

Preparation and Properties of Polyamide 6 Fibers Prepared by the Gel Spinning Method

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ABSTRACT: Polyamide 6 (PA6) fibers were prepared by CaCl₂ complexation and the gel spinning technique. PA6 was partially complexed with CaCl₂ for the purpose of suppressing interchain amide group hydrogen bonding. The fibers were characterized with scanning electron microscopy, X-ray diffraction (XRD), differential scanning calorimetry (DSC), and Fourier transform infrared (FTIR) spectroscopy. In the gel spinning process, a mixed tetrachloroethane and chloroform solution was chosen as the coagulation bath after a comparison of different types of solutions. From our investigation of the morphology, structure, and mechanical properties of gel-spun and

hot-drawn fibers, it was indicated that the modulus and tensile strength increased with increasing draw ratio, the orientation of the fibers was improved, and the cross section of the PA6 gel fibers became more smooth and tight. The results from the XRD, DSC, and FTIR tests indicated that calcium metal cations complexed with the carbonyl oxygen atoms of PA6. The maximum modulus and tensile strength values obtained in this study were 28.8 GPa and 413 MPa, respectively, at a draw ratio of 8. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 5165–5171, 2012

Key words: fibers; polyamides; structure

INTRODUCTION

Although the theoretical modulus of polyamide 6 (PA6) fibers is 263 GPa,¹ the highest reported initial modulus of PA6 was 19 GPa,² which is much lower than its theoretically calculated value. Unlike polyethylene, polyamides have hydrogen bonds between their molecular chains. Hydrogen bonds play an important role in making polyamides into engineering plastics. At the same time, hydrogen bonds prohibit high-draw-ratio processing in polyamides, which have a maximum draw ratio of approximately 5. For this reason, efforts have been made to overcome this low maximum draw ratio with various processing techniques. However, the draw ratios and

mechanical properties of polyamide fibers have not been improved markedly.^{3,4}

Wyzgoski and Novak⁵ reported that stress cracking appeared in dry nylon after it was blended with calcium chloride in a methanol solution. Sun and Chin⁶ found that calcium chloride formed a complex compound with polyamide 66 (PA66) by breaking the hydrogen bonds. In our previous study,⁷ we investigated the effects of the molar ratio of calcium chloride to PA6, solvent types, decomplexing agents, and decomplexing time on the structures and properties of PA6 in detail, and PA6 fibers with a high initial modulus around 48 GPa were obtained by a dry spinning method. Those results demonstrate that the complexation of calcium chloride and PA66 or PA6 could be used to temporarily suppress hydrogen bonding during drawing and allow orientation to the desired degree before re-formation of the hydrogen bonds in the oriented state. However, we found few reports on the gel spinning of PA6/calcium chloride complexes.

Gel spinning is an efficient technique for preparing high-strength and high-modulus fibers from flexible chain polymers; it has been successfully used in the production of ultra high molecular weight polyethylene (UHMWPE) fibers⁸ and some other polymer fibers.^{9,10} Many efforts during the last decade have been made to produce high-modulus polyamide fibers with gel spinning, but the research has not

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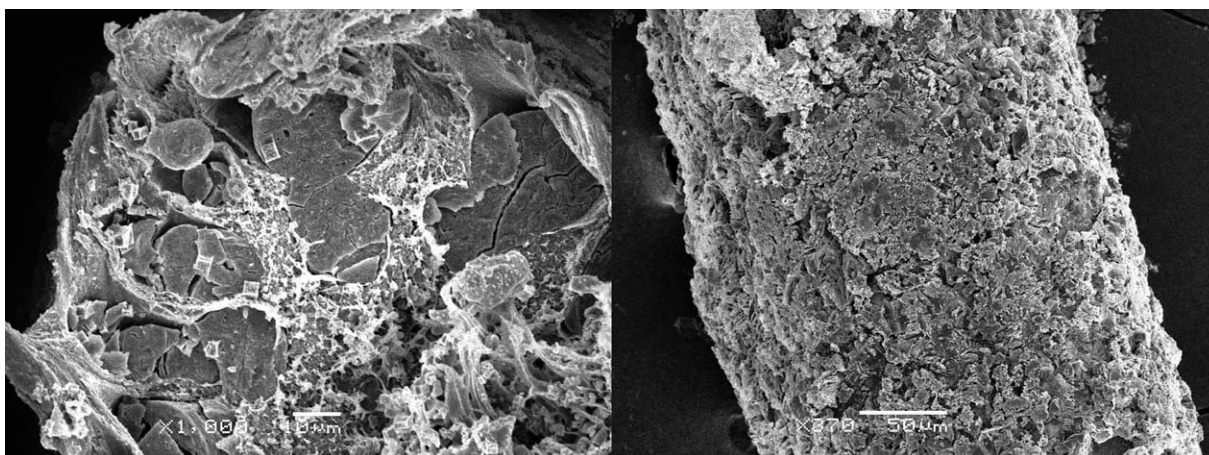


Figure 1 SEM figures of the PA6 gel fibers with dimethyl sulfoxide as the coagulation bath.

achieved a big breakthrough. Matsuo et al.¹¹ obtained PA6 films by gelation/crystallization from a formic acid/chloroform mixture. Chuah and Porter¹² produced PA6 gel by cooling a PA6 solution with benzyl alcohol from 165°C to room temperature and obtained a dried gel film with a modulus of 5.7 GPa at a draw ratio above 3.7. On the basis of this result, Cho et al.¹³ investigated the mechanism of PA6/benzyl alcohol gel fibers, and the maximum draw ratio and modulus obtained were 6.2 and 6.2 GPa, respectively. Up to this point, little progress in PA6 gel spinning has been achieved, and there is a long way to go in this field.

In this study, PA6 fibers with high draw ratios were first obtained by the gel spinning of a calcium chloride/PA6 complex, and the composition of the coagulation bath and the mechanical properties of PA6 fibers prepared by gel spinning were investigated in detail.

EXPERIMENTAL

Materials

PA6 powder with a relative viscosity of 19.44 was used; it was prepared by anionic slurry polymerization with sodium hydroxide as a catalyst, aliphatic isocyanate as an activator, and inert aliphatic hydrocarbon as a dispersant. Formic acid (98 wt %) was used as a solvent, and anhydrous CaCl_2 was the complexant.

Gel spinning of the fibers

The spinning solutions were prepared by the dissolution of PA6 in a $\text{CaCl}_2/\text{HCOOH}$ solution under nitrogen at room temperature. The concentration of PA6 here was 16 wt %, and the molar ratio of the CaCl_2 and PA6 repeating unit was 0.15. Before spinning, PA6 was dried for 24 h at 70°C in a vacuum oven. The spinning apparatus, described by Jung

et al.,¹⁴ was used for the gel spinning. After complete dissolution, the solution was spun at 40°C through a conical die with a diameter of 0.25 mm and a length of 2.5 mm. The as-spun fibers were quenched to 18°C in a coagulation bath to form the gel fibers and collected on bobbins. The gel fibers were then dried under ambient conditions. The coagulation bath had a length of 50 cm, and different solutions were studied. One solution was finally chosen after comparison of the fiber structures.

Drawing and decomplexation processes

The drawing of the gel fibers was carried out by a two-stage draw. The first-stage drawing was done at ambient temperature to 2–7 times the original fiber length. Then, the fiber was immersed in a mixture of 50 vol % ethanol and 50 vol % water in a beaker for 2 h. In the next step, the second-stage drawing was carried out at 200°C to various draw ratios. The draw ratio was determined by measurement of the displacement of ink marks on the sample before and after drawing. The decomplexed and drawn fibers are referred to as *regenerated fibers*.

Measurements of the properties of the samples

The morphology of the fibers was observed with a field emission scanning electron microscope (JSM-6360SEM, JEOL Co., Tokyo, Japan).

Wide-angle X-ray scattering was carried out with Rigaku Dmax-B X-ray diffractometer (Tokyo, Japan) with curved crystal monochromatized $\text{Cu K}\alpha$ radiation (1.54 Å) generated at 40 kV and 50 mA. Equatorial scans were obtained in the 2θ range 6–36°, with intensity data collected at 2°/min.

Differential scanning calorimetry (DSC) analysis was performed on a Seiko DSC 6200 instrument (Tokyo, Japan) under a nitrogen atmosphere in the

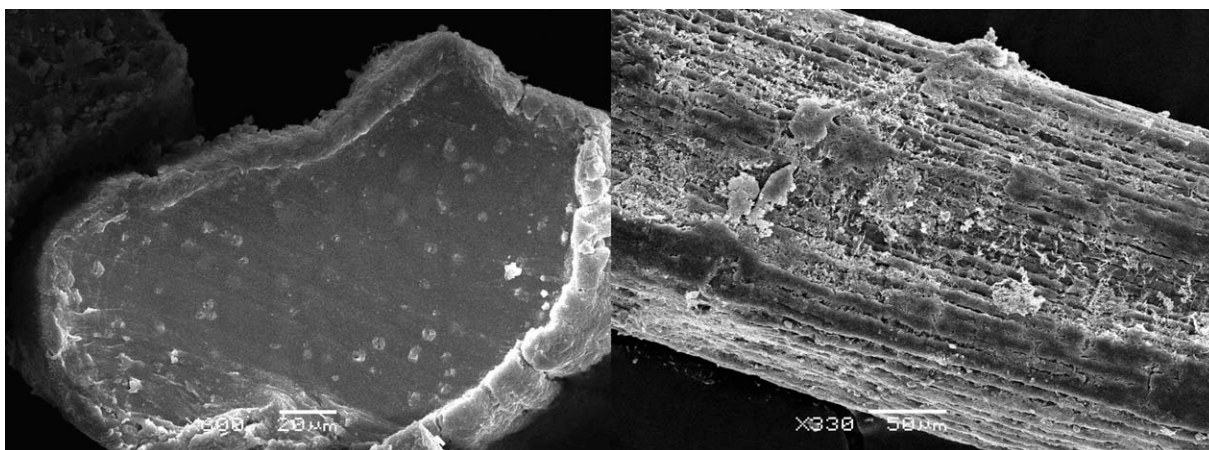


Figure 2 SEM figures of the PA6 gel fibers with ether as the coagulation bath.

temperature range from 25–250°C at a scanning rate of 10°C/min for each run. Measurement of all of the samples consisted of three scans: heating (to remove the heat history), cooling, and heating. An empty sample pan was taken as the reference, and each sample was weighted to about 3 mg. The melting points of the samples were taken at the maximum of the melting curves, and the glass-transition temperature (T_g) values were taken at the midpoint.

Fourier transform infrared (FTIR) spectra were obtained from attenuated total reflectance on a Nicolet Nexus 670 spectrometer (Thermo Co., Madison, WI). At least 64 scans were obtained at attenuated total reflectance to achieve an adequate signal-to-noise ratio.

The tensile properties of the fibers were measured with an Instron 1122 (High Wycombe, England) at a clamping length of 20 mm and a tensile speed of 40 mm/min. Testing conditions of $23 \pm 1^\circ\text{C}$ and 30% relative humidity were retained during the testing. Each strength and initial modulus value shown here represents an average of five individual measurements.

RESULTS AND DISCUSSION

Comparison of the coagulation bath types

To make the gel fiber form rapidly and to keep the complex of PA6 at the same time, the reaction between the coagulation bath and fibers was just a heat exchange that belonged to the physical reaction, not a chemical reaction, and the inner chemical bonds were not changed. By comparing different solutions to get the appropriate coagulation bath, we found that those solvents could be divided into three types.

With the first type, the face color of gel fibers turned white immediately when they were sunk into the coagulation bath. Such solvents included acrylonitrile, acetone, dimethyl sulfoxide, and tetrahydrofuran. Scanning electron microscopy (SEM) photos of the PA6 gel fibers with the dimethyl sulfoxide solution as the coagulation bath are shown in Figure 1. The fiber exhibited an awful surface with an old bark structure, and lacuna and a skin-core structure existed. The formation of this structure was attributed to the quick dissolution of the solvent and

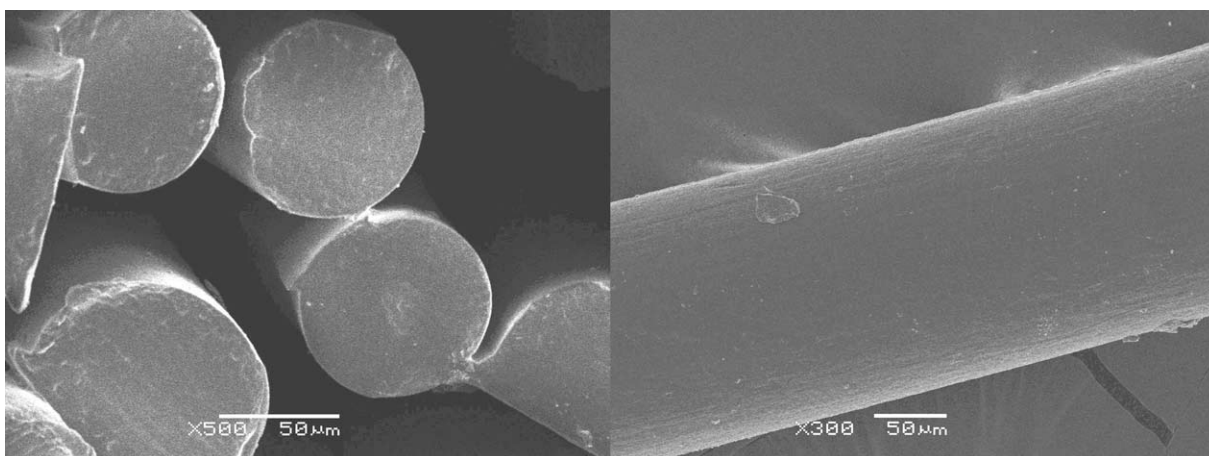


Figure 3 SEM figures of the PA6 gel fibers with a mixed tetrachloroethane and chloroform solution as the coagulation bath.

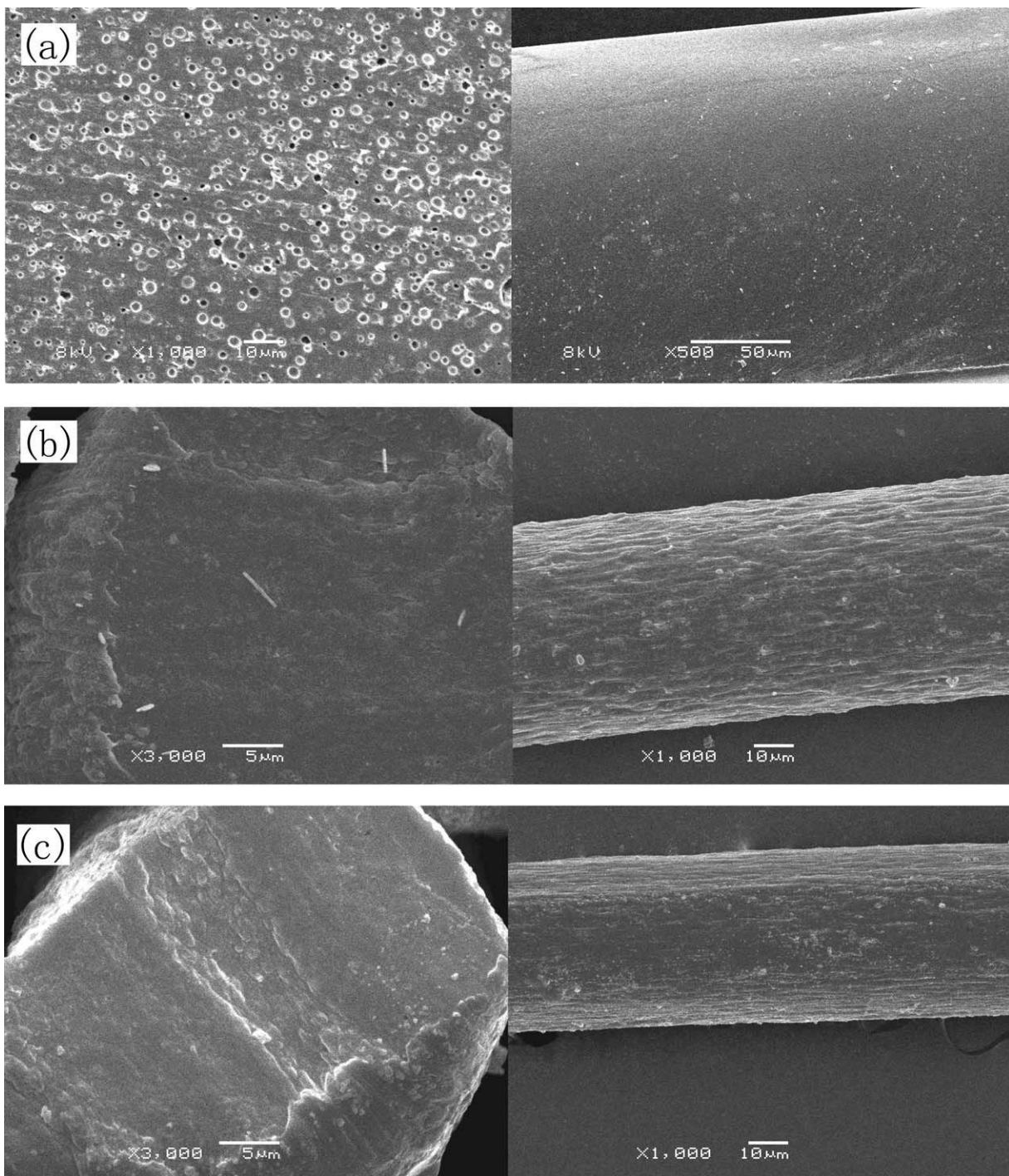


Figure 4 SEM figures of the PA6 gel fibers with different draw ratios: (a) 1.0, (b) 5.2, and (c) 8.0.

complexant in the coagulation bath. It seriously reduced the mechanical properties of the fibers. This type of solvent could not be used as a coagulation bath.

With the second type of solvent, the gel fibers could not form easily, and the filaments stuck together. Those solvents dissolved the formic acid solvent slightly, but no decomplexation was observed. This type was represented by heptane, anhydrous

ether, toluene, and olefin. SEM photos of the PA6 fiber with ether as the coagulation bath were taken. Figure 2 shows the existence of a skin-core structure in the cross section and the weak links of the fibers. The fibers demonstrated a rough and fragmented surface; this would not benefit the stretch performance and reduced the mechanical properties of the fibers. The fibers had a porous and lamellar-like structure in the longitudinal section. The formation

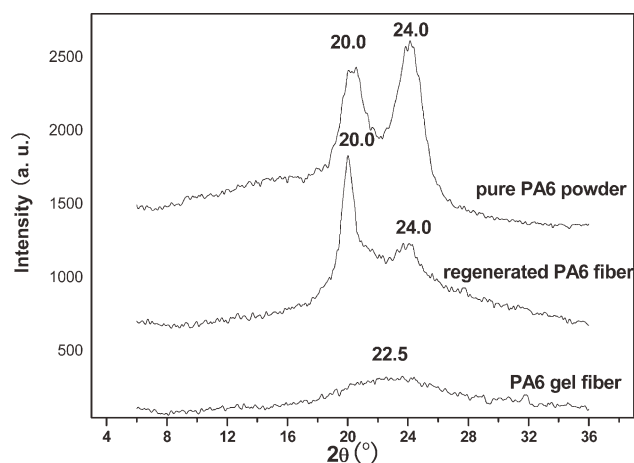


Figure 5 XRD patterns of the pure PA6 powder, PA6 gel fibers, and regenerated PA6 fibers.

of this lamellar-like structure was possibly due to stretching before the fibers were placed in the coagulation bath. This type of solvent also could not be used as a coagulation bath.

With the third type, the gel fibers formed well with little stickiness, and there was no decomplexation or double diffusion. The coagulation bath hardly dissolved the formic acid solvent and complexant. These solvents included tetrachloroethane, chloroform, methyl chloroform, and methylene dichloride. Figure 3 shows SEM figures of PA6 gel fibers with a tetrachloroethane and chloroform mixed solution as the coagulation bath. The fibers exhibited a compact structure and a relatively smooth surface. This type of solvent could be used as a coagulation bath.

In the following discussion, the coagulation bath used was mixture of 75 vol % tetrachloroethane and 25 vol % chloroform.

SEM photos of the regenerated PA6 Fibers

Figure 4 shows the surface and cross section of PA6 fibers with different draw ratios. The spherical gels changed to a fibrillar structure as the draw ratio increased. With increasing draw ratio, the orientation of the fibers was improved, and the cross section of the PA6 gel fibers became smoother and tighter. The flaws were almost diminished at a draw ratio of 8. However, the surface of the drawn fibers was filled with CaCl_2 particles. The existence of CaCl_2 was likely to hinder the elongation of the fibers to higher draw ratios and to cause flaws on the surface of the fibers in the drawn samples.

X-ray diffraction (XRD) analysis

Figure 5 shows the XRD patterns of PA6 samples prepared in different spinning stages. There was

only one broad peak centered at $2\theta = 22.5^\circ$ in the pattern of the PA6 gel fibers; this was not the reflection of the α -crystalline phase, which suggests that the crystal phase changed and the complex was completely amorphous. This was attributed to the existence of some CaCl_2 among the PA6 chains, which complexed with PA6, suppressed hydrogen bonding, reduced the original crystal phase, and then weakened the crystallization of PA6. The diffraction patterns of the pure PA6 powder and regenerated PA6 fiber were very similar. However, the intensity of the peak at $2\theta = 24^\circ$ of the regenerated PA6 fibers was weaker than that of pure PA6 because of the incomplete process of the decomplexation.

Thermal properties

Figure 6 gives the DSC results obtained for the pure PA6 powder, complexed PA6 film, PA6 gel fibers, and regenerated PA6 fibers upon heating. The DSC scans of the complexed PA6 film and PA6 gel fibers displayed T_g 's at 148.6 and 152.2°C, respectively. Both samples were complexed, and the regularity of chains was disrupted, so they showed amorphous characteristics and had no melting transition in DSC. The T_g of the complexed PA6 film was 3.6°C lower than that of the PA6 gel fiber; this may have been due to a slight orientation of PA6 chains through the spinneret during the gel spinning process. The melting temperature value of 216.8°C for the regenerated fibers was very close to that of the pure PA6 powder, and the small reduction of 3.5°C could be ascribed to the incomplete process of decomplexation, which was in accordance with the results of XRD.

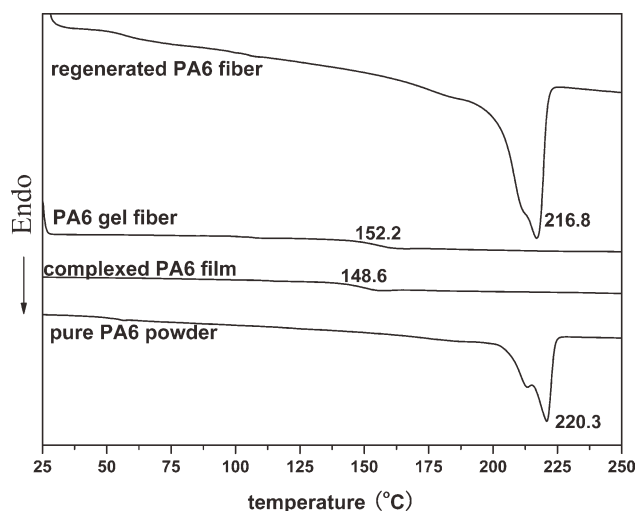


Figure 6 DSC scans observed upon heating of different PA6 samples.

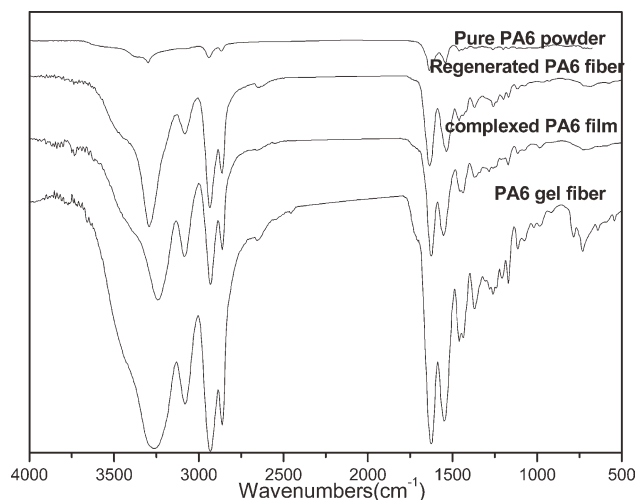


Figure 7 FTIR patterns of the pure PA6 powder, PA6 gel fibers, and regenerated PA6 fibers.

FTIR spectroscopy

Figure 7 shows the FTIR patterns of the pure PA6 powder, PA6 gel fibers, and regenerated PA6 fibers. The data of the IR absorption spectra for the main groups of all of the samples are shown in Table I. The infrared spectrum of pure PA6 powder showed an N—H stretching band at 3299 cm^{-1} , C=O stretching at 1638 cm^{-1} , and a C—N stretching band at 1543 cm^{-1} . The infrared spectra of the pure PA6 powder and the regenerated PA6 fibers were very similar and suggested that little complexed structure existed in the latter sample.

In contrast to the $\text{GaCl}_3/\text{PA6}$ system,¹⁵ it is apparent from Table I that the N—H stretching band was shifted to 3266 cm^{-1} and that the C=O stretching band was shifted to 1626 cm^{-1} in the $\text{CaCl}_2/\text{PA6}$ complexed gel fiber. These observations indicated that hydrogen bonding was destroyed during the complex formation. The C—N stretching band was shifted to 1550 cm^{-1} in these PA6 gel fibers. Because the calcium ion possesses a much stronger positive charge-inducing action, it could take the place of the N—H bond to form a complexation with the C=O bond. This complexation could have restricted the stretching vibration of the N—H and C=O bonds, so the absorption

TABLE I
Data of the IR Absorption Spectra for the Main Groups of the Pure PA6 Powder, PA6 Gel Fibers, and Regenerated PA6 Fibers

Sample	$\nu_{\text{N-H}}$ (cm^{-1})	$\nu_{\text{C=O}}$ (cm^{-1})	$\nu_{\text{C-N}}$ (cm^{-1})
Pure PA6 powder	3299	1638	1543
Regenerated PA6 fibers	3293	1636	1537
PA6 gel fibers	3266	1626	1550
Complexed PA6 film	3242	1626	1555

TABLE II
Mechanical Properties of PA6 Fibers with Different Draw Ratios

Draw ratio	Initial modulus (GPa)	Tensile strength (MPa)	Ultimate elongation (%)
3	3.7	44.7	57.4
5.2	17.5	61.4	56.3
8	28.8	345.2	50.2

bands of both shifted to lower wave numbers. Also, the π - π conjugation between the NH bond with the C=O bond was weakened; this favored the stretching vibration of the C—N bond and made its absorption band shift to the direction of the short wave. Compared with the complexed PA6 film, the spectra of the PA6 gel fiber showed smaller shifting at the bands of N—H and C=N. This observation indicated that a few crystalline structures existed in the PA6 gel fibers because of the chain orientation during the process of passing the spinneret.

Mechanical properties

The presence of long-chain branches and hydrogen bonds in the system was likely to restrict the slippage of the chains and chain defects through the crystal lattice, which hindered the achievement of higher draw ratios and better orientation. Generally, PA6 cannot be drawn more than five times because of strong intermolecular hydrogen bonding between its amide linkages. When the polymer is complexed with CaCl_2 , the hydrogen bonding is partially eliminated, and therefore, it is possible to reach these high draw ratios. In this study, PA6 was partially complexed with a small quantity of CaCl_2 , and we reserved part of the hydrogen bonds. One advantage of the gel spinning method is a reduction in molecular entanglements in the gel and the improvement of the efficient stretching of chains in the flow field. So the slippage of the chains and ineffective stretching were reduced, and then, a high modulus of the PA6 fibers was achieved. The mechanical properties of the fibers with different draw ratios are given in Table II. It was apparent that the tensile strength and initial modulus of the PA6 fibers under investigation increased with increasing draw ratio, and the ultimate elongation decreased. The maximum draw ratio achieved in this study was 8 for the two-stage draw. At this draw ratio, fibers with an initial modulus of 28.8 GPa were achieved.

CONCLUSIONS

A PA6 complex solution was prepared by the addition of PA6 powder into a mixed calcium chloride and formic acid solution. On the basis of the

investigation of the morphology, structure, and properties of the PA6 fibers, the coagulation bath was selected, and PA6 fibers with a maximum draw ratio of 8 and an initial modulus of 28.8 GPa were obtained by the gel spinning process.

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