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Effect of Molecular Orientation on the Biodegradability of Aliphatic Polyester

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SUMMARY: The effect of morphological microstructure on the biodegradability of aliphatic polyester, poly(ε -caprolactone) (PCL) was studied in terms of crystallite size, crystallinity and amorphous and crystalline orientation factors. Microstructural changes during hydrolysis/biodegradation of the drawn PCL films were investigated by the conventional small and wide angle X-ray scattering methods. The lower was the draw ratio, the higher the hydrolytic degradability or biodegradability. With the increase of the hydrolysis time, the long period, at earlier stage, decreased; then slightly recovered and the crystallinity increased while the lamellar thickness remained unchanged. The amorphous orientation factors start to decrease at earlier stage and gradually go down to zero before the end of hydrolysis. In the case of crystalline orientation factor, although the values decrease with increasing hydrolysis time, they do not reach zero point. After the biodegradation for 60 days, crystallinity, crystal lateral size and lamellar thickness in all drawn PCL films decreased, and then it was confirmed that even crystalline regions were degraded for long term biodegradation test.

Introduction

Aliphatic polyester has been known as the environmental biodegradable polymer and there were so many reports on degradation mechanisms of aliphatic polyesters and their blends or copolymers with other common polymer. It is well known that hydrolytic attack could be initiated in the amorphous regions of the polymer[1-5]. The amorphous regions of polymer are more open and less dense than the crystalline regions and are more susceptible to be attacked by reacting species or solvent than the crystalline regions. By the way, it has been reported that the biodegradability was improved with not only the increase of amorphous contents but also the lower melting temperature due to low perfectness of crystals[6-8]. The biodegradability of crystalline polymers usually depends on the crystalline, amorphous microstructure such as size and perfectness of crystallites, crystallinity and degree of orientation[9-11]. There were, however, few reports on the relationship between microstructure and biodegradability.

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The aim of this work is to identify the effect of morphological microstructure in the amorphous and crystalline region on the biodegradability of aliphatic polyester, poly(ε - caprolactone) (PCL). The molecular orientations in crystalline and amorphous regions of drawn PCL (poly ε -caprolactone) were measured by the X-ray azumithal scanning method and the microstructural changes during degradation of the drawn films were investigated by the conventional small and wide angle X-ray scattering methods.

Experimentals

The PCL films were prepared by quenching in the cold water after being melt-pressed. The films, then, were drawn at the temperature of -55℃ which is a little higher than the glass transition temperature of PCL. The quenched film thickness was controlled so that the drawn films had the almost same thickness, because the surface area of samples is a very important factor of the degradation test. The different morphological parameters depending on two degradation test methods - the biodegradation method in activated sludge and the hydrolytic degradation method – were investigated. By using the wide angle X-ray azimuthal scan, the molecular orientation of amorphous and crystalline regions and the crystallinity of drawn samples were measured. A small angle X-ray diffractometer was used for investigating the variation of long period during the degradation.

Results and discussion

Tab. 1 denotes the fine structures of drawn PCL films measured by wide- and samll angle X-ray diffractometer. In the meridional SAXS intensity profiles (lamellar intensity) with draw ratio, the maximum of peak intensity moves to lower angle and the lamellar intensity increases with increasing draw ratio. It is well known that the increase of SAXS intensity is usually attributed to an increase in the crystallinity and crystalline order, and a decrease in interlamellar density[12,13]. In Tab. 1, the long period increases with draw ratio. From the value of long period and crystallinity, the lamellar thickness was calculated[14,15]. With increasing the draw ratio, the size of crystallite along the draw direction, lamellar thickness, appears to increase and that perpendicular to the draw direction to decrease. The crystallinity slightly increases as the draw ratio increases. WAXS profile obviously shows two sharp peaks, 110 plane and 200 plane reflections. The d-spacing of 110 and 200 planes was not changed by drawing PCL films. That is, drawing does not affect the crystal structure.

The variations of crystal orientation factor, f_c, and amorphous orientation factor, f_{am}, with drawing ratio were presented in Tab. 1. Orientation factor f_c drastically increases at the lower elongation and then the increment rate is reduced with further elongation. This is the typical trend of the oriented polymer.

Tab. 1. Fine structure parameters of drawn PCL films measured by wide- and small-angle X-ray diffractometer

Draw Ratio	Crystallinity (%)	f_c	f_{am}	Crystallite Size (Å)			Crystal Volume (Å^3)
				L (110)	L (200)	Lamellar Thickness	
1 (undrawn)	34.3	0	0	73.6	68.7	57.6	349,500
2	35.1	0.48	0.28	68.6	65.5	61.4	331,000
3	35.3	0.69	0.56	67.7	63.8	64.2	332,700
4	37.8	0.81	0.71	65.8	61.8	70.6	344,500
5	40.6	0.84	0.79	64.9	60.5	76.7	361,400

Fig. 1 shows the variation of degradability of PCL films with different draw ratio as a function of hydrolysis time. After 20 days hydrolysis, the films could not keep their shape so that the measurement of weight was impossible. The lower the draw ratio, the higher the degradability and the faster the starting of notable degradation. The molecular density in the amorphous region becomes high as the orientation increases. The higher molecular density might interrupt the penetration of active species between the molecular chains, resulting in the delayed starting point of the degradation and the less degradability when the draw ratio is high.

The characteristics of SAXS intensity profiles for the PCL films, such as the position of maximum intensity, curve shape and maximum intensity, depended on the hydrolysis time. The position of maximum intensity moved to higher angle with hydrolysis time, which means the decrease of the long period. The lamellar intensity increased with increasing hydrolysis time due to the increase of electron density difference between crystalline and amorphous regions by hydrolysis. The long periods were calculated and plotted versus hydrolysis time in Fig. 2. In the case of the films with 3 and 4 draw ratio, the values of long period, at earlier stage, decrease, and then slightly recover. The same phenomenon was reported by R. E. Cameron$^{16)}$ for the poly(glycolic acid), even though undrawn, molded

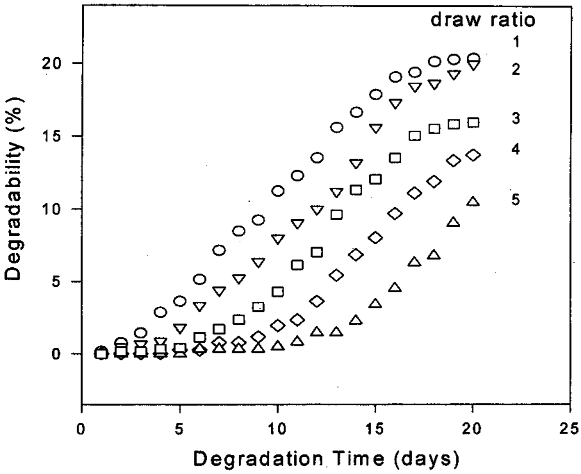

Fig.1. The variation of degradability of the PCL films with various draw ratio. The degradability by hydrolysis was calculated from the weight loss.

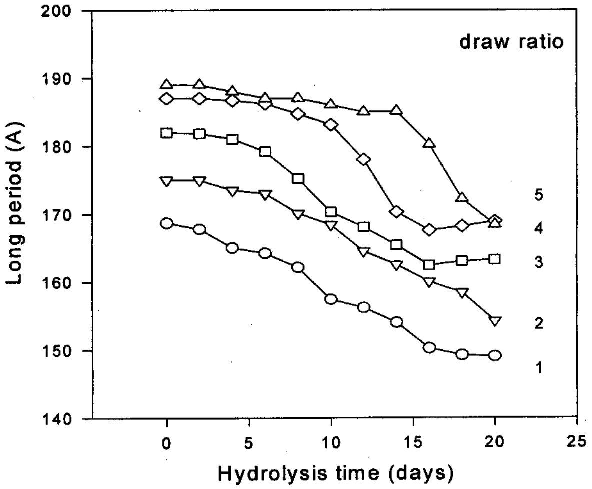

Fig.2. The variation of long period for the PCL films with hydrolysis time. The values are obtained by applying the Bragg equation to the peak positions of the Lorentz corrected SAXS intensity profiles.

sample was used. Our undrawn or little drawn samples showed no recovery of long period with the hydrolysis time. In the process of hydrolytic degradation, the molecular chains in amorphous regions were selectively attacked and degraded. Accordingly, the long period was reduced because the tie molecules in amorphous regions were removed. However, at the final stage of hydrolysis, the long period was slightly increased due to the volume increase of degraded amorphous chains and voids. The reason this phenomenon could not be observed in the undrawn or low-drawn samples might be that they have comparatively low density in amorphous region. .

Fig. 3 shows the crystallinity variation with different draw ratio as hydrolysis time increases. It is sure that the crystallinity increases due to the removal of molecular chains in amorphous region. After 20 days hydrolysis, the crystallinity reached reasonable values, meaning that these crystallinities were a little lower than those calculated from the weight loss after 20 days hydrolysis in the assumption that the whole weight loss corresponds to the amorphous regions. On the proceeding of the hydrolysis, the variation of lamellar thickness was traced by using the crystallinity of each sample measured from WAXS intensity profiles and long period from SAXS intensity profiles (Fig. 4). Lamellar thickness remained unchanged for all the samples during hydrolysis.

Even though it was possible that the constraints between the crystallites could be reduced as the tie molecules in amorphous region were removed, the effect of degradation on the unit cell dimensions was almost negligible in this work. That is, the crystal density was unchanged by the degradation. We could get some information about average lateral crystal size from the width of the WAXS peaks 110 and 200 using Debye Scherrer equation. The slight decrease in the width of 110 and 200 is observed with hydrolysis time. It means that the average lateral crystal size increased because so smaller crystallites were more readily removed due to their large surface area.

In Fig. 5, the changes of amorphous orientation factors were represented with the hydrolysis time. The amorphous orientation factors start to decrease at earlier stage and continually go down to zero before the end of hydrolysis, meaning that the orientation of molecular chains in amorphous region randomized from the earlier stage of hydrolysis. In the case of crystalline orientation factor in Fig. 6, although the values decrease with increasing hydrolysis time, they do not reach zero point. It means that the crystallites keep their orientation to some extent after hydrolytic degradation.

The biodegradability was evaluated by the amount of CO_2 creation from PCL in the activated sludge. The biodegradation behavior is similar to the results of hydrolytic degradation. The lower was the draw ratio, the higher the degradability. Tab. 2 denotes the change of fine structure for drawn PCL films measured by WAXS and SAXS after

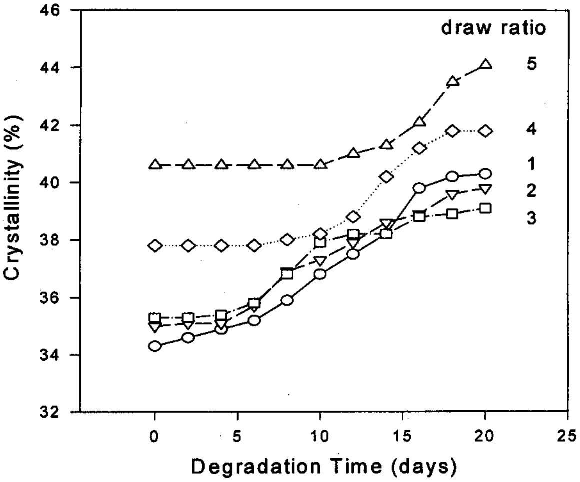

Fig.3. The crystallinity of the PCL films calculated from the WAXS intensity profiles for samples with different draw ratio.

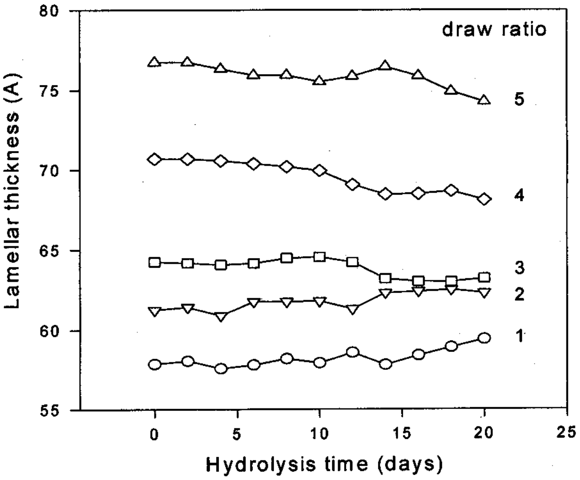

Fig.4. The variation of lamellar thickness for the PCL film with hydrolysis time. The thickness were calculated from the values of long period and crystallinity

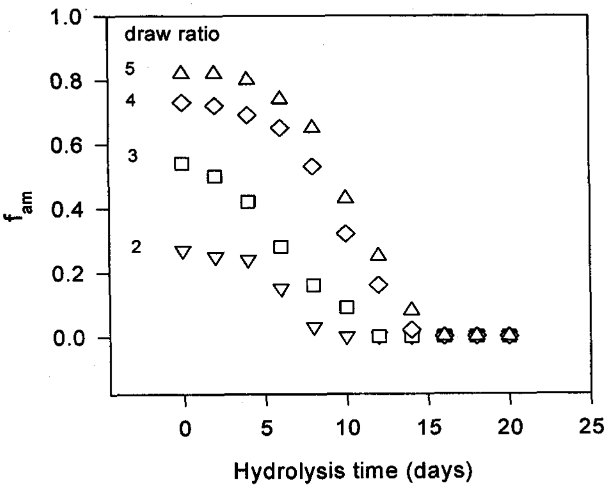

Fig.5. The variation of amorphous orientation function for PCL films depending on the hydrolysis time.

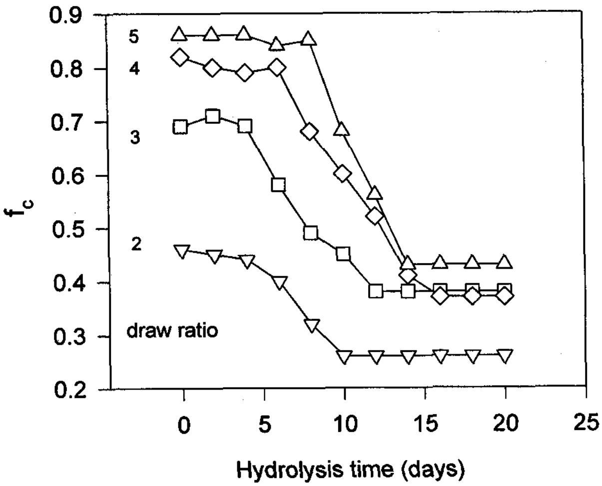

Fig.6. The variation of crystalline orientation function for PCL films depending on the hydrolysis time.

biodegradation in activated sludge. In the course of hydrolytic degradation, we suggested that the amorphous regions were mainly degraded including some very small and imperfect crystallites. So, the average lateral crystallite size increased with hydrolysis time. After the biodegradation for 60 days, however, crystallinity, crystal lateral size and lamellar thickness in all drawn PCL films decreased. Therefore, we confirmed that even crystalline regions were degraded for long term biodegradation test.

Tab. 2. Fine structures of drawn PCL films before and after biodegradation in activated sludge measured by wide- and small-angle X-ray diffractometer

Draw Ratio	Degradation Test	Quenched film				
		Crystallinity (%)	Crystallite Size (Å)			Crystal Volume (Å^3)
			L (110)	L (200)	Lamellar Thickness	
1	Before	34.3	73.6	68.7	57.6	349,500
	After	31.8	69.2	63.1	53.1	277,800
2	Before	35.1	68.6	65.5	61.4	331,000
	After	33.6	62.1	61.3	55.4	253,000
3	Before	35.3	67.7	63.8	64.2	332,700
	After	32.1	62.2	58.9	60.1	262,900
4	Before	37.8	65.8	61.8	70.6	344,500
	After	34.5	58.4	54.3	64.3	244,700
5	Before	40.6	64.9	60.5	76.7	361,400
	After	33.4	57.1	55.4	69.6	264,200

Conclusion

The effect of morphological microstructure on the biodegradability of aliphatic polyester, poly(ε -caprolactone) (PCL) was studied in terms of crystallite size, crystallinity and amorphous and crystalline orientation factors. The lower was the draw ratio, the higher the degradability. The values of long period, at earlier stage, decrease, and then slightly recover. The long period was reduced because the tie molecules in amorphous regions were removed. However, at the final stage of hydrolysis, the long period was slightly increased due to the volume increase of degraded amorphous chains and voids. The crystallinity increases due to the removal of molecular chains in amorphous region and lamellar thickness remained unchanged for all the samples during hydrolysis.

The amorphous orientation factors start to decrease at earlier stage and gradually go down to zero at the middle term of hydrolysis, meaning that the orientation of molecular chains in amorphous region randomized from the earlier stage of hydrolysis. In the case of crystalline orientation factor, although the values decrease with increasing hydrolysis time, they do not reaches to zero point. It means that the crystallites keep their orientation to some extent after hydrolytic degradation.

The behavior of the biodegradation in activated sludge is similar to the results of hydrolytic degradation. The lower was the draw ratio, the higher the degradability. After the biodegradation for 60 days, however, crystallinity, crystal lateral size and lamellar thickness in all drawn PCL films decreased. Therefore, we confirmed that even crystalline region was affected in the long termed biodegradation test.

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