

Influence of Interchain Forces and Supermolecular Structure on the Drawing Behavior of Nylon 66 Fibers in the Presence of Supercritical Carbon Dioxide

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ABSTRACT: The drawing behavior and mechanical properties of as-spun and highly oriented nylon 66 fibers drawn in supercritical carbon dioxide (SCCO₂) were investigated. Conditions including different temperatures, CO₂ pressures, and plasticizers with different polarity were systematically studied. Results indicate that CO₂ is an efficient plasticizer for as-spun nylon 66 fibers as shown by decreases in the draw stress. In contrast, CO₂ shows only a slight influence on the drawability of highly oriented nylon 66 fiber. The effect of other plasticizers such as water, methanol, and ethanol on the drawability of nylon 66 fibers is very similar to that of CO₂. Tenacity and modulus of one-stage drawn

fibers were less than 0.8 and 5.0 GPa, respectively. Fibers with the highest tenacity and modulus, 0.96/5.04 and 1.06/5.04 GPa, were obtained by two-stage drawing in SCCO₂ from as-spun and drawn nylon 66 fibers, respectively. The main reason for the extremely low draw ratios (<6.0) of nylon 66 fibers was the presence of hydrogen bonds in the crystalline phase. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2282–2288, 2004

Key words: nylon; drawing; mechanical properties; supercritical carbon dioxide; modulus

INTRODUCTION

For nearly a century, scientists have studied the use and development of synthetic and natural fibers.¹ The ideal fiber properties are high tenacity and modulus, or a combined balance of properties like those of spider major ampullate silk (high tensile strength, stiffness, and toughness). To date, two major research directions have been taken to produce high-performance fibers.

The first direction involves the production of fibers using synthesis of new polymers, or by special spinning techniques different from traditional melt, wet, and dry spinning. The fibers produced depend on the type of raw material used and there are two basic classes: (1) rigid rod or liquid crystalline polymers such as aromatic polyamides (Kevlar, Nomex), aromatic polyesters (Vectra), aromatic polyimides (Polyimide 2080), aromatic heterocyclic polymers (PBI, PBO),² and PIPD or "M5" fibers^{3,4}; and (2) flexible chain polymers in highly oriented structures such as ultrahigh molecular weight polyethylene (UHMWPE) and poly(vinyl alcohol).^{5,6}

A second and relatively new direction involves the use of man-made silks and silk-like polymers based on biotechnology for novel high-performance fibers,^{7,8} although to obtain the ultimate high performance, the productivity and cost are out of consideration.

Most recently another direction has been considered, which focuses on the use of conventional semicrystalline polymers and commercially manufactured synthetic fibers to improve the fiber properties at a reasonable additional cost. According to the recent data,⁹ by far no other synthetic fibers are substantially better and cheaper than the present polyester and polyamide fibers. Also surprising is that the tensile strength of these fibers (<1.0 GPa) is much lower than their theoretical strength, and the tensile modulus is also only 1/20–1/5 of their theoretical lattice modulus.^{10–12} This suggests that additional posttreatment processes might expand their property range and applications.

One such method involves postdrawing fibers in the presence of subcritical or supercritical carbon dioxide (SCCO₂). This process has shown to successfully improve the mechanical properties of polyethylene terephthalate (PET) fiber and UHMWPE fiber.^{13,14} Initial studies have also been done on nylon 66 fiber. Compared to PET, high-density polyethylene (HDPE) fiber, drawing nylon 66 fiber in SCCO₂ presents a larger complexity of variables attributed to both the chemical structure and the supermolecular structure.

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Therefore, it is necessary to carry out systematic studies related to the influence that CO₂ and other plasticizers have on the fiber's drawability, orientation, and crystalline morphology, and ultimate mechanical properties. This article reports results from such a study.

EXPERIMENTAL

Materials and preparation of samples

The fibers used in this study include nylon 66 as-spun tire cord, as-spun carpet fiber, and drawn Solutia fiber, all supplied by Solutia Inc. (St. Louis, MO). Methanol (CAS 67-56-1), ethanol (CAS 64-17-5), and 2-propanol were purchased from Fisher Scientific Co. (Pittsburgh, PA) and used as received.

The drawing of nylon 66 fibers in CO₂ was performed in a custom high-pressure drawing apparatus. Details of the apparatus were reported previously.¹³ Coleman grade CO₂ was supplied through a Hydro-Pac, Inc. (Fairview, PA) high-pressure carbon dioxide pump. All samples were soaked 30 min before drawing and drawn at a strain rate of 0.1/60 s. When drawing in different plasticizers such as water and methanol, there is enough liquid plasticizer at the bottom of the vessel to keep the nylon 66 fibers in a saturated atmosphere. Stress values were calculated from force measurements normalized by the fiber cross-sectional area. The draw ratio is calculated from the ratio of $(D_0/D_1)^2$, where D_0 and D_1 represent the diameter before drawing and after drawing. Because the increase in density of nylon 66 after drawing is very small (<1%), the draw ratio from $(D_0/D_1)^2$ will be equal to the draw ratio defined on the basis of extension in length for a constant volume system.

Characterization

Differential scanning calorimetry (DSC) measurements were carried out using a TA Instruments 2910 DSC (DuPont/TA Instruments, New Castle, DE) from 20 to 290°C, at a heating rate of 10°C/min. X-ray measurements were conducted on a Phillips/Norelco PW-1830 diffractometer in transmission mode using a nickel-filtered Cu-K_α radiation ($\lambda = 0.154$ nm) operated at 40 kV and 30 mA. A Fuji (Osaka, Japan) AS-Va image plate was used to collect data. Single fibers were mounted on a cardboard template with a gauge length of 20 mm using a 5-min epoxy adhesive. Tensile tests were performed on an Instron (Canton, OH) 5500R with a 50 N load cell at a strain rate of 1.0/60 s. The fiber diameter was measured on an Olympus (Osaka, Japan) optical polarizing microscope calibrated with a micrometer scale. Birefringence measurements were also made on the same Olympus polarizing microscope, equipped with a 1/20th λ Berek compensator

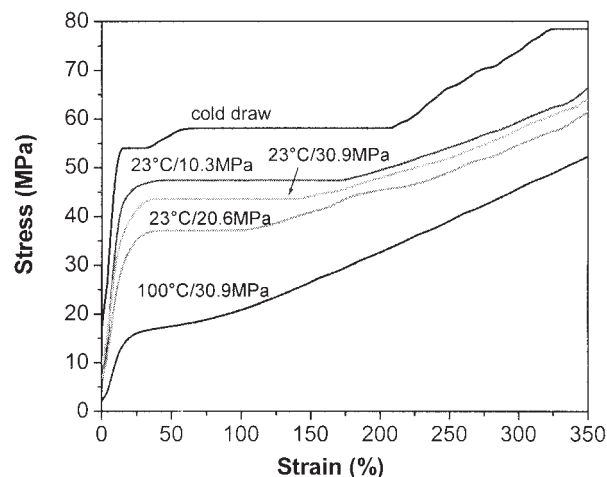


Figure 1 Stress-strain curves of tire-cord fibers drawn in CO₂ at different temperatures and pressures.

(Olympus). The retardation was measured by using both thick and thin Berek compensators with individual filaments.

RESULTS AND DISCUSSION

Drawing behavior in SCCO₂

The stress-strain curves of tire-cord fibers drawn at different temperatures and pressures are presented in Figure 1. The drawing stress or yield stress (σ) of a cold-drawn sample is around 59 MPa. At the same drawing temperature, σ initially decreases as a function of CO₂ pressure and then increases at higher pressures. σ of fiber drawn at 30.9 MPa is 48 MPa, which is higher than that of the sample drawn at 20.6 MPa and lower than that of the sample drawn at 10.3 MPa. As expected, increasing the draw temperature causes a reduction in yield stress of polymers¹⁵ and it is the same case for tire-cord fibers (Fig. 2). Note that the drawing response alters at around 80°C, with the deformation becoming affine (i.e., neck formation is suppressed). Compared to samples drawn at 100°C and 30.9 MPa (Fig. 1), σ of a sample drawn at 100°C without CO₂ is 25 MPa and 10 MPa higher. This indicates the effect of CO₂ is still present even at these elevated temperatures.

The fact that σ decreases, even at very low pressures and temperatures, indicates that CO₂ can effectively plasticize the semicrystalline nylon. It acts as a diluent or plasticizer, penetrates the amorphous regions, and improves the mobility of nylon 66 chains. If compared to the stress-strain curves of PET fibers (Figs. 5 and 6 in Hobbs and Lesser¹³), the influence of CO₂ on the drawing behavior of nylon 66 is obviously different. Note that the amount of decrease in σ for PET and nylon is very different. The reduction in σ is around 85–98% for PET when drawing was carried out, even

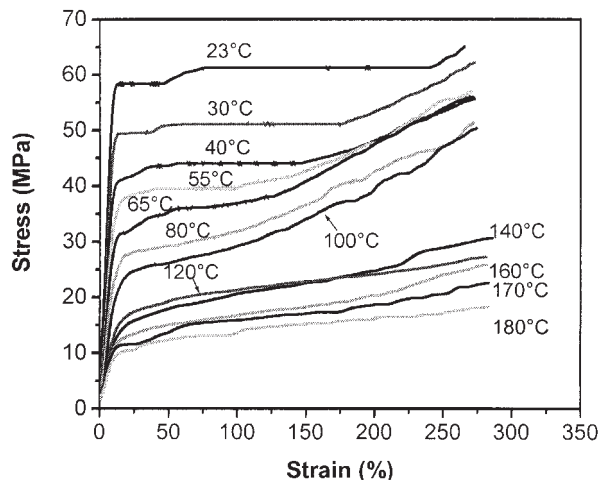


Figure 2 Stress-strain curves of tire-cord fibers drawn in air at different temperatures.

in subcritical CO_2 and supercritical CO_2 at 35°C. For nylon 66, the decrease in drawing stress is only about 28.8–45%. The maximum reduction in σ is less than 75% in our research for nylon 66. The other absolute difference exists in the draw ratio. Although drawing in CO_2 can decrease the drawing stress, there is no commensurate increase in the draw ratio of nylon 66 fibers (regardless of whether they were as-spun or highly oriented fibers), over the range of test temperatures or pressures. In comparison, an increase in the draw ratio of about 2–3 times was obtained in PET fiber when the stress-induced and CO_2 -enhanced crystallization were relatively hindered.

There are several possible reasons for these differences in the drawability between PET and nylon 66 fibers. The first reason may be associated with the different interchain interactions resulting from secondary bonds. UHMWPE fiber shows the weakest interchain interaction (van der Waals forces). PET contains higher interchain forces attributed to dipole interaction. Compared to PET and UHMWPE, nylon 66 has the highest interchain interaction arising from its higher polarity and the well-known hydrogen bonds between amide groups between adjacent chains. The cohesive energy density is a quantitative description of these interchain interactions. The cohesive energy densities of PE, PET, and nylon 66 are 8.4, 60.3, and 163.4 kJ/mol, respectively.¹⁶ To further explore the influence of interchain force on the drawing behavior, other solvents with higher polarity such as water, methanol, ethanol, and 2-propanol were used in our research. It is expected that the small molecules can penetrate the amorphous region of nylon 66 and even get to the surface of crystallites. Hydrogen bonds between the small molecules and nylon may replace part of the hydrogen bonds between nylon-nylon, which could, in turn, weaken the interchain forces. The

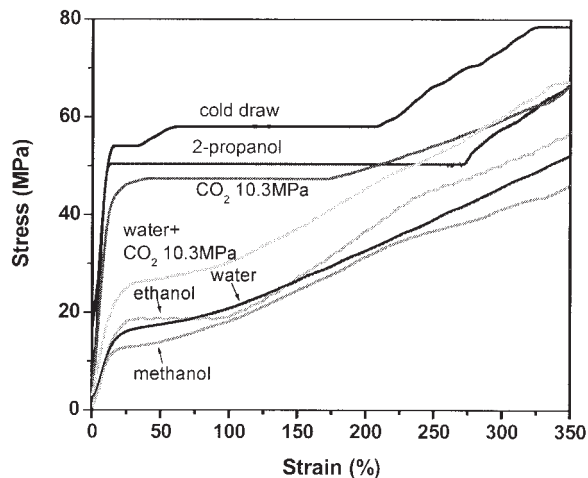


Figure 3 Stress-strain curves of tire-cord fibers drawn in different plasticizers.

stress-strain curves of tire-cord fiber drawn in these solvents at 23°C are presented in Figure 3. The results indicate that methanol and water are more effective plasticizers than CO_2 and 2-propanol. The reduction in σ is about 85%, which is higher than that of fibers drawn at high temperature in CO_2 . Weakening the hydrogen bonds can result in better drawability. Note, however, that the draw ratio is close to that of drawn samples drawn in SCCO_2 . This implies that the overall orientation cannot be significantly affected or improved using this method on nylon 66 fibers.

Yield stresses σ (solid square) of nylon 66 tire-cord fibers drawn at different temperatures versus the ratio of drawing temperature (T_d) and glass-transition temperature (T_g , 50°C) of nylon 66 (T_d/T_g) are plotted in Figure 4. σ is described by an exponential relationship

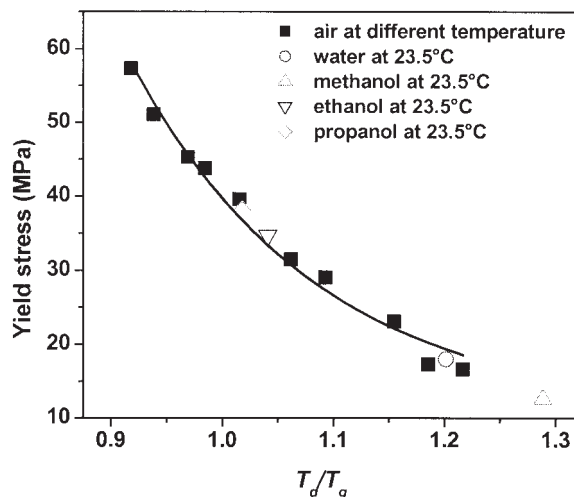


Figure 4 Plot of yield stresses of tire-cord fibers drawn at different temperatures and in different plasticizers versus the ratio of drawing temperature (T_d) and glass-transition temperature (T_g) of nylon 66.

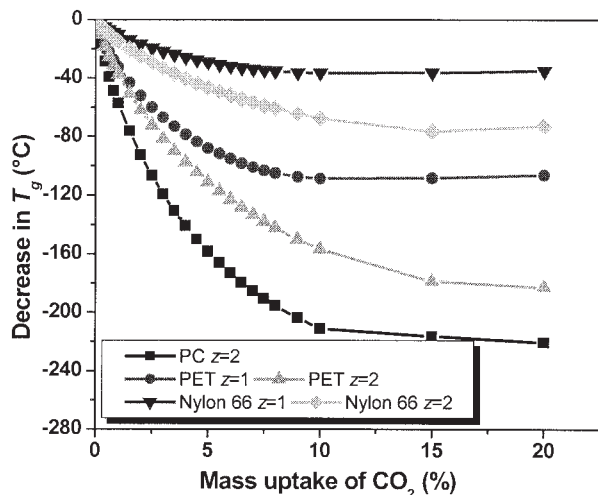


Figure 5 Decrease in T_g versus mass uptake of CO_2 of PC, PET, and nylon 66 calculated from the Chow model.

with T_d/T_g :

$$\sigma = 2408.1 \exp(-4.0756 \times T_d/T_g) \quad (1)$$

The correlation coefficient for this fit is 0.988. The yield stresses of fibers drawn in water, methanol, ethanol, and propanol at 23.5°C are 18.0, 12.6, 34.6, and 38.0 MPa, respectively. Effective T_g values of the plasticized fibers calculated from the above equation of nylon 66 fibers in saturated water, methanol, ethanol, and propanol atmosphere are -28, -44.9, 9.9, and 16.3°C, respectively. All of these data are also plotted in Figure 4 by open symbols. The depression in both the T_g and the efficiency in plasticization of nylon 66 decreases in the following order: methanol, water, ethanol, and propanol. These results are in accordance with Birkinshaw's research on the plasticization of water and alcohol on nylon 66 by dynamic mechanical analysis.¹⁷

Another consideration that significantly affects the drawability of nylon 66 fibers is the intrinsic crystallization characteristics of the polymer, and the crystallinity both before and that developed during drawing. Crystallites act as physical crosslinks and restrict drawing to high draw ratios. The crystallinity of the as-spun tire cord and carpet nylon 66 fiber is about 33% (considerably higher compared to that of amorphous PET fibers). In fact, the effect of crystallinity on the drawability was also observed in the PET drawing in the presence of CO_2 . The drawability decreased dramatically when the crystallization became more pronounced at increased pressures. This was observed even when the draw temperature was very low (35°C).¹³

Our research on drawing of polycarbonate (PC) in SCCO_2 further supports both of the above discussions.¹⁸ Because of the extremely slow kinetics of crys-

tallization of PC, the crystallization during drawing can be controlled. Therefore, the draw ratio of samples drawn in SCCO_2 is about 7–8 times higher than that of PC drawn without CO_2 , even at high temperatures. The drawing stress is even lower than that of PET drawing in SCCO_2 . The increase in drawability of PC is even much better than that of PET in SCCO_2 .

Finally, the overall drawability of nylon 66 is also affected by the equilibrium mass uptake of CO_2 . The thermodynamically determined solubility or mass uptake of CO_2 in different polymers has been investigated. According to Chow's model,¹⁹ the decreases in T_g as a function of mass uptake of CO_2 of PC (calculated with $z = 2$, $T_g = 150^\circ\text{C}$, an average value of $\Delta C_p = 0.0585 \text{ cal g}^{-1} \text{ K}^{-1}$ ^{20,21}), PET (calculated with $z = 1$ and 2, $T_g = 77^\circ\text{C}$, and $\Delta C_p = 0.0806 \text{ cal g}^{-1} \text{ K}^{-1}$ ^{16,20}), and nylon 66 (calculated with $z = 1$ and 2, $T_g = 50^\circ\text{C}$, and $\Delta C_p = 0.01258 \text{ cal g}^{-1} \text{ K}^{-1}$ ²²) are plotted in Figure 5. It is obvious that the decrease in T_g of PC is much faster than that in PET and nylon 66 at the same CO_2 mass uptake. The depression in T_g of nylon 66 by SCCO_2 is very slight. Previous research also shows that the mass uptake of CO_2 in nylon 66 is much lower than that in PET, and polyvinylidene fluoride (PVDF) at a given temperature and pressure.²³ The measured mass uptake of CO_2 in PC right after depressurization is about 3.0–3.5 wt % and is much higher than that of nylon 66. The significant depression in T_g greatly increases the mobility of rigid PC chains and drawability. It seems that the nature of nylon 66 is not favorable for high solubility of CO_2 .

Incorporating all of the above considerations, the influence of SCCO_2 on the drawability of highly oriented and crystallized Solutia nylon 66 fiber should be much less significant than that on the as-spun fiber. Figure 6 shows the stress–strain curves of Solutia ny-

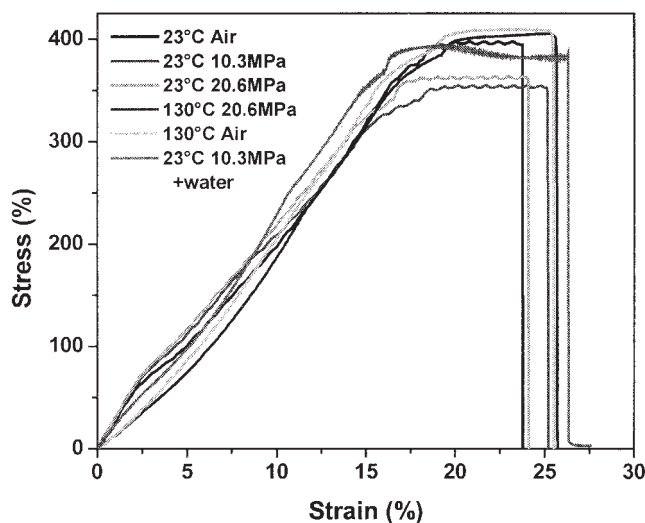


Figure 6 Stress–strain curves of Solutia fibers drawn at different conditions.

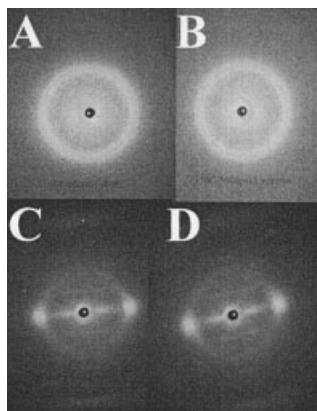


Figure 7 WAXD patterns of tire-cord fibers: (A) as-spun, (B) 150°C/34.3 MPa soaked for 30 min, (C) 100°C/27.4 MPa drawn, and (D) 100°C/air drawn.

lon 66 fibers drawn in CO₂, different plasticizers. Except for subtle differences in moduli, the strength and elongation at break of the samples drawn under different conditions are very close.

Crystalline morphology and orientation

Typical WAXD patterns of as-spun tire-cord fiber (A), as-spun fiber soaked at 150°C/34.3 MPa for 30 min (B), fiber drawn at 100°C/27.4 MPa (C), and fiber drawn at 100°C/air (D) are presented in Figure 7, respectively. The undrawn as-spun fibers have a typical triclinic unit cell with very low orientation. There is no obvious change in reflection intensity of the 100 and 010 reflection plane, even though the as-spun fibers were soaked at 150°C and 34.3 MPa for 30 min. Also, their crystallinities, as measured by DSC, are very close. This is different from the soaking of PET¹³ and even high molecular weight PC²⁴ in SCCO₂, where the crystallization is greatly enhanced at this high temperature and high pressure. After drawing, the WAXD patterns show a highly oriented structure with the crystallographic planes perpendicular to the fiber axis. The total average orientation factor (f_{av}) calculated from birefringence of undrawn tire-cord as-spun fiber is 0.0620. The f_{av} values of drawn tire-cord fibers are in the range of 0.63 to 0.71. The increase in f_{av} is about 10-fold. The f_{av} value of undrawn Solutia fiber is 0.6495, and those of the drawn Solutia fibers are also in the range of 0.63 to 0.71. Because the Solutia fiber is already highly oriented, there is no evident increase in orientation by drawing in CO₂. There is no obvious difference in the WAXD patterns between samples drawn with and without CO₂. It appears that the high pressure imposed by CO₂ does not affect the crystal structure of nylon 66 during the drawing procedure. The crystallinity of the tire-cord fiber and Solutia fiber is 33%. The range of crystallinities of the drawn tire-

cord fibers is around 36 to 42%. Drawing in CO₂ does not show a substantial influence on the crystallinity of drawn fibers.

Mechanical properties

The one-stage drawing results indicate that fibers drawn between 120 and 140°C in CO₂ have a better combination of mechanical properties, and low-pressure processing (10.3 MPa) produces the best results. Fibers drawn to a higher draw ratio have a higher degree of orientation and tenacity. Tenacity and modulus (E) versus draw ratios of one-stage drawn tire-cord fibers at different conditions are shown in Figure 8. The tenacity demonstrates a much better linear relationship with draw ratio than does modulus. It can be clearly seen that the maximum draw ratio, maximum tenacity, and maximum modulus are less than 5, 0.8 GPa, and 5.0 GPa, respectively.

Table I shows the mechanical properties of two-stage drawn fibers under different conditions. Fibers with the highest tenacity and modulus values (0.96/5.04 and 1.06/5.04 GPa) were obtained by two-stage drawing in SCCO₂ from as-spun and drawn nylon 66 fibers, respectively. Compared to one-stage drawing, two-stage drawing can further increase the tenacity and modulus of nylon 66 fibers. Drawing in plasticizers such as water, other supercritical fluids such as nitrogen do not result in better mechanical properties.

Although two-stage drawing in CO₂ can increase the mechanical properties of nylon 66 fibers, the draw ratio is lower than 6.0 and still very low. Even for highly oriented UHMWHDPE fiber, with crystallinity > 90%, the maximum draw ratio of fiber drawing in SCCO₂ could reach around 2.0.¹³ Therefore, the relatively high crystallinity is not the only reason for this. Hydrogen bonding plays a significant role in this

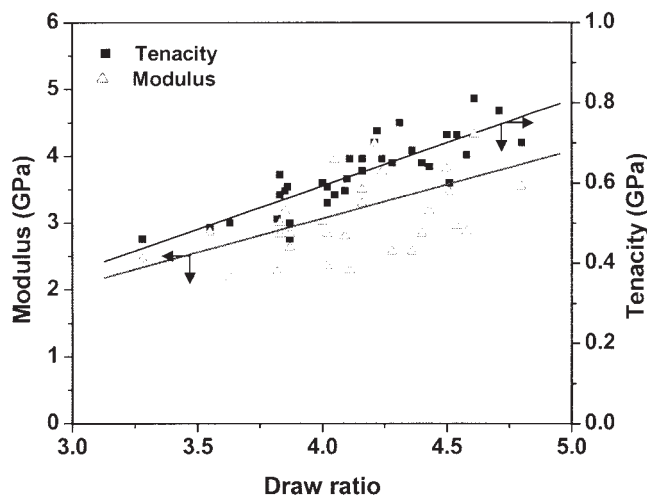


Figure 8 Tenacity and modulus versus draw ratio of one-stage drawn tire-cord fibers at different conditions.

TABLE I
Tenacity, Modulus (E), and Elongation at Break (ϵ) of Nylon 66 Fibers Drawn at Different Conditions

Drawing conditions		Tenacity (GPa)	E (GPa)	ϵ (%)
Stage 1	Stage 2			
140°C/10.3 MPa ^a	140°C/32.6 MPa	0.85	4.34	21.07
23°C/air ^a	130°C/air	0.87	4.30	20.78
23°C/10.3 MPa ^a	130°C/32.6 MPa	0.96	5.04	20.16
23°C/10.3 MPa ^b	130°C/10.3 MPa	0.83	5.34	23.06
23°C/air ^b	130°C/air	0.71	5.29	30.93
23°C/10.3 MPa ^b	130°C/32.6 MPa	0.66	4.76	21.06
23°C/air ^c	130°C/air	0.96	4.32	26.11
23°C/10.3 MPa ^c	130°C/10.3 MPa	1.06	5.04	23.94
23°C/32.6 MPa ^c	130°C/32.6 MPa	1.30	5.08	22.79
23°C/water ^a	130°C/air	0.80	4.14	19.26
23°C/water ^a	130°C/10.3 MPa	0.77	4.68	18.75

^a As-spun carpet fiber.

^b As-spun tire-cord fiber.

^c Solutia, Inc.

case.²⁵ Plasticizers with high polarity penetrate the amorphous regions, thereby weakening the hydrogen bonds between nylon chains. This, in turn, lowers the drawing stress but does not affect the overall draw ratio. However, the hydrogen bonds in the crystalline phase, together with the high crystallinity, are the factors that govern the draw ratio of these fibers. This is in accordance with the molecular dynamics simulations and NMR characterization of molecular motions in nylon 66, which indicates the hydrogen-bonded amide groups in crystallites are relatively immobile at all temperature below 230°C.²⁶ In a normal crystal stem length of nylon 66, there are around 20 hydrogen bonds, and the energy required to disassociate all of these bonds is near equivalent to the disassociation energy of a covalent bond.^{27,28} Consequently, chain scission takes place before chain pullout, which restricts the drawing of nylon 66 fiber to high draw ratio. To achieve high drawability and further improve the strength and moduli of these fibers, complete scission of the hydrogen bonds before drawing is necessary. "Unzipping" the hydrogen bonds using Lewis acid-base complexation,²⁹ drawing the subsequent amorphous fiber to high orientation in SCCO₂, and "zipping" the nylon 66 chains to recover the hydrogen bonds, as well as high crystallinity under load with or without SCCO₂, are ongoing research directions in our laboratory.

CONCLUSIONS

CO₂ is an efficient plasticizer for as-spun nylon 66 fibers and can decrease the drawing stress. CO₂ shows slight influence on the drawability of highly oriented drawn nylon 66 fiber. The effect of other plasticizers such as water, methanol, and ethanol on the drawability of nylon 66 fibers is very similar to that of CO₂. Strength and modulus of one-stage drawn fibers are

less than 0.8 and 5.0 GPa, respectively; lower than those of two-stage drawn fibers. Fibers with highest tenacity and modulus 0.96 GPa/5.04 GPa and 1.06 GPa/5.04 GPa were obtained by two-stage drawing in SCCO₂ from as-spun and drawn nylon 66 fibers, respectively.

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