

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 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 three stretching methods and film properties, so it was not clarified why the film has big differences in its 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 high stretching 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. As blends of PA6 improved the properties of easy straight line cut and high barrier by blending meta-Xylene diamine (MXD6), 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.

1. Introduction

Environmental problems have come into question in the packaging industry in recent years. Dechlorination and waste reduction have been addressed as serious problems in this industry. For example, to produce a standing repackage pouch, thin and strong biaxially oriented PA6 film is indispensable. The demand for biaxially oriented PA6 film has been increasing [1-7].

The biaxial stretching PA6 film is widely used for food and industrial products packaging, because it has good physical properties, such as high toughness, hard wearing properties and gas barrier properties[1]. It is expected to improve film formability and performance for 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 is no report which described the difference among three stretching methods and film properties, so it was not clarified why the film has big difference in its properties.

Also, as blends of PA6 improved the properties of easy straight line cut and high barrier by blending meta-Xylene diamine (MXD6) [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 three stretching methods and to develop the biaxial stretching film of polyamide which has good stretchability and good physical properties.

Furthermore, it is to investigate the blend effects of MXD6 to PA6 and dynamics analyses.

2. Experiment

2.1 Experimental Equipment

The film samples of PA6 were used to study the biaxial stretchability and the super structure formation by using a biaxial stretcher. The biaxial stretcher SDR-527K, which was designed by our group and made by Etoh Corporation, was used[11].

The schematic view of this equipment is shown in Fig.1. Various data could be obtained at the same time, such as stress strain curve (S-S), refractive indexes in three directions and light scattering data. The stretching conditions are shown in Table 1.

Table 1 Stretching conditions

Stretching mode	Sequential biaxial stretching
Stretching speed	10mm/s
Stretching ratio	MD 5 times \times TD 7 times
Stretching temp.	159°C
Preheating time	2min

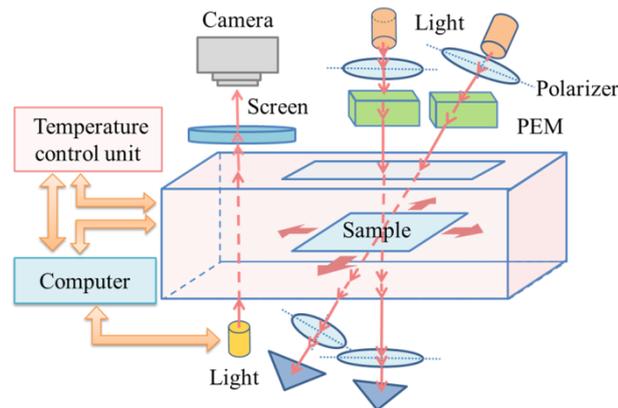


Fig.1 Schematic diagram of biaxial stretching machine

2.2 Materials

PA6 was Ube Nylon 1023FD with mean molecular weight of 23,000 and the relative viscosity of $\eta_r=3.5$ in 98% sulfuric acid as a solvent.

MXD6 was Mitsubishi Gas Chemical MX Nylon 6007 with mean molecular weight of 25,000 and the relative viscosity of $\eta_r= 2.7$ in

96% sulfuric acid as a solvent. The chemical structure of both Nylon6 and MXD6 are shown in the Fig.2.

2.3 Experimental Conditions

The 50 μ m PA6 film thickness samples were used. The film samples were stretched using the biaxial stretcher under the conditions of preheating time 2minutes, stretching temperature 106°C, stretching speed 10mm/s and various stretching ratio. In-situ measurement of stress and strain curves and birefringence were obtained. The stretching ratio conditions of the sequential stretching were MD \times TD 1.5 \times 1, 2 \times 1, 2.5 \times 1, 3 \times 1, 3 \times 1.5, 3 \times 2, 3 \times 2.5, 3 \times 3, respectively. The stretching ratio conditions of the simultaneous stretching were MD \times TD 2 \times 2, 2.5 \times 2.5, 3 \times 3, respectively. The stretching ratio condition of the double bubble tubular stretching using a production line was MD \times TD 3 \times 3. Each sample was also measured polarizing microscope observation and three dimensional birefringence.

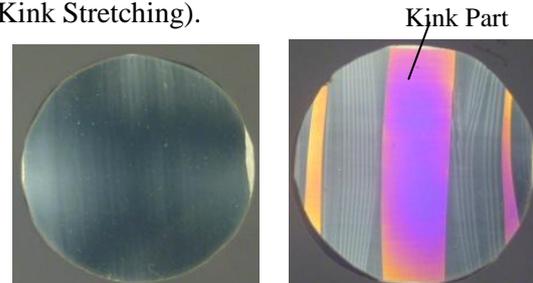
Furthermore, 80 μ m film thickness of the blends of MXD6 to PA were used as a base film for stretching. The stretching conditions were preheating time 2minutes, stretching temperature 110°C, stretching speed 10mm/s and stretching ratio MD \times TD 3 \times 3 by the simultaneous biaxial stretching.

3. Results and Discussion

3.1 PA stretching film

The polarizing microscope observation of the simultaneous biaxial stretching and the sequential biaxial stretching are shown in Fig.2.

The polarizing microscope observation of the simultaneous biaxial stretching shows very uniform biaxial stretching, but the polarizing microscope observation of the sequential biaxial stretching film shows ununiform stretching (Kink Stretching).



Simultaneous biaxial stretching Sequential biaxial stretching
Fig.2 Pictures of PA6 films through polarizing plate

Fig.2 shows pictures of both the simultaneous biaxial stretching film and the sequential biaxial stretching film through polarizing plate.

Fig.3 shows the stress and strain curve and retardation as a function of total strain ratio under the simultaneous biaxial stretching MD×TD 3×3.

The simultaneous biaxial stretching shows almost same stress of X and Y and keeps very low retardation.

Fig.4 shows three dimensional refractive indexes as a function of total strain ratio under the simultaneous biaxial stretching.

The refractive indexes of Nx and Ny increase with increasing total strain ratio. It means that the simultaneous biaxial stretching increases both MD and TD molecular orientations in the parallel to film plane and gives low retardation.

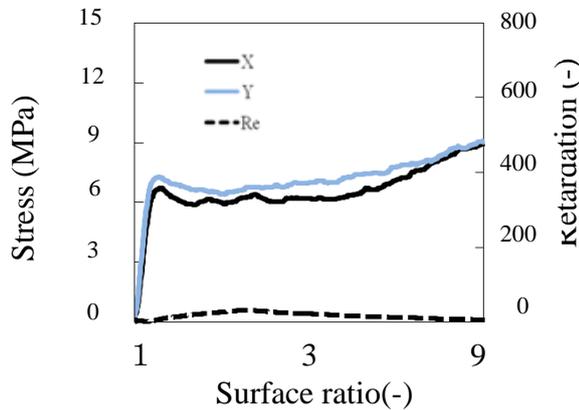


Fig.3 Stress-Total stretching ratio curves and retardation-Total stretching ratio curve of the simultaneous biaxial stretching

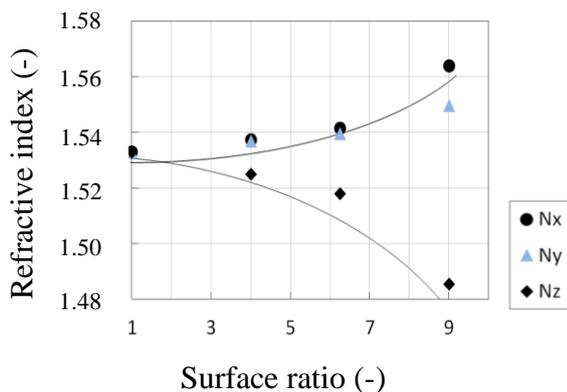


Fig.4 Refractive index and Total stretching ratio curve of simultaneous biaxial stretching

Fig.5 shows stress-strain curve and retardation under the sequential biaxial stretching and stretching ratio MD×TD 3×3.

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.6 shows three dimensional refractive indexes as a function of total strain ratio.

MD stretching increases only Nx which means molecular orientation in MD direction.

TD stretching increases Ny which means TD molecular orientation proceeds. In the unstretched zone, the refractive index during TD stretching does not change and keeps orientation constant.

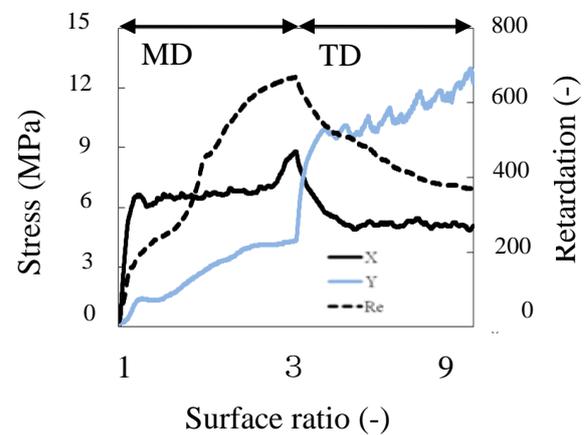


Fig.5 Stress-area stretching ratio curves and retardation-area stretching ratio curve of sequential biaxial stretching

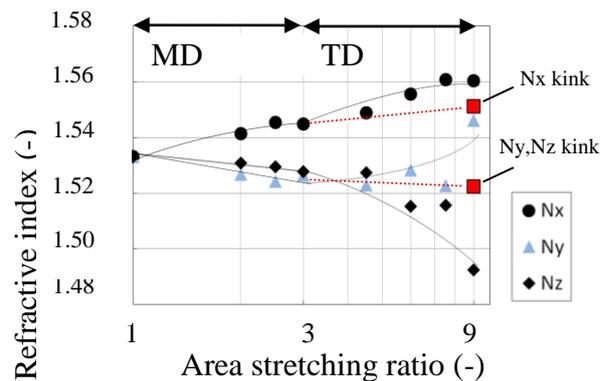


Fig.6 Refractive index and Area stretching ratio curve of sequential biaxial stretching

From these results, the sequential biaxial stretching shorten the distance between hydrogen bonds and makes hydrogen bond strong, and then increases TD stretching stress.

Owing to this strong TD stretching stress, it is considered that it is difficult to stretch uniformly and increase the retardation.

Fig.7 shows the distribution of the phase contrast at different stretching methods. These results show that orientation balance is the best for double bubble tubular film and the worst for sequential biaxial stretched film.

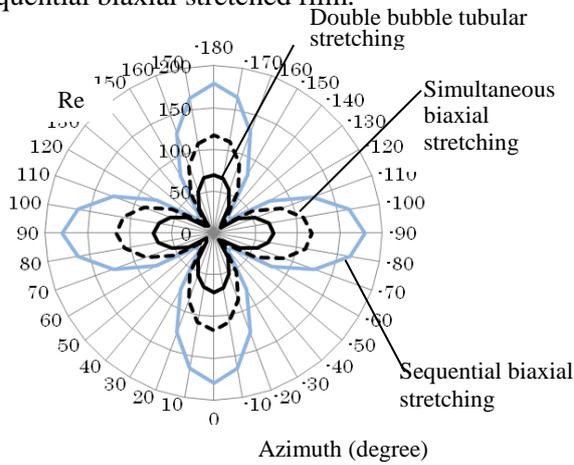


Fig.7 Distribution of phase contrast at different stretching methods

3.2 PA/MXD6 blend stretching film

The blend of MXD6 to PA6 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. Furthermore, the stress behavior is also changed after the stretching stress passes the yield stress. PA6 has larger stress build up than PA6/MXD6.

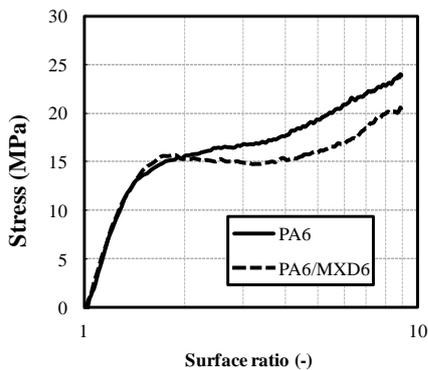


Fig.8 Stress-surface ratio curves of PA6, PA6/MXD6 blends at 110°C

3.2.1 Effect of Stretching Temperature

The stretching temperature was changed at 90°C, 100°C, 110°C, 120°C, 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 temperature.

It was found that both PA6 and PA6/MXD6 blend decrease with increasing stretching temperature. PA6/MXD6 blend was much stronger temperature dependence than PA6.

From this result, it is considered that the stretching temperature window of PA6/MXD6 is narrower than the one of PA6.

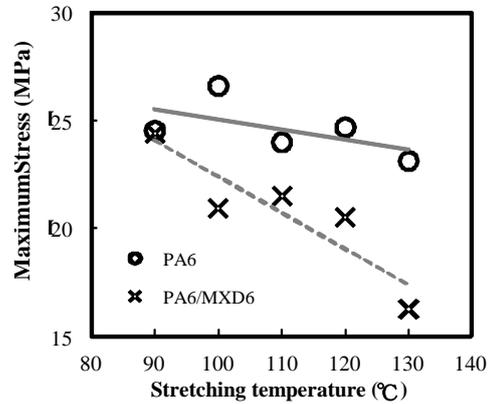


Fig.9 Relationships between maximum stress and stretching temperature

3.2.2 Effect of Stretching ratio

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

Table 2 shows the summary of the maximum stretching ratio, the maximum stretching stress and degree of orientation.

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

Table 2 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.

As the blending of MXD6 to PA6 prevents the hydrogen bond of PA6, the stretching stress is reduced. It was observed that the stretching stress between 25~30MPa makes film break during the biaxial stretching.

From these results, PA6/MXD6 blend can obtain the film having high orientation and high physical properties by increasing stretching ratio.

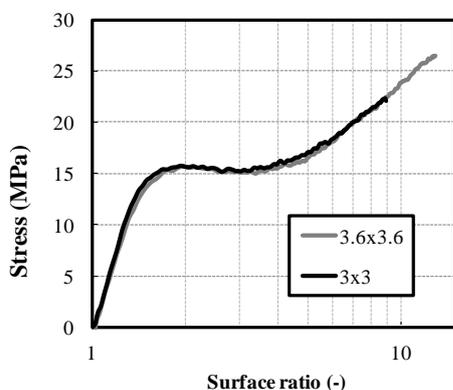


Fig.10 Stress-surface ratio curves of PA6/MXD6 blends at several different surface ratio

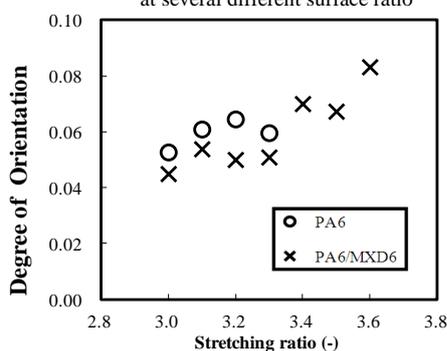


Fig.11 Degree of orientation-stretching ratio curves of PA6 and PA6/MXD6 blends at several different stretching ratios

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

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

3.4 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 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 smaller standard deviation than PA6/MXD6. This result comes from the stress build up ratio after the yield stress passes. The higher stress build up of the stress and strain shown in Fig.12 improves better thickness uniformity.

In other words, as higher stress build up means the thicker film part is much more stretched 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 decreases with increasing the stretching ratio and are almost same at the maximum stretching ratio. This means that the film thickness uniformity of PA6/MXD6 is almost same level as PA6, because as PA6/MXD6 has lower stretching stress and can be set at higher maximum stretching ratio.

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

4. 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 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 in MD and TD 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 and easy tear properties and low stretching stress, but poor thickness uniformity. To increase stretching ratio improves stress

build up and film thickness uniformity and produces high orientation film.

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