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Photodegradation Behavior of Polycaprolactone-Poly(ethylene glycol) Block Copolymer

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Abstract: The biodegradation behavior *in vitro* and *in vivo* of polycaprolactone-poly (ethylene glycol) block copolymer (PCE) was reported in detail. In this paper, photodegradation test of PCE was performed by exposure to UV light. The mechanical properties and the inherent viscosity of PCE samples which are subjected to photodegradation were determined. The experimental results indicated that poly (ethylene glycol) (PEO) segment in PCE copolymer is photosensitive. The photodegra-dation rate of the PCE was increased with increasing poly (ethylene glycol) content.

Keywords: Photodegradation, polycaprolactone -poly (ethylene glycol).

Polycaprolactone-poly (ethylene glycol) (PCE) block copolymer is a biodegradable polymer. The biodegradation characterisation *in vitro* and *in vivo* of the PCE was reported[1,2]. It was found that the degradation rate of the PCE was increased with increasing poly (ethylene glycol) content, temperature, acidity and alkalinity and it was accelerated by the presence of enzyme. The fastest degradation rate was observed in the physiological condition of the sample being implanted in the body of animals. So PCE copolymer possesses a good prospect to be bio-medical materials[3].

Most polymers are subjected to photooxidative degradation upon exposure to sunlight, and additives and impurities catalyze the breakage of the polymer chains by a series of UV initiated free radical reaction[4]. For example, the addition of photosensitive species, such as carbonyl groups or metal complexes can accelerate these processes. Thus we tried to add photosensitizer benzophenone into the PCE block copolymer to make it photobiodegradable . The experimental results are surprising, that the PCE block copolymer can be easily photodegraded without any photosensitizer. In this paper, the photodegradation characterisation of the PCE are determined. The dependence of photodegradation rate on composition of the PCE block copolymer is discussed. A photo-biodegradable polymer-- PCE was obtained.

The PCE block copolymer was synthesized by copolycondensation of a prescribed amount of ε-caprolactone (CL) and poly(ethylene glycol) (EO) at 160℃with stannous octate as the catalyst for 6-8 hrs[1]. A solution of 8% polymer and (with 0.3% or without benzophenone) in chloroform was cast on a clean glass plate to obtain polymer film for photodegradation test.

The photodegradation test was carried out in Xenotest Light and Weather Fastness Testor with a 450 xenon lamp as light source.

After a certain irradiation time interval, the PCE copolymer film was removed and mechanical properties and inherent viscosity of PCE films were determined. The measurement of the mechanical properties of PCE samples was performed by a Shinkch Tensile Test machine.

The viscosity η of the PCE copolymer at a concentration (C) of 0.5 g/dl in chloroform was determined by a Ubbelodhe viscometer at 30℃ and its inherent viscosity was calculated from η_r by "one point method"

$$[\eta] = 2(\eta_{sp} - \ln \eta_r) / C$$

where η and η_o are the viscosity of solution and solvent respectively, $\eta_r = \eta / \eta_o$, $\eta_{sp} = \eta_r - 1$, and $[\eta]$ expressed in dl/g.

The molecular weight of PCE was measured with Waters high-performance liquid chromatograph, model 510 at 35℃ at a chloroform flow rate of 1 ml/min through the Shodex GPC KF-800 series column. The number-average molecular weight (M_n), the weight-average molecular weight (M_w) and the molecular weight distribution (M_w/M_n) of PCE copolymers were calibrated by using standard polystyrene samples.

Effects of photosensitive additive benzophenone on photodegradation of PCL homopolymer and PCE copolymer

For making photodegradable materials, 0.3 wt% benzophenone was added into PCL homopolymer and PCE copolymer. The results of photodegradation of PCL and PCE are shown in **Table 1**.

Table 1. Dependence of mechanical properties of PCL and PCE on irradiation time*

Irradiation time (hr)	PCL		PCL + 0.3% Benzophenone		PCE		PCE + 0.3% Benzophenone	
	Retention percent (%)							
	T.S.	E	T.S.	E	T.S.	E	T.S.	E
0	100	100	100	100	100	100	100	100
30	96.1	52.3	104.5	94.6	55.4	23.3	50.5	36.8
54	95.1	78.0	107.0	108.0	19.8	13.3	36.9	21.1
78	91.1	44.6	99.2	56.8				

*Irradiation condition: a 4500W Xe lamp under 6-14RH% at 30℃

T.S.: Tensile Strength; E: Elongation at break

Table1 shows that photosensitizer benzophenone did not accelerate photodegradation of PCL and PCE. However, it is found unexpectedly that the PCE block copolymer itself can be readily photodegraded. After 78 hours of irradiation at 30 ℃ under UV light, the change of mechanical properties of PCL homopolymer is not obvious, but PCE block copolymer lost almost completely. At the same time the inherent viscosity of PCL has no change, but decreased by 38% for PCE. Obviously, the photodegradability of PCE might be caused by the component of poly (ethylene glycol) (PEO) in the copolymer. To prove this important finding, a more detailed investigation on photodegradation behavior of PCE was carried out.

Table 2. Composition of PCE copolymers

Sample	Composition [CL/EO] (mol%)		[η](dl/g)
	in feed	in polymer*	
PCL-1	100/0		1.06
PCE-2	90/10	89.5/10.5	1.79
PCE-3	80/20	79.5/20.5	1.06
PCE-4	70/30	69.2/30.8	0.95
PCE-5	60/40	59.4/40.6	0.94

* Calculated buy ^{1}H-NMR

Effect of composition on Photodegradation behavior of PCE block copolymer

A series of PCE copolymers with different compositions were synthesized as shown in **Table 2**. The PCE copolymers were exposed to 4500W of Xe lamp. Samples were removed periodically to determine inherent viscosity and measure tensile properties. The results are shown in **Figure 1** and **2**. **Figure 1** illustrates that the tensile strength of the samples in which polyethylene glycol [EO] unit content is below 30% (mol%) was essentially unchanged, but that of samples with [EO] content of 30 or 40 mol%, decreased by 50-60 %.

Figure 2 indicates more obviously that elongation at break of the samples decreased with the increase of content of the EO unit in PCE copolymer. GPC results of PCE ([CL]/[EO] = 60/40) film photodegraded over irradiation time are given in **Figure3**. The photodegraded PCE copolymer shows a shift of molecular weight peak toward lower

Figure 1. The changes in tensile strength of PCL and PCE samples with irradiation time by a 4500W of Xe lamp at 25℃ CL/EO (mol%) -■- 100/0; -●- 90/10; -▲- 80/20; -∀- 70/30; -◆- 60/40

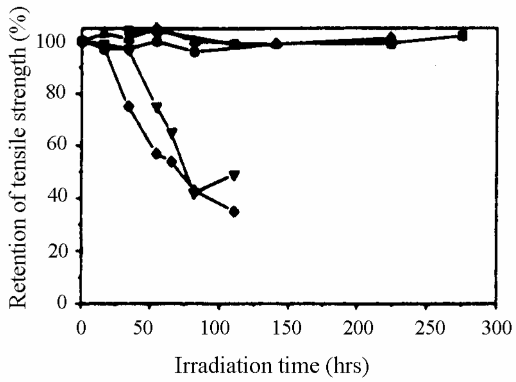


Figure 2. The changes in elongation at break of PCL and PCE samples with irradia- tion time by a 4500W of Xe lamp at 25℃ CL/EO (mol%) -■- 100/0; -●- 90/10; -▲- 80/20; -∀- 70/30; -◆- 60/40

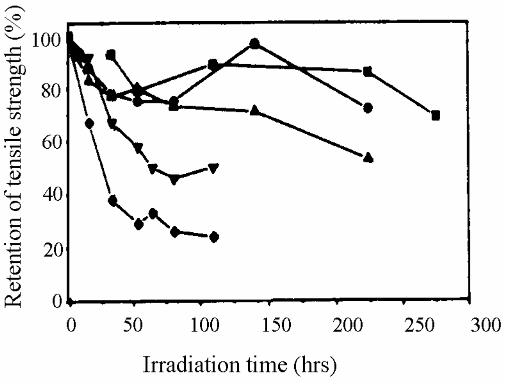


Figure 3. GPC results of PCE-5 film photodegraded over irradiation time

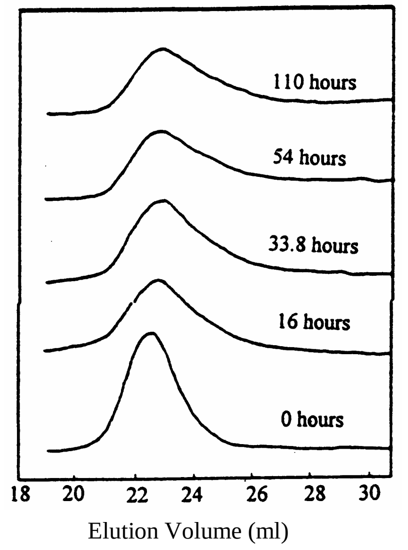
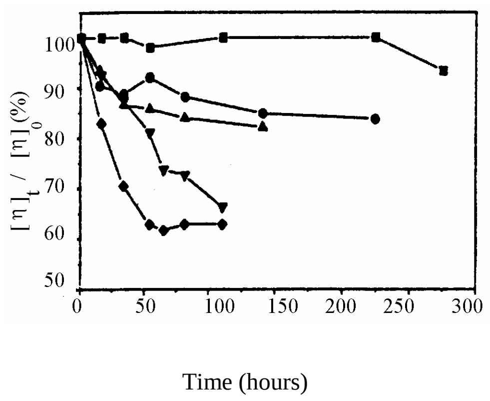


Figure 4. The changes in inherent viscosity of PCL and PCE samples with irradiation time by a 4500W of Xe lamp at 25℃ CL/EO (mol%) -■- 100/0; -●- 90/10;-▲- 80/20; -▼ 70/30; -◆- 60/40



molecular weight and a wide molecular weight distribution with irradiation time. The results of inherent viscosity determination are shown in **Figure 4**. It revealed that the inherent viscosity of PCL homopolymer was entirely unchanged even after UV irradiation for 224 hrs, but that of PCE copolymer rapidly decreased with increasing irradiation time and component of polyethylene glycol in PCE copolymers. The experimental result above described clearly illustrate that photodegradation rate of PCE depends on the content of poly (ethylene glycol) segment in PCE, and the latter is photosensitive. It can be expected that with suitable content of EO in PCE, a new photo-biodegradable polymer would be obtained. The photodegradation mechanism of PCE is being in investigation and will be reported elsewhere.

Acknowledgments

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