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# 一軸延伸한 PET필름의 손실 tangent의 異方性

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# Anisotropy of the Mechanical Loss Tangent of Uniaxially Drawn PET Films

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**요약** : 일축 연신한 PET필름의 손실 tangent의 이방성을 연신비와 열처리온도의 변화에 대한 의존성을 조사 검토하였다. 연신축과 평행한 방향의 최대 $\tan\delta_{/\!/}$의 강도는 연신축과 수직한 방향의 그것보다 높았으며, 한편 최대 $\tan\delta$를 나타내는 온도는 연신축과 평행방향이 수직방향보다 낮았다. 최대 $\tan\delta_{/\!/}$는 연신비가 2.5일때까지 증가하다가 그 이상일 때는 급격하게 감소한 반면 최대 $\tan\delta_{\perp}$는 연신비가 증가할수록 단조 감소하였다. $\tan\delta_{/\!/}$와 $\tan\delta_{\perp}$ 공히 열처리 온도가 증가할수록 감소하였다. 최대 $\tan\delta_{/\!/}$와 최대 $\tan\delta_{\perp}$의 비는 연신비에 따라 증가하였으나 열처리 온도에 따라서는 감소하였다. 즉 이방성은 연신비에 따라 비례적으로 증가한 반면 열처리 온도에 따라서는 감소하였다.

**ABSTRACT:** The anisotropy of the loss tangent of uniaxially stretched PET films was investigated. The intensity of maximum tan $\delta_{/\!/}$(parallel to the drawing direction) was higher than that the maximum tan $\delta_{\perp}$ (perpendicular to the drawing direction) and the maximum tan $\delta$ temperature was lower in the parallel direction than in the perpendicular one.

Maximum tan $\delta_{/\!/}$ increased with the draw ratio of up to 2.5 above which it decreased rapidly while maximum tan $\delta_{\perp}$ decreased monotonously with the draw ratio. On the other hand, both of them decreased with increasing annealing temperature.

The ratio of maximum tan $\delta_{/\!/}$ to maximum tan $\delta_{\perp}$ increased with the draw ratio and decreased with increasing annealing temperature, indicating that the anisotropic behavior increased with the draw ratio but decreased with increasing annealing temperature.

## 1. INTRODUCTION

The dynamic mechanical behavior of poly (ethylene terephthalate) has been the subject of many previous investigations.[1,2] The relaxation of PET occurs in the temperature range

of 80~125°C, the exact position being very dependent on structural factors such as crystalinity and orientation.[3] In general, the $\alpha$-relaxation broadens and moves to higher temperature with increasing crystallinity while its intensity is much reduced. The $\alpha$-relaxation has therefore been explained to be associated with the amorphous phase of polymers although it is strongly influenced by the type of crystal structure and degree of crystallinity. As a matter of fact, there are no clear-cut explanations about the molecular origins of $\alpha$-relaxation although it has been generally agreed that the $\alpha$-relaxation is due to the initiation of micro-Brownian motion in molecular chains.

It has been well known that numerous polymers have anisotropic properties in the thermal conductivity[4], thermal expansion coefficient[4,5], refractive index, elastic modulus[6~8], and compressibility[4]. Such polymeric materials are fibres, wood, oriented amorphous and crystalline polymers, injection-molded plastics, fiber-filled composites, and single crystals etc.[9] Extensive studies on the anisotropic mechanical behavior of polymers have been carried out by Ward and reviewed in his book[7]. However, the studies of the effect of anistropy on loss tangent have been comparatively few.

Takayanagi et al[10], measured the complex moduli of oriented specimens of polyethylene, polypropylene, polyoxymethylene, poly(ethylene oxide), and polytetrahydrofuran in a sheet form as a function of direction. They suggested a model that the crystalline region and the amorphous region are arranged in series along the stretched direction and at the same time the crystalline region should be more or less continuous along the 90° direction. Stachurski and Ward[11,12] investigated the anisotropy of viscoelastic behavior of cold-drawn low-density and high-density polyethylene sheets. They found that LDPE and HDPE exhibit an anisotropic behavior at $\alpha$-and $\beta$-transition, respectively. Davies and Ward[13] investigated the anisotropy of the $\alpha$ and $\beta$-relaxations of oriented poly (ethylene terephthalate) by dynamic mechanical and dielectric relaxation measurements. They reported that both the extruded rod and drawn film are anisotropic. According to them, since the mechanical anisotropy cannot be as simply related to the lamellar orientation as in the case of lowdensity polyethylene, it is concluded that other morphological factors should be taken into account. One of the factors may be the nature of the coupling between crystalline and amorphous region in the Takayanagi model.[10] They also concluded that all or some of the components of the $\beta$-process occur at least in part in the crystalline phase.

In this study, the anisotropy of mechanical loss tangent of PET film, which was drawn at different draw ratios and annealed at various temperatures, was investigated by the technique of dynamic mechanical measurement. It is of our particular interest to examine the effect of draw ratio and annealing temperature on anisotropy of $\alpha$-relaxation. It is also attempted to interpret the results in terms of the molecular montion of amorphous region.

## 2. EXPERIMENTAL

### 2-1. Preparation of Samples

Undrawn PET film sheet was obtained with the courtesy of Sunkyung Chemical Co. Ltd. Seoul, KOREA. The PET film was drawn 1.5 X, 2.0 X, 2.5 X, and 3.0 X of its original length with an Instron testing machine at a rate of 600%/min., at constant drawing temperature (80°C). Ink dots were marked at 1 cm intervals along the length of the specimen so that the draw ratio could be read. The specimens, both

undrawn and drawn, were heat-treated with the constraint at constant length in direction of drawing under vaccum at various annealing temperatures (100°C, 125°C, and 150°C) for 30 minutes. Rectangular strips were cut out from the specimen, with long side parallel and perpendicular to the drawing direction.

### 2-2. Loss Tangent Measurement

The mechananical loss tangent was measured at a fixed frequency of 110 Hz while the samples were heated from room temperature to 200°C on a direct-reading Rheovibron DDV-II viscoealstometer, a type of stretch vibrometer, made by Toyo measuring Instruments, Ltd., Tokyo. The sinusoidal strain was always applied parallel to the length of the sample. Measurements were made at 4°C intervals when the sample was heated at a constant heating rate of 2°C/min from room temperature, except near the transition region where narrower temperature intervals were employed.

Magnitude of dynamic complex modulex, $|E^*|$ is obtained from the following formula:[14]

$$|E^*| = 2 \times \frac{1}{A \times D} \times \frac{L}{S} \times 10^9 \quad (\text{dyne/cm}^2) \cdots\cdots (1)$$

where $L$ : Length of specimen (cm)
$S$ : Sectional area ($\text{cm}^2$)
$A$ : Amplitude factor
$D$ : The value of Dynamic Force dial when measuring tan $\delta$

Storage modulus $E'$ and Loss modulus $E''$ are given by Equations (2) and (3):

$$E' = |E^*| \cos \delta \cdots\cdots (2)$$

$$E'' = |E^*| \sin \delta \cdots\cdots (3)$$

### 2-3. Crystallinity Measurement

Density of the sample was measured at 20°C by using Direct Reading Density Measuring Apparatus (Shibayama Scientific Co. Ltd. Tokyo). The density gradient column was filled with the mixtures of xylene and carbon tetrachloride of progressively varied composition The crystallinity was calculated from the following formula:

$$\text{Crystallinity}(\%) = \frac{\frac{1}{d} - \frac{1}{d_{\text{amor.}}}}{\frac{1}{d_{\text{cry.}}} - \frac{1}{d_{\text{amor.}}}} \times 100 \quad (4)$$

where $d$, $d_{\text{amor.}}$ (=1.335) and $d_{\text{cry.}}$ (=1.455) are densities of the specimen, entirely amorphous and crystalline material of PET, respectively.[15,16]

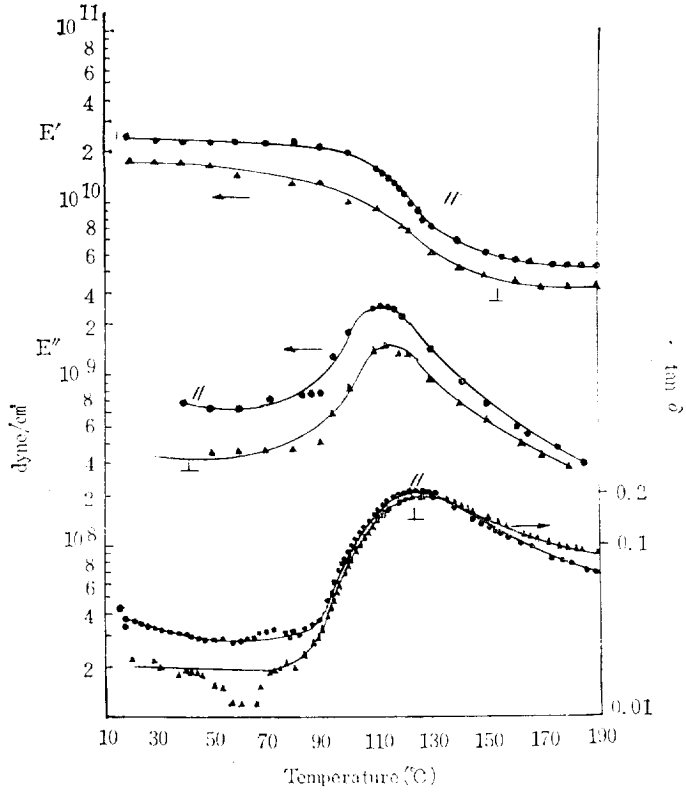


**Fig. 1.** Dynamic mechanical data of PET film drawn 3X and annealed at 125°C.

## 3. RESULTS AND DISCUSSION

### 3-1. Anisotropy of Dynamic Mechanical Properties

Fig. 1 shows tan $\delta$, $E'$, and $E''$ versus temperature for PET film drawn 3X and annealed at 125°C. The maximum in tan $\delta_{/\!/}$ is higher than in tan $\delta_{\perp}$ and the peak temprature is lower in the parallel direction than in the perpendicular one. The $E'$ curves run parallel to one another, with $E'$ higher in all the temprature range scanned in the drawing direction. The loss modulus $E''$ goes through a peak at a slightly lower temperature than the loss tangent does. In addition, $E''$ is higher in all the temperature range scanned in the parallel direction than in the perpendicular one. The maximum

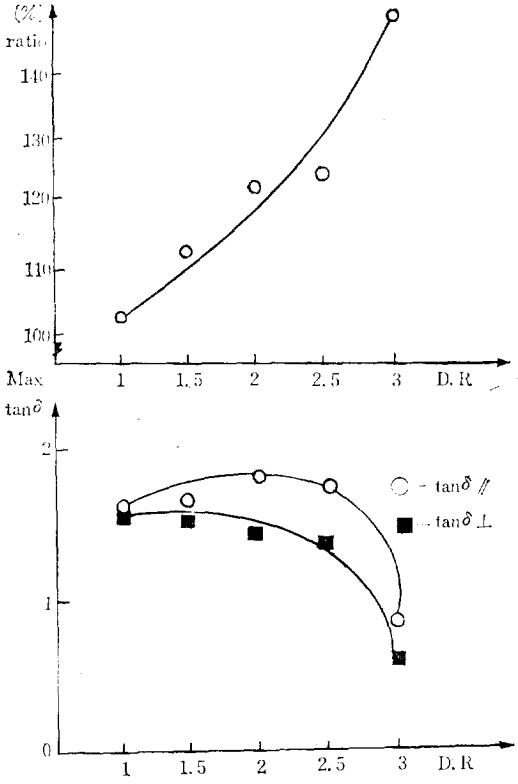


**Fig. 2.** Effect of draw ratio on max. tan $\delta_{/\!/}$ max-tan$\delta_{\perp}$ and their ratio for PET film un. annealed.

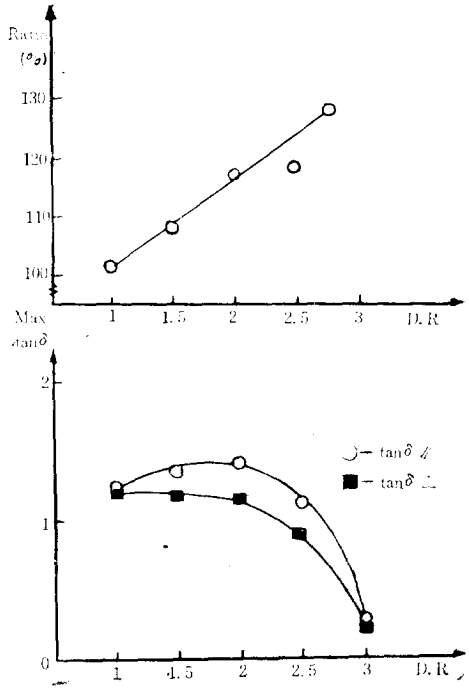


**Fig. 3.** Effect of draw ratio on max. tan$\delta_{/\!/}$, max. tan$\delta_{\perp}$ and their ratio for PET film annealed at 100°C.

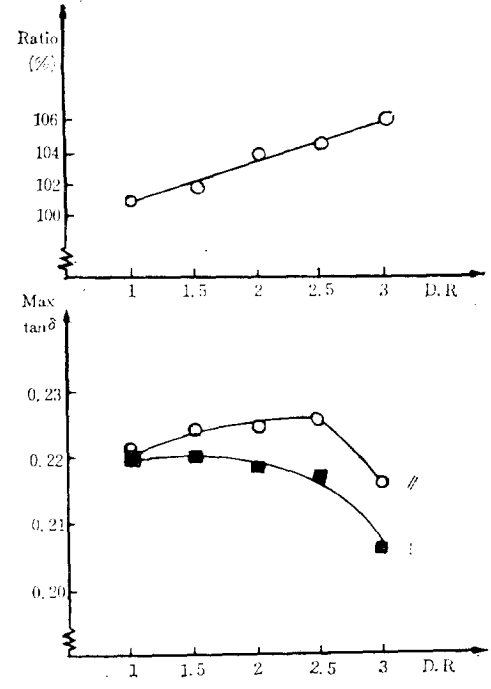


**Fig. 4.** Effect of draw ratio on max. tan$\delta_{/\!/}$, max. tan$\delta_{\perp}$ and their ratio for PET film annealed at 125°C.

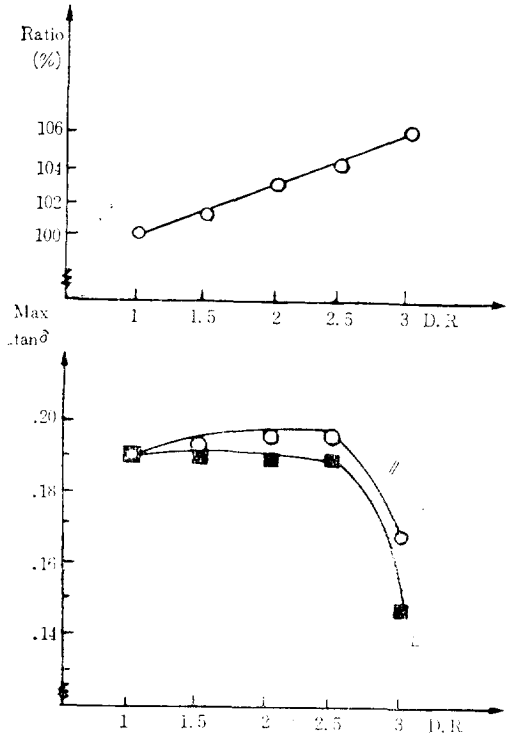


**Fig. 5.** Effect of draw ratio on max. tan$\delta_{/\!/}$, max. tan$\delta_{\perp}$ and their ratio for PET film annealed at 150°C.

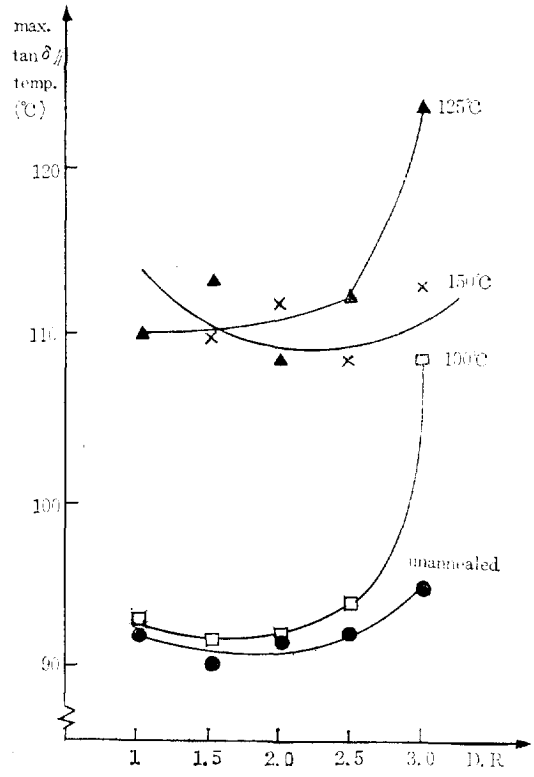


**Fig. 6.** Effect of draw ratio on maximum tan$\delta_{/\!/}$ temp. at various annealing temperature.

heat dissipation per unit deformation occurs at the temperature where $E''$ is maximum.

### 3-2. Effect of Draw Ratio

Fig. 2 shows the effect of draw ratio on maximum tan $\delta_{/\!/}$, maximum tan $\delta_{\perp}$ and their ratio for the samples unannealed. Maximum tan $\delta_{/\!/}$ increases with the draw ratio of up to 2～2.5 above which it decreases rapidly, while maximum tan $\delta_{\perp}$ decreases monotonously with the draw ratio with a large fall near the draw ratio of 2.5. This implies that a certain remarkable change may occur in the molecular conformation near the draw ratio of 2.5. The reason will be explained later in this section. As is also shown in Fig. 2, the ratio of maximum tan $\delta_{/\!/}$ to maximum tan $\delta_{\perp}$ increases with the draw ratio, suggesting that an anisotropic behavior increases with the draw ratio as expected from the molecular orientation. Similarly, maximum tan $\delta_{/\!/}$ of the samples annealed at 100°C, 125° and 150°C increase with the draw ratio of up to about 2～2.5 where it begin to decrease and maximum tan $\delta_{\perp}$ decrease with the draw ratio (Fig. 3～5). However, the ratio which may be a measure of anisotropy increases almost linearly with draw ratio.

As indicated in Fig. 6 and Fig. 7, the peak temperature is not affected by the draw ratio of up to 2.5 above which it increases rapidly. This is coincident with the phenomenon that the intensity of tan $\delta$ decreases rapidly near the draw ratio of 2.5. It is apparent from the above phenomenon that there would be a kind of great change in the molecular conformation

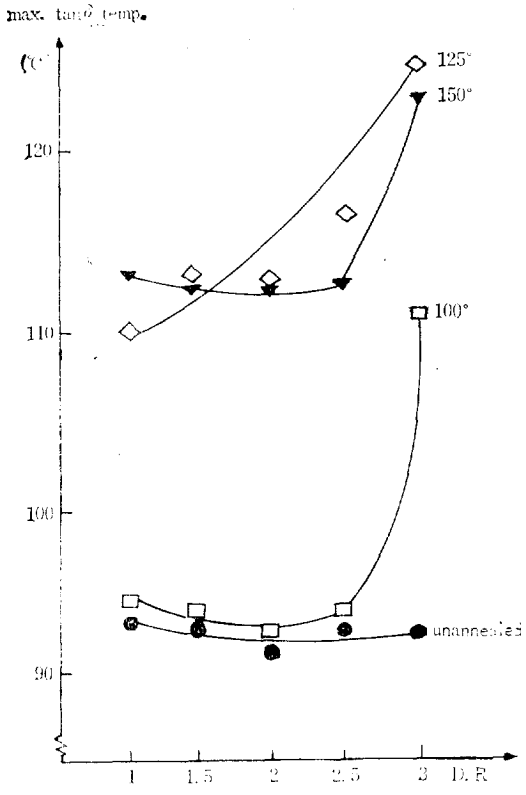


**Fig. 7.** Effect of draw ratio on maximum $\tan\delta_{\perp}$ temperature.

near the draw ratio of 2.5. The reason for this phenomenon is too complex to be explained clearly at present, however, the following explanations may be proposed.

Many polymers, when rapidly cooled from the molten state, form an amorphous structure. This structure is considered to be a random tangle of molecular chains. Since the loss tangent, in general, is mostly due to the amorphous phase, the contribution of crystalline phase to the $\alpha$-transition could be excluded. If the chain length of amorphous region in the drawing direction is statistically the same as that in the perpendicular direction, the contribution of an amorphous chain to the $\alpha$-peak in the parallel direction would be the same as in the perpendicular one, that is, completely isotropic. When

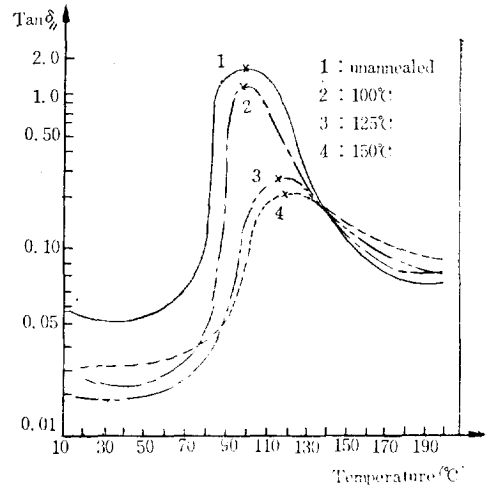


**Fig. 8.** $\tan\delta_{/\!/}$ vs. temperature for undrawn PET film annealed at various temperatures.

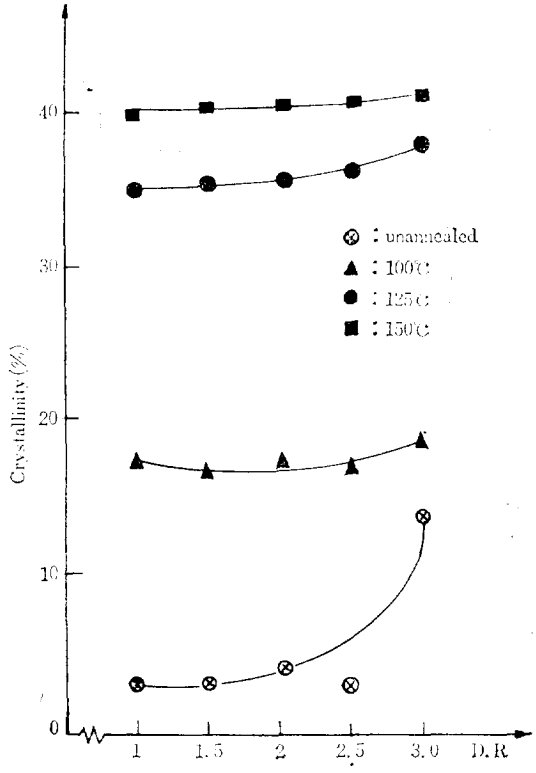


**Fig. 9.** Crystallinity vs. draw ratio at various annealing temperatures.

the isotropic material is drawn 1.5X, the isotropic amorphous phase would be distorted to give more amorphous chains in the drawing

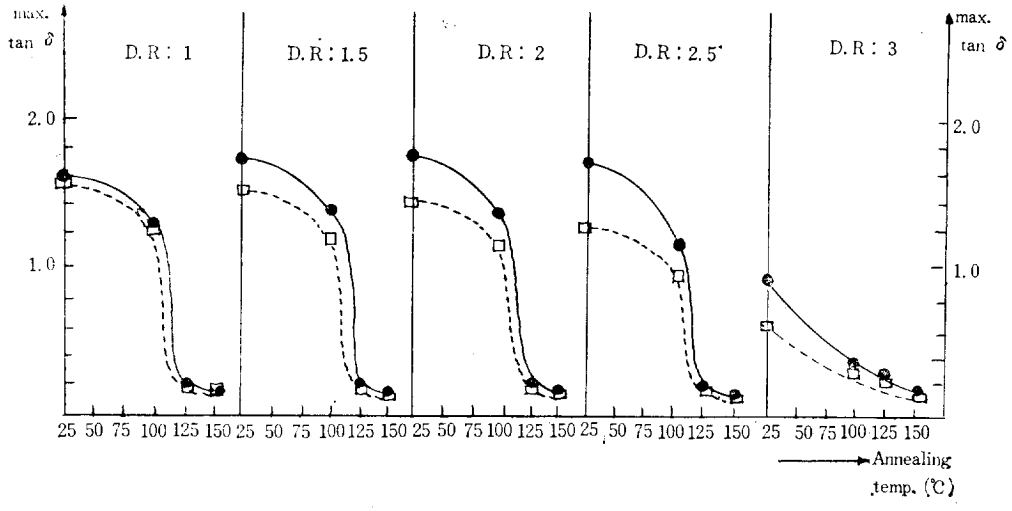


**Fig. 10.** Effect of annealing temperature on max. $\tan_{/\!/}$(●) and max.$\tan\delta_{\perp}$(□) at various draw ratios.

direction and thus the contribution to the $\alpha$-transition would increase in the parallel direction but it would decrease in the perpendicular one. The more this chain molecule is drawn, the more the contribution would increase in the parallel direction but it would descrease in the perpendicular one. However, above a certain draw ratio (2.5 in our experiments), the chain molecule of amorphous region would be almost stretched and subject to the restraint of crystalline region and it would therefore become nearly immobile. Consequently the intensity of tan $\delta$ decreases rapidly near the draw ratio of 2.5.

### 3-3. Effect of Annealing Temperature

It is known that the crystal sizes of PET increase with increasing annealing temperature from 102°C to 245°C and that the tan$\delta$-curve becomes broader and the intensity decreases with increasing annealing temperature.[17] As shown in Fig. 8, maximum tan $\delta$ decreases rapidly between annealing temperature of 100°C and 125°C, suggesting that the crystallization occurs intensely in this temperature range. The fact is again supported by the crystallinity measurement.

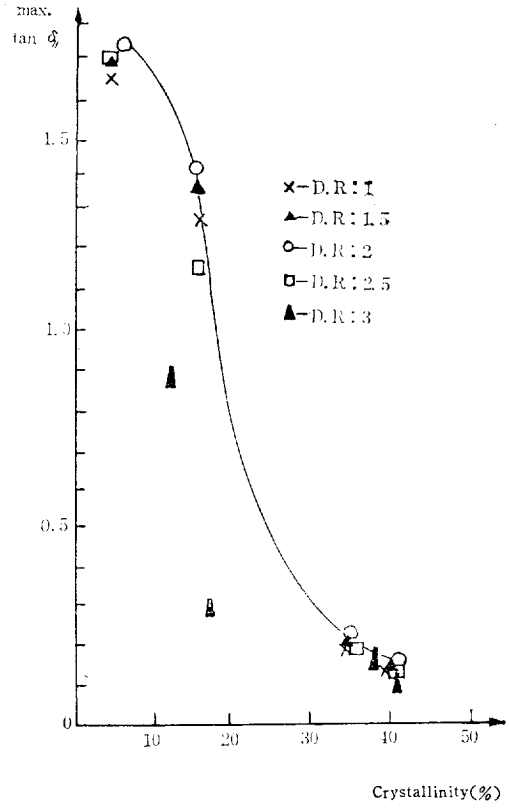


**Fig. 11.** Maximum $\tan\delta_{/\!/}$ vs. crystallinity for PET of various draw ratios.

Fig. 9 shows that the orientation affects cry-

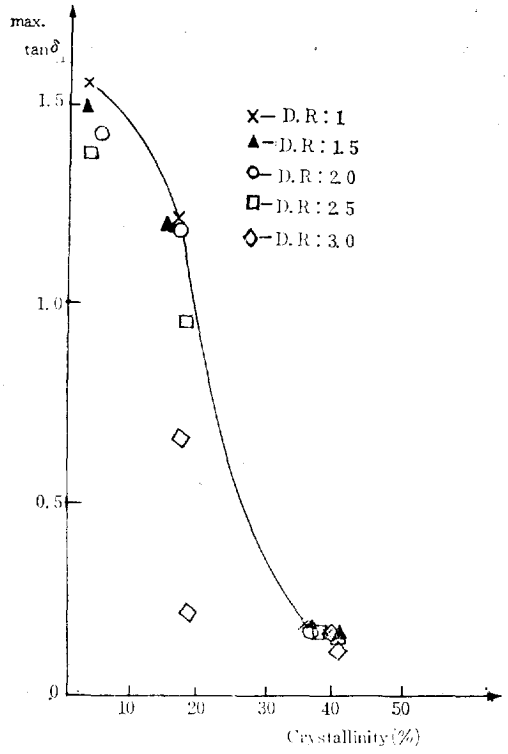


**Fig. 12.** Maximum $\tan\delta_{\perp}$ vs. crystallinity for PET of various draw ratios.

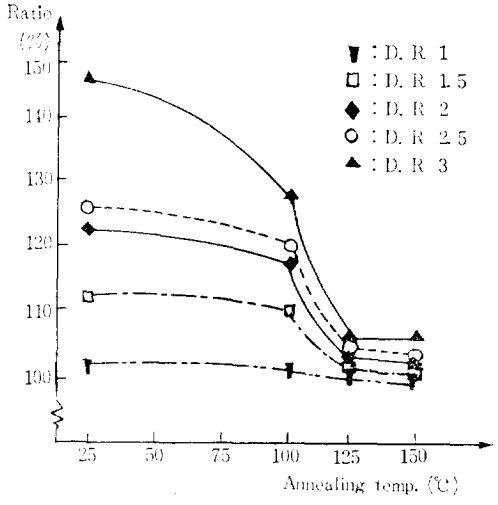


**Fig. 13.** Effect of annealing temperature on the ratio of max. $\tan\delta_{/\!/}$ to max. $\tan\delta_{\perp}$

stallinity less than the annealing temperature does and that crystallinity increases rapidly between 100°C and 125°C. Hence the intensity

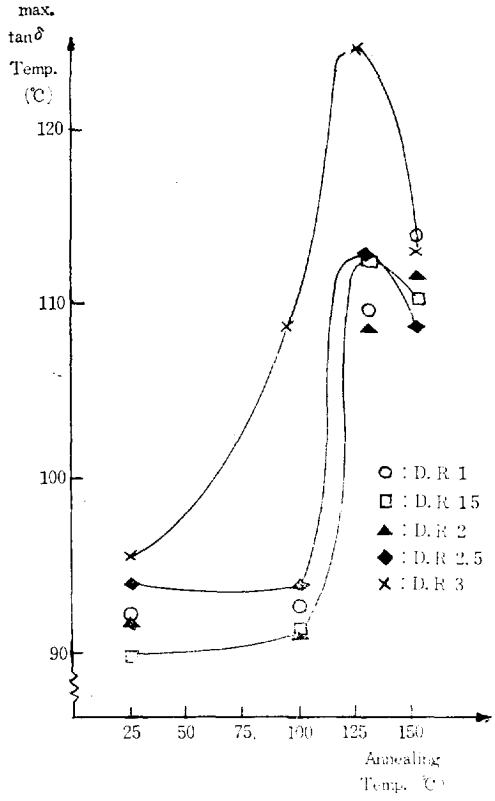


**Fig. 14.** Effect of annealing temperature on maximum $\tan\delta_{/\!/}$ temperature.

of the loss tangent decreases rapidly in this range. The effect of annealing temperature on maximum tan $\delta_{/\!/}$ and maximum tan $\delta_{\perp}$ at various draw ratios is shown in Fig. 10. It is noted that both maximum tan $\delta_{/\!/}$ and maximum tan $\delta_{\perp}$ decrease with the annealing temperature followed by a large fall from 100°C to 125°C.

It is evident, in Fig. 11 and Fig. 12, that the intensity of tan $\delta$ decreases with the increase of degree of crystallinity. The intensity of the loss tangent is often given by the equation,[18]

$$\tan\delta = Wc(\tan\delta)c + (1-Wc)(\tan\delta)a \cdots (5)$$

where Wc is the degree of crystallinity, and the subscripts a and c refer to the amorphous and crystalline phase, respectively. Since the loss tangent is mostly due to the amorphous

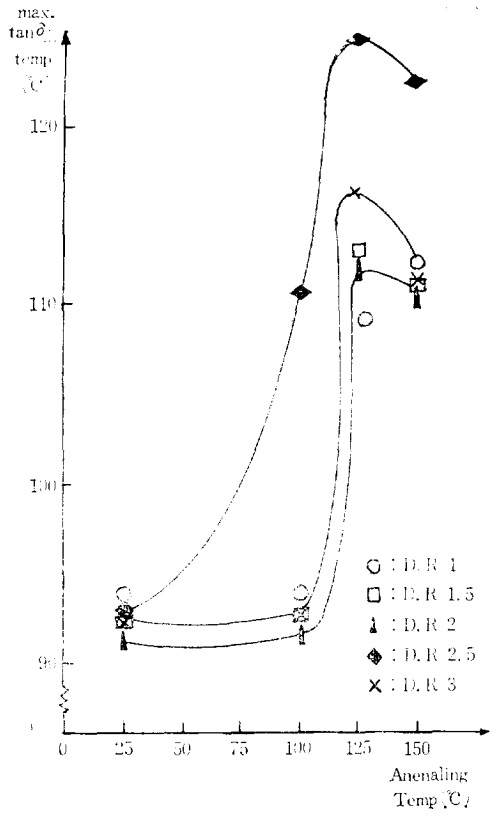


**Fig. 15.** Effect of annealing temperature on maximum tan$\delta_\perp$ temperature.

phase, the equation (5) is simplified to tan $\delta$= (1−Wc) (tan $\delta$)a, which shows that the intensity decreases with increasing degree of crystallinity.

Fig. 13 shows that the ratio of maximum tan $\delta_{/\!/}$ to maximum tan $\delta_\perp$ decreases with the annealing temperature, i. e, the anisotropic behavior decreases with the annealing temperature. Since all the samples were annealed under constraint at constant length in the direction of drawing, the larger number of amorphous chain segments might be converted into crystallites in the parallel direction than in the perpendicular one. Thus the anisotropic behavior already developed by the drawing process would reduce gradually with increasing annealing temperature.

Fig. 14 and Fig. 15 show the effect of annealing temperature on maximum tan $\delta_{/\!/}$ temperature and maximum tan $\delta_\perp$ temperature respectively. Maximum tan $\delta$ temperature increases with the annealing temperture of up to 125°C above which it begins to decrease. This could be explained by the shift-back phenomenon. In other words, although the $\alpha$-transition initially shifted to higher temperature with crystallinity, it began to shift back above a certain crystallinity.[2] This behavior could be attributed to the effect of crystal size on the amorphcus region.[19] At low to medium crystallinities there would be many small crystallites, which would act like crosslinks and inhibit the motion of amorphous chain, while at high crystallinities the crystallites would be larger and fewer, and thus would allow the amorphous chain more freedom. Our experimental data of crystallinity showed that the $\alpha$-peak shifted to higher temperatures for crystallinities up to about 35% above which it shifted toward lower temperatures. This is nearly agreed with the result of others.[19] They showed that the crystallinity at which the $\alpha$-peak shifted back was 30%.

## 4. CONCLUSIONS

1) The intensity of maximum tan $\delta_{/\!/}$ is higher than that of maximum tan $\delta_\perp$. The peak temperature is lower in the parallel direction than in the perpendicular one.
2) Maximum tan $\delta_{/\!/}$ increases with the draw ratio up to 2.5 above which it decreases rapidly. Maximum tan $\delta_\perp$ decreases monotonously with the increase of draw ratio. And both of them decrease with increasing annealing temperature.
3) The ratio of maximum tan $\delta_{/\!/}$ to maximum tan $\delta_\perp$ increases with the draw ratio while it decreases with increasing annealing tem-

perature.

4) Maximum tan $\delta_{/\!/}$ temperature and maximum tan $\delta_{\perp}$ temperature are not affected by the draw ratio of up to 2.5 above which they increase rapidly. And the values increase with the annealing temperature but begin to decrease above a certain temperature (125°C).

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