PREPARATION OF WELL-ALIGNED AND WELL-ORIENTED *ALL*-POLYIMIDE NANOFIBER COMPOSITE

K. Mizoguchi[a*], C.Hongo[a], M.Kotera[a], T.Nishino[a]

[a] *Department of Chemical Science and Engineering, Kobe University, Rokko, Nada, Kobe, Japan*
**tnishino@kobe-u.ac.jp*

Keywords: Polyimide, Nanofiber, Nanocomposite, Mechanical Properties

Abstract
Polyimide (PI) possesses the outstanding mechanical properties, high temperature stability, and high chemical resistance. In the high technology fields, such as aerospace and electronic industries, PI is widely used. In this study, a simple method for preparing all-polyimide (PI) nanocomposite was proposed. Well-aligned and well-oriented BPDA-PPD type PI nanofibers were electrospun with rotating disk-shaped collector, then these well-aligned and well-oriented PI nanofibers were impregnated into PI precursor solution, followed by thermal imidization, and finally all-PI nanocomposite was obtained. These electrospun PI nanofibers and all-PI nanocomposite were found to possess excellent mechanical properties.

1. Introduction

Polyimide (PI) possesses the outstanding mechanical properties, high temperature stability, and high chemical resistance. In the high technology fields, such as aerospace and electronic industries, PI is widely used. Especially, BPDA-PPD type PI, from biphenyl tetracarboxylic dianhydride (BPDA) and *p*-phenylene diamine (PPD), has linear and rigid skeleton, and its crystallites are known to be well oriented by slight drawing, which results in high mechanical performance, *that is*, high modulus and high strength [1]. In addition, these properties depend on heat treatment process [2, 3].

In a past few decades, nanoscale materials are the subject of extensive worldwide researches in both industry and academia because of their novel functionality and high performance. Electrospinning (ES) is known as a low cost but effective method to produce polymer nanofibers [4, 5]. Thus, ES became well-recognized method and has already created interesting applications in drug delivery system, wound dressing, scaffolds in tissue engineering, and sensors in electronics [6-8]. In general, ES is used to make nonwoven fabric.

In this study, we basically used this ES technique but there is one distinguished different point. Instead of using flat plate collector, we here used a rotating disk-shaped collector, which make fibers highly aligned. Then it becomes also possible to make uniaxial orientation of molecular chain by drawing, which is expected to result in higher mechanical properties. In addition, we tried to use these nanofibers as reinforcement in this study.

Recently, polymer composites have excellent properties so that they are used in wide range of applications such as automobiles, ICT and electronic devices, and medicals [9]. As the reinforcing elements, glass fibers or carbon fibers are often used. In general, these composites have interface between the matrix and the reinforcements. This interface often causes problems such as poor adhesion, imperfect stress transfer and high water uptake. These problems may reduce the properties of the whole composites. From this point of view, the concept of single polymer composites has proposed [10]. The composites are made by similar or identical materials for both matrix and reinforcement, so they have advantage in terms of recyclability and interfacial compatibility [11]. Following this pioneering work, a number of studies have been carried out on the preparation and characterization of single polymer composite. Our laboratory has also engaged in these works, e.g. *all*-Polypropylene, *all*-Aramid, *all*-Cellulose composite and so on [12-14].

In this work, a simple method of preparing well-aligned and well-oriented BPDA-PPD PI nanofibers were first proposed using electrospinning with rotating disk-shaped collector. Second, these well-aligned and well-oriented PI nanofibers were impregnated in PI precursor, polyamic acid (PAA) solution, followed by thermal imidization, and finally *all*-PI nanocomposite was obtained. The microstructures and the mechanical properties of electrospun PI nanofibers and *all*-PI nanocomposite were investigated.

2. Materials and testing methods

2.1. Materials

para-phenylene diamine (PDA; Wako Pure Chemical Industries, Ltd.) is broken in granular shape with the diameter of about 1 mm. 3,4:3',4'-biphenyl tetracarboxylic dianhydride (BPDA;Wako Pure Chemical Industries, Ltd.) was dried in 200 °C oven overnight. *N*,*N*-dimetylacetamide (DMAc; Nacalai Tecque, Inc.) was distilled under nitrogen at reduced pressure.

2.2. Sample preparation

PAA polymerization. First, we polymerized PAA solution. PDA was dissolved in DMAc while stirring at 300 rpm under N_2 flow in 60 °C for 1.5 h. Then, BPDA was added and stirred at 300 rpm and flowing N_2 for another 4 h. PAA from BPDA-PDA solution (10 wt%) was obtained.

PI cast film. PAA solution was cast in petri dish and vacuum dried for 24 h at 60 °C. Then, these PAA films were imidization by heat treatment for 1 h at 200 °C and another 1 h at 400 °C in N_2 atmosphere.

PI nanofibers. We made PAA nanofiber by electrospininng (MECC, Ogori, Japan) using rotating disk-shaped collector. The distance between the needles tip and collector was 15 cm and the applied voltage over the gap was 20 kV. The ambient temperature and humidity were 20-25 °C and 20-40 %, respectively. Disposable needle (the inner diameter: 0.70 mm) was used. PAA solution (4.3 wt%) was fed by syringe pump with flow rate of 1.0 mL/h. Electrospun fibers were collected onto rotation disc whose diameter was 20 cm. These collected PAA nanofibers were alligned, then they were imidization by heat treatment for 1 h at 200 °C and another 1 h at 400 °C in N_2 atmosphere under constant stress.

***All*-PI nanocomposite.** PAA solution was impregnated these PI nanofibers bundle. Then, it was vacuum dried at 60 °C for 24 h, followed by curing by two steps as the same conditions with fibers.

2.3. Characterization

Fourier transferred infrared (FTIR) spectrometery (Spectrum GX FT-IR System I-KS, Perkin Elmer) was performed at a resolution of 2 cm^{-1}. The accumulated number of the scans was 10. Scanning electron microscopy (SEM) was performed to study the surface morphology of nanofibers with a JSM-5610LSV (JEOL Ltd., Japan), at an accelerating voltage of 15 kV. Pt/Pd was deposited on the surface prior to the observation. Wide angle X-ray diffraction were carried out using the CuKα (λ=1.5418 Å) radiation, generated with an RINT-2000 (Rigaku Co.) at 40 kV, 20 mA. The X-ray beam was irradiated perpendicular to the surface of the specimen. Exposure time was 20 min for each specimen. The tensile test was conducted using a tensile tester (Autograph AGS-1kND (Shimadzu Co.)) with a cross head speed of 1 mm/min. More than ten specimens were tested with the initial length of 20 mm. The cross-sectional area was determined from the density (floatation method with tetrachloromethane / benzene system at 30 °C), weight and length.

3. Results and discussion

3.1 Characteristics

Figure 1 (a) shows the FTIR spectra of as electrospun PAA nanofibers and annealed ones (PI nanofibers). The spectra show the characteristic absorption bands of PAA and PI, respectively. For as-spun PAA nanofibers, the band at 1665 cm^{-1} can be assigned to the stretching vibration of C=O. The bands at 1558 cm^{-1} and 1319 cm^{-1} are attributed to C-NH symmetric stretching and COO^- asymmetric stretching, respectively. After annealing, the bands originated from

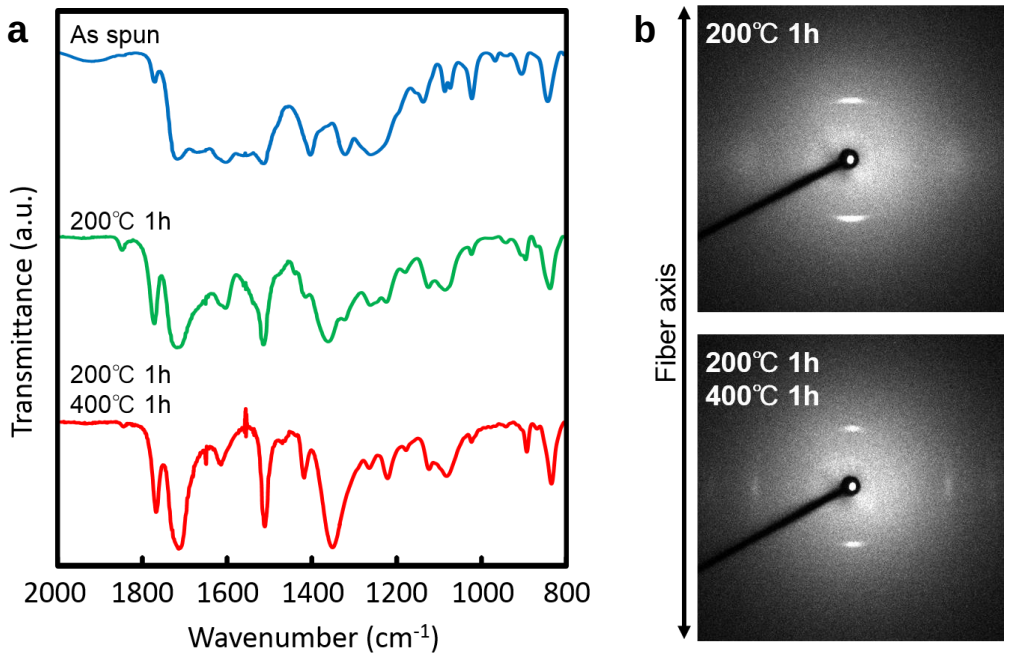

Figure 1. (a) FT-IR spectra of as spun and annealed electrospun fiber of PAA and (b) X-ray fiber photographs of PI nanofibers after curing at 200 °C for 1 h , then curing another 1 h at 400 °C.

PAA disappeared and the peculiar absorption bands from PI appeared. The bands at 1775 cm^{-1} and 1733 cm^{-1} can be assigned to C=O symmetric stretching and asymmetric stretching, respectively. The band at 1375 cm^{-1} is attributed to the stretching vibration of C-N. The band at 1088 cm^{-1} is assigned to C-H bending vibration [15, 16].

Figure 1 (b) shows X-ray fiber photographs of PI nanofibers after curing at 200 °C for 1 h and after curing for 1 h at 200 °C and another 1 h at 400 °C. After annealing for 1 h at 200 °C, the amorphous halo concentrated on the equatorial direction, and the crystalline reflections of PI were observed on the meridional direction. On the other hand, spot-like reflections were focused on the equatorial direction after annealing at 400 °C. These suggest that PI molecular chains were packed tightly after heat treatment at 400 °C for 1 h.

Figure 2 (a) shows the X-ray fiber photographs of the PI nanofibers cured up to 400 °C under free-stress and constant stress, respectively. For the PI nanofibers annealed without stress, the amorphous halo appeared on the equatorial direction, and the crystalline reflections of PI were only slightly observed on the meridional direction. These show that crystallites were slightly oriented only by fiber spinning [17]. On the other hand, spot-like reflections were focused on the equatorial direction for PI fibers annealed with stress. This suggests that PI molecular chains were highly packed and oriented by the heat treatment under stress.

Figure 2 (b) shows the degree of crystallite orientation (Π) of PI nanofibers to rotating speed of dick-shaped collector. The Π values was calculated as

$$\Pi = \frac{180 - H}{180} \quad , \tag{1}$$

where, H is the peak width at half maximum in the intensity profile along the Debye-Scherrer ring. It shows that all fibers are highly oriented even under low rotating speed of collection. So the correlation between the degree of orientation and the rotating speed was hardly observed.

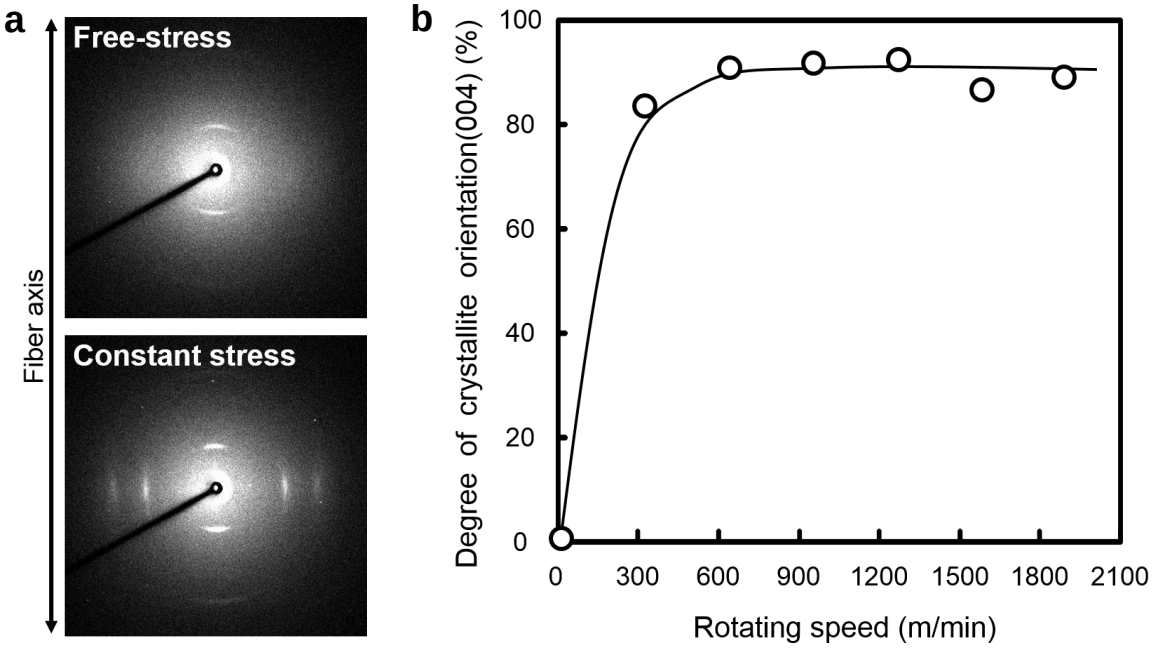

Figure 2. (a) The X-ray fiber photographs of the PI nanofibers cured under free-stress and constant stress and (b) degree of (004) crystallite orientation calculated from the intensity profile along the Debye-Scherrer ring.

Figure 3 shows SEM photographs of fibers collected with different rotating speed and the frequency distributions of fibers angle along the rotating collector. The distributions are quantified by the ImageJ software analysis of SEM photographs. A total of 150 fibers randomly selected from SEM images were measured. SEM photographs revealed that all of the electrospun fibers were smooth, nonporous and almost free of defects such as beads, and the diameter of fibers is about 500 to 750 nm. It can be observed that the degree of fibers alignment at 1260 mm/min of rotating speed is the highest among that of these conditions. In addition, the distribution also shows that the fibers collected with the 1260 mm/min were most highly aligned. With increasing the rotation speed, the degree of alignment increased. However, when rotating speed becomes large too much, fibers are scattered along the disk collector, which may be brought by the wind through by the rotation.

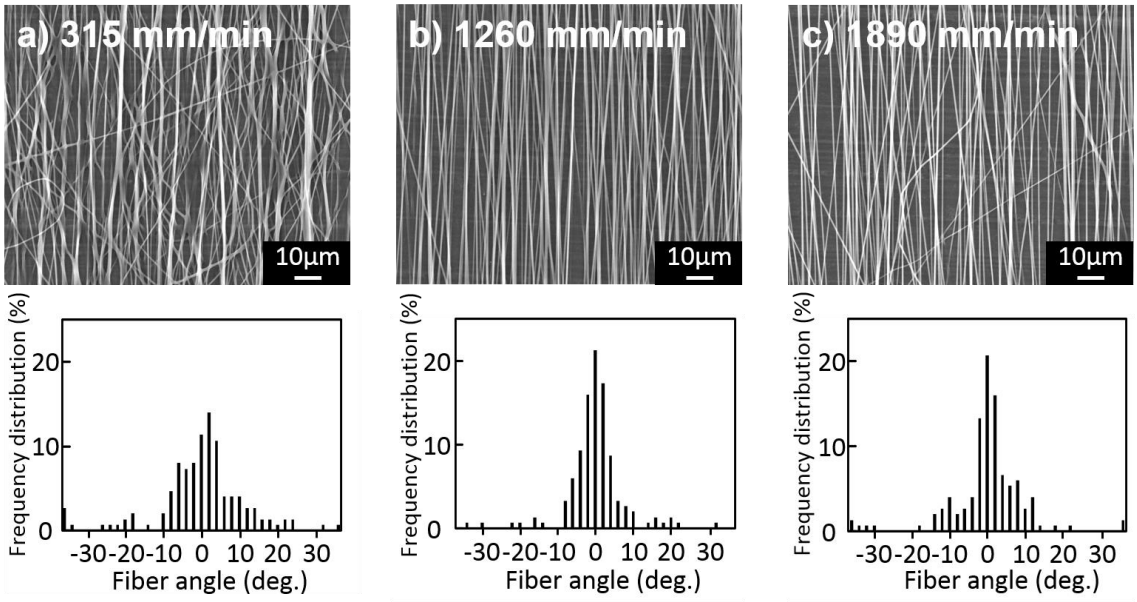

Figure 3. Scanning electron micrographs of PAA nanofibers collected with different rotating speed and frequency distribution of nanofibers alignment as quantified by the ImageJ software. A total of 150 fibers randomly selected from SEM images were measured. Rotating speed of disk are a) 315 mm/min, b) 1260 mm/min and c) 1890 mm/min.

3.2 Mechanical properties

Figure 4(a) shows the stress (σ)-strain (ε) curves of the PI cast film and PI nanofibers electrospun with the rotating speed of 1260 mm/min and 630 mm/min, respectively. It can be seen that PI nanofibers at rotating speed 1260 mm/min and 630 mm/min have higher Young's modulus (E) and tensile strength (σ) compared to PI cast film. In addition, highly alligned fibers at rotating speed 1260 mm/min show the highest mechanical properties. The E value of nanofibers at 1260 mm/min (22 GPa) is more than 6 times that of cast film (3.5 GPa) and the σ value (1.1 GPa) is about 4 times that of cast film (0.35 GPa).

Figure 4(b) shows the relationships between mechanical properties and the degree of fibers alignment. With increasing the degree of alignment, mechanical properties increased. This suggests that the degree of nanofiber alignment can be well correlated to the mechanical properties.

Figure 5 (a) shows the stress (σ)-strain (ε) curves and Table 1 shows the values of mechanical properties of *all*-PI nanocomposite and PI cast film. The *all*-PI nanocomposite reveals significant increases of E value and σ value. *All*-PI nanocomposite shows the E value of 27

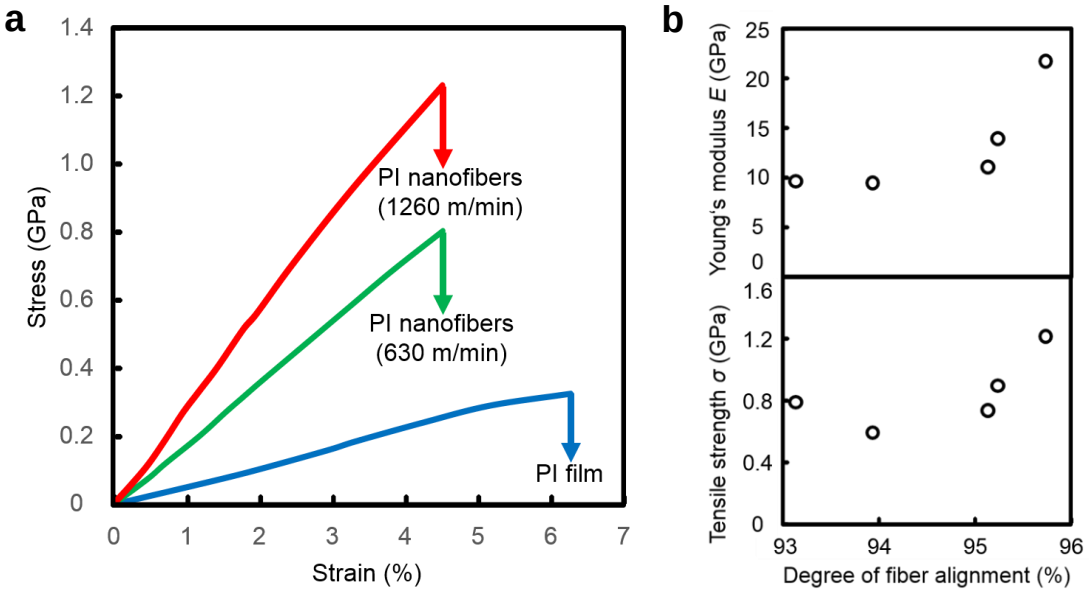

Figure 4. (a) Stress (σ)-strain (ε) curves of the PI cast film and PI nanofibers at rotating speed of 1260 mm/min and 630 mm/min and (b) the relationships between mechanical properties and the degree of alignment of PI nanofibers.

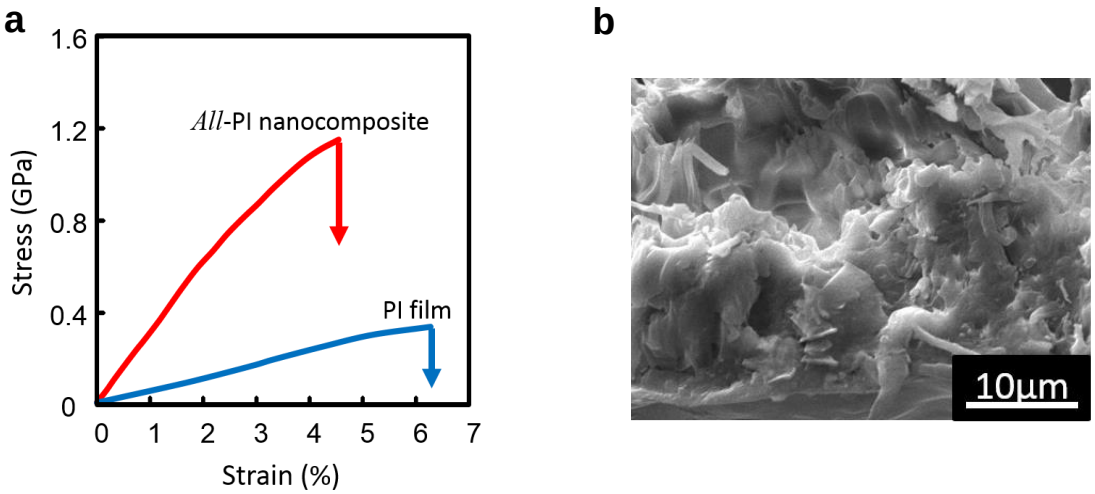

Figure 5. (a) The stress (σ)-strain (ε) curves of *all*-PI nanocomposite and PI cast film and (b) SEM image of broken out section for *all*-PI nanocomposite.

	Young's modulus	Tensile strength
	GPa	GPa
PI film	3.5±0.7	0.35±0.07
All-PI nanocomposite	27±1.6	1.1±0.1

Table 1. Young's modulus and tensile strength of PI cast film and *all*-PI nanocomposite.

GPa and the σ value of 1.1 GPa, which were higher for *all*-PI nanocomposite compared to those of PI cast film.

Figure 5 (b) shows the SEM image of tensile broken surface of PI nanocomposite. It can be seen that PAA solution penetrated into PI nanofibers bundle and there are few void in *all*-PI nanocomposite.

Conclusions

Single polymer nanocomposite composed of only PI was prepared using electrospinning and the structure and properties were investigated. PI nanofibers were prepared via electrospinning. Using rotating disk-shaped collector and optimizing rotating speed, electrospun nanofibers were highly aligned. In addition, by curing PAA nanofibers under constant stress, PI molecular chain was highly packed and highly oriented. Therefore, PI nanofibers shows high mechanical properties. Futhermore, using the PI nanofibers as reinforcement fiber, the *all*-PI nanocomposite showed higher Young's modulus and higher tensile strength compared with those of PI film.

References

[1] N.Miki, Y.Matsuoka, T.Nishino, K.Nakamae, T.Saito,T.Kikuchi. Elastic modulus of the crystalline regions of polyimide derived from poly (amic acid)–biphtalic dianhydride and *p*-phenylene diamine. *J, Polym. Sci. Part B, Polym. Phys.*, 37 (22): 3294-3301, 1999

[2] M. Kotera, T. Nishino, K. Nakamae. Imidization processes of aromatic polyimide by temperature modulated DSC. *Polymer*, 41 (10): 3615-3619, 2000

[3] T. Nishino, M. Kotera, N. Inayoshi, N. Miki, K. Nakamae. Residual stress and microstructures of aromatic polyimide with different imidization processes. *Polymer*, 41 (18): 6913-6918, 2000

[4] N. Bhardwaj, Subhas C. Kundu. Electrospinning: A fascinating fiber fabrication technique. *Biotechnol. Adv.*, 28: 325-347, 2010

[5] A.L.Andrady. *Science and technology of polymer nanofibers*. Willy-interscience, 2008

[6] J.F. Rabolt, M.V. Kakade, S. Givens, K. Gardner, K.H. Lee, D.B. Chase. Electric Field Induced Orientation of Polymer Chains in Macroscopically Aligned Electrospun Polymer Nanofibers. *J.Am.Chem.Soc.*, 129: 2777-2782, 2007

[7] H. Tsuji, M. Nakano, M. Hashimoto, K. Takashima, S. Katsura, A. Mizuno. Electrospinning of Poly (lactic acid) Stereocomplex Nanofibers. *Biomacromolecules*, 7: 3316-3320, 2006

[8] B. Chu, X.Zonga, K. Kima, D. Fangb, S.Rana, B. S. Hsiao. Structure and process relationship of electrospun bioabsorbable nanofiber membranes. *Polymer*, 43: 4403-4412, 2002

[9] J. Leng and A. Kin-tak. *Multifunctional Polymer Nanocomposites*. CRC press, Florida, 2011

[10] N.J. Csapiati and R.S. Porter. The concept of one polymer composites modeled with HDPE. *J. Mater. Sci.*, 10: 1671-1677, 1975

[11] T. Peijs. Composites for recyclability. *Materials today*, 30-35, 2003

[12] J.M.Zhang, Z.Mousavi, N.Soykeabkaew, P.Smith, T.Nishino, T.Peijs. *All*-Aramid composite by partial fiber dissolution. *ACS Applied Material & Interfaces*, 2 (3): 919-926, 2010

[13] T.Nishino, N. Arimoto, *All*-cellulose composite prepared by selective dissolving of fibersurface. *Biomacromolecules*, 8: 2712-2716, 2007
[14] T. Nishino, I. Matsuda, and K. Hirao. *All*-Cellulose Composite. *Macromolecules*, 37: 7683-7687, 2004
[15] J. T. Young , W. H. Tsai , F. J. Boerio. Characterization of the interface between pyromellitic dianhydride/oxydianiline polyimide and silver using surface-enhanced Raman scattering. *Macromolecules*, 25 (2): 887-894, 1992
[16] S. Diaham, M.L. Locatelli, T. Lebey, D. Malec. Thermal imidization optimization of polyimide thin films using Fourier transform infrared spectroscopy and electrical measurements. *Thin Solid Films*, 519 (6): 1851-1856, 2011
[17] W.A.Yee, M.Kotaki, Y.Liu, X.Lu. Morphology, Polymorphism Behavior and Molecular Orientation of Electrospun Poly (vinylidene fluoride) Fibers. *Polymer*, 48 (12): 512-521, 2007