

Dynamics and Structure Development for Biaxial Stretching PA6 Films

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Abstract: The biaxial stretching film of polyamide 6 (PA6) is widely used for food and industrial products packaging, because it has good physical properties, such as high toughness and gas barrier properties. It is expected to improve film formability and performance for a larger market. So, in this research, both the stretching methods and PA6 blends were investigated in terms of dynamics and structure development for biaxial stretching films. There are three different stretching methods which can produce polyamide 6 films, namely the simultaneous biaxial stretching, the sequential biaxial stretching, and the double bubble tubular process. There are no reports which describe the difference among the three stretching methods and film properties, so it was not clarified why the films have big differences in their properties. For this reason, the higher order structure and stretching behaviours of the three stretching methods were studied. As a result, the sequential biaxial stretching shows strong stretched effect and molecular orientation in the transverse direction. In the simultaneous biaxial stretching, the molecule orientation was equal both in the machine direction and in the transverse direction of the stretched plane. The double bubble tubular process produced well balanced film and equal orientation in any directions, in terms of the phase difference in the plane of film. Blends of PA6 to meta-Xylene diamine (MXD6) improved the properties of easy straight line cut and high barrier, but did not have good stretchability. For this reason, they were also studied to develop the biaxial stretching film of polyamide which improved stretchability and physical properties. Furthermore, blend effects of MXD6 to PA6 and dynamics analyses were investigated.

INTRODUCTION

The biaxial stretching PA6 film is widely used for food and industrial products packaging, because it has good physical properties, such as high toughness, high tensile strength, hard wearing properties and gas barrier properties[1]. It is expected to improve film formability and performance for a larger market. So, in this research, both the stretching methods and PA6 blends were investigated in terms of dynamics and structure development for biaxial stretching films.

There are three different stretching methods which can produce polyamide 6 films, namely the simultaneous biaxial stretching[5], the sequential biaxial stretching[6], and the double bubble tubular process[1-4,8,9]. There are no reports which described the difference among the three stretching methods and film properties, so it was not clarified why the films have big differences in their properties. Also, as blends of PA6 to meta-Xylene diamine (MXD6) improved the properties of easy straight line cut and high barrier[10], they were studied to develop the biaxial stretching film of polyamide which has good stretchability and good physical properties. Furthermore, blend effects of MXD6 to PA6 and dynamics analyses were investigated. For these reasons, our study is to investigate the higher order structure and stretching behaviors of the three stretching methods and to develop the biaxial stretching film of polyamide which has good stretchability and good physical properties.

Experimental Conditions

The 50 μ m thickness PA6 film samples were produced using an extruder with a die extruded at a resin temperature of 265°C and chilled water bath of 18°C to prevent crystallization. By using a 40 ϕ mm extruder (L/D=24) with a circular die of the diameter of 75mm and the lip clearance of 1mm and with a water-cooling ring having the diameter of 90mm, non-stretched film was produced at a resin temperature of 265°C and a blow-up ratio of 1.2.

The film samples were stretched using the biaxial stretcher under the conditions of preheating time 2 minutes, standard stretching temperature 106°C, standard stretching speed 10mm/s and various stretching ratios. In-situ measurement of stress and strain curves and birefringence were obtained. The stretching ratio conditions of the sequential stretching were MD×TD 1.5×1, 2×1, 2.5×1, 3×1, 3×1.5, 3×2, 3×2.5, 3×3, respectively. The stretching ratio conditions of the simultaneous stretching were MD×TD 2×2, 2.5×2.5, 3×3, respectively.

The double bubble tubular film process was also produced in order to compare with tenter stretching films. Non-stretched films were produced under the same extrusion conditions as the above conditions. While passing through the part of apparatus for second blowing, which is composed of two pairs of pinch rolls and a heating furnace (a far infrared radiation heater is self-contained), this raw film was stretched simultaneously in the machine and transverse directions by using internal bubble air. The stretching ratio condition of the double bubble tubular stretching using a production line was MD×TD 3×3. Each sample was also measured by the polarizing microscope and three dimensional birefringences.

Furthermore, 80 μ m thickness films of the blends of MXD6 to PA were used as a base film for stretching. The stretching conditions were preheating time 2 minutes, stretching temperature 110°C, stretching speed 10mm/s and stretching ratio MD×TD 3×3 by the simultaneous biaxial stretching.

RESULTS AND DISCUSSION

PA stretching film

The photographic images through the polarizing plate for both the simultaneous biaxial stretching film and the sequential biaxial stretching film are shown in Fig.2. The photographic image through the polarizing plate of the simultaneous biaxial stretching film shows very uniform biaxial stretching, but the photographic image through the polarizing plate of the sequential biaxial stretching film shows ununiform stretching (Kink Stretching).

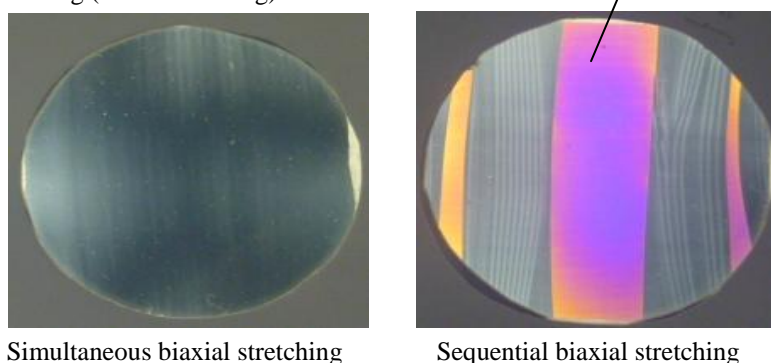


Fig.2 Pictures of PA6 films through polarizing plate

At first the sequential biaxial stretching results are shown. Fig.3 shows the stress and strain curve and retardation as a function of total strain ratio (surface ratio) under the simultaneous biaxial stretching MD×TD 3×3. The simultaneous biaxial stretching shows almost the same stress of X and Y and keeps very low retardation.

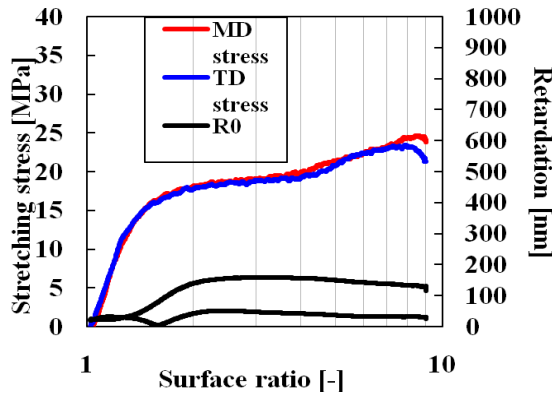


Fig.3 Stress-total stretching ratio curves and retardation-total stretching ratio curve of the simultaneous biaxial stretching

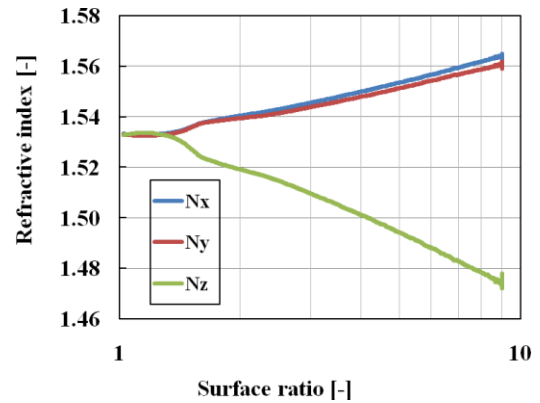


Fig.4 Refractive index and total stretching ratio curve of simultaneous biaxial stretching

Fig.4 shows three dimensional refractive indexes as a function of total strain ratio under the simultaneous biaxial stretching. The refractive indexes of N_x and N_y increase with increasing total strain ratio. It means that the simultaneous biaxial stretching increases both the MD and TD molecular orientations in the parallel to film plane and gives low retardation.

Next the sequential biaxial stretching results are shown. Fig.5 shows the stress-strain curve and retardation under the sequential biaxial stretching and stretching ratio MD \times TD 3 \times 3. Y stress (TD stretching stress) becomes larger than X stress (MD stretching stress). Furthermore, the retardation increases with increasing MD stretching ratio and then decreases with increasing TD stretching ratio.

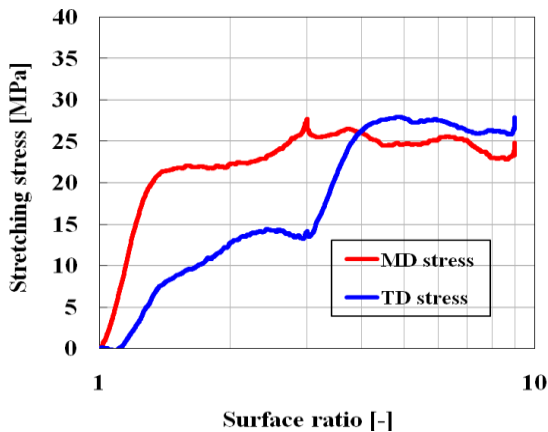


Fig.5 Stress-area stretching ratio curves of sequential biaxial stretching

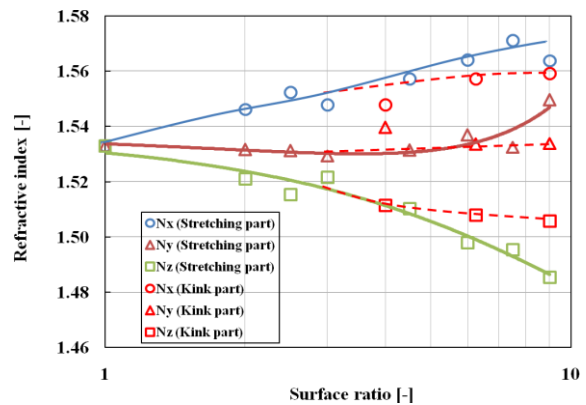


Fig.6 Refractive index and area stretching ratio curve of sequential biaxial stretching

Fig.6 shows three dimensional refractive indexes as a function of total strain ratio of the sequential biaxial stretching. MD stretching increases only N_x which means molecular orientation in MD. TD stretching increases N_y which means TD molecular orientation proceeds. In the unstretched zone, the refractive index during TD stretching does not change and keeps orientation constant.

From these results, the sequential biaxial stretching shortens the distance between the hydrogen bonds and makes the hydrogen bonds strong, and then increases TD stretching stress. Owing to this strong TD stretching stress, it is considered that it is difficult to stretch uniformly.

Fig.7 shows the distribution of the phase contrast at three different stretching methods. These results

show that orientation balance at any angle is the best for the double bubble tubular film and the worst for the sequential biaxial stretched film.

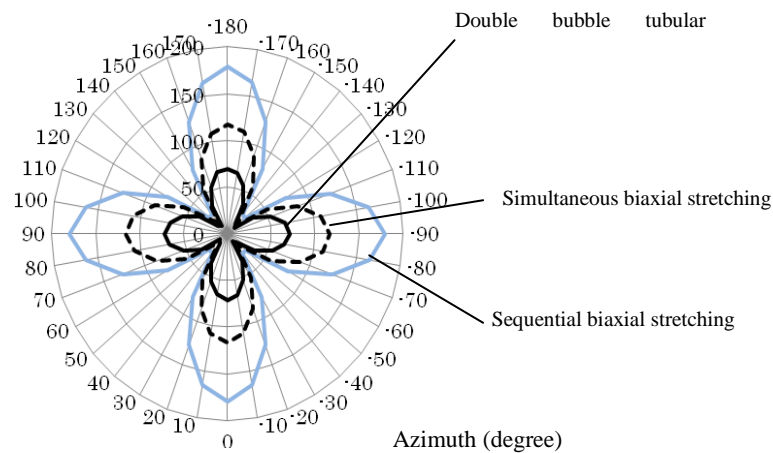


Fig.7 Phase contrast distribution of at whole angles produced by different stretching methods

PA/MXD6 blend stretching film

The blend of MXD6 to PA6 was studied to improve the gas barrier and easy tear properties. It was stretched and the stretching stress of the blend was evaluated, compared with PA 6. The results are shown in Fig.8.

Fig.8 shows blending of MXD6 to PA6 makes PA6 stretching stress decrease. This result means the hydrogen bond caused by PA6 was reduced by blending MXD6. Furthermore, the stress behavior is also changed after the stretching stress passes the yield stress. PA6 has larger stress build up than PA6/MXD6.

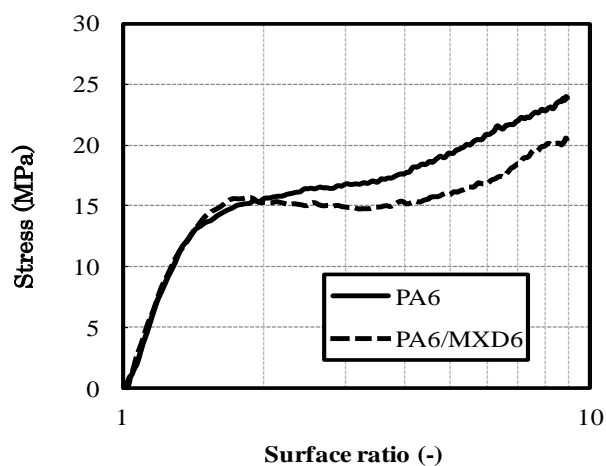


Fig.8 Stress-surface ratio curves of PA6, PA6/MXD6 blends at 110°C

Effect of Stretching Temperature

The stretching temperature was changed at 90°C, 100°C, 110°C, 120°C and 130°C. The maximum stretching stress as a function of stretching temperature was plotted in Fig.9 in order to evaluate stretchability and stretching stress. The larger slope means the stronger stretching stress dependent on the temperature.

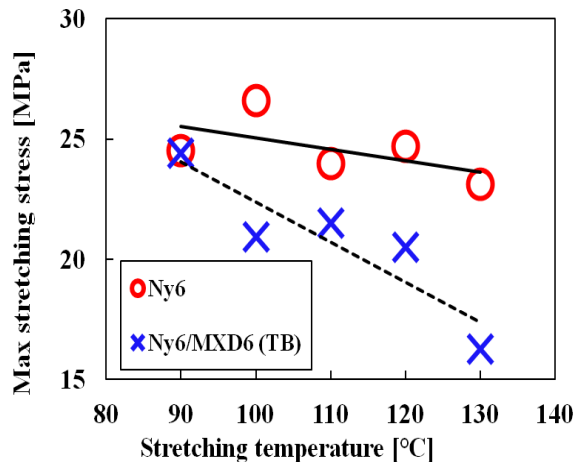


Fig.9 Relationships between maximum stress and stretching temperature

It was found that both PA6 and PA6/MXD6 blend decrease with increasing stretching temperature. PA6/MXD6 blend had much stronger temperature dependence than PA6. From this result, it was considered that the stretching temperature window of PA6/MXD6 was narrower than the one of PA6.

Effect of Stretching Ratio

Fig.10 shows the stretching stress and stretching ratio of PA6/MXD6 blends in order to evaluate the stretchability by changing stretching ratio of MD and TD. The degree of orientation in the plane of the film for PA6 and PA6/MXD6, which was calculated by three dimensional refractive indexes shown below, was plotted as a function of stretching ratio shown in Fig.11.

The degree of orientation in the plane of the film = $[(N_x + N_y) / 2] - N_x$

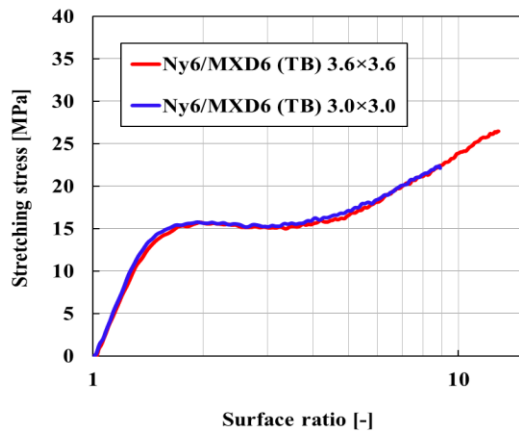


Fig.10 Stress-surface ratio curves of PA6/MXD6 blends at several different surface ratio

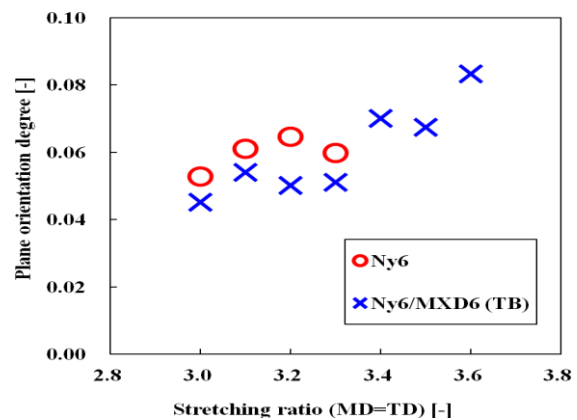


Fig.11 Degree of orientation-stretching ratio curves of PA6 and PA6/MXD6 blends at several different stretching ratios

Fig.10 shows the stretching stress increases with increasing the stretching ratio. Fig.11 shows the degree of orientation in the film plane of MD and TD for both samples increase with increasing the stretching ratio.

Table 2 shows the summary of the maximum stretching ratio, the maximum stretching stress and the degree of orientation. It shows the blending of MXD6 to PA6 reduces stretching stress, compared with PA6. So the blend can increase the stretching stress by increasing higher stretching ratio than PA6 without film break during the biaxial stretching.

Table 2 Maximum stretching ratio and maximum stress of PA6, PA6/MXD6 blends

	Maximum stretching ratio (-)	Maximum stress (MPa)	Degree of orientation (-)
PA6	3.3	29.0	0.060
PA6/MXD6	3.6	26.5	0.083

As the blending of MXD6 to PA6 prevents the hydrogen bond of PA6 from forming, the stretching stress is reduced. It was observed that the stretching stress between 25~30MPa causes film break during the biaxial stretching. PA6/MXD6 blend can be stretched at a higher stretching ratio without film break than PA6. From these results, PA6/MXD6 blend can produce the film having high orientation and high physical properties by increasing stretching ratio.

Film Uniformity

The retardation was measured and then the standard deviation of retardation was calculated to evaluate the film thickness uniformity. The result is shown in Table 3. It was found that the standard deviation of the retardation is closely related to the film thickness uniformity.

Table 3 shows PA6 has better uniformity than PA6/MXD6 at the stretching ratio 3 as PA6 has lower standard deviation than PA6/MXD6. This result comes from the stress build up ratio (maximum stretching stress / stretching stress at the yield point) after the yield stress passes. The higher stress build up of the stress and strain shown in Fig.12 improves thickness uniformity.

Table 3 Stretching ratio and standard deviation of retardation of PA6, PA6/MXD6 blends

	Stretching ratio (-)	Standard deviation of retardation (-)
PA6	3.0	7.6
PA6	3.3	6.1
PA6/MXD6	3.0	8.3
PA6/MXD6	3.6	5.8

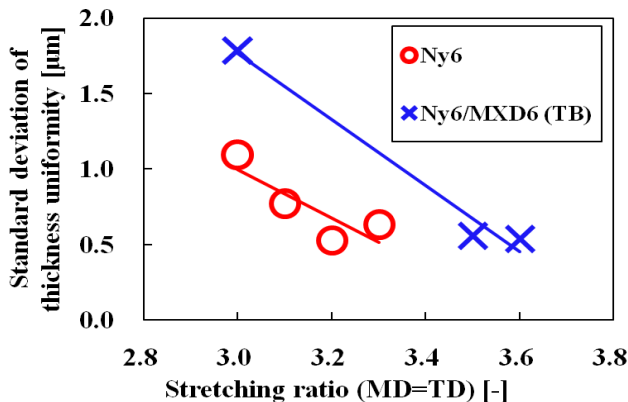


Fig.12 Relationship between standard deviation of thickness uniformity and surface ratio

In other words, as higher stress build up means the thicker film part is stretched much more than the thinner film part, PA6 which has higher stress build up and better thickness uniformity was produced, compared with PA6/MXD6.

Furthermore, the standard deviations of both samples decrease with increasing the stretching ratio and are almost the same at the maximum stretching ratio. This means that the film thickness uniformity of PA6/MXD6 is almost the same level as PA6, because as PA6/MXD6 has a lower stretching stress and can be set at a higher maximum stretching ratio.

CONCLUSION

1) Three different stretching methods, which can produce polyamide 6 films, namely the simultaneous biaxial stretching, the sequential biaxial stretching, and the double bubble tubular stretching, were investigated.

① Sequential Biaxial Stretching Process

Both the stretched part and the unstretched part were existed owing to the hydrogen bond during TD stretching. The stretched part shows high TD orientation. The unstretched part shows low TD orientation and high MD orientation, because of very low TD stretching effect. The ununiform part causes retardation distribution and the film balance to worsen

② Simultaneous biaxial stretching process

The polymer chain was oriented in MD or TD and almost the same orientation in MD and TD, so the orientation balance is good

③ Double bubble tubular process

Uniform stretching stress and orientation in every direction and good balanced film in every direction were obtained.

2) Low stretching temperature, slow stretching speed and high stretching ratio are important to obtain highly oriented film with high physical properties.

3) Blending of MXD6 to PA6 gives high gas barrier, easy tear properties and low stretching stress, but poor thickness uniformity. To increase stretching ratio increases stress build up and improves film thickness uniformity and produces high orientation film.

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