

Preparation of Polysaccharide Nanofiber Fabrics by Electrospray Deposition: Additive Effects of Poly(ethylene oxide)

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ABSTRACT: Polysaccharide—chitosan, sodium chondroitin sulfate, and pectin—nanofibrous fabrics were prepared from the respective polysaccharide/poly(ethylene oxide) (PEO) blend solutions by electrospray deposition (ESD). The surface morphologies of the electrosprayed fabrics were observed by scanning electron microscopy (SEM). Unblended polysaccharide solutions showed low ESD processability; *viz.*, the solutions could not be electrosprayed, or provided a non-fibrous morphology composed of spherical entities when ESD was applicable. The addition of high-molecular-weight PEO ($M_w = 500,000$) to chitosan solutions significantly enhanced the formation of a fibrous structure. Sodium chondroitin sulfate/PEO and pectin/PEO blend solutions were generally too viscous to be sprayed at 25 °C; at 70 °C, however, we succeeded in forming the fibrous structure from these solutions by ESD. The results indicate that adequate heating is effective to improve the processability of such highly viscous blend solutions into the electrostatic fiber formation. [DOI 10.1295/polymj.37.391]

KEY WORDS Polysaccharides / Chitosan / Sodium Chondroitin Sulfate / Pectin / Nanofiber /
Electrospray Deposition /

Electrospray deposition (ESD) is a straightforward and versatile method for forming thin films. This method has the following advantages: (i) applicability to solute molecules which have a wide range of molecular weights (*e.g.*, inorganic molecules, synthetic polymers, proteins, and DNA); and (ii) ability to deposit polymer thin films with nano-microscaled structures, which range from spheres to fibers.^{1–10} The ESD methods consist of the following steps: (i) a strong electric field is applied between a polymer solution placed in a nozzle and a conductive substrate; (ii) when the voltage reaches a critical value, electrostatic forces overcome the surface tension of the solution; (iii) charged droplets (or jets) are sprayed from the tip of the nozzle, in a dry atmosphere; and (iv) the dried droplets (or jets) are finally collected on the substrate to form a thin film. One major advantage of the ESD technology is forming nano-microscaled fibrous fabrics (typically nonwoven fabrics).

Chitosan, which is obtained by deacetylation of chitin in concentrated alkaline solution at a high temperature, is one of the muco-polysaccharides with a β -1,4 bonded structure of the glucosamine residue, having an amino group at the C-2 position and two hydroxyl

groups at the C-3 and C-6 positions.¹¹ *Chondroitin sulfate* is widely distributed over the inside of human body in the form of proteoglycan which is combined with non-collagenic protein, as a matrix component such as cartilage, tendons, blood vessel walls and skins.¹² It is an acidic muco-polysaccharide, which consists of *N*-acetyl-D-galactosamine and uronic acid and is extracted from shark or bovine cartilage. *Pectin* is a vegetative phlegmatic material widely distributed over the leaves, stalks, and fruits of seaweeds and plants. It is formed in a β -1,4 bonded structure with D-galacturonic acid partially methyl-esterified.¹³ These polysaccharides have high biocompatibility, biodegradability, and bioactivity such as wound healing and antimicrobial effects.^{14–16}

There have been many studies on electrostatic fiber formation, or “electrospinning”.^{17–19} Electrostatic fiber formation has drawn strong attention in many fields including biomedical engineering (*e.g.*, scaffolds for tissue engineering²⁰ and drug delivery systems²¹). The combination of functional biomacromolecules, polysaccharides, and nano-microfabrication technology, ESD, is a promising option to provide novel biomedical devices. Since polysaccharide

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solutions generally show a lower ESD processability, water-soluble polymer may be useful as the additive of polysaccharide solution to improve the electrostatic spinnability. Several papers have been published on the electrostatic fiber formation of polysaccharides and their mixtures with water-soluble polymers (*e.g.*, cellulose,²² dextran,²³ hyaluronic acid,²⁴ chitin,²⁵ chitosan,²⁶ a chitosan/poly(ethylene oxide) (PEO) mixture,²⁷ a chitosan/poly(vinyl alcohol) (PVA) mixture,²⁶ and cellulose acetate/PVA mixtures²⁸). However, there have been few systematic studies on the additive effect of water-soluble polymers on the electrostatic spinnability of polysaccharide solution. To the best of our knowledge, the electrostatic fiber formation from sodium chondroitin sulfate and pectin solutions has never been accomplished.

Our previous paper provided a systematic information for the morphology control of PEO thin films by ESD.⁸ In the present work, we attempt to thoroughly examine the additive effect of PEO, which is a biocompatible polymer,²⁹ to solutions of different polysaccharides, chitosan, sodium chondroitin sulfate, and pectin, on forming their fibrous structure. The aim of this paper is to present a comprehensive findings on the electrostatic spinnability from the polysaccharide/PEO blend solutions by ESD.

EXPERIMENTAL

Materials

Three chitosans, with mutually different average molecular weights, $M_w = 36,000$ (CH-36k; Degree of deacetylation, DAC = 87%), 70,000 (CH-70k; DAC = 85%), and 120,000 (CH-120k; DAC = 85%), were supplied from Kyowa Tecnos, Japan. Sodium chondroitin sulfate of $M_w = 110,000$ (CHON) and pectin of $M_w = 510,000$ (PEC) were purchased from Laiyang Xianghe Biochemical Products, China, and Wako Pure Chemicals, Japan, respectively. The molecular weights of these polysaccharides were estimated by gel permeation chromatography using an apparatus equipped with a column (Shodex Asahipack GF-7MHQ, Showa Denko, Japan) and a refractive index detector (L-7490, Hitachi, Japan). 0.2 M Acetic acid–0.2 M sodium acetate buffer was used as an eluent. Poly(ethylene oxide)s of nominal average molecular weights, $M_w = 20,000$ (PEO-20k), 100,000 (PEO-100k), and 500,000 (PEO-500k), were purchased from Wako Pure Chemicals, Japan (for PEO-20k and -500k) and Polysciences, USA (for PEO-100k). Acetic acid of extra-pure grade was obtained from Wako Pure Chemicals, Japan.

Ultrapure water was prepared in a water purification system (Milli-Q Academic A10, Millipore, USA) and used in the preparation of aqueous polymer

solutions.

Aluminum sheets (AL-013 Series, Nilaco, Japan) were used as a conductive substrate.

Preparation of Spray Solutions

Chitosan (CH) was dissolved in 5 wt % acetic acid aqueous solution to give a 10 wt % CH solution (chitosan:acetic acid = 2:1 w/w). On the other hand, 5 wt % PEO aqueous solutions were prepared using three kinds of PEOs with different molecular weights. A CH-36k solution was blended with the 5 wt % PEO solutions at volume proportions 8:2, 6:4, 4:6, and 2:8. The actual blending ratios of the two polymer solutes, CH-36k/PEO, are 8/1, 6/2, 4/3, and 2/4 in w/w for the three kinds of blended systems, CH-36k/PEO-20k, CH-36k/PEO-100k, and CH-36k/PEO-500k. Two additional solutions of CH-36k/PEO-500k = 9.5/0.25 and 9/0.5 were also prepared.

Sodium chondroitin sulfate (CHON) aqueous solutions were prepared at 1, 10, and 20 wt %. They were blended with a 5 wt % PEO-500k solution at volume proportions of 8:2, 6:4, 4:6, and 2:8; corresponding to actual solute ratios of 0.8/1, 0.6/2, 0.4/3, and 0.2/4 (w/w) for 1 wt % CHON/PEO; 8/1, 6/2, 4/3, and 2/4 (w/w) for 10 wt % CHON/PEO; and 16/1, 12/2, 8/3, and 4/4 (w/w) for 20 wt % CHON/PEO.

Pectin (PEC) aqueous solutions were prepared at 1, 3, and 5 wt %. They were blended with a 5 wt % PEO-500k solution at volume proportions of 8:2, 6:4, 4:6, and 2:8. The blending ratios of the solutes are 0.8/1, 0.6/2, 0.4/3, and 0.2/4 (w/w) for 1 wt % PEC/PEO; 2.4/1, 1.8/2, 1.2/3, and 0.6/4 (w/w) for 3 wt % PEC/PEO; and 4/1, 3/2, 2/3, and 1/4 (w/w) for 5 wt % PEC/PEO.

Solution viscosities were measured with an oscillating type viscosity meter (VM-100A, CBC Materials, Japan) at 25 °C and 70 °C. Surface tensions of the polymer solutions were determined by the Whilhelmy plate method using a full automatic surface tensiometer (CBVP-Z, Kyowa Interface Science, Japan) at 25 °C. Solution conductivities were measured using a conductivity meter (CM-20S, TOA, Japan) equipped with a conductivity cell (CG-511B, TOA, Japan) at 25 °C.

Electrospray Deposition (ESD)

Electrospraying was carried out using an electro-spray deposition device (ESD200S, Fuce, Japan), which is shown in Figure 1. Polymer solutions were sprayed through a glass capillary with an internal platinum microelectrode. Glass capillaries of 50 μm diameter were prepared using a glass microelectrode puller (PC-10, Narishige, Japan). The distance between the capillary tip and the substrate surface was 80 mm. The voltage applied between the capillary and the substrate was typically 6.4–16.6 kV corresponding to

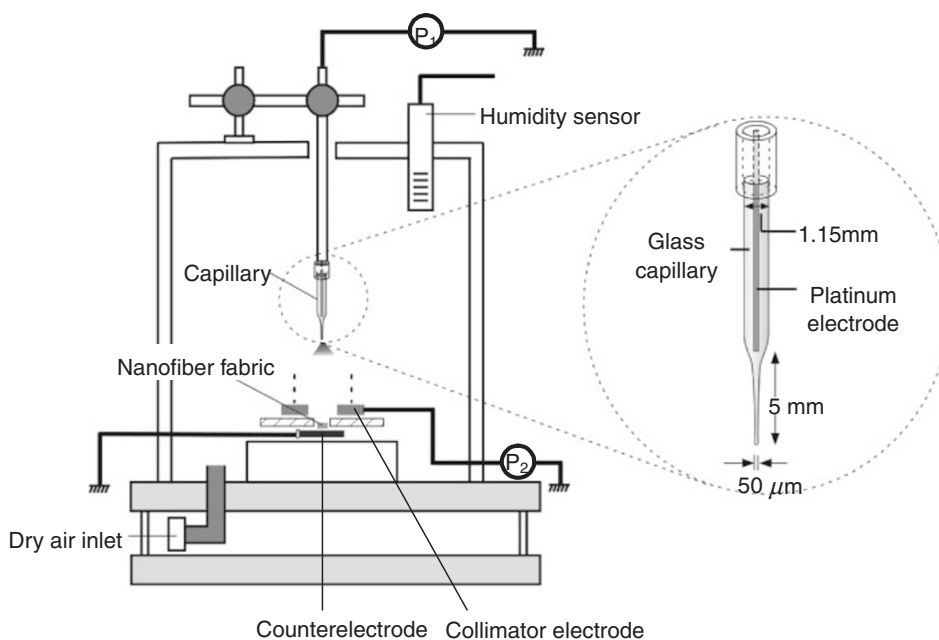


Figure 1. Schematic diagram of the ESD device. P1, DC power source for ESD; P2, DC power source for collimator.

near the lower critical spraying voltage for each solution. Deposition was performed in an acrylic chamber filled with dry air (typically the relative humidity is 20% and the temperature is about 25 °C).

Observation of Surface Morphologies of Fabrics

The surface morphologies of the deposited thin fabrics were observed using a scanning electron microscope (SEM; SM-200, Topcon, Japan) operated at 4–7 kV. All samples were sputter-coated with Au.

Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared spectra were measured with a Fourier transform infrared spectrometer (FT/IR-410, JASCO, Japan) with 16 scans at a 4 cm⁻¹ resolution from 4000 to 400 cm⁻¹.

RESULTS AND DISCUSSION

ESD of Unblended Chitosan Solutions

Before examination of PEO addition effect, we tried to deposit from unblended chitosan solutions. Here, we prepared three kinds of 10 wt % chitosan solutions with different molecular weights, CH-36k, CH-70k, and CH-120k. The viscosity of the chitosan solutions became higher conspicuously as the molecular weight rose. We could deposit thin fabrics from the CH-36k solution at 25 °C, but their surface morphology was usually made up of spherically structured entities. To the contrary, the CH-70k and CH-120k solutions were unable to be sprayed even at 20 kV. (Our previous study showed that the drawing of a higher-viscosity solution in a capillary by electrostatic force

was more difficult.⁸) When the CH-70k and CH-120k solutions were heated at 70 °C, however, it became possible to spray them due to the decrease in solution viscosity. Even then, again we obtained only spherically structured deposits from these solutions.

Additive Effects of PEO on ESD processability of Chitosan Solutions

It has been found so far that the addition of water-soluble polymer can improve the electrostatic spinnability.^{26–28,30} In the present study, we used CH-36k showing a good ESD processability previously mentioned, and three kinds of PEOs, PEO-20k, PEO-100k, and PEO-500k, as additives. The basic properties and spinnability of the prepared CH/PEO solutions are summarized in Table I. Figure 2 shows the effect of molecular weight of adding PEO on the surface morphologies of electro-spray-deposited fabrics from C2, C7, and C15 solutions, where the CH concentration and CH/PEO ratio are fixed at 6 wt % and 6/2, respectively. The SEM data given there indicate that the addition of higher-molecular-weight PEO tends to develop a fibrous structure. Our previous study revealed that plain high-molecular-weight PEO showed good spinnability.⁸ As can be seen in Table I, the conductivity of CH/PEO blend solutions increased with an increase in the CH concentration. Therefore, applied voltages, which are near the lower critical spraying voltage, also increased with an increase in the CH concentration. (Our previous study demonstrated that the charging of higher-conductivity solution at the tip of the capillary under application of voltage was more difficult.⁸) Figure 3 shows the poly-

Table I. Properties of CH/PEO blend solutions and their spinnability by ESD*

| Spray Solution | CH ^a -36k (g) | PEO ^b (g) | HAc ^c (g) | Water (g) | Conductivity (mS/cm) | Viscosity (mPas) | Surface tension (mN/m) | Spraying Temp. (°C) | Spraying Voltage (kV) | Surface morphology |
|----------------|--------------------------|----------------------|----------------------|-----------|----------------------|------------------|------------------------|---------------------|-----------------------|--------------------------|
| C1 | 8 | 20k | 1 | 4 | 87 | 9.34 | 58.2 | 25 | — | — |
| C2 | 6 | | 2 | 3 | 89 | 7.58 | 35.9 | 25 | 16.54 | spherical |
| C3 | 4 | | 3 | 2 | 91 | 5.86 | 20.0 | 25 | 16.54 | spherical |
| C4 | 2 | | 4 | 1 | 93 | 3.84 | 10.7 | 25 | 13.58 | spherical |
| C5 | 0 | | 5 | 0 | 95 | 0.0948 | 4.5 | 25 | 6.47 | spherical |
| C6 | 8 | 100k | 1 | 4 | 87 | 9.33 | 79.8 | 25 | 14.40 | spherical |
| C7 | 6 | | 2 | 3 | 89 | 6.89 | 62.1 | 25 | 14.00 | spherical |
| C8 | 4 | | 3 | 2 | 91 | 5.21 | 48.2 | 25 | 11.54 | spherical |
| C9 | 2 | | 4 | 1 | 93 | 3.09 | 36.2 | 25 | 11.28 | spherical |
| C10 | 0 | | 5 | 0 | 95 | 0.191 | 25.0 | 25 | 8.50 | spherical |
| C11 | 10 | 500k | 0 | 5 | 85 | 10.4 | 82.9 | 25 | — | — |
| C12 | 9.5 | | 0.25 | 4.75 | 85.5 | 10.2 | 92.5 | 25 | 16.54 | s/f mixture ^d |
| C13 | 9 | | 0.5 | 4.5 | 86 | 9.91 | 95.5 | 25 | 14.70 | fibrous |
| C14 | 8 | | 1 | 4 | 87 | 9.40 | 117 | 25 | 12.61 | fibrous |
| C15 | 6 | | 2 | 3 | 89 | 7.56 | 126 | 25 | 11.20 | fibrous |
| C16 | 4 | | 3 | 2 | 91 | 5.36 | 130 | 25 | 10.86 | fibrous |
| C17 | 2 | | 4 | 1 | 93 | 2.92 | 146 | 25 | 9.08 | fibrous |
| C18 | 0 | | 5 | 0 | 95 | 0.0374 | 197 | 25 | 6.80 | fibrous |

^aCH: chitosan; ^bPEO: poly(ethylene oxide); ^cHAc: acetic acid; ^ds/f mixture: mixture of spherical and fibrous shapes.

*All solution properties were measured at 25 °C.

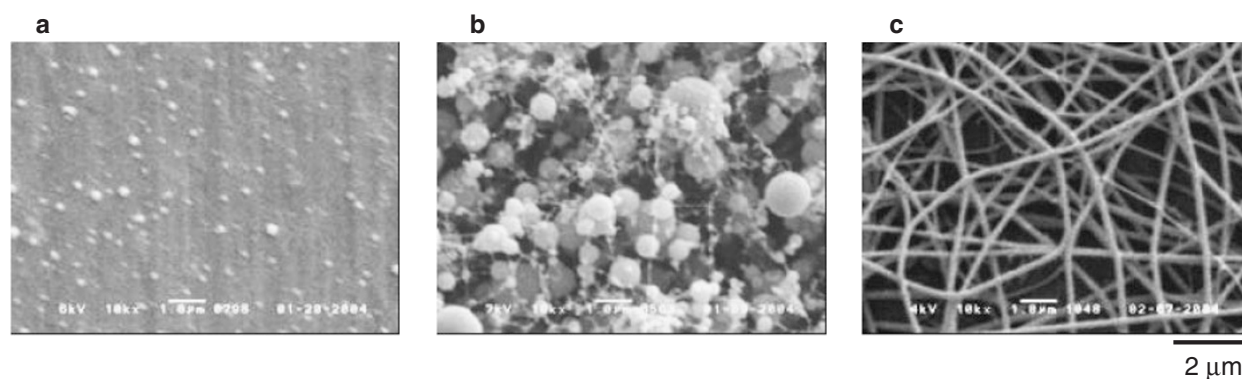


Figure 2. Effect of molecular weight of adding PEO on the surface morphology of electrospay-deposited CH/PEO blend fabrics: sprayed from (a) C2, (b) C7, and (c) C15 solutions (see Table I).

mer composition dependence of the viscosity and electrostatic spinnability for CH/PEO blend solutions C1–C18 (see Table I). The viscosity of the blend solutions decreased with an increase in the CH/PEO ratio for the CH-36k/PEO-500k solutions (C11–C18), because the value for the 5 wt % CH-36k (C11) solution, 82.9 mPas, is smaller than that for the PEO-500k (C18) solution of the same concentration, 197 mPas. Conversely, the viscosity of the CH-36k/PEO-20k and CH-36k/PEO-100k blend solutions increased with an increase in the CH/PEO ratio, because the value for the 5 wt % CH-36k (C11) solution, 82.9 mPas, is larger than those for the PEO-20k (C5) and PEO-100k (C10) solutions of the same concentration, 4.5 and 25.0 mPas, respectively. All the solutions with higher viscosity than 95.5 mPas showed good spinnability:

the spray solutions with the higher-molecular-weight PEO and/or the lower CH/PEO-500k ratio (*i.e.*, higher PEO concentration) tend to form the fibrous structure by ESD. The tendency corresponds to the effect of solution viscosity described in our previous paper.⁸ This result also confirmed that the addition of such a small content of PEO-500k, whose concentration in the blend solution is 0.5 wt % (C13), was already effective for the fiber formation. An effect of the CH/PEO ratio on the diameter of produced fibers for CH-36k/PEO-500k blend fabrics is shown in Figure 4. The fiber diameter increased rapidly at CH-36k contents higher than 75 wt % from 150 to 350 nm. Figure 5 shows an FT-IR spectrum of an electrospay-deposited CH/PEO fabric prepared from the C15 solution, in comparison with that of a pure PEO fabric

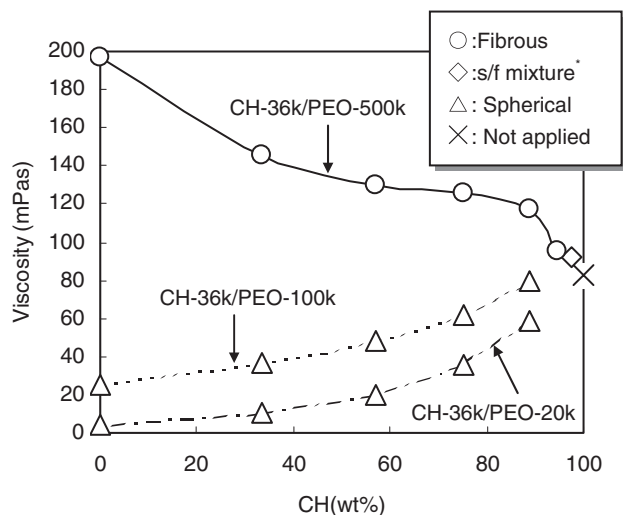


Figure 3. Polymer composition dependence of the viscosity and electrostatic spinnability for CH/PEO blend solutions C1–C18 (see Table I). The composition is denoted by wt % CH calculated as $\text{CH}/(\text{CH} + \text{PEO})$ (w/w) $\times 100\%$. *s/f mixture: mixture of spherical and fibrous shapes.

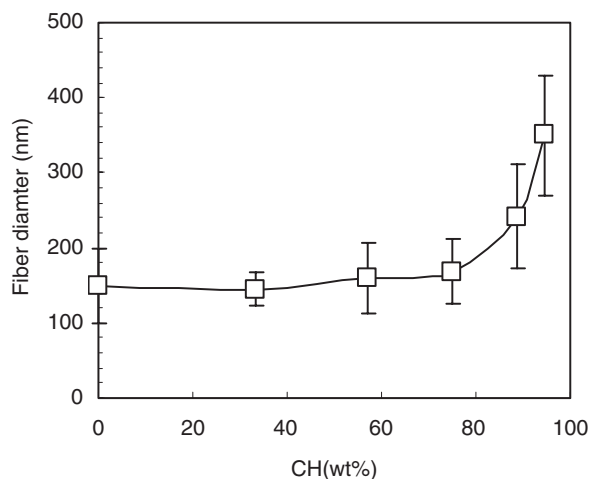


Figure 4. Polymer composition dependence of the diameter of fibers produced from CH/PEO blend solutions C13–C18 (see Table I). The composition is denoted by wt % CH calculated as $\text{CH}/(\text{CH} + \text{PEO})$ (w/w) $\times 100\%$.

from C18 solution. The characteristic adsorption peaks were observed at 3365 and 1658 cm^{-1} for the CH/PEO blend fabric. These peaks indicate the presence of $-\text{OH}$ and $-\text{NH}$ groups, and the presence of $\text{C}=\text{O}$ groups, respectively, derived from the chitosan component, which was undoubtedly involved in the fiber fabrication.

Heating Effect on CHON/PEO Blend Solutions

The properties of spraying CHON/PEO solutions and their spinnability by ESD are summarized in Table II. At 25°C , we could obtain spherically structured deposits from the blend solutions with lower CHON concentrations (S1–S4), but failed to spray

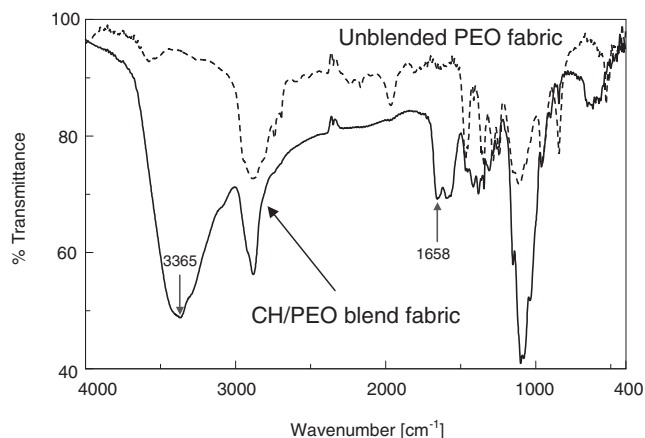


Figure 5. FT-IR spectrum of an electro spray-deposited CH/PEO blend fabric, compared with that of an unblended PEO fabric. These fabrics were sprayed from C15 and C18 solutions, respectively (see Table I).

the CHON/PEO solutions (S5–S12) with higher CHON concentrations. Therefore, we attempted to spray the relevant solutions heated at 70°C for 20 min. The solution viscosities then decreased by the heating treatment, e.g., from 15 to 6.27 mPas for S1; from 103 to 31 mPas for S5; and from 531 to 130 mPas for S9. The heating effect on the ESD processability and an effect of CHON concentration on the surface morphologies of electro spray-deposited fabrics are shown in Figure 6 for the cases from S1, S5, and S9 solutions, where the respective PEO concentrations are all fixed at 1 wt %. Thus we could spray all the solutions at 70°C . As demonstrated by SEM images in the Figure, the blend solutions with higher CHON concentrations tended to form a finer fibrous structure.

As seen in Table II, the conductivity of CHON/PEO blend solutions increased with an increase in the CHON concentration. Therefore, the spraying voltage (but near the lower critical spraying voltage) also increased with an increase in the CHON concentration.⁸ Conversely, the viscosity of blend solutions decreased with an increase in the CHON concentration, because the molecular weight of CHON (110k) is considerably smaller than that of PEO (500k). There was thus a general trend that the spray solutions with higher PEO concentrations formed a fibrous structure by ESD; correspondingly, the solutions with a viscosity higher than 31 mPas showed better spinnability. The diameter of fibers was in a narrow range ca. 150–200 nm and the effect of solution composition on the fiber diameter was less indicative.

Heating Effect on PEC/PEO Blend Solutions

The properties of spraying PEC/PEO solutions and their spinnability are summarized in Table III. At

Table II. Properties of CHON/PEO blend solutions and their spinnability by ESD

| Spray Solution | CHON ^a -110k (g) | PEO ^b -500k (g) | Water (g) | Conductivity (mS/cm) | Viscosity* (mPas) | Surface tension (mN/m) | Spraying Temp. (°C) | Spraying Voltage (kV) | Surface morphology |
|----------------|-----------------------------|----------------------------|-----------|----------------------|-------------------|------------------------|---------------------|-----------------------|--------------------------|
| S1 | 0.8 | 1 | 98.2 | 1.369 | 6.27 | 61.1 | 70 | 9.45 | spherical |
| S2 | 0.6 | 2 | 97.4 | 0.908 | 14.2 | 60.2 | 70 | 8.68 | s/f mixture ^c |
| S3 | 0.4 | 3 | 96.6 | 0.613 | 40.1 | 58.8 | 70 | 7.61 | fibrous |
| S4 | 0.2 | 4 | 95.8 | 0.286 | 88.1 | 59.2 | 70 | 6.84 | fibrous |
| S5 | 8 | 1 | 91 | 9.81 | 31 | 58.1 | 70 | 16.56 | fibrous |
| S6 | 6 | 2 | 92 | 7.36 | 42 | 59.3 | 70 | 14.38 | fibrous |
| S7 | 4 | 3 | 93 | 4.22 | 60 | 56.1 | 70 | 11.30 | fibrous |
| S8 | 2 | 4 | 94 | 2.27 | 111 | 59.3 | 70 | 7.09 | fibrous |
| S9 | 16 | 1 | 83 | 17.64 | 130 | 57.5 | 70 | 16.56 | fibrous |
| S10 | 12 | 2 | 86 | 12.11 | 150 | 59.2 | 70 | 14.86 | fibrous |
| S11 | 8 | 3 | 89 | 9.09 | 162 | 60.0 | 70 | 12.25 | fibrous |
| S12 | 4 | 4 | 92 | 4.59 | 160 | 57.5 | 70 | 12.20 | fibrous |

^aCHON: sodium chondroitin sulfate; ^bPEO: poly(ethylene oxide); ^cs/f mixture: mixture of spherical and fibrous shapes.

*Viscosity data were measured at 70 °C. Other solution properties were measured at 25 °C.

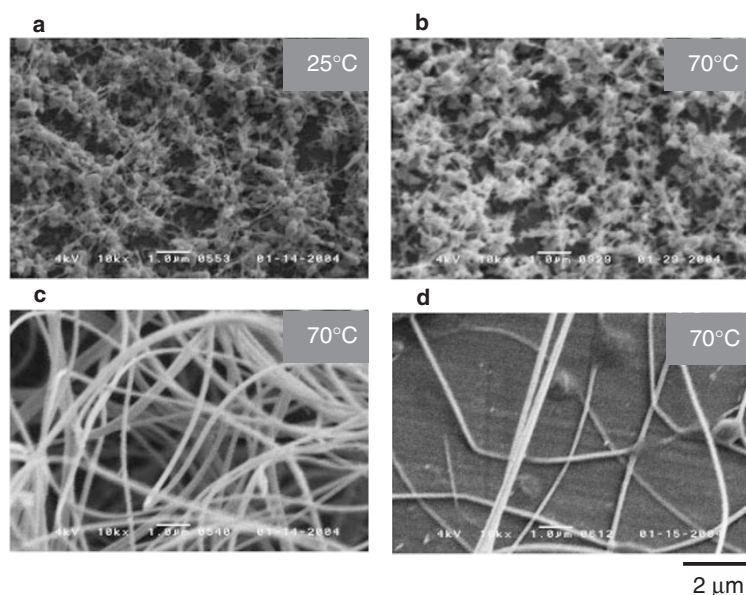


Figure 6. Heating effect on the ESD processability and CHON-concentration effect on the surface morphology of electro-spray-deposited CHON/PEO blend fabrics: sprayed from (a) S1 solution at 25 °C (S5 and S9 solutions could not be sprayed at 25 °C.); (b) S1, (c) S5, and (d) S9 solutions at 70 °C (see Table II).

25 °C, we could deposit spherically structured deposits from the blend solutions with lower PEC concentrations (P1–P4), but failed to spray the PEC/PEO solutions (P5–P12) with higher PEC concentrations. Therefore, again, we attempted to spray the corresponding solutions heated at 70 °C. The solution viscosity decreased by the heating, *e.g.*, from 29.7 to 13.2 mPas for P2; from 71.8 to 30.4 mPas for P6; and from 178 to 39.2 mPas for P10. SEM photographs in Figure 7 indicate the heating effect on the ESD processability and an effect of PEC concentration on the surface morphologies of electro-spray-deposited fabrics prepared from P2, P6, and P10 solutions, the PEO concentration being fixed at 2 wt% in any of

the solutions. As demonstrated there, we could spray all solutions at 70 °C. The SEM observations revealed clearly a changing manner of the surface morphology from a spherical structure to a fibrous one *via* spindle-shaped stage with an elevation in the PEC concentration.

The conductivity of PEC/PEO blend solutions increased with an increase in the PEC concentration (see Table III), and hence the spraying voltages also increased correspondingly.⁸ Generally, the spraying solutions with higher PEO concentrations tended to form the fibrous structure by ESD, while the solutions with higher PEC concentrations tended to form the spherical structure in the deposition. The diameter of

Table III. Properties of PEC/PEO blend solutions and their spinnability by ESD

| Spray Solution | PEC ^a -510k (g) | PEO ^b -500k (g) | Water (g) | Conductivity (mS/cm) | Viscosity* (mPas) | Surface tension (mN/m) | Spraying Temp. (°C) | Spraying Voltage (kV) | Surface morphology |
|----------------|----------------------------|----------------------------|-----------|----------------------|-------------------|------------------------|---------------------|-----------------------|--------------------------|
| P1 | 0.8 | 1 | 98.2 | 0.397 | 4.4 | 56.4 | 70 | 14.86 | spherical |
| P2 | 0.6 | 2 | 97.4 | 0.298 | 13.2 | 59.6 | 70 | 11.79 | spherical |
| P3 | 0.4 | 3 | 96.6 | 0.198 | 32.7 | 58.1 | 70 | 9.09 | s/f mixture ^c |
| P4 | 0.2 | 4 | 95.8 | 0.103 | 53.5 | 57.8 | 70 | 7.51 | fibrous |
| P5 | 2.4 | 1 | 96.6 | 0.805 | 25.8 | 59.2 | 70 | 15.47 | spherical |
| P6 | 1.8 | 2 | 96.2 | 0.655 | 30.4 | 59.6 | 70 | 13.79 | spindle-shaped |
| P7 | 1.2 | 3 | 95.8 | 0.425 | 28.0 | 58.1 | 70 | 8.67 | fibrous |
| P8 | 0.6 | 4 | 95.4 | 0.209 | 25.8 | 57.8 | 70 | 7.16 | fibrous |
| P9 | 4 | 1 | 95 | 1.140 | 41.5 | 58.0 | 70 | 16.52 | spherical |
| P10 | 3 | 2 | 95 | 0.901 | 39.2 | 54.8 | 70 | 15.89 | fibrous |
| P11 | 2 | 3 | 95 | 0.623 | 32.1 | 59.0 | 70 | 13.78 | fibrous |
| P12 | 1 | 4 | 95 | 0.349 | 35.6 | 61.3 | 70 | 10.89 | fibrous |

^aPEC: pectin; ^bPEO: poly(ethylene oxide); ^cs/f mixture: mixture of spherical and fibrous shapes.

*Viscosity data were measured at 70 °C. Other solution properties were measured at 25 °C.

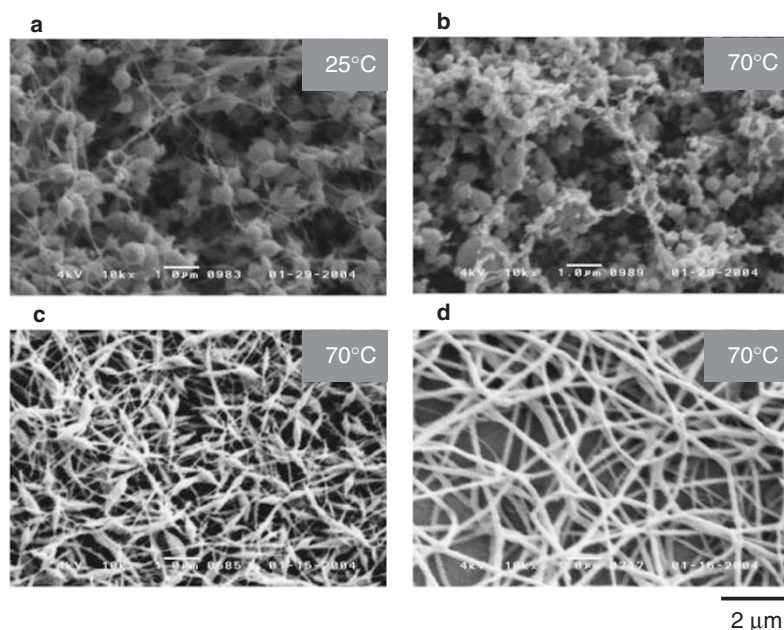


Figure 7. Heating effect on the ESD processability and PEC-concentration effect on the surface morphology of electro spray-deposited PEC/PEO blend fabrics: sprayed from (a) P2 solution at 25 °C (P6 and P10 solutions could not be sprayed at 25 °C.); (b) P2, (c) P6, and (d) P10 solutions at 70 °C (see Table III).

the produced fibers was about 100 nm and the effect of solution composition on the fiber diameter could be undiscernible for this system, too.

CONCLUSIONS

Chitosan, chondroitin sulfate, and pectin nanofibrous fabrics were prepared successfully from the respective polysaccharide/PEO blend solutions by ESD. The effect of PEO addition, and that of the molecular weight and concentration on the formation of the structure and morphology of the produced fabrics were systematically examined. The addition of PEO

with higher-molecular-weights and/or at higher concentrations improved significantly the electrostatic spinnability of the chitosan (CH) solutions. The high-molecular-weight PEO was also advantageous for the fibrous formation even if the addition amount was small: a CH solution blended with only 0.5 wt% PEO was already effective for the fiber formation. An optimal viscosity limit for the fiber formation from the CH/PEO blend solutions was determined as >95.5 mPas. The heating of the spraying solutions at 70 °C enhanced the electrostatic fiber formation from both solutions of chondroitin sulfate (CHON)/PEO and pectin (PEC)/PEO blends. We accomplished well

the fiber formations of chondroitin sulfate and of pectin by the combined use of PEO addition and high-temperature ESD. Further studies on characterization of the polysaccharide/PEO blend fabrics insolubilized after their deposition are now in progress and the result will be reported elsewhere.

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