Coextrusion of it-Polypropylene Film

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Synopsis

it-Polypropylene films were coextruded by using dies of varying extrusion draw ratio (EDR) from 2–10. Among the resulting films, the film coextruded at EDR 9 possesses the most attractive superstructure and the highest modulus. The dynamic modulus at room temperature was 7 GPa and an α_c dispersion peak occurred at 100°C in E″-temperature curves, which is higher by about 20°C than that of the multistep zone-drawn and zone-annealed fibers previously reported. Further, to prepare films with higher draw ratio and higher modulus, repetition of the coextrusion was attempted. Consequently, the draw ratio and the E′ at room temperature reached 12 and 13 GPa, respectively. The present paper discusses changes in molecular orientation, crystallinity, uniformity of the superstructure, and dynamic viscoelasticity, with increasing of the used EDR and repeating the coextrusion with some combinations of EDR.

INTRODUCTION

On the basis of the information regarding solid-state extrusion method, Porter and his coworkers proposed[1,2] the coextrusion method of 1979 as a new development in the solid-state extrusion. Since then, the coextrusion method has been applied to a wide variety of semicrystalline and amorphous polymers, such as polyethylene,[1,3,4] nylons 6[5,6] and 11,[5] poly(vinylidene fluoride),[7] polystyrene,[8-10] and poly(ethylene terephthalate).[11-15] Furthermore, the application of this method to ultra-high molecular weight single crystal mats of polyethylene[16] and polypropylene[17] was remarkably successful and attained particularly the moduli of 222 GPa and 33 GPa, which are very close to theoretical values, respectively.

In the present study, the coextrusion method has been applied to as-extruded isotactic-polypropylene films by the use of dies with varying extrusion draw ratio (EDR). As a new development, a two-step coextrusion method also was attempted. The two-step coextrusion shows a significant effect on improving the mechanical properties. For example, the modulus at room temperature has become almost doubled by the new method. The purpose of the present paper is to report the results for superstructure and mechanical properties of the one- and two-step coextruded it-polypropylene films.

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EXPERIMENTAL

Material

The original material used in the present study is as-extruded it-polypropylene film of about 90 μm in thickness, supplied by Toray Industries Ltd. The film has a crystallinity of 53.5% and a birefrigence of 0.14×10^{-3}.

Coextrusion

Strips were cut into a size of 2 × 90 mm from the original film. The strip was interposed between half-cut billets of polyethylene. The billets with the it-polypropylene strip were inserted into a cylinder of an extruder equipped with a die. The dies have various ratios of inlet diameter/outlet one. The ratio is represented by EDR. In this study, EDR 2, 3, 4, 5, 6, 7, 8, 9, and 10 were used. The billets interposed it-polypropylene strips were extruded by a planger moving at a downspeed of 1 mm/min and at 120°C. As the real draw ratio of coextruded film differ from EDR, it was estimated from the distance between ink marks on the film surface.

Measurements

The birefringence was measured with a usual polarizing microscope equipped with Berek compensator. The density was measured at 25°C by a flotation method using water–methyl alcohol mixtures. The crystallinity (Xc) was calculated from the density (d) by the following equation using a crystal density (d_c)[18] of 0.936 and an amorphous region density (d_a)[18] of 0.850 g/cm^3.

$$Xc = [d_c(d - d_a)/d(d_c - d_a)] \times 100$$

The dynamic viscoelasticity, i.e., dynamic modulus E′, loss modulus E″, and tan δ, were measured at 110 Hz at a heating rate of 1.4°C/min from room temperature to 140°C in air with a viscoelastmeter, VIBRON DDV-II (Orientec Co.). The dimensional stability, i.e., shrinkage or elongation, was measured in silicon oil heating at a rate of 1°C/min. Furthermore, the wide angle X-ray photographs, SEM photographs, and polarizing microscope photographs were taken. DSC curves were obtained at a heating rate of 10°C/min in air.

RESULTS AND DISCUSSION

Changes in Superstructure with Coextrusion

Table I shows the relation between the real draw ratio of films and the EDR of dies used for coextrusion. The real draw ratio is always smaller than EDR. The maximum draw ratio 8.78 was obtained on the film coextruded at EDR 10. At EDR more than 10, the film could not be drawn and was broken into small flakes. The value of birefringence increased with increasing EDR, as seen Figure 1. The value reached 0.0382, which is fairly higher than the maximum value for the multistep zone-drawn and zone-annealed fiber,[19] 0.0369. The crys-

TABLE I
Relation between EDR and Real Draw Ratio

EDR	Real draw ratio
2	1.80
3	2.76
4	3.66
5	4.54
6	5.44
7	6.18
8	7.00
9	7.76
10	8.78
7 × 2	12.07

tallinity (Xc) was almost constant over a range of EDR 2–9, as shown in Figure 2. The level of Xc is 70–74%, which is increased by 16–20%, compared with the Xc of the original film, 53.5%. In the case of EDR 10, however, the Xc was rapidly decreased to 47%. It is not clear whether the decrease depends on the drop in Xc or not because the exact measurement of density is prevented by cracks generated on excessive drawing.

Figure 3 shows the wide-angle X-ray photographs for the original film and the coextruded films. The X-ray pattern of the original film consists of rings, and indicates no orientation of the molecular chains, as well as the result of birefringence measurement. By the extrusion with EDR 2, the crystallinity was clearly increased, but the orientation is still low. The results agree with those indicated in Figures 1 and 2. The X-ray scattering spots become step by step sharper at above EDR 3. The pattern of the EDR 8 film indicates a very high orientation of the crystallites.

Some of the polarizing microscope photographs are shown in Figure 4. The EDR 6 film has an nonuniform structure, although the molecular orientation

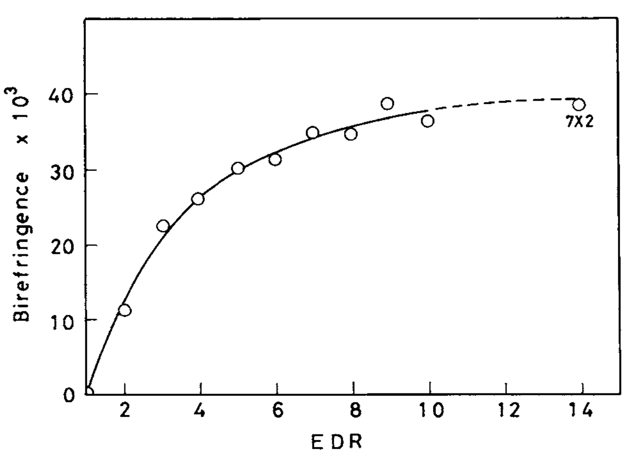

Fig. 1. Relation between the extrusion draw ratio (EDR) and the birefringence.

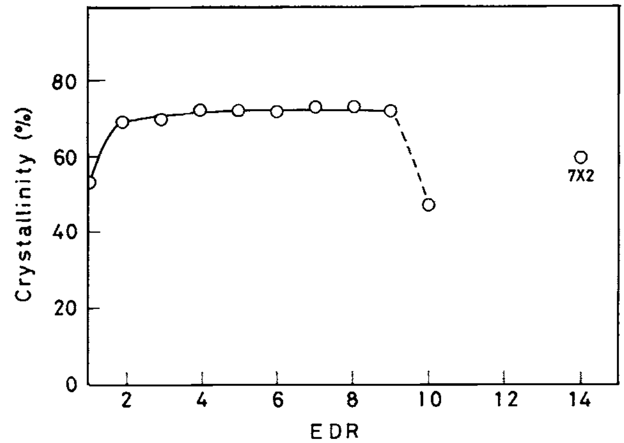

Fig. 2. Relation between EDR and crystallinity.

is fairly good. However, the structural uniformity increases with increasing EDR up to EDR 9. When the EDR 10 die is used, however, the film again becomes nonuniform. Partial slips and fractures are considered as the origins. These may be related to widening of the X-ray diffraction spots in Figure 3 and to the rapid drop of density in Figure 2. In the photographs of EDR 6 and 8, rough network patterns are observed. In the coextrusion, the characteristic patterns appears strongly. The shear stress and compression force act in cooperation on the interposed films in the die, and forcibly tilt the lamellae and then effectively withdraw the molecular chains. In the photograph of EDR 10 film, however, the streaks perpendicular to drawing direction became brighter. The fact suggests that the deformation of the film becomes difficult at EDR 10. The films broke into flakes when dies greater than EDR 10 were used. Similar structure changes were observed in SEM photographs of the coextruded films.

Table II indicates the changes of crystal melting peak temperature in DSC curves with EDR. The melting point shifts to higher temperatures with increasing EDR in order. The temperature difference between the original film and the EDR 9 film is 6°C. Although the melting peak temperature for the EDR 10 film reached 171.5°C, the peak became fairly sharp and small.

The changes in length on heating for each EDR film are shown in Figure 5. The original film lengthened gradually with an increase in temperature, the maximum elongation being about 3% at 140°C. On the other hand, the coextruded films shrank upon heating in silicon oil. The percentage of shrinkage did not exceed 4–5% in the coextruded films except for the EDR 10 film. These films show a very high dimensional stability.

Change in Dynamic Viscoelastic Properties with Coextrusion

Figure 6 shows the temperature dependence of dynamic modulus E′ for the original film and the coextruded films. Up to EDR 9, the modulus increases with increasing the EDR step by step. The E′ value of the EDR 10 film is

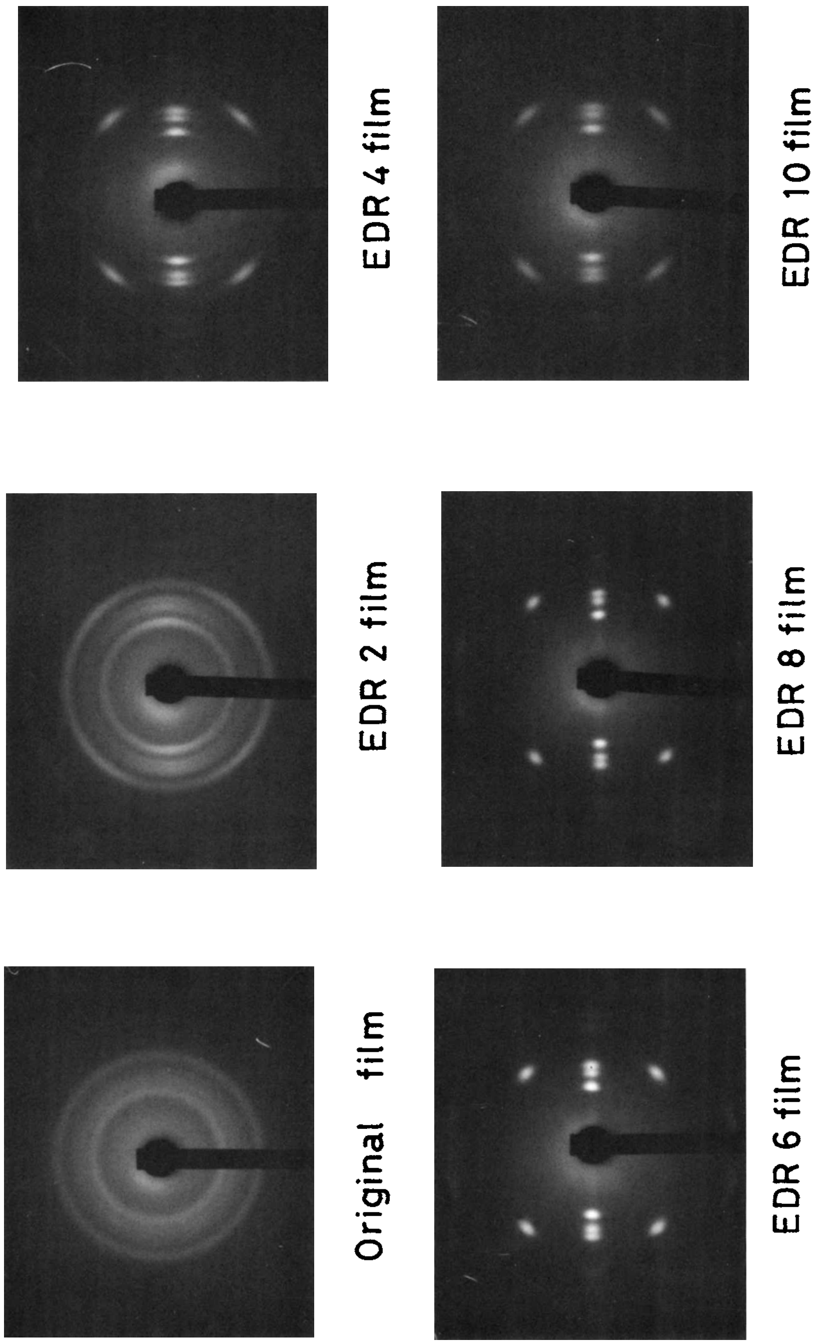

Fig. 3. Wide-angle X-ray photographs of the coextruded films.

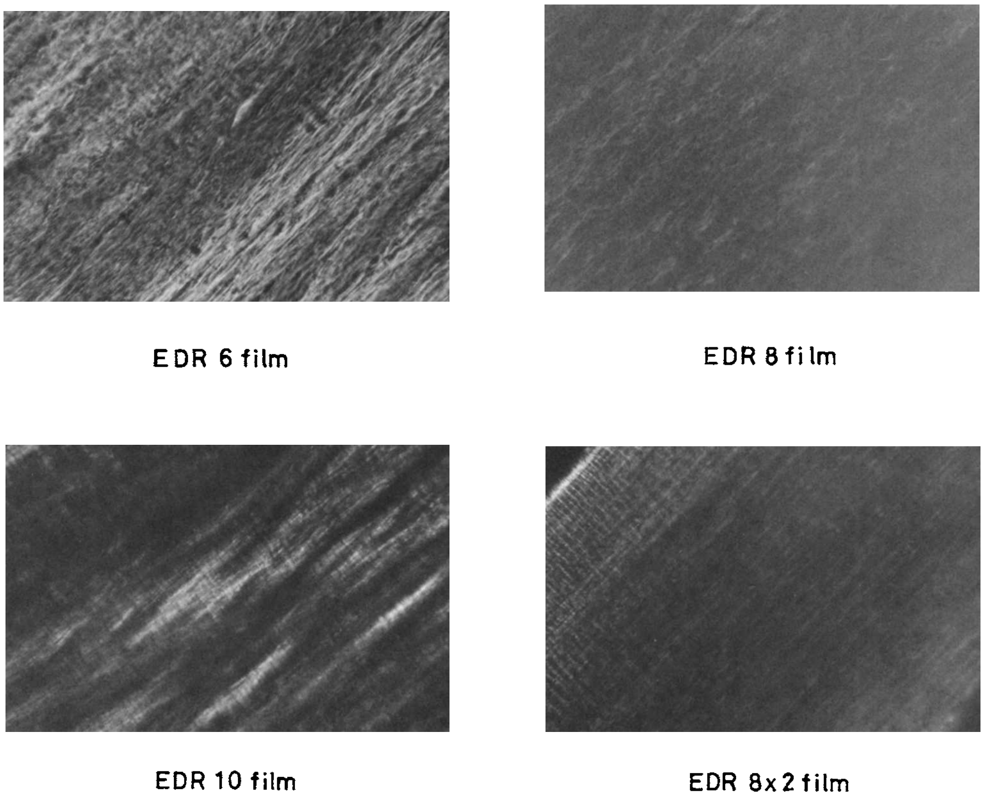

Fig. 4. Polarizing microscope photographs of the coextruded films.

slightly lower than that of the EDR 9 film. The maximum E′ value at room temperature is 7.3 GPa. As the room temperature modulus is higher, the moduli at elevated temperatures are higher. It is interesting that the higher level maintains even in the temperature range above α_c dispersion, suggesting that the crystals in the coextruded films are hard and play an important role in improvement of mechanical properties. Figure 7 shows the temperature dependence of loss modulus E″ for the same films as those in Figure 6. The E″ value also increases with increasing the EDR. The α_c dispersion peak appears at about 100°C for the films above EDR 4. The peak increased in height in order,

TABLE II
Change in Melting Point with Coextrusion

Sample	Melting point (°C)
Original film	165
EDR 4 coextruded film	167
EDR 6 coextruded film	169
EDR 8 coextruded film	170
EDR 10 coextruded film	172

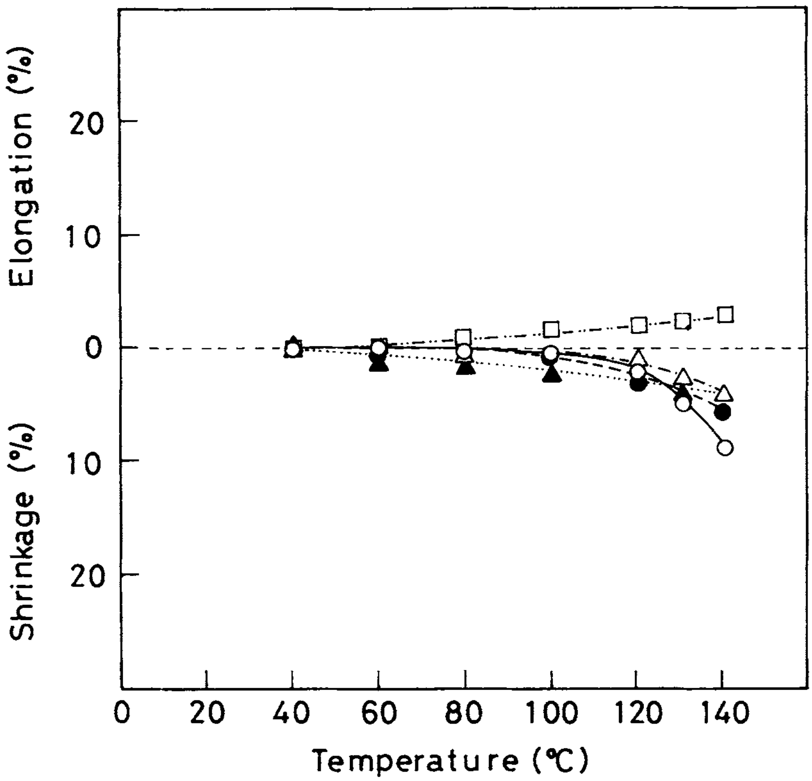

Fig. 5. Changes in length of the original and coextruded films on heating in silicon oil at a heating rate of 1°C/min; (□) original film; (▲) EDR 4 film; (△) EDR 6 film; (●) EDR 8 film; (○) EDR 10 film.

but arose at the same temperature of ca. 100°C, which is higher than those of the multistep zone-drawn and zone-annealed polypropylene fibers (80–85°C) previously reported. It indicates that the crystal relaxation in the coextruded films is remarkably difficult.

Repetition of the Coextrusion

As described above, the film coextruded at EDR 10 has many undesirable properties, e.g., a low density, an inhomogeneous structure, a higher shrinkage (8% at 140°C), and a slightly lower modulus than that of the EDR 9 film. In addition, the coextrusions at above EDR 10 were not entirely successful.

To obtain films having a higher draw ratio and more excellent mechanical properties, the repetition of coextrusion was attempted. For example, the film extruded at EDR 6 was again coextruded by using the die of EDR 3 and a set of newly prepared billets. This procedure is abbreviated as EDR 6 × 3. In this study, EDR 6 × 3, EDR 7 × 2, EDR 8 × 2, and EDR 9 × 2 were successful.

The EDR 7 × 2 film, as one example, has the total draw ratio of 12.1, the birefringence of 0.0379, and the crystallinity of 59.9%. In Figure 8, the

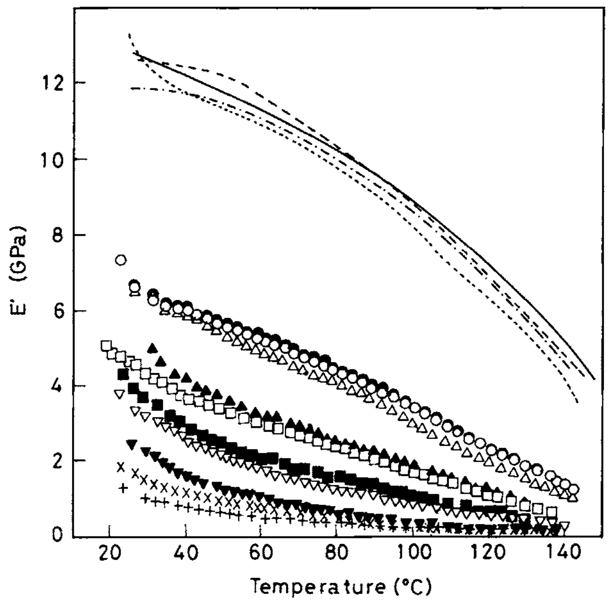

Fig. 6. Temperature dependence of the dynamic modulus (E′) for the coextruded films and the two-step coextruded films; (+) original film; (×) EDR 2 film; (▼) EDR 3 film; (▽) EDR 4 film; (■) EDR 5 film; (□) EDR 6 film; (▲) EDR 7 film; (△) EDR 8 film; (●) EDR 9 film; (○) EDR 10 film; (–•–•–) EDR 6 × 3 film; (• • •) EDR 7 × 2 film; (---) EDR 8 × 2 film; (——) EDR 9 × 2 film.

changes in wide-angle X-ray photographs with repeating the coextrusion are shown. Although the draw ratio increased up to 12–13, the birefringence remained in the order of about 0.038; in addition, the crystallinity estimated by the density method was decreased as shown in Figure 2. As seen in the photograph of the EDR 8 × 2 film (Fig. 4), the cross-streaks appeared more densely and clearly than those of the EDR 10 film. The detailed description of the superstructure of two-step coextruded films is not discussed in this paper because the morphology has not yet been shown conclusively.

The mechanical properties were strikingly improved. As shown in Figure 6, the E′ values of the two-step coextruded films are remarkably higher than that of the EDR 9 film over the whole temperature range measured. Also, it is very interesting that the E′ values are almost at the same level for the four examinations. The E′ value at room temperature is 12–13 GPa, corresponding to two times that of the EDR 9 film. Furthermore, the high level of E′ value was maintained at elevated temperatures: 9 GPa at 100°C, 7 GPa at 120°C, and 4.5–5 GPa even at 140°C. These results suggest that the fibers can be used in applications over a broad temperature range. The α_c dispersion peak shifted to a higher temperature and became much higher in intensity with repeating the coextrusion. The peak temperatures were about 120°C, which is further higher by 20°C than that of the EDR 9 film. This indicates that the crystal structure is very hard and the molecular movements in the crystallites are strongly prevented.

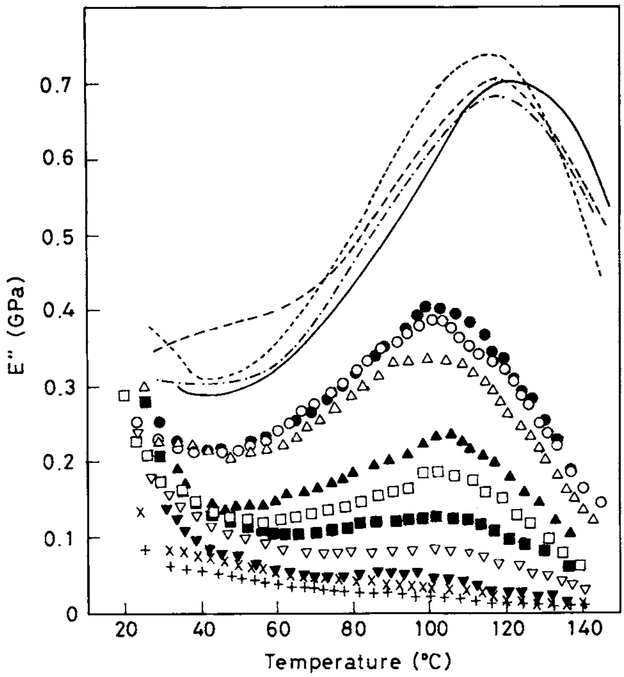

Fig. 7. Temperature dependence of the loss modulus (E″) for the coextruded films and the two-step coextruded films; (+) original film; (×) EDR 2 film; (▼) EDR 3 film; (▽) EDR 4 film; (■) EDR 5 film; (□) EDR 6 film; (▲) EDR 7 film; (△) EDR 8 film; (●) EDR 9 film; (○) EDR 10 film; (- • - • -) EDR 6 × 3 film; (• • •) EDR 7 × 2 film, (---) EDR 8 × 2 film; (——) EDR 9 × 2 film.

CONCLUSION

1. The coextrusion method has been successfully applied to it-polypropylene film. The film coextruded at EDR 9 has a birefringence of 0.0382, a crystallinity of 74%, and a dynamic modulus of 7GPa.
2. The film coextruded at EDR 10 possesses undesirable properties: a lower density, a nonuniformal superstructure, and a lower modulus than those of the EDR 9 film. It was found that the films were broken to small pieces with the dies of EDR above 11.
3. To obtain films with higher draw ratio and improved properties, the two-step coextrusion method was used. In spite of relatively lower birefringence and crystallinity, the films obtained by this method indicated higher draw ratios near 12 and had excellent mechanical properties. The E′ value at room temperature was increased to 13 GPa. In addition, the E′ value maintains a strikingly high level even at elevated temperatures. The α_c dispersion peak occurred at 120°C, which was much higher than those of the EDR 9 film (100°C) and the zone-drawn and zone-annealed fiber (ca. 85°C).

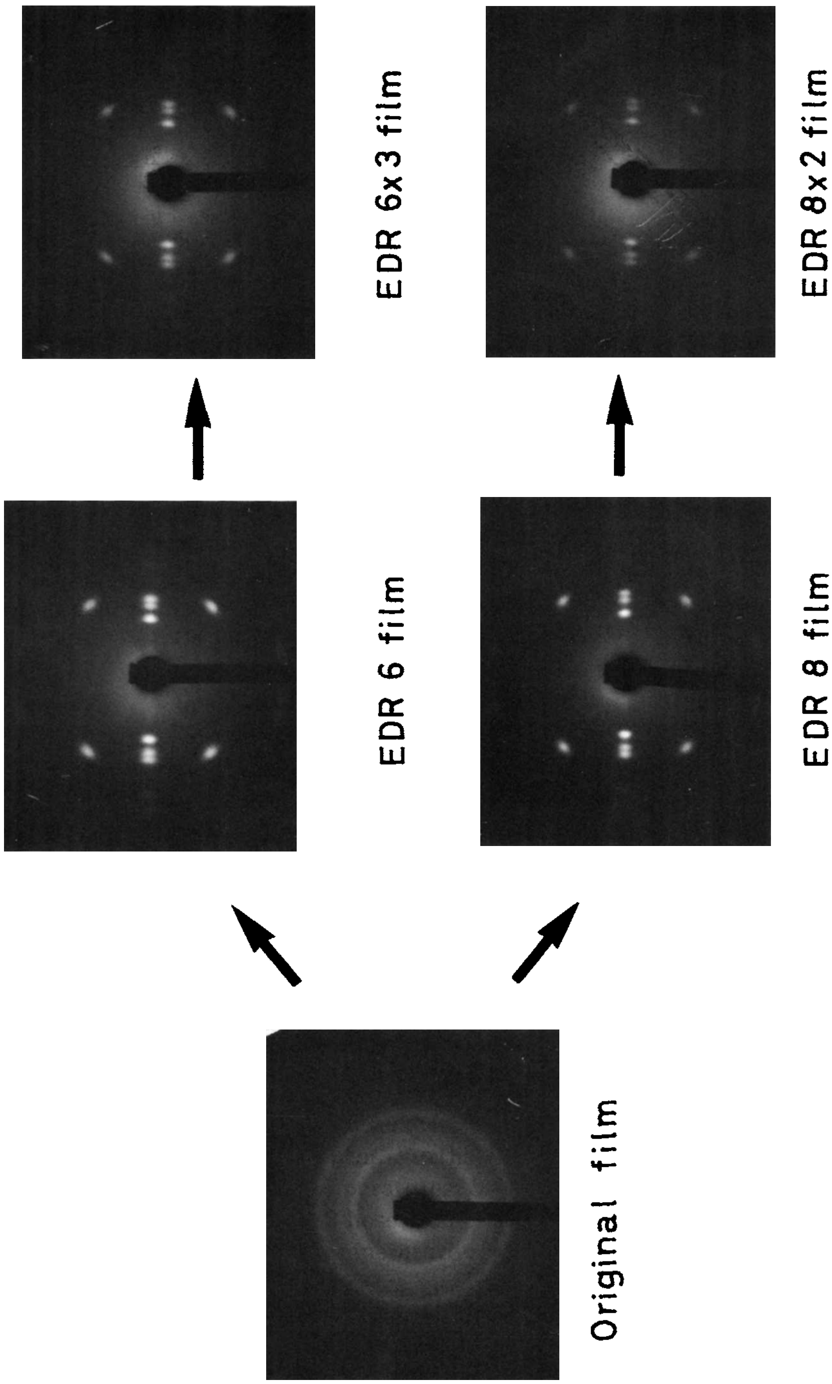

Fig. 8. Wide-angle X-ray photographs for the original film and the coextruded and two-step coextruded films.

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