

Combined Effects of Stretching and Nanofillers on the Crystalline Structure and Mechanical Properties of Polypropylene and Single-walled Carbon Nanotube Composite Fibers*

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Abstract The combined effects of stretching and single-walled carbon nanotubes (SWCNTs) on crystalline structure and mechanical properties were systematically investigated in melt-spun polypropylene (PP) fibers prepared at two different draw ratios. The dispersion, alignment of the SWCNT bundles and interfacial crystalline structure in the composite fibers are significantly influenced by the stretching force during the melt spinning. The nanohybrid shish kebab (NHSK) superstructure where extended PP chains and aligned SWCNT bundle as hybrid shish and PP lamellae as kebab has been successfully obtained in the composite fibers prepared at the high draw ratio and the related formation mechanism is discussed based on the results of morphological observations and 2d-SAXS patterns. Large improvement in tensile strength and modulus has been realized at the high draw ratio due to the enhanced orientation and dispersion of SWCNT bundles as well as the formation of NHSK.

Keywords: Stretching; SWCNTs; Nanohybrid shish kebab; Mechanical properties.

INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) possess impressive mechanical performances, such as the Young's modulus of 1TPa and the tensile strength of 150 GPa^[1–3], and thus, are theoretically an ideal candidate to prepare the polymer-based composites with high mechanical properties^[4–6]. However, most investigations of the SWCNT-reinforced polymers did not show a substantial improvement in mechanical properties, only modest enhancements were achieved and it was demonstrated that the remarkable reinforcement of SWCNT in polymer matrix not only relied on its excellent intrinsic properties, but also on the SWCNT dispersion and alignment and especially the interfacial adhesion between the SWCNT and matrix^[7–10]. Generally, it is considered that the chemical-bond formation between the carbon nanotubes (CNTs) and the polymer matrix could be an effective way to produce a strong interface, and some investigations have proven that the CNTs grafted with polymers in composites exhibit a strong interfacial adhesion^[6, 11, 12]. However, the chemical functionalization might introduce some defects on CNT surfaces or/and shorten the CNTs and thus lower the intrinsic mechanical and electrical properties of CNTs. In addition, the common non-covalent functionalization using surfactant, oligomers and polymer to wrap CNTs usually exhibits a weak CNT-polymer interfacial adhesion^[13, 14]. Thus, the continued challenge is to develop a new and efficient physical way to control the CNT-polymer interface.

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In semicrystalline polymer/SWCNT systems, SWCNT was reported as a good nucleating agent and could efficiently template the orientated polymer crystallization^[15–17]. The induced structure might bring a strong interfacial adhesion and thus it is of particular interest for scientists. One of the typical structure of semicrystalline polymer patterning SWCNTs is nanohybrid shish kebab (NHSK) superstructure first observed by Li *via* solution crystallization where the nanotubes act as shish and PE lamella serves as kebab^[18]. However, such a NHSK superstructure is mostly obtained in strict solution crystallization procedure. It is more interesting and important to replicate such a NHSK superstructure in polymer/SWCNT composites *via* melt blending method for an applicable composite with high mechanical performance.

On the other hand, the most successful polymers used to prepare NHSK superstructure are generally in a planar zigzag conformation, such as PE^[19–20], PVA (poly(vinyl alcohol))^[21], PA66 (nylon 66)^[22], PVDF (poly(vinylidene fluoride))^[19], PBT (poly(butylene terephthalate))^[15]. It is difficult to form NHSK for the polymers with a helical conformation due to their large diameter which hinders a close contact between the polymer chains and CNTs, and therefore the alignment of polymer chains on CNTs surface is difficult^[23–25]. Recently, it has been reported that SWCNT bundles can facilitate the orientation of polymer chains and thus are helpful to form the NHSK formation with helical polymer *via* solution crystallization method^[26]. Besides, the external flow, which commonly exists in common polymer processing has been proven helpful in inducing the polymer chains with a coiled conformation to undergo a coil-to-stretch transition and producing oriented nuclei in a lower nucleation barrier^[27, 28], thus enhancing the crystallization process. So, it is meaningful to explore the possibility to obtain the NHSK superstructure by using polymer with a helical conformation combining the influences of the existences of SWCNT bundles and extensional flow. We believe the results can enlarge the application of NHSK in polymer composites.

In current work, PP with a helical conformation is chosen as the matrix and melt-spinning technology is used to prepare PP/SWCNT composite fibers. We mainly focus on the effect of stretching on the dispersion, alignment of SWCNTs in the fibers and especially the possible crystalline structures in the composites. Furthermore, the relationship between the structure and mechanical properties is also discussed.

EXPERIMENTAL

Materials

Isotactic polypropylene (*i*PP) (T30S), $M_w = 39.9 \times 10^4$ g/mol and $M_w/M_n = 4.6$, was supplied by Dushanzi Petroleum Chemical Incorporation (Xinjiang, China).

Single-walled carbon nanotubes (SWCNTs) were purchased from Chengdu Institute of Organic Chemistry of the Chinese Academy of Science (Chengdu, China) with purity of more than 90 wt%. The as-received SWCNTs stack together as bundles due to strong Van der Waals' interaction between the tube walls^[29], as shown in Fig. 1. The average diameter and length of SWCNTs was 1–2 nm and 50 μ m, respectively.

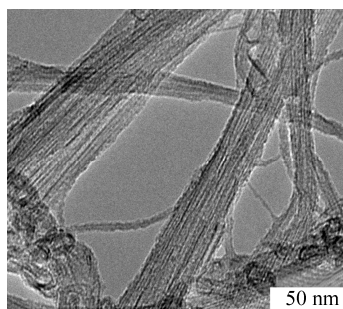


Fig. 1 The TEM image of the morphology of pristine SWCNTs

Sample Preparation

Polypropylene and SWCNTs (2 wt%) were first melt blended in an internal mixer (Rheocord 9000, Haake Co., Ltd. Germany) and then the mixture was diluted to 0.5 wt% SWCNTs content by a TSSJ-25 co-rotating twin-screw extruder with the barrel temperature of 170–200 °C and the screw speed of 120 r/min, and then pelletized as granules. The pure *i*PP was also processed in the same procedure as the control group. After dried for 12 h in a vacuum oven, the granules were melt spun into monofilaments at 200 °C by using a capillary rheometer (Rosand RH70, Malvern, Bohlin Instruments) with a die diameter of 1.0 mm and length-to-diameter ratio of 16. All the extruded composite fibers were air-cooled and collected under tension by a windup spool. By adjusting the take-up speed, fibers at two different draw ratios were prepared. The draw ratio (DR) defined as the section area of the capillary die versus that of the fibers is about 20 for 20 m/min take-up speed and 200 for 150 m/min take-up speed which were served as the low draw ratio (DR-20) and high draw ratio (DR-200), respectively. The typical diameter is 70 μm and 240 μm for the fibers obtained through high and low draw ratio.

The as-spun fibers are labeled according to the draw ratio in a terse manner: for example, SPP-20 and SPP-200 represent the composite fibers with 0.5 wt% SWCNTs prepared at 20 and 200 draw ratios, respectively. In the same way, pure *i*PP fibers fabricated at the two different draw ratios are marked as PP-20 and PP-200.

Characterization and Measurements

An FEI Tecnai G2 F30 TEM (Transmission Electron Microscope) was used to obtain the high definition images of SWCNTs at an accelerating voltage of 200 kV.

Raman spectrum measurement was conduct on a micro-Raman spectrometer (Renishaw) equipped with a Leica microscope. The laser with 514.5 nm was excited by 136 M He+ resource. The laser power is 1.7 mW and the laser spot is 2 μm in diameter. To estimate the orientation of the SWCNTs in composite fibers, two measurements were carried out with the fiber parallel and perpendicular to the polarization direction of the laser light.

For direct observing the alignment of SWCNTs, the composite fibers were etched in xylene solution; and for characterizing the interfacial crystallization structure of the fibers, the melt-spun fibers were etched for 2 h in a solution containing 1.3 wt% potassium permanganate (KMnO₄), 32.9 wt% concentrated sulfuric acid (H₂SO₄) and 65.8 wt% concentrated phosphoric acid (H₃PO₄), according to the procedure proposed by Olley and Bassett^[30]. Both these etched samples were then coated with a layer of gold and observed by an FEI Inspect F scanning electron microscope (SEM) instrument at an acceleration voltage of 20 kV.

The 2D-SAXS measurements on a bundle of fibers were carried out with a Shanghai Synchrotron Radiation Facility. The radiation wavelength is 0.124 nm and the sample-to detector distance is 5120 mm. The orientation could be estimated by calculating the orientation parameter f combining formula (1) and (2):

$$f = \frac{3\langle \cos^2 \phi \rangle - 1}{2} \quad (1)$$

$$\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \sin \phi \cos^2 \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \quad (2)$$

Where ϕ is the angle between the normal direction of a given (hkl) crystal plane and the stretching direction, and $I(\phi)$ is the scattering intensity at ϕ .

A Perkin-Elmer Pyris I differential scanning calorimeter (DSC) with nitrogen as the protective atmosphere was used to investigate the melting and crystallization behavior of all the melt-spun fibers. The weight of each sample was about 5 mg. The sample was heated from 50 °C to 200 °C at a heating rate of 10 K/min and maintained at 200 °C for 5 min to erase the thermal history, and then cooled down to 50 °C at a cooling rate of 10 K/min. The overall degree of crystallinity (X_c) of the samples was calculated from the formula $X_c = \Delta H_i / \phi_i \Delta H_i^m$, where ΔH_i is the enthalpy of fusion of the samples, ϕ_i is the mass fraction of *i*PP matrix, and ΔH_i^m is

the enthalpy of fusion for 100% crystalline *i*PP, which is assigned as 209 J/g^[31].

The tensile tests for the fibers were carried out on an Instron 5567 universal testing machine with a 100 N load cell and a crosshead speed of 50 mm/min at room temperature (23 ± 2 °C). The gauge length was 10 mm and all the values were calculated as the average of at least five specimens for each composition.

RESULTS AND DISCUSSION

The Dispersion and Alignment of SWCNTs in Fibers

The uniform dispersion of SWCNTs is a fundamental premise for preparing high performance polymer composites. The cross section of the cryogenically fractured composite fibers was observed by SEM, and the results are shown in Fig. 2. One can clearly find some aggregates of SWCNTs (pointed by the black circles) in the surface of DR-20 composite fibers, as shown in Fig. 2(a). On the contrary, in Fig. 2(b), no obvious agglomerates can be observed, which suggests that the SWCNTs are relatively homogeneously dispersed in DR-200 composite fibers. Therefore, the increased stretching force at high draw ratio seems to be favorable to the dispersion of SWCNTs in *i*PP matrix. Such a phenomenon might be contributed to stress-induced-dispersion effort. As we know, during the melt-spinning, when a stretching force is applied along the fiber, the difference in the strain rate between fillers and matrix usually causes a vertical force to these SWCNTs when they are not parallel to the fiber according to the law of resolution of forces. This vertical force brings two possible consequences to the fiber: 1) rotating (aligning) the SWCNTs till they are parallel to the fiber; 2) the SWCNT aggregates separated (into bundles) during the rotating.

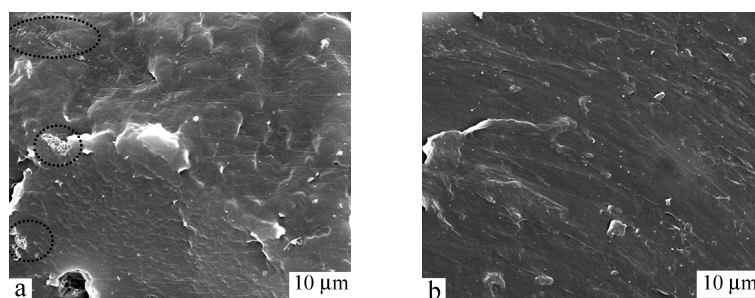


Fig. 2 SEM images for cross section of the fibers showing the SWCNTs dispersion in composite fibers prepared at (a) DR-20 and (b) DR-200

In order to characterize the alignment of the SWCNTs, the polarized Raman measurement was employed, and the spectra are shown in Fig. 3(a and b). The degree of the SWCNT orientation can be assessed by the intensity ratio of tangential mode G band at 1588 cm^{-1} in parallel and perpendicular to the fiber direction ($G_{//} / G_{\perp}$), which relies on the fact that the Raman intensity of tangential mode is sensitive to the polarization angle. Usually, the G band intensity reaches a maximum when the polarization direction of light is parallel to the SWCNTs and significantly decreases as the angle between the SWCNTs and polarization direction of light approaches to 90° . A ($G_{//} / G_{\perp}$) value close to unity indicates an isotropic morphology, whereas a value ($G_{//} / G_{\perp}$) higher than unity implies preferential orientation of CNTs along the fiber stretching direction. Comparing Figs. 3(a) and 3(b), one can see that the spectrum for SPP-200 shows a sharper peak at 1588 cm^{-1} , and the calculated $G_{//} / G_{\perp}$ is larger than that of SPP-20 (values are about 1.98 and 3.29 for SPP-20 and SPP-200, respectively). Therefore, except for improving the dispersion level, the higher stretching force also promotes SWCNTs to preferentially align along the fiber axis as expected. Another evidence for the preferential orientation of SWCNTs along the fiber axis can be confirmed by SEM observation of the etched SPP-200 fibers. As shown in Fig. 3(c), most SWCNTs, indicated by the red arrows, preferentially orient along the stretching direction.

Besides, the observed diameter of the SWCNT in Fig. 3(c) is about 20–50 nm which is much larger than that of a single SWCNT (1–2 nm) and approximately the diameter of the pristine SWCNT bundles. Therefore, the dispersed SWCNTs in the fibers are also in the form of bundles consisting of several individual SWCNTs due to the strong Van der Waals' interaction between the tube walls. Meanwhile, the surface of the SWCNT bundles is quite rough, which means the bundles are wrapped by *i*PP chains. It can partly indicate the good interaction between the SWCNTs and *i*PP matrix in composite fibers prepared at the high draw ratio.

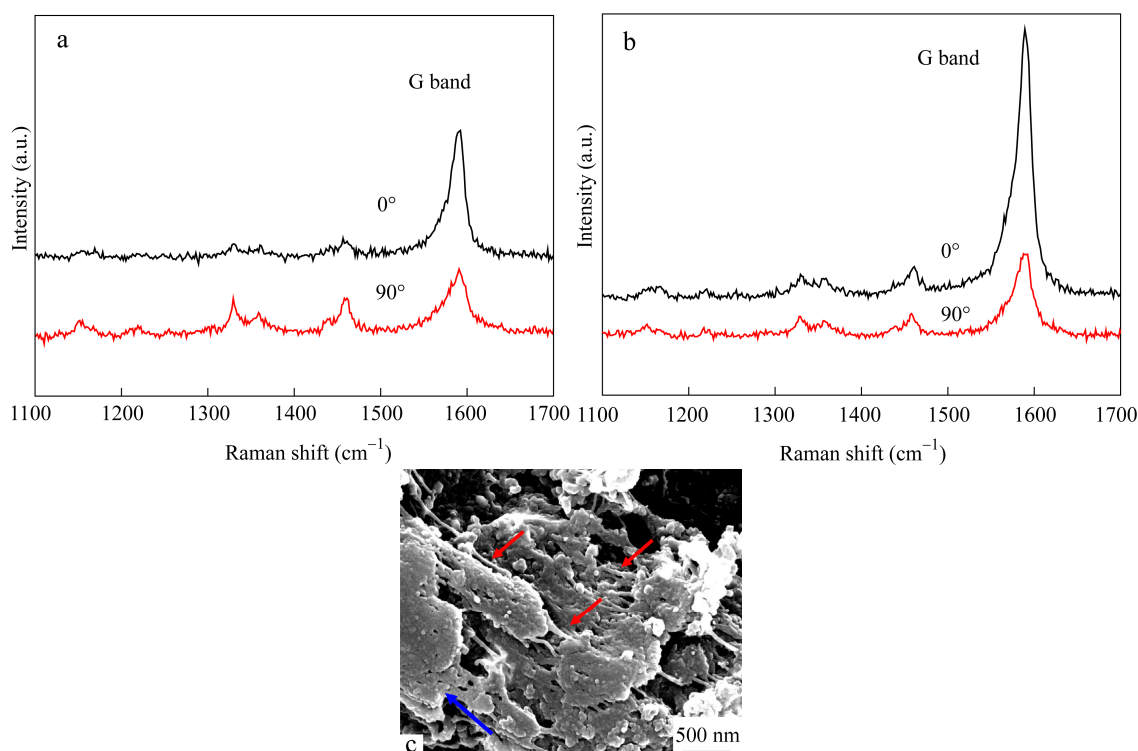


Fig. 3 Polarized Raman spectra of the composite fibers parallel and perpendicular to the polarization direction: (a) DR-20, (b) DR-200 and (c) the SEM image of SPP-200 after etched by xylene solution (The blue arrow shows the stretching direction.)

The Interfacial Crystalline Structure and Crystallization of *i*PP/SWCNT Composite Fibers

The interfacial adhesion between the two components in the *i*PP/SWCNT composites can be significantly affected by the interfacial crystalline structures. Therefore, the chemically etched composite fibers were then characterized by SEM, and the results are presented in Fig. 4.

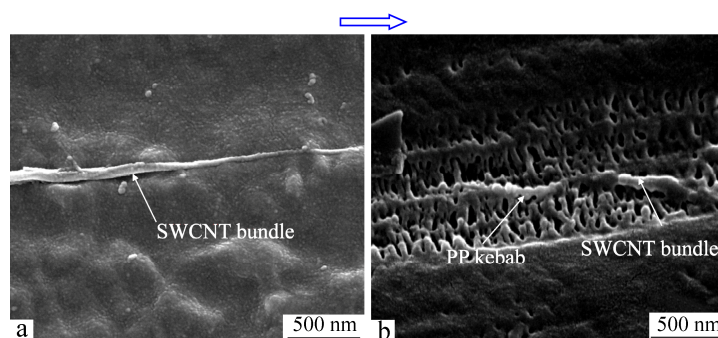


Fig. 4 SEM images of the typical interfacial crystalline morphology in (a) SPP-20 and (b) SPP-200 (The arrow presents the stretching direction.)

The typical shish-kebab structure along the stretching direction is clearly seen in SPP-200 (Fig. 4b) where the dense lamellae of *i*PP are perpendicular to the long axis of aligned SWCNT bundles. However, for SPP-20, only the relative smooth surface of a SWCNT bundle is observed (Fig. 4a). Therefore, the high stretching force during melt-spinning plays a key role in the formation of the NHSK superstructure in the composite fibers.

The two-dimensional SAXS technology was then performed to obtain the detailed information of the crystal structure formed during melt-spinning. Figure 5 presents the SAXS patterns of pure *i*PP and composite fibers, where the background scattering has been subtracted. And the lamellae orientation parameters (f) were calculated using Eqs. (1) and (2). The f for PP-20, PP-200, SPP-20 and SPP-200 are 0.58, 0.85, 0.78 and 0.88, respectively. Comparing these values, one can find that both the addition of SWCNTs and draw ratio influence the orientation of *i*PP lamellae remarkably, but the composite sample shows a stabilized value of f compared with that of pure *i*PP samples. Combining the results of Raman measurements, we believe that the different increments of *i*PP and SPP fibers under different draw ratios are the outcome of the addition of SWCNTs and application of stretching force. For the *i*PP fibers, it is easy to draw the conclusion that the high stretching force causes the *i*PP lamellae to orient along the stretching direction. As for the composite fibers, it seems contradictory that the high stretching force and SWCNT orientation (reflected by $G_{//} / G_{\perp}$) did not bring a higher f value for SPP-200. As we know the addition of SWCNTs brings heterogeneous nucleation sites of *i*PP chains and the aligned SWCNTs make the *i*PP lamellae highly oriented, which is the reason why the value of f jumped from 0.58 for PP-20 to 0.78 for SPP-20. But the beneficial effects brought by the highly aligned SWCNTs and stretching force are limited; higher stretching force under high draw ratio also restrains the *i*PP chains to fold back and forward to form the lamellae. Under the stretching, these factors work together in a complex way and the outcome is that the addition of SWCNTs “stabilizes” the influence of the different draw ratios. On the other hand, as the SWCNTs incorporated, the scattering intensity in the meridian direction is increased greatly especially for the SPP-200, indicating the existence of SWCNTs can facilitate the formation of the *i*PP lamellae (kebabs). Moreover, the increased scattering intensity of the equatorial streak originating from fibrillar structures (shish) of SPP-200 compared with that of PP-200 suggests that more shish on the surface of SWCNT bundles are formed, demonstrating that the extended *i*PP chains and SWCNT bundles are serving as the hybrid shish in the NHSK superstructure.

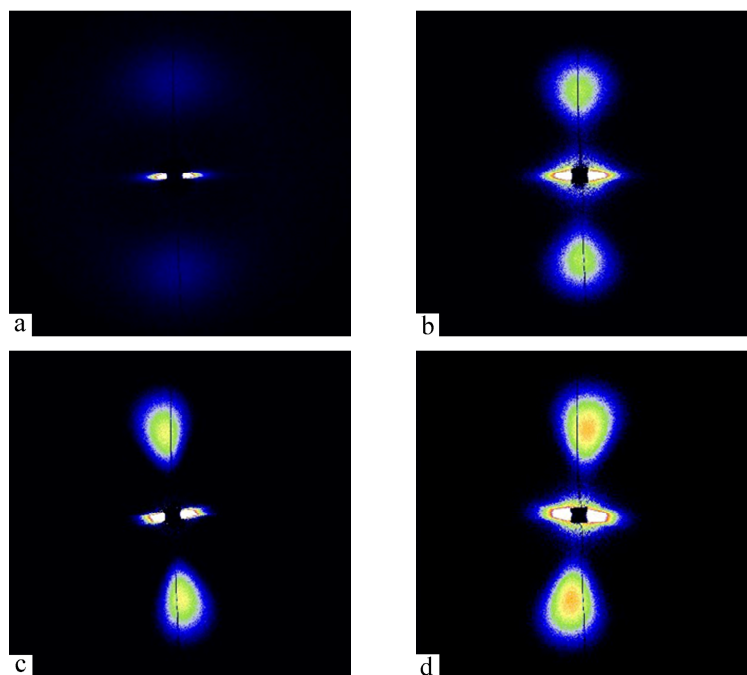


Fig. 5 Two dimensional SAXS patterns of (a) PP-20, (b) SPP-20, (c) PP-200 and (d) SPP-200

Based on the results and discussion above, a possible mechanism for the NBSK superstructure formation in composite fibers is proposed in Fig. 6. It is worthy to note that the SWCNTs exist in bundles mostly, because even after the processing machine it is hard to separate each SWCNTs apart. Such a SWCNT bundle produces grooves between SWCNTs. Our previous study on the early stage of *i*PP crystallization on the surface of SWCNTs bundles using molecular dynamic simulation has revealed that such a groove structure is helpful for the stabilization of polymer chains thus facilitating the orientation of *i*PP chains along the long axis of SWCNTs,

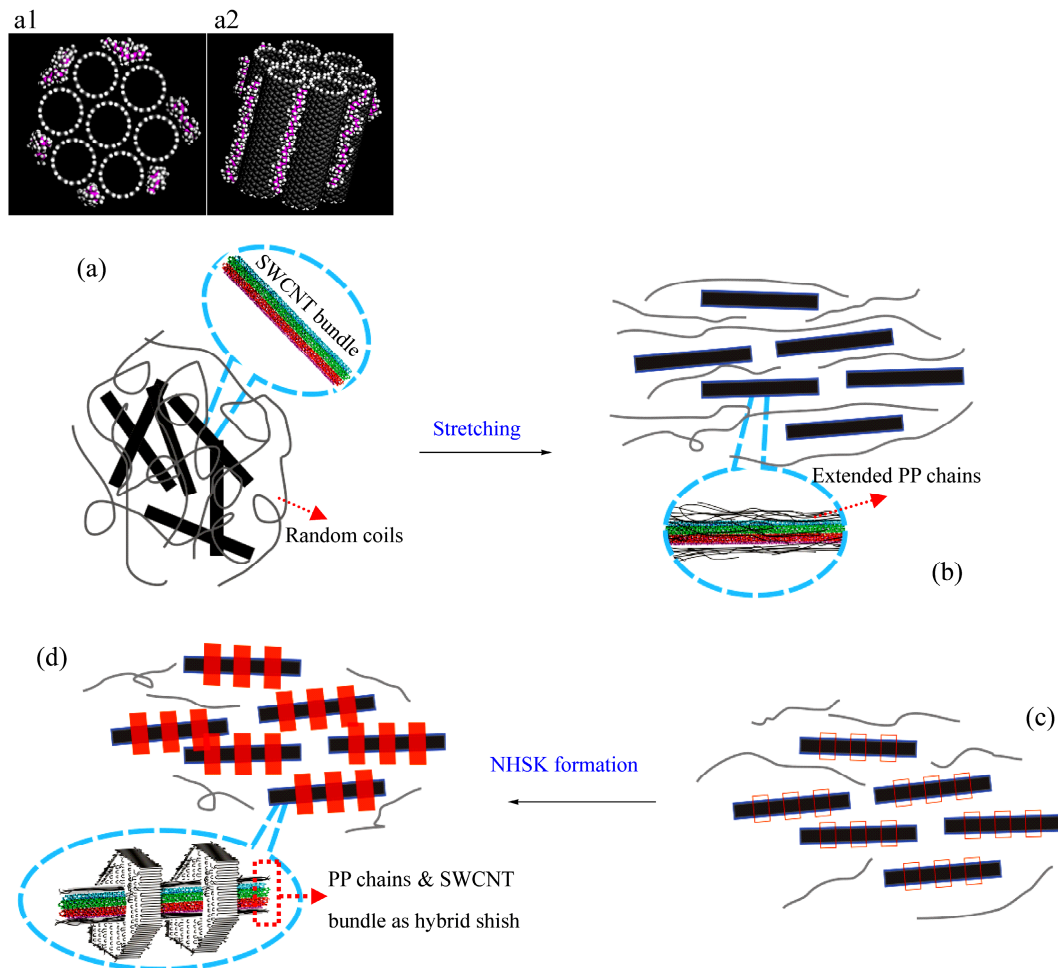


Fig. 6 Schematic illustration of the possible mechanism of the NBSK superstructure formation in SPP composite fiber fabricated at high draw ratio

as shown in Fig. 6(a1 and a2). So, at the initial state of the *i*PP melt, SWCNT bundles are surrounded by *i*PP chains and some *i*PP chains are absorbed on the surface of SWCNT bundles and may especially rich in the grooves to decrease the high surface free energy of SWCNT bundles. When the high draw ratio is applied, the high stretching force promotes *i*PP chains to disentangle and orient along the grooves regardless of the influence of the side groups of *i*PP chains. Moreover, the grooves of the stacked SWCNT arrays can stabilize the oriented *i*PP chains and hinder their relaxation especially for the short extended chains (see Fig. 6b), indicating by the results of the SAXS that more shishs are formed after incorporating with SWCNTs under high draw ratio. At the later stage, due to the reduced nucleation barrier of extended *i*PP chains, nuclei stabilize and then *i*PP chains begin to fold, and start the crystallization growth perpendicular to the axis of SWCNT bundles (shown in Fig. 6c). Finally, the NBSK superstructure where extended-chains of *i*PP and SWCNT bundles as hybrid shish

and *i*PP lamellae as kebab is formed, as shown in Fig. 6(d). The formation of NHSK superstructure in such helical polymer/SWCNT composites *via* melt spinning technology is mainly caused by the special surface topography of SWCNT bundles (grooves) and the stretching effect. Such a special interfacial crystalline structure is expected to enhance the interfacial adhesion and causes enhancements in mechanical properties of the fibers, as reported in other polymer/CNT system^[32, 33].

The melting and crystallization behavior of the composite fibers were further studied by DSC experiments, and the results are shown in Fig. 7 and Table. 1. It can be found in Table. 1 that the degree of crystallinity of pure *i*PP fiber is slightly increased by using the high draw ratio and incorporation of the SWCNT bundles; the melting point of the composite fibers is improved from 163.3 °C to 164.6 °C by increasing the draw ratio, which suggests that the SWCNT bundles produce more condensed crystallites and the high stretching force results in more thick *i*PP lamellae. The prominent nucleation effect of the SWCNT bundles for *i*PP matrix was reflected by the DSC cooling curves, as shown in Fig. 7(b) and Table. 2. The peak temperature of crystallization of SPP-20 (126.1 °C) is about 10 K higher than that of PP-20 (115.9 °C), though with only 0.5 wt% SWCNTs. Moreover, the crystallization temperature of SPP shifts to even higher temperature (127.5 °C) when high draw ratio is adopted. It should be noted that the thermal history of the composite fiber prepared both at DR-20 and DR-200 has been eliminated after being annealed at 200 °C for 5 min and the orientation of *i*PP chains is expected to be hardly preserved due to the sufficient relaxation. The crystallization temperature of SPP-200 is 1.4 K higher than that of SPP-20, which could be the result of the uniformly dispersed SWCNT bundles in SPP-200 providing more heterogeneous nucleation sites for *i*PP crystallization. Meanwhile, the NHSK structure in melt may partially maintain their molecular orientation due to the geometrical confinement of SWCNT bundles; the nucleation barrier of the *i*PP chains would be reduced during the recrystallization process. So, the recrystallization of SPP-200 can occur at higher temperature compared to that of SPP-20. It can be concluded that the high stretching force enhances the nucleation ability of the SWCNT bundles and results in more thick and complete *i*PP lamellae decorating on the surface of the SWCNT bundles.

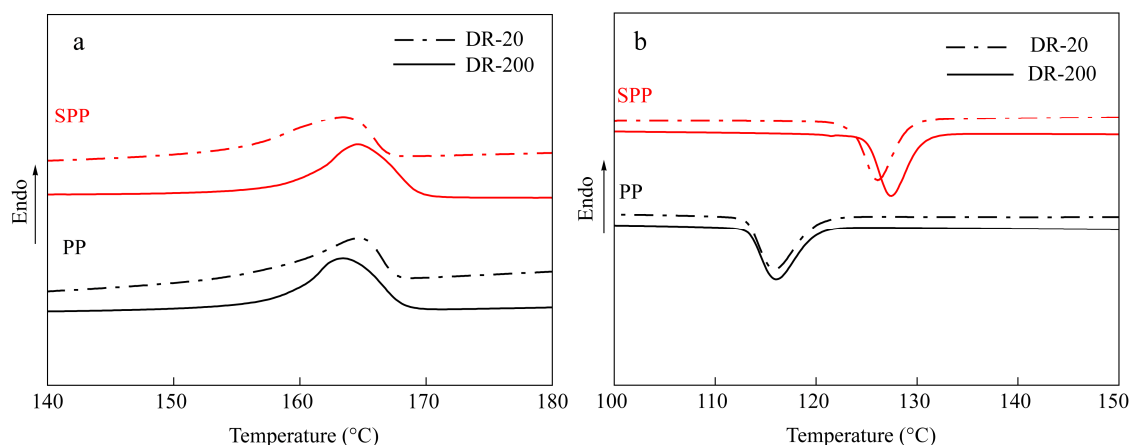


Fig. 7 DSC curves of the PP and SPP fibers fabricated at DR-20 and DR-200: (a) first melting and (b) the subsequent cooling at the cooling rate of 10 K/min

Table 1. The melt and the non-isothermal crystallization data of the samples (melting point (T_m), crystallinity (X_c) and the peak crystallization temperature (T_c))

	DR-20			DR-200		
	T_m (°C)	X_c (%)	T_c (°C)	T_m (°C)	X_c (%)	T_c (°C)
PP	164.6	36.6	115.9	163.4	37.7	116
SPP	163.4	37.2	126.1	164.6	40.5	127.5

Mechanical Properties of *i*PP/SWCNT Composite Fibers

As we known, the well dispersion and alignment of fillers, the oriented crystal structure and the good interaction brought by interfacial crystallization often give birth to an enhancement in the mechanical properties of the composites. So, the tensile test was then carried out, and the results are shown in Fig. 8. For the fibers prepared at DR-20, the Young's modulus is improved from 0.82 ± 0.065 GPa (PP-20) to 1.12 ± 0.114 GPa (37% increment) after adding 0.5 wt% SWCNTs. The SWCNT aggregation (see in Fig. 2a) leads to the minor improvement of the tensile strength of SPP-20 (only 8% increment compared with PP-20). As for the fibers prepared at DR-200, one can easily find that the improvement of the tensile properties is higher than that of DR-20 composite fibers. The tensile strength and modulus of *i*PP fibers are improved from 150 ± 11 MPa to 240 ± 8.1 MPa (60% increment) and 1.12 ± 0.039 GPa to 1.97 ± 0.21 GPa (76% increment) with 0.5 wt% SWCNTs addition. Obviously, the mechanical properties of the fibers are significantly affected by the addition of SWCNTs and the draw ratio adopted. The high draw ratio is favorable for a better mechanical properties and a higher reinforcing efficiency, which is mainly attributed to the well dispersion and alignment of SWCNTs, and the improved interaction of the two components caused by the formation of NSHK superstructure.

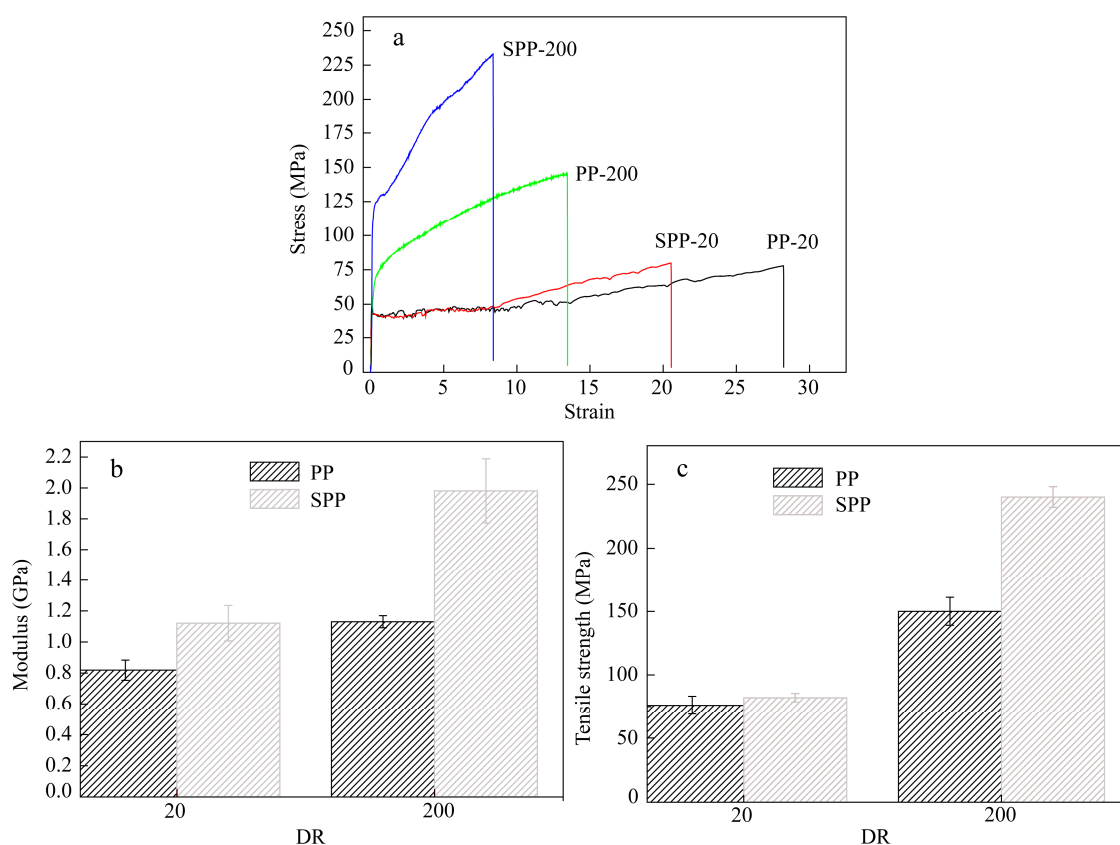


Fig. 8 (a) The typical stress-strain curves of pure PP and composite fibers; (b) and (c) the average Young's modulus and tensile strength of the composite fibers prepared at DR-20 and DR-200

CONCLUSIONS

In current work, the pure *i*PP and *i*PP/SWCNT composite fibers are successfully prepared by melt spinning technology at two different draw ratios (DR-20, DR-200). The SEM observation reveals that the SWCNTs in the fibers stack together in the form of bundles due to strong Van der Waals' interaction between the tube walls. The level of the dispersion and alignment of SWCNT bundles along the fiber axis are greatly improved by the stretching force under high draw ratio. Moreover, NSHK superstructures where extended *i*PP chains and

SWCNT bundle as hybrid shish and thick *i*PP lamellae as kebab are formed under the influences of the stretching and special topographic structure of SWCNT bundles. As a result, more noticeable improvement of mechanical properties of the composite fibers obtained at high draw ratio is achieved, which is attributed to the uniform dispersion, preferential alignment and most importantly, the good interfacial adhesion between SWCNT bundles and *i*PP matrix caused by the NHSK superstructure.

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