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THE STRUCTURE OF HIGHLY DRAWN PET FILM WITH TRANSVERSE LINES AND ITS POLARIZED LIGHT SCATTERING

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ABSTRACT

When the PET film is drawn to about 4 times at first stage, the transverse line structure is observed under the polarized optical microscope (POM) and the scanning electron microscope (SEM). These transverse lines extended and slightly undulated perpendicular to the draw direction. Consequently, the transverse lines are distributed perpendicular to the draw direction.

From the observation of the POM and the SEM and the results of the S-S curve and of the birefringence of PET films, it can be considered that the transverse line structure is composed of the "squeezed structure" and the relaxed craze-like structure.

PET film with the transverse line structure shows the unique polarized light scattering patterns when the incident beam has the component perpendicular to the draw direction, and that the light in this pattern oscillates in the draw direction.

The "polarized pattern" shows four leaf-shaped patterns not only in the front but also in the back. The intensity of the "polarized pattern" in the negative direction is weak.

Such "polarized pattern" can be observed when the transverse line structure extends perpendicular to the draw direction. When the transverse lines are inclined perpendicular at 3.8° , the "polarized pattern" is changed into the pair of two leaf-shaped patterns.

The incident beam reflects and transmits repeatedly at the boundary between two layers which have different densities and refractive indices. Consequently it is considered that polarized light vibrating in the horizontal plane is observed.

Such optical property of the PET film is similar to a half-wave plate or an optically active substance, which is, however, substantially different from the PET film. This is because the "polarized pattern" in this paper does not depend on the thickness of the sample films and light vibrating perpendicularly to the draw direction is changed into the one vibrating in parallel to the draw direction and not vice versa. There is a possibility of applying the PET film to an optical element, such as an optical isolator and an opto electric integrated circuits.

1. INTRODUCTION

Many crystalline polymers are developed by drawing. It is widely known that piled lamellae and their aggregates which grow perpendicular to the draw direction exist in the oriented and crystallized polymers.¹⁾²⁾

It has been found out by the scanning electron microscope (SEM) that the piled lamellae structure also exists in the highly drawn and highly oriented

poly(ethylene terephthalate) (PET). This structure was reported previously as the transverse line structure of PET.³⁾⁴⁾ PET film with the transverse line structure shows specific polarized light scattering patterns.⁵⁾

There are two aims in this paper. One is to reveal the mechanism, how the transverse line structure is produced. The other is to clarify the relation between the transverse line structure and the specific polarized light scattering patterns.

2. EXPERIMENTAL

2.1 Sample preparation

An undrawn PET film which showed no orientation and amorphous pattern in x-ray diffraction was drawn at a rate of 1%/sec. in water at 65°C. The thickness of the undrawn film is 392 μm . The draw ratio was calculated based on the change in the length between marks on the specimen.

2.2 Microscopy

A Nihonkogaku polarizing microscope was used. When we measure the degree of birefringence, a Berek compensator was attached to it. For a scanning electron microscope (SEM), JEOL JSM-25 was used.

2.3 Measuring of light scattering

Fig. 1 shows a measurement system of light scattering. A He-Ne gas laser (wave length of 0.6328 μm) was used as a light source. The light which has passed through a polarizer scatters at the film. This scattering light goes through an analyzer, and after this stage, the scattering light forms an image on a screen. The power of scattering light was measured by a power meter. The angle between scattering patterns (2ϕ) was measured.

Fig. 1 The measurement system of light scattering.

The co-ordinate of the scattering system is shown in Fig. 1. The x-axis is directed toward the horizontal (H) direction ($\theta=0^\circ$). The y-axis is directed toward the vertical (V) direction ($\theta=90^\circ$). We decided to fix the draw direction of the specimen toward H direction. Various combinations are possible regarding directions of polarizer and of analyzer. For example, one possible combination is as follows: The angle of polarization is H, the draw direction of the film is H (fixed), and

the analyzer is V. In this case, we indicate this combination as HHV. We conducted an experiment by the following method. We rotated the draw direction of the film around the y-axis in the x-z plane. At this stage, we define χ as an angle between the x-axis and the draw direction.

3. RESULTS AND DISCUSSION

3.1 The transverse line structure

Photographs of the polarizing microscope (POM) and SEM of the transverse line of PET film are shown in Fig. 2 and Fig. 3 respectively. The specimen in Fig. 3 is etched by alkali in order to clear the transverse line. The transverse lines are generally observed to be extending perpendicular to the draw direction. From the photograph we can observe small undulations in the transverse line. Consequently transverse lines are distributed perpendicular to the draw direction.

When the film is not drawn homogeneously, the

Fig. 2 POM photograph of transverse lines of PET film. Drawn to 55% at 65°C in water.

Fig. 3 SEM photograph of transverse lines of PET film. Drawn to 55% at 65°C in water.

Fig. 4 SEM photograph of transverse lines which are inclined perpendicular direction. Drawn to 46% at 65°C in water.

transverse lines are inclined at 3.8° not being perpendicular as shown in Fig. 4.

Fig. 5 shows stress strain curve (S-S curve) of the drawn PET film with a transverse line structure and the undrawn PET film. This curve reveals not only the primary yield point but also the secondary yield point. However, the undrawn film reveals only the primary yield point. If the

Fig. 5 The stress strain curves of the drawn (with transverse line) and undrawn PET films. The drawn PET films with the transverse lines were stretched again at 6% and they were stretched again after they are left without being stressed for 1 sec., 10 min. and 2 days respectively.

undrawn film is drawn beyond the yield point, a necking phenomenon occurs. When the film in which necking occurred is extended again, the S-S curve is different from the original curve before necking occurs. In the case of PET film with transverse line, the S-S curve which has been once extended approaches to the original shape as the recovery time is longer (see Fig. 5). Such a phenomenon is observed in a material called "hard elastic".⁶⁾ It is known that these materials consist of lamellae stacked perpendicular to the draw direction.²⁾ The mechanism of this behavior is considered that the separation between lamellae takes place by extension and after the stress is removed separated parts will gradually recombine with each other.²⁾

The width of the transverse line was about several thousand of Å. This width was one digit greater than that of the lamella of hard elastic materials.⁷⁾ It is considered, however, that extensional recovery behavior of transverse line materials is similar to that of hard elastic materials. That is, the distance between transverse lines increases by extension and it gradually decreases after stress is removed. It means that it returns to its original structure gradually.

Fig. 6 showed the relation between the draw ratio and the degree of birefringence of PET films, which was drawn in water at 65°C. The transverse line structure occurred when the draw ratio was beyond about 4 times. Birefringence increases linearly before the transverse line structure occurs. However, after the transverse line structure occurs,

Fig. 6 The relation between the draw ratio and the degree of birefringence (Δn) of PET films. Drawing conditions; 65°C in water. ●—● without transverse lines, ○—○ with transverse lines.

the increase in the birefringence become small. Therefore it is considered that the increase in the orientation of the film with transverse line is smaller than that of the film before the transverse line structure occurs.

Taking into account all the results of our experiments mentioned so far, let us here propose a model in which the transverse line structure is produced. What we propose are as follows:

(1) At the initial stage, the film is deformed by the shear stress. Namely, when the extensional stress works on the undrawn PET film, the shear stress generates and the direction of the greatest shear stress is 45° . This shear stress plays the role of arranging polymer molecular chains in a bundle. We call this structure "arranged structure". The formation of the "arranged structure" occurs only where the plastic deformation is easy to generate by the shear stress and this structure is regarded as identical with so-called Lüders line. This "arranged structure" attracts crystallites, and the molecular axis of the crystallites turns to the molecular chain direction of the "arranged structure" (Fig. 7a).

(2) At the middle stage, the more extensional stress works, the more "arranged structure" are formed. The "arranged structure" turns to the extensional direction from 45° . As a consequence, the axis of the molecular chains bounded by the "arranged structures" turns to the extensional direction. The "arranged structure" which is three dimensionally formed in specimen develops as the structure of a three-dimensional network. We call such a structure "squeezed structure" meaning a drawn out structure that contains countless minute lamellae (see Fig. 7b).

(3) At the final stage, when excessive extensional stress is applied, homogeneous deformation of the collective "squeezed structure" does not take place. Then its partial destruction begins. This destruction phenomenon is considered to be similar to that we generally call the crazed structure (see Fig. 7c). When the extensional force is removed, this crazed structure transforms into a relaxed craze-like structure. This structure functions in lowering the degree of birefringence as shown in Fig. 6.

We have considered the mechanism of the behavior in Fig. 5 as below. When the stress is

Fig. 7 The model of formation of the transverse line structure by drawing. (a) at the initial stage, (b) at the middle stage, (c) at the final stage.

applied to the transverse line structure, the relaxed craze-like structure is extended into the crazed structure. Once the stress is removed from the extended transverse line structure, it takes the crazed structure long time to return to the original state of relaxed craze-like structure. The S-S curves of a sample which has been once extended approach to the original shape as the recovery time is longer. If we extend these specimen furthermore beyond the secondary yield point, the S-S curve of these specimens shows the primary yield point.⁸⁾⁹⁾ It may be considered that the primary yield point is caused by the destruction of the crazed structure and/or of "squeezed struc-

ture".

It can be considered that the transverse line structure is composed of the "squeezed structure" and the relaxed craze-like structure.

3.2 Polarized light scattering pattern

Fig. 8 shows VHH light scattering pattern which is obtained from PET films with the transverse lines mentioned above. This pattern shows four leaf-shaped patterns in the front and another four similar weak patterns in the back (in this figure only two patterns are shown for the back scattering). The scattering angles of these leaf-shaped patterns were about 40° at their centers. The angle between scattering patterns (2φ) was 7.6° . Moreover, this pattern can not be observed in VHV light scattering where analyzer is rotated by 90° from the position in VHH light scattering, so this scattering from the film is composed of polarized light vibrating to the horizontal plane. This pattern will be described as "polarized pattern" in this paper. In HHH light scattering, however, "polarized pattern" is not observed and only strong and horizontal streak emerging on both sides from the scattering center is observed

(Fig. 9). It will be found from these results that the "polarized patterns" can not be observed when incident beam vibrates in parallel to the draw direction of specimens, but can be observed when incident beam vibrates perpendicularly to the draw direction. The strong and horizontal streak in HHH light scattering is produced by scattering which is due to the variation of density or refractive index in the sample showing transverse lines.

The intensity of θ HH "polarized pattern" obtained by rotation of the polarizer in the x-y plane by θ from the horizontal position agrees with $\sin^2\theta$ as shown in Fig. 10. Both VHH and HHH light scattering patterns are observed in θ HH light scattering. An amplitude component in the y-axis direction for the light vibrating in the θ direction is in proportion to $\sin\theta$, so that the intensity of this component is in proportion to $\sin^2\theta$. Hence, it can be considered that a vertical component of incident light is changed into the polarized light vibrating horizontally by the PET film with the transverse lines.

Fig. 11 shows one of the structure models

Fig. 8 VHH light scattering pattern which is obtained from PET film with the transverse lines.

Fig. 9 VHH and HHH light scattering patterns of the transverse line PET film.

Fig. 10 The intensity of θ HH light scattering patterns of the transverse line PET film.

Fig. 11 The structure model producing "polarized patterns"

producing "polarized patterns" As described above, transverse lines are composed of the two-layer structure where the two layers have different densities and refractive indices and arranged perpendicularly to the draw direction. These transverse lines are not perfectly perpendicular to the draw direction. They are little undulated and consequently locally inclined. When the incident light passing through the specimen is reflected and transmitted at the boundary of two layers, the reflecting or transmitting behavior depends on vibrating direction of the light. The light vibrating perpendicularly to the boundary plane is easy to transmit, but the light vibrating in parallel to the boundary plane is fairly reflected at the boundary. In VHH light scattering, the light reflected at the boundary stimulates the scattering elements of the specimen to induce secondary wave. Because the scattering elements are inclined, the secondary

waves have both vertical and horizontal components. The vertical component is fairly reflected at the boundary, and passes through the specimen in the same way as incident light (primary light) does. On the other hand, the horizontal component of secondary waves at a wider scattering angle transmits the boundary to produce the "polarized pattern".

It is difficult to explain perfectly by only this model of how the "polarized pattern" is developed. It might be better to take into consideration possible interferences of secondary wave.

A half-wave plate and an optically active substance have some functions similar to that of the PET film. However, the former two functions are substantially different from the latter. This is because the "polarized pattern" in this paper does not depend on the thickness of the sample films, and light vibrating perpendicularly to the draw direction is changed into the one vibrating in parallel to the draw direction and not vice versa.

When the transverse lines are inclined at 3.8° (Fig. 4) not being perpendicular to the draw direction, VHH "polarized pattern" is changed into the pair of two leaf-shaped pattern on both sides as shown in Fig. 12. The inclination of 3.8° as observed Fig. 4 agrees with the half angle between scattering patterns ($2\varphi=7.6^\circ$). This result shows that the "polarized pattern" is related to the inclination of the transverse lines or the boundary plane. For this reason the boundary reflection model shown in Fig. 11 may be valid.

Fig. 13 shows how the VHH "polarized pattern" changes with the χ -rotation of the specimen around the y-axis. The "polarized pattern" rotates with rotation of the draw direction of specimen, as shown in Fig. 13 a, b and c. The boundary

Fig. 12 VHH "polarized pattern" which is obtained from PET film with the inclined transverse lines.

$\chi = 0^\circ$
(a)

$\chi = 30^\circ$
(b)

$\chi = 60^\circ$
(c)

Fig. 13 VHH "polarized pattern" which is obtained with χ -rotation of the transverse line PET film around y-axis.

reflection model also receives a support from this result.

Fig. 14 shows the light scattering pattern (VH0) from without analyzer in VHH arrangement. When PET film with transverse lines is stretched, the scattering angle of the "polarized pattern" does not change, but its intensity fairly decreases (Fig. 14 b, 1% stretched) and disappears at the stretching of 12% (Fig. 14 c). In Fig. 14 b, the strong streak is observed while the "polarized pattern" is weak. Though the reason why these phenomena are observed is now under examination in our laboratory, the PET film with the transverse lines may be applied to a stress sensor.

Fig. 15 shows the ratio of scattering energy of

0 %
(a)

1 %
(b)

12 %
(c)

Fig. 14 VHO "polarized patterns" which is obtained stretching the transverse line PET film.

Fig. 15 The ratio of scattering energy to that of the incident light. Total ratio of them is 89% and 11% is not measured. Scattering energy of the "polarized patterns" is enclosed with a circle.

the "polarized pattern" to that of the incident light. The ratio is about 9% and very small. Although this is a difficult problem to be solved, there is a possibility of applying the PET film to an optical element, such as an optical isolator and an opto electric integrated circuits.

4. CONCLUSION

In this paper, the mechanism of formation of the transverse line structure in the highly drawn and highly oriented PET film was studied. And the relation between transverse line structure and the specific polarized light scattering pattern of PET film with the transverse line structure was also studied. Results are as follows:

1) The transverse line structure occurred when draw ratio was beyond about 4 times. The transverse lines extend perpendicularly to the draw direction, and small undulations are observed in the transverse line.

2) When the transverse line structure occurs, an increase in birefringence becomes small.

3) The S-S curve of PET films with the transverse line structure shows the primary yield point and the secondary yield point. These curves of the sample which has been once extended approach to the original shape as the recovery time is longer.

4) The shear stress plays the role of arranging polymer molecular chains in a bundle when amorphous and unoriented PET films are drawn. The "squeezed structure" is formed from such "arranged structure" by the successive extension. With further stretching, a partial destruction occurs in "squeezed structure" to generate crazed structure. When the film is relaxed, the molecular chains of the crazed structure are also relaxed. It can be considered that the transverse line structure is composed of the "squeezed structure" and the relaxed craze-like structure.

5) The "polarized pattern" can be observed in the sample with the transverse line structure.

6) The "polarized pattern" is observed only when the incident beam has the component perpendicular to the draw direction.

7) The "polarized pattern" shows four leaf-shaped patterns not only in the front but also in the back. The intensity of the "polarized pattern" in the negative direction is weak.

8) When the transverse lines are out of perpendicular to the draw direction and they are inclined on one side at 3.8° , the "polarized pattern" is changed into the pair of two leaf-shaped patterns. The angle between scattering patterns (7.6°) is equal to two times of the inclined angle (3.8°).

9) The scattering light reflects and transmits repeatedly at the boundary between two layers which have different densities and refractive indices, so that the polarized light vibrating in the horizontal plane becomes to be observed.

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高配向ポリエチレンテレフタレートフィルムの 横縞構造と偏光散乱

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ポリエチレンテレフタレート (PET) フィルムを延伸すると、横縞構造が約 4 倍の延伸比以上で、偏光顕微鏡あるいは走査型電子顕微鏡により観察される。この横縞構造は延伸方定にはほぼ直角な方向を向いているが、小さなうねりを有しているため、部分的には延伸方向に直角な方向を中心としてゆらぎを有している。

横縞構造の顕微鏡による観察、未延伸フィルムと横縞構造発生フィルムにおける S-S 曲線および伸張一回復曲線の相違、複屈折度の延伸比に対する変化の挙動などから、横縞構造は“絞りこみ構造”の集合体とそれが部分的に破壊された構造の二層構造と考えることができる。

このような横縞構造をもつ PET フィルムは、特殊な光散乱特性を示す。すなわち、PET フィルムに入射する光が、延伸方向と直角の方向に振動面をもつかあるいは直角成分を有しているとき、延伸方向に平行な振動面をもつ偏光散乱パターンが観察される。この偏光散乱は、

入射光線に対し前方と後方にそれぞれ 4 つの長円状のパターンが、散乱角約 40° を中心として観察される。しかし、横縞構造全体が延伸方向に対しどちらか一方に傾いて出現した場合には、4 つの長円状のパターンのうち 2 つのペア散乱が観察されるのみである。以上のような現象は、散乱光が密度の異なる横縞の境界で、選択的反射や透過を繰り返すことにより、延伸方向に平行な方向に振動する散乱光として観察されることになるためと考えられる。

このような現象と類似したものに、たとえば $\lambda/2$ 波長板や旋光があるが、この横縞構造フィルムはこれらと本質的に異なり、フィルムの延伸方向に垂直な成分光に対して、それを平行な成分に変換する機能をもつものである。このような偏光散乱の特殊性から、このフィルムは光アイソレーターや光集積回路の素子としての可能性がある。