10F06

The Effect of Molecular Orientation on Degradation of Poly(ε -caprolactone)

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1. 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]. The biodegradability of crystalline polymers usually depends on the crystalline, amorphous microstructure such as size and perfectness of crystallites, crystallinity and degree of orientation. There were, however, few reports on the relationship between microstructure and biodegradability.

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 changinsing degradation of the drawn films were investigated by the conventional small and wide angle X-ray scattering methods.

2. Experimetals

The PCL films were prepared by quenching in the cold water after being melt-pressed. The films, then, were drawn at the temperature of -5 5℃ 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.

3. Results and Discussion

Tab. 1 denotes the fine structures of drawn PCL films measured by wide- and samll angle X-ray diffractometer. 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. The variations of crystal orientation factor, f_c, and amorphous orientation factor, f_{am}, with drawing ratio were presented in Tab. 1, too. 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.

Fig. 1 shows the variation of degradability of PCL films with different draw ratio as a function of hydrolysis time. 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.

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

Draw Ratio	Crystallinity (%)	fc	fam	Crystallite Size (Å)			Crystal Volume (Å3)
				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

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.

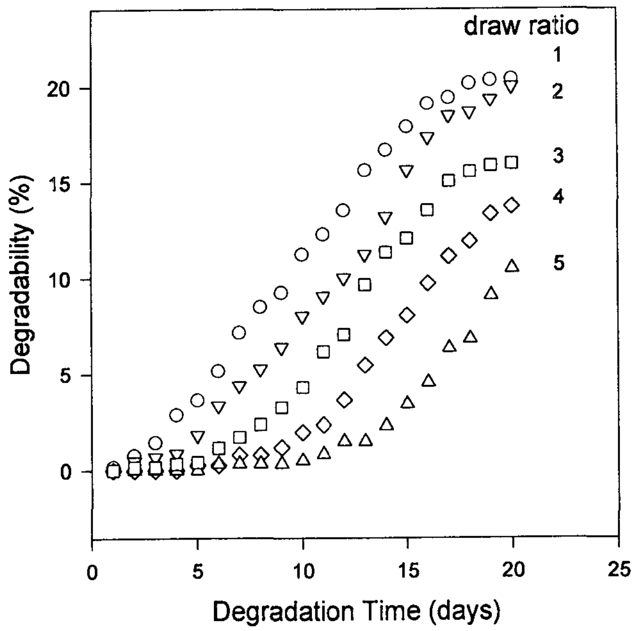

Fig. 1. The variation of degradability of the PCL films with various draw ratio. The degradability by hydrolysis was calculated from the weight loss.

4. Reference

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