

Preparation of Atactic Poly(vinyl alcohol)/Sodium Alginate Blend Nanowebs by Electrospinning

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ABSTRACT: Through the blending of a rigid polymer, sodium alginate (SA), and a flexible polymer, atactic poly(vinyl alcohol) (PVA), with various ratios of SA and PVA and through the electrospinning of SA/PVA solutions, SA/PVA blend nanowebs were successfully prepared. The structure and morphology of the SA/PVA blend nanowebs were investigated through a series of instrumental analyses. Through the examination of the morphological variations of each blend web, it was found that with only PVA, the electrospun nanowebs had very uniform and fine fiber structures, but the SA/PVA blend nanowebs had a mixture of

large beads and fibers, which were generated with increasing SA content. A thermal analysis indicated that the endothermic peaks of the SA/PVA blend nanowebs decreased with an increase in the SA content. The SA content was determined by the observation of the changes in the SA peak intensity via Fourier transform infrared spectroscopy. The tensile strength decreased with increasing SA content. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1337–1342, 2007

Key words: PVA; alginate; blend; electro-spinning

INTRODUCTION

Electrospinning is a unique method that produces polymeric fibers with diameters in the range of nanometers to a few micrometers, using an electrically driven jet of a polymer solution or melt.^{1,2} This technique has been developed since its introduction by Formhals in 1934.³ It is used to produce the electrostatic force for making fibers. A high-voltage power supply is required to create an electrically charged jet of a polymer solution or melt. An electric field between a capillary tip and a collector is created, and it induces a charge on the surface of the solution or melt. As the electric field increases, the hemispherical shape of the pendant drop at the end of the capillary tip is charged into a conical shape. This is known as a Taylor cone.⁴ If an electric field is induced above a critical value, it is ejected from the vertex of the cone toward the grounded collector. The charged jet comes from the polymer liquid, and it moves as a straight jet for some distance and then travels a spiral path. It is triggered by the electrically driven bending instabil-

ity,⁵ which is alternatively called whipping instability.⁶ The solvent evaporates as the jet proceeds to the collector and accelerates because of the electric field that forms between the capillary tip and grounded collector. The solidified fibers are collected on the grounded collector.

Electrospun nonwoven mats have a small pore size, high porosity, and high surface area; therefore, they can be used in a wide variety of applications, such as reinforcing fibers in composite materials^{7,8} and scaffolds in tissue engineering.^{7,9} The morphology of electrospun fibers depends on various parameters, such as (1) solution parameters, including the viscosity, conductivity, and surface tension; (2) controlled variables, including the hydrostatic pressure in the capillary, electric potential at the tip, and tip-to-collector distance (TCD); and (3) ambient parameters, including the temperature, humidity, and air velocity in the electrospinning chamber.¹⁰ Therefore, nanofibers can be prepared through the control of these parameters. Moreover, a significant implication of the mechanism of electrospinning is that materials derived from polymer blends will likely not be an admixture of two different fibers but rather will be fibers containing both components.

Polymer blending constitutes a very useful method for the improvement or modification of the physicochemical properties of polymeric materials. Therefore, polymer blends have attracted increasing interest in

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both industrial and scientific fields. Some polymer blends exhibit unusual properties that are absolutely different from those of the homopolymers. An important property of a polymer blend is the miscibility of its components because it affects the mechanical properties, the morphology, and the permeability and degradation. Polymer blends are physical mixtures of structurally different polymers or copolymers that interact with secondary forces with no covalent bonding,¹¹ such as hydrogen bonding, dipole–dipole forces, and charge-transfer complexes for homopolymer mixtures.^{12–14}

Poly(vinyl alcohol) (PVA) is a semicrystalline polymer that is biocompatible and water-soluble, and it has a good formation ability for fibrous materials. Its flexibility and toughness are good, so it is a typical synthetic polymer that is used to improve the physical properties through mixing with other materials that have poor physical properties. PVA with functional groups is useful in practical investigations of functional polymers because of its easy preparation as a bulk material, films, and fibers.

Natural polymers, including polysaccharides, may be of great significance because of the wider utilization and new functionalization of abundant biomass. Sodium alginate (SA), obtained from brown seaweeds, is a linear copolymer of 1,4-linked β -D-mannuronate (M) and α -L-guluronate (G) residues arranged in different M/G ratios. These residues are arranged in a blockwise fashion, constructed not only of homopolymer blocks of MM or GG but also of alternating blocks of M and G, as shown in Figure 1. SA is known to be a nontoxic, biocompatible polymer. Recently, SA has been investigated for such uses as matrices for drug delivery,^{15,16} scaffolds for specific cell cultures,¹⁵ and wound dressings.¹⁷ Clinical observations of SA as a wound dressing have indicated that SA initiates or accelerates the healing of chronic wounds after the treatment of the underlying pathology.

This carbohydrate polymer has been reevaluated recently as an attractive natural resource possessing the potential to be further developed for medical, pharmaceutical, biological, and other industrial applications. One of the useful characteristics of alginate is the ability to form hydrogels.¹⁸ An aqueous solution of alginate is readily transformed into a hydrogel upon the addition of metallic divalent cations such as Ca^{2+} ,^{19,20} and the gelation behavior has been investigated in various ways,²¹ such as a thermodynamic model treatment²² and ^{13}C -NMR spectroscopy.²³ It has been generally accepted that in the gelation mechanism, crosslinks are formed by the coordination of divalent metal cations to interchain cavities made up of guluronate blocks, resulting in the development of a so-called egg-box junction zone. In contrast to the numerous studies of the physical properties and

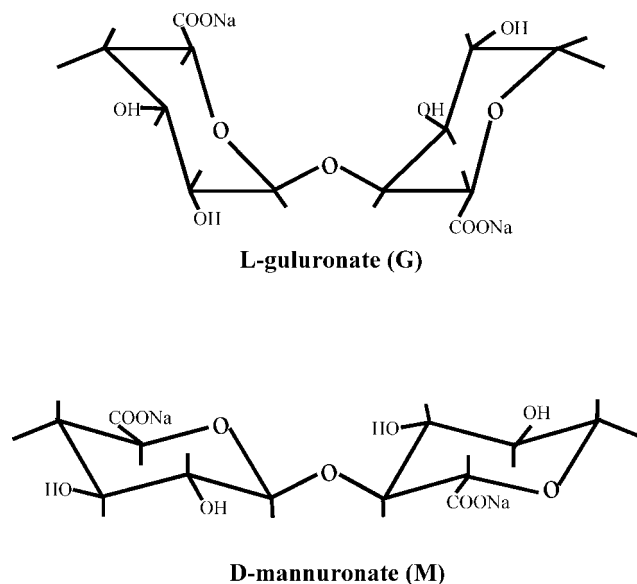


Figure 1 Structures of the G and M units of SA.

industrial applications of alginate gels, there have been only a few examples of studies dealing with alginate/synthetic polymer blends.^{24,25} The rigid and fragile nature of gelatinous alginates may also be unfavorable for processing into nonspherical forms such as films and filaments via the gel state. A method to overcome this drawback is blending the polysaccharide with a compatible flexible vinyl polymer.

In this study, a rigid polymer, SA, was blended with a flexible polymer, PVA, to enhance the mobility of polymer chains during an electrospinning process and to vary the physical properties of electrospun webs. In addition, SA/PVA blend nanowebs prepared by electrospinning were characterized with various techniques.

EXPERIMENTAL

Materials

PVA was purchased from Dongyang Chemical Co. (Seoul, Korea). The number-average degree of polymerization and degree of saponification of PVA were 1700 and 99.9%, respectively. SA (chemical-grade) powder was purchased from Aldrich Chemical Co. (St. Louis, MO). The viscosity was 200–400 cps. Ultrapure deionized water was used. All chemicals were used without any further purification.

Electrospinning

Different blend solutions of SA and PVA with mass percentage ratios of 0/100, 1/100, 5/100, 10/100, 20/100, and 30/100 were placed in separate beakers and dissolved in 100 mL of ultrapure deionized water.

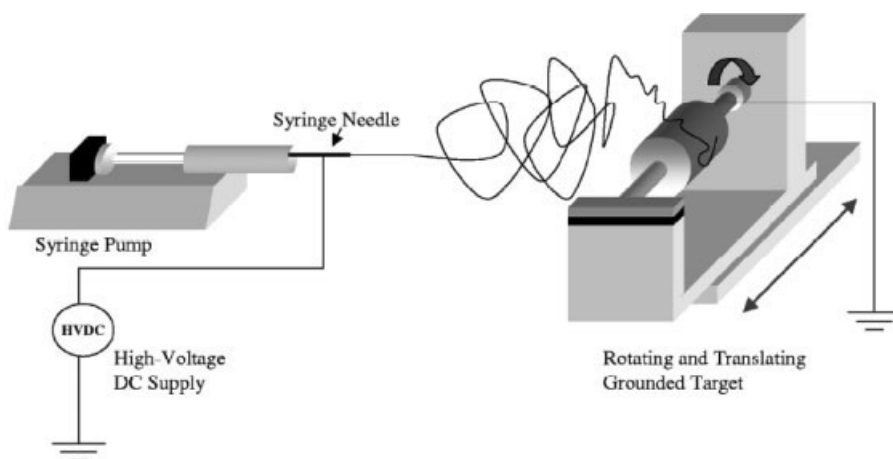


Figure 2 Experimental setup device for the electrospinning process (DC = direct current).

The concentrations of the PVA solutions ranged from 8 to 11 wt %. The blend solutions were filtered to remove any undissolved solids such as impurities. The experimental setup device used for the electrospinning process is shown in Figure 2. A variable high-voltage power supply (Dongyang Co., Daegu, Korea) was used to produce voltages ranging from 0 to 90 kV. Each blend solution was poured into a 30-mL syringe attached to a capillary tip with a 1-mm diameter. The positive electrode of the high-voltage power supply was attached to a copper wire inserted into the polymer solution. The negative electrode was attached to the grounded collector. The applied voltage and TCD were fixed at 15 kV and 20 cm, respectively.

Characterization

The structure and morphology of the SA/PVA blend nanowebbs were observed with scanning electron microscopy (SEM; S-4200, Hitachi Co., Tokyo, Japan). A small section of the fiber mat was placed on the SEM sample holder and sputter-coated with gold (E-1030, Hitachi, Tokyo, Japan). An accelerating voltage of 15 kV was employed to take the photographs.

The thermal behavior of the SA/PVA blend nanowebbs was investigated with differential scanning calorimetry (DSC; TA 2010, TA Instruments, Dupont, New Castle, DE). The DSC thermograms were recorded from 25 to 250°C at the heating rate of 10°C/min under a nitrogen atmosphere.

Fourier transform infrared spectroscopy (FTIR) was used to identify the structure of the SA/PVA blend nanowebbs. The spectra were scanned between 400 and 4000 cm^{-1} (IFS-66V/S, Bruker, Ettlingen, Germany).

The mechanical properties of the SA/PVA blend nanowebbs were determined with an Instron 4301 automated materials testing system (1.23, series IX, Instron Ltd., Buckinghamshire, England) at room

temperature. The experiments were performed at a constant crosshead speed of 10 mm/min. The specimens were prepared in the cross direction and machine direction (20 mm wide, 50 mm long, and 20–30 μm thick).

RESULTS AND DISCUSSION

Microscopic and fiber diameter distribution studies for evaluating the optimum electrospinning conditions of various polymer systems have been conducted by several researchers. Demir et al.²⁶ reported the effects of these parameters on the electrospinning behavior of an elastomeric polyurethane copolymer, using microscopic methods, including optical microscopy, SEM, and atomic force microscopy. The effects of electrospinning parameters on morphological changes, especially the beaded structures of nanofibers, were examined by Fong et al.²⁷ Morphological studies were also performed by Deitzel et al.,²⁸ Suki-gara et al.,²⁹ Pawlowski et al.,³⁰ and Ohgo et al.³¹ They used SEM as the main characterization method in numerous studies to determine the optical electric field, solution concentration, and TCD for PVA electrospun fibers with respect to the fiber diameter and morphology. According to the literature, optimum electrospinning conditions for PVA nanofabrics with average diameters of 250 and 300 nm have been successfully produced. The average diameter of PVA nanowebbs slightly decreases with an electric potential and with decreases in the TCD and solution concentration.³² However, there are no reports in the literature describing electrospun nanowebbs of SA because of the poor web-forming ability of SA. On the basis of these results, we subsequently investigated various blend ratios of SA and PVA in ultrapure deionized water to produce electrospun nanowebbs.

SEM microphotographs of SA/PVA blend nanowebbs are presented in Figure 3. The individually electrospun PVA fibers appeared to be finer fiber

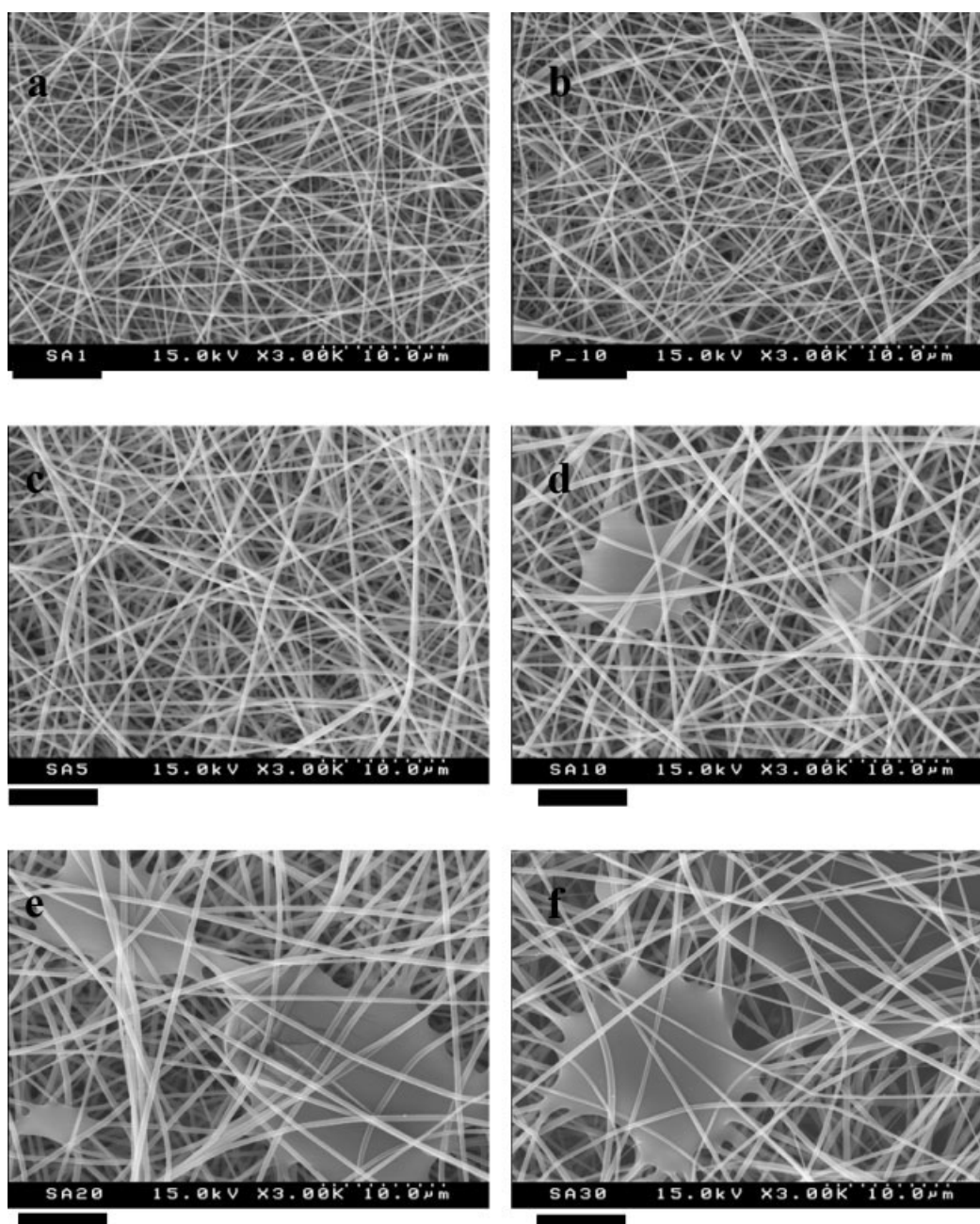


Figure 3 SEM photographs of SA/PVA blend nanowebs with blend ratios of (a) 0/100, (b) 1/100, (c) 5/100, (d) 10/100, (e) 20/100, and (f) 30/100 wt %/wt %.

structures without the present of any beads [Fig. 3(a)]. In addition, finer fiber structures and less beaded nanowebs were observed in the lower SA content specimen [Fig. 3(b)] versus the higher one [Fig. 3(f)]. The morphologies of beaded nanowebs were prone to form [Fig. 3(d)]. The diameters of the beads were smaller and the average distance between the beads on the nanowebs was longer with a lower content of SA. In addition, the diameters of the beads became bigger and the average distance between the beads became shorter as the content of SA increased. Vollrath and Edmonds³³ reported that beads, re-

garded as byproducts, are often formed in electrospinning. In this study, the formed beads were widely observed in electrospun SA/PVA blend nanowebs prepared with lower concentrations of PVA.

The FTIR spectra of SA/PVA blend nanowebs with different compositions are shown in Figure 4. The FTIR spectra of the PVA nanowebs show absorption bands attributed to the resonances at 3322 (OH stretching), 2937 (CH₂ bending), 1434 (CH—OH bending), 1328 (CH—OH bending), 1094 (C—O out of plane bending), and 849 cm⁻¹ (C—C out of plane bending). A broad band appearing at 3400 cm⁻¹ cor-

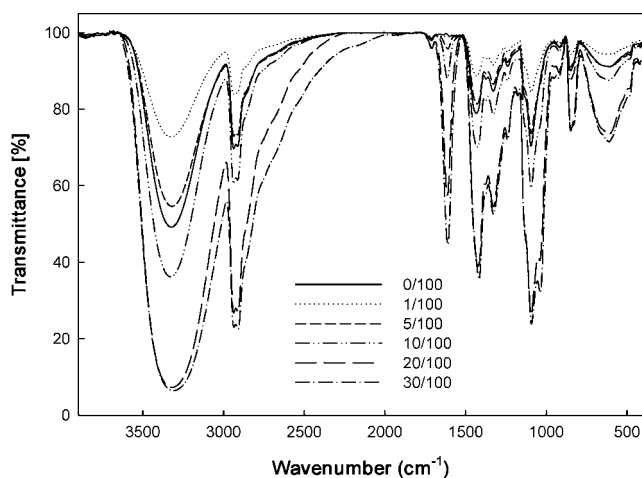


Figure 4 FTIR spectra of SA/PVA blend nanoweb samples with blend ratios of 0/100, 1/100, 5/100, 10/100, 20/100, and 30/100 wt %/wt %.

responds to the associated OH stretching; the peak appearing at 1610 cm^{-1} corresponds to the deformation of the carbonyl group of SA. The content of SA in the nanoweb was confirmed by a strong absorption band at 1610 cm^{-1} ($-\text{COO}-$ asymmetric stretching), which corresponds to SA with an increasing blend ratio of SA. The characteristic peaks of PVA in the SA/PVA blend nanoweb did not change with the blending ratios of the two polymers because either the two polymers did not mutually interact or their interaction was too weak to be detected by FTIR spectroscopy.

SA/PVA mixed polymer solutions showed good transparency to the naked eye over the whole range of compositions. Thus, a visual inspection gave no indication of phase separation in any of the blends. One of the methods most commonly used to estimate polymer-polymer miscibility is the determination of

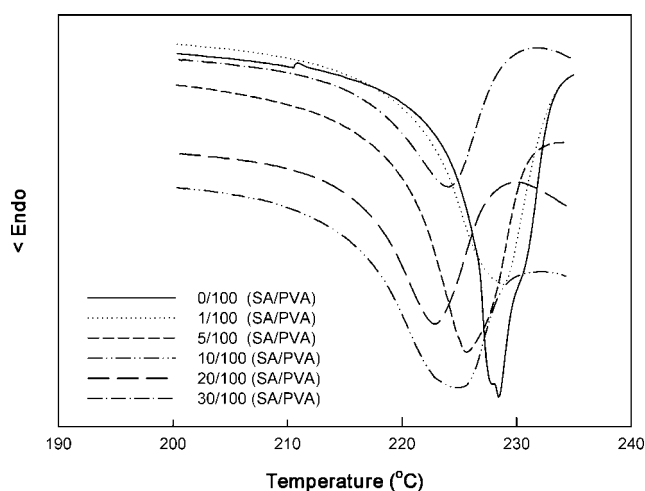


Figure 5 DSC thermograms of SA/PVA blend nanoweb samples with different blend ratios of 0/100, 1/100, 5/100, 10/100, 20/100, and 30/100 (wt %/wt %).

the glass-transition temperature of the blend versus the glass-transition temperatures of the individual homopolymers. When one component is crystalline, the observation of a melting point depression of that polymer may also be used as evidence to support the miscibility of the polymer pair. Figure 5 compiles selected data of DSC thermograms obtained for a series of SA/PVA blend samples. The melting temperature of the SA/PVA component was depressed to lower temperatures with increasing SA content. In addition, the magnitude of the endothermic peak area was reduced disproportionately with the SA/PVA blend ratio. Such effects on the thermal transition behavior observed for this system, the depression of the melting temperature and the repression of the degree of crystallinity of the crystallizable component (i.e., PVA) due to the addition of the second component (i.e., SA), are common features that are shared with other crystalline/amorphous polymer pairs that are capable of forming a miscible phase in their blends.

The tensile properties of SA/PVA blend webs are very important because it is impossible for homo-SA to form fibrous nanoweb through electrospinning, and this is ascribed to the poor toughness of the SA polymer. Therefore, to be used as composite materials, filters, scaffolds, and so forth, SA/PVA blend nanoweb should have a certain range of tensile strengths. The tensile strength of SA/PVA blend nanoweb of all five blend systems decreased with increasing SA content. A definite trend in the variation of the tensile strength with the SA content is clearly reflected in Figure 6; in general, the tensile strength registered a sharp and almost linear decrease with SA contents up to about 10 wt % (on PVA). Beyond this, the tensile strength decreased with

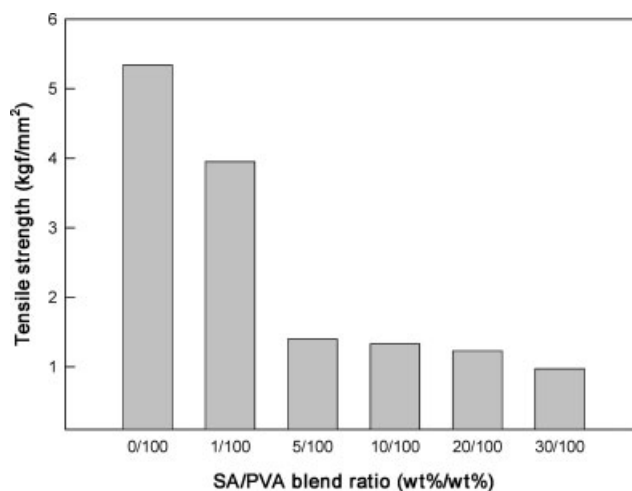


Figure 6 Tensile strengths of SA/PVA blend nanoweb samples with blend ratios of 0/100, 1/100, 5/100, 10/100, 20/100, and 30/100 wt %/wt %.

increasing SA content. The tensile strength of the SA/PVA blend nanoweb prepared with an SA content of 30 wt % was much lower than that of homo-PVA.

CONCLUSIONS

SA/PVA blend nanowebs were prepared by electrospinning through the blending of a rigid polymer, SA, and a flexible polymer, PVA, with various blend ratios. The structural and physical properties of the SA/PVA blend nanowebs were characterized with FTIR spectrometry, DSC, SEM, and an Instron instrument. The morphologies of the nanowebs showed numerous beads with increasing SA contents in the nanowebs. The contents of SA in the nanowebs were confirmed from a strong absorption band at 1610 cm^{-1} ($-\text{COO}-$ asymmetric stretching), which corresponded to SA with an increasing blend ratio of SA. Moreover, DSC showed that the endothermic peak of SA/PVA blend nanowebs decreased with increasing SA content. As the SA content in blends increased, the tensile strength of the webs decreased. SA/PVA blend nanowebs prepared by electrospinning are expected to have large surface areas, which should impart to them excellent properties suitable for biomedical applications. In the near future, we will report on the electrospinning of SA/stereoregular PVA blends.

References

- Baumgarten, P. K. *J Colloid Interface Sci* 1971, 36, 71.
- Larronda, L.; John Manley, R. S. *J Polym Sci Polym Phys Ed* 1981, 19, 909.
- Formhals, A. U.S. Pat. 1,975,504 (1934).
- Taylor, G. I. *Proc R Soc London Ser A* 1969, 313, 453.
- Reneker, D. H.; Yarin, A. L.; Fong, H.; Koombhongse, S. *J Appl Phys* 2000, 87, 4531.
- Shin, Y. M.; Hohman, M. M.; Brenner, M. P.; Rutledge, G. C. *J Appl Phys* 2001, 78, 1149.
- Doshi, J.; Reneker, D. H. *J Electrostat* 1995, 35, 151.
- Gibson, P. W.; Schreuder-Gibson, H. L.; Riven, D. *AIChE J* 1999, 45, 190.
- Buchko, C. J.; Chen, L. C.; Shen, Y.; Martin, D. C. *Polymer* 1999, 40, 7397.
- Reneker, D. H.; Chun, I. *Nanotechnology* 1996, 7, 216.
- Krause, S. In *Polymer Blends*; Paul, D. R.; Newman, S., Eds.; Academic: New York, 1979; p 1.
- Varnell, D. F.; Coleman, M. M. *Polymer* 1981, 22, 1324.
- Varnell, D. F.; Runt, J. P.; Coleman, M. M. *Polymer* 1983, 24, 37.
- Woo, E. M.; Barlow, J. W.; Paul, D. R. *J Appl Polym Sci* 1986, 32, 3889.
- Kikuchi, A.; Kawabuchi, M.; Watanabe, A.; Sugihara, M.; Sakurai, Y.; Okano, T. *J Controlled Release* 1999, 58, 21.
- Lai, H. L.; Abu'Khalil, A.; Craig, D. Q. M. *Int J Pharm* 2003, 251, 175.
- Häuselmann, H. J.; Mauda, K.; Hunziker, E. B.; Neidhart, M.; Mok, S. S.; Michel, B. A.; Thonar, E. *Am J Physiol Cell Physiol* C 1996, 271, 742.
- Clark, A. H.; Ross-Murphy, S. B. *Adv Polym Sci* 1987, 83, 57.
- Grant, G. T.; Morris, E. R.; Rees, D. A.; Smith, P. J. C.; Thom, D. *FEBS Lett* 1973, 32, 195.
- Smidsrød, O.; Haug, A. *Acta Chem Scand* 1972, 26, 2063.
- Morris, E. R.; Rees, D. A.; Thom, D. B. *J Carbohydr Res* 1978, 66, 145.
- Nilsson, S. *Biopolymers* 1992, 32, 1311.
- Wang, Z. Y.; Zhang, Q. Z.; Konno, M.; Saito, S. *Biopolymers* 1993, 33, 703.
- Nagura, M.; Murai, J.; Ohkoshi, Y. *Kobunshi Ronbunshu* 1991, 48, 775.
- Yonese, M.; Baba, K.; Kishimoto, H. *Polym J* 1992, 24, 395.
- Demir, M. M.; Yilgor, I.; Yilgor, E.; Erman, B. *Polymer* 2002, 43, 3303.
- Fong, H.; Chun, I.; Reneker, D. H. *Polymer* 1999, 40, 4585.
- Deitzel, J. M.; Kleinmeyer, J.; Harris, D.; Beck Tan, N. C. *Polymer* 2001, 42, 261.
- Sukigara, S.; Gandhi, M.; Ayutsede, J.; Micklus, M.; Ko, F. *Polymer* 2003, 44, 5721.
- Pawlowski, K. J.; Belvin, H. L.; Raney, D. L.; Su, J.; Harrison, J. S.; Siochi, E. J. *Polymer* 2003, 44, 1309.
- Ohgo, K.; Zhao, C.; Kobayashi, M.; Asakura, T. *Polymer* 2003, 44, 841.
- Lee, J. S.; Choi, K. H.; Ghim, H. D.; Kim, S. S.; Chun, D. H.; Kim, H. Y.; Lyoo, W. S. *J Appl Polym Sci* 2004, 93, 1638.
- Vollrath, F.; Edmonds, D. T. *Nature* 1989, 340, 305.