peak temperature of PE21Cl is 102.1 °C measured by fast-scan differential scanning calorimetry, which is 13 °C higher than that measured by traditional DSC. The melting temperature shifted to higher temperature compared with traditional DSC because of supper heating effect [48,49] and thermal lags [47].

We can observe from Fig. 5a that the melting temperatures of PE21Cl/SWCNT nanocomposites is 81.0 °C, which is 21 °C lower than that of PE21Cl. It suggests that the thickness of lamellae formed on SWCNT is much smaller than that of PE21Cl. The melting temperatures increase as the increasing crystallization temperature, from 99.7 °C at 70 °C to 104.2 °C at 80 °C. The increase rate of melting temperature is higher than that of PE21F/SWCNT nanocomposites [45]. It indicates that PE21Cl needs higher crystallization temperature for incorporating more substituents to form longer methylene sequence due to the hindering of more larger substituent. Surprisingly, the melting temperatures of PE21Cl/RGO nanocomposites is 145.6 °C for crystallizing at 60 °C (Fig. 5b), which is 43 °C higher than that of PE21Cl. Moreover, the melting temperatures of PE21Cl/RGO nanocomposites increased to 156.1 °C and 177.7 °C at the crystallization temperature of 70 and 80 °C. It should be noted that the thickness of PE21Cl/RGO crystals is almost same with that of PE21Cl/SWCNT nanocomposites as mentioned above.
The speculation of remarkably higher melting temperatures caused by thicker lamellae formed on RGO is ruled out. It is worth mentioning that the melting temperature of PE21Cl/RGO nanocomposites is slightly lower than that of PE. PE21Cl has lower melting temperature compared with PE21F due to bulkier substituent Cl disturbs length of continuous methylene sequences [50]. However, PE21Cl/RGO nanocomposites possess particularly higher melting temperatures. It can be summarized from the previous papers that only the common addition of carbon nanofillers has little effect on polymer melting temperature measured by DSC. There is no additional chemical bond between PE21Cl and RGO. Consequently, these results above suggest that RGO may induce PE21Cl to form crystals with different structure. We can also find from Table 5 that melting range (span of onset-end) of PE21Cl/RGO composites is smaller than that of PE21Cl/SWCNT composites prepared at same crystallization temperature, which is consistent with the result that the uniformity of the thickness of crystals on RGO is better than that on CNT. It is impossible that melting recrystallization occurs at so fast scanning rate. Therefore, the melting range of polymer is the reflection of the uniformity of lamellae thickness if there is not different structure in each kind of crystal.

For the purpose of investigating the influence of supercritical CO$_2$ on the melting behavior of PE21Cl crystals, we took PE21Cl/nanofillers composites produced at 70 °C and 15 MPa SC CO$_2$ pressure as example. The melting curves measured by fast-scan differential scanning calorimetry are shown in Fig. 6, and the melting temperatures are listed in Table 6. We can find from Table 6 that the melting peak temperature of PE21Cl/SWCNT nanocomposites produced at 70 °C is 100.5 °C for 15 MPa, which is almost consistent with that prepared by traditional solution crystallization (99.7 °C). The same result is also observed in PE21Cl/RGO nanocomposites. This further suggests that supercritical CO$_2$ can promote the lateral growth of lamellae on CNT and RGO, but the thickness of the crystal lamellae is directly related to crystallization temperature. We can also find from Fig. 6 and Table 6 that double melting peaks appeared in PE21Cl/RGO nanocomposites system. The higher melting peak temperature of PE21Cl/RGO produced with the assistance of supercritical CO$_2$ 156.1 °C, is consistent with that prepared by traditional solution crystallization (Table 5). The lower melting peak temperature of PE21Cl/RGO produced with the assistance of supercritical CO$_2$ located at 146.5 °C. This may be because that the amount and speed of the PE21Cl precipitation from supercritical CO$_2$ is large, leading to the formation of more lamellae with inhomogeneous thickness. The melting range of PE21Cl/SWCNT and PE21Cl/RGO nanocomposites prepared at 70 °C and 15 MPa SC CO$_2$ pressure is 67.1 and 36.5 °C, respectively, which is larger than that prepared by traditional solution crystallization (49.7 and 28.9 °C shown in Table 5). This also suggests that more lamellae with inhomogeneous thickness formed with the assistance of supercritical CO$_2$. Similar to that produced by traditional solution crystallization, the melting range of PE21Cl/RGO nanocomposites is smaller than that of PE21Cl/SWCNT nanocomposites at SC CO$_2$.

**3.3. Crystalline structure of PE21Cl/nanofillers composites**

To investigate the structure of PE21Cl/nanofillers composites, X-ray diffraction (XRD) and selected area electron diffraction (SAED) were conducted. As shown in Fig. 7a and Table 7, two peaks located at 21.4° and 22.9° in XRD pattern of PE21Cl/SWCNT nanocomposite can be assigned to pure PE21Cl, indexed as (100) and (010) crystalline planes of triclinic form [52]. All the peaks for PE21Cl and SWCNT are found in the XRD pattern of PE21Cl/SWCNT nanocomposite without obvious peak shift. This indicates that SWCNT has no influence on the crystal structure of PE21Cl. X-ray diffractograms of PE21Cl/RGO nanocomposites are shown in Fig. 7b. Two peaks located at 21.8° and 24.4° was observed from PE21Cl/RGO nanocomposites produced at 100 °C, which can be indexed as (110) and (200) crystalline planes of orthorhombic form (Table 7). The orthorhombic form structure also can be determined according to higher 20 peaks, 36.5° and 39.9°, which are indexed as (020) and (011) crystalline planes of orthorhombic form respectively. The other peaks can be assigned to the contribution of RGO. As increasing the crystallization temperature of PE21Cl/RGO nanocomposite to 70 and 80 °C, two peaks of 21.8° and 24.4° disappear, and the new peak of 29.9° (which can be indexed as (210) crystal plane of orthorhombic form of PE21Cl) appears. This may be due to the fact that the quantity of epitaxial crystallized lamellae is small at lower undercooling degree (Fig. 2b, c), which results in weak diffraction intensity of (110) and (200) crystalline planes and covered by the diffraction peak of RGO. The XRD results above indicate that crystal structure of PE21Cl epitaxial crystallized on the surface of RGO transformed from triclinic to orthorhombic form. The orthorhombic lattice parameter of PE21Cl/RGO nanocomposite is calculated to be $a = 7.314$, $b = 4.920$, $c = 2.541$, which is smaller than that of PE21F ($a = 7.515$, $b = 4.989$, $c = 2.547$) [43] and even...
Much more ordered although PE21Cl has larger volume of substituent. X-ray diffractograms of PE21Cl/nanofiller composites prepared with assistance of supercritical CO2 (Supporting Information Figs. S2 and S3) show the similar results, which confirm the structural results of PE21Cl epitaxial crystallized on CNT and RGO by traditional solution crystallization. This also indicates that although it can promote effectively the lateral growth of lamellae smaller than that of HDPE (a = 7.410, b = 4.934, c = 2.547). It suggests that lattice structure of PE21Cl lamellae formed on RGO is on CNT and RGO, supercritical CO2 can not change the crystal structure of PE21Cl/nanofillers composites.
Fig. 8b shows selected area electron diffraction (SAED) pattern from the circled area of Fig. 8a. The reflection spots of PE21Cl orthorhombic form can be observed, six symmetric weak PE21Cl (002) reflection spots are close to RGO (2−1−10) reflections, and the (310) PE21Cl diffraction are over lapped with RGO (10−10) diffractions. This confirms that the PE21Cl chains in the edge-on crystal are parallel to the basal plane of RGO sheets. The rod-like crystal lamellae prefer to arrange at three directions that are about 60° apart from each other. This result is also consistent with cases of epitaxial growth of polyethylene crystals on the surfaces of graphite [51], HOPG [35], and RGO [46].

It is generally believed that substituent has certain effect on the chain packing of PE crystals as the defect of chain. It is confirmed from the previous paper that chlorine, as one kind of smaller side groups, can be incorporated into the crystalline lattice of PE [50,52,53]. This is also evidenced by the fact that the thickness of PE21Cl lamellae formed on RGO or CNT is well above 2.55 nm that corresponds to the length of 20 all-trans methylene units. Compared to the orthorhombic packing displayed by PE and PE with F substitutions, the triclinic pattern is degeneration since reduced order is needed to facilitate minimum spatial requirements to accommodate the bulky Cl groups between adjacent molecules in the crystal of pure PE21Cl. However, the epitaxial crystallization on the RGO changes this structure of PE21Cl as can be concluded from the results described above. The analysis of PE21Cl epitaxial crystallization on the RGO can refer to the PE on the HOPG since the structure of PE21Cl is analogous to PE and that of RGO is same with HOPG. On the basis of structural analysis of epitaxial crystallization, the chain direction, <001>, and the plane (110) of the orthorhombic PE21Cl are parallel to the <2−1−10> direction and the (0001) plane of RGO, respectively [35,46]. However, only chain axis of PE21Cl, <010>, can be indexed as parallel to the <2−1−10> RGO [35,51]. An important quantity in epitaxy is the lattice mismatch $R$ between an epitaxial crystal and a substrate crystal.

$$R[\%] = \frac{d_E - d_S}{d_S} \times 100$$  

(1)

Where $d_E$ and $d_S$ are spacings of 2-dimensional lattices at the interface of the epitaxial crystal and the substrate crystal, respectively. Using the lattice parameters of PE21Cl and RGO, we can calculate the lattice mismatch value, along the chain axis of PE21Cl it is 3.3% for orthorhombic form, along the direction perpendicular to the chain axis, the lattice mismatch is 3.8% [35,51]. The periodic of PE21Cl triclinic form along the chain axis can not be found in the literature, if the value of similar polymer, PE21Br, is used for reference (5.27 nm) [54], the periodic value is much larger than the periodic value of RGO (0.246 nm), consequently it is much difficult that the lattice match between PE21Cl with triclinic form and RGO. Therefore, PE21Cl can epitaxial crystallized on RGO only with orthorhombic form. If the lattice parameters of an epitaxial crystal have to fit to those of substrate, it is easier to understand that the epitaxial PE21Cl compresses its crystal cell, this could account for that the lattice parameter of PE21Cl lamellae formed on RGO is smaller than that of HDPE. It is generally believed that the melting temperature is extensively affected by the structural of polymer crystals. The melting temperature of PE15Cl increased by 10 °C when the conformation around the Cl substitution transformed from all-trans packing to TG while the main CH2 sequence remains the triclinic lattice [55]. Although chlorine as the defect of chain significantly impacts the chain ordering of substituted polyethylene and alter the orthorhombic unit cell packing of the linear chain to triclinic lattice [50], RGO transform triclinic form of PE21Cl to orthorhombic form. Therefore, we can conclude that RGO can induce PE21Cl to form ordered lattice structure under the existence of crystal defects, but one-dimensional CNT can not induce the transformation of crystal form because of absent strict epitaxial crystallization. Markedly increased melting temperature of precisely chlorine-substituted polyethylene caused by epitaxial crystallization allows models for fabricating functional Polyolefin materials with high service temperature.

4. Conclusion

PE21Cl epitaxial crystals on low-dimensional carbonaceous nanofillers were prepared by traditional solution crystallization and supercritical CO2 assisted solution crystallization. Low-dimensional carbonaceous nanofillers induced PE21Cl to form kebab-like and rod-like crystals on CNT and RGO, respectively. Triclinic crystal lattice structure of PE21Cl remained unchanged in PE21Cl/CNT composites. However, RGO induced structural transformation of PE21Cl caused by epitaxial crystallization from triclinic form to orthorhombic form, which generated markedly high melting temperature. The increased melting temperature of precisely chlorine-substituted polyethylene caused by epitaxial crystallization provides model for fabricating substituted or branched polyolefin materials with high service temperature. This finding will intrigue our interesting in further investigation on the epitaxial crystallization behavior of other precision systems with bulkier substituents and higher content of substituents.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2016.04.022.

References
