

A STUDY OF STRUCTURE AND PROPERTY CHANGES OF BIODEGRADABLE POLYGLYCOLIDE AND POLY(GLYCOLIDE-*co*-LACTIDE) FIBERS DURING PROCESSING AND *IN VITRO* DEGRADATION*

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Abstract Structure and properties of bioabsorbable polyglycolide (PGA) and poly(glycolide-*co*-lactide) (PGA-*co*-PLA) fibers were investigated during several industrial processing stages and *in vitro* degradation by means of wide-angle X-ray diffraction (WAXD), dynamic mechanical analysis (DMA) and mechanical property tests. In the orientation stage, the PGA fibers were found to have higher degrees of crystallinity than corresponding PGA-*co*-PLA samples produced under similar conditions. In the hot-stretching and post-annealing stages, after fibers were braided, PGA samples were found to gain more crystallinity and higher T_g than PGA-*co*-PLA samples. The higher crystallinity in PGA fibers resulted in a slower rate of degradation. DMA results showed that a great deal of internal stress that was built during orientation and hot-stretching stages was released in the post-annealing stage for all PGA and PGA-*co*-PLA samples. During earlier stages of *in vitro* degradation, both PGA and PGA-*co*-PLA samples exhibited the typical cleavage-induced crystallization mechanism. The heat shrinkage in the glass transition area was found to disappear after 6–8 days of degradation for all PGA and PGA-*co*-PLA samples, indicating the amorphous portions of the polymers lost orientation after a short period in the buffer solution, most likely due to relaxation of the cleaved chains.

Keywords Polyglycolide, Poly(glycolide-*co*-lactide), Bioabsorbable, Fiber processing, *in vitro* Degradation

INTRODUCTION

Bioabsorbable polymers are an important class of synthetic biomaterials that are widely used in therapeutic applications such as wound closure, scaffolds for tissue regeneration and vehicles for drug delivery. Among the bioabsorbable polymers developed thus far, polyglycolide (PGA), poly(*L*-lactide) (PLA) and their copolymers (PGA-*co*-PLA) attract the most attention in commercial applications. For many surgical repair applications, they possess suitable bioabsorbable properties as well as suitable mechanical properties. For example, a commercial product having a proven record in clinical applications is a VICRYL (a trademark of Ethicon) suture; it is based on one of the (PGA-*co*-PLA) copolymers.

In order to produce absorbable sutures of high quality, two important properties have to be assured. One is the initial mechanical performance^[1–7], especially the tensile strength of the suture that determines the capability of holding the wound tissues together. This property is closely associated with processing conditions^[1, 2, 6].

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Another aspect of sutures is the biological performance, which is related to the absorption and tissue reaction profiles that are exhibited by the implanted material. In fiber processing, two typical processes are routinely used to manipulate the fiber properties. One technique involves the orientation process and the other technique involves the annealing process (or heat-setting process). The orientation process imposes a mechanical stretching of the polymer chains and crystallites, resulting in an increase of amorphous and crystalline orientation, as well as a frequent increase in crystallinity. These changes in structure usually yield an increase in tensile strength but a decrease in elongation. During the annealing process (heat-setting), the polymer chains gain mobility at elevated temperatures. As a result, the molecular segments in lower ordering tend to crystallize. This process often yields an increase in crystallinity, but may lose a certain degree of amorphous and crystalline orientation and cause the fiber to shrink if unconstrained. Seemingly identical materials can behave very differently with regard to their biological and mechanical performances if they display different crystal ordering and morphology. Many studies have been carried out to investigate the structure and property relationship in PGA and PLA fibers. It was found that higher crystallinity and molecular orientation usually resulted in higher tensile strength and lower degradation rate. During degradation, it has been reported that the hydrolysis process consists of two major mechanisms^[8–15]. In the first mechanism, water molecules diffuse into the amorphous region, resulting in scission of some chains. The densely ordered crystalline phase stays largely unaffected. As water molecules react with the amorphous chain segments, the additional degree of freedom facilitates the formation of new crystalline regions and increases the overall crystallinity. This phenomenon is termed “cleavage-induced crystallization”. As a result, the crystallinity will reach a maximum, which marks the domination of the second mechanism. At the second stage, water molecules slowly attack the crystalline phase resulting in chain segments small enough to be water soluble and susceptible to metabolism.

In our previous paper^[16], we have studied the structure and property relationships of poly(glycolide-co-lactide) (PGA-co-PLA) fibers during different processing stages and also *in vitro* degradation using wide-angle X-ray diffraction (WAXD), dynamic mechanical analysis (DMA) and mechanical property tests. The fibers were processed through orientation, hot-stretching and annealing stages. It was found that the fiber structure and properties changed significantly after each of the fiber processing stages. The fibers that had different structure and properties also exhibited different performance in *in vitro* degradation. In this paper, we intend to extend our investigation to include PGA fibers. Emphasis will be placed on comparing the difference between the PGA homopolymer and PGA-co-PLA copolymers.

EXPERIMENTAL

PGA-co-PLA samples used in this study were random copolymers based on approximately 90 mol% of glycolide and 10 mol% of *L*-lactide (90/10 PGA-co-PLA). This resin had an M_w of 62,000 g/mol, an M_n of 22,000 g/mol and a polydispersity of 2.8. PGA samples were homopolymers having an M_w of 60,000 g/mol, an M_n of 22,000 g/mol and a polydispersity of 2.7. The polymer was stored under vacuum before extrusion. The polymer was extruded and processed using the procedures schematically shown in Fig. 1 (reproduced from our previous paper^[16]). The identification of the samples is shown in Table 1. Drawn fibers were labeled as V2A to V2C for PGA-co-PLA copolymers and P1A to P1F for PGA homopolymers. Samples after the braiding and scouring stages were labeled by adding two letters, “BS”, after the corresponding name of the drawn fibers. For instance, sample V2A became V2A-BS for braided fibers. The hot-stretched samples were indicated by adding a letter “H”. For instance, sample V2A-BS became V2A-BSH. The annealed samples were designated by adding a letter “A” after the corresponding name of the hot-stretched samples.

The post-annealed samples were placed in a buffer solution (pH = 7.79) at 40.9°C for *in vitro* degradation studies. A small amount of sample was taken out and dried after a certain period of time for structure and property studies. We note that there was no tension applied on sutures during *in vitro* degradation. The *in vitro* degraded samples were named by adding the number of days of exposure. For instance, after 8 days of degradation, sample V2A-BSHA became V2A-BSHA-8D.

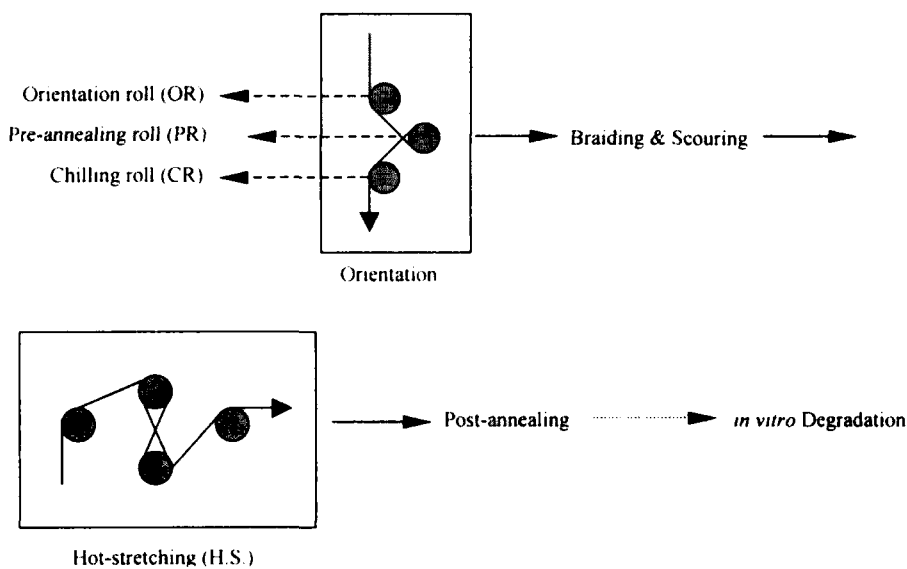


Fig. 1. Schematic drawing of the various suture processing stages

Table 1. Structure and property parameters of PGA-co-PLA and PGA fibers produced at different PR temperatures in the orientation stage

Sample ID	Crystallinity (%)	Crystal size (Å)	Tenacity (gpd)	Elongation at break (%)	Processing temperatures
V2A	26	44	6.8	23	PGA-co-PLA, OR = 84°C, PR = 131°C
V2B	25	43	7.0	24	PGA-co-PLA, OR = 84°C, PR = 101°C
V2C	20	42	6.5	27	PGA-co-PLA, OR = 84°C, PR = 71°C
P1A	30	47	7.3	25	PGA, OR = 88°C, PR = 120°C
P1B	33	46	8.3	27	PGA, OR = 88°C, PR = 110°C
P1C	30	46	7.4	26	PGA, OR = 88°C, PR = 100°C
P1D	30	45	7.3	26	PGA, OR = 88°C, PR = 90°C
P1E	29	44	8.2	27	PGA, OR = 88°C, PR = 80°C
P1F	27	41	6.7	24	PGA, OR = 88°C, PR = 70°C

Wide-angle X-Ray Diffraction (WAXD)

The X-ray measurements were carried out on a Siemens Hi-Star™ unit with Cu Kα radiation at a wavelength of 1.542 Å. The instrument was operated at 40 kV and 40 mA with a collimator size of 0.5 mm. The fiber sample was mounted on a goniometer, normal to the X-ray beam. The exposure time for each sample was 300 seconds. The calculation of the crystallinity content was performed with DIF-FRAC PLUS™ software developed by Siemens. A 2θ-intensity profile was first achieved by integration of azimuthal scans with the beam stop as the center. The profile was then peak-fitted to separate the amorphous peak (a Pearson VII split peak determined by a quenched extrudate) and three Gaussian crystalline peaks (110, 020, 002 reflection from an orthorhombic unit cell of PGA crystals). Dividing the area of the crystalline peaks, I_c , by the overall area I_{total} (amorphous and crystalline areas combined), we obtained the total crystallinity of the sample. The 110-reflection peak was used to determine the crystallite size. This measurement was performed using the Scherrer equation:

$$D_{hkl} = 57.3K\lambda / (B - b) \cos\theta \tag{1}$$

where K is the shape factor (= 0.9), λ is the wavelength (1.54 Å), B is the experimental breadth at the maximum intensity, and b is the instrumental correction coefficient (0.6781).

Dynamic Mechanical Analysis (DMA)

DMA was performed using a DMS 120 instrument (Seiko Instrument) operated in the tensile mode. The sample was mounted on the machine with a constant 20-gram tension applied during measurements. The experiment was performed at 1 Hz with a stretching ratio of 0.1%. Samples were heated from room temperature to 180°C at 2 K/min. The heat shrinkage was monitored by comparing the sample length changes to the original sample length (20 mm). The authors note that the T_g indicated in this paper is the $\tan\delta$ peak, which is usually not equal to the T_g from differential scanning calorimetry (DSC).

Mechanical Property Test

Mechanical property testing was performed using an Instron tensile machine (model 4201) with a crosshead speed of 12 inch/min. The stress-strain curves were obtained at room temperature. The maximum tensile strength and elongation at break were obtained by taking the averaged values from 8 separate measurements. The standard deviation of all mechanical property tests was very small (less than 5%).

RESULTS AND DISCUSSION

The Effect of Draw Temperature on Fibers

Table 1 shows the structure and property parameters of the chosen PGA and PGA-co-PLA fibers. V2A to V2C represent PGA-co-PLA fibers produced at different pre-annealing roll (PR) temperatures, and P1A to P1F represent PGA fibers produced at different PR temperatures. As seen, the PR temperature has significant influence in the structure development of PGA-co-PLA drawn fibers. For instance, sample V2A (PR = 131°C) exhibited higher crystallinity and slightly larger crystal size than sample V2C (PR = 71°C). In contrast, PGA fibers showed relatively weak temperature dependence in crystallinity changes. It was noted that the PGA samples generally had higher degrees of crystallinity than the PGA-co-PLA samples (the average crystallinity of the PGA sample was 30%, while the PGA-co-PLA sample was only 25%). This is quite reasonable as the PLA component in PGA-co-PLA copolymer can hinder the crystallization process of PGA, probably following an exclusion model proposed by Flory^[17]. The tenacity and elongation at break of PGA and PGA-co-PLA fibers was observed to have minimal changes at different PR temperatures.

Since the braiding process does not impact structure changes in the fibers, the mechanical properties of braided fibers are expected to be the same as the initial fibers. The heat shrinkage properties of the braided fibers were evaluated by DMA. These properties are reflective of the internal stress build-up in the fibers, which also has a direct impact in *in vivo* performance. Figure 2(a) shows the heat shrinkage profiles during a DMA scan on three PGA-co-PLA braids produced at different PR temperatures. As pointed out in our previous paper^[16], there are three relaxation regions that can be identified. The first is the region of $T < T_g$. Since the polymer chains have very limited mobility in this region, materials usually do not show heat shrinkage. The second is the glass transition region, where $T \sim T_g$. The polymer chains begin to gain mobility to disorient, which causes significant heat shrinkage. In this stage, the internal stress release is mostly associated with the amorphous chain. Very often, this region is referred to as the amorphous relaxation region. The last is the post- T_g region, where $T_g < T < T_m$. In this region, the crystalline phase is changed due to the reorganization of the crystal phase (defect annihilation) and recrystallization of the amorphous chains, which will cause another significant dimensional change. This region can be referred to as the crystalline relaxation region (assuming that the internal stress in the amorphous phase can be totally released by a slow heating at 1–2 K/min). As seen in Fig. 2(a), the most distinct difference among the three samples is in the glass transition area, ranging from 50°C to 120°C. Sample V2C-BS, which was produced under the lowest PR temperature, has the most significant heat shrinkage in this region. This suggests that at low pre-annealing temperature, the fiber has less opportunity to release the internal stress in the amorphous region due to the insufficient kinetics energy supplied. What may be even more important, however, is that this sample has not developed enough crystallinity (only 20%) to adequately resist the entropic driving force resulting in significant dimensional changes when raised to the glass transition temperature range. The PGA samples showed similar but much less pronounced behavior in the glass transition area (Fig. 2b). It is noted that

the PGA sample exhibits much less shrinkage than PGA-co-PLA samples. This is most likely due to the fast crystallization rate and better crystallization capability of PGA. The inclusion of the lactyl component retards the crystallization behavior of PGA. As a result, the structure and properties of PGA-co-PLA samples are more sensitive to heat.

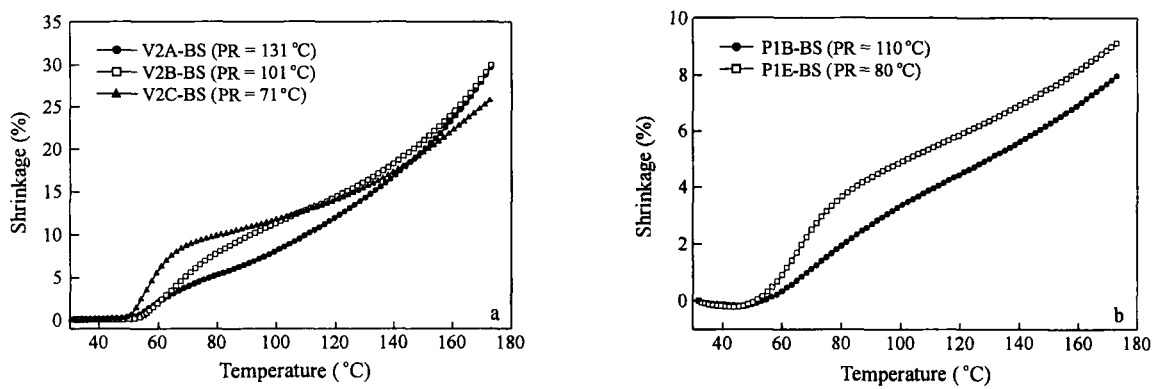


Fig. 2 DMA temperature scans of PGA-co-PLA (Fig. 2a) and PGA (Fig. 2b) braids produced at different pre-annealing roll (PR) temperatures

Structure and Property Evaluation During Post-Orientation Stages

Two PGA-co-PLA (V2A, V2C) samples and two PGA samples (P1B, P1E) were selected to evaluate the structure and properties of the final suture products. All four samples were hot-stretched at 101 °C and annealed at 124 °C. The results are summarized in Table 2. As seen, the crystallinity of sample V2A increased by a factor of approximately 1.4X (from 26% to 36%) after two processing steps: hot-stretching and post-annealing. The crystallinity of sample V2C, which was lower than V2A after the orientation process, increased more than a factor of 1.6X (from 20% to 33%). A similar behavior was also observed in PGA samples, where the samples of lower initial crystallinity gained more crystallinity after hot-stretching and annealing stages. In general, samples gain slight crystallinity after hot-stretching stages, and the crystal size was usually unaffected. The annealing process, however, usually resulted in notable increases in crystallinity and crystal size. This suggests that only some secondary crystallites are generated by the hot-stretching process, where the crystallinity increase is small and the average crystal size is about constant. In contrast, in the annealing process, the increased chain mobility enhances the crystal perfection process, resulting in the increase of both crystallinity and crystal size. All these factors have a direct impact on the material properties. As seen in Table 2, the strength at break of all samples was increased after each step. Figure 3(a) shows the DMA heating scans of sample V2A during the hot-stretching and annealing processes. As seen, the position of $\tan\delta$ peak (identified as T_g) and the peak-width did not change much after the hot-stretching stage. After the annealing process, sample V2A showed a broader $\tan\delta$ peak and higher T_g . This phenomenon is very consistent with the crystallinity observation, where the annealing process usually increases the crystallinity by promoting the chain mobility. It was also observed that the heat shrinkage in the glass transition temperature region slightly increased after the hot-stretching process, but significantly decreased after the annealing process. The increase in heat shrinkage agrees well with the increase of internal stress that was produced during the orientation and hot-stretching processes. The decrease in heat shrinkage after annealing is due to the increased crystallinity (which can resist the entropic driving force to shrink) and the decrease of internal stress by reorganization during the annealing process, which has been extensively discussed in our previous paper^[16]. Figure 3(b) shows the DMA heating scans of sample P1E at different industrial stages. As seen, the PGA samples had broader glass transition regions than the PGA-co-PLA samples although their $\tan\delta$ evolution profiles were similar to the PGA-co-PLA samples. The shrinkage profiles also followed the same trend as PGA-co-PLA samples, but had significantly lower shrinkage (less than 10%) in all temperature zones. In Table 2, both PGA-co-PLA samples exhibit a $\tan\delta$ half-width (defined as the FWHM of the $\tan\delta$ transition peak)

of 30 °C after the annealing process, compared to 35 °C for the PGA samples. The $\tan\delta$ half-width is known to be associated with the elasticity of a sample. Since $\tan\delta$ peak is mostly due to the amorphous phase in general, the decrease of the intensity of $\tan\delta$ peak (hence a broader $\tan\delta$ half-width) usually indicates an increase of crystallinity in semi-crystalline polymers. It is indeed the case in our observations of PGA and PGA-co-PLA

Table 2. Structure and property parameter changes of PGA-co-PLA and PGA sutures after each industrial process stages

Sample ID	Crystallinity (%)	Crystal size (Å)	Strength at break (kg)	$\tan\delta$ Half-width ^a (°C)	T_g (°C)	Shrinkage at 80 °C (%)	Processing temperatures
V2A-BS	26	44	7.2	24.8	66.5	5.3	OR = 84 °C, PR = 131 °C
V2A-BSH	28	45	7.2	21.6	66.1	6.5	H.S. temp. = 101 °C
V2A-BSHA	36	44	7.3	30.8	73.7	3.9	Annealing temp. = 124 °C
V2C-BS	20	42	6.3	20.1	60.9	9.8	OR = 84 °C, PR = 71 °C
V2C-BSH	28	42	7.1	23.8	64.9	9.2	H.S. temp. = 101 °C
V2C-BSHA	33	46	7.4	30.1	73.2	3.2	Annealing temp. = 124 °C
P1B-BS	33	46	7.5	23.6	69.0	1.9	OR = 88 °C, PR = 110 °C
P1B-BSH	35	43	7.7	33.7	70.7	1.7	H.S. temp. = 101 °C
P1B-BSHA	40	45	7.9	35.6	76.9	1.2	Annealing temp. = 124 °C
P1E-BS	29	44	7.1	27.0	68.7	3.6	OR = 88 °C, PR = 80 °C
P1E-BSH	36	43	7.2	27.1	69.7	3.6	H.S. temp. = 101 °C
P1E-BSHA	41	47	7.5	34.4	77.1	1.1	Annealing temp. = 124 °C

^a Defined as the FWHM of $\tan\delta$ peak in glass transition region

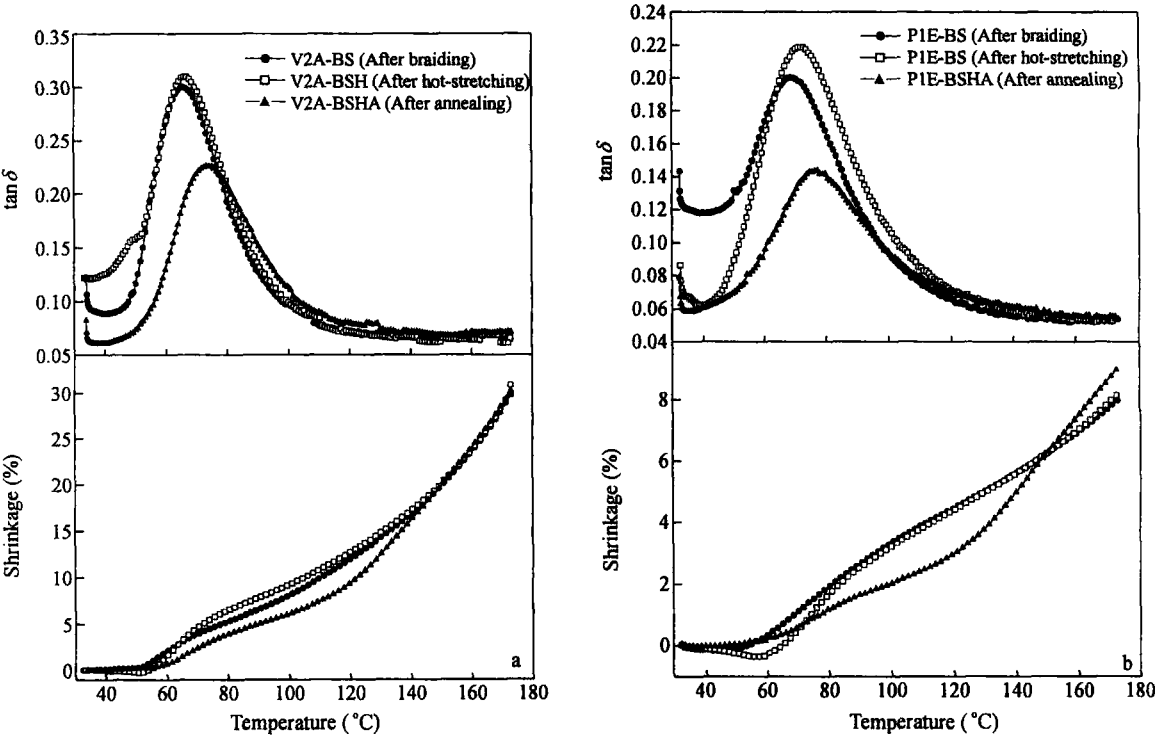


Fig. 3 An example of the $\tan\delta$ and heat shrinkage evolution of PGA-co-PLA (Fig. 3a) and PGA (Fig. 3b) sutures during the entire industrial process

samples. It was also observed that the T_g of PGA-co-PLA samples ($\sim 73^\circ\text{C}$) was considerably lower than that of PGA samples ($\sim 77^\circ\text{C}$), which corresponded well to the higher crystallinity of the PGA samples.

Structure and Property Relationships During in Vitro Degradation

Four post-oriented PGA (P1B and P1E) and PGA-co-PLA samples (V2A and V2C) were subjected to *in vitro* degradation. As shown in Fig. 4(a), PGA-co-PLA samples V2A and V2C exhibited approximately 20% tensile strength left after 18 days. Ranging from 33% to 38%, the crystallinity increased only very slightly with *in vitro* exposure until about 14 days, whereafter a rather significant jump was observed. The crystallinity of V2A jumped from 35% to 48% and that of V2C jumped from 37% to 45% in the *in vitro* time period between 14 and 18 days. This rapid increase is consistent with a cleavage-induced crystallization mechanism. Figure 4(b) shows the degradation behavior of PGA samples (P1B and P1E). The PGA samples showed similar losses in mechanical properties as the PGA-co-PLA samples. However, the crystallinity changes are different between the PGA and the PGA-co-PLA samples. It is interesting to note that the crystallinity of PGA samples did not show a major jump, increasing only slowly from 40%–41% to a high of 46%–48% after 16 days of exposure. This increase might be due to the higher starting crystallinity of the PGA samples, which provided little room for further crystal growth. Figure 5 shows the DMA heating scans of PGA-co-PLA samples during *in vitro* degradation. It was seen that T_g shifted slightly to lower temperatures. This slight drop in T_g is consistent with water molecules reacting with the ester groups of the amorphous phase, producing more polar acid and alcohol moieties. This environment invites even more water molecules to further plasticize the material resulting in a lower T_g . Heat shrinkage in the glass transition region disappeared after 7 days of *in vitro* exposure indicating that the amorphous portion of the polymer had lost orientation after this short period of time in the buffer solution, most likely due to the relaxation of the now cleaved chains.

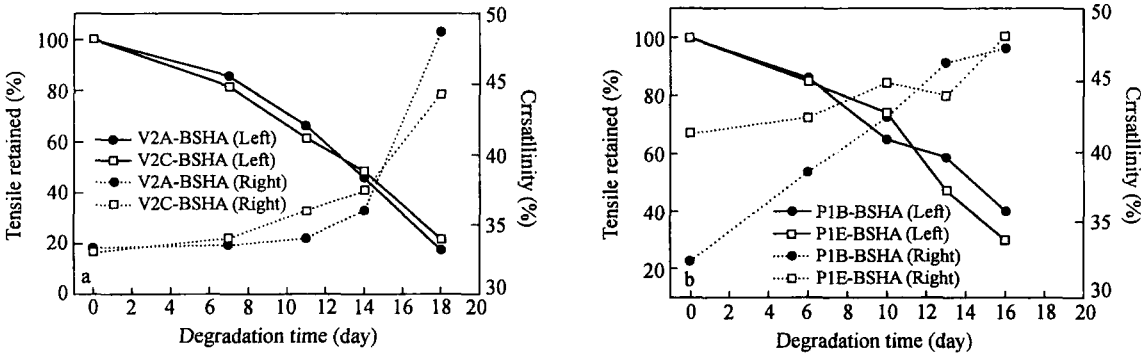


Fig. 4 The crystallinity and tensile retained percentage changes of PGA-co-PLA (Fig. 4a) and PGA (Fig. 4b) sutures during *in vitro* degradation

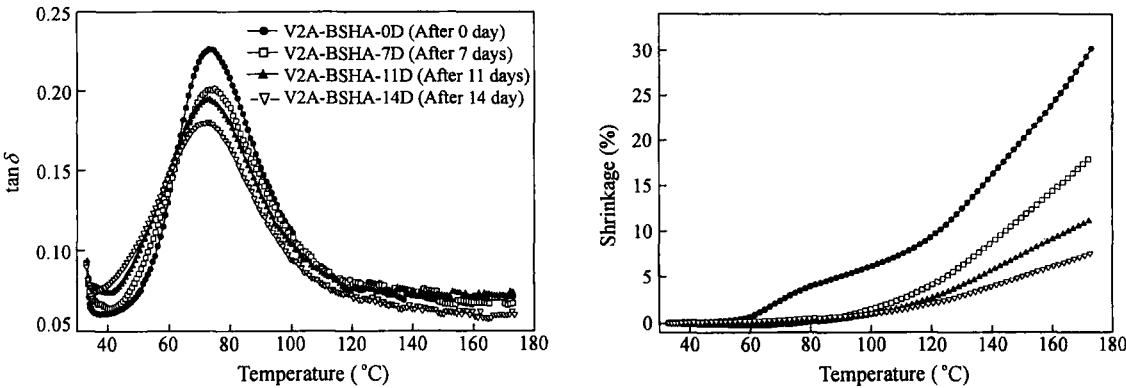


Fig. 5 An example of the $\tan \delta$ and heat shrinkage evolution of PGA-co-PLA suture during *in vitro* degradation

Figure 6 shows the heat shrinkage profiles of the PGA samples during *in vitro* degradation. As seen, the general behavior in PGA was similar to that in PGA-co-PLA. There is, however, some notable difference between the two. For instance, the glass transition region of PGA was found to be broader than that of PGA-co-PLA. This is consistent with the more rigid molecular structure of the PGA chains. The heat shrinkage of PGA samples was virtually unseen after 16 days. This could be attributed to the high initial crystallinity. Table 3 summarizes the structure and property changes of both PGA and PGA-co-PLA during *in vitro* degradation. It was found that the crystal size of both PGA and PGA-co-PLA remained stable during degradation. The intensity of tan δ peak of PGA-co-PLA samples was observed to slightly decrease after degradation, and the peak shape

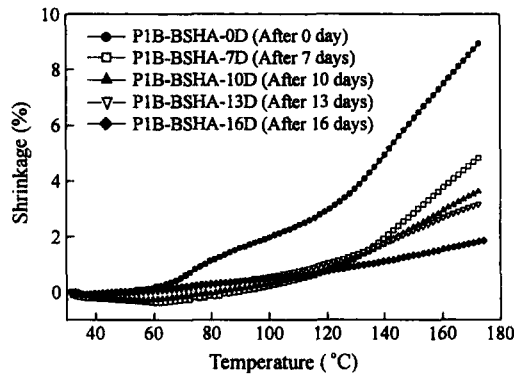


Fig. 6 An example of the heat shrinkage evolution of PGA suture during *in vitro* degradation

Table 3. Structure and property parameter changes of PGA-co-PLA and PGA sutures during *in vitro* degradation

Sample ID	Strength at break (kg)	Tensile retained (%)	Crystallinity (%)	Crystal size (Å)	T_g (°C)	Half-width (°C)	Shrinkage at 120°C (%)	M_w	M_w/M_n
V2A-BSHA-0D	7.3	100	36	45	73.7	30.8	12	62,000	2.8
V2A-BSHA-7D	6.3	85.6	36	46	75.3	33.3	4.0	41,000	2.4
V2A-BSHA-11D	4.9	66.3	36	48	73.4	32.8	2.7	28,000	2.3
V2A-BSHA-14D	3.4	45.9	38	47	72.5	32.9	2.1	18,000	2.0
V2A-BSHA-18D	1.3	17.3	45	45	75.8	33.1	1.0	8,800	1.7
V2C-BSHA-0D	7.4	100	33	46	73.2	30.1	14	62,000	2.8
V2C-BSHA-7D	6.1	81.7	34	46	74.5	32.1	3.7	43,000	2.5
V2C-BSHA-11D	4.6	61.6	36	45	73.9	33.9	2.5	29,000	2.2
V2C-BSHA-14D	3.6	48.6	37	48	72.8	33.6	2.1	19,000	2.1
V2C-BSHA-18D	1.6	21.9	44	45	72.5	31.1	2.0	9,500	1.7
PIB-BSHA-0D	7.9	100	40	45	76.9	35.6	2.9	60,000	2.7
PIB-BSHA-6D	6.8	86.1	43	46	74.0	31.3	0.8	47,000	2.5
PIB-BSHA-10D	5.1	64.9	44	45	74.4	27.7	0.9	35,000	2.3
PIB-BSHA-13D	4.6	58.8	46	47	74.6	35.6	1.0	24,000	2.2
PIB-BSHA-16D	3.2	40.0	46	47	73.3	32.0	0.8	15,000	2.1
PIE-BSHA-0D	7.5	100	41	47	77.1	34.4	6.3	60,000	2.7
PIE-BSHA-6D	6.4	84.9	43	47	76.3	31.2	1.3	47,000	2.6
PIE-BSHA-10D	4.6	74.1	45	45	74.1	31.1	0.9	34,000	2.4
PIE-BSHA-13D	3.5	47.1	44	46	74.5	35.0	1.0	25,000	2.3
PIE-BSHA-16D	2.3	30.0	48	46	73.3	34.7	0.6	14,000	1.9

became broader (broader $\tan\delta$ half-width). This observation is consistent with crystallinity growth after degradation. The half-widths of the $\tan\delta$ peaks of the PGA samples were observed to change very little during the 16 days of *in vitro* degradation, consistent with the little change in crystallinity observed for these samples. Both the weight average and the number average molecular weight of all the samples tested were observed to decrease almost linearly with *in vitro* exposure time. Polydispersity of all the samples decreased during *in vitro* degradation; weight average molecular weight decreased faster than number average molecular weight, even on a percent basis. This is elegant evidence of a greater likelihood of larger molecules undergoing chain cleavage; the greater the length of the chain, the greater is the probability of cleavage.

CONCLUSION

In this study, we have studied the structure and property changes of polyglycolide (PGA) and poly(glycolide-co-lactide) (PGA-co-PLA) biodegradable fibers during different processing stages and *in vitro* degradation. These stages include the orientation stage, the hot-stretching stage and the annealing stage. In the orientation stage, we found that the pre-annealing roll (PR) temperature had less influence on PGA fibers than PGA-co-PLA fibers. In general, homopolymeric PGA fibers have higher crystallinity and a faster crystallization rate. In the hot-stretching and annealing stages, samples increased in strength — at-break, crystallinity, crystal size, and T_g . The annealing stage was important for producing a morphology that was heat stable. Both PGA and PGA-co-PLA samples showed typical cleavage-induced crystallization during *in vitro* degradation. It was found that the heat shrinkage in the amorphous relaxation region (the same as the glass transition region) disappeared after 6–8 days of degradation.

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REFERENCES

- 1 Penning, J.P., Dijkstra, H. and Pennings, A., J., *Polymer*, 1993, 34: 942
- 2 Leenslag, J.W. and Pennings, A.J., *Polymer*, 1987, 28: 1695
- 3 Okuzaki, H., Kubota, I. and Kunugi, T., *J. Polym. Sci., Polym. Phys.*, 1999, 37: 991
- 4 Schmack, G., Tandler B., Vogel, R., Beyreuther, R., Jacobsen, S. and Fritz, H.G., *J. Appl. Polym. Sci.*, 1999, 73: 2785
- 5 Postema, A.R. and Pennings, A.J., *J. Appl. Polym. Sci.*, 1989, 37: 2351
- 6 Postema, A.R., Luiten, A.H. and Pennings, A.J., *J. Appl. Polym. Sci.*, 1990, 39: 1265
- 7 Martin, O. and Averous, L., *Polymer*, 2001, 42: 6219
- 8 Chu, C.C., *J. Appl. Polym. Sci.*, 1981, 26: 1727
- 9 Chu, C.C., *J. Biomed. Mater. Res.*, 1981, 15: 19
- 10 Ginde, R.M. and Gupta, R.K., *J. Appl. Polym. Sci.*, 1987, 33: 2411
- 11 Fredericks, R.J., Melveger, A.J. and Dolegiewitz, L.J., *J. Polym. Sci., Polym. Phys.*, 1984, 22: 57
- 12 King, E. and Cameron, R.E., *J. Appl. Polym. Sci.*, 1997, 66: 1681
- 13 Zhou, J.J., Samon, J.M. and Dormier, E., *J. Appl. Med. Polym.*, 1999, 3: 55
- 14 Zong, X.H., Wang, Z.H., Hsiao, B.S., Chu, B., Zhou, J.J., Jamiolkowski, D. D., Muse, E. and Dormier, E., *Macromolecules*, 1999, 32: 8107
- 15 Wang, Z.G., Hsiao, B.S., Zong, X.H., Yeh, F., Zhou, J.J., Dormier, E. and Jamiolkowski, D.D., *Polymer*, 2000, 41: 621
- 16 Fu, B.X., Hsiao, B.S., Chen, G., Zhou, J., Koyfman, I., Jamiolkowski, D.D. and Dormier, E., *Polymer*, 2002, 43:5527
- 17 Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, p.570