Nylon 66 Nanofiber Sheets Prepared by Carbon Dioxide Laser Supersonic Multi-drawing

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Abstract  Carbon dioxide (CO2) laser supersonic drawing is a new technique for preparation of nanofibers in a vacuum chamber using a CO2 laser and a supersonic air jet formed directly below the fiber supply orifice. In this study, we have applied a CO2 laser supersonic multi-drawing method to nylon 66 to produce nanofiber sheets. A fiber of 182 µm in diameter was drawn at a drawing speed of 223 m s\(^{-1}\) and a draw ratio of approximately 1.3×10^5 to obtain a nanofiber sheet having 25 cm length, 17 cm width, 61.5 µm thickness, and an average nanofiber diameter of approximately 0.5 µm.

The nanofiber sheet exhibited two melting temperature (\(T_m\)), 259°C (\(T_m^1\)) and 270°C (\(T_m^2\)). \(T_m^2\) is approximately 10°C higher than the \(T_m\) value of nylon 66 at usual. The sheet showed no drastic fiber shrinkage during heating, and the fiber form was held even at the temperature of the usual melting temperature or higher.

Keywords  Nylon 66, Nanofiber, CO2 laser supersonic multi-drawing, DSC, Melting temperature

Introduction

It has been reported that nanofibers with a diameter smaller than 1 µm exhibit markedly improved electrical, mechanical, thermal and other properties owing to their heightened molecular chain orientation1–2). Nanofibers for industrial use can be manufactured by various methods, including the sea-island conjugated melt spinning process3) and the melt blowing process4), among others. Another method that has reached the level of practical use in recent years is electrospinning in which a polymer material is dissolved in a solvent and spun into nanofibers under the application of a high voltage5).

Suzuki et al. developed a carbon dioxide (CO2) laser supersonic drawing (CLSD) method for producing long nanofibers in a single process without using any chemical solvents, which are feared to adversely affect the environment and living organisms. To date it has been reported that this new method of producing nanofibers is applicable to various thermoplastic polymers such as poly-L-lactide acid (PLLA)6), polyethylene terephthalate (PET)7), polyethylene naphthalate (PEN)8), and polyglycolic acid (PGA)9). With the CLSD method, nanofibers are produced using a CO2 laser and a supersonic air jet created directly below the fiber supply orifice installed in a vacuum chamber. The results of a flow analysis conducted with a 3D finite element method revealed that the fiber spinning velocity in this process is more than three times faster than the usual ultrahigh-speed spinning velocity of 91–133 m s\(^{-1}\) and exceeds the speed of sound of 346.5 m s\(^{-1}\)10–12). Moreover, a CO2 laser supersonic multi-drawing (CLSMD) process using an improved apparatus has been developed that is capable of drawing multiple strands of an original fiber simultaneously to produce a nanofiber sheet and has been applied to manufacture sheets of PET13), polypropylene (iPP)14) and other polymers.

In our research on the production of nylon 66 nanofibers by CLSD, we have reported that nylon 66 nanofibers were obtained that contained crystals having a melting temperature10–15°C higher than that ordinarily observed for nylon 6615). The quantity of such crystals having a higher melting temperature is related to the molecular orientation and an increase in the trans/gauche ratio. This implies that various phenomena may occur in the nanofibers such as higher crystal perfection due to improved packing of the molecular chains, the formation of tie molecules or increased crystal thickness16). A higher melting temperature is an important characteristic because it increases the thermal re-
sistance of a material and thus expands its potential range of application.

In this study, the CLSMD process was applied to nylon 66 to investigate the production of nanofiber sheets possessing higher-melting-temperature crystals.

**Experimental**

**Samples**

Commercial nylon 66 pellets manufactured by Sigma-Aldrich Corp. were used as the raw material in this study. The pellets were first dried under reduced pressure at 80°C for 24 hr and then melt-spun into the original fiber of 182 μm in diameter using a high-temperature, vacuum-gas-replacement, twin-rotor kneading and discharging machine made by Musashino Kikai Co., Ltd. The melt spinning conditions were a spinning temperature of 285°C, a fiber discharge rate of 6 ml min⁻¹, and a winding speed of 145 m min⁻¹.

**CO₂ laser supersonic multi-drawing system**

The configuration of the CLSMD system used in this study is shown schematically in Figure 1. This system consists of a spool for supplying the original fiber, a continuous-wave CO₂ laser emitter (wavelength: 10.6 μm; diameter: 1.8 mm), a vacuum chamber fitted with zinc selenide (ZnSe) windows, fiber supply orifices, a winding spool, a power meter and a vacuum pump, among other devices. The vacuum chamber sits on a turntable, the movement of which can be finely adjusted in the lateral, vertical and rotational directions.

A 3D finite element flow analysis was conducted to calculate the flow velocities of the air jets directly below the fiber supply orifices at three levels of reduced chamber pressure (Pch). The calculated flow velocity distributions are shown in Figure 2. The data indicate that the maximum flow velocity occurred at approximately 1 mm from the orifice exit under all three Pch levels.

Table 1 shows the maximum flow velocity (ν) and minimum temperature (T) of the supersonic air jet emitted from a fiber supply orifice under three different Pch levels of 10 kPa, 20 kPa and 30 kPa. It is seen that ν of the supersonic air jet increased whereas T decreased as Pch was reduced. Among the three pressure levels, ν exceeded the speed of sound of 346.5 m s⁻¹ at Pch=10 kPa and 30 kPa, indicating that a supersonic air jet was attained.

When the original fiber is supplied in supersonic air jets and melted by the CO₂ laser, it is immediately changed into nanofibers drawn at a supersonic speed. For example, when an original fiber with a 200 μm diameter is drawn into nanofibers of 0.5 μm in diameter, the draw ratio (λ) is calculated with Eq. (1) below to be 1.6×10⁵, where L is the original fiber length, ℓ is the drawn fiber length, d₀ is the original fiber diameter and dₐv is the average drawn fiber diameter.

\[ \lambda = \left( \frac{d_0}{d_{av}} \right)^2 \]  

The drawing speed (S₀) is calculated with Eq. (2), where S₀ is the fiber supply speed.

\[ S_0 = \left( \frac{d_0}{d_{av}} \right)^2 S_0 = \lambda S_0 \]  

**Observation of fiber form and measurement of fiber**
diameter

Scanning electron microscopes (JCM-5700 and JSM-6060LV) made by JEOL Ltd. were used to observe the fiber form and to measure the fiber diameter. After attaching fiber samples to double-sided conductive aluminum foil tape, they were mounted on the sample stage and coated with platinum. The sample stage was placed in the microscope chamber and SEM images were obtained at an accelerating voltage of 15 kV. From the SEM images, the length of 100 fibers selected at random was measured and the average fiber diameter ($d_{av}$) was determined.

Measurement of melting temperature

The melting temperature of fiber samples was measured using a Thermo Plus 2 DSC823 differential scanning calorimeter (DSC) made by Rigaku Corporation. A 2.0 mg sample was measured in a temperature range of 25°C to 300°C at a temperature rise rate of 10°C min$^{-1}$. Nitrogen gas was injected into the sample chamber during the measurement to prevent sample oxidation. The heat of fusion ($\Delta H_m$) thus obtained was input into Eq. (3) below to calculate the degree of crystallinity ($X_c$), where the value of $-192 \text{ J g}^{-1}$ in the equation is the heat of fusion of nylon 66$^{(7)}$.

$$X_c = \frac{\Delta H_m}{-192} \times 100$$ (3)

Observation of fiber form during heating

An Olympus BX50 microscope and a heating stage were used to observe the fiber form. A sample was cut from a fabricated nanofiber sheet and sandwiched between two glass microscope slides together with a silicone oil for observation. The temperature range was controlled between 30–300°C. Nitrogen gas was injected into the sample chamber to prevent sample oxidation during heating.

Results and Discussion

Nanofiber sheet preparation conditions

The conditions for preparation nanofiber sheets by CLSMD were determined in reference to those for preparation single nylon 66 nanofibers using the CLSD system$^{(15)}$. Table 2 compares the drawing conditions used for preparation nylon 66 nanofibers with the CLSMD and CLSD systems. The parameters examined in this study using the CLSMD system were the laser power, chamber pressure and winding speed.

Investigation of laser power

Seven fiber supply orifices were used in this study to
produce nanofiber sheets. The orifices were spaced at 10 mm intervals in relation to the irradiation direction of the CO\textsubscript{2} laser beam. Therefore, it was necessary to ensure that all seven strands of the original fiber supplied from the orifices would be irradiated uniformly by the CO\textsubscript{2} laser. Additionally, because the portion of the fibers irradiated by the CO\textsubscript{2} laser would reach a high temperature, the laser power ($P_L$) had to be set so that the fibers would not break, thermally decompose or suffer any other damage.

Figure 3 shows the average diameter ($d_{av}$) of nanofibers drawn at $P_L=10$, 15, 20, 25 and 30 W at various points along the length (L) of the winding spool. The chamber pressure and winding speed were set at 10 kPa and 1.0 m min\textsuperscript{-1}, respectively. It is seen that $d_{av}$ was less than 1 \textmu m at $P_{ch}=10$ kPa and 20 kPa, thus confirming that nanofibers were obtained. Little variation is seen in Table 2.

Table 2. Drawing conditions for nanofiber sheets.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CLSD</th>
<th>CLSMD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser power/W</td>
<td>10</td>
<td>10, 20, 30</td>
</tr>
<tr>
<td>Chamber pressure/kPa</td>
<td>20</td>
<td>10, 20, 30, 40</td>
</tr>
<tr>
<td>Winding speed/m min\textsuperscript{-1}</td>
<td>—</td>
<td>1.0, 2.5, 5.0, 10.0</td>
</tr>
<tr>
<td>Fiber supply speed/m min\textsuperscript{-1}</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Distance from orifice/mm</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Orifice diameter/mm</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Figure 4 presents the DSC curves obtained for the original fiber and nanofiber sheets produced at the five $P_L$ levels. The original fiber showed a melting temperature ($T_m$) at 259°C, whereas the nanofiber sheets exhibited two $T_m$ points, one each at a lower and a higher temperature. The lower melting temperature ($T_{m1}$) was nearly the same as that of the original fiber, while the higher melting temperature ($T_{m2}$) was 8–12°C above that of the original fiber. It is seen that the temperature of $T_{m2}$ rose with a lower $P_L$ level.

Figure 5 shows the degree of crystallinity ($X_c$) of the nanofiber sheets as a function of $P_L$. The results indicate that $X_c$ at $T_{m1}$ increased with a lower $P_L$ level, whereas $X_c$ at $T_{m2}$ decreased.

The foregoing results revealed that drawing nanofibers at a lower $P_L$ level is effective in producing nanofibers having a large quantity of crystals with a higher melting temperature.

Investigation of chamber pressure

The chamber pressure ($P_{ch}$) is an important parameter for adjusting the flow velocity of the supersonic air jets, i.e., the drawing speed. Figure 6 shows the average diameter ($d_{av}$) of nanofibers produced at $P_{ch}=10$, 20, 30 and 40 kPa at various points along the length (L) of the winding spool. The laser power and winding speed were set at 10 W and 1.0 m min\textsuperscript{-1}, respectively. It is seen that $d_{av}$ was less than 1 \textmu m at $P_{ch}=10$ kPa and 20 kPa, thus confirming that nanofibers were obtained. Little variation is seen in
dav at each point, which indicates that the seven strands of the supplied original fiber were stably drawn at these two chamber pressures. However, because fiber breakage often occurred at $P_{ch} = 10 \text{kPa}$, it was judged that this chamber pressure is not suitable for producing large area nanofiber sheets with the present system.

At $P_{ch} = 30 \text{kPa}$ and $40 \text{kPa}$, $d_{av}$ was larger than 1 $\mu \text{m}$, indicating that nanofibers were not obtained. Additionally, at distances greater than $L = 8 \text{cm}$, $d_{av}$ increased and was not uniform.

Figure 7 presents the DSC curves obtained for the original fiber and the nanofiber sheets produced at the four $P_{ch}$ levels. Like the results seen for the different $P_{ch}$ levels, two melting temperatures were observed for the nanofiber sheets, one each at a lower temperature ($T_{m1}$) and at a higher temperature ($T_{m2}$).

Figure 8 shows the degree of crystallinity ($X_c$) of the nanofiber sheets as a function of $P_{ch}$. It is seen that $X_c$ at $T_{m2}$ increased with a lower $P_{ch}$ level, whereas $X_c$ at $T_{m1}$ decreased.

These results revealed that drawing nanofibers at a lower $P_{ch}$ level is effective in producing nanofibers having a large quantity of crystals with a higher melting temperature.

Investigation of winding speed

The winding speed ($S_w$) is an important parameter that influences not only the evaluation of the nanofiber sheet form and appearance but also its various properties. 
Figure 9 presents photographs of nanofiber sheets produced at $S_w=1.0$, 2.5, 5.0 and 10.0 m min$^{-1}$. The laser power and chamber pressure were set at $P_L=10$ W and $P_{ch}=20$ kPa, respectively. Except for the sheet produced at $S_w=1.0$ m min$^{-1}$, the sheets obtained at the other $S_w$ levels display vertical lines representing the boundaries of the nanofibers supplied from the orifices in the winding direction, thus indicating the nonuniform form of the sheets.

These results revealed that drawing nanofibers at a lower $S_w$ level is effective in producing nanofiber sheets having a uniform form.

Figure 10 presents photographs of the sheet appearance, an SEM image of the fibers and the distribution of the average fiber diameter for a nylon 66 nanofiber sheet produced under the optimal conditions of $P_L=10$ W, $P_{ch}=20$ kPa and $S_w=1.0$ m min$^{-1}$. The winding spool on which the nanofiber sheet was wound measured 8 cm in diameter by 19 cm in width and the collection time was

Figure 9. Photographs of nanofiber sheets obtained at various winding speeds ($S_w$).

Figure 10. Nanofiber sheet produced under optimal conditions. (a) Photos of appearance, (b) SEM image of fibers and (c) distribution of average fiber diameter.
30 min.

The size of the nanofiber sheet was 17 cm width, 25 cm length and 61.5 μm thickness, and the average fiber diameter ($d_{av}$) was approximately 0.5 μm. The draw ratio ($\lambda$) and drawing speed ($S_D$) were calculated to be $\lambda \approx 1.3 \times 10^5$ and $S_D = 223$ m s$^{-1}$.

Figure 11 presents the DSC curve of the nanofiber sheet produced under the optimum conditions. Two melting temperatures were observed for the nanofiber sheet, $T_{m1}$ at 258°C and $T_{m2}$ at 270°C. The degree of crystallinity ($X_c$) was 39% at $T_{m1}$ and 14% at $T_{m2}$.

**Observation of fiber form in nanofiber sheets during heating process**

![DSC curve of nylon 66 nanofiber sheet](image)

**Figure 11.** DSC curve of the nylon 66 nanofiber sheet produced under optimum conditions.

Figure 12 shows photographs of the fiber form obtained in the process of heating the nanofiber sheet from 30°C to 300°C. The nanofiber sheet did not show any evidence of drastic fiber shrinkage during the heating process, and the fiber form was maintained even above $T_{m1} = 260°C$, which is the ordinary melting temperature of nylon 66.

**Conclusions**

This study investigated the application of the CO$_2$ laser supersonic multi-drawing (CLSMD) process to produce nylon 66 nanofibers possessing crystals with a higher melting temperature. The results obtained are summarized below.

1) It was found that setting the laser power ($P_L$) and chamber pressure ($P_{ch}$) at low levels is effective in producing nanofiber sheets containing a large quantity of crystals with a higher melting temperature. In the present study, the largest proportion of crystals with a higher melting temperature increased under the conditions of $P_L = 10$ W and $P_{ch} = 10$ kPa.

2) The results revealed that setting the winding speed ($S_w$) at a low level is effective in obtaining a nanofiber sheet having a uniform sheet form. In the present study, $S_w = 1.0$ m min$^{-1}$ was the optimal condition in this regard.

3) The conditions for preparation nanofiber sheets having crystals with a higher melting temperature, a uniform sheet form and drawing stability were found to be $P_L = 10$ W, $P_{ch} = 20$ kPa and $S_w = 1.0$ m min$^{-1}$. Under these...
conditions, the average fiber diameter was approximately 0.5 µm and a nanofiber sheet was obtained that was 17 cm width, 25 cm length and 61.5 µm thickness. This nanofiber sheet exhibited two melting temperatures ($T_m$), 259°C and 270°C. The degree of crystallinity at the higher $T_m$ of 270°C was 14%.

4) The sheet showed no drastic fiber shrinkage during heating, and the fiber form was held even at the temperature of the usual melting temperature or higher.

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