Bowing Phenomenon of Double Bubble Tubular Film Process for Nylon6 Film

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ABSTRACT

This report is discussed on the bowing phenomenon and the sag elimination tension for biaxially oriented nylon6 film process which consists of double bubble tubular film process and thermosetting tentering one.

The bowing phenomenon does not occur in the heat set of the triple bubble tubular process. However, there is a serious problem of the bubble stability when the sufficient thermosetting by the tubular process is carried out, so the heat set by the tenter process is required.

The bowing phenomenon arises when the thermosetting is carried out by the tenter method. The bowing ratio becomes large when the thermosetting temperature is high and film relaxation ratio is large.

It is possible to reduce the bowing ratio when thermosetting is carried out in the two steps of tenter process. Shrinkage stress of the stretched film was relaxed in the heat treatment of the second step whose temperature is higher than the first one. Two steps heat treatment was able to decreased the bowing ratio compared with the one step heat treatment.

When the bowing phenomenon occurred, shrinkage percentage in hot water changes along the cross-direction of a film. The humidity expansion coefficient in the film increases with increasing shrinkage percentage in hot water which is related to the molecular orientation. The sag also increased with increasing the bowing ratio. The bowing ratio and the sag elimination tension have the proportional connection.

1. Introduction

The plastic film is used in the various application, and the required film quality is more severe year by year in proportion to the diversification of the application. Therefore, the advanced production technology of the plastic film is needed, and especially, further technology upgrading is required in order to demonstrate features of the nylon6.

Research of the biaxial stretching film remains for the basic research which requires large scale research machine.

There are bowing phenomenon and film thickness ununiformity as a technological problem of stretch film. Bowing is a phenomenon related to the discrepancy between the direction of the molecular orientation axis of the center and the edge of the film width and causes the anisotropy of film characteristics such as heat shrinkage, optical refractive index and mechanical properties. When customers require film having no bowing in property, film manufacturers usually supply the film obtained at the center part of the film width by slitting. Reducing the bowing is one of the most important technical problem for biaxial film producers.

Papers on the bowing phenomenon have been published by Kase et al. [1 - 4] and Sakamoto [5 - 7]. Kase et al. theoretically analyzed the deformation behavior of thin, and uneven elastic film in the tenter process by using the finite difference method. Sakamoto investigated changes of the refractive index ellipsoid by biaxial drawing of PET film which was conducted by a laboratory batch drawing. But as far as bowing phenomena are concerned, there is no proof that such a batch drawing is equivalent to industrial tenter drawing. He also reported the theoretical analysis of the refractive index ellipsoid due to bowing which occurs in industrial tenter process. However, these theoretical predictions have not been confirmed experimentally. Previous study reported by the authors was concerned about observations of bowing phenomena throughout a tenter. Their analyses was used finite element method calculation discussing the countermeasure for reducing bowing ratio. But these papers are not systematically described.

Afterwards, the research using biaxial tenter stretching production machine on the polyester film was carried out by Yamada, Nonomura, Matsuo et al. [8 - 13].

However, the research of heat set technology on the nylon6 film was not carried out in detail.

Though the research of the tenter method biaxial stretching technology has been reported until now, the research on the bouble bubble tubular biaxial technology has not been made. Especially thermosetting technology in double bubble tubular process should be studied this time.

In order to commercialize biaxial stretching nylon6 film for application such as the retorting, the reliable heat set is necessary.
Above the reason, it is necessary to carry out the thermosetting using the tenter equipment. But the bowing phenomenon arises as a destiny, when the thermosetting is carried out using the tenter equipment.

After the tubular biaxial stretching , the reduction of the bowing phenomenon in the tenter thermosetting is required. This is the main purpose in this study.

It is a problem that biaxially stretched nylon6 film absorbs moisture .
When moisture is absorbed, sag is caused. Sag cause the trouble in printing and in the laminate. Therefore, it is important to reduce the bowing phenomenon and minimizes sag and these control factors should be examined in detail informed.

2. Experimental

2.1 Experimental Equipment

The apparatus of the double bubble tubular film process shown in Figure 1 was used. Using an extruder (L/D=24) with the diameter of 40mm as well as a circular die with the diameter of 75mm and the lip clearance of 1mm, non-stretched film was produced at the condition of the resin temperature at 265^0C , blow up ratio of 1.2, and it was cooled and solidified it with a water-cooling ring having the diameter of 90mm.

This raw film is stretched simultaneously in the machine direction and transverse one by inside bubble air, using a drawing machine composed of two pairs of pinch rolls and a heating furnace (a far infrared radiation heater is self-contained). (Fig. 1)

The stretched film is heat-set using tube method heat set equipment and tenter method heat set equipment.（Fig. 2）

By letting film for evaluating the sag elimination tension using the slitter machine, the bubble tension by using a pair of the roll was quantitatively measured.

2.2 Material

The material is Ube Nylon 1024FDX14 (Nylon 6) with the relative viscosity of ηr=3.75 (sulfuric acid concentration 98%), and mean molecular weight of 24000.

2.3 Definition of Bowing Ratio

Bowing phenomena has two meanings. One is the geometrical bowing, in which a straight line drawn across the film width at the entrance of a tenter changes into bow shape at the exit of the tenter. Another is the characteristic bowing it means the anisotropical main axis of film characteristics such as heat shrinkage, optical refraction index, and mechanical properties is varied along the film width. In this paper, the geometrical bowing is dealt under the assumption that it corresponds to the characteristic bowing.

As shown in Figure 3, bowing ratio（B.R）is expressed as the percentage of bowing distance ΔB divided by the film width L.
When the film center lags behind the film edge, the bowing distance ΔB is considered to be positive.

$$B.R = \Delta B / L \times 100 \quad (\%)$$

2.4 Experimental Method

Using the stretched film produced by double bubble tubular film process, the comparative evaluation by two kinds of heat set method of tubular method and tenter one was carried out.

The process conditions of non-stretched film are 265^0C for resin temperature at the die exit, 1.2 for blow up ratio, and 6.0 for draw down ratio respectively. A water cooling method was used to reduce crystallinity. The cooling water temperature was adjusted to be 18^0C. The stretching process consists of a heating/ stretching furnace and an air ring device. The air ring device was installed at the upper part of the heating furnace so as to fix the stretching start point, and it injected air downward at the angle of 45^0.

The standard condition for stretching process was set at 310^0C for process temperature (heater set temperature) and MD (Machine Direction)/ TD (Transverse Direction) =3.0 /3.2 for stretching ratio respectively.
The film thickness was 130 μ for non-stretched film, and it became 13.5 μ after stretching. The stretched film was subjected to heat treatment, using a heat treatment device to prevent shrinkage , thereby there is no disturbance due to film shrinkage permitting the measurement of film thickness and physical properties alike.

2.5 Thermosetting Conditions

The bowing ratio and film orientation were evaluated by the change of thermosetting temperatures, film relaxation ratio, bowing ratio and effect on the film oriented state, etc.

① Thermosetting temperature （180, 190, 200, 210, 220 ℃）
② Relaxation ratio (0, 10, 20, 30 %)
③ Thermosetting stage（1 stage, 2 stage）
④ Tubular thermosetting process

2.6 Evaluation of Film shrinkage percentage and Film density

In the nylon film for retort food, it is soaked in hot water of high temperature in order to conduct the sterilization and processing.
It is necessary to hold the shrinkage percentage of a film small by thermosetting.
The relationship among thermosetting temperature, film shrinkage percentage and film density was examined.

2.7 Evaluation of Bowing ratio

Many straight lines across the non-stretching film width were drawn on the surface of the film at the entrance of the stretching furnace. After the film winding, the line sample was collected. The evaluation procedure for bowing phenomenon was followed by Figure 3.

2.8 Evaluation of Film shrinkage percentage in-plane

By changing heat set and cross-direction position, the value of the shrinkage percentage pattern was measured.

By measuring the length of the marked line under the 23℃-50％ relative humidity after a day drying as a conditioning after the shrinkage percentage pulled the table line in each direction in the film in-plane every 100mm and after it spread in the hot water of 120℃ condition for 30 minutes, the shrinkage percentage was calculated.

2.9 Evaluation of Film Orientation

Molecular orientation condition of the film in-plane was evaluated using the ultrasonic wave orientation equipment. This equipment can evaluate the in-plane orientation using the elastic modulus proportional for the square of conduction velocity of ultrasonic wave.

2.10 Evaluation of Sag Elimination Tension

Using the slitter machine, sag elimination tension was measured.

Slit sample of the 800mm width was collected by the change of the thermo-setting temperature, and each sag elimination tension was evaluation using the slitter machine.

The relationship between bowing ratio and sag elimination tension was evaluated.

2.11 Evaluation of Film Humidity Expansion

Using the humidity expansion measuring instrument（Nihon sinku）, the relationship between film position and humidity expansion coefficient of a film was quantitatively evaluated. The humidity expansion coefficient should be obtained by the sampling of the film position of diagonal 45°.

The relative humidity was made to rise from 20% to 80%, and the humidity expansion coefficient was calculated by the measurement of the elongation percentage of a film.

3. Results and Discussion

3.1 Effects by Heat set Temperature and Relaxation ratio

The shrinkage percentage of a film is reduced by increasing thermosetting temperature.（Fig. 4）The density of a film increases with the rise in the thermosetting temperature.（Fig. 5）It is necessary to reduce less than 5% shrinkage percentage of a film for the application of the retorting.

It is necessary to set the thermosetting temperature near 210℃ for this reason.

The bowing ratio tend to increase rapidly over the thermo-setting temperature over 200℃. (Fig. 6) The crystallinity increased with increasing temperature.

The bowing line showed the bilaterally symmetric shape.

When the film relaxation ratio is increased, the bowing ratio proportionally increases. (Fig. 7) It is based on also influencing in the wait of the contraction stress of the MD direction, since film width orientation tensile force lowers.

The effective product width decreases too.

3.2 Thermosetting of the triple bubble tubular process

The line pulled in non-stretched film before the stretching straight completely did not change in stretching, after the strain was not generated.

The bowing phenomenon completely did not arise from this in the heat set of the triple bubble tubular process from the experiment.

However, the bubble showed the gourd phenomenon with heightening the heat set temperature , and some tendencies were unstable shown, and the good sample became difficult to be obtained. Mechanical heat set using the tenter equipment is necessary in order to carry out sufficient heat set.

3.3 Thermosetting of the two stage tenter process

The bowing ratio increased in the tenter method heat set. Then tenter heat set was conducted in the two stage and the influence on the bowing ratio was examined. (Fig.8)
It was possible to hold the bowing ratio small than one stage heat treatment system in the two stage heat treatment system. (Table.1)
As the result, one step small bowing phenomenon, however, it was found that the bowing ratio is held small, because to considerably reduce the contraction stress is possible, and because the initial shrinkage stress is small as a result in the heat set of two steps in high-temperature range, was possible.

3.5 Film shrinkage percentage and Film orientation

In the edge, the tendency in which the shrinkage percentage of diagonal 45 ° differed was shown, though the central had as a result of evaluating the film shrinkage percentage pattern in the each direction. (Fig. 9)
Both edges showed the symmetrical shrinkage percentage pattern for the central axis.

In the edge, the main shaft had turned to the MD direction on the central as a result of evaluating the film orientation pattern, and the tendency in which the main shaft tilted a little was shown.
Both edges showed the symmetrical orientation pattern for the central axis.

3.6 Sag Elimination Tension

The roll film of the fixed width was collected from the film in which the thermosetting temperature changed, and the sag elimination tension was calculated using the slitter machine. (Fig. 10)

The tendency in which the sag elimination tension as a film in which the big thermosetting temperature of the bowing ratio as a result is high increased was shown. (Fig. 11)
There was in the proportional connection shown in the Figure.12 , when this result was arranged in the relationship between sag elimination tension and bowing ratio.
It is important to reduce the bowing ratio in order to decrease the film sag.

3.7 Shrinkage percentage and Humidity Expansion

It is considered that the phenomenon of sag originates from the elongation of the minute quantity of a film in the film width orientation. It is considered that the elongation of film is influenced by humidity expansion in the moisture absorption. (Fig. 13)
It tried to compare the humidity expansion coefficient in the direction in which the shrinkage percentage in the place where the anisotropy is big in the product edge differed, it is greatly different in film and edge in the central , when humidity expansion coefficient at 45 ° and 135 ° was measured.（Table. 2）

The humidity expansion coefficient of the direction of the big hot water shrinkage percentage showed the high value. Reversely, the humidity expansion coefficient of the smallish direction
of hot water shrinkage percentage showed the small value.
It is regarded as sag arising , since the strain of the edge by bowing is extended by the moisture absorption excessively.

The tension by slitter machine had to be heightened in order to remove sag which occurs in extending the film edge. It is understood that there is the correlation as a result between bowing ratio and sag elimination tension. (Fig.14)
The printing can smoothly carry out it, if there is no sag of a film.

3.8 Shrinkage Stress

The double bubble tubular film process is a method for biaxial stretching by the inside bubble pressure, using the device shown in Figure 15. In principle, stretching stress etc. may be calculated in accordance with the tubular theoretical equation analyzed by the authors et al. ［14］
The stresses at the end point of heat set may be obtained by the following equation.

$$\sigma = \triangle P \cdot D / 2t$$

where σ : Shrinkage stress in the TD direction
$\triangle P$: Inside bubble pressure
D : Bubble diameter at end point of heat set
t : Film thickness at end point of heat set

In the double bubble tubular film process, the shrinkage stress in the width direction may be calculated by measuring the inside bubble pressure. Figure 16 shows the relationship between shrinkage stress and thermosetting temperature, illustrating that the larger thermosetting temperature is, the lower shrinkage stress is. Figure 17 shows the relationship between shrinkage stress and relaxation ratio, illustrating that the larger relaxation ratio is, the lower shrinkage stress is.
It was verified that the tensile force which work in back direction in heat set increased and that the bowing ratio increase as a result, as the shrinkage stress was bigger. It is regarded as reducing the shrinkage stress in the 1 stage heat set, when heat set was carried out from this fact in 2 stage, and reducing bowing ratio in heat set of high temperature of 2 steps as a result.

4. Conclusion

The bowing phenomenon caused by thermosetting process of both tenter process and bubble process was quantitatively examined for nylon6 film.

(1) The bowing phenomenon does not occur in the thermosetting of the triple bubble tubular process. However, there is a problem of the bubble stability when the sufficient thermosetting by the tubular process is carried out.
(2) The bowing phenomenon arises when the thermosetting is carried out by the tenter method.
(3) Bowing ratio becomes large when the thermosetting temperature is high and film relaxation ratio is large.
(4) It is possible to reduce the bowing ratio when thermosetting is carried out in the twostep of tenter process.
(5) Shrinkage stress of the stretched film was relaxed in the thermosetting of the second step

whose temperature is higher than the first one.
Two step thermosetting was able to decreased the bowing ratio compared with the one step of tenter process.

(6) When the bowing phenomenon occurred, shrinkage percentage in hot water changed along the cross- direction of a film.

(7) The humidity expansion coefficient in the film increases with increasing hot water shrinkage percentage which is related to the orientation of the molecule.

(8) The sag also increased with increasing the bowing ratio.

(9) The bowing ratio and the sag elimination tension have the proportional relation.

(10) It is necessary to decrease the sag of a film in order to carry out smooth and clear printing.

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Table

Table １ Relationship between 1 stage thermosetting and 2 stage thermosetting system

Table ２ Film shrinkage percentage and humidity expansion coefficient

Figure

Fig. 1. Schematic view of double bubble tubular film process

Fig. 2. Schematic view of triple bubble tubular thermosetting machine

Fig. 3. Bowing phenomenon

Fig. 4. Relationship between film shrinkage percentage and thermosetting temperature

Fig. 5. Relationship between film density and thermosetting temperature

Fig. 6. Relationship between bowing ratio and thermosetting temperature
(1 stage thermosetting process)
Fig. 7. Relationship between bowing ratio and relaxation ratio
(1 stage thermosetting process)
Fig. 8. Relationship between bowing ratio and thermosetting temperature
(2 stage thermosetting process)
Fig. 9. Film shrinkage percentage pattern and film orientation
Fig. 10. Schematic view of slitter machine
Fig. 11. Relationship between sag elimination tension and thermosetting temperature
(2 stage thermosetting process)
Fig. 12. Relationship between bowing ratio and sag elimination tension
Fig. 13. Film humidity expansion coefficient
Fig. 14. Relationship between film shrinkage percentage and film humidity expansion coefficient
Fig. 15. Measurement method of shrinkage stress
Fig. 16. Relationship between film shrinkage stress and thermosetting temperature
Fig. 17. Relationship between film shrinkage stress and relaxation ratio in TD

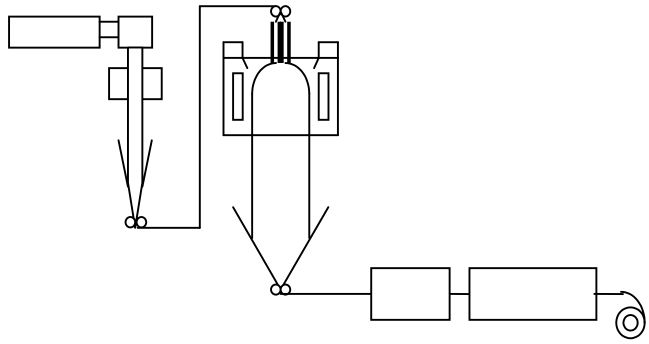


Figure 1 Schematic view of double bubble tubular film

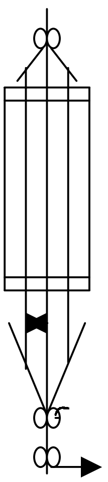


Figure 2 Schematic view of triple bubble tubular thermosetting machine

Figure 3 Bowing Phenomenon

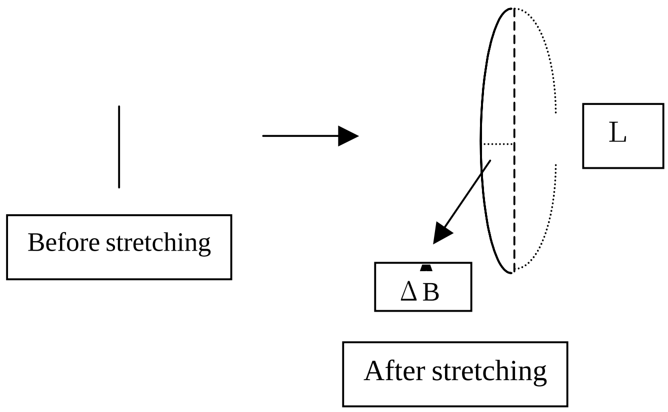


Fig. 4

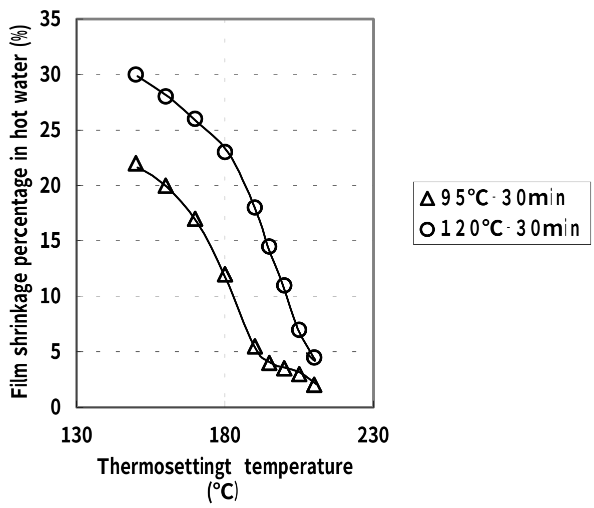


Fig. 5

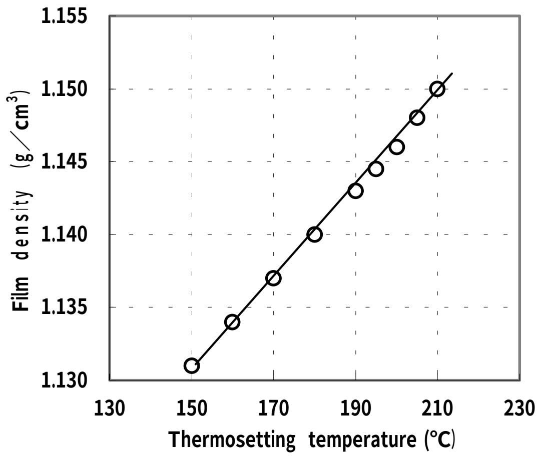


Fig. 6

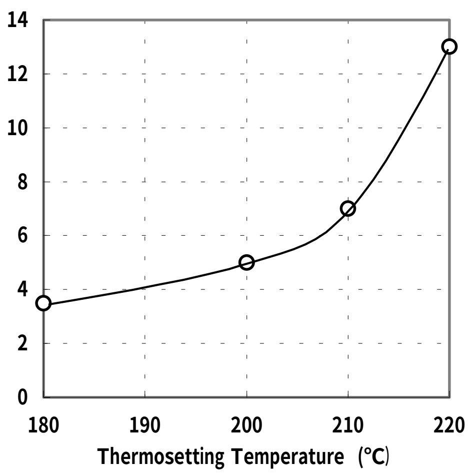


Fig. 7

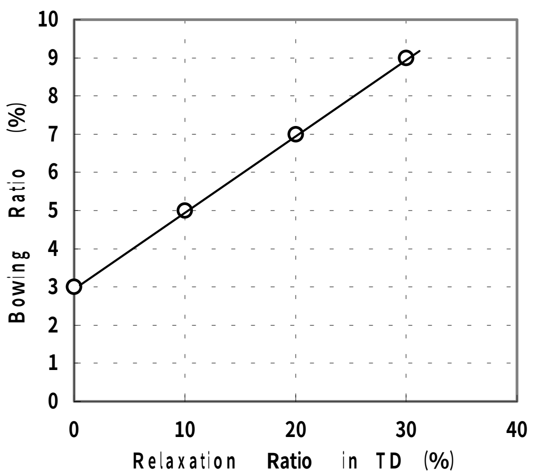


Table.1 Relationship between 1st stage thermosetting and 2nd stage thermosetting system

	Thermosetting system	Bowing Ratio （%）
①	Tubular thermosetting system	0
②	Tenter 1 stage	10
③	Tenter 2 stage	5

Fig. 8

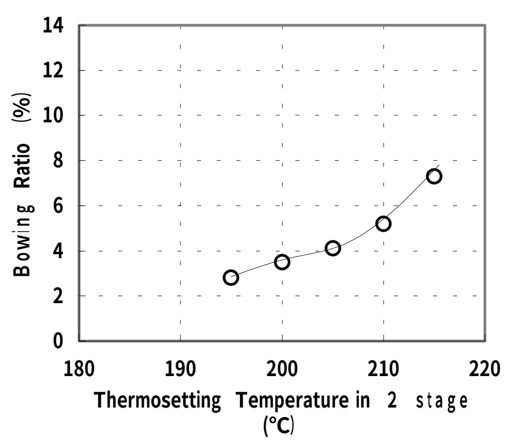
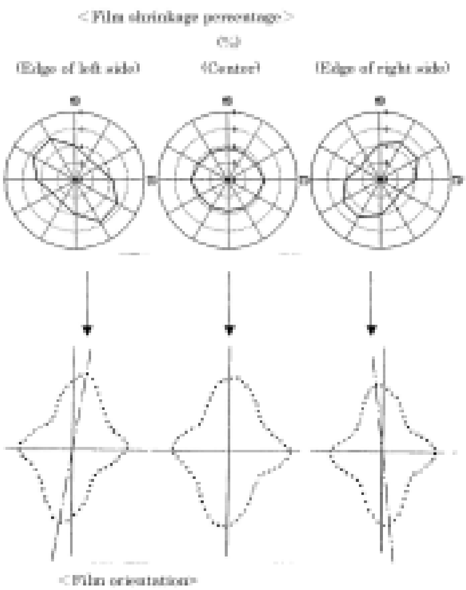


Fig.9 Film shrinkage percentage and film orientation



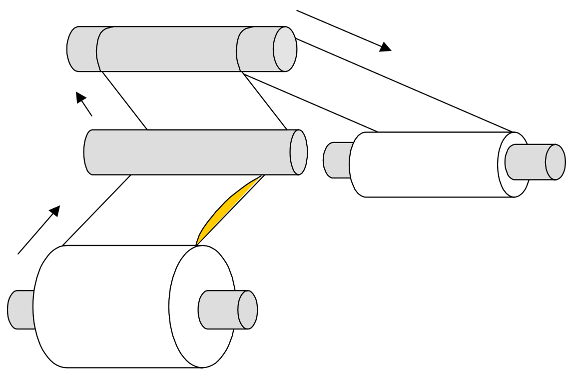
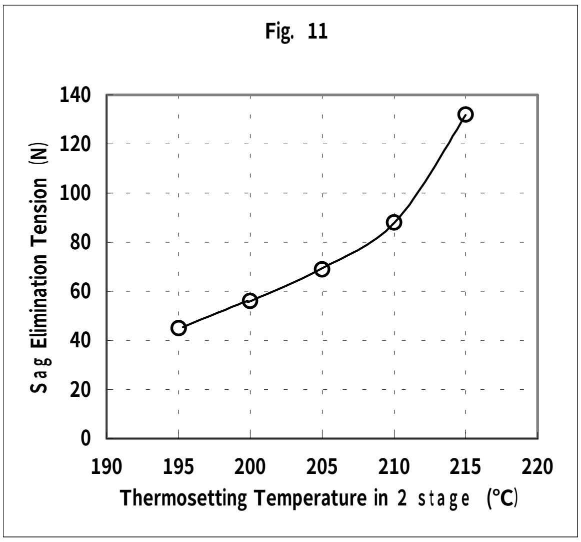
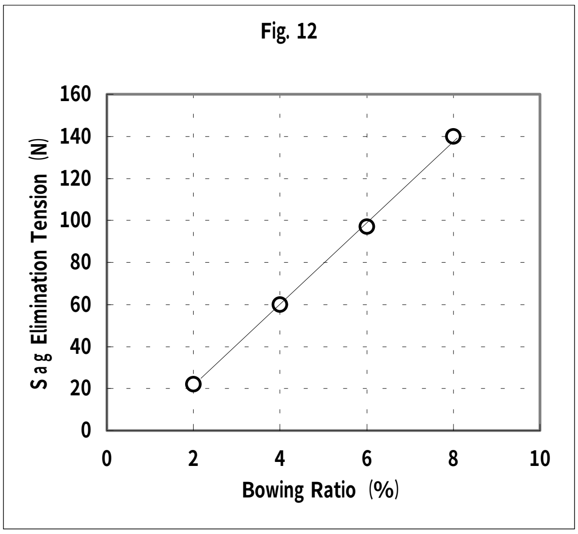


Fig. 10　Schematic view of slitter machine





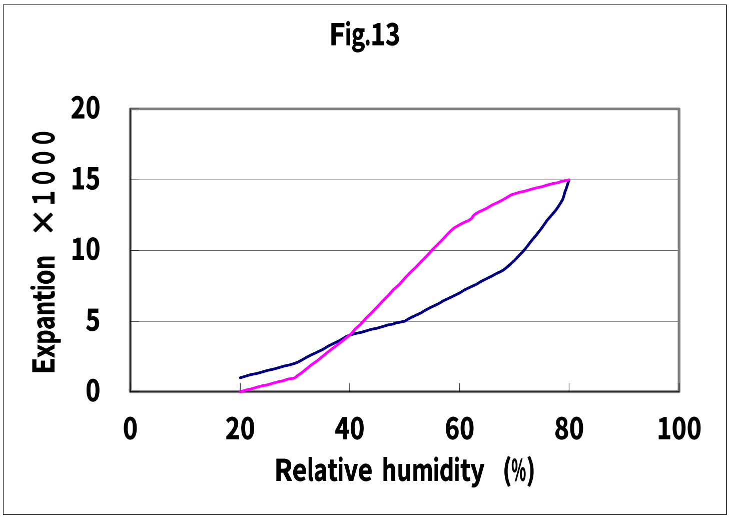


Table.2 Film shrinkage percentage pattern and humidity expansion coefficient

Position	Film shrinkage percentage (%)	Humidity expansion coefficient (1／%)
① Center 45 °	3.7	2.4 × 10^{-4}
② Center 135 °	3.8	2.5 × 10^{-4}
③ Edge 45 °	5.7	2.9 × 10^{-4}
④ Edge 135 °	2.2	1.8 × 10^{-4}

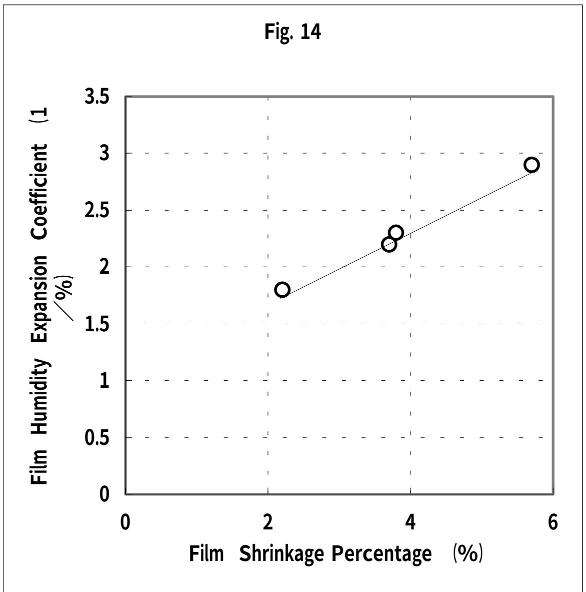


Fig. 15. Measurement method of shrinkage stress