CHAPTER 5

IN VITRO BIODEGRADATION OF HOMO- AND COPOLYMERS

5.1 Experimental Procedure

The samples originally chosen for this study were poly(δ-valerolactone), synthesized in bulk at 100°C using stannous octoate as initiator, and poly(glycolic acid) and poly(glycolic acid-co-valerolactone) synthesized at 150°C using stannous octoate as initiator.

All glassware items were sterilized before use by steam autoclaving at 120°C for 20 mins. In this research project, a 0.2 M phosphate buffer of pH 7.40 was used as the immersion medium. This type of immersion medium is commonly used in polymer biodegradation studies [55].

Phosphate Buffer Immersion Medium (pH 7.40)

A 0.2 M phosphate buffer of pH 7.40 was prepared from anhydrous disodium hydrogen orthophosphate, Na_2HPO_4 (salt), and sodium dihydrogen phosphate 2-hydrate, $NaH_2PO_4.2H_2O$ (acid). From the Henderson-Hasselbach Equation [5.1] :

$$pH = pKa + \log\frac{[Salt]}{[Acid]} \qquad (5.1)$$

$$pH = pKa + \log\frac{[Na_2HPO_4]}{[NaH_2PO_4.2H_2O]} \qquad (5.2)$$

and the "Handbook of Chemistry and Physics" [56], the pKa of this phosphate mixture is 7.21. By calculation, a 0.2 M phosphate buffer (pH 7.40) was prepared from 17.2584 g of Na_2HPO_4 and 12.2401 g of $NaH_2PO_4.2H_2O$ dissolved in 1 l of deionized water. The pH of the solution, which was almost 7.40, was adjusted to exactly 7.40 with 2 M NaOH.

Sample Preparation

All the samples were made in the physical form of monofilament fibres (diam. ≈ 0.5 mm) using a simple prototype melt spinning apparatus [57]. It was found that all of the samples could be extruded in fibre-form except for the PGA samples. The reason why the PGA could not be melt spun was probably due to a combination of factors, most notably the polymer's low molecular weight and its thermal instability at the processing temperature. Therefore, only the PVL and P(GA-co-VL) samples were studied with respect to their in vitro biodegradation. A total of 72 samples (3 sets of 24) were dried in a vacuum oven (at 30°C for the PVL and at 70°C for the P(GA-co-VL) samples) to constant weight and their weights accurately recorded. They were then immersed individually in 30 ml screw-top glass bottles, each containing 20 ml of the pH 7.40 phosphate buffer. The bottles were then immediately placed in an incubator (see Fig. 5.1), thermostatically controlled at 37.0 ± 0.5°C, for the in vitro biodegradation experiments which lasted for a total of 24 weeks.

Sampling Procedure

At time intervals of 1 week, one set of 3 bottles was removed from the incubator and the samples filtered off, washed carefully with deionized water and dried to constant weight in a vacuum oven at room temperature for PVL and 70°C for P(GA-co-VL). Their weights were accurately recorded. Various properties of the samples were then tested, such as % weight retention, melting point, heat of fusion and intrinsic viscosity. The pH of the medium was also re-measured since the hydrolytic mechanism of polyester biodegradation is well-known to be pH-dependent.

Fig. 5.1 : Incubator used for in vitro biodegradation experiments.

5.2 Property Changes from Biodegradation

5.2.1 Weight Loss Profiles

An analytical balance, accurate to ± 0.0001 g, was used to weigh the samples. After vacuum drying to constant weight, the % weight retention was calculated as follows :

$$\% \text{ weight retention} = \frac{w_f \times 100\%}{w_0} \qquad (5.3)$$

where :

W_0 = initial dry weight of sample (before immersion)
W_f = final dry weight of sample (after immersion)

The weights and % weight retentions are shown in Tables 5.1-5.3 for each of the 3 sets of samples. The corresponding weight loss profiles are plotted in Fig. 5.2.

Table 5.1 : Weights and % weight retentions of PVL fibres immersed in pH 7.40 phosphate buffer solution at 37°C.

Time (weeks)	Initial Weight ± 0.0001 (g)	Final Weight ± 0.0001 (g)	% Weight Retention ± 0.1 (%)
1	0.4177	0.4160	99.6
2	0.4244	0.4223	99.5
3	0.4029	0.4000	99.3
4	0.3926	0.3891	99.1
5	0.4025	0.3953	98.2
6	0.4106	0.4020	97.9
7	0.4188	0.4083	97.5
8	0.4079	0.3965	97.2
9	0.4036	0.3903	96.7
10	0.4131	0.3933	95.2
11	0.3994	0.3742	93.7
12	0.4020	0.3714	92.4
13	0.4054	0.3725	91.9
14	0.4173	0.3764	90.2
15	0.4094	0.3660	89.4
16	0.4110	0.3600	87.6
17	0.4246	0.3622	85.3
18	0.4057	0.3424	84.4
19	0.4063	0.3380	83.2
20	0.4113	0.3373	82.0
21	0.4005	0.3268	81.6
22	0.4361	0.3559	81.5
23	0.4054	0.3284	81.0
24	0.4083	0.3283	80.4

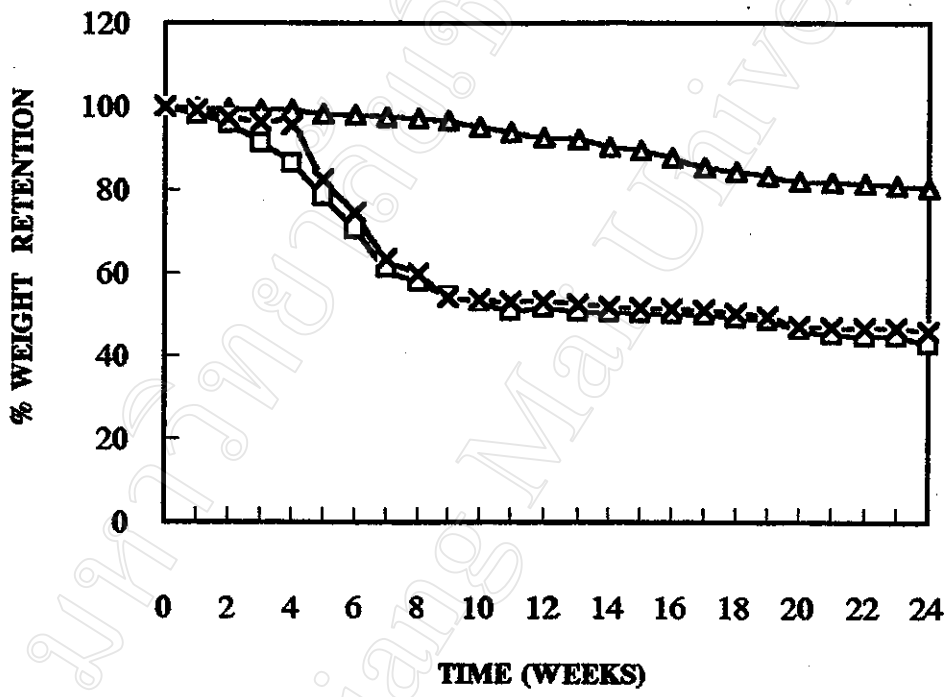
Table 5.2 : Weights and % weight retentions of P(GA-co-VL) fibres, comonomer mole ratio 2:1, immersed in pH 7.40 phosphate buffer solution at 37°C.

Time (weeks)	Initial Weight ± 0.0001 (g)	Final Weight ± 0.0001 (g)	% Weight Retention ± 0.1 (%)
1	0.4089	0.4007	98.0
2	0.4051	0.3805	95.9
3	0.4080	0.3717	91.1
4	0.4071	0.3517	86.4
5	0.4045	0.3171	78.4
6	0.4045	0.2852	70.5
7	0.4057	0.2481	61.2
8	0.4039	0.2331	57.7
9	0.4115	0.2239	54.4
10	0.4068	0.2160	53.1
11	0.4006	0.2043	51.0
12	0.4053	0.2095	51.7
13	0.4041	0.2081	50.5
14	0.4095	0.2100	50.3
15	0.3989	0.2046	50.4
16	0.4091	0.2050	50.1
17	0.4019	0.2001	49.8
18	0.4025	0.1976	49.1
19	0.4033	0.1960	48.6
20	0.4037	0.1873	46.4
21	0.4101	0.1855	45.2
22	0.4107	0.1836	44.7
23	0.3996	0.1782	44.6
24	0.4049	0.1741	43.0

Table 5.3 : Weights and % weight retentions of P(GA-co-VL) fibres, comonomer mole ratio 1:1, immersed in pH 7.40 phosphate buffer solution at 37°C.

Time (weeks)	Initial Weight ± 0.0001 (g)	Final Weight ± 0.0001 (g)	% Weight Retention ± 0.1 (%)
1	0.4019	0.3987	99.2
2	0.4033	0.3932	97.5
3	0.4091	0.3989	96.4
4	0.4089	0.3909	95.6
5	0.3944	0.3250	82.4
6	0.4113	0.3064	74.5
7	0.4090	0.2593	63.4
8	0.4060	0.2428	59.8
9	0.4031	0.2189	54.3
10	0.3991	0.2143	53.7
11	0.4027	0.2142	53.2
12	0.4160	0.2209	53.1
13	0.4072	0.2134	52.4
14	0.4004	0.2082	52.0
15	0.4128	0.2134	51.7
16	0.3979	0.2041	51.3
17	0.4260	0.2177	51.1
18	0.4071	0.2052	50.4
19	0.4002	0.1985	49.6
20	0.4201	0.1983	47.2
21	0.4199	0.1974	47.0
22	0.3989	0.1867	46.8
23	0.4084	0.1907	46.7
24	0.4096	0.1880	45.9

WEIGHT LOSS PROFILES



Δ = PVL □ = P(GA-co-VL) 2:1 × = P(GA-co-VL) 1:1

Fig. 5.2 : Comparison of the weight loss profiles of the PVL and P(GA-co-VL) fibres during the period of the in vitro biodegradation experiments.

The results in Tables 5.1-5.3/Fig. 5.2 show the different weight loss profiles of the PVL and P(GA-co-VL) samples. The weight loss from the PVL samples over the 24-week duration of the experiment was slow and continuous. In contrast to this, the weight loss profiles of the P(GA-co-VL), comonomer mole ratios 2:1 and 1:1, showed sudden increases in weight loss after about weeks 2 and 4 respectively. When comparing the P(GA-co-VL) samples, the P(GA-co-VL) 2:1 showed a faster weight loss than the 1:1. In other words, it is clear that the weight loss profile is composition-dependent. As the VL content in the copolymer increases, the rate of weight loss decreases. This is as would be expected from the lower hydrophilicity and hydrolysability of the VL units compared with the GA units. The weight loss profile of PVL emphasizes this point, with about 80% of the weight still remaining at the end of the 24 weeks immersion period.

With reference to previous work carried out under identical conditions, it is interesting to compare the weight loss profiles of the P(GA-co-VL) samples and PGA (DEXON) sutures from a previous study [58].

Table 5.4 : Comparison of the % weight retentions of the P(GA-co-VL) fibres from this study and commercial PGA (DEXON) sutures from a previous study [58] after immersion in a pH 7.40 phosphate buffer solution at 37°C.

Time (weeks)	% Weight Retention ±0.1 %		
	P(GA-co-VL) 2:1*	P(GA-co-VL) 1:1**	DEXON sutures***
1	98.0	99.2	99.9
2	95.9	97.5	9708
3	91.1	96.4	8809
4	86.4	95.6	75.8
5	78.4	82.4	51.7
6	70.5	74.5	34.9
7	61.2	63.4	22.0
8	57.7	59.8	18.5
9	54.4	54.3	3.4
10	53.1	53.7	1.0
11	51.0	53.2	-
12	51.7	53.1	-
13	50.5	52.4	-
14	50.3	52.0	-
15	50.4	51.7	-
16	50.1	51.3	-
17	49.8	51.1	-
18	49.1	50.4	-
19	48.6	49.6	-
20	46.4	47.2	-
21	45.2	47.0	-
22	44.7	46.8	-
23	44.6	46.7	-
24	43.0	45.9	-

* **P(GA-co-VL) 2:1 data taken from Table 5.2**

** **P(GA-co-VL) 1:1 data taken from Table 5.3**

*** **DEXON data taken from Reference [58]**

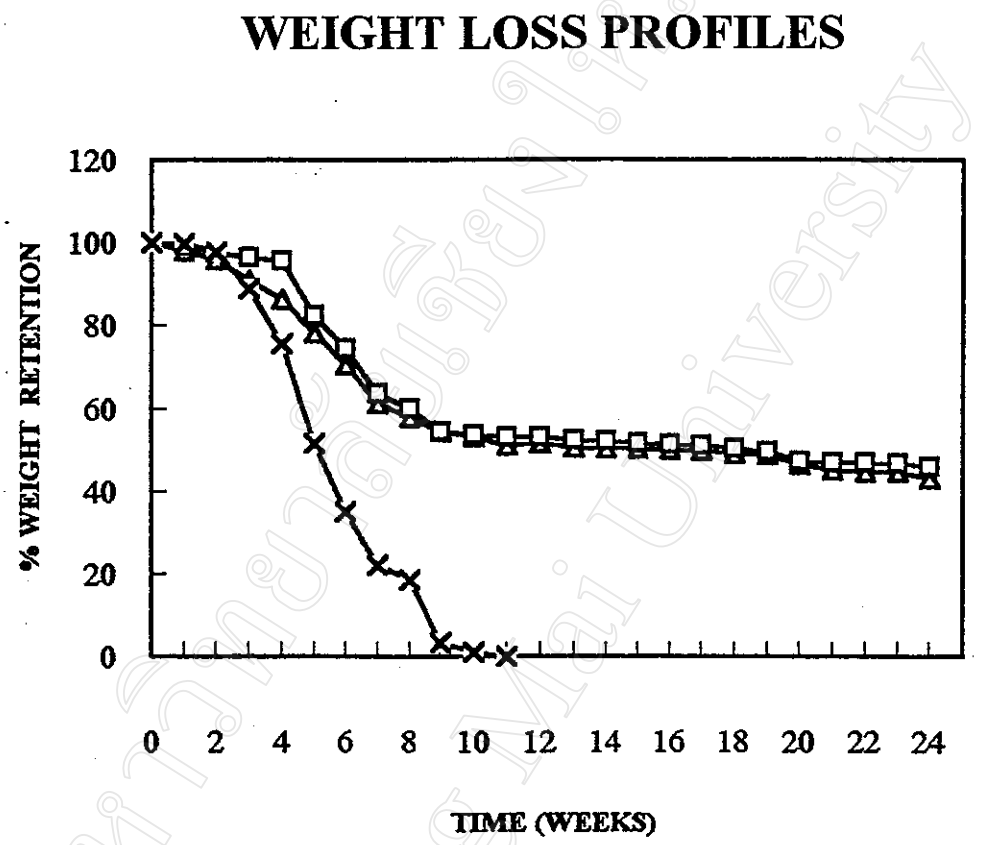


Fig. 5.3 : Comparison of the in vitro weight loss profiles of the P(GA-co-VL) fibres from this study and commercial PGA (DEXON) sutures from a previous study [58] after immersion in a pH 7.40 phosphate buffer solution at 37°C.

The results shown in Table 5.4/Fig. 5.3 show there to be very little weight loss in the PGA (DEXON) sutures and the P(GA-co-VL) samples during the first 2 weeks. However, after about week 2, the PGA (DEXON) sutures started to lose weight rapidly while there was no significant weight decrease in the 2:1 and 1:1 P(GA-co-VL) copolymers until after about weeks 2 and 4 respectively.

The PGA (DEXON) sutures then showed an increasing weight loss from 2-5 weeks followed by a gradual slowing down until weight loss was completed at week 10. In marked contrast to this, as the time progressed, weight loss from the P(GA-co-VL) fibres slowed down considerably, such that about 40-50 % weight still remained at the end of the 24-week immersion period.

Similarly, it is interesting to compare the weight loss profiles of the P(GA-co-VL) samples with commercial P(GA-co-TMC) (MAXON) sutures from a previous study [14]. The results are shown in Table 5.5 and Fig.5.4.

These differences in the rates of weight loss are believed to be due to a combination of both chemical and physical factors. Chemically, the inclusion of VL units will certainly slow down the hydrolysis rate of PGA, as previously mentioned. However, since the VL contents in the P(GA-co-VL) copolymers are relatively small, especially in the 1:1 sample, this alone cannot account for the large differences in their profiles. Instead, it is more likely to be physical characteristics such as geometric configuration and surface-to-bulk ratio which determine the weight loss profile. In this respect, PGA (DEXON), being a braided multifilament suture, would have the highest surface-to-bulk ratio and would therefore allow greater access of water to the polymer surface. Since hydrolysis must start at the surface, it is therefore understandable that DEXON hydrolyses much faster. The P(GA-co-VL) fibres studied here, being monofilaments, are therefore more comparable with the MAXON sutures which are also monofilaments.

Table 5.5 : Comparison of the % weight retentions of the P(GA-co-VL) fibres from this study and commercial P(GA-co-TMC) (MAXON) sutures from a previous study [14] after immersion in a pH 7.40 phosphate buffer solution at 37°C.

Time (weeks)	% Weight Retention ±0.1 %		
	P(GA-co-VL) 2:1*	P(GA-co-VL) 1:1**	MAXON sutures***
1	98.0	99.2	100.0
2	95.9	97.5	100.0
3	91.1	96.4	99.8
4	86.4	95.6	99.6
5	78.4	82.4	98.9
6	70.5	74.5	98.2
7	61.2	63.4	97.2
8	57.7	59.8	95.6
9	54.4	54.3	90.4
10	53.1	53.7	84.5
11	51.0	53.2	80.7
12	51.7	53.1	76.9
13	50.5	52.4	75.1
14	50.3	52.0	70.5
15	50.4	51.7	67.3
16	50.1	51.3	50.3
17	49.8	51.1	47.3
18	49.1	50.4	32.6
19	48.6	49.6	30.1
20	46.4	47.2	30.0

* **P(GA-co-VL) 2:1 data taken from Table 5.2**

** **P(GA-co-VL) 1:1 data taken from Table 5.3**

*** **MAXON data taken from Reference [14]**

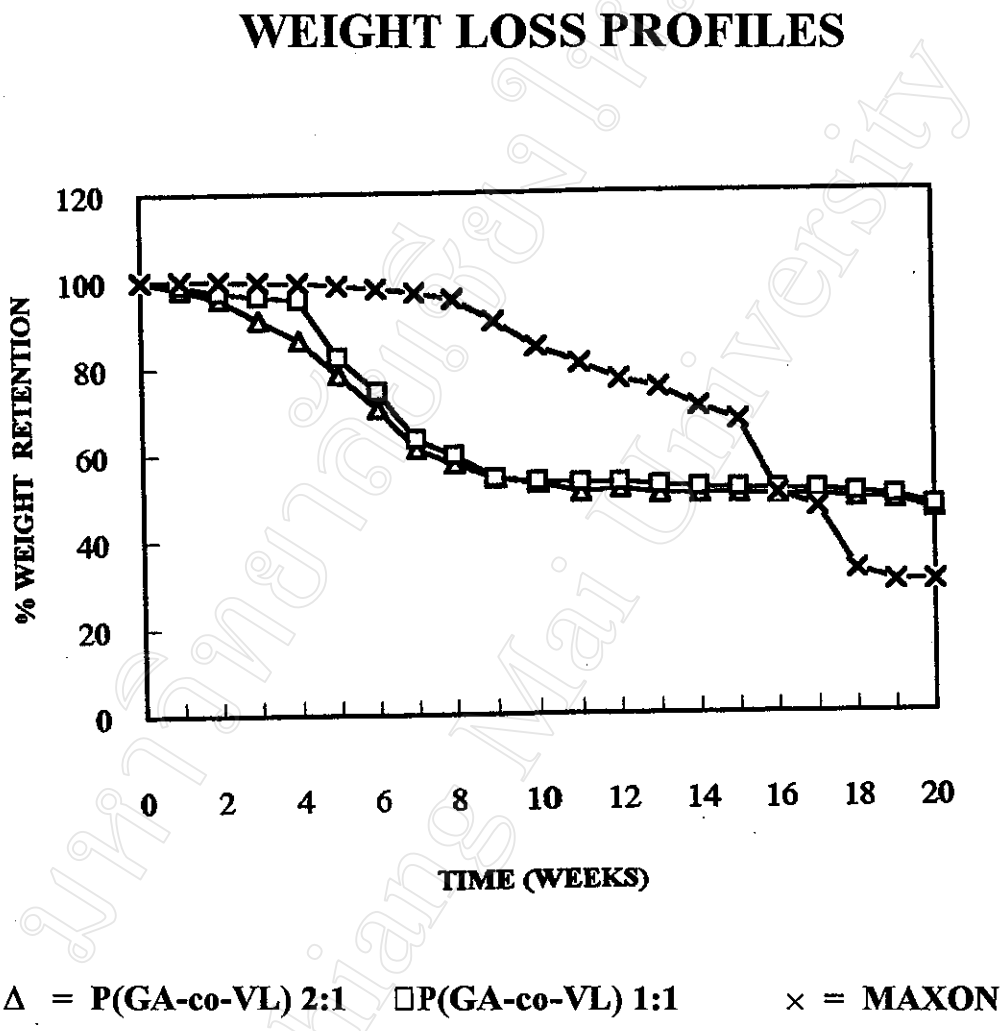


Fig. 5.4 : Comparison of the in vitro weight loss profiles of the P(GA-co-VL) fibres from this study and commercial P(GA-co-TMC) (MAXON) sutures from a previous study [14] after immersion in a pH 7.40 phosphate buffer solution at 37°C.

Finally, an interesting comparision can also be made between the weight loss profiles of the P(GA-co-VL) fibres from this study and the compressed P(GA-co-VL) discs from a previous study [33]. This comparison is made in Table 5.6 and Fig. 5.5.

Table 5.6 : Comparison of the % weight retentions of the P(GA-co-VL) fibres from this study and P(GA-co-VL) discs from a previous study [33] after immersion in a pH 7.40 phosphate buffer solution at 37°C.

Time (weeks)	% Weight Retention ± 0.1 %			
	FIBRES		DISCS	
	P(GA-co-VL) 2:1*	P(GA-co-VL) 1:1**	P(GA-co-VL) 2:1***	P(GA-co-VL) 1:1****
1	98.0	99.2	90.6	89.5
2	95.9	97.5	77.7	82.9
3	91.1	96.4	76.0	82.5
4	86.4	95.6	74.0	79.9
5	78.4	82.4	71.6	80.8
6	70.5	74.5	70.9	78.8
7	61.2	63.4	69.4	76.6
8	57.7	59.8	68.2	74.8
9	54.4	54.3	65.6	74.4
10	53.1	53.7	65.3	73.8
11	51.0	53.2	65.0	72.2
12	51.7	53.1	61.9	70.7

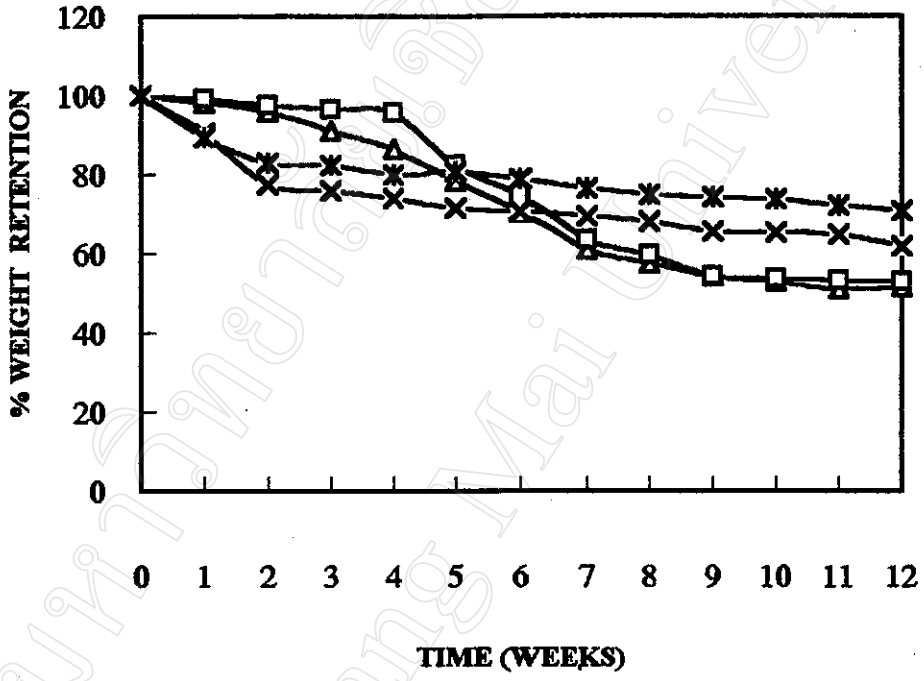
* **P(GA-co-VL) 2:1 data taken from Table 5.2**

** **P(GA-co-VL) 1:1 data taken from Table 5.3**

*** **P(GA-co-VL) 2:1 data taken from Reference [33]**

**** **P(GA-co-VL) 1:1 data taken from Reference [33]**

WEIGHT LOSS PROFILES



Δ = P(GA-co-VL) 2:1 fibres □ = P(GA-co-VL) 1:1 fibres
× = P(GA-co-VL) 2:1 discs * = P(GA-co-VL) 1:1 discs

Fig. 5.5 : Comparison of the in vitro weight loss profiles of the P(GA-co-VL) fibres from this study and P(GA-co-VL) discs from a previous study [33] after immersion in a pH 7.40 phosphate buffer solution at 37°C.

From the results shown in Table 5.6/Fig. 5.5, the differences in the weight loss profiles must be due to the different physical forms of the samples. Because they were formed by compression rather than by melting, the P(GA-co-VL) discs would have had more "open" surfaces allowing easier penetration of water into the porous interior. This would also have facilitated the passage of hydrolysis products out of the discs resulting in more immediate weight losses. However, after the first 2 weeks, these weight losses slowed down dramatically. This was thought to be due to the internal pore channels becoming "clogged up" with degrading material [33]. The fibres, having been melt extruded, had less porous surfaces resulting in a delayed initial weight loss until water had penetrated into the bulk interior.

5.2.2 Melting Point and Heat of Fusion Profiles

For each DSC sample analysis, approximately 3-5 mg of sample were weighed accurately. The DSC melting point and heat of fusion data are shown in Table 5.7 for each of the 3 sets of samples. The results are also plotted graphically in Figs. 5.6 and 5.7.

From the results shown in Table 5.7/Fig. 5.6, the melting points show initial decreases during the first 3 weeks. A possible explanation for this is an increase in molecular disorder (disorientation) brought about by hydrolytic chain scission. Following melt spinning, there should be a certain amount of molecular orientation in the polymer matrix as a result of the shear forces exerted on the molten polymer as it is forced under pressure through the spinnerette. This will enhance the polymer's tendency to crystallize as it cools. However, following its immersion in the pH buffer, diffusion of water into the matrix leading to hydrolysis results in a "stress relaxation" of the oriented chains, both in the amorphous and crystalline regions. Thus, a slight lowering of the melting point is observed. However, this trend is subsequently reversed with the melting point increasing back towards its former value. This is probably due to an increase in the number of free chain ends, as hydrolysis proceeds further, facilitating molecular motion and enabling the shorter chain segments to realign themselves within an adjoining crystallite. This view is supported by the heat of fusion profiles in Fig. 5.7. The slight upward trend in each sample indicates that the % crystallinities of the samples are increasing with time. Another factor which may be expected to contribute to contribute to

an increase in % crystallinity is the preferential hydrolysis in the amorphous regions. As the more loosely-packed amorphous regions hydrolyse first, the matrix as a whole increases in crystallinity and maintains a constant value even after substantial weight loss (>50%) has already occurred.

The heats of fusion given in Table 5.7 are computed from the normalized DSC melting peaks areas. They are directly related to the % crystallinity of the samples. To calculate the % crystallinity of a sample from its heat of fusion, a reference value of the heat of fusion of a theoretical 100% crystalline sample must be known, usually from the tables of data available in the "Polymer Handbook" [37]. Unfortunately, for the PVL and P(GA-co-VL) copolymers studied here, this reference data is not available and so their % crystallinities cannot be calculated.

Table 5.7 : DSC melting peak data for the PVL and P(GA-co-VL) 2:1 and 1:1 fibres, immersed in a phosphate buffer medium at 37°C, pH 7.40.

Time (weeks)	PVL		P(GA-co-VL) 1:1		P(GA-co-VL) 2:1	
	Melting Point (°C)*	Heat of Fusion (J/g)	Melting Point (°C)*	Heat of Fusion (J/g)	Melting Point (°C)*	Heat of Fusion (J/g)
0	52.64	121.44	180.67	66.89	205.15	57.87
1	50.28	99.27	176.20	60.15	185.98	99.35
2	50.38	106.97	173.48	62.24	181.80	64.52
3	51.26	112.24	171.86	92.95	184.06	68.99
4	60.47	57.24	200.55	113.75	204.78	65.48
5	58.23	56.89	200.06	117.18	200.05	93.86
6	59.43	57.74	199.51	119.43	198.60	91.73
7	58.58	57.98	197.78	123.16	196.61	90.85
8	58.86	56.29	197.66	124.35	196.50	91.55
9	58.46	66.25	200.86	125.40	198.51	89.87
10	58.91	64.80	200.55	124.77	198.39	88.57
11	58.86	63.59	200.06	124.21	198.38	88.65
12	58.60	61.66	203.50	126.31	198.73	92.28
13	58.00	61.21	199.87	126.87	196.94	95.82
14	57.46	63.07	200.95	131.65	196.79	97.43
15	56.35	62.86	201.13	131.74	196.48	96.58
16	56.17	64.85	199.93	132.92	196.78	95.70
17	56.91	72.24	198.47	136.82	195.60	97.89
18	56.46	65.56	198.31	137.05	195.20	93.21
19	55.38	69.96	198.96	138.92	195.31	95.75
20	55.03	73.19	192.20	137.24	188.26	98.35
21	55.82	72.67	191.04	137.18	186.70	97.71
22	55.43	84.99	191.55	136.98	185.26	99.27
23	55.73	79.16	190.78	138.16	185.53	97.22
24	54.85	97.98	190.40	139.75	185.56	97.79

*** taken as the melting peak maximum temperature ; scanning rate = 10°C/min.**

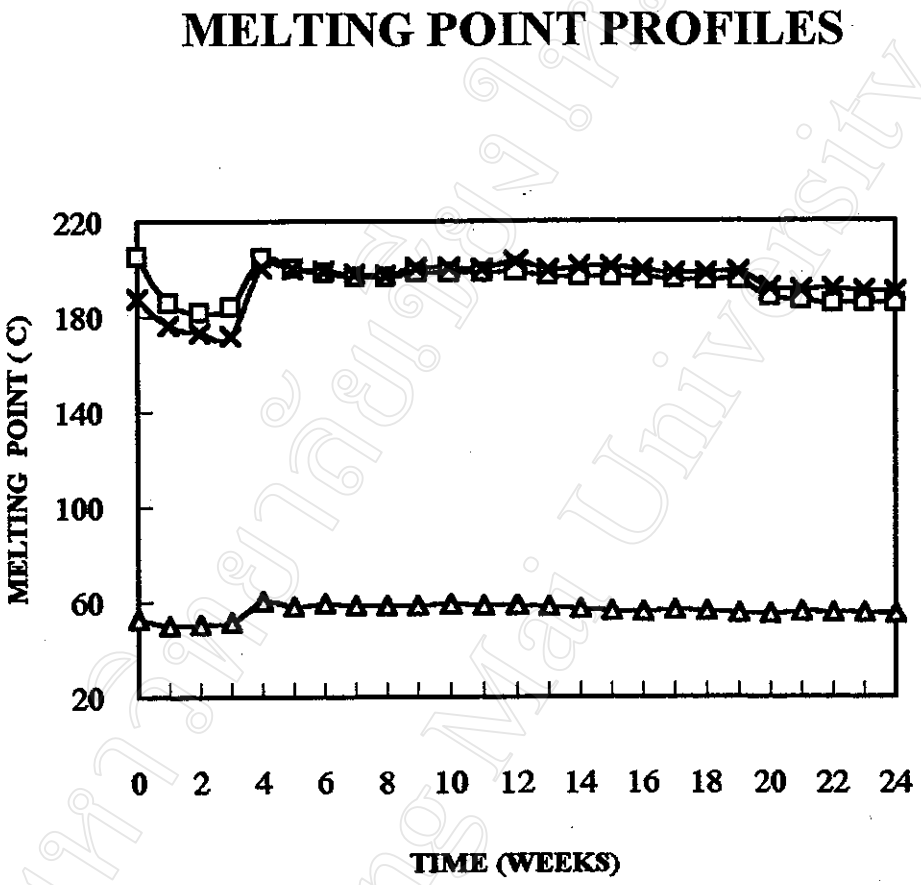
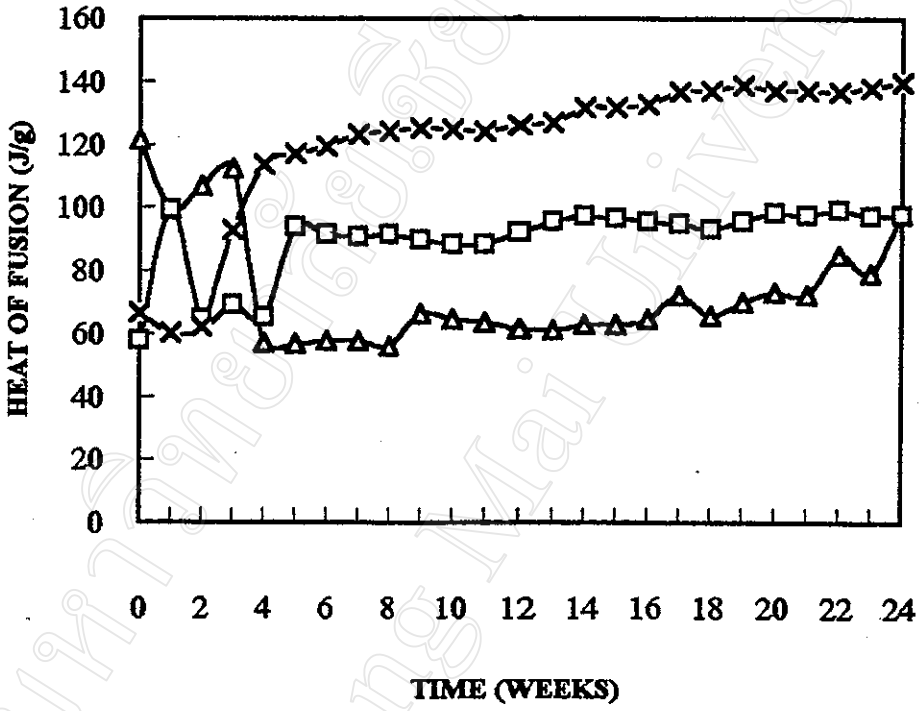


Fig. 5.6 : Comparison of the melting point profiles of the PGA and P(GA-co-VL) 2:1 and 1:1 fibres over the period of the biodegradation experiment.

HEAT OF FUSION PROFILES



Δ = PVL □ = P(GA-co-VL) 2:1 × = P(GA-co-VL) 1:1

Fig. 5.7 : Comparison of the heat of fusion profiles of the PGA and P(GA-co-VL) 2:1 and 1:1 fibres over the period of the biodegradation experiment.

5.2.3 Intrinsic Viscosity

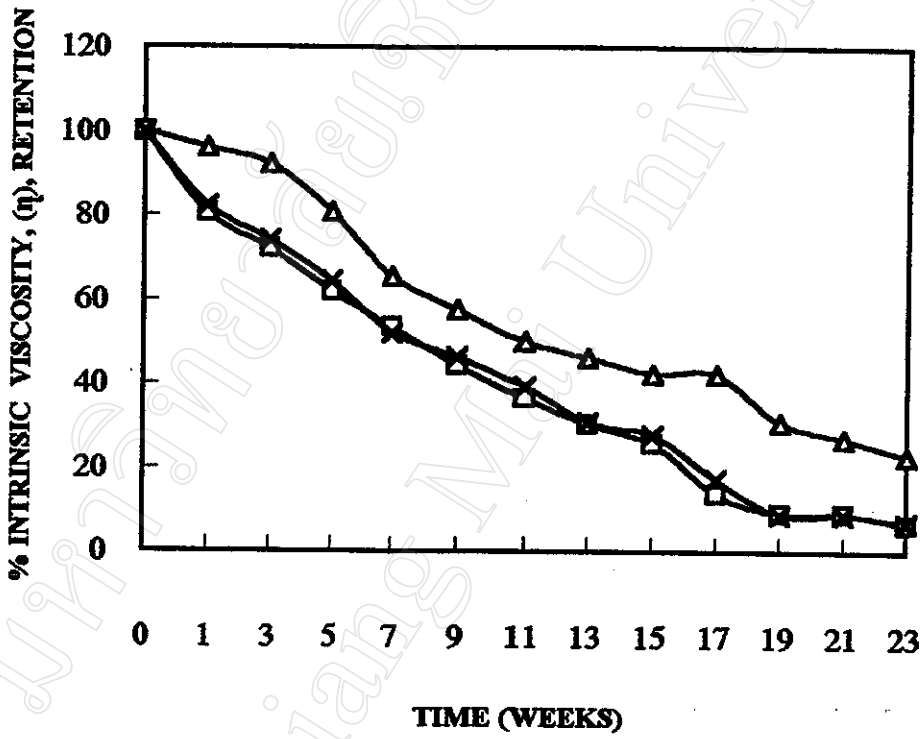
5.2.3.1 Experimental Procedure

Approximately 0.25% w/v PVL and P(GA-co-VL) solutions were accurately prepared using chloroform and DMSO as solvents respectively. Their flow-times were then determined at 30.0 ± 0.1°C and 90.0 ± 0.1°C respectively using a Schott-Gerate micro-Ubbelohde viscometer (type No. 537 10, capillary size I). By using the One-Point Approximation Method, the intrinsic viscosities, [η], of each sample were calculated from the Solomon-Ciuta Equation. Their values are given in Table 5.8 and plotted in Fig. 5.8.

Table 5.8 : Comparison of intrinsic viscosities and their % retentions for PVL and P(GA-co-VL) immersed in pH 7.40 phosphate buffer solution at 37°C.

Time (weeks)	PVL		P(GA-co-VL) 1:1		P(GA-co-VL) 2:1	
	[η] ±0.01 dl/g	% Retention of [η] ±0.1	[η] ±0.01 dl/g	% Retention of [η] ±0.1	[η] ±0.01 dl/g	% Retention of [η] ±0.1
0	0.26	100.0	0.41	100.0	0.33	100.0
1	0.25	96.1	0.34	82.3	0.27	80.6
3	0.24	92.3	0.30	74.2	0.24	72.1
5	0.21	80.8	0.26	64.5	0.20	61.8
7	0.17	65.4	0.21	52.0	0.18	53.5
9	0.15	57.7	0.19	46.3	0.15	44.3
11	0.13	50.0	0.16	39.2	0.12	36.5
13	0.12	46.2	0.13	30.8	0.10	30.2
15	0.11	42.3	0.11	27.7	0.08	25.7
17	0.11	42.3	0.07	17.4	0.05	13.8
19	0.08	30.8	0.04	9.0	0.03	9.2
21	0.07	26.9	0.04	9.0	0.03	9.2
23	0.06	23.0	0.03	7.1	0.02	6.5

INTRINSIC VISCOSITY LOSS PROFILES



Δ = PVL □ = P(GA-co-VL) 2:1 × = P(GA-co-VL) 1:1

Fig. 5.8 : Comparison of intrinsic viscosity loss profiles of the PGA and P(GA-co-VL) 2:1 and 1:1 fibres over the period of the biodegradation experiment.

The [η] loss profiles in Fig. 5.8 indicate a fairly constant rate of molecular weight decrease throughout. This is hardly surprising considering that the polymer molecular weights are low to start with. The decrease is the result of hydrolytic chain scission of the ester bonds in the polymer chain. As would be expected, the PVL shows a slower rate of decrease due to its lower hydrophilicity and, therefore, lower hydrolysability.

5.2.4 pH Stability of Phosphate Buffer Immersion Medium

Finally, the pH of the phosphate buffer immersion medium was monitored throughout the period of the experiment. It was found that the initially adjusted pH of 7.40 decreased during the period of the experiment, as shown in Table 5.9 and Fig. 5.9. No attempt was made to readjust the pH to 7.40 since it was of interest to note how the pH changed.

From Fig. 5.9, it can be seen that the pH of each of the phosphate buffer solutions decreased continuously throughout the course of the experiments. It is thought that this decrease in pH is caused by the release into solution of water-solution acidic compounds formed as the products of the samples' hydrolytic breakdown. This view is supported by the fact that the order of the pH decreases in Fig. 5.9 corresponds with the order of the previous sample weight decreases in Fig. 5.3 ; i.e.

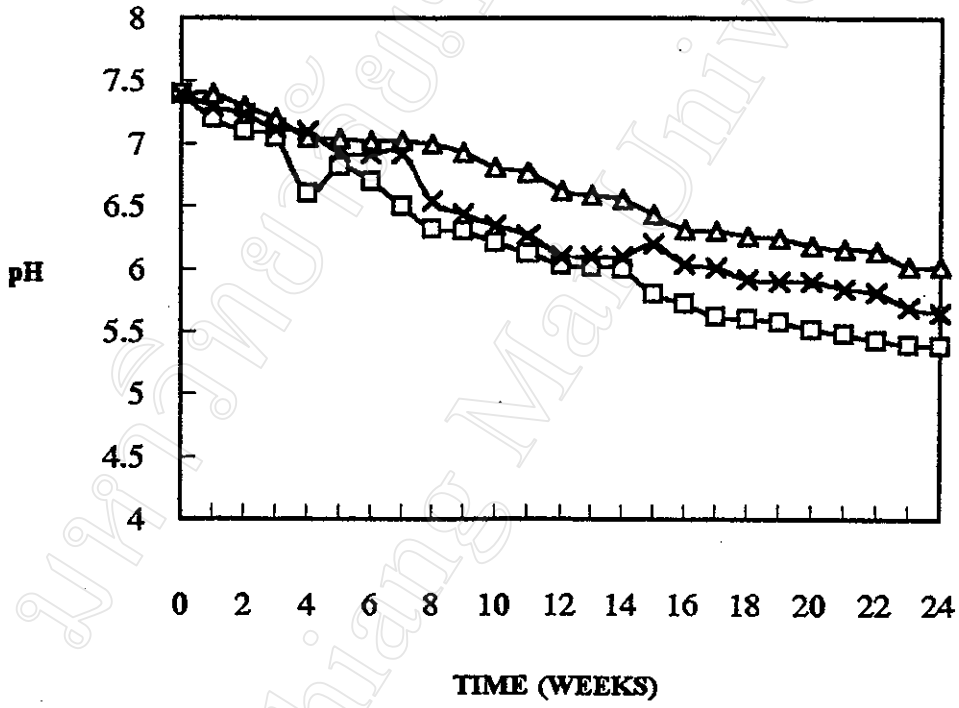
P(GA-co-VL) 2:1 > P(GA-co-VL) 1:1 > PVL

These changes in the pH of the immersion media may have an important influence on the respective degradation rates since the kinetics of ester hydrolysis are known to be pH-dependent. As the pH decreases below 7, indicating acidity, acid-catalysis of the hydrolysis reaction may have a significant accelerating effect.

Table 5.9 : Variations in pH of the phosphate buffer solutions containing the PVL and p(GA-co-VL) 2:1 and 1:1 samples during the 24-week period of the biodegradation experiment.

Time (weeks)	pH of Phosphate Buffer		
	PVL	P(GA-co-VL)	P(GA-co-VL)
0	7.40	7.40	7.40
1	7.40	7.20	7.30
2	7.30	7.10	7.24
3	7.20	7.05	7.12
4	7.05	6.60	7.10
5	7.04	6.82	6.93
6	7.02	6.70	6.92
7	7.02	6.50	6.92
8	7.00	6.32	6.54
9	6.93	6.30	6.44
10	6.81	6.21	6.35
11	6.77	6.12	6.27
12	6.62	6.03	6.10
13	6.59	6.01	6.10
14	6.55	6.00	6.10
15	6.43	5.80	6.20
16	6.31	5.72	6.04
17	6.30	5.62	6.01
18	6.26	5.60	5.92
19	6.24	5.58	5.90
20	6.18	5.52	5.90
21	6.16	5.48	5.84
22	6.14	5.43	5.82
23	6.02	5.40	5.70
24	6.02	5.39	5.65

VARIATION IN pH PROFILES



Δ = PVL □ = P(GA-co-VL) 2:1 × = P(GA-co-VL) 1:1

Fig. 5.9 : Variations in pH of the phosphate buffer solutions containing the PVL and P(GA-co-VL) 2:1 and 1:1 samples during the period of the biodegradation experiments.