

Study on Dry Spinning and Structure of Low Mole Ratio Complex of Calcium Chloride-Polyamide 6

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ABSTRACT: Polyamide 6 (PA 6) filaments with initial modulus around 48 GPa were produced by dry spinning from low mole ratio (MR) complex of calcium chloride and high molecular weight PA 6 (CaCl₂-PA 6) in formic acid. From the results of XRD, DSC, FTIR, and SEM, the complexation of CaCl₂-PA 6 in the MR range of 0.15–0.3 was efficient. The spinnability of the complex solution was excellent, which allowed a maximum draw ratio of 14.4 for as-spun fibers. After decomplexing and annealing, the birefringence of drawn fiber could reach around 0.08. Porous structure was found in fibers spun from formic acid-chloroform cosolvent but not observed by using pure

formic acid. When MR of CaCl₂/PA 6 exceeded 0.3, some irregular particles formed on the fiber surface due to the recrystallization of CaCl₂. However, fibers with smooth surface could be obtained when the MR decreased to 0.15. During the process of decomplexing in ethyl alcohol, an axial shrinkage of drawn fibers in a relaxed state was observed. It turned out that this shrinkage could be avoided by decomplexing the fibers under tension. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1996–2004, 2010

Key words: polyamide 6; complex; dry spinning; high modulus

INTRODUCTION

During last decades, much efforts have been spent on producing high strength and high modulus fiber from high-molecular weight aliphatic polymers, such as ultra-high molecular weight polyethylene (UHMWPE),¹ polyvinyl alcohol (UHMWPVA),² polyacrylonitrile (UHMWPAN),³ and polyamide (UHMWPA),⁴ etc. Among them, great success has been made in UHMWPE. UHMWPE can be achieved through conversion of flexible chains into highly oriented and extended chain conformations, which substantially increased the tensile properties.¹ Unlike polyethylene, polyamide has hydrogen bonds between molecular chains, which greatly prohibit its high value of drawn ratio. It was reported that the maximum draw ratio(DR) of only 5 could be obtained.⁴ Therefore, highly oriented polyamide could be obtained either by suppressing its crystallinity or reducing the number and strength of hydrogen bonds between molecular chains. For this reason,

many researchers attempted to increase maximum DR by using various processing techniques, such as plasticizers,^{5,6} dry spinning,⁷ gel spinning,⁸ wet spinning,⁹ zone drawing, and annealing etc.¹⁰

A remarkable study on the dry spinning of PA 6 from formic acid/chloroform cosolvent system was performed by Gogolewski and Pennings.⁷ With a DR of 10, they obtained a tensile strength up to 1 GPa and initial modulus of 16–19 GPa, respectively. They proposed that, because of the presence of chloroform in the spinning solution, a better entanglement network containing fewer topological irregularities was formed because chloroform is a non-solvent of PA 6. The formation of such an optimum entanglement network could be enhanced by increasing the rate of fiber drying, which reduced the chance of the chains being involved in numerous newly formed entanglements. The DR of 10 was almost two times higher than that obtained for the melt-spinning fiber. However, the DR of such a PA 6 fiber was still much lower than that of the ultra high modulus and high strength polyethylene fiber.

The hydrogen bonding between chains in PA 6 and chain defects in the crystal lattice restrict the molecular orientation. Therefore, it hinders the achievement of higher DR. It was found that, with high concentrations of PA 6 non-solvent in the spinning solution, the as-spun PA 6 fibers contained ball-like structures, which was possibly due to the liquid-liquid phase separation in the polymer/

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solvent/non-solvent ternary system. The formation of ball-like structures reduced the ultimate mechanical properties of hot-drawn PA 6 fibers.⁷

Another approach to disrupt hydrogen bonding in polyamide is to complex carbonyl groups with Lewis acids. Jenekehe et al.^{11–13} investigated Lewis acid complexed with various polyamides. Vasanthan et al.¹⁴ prepared GaCl₃-PA 66 complex in nitromethane and stretched the complexed film up to 4,000%. Jung et al.¹⁵ also prepared a complex solution of high molecular weight PA 66-GaCl₃ with the complexation ratio of GaCl₃/carbonyl group 1 : 0.8–1 : 0.9. They adopted a process for preparing high initial modulus and high tensile strength nylon fibers. The process consists of dry-jet wet spinning, fibers drying, drawing, and fiber soaking in solvent to remove the GaCl₃. The initial modulus and tenacity of produced fibers could reach 30.1 GPa and 2.5 GPa, respectively. It is a promising process to improve the drawability and strength of fibers from polymers with strong intra- or interactions between molecular chains. However, high complexation could result in a non-efficient drawing due to a complete suppression of hydrogen bonds, which led to more chain slippage than extension. A similar result was found by Lee and Porter.¹⁶

The work in this article involved with a low mole ratio (MR) complex system of CaCl₂-PA 6. The partially complexed fibers were produced from the complex solution by dry spinning. Because hydrogen bonds between molecular chains were partially maintained, the elongation and orientation of polymer chain could be efficiently improved during fiber drawing. The effects of CaCl₂ on structure-property relations of the complex fibers were also investigated.

EXPERIMENTAL

Materials

PA 6 powder with weight-average molecular weight in the range of $3.0\text{--}4.0 \times 10^5$ was prepared by slurry anionic polymerization of ϵ -caprolactam, in which sodium hydroxide was used as catalyst and diisocyanate as activator. The weight-average molecular weight of the samples was calculated according to the following equation proposed by Ueda et al.¹⁷

$$M_w = 2.81 \times 10^4 \times [\eta]^{1.35}$$

ϵ -Caprolactam monomer was purchased from Shijiazhuang Chemical Fiber Group Co. (Shijiazhuang, Hebei Province, China). Sodium hydroxide (NaOH), diisocyanate, sulfuric acid, and other analytical-grade reagents were purchased from Shanghai Sinopharm Chemical Co. (Shanghai, China) and

the Joint Institute for Chemical Reagents (Chengdu, Sichuan Province, China) respectively, and used as received.

Preparation of CaCl₂-PA 6 complex film

The CaCl₂-PA 6 complex solution was prepared by dissolving the polymer and CaCl₂ at 50°C in 98% formic acid or formic acid/chloroform cosolvent (75/25 v/v) with the MR of CaCl₂/PA 6 ranged from 0.15 to 0.50 (CaCl₂/PA 6 repeating unit) under nitrogen atmosphere. Then the solution was cast onto glass sheets (thickness, 0.25 mm) for film formation at room temperature. The as-cast films were cut into 15 mm wide strips and annealed at 140°C for 20 min in a vacuum oven for testing.

Fiber spinning and drawing

PA 6 powder was dried for 12 h at 90°C in a vacuum oven. Complex solution was prepared following the same method as above-mentioned. A mechanical stirring was used to ensure complete dissolving of the polymer. Concentrations of the polymer were in the range of 15 to 20 wt %. MRs of CaCl₂/PA 6 were controlled in the range of 0.15–0.50 (CaCl₂/PA 6 repeating unit). Fibers were spun at 50°C through a spinneret with a diameter of 0.5 mm and a length of 5 mm, and then passed through a 1.2 m spinning tunnel, in which temperature was controlled in the range of 120–150°C. The take-up rate was adjusted in the range of 2–20 m/min.

Fibers were drawn in two stages. The first stage of 3 to 8 times drawing was done at room temperature and then immersed into water or ethyl alcohol for 0.5–24 h for decomplexing. The second stage of drawing was performed at 200°C.

Characterizations

DSC analysis was performed on a Seiko DSC 6200 instrument (Tokyo, Japan) under a nitrogen atmosphere at a constant heating rate of 10°C min⁻¹. The samples were scanned in the range of 15–312°C.

Measurements of wide angle X-ray diffraction (WAXD) were performed on a Rigaku Dmax-B X-ray diffractometer (Tokyo, Japan) with Cu K α_1 radiation (wavelength = 0.154 nm) generated at 40 kv and 50 mA.

Fourier transform infrared (FTIR) spectra were measured on a Nicolet Nexus 670 spectrometer (Madison, WI). At least 64 scans were obtained to achieve an adequate signal to noise ratio. The spectral resolution was 8 cm⁻¹.

SEM observations were carried out with a JOEL 6360 LV scanning electron microscope (Tokyo, Japan). The surfaces of the samples were sputtered

with gold and then observed and photographed. The birefringence (Δn) was obtained with an XP-1 double-refracting interference microscope (Xintian Optical Instruments Co., Guiyang, China).

Mechanical properties of single fiber were tested by an INSTRON 1122 universal material testing machine (High Wycombe, England) with a gauge gap of 10 cm and a tensile speed of 40 mm/min. The testing was carried out at a temperature of 20°C and a relative humidity of 65%.

RESULTS AND DISCUSSION

Effects of CaCl_2 on the structure and properties of PA 6

Crystalline structure of the films was examined by WAXD, as shown in Figure 1. The diffraction pattern of uncomplexed reference PA 6 film displayed peaks at scattering angles (2θ) of 20° and 24°, corresponding to the reflections of crystalline plane (200) and combined planes (002/202), respectively. It indicated the typical monoclinic α -phase morphology. However, the WAXD pattern of complexed films showed broad halos, implying that the complexed films were completely amorphous after annealing treatment, even at a low complex MR of 0.15. This fact was due to the decrease in crystallinity as a consequence of the reduced number of hydrogen bonds between NH and C=O groups.^{18,19} It is similar to the data in other literatures.^{14,20}

DSC thermal analysis was carried out to study the thermal properties of the low MR complexed films, as shown in Figure 2.

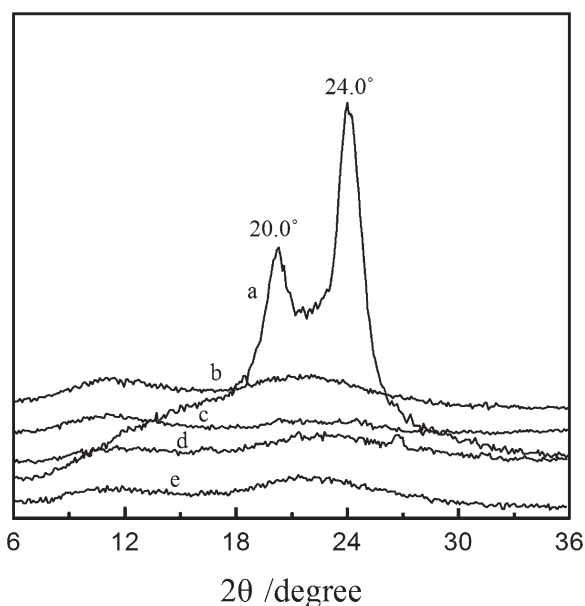


Figure 1 X-ray diffraction spectra for complexed films with different MRs of $\text{CaCl}_2/\text{PA 6}$: (a) 0, (b) 0.15, (c) 0.20, (d) 0.25, and (e) 0.30.

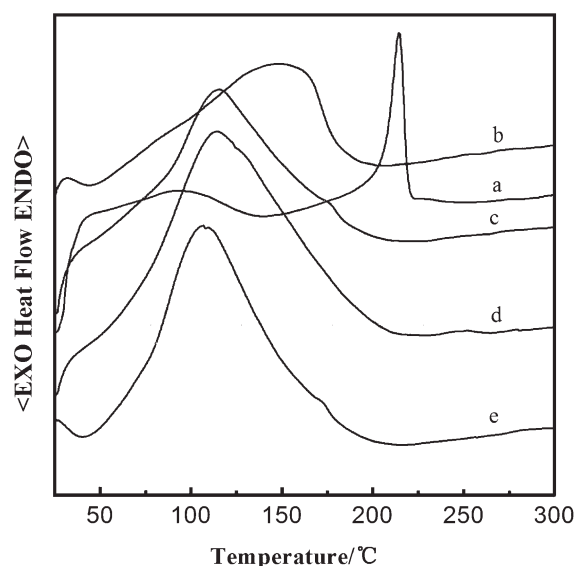


Figure 2 DSC profiles of complexed films with different MRs of $\text{CaCl}_2/\text{PA 6}$: (a) 0, (b) 0.15, (c) 0.20, (d) 0.25 and (e) 0.30.

The DSC result of uncomplexed PA 6 sample displayed a single melting peak at 212°C. All the complexed samples showed much broad endothermic peaks in the range of 100–140°C, indicating no crystallization structures formed during casting, even for the sample with very small amount of complexing agent CaCl_2 . It agreed well with the result obtained from the WAXD.

Figure 3 shows the FTIR spectra of uncomplexed PA 6 and complexed CaCl_2 -PA 6 films with MR of 0.15 and 0.30, respectively. The band assignments of the spectra are listed in Table I. The uncomplexed PA 6 presented strong absorption bands at 3295.07 cm^{-1} (amide A, N–H stretch vibration), 1636.83 cm^{-1}

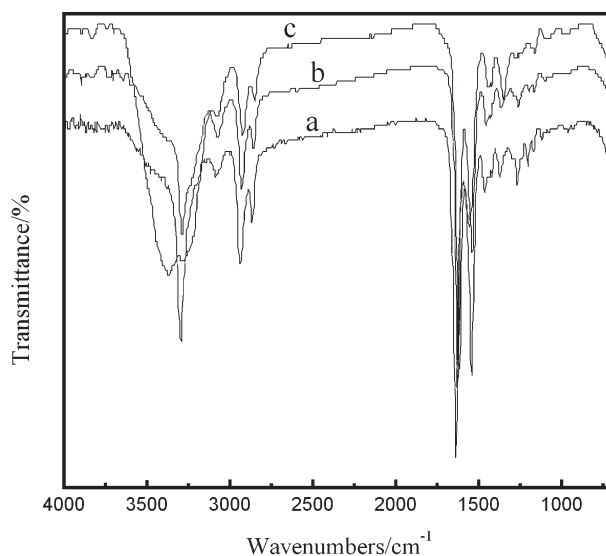


Figure 3 FTIR spectra for complexed films with different MRs of $\text{CaCl}_2/\text{PA 6}$: (a) 0, (b) 0.15, and (c) 0.30.

TABLE I
FTIR Spectra Band Assignment of CaCl₂-PA 6 Complexed Films with Different Molar Ratios (Peak Position in cm⁻¹)

Samples	N-H Structure	Amide I	Amide II	sCH ₂	asCH ₂
a	3295.07	1636.83	1542.75	2865.23	2937.68
b	3295.78	1635.04	1545.53	2863.18	2935.67
c	3297.56	1631.40	1571.94	2861.74	2937.26

a, 0; b, 0.15; and c, 0.30.

(amide I, C=O stretch vibration), and 1542.75 cm⁻¹ (amide II, N-H deformation), which were characteristic peaks of the amide groups existing in the *trans* planar conformation.^{19,21} Because free NH and C=O groups generated absorption bands at about 3400 cm⁻¹,²² hydrogen-bonding might exist between the NH and C=O groups. Another two strong absorption at 2865.23 and 2937.68 cm⁻¹ were assigned to symmetric CH₂ stretching vibration and to asymmetric CH₂, respectively.

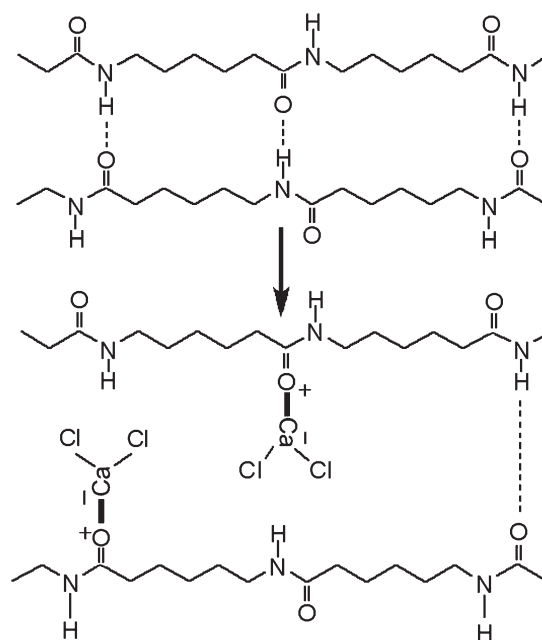
Compared with uncomplexed PA 6, the 3295.07 cm⁻¹ band shifted to 3295.78 cm⁻¹ and to 3297.56 cm⁻¹ for the complexed films with MR of 0.15 and 0.30, respectively. It also presented a small increase of the N-H stretching frequency in the complexed samples. An explanation of this fact was that CaCl₂ weakened the hydrogen bonds via complexing with carbonyl in the PA 6.¹⁸ Therefore, the complexed films contained "free" N-H groups and "complexed" C=O groups as illustrated in Scheme 1, which caused the N-H vibrational band shifted to a higher frequency. Furthermore, the addition amount of CaCl₂ was quite small, so that the change was not significant.

In comparison of uncomplexed film, C=O stretching bands in the complexed samples with MR of 0.15 and 0.30 shifted from 1636.83 cm⁻¹ to 1635.04 cm⁻¹ and 1631.40 cm⁻¹, respectively. It was because CaCl₂ (Lewis acid) had a stronger electron-withdrawing effect on C=O than does hydrogen bonding, which led to a shift of C=O band to a lower frequency. As seen from Table I, N-H in-plane bending vibration (amide II band) shifted to a higher frequency for all of complexed samples. This might be mainly due to the increased overlap of the amide I and amide II modes in the complex.¹² There was no obvious shift of CH₂ symmetrical and asymmetric stretching vibration band, because CH₂ did not play major roles in complexing.¹⁴ The result indicated that addition of CaCl₂ disturbed the original hydrogen bond formation in PA 6 chains even at a low MR of 0.15–0.3. The disturbance was more significant with a higher addition amount of CaCl₂. In other words, the number of hydrogen bond in PA 6 chains can be controlled to some extent.

Figure 4 shows the SEM images of CaCl₂-PA 6 films with different MR, which were cast from for-

mic acid or in benzyl alcohol solution. The films were annealed at 140°C in vacuum oven for 20 min before the measurement. The uncomplexed PA 6 films cast from either formic acid or benzyl alcohol solution both exhibited spherulite structure. The presence of such spherulite could hinder fibers to be elongated to a high DR. The complexed film, however, showed homogeneous lamellar structure, due to the reduced number of hydrogen bond. It was likely that the lamellar structure was helpful in increasing the extension capability of the complex. In Figure 4(d), the lamellar changed to a fibrillar structure as the DR increased. It was obviously different from the regular spherulite structure and probably responsible for the improvement of drawability of the polymer.

Table II shows the relations among maximum DR of the film, MR of CaCl₂/PA 6 and solvent. It was clear that the maximum DR of films increased with the increasing of amount of CaCl₂. For the same amount of CaCl₂, the maximum DR of film cast from formic acid/chloroform cosolvent was higher than that cast from pure formic acid. These were



Scheme 1 Schematic illustration of hydrogen-bonded sheet structure of PA 6 and CaCl₂-PA 6 complex.

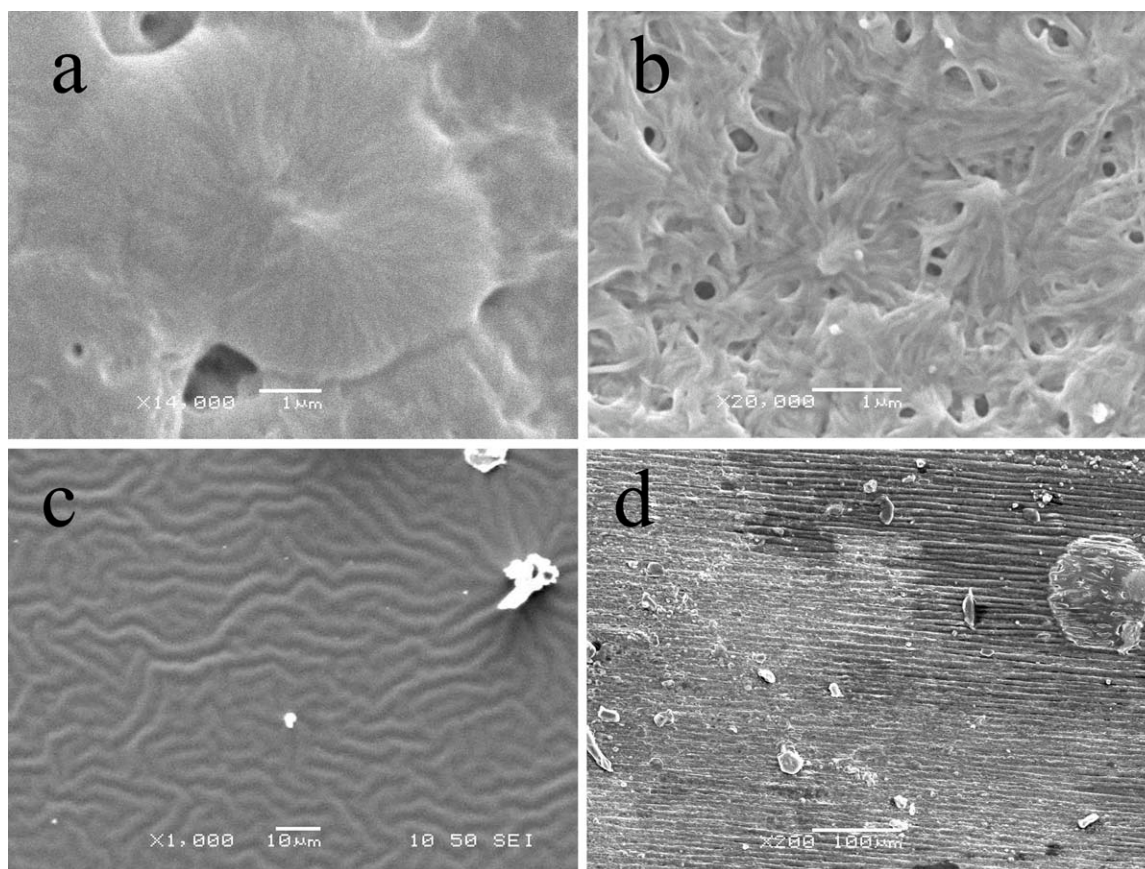


Figure 4 SEM images of uncomplexed PA 6 and complexed film: (a) PA 6 film cast from formic acid solution, (b) PA 6 film cast from benzyl alcohol solution, (c) complexed CaCl_2 -PA 6 film with molar ratio of 0.3, cast from formic acid solution, and (d) complexed CaCl_2 -PA 6 with molar ratio of 1.0, cast from formic acid solution and drawn 5.0 times.

due to the reduced number of hydrogen bonds in the PA 6 and better entanglement network of PA 6 chains formed in the cosolvent.⁷ It is well known that the difficulty of the ultradrawing of PA 6 is largely due to the presence of intermolecular hydrogen bonding between adjacent amide groups in PA 6. As the amount of CaCl_2 increased, the number of hydrogen bond in PA 6 decreased gradually due to the increase of complexation of CaCl_2 with amide groups.

Dry spinning of low MR complex of CaCl_2 -PA 6

As mentioned above, the addition of CaCl_2 had a significant effect on the tensile properties of PA 6. The SEM pictures [Fig. 5(a-d)] of uncomplexed and complexed CaCl_2 -PA 6 fibers provide the information on the morphology change with different addition of CaCl_2 . All the fibers in this Figure 5 were produced by using formic acid as the solvent. In Figure 5(a) (0.15 MR of CaCl_2 /PA 6), the fiber exhibited a compact structure and a relatively smooth surface. However, with the increase of CaCl_2 , lots of grains and irregular particles were found on the surface of the as-spun fiber, as shown in Figure 5(c,d). It was

mainly due to the recrystallization of CaCl_2 accompanied with the formic acid evaporation. The similar structures were found in the fiber spun from formic acid/chloroform cosolvent. These structures imparted opposite effects on mechanical properties and on following processing of the fibers. Eventually, the MR of 0.15 was chosen as the optimal addition of CaCl_2 .

It is well known that solvent play an important role in dry-spun fiber formation and has a great influence on the mechanical properties of the fiber.

TABLE II
Maximum DR of CaCl_2 -PA 6 Complexed Films Cast from Different Solvents

No.	Solvent	MR of CaCl_2 /PA 6	Maximum DR
1	Formic acid	0	4.0
2	Formic acid	0.15	5.0
3	Formic acid	0.30	5.5
4	Formic acid	0.50	6.5
5	F75/C25	0	5.5
6	F75/C25	0.15	6.0
7	F75/C25	0.30	7.5
8	F75/C25	0.50	10.0

F75/C25 refers to formic acid 75/chloroform 25.

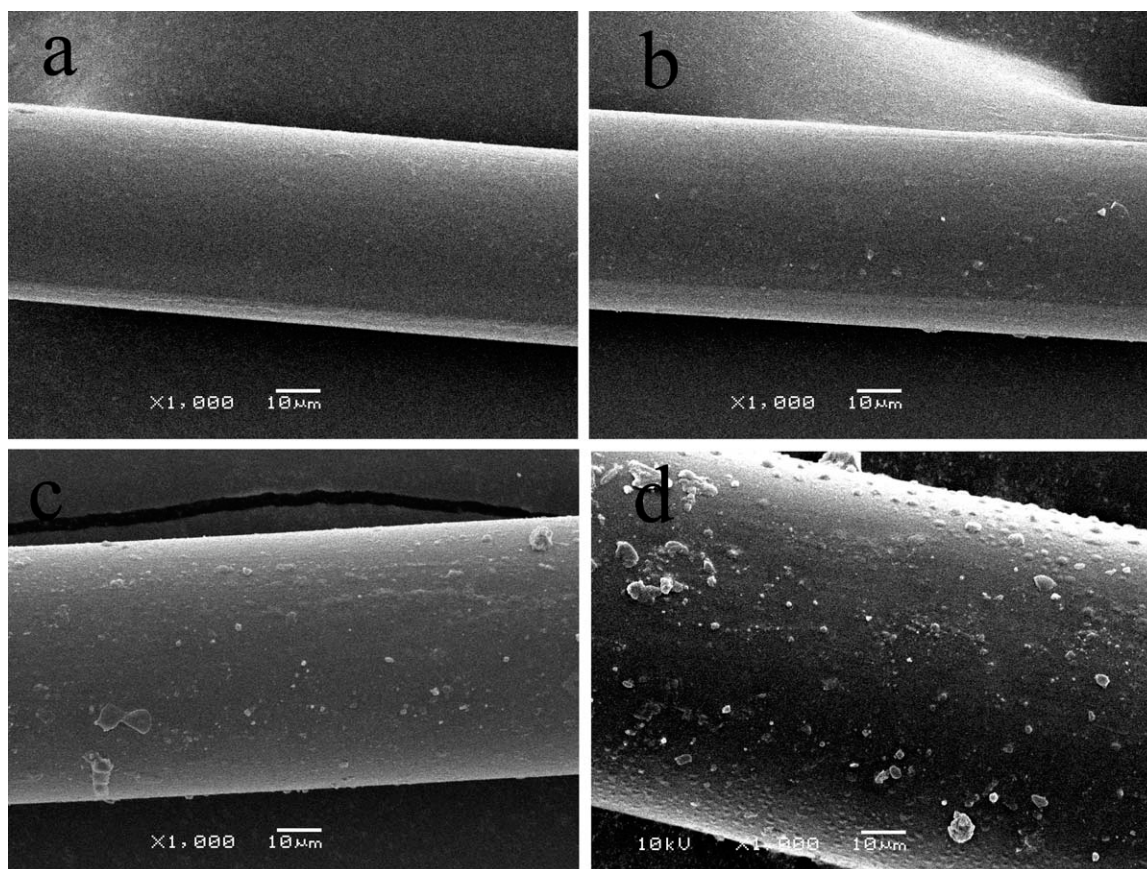


Figure 5 SEM images of complexed fibers with different MR of CaCl₂/PA 6: (a) 0.15, (b) 0.30, (c) 0.40 and (d) 0.50.

Table III shows the maximum DR of fibers spun from different solvent systems. It could be found that maximum DR of the fiber spun from pure formic acid was higher than that from cosolvent system. This did not agree with the result obtained from films drawing test as listed in Table II and indicated that there must be other reasons that influence the drawing properties of the fiber. So, to figure out the influencing factors, a test of the cross section of the fibers was conducted.

Figure 6 shows the SEM images of cross section of the fibers. Lots of pores were found in the cross section of fiber spun from F75/C25 cosolvent system, which were due to the evaporation of chloroform for its low boiling point (65°C). These porous structures reduced coherence of the fibers and led to low drawability and worse mechanical properties of the fibers. This, we think, may account for the inconsistency of our results in Tables III and II. However, cross section of the fiber spun from pure formic acid showed compact and smooth structure [Fig. 6(b)]. It indicated that chloroform was not appropriate for fiber spinning, because the temperature of spinning tunnel was around 120–150 °C in our study, which was much higher than its boiling point. Fortunately, the drawability of PA 6 fiber was greatly improved

by low MR complexation of CaCl₂-PA 6 in pure formic acid and the maximum could reach 14.4.

The as-spun fibers were drawn at room temperature and then soaked in water or ethanol for 24 h or 0.5 h to remove CaCl₂. Scroll structure was observed on the fiber surface after decomplexed in ethanol for 0.5 h under relaxed condition, as shown in Figure 7(a). It suggested that axial shrinkage occurred during the process, which was due to the deorientation of molecule chains of the complexed fiber with very low crystallinity. It also implied that more molecule chain extension than slippage was obtained during the drawing process. In the following experiment, the fiber was regenerated under tension and no scroll structure was found on surface of the fibers [Fig. 7(b)].

TABLE III
Maximal DR of Fiber Dry-spun From Different Solvent System

Solvent	Maximal DR
Formic acid	14.4
F75/C25	12.0

F75/C25 refers to formic acid 75/chloroform 25.

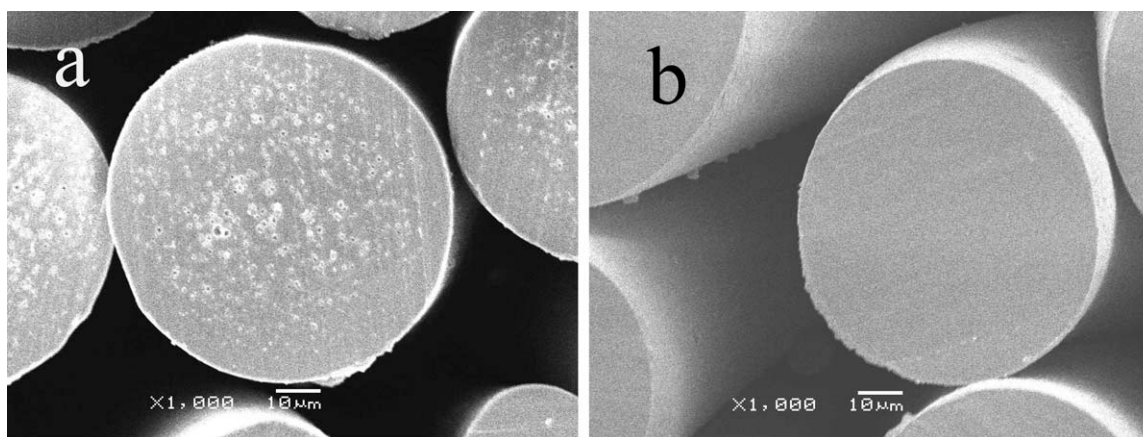


Figure 6 SEM images of the cross section of the complexed fibers dry-spun from different solvent system: (a) formic acid 75/chloroform 25, (b) pure formic acid (MR of CaCl_2 /PA 6 is 0.15).

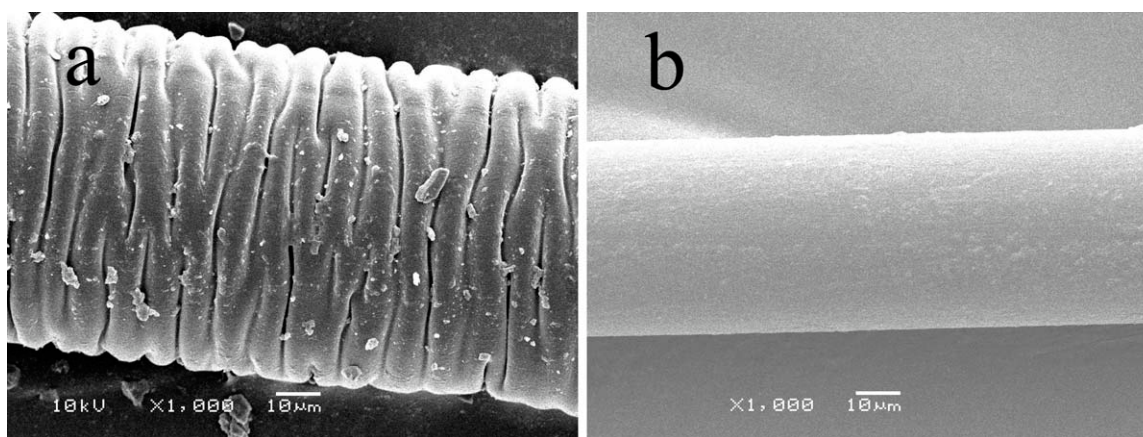


Figure 7 SEM images of longitudinal section of decomplexed filament: (a) decomplexed by ethyl alcohol for 0.5 h under relaxation (fiber was drawn 3.5 times before regenerating), (b) decomplexed by ethyl alcohol for 24 h under tension (fiber was drawn 6.0 times before regenerating).

All regenerated PA 6 fibers were annealed at 140°C for 20 min and investigated by XRD. As shown in Figure 8, the WAXD pattern of fiber decomplexed by water for 24 h showed a single diffraction peak centered at 21.5° , attributing to γ -crystalline phase reflection. In contrast, the fiber decomplexed by ethanol for 24 h showed two diffraction peaks centered at 20.2° and 23.9° , respectively, which attributed to typical α -crystalline reflection. Crystalline structure was regenerated compared with the complexed samples in Figure 1. It is well recognized that α -crystal is more stable and all the hydrogen bonding is formed between molecular chains. In the γ -crystalline phase, however, only half number of hydrogen bonding can form. It is obvious that crystalline property of the regenerated fibers is affected by the decomplexing condition.

Table IV shows the mechanical properties of uncomplexed and complexed fibers. The complexed fibers were obtained in the following process: partial complexed CaCl_2 -PA 6 dry spun from formic acid system, drawn at room temperature, regenerated by

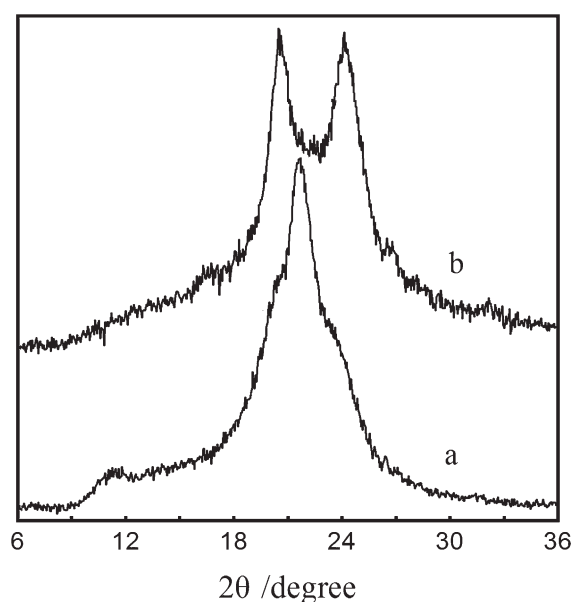


Figure 8 X-ray diffraction spectra for regenerated fiber decomplexed by different solution: (a) water 24 h, (b) ethanol 24 h.

TABLE IV
Mechanical Properties of Uncomplexed and Complexed Fibers

Solvent	MR of CaCl ₂	Total DR	Tenacity (MPa)	Modulus (GPa)	Strain (%)
Formic acid	0	5	395.4	13.7	32.3
Formic acid	0.15	7	660.4	14.7	51.6
Formic acid	0.15	12.6	610.0	45.4	17.3
Formic acid	0.15	12.8	570.0	42.4	15.1
Formic acid	0.15	14.4	660.0	48.0	17.3

MR refers to molar ratio of CaCl₂/PA 6.

water for 24 h and drawn at 200°C. It was obvious that drawability and mechanical properties of the fibers spun in pure formic acid were improved greatly compared with that of uncomplexed. The complexed as-spun fibers were rubbery and easy to draw compared with that of commercial PA 6 fibers. The highest DR of 8.0 was obtained for low MR CaCl₂-PA 6 complex as-spun fibers at room temperature, and a DR of 1.2–1.8 was further obtained at the temperature of 200°C after decomplexing treatment. The highest initial modulus of 48.0 GPa was achieved, which is much higher than the highest value (30.1 GPa) reported for nylon 66 fibers¹⁵ prepared by dry-jet wet spinning from complexed high molecule weight PA 66-GaCl₃-nitromethane solution. The modulus increased along with the increasing of DR, due to the increased degree of orientation, which could be reflected by the data of birefringence (Fig. 9). The optimum processing conditions are under investigation, which are promising to further enhance the mechanical properties of the complexed fibers and will be reported later on.

In addition, good aligned fibrillar structure was found in the complexed fiber with the highest total DR of 14.4, as seen in Figure 10. Similarly, it was

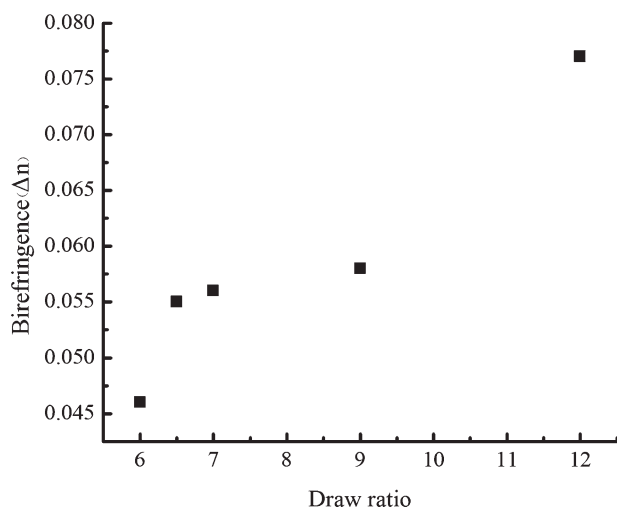


Figure 9 Birefringence vs. DR of CaCl₂-PA 6 complexed fibers.

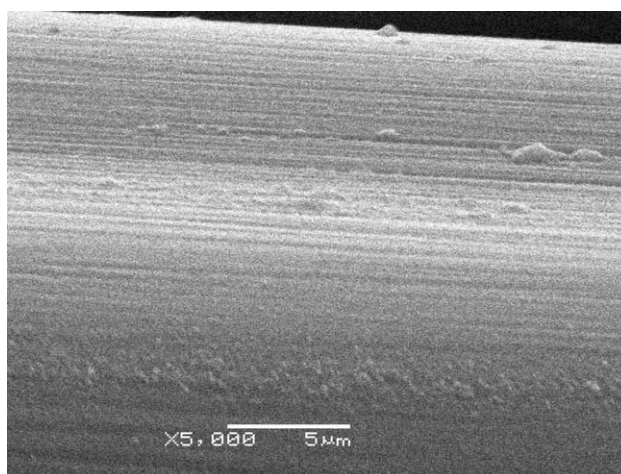


Figure 10 SEM images of the fiber drawn 14.4 times.

reported that SEM observation of UHMWPE gel-spun from a decalin solution showed a fibrillar texture like spongy tissue and its drawn sample had nearly perfectly extended chains.^{23,24}

CONCLUSIONS

Spinnability and drawability of high molecular weight PA 6 dry spun fiber were greatly improved by means of preparing low MR complex of CaCl₂-PA 6 in formic acid. The optimal addition of CaCl₂ was 0.15 (molar ratio of CaCl₂/PA 6). A maximum DR of 14.4 for the as-spun fiber was obtained and its birefringence value was around 0.08. Among the enhanced mechanical properties, the initial modulus of the drawn and annealed fiber was significantly increased to 48.0 GPa. These results implied that not only hydrogen bonds between PA 6 chains were partially disrupted but also chain slippages were effectively reduced for the low MR complexation of CaCl₂-PA 6.

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