

ANNEALING INDUCED VARIATION OF CRYSTALLINE STRUCTURE AND MECHANICAL PROPERTIES OF SYNDIOTACTIC POLYPROPYLENE FIBERS*

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Abstract Syndiotactic polypropylene (sPP) as-spun fiber (sPP1) and drawn fiber (sPP2) were prepared by melt-spinning and melt-spinning/hot-drawing, respectively. The structure transition of the two fibers induced by annealing at different temperatures and the corresponding mechanical properties were subsequently investigated by the combination of Fourier transform infrared spectroscopy (FTIR), wide-angle X-ray diffraction (WAXD) and tensile testing. The results indicate that the chain conformation and crystal forms of the two sPP fibers are not obviously changed at low annealing temperature (40°C). With increasing the annealing temperature, the trans-planar conformation and mesophase in sPP1 and sPP2 fibers can be completely transformed to helical conformation and crystal form I under tension. Upon removing the tension, a small amount of mesophase and trans-planar conformation will be regained. The mechanical properties of the annealed fibers are manifestly dependent on their initial structure and the annealing temperature.

Keywords: Syndiotactic polypropylene fiber; Annealing treatment; Crystal form transition; Mechanical properties.

INTRODUCTION

Compared with conventional elastomers, syndiotactic polypropylene (sPP) is a new thermoplastic elastomer with high crystallinity and large modulus, which has aroused extensive research interests in recent years^[1–9]. One of the most distinctive characteristics of sPP is its complex polymorphisms, the transition among which is believed to be responsible for the adjustable elasticity of sPP fibers and films. It is generally recognized that sPP has four crystal modifications and one mesomorphic form, which are formed under specific crystallization conditions or by appropriate treatment^[10–17]. Crystal forms I and II are characterized by chains in $(t_2g_2)_n$ helical conformation packing in different orthorhombic crystals, whereas crystal form III or mesophase and crystal form IV present chains in trans-planar and $(t_6g_2t_2g_2)_n$ conformation, respectively. Crystal form I is the most stable form and crystal forms II, III, IV and mesophase are unstable. Under reasonable temperature and stress^[18–30], phase transition among different crystal forms may occur, which provides sPP with excellent mechanical properties, such as superior elasticity.

De Rosa investigated the relationship between structure transition and elasticity of sPP films^[4–6]. It was found that the transition of crystalline forms can produce an enthalpy gain in the process of stretching and relaxing processes, thus enduing sPP with excellent elasticity. With increasing stretching temperature, no crystalline transition happens, which decreases the elasticity of sPP. Furthermore, the initial structure of sPP, including the crystalline forms, crystallinity, orientation degree and crystallite dimensions, significantly

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influence the structure transition and elastic properties. Although there have been extensive reports on the relationship between structure and properties of *s*PP films, up to date the structure and mechanical properties of *s*PP fibers prepared by melt spinning have been seldom involved.

*s*PP fiber shows complex polymorphic variation during melt spinning. At low spinning velocity, the fiber adopts crystal form I with helical conformation, while at high spinning velocity, mesophase with trans-planar conformation is the major form^[31–33], which is unstable and easy to transform into stable form in the temperature range of 40–60°C. Such instability drawback needs to be complemented in practical applications. A simple method is to anneal the unstable *s*PP fibers at high temperatures under tension so as to acquire fibers with stable crystal form I. Therefore, in the present investigation, *s*PP fibers were prepared first by melt spinning and then processed by hot-drawing. The structure variation and performance of the obtained fibers through different routes, were systematically investigated by the combination of rheo-optical FTIR spectroscopy, WAXD and mechanical property measurements. The results provide comprehensive understanding of the variation of crystal structures as well as the relationship between the structure transition and mechanical performance of *s*PP fibers.

EXPERIMENTAL

Materials

Syndiotactic polypropylene (*s*PP-EOD) was obtained from AtoFina Company with M_w of 9.11×10^4 and $M_w/M_n = 3.37$ (measured with Waters-GPCV2K). The melting temperature ($T_m = 130^\circ\text{C}$) was obtained by Perkin-Elmer DSC-7 with a heating rate of 10 K/min (the first heating). The chain sequence was analyzed by ^{13}C -NMR spectroscopy with a Bruker AM-300 FT-NMR spectrometer. The polymer shows 80% syndiotactic pentads.

Fiber Preparation

The melt spinning of *s*PP fibers was carried out on a single-screw extruder (diameter = 30 mm, $L/D = 25$) with a spinneret containing one orifice of 0.3 mm diameter. The extruder barrel was set at five temperature zones of 185°C, 205°C, 210°C, 205°C, and 190°C, corresponding to the feed, metering, melt-blending, die and spinneret sections, respectively. The as-spun *s*PP1 filament was collected at a take-up speed of 300 m/min, and one-step thermo-drawing of 1.5 times elongation at 70°C and a following thermo-fixing process at 90°C were carried out to obtain fiber *s*PP2. The duration time of thermo-fixing was about 1 s.

The obtained *s*PP fibers were annealed at different temperatures on a homemade tensile machine with a temperature-variable cell^[34], inside which the fibers were kept under tension to avoid losing of orientation. The homemade tensile device was installed in the IR detection chamber and the infrared spectra of *s*PP fibers during annealing were *in situ* measured. The chosen annealing temperatures (T_a) were 40°C, 80°C, and 105°C. The annealing time (t_a) was 120 min at 40°C and 80°C, and 60 min at 105°C, respectively. After removing the tension, the acquired fibers were characterized by FTIR, WAXD and mechanical measurements at room temperature.

Characterization

Infrared spectra were accumulated by using a Bruker EQUINOX 55 spectrometer with resolution of 4 cm^{-1} and 32 scans. WAXD data between 5° and 30° were collected using a Philips X'pert X-ray diffractometer with Cu $K\alpha$ radiation at a generator voltage of 40 kV and current of 40 mA.

The uniaxial tensile deformation of the annealed fibers was measured on an Instron 3365 universal mechanical testing machine at room temperature, with a crosshead speed of 20 mm/min. The initial length of the fibers was 30 mm. The stress-strain curves were recorded. The modulus, elongation at break, and strength of fibers were acquired.

The elastic recovery test was carried out on an Instron 3365 testing machine at room temperature. The fiber with initial length $L_0 = 30\text{ mm}$ was stretched up to a length of L_1 (strain 100%) at a crosshead speed of 20 mm/min, then the tension was released and the final length (L_2) of the relaxed specimen was measured after 2 min. The elastic recovery was calculated as^[4]:

$$\varepsilon (\%) = (L_1 - L_2)/(L_1 - L_0) \times 100\%$$

The reported values of all the mechanical properties were averaged over five independent measurements.

RESULTS AND DISCUSSION

Annealing Induced Variation of Conformations and Crystal Forms

Infrared spectroscopy is a powerful tool to detect the chain conformation of macromolecules, especially for long chain *n*-alkanes and linear polyolefins. During the annealing process under tension, the transition of crystal form and chain conformation of sPP fibers can be *in situ* characterized by FTIR. Figure 1 shows that sPP1 fiber crystallizes into form I with helical conformation and minor mesophase with trans-planar conformation. The absorption bands of the helical conformation, appearing at 977, 810 and 1005 cm^{-1} , are strong, whereas the intensity of trans-planar bands at 963, 831 and 1130 cm^{-1} is relatively low. After annealed at 40°C for 2 h, the peak intensity of both helical and trans-planar conformations of the fiber shows no obvious change, indicating almost no transformation of crystal form and chain conformation. The intensity of *trans*-planar conformation band at 1130 cm^{-1} decreases obviously as annealed at 80°C under tension, and at last exists as a shoulder peak. The band intensity of 977 cm^{-1} (helical) and 963 cm^{-1} (*trans*-planar) in amorphous region appears no obvious change. As increasing the annealing temperature to 105°C, the 1130 cm^{-1} band disappears, indicating that the *trans*-planar chains have been transformed to helical ones at high annealing temperatures under tension.

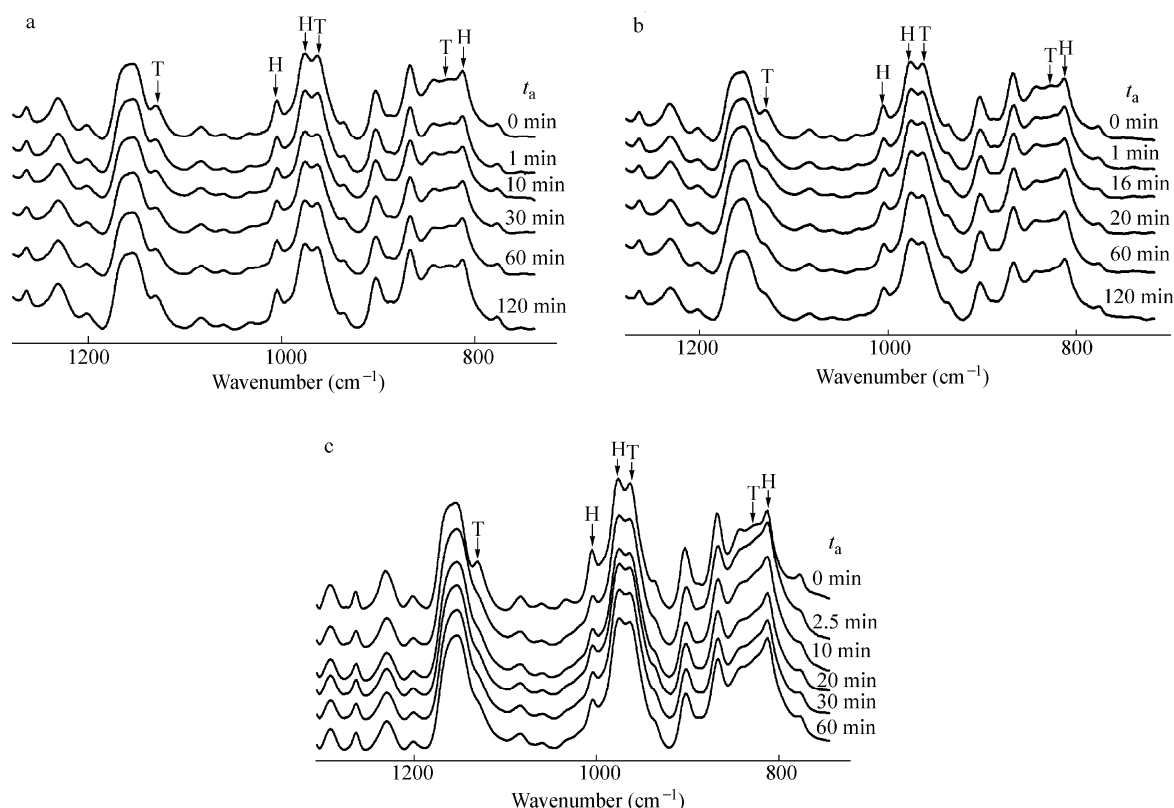


Fig. 1 *In situ* FTIR spectra of the sPP1 fibers annealed at different temperatures under tension a) 40°C; b) 80°C; c) 105°C; T: *trans*-planar conformation; H: helical conformation

The absorbance of 1130 cm^{-1} increases for annealed sPP1 fibers after releasing tension (Fig. 2). WAXD results (Fig. 3) indicate that the main crystal form of sPP1 initial and annealed fibers is the usual form I ($2\theta = 16.0^\circ$) with a shoulder at $2\theta = 17.0^\circ$ (see the arrow), the typical peak of mesophase with the *trans*-planar

conformation^[17]. The width of $2\theta = 16.0^\circ$ peak for sPP1 fibers annealed at 80°C and 105°C is narrower than that of the sPP1 initial fiber, corresponding to the decrease of mesophase content. Combining the results of FTIR and WAXD, the conformation and crystal form of sPP1 fiber undergoing annealing keep always unchanged, only the content of mesophase with *trans*-planar conformation decreases slightly for the sPP1 fibers annealed at 80°C and 105°C .

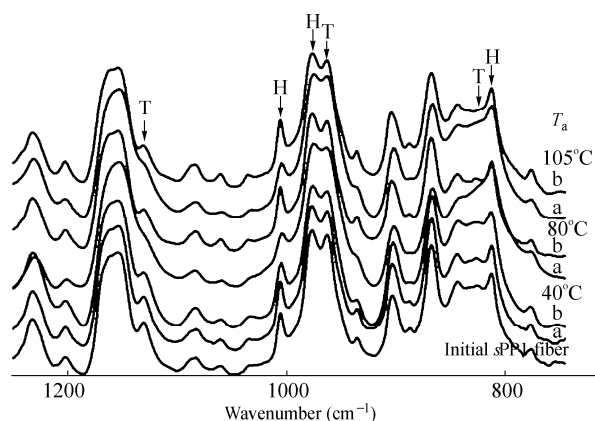


Fig. 2 FTIR spectra of the initial sPP1 fiber and sPP1 fibers (a) annealed under tension at the indicated temperatures and (b) annealed and after removing the tension

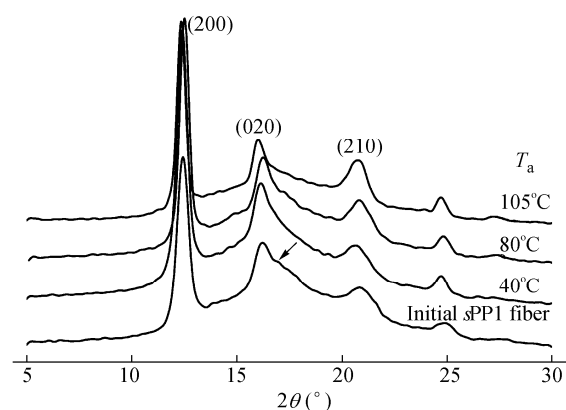


Fig. 3 WAXD profiles recorded at room temperature for the initial sPP1 fiber and sPP1 fibers annealed under tension at the indicated temperatures and after tension removal

The FTIR spectra of sPP2 fiber annealed at 40°C under tension show no obvious changes, and mesophase with *trans*-planar conformation is still the dominating form (Fig. 4). The 1005 and 810 cm^{-1} peaks of crystal form I with helical conformation are absent. According to previous reports^[19, 21], mesophase in sPP will melt or transform into crystal form I in the temperature range of 15 – 60°C , depending on the thermal history the fibers undergo. The mesophase transition and melting temperatures of sPP2 are increased due to the thermo-drawing and thermo-fixing processes. Therefore, the mesophase of sPP2 fiber is stable at 40°C , with no occurrence of obvious phase transition or melting. Increasing the annealing temperature to 80°C , the bands of 1005 and 810 cm^{-1} corresponding to crystal form I emerge, the intensity of which gradually rises with the increase of annealing time. On the contrary, the intensity of 1130 and 831 cm^{-1} bands (mesophase) decreases rapidly, and finally they exist as shoulders. Similarly, the intensity of 963 cm^{-1} (*trans*-planar) decreases, while that of 977 cm^{-1} (helical) increases with annealing time. As the annealing temperature further reaches 105°C , the 1130 and 831 cm^{-1} bands (mesophase) disappear completely. The 977 cm^{-1} band (helical) becomes stronger than that of 963 cm^{-1} (*trans*-planar). Therefore, it is concluded that with increasing the annealing temperature, mesophase in the drawn sPP fiber can be transformed into stable crystal form I with helical conformation.

After removing the tension, WAXD results and FTIR spectra of sPP2 and annealed fibers were also measured at room temperature (Figs. 5 and 6). Figure 5 shows that the initial sPP2 fiber is characterized by a strong and broad reflection peak at $2\theta = 17^\circ$, corresponding to the mesomorphic form. After annealing at 40°C , the diffraction pattern of the fiber exhibits no obvious change, indicating that the mesophase is stable and no crystalline transition occurs. The FTIR spectrum of the annealed fiber at 40°C in Fig. 6 also shows no obvious change. As the sPP2 fiber was annealed at 80°C or 105°C , the *trans*-planar mesomorphic form transforms into stable crystal form I, as indicated by the emerging of peaks $2\theta = 12.0^\circ$, 16.0° and 20.8° , corresponding to the reflection of (200), (020), and (210) crystal planes, respectively. The content of crystal form I increases with increasing the annealing temperature, indicated by the increase of diffraction intensity of (200) and (020) crystal planes. However, the 17.0° peak still exists, meaning that for drawn and thermal-fixed sPP2 fiber, a small amount of mesophase can be retained, even treated at high temperatures. The FTIR spectra of the fibers annealed at 80°C and 105°C show that the 1130 and 831 cm^{-1} bands corresponding to mesophase exist as

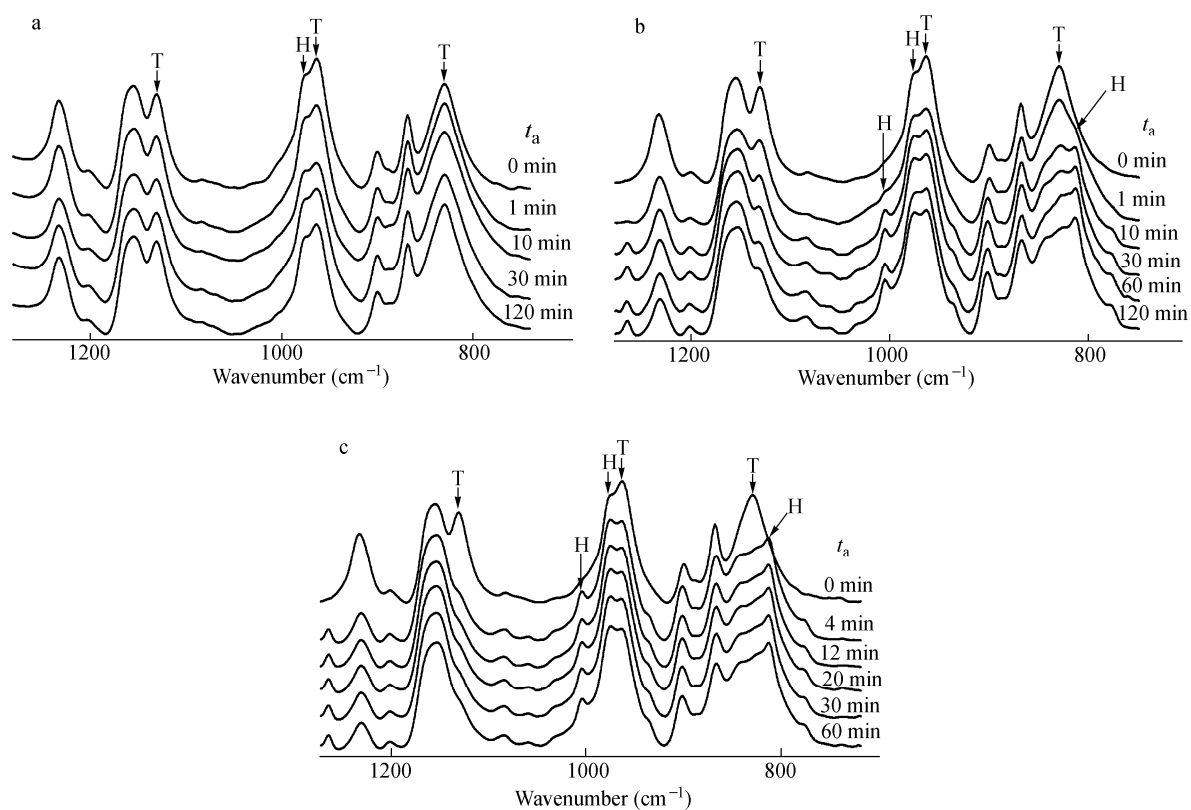


Fig. 4 *In situ* FTIR spectra of the sPP2 fiber annealed at different temperatures under tension a) 40°C; b) 80°C; c) 105°C; T: *trans*-planar conformation; H: helical conformation

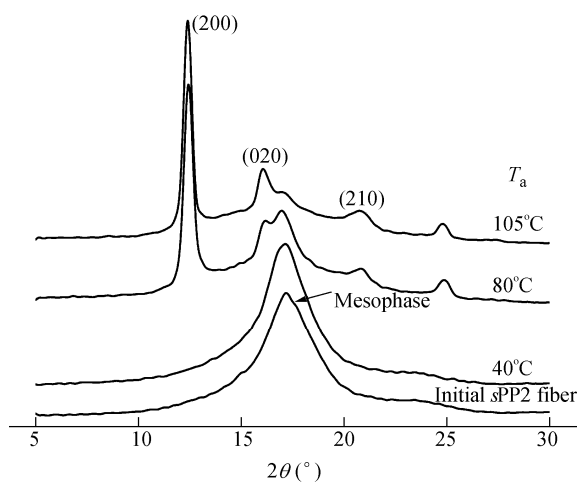


Fig. 5 WAXD profiles recorded at room temperature of the initial sPP2 fiber and sPP2 fibers annealed under tension at the indicated temperatures and after tension removal

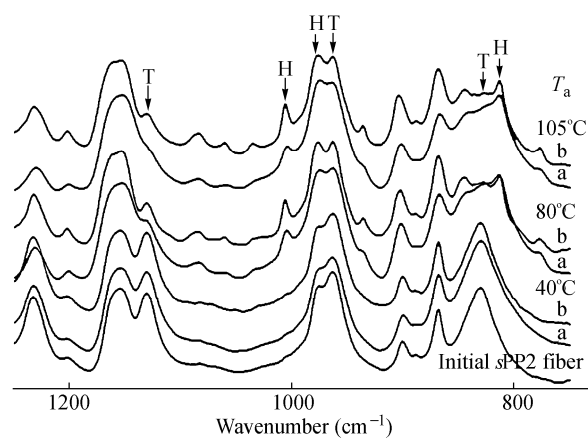


Fig. 6 FTIR spectra of the initial sPP2 fiber and sPP2 fibers (a) annealed under tension at the indicated temperatures and (b) annealed and after removing the tension

shoulder peaks (Fig. 6). This result is consistent with that of WAXD analysis in Fig. 5. Compared with sPP1 fiber, sPP2 fiber annealed at relatively high temperatures under tension displays the melting or transition of mesophase and the formation of crystal form I. After releasing tension, minor mesophase with *trans*-planar conformation still exists in sPP2 fibers annealed at high temperatures.

From the above analysis, it is clear that sPP1 initial fiber and annealed fibers consist of crystals of form I with helical conformation and minor mesophase with *trans*-planar conformation. For sPP2 initial fiber and fiber annealed at 40°C, the major structure is the *trans*-planar mesophase, while the sPP2 fibers annealed at 80°C and 105°C allow the prevalent crystallization of form I. The mechanical properties of the sPP fibers with different crystal structures will be discussed below.

Correlation between Structure Variation and Mechanical Properties of sPP Fibers

The mechanical properties of polymer materials are greatly influenced by the crystallization and orientation behavior of polymers. The stress-strain curves of sPP1 and its annealed fibers show usual plastic deformation *via* necking and high value of elongation at break (Fig. 7). However, no necking is observed on the stress-strain curves for the sPP2 and its annealed fiber at 40°C (Fig. 8). With increasing the annealing temperature, the deformation ability of the sPP2 fibers annealed at 80°C and 105°C increases and the stress-strain curves present a yielding point. Table 1 lists the mechanical properties of sPP fibers undergoing different thermal history. The results indicate that the break strength of sPP2 and its annealed fibers is much higher than that of sPP1 and its annealed fibers. The modulus of sPP2 and its annealed fiber at 40°C is relatively low. With increasing of the annealing temperatures to 80°C or 105°C, the modulus increases rapidly and is much larger than that of the annealed sPP1 fibers. The break elongation of the annealed sPP2 fibers increases, and the elastic recovery is larger than that of sPP1 fibers under the same experimental condition. However, annealing at high temperature induces the decrease of break strength for the two sPP fibers. The difference of the mechanical properties among the sPP fibers can be attributed to the change of the orientation and crystal structures, determined by the initial morphology and thermal history.

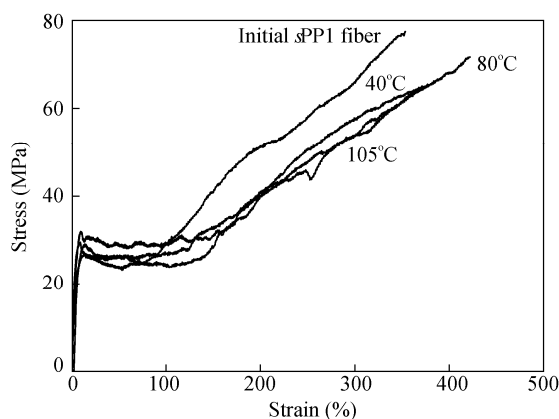


Fig. 7 Stress-strain curves of the sPP1 fiber and of fibers obtained by annealing the sPP1 fiber at 40°C, 80°C and 105°C

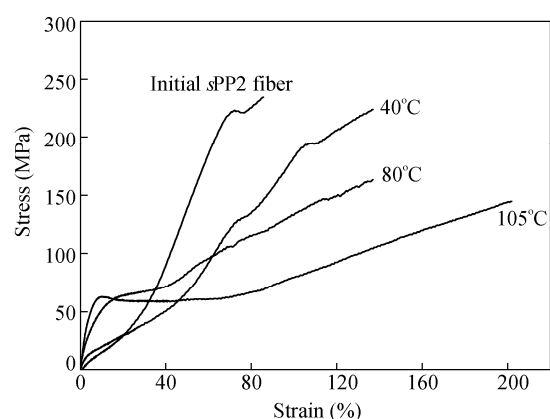


Fig. 8 Stress-strain curves of the sPP2 fiber and of fibers obtained by annealing the sPP2 fiber at 40°C, 80°C and 105°C

An interesting phenomenon is that the mechanical properties of annealed sPP1 fibers show minor changes compared with those of the initial sPP1 fiber (Fig. 7), in accordance with no obvious crystal structure variation at different annealing temperatures (Fig. 3). The decrease of break strength for the annealed sPP1 fiber can be attributed to the relaxation of molecular chains and the loosening of partial orientation during annealing. On the contrary, for sPP2 fibers annealed at different temperatures, the mechanical properties are obviously different. The modulus of sPP fibers with mesophase is very low (sPP2 fiber and sPP2 fiber annealed at 40°C) and the stress-strain curves do not present a yielding point. The modulus increase of the annealed sPP2 fibers at 80°C and 105°C (Fig. 8) corresponds to the crystal transition from mesophase to crystal form I (Fig. 5). On the other

hand, the orientation of sPP2 fiber series is higher than that of sPP1 fibers, resulting in larger break strength and elastic recovery (Table 1).

Table 1. The mechanical properties of initial sPP fibers and of fibers obtained by annealing sPP fibers at the indicated temperatures

Samples	Modulus (MPa)	Elongation at break (%)	Break strength (MPa)	Elastic recovery (%)
sPP1	605	359	80	52
sPP1 (40°C)	698	378	69	54
sPP1 (80°C)	715	443	74	59
sPP1 (105°C)	755	329	52	64
sPP2	—	80	251	—
sPP2 (40°C)	—	144	226	82
sPP2 (80°C)	793	139	171	69
sPP2 (105°C)	1523	215	133	71

CONCLUSIONS

The crystal form transition and mechanical properties of sPP fibers annealed at different temperatures have been investigated. The results indicate that the dominating crystal form of as-spun sPP1 and annealed fibers is form I with helical conformation. Annealing sPP1 fibers at different temperatures (40°C, 80°C and 105°C) induces no obvious crystal structure variation. The sPP2 fiber comprises mainly mesophase with *trans*-planar conformation. Annealing sPP2 fiber at 40°C has no influence on the mesophase. With increasing the annealing temperature to 80°C and 105°C, the *trans*-planar mesophase of sPP2 fiber transforms to the crystal form I with helical conformation. After releasing the tension, the sPP2 fibers annealed at 80°C and 105°C still retain a minor content of mesophase. The mechanical properties of sPP fibers depend on their crystal structure and orientation.

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