Investigations of the Preparation Technology for Polyglycolic Acid Fiber with Perfect Mechanical Performance

Qing Yang, Xinyuan Shen, Zhiqing Tan

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, 200051 Shanghai, People's Republic of China

Received 11 July 2006; accepted 28 February 2007
DOI 10.1002/app.26392
Published online 30 May 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polyglycolic acid (PGA) fibers were prepared by melt-spinning process in this report. The effects of spinning parameters, such as windup rates and drawn ratio, on the mechanical properties of the fibers were discussed by analyzing the internal stress of as-spun fibers, axial sound velocity, fiber tenacity, etc. The results showed that windup rate had a slight effect on the macromolecular orientation degree of the as-spun fibers, which was quite unusual for melt spinning, whereas, the subsequent drawing process effectively increased the macromolecular orientation degree of the PGA fibers and consequently increased the tensile strength of the fibers. Low internal stress of as-spun fibers obtained at lower windup rate led to higher drawing ratio, and the drawn fibers possessed relatively excellent mechanical properties. As a contrast, higher windup rate resulted in the strong internal stress of the as-spun fibers, which had a negative influence on the drawing process, and so the tensile strength of the drawn fibers was relatively poor. Therefore, PGA fiber with perfect mechanical performance could be prepared at the technical parameters of lower windup rate and higher drawing multiples as well as slow drawing rate. J Appl Polym Sci 105: 3444–3447, 2007

Key words: polyglycolic acid (PGA); fibers; spinning technology; mechanical properties; orientation

INTRODUCTION

Biomacromolecular materials have been extensively applied in medicine area. In addition to required intensity, rigidity, tenacity, and biocompatibility, the medical polymers should possess outstanding biodegradability, so that they can be absorbed or metabolized in human body. Up to the present, tens of absorbable and degradable polymers have been discovered, but only a few of them are verily applied in clinic. Among them, polyglycolic acid (PGA), a biodegradable aliphatic polymer, has been extensively applied in medical area because of its excellent biocompatibility and mechanical properties. PGA can be used to prepare special sleeves for reinforcing staple-lines to reduce air leaks after resection of emphysematous lung,[1] cell carrier for tissue engineering,[2,3] tape for use in hepatic mass ligation,[4] mesh on intestinal adhesion formation,[5] and self-reinforced rods for osteochondritis.[6] On the other hand, the most important application of PGA is focused on absorbable medical suture.[7] PGA is a kind of highly crystallizable polyester and PGA fibers possess excellent physicochemical and mechanics properties. PGA suture has become a main absorbable product for subcutaneous operation because of its relatively high tensile strength and elastic modulus.

Melt-spinning technology is easily used to prepare PGA fibers. However, some formation and drawing parameters for producing the fibers have not been published, even though some commercial PGA sutures have been existing in market. In this article, the spinning technologies are discussed with the purpose of preparing the PGA fiber with high mechanical performance.

EXPERIMENTAL

Preparation of PGA as-spun fibers

PGA chips were supplied by PURAC Biochem Company (The Netherlands), and the properties of the polymer are listed in Table I.

Spinning process was conducted on a microscale spinning machine made by Shanghai Tianqing Biomaterial (Shanghai, China). The spinning temperature of PGA melt was controlled at 255°C. The windup rates were adjusted at 30, 50, 100, 200, 300, and 400 m/min, and the corresponding samples are numbered from 1 to 6, respectively.

Measurement of fiber sound orientation factor f_s

The fiber axial sound velocity C was measured by SCY-III Sound Velocity Instrumentation made by

Correspondence to: Q. Yang (yangqing@dhu.edu.cn).

TABLE I
Properties of PGA Chips Used in the Report

Items	Parameters
Inherent viscosity (HFIP, 25°C, intrinsic viscosity $c = 0.1$ g/dL)	1.54 dL/g
Melting range (DSC, 10°C/min)	195.2–207.3°C
Heat of fusion (DSC, 10°C/min)	71.2 J/g
Residual solvent	<0.1%
Residual monomer (by drying)	<1%

Donghua University, and sound orientation factor f_s and sonic modulus E are calculated by eqs. (1) and (2), respectively:

$$f_s = 1 - \frac{C_u}{C^2} \tag{1}$$

$$E = 0.997C^2(\mathrm{N/tex}) \tag{2}$$

where C_u and C represent the axial sound velocity (km/s) in a randomly oriented state and measured state, respectively.

According to Moseley,[8] if sound is sent across an array of parallel molecules, sonic energy is presumed to be transmitted from one molecule to another by stretching of intermolecular bonds. On the other hand, if sound is sent along the length of a bundle of parallel polymer molecules, the sonic energy is presumed to be transmitted principally by stretching of the chemical bonds in the backbone of the polymer chain. In the case of partially oriented polymer molecules, the molecular motion due to sound transmission is presumed to have right angle components, along and across the direction of the molecular axis. The magnitude of either of these two components is taken to be a function of the angle between the molecular axis and the direction of sound propagation θ.

The earlier considerations lead to eq. (1) that relates the sound velocity in a sample to its molecular orientation in terms of certain constants characteristic of the polymer structure. The value of $\overline{\cos^2\theta}$ varies from one-third for a randomly oriented material to unity for a theoretically perfectly oriented sample. The sound orientation factor f_s is termed the total molecular orientation. The term total is used to indicate that the measured orientation is an average for all molecular segments, both crystalline and amorphous. The sonic modulus in units of newtons per tex is directly proportional to the square of the sonic velocity and is given by eq. (2).

Measurement of boiling water shrinkage of as-spun fibers

To understand the internal stress of PGA as-spun fibers under various windup rates, the as-spun fibers were put into boiling water in stress-free condition for 10 min. Then, the fiber shrinkage S is measured by eq. (3):

$$S = \frac{l_0 - l}{l_0} \times 100\% \tag{3}$$

where l_0 and l represent the length of a sample before and after treatment in boiled water, respectively.

Tensile strength measurement of drawn fibers

PGA as-spun fiber samples were drawn in drawing machine under certain temperatures, drawing ratios, and rates. The fiber tensile strength was tested by XL-1 Yarn Tension and elongation tester, with the condition of cramp length of 250 mm, preset a tension of 0.1 N/dtex, and a drawing speed of 250 mm/min.

RESULTS AND DISCUSSION

Influence of windup rates on the macromolecular orientation degree of as-spun fibers

Sound velocity C_u, in randomly oriented state, is necessary for measuring the sound orientation factor f_s of fibers. Because the C_u of PGA fiber is unavailable, an unoriented film was cast and the sound velocity of 1.325 km/s was measured as C_u.

Table II shows the f_s and E of PGA as-spun fibers at different windup rates. The data indicate that f_s values change a little as windup rate increases, fluctuating in the narrow range of 0.48–0.54 and seem indifferent to windup rates, which disagree with conventional synthetic fibers. Ziabicki[9] reported that for most fiber-forming polymers, the molecular orientation degree of as-spun fibers increases with increasing windup rates. Other researches about melt spinning also expressed a similar viewpoint.[10–12] The difference between our results and the previous reports may be caused by the following: PGA is a kind of easy-crytallizable polymer, and its spinning temperature is usually not high lest macromolecule degradation, and so the melt viscosity is quite great in the case. The high viscosity prevents macromolecules from flowing and orienting freely under external force, so that the molecular orientation degree of PGA as-spun fibers is less affected by windup rates. For other fiber-forming polymers, their melt viscosities are usually not high, either due to self structure or high spinning temperature. Therefore, the melt fluidity is quite good, and macromolecular chains are easily oriented and form crystallization structure under strong axial tension at high windup rates, and the as-spun fiber will possess excellent tensile strength. For example, polyethylene terephthalate chips are spun at very high speeds, and the highly

TABLE II
Sound Orientation Factors f_s and Sonic Modulus E of PGA As-Spun Fibers at Different Windup Rates

Sample	Windup rate (m/min)	Drawing ratio	Sound velocity (km/s)	Modulus (N/tex)	Sound orientation factor f_s
1–0	30	–	1.94	3.75	0.53
2–0	50	–	1.90	3.60	0.51
3–0	100	–	1.95	3.79	0.54
4–0	200	–	1.93	3.71	0.53
5–0	300	–	1.83	3.34	0.48
6–0	400	–	1.90	3.60	0.51
1–5	30	5.0	6.06	36.61	0.95
6–2	400	2.0	1.98	3.91	0.55

oriented as-spun fibers with high modulus low shrinkage, good uniformity, and improved drive behavior can be used directly for weaving without further posttreatment.[13]

Drawability of the as-spun fibers

Table III shows the influence of windup rates on the maximum drawing ratio and break strength of PGA fiber. The data indicates that with the increase of spinning speed, the maximum drawing ratio and fiber break strength are gradually stepped down. As we know from the previous discussion, windup rates have little influence on the molecular orientation of PGA fiber, and the drawing process plays an important role in the fiber molecular orientation as well as the fiber tensile strength.

The reason for the decrease in the fiber maximum drawing ratio with increasing windup rates can be inferred as that the acting force among PGA macromolecules is larger, which leads to a longer response time for macromolecular movement under external force of winding. The microstructure units in crystalline and amorphous region deform under larger axial tension. The external force is transformed to cohesive energy inside the as-spun fiber, which leads to larger internal stress. The internal stress would further impede subsequent drawing process. The higher the windup rate is, the larger is the internal stress and the less is the drawing ratio.

TABLE III
Influence of Windup Rates on the Maximum Drawing Ratio and Break-Down Strength of PGA Fibers (25°C)

Sample no.	Windup rate (m/min)	Maximum drawing ratio	Tensile strength (cN/dtex)
1	30	5.0	6.45
2	50	4.8	6.32
3	100	4.2	5.87
4	200	3.4	4.77
5	300	3.1	3.45
6	400	2.0	2.33

To confirm the aforementioned inference, the changes of boiling water shrinkage of PGA as-spun fiber with various windup rates was measured, as shown in Figure 1. As a result, the internal stress of fibers is obviously affected by windup rates. When windup rate is 30 m/min, the boiling water shrinkage of the as-spun fiber is only 3.4%, while the rate is up to 400 m/min, and it is excessive at 40%. The fact confirms that windup rates indeed have a great influence on the internal stress of PGA as-spun fibers.

Furthermore, the data in Tables II and III indicate that the as-spun fiber by windup rate of 30 m/min can be drawn five times. The sound velocity C of the drawn fibers greatly increased with the f_s of 0.95, modulus E evidently strengthens, and the fiber tensile strength is raised to 6.45 cN/dtex. Although, the as-spun fiber obtained by a windup rate of 400 m/min can only be drawn two times with a slight change of C, f_s, and E, the fiber tensile strength is just 2.33 cN/dtex.

According to the viewpoint of spinning technology, lower windup rates are preferred for preparing PGA fiber with excellent drawability and mechanical

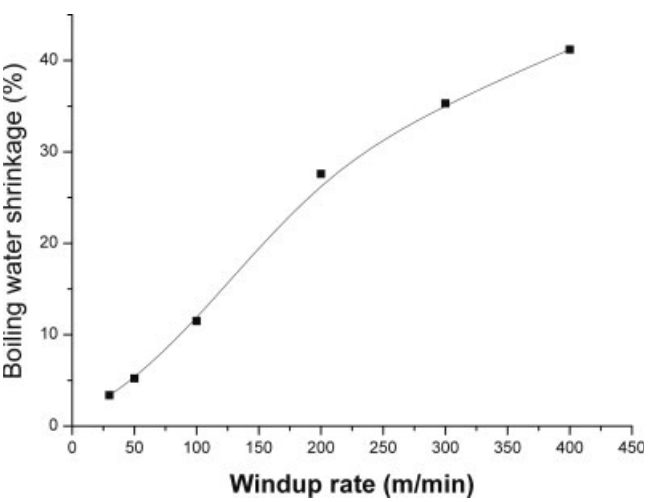

Figure 1 Influence of windup rates on boiling water shrinkage of PGA as-spun fibers.

properties. The as-spun fibers by lower windup rate possess lower internal stress, and the macromolecular chains are in a state of disorder with lower crystallinity, which is profitable to subsequent drawing. The macromolecular chains or the aggregate structure units inside the as-spun fibers adequately stretch at a high drawing ratio, and the axial molecular orientation degree in disordered region is greatly raised. After drawing process, the higher molecular orientation degree induces perfected crystal structure that leads to excellent fiber mechanics properties. On the other hand, the as-spun fibers with higher internal stress, spun at higher windup rates, are difficult to ''stand'' high drawing ratio process. Therefore, the supermolecular structure of the drawn fiber is not quite ideal because of the disorder macromolecule chains and the imperfect crystal structure, which results in poor mechanical properties of the biodegradable fiber.

Influence of drawing process on fiber tensile strength

Figure 2 shows the influence of drawing rates and temperatures on fiber tensile strength. The curves demonstrate that the fiber tenacity increases with elevation of the temperature of the heating plate below 45°C, while it obviously decreases down when the temperature is beyond 45°C. The possible reason is maybe that the activity of macromolecular chains is strengthened with the elevation of temperature at a certain range, which is helpful for the macromolecular chains to form oriented crystallization structure. However, overheating will cause deorientation of macromolecular chains and lead to negative effect of tensile strength of the drawn fibers.

Drawing rates are also playing an important role, affecting the tensile strength of PGA fibers. Generally, in the drawing process, somewhat lower rate is traditionally required than can be achieved in spinning.[14] The tensile strength decreased with the increase of drawing rate, and this is because the interacting force among PGA macromolecules are great, which hampers their responsiveness to external force. At the same time, macromolecular chains need enough time to overcome the interacting force and rearrange for orientation, and if the drawing rate is too fast, macromolecules cannot be adequately oriented, and so the fiber tenacity would drop down with the increase in drawing rate.

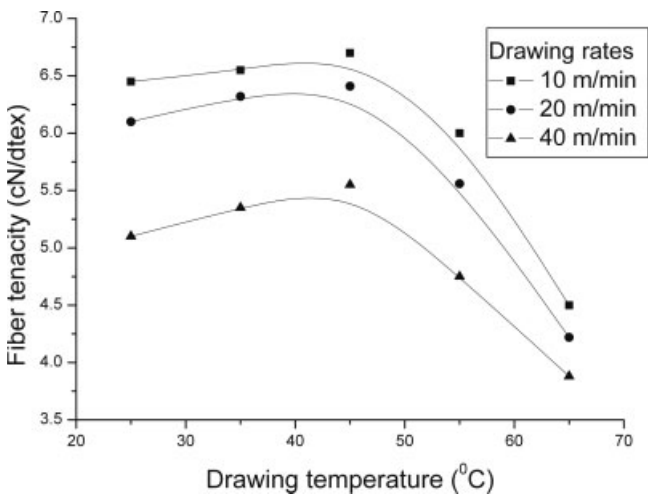

Figure 2 Influence of drawing temperatures and rates on fiber tensile strength.

CONCLUSION

Contrasting to current polymer spinning process, it is very unusual that the molecular orientation degree of PGA as-spun fibers is hardly affected by windup rates. The postdrawing process effectively enhances the fiber macromolecular orientation degree. The weak internal stress of the as-spun fiber by lower windup rate is useful for a higher drawing ratio of the as-spun fiber being high-ratio drawn and leading to good mechanical properties. Low drawing rate with suitable temperature is of benefit for preparing the PGA fibers with the relative high tensile strength. Generally, PGA fibers with perfect mechanical performance can be prepared at the spinning condition of lower windup rate and higher drawing multiple as well as slow drawing rate.

References

1. Yukihito, S.; Hideyasu, O.; Yuzo, S.; Ken-ichiro, M.; Hiroji, I. Surg Today 2002, 32, 297.
2. Kim, B. S.; Baez, C. E.; Atala, A. World J Urol 2000, 18, 2.
3. Harding, S. I.; Afoke, A.; Brown, R. A.; MacLeod, A.; Shamlou, P. A.; Dunnill, P. Bioprocess Biosyst Eng 2002, 25, 53.
4. Suzuki, M.; Fukuhara, K.; Unno, M.; Rikiyama, T.; Takeuchi, H.; Uchiyama, T.; Matsuno, S. J Hepatobiliary Pancreat Surg 1998, 5, 292.
5. Baykal, A.; Onat, D.; Rasa, K.; Renda, N.; Sayek, I. World J Surg 1997, 21, 579.
6. Tuompo, P.; Arvela, V.; Partio, E. K.; Rokkanen, P. Int Orthopaed (SICOT) 1997, 21, 355.
7. Moreno, M.; Magos, F. J.; Arcovedo, R.; Olachea, P.; Palacios, J. A.; Salazar, A.; Ramirez, M. E.; Herrera, J. J. Surg Endosc 2004, 18, 157.
8. Moseley, W. W. J Appl Polym Sci 1960, 3, 266.
9. Ziabicki, A. Melt Spinning, Fundamentals of Fibre Formation; Wiley-Interscience: New York, 1976; Chapter 3.
10. Akahane, T.; Mochizuki, T.; Nakayasu, H.; Kawai, S. J Soc Fiber Sci Technol Jpn 1980, 36, 319.
11. Overturf, J. Fundam Melt Spinning Synth Yarn Prod 1997, 14/15, 26.
12. Anazawa, T.; Ohbayashi, A. J Soc Fiber Sci Technol Jpn 1999, 55, 112.
13. Taurat, D. O. Chem Fibers Int 2001, 8, 62.
14. Billmeyer, F. W. Textbook of Polymer Science, 3rd ed.; Wiley: New York, 2000.