

# Viscoelastic Properties and Structure of the Zone-Drawn Polyaniline Films

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Received 11 May 1999; accepted 21 May 1999

**ABSTRACT:** The zone-drawing method was applied to chemically synthesized polyaniline cast films of emeraldine base under various applied tensions and drawing temperatures. The changes in the microstructure and viscoelastic properties of the resulting films were investigated. It was found that the microstructure was strongly affected by the drawing temperature ( $T_d$ ). The crystallinity, crystallite size, and orientation factor of crystallites, respectively, attained 42%, 23 Å, and 0.975 for the film zone-drawn at  $T_d = 170^\circ\text{C}$ , whereas a further increase in the  $T_d$  brought about a decrease of these values. The viscoelastic measurements indicated that the dynamic storage modulus attained 12 GPa at room temperature and was 5 GPa at  $280^\circ\text{C}$  for the film zone-drawn at  $T_d = 210^\circ\text{C}$ , which was comparable to that of the typical engineering plastics. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 566–571, 2000

**Key words:** polyaniline film; zone-drawing; viscoelastic properties; crystallinity; high-modulus

## INTRODUCTION

During the last decade, conducting polymers have been given much attention because of their potential applications in electric or optical devices such as batteries,<sup>1</sup> light-emitting diodes,<sup>2</sup> or transistors.<sup>3</sup> Among the conducting polymers, polyaniline (PANI) has advantages in solubility, processability, and environmental stability. Most of the previous work has focused on the electrical conductivity,<sup>4–7</sup> crystalline structures,<sup>8</sup> and thermal properties,<sup>9–11</sup> and a few reports on the mechanical properties<sup>6,7,12</sup> suggest that the PANI is a high-performance polymer because of its rigid structure and crystallinity.

We have succeeded in preparing high-performance films and fibers from commercial poly-

mers, such as polyolefines,<sup>13</sup> polyesters,<sup>14</sup> and polyamides<sup>15</sup> by the use of the zone-drawing technique, developed in our laboratory. Although the apparatus is simple and the procedure is quite easy, this method has the following advantages: 1. the heat and tension act effectively and uniformly on a quite narrow area of the specimen; 2. various thermal reactions or removal of solvent can be performed simultaneously with drawing; 3. oxidation of the specimen can be minimized even in air because the heating time is very short, about a few seconds. Thus, this technique is applicable to various thermally unstable biopolymers or functional polymers for the purpose of improving their mechanical properties.

In the present report, the zone-drawing method was applied to chemically synthesized PANI cast films of emeraldine base under various applied tensions and drawing temperatures. The changes in the microstructure and viscoelastic properties of the resulting films were investigated. The temperature dependence of viscoelas-

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*Journal of Applied Polymer Science*, Vol. 75, 566–571 (2000)

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CCC 0021-8995/00/040566-06

tic properties can provide us with information on dynamic and loss moduli, mechanical dispersion, and thermal stability.

## EXPERIMENTAL

### Preparation of PANI Films

The PANI was synthesized by oxidation of aniline in the presence of ammonium persulfate.<sup>16</sup> The aniline monomer (0.43M) and ammonium persulfate (0.1M) were dissolved in an aqueous solution of 1N HCl containing 5.6M of LiCl. The polymerization was performed at  $-30^{\circ}\text{C}$  for 3 h. The obtained PANI emeraldine salt was filtered and deprotonated by washing with an aqueous solution of 0.1N  $\text{NH}_4\text{OH}$  several times. After drying under vacuum, a powder in the form of emeraldine base (EB) was obtained. The PANI film was prepared by casting the 3 wt % of *N*-methyl-2-pyrrolidone (NMP) solution of the EB powder and allowing it to solidify by evaporation of solvent at  $50^{\circ}\text{C}$  for 24 h. The PANI films were flexible, having a thickness of about 50  $\mu\text{m}$ . The elemental analysis indicated that the as-cast original film contained  $\approx 15$  wt % of residual NMP solvent.

### Zone-Drawing

The zone-heater (2-mm thick), consisting of nichrome wire and thermocouple placed between two asbestos plates, was mounted on the cross-head of a tensile tester, where the heater temperature was controlled by a thermoregulator. The upper end of the original film (50-mm long, 2-mm wide, and 50- $\mu\text{m}$  thick) was fixed to the tensile tester and then the desired tension was applied to the lower end by mounting a dead weight. The zone-heater was moved in the direction from the lower to the upper end at a constant speed of 20  $\text{mm min}^{-1}$  in air.

### Measurements

The draw ratio ( $\lambda$ ) was determined by measuring the distance between marks put on the surface of the film before drawing. Thermogravimetric (TG) analysis was performed with a TG-DTA 2000S (MAC Science Co., Ltd.). Approximately 10 mg of film was weighed in an aluminum pan and the measurement was performed at a heating rate of  $3^{\circ}\text{C min}^{-1}$  in an argon atmosphere. The content of NMP remaining in the film was defined as the weight loss between 100– $250^{\circ}\text{C}$ . The degree of

crystallinity ( $X_c$ ), defined as the ratio of the peak area of the diffraction from crystallites to total diffraction, was measured from wide-angle X-ray diffraction patterns. The apparent crystallite size normal to the (hkl) plane ( $D_{\text{hkl}}$ ) was estimated from Scherrer's equation:

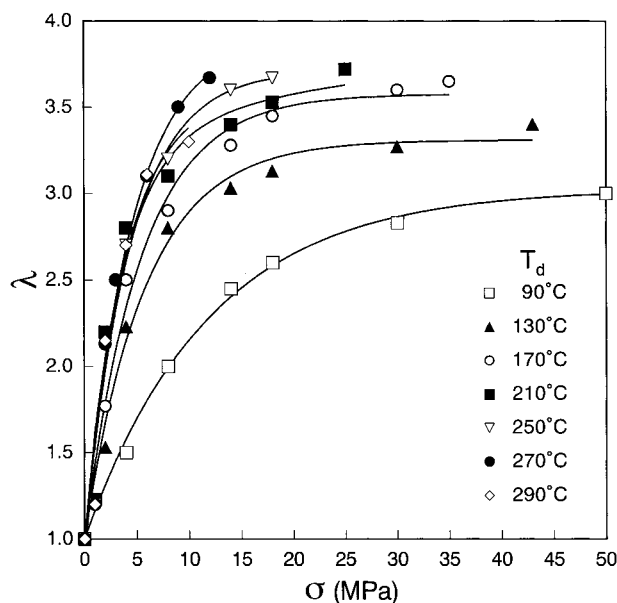
$$D_{\text{hkl}} = \frac{0.9\Lambda}{\beta \cos \theta_{\text{hkl}}} \quad (1)$$

where  $\Lambda$ ,  $\beta$ , and  $\theta_{\text{hkl}}$  were the wavelength of the  $\text{CuK}\alpha$  beam (1.542  $\text{\AA}$ ), the half-width of the diffraction peak in unit of radian, and one-half of the diffraction angle, respectively. The orientation factor of crystallites ( $f_c$ ) was evaluated by the Wilchinsky<sup>17</sup> method using diffractions from (110) and (200) planes of orthorhombic unit cell for the PANI EB crystal. The dynamic viscoelastic properties, storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ), were measured with a dynamic viscoelastometer, VIBRON DDV-II (Orientec Co., Ltd.) at 110 Hz over a temperature range from room temperature to  $350^{\circ}\text{C}$  at a heating rate of  $2.5^{\circ}\text{C min}^{-1}$  in a nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Zone-Drawing

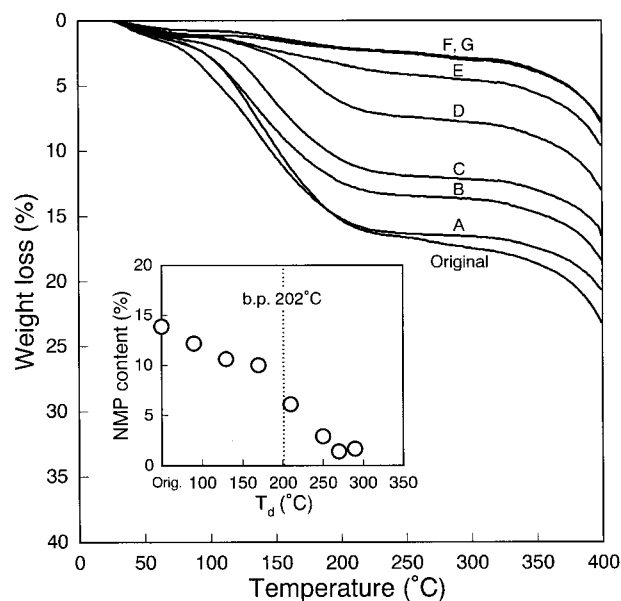
Figure 1 shows the relation between draw ratio ( $\lambda$ ) and applied tension ( $\sigma$ ) at various drawing temperatures ( $T_d$ ). At  $T_d < 90^{\circ}\text{C}$ , the film could not be drawn uniformly, whereas at  $T_d > 290^{\circ}\text{C}$  a neck went out above the zone-heater or the film broke during the drawing even under the small  $\sigma$  values. Thus, the zone-drawing was performed in a  $T_d$  range of  $90$ – $290^{\circ}\text{C}$ . It can be seen from Figure 1 that  $\lambda$  rises as values of  $\sigma$  and  $T_d$  become higher, whereas the attainable  $\lambda$  values are nearly the same at  $\approx 3.7$  in the  $T_d$  range of  $170$ – $270^{\circ}\text{C}$ . The drawability of PANI films is quite different compared with the electrochemically synthesized polypyrrole films<sup>18</sup>: there is a critical  $\sigma$  value at which the film can be zone-drawn and the film is stretched by up to twice its original length at  $T_d = 150^{\circ}\text{C}$ . This means that the PANI film is more deformable, which can be explained by the plasticizing effect due to the NMP remaining in the film.<sup>11</sup> However, the high boiling point of NMP ( $T_b = 202^{\circ}\text{C}$ ) represents a drawback if one wants to remove it completely from the film. According to the literature, the NMP content decreased to 3% after curing at  $120^{\circ}\text{C}$  under the



**Figure 1** Relation between applied tension ( $\sigma$ ) and draw ratio ( $\lambda$ ) for the PANI films at different drawing temperatures ( $T_d$ ). The zone-drawing was performed at a constant heater speed of  $20 \text{ mm min}^{-1}$  in air.

reduced pressure ( $<1$  torr) for 2 h, and it became negligible after 5 h.<sup>19</sup> Wei et al.<sup>11</sup> performed the removal of NMP by a repeated doping-undoping method: the film was doped with  $1M$  HCl and then undoped in a  $0.1M$   $\text{NH}_4\text{OH}$  aqueous solution. These methods, however, require much time and labor. Furthermore, formation of various structural defects or relaxation of molecular orientation would occur during the processes. Therefore, we consider that the zone-drawing technique will be useful for the removal of volatile solvent with a minimum of structural deterioration because the sample is heated very locally and briefly.

A clear indication of the importance of zone-drawing method for the removal of NMP is demonstrated in Figure 2. The films having the largest  $\lambda$  value at each  $T_d$  are used as samples, and conditions for the zone-drawing are listed in Table I. It is seen from Figure 2 that the original film has three major steps in the weight loss: the first small weight loss (1–2%) at 25–100°C is associated with the elimination of moisture sorbed and the second one at 100–250°C with evaporation of the residual NMP. On the other hand, the third weight loss  $> 300^\circ\text{C}$  may be due to decomposition of polymers.<sup>9,11</sup> It is found that the second weight loss of the original film is  $\approx 14\%$  which coincides with the NMP content calculated from the ele-

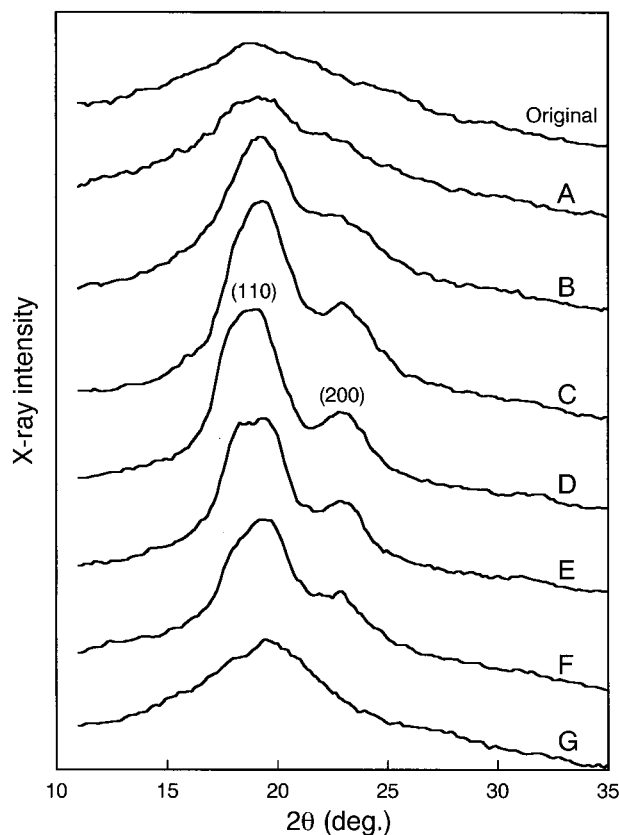


**Figure 2** TG thermograms for various PANI films zone-drawn at different drawing temperatures ( $T_d$ ) measured at a constant heating rate of  $3^\circ\text{C min}^{-1}$  in an argon atmosphere. The NMP content was defined as the weight loss at 100–250°C.

mental analysis. The weight loss for the first and second steps decreases as the  $T_d$  becomes higher and the thermograms tend to be identical at  $T_d > 270^\circ\text{C}$ , whereas the third step is less dependent on the  $T_d$ . This is clear evidence that the moisture and NMP are removed during the zone-drawing. Indeed, the NMP content, defined as the second step weight loss, gradually decreases with increasing  $T_d$  and the value becomes  $\approx 1\%$  at  $T_d > 270^\circ\text{C}$  (Fig. 2 insert). It seems to be rather surprising because the heating time is very short,  $\approx 6$  s and the actual temperature the sample experiences during the zone-drawing will be lower than the  $T_d$ .<sup>20</sup> The results obtained, however, al-

**Table I** Conditions for the Zone-Drawing at Various Drawing Temperatures

Sample No.	$T_d$ ( $^\circ\text{C}$ )	$\sigma$ (MPa)	$\lambda$
A	90	50	3.0
B	130	43	3.4
C	170	35	3.7
D	210	25	3.7
E	250	18	3.7
F	270	12	3.7
G	290	10	3.3



**Figure 3** Change in the X-ray diffraction patterns for various PANI samples.

low us to consider that the heating time is enough to draw and remove the NMP, which is presumably due to the heat and tension acting effectively and uniformly on the quite narrow area of the sample. On the other hand, the film zone-drawn at the higher heater speed of  $200 \text{ mm min}^{-1}$  still has a large NMP content. The fact demonstrates that a cooperation between  $T_d$  and heater speed would be predominant for the effective removal of the solvent. The heater speed of  $20 \text{ mm min}^{-1}$ , used in this experiment, is the lowest limit of the apparatus.

#### Changes in Microstructure

Figure 3 shows X-ray diffraction patterns for various samples. A broad diffraction for the original film changes into two peaks at  $2\theta = 19.4^\circ$  ( $d = 4.6 \text{ \AA}$ ) and  $22.9^\circ$  ( $d = 3.9 \text{ \AA}$ ) for the samples C and D, corresponding to the diffractions from (110) and (200) planes of the PANI EB crystal.<sup>8</sup> On the other hand, a further increase in the  $T_d$  brings about a decrease and broadening of the diffraction peak even though the  $\lambda$  values are nearly the

same (samples E–G). This may be ascribed to the heat and/or evolution of NMP gases, which increases the structural disorder. The crystallinity ( $X_c$ ), crystallite size normal to the (110) planes ( $D_{110}$ ), and orientation factor of crystallites ( $f_c$ ) for various samples are summarized in Table II. As indicated from Figure 3, sample C has the largest  $X_c$  and  $D_{110}$  values of 42% and 23 Å, respectively. Compared with the thermally stretched PANI films or fibers, the crystallinity is comparable<sup>21</sup> but the size is considerably small (the  $D_{110}$  for the thermally stretched films is 50–100 Å).<sup>8</sup> This fact indicates an increase of the crystallites in number. This may be associated with the characteristics of this method: the large deformation and crystallization of molecular chains occur at the zone-heater, but the rapid elongation of the film results in the immediate cooling of the film outside the zone-heater. This would quench the crystal growth; consequently, the numerous small crystallites are fixed in the polymer matrix. On the other hand, the values of  $f_c$  indicate the high orientation of crystallites in the drawing direction, whereas the values for the original, sample A and G could not be obtained because of any apparent diffraction from the (200) plane.

#### Viscoelastic Properties

Figure 4 shows temperature dependence of storage modulus ( $E'$ ) for various samples. The  $E'$  values of all samples increase over the whole experimental temperature range by the zone-drawing, whereas the  $E'$ -temperature curve strongly depends on the  $T_d$ . A drop of  $E'$  in the temperature range of 90–230°C for the films zone-drawn at  $T_d$  below 250°C is associated with the evapo-

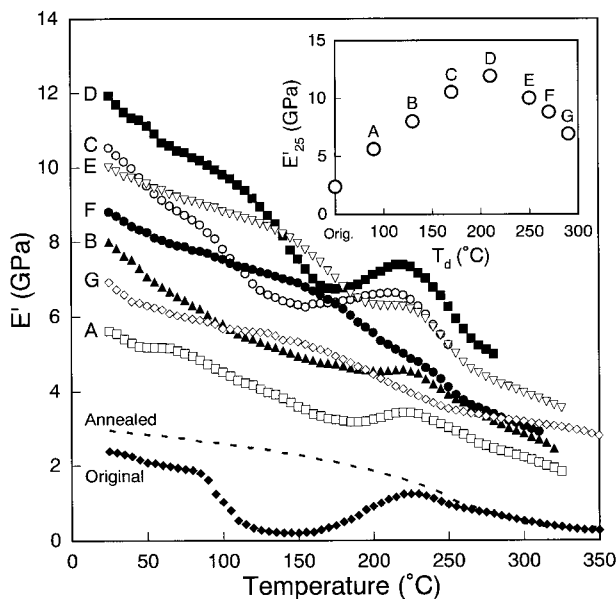
**Table II** Crystallinity ( $X_c$ ), Crystallite Size Normal to the (100) Plane ( $D_{110}$ ), and Orientation Factor of Crystallites ( $f_c$ ) for Various Zone-Drawn Films

Sample No.	$X_c$ (%)	$D_{110}$ (Å)	$f_c$
Original	13.3	10.6	—
A	20.8	14.4	—
B	32.5	19.7	0.948
C	42.0	23.0	0.975
D	38.0	21.5	0.973
E	35.7	20.5	0.971
F	30.3	19.2	0.967
G	18.7	12.8	—

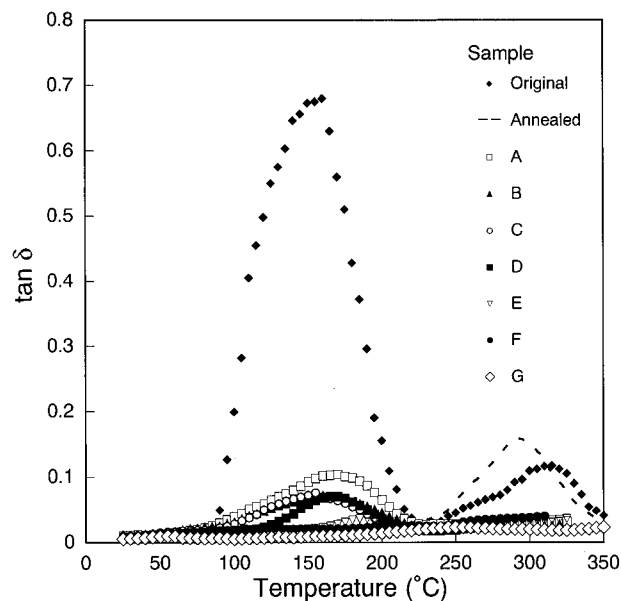


ration of NMP. If the original film is annealed at 230°C for 1 h in a nitrogen atmosphere with an electric furnace, no notable drop of the  $E'$  is observed in that temperature range (broken line). It is noted that the  $E'$  at 25°C ( $E'_{25}$ ) monotonically increases with  $T_d$  and attains 12 GPa for the sample D ( $T_d = 210^\circ\text{C}$ ). The value is comparable to that of the typical engineering plastics such as poly(*p*-phenylene sulfide)<sup>22</sup> ( $E'_{25} = 7.2$  GPa) or poly(ether ether ketone)<sup>23</sup> ( $E'_{25} = 13.3$  GPa) prepared by the zone-drawing/zone-annealing method. On the other hand, the decrease of  $E'_{25}$  at  $T_d$  higher than 250°C would be connected with the increase of structural disorder as indicated from the decrease of  $X_c$ ,  $D_{110}$ , and  $f_c$  values.

Figure 5 shows temperature dependence of  $\tan \delta$  for various samples. One can see that the original film has two apparent mechanical dispersions at 150 and 310°C. The dispersion at the lower temperature, relating to the drop of  $E'$ , is associated with an apparent glass transition of the PANI in the presence of NMP,<sup>11</sup> where the NMP gases evolved behave as a plasticizer and enhance the molecular motion. Here, the fact that the samples A–E have a broad dispersion at 100–200°C, clearly demonstrates that the films still



**Figure 4** Temperature dependence of storage modulus ( $E'$ ) for the original and various zone-drawn films at different drawing temperatures ( $T_d$ ) measured at a constant heating rate of  $2.5^\circ\text{C min}^{-1}$  in a nitrogen atmosphere under a frequency of 110 Hz. The annealing was performed on the original film at  $230^\circ\text{C}$  for 1 h in a nitrogen atmosphere with an electric furnace.



**Figure 5** Temperature dependence of loss tangent ( $\tan \delta$ ) for the original and various zone-drawn films at different drawing temperatures ( $T_d$ ) measured at a constant heating rate of  $2.5^\circ\text{C min}^{-1}$  in a nitrogen atmosphere under a frequency of 110 Hz.

contain NMP. On the other hand, the dispersion at the higher temperature will be a “real” glass transition of the PANI because the annealed film has only one dispersion peak near  $300^\circ\text{C}$ . It is noted that the zone-drawn films have no notable dispersion at the higher temperature range. Because the  $\tan \delta$ , defined as the ratio of storage and loss moduli ( $E''/E'$ ), reflects in the molecular motion, the result obtained demonstrates that the micro-Brownian motion of amorphous chains is highly restricted for the zone-drawn film. This is attributed to the numerous crystallites that behave as crosslinking points and hinder the motion of amorphous chains.

Thus, the zone-drawing technique is found to be effective in the improvement of mechanical properties of the PANI films. Furthermore, this method is easier and more convenient compared with the thermal stretching because the removal of solvent can be performed within a few seconds in air simultaneously with drawing.

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