

Effect of Orientation on the Biodegradability of Uniaxially Stretched Aliphatic Copolyester Films

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ABSTRACT: The effects of uniaxial drawing conditions on the orientation of aliphatic copolyester films were investigated by using both Fourier transform infrared–attenuated total reflection (FTIR–ATR) dichroism and wide angle X-ray diffraction (WAXD) methods. The results showed that orientation in uniaxially drawn films was determined by the drawing rate and drawing temperature. At higher drawing rates and higher drawing temperatures, higher orientation was obtained due to a large deformation of spherulites. The WAXD patterns of drawn films exhibited the preferential orientation of lamellar crystallites. The results of microbial degradation indicated that development of crystalline orientation evidently depressed biodegradability of samples. Video microscopy observations revealed that the degree of orientation played a dominant role in determining the rate of surface erosion. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1999–2006, 1997

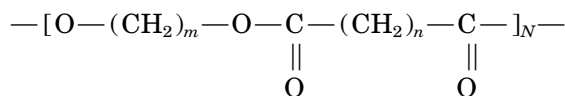
Key words: aliphatic copolyester; orientation; biodegradation

INTRODUCTION

The amount of municipal and industrial waste has markedly increased throughout the world in the last few years. Waste disposal is becoming a serious environmental problem because of limited landfill capacity and incineration facilities. Environmental concerns have caused scientists to accelerate their activities in the design and study of materials that are constructed to degrade to safe components in a desirable frame under specified environmental conditions.

It is well known that aliphatic polyesters have a high level of biodegradability. Aliphatic polyesters are usually synthesized by polycondensation

or ring-opening polymerization of lactones. For poly(caprolactone) (PCL), its low melting point is a problem for use in biodegradable plastics. Therefore, various PCL copolymers and blends have been developed.^{1–5} Regarding the use of condensation polymerization, it has been proven that it is difficult to synthesize high-molecular-weight aliphatic polyesters via this method. However, some companies have recently succeeded in raising molecular weight up to $3–4 \times 10^4$ in M_n . A crystalline aliphatic copolyester produced from aliphatic dicarboxylic acids and glycols seems to be the most promising biodegradable plastics because of its low price, good physical and mechanical properties, and high biodegradability. Its main unit structure is



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The biodegradability of aliphatic polyesters is dependent on molecular weight, degree of crystallinity, and polymer morphology. Takiyama and Fujimakim⁶ have indicated that for aliphatic copolyesters, M_n has to be raised above 30,000 in order to obtain high mechanical strength; but above 50,000, its biodegradability decreases. They emphasized that the biodegradation rate can be controlled by varying the chemical composition of copolyesters. Tokiwa⁷ has shown that the development of crystallinity depressed the microbial degradability. This suggests that the biodegradation in the amorphous state should be easier than in the crystalline state. He has also reported that the size of spherulites was a more important factor than crystallinity in the biodegradability of PCL.

Films used in packaging materials could be a large potential market for biodegradable plastics. Agricultural films are also considered to be a potential market. Selection of the best film for any particular use is a matter of matching film properties against the performance required. One important property of biodegradable plastics films is the rate of biodegradation. The rate of film biodegradation can be greatly modified by controlling the degree of crystallinity and orientation. Various information relating to the morphology and biodegradability of crystalline polymers is available,⁸⁻¹³ but most of this has addressed the effect of crystallinity and spherulite size, rather than orientation.

In this work, the orientation of biodegradable films stretched at various drawing temperatures and rates was analyzed using Fourier transform infrared (FTIR), attenuated total reflection (ATR), and wide angle X-ray diffraction (WAXD) methods. The biodegradation of samples with a different degree of orientation was measured by liquid culture experiments. The attention was focused on the role of orientation in the biodegradation of aliphatic copolyester films.

EXPERIMENTAL

Materials

This study was performed with the following two types of aliphatic copolyesters manufactured by SKI, Ltd. of Korea: SG1109, a copolyester of succinic acid-(1,4-butanediol/ethylene glycol); and SG2109, a copolyester of (succinic acid/adipic acid)-(1,4-butanediol/ethylene glycol).

Undrawn films were prepared by conventional flat-film extrusion. The molten polymer was extruded through a slit-die followed by a chilled roller. The temperatures of hoper, melting zone, and die were set to 120, 140, and 150°C, respectively. The undrawn films (dimensions of 10 × 10 cm with a thickness of 160 μm) were placed in a uniaxial drawing device, which was preheated to drawing temperature. Uniaxial drawing was carried out at 45–65°C with a drawing rate of 0.25, 0.5, 1.0, or 2.0 m/min. Uniform film drawing was not obtained, even though draw ratios approached 3.0. Above a draw ratio of 4.5, the films ruptured during stretching. Therefore, we set the draw ratio at 4. Samples were cooled quickly following drawing to reduce annealing effect.

ATR Analysis

Because of its sensitivity to molecular structural details, IR spectroscopy by ATR using a plane-polarized IR beam is a preferred method to probe molecular orientation at a surface depth of a few microns. In IR-ATR dichroism techniques, both the polymer film and polarizer can be rotated by 90 degrees, producing four reflection spectra from which three spatial absorbances (A_x , A_y , and A_z) need to be calculated according to the following equations derived by Flournoy and Schaeffers¹⁴:

$$A_{TE,x} = \alpha A_x$$

$$A_{TM,x} = \beta A_y + \gamma A_z$$

$$A_{TE,y} = \alpha A_y$$

$$A_{TM,y} = \beta A_x + \gamma A_z$$

In these equations, α , β , and γ are constants determined by the refractive indices of the sample, the reflective crystal, and the angle of incidence. The ATR intensities for transverse electric (TE) and transverse magnetic (TM) polarization are represented by $A_{TE,x}$ (or $A_{TE,y}$), and $A_{TM,x}$ (or $A_{TM,y}$), where the x axis is the draw direction in the case of uniaxial stretching, and the y and z axes are the transverse to draw direction and the thickness direction, respectively. The dichroic ratio $D_{xy} = A_x/A_y$ is used to calculate the orientation function, as defined by

$$f_{xy} = \left(\frac{D_{xy} - 1}{D_{xy} + 2} \right) \left(\frac{D_0 + 2}{D_0 - 1} \right)$$

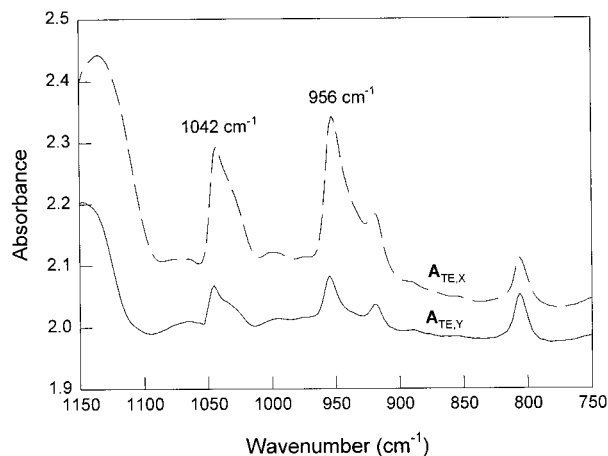


Figure 1 FTIR-ATR spectra obtained from the surface of uniaxially drawn film using a 45 degree incident angle with TE polarization.

where $D_0 = \cot^2 \alpha$, with α being the angle between the transition moment vector for the vibrational mode considered and the chain axis. The angle α for each absorption band is not accurately known. As a first approximation, 0 degrees for all parallel bands and 90 degrees for all perpendicular bands are used. If the angle is between 0 and 90 degrees, the orientation functions calculated assuming 0 or 90 degrees should be underestimated, and therefore minimum, orientation values.¹⁵

X-ray Diffraction Measurement

To identify a preferred orientation of crystallites, WAXD photographs on selected samples were obtained using a Rigaku Rotaflex system equipped with an evacuated camera. The X-ray generator was operated at 40 KV and 20 mA. The exposure time was about 4 h. To measure the degree of crystallinity of samples, the X-ray diffraction (XRD) patterns were recorded in the range of $2\theta = 5-60$ degrees at scan speed of 1 degree/min. X-ray crystallinities were calculated by using a basic method for differentiation between crystalline and amorphous scattering in diffraction intensity curves.¹⁶

Biodegradation Test

The biodegradation test was done by liquid culture experiments along the general lines of ASTM D5247. The test method consists of selecting specific

microorganisms for the determination of aerobic biodegradability, preparing inoculum, exposing samples to the activated inoculum, measuring CO_2 that evolved as a function of time, and assessing the degree of biodegradability. In this work, *Aspergillus niger* was used for the biodegradation test. All the biodegradation data was reported as the percentage of carbon converted to CO_2 based on original carbon content. To be more accurate, this test was conducted four times simultaneously, and all the data was averaged. From the average of four tests, the deviation value was so small that it could be ignored.

RESULTS AND DISCUSSION

Orientation

Figure 1 shows representative FTIR-ATR spectra obtained from the surface of a uniaxially drawn SG1109 film by rotating the sample using a 45 degree incident angle with TE polarization. Under this experimental condition, the penetration depth achieved by TE polarization is about 5 μm at 1000 cm^{-1} . Strong dichroism is observed for the parallel bands at 1042 and 956 cm^{-1} . The good signal-to-noise ratio allowed us to measure dichroic ratios from which the orientation function was calculated. We used a parallel band at 1042 cm^{-1} to study the effects of drawing conditions on the molecular orientation of aliphatic copolyesters. The band at 1042 cm^{-1} is associated with the asymmetric stretching vibration of O—C—C group of esters.¹⁷

Figure 2 illustrates a sample with a drawing

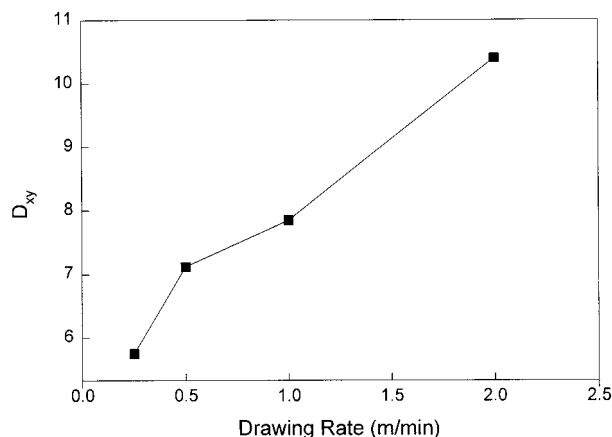


Figure 2 Dichroic ratio D_{xy} of 1042 cm^{-1} as a function of drawing rate at 55°C .

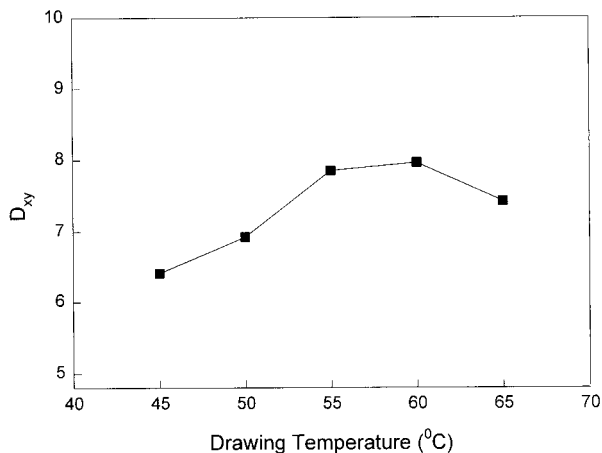


Figure 3 Dichroic ratio D_{xy} of 1042 cm^{-1} as a function of drawing temperature at drawing rate of 1 m/min.

temperature of 55°C , as a function of drawing rate. The faster drawing rate results in a greater value of D_{xy} . Similar trends have been observed when drawing temperature was either at 45 or 65°C . These results are apparently consistent with the finding of abundant work on the orientation produced by uniaxial stretching of amorphous poly(ethylene terephthalate) (PET).^{18–21} However, it is worth noting that there is a difference in mechanisms of orientation between aliphatic copolyesters and amorphous PET. When PET is drawn in the temperature range of 80 – 100°C , amorphous chains become oriented. Some of the oriented chains can crystallize, while some may relax back to unoriented chain or stay as an oriented amorphous chain.²¹ At slow drawing rates, the chain relaxation becomes an important process in decreasing the orientation in PET. The T_g of aliphatic copolyesters used in this study was about -30°C . The undrawn film was, therefore, precrystallized even though rapidly quenched by a chilled roller. There were no significant changes in crystallinity with stretching. The mechanism of orientation in precrystallized films involves spherulitic deformation, disruption of chain-folded lamellae, and subsequent alignment of lamellar crystallites in the draw direction.²² However, the orientation of amorphous PET occurs through an uncoiling motion of molecular chain segments, followed by crystallization. The faster the drawing rate, the higher the drawing stress. This implies more spherulitic deformation. With faster drawing rates, the internal temperature of the sample can increase by viscous dissipation, which also allows of a large deformation of spher-

ulites. These two effects played an important role in increasing the orientation of the pre-crystallized films through drawing rate.

The effect of drawing temperature at a constant drawing rate is shown in Figure 3. The deformation of spherulites is a predominant feature in the drawing process of pre-crystallized samples. As the drawing temperature increases, the spherulites deform more easily, resulting in an increase of preferential orientation of lamellar crystallites in the draw direction. At 65°C , the dichroic ratio D_{xy} , dropped slightly. This is likely to be due to the partial melting behavior of lamellar crystals during stretching. Figure 4 is a DSC thermogram of SG1109 at a heating rate of $10^{\circ}\text{C}/\text{min}$. The DSC curve exhibits the beginning of melting around 60°C and the melting peak at around 85°C . At a drawing temperature of 65°C , which is above the onset of melting the samples, drawing becomes less effective, decreasing the orientation in the films. The reduced orientation of lamellar crystallites is also attributed to a lower drawing stress at elevated temperatures.

In order to complement the FTIR–ATR dichroism technique, the WAXD method was used as an independent method for crystalline orientation determination of biodegradation test samples. Figure 5 shows WAXD patterns observed from the SG-1109 samples, which were placed with draw direction perpendicular to the incident beam. The XRD profile of the melt-crystallized sample shows Debye–Scherrer rings. This indicates that the sample does not have a crystalline orientation. The melt-crystallized film with the same thickness as the drawn films, $40\ \mu\text{m}$, was prepared in a

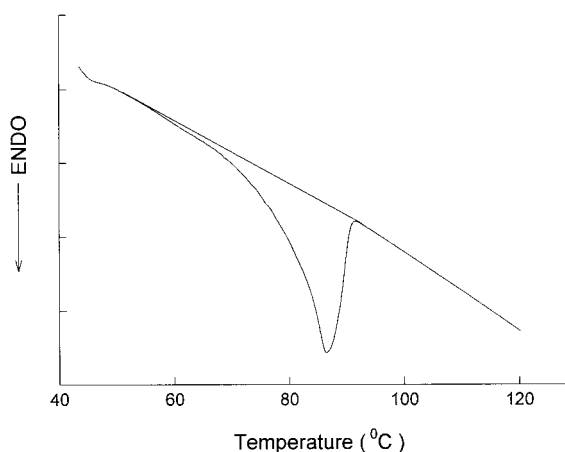


Figure 4 DSC thermogram of SG-1109 at heating rate of $10^{\circ}\text{C}/\text{min}$.

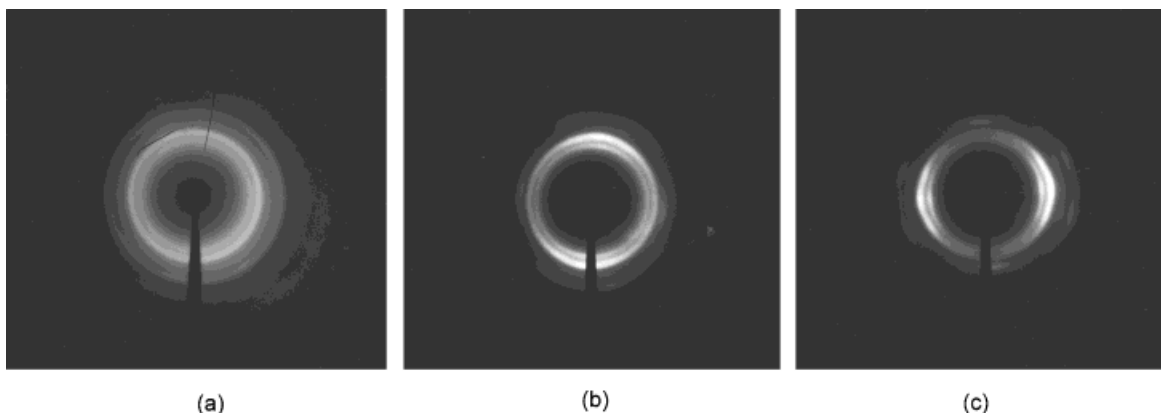


Figure 5 WAXD patterns: (a) melt-crystallized film; (b) drawn film at 55°C and 0.5 m/min; and (c) drawn film at 55°C and 2.0 m/min.

hot press set at 120°C by gently pressing undrawn film after melting for 5 min between two Teflon™ coated stainless steel plates with a spacer. The film was cooled to room temperature at ca. 20°C/min. The WAXD pattern in Figure 5(c) indicates the preferential orientation of crystal lamellae. This means that the drawn film is composed of lamellar crystallites, which are highly oriented with their flat faces parallel to the film surface. The WAXD pattern in Figure 5(b) shows basically the same type as Figure 5(c) but with lower scattered intensity because of a lower crystalline orientation.

Biodegradation

Figure 6 shows microbial degradation of the SG-1109 samples with a different degree of orienta-

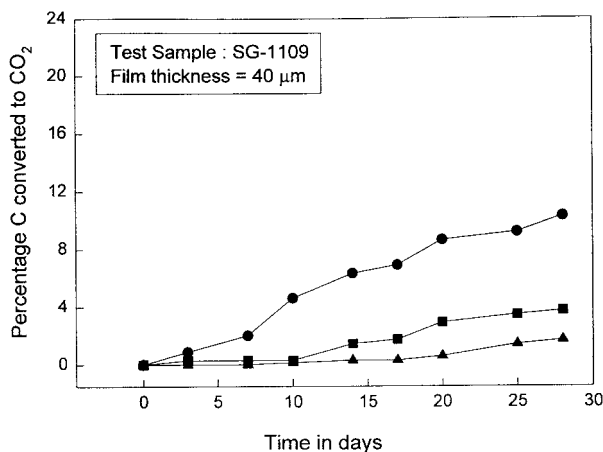


Figure 6 Percentage C converted to CO₂ with time: (●) melt-crystallized film; (■) drawn film at 55°C and 0.5 m/min; and (▲) drawn film at 55°C and 2.0 m/min.

tion. The rate of biodegradation decreased with increasing orientation of lamellar crystallites in the draw direction. The fungal degradation of crystalline aliphatic polyesters proceeds in a selective manner, with the amorphous regions being degraded prior to the degradation of crystalline regions.^{8,13} This suggests that the degree of crystallinity is a dominant factor in determining degradability on the fungal degradation. However, the effect of the degree of crystallinity on the biodegradation rate can be ignored in this study because the crystallinity values of the drawn samples were almost equal to that of the melt-crystallized sample. (The X-ray crystallinity of the melt-crystallized sample was 28.7%, and the crystallinity values of drawn samples were in the range of 29.5–30.3%.) As mentioned previously, the orientation of the films is accompanied with a crystallite alignment parallel to the surface. After the amorphous regions on the surface are degraded, the surface is covered by a layer of relatively inactive crystal lamellae with their large flat faces parallel to the film surface. Therefore, an increase of the oriented lamellar crystallites in the surface causes the deceleration of biodegradation of the drawn films.

The biodegradation of copolyesters appears to occur by colonization of the film surface by bacteria or fungi, which secrete an extra cellular depolymerase that degrades the polymers.^{13,23} This surface erosion mechanism is favored by a large surface area, and the biodegradation rate of the samples does increase with increasing surface area. Biodegradation tests on BIOPOL films of various thicknesses indicated an increase in biodegradation rate with decreasing film thickness.²³

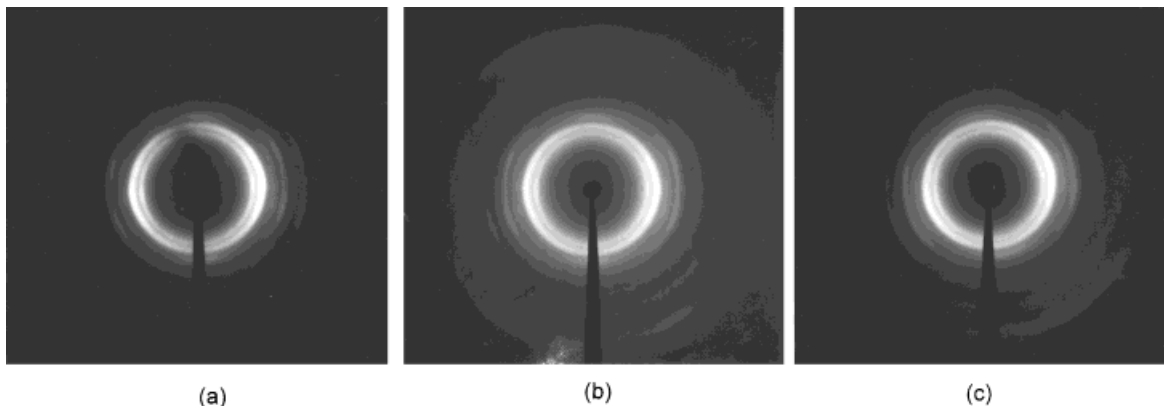


Figure 7 WAXD patterns of melt-drawn samples with various film thicknesses: (a) 20, (b) 40, and (c) 80 μm .

In this study, SG-2109 cast films with thicknesses of 80, 40, and 20 μm were made by changing roll speed in the chill roll casting process. The films were melt-drawn in the machine direction at draw ratios of 2, 4, and 8. Figure 7 shows WAXD patterns of the melt-drawn samples. The WAXD patterns indicate that higher draw ratios lead to an increase in the preferential orientation of crystallites parallel to the film surface. Since the melt-drawing process was less effective in the orientation due to large chain relaxation during the stretching, the scattered intensity of the melt-drawn samples was somewhat weak.

The effects of the film thicknesses on the microbial degradation can be seen in Figure 8. The rate of biodegradation was faster in 40 μm thick film compared with 20 μm thick film. But the films

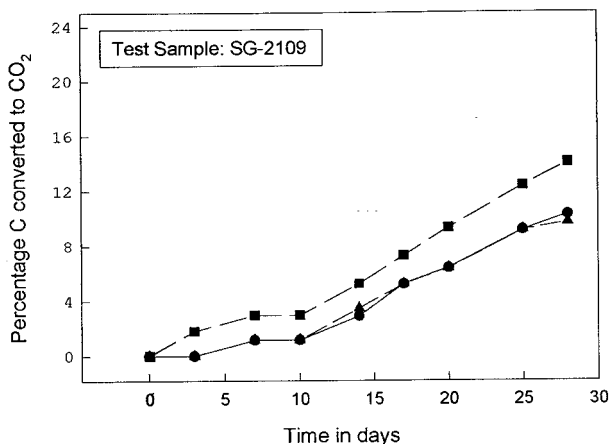


Figure 8 Percentage C converted to CO_2 with time. Thickness of melt-drawn films: (●) 20, (■) 40, and (▲) 80 μm .

with thicknesses of 20 and 80 μm exhibited similar biodegradation rates. When considering the thickness effect described above, this trend may appear contradictory. However, the biodegradation rate of the drawn films depends on the degree of orientation as well as on the film thickness. In the 20 μm thick film, the degree of orientation was high; thus, the rate of biodegradation was depressed, while the microbial degradation in the 80 μm thick film proceeded slowly due to the thickness effect. Therefore, the fastest biodegradation rate was obtained in the film of intermediate thickness.

To clarify the microbial degradation of the melt-drawn films, the surface morphology of the degraded films was examined by using a video microscope system equipped with a color printer (in this study, SEM analysis failed because surface morphology was severely changed due to the lower melting point of the film during sample preparation, which requires sputter-coating with metal). After an incubation at 27°C for 28 days, the degraded samples were removed, vigorously washed with fresh water, and dried in a vacuum oven at room temperature. Video micrographs in Figure 9 illustrate changes in surface morphology as a result of biodegradation. For a melt-drawn film, the original surface was found to be smooth. An exposure to the activated inoculum caused material removal from the surface, increasing film surface roughness. Even though degradation patterns were similar, the surface of the degraded sample with a thickness of 80 μm was much coarser compared with that of the 20 μm thick sample. This means that surface erosion proceeded faster in the 80 μm thick sample. The bio-

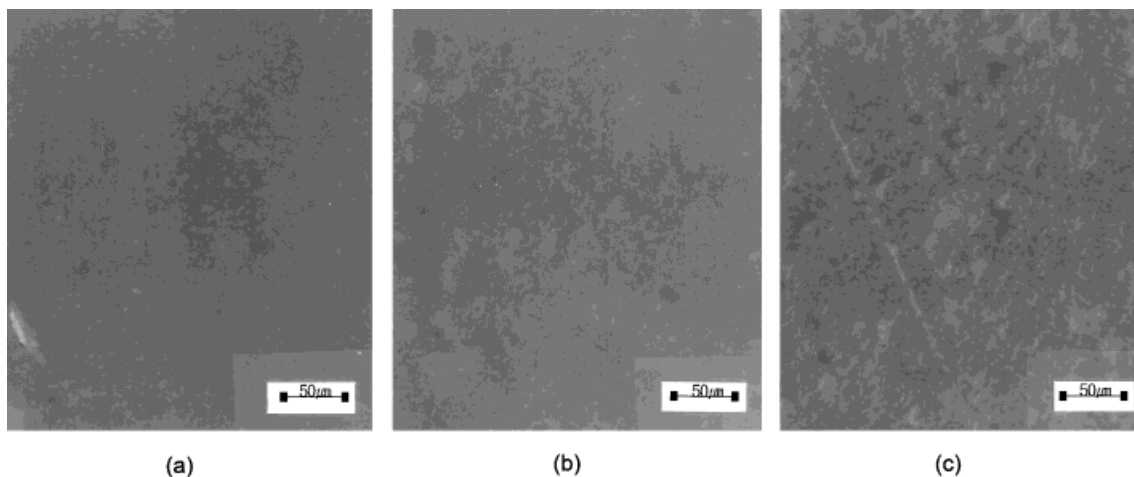


Figure 9 Video micrographs: (a) original film surface; (b) degraded surface of 20 μm thick film; and (c) degraded surface of 80 μm thick film.

degradation rate depended primarily on film thickness. On the other hand, surface erosion appears to depend much more on the degree of crystalline orientation in the films; at a given film thickness, higher orientations give lower rates of surface erosion, consequently causing a decrease in biodegradation rate.

CONCLUSION

The orientation in uniaxially drawn films was found to be determined by stretching conditions. At higher drawing rates and higher drawing temperatures, the deformation of spherulites occurred more easily, resulting in an increase of the degree of orientation. Biodegradation tests showed that the rate of microbial degradation was significantly dependent on the degree of orientation. The orientation of lamellar crystallites with their large flat faces parallel to the film surface depressed the biodegradability by reducing the possibility of preferential degradation of amorphous regions. Video microscopy observations indicated that the degree of orientation played a dominant role in determining the rate of surface erosion. Therefore, the combined effects of film thickness and degree of orientation should be carefully considered in evaluating biodegradability of drawn films.

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REFERENCES

1. Y. Tokiwa and T. Suzuki, *J. Appl. Polym. Sci.*, **26**, 441 (1981).
2. L. Tilstra and D. Johnsonbaugh, *J. Environ. Polym. Degrad.*, **1**, 257 (1993).
3. A. Iwamoto and Y. Tokiwa, *J. Appl. Polym. Sci.*, **52**, 1357 (1994).
4. F. Gassner and A. J. Owen, *Polymer*, **35**, 2233 (1994).
5. C. Bastioli, A. Cerutti, I. Guanella, G. C. Romano, and M. Tosin, *J. Environ. Polym. Degrad.*, **3**, 81 (1995).
6. E. Takiyama and T. Fujimaki, *Plastics*, **43**, 87 (1992).
7. Y. Tokiwa et al., *Polym. Prepr. Japan*, **42**, 3769 (1993).
8. C. V. Benedict, W. J. Cook, P. Jarrett, J. A. Cameron, S. J. Huang, and J. P. Bell, *J. Appl. Polym. Sci.*, **28**, 327 (1983).
9. P. J. Barham, A. Keller, E. L. Otun, and P. A. Holmes, *J. Mat. Sci.*, **19**, 2781 (1984).
10. P. J. Barham and A. Keller, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 69 (1986).
11. M. Kunioka, A. Tamaki, and Y. Doi, *Macromolecules*, **22**, 694 (1989).
12. Y. Doi, Y. Kanesawa, and M. Kunioka, *Macromolecules*, **23**, 26 (1990).

13. H. Nishida and Y. Tokiwa, *J. Environ. Polym. Degrad.*, **1**, 65 (1993).
14. P. A. Flournoy and W. J. Schaeffers, *Spectrochim. Acta*, **22**, 5 (1966).
15. A. de Vries, *J. Pure Appl. Chem.*, **53**, 1011 (1981).
16. J. F. Rabek, *Experimental Methods in Polymer Chemistry*, Wiley, New York, 1980.
17. G. Socrates, *Infrared Characteristic Group Frequencies*, Wiley, New York, 1994.
18. A. Cunningham, I. M. Ward, H. A. Willis, and V. Zichy, *Polymer*, **15**, 749 (1974).
19. G. LeBourvellee, L. Monnerie, and J. Jarry, *Polymer*, **27**, 856 (1986).
20. S. Sharma and A. Misra, *J. Appl. Polym. Sci.*, **34**, 2231 (1987).
21. K. H. Lee and C. S. P. Sung, *Macromolecules*, **26**, 3289 (1993).
22. S. A. Jabarin, *Polym. Eng. Sci.*, **31**, 1071 (1991).
23. M. K. Cox, in *Biodegradable Polymers and Plastics*, M. Vert et al., Ed., Royal Society of Chemistry, Cambridge, 1992, p. 95.