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Properties of films and fibers obtained from Lewis acid–base complexed nylon 6,6

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Abstract

A nylon 6,6 complex with $GaCl_3$ in nitromethane (4–5 wt% nylon 6,6) was prepared at 50–70 °C over 24 h for the purpose of disrupting the interchain hydrogen bonding between nylon 6,6 chains, resulting in amorphous nylon 6,6, and increasing the draw ratio for improving the performance of nylon 6,6 fibers. After drawing, complexed films and fibers were soaked in water to remove $GaCl_3$ and regenerate pure nylon 6,6 films and fibers. FTIR, SEM, DSC, TGA, and mechanical properties were used for characterization of the regenerated nylon 6,6 films and fibers. The amorphous complexed nylon 6,6 can be stretched to high draw ratios at low strain rates, due to the absence of hydrogen bonding and crystallinity in these complexed samples. Draw ratios of 7–13 can be achieved for complexed fibers, under low strain rate stretching. This study indicates that nylon 6,6 fibers made from the $GaCl_3$ complexed state, using a high molecular weight polymer, can reach initial moduli up to 13 GPa, compared to initial moduli of 6 GPa for commercial nylon 6,6 fibers. Lewis acid–base complexation of polyamides provides a way to temporarily suppress hydrogen bonding, potentially increasing orientation while drawing, and following regeneration of hydrogen bonding in the drawn state, to impart higher performance to their fibers.

Keywords: Nylon; Complexation; $GaCl_3$

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1. Introduction

A number of attempts to produce high modulus fibers have been made [1–7]. However, from the theoretical point of view, there are only two fundamental methods to produce such fibers. The first technique involves the synthesis and assembly of polymers with rigid and linear backbone molecular structures. The second method transforms conventional flexible, semi-crystalline polymers that usually have relatively low modulus and strength, into highly oriented materials. In the first case, *para*-substituted aromatic rings in the polymer backbone are used. These inherently rigid polymers can produce fibers of very high stiffness and strength, either by wet spinning to produce aramid fibers or by melt spinning if thermotropic liquid crystalline polymers are used. In the second case, the inherently flexible chains of most semi-crystalline polymers must be converted into highly oriented and extended chain conformations. Drawing, a processing technique, is often used to enhance orientation and the mechanical properties of fibers. Ultra drawn high molecular weight polyethylene is one good example. Zachariades and Kanamoto [2] have successfully drawn ultra-high molecular weight polyethylene more than 200 times and obtained almost the theoretical modulus (240–340 GPa) at that draw ratio.

Unlike polyethylene, polyamides possess intermolecular hydrogen bonding and have high melting temperatures. Hydrogen bonds play an important role in making polyamides engineering plastics. At the same time, to date they have prohibited high draw ratio processing in polyamides, which have a maximum draw ratio of only ∼5 [8]. Therefore, highly oriented polyamides obtained by tensile drawing can potentially be achieved either by suppression of crystallinity or by modification of the number

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and strength of the hydrogen bonds between their chains. For this reason, many researchers have attempted to overcome the normally low nylon draw ratios by using various processing techniques, such as, plasticizers, dry spinning, gel spinning, wet spinning, zone drawing, annealing, etc. [9–18]. In this report, we have investigated Lewis acid–base complexation as a method to temporarily break hydrogen bonding and suppress crystallinity in nylon 6,6. Fibers were spun from complexed solutions through a dry-jet wet spinning process, followed by decomplexation/regeneration of the drawn nylon 6,6 fibers by soaking them in water. We observe these fibers to exhibit high initial moduli, when a high molecular weight nylon 6,6 is employed.

2. Experimental

2.1. Materials

High molecular weight nylon 6,6 ($M_w = 175{,}000$–$200{,}000$ g/mol) was prepared by solid-state polymerization [19,20], beginning with commercial nylon 6,6 chips (Zytel® 101, $M_w = 30{,}000$ g/mol), which were supplied by Du Pont Co. $GaCl_3$, nitromethane, and all coagulation bath solvents were obtained from Aldrich Co.

Viscosity average molecular weights were obtained using the Mark–Houwink equation. The constants K and a used for the nylon 6,6/formic acid system at 25 °C are 35.3×10^{-5} dL/g and 0.786, respectively [21]. The viscometric measurements were conducted at 25 °C with an Ubbelohde viscometer. The limiting viscosity number was determined from the following Eq. (1):

$$[\eta] = \frac{2}{C}\left(\eta_{\mathrm{rel}}^{1/2} - 1\right) \tag{1}$$

where C is the polymer concentration, $[\eta]$ is the intrinsic viscosity, and η_{rel} is the relative viscosity.

2.2. Preparation of nylon 6,6/$GaCl_3$ complex solutions

Nylon 6,6/$GaCl_3$ complex solutions with 4–5 wt% concentration of nylon 6,6 were prepared as follows. A specific amount of $GaCl_3$ (5 g) was added to nitromethane refluxing under nitrogen. This mixture was stirred at 70 °C until $GaCl_3$ was completely dissolved. Predetermined weights of nylon 6,6 chips corresponding to different stoichiometric ratios of $GaCl_3$ to amide groups (as an example, for a stoichiometric ratio of 1:1, 3.21 g nylon 6,6 and 5 g $GaCl_3$) were then added to the solution and the mixture was stirred under nitrogen until the polymer was completely dissolved (16–24 h). Stoichiometric ratios (1:1 and 1.1:1) of $GaCl_3$ to amide groups were used to achieve complete suppression of hydrogen bonding in nylon 6,6. It is important to mention that solutions of nylon 6,6 complexed with $GaCl_3$ are sensitive to moisture, due to the high reactivity between $GaCl_3$ and H_2O, leading to reduced solution viscosities.

2.3. Preparation of nylon 6,6/$GaCl_3$ complex films

The nylon 6,6/$GaCl_3$ complexes were made using both low ($M_w \sim 30{,}000$ g/mol) and high ($M_w \sim 175{,}000$–$200{,}000$ g/mol) molecular weight nylons. Complexed films were made by evaporating the solvent in vacuum.

2.4. Dry-jet wet spinning of the complexed nylon 6,6 solutions

A dry-jet wet spinning method was used for producing nylon 6,6/$GaCl_3$ complex fibers. High molecular weight nylon 6,6 (4–5 wt.% concentration) in $GaCl_3$ complexed nitromethane solutions were used as the spinning dope, and isopropanol was used as the non-solvent in a coagulation bath held at 25 °C. Spinning temperature was about 60–70 °C and the pressure for the extrusion was in the range 100–150 psi. The cylindrical single orifice spinneret dimensions were $D = 0.01''$ and $L = 0.02''$. The as-spun fibers were carefully collected on a bobbin at take-up speed around 20 m/min, and then dried in a desiccator. Due to the coagulation process in wet spinning, fiber cross-sections were not completely round, but were somewhat collapsed.

To control spinning speed, throughput of the complexed spinning solution was measured to understand the polymer flow behavior at different pressures and times at room temperature (data not shown).

2.5. Wide angle X-ray diffraction

Measurement of wide angle X-ray scattering (WAXD) was carried out using a Philips X-ray diffractometer in the transmission mode, with curved crystal monochromatized Cu Kα radiation (1.54 Å) generated at 30 kV and 20 mA. Equatorial scans were obtained in the 2θ range 10–40°, with intensity data collected every 0.1°. Nylon 6,6 fibers presented a characteristic two peak equatorial X-ray scattering pattern for an alpha structure as described by several authors [22]. The observed peak maxima for nylon 6,6 fibers were $2\theta \approx 20.8°$ and $\approx 23°$ corresponding to the (100) and (010) diffraction planes, respectively.

To probe the orientation of pseudohexagonal [23] hot-drawn nylon 6,6 fibers, we used the 010 equatorial reflection [24]. The orientation factor is given by Eq. (2):

$$f_j = \left(3\cos^2\phi_{j,z} - 1\right)/2 \tag{2}$$

where $\cos^2\phi_{j,z}$ is the average value of the square of the cosine of the angle between the fiber axis z and the j crystallographic axis ($j = a$, b, or c). Assuming rotational symmetry about the fiber axis, the value of $\cos^2\phi_{j,z}$ is given as follows:

$$\cos^2\phi_{j,z} = \frac{\int_0^{\pi/2} I_{hkl}\left(\phi_{j,z}\right)\cos^2\phi_{j,z}\sin\phi_{j,z}\,\mathrm{d}\phi_{j,z}}{\int_0^{\pi/2} I_{hkl}\left(\phi_{j,z}\right)\sin\phi_{j,z}\,\mathrm{d}\phi_{j,z}} \tag{3}$$

$$\cos^2\phi_{c,z} = 1 - 2\cos^2\phi_{010,z} \tag{4}$$

$$f_a = f_b = -f_c/2 \tag{5}$$

where $I_{hkl}(\phi_{j,z})$ is the intensity of the beam diffracted from the (hkl) planes that are normal to the j crystallographic axis.

2.6. FTIR spectroscopy

Attenuated total reflectance (ATR) spectra were collected on a Nicolet 560 FTIR spectrometer equipped with an Advantage microscope and using a liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detector. At least 256 scans were obtained to achieve an adequate signal to noise ratio. The spectral resolution was 2 cm^{-1}.

2.7. Thermal analysis

2.7.1. Differential scanning calorimetry

Melting temperatures and heats of fusion were measured with a Perkin–Elmer differential scanning calorimeter (DSC 7) on 3–5 mg samples. Each thermogram was obtained from 25 to 280 °C at a heating and cooling rate of 20 °C/min, and the instrument was calibrated using indium. The heat of fusion for the totally crystalline nylon 6,6 was taken from the literature as 191 J/g [20b].

2.7.2. Thermal gravimetric analysis

A Perkin–Elmer Pyris 1 thermal gravimetric analyzer (TGA) was used to determine the thermally induced weight loss of solid complexed nylon 6,6 film (after solvent evaporation) and as-received nylon 6,6 chips. Approximately 20–30 mg samples were heated from 25 to 650 °C at a rate of 20 °C/min in a nitrogen environment. As the sample is heated, the mass is measured as function of temperature. The % mass remaining is calculated by dividing the mass at the temperature of interest by the initial mass before heating.

2.8. Drawing and tensile properties

A tensile tester was used for slow drawing of the complexed filaments and films at different strain rates from 2 to 50 mm/min. The gauge length was 1″. For the first set of fibers in our experiments, after cold drawing in the Instron, the complexed filaments were held under slight tension on a rectangular glass frame and soaked in water to obtain decomplexed and regenerated filaments. The decomplexation time was about 1 day. Tensile properties of decomplexed filaments were measured on an Instron machine with a 50 mm/min (0.032 s^{-1}) strain rate, at 65% relative humidity and 25 °C, after being conditioned in this environment for 24 h.

After 1 day soaking in water, a second set of regenerated continuous fibers were drawn over a hot plate at 150–230 °C using rollers operating at different speeds. Draw ratios were initially equated to the ratios of take-up to feed velocities V_1 and V_0, respectively (Fig. 1). More exact draw ratios were determined by measuring the distances between ink marks on the fibers before and after drawing. Fiber denier was measured by weighing predetermined lengths (1–2 m) of fibers.

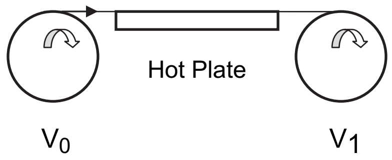


Fig. 1. Schematic diagram of hot drawing apparatus.

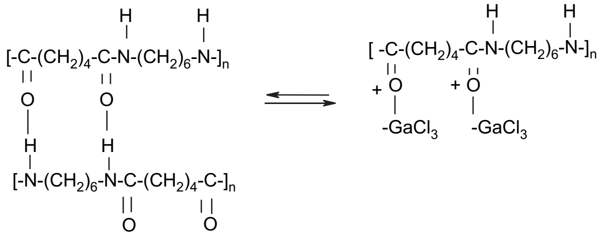
2.9. Scanning electron microscopy

Cross-sections of regenerated nylon 6,6 fibers were observed with a Hitachi S-3200N scanning electron microscope (SEM). Fiber samples were submerged in liquid nitrogen and were cut with a razor blade. The surface of the cut fiber was coated with a layer of gold before viewing.

3. Results and discussion

3.1. Complexation of nylon 6,6 with gallium trichloride

The complexation of nylons with Lewis acids was first reported by Roberts and Jenekhe at the beginning of the 1990s [25,26]. These authors discovered that the complexation of nylon 6 with $GaCl_3$ (see Scheme 1) can be accomplished in nitromethane, where the nylon chains do not remain fully extended and in crystalline register. Generally, pure un-complexed nylon 6 does not dissolve in this solvent. Our extensive studies of nylon 6,6 determined that its complexation with gallium trichloride can also be done in nitromethane. However, the complex forms and dissolves in this solvent at elevated temperatures, only when at least the stoichiometric amount of this Lewis acid is used. Furthermore, the complexation must be carried out under anhydrous conditions. Usually a highly viscous, heterogeneous (for stoichiometric ratio 1:1) mixture first forms when nylon chips are mixed with $GaCl_3$ in nitromethane at 70 °C. The viscosity of this system tends to increase and the maximum viscosity is often only reached after 2 h. It usually takes about 24 h (for stoichiometric ratio 1:1) to fully dissolve nylon 6,6 chips in nitromethane.



Scheme 1.

A 4–5 wt.% solution of nylon 6,6 complexed with $GaCl_3$ in nitromethane is transparent and has a yellowish color. The nylon 6,6/$GaCl_3$ solutions are stable if kept under N_2 environment. As mentioned earlier, $GaCl_3$/nylon 6,6 complex solutions in nitromethane can be prepared only by adding at least 1 mol of $GaCl_3$ per mole of amide groups, while other ratios, namely 1:1.5 and 1:2, did not lead to dissolution of the complex. However, if we increased the amount of Lewis acid compared to the polymer, then the time needed for fully dissolving nylon 6,6 chips was reduced to around 18 h for a stoichiometric ratio of 1.1:1, and the solution was very homogeneous with no undissolved polymer chips and no swollen polymer.

3.2. Properties of nylon 6,6/GaCl$_3$ complexed and regenerated films

Nylon 6,6/GaCl$_3$ complexed films and fibers before regeneration are amorphous, rubbery, soft, and very sticky. The complexed films can be easily stretched when pulled by both hands at room temperature. The glass transition temperature of the complexed film is ∼−32 °C, as found in the DSC thermogram (not shown) [27]. Generally, nylon 6,6 cannot be drawn post-spinning more than five times, because of strong intermolecular hydrogen bonding present between the amide linkages and crystallinity. When nylon 6,6 is complexed with gallium trichloride, interchain hydrogen bonding and crystallinity are fully eliminated (Scheme 1), and therefore it is possible to draw the complexed films to very high draw ratios. Consequently, complexed nylon 6,6 films or filaments with possibly a higher degree of molecular orientation can be obtained.

In our previous paper, we demonstrated that nylon 6,6/GaCl$_3$ complexed films could be drawn at room temperature to draw ratios up to 30 at low strain rate using a tensile tester [25]. It is obvious that the draw ratio of 30 obtained there is much higher than the draw ratio of 5 usually obtained in the conventional drawing of melt-spun nylon 6,6. The theoretical draw ratio for low molecular weight nylon 6,6 (30,000 g/mol) is ∼10. Therefore, in addition to the elastic stretching of complexed nylon 6,6 chains upon drawing, irreversible elongational plastic flow is also expected to have occurred. High draw ratios could not be achieved by increasing the strain rate. This indicated insufficient time available for molecular relaxation of the relatively bulky, complexed nylon 6,6 chains to slide past each other. In other words, increased frictional forces appear to obstruct drawability, at higher strain rates, even in the absence of interchain hydrogen bonding. Figs. 2 and 3 show that increasing molecular weight from 30,000 to ∼200,000 g/mol increased the drawability of films and led to increasing tenacities and moduli.

As shown in Fig. 4, nylon 6,6/GaCl$_3$ and regenerated nylon 6,6 fibers were examined by wide angle X-ray diffraction (WAXD). The WAXD pattern of nylon 6,6/GaCl$_3$ shows a broad halo, suggesting that the complex is completely amorphous. Diffraction patterns of regenerated nylon 6,6 and as-received nylon 6,6 (not shown) are similar, which demonstrates that the regeneration was complete.

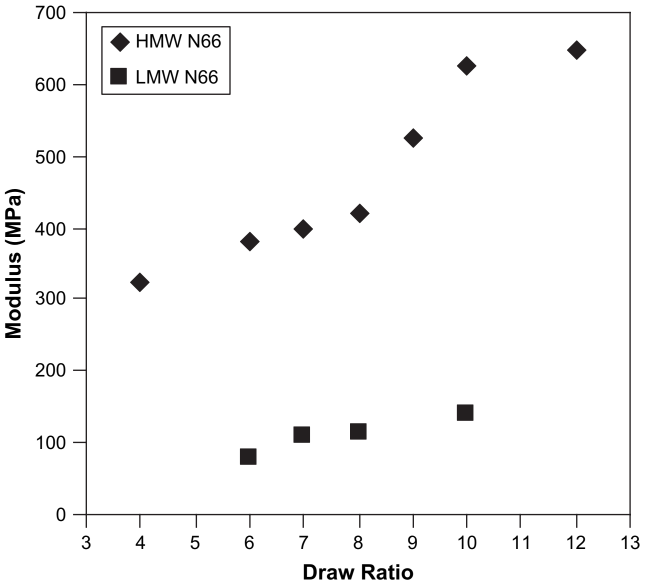


Fig. 2. Initial moduli of drawn regenerated nylon 6,6 films.

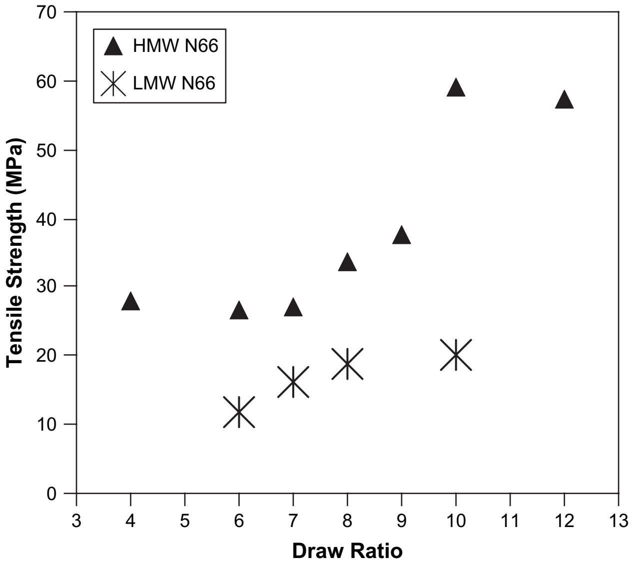


Fig. 3. Tensile strengths of drawn regenerated nylon 6,6 films.

From the FTIR spectra shown in Fig. 5 we can see bands at 3300 and 1640 cm^{-1}, which have been attributed to N−H and C=O stretching vibrations. Ga^{+3} metal coordination leads to breaking of the hydrogen bonds between nylon 6,6 chains (see Scheme 1). Since GaCl$_3$ forms a complex with the C=O group, the N−H bond is free. This causes the N−H vibrational band to shift to higher frequency (red shift from 3300 to 3366 cm^{-1}), while the C=O vibrational band shifts to lower frequency (blue shift from 1640 to 1617 cm^{-1}), due to the reduction in bond order [27]. Also the infrared spectra of initial and regenerated nylon 6,6 films are similar, suggesting complete removal of the Lewis acid from the complexed sample. Decomplexation occurs by soaking the complexed nylon 6,6 films or filaments in water. In order to remove all gallium trichlorides, the films must be soaked in water for at least 72 h [27]. In most cases, however, after 24 h the films contained only traces of gallium trichloride. Fig. 5 shows the FTIR spectra taken from the nylon 6,6/GaCl$_3$ complex with a stoichiometric ratio 1:1.1. In complexed films with a stoichiometric excess of GaCl$_3$, there are two new vibrational bands at 1681 and 3542 cm^{-1}, probably related to a different complex structure.

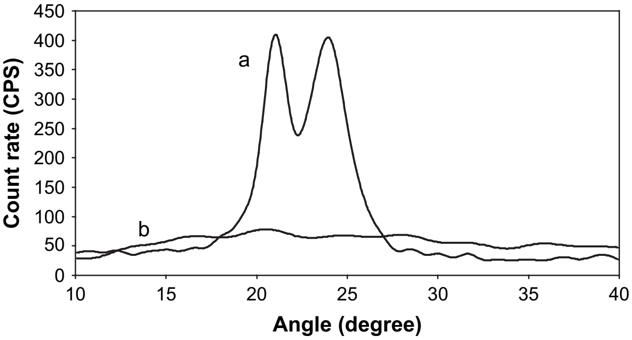


Fig. 4. WAXD diffractograms of (a) decomplexed and drawn nylon 6,6 fiber and (b) nylon 6,6/$GaCl_3$ complexed fiber.

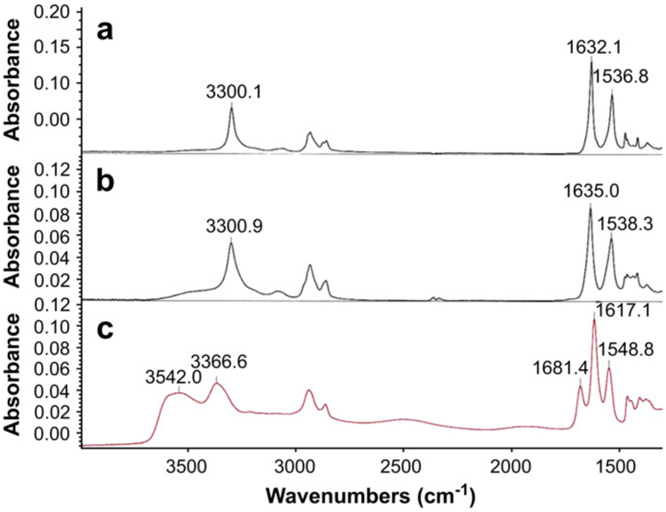


Fig. 5. FTIR spectra of (a) as-received nylon 6,6, (b) decomplexed undrawn nylon 6,6, and (c) nylon 6,6/$GaCl_3$ complex (ratio 1:1.1).

Fig. 6 (a and b) presents the TGA thermograms of nylon 6,6 chips and nylon 6,6/$GaCl_3$ (stoichiometric ratio 1:1.1) complexed film, respectively. The complexed film contains 63% by weight $GaCl_3$ and 10% of that (6.3% of total sample weight) is in excess compared to the 1:1 stoichiometric sample. In fact an ∼6% decrease in the weight of the sample occurs at ∼200° C, near the boiling point of $GaCl_3$ (201 °C). The remaining 1:1 nylon 6,6/$GaCl_3$ complexed film then begins to thermally degrade above 300 °C, or ∼100 °C below the pure nylon 6,6 chips. A substantial portion of this ∼70% weight loss must be due to $GaCl_3$ degradation, because below 300 °C the stoichiometric complex contains 61% $GaCl_3$ and 39% nylon 6,6. Unlike the pure nylon 6,6 chips, which begin to decompose above ∼400 °C, the complexed nylon 6,6 reaches a stable weight at this temperature and must now be predominantly nylon 6,6. Though these interesting observations warrant further study by mass spectrometry, it appears that aliphatic nylons may be rendered more thermally stable through complexation with Lewis acids, such as $GaCl_3$.

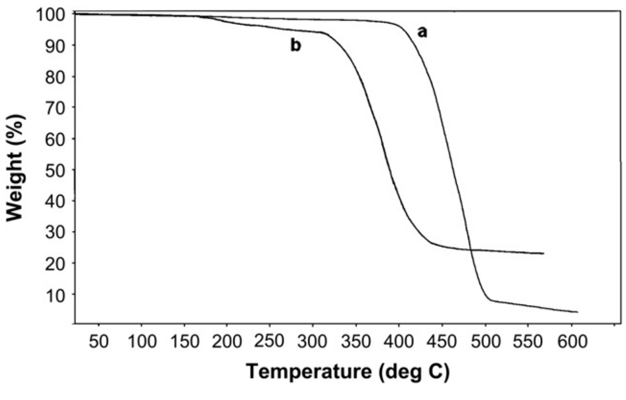


Fig. 6. TGA thermograms of (a) nylon 6,6 chips and (b) nylon 6,6/$GaCl_3$ film with stoichiometric ratio 1:1.1.

Differential scanning calorimetry was carried out to obtain melting and crystallization temperatures. Fig. 7 shows the DSC scan of the nylon 6,6/$GaCl_3$ complexed film. No melting and crystallization transitions are observed during heating and cooling, respectively, for complexed nylon 6,6, suggesting that the complex is essentially amorphous. Fig. 8 shows the DSC scans obtained for the regenerated undrawn nylon 6,6 film, which clearly show melting and crystallization transitions, and confirm the regeneration of crystallinity. The same results were observed for complexed and regenerated nylon 6,6 fibers (not shown). The crystallinity of the regenerated undrawn film based on its fusion enthalpy of melting is about 26%.

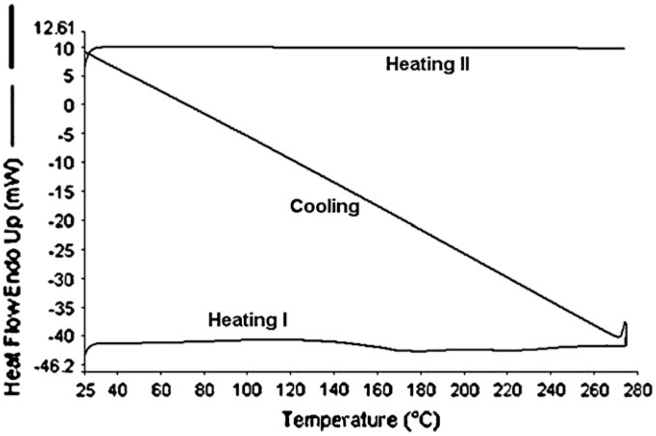


Fig. 7. DSC thermogram of nylon 6,6/$GaCl_3$ film with stoichiometric ratio 1:1.1.

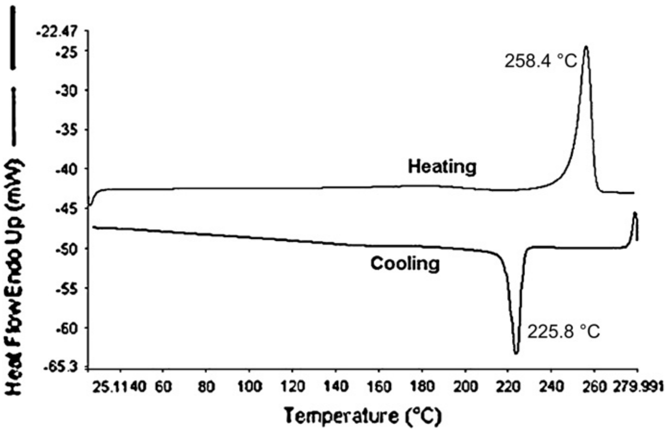


Fig. 8. DSC thermogram of regenerated undrawn nylon 6,6/$GaCl_3$ film.

3.3. Fiber spinning and fiber properties

Spinnability of a polymer solution can be easily determined by immersing a small spatula or a glass rod in the polymer solution and pulling it upwards. Generally, a liquid jet will form if a polymer solution has fiber-forming properties. If its viscosity is too low, then dripping occurs. For establishing the dry-jet wet spinning conditions, throughput at different pressures was measured at room temperature.

The viscosity dramatically decreases 2–4 days after preparing the nylon 6,6/$GaCl_3$ complex due to moisture in the air, and tends to level off thereafter, losing spinnability for producing fibers. This type of rheological instability can be explained by the interaction of $GaCl_3$ with moisture during the experiment. Therefore, it is very important to prepare and handle the nylon 6,6/$GaCl_3$ complex/nitromethane solution in the presence of dry nitrogen to prevent moisture absorption.

The non-solvent in the coagulation bath can also play a very important role in wet spinning. In order to coagulate nylon 6,6/$GaCl_3$, various liquids including methanol, ethanol, *n*-propanol, 2-propanol, *n*-butanol, acetone, and water were investigated. Among these potential coagulants, 2-propanol was found to be the only liquid that was suitable for the coagulation of the complex. In all the other liquids, the fibers were either brittle or did not coagulate completely to hold structure and form fibers. In water, for example, the coagulation was very fast and so the fibers were brittle.

In an attempt to achieve filament orientation we used the dry-jet wet spinning method. The gap between the spinneret and the coagulation bath was 2″. Fig. 9 shows a schematic of our dry-jet wet spinning system. The cylinder containing the spinning dope was well insulated to prevent heat losses and rapid changes in dope viscosity. The cylinder was equipped with a single orifice spinneret. The dry-jet wet spinning method is usually used for making Kevlar fibers, and differs from conventional wet spinning. In conventional wet spinning, the spinneret is located in the coagulation bath. However, in the dry-jet wet spinning, the spinneret is located above the coagulation bath (see Fig. 9).

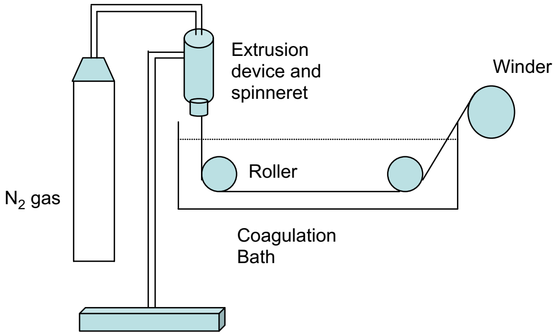


Fig. 9. Schematic of dry-jet wet spinning.

3.3.1. Cold drawing of short complexed fibers

The short complexed filaments made by this method were carefully drawn at room temperature using a tensile tester with drawing rates from 2 to 50 mm/min. The draw ratios obtained by cold drawing these complexed filaments show a range from 4 to 7. When the dry-jet wet spun complexed filaments had an even thickness and shape, high draw ratios were obtained. On the other hand, if the shape of the as-spun complex filaments was not even or had an irregular external appearance, low draw ratios were obtained. The complexed filaments were very weak and could be easily stretched compared to melt-spun nylon 6,6 fibers due to complete suppression of hydrogen bonding and crystallinity. The ability to be drawn and other characteristics of nylon 6,6/$GaCl_3$ complexed materials were discussed in our previous paper [27]. We obtained high draw ratios with complexed filaments in these experiments at a 5 mm/min (0.003 s^{-1}) strain rate. The stretched complex filaments were fixed on a rectangular glass frame and then soaked in water for 24 h to remove $GaCl_3$. Decomplexed or regenerated drawn nylon 6,6 filaments were prepared for tensile testing, and Table 1 summarizes the results of the tensile tests for the regenerated nylon 6,6 filaments. Initial moduli of these regenerated filaments were near to commercial melt-spun fibers, with initial moduli of about 6 GPa.

The draw ratio range varied from 4 to 7 for cold drawing, and depended on the morphology of the spun filaments. The measured tenacities showed low values, which can be related to defects in the structure of these fibers, presumably pores or voids. Initial moduli can be calculated from the initial slope of each load–extension curve (not shown), and increased with increasing draw ratios. At a draw ratio of 7, the initial slope was high compared to those fibers with lower draw ratios. The higher draw ratio was obtained by careful drawing of the short complexed fibers, which have no hydrogen bonding between their nylon 6,6 chains, at room temperature in the Instron. Our regenerated nylon 6,6 fibers showed an initial modulus up to 5 GPa at a draw ratio of 7.

3.3.2. Hot drawing of regenerated continuous fibers

Continuous complexed filaments were produced by dry-jet wet spinning (the spinning temperature was about 65 °C, and the coagulation bath temperature was 25 °C) after cold drawing during spinning, subsequent decomplexation, and finally careful drawing over a hot plate (150–230 °C) at different draw ratios by operating feed and take-up rollers at different speeds. When the dry-jet wet spun complex filaments had an even thickness and shape and low denier, then high hot-draw ratios were obtained. If the shape of the spun complex filaments

Table 1
Physical properties of high molecular weight (200,000 g/mol) regenerated nylon 6,6 cold-drawn short filaments obtained at a drawing speed of 2.5 mm/min

Draw ratio	Temperature of drawing (°C)	Tenacity (GPa)	Modulus (GPa)	Elongation at break (%)
Undrawn	–	0.075 ± 0.01	2.9 ± 0.9	203.8 ± 84.4
4	25	0.25 ± 0.02	3.2 ± 0.27	40.4 ± 13.06
5	25	0.24 ± 0.07	3.2 ± 0.4	36.3 ± 16
6	25	0.29 ± 0.07	4.7 ± 0.9	25.4 ± 1.14
7	25	0.39 ± 0.12	5.2 ± 0.7	42.2 ± 12.06

Dope concentration of nylon 6,6 in complex: 4–5 wt%; temperature of spinning: 60–70 °C.

Table 2
Physical properties and orientation factor of crystalline regions of high molecular weight (200,000 g/mol) regenerated nylon 6,6 continuous filaments initially spun at 1 m/min following hot drawing

Draw ratio	Temperature of drawing (°C)	Tenacity (GPa)	Modulus (GPa)	Elongation at break (%)	f_c
Undrawn	–	0.075 ± 0.01	2.9 ± 0.93	203.8 ± 84.4	–
4	150	0.195 ± 0.03	9.5 ± 1.27	18.6 ± 6.01	–
13.8	200	0.342 ± 0.07	10.5 ± 3.21	16.5 ± 5.6	–
9.2	230	0.253 ± 0.02	10.7 ± 1.20	15.3 ± 8.6	0.78
13.8	230	0.343 ± 0.07	12.8 ± 1.97	12.3 ± 6.9	0.85

Dope concentration of nylon 6,6 in complex: 4–5 wt%; temperature of spinning: 60–70 °C.

was not even or had an irregular external appearance and high denier, then low hot-draw ratios were obtained. By increasing the denier of fibers, their drawability decreased. The complexed filaments were very stretchable and could be easily extended compared to melt-spun nylon 6,6 fibers due to complete suppression of hydrogen bonding.

Table 2 summarizes the results of the tensile tests for the regenerated hot-drawn continuous nylon 6,6 filaments. Initial moduli of these regenerated filaments were high compared to melt-spun nylon 6,6 fibers. Initial moduli increased as the draw ratio increased. The draw ratio range varied from 5 to 13. All regenerated hot-drawn filaments were broken at low strain levels. The high modulus of these fibers presumes, and is in accord with long times to break, that the regenerated filaments were likely highly oriented at a draw ratio of 13. The crystallinity of the fiber hot-drawn at 200 °C to a draw ratio of 13 is about 46%, based on its observed enthalpy of melting. The low tenacities for this series of continuous fibers are probably due to non-uniformity or defects (voids or pores) in the fibers. The SEM cross-sections of these continuous high modulus regenerated nylon 6,6 fibers are shown in Fig. 10 (a–g). Our fibers do not show a perfectly smooth round shape. Because of the nature of the wet spinning process, the cross-section of fibers are somewhat collapsed. The fiber surface does not show voids, but the morphology of undrawn regenerated fibers

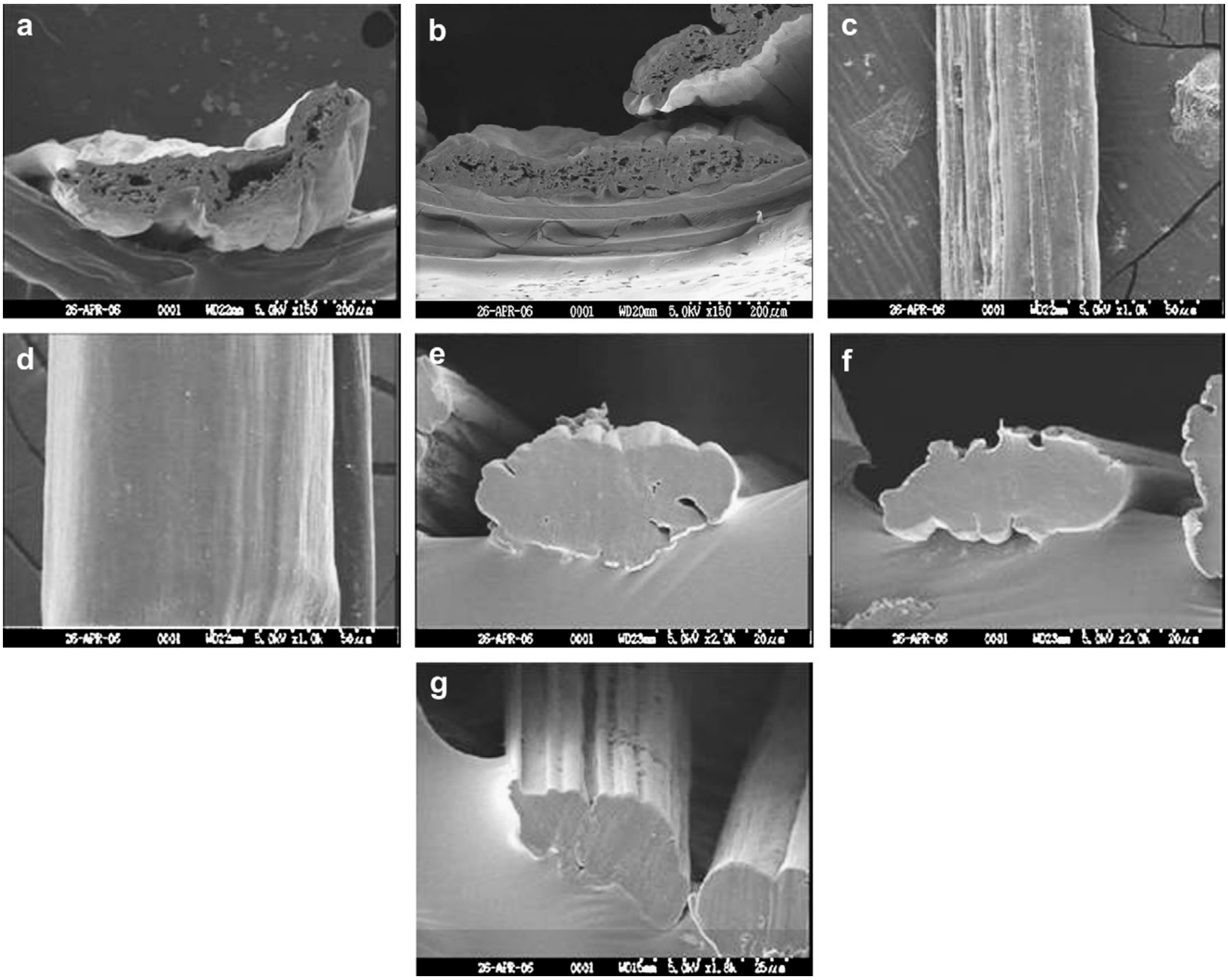


Fig. 10. SEM micrographs of cross-sectional and longitudinal views of regenerated undrawn and drawn nylon 6,6 fibers: (a) cross-sectional view of regenerated undrawn nylon 6,6 fiber; (b) cross-sectional view of regenerated undrawn nylon 6,6 fiber; (c) longitudinal view of regenerated undrawn nylon 6,6 fiber; (d) longitudinal view of regenerated hot-drawn (150 °C, DR ~ 4) nylon 6,6 fiber; (e) cross-sectional view of regenerated hot-drawn (150 °C, DR ~ 4) nylon 6,6 fiber; (f) cross-sectional view of regenerated hot-drawn (200 °C, DR ~ 13.8) nylon 6,6 fiber; (g) longitudinal view of regenerated hot-drawn (200 °C, DR ~ 13.8) nylon 6,6 fiber.

is very porous. By measuring the surface area of fiber cross-sections and the weight of fibers, and considering the density of nylon 6,6 as 1.14 g/cm^3, a fiber porosity of ~70% was calculated. Though the SEM micrographs of hot-drawn regenerated fibers show compact structures with very low apparent porosity, their low tenacities are likely due to the presence of voids lying along the fiber axis perpendicular to the fiber cross-section, which lead to stress concentration.

The observed orientation factors of crystalline regions for regenerated fibers hot-drawn to draw ratios 9.2 and 13.8 are presented in Table 2. They show that nylon 6,6 chains are predominantly oriented during the drawing process, and, therefore, chain slippage is not dominant. The orientation factors observed here for the crystalline regions of regenerated hot-drawn fibers agree with orientation factors of melt-spun drawn fibers reported in the literature [28,29]. However, we need to mention that in WAXD measurements, the contributions of small crystals are often difficult to detect [30].

In the following publications a full evaluation of the morphology and mechanical properties of fibers produced by continuous spinning of complexed nylon 6,6/$GaCl_3$ in nitromethane solutions and using different coagulants and heat treatments (annealing) will be given.

4. Conclusions

Disruption of the interchain hydrogen bonding between high molecular weight nylon 6,6 chains made possible by complexation with $GaCl_3$ led to the production of strong fibers upon regeneration (removal of $GaCl_3$) and subsequent hot drawing. Stable nylon 6,6/$GaCl_3$ complex solutions were obtained under nitrogen in nitromethane. High modulus fibers were produced from $GaCl_3$/high molecular weight nylon 6,6 complexes. Different draw ratios were obtained by low strain rate stretching of complexed fibers made by using a dry-jet wet spinning process. The complexed fibers, which are rubbery, soft and very sticky, similar to their films, can be stretched at low strain rates by using a tensile tester. The maximum draw ratio achieved for fibers in our experiments was about 13. It has been demonstrated earlier, as well as in this work, that Lewis acid complexation of aliphatic nylons provides a way to temporarily suppress the effects of hydrogen bonding, while drawing, allowing a potential increase in orientation, and then, upon decomplexation/regeneration, to restore hydrogen bonding to the highly oriented fiber, resulting in high modulus. Continued research will focus on using different coagulants and trying to produce more uniform continuous filaments, with more compact pore-free structures, for subsequent (cold and hot) drawing to increase fiber tenacity and further improve modulus. Detailed study of fiber morphologies will hopefully lead us to some understanding of the relationships between the orientations of amorphous and crystalline regions and the physical properties of the fibers, following decomplexation/regeneration by removing the $GaCl_3$, both before and after they are drawn.

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