Yong Liu,
Ji-Huan He,
Jian-Yong Yu

Modern Textile Institute, Donghua University,
1882 Yan'an Xilu Road,
Shanghai 200051, China
E-mail: jhhe@dhu.edu.cn

Preparation and Morphology of Poly(butylene succinate) Nanofibers via Electrospinning

Abstract
An electrospinning method was used to produce Poly(butylene succinate) (PBS) nanofibres. The morphology of the fibres was studied considering fibres of different weight concentrations of PBS/CF solution and spun with different diameters of needle-orifice. The results show that the electrospinning process is very difficult and the products are only by few fibres when the weight concentration equals 8%. When the concentration is increased, the efficiency is high and the process becomes easy. The morphology of the fibres is more uniform when are spun with a larger diameter of the needle-orifice. The electrospinability ranges between 8 wt% and 14wt% of PBS/CF weight concentration. The thermal properties and the crystallisation of the PBS polymer pellets and electrospun PBS nanofibers were measured by differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD), respectively. In addition, the hydrolytic degradation behaviour of electrospun PBS nanofibres in 1N NaOH solution was observed by using scanning electron microscopy (SEM).

Key words: *electrospinning, PBS, nanofibers, morphology, characterization.*

Introduction

It is known that biodegradable polymers have received growing interests in recent decades because of increasing global waste-plastic pollution. Poly(butylene succinate) (PBS) , as one of the aliphatic polyesters, which are biodegradable and easily decomposed in an acidic or basic condition and thus considered as promising polymers to solve the problem, has been investigated by many researchers [1 - 5]. Because of their excellent biodegradability, melt processability and thermal and chemical resistance, the application fields of their products, especially those combined with the electrospinning process, may be extended further to textiles, medical treatment, environmental engineering and biotechnology, defence and security application, etc. [6, 7]. Thus the importance of research into electrospinning PBS nanofibres is self-evident.

On the other hand, the electrospinning process and the electrospinning of other biogradable and biocompatible polymers such as poly(lactide) (PLA), poly(D,L-lactide), poly(L-lactic acid) (PLLA), poly(lactic-co-glycolic acid) (PLGA), chitosan fibres and their application have been popularly investigated in recent several years [8 - 20]. Unfortunately, there is very little literature that focuses on the electrospinning of PBS fibres. Eun Hwan Jeong et al. studied the electrospinning of PBS along with the thermal and structural properties of ultrafine PBS fibres for the first time [21]. Our group investigated micro-spheres with nanoporosity [22] and the effect of voltage on morphology and diameter of electrospun PBS nanofibers [23]. However, it is necessary to perform more experiments to understand and optimise this process. It was reported in open literature that solution concentration has a significant effect on the morphology and diameter of the electrospun fibres [24 - 26]. In this study, we investigate the morphology of the PBS nanofibers via electrospinning under different weight concentrations and needle-orifice diameters. Additionally, the thermal properties and crystallisation of electrospun PBS fibres were characterised by DSC and WAXD. The hydrolytic degradation behaviour was observed by using scanning electron microscopy.

Experimental

Materials

The PBS polymer was provided by Shanghai Institute of Organic Chemistry, Chinese Academy of Science. The molecular weight is about 200,000 - 300,000 g/mol. The solvent system was chloroform (CF) from Shanghai Chemical Reagent Co., Ltd. China. All the chemicals in this study were used as received without further purification.

Four PBS solutions of about 8, 10, 12 and 14 wt% were prepared by dissolving PBS pellets in CF solvent at 40 °C and stirring vigorously for 2 h. All the solutions were cooled to room temperature before electrospinning.

Electrospinning process

The electrospinning setup with a F180-L variable DC high-voltage power generator (of 0 - 100 kV, Shanghai Fudan High School) was used in this study. The schematic is illustrated in Figure 1. The electrospinning process was performed using the above-mentioned PBS polymer solutions. The polymer solution was placed into a 20 ml plastic syringe with a stainless steel needle. The spinning process was carried out under room temperature in a vertical spinning configuration. The orifices of the needles were 0.5, 0.7, and 0.9 mm and the spinning distance between the orifice and the collector was

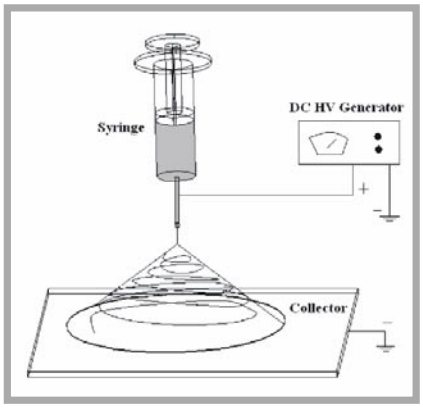

Figure 1. *Electrospinning setup.*

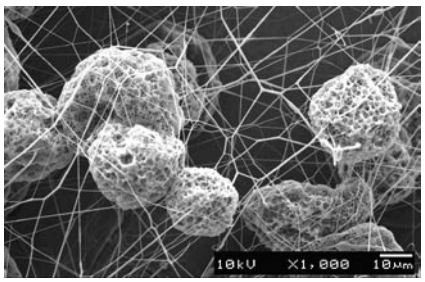

Figure 2. *SEM photograph of PBS electrospun fibers. The concentration and voltage are 8 wt% and 10 kV. The diameter of the needle orifice is 0.5 mm.*

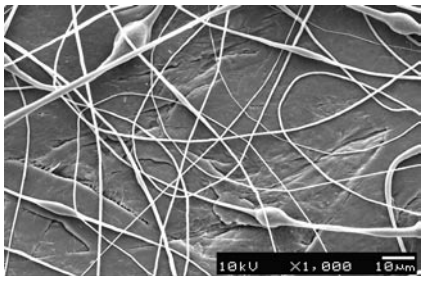

Figure 4. *SEM photograph of PBS electrospun fibers. The concentration and voltage are 12 wt% and 10 kV. The diameter of the needle orifice is 0.5 mm.*

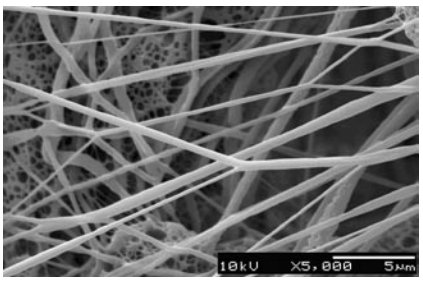

Figure 3. *SEM photograph of PBS electrospun fibers. The concentration and voltage are 10 wt% and 10 kV. The diameter of the needle orifice is 0.5 mm.*

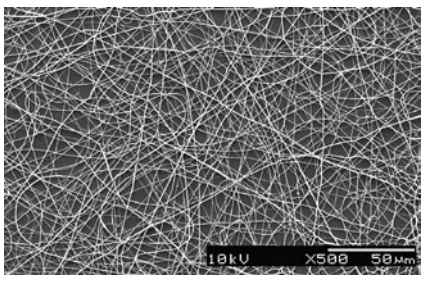

Figure 5. *SEM photograph of PBS electrospun fibers. The concentration is 14 wt% and the applied voltage is 10 kV. The diameter of the needle orifice is 0.5 mm.*

about 5 cm. The applied was 10 kV connected to the needle by the high-voltage power supply via an alligator clip.

Characterisation

The diameter and morphology of the electrospun PBS fiber mats were determined by a JSM-5610 scanning electron microscope (SEM, Japan). Each sample was collected on a SEM disk and then coated with gold. A Perkin–Elmer, Pyris 1 differential scanning calorimeter (DSC) was employed to evaluate thermal properties. About 5 mg samples were placed in an aluminum pan and were heated to 160 °C at a rate of 20 °C/min. under a nitrogen atmosphere. An X-ray measurement was carried out using a D/max-2550 PC X-ray diffractometer (Rigaku Corporation, Japan), where Cu K target was used at 40 kV and 300 mA (λ = 0.154 nm) within the 2θ, range of 5 - 60°.

Results and discussion

Morphology

The electrospinning process was performed to observe the fibre formation efficiency. The morphologies of the fibres in different weight concentrations and diameters of the needle orifice were observed through SEM photos. SEM micrographs of the products are illustrated in Figures 2 - 5. When the weight concentration was 8%, the electrospinning process was difficult and the products were some balls with few fibres (Figure 2). The process was somewhat difficult and the products were fibres with few balls at 10 wt% (Figure 3). In addition to very few small beads, the process was easy and the products were fibres at 12 wt% (Figure 4). The efficiency of the electrospinning process is high at the high weight concentration and the products are predominately fibres (Figure 5). It was obvious that the products became fibers completely when the weight concentration arrived at 14 wt%. However, the process was almost impossible in the case of 15 wt% because of the too high viscosity of the solution. We found inelectrospinability in the PBS/CF solution when the concentration got below 8% or over 14%. The reason for this phenomenon might be that the solvent, chloroform (CF), was evaporated quickly at the exit orifice of the needle in the case of low weight concentration and high viscosity of 14 wt% solution. SEM analysis of electrospun PBS fibres revealed that the diameters of the fibres ranged between 200 nm and 1 μm, depending on the needle orifice as shown in Figure 9 (see page 32). When the diameter of the needle was smaller, it seemed that the diameter of the fibres became less uniform (see Figure 6). The average diameter of electrospun nanofibres was about 960 nm when the diameter of the needle orifice was 0.5 mm. With the larger diameter of the needle, the uniformity improves (see Figures 7 and 8). The average diameters of electrospun nanofibres were about 600 nm and 500 nm when the diameters of the needle orifice were 0.7 and 0.9 mm, respectively.

Thermal properties and crystallisation

DSC and WAXD were used to characterise the thermal properties and crystal structures of PBS pellets and electrospun PBS nanofibres, which were fabricated under the condition of 14 wt%. Figure 10 (see page 32) showes the DSC thermograms of PBS pellets and electrospun PBS nanofibres. The thermogram for PBS pellets showes typical double melt-

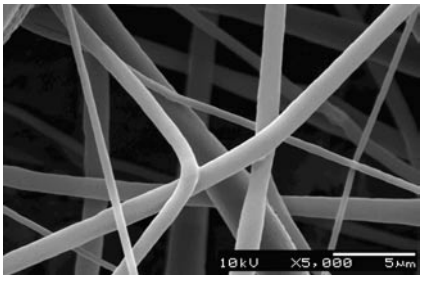

Figure 6. *SEM photograph of PBS electrospun fibers. The concentration and voltage are 12 wt% and 10 kV. The diameter of the needle orifice is 0.5 mm.*

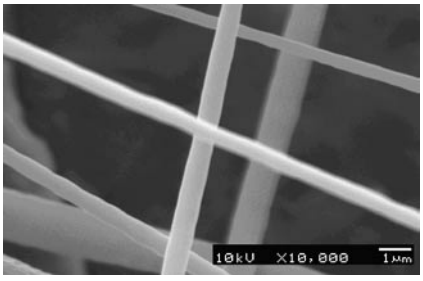

Figure 7. *SEM photograph of PBS electrospun fibers. The concentration and voltage are 12 wt% and 10 kV. The diameter of the needle orifice is 0.7 mm.*

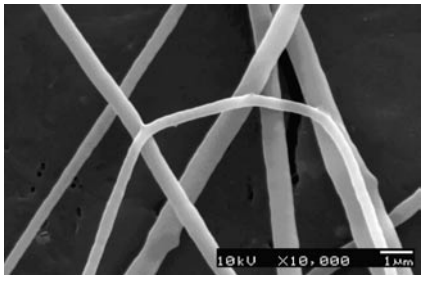

Figure 8. *SEM photograph of PBS electrospun fibers. The concentration and voltage are 12 wt% and 10 kV. The diameter of the needle orifice is 0.9 mm.*

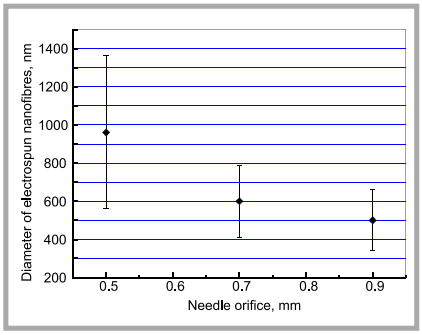

Figure 9. *Electrospun PBS fiber diameters as a function of needle orifice.*

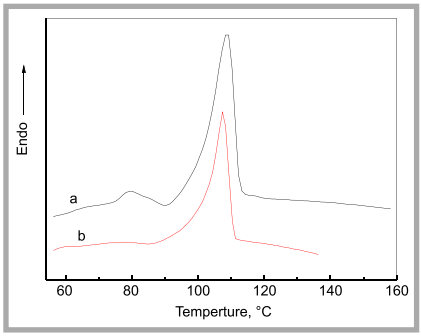

Figure 10. *DSC thermograms of (a) PBS pellets and (b) electrospun PBS fibers.*

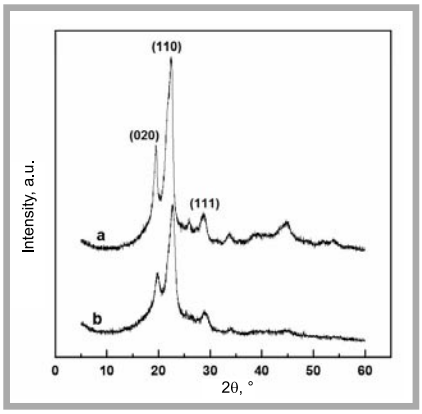

Figure 11. *Wide angle X-ray diffraction patterns for (a) PBS pellets and (b) electrospun PBS fibers.*

ing behaviour [27], while the thermal properties of the electrospun PBS nanofibres were similar to those of PBS pellets except for the melting peak at 79 °C (not visible for PBS nanofibres) as illustrated in Figure 10 and Table 1, respectively. The crystallisation of electrospun PBS nanofibres is 45.01%. In order to compare with the results in open literature [21, 28], we calculated its crystallisation based on the heat of the fusion for PBS being 200 J/g. The WAXD patterns of PBS pellets and electrospun PBS fibres in Figure 11 showed that the two samples had similar characteristic peaks and patterns. The characteristic peaks, (020), (110) and (111), were located at 2θ = 19.6°, 22.36°, and 28.64°, respectively [21, 29, 30]. The crystallisation of electrospun PBS nanofibres was 69.16%. The reason for the difference between the two crystallisations was mainly the different methods used.

Hydrolytic degradation

For degradation study, electrospun PBS nanofiber specimens were immersed in 1N NaOH solution at 37 °C for 1, 2 and 3 hours, respectively. The specimens were dried in a drying oven and then observed through SEM photography. Figures 12.a, 12.b and 12.c revealed their SEM images of the fibres after hydrolytic degradation for 1, 2, and 3 hours, respectively. The effect of hydrolytic degradation on PBS nanofibres was indistinct in an hour. As time passed, the nanofibres degraded rapidly and some fibres were broken down (see Figure 12.b). After 3 hours, all of the nanofibres were broken down completely. The reason for the fast degradation might be that the nanofibres had a higher ratio of surface-to-volume than fibres with larger dimensions [21]. The crystallisation also played an important role in the polymer hydrolytic degradation, which happened in the amorphous region at an earlier stage.

Conclusions

Four weight concentration PBS/CF solutions, 8, 10, 12, 14 wt%, and three diameters of the needle orifice, 0.5 mm, 0.7 mm, 0.9 mm, have been used to investigate the morphology of the PBS fibres via electrospinning. The electrospinning process was very difficult and the efficiency was very low when the weight concentration was below 10%. The products were some balls besides a few fibres. The fibres are in the majority when the weight concentration is equal to or over 12%. The morphology of the fibres became more uniform when the diameter of the needle became larger. The thermal properties of the electrospun PBS nanofibres were similar to those of PBS pellets. The crystallisation of electrospun PBS nanofibres was 69.16% measured by WAXD. The speed of hydrolytic degradation of electrospun PBS nanofibres was rapid and all the fibres were broken down after 3 hours in 1 N NaOH solution.

Table 1. *Thermal properties of PBS pellets and electrospun PBS fibers*

Sample	T_m, °C	ΔH_m, J/g	Crystallinity, %
PBS pellets	108.911	86.219	43.11
PBS fibers	107.755	90.011	45.01

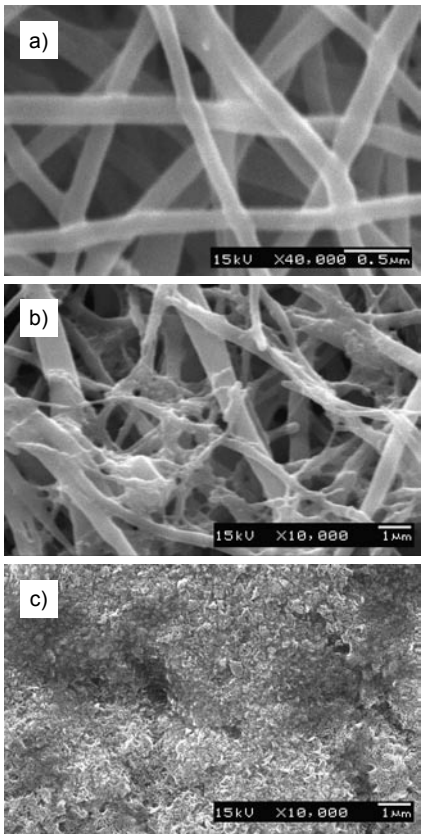

Figure 12. *SEM photographs of the electrospun PBS nanofibers after hydrolytic degradation in a 1 N NaOH solution for (a) 1 h and (b) 2 h (c) 3 hours respectively.*

Acknowledgement

The financial support from National Natural Science Foundation of China under grant No. 10372021 and the Program for New Century Excellent Talents in University is greatly appreciated.

References

1. *Kim H. -S., Kim H. -J., Lee J. -W., et al.; Polymer Degradation and Stability, Vol. 91 (2006) pp. 1117-1127.*
2. *Haiyan L., Jiang C., Amin C., Junying W.; Macromolecular Bioscience, Vol. 5 (2005) pp. 433-440.*
3. *Bahari K., Mitomo H., Enjoji T., et al.; Polymer Degradation and Stability, Vol. 62 (1998) pp. 551-557.*

4. *Chrissafis K., Paraskevopoulos K. M.; Bikiaris D.N. Thermochimica Acta Vol. 435 (2005) pp. 142-150.*
5. *Someya Y., Nakazato T., Teramoto N., et al.; Journal of Applied Polymer Science, Vol. 91 () pp. 1463-1475.*
6. *Ramakrishna S., Fujihara K., Teo W. - E., et al.; Materials Today, Vol. 9 (2006) pp. 40-50.*
7. *Rho K. S., Jeong L., Lee G., et al.; Biomaterials, Vol. 27 (2006) pp. 1452-1461.*
8. *Tomaszewski W., Szadkowski M. Fibres & Textiles in Eastern Europe (2005); Vol. 13 No. pp. 22-26.*
9. *He J. -H., Wan Y. -Q.; Polymer Vol. 45 (2004) pp. 6731-6734.*
10. *He J.-H., Wan Y.-Q., Yu J.-Y. Polymer (2005); 46:2799-2801.*
11. *Spivak A.F., Dzenis Y.A., Reneker D.H. Mech Res Commun (2000); 27:37-42.*
12. *Reneker D.H., Yarin A.L., Fong H., et al. J Appl Phys (2000); 87:4531-4547.*
13. *Kim K., Luu Y.K., Chang C., et al. J Control Release (2004); 98:47-56.*
14. *Kim K., Yu M., Zong X., et al. Biomaterials (2003); 24:4977-4985.*
15. *Shu-Ying Gu J.R. Macromol Mater Eng (2005); 290:1097-1105.*
16. *Young You S.J.L.B.-M.M.W.H.P. J Appl Polym Sci (2006); 99:1214-1221.*
17. *Blasinska A., Krucinska I., Chrzanowski M. Fibres & Textiles in Eastern Europe (2004); 12:51-55.*
18. *Wu Y., Yu J.-Y., He J.-H., et al. Chaos, Solitons & Fractals (2007); 32:5-7.*
19. *Zeng Y.-C., Wu Y., Pei Z., et al. International Journal of Nonlinear Sciences and Numerical Simulation (2006); 7: 385-388.*
20. *He J.-H., Wan Y., Yu J. International Journal of Nonlinear Sciences and Numerical Simulation (2004); 5:253-262.*
21. *Jeong E.H., Im S.S., Youk J.H. Polymer (2005); 46:9538-9543.*
22. *He J.-H., Liu Y., Xu L., et al. Chaos, Solitons & Fractals (2007); 32:1096-1100.*
23. *Liu Y., He J.-H., Xu L., et al. International Journal of Electrospun Nanofibers and Applications (2007); 1:7-15.*
24. *Megelski S., Stephens J.S., Chase D.B., et al. Macromolecules (2002); 35:8456 -8466.*
25. *Deitzel J.M., Kleinmeyer J., Harris D., et al. Polymer (2001); 42:261-272.*
26. *Thandavamoorthy Subbiah, Bhat G.S., Tock R.W., et al. J Appl Polym Sci (2005); 96:557-569.*
27. *Cho K., Lee J., Kwon K. Journal of Applied Polymer Science (2001); 79:1025-1033.*
28. *Miyata T., Masuko T. Polymer (1998); 39: 1399-1404.*
29. *Gan Z., Abe H., Kurokawa H., et al. Biomacromolecules (2001); 2:605-613.*
30. *Park J.W., Kim D.K., Im S.S. Polymer International (2002); 51:239 - 244.*

Received 11.01.2007 Reviewed 29.06.2007

TEXMEDECO NET

TEXTILES & HEALTH INTERNATIONAL SCIENTIFIC NETWORK

The **TEXTILES & HEALTH POLISH SCIENTIFIC NETWORK** was established as an initiative of the **Textile Research Institute**, Łódź, Poland (Instytut Włókiennictwa – IW) and other R&D centres working in the area of textiles, medicine and occupational medicine.

The **TEXTILES & HEALTH SCIENTIFIC NETWORK** (with the acronym of **TEXMEDECO NET**) was formally registered at the State Committee for Scientific Research in Warsaw on the basis of an official decision of 31 January 2003. Due to a new decision of 26 January 2005 it received the formal status of the **INTERNATIONAL SCIENTIFIC NETWORK**.

The Textile Network area covers the following fields:

- MED-TEXTILES: textiles for medical treatment,
- ECO-TEXTILES: textiles safe for human health,
- ENVIRO-TEXTILES: textiles, which protect against physical, chemical and biological hazards.

- The MED-TEXTILES group covers research into all textile fabrics assisting medical treatment and prophylaxis. It requires collaboration of scientists from various disciplines: textile technology, chemistry, biology, medicine, epidemiology, and medical engineering. Textile wound coverings, antibacterial fabrics, textile prostheses & implants, and modern intelligent textiles applied in medical diagnostics & treatment belong to this group.

- The ECO-TEXTILES group covers research works and studies aimed at protecting human (skin, respiratory and thermo-regulating systems), and against the negative effects of textile fabrics.

- The ENVIRO-TEXTILES group comprises textile fabrics protecting humans against the harmful effects of external factors (electromagnetic and electrostatic fields, UV and IR radiation, microorganisms).

The **TEXTILES & HEALTH NETWORK** comprises 17 Polish and 5 foreign R&D institutions covering the following areas: textiles, medicine, occupational medicine and the leather industry (List of Member Institutions www.texmedeco.net).

The Institute acts as the coordinating institution of this Network, represented by the network coordinator Jadwiga Sójka-Ledakowicz Ph. D., Eng.

The network acts on the basis of the 'Network Status' and the 'Regulations' (of the Network Steering Committee and of the Network Work Groups). The coordinator, the vice-coordinators and the chairmen of Work Groups (Med, Eco and Enviro) form the structure of the Steering Committee which is the executive body. The General Assembly is the highest authority of the network. The authorised representatives of all members (one from each member institution) take part in the meetings of the General Assembly.

The **TEXTILES & HEALTH INTERNATIONAL SCIENTIFIC NETWORK** has an open character.

We welcome any new members both from Poland and abroad.

Interested parties should contact the Network Coordinating Office:

INSTYTUT WŁÓKIENNICTWA - TEXTILE RESEARCH INSTITUTE
address: Brzezińska 5/15, 92-103 Łódź, POLAND
www.texmedeco.net

Jadwiga Sójka-Ledakowicz Ph. D., Eng. - network coordinator
tel (+4842) 6163 110 ; e-mail: ledakowicz@mail.iw.lodz.pl

Katarzyna Grzywacz (Ms) – info officer ; network secretary
phone: (+4842) 6163 195, fax (+4842) 6792638, e-mail: grzywacz@mail.iw.lodz.pl