The probable influence of in situ thermal reduction of graphene oxides on the crystallization behavior of isotactic polypropylene

Jiashu Fan, Ruijin Huang, Shibing Ye, Tianjiao Li, Jiachun Feng*

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, PR China

A R T I C L E   I N F O

Article history:
Received 29 December 2013
Received in revised form 29 May 2014
Accepted 1 June 2014
Available online 9 June 2014

Keywords:
Polypropylene
Crystallization
Graphene oxide

A B S T R A C T

The influence of in situ thermal reduction of graphene oxides (GO) on the isotactic polypropylene (iPP) crystallization were systematically investigated by comparing the crystallization behavior of iPP with different annealing procedures at 200 °C. Polarizing optical microscopy and differential scanning calorimetry results show that, for iPP/GO composite after annealing, both the number of nucleation sites and the rate of crystallization decrease with the increase of annealing time, while this effect cannot be observed for neat iPP. Comparative experiments on iPP containing reduced GO demonstrate that the crystallization behavior of iPP cannot be affected by annealing if GO is already highly reduced. Further investigation by temperature dependent Fourier transform infrared spectra indicates that the negative influence of annealing on iPP/GO crystallization is associated with the decrease in the degree of conformational ordering during the process of crystallization. Our results suggest that the melt annealing can alter the crystallization behavior of iPP with GO and this alteration is probably caused by the thermal reduction-induced chemical changes on GO sheets.

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1. Introduction

Nucleation is an essential part of crystallization process, which may be homogenous (nuclei form within the melt itself) or heterogenous (nuclei form on a surface such as an interface or a colloidal solid like catalytic remnants or dust particles). Generally, heterogenous nucleation takes place more readily than homogenous nucleation at higher temperatures which will accelerate the crystallization process greatly. Although the mechanism of heterogenous nucleation is still far from being fully understood, it has been widely accepted that the interface between foreign particle and melt or solution plays a key role in the origin of heterogenous nucleation. In recent several decades of development in polymer science, special emphasis has been placed upon the influence of intrinsic characteristics of heterogenous surface on heterogenous nucleation behavior, for example, the crystal structure and geometry of heterogenous surface [1–6]. Among all these characteristics, the chemical structure of heterogenous surface stands out as the most essential factor that dominates the heterogenous nucleation efficiency. In the serial studies on the heterogenous nucleation in the crystallization of polyolefins in 1970s, Binsbergen concluded that almost all nucleating agents consist of both hydrocarbon groups (resembling good solvents for the polymers) and either polar groups or a condensed aromatic structure (rendering the agents insoluble in the polymer melt) [7–10]. Nucleating agents expose a hydrocarbon surface on which the hydrocarbon groups are arranged in rows leaving shallow ditches between them, which makes subsequent epitaxial crystallization of polymers possible [7–10]. Maiti and Okamoto observed the exclusive formation of the γ-phase of nylon-6 and a shish–kebab structure with clay acting as shish and nylon-6 γ-phase lamella as kebab, which was ascribed to hydrogen bonding formed by the silicon hydride chemical bonds on the surface of clay and amino bonds of nylon-6 [11]. Li’s work suggests that the surface modification of carbon nanotubes by octadecylamine prohibited the polyethylene single crystal growth on the surface [12]. These results demonstrates the important role of surface chemical structure on heterogenous nucleation. If the chemical structure is changed, the heterogenous nucleation behavior can also be altered, which will lead to a different crystallization behavior.

Graphene, as a two-dimensional crystal of sp² conjugated carbon atoms, has become one of the most promising nanofillers for polymer composites due to its extraordinary mechanical, electrical, and thermal properties [13–17]. Considering the challenges of producing large scale quantities of high quality graphene sheets and the irreversible aggregation in polymer matrix, graphene oxide...
(GO), which can be easily made from natural graphite, is commonly used as the starting material for the scalable preparation of graphene nanosheets. After oxidation procedures of GO preparation, GO possesses considerable amounts of oxygen-containing groups, such as, hydroxyl, epoxide, and carboxyl groups, which is chemically different from graphene [18–20]. In fact, GO is also a kind of nanofillers for preparing polymer composites due to its large aspect ratio, relatively high mechanical strength and abundant functional groups [21–23]. Up to now, there are mainly three effective techniques to prepare polymer/GO composite, in situ polymerization [24–26], solution coagulation [27,28] and melt mixing [29,30]. No matter how the composite is prepared, it has to undergo melt processing before made into specimens for mechanical measurements or products for practical applications. For most polymers, this environmentally friendly processing technique is generally operated at temperatures ranging from 100 to 300 °C, which has already been reported to lead to inevitable reduction of GO in a polymer matrix [31–33]. Reduction of GO will result in changes in the surface structure of GO sheets, for example the partial removal of oxygen-containing groups. This may have a non-ignorable influence on the properties of polymer/GO composite. If the polymer matrix is crystallizable, this influence may be more tremendous. Many pioneer studies have already demonstrated that the addition of GO may accelerate the crystallization of various polymer [34–39]. However, whether the in situ reduction of GO during melt processing will change the crystallization behavior especially heterogenous nucleation has rarely been studied. Considering the importance of melt processing for polymer-based composites, the potential effect of GO reduction on crystallization behavior, which may bring enormous influence on the properties of materials for final usage, is sure to attract strong interests in both academy and industry.

In present work, we investigated the influence of melt processing on the crystallization behavior of iPP/GO composite. Although the crystallization of iPP/GO composite has been studied in recent years and efforts have been made to enhance the heat resistance, thermal and electrical conductivity for the iPP, the probable influence of melt processing on iPP/GO crystallization still needs to be explored. By various experimental methods, we find that the thermal reduction of GO during melt processing in PP matrix will alter the crystallization behavior of iPP. Particular attention is paid to the change of conformation ordering caused by the in situ GO reduction, which may be helpful to reveal the alteration mechanism on the phenomenon we observed.

2. Experimental section

2.1. Materials

Natural graphite flakes were supplied by Qingdao BCSM Co., Ltd., (Qingdao, China) for the preparation of GO. Ziegler–Natta iPP (F401) employed in this study was supplied by Yangzi Petrochemical Co., SINOCPE (Nanjing, China) with a weight-average molecular weight (Mw) of 22.0 × 10⁴ g/mol and a polydispersity index of 4.85. All other reagents and solvents were purchased from Aladdin Reagent Company (Shanghai, China) and used as received.

2.2. Preparation of iPP/GO and iPP/reduced graphene oxide (RGO) composites

GO was prepared by oxidation of natural graphite according to a modified Hummers method [40]. Solution coagulation was utilized to prepare iPP/GO nanocomposite with a GO content of 0.1 wt% as follows: 10 g of iPP pellets were firstly dissolved in 100 mL of xylene at 138 °C in an oil bath with constant stirring; secondly, 10 mg of GO, which had been exfoliated in 100 mL of N,N-dimethylformamide (DMF) with the aid of ultrasonication for 15 min, was mixed into xylene/iPP solution with the coagulations precipitated incessantly; a mess of methanol was then poured into the mixture until no coagulations precipitated; finally the mixture was transferred to evaporating dishes for 24 h at room temperature and dried in vacuum oven for another 24 h to evaporate any residual solvent.

For comparison purpose, neat iPP and iPP with 0.1 wt% RGO was also prepared by solution coagulation. The RGO used was made by annealing GO at 800 °C for 1 h in a tube furnace (Shanghai Guangshu Electrical Co., Ltd., China) under a stream of Ar.

2.3. Characterizations

2.3.1. Polarizing optical microscopy (POM)

POM observations were performed using a Leica polarizing microscope (DM2500P, Leica, Germany) with a camera for photography and a Linkam hot stage (THMS600) to control the experimental temperature, the sensor accuracy of which is ±0.1 °C. The samples were firstly hot pressed in the hot stage at 200 °C between two glass slides and then held at 200 °C for 5 min to erase prior hot history. Annealing was achieved by holding at 200 °C for 30 min before observations and the samples were named as iPP/GO-30 min, iPP-30 min and iPP/RGO-30 min respectively. Correspondingly, the samples which were immediately cooled to 135 °C at a rate of 30 °C/min after erasing prior hot history and then isothermally crystallized for POM observations were named as iPP/GO-0 min, iPP-0 min and iPP/RGO-0 min respectively. Considering the protocol of erasing prior hot history, a necessary step for studies on polymer crystallization, which also leads to an inevitably annealing effect and has the possibility to induce the thermal reduction of GO, the annealing effect studied in the present work actually is the effect of further annealing after erasing prior hot history. To avoid thermal oxidative degradation, all experiments were performed in a nitrogen atmosphere.

2.3.2. Differential scanning calorimetry (DSC)

A DSC 821e thermal analysis system (Mettler Toledo Instruments Inc., Switzerland) with temperature accuracy of ±0.05 °C was used to measure the thermal properties. To ensure reliability of the data obtained, indium (Tm = 156.60 °C and ΔHm° = 28.45 J/g) was used to calibrate the temperature scale as a standard. All experiments were carried out in a nitrogen atmosphere to avoid oxidative degradation. Following procedures were performed for melting and crystallization: samples were heated to 200 °C and held there for 5 min to erase any previous thermal history; subsequently, samples with or without further annealed at 200 °C were cooled to 25 °C at a rate of 10 °C/min and the crystallization thermograms were recorded; again they were heated to 200 °C at a rate of 10 °C/min to record the melting thermograms. For isothermal crystallization, samples with different annealing procedures were cooled from 200 to 135 °C at a rate of 30 °C/min and held for 120 min to record the isothermal crystallization curves.

2.3.3. Fourier transform infrared spectra (FTIR)

IR spectra were collected with a Nicolet Nexus 470 Infrared Spectrometer (Thermal Nicolet, America) in the region of 750–1350 cm⁻¹. All collected spectra were the averages of 32 scans with a resolution of 4 cm⁻¹ for an acceptable signal-to-noise ratio. An electronic cell holder was occupied for manually controlling experimental temperatures at rates of ca. 0.3 °C/min with an increment of 1 °C. Baselines of raw spectra were corrected by the software Omnic, ver. 6.1a.
3. Results and discussion

3.1. Crystallization morphologies of iPP/GO composite before and after annealing

We firstly investigated the morphology development and number of spherulites of iPP/GO composite before and after annealing by POM. With the equipment of hot stage and digital camera, real-time process of isothermal crystallization could be observed and the evolution of crystalline morphology could be recorded. 135 °C was finally chosen as the identical temperature of isothermal crystallization for all samples tested in our work after a series of attempting efforts. Following the operation protocol described in Section 2.3.1, the morphological evolution of iPP/GO sample annealed at 200 °C for 0 min and 30 min after erasing prior hot history was photographed as shown in Fig. 1. At 2 min, some sporadic nuclei were already visible for iPP/GO-0 min sample, indicating the beginning of isothermal crystallization. However, after annealed for 30 min, the number of nuclei decreased so substantially that almost no nuclei could be observed for iPP/GO-30 min. The number of nucleation sites of both iPP/GO-0 min and iPP/GO-30 min samples continues to increase at 4 min. With the comparison of the images of both samples captured at 4 min, it is clear that the number of nucleation sites of iPP/GO-30 min is much less than that of iPP/GO-0 min. The number of nucleation sites of iPP/GO-0 min sample is 78, whereas that of iPP/GO-30 min sample is 23. These results indicate that anneal can cause severe suppression in heterogeneous nucleation behavior of iPP/GO composite. After 4 min, the formed spherulites began to impinge on each other at 6 min, while this phenomenon did not become evident until 10 min for sample iPP/GO-30 min which resulted from the much less nucleation sites. Further observations revealed that the subsequent growth of crystallization almost stopped at 16 min. However, the spherulites of iPP/GO-30 min sample were still growing until 16 min and the crystallization was still far from saturation. The spherulites’ size of iPP/GO-30 min was also much larger than that of iPP/GO-0 min due to the lower nucleation density. These results indicate that the growth rate of crystallization of iPP/GO-30 min is slower than that of iPP/GO-0 min. Therefore, it is clear that the nucleation and overall crystallization rate of iPP/GO can be suppressed with annealing procedure.

The crystalline morphologies of neat iPP with different annealing procedures were also observed by POM as shown in Fig. 2. By comparing the POM image at 4 min of iPP-0 min with that of iPP-30 min, it can be found that the effect of anneal on the nucleation process of iPP without GO is much less prominent than that of iPP/GO sample. The number of nucleation sites of neat iPP stays almost unchanged after annealed for 30 min Fig. 2 also shows that the crystallization process of iPP-0 min needs more time (about 30 min) to reach saturation than iPP/GO-0 min sample without anneal. This phenomenon demonstrates that the addition of GO accelerates the crystallization of iPP dramatically because of the effect of heterogenous nucleation, which is in agreement well with Li's report [37–39]. The spherulite growth process of neat iPP with different annealing procedures shows no prominent difference. The evident discrepancy in the influence of anneal on the crystallization behavior of iPP with and without GO manifests that the melt annealing-induced decrease in crystallization ability is not caused by the possible variations of iPP such as thermal oxidative degradation. The alteration in crystallization may be in strong relation with the change of GO during melt annealing.

3.2. Nonisothermal and isothermal crystallization of iPP/GO composite with different annealing procedures investigated by DSC

DSC was also utilized to investigate the annealing-induced change in crystallization behavior of iPP/GO composite. Fig. 3 shows the nonisothermal crystallization and subsequent melting curves of both iPP/GO and neat iPP sample with different annealing procedures. As is shown in Fig. 3a, the crystallization peak temperature of iPP/GO-0 min is around 114.9 °C while that of iPP-0 min is 112.6 °C. This 2.3 °C rise indicates an acceleration in crystallization, which can be attributed to the heterogeneous nucleation

![Fig. 1. Morphologies development of iPP/GO-0 min and iPP/GO-30 min samples crystallized isothermally at 135 °C.](image-url)
induced by GO. However, despite of the melt annealing-induced distinct variation in POM observation, the nonisothermal crystallization behavior of iPP/GO with different annealing procedures at 200 °C shows no evident difference. The DSC melting curves of samples with different annealing procedures in Fig. 3b exhibit the similar results as well. These results suggest that the effect of annealing on the crystallization behavior, although obvious in isothermal crystalline morphology, may be not significant enough to be detected in DSC nonisothermal scanning at a relatively fast scanning rate.

To confirm the annealing-induced change in crystallization behavior of iPP/GO composite observed in POM experiments, DSC isothermal crystallization was also carried out at the temperature of 135 °C, which is the same as that of POM observation. The crystallization curves of both iPP/GO and neat iPP with annealing at 200 °C for different time are shown in Fig. 4. The half crystallization time \( t_{1/2} \) of iPP/GO-0 min is ca. 905 s, while that of iPP/GO-5 min is ca. 1233 s. We can see clearly that the crystallization rate of iPP/GO composite decreases obviously after annealing. The \( t_{1/2} \) of iPP/GO shows no further variations with annealing time increasing from 5 min to 30 min, which might suggest that the annealing induced change in iPP/GO composite is accomplished with 5 min at 200 °C. Comparatively, the crystallization of iPP with different annealing procedures ends at ca. 5000 s and shows no evident change, which indicates that melt annealing has no significant influence on the isothermal crystallization behavior of iPP. These results demonstrate that melt annealing will result in a decrease in the number of nucleation sites and deceleration of crystallization of iPP/GO composite but have no evident impact on the crystallization of neat iPP, which is consistent well with that of POM observations. Our TEM results of iPP/GO-0 min and iPP/GO-30 min showed that GO sheers were well exfoliated and dispersed in the iPP matrix of both samples, which excluded the influence of annealing on GO dispersion (see Supporting Information Figure S1). Therefore, we can conclude from our results that the significant difference may be closely related with the chemical structural changes GO during annealing.

Considering the possible structural change of GO sheets, various studies have demonstrated that GO can be reduced at relatively low temperatures [30–33]. The annealing temperature in our experiment is 200 °C and GO may be possible to be reduced during the

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**Fig. 2.** Morphologies development of iPP-0 min and iPP-30 min samples isothermally crystallized at 135 °C.

**Fig. 3.** Nonisothermal crystallization (a) and melting (b) curves of iPP/GO and neat iPP samples with different annealing procedures.
annealing process. Following the method developed by Glover and Schniepp et al. [31], we also studied the reduction of GO at low temperatures using DSC scanning and found that GO used in this study could be reduced in the atmosphere of N2 at temperatures ranging from 100 to 250 °C (see Supporting Information, Figure S2). Although the reduction of GO can proceed at different temperatures in various polymer matrixes as revealed in our previous study [33], we suppose that, in the present study, GO will be probably reduced in iPP when annealing at 200 °C for 30 min. The in situ thermal reduction of GO in iPP matrix may be the key reason for the melt annealing induced change in iPP/GO crystallization.

3.3. Role of reduction of GO on the alteration in crystallization behavior

From the above result, we deduce that the variation of iPP/GO crystallization results from the in situ reduction of GO during annealing. It is well known that GO can be simultaneously reduced and exfoliated when heated to a relatively high temperature (ranging from 550 to 1100 °C) under Ar or H2 and the extent of reduction is in close relation with the temperature [41–43]. At low temperatures, reduction is only the removal of a small amount of oxygen-containing groups that can easily drop and those in strong interaction with GO surface still remain on the sheets. These residual oxygen-containing groups can only be removed at higher temperatures. That is to say the RGO already reduced at a higher temperature should not be further reduced when heated again at a lower temperature. If our deduction makes sense, then melt annealing process will have little effect on the crystallization of iPP with RGO reduced at high temperatures. Based on these considerations, RGO with a high degree of reduction was prepared by annealing GO at 800 °C for 1 h in a tube furnace. The C:O ratio of RGO is 18.1, which is much higher than the 2.2 of GO (see detailed XPS structural comparison of GO and RGO in Supporting Information, Figure S3). Through studying the effect of anneal on the crystallization behavior of iPP/RGO composite, we are able to confirm the role of reduction of GO on the annealing induced alteration in crystallization behavior of iPP/GO composite.

The crystalline morphologies of iPP/RGO composite were observed by POM. Comparing the POM observations of iPP/RGO
(Fig. 5) with that of iPP/GO and neat iPP (Figs. 1 and 2), it can be found that the crystalline morphology evolution of iPP/RGO with different annealing procedures differs greatly from that of iPP/GO. Firstly, the number of nucleation sites stays almost unchanged with different annealing procedures. Secondly, the rate of spherulite growth is slower than that of iPP/GO but still faster than that of neat iPP. This difference can be further proved by isothermal and non-isothermal crystallization behavior characterized by DSC. As shown in Fig. 6a, anneal has little effect on the isothermal crystallization behavior of iPP/RGO even for samples annealed at 200 °C for 30 min under what condition the iPP/GO sample has already shown evident changes. Nonisothermal crystallization behavior in Fig. 6b also shows no big difference with different annealing process. All these results suggest that anneal has no significant influence on the crystallization of iPP/RGO composite, which is different from that of iPP/GO. To further confirm the influence of reduction extent of GO on iPP crystallization, additional experiments were also performed on iPP/GO composites containing GO with two different reduction extent (Figure S4 in Supporting Information). With the same procedures, it was found that the iPP/GO with a lower reduction extent has stronger crystallization abilities than that with a higher reduction extent. Combining all these results, it can be confirmed that it is the annealing induced in situ reduction of GO in iPP matrix that result in the deceleration of crystallization of iPP/GO.

3.4. Changes in conformation ordering of iPP/GO crystallization investigated by temperature dependent FTIR

The change in annealing-induced crystallization behavior of iPP/GO should be accompanied by the alteration in the conformation ordering. FTIR has already been proved to be a powerful and sensitive method to study the conformation ordering of iPP molecular chains during crystallization [39,44–46]. Therefore, we adopt this method to detect the crystallization process of iPP/GO sample with different annealing procedures, aiming to explore the influence of melt annealing on conformation changing of iPP/GO during crystallization. Fig. 7 gives the temperature dependent FTIR spectra recorded during crystallization of iPP/GO with different annealing procedures. As temperature decreases, intensity changes and band shifts of the crystalline-sensitive bands apparently occur, indicating the beginning and evolution of crystallization.

The IR bands of different wave numbers refer to 31 helical structures of different order degree, which can be used to evaluate the conformation evolution of iPP molecular chains [46]. During crystallization, short helices must experience some transformation to construct longer helices. According to Doi-Edward’s dynamics theory, the critical persistence length of iPP for isotropic-to-nematic transition is 11 monomers in helical conformation [47,48]. The conformational band corresponding to 10 monomer units is 998 cm⁻¹, which is therefore reasonably chosen for statistical analysis of the conformation evolution during crystallization. The 1303 cm⁻¹ bond corresponding to the helical length with 13 monomers can be taken as the crystalline signal.

Following Li’s method [39], in order to evaluate the degree of conformation ordering and the development of crystals, semi-logarithm curves of I₉₉₈ with the development of I₁₃₀₃ for iPP/GO composite with different annealing procedures were calculated according to FTIR spectra in Fig. 8. At the initial stage, the I₉₉₈ deviates positively from I₁₃₀₃, which suggests that conformational ordering does occur prior to crystal growth. With temperature decreases, conformational ordering and crystal growth develop synchronously because of continuously packing of long helices into a crystal lattice or lamellar layer. However, it is interesting to find that the increase of I₉₉₈ with the development of I₁₃₀₃ for iPP/GO-
30 min is less salient than that of iPP/GO-0 min. This deviation indicates the degree of conformational ordering during crystallization lowers with the introduction of anneal. According to Li et al., the presence of GO sheets facilitates the formation of long helical segments and therefore leads to a considerable enhancement in crystallization of iPP [39]. In our experiment, the annealing induced decrease of conformational ordering indicates that the partial removal of oxygen-containing groups and a change in the graphitic network of sp² bonds on GO sheets may make GO, which are partially reduced at low temperatures, less favorable for the formation of long helical segments than original GO and therefore result in a negative influence of annealing on the heteroatomic nucleation of iPP.

4. Conclusions
In this work, we systematically studied the influence of annealing on the crystallization behavior of iPP/GO composite by POM and DSC. It was found that the decrease in both the number of nucleation sites and the overall crystallization rate after melt annealing might be caused by the in situ thermal reduction of GO in PP matrix. Combining further results of comparative experiments carried out on neat iPP and iPP/RGO and temperature dependent FTIR, we suppose that the reduction-induced partial removal of oxygen-containing groups and a change in the graphic network of sp² bonds on GO sheets may be probably the reason for the negative influence of annealing on iPP/GO crystallization. Our work demonstrates the non-ignorable change in chemical composition and properties of polymer composite during processing, which is of great importance for determining proper processing conditions and optimizing the final properties.

Acknowledgments
We gratefully acknowledge the financial support from the Natural Science Foundation of China (Nos. 21174032 and 51373042).

Appendix A. Supplementary data
Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.06.003.

References

Fig. 8. Normalized intensity of the 998 cm⁻¹ band with the evolution of the normalized intensity of the 1303 cm⁻¹ band during crystallization process for iPP/GO with different annealing procedures.