

## Barus Effect in Nylon 6 Polymer Melts

TOHRU ISHIBASHI, *Tsuruga Nylon Plant, Toyobo Co., Ltd., Kurehacho, Tsuruga, Fukui 914, Japan*

### Synopsis

The maximum diameter of broadening of nylon 6 polymer melts due to the Barus effect  $d_{\max}$  were measured under various conditions of spinneret die dimensions and polymer temperatures. The results obtained were formulated and compared with the typical past theories on the mechanism of occurrence of the Barus effect. The Barus effect was formulated by using the relation between stress and strain in the theory of rubber elasticity:

$$\frac{\tau_s}{T} = \text{const.} \left( \lambda^2 - \frac{1}{\lambda} \right) = \text{const.} \left( \frac{d_{\max}}{d_0} \right)^4 - \left( \frac{d_0}{d_{\max}} \right)^2$$

where  $\tau_s$  is the shear stress generated inside the spinneret die,  $T$  is the absolute temperature of polymer melts,  $\lambda$  is the elongation ratio parallel to the polymer stream, and  $d_0$  is the diameter of spinneret die. This formula coincides with the experimental results.

### INTRODUCTION

When polymer melts are extruded from a spinneret (a capillary), the stream of polymer extruded swells on emergence from the spinneret and the diameter of the stream becomes larger than that of the spinneret. This phenomenon is known as the Barus effect.

For the mechanism of occurrence of the Barus effect, several theories have so far been reported: (i) interpretation by the theory of rubber elasticity (so-called orientation effect),<sup>1,2,3</sup> (ii) interpretation by the theory of viscoelasticity,<sup>4,5</sup> (iii) interpretation<sup>6</sup> by the contributions of (i) and (ii), and (iv) normal-stress effect.<sup>7,8</sup> However, there is no established theory which can explain the phenomenon irrespective of the types of polymers. Theory (iv) is neglected, because it alone can not explain the Barus effect.<sup>6,9</sup> In the present report, the maximum diameter of broadening of nylon 6 due to the Barus effect  $d_{\max}$  was measured under various spinning conditions. The results obtained were formulated and compared with the typical past theories on the mechanism of occurrence of the Barus effect.

### EXPERIMENTAL

A nylon 6 polymer with a number-average molecular weight  $\bar{M}_n$  of  $2.4 \times 10^4$  was used throughout this work. Polymer melts are extruded from the various spinneret dies as shown in Figure 1 and Table I. The temperature of polymer melts were varied within the range of 250°C to 280°C. The

TABLE I  
 Dimensions of Dies

No.	$d_0$ , cm	$l_0$ , cm	$l_0/d_0$
1	0.03	0.06	2
2	0.03	0.09	3
3	0.03	0.24	8
4	0.04	0.08	2
5	0.04	0.12	3
6	0.04	0.28	7
7	0.05	0.10	2
8	0.05	0.15	3
9	0.05	0.40	8

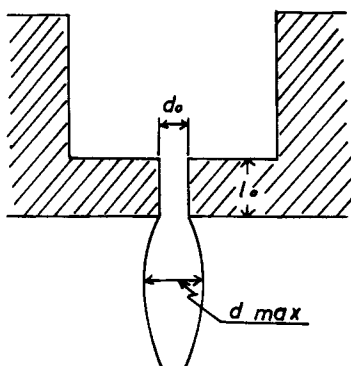


Fig. 1. Schematic of die dimension and profile of polymer stream.

extruding velocity was kept constant ( $1.47 \times 10^{-2}$  cm<sup>3</sup>/sec). The maximum diameter of broadening of polymer melts due to the Barus effect  $d_{\max}$  (see Fig. 1) and the die pressure  $P_i$  was measured under various experimental conditions as mentioned above. An optical microscope ( $\times 50$ ) was used to measure the  $d_{\max}$ .

## RESULTS AND DISCUSSION

The effects of dimensions of the die and temperature on the Barus effect are shown in Figure 2. The Barus effect becomes larger, as the diameter of die and  $l_0$  are smaller, and the temperature of polymer is lower. Figure 3 shows the effects of the dimension of die and temperature on the die pressure  $P_i$  (the internal stress at the inlet of capillary) measured together with  $d_{\max}$ . Even at  $l_0/d_0 = 0$ ,  $P_i = 0$  is not observed. This proves the existence of the so-called endeffect.

Using these data, the mechanism of occurrence of the Barus effect will be discussed.

Ziabicki and Kedzierska<sup>4</sup> defined the Barus effect  $q$  by the following equation:

$$q = \left( \frac{d_{\max}}{d_0} \right)^2 - 1 = \lambda - 1 \quad (1)$$

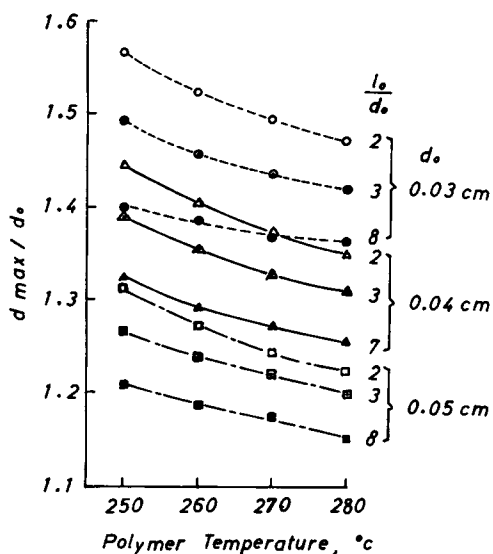


Fig. 2. Effects of dimension of die and temperature on Barus effect ( $d_{max}/d_0$ ).

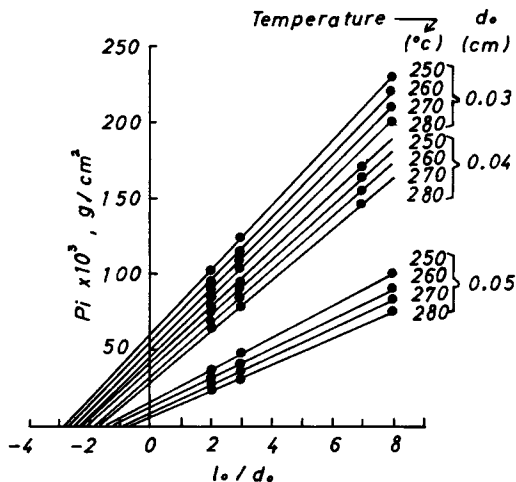


Fig. 3. Effects of dimension of die and temperature on die pressure  $P_i$ .

where  $\lambda$  is the elongation ratio parallel to the polymer stream,  $d_{max}$  is the maximum diameter of polymer stream due to the Barus effect, and  $d_0$  is the diameter of the capillary. Assuming that the Barus effect  $q$  is proportional to the internal stress  $P_i$  at the outlet of a capillary, the following equation is derived:

$$q \cong P_i = P_i \exp\left(-\frac{t}{\tau}\right) \tag{2}$$

where  $t$  is the transit time through the capillary,  $\tau$  is the relaxation time, and  $P_i$  is the internal stress at the inlet.

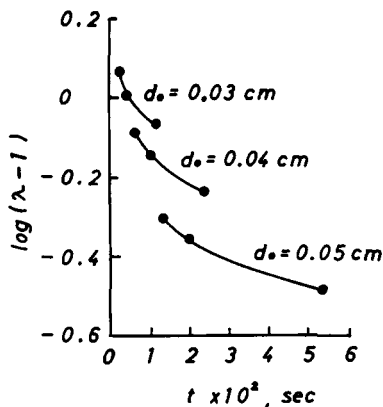


Fig. 4. Relation between time in which polymer melt (280°C) moves through the capillary die  $t$  and  $\log(\lambda - 1)$ ; plots of eq. (2).

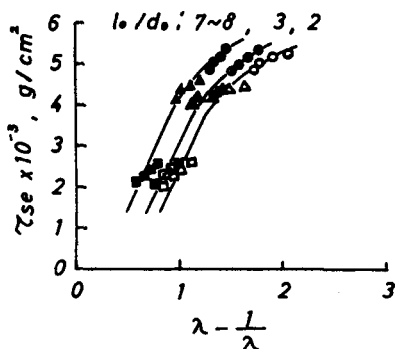


Fig. 5. Relation between  $\lambda - (1/\lambda)$  and end-corrected shear stress  $\tau_{se}$ ; plots of eq. (3). Symbols are same as in Fig. 2.

Figure 4 shows an example of Ziabicki's plot, adaptability of eq. (2). A straight line is not obtained. This indicates that eq. (2) does not satisfy the experimental results. This discrepancy seems to be attributable to the inadequacy of the definition of eq. (1). In addition, if a Maxwell model is assumed for a polymer melt, the period in which the effect of stress relaxation appears is at least more than 0.1 sec,<sup>10</sup> whereas the time in which the polymer melt moves through the capillary is the order of 0.05 sec under the conditions of this experiment (within the ranges of ordinary spinning conditions). Therefore, the contribution of viscoelastic relaxation does not seem to be necessary to be taken into consideration.

Spencer and Dillon<sup>1</sup> have derived the following equation:

$$\tau_{se} = G \left( \lambda - \frac{1}{\lambda} \right) \quad (3)$$

where  $\tau_{se}$  is the effective shear stress corrected for the end effect and  $G$  is the shear modulus.

Figure 5 shows the plots according to eq. (3). The plots of  $\tau_{se}$  against  $\lambda - (1/\lambda)$  do not become linear, and eq. (3) does not explain the present experimental results satisfactorily. Furthermore, although the figure was omitted, similar result was obtained on the plots of  $\tau_s$  against  $\lambda - (1/\lambda)$ . This disagreement is attributed to the inadequate description of  $\lambda - (1/\lambda)$ . It is said that the theory of rubber elasticity is employed to derived eq. (3), but the relation between stress and elongation in the theory of rubber elasticity is not used in the original form as indicated later.

According to the theory of rubber elasticity, the tensile stress  $\sigma$  acting on a stretched rubber sample is given by the following equation:

$$\sigma = NkT \left( \lambda - \frac{1}{\lambda^2} \right) \quad (4)$$

where  $N$  is the number of network chains per cubic centimeter,  $k$  is Boltzmann's constant, and  $T$  is absolute temperature. In this equation,  $\sigma$  is calculated on the original (unstretched) cross-sectional area. If the stress is calculated on the stretched cross-sectional area, the following equation is thought to be adequate<sup>10</sup>:

$$\sigma = NkT \left( \lambda^2 - \frac{1}{\lambda} \right). \quad (5)$$

Now in Figure 1, the polymer stream during the spinning expands from the diameter of the die  $d_0$  to  $d_{max}$  as a result of the Barus effect. When the theory of rubber elasticity is applied, it is supposed that the sample with a diameter of  $d_{max}$  deforms to diameter  $d_0$  by stretching. It is assumed that the tensile stress after deformation  $\sigma$  is proportional to the shear stress generated inside the die  $\tau_s$ . That is to say,

$$\sigma = \text{const. } \tau_s. \quad (6)$$

Accordingly, from eqs. (5) and (6), the following equation is obtained:

$$\frac{\tau_s}{T} = \text{const.} \left( \lambda^2 - \frac{1}{\lambda} \right). \quad (7)$$

$\tau_s$  has the following relation with the internal stress (die pressure) at the inlet of the die  $P_t$ :

$$\tau_s = \frac{P_t d_0}{4l_0}. \quad (8)$$

If the end correction is necessary,

$$\tau_{se} = \frac{P_t}{4 \left( \frac{l_0}{d_0} + \nu_e \right)} \quad (9)$$

where  $\nu_e$  is the correction factor.

Figure 6 shows plots according to eq. (7) obtained by the author. A good linear relationship is obtained between  $\tau_s/T$  and  $\{\lambda^2 - (1/\lambda)\}$ , and eq.

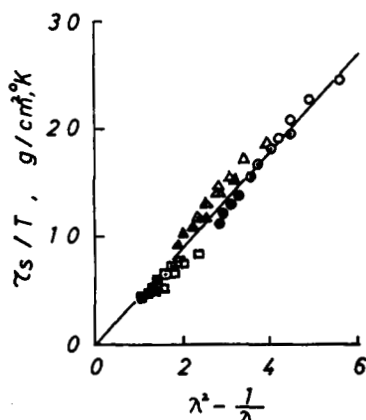


Fig. 6. Relation between  $\lambda^2 - (1/\lambda)$  and  $\tau_s/T$ ; plots of eq. (7). Symbols are same as in Fig. 2.

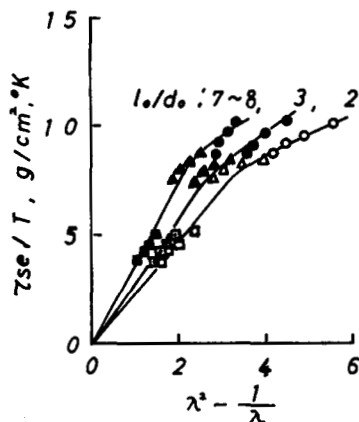


Fig. 7. Relation between  $\lambda^2 - (1/\lambda)$  and  $\tau_{se}/T$ . Symbols same as in Fig. 2.

(7) satisfies the experimental results. The following experimental formula is derived from Figure 6:

$$\frac{\tau_s}{T} = 4.4 \left( \lambda^2 - \frac{1}{\lambda} \right). \quad (10)$$

On the other hand, Figure 7 shows the plots in which  $\tau_{se}$  (calculated from the end correction factor  $\nu_e$  from Figure 3 using eq. (9)) is used instead of  $\tau_s$  in eq. (7). As observed from this figure, no linear relation is obtained.

The reason why the apparent shear stress  $\tau_s$ , neglecting the end effect satisfies the experimental results is not clear. But, if the effect of orientation mentioned above is assumed as the mechanism of the Barus effect, it is supposed that the streaming orientation proceeds even in the capillary region, in which steady flow is not attained and the end correction is necessary, and that practically no stress relaxation (relaxation of orientation)

occurs inside the capillary. The orientation which occurred in this region is maintained after passing the inlet region, and supposedly contributes to the Barus effect in addition to the orientation occurring in the following steady flow region.

The author wishes to thank Prof. Toshiyuki Shōno of Osaka University and Dr. Jirō Furukawa of Toyobo Co., Ltd., for their advice and encouragement given in this research.

### References

1. R. S. Spencer and R. E. Dillon, *J. Colloid Sci.*, **11**, 251 (1967).
2. L. R. G. Treloar, *The Physics of Rubber Elasticity*, Oxford University Press, 1958, Chap. 5.
3. E. B. Bagley, S. N. Storey, and D. C. West, *J. Appl. Polym. Sci.*, **7**, 1661 (1963).
4. A. Ziabicki and K. Kedzierska, *Kolloid-Z.*, **171**, 111 (1960).
5. T. Arai and H. Aoyama, *Trans. Soc. Rheol.*, **7**, 333 (1963).
6. K. Kamide, Y. Inamoto, and K. Ohno, *Kobunshi Kagaku (Chem. High Polym.)*, **22**, 505 (1965).
7. W. Phillipoff, *Trans. Soc. Rheol.*, **1**, 95 (1957).
8. A. B. Metzner, W. T. Houghton, R. A. Sailor, and J. L. White, *Trans. Soc. Rheol.*, **5**, 133 (1961).
9. M. Yamamoto, *Rheology*, Maki Shoten, 1964, Chap. 7.
10. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962.

Received December 20, 1973