Fabrication and Characterization of a Persimmon Leaves (PL)/poly(acrylonitrile) (PAN) Blend Bio-fiber

De-Lan Li,[1] Qing Shen,[1,2] Hong-Gui Ding,[1] Qing-Feng Gu,[1] Zhi-Xin Wang[1]

[1]*Department of Polymer Material and Engineering, Donghua University, 200051 Shanghai, People's Republic of China*
[2]*State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, 200051 Shanghai, People's Republic of China*

Received 1 June 2005; accepted 11 July 2005
DOI 10.1002/app.22612
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Adopting persimmon leaves, PL, as a biomaterial to blend with poly(acrylonitrile) (PAN) via the wet spinning method, a PL/PAN blend biofiber was fabricated. On the basis of mechanical measurements, X-ray diffraction, and DSC characterization, it was found that this biofiber has acceptable mechanical properties for further applying to different cases. Results also showed that though the crystal structure, especially the crystal size, is changed indeed for blend fiber, it seems to be of less influence on the thermal properties, especially the crystallization temperature, T_c.
 J Appl Polym Sci 101: 2810–2813, 2006

Key words: persimmon leaves; poly(acrylonitrile); blend fiber; wet spinning; structure; properties

INTRODUCTION

With respect to the several findings on persimmon leaf, PL, that this natural material provided better effects for applying to medical area,[1–6] different PL-based medicinal products have been therefore innovated, as can be seen elsewhere.[1–7] Recently, by analysis of the material components of PL (e.g., lignin, cellulose, and hemicellulose components[8]) and surface properties (e.g., the Lifshitz-van der Waals, Lewis acid-base components[9]), we have successfully prepared a cellulose/PL blend fiber.[7] Of that case,[7] a comparison with reference to cellulose fiber prepared via the same route showed that the mechanical properties of PL/cellulose blend fiber are also acceptable, indicating the blend biofiber can be further fabricated to fit different cases, including biotextiles. On the basis of previously obtained results,[7] it was further considered that PL might also be blended with other polymers, especially synthetic polymeric materials, to provide new insight than previous obtained PL/cellulose blend fiber.[7]

The condition of wet spinning method is capable of protecting the medical substances for biomaterials as previous adopted, and poly(acrylonitrile) (PAN) can be dissolved in solvent to fit such conditions.[10] The aims of this work were therefore proposed initially to prepare a PAN/PL blend fiber; then to characterize the properties of the obtained fiber, meanwhile comparing it with a referenced PAN fiber that was prepared with the same method and condition as that of this case.

Correspondence to: Q. Shen (sqing@dhu.edu.cn).
Contract grant sponsor: Chinese Education Ministry; contract grant numbers: 2B10601.

EXPERIMENTAL

Materials

As previously described in detail,[7–9] the persimmon leaves (PL) were picked from the campus of Donghua University, Shanghai, and prepared in powder form with a size of about 40 meshes.

Commercial PAN with known molecular weight, M_n, of about 18 kDa was obtained from Shanghai Jinshan Chemical Co. and used without further treatment. Previously, this PAN powder has been also used and described.[10]

An analytical grade *N*,*N*-dimethylacetamide, DMAc, solvent purchased from a chemical company located at Shanghai was adopted. This solvent was used as received without further purification.

Preparation of spinning solution and spinning of blend fiber

In the process of spinning solution preparation, the PAN powders were initially heated to about 80°C, and kept for about 12 h. Then, PAN powders were dissolved in DMAc solvent for about 3–4 h until dissolution phenomena was fully observed. After that, PL powders were added to PAN/DMAc solution and was further heated for about 1 h to yield a uniform

solution. Before spinning, the blend solution was filtrated to fit the conditions of spinning.[7]

A laboratory scale wet spinning process was carried out as described earlier.[7] Briefly, the fiber was spun under a pressure of about 300 kPa, controlled by a metering pump with a flow rate of about 0.2 g/min. The fiber was initially formed by a spinneret with the diameter of 100 μm and a L/D ratio of 1.0, then be solidified throughout by two water baths, i.e., the former was a coagulation bath with a temperature of about 55°C, and the latter was a boiling bath with a temperature of about 95°C. Finally, the obtained filament was washed with distilled water and dried in a vacuum oven at 50°C for 24 h. Before analysis, the filament was held at a container under a condition of 20°C and 65% relative humidity. Similarly, a pure PAN fiber was prepared as a reference.

Fiber analysis and characterization

As mentioned in the previous work,[7] the mechanical properties of obtained filaments were measured using several self-made (Donghua University) fiber analysis instruments, e.g., XQ-1, YG086, and YG001A. During measurement, the gauge length and crosshead speed were chosen as 500 mm and 7.5 mm/min, respectively. All reported values were averaged based on 10–30 independent measurements.

The X-ray diffractograms of fibers were recorded using Rigaku III Dmax 2500 type X-ray diffractometer. Nickel-filtered (λ = 0.1542 nm) Cu Kα radiation was used for all measurements. The Sherrer equation was employed to calculate crystal grain size corresponding to $2\theta = 14°$.[7,11,12] For DSC analysis, a Mettler-Toledo 822e Differential Scanning Calorimeter was employed, and the temperature was increased from 20 to 300°C at a rate of 10°C/min.

To analyze the orientation of fiber, a sonic velocity measurement was carried out using a self-made tester and the method of Moseley,[12] as mentioned earlier.[7]

RESULTS AND DISCUSSION

In general, blending of polymeric material with PL is based on the fact that this natural material is rich in macromolecules components.[8] For example, by analysis of its material components, it was primarily known that PL consists of cellulose (about 68%), hemicellulose (about 8%), and lignin (about 12%), respectively,[8]. However, in the case of PL/cellulose blend fiber,[7] it was exactly found that the effects from the low-molecular-weight components and anomalous macromolecules of PL are obviously on the structure and mechanical properties of obtained blend fiber. Additionally, influences from spinning process, e.g., the temperature of coagulation bath and the concentration of spinning solution, are visible.[7] Furthermore, the amount of PL added is also an important factor.[7]

TABLE I
Influence of Temperature of Coagulation Bath on Drawing and Mechanical Properties of PL/PAN Blend Fiber

Temperature of coagulation bath (°C)	Drawing behavior of the fiber	Breaking intensity of the fiber (cN/dtex)
20	Breaks easily	1.6
30	Good drawing	2.1
40	Good drawing	2.2
50	Breaks easily	1.9

Influence of the temperature of coagulation bath on preparation and mechanical properties of PL/PAN blend fiber

To vary the temperature of coagulation bath from 20 to 50°C and take fiber drawing and breaking intensity as two targets, the influence of coagulation bath on preparation of PL/PAN fiber was evaluated (Table I). Both the lowest and the highest temperatures (e.g., 20 and 50°C, respectively) caused bad results, indicating that these temperatures are not suitable for the preparation of the PL/PAN blend fiber. According to Table I, the best temperature for coagulation bath seems to be about 40°C. Since this temperature is smaller than that for the preparation of PL/cellulose blend fiber previously adopted,[7] the solidification of PL/PAN blend fiber is easier than that of PL/cellulose blend fiber. Probably, this may be of benefit to the enhancement of the mechanical properties for PL/PAN blend fiber.

Influence of the concentration of spinning solution on mechanical properties of PL/PAN blend fiber

By fixing the amount of PL added at about 5 wt % and varying the concentration of spinning solution from 14 to 18 wt %, the influence of the concentration of spinning solution on fiber was evaluated (Table II). The lower concentration of spinning solution, e.g., 14 and 15%, are found to be inappropriate for PL/PAN blend fiber preparation mainly because of difficult drawing.

According to Table II, it was noted that the mechanical properties of PL/PAN blend fiber seem to be increased with the increase of the concentration of spinning solution, especially up to about 18%. This is important and generally expected for preparation of a qualified polymeric filament.[12]

Influence of the added amount of pl on the preparation and mechanical properties of PL/PAN blend fiber

To prepare a PL/PAN blend fiber, the amount of PL added is expected in high. However, the amount

TABLE II
Influence of the Concentration of Spinning Solution on Drawing and Mechanical Properties of PL/PAN Blend Fiber

Concentration of spinning solution (wt %)	Amount of persimmon leaves added (wt %)	Drawing behavior of the fiber	Breaking intensity of the fiber (cN/dtex)
14	5	Difficult drawing	–
15	5	Breaks easily	1.8
16	5	Gooddrawing	2.1
18	5	Good drawing	2.2

added is considerable to influence polymer's structure and to influence related mechanical properties. The reason is PL with various low-molecular-weight substances[8] would influence the polymer net and extend to the orientation of fiber.[7] To understand the amount of PL added is how to influence blend fiber, the PL added in spinning solution was thus varied from 0, 2.0, 5.0 to about 10% in weight, respectively. Of which, the zero represents the referenced PAN fiber.

According to X-ray measurement presented in Figure 1, the influence of the addition of PL on PAN is evident as intense peaks shifted. Moreover, the visible change seems to be at the 100 and 101 peaks for blend fiber due to the former smaller and latter greater in comparison of PAN fiber (Fig. 1). This thus indicated that the crystal structure of PAN was changed by the addition of PL. Figure 2 further showed that the crystallinity of PAN was rapidly decreased with the increase in the amount of PL added. As a support, Figure 3 showed that the orientation of blend fiber was greatly reduced with the increase in the amount of PL

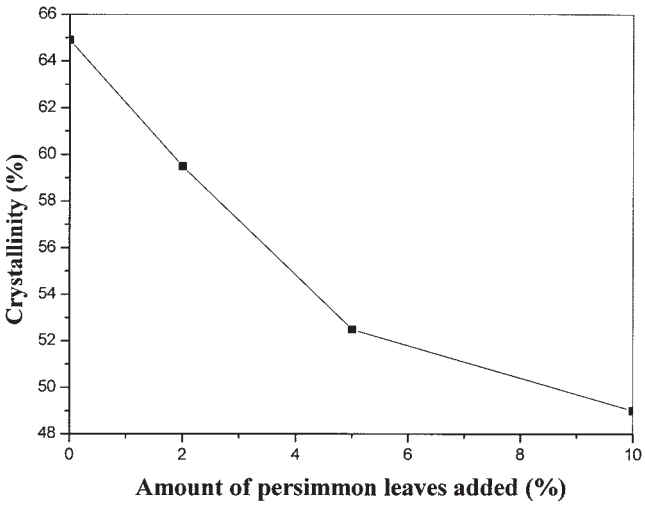

Figure 2 The crystallinity of PL/PAN blend fiber as a function of the added amount of persimmon leaves.

because of the change of crystal structure. Figure 4 furthermore described that the change of the crystal structure is indeed to influence the mechanical properties of blend fiber. This suggests that for the preparation of PL-based biofiber a suitable concentration needs to be chosen to fit the request of the biocomponent or the mechanical properties.

On the basis of Figure 1, the change of the crystal structure is described in detail in Table III. The change of the crystal structure is attributable to the change in crystal grain size. This thus furthermore indicated that the low-molecular-weight substances remained in PL would cause poor compatibility for blend polymer where beyond a critical concentration in the absence of strong intermolecular interactions based on the interference of the random coil polymer with a mutual

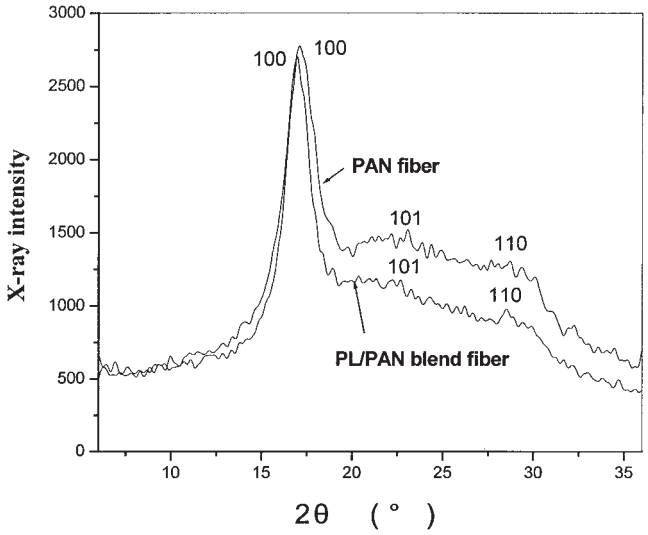

Figure 1 A comparison of the X-ray diffractograms for PL/PAN blend fiber and referenced PAN fiber.

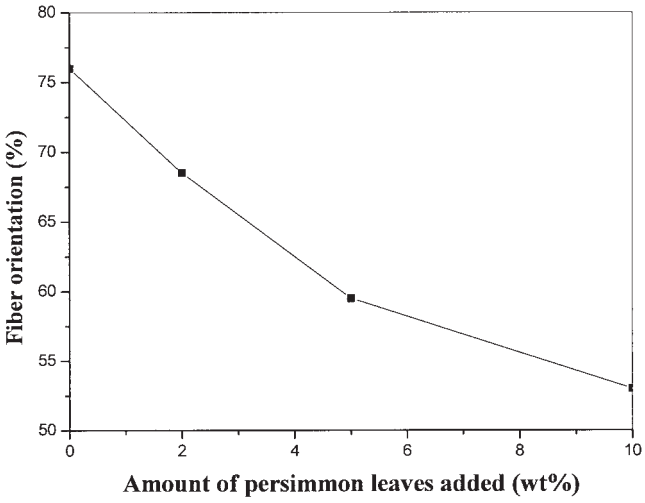

Figure 3 The orientation of PL/PAN blend fiber as a function of the added amount of persimmon leaves.

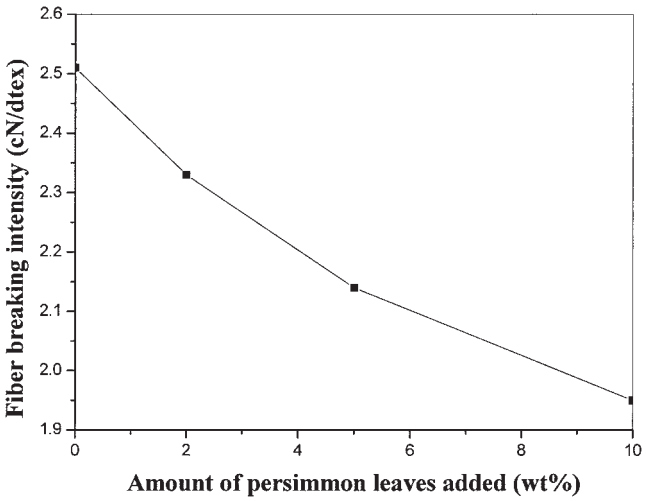

Figure 4 The breaking intensity of PL/PAN blend fiber as a function of the added amount of persimmon leaves.

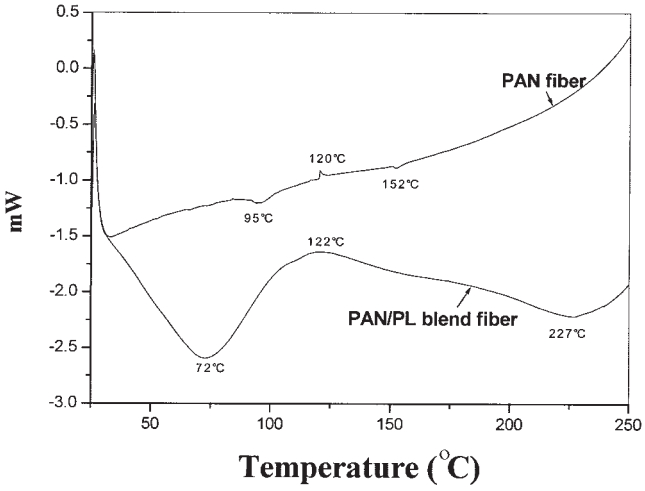

Figure 5 A comparison of DSC curves for PL/PAN blend fiber and referenced PAN fiber.

orientation of the molecules of the rod-like polymer molecules.[12] This is possible and has been ascribed to that the low-molecular-weight polymers played as a plasticizer to facilitate polymer chains.[13]

Acomparison of the thermal behaviors for PL/PAN blend fiber and referenced PAN fiber

To understand the difference between PL/PAN blend fiber and PAN fiber, DSC curves for these two fibers were recorded and presented in Figure 5. A comparison of these curves showed that the glass transition temperature, T_g, for blend fiber is less (at about 72°C) than that for PAN fiber (at about 95°C). Furthermore, the comparison of the crystallization temperature, T_c, for both blend and pure fibers however showed that it seems to be similarly without influenced. This is of interest since thermal phenomena presented by Figure 5 seems to be contradict that presented by Figure 1. Thus, it is considered that the addition of PL into PAN is acceptable for fabrication of a bio-blend fiber.

TABLE III
A Comparison of the Crystal Structure for PL/PAN Blend Fiber and PAN Fiber

Fibers	Amount of added persimmon leaves (wt %)	Crystal grain size (nm)		
		100	101	110
PAN	0	3.34	0.34	0.23
PL/APN blend	10	2.74	0.40	0.22

CONCLUSIONS

Applying wet spinning method, a PL/PAN bio-blend fiber was fabricated. According to structure analysis and mechanical properties determination, as well as compared with a referenced PAN fiber prepared via the same method as that of this case, it was found that this bio-blend fiber is suitable for further application though the change in the crystal structure seeming to be visible because the addition of PL also induced several low-molecular-weight substances.

References

1. Funayama, S.; Hikino, H. Chem Pharm Bull 1979, 27, 2865.
2. Kameda, K.; Takaku, T.; Okuda, H. J Nat Prod 1987, 50, 680.
3. Kotani, M.; Fujita, A.; Tanaka, T. J Jpn Soc Food Sci 1999, 52, 147.
4. Kotani, M.; Matsumoto, M.; Fujita, A.; Higa, S.; Wang, W.; Suemura, M.; Kishimoto, T.; Tanaka, T. J Allergy Clin Immunol 2000, 106, 159.
5. Matsumoto, M.; Kotani, M.; Fujita, A.; Higa, S.; Kishimoto, T.; Suemura, M.; Tanaka, T. Br J Dermatology 2002, 146, 221.
6. Tanaka, T.; Higa, S.; Hirano, T.; Kotani, M.; Matsumoto, M.; Fujita, A.; Kawase, I. Curr Med Chem Anti Inflamm Anti Allergy Agents 2003, 2, 57.
7. Wang, Z. X.; Shen, Q.; Gu, Q. F. Carbohydrate Polymer 2004, 57, 415.
8. Hu, J. F.; Zuo, T. L.; Zhang, H.; Shen, Q. J Inner Mongolia Polytechnic Univ 2002, 21, 272 (in Chinese).
9. Shen, Q.; Ding, H. G.; Zhong, L. Colloids Surf B 2004, 37, 133.
10. Shen, Q.; Gu, Q. F.; Hu, J. F.; Teng, X. R.; Zhu, Y. F. J Colloids Interface Sci 2003, 267, 333.
11. Alexander, L. (Ed.) In X-ray Diffraction Method in Polymer Science; Wiley-Interscience: New York, 1969; p 137.
12. Billmeyer, F. W., Jr. (Ed.). In Textbook of Polymer Science, 3rd ed.; Wiley: New York, 2000.
13. Focher, B.; Marzetti, A.; Conio, G.; Marsano, E.; Cosani, A.; Terbojevich, M. J Appl Polym Sci 1994, 51, 583.