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Morphologies of iPP induced by its partially carbon-coated homogeneity fibers

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Abstract

Homogeneity fiber/matrix composites of isotactic polypropylene (iPP) were prepared with both partially carbon-coated and non-carbon-coated iPP fibers. Their morphologies produced by melt recrystallization were studied by means of polarized optical microscopy. The results show that through vacuum evaporating a thin carbon film partially on the surface of iPP fiber, the nucleation ability of the molten iPP matrix during the course of recooling has been enhanced tremendously. The early formation and high density of the iPP row nuclei formed along the partially carbon-coated iPP fibers lead to the formation of an apparent iPP transcrystalline zone in the vicinity of its precoated fiber. The high nucleation ability of the carbon-coated iPP fiber towards its homogeneity matrix may originate from the surface fixing effect of the vacuum evaporated carbon layer on the polymer samples.

Keywords: Isotactic polypropylene; Fiber/matrix composite; Vacuum carbon evaporation

1. Introduction

Polymer based fiber/matrix composites have attracted much attention in the past few decades. It was well known that the resulting interfacial morphologies between the fibers and the polymer matrices have profound influence on the mechanical properties of the semicrystalline polymer composites [1–5]. Therefore, much effort has been devoted to investigating the origin and development of the interfacial morphologies of the fiber/polymer composite systems [6–15]. Among them, the interfacial morphologies of isotactic polypropylene (iPP) generated by various fibers, such as PTFE, carbon, Kevlar, glass, and PET fibers, have been most extensively studied [6–12].

In the past few years, due to the expected ideal recyclability and interfacial bonding, a growing interest in homogeneity fiber reinforced polymer composites was seen. Up to now, a number of investigations have been conducted on such self-reinforced polymer composites, which include polyethylene fiber reinforced polyethylene composites [16–22] and polypropylene fiber reinforced polypropylene composites [23]. In our recent work, through introducing iPP fibers into their supercooled homogeneity matrix, the interfacial morphologies of the self-reinforced iPP system have been studied in detail [24,25].

On the other hand, in our previous work on the recrystallization behavior of carbon-coated preoriented polymer thin films, it was found that the vacuum evaporated ultrathin carbon layer on the top surface of highly oriented polymer thin films can preserve their high orientation after complete melting and recrystallization [26–28]. This has been explained in terms of surface fixing confined recrystallization, namely, the vacuum evaporated carbon layer has a strong fixing effect on the thin polymer films. This has prevented the surface monolayer extended macromolecular stems previously included in the crystalline lamellae from melting or at least from a complete relaxing during the high temperature annealing. These locally ordered extended macromolecular bundles may act as self-nuclei during the course of recooling and initiate the oriented recrystallization. This kind of fixing effect may also be expected for the vacuum carbon evaporated iPP fibers.

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But a direct morphological study on the carbon-coated fibers has its difficulty. Considering that the interfacial morphologies of fiber reinforced polymer systems have already been well documented, morphological studies on homogeneity fiber/matrix systems composed of partially carbon-coated fibers, e.g. vacuum evaporating the top side of the cylindrical fibers, may provide us some indirect information about the influence of vacuum evaporated carbon layer on the melt recrystallization behavior of the highly oriented polymer fibers.

The purpose of this paper is to present some detailed information about the experimental setup and the melt recrystallization produced morphologies of the iPP fiber/-matrix homogeneity composite systems with the iPP fibers being partially carbon-coated.

2. Experimental

The matrix polymer used in this work was iPP, GB-2401, with melting flow index of 2.5 g/10 min and melting temperature of 170 °C, produced by Yanshan Petroleum and Chemical Corporation, China. The granular iPP materials were used without any additional treatment. The iPP matrix films, with a thickness of 30 ~ 50 μm, were prepared by hot-pressing the iPP pellets at 190 °C for 10 min and then quenched to room temperature. The iPP fibers, with diameter of about 20 μm and melting point of ~170 °C, were produced by a home-made melt-spinning device at temperatures of 200 ~ 240 °C. The resulting iPP fibers were then subjected to a cold-draw procedure at 110 °C with a draw ratio of 6. To remove the sizing agents on the fiber surface, the fibers were rinsed for 4 h in a distillation flask with acetone and then dried in a vacuum oven at 40 °C for 24 h.

To prepare the aforementioned iPP homogeneity composites, the iPP fibers with both ends fixed on a glass slide were first vacuum evaporated with a thin carbon layer (Fig. 1(a)), and then either transferred onto the surfaces of the compression molded iPP films supported by glass slides (Fig. 1(b)) or sandwiched between two pieces of compression molded iPP films (Fig. 1(c)). To get a direct comparison, iPP fibers free of carbon coating were also used in some of the samples. The samples thus prepared were subsequently melt-recrystallized at different conditions.

For polarized optical microscopic (POM) observation, an Olympus BH-2 optical microscope equipped with a Mettler FP52 hot stage was employed. The isothermal crystallization was conducted by melting the stacked sample at 190 °C for 10 min and then kept at 140 or 135 °C for in situ observation. The constant cooling process was carried out by heating the composite sample to 190 °C for 10 min and subsequently cooled at a rate of 1 °C/min to room temperature.

Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo Star^e thermal analyzer. The pure iPP fiber and carbon-coated iPP fiber were measured individually at a heating/cooling rate of 10 °C/min. The weight of both samples was 1.5 mg.

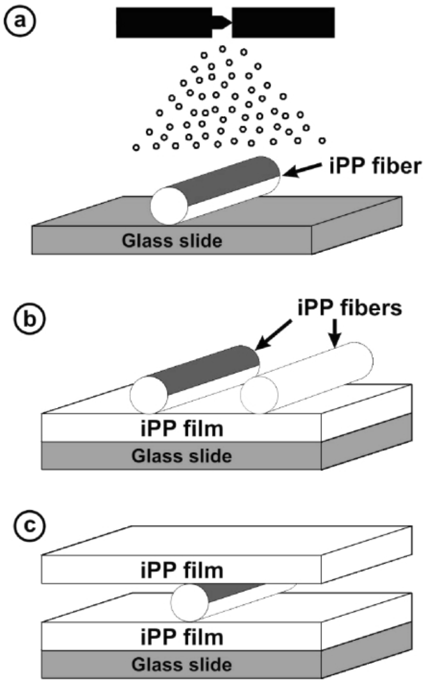

Fig. 1. A schematic diagram shows the sample preparation process.

3. Results and discussion

Fig. 2 shows a series of POM micrographs of a homogeneity iPP fiber/matrix composite. The sample was prepared according to the procedure shown in Fig. 1(a) and (b). Fig. 2(a) presents an optical micrograph of the as prepared sample. Two iPP fibers ca. 75 μm apart from each other were parallel aligned in the sample. The left one is carbon-coated, while the right one is free of carbon coating. When the composite was heated to 190 °C, the whole visual field became dark (Fig. 2(b)). This is not beyond expectation, since this temperature is well above the melting temperatures of both the iPP fibers and matrix film and therefore no iPP crystals can survive at such a condition. As shown in Fig. 2(c), after the sample was quenched from 190 to 135 °C and kept at this temperature for 10 min, a row of small iPP spherulites were formed along the axis of the partially carbon-coated iPP fiber. There is, however, no detectable change in the position of the bulk iPP fiber. This clearly demonstrates that the nucleation of iPP in contact with its carbon-coated fiber is more favorable than that in contact with its non-carbon-coated fiber. As the crystallization continues, the small spherulites generated by the carbon-coated iPP fiber propagate towards the remaining non-crystallized area. Since spherulitic segments from the nuclei densely spaced along the carbon-coated iPP fiber axis mutually hinder their lateral growth, the crystallites can only

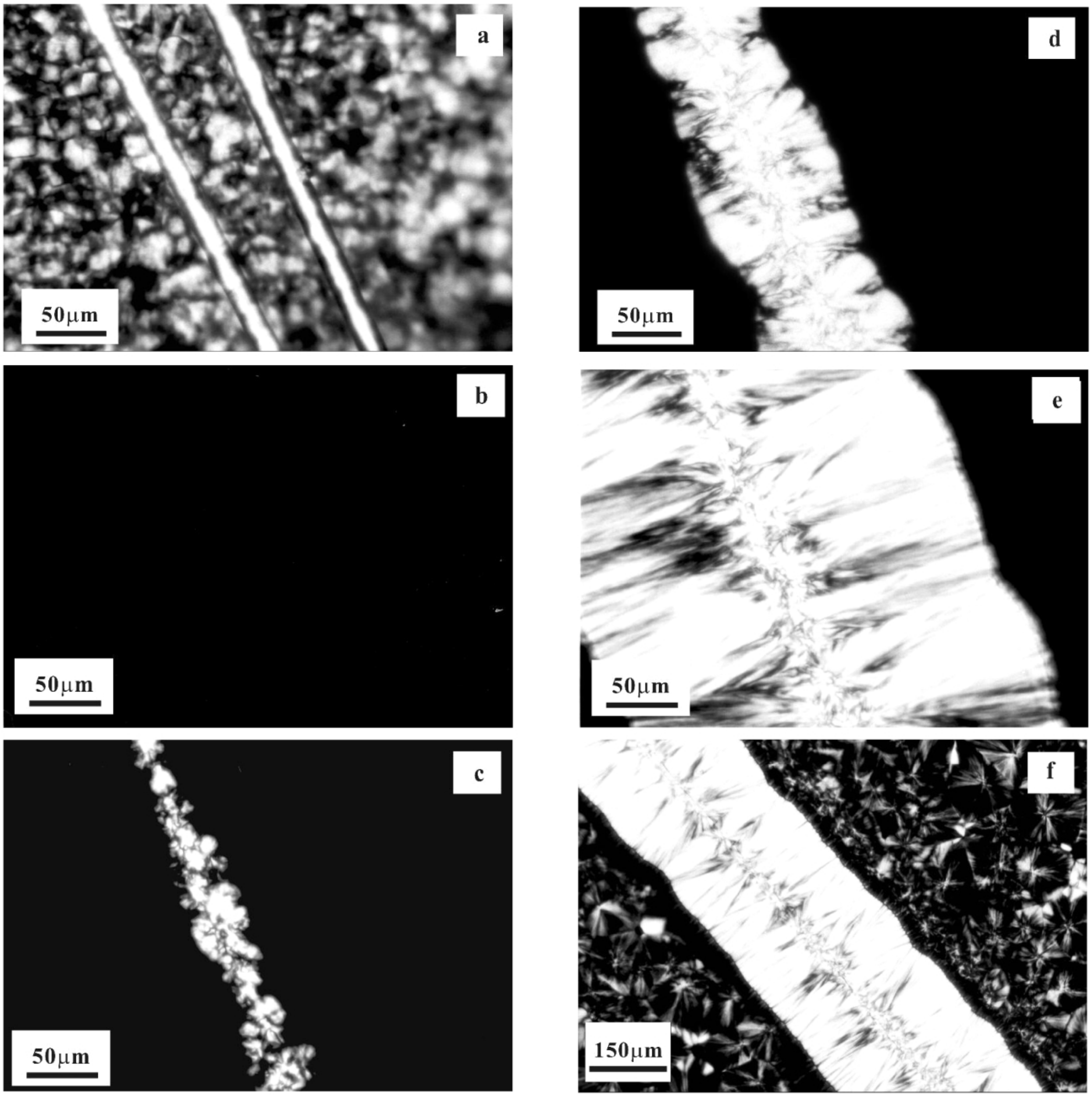

Fig. 2. (a) POM micrograph of an iPP fiber/matrix homogeneity composite containing two iPP fibers. The fiber on the left side is carbon-coated iPP, while the one on the right side is free of carbon coating. The sample was heated to 190 °C for 10 min (b), subsequently isothermally crystallized at 135 °C for 10 min (c), 30 min (d), 90 min (e), and finally quenched to room temperature (f).

grow in the direction perpendicular to the fiber axis. As a result, a transcrystalline growth front has emerged parallel to the axis of the carbon-coated iPP fiber (Fig. 2(d)). After 90 min isothermal crystallization, Fig. 2(e), a ca. 125 μm transcrystalline layer has been developed, while the remaining area was still in the molten state. It should be pointed out that the transcrystalline zone has already grown across the position where the non-carbon-coated iPP fiber located. This means that the non-carbon-coated iPP fiber exhibits no nucleation capacity towards the iPP matrix at all and is now rearranged in the transcrystalline zone. By taking the sample out of the microscope hot stage, the remaining iPP melt crystallizes rapidly and forms a great number of small spherulites (Fig. 2(f)). From the above results, it can be concluded that iPP fiber partially covered with vacuum evaporated thin carbon layer can conspicuously promote the nucleation and crystallization of iPP.

The above mentioned morphological features have also been observed in the samples subjected to repeated melting and recrystallization process. As an example, Fig. 3 presents the POM micrographs of the same iPP fiber/matrix homogeneity composite used for Fig. 2, which was heat-treated at 190 °C again for 10 min and then cooled at a rate of 1 °C/min to room temperature. As in the case of Fig. 2,

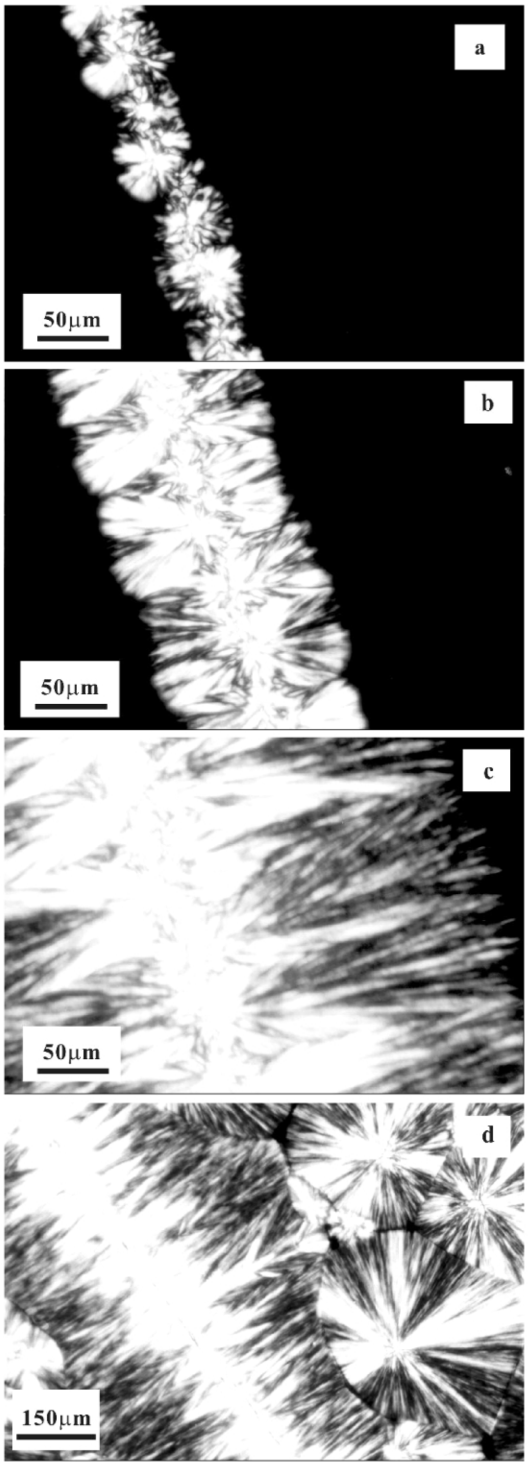

Fig. 3. POM micrographs of the same sample as used in the case of Fig. 2, which has been heat-treated at 190 °C again for 10 min and then cooled at a rate of 1 °C/min to room temperature. The pictures were taken at (a) 130, (b) 125, (c) 120, and (d) room temperature.

when the sample was heated to 190 °C, the birefringence of the whole sample disappeared and the view field became completely dark. During the cooling process, when the temperature reached 130 °C, a strip of row nuclei appeared along the axis of the previously carbon-coated iPP fiber, Fig. 3(a). This resembles what happened in the isothermal crystallization condition and indicates an early nucleation of the iPP in contact with the vacuum evaporated carbon layer. With the further decrease of temperature, the microspherulites propagate gradually towards the direction perpendicular to the fiber axis. As a result, a transcrystalline growth front appeared (Fig. 3(b) and (c)). As the crystallization of iPP completed, Fig. 3(d), a morphological structure consisting of a transcrystalline zone around the carbon-coated iPP fiber and some spherulites far away from the carbon-coated iPP fiber was observed. This again indicates that the vacuum evaporated thin carbon film has enhanced the crystallization ability of the iPP matrix during the melt-recrystallization process.

It should be pointed out that in the above experiments, both the iPP fibers with and without carbon coating were simply placed on the top surface of the iPP compression molded film. In order to get some more information about the influence of partially vacuum carbon evaporated iPP fibers on the melt crystallization behavior of its homogeneity matrix, the isothermal recrystallization process of sandwich samples, in which the iPP fibers with and without carbon coating were embedded between two pieces of compression molded iPP films (Fig. 1(c)), was also studied. Fig. 4 shows the POM micrographs of the sandwich samples, which were first heat-treated at 190 °C for 10 min, then crystallized isothermally at 140 °C for 4 h, and finally quenched to room temperature on air. Fig. 4(a) and (b) show apparently the difference between morphologies of the two composite samples. For the sample comprising non-carbon-coated iPP fiber, Fig. 4(a), there are several big spherulites sporadically dispersed in the iPP matrix. The dimension of the iPP spherulites is about 350 μm. In the sample composed of partially carbon-coated iPP fiber, there is, however, a very clear transcrystalline zone around the axis of the carbon-coated fiber (Fig. 4(b)). The transcrystalline morphology has a close resemblance with that observed in Fig. 2(f). In the area far away from carbon-coated iPP fiber, there are also a few spherulites randomly dispersed in the iPP matrix. Because of the exactly identical thermal condition of the two samples, the size of the spherulites shown in Fig. 4(a) and (b) is the same. From this contrast experiment, it can be seen once again that the vacuum deposited carbon has a striking effect on the melt recrystallization behavior of the iPP fiber/matrix homogeneity composites, regardless of how the partially carbon-coated fibers are placed in the composites.

From all of the aforementioned results, it can be concluded that vacuum evaporating a thin carbon layer partially on the surface of iPP fibers can evidently enhance the crystallization ability of the relating composites during the subsequent melt recrystallization process. One may suggest that the observed phenomenon is caused by the well known superheating or memory effects. But considering that (i) the birefringence of both iPP fibers and matrix has completely disappeared at 190 °C under crossed polarizers,

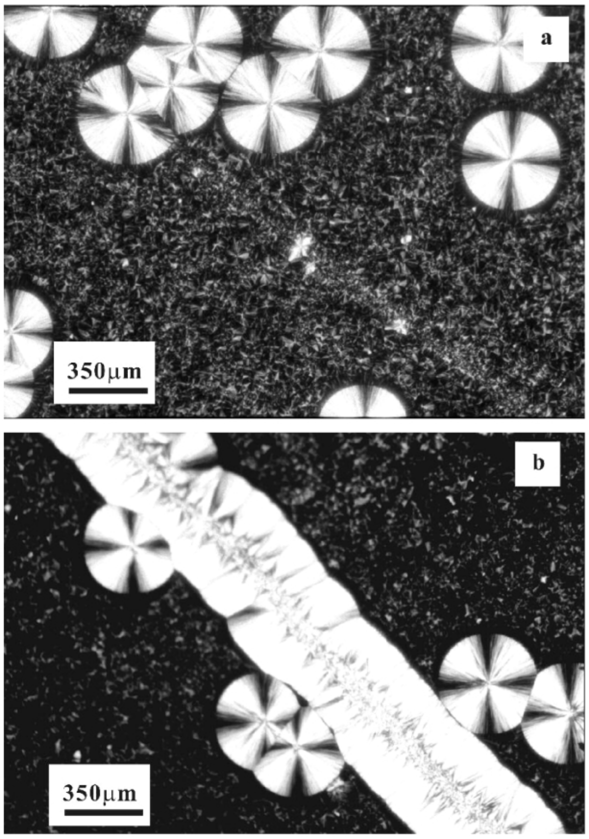

Fig. 4. POM micrographs of the iPP fiber/matrix homogeneity composites with the iPP fibers embedded between two pieces of compression molded iPP films. The fiber in (a) is free of carbon coating, while that in (b) is partially carbon-coated. Both samples were heat-treated at 190 °C for 10 min and then crystallized isothermally at 140 °C for 4 h before quenched to room temperature.

and (ii) the iPP fibers free of carbon evaporation exhibit no nucleation capacity towards iPP matrix at present experimental conditions, it is fair to state that the strong nucleation ability of partially carbon-coated iPP fiber towards its homogeneity matrix does not originate from the superheating and/or memory effects. Consequently, other mechanisms should be discussed here.

It should be pointed out that transcrystalline crystallization is frequently observed in the case of inorganic or high-melting-temperature (higher than the T_m of iPP film) polymeric fiber reinforced heterogeneity iPP composites. For these systems, the fibers remain in solid state during processing, and interfacial stresses may be expected during the cooling process of the composites due to the different thermal expansion coefficient. Therefore, transcrystalline nucleation is assumed to be induced by these interfacial stresses [10,11]. In the present case, except for the vacuum evaporated carbon layer, the fibers and matrix materials are all molten. But the studies on the crystallization behavior of iPP placed simply on the preformed carbon supporting film show that the vacuum evaporated carbon layer has no detectable nucleation efficiency towards iPP. On the other hand, the molten fibers and matrix are of the same materials and have exactly the same thermal expansion behavior. This clearly indicates that the transcrystalline crystallization observed here differs from that of the heterogeneity fiber reinforced thermoplastic polymers.

As mentioned in the Section 1, it was reported that vacuum evaporating a thin carbon layer on the top surface of highly oriented ultrathin polymer films can maintain their high degree of orientation after complete melting and recrystallization [26–28]. Systematic studies on the orientation fixing effect have recognized a strong fixing effect of vacuum evaporated carbon layers on the polymer films. Although the exact mechanism of the fixing effect of vacuum evaporated carbon layers on the thin polymer films is not quite clear yet, the recognition of the fixing effect has helped to explain the oriented recrystallization phenomenon of the carbon coated pre-oriented thin polymer films. That is to say, the vacuum evaporated carbon layer on the polymer thin film has prevented the surface extended macromolecular stems previously included in the crystalline phase from relaxing during high temperature annealing. These locally ordered macromolecular stems have, in turn, induced the oriented recrystallization of the thin polymer molten layer. In the present case, the same fixing effect of the directly vacuum evaporated carbon layer on the iPP fibers should exist. The fixed locally ordered iPP chain stems may act as self-nuclei during the course of recooling and result in an early crystallization of the molten iPP at a higher temperature. As a result, row nuclei along the partially carbon-coated iPP fiber are generated.

To check the validity of the above discussion, DSC measurements were performed for the iPP fibers with and without carbon coating. In Fig. 5 the DSC cooling curves of both samples with the same weight and thermal history are presented. Clearly, both the onset crystallization

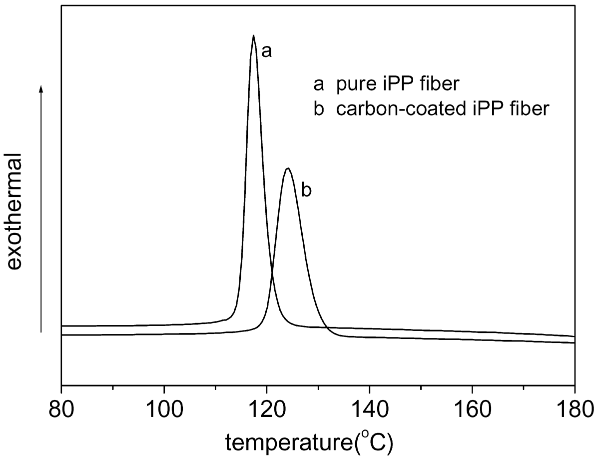

Fig. 5. DSC cooling curves of iPP fibers with and without carbon coating. Both samples were heated to 190 °C for 10 min and subsequently cooled at a rate of 10 °C/min to room temperature. (a) Pure iPP fiber, (b) carbon-coated iPP fiber.

temperature and the peak crystallization temperature of the carbon-coated iPP fiber are much higher than those of its non-carbon-coated counterpart. Through carbon evaporation, the onset crystallization temperature of the iPP fiber shifts from 121 to 130 °C, while the peak crystallization temperature shifts from 117 to 124 °C. This indicates unambiguously that the recrystallization of carbon-coated iPP fiber during the recooling process takes place at a higher temperature and confirms the above explanation of the POM investigations.

4. Conclusions

In conclusion, POM observations show that the recrystallization of the iPP in the vicinity of the carbon-coated iPP fiber starts much earlier than that in the areas with the non-carbon-coated iPP fiber and bulk iPP matrix. The early formation and high density of the iPP row nuclei formed along the partially carbon-coated iPP fibers lead to the formation of an apparent transcrystalline zone of the iPP in the vicinity of its precoated fiber. DSC measurements indicate that the recrystallization of the carbon-coated iPP fiber takes place at a temperature 9 °C higher than that of the iPP fiber free of carbon coating. All of these unambiguously demonstrate that through vacuum evaporating a thin carbon layer partially on the surface of iPP fiber, the nucleation ability of the iPP in the homogeneity fiber/matrix composite has been enhanced tremendously during the recrystallization process. The high nucleation ability of the carbon-coated iPP fiber towards its homogeneity matrix may originate from the surface fixing effect of the vacuum evaporated carbon layer on the polymer surface. In other words, the vacuum evaporated carbon layer on the surface of iPP fibers has fixed the surface monolayer well ordered iPP chain stems included in the crystalline state and prevented them from melting or at least a complete relaxing during high temperature annealing. These extended or relatively extended iPP chain stems, in turn, act as self-nucleation sites during the course of recooling and induce an early crystallization at higher temperature.

Acknowledgements

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