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Dynamics and structure development for biaxial stretching PA6/MXD6 blend packaging 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 gas barrier and easy straight cut performance for a larger market such as food packaging. So, in this research, blends of poly(m-xylene adipamide) (MXD6) to PA6 which are immiscible were investigated in terms of dynamics and structure development for biaxial stretching films. For this reason, the higher order structure and stretching behaviors of the blends were studied. As a result, blends of MXD6 to PA6 which had cylindrical structures improved the properties of easy straight cut and high barrier, but did not have good stretchability and film thickness uniformity. For these reasons, they were studied to develop the biaxial stretching film of polyamide which improved stretchability and film thickness uniformity. Furthermore, blend effects of MXD6 to PA6 and dynamics analyses were investigated.

KEYWORDS

barrier, biaxiality, blends, films, polyamides

1 | INTRODUCTION

The biaxial stretching polyamide 6 (PA6) film is widely used for food and industrial products packaging, because it has good physical properties, such as high toughness, high tensile strength, heat resistance, solvent resistance, hard wearing properties, and gas barrier properties. For this reason, PA6 becomes more important for food packaging and industrial usage. So there are many papers which reported PA6 film.[1–15]

Polyamide 6 film has inferior oxygen gas barrier performance. K-coated film, which coats the surface of biaxial stretching PA6 film with polyvinylidene chloride raise the oxygen barrier performance, is used. When this film is incinerated, it generates toxic gas such as chlorine gas and dioxin. The development of oxygen gas barrier film without K-coated layer is desired.

As a gas barrier resin, poly (m-xylene adipamide) (MXD6) was selected. The previous report discussed an oxygen gas barrier PA6/MXD6 blend film which satisfied formability and physical property using blending technology.[7] The patent describes PA 6 and MXD6 multi-layered film,[2,3] but the

property of easy straight line cut is not available. The bag is sometimes required to open easily and safely, for children and elderly people. The retort food is heated in the boiling water and then is opened at high temperature. In the medical field, there are many applications, where we cannot use a pair of scissors for safety and hygiene reasons, so the development of a film with the easy open access is desired.

For this reason, it is expected to improve gas barrier and easy straight cut performance for a larger market. So, in this research, both the stretching methods and PA6 blends, which influenced physical properties, 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,[16,17] the sequential biaxial stretching,[16,17] and the double bubble tubular process.[1,10–20] The difference among the three stretching methods and film properties was reported in the previous paper.[21] It was found that the simultaneous biaxial stretching process is fit for PA6, because PA6 had a high crystallization speed and the hydrogen bond was easily created

during MD stretching in the case of the sequential biaxial stretching.

As blends of (MXD6) to PA6 improved the properties of easy straight line cut and high barrier[7] which are very important properties for food packages, they were studied to develop the simultaneous biaxial stretching film of polyamide which has good stretchability and good physical properties. During our research, there were some problems with poor film thickness uniformity. We tried to improve the thickness uniformity to the same level as PA6 film. Furthermore, blend effects of MXD6 to PA6 and dynamics analyses were investigated. For these reasons, our study was to investigate the biaxial stretching behavior under various stretching conditions and to develop the biaxial stretching film of polyamide which has good thickness uniformity, stretchability, and high physical properties using a newly developed tenter test machine.[22,23]
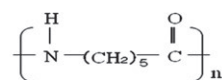
2 | EXPERIMENT

2.1 | Experimental equipment

The film samples of PA6 were used to study the biaxial stretchablity and the super structure formation during the simultaneous biaxial stretching using a biaxial stretcher. The biaxial stretcher SDR-527K, which was designed by our group and made by Etoh Corporation, was used.[22,23]

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

2.2 | Materials

Polyamide 6 and MXD6 were used for our research. PA6 was Ube Nylon 1023FD with a mean molecular weight of 23,000 and the relative viscosity of $\eta_r = 3.5$ in 98% sulfuric acid as a solvent. MXD6 which is Poly (m-xylene adipamide 6) was Mitsubishi Gas Chemical MX Nylon 6007 with a 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 PA6 and MXD6 are shown below.

Polyamide 6 (PA6)
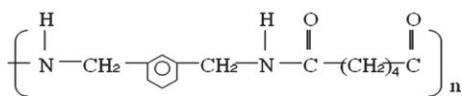
Poly (m-xylene adipamide 6) (MXD6)

2.3 | Experimental conditions

The 80 μm thickness PA6 and PA6/MXD6 blend film samples as nonstretched films were produced using a 40 ϕ mm extruder (L/D = 24) with a circular die of the diameter of 75 mm and the lip clearance of 1 mm at a resin temperature of 265°C and a chilled water bath of 18°C to prevent crystallization, and a blow-up ratio of 1.2 with a water-cooling ring having the diameter of 90 mm. The standard blend ratio of PA6/MXD6
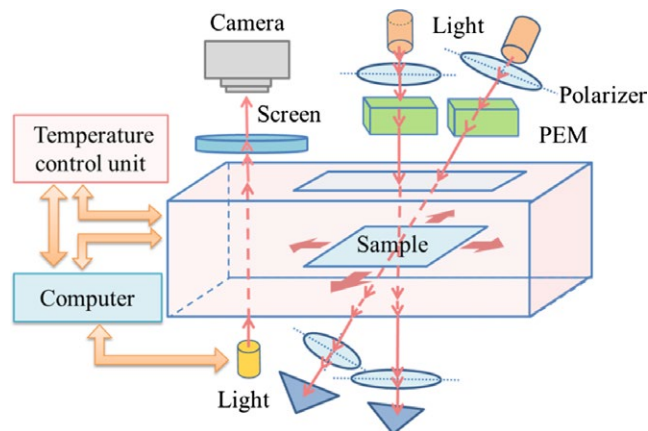

FIGURE 1 Schematic diagram of biaxial stretching machine

TABLE 1 Stretching conditions

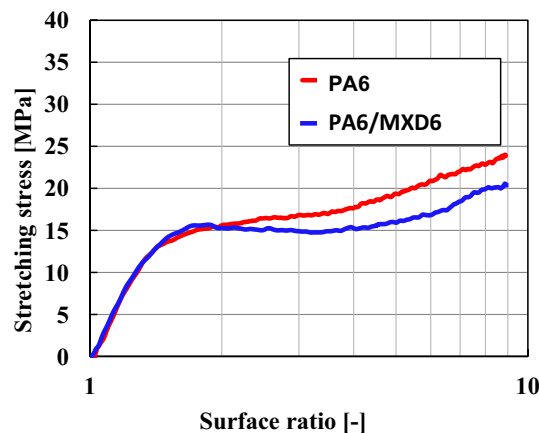|	
Stretching mode	Simultaneous biaxial stretching
Stretching speed	10 mm/s
Stretching ratio	MD 3 times × TD 3 times (standard condition)
Stretching temp.	110°C
Preheating time	2 min

FIGURE 2 Stretching stress-surface ratio curves of simultaneous biaxial stretching for polyamide 6 (PA6) and PA6/MXD6 films

blend was PA6 70% and MXD6 30% which could obtain easy straight cut property and proper thickness uniformity.

The film samples were stretched using the biaxial stretcher under the conditions of preheating time 2 min, the standard stretching temperature 110°C, the standard stretching speed 10 mm/s, and various stretching ratios. The in situ measurement of stress and strain curves and birefringence were obtained. The stretching ratio conditions of the simultaneous stretching were MD × TD 3.0 × 3.0, 3.3 × 3.3, and 3.6 × 3.6, respectively.

3 | RESULTS AND DISCUSSION

3.1 | PA/MXD6 blend stretching film

The blend of MXD6 to PA6 was studied to improve thickness uniformity of biaxial stretching film keeping gas barrier and
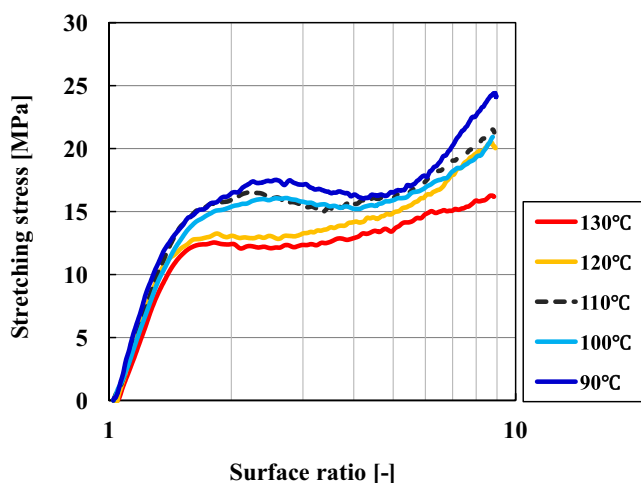
FIGURE 5 Relationship between plane orientation degree and stretching temperature for polyamide 6 (PA6) and PA6/MXD6 films

FIGURE 3 Stretching stress-surface ratio curves of simultaneous biaxial stretching at different stretching temperatures for PA6/MXD6 blend. PA6, polyamide 6
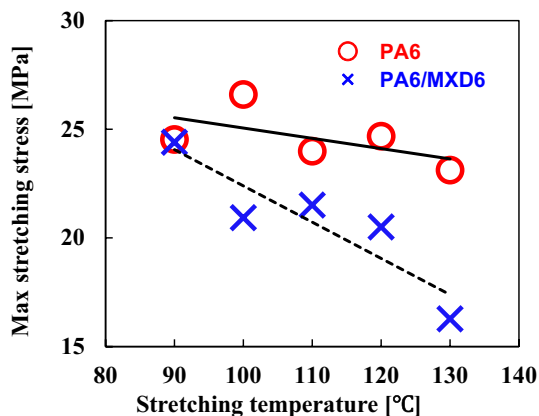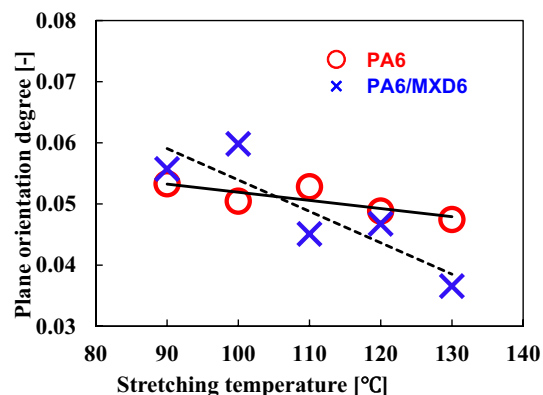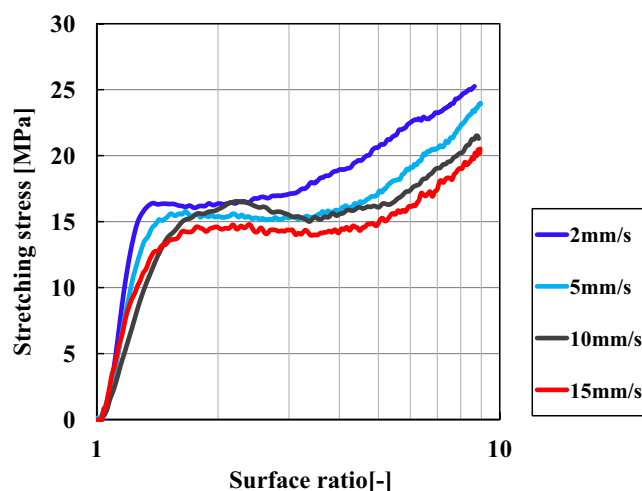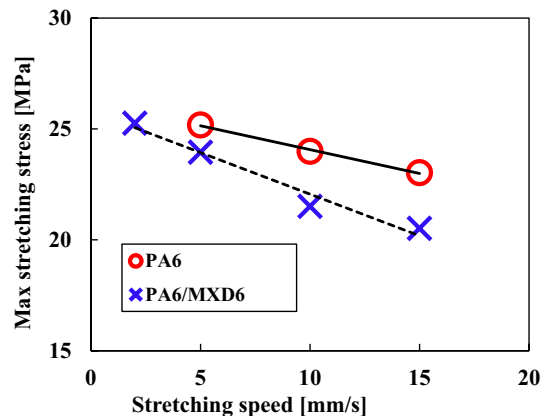
FIGURE 6 Stretching stress-surface ratio curves of simultaneous biaxial stretching at different stretching speeds

FIGURE 4 Relationship between max stretching stress and stretching temperature for polyamide 6 (PA6) and PA6/MXD6 films

FIGURE 7 Relationship between max stretching stress and stretching speed for polyamide 6 (PA6) and PA6/MXD6 films
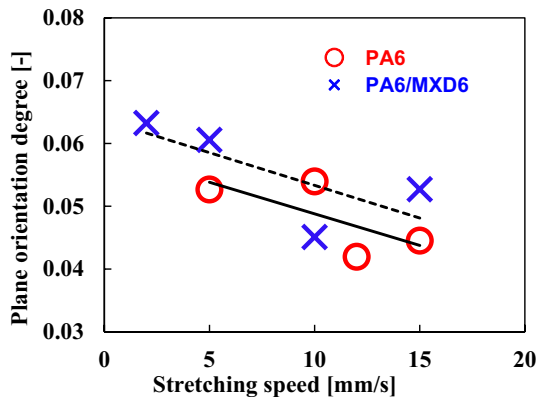
FIGURE 8 Relationship between plane orientation degree and stretching speed for polyamide 6 (PA6) and PA6/MXD6 films
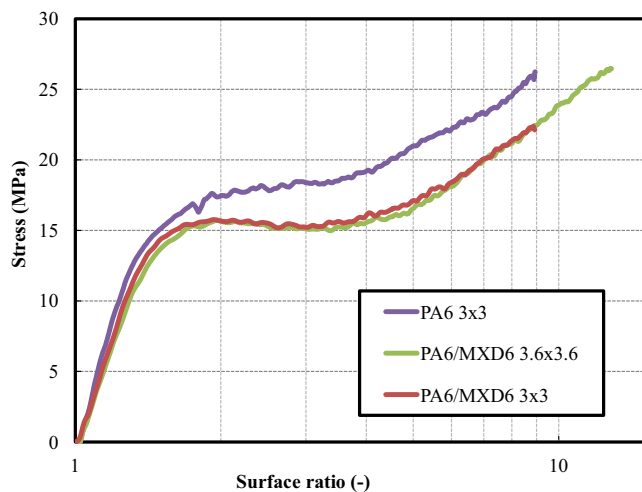

FIGURE 9 Relationship between the stretching ratio and the stretching stress of polyamide 6 (PA6) and PA6/MDX6
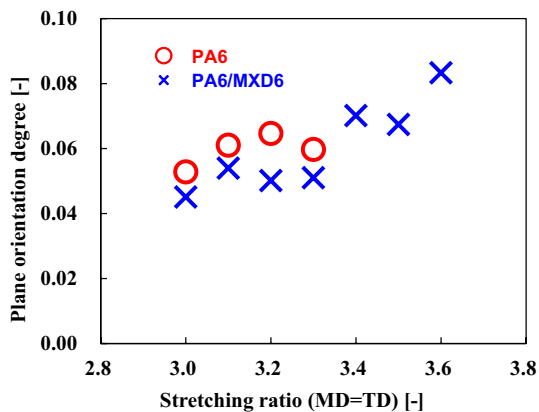

FIGURE 10 Relationship between plane orientation degree and stretching speed for polyamide 6 (PA6) and PA6/MXD6 films

easy straight cut properties. It was stretched and the stretching stress of the blend was evaluated, compared with PA6. The results are shown in Figure 2. It shows that 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 buildup (maximum stress/yield stress) than PA6/MXD6.

3.2 | Effect of stretching temperature

The stretching temperature was changed at 90, 100, 110, 120, and 130°C. Figure 3 shows the stretching stress as a function of stretching ratio for PA6/MXD6 blends. The maximum stretching stress as a function of stretching temperature for PA6 and PA6/MXD6 blends was plotted in Figure 4 to evaluate stretchability and stretching stress. The steeper slope means the stronger stretching stress dependent on the 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, because MXD6 has benzene ring in the main chain. From this result, it was considered that the stretching temperature window of PA6/MXD6 was narrower than that of PA6.

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

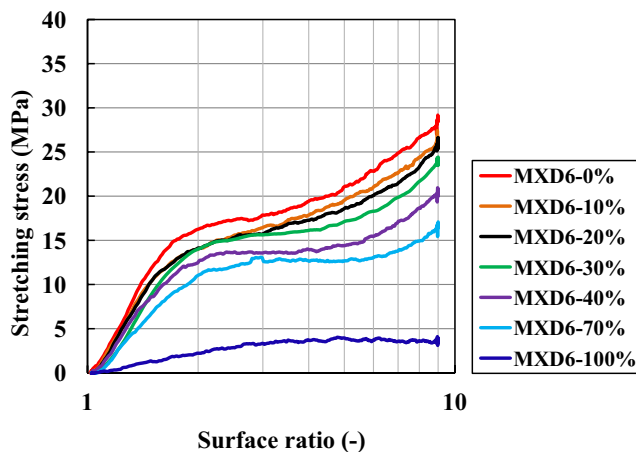|	Maximum stretching ratio (−)	Maximum stress (MPa)	Degree of orientation (−)
PA6	3.3	29.0	0.060
PA6/MXD6	3.6	26.5	0.083

PA6, polyamide 6.

FIGURE 11 Stretching stress-surface ratio curves of simultaneous biaxial stretching at different MXD6 blending ratios

Figure 5 shows the plane orientation P as a function of the stretching temperature. The plane orientation *P* was calculated by Equation (1);

$$P = [(Nx + Ny)/2] - Nz \qquad (1)$$

Nx, refractive index in MD (machine direction); Ny, refractive index in TD (transverse direction); Nz, refractive index in ND (normal direction).

The blend of MXD6 to PA6 showed that the plane orientation increased with decreasing the stretching temperature, because the stretching stress increased with decreasing the stretching temperature.

3.3 | Effect of stretching speed

The stretchability, stretching stress, and orientation as a function of the stretching speed for PA6/MXD6 blend were investigated. The relationship between the stretching stress and stretching ratio under various stretching speeds is shown in Figure 6. The relationship between the maximum stretching stress and stretching speed is shown in Figure 7.

The stretching stress of PA6/MXD6 blend decreased with increasing the stretching speed, because of the hydrogen bond of PA6. Increasing the stretching speed makes the molecular orientation time shorten during the stretching process and the hydrogen bond weaken. Furthermore, PA6/MXD6 blend which had much wider stretching speed range could be stretched even at a stretching speed 2 mm/s lower than PA6 at 5 mm/s. These results also came from reducing the hydrogen bond by blending MXD6.

The plane orientation P as a function of the stretching speed is shown in Figure 8. The plane orientation P increased with decreasing the stretching speed. This is because the stretching stress increased with decreasing the stretching speed.

3.4 | Effect of stretching ratio

Figure 9 shows the stretching stress and stretching ratio of PA6/MXD6 blends 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 and using
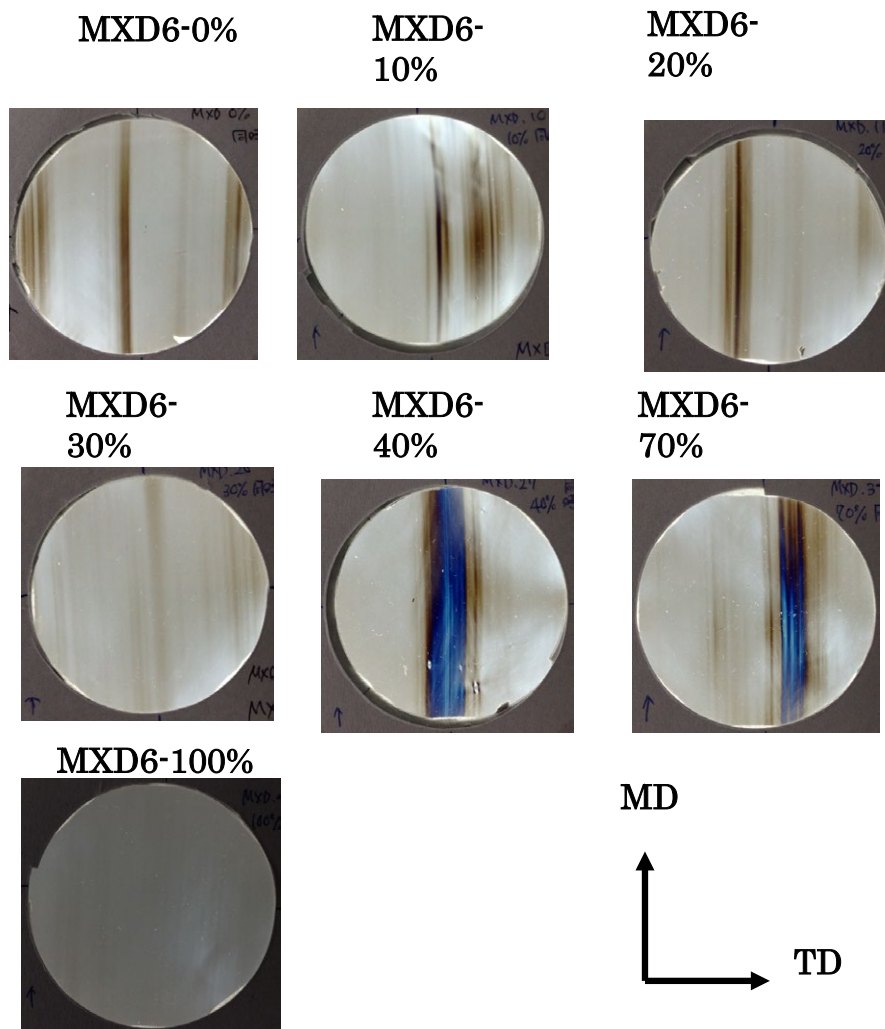

FIGURE 12 Observation of the MXD6 blending ratio change sample using polarizing plates. Stretching ratio: MD × TD 3 × 3

Through view **End view** **Edge view**

MXD6-0%

MXD6-10%

MXD6-20%

MXD6-30%
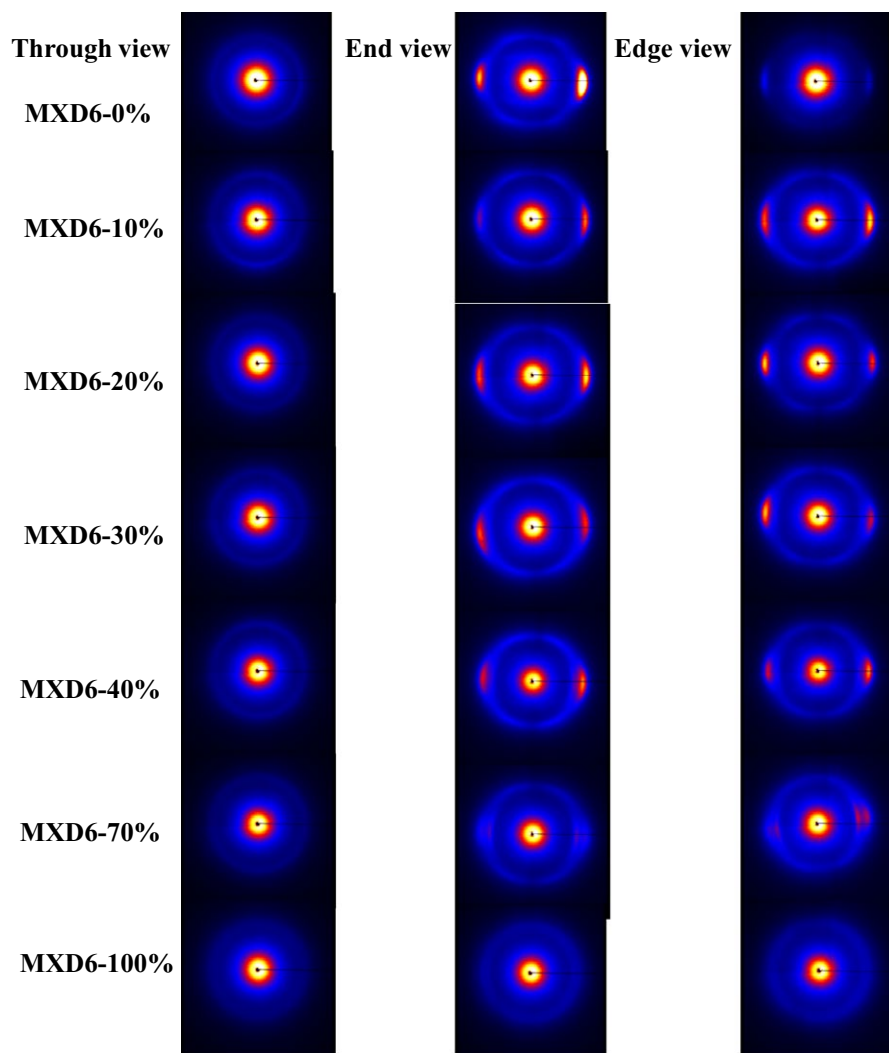
MXD6-40%

MXD6-70%

MXD6-100%

FIGURE 13 The result of wide angle X-ray diffraction patterns of simultaneous biaxial stretching at different MXD6 blending ratios

Equation (1), was plotted as a function of stretching ratio shown in Figure 10.

Figure 9 shows the stretching stress increases with increasing the stretching ratio. Figure 10 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 PA6/MXD6 blend can increase stretching ratio higher than PA6 without film break during the biaxial stretching, because the blend of MXD6 to PA6 can reduce the stretching stress.

As the blending of MXD6 to PA6 weakens the hydrogen bond of PA6, the stretching stress is reduced. It was observed that the stretching stress between 25 and 30 MPa 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 the 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

PA6, polyamide 6.

3.5 | Effect of blending ratio

The stretchability, stretching stress, and plane orientation as a function of the blend ratio of MXD6 were investigated. The gas barrier and the easy straight cut properties increased with increasing the MXD6 ratio[1].

The stretching stress as a function of the stretching ratio under various blend ratios is shown in Figure 11. The stretching stress and the yield stress decreased with increasing the MXD6 blend ratio except 100% MXD6. This means the

hydrogen bond became weak with increasing the ratio of MXD6.

Figure 12 shows the observation of PA6 and MXD6 blends changing MXD6 blend ratio using the polarizing plate. The film uniformity became worse with increasing the MXD6 blend ratio, because the stress buildup ratio decreased.

Figure 13 shows the wide angle X-ray diffraction patterns observation of PA6 and MXD6 blends at stretching ratios MD 3 × TD 3 under various MXD6 blend ratios. It shows the diffraction patterns of the through view were not changed under various blending ratios of MXD6, but the diffraction patterns of the end view and the edge view show strong diffraction patterns in equator direction which mean planar orientation, and furthermore, it shows slightly different diffraction patterns over the blend ratio of MXD6 70%.

As a result, some crystalline of MXD6 was molten, because the experiments were performed at the same stretching temperature. In the case of high content MXD6 sample, the sharp peak of (002) plane became weaker and broader and then the hydrogen bond became weaker.
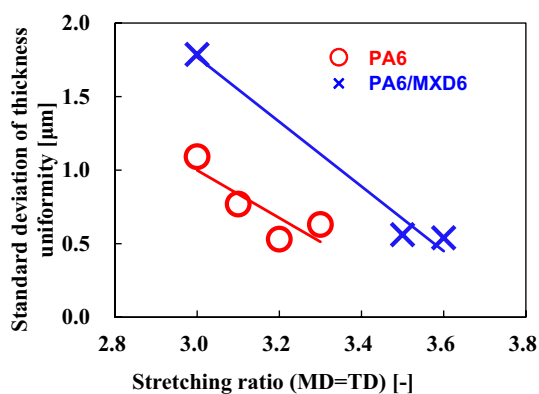
3.6 | Film uniformity

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 buildup ratio (maximum stretching stress/stretching stress at the yield point) after the yield stress passes. The relationship between thickness uniformity and the stretching ratios is shown in Figure 14 and thickness uniformity improved by increasing the stretching ratio.

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

FIGURE 14 Relationship between standard deviation of thickness uniformity and surface ratio for polyamide 6 (PA6) and PA6/MXD6 films
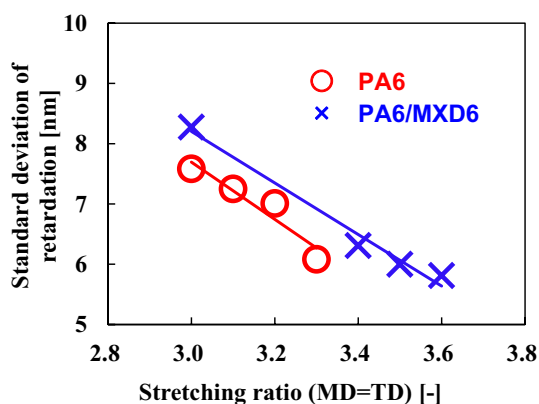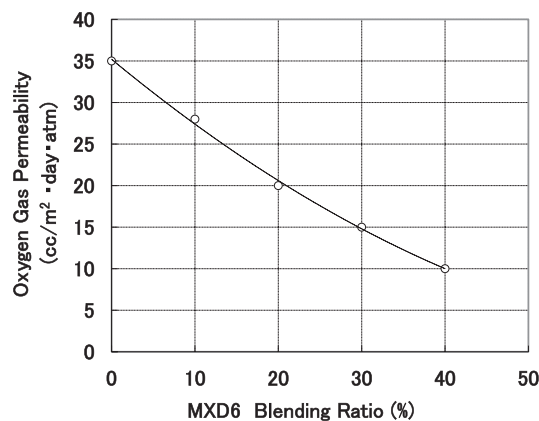
FIGURE 16 Relationship between MXD6 blending ratio and oxygen permeability

FIGURE 15 Relationship between standard deviation of retardation and surface ratio for polyamide 6 and PA/MXD6 films
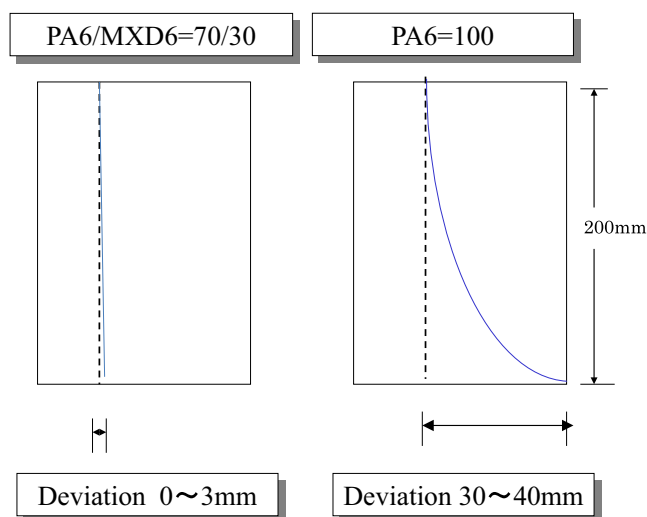
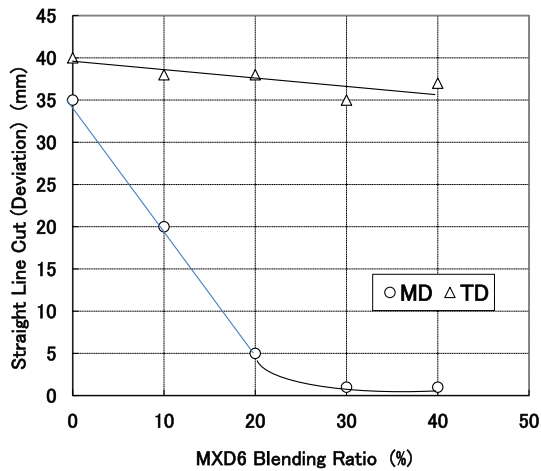**FIGURE 17** Straight line cut of biaxial polyamide 6 film

FIGURE 18 Relationship between MXD6 blending ratio and straight line cut

Furthermore, the standard deviations of both samples decrease with increasing the stretching ratio and are almost the same value at the maximum stretching ratios of PA6 3.3 and PA6/MXD6 blend 3.6. This means that the film thickness uniformity of PA6/MXD6 is almost the same level as PA6, because PA6/MXD6 has a lower stretching stress and can be set at a higher maximum stretching ratio.

Figure 15 shows the standard deviation of retardation as a function of the stretching ratio for PA6 and PA6/MXD6 blend. The standard deviation of retardation was calculated by the measurement results of retardation mapping which was equipped in the biaxial stretching machine. As the standard deviation of retardation comes from optical ununiformity, it is closely related to the data of the film thickness uniformity shown in Figure 14.

From the results, it was found that the blending of MXD6 to PA6 reduced the stress buildup ratio and then the thickness uniformity became worse. But as the blend of MXD6 to PA6 has low stretching stress, the stress buildup ratio increased with increasing the stretching ratio and the thickness uniformity of PA6/MXD6 blend became almost the same level as PA6 film.

3.7 | Film properties

The film physical properties were evaluated by the change in blending ratio of PA6 and MXD6. Figure 16 shows the relationship between blending ratio and oxygen gas permeability. Oxygen gas permeability of the blending sample of PA6 and MXD6 was more excellent than the PA6 film. The oxygen gas permeability was also improved, as blending ratio of the MXD6 resin increased.

Figure 17 shows the measurement method of straight line cut in film. The straight line cut level was expressed using the deviation length. Figure 18 shows the relationship between blending ratio and straight line cut. The deviation length of MD drastically decreased with increasing MXD6 blending ratio. But the deviation length of TD was not changed in all MXD6 blending ratio. In PA6 film, the deviation length was about 35 mm. But in 30% MXD6 blending film, the deviation length was about 0 mm in MD. It was found that MXD6/PA6 film blended MXD6 between 30% and 40% has the straight
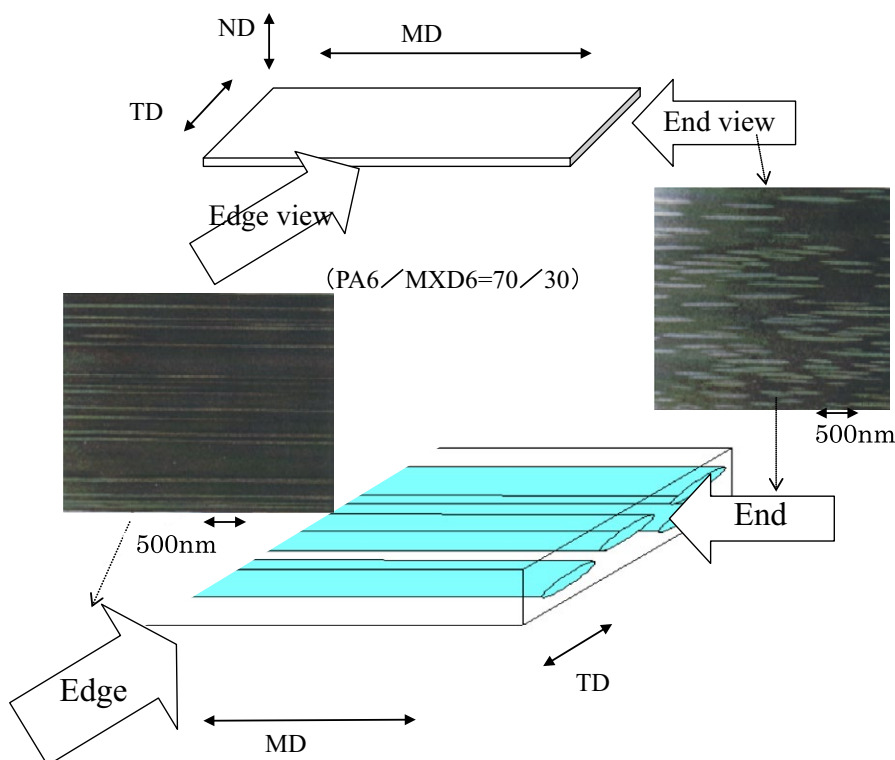

FIGURE 19 TEM Observation of biaxially stretched PA/MXD6 film TEM

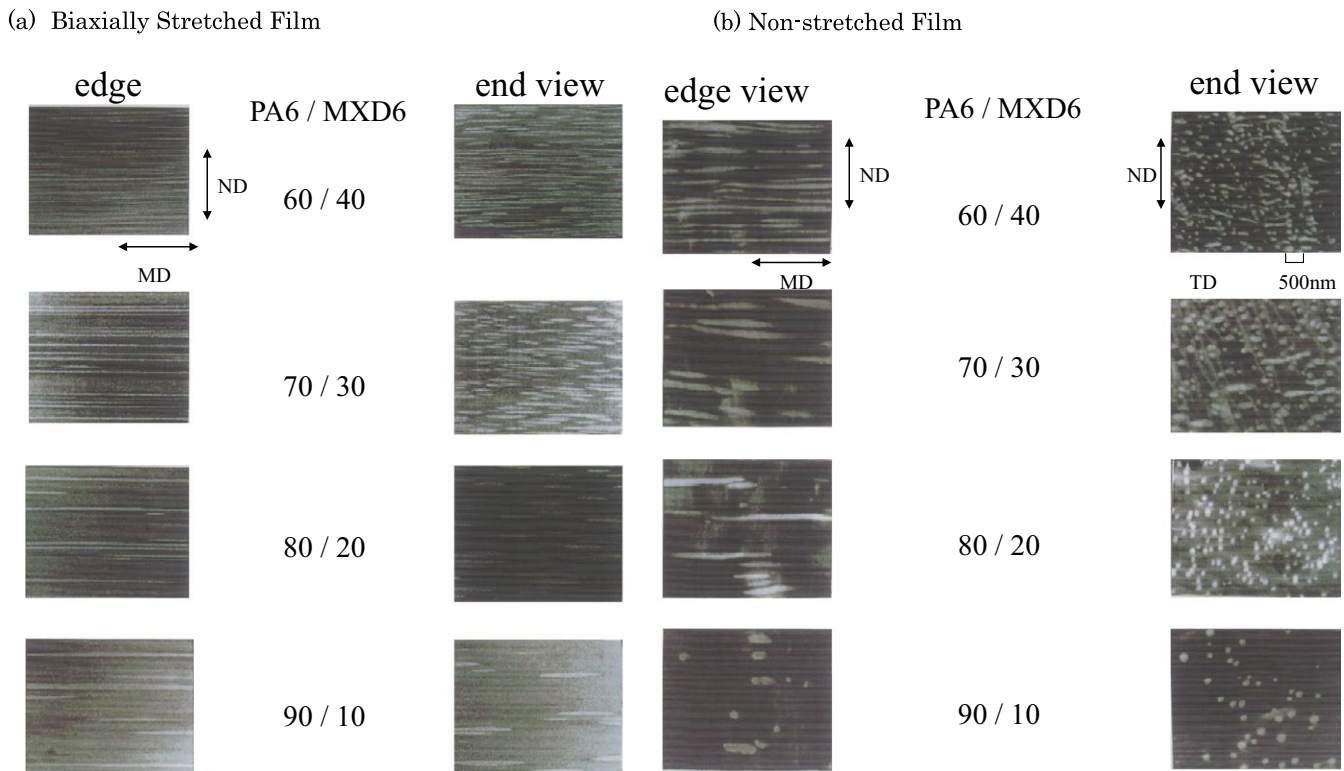(a) Biaxially Stretched Film   (b) Non-stretched Film

FIGURE 20 Observation of TEM for polyamide 6/MXD6 blends. (a) Biaxially Stretched Film. (b) Nonstretched Film

line cut property in MD which means the deviation length is almost 0. The property of the straight line cut disappeared, when MXD6 blend ratio is below 15%. In the case of PA6 film, it has 35 mm.

TEM photograph of the edge view and the end view for biaxially stretched 30% MXD6 blended film was shown in Figure 19. It was found that the blending film had a plate-like cylinder structure consisting of MXD6 domains. The MXD6 domain is highly oriented. The difference of tearing anisotropy is due to this domain structure. MXD6 has formed dispersed phase in the blend film. The slender MXD6 domain is several hundred nm width and several thousand nm length from the electron microscopy. And the domain has lined up in MD. Figure 20 shows TEM photographs of the edge view and the end view for various biaxially stretched MXD6 blended films. The easy straight cut property is owing to the controlled matrix and domain morphology. The low blend content of MXD6 is not enough to have the easy straight cut property and the high content of MXD6 such as 30 wt% is the proper content to obtain the easy straight cut property.

4 | CONCLUSIONS

Blending of MXD6 to PA6 gives high gas barrier, easy straight cut properties, and low stretching stress, but poor thickness uniformity. As blending of MXD6 to PA6 reduces the hydrogen bond, the stretching stress can be reduced and higher stretching ratio can be achieved without film break. The stress buildup value (final stress/yield stress) increases with increasing the stretching ratio and improves film thickness uniformity and produces high orientation film. Finally, blend film of MXD6 to PA6 has high gas barrier, easy straight cut properties, and good thickness uniformity and is suitable for food packaging.

By the dynamic observation and the in situ orientation analysis during the biaxial stretching process, the following results were obtained.

- The blend of MXD6 to PA6 has lower stretching stress and plane orientation than PA6, because PA6 hydrogen bond was weakened by the steric hindrance of MXD6.
- The blend of MXD6 to PA6 has narrower stretching temperature window than PA6. As the plane orientation increased with increasing the stretching stress, the stretching temperature should be reduced to produce high oriented film by considering the stretchability.
- The blend of MXD6 to PA6 could be stretched at a lower stretching speed which could produce the biaxial stretching film having higher plane orientation.
- The blend of MXD6 to PA6 could reduce the stretching stress. It had lower plane orientation than PA6 at the same stretching ratio, but as the stretching stress of the blend PA6/MXD6 increased with increasing the stretching ratio,

it was possible to obtain the high oriented film. To obtain the highly oriented biaxial stretching film, it should be stretched at a high stretching ratio considering the stretchability.

- As the stress buildup ratio decreased with increasing the MXD6 blend ratio, the biaxial stretched film thickness uniformity of the blend of MXD6 became worse with increasing the MXD6 blend ratio. However, as the blend of MXD6 could reduce the stretching stress, stress buildup ratio was increased and thickness uniformity of the blend film was improved by increasing the stretching ratio and then the same level of thickness uniformity as PA6 was achieved. Finally, the blend of MXD6 to PA6 had high barrier, straight cut properties, and film thickness uniformity.

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