Polymer−Micelle Complex as an Aid to Electrospinning Nanofibers from Aqueous Solutions

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We propose and demonstrate the concept that a polymer−micelle complex can be used as an aid to preparing nanofibers from aqueous solutions by the electrospinning process. This is based on the recognition that a polymer−micelle complex can simultaneously contribute to an increase in solution viscosity, decrease in surface tension, and increase in electrical conductivity, all of which favor the formation of nanofibers by electrospinning. By incorporating the polymer−micelle complex as a secondary ingredient, electrospinning of sparingly soluble or low molecular weight polymers is made possible, as is illustrated here using a PEO−SDS complex to electrospin a gel forming, genetically engineered silk-elastin biopolymer. The wide choice of polymers and surfactants available to form the polymer-micelle complex with a range of viscosity, surface tension and electrical conductivity properties, potentially allows for a variety of solutions and dispersions to be electrospun from the aqueous medium.

Introduction

Polymeric nanofibers are a new class of nanomaterials in the size range of 10−1000 nm that have been prepared from nearly 50 or more synthetic as well as biological polymers.[1] Numerous applications in membrane systems,[2] catalysis,[3] immobilized enzymes,[4] chemical and biological defense,[5,6] fiber-reinforced composite materials,[7] tissue engineering,[8] wound healing,[9] sensors and photonics,[10] etc, are being developed taking advantage of the large surface-to-volume ratio of these nanofibers and the ability to modify and functionalize the nanofiber surfaces. Polymeric nanofibers are efficiently produced by the process of electrospinning, a process invented about 70 years ago by Formhals.[11] In electrospinning, a fluid jet is generated by the application of an electric field and the jet, subjected to electrostatic, viscous, and surface tension forces, experiences various instabilities. Fluid mechanical analysis[12−17] suggests that in most cases, the jet experiences a whipping instability giving rise to the bending and stretching of the jet and resulting in the generation of nanofibers.

One can expect the morphology and the properties of the nanofiber to be influenced by (i) the properties of the polymer solution such as the viscosity, dielectric constant, surface tension, density, and solvent vapor pressure, (ii) the operational variables such as the solution flow rate, applied electric field, and the electric current, and (iii) the equipment variables such as the nozzle size and the distance between the nozzle end and the fiber collector. Uniform nanofibers are not produced from all polymer solutions. The stability of the jet depends on the viscous and viscoelastic properties of the polymer solution, and unstable jets (corresponding to low viscosity solutions) result in breakup into droplets and the formation of beaded structures.[17] Reduced surface tension favors the formation of fibers without beads. Also, a direct dependence of the fiber diameter on the surface tension has been established by fluid mechanical analysis.[17] The electrical forces are responsible for the initiation of the jet and the stretching during whipping instability. Therefore, high solution conductivity and large solvent dielectric constant are favorable to produce thinner fibers.

Many solvents including formic acid, dimethyl formamide, dimethyl acetamide, chloroform, tetrahydrofuran, methylene chloride, ethanol, isopropanol, hydrochloric acid, camphorsulfonic acid, trifluoroacetic acid, carbon disulfide, hexafluoroisopropanol, water, and mixtures of these solvents have been employed for electrospinning.[7] In practice, the solvent is selected mainly on the basis that the polymer can dissolve in large enough concentration to make the solution adequately viscous. For all organic solvents listed here, the surface tensions are in the range 20−40 mN/m, dielectric constants lie between 5 and 40, and the electrical conductivities are quite small, typically below 4 mS/m (in most cases, below 1 mS/m).

For the large scale production of nanofibers, electrospinning from aqueous solutions is desirable, from an environmental point of view. Common water-soluble polymers such as polyethylene oxide (PEO), polyvinyl pyrrolidone (PVP), and polyvinyl alcohol (PVOH) have been successfully electrospun into nanofibers from aqueous solutions. However, polymers that have low aqueous solubility, low molecular weight polymers, and polymers with rigid or globular structures do not generate necessary viscosity in aqueous solutions and are not easily electrospun into uniform fibers. Some polymers may undergo gelation at low concentrations, making available only solutions of low viscosity for electrospinning. To overcome the limitations listed above and to facilitate electrospinning from aqueous solutions, we propose an approach that makes use of a polymer−micelle complex as a secondary ingredient in the aqueous solution.

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Figure 1. Schematic representation of a polymer-micelle complex formed from the nonionic polymer, polyethylene oxide and the anionic surfactant, sodium dodecyl sulfate, in aqueous solutions.
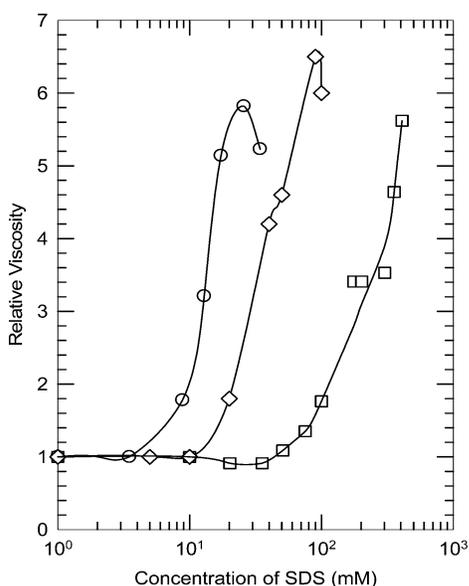

Figure 2. Relative viscosity of a PEO + SDS aqueous solution containing polymer-micelle complex (defined with respect to a PEO solution with no SDS). Circles:[19] 0.1 wt % PEO (M_w = 5 × 10⁶), Diamonds:[20] 0.5% w/v PEO (M_w = 885 000), Squares:[21] 1.15% w/v PEO (M_w = 250 000) plus 0.02 M NaCl. All measurements are at 25 °C.

A schematic representation of the nonionic polymer-ionic micelle complex[18,19] is presented in Figure 1. The segments of the polymer molecule wrap around the micelles with the polymer segments partially penetrating the polar head group region of the micelles and reducing the hydrophobic micelle core-water contact. The size of the polymer-bound micelle depends on the nature of polymer-micelle interactions,[19] whereas the number of micelles bound per polymer depends on the polymer molecular weight. The ionic micelles make the nonionic polymer behave like a polyelectrolyte because of inter-micelle repulsions and contribute to significant expansion of the polymer coil upon complex formation. As the surfactant concentration continues to increase, the ionic strength of the solution also increases, which reduces the inter-micelle repulsions and causes a reduction in the magnitude of polymer expansion. As a result, the solution viscosity first increases, exhibits a maximum, and then decreases with increasing concentration of the surfactant.
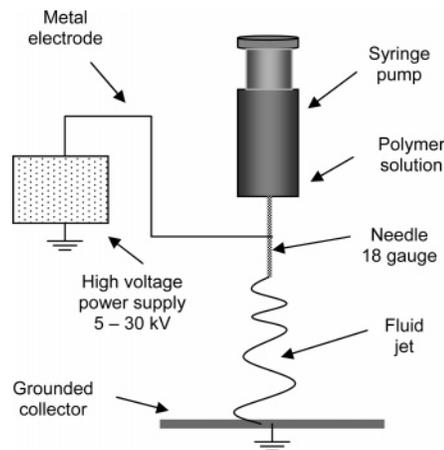

Figure 3. Schematic representation of electrospinning process with the main components being a high voltage power supply, a syringe pump system for controlled flow, and a grounded collector.

Experimentally determined[19−21] relative viscosities of the polyethylene oxide-sodium dodecyl sulfate solution (defined as the ratio between the viscosity of the polymer + surfactant solution and the viscosity of the polymer solution, both at the same polymer concentration) have been plotted in Figure 2 as a function of the surfactant concentration for different molecular weights and concentrations of polyethylene oxide. In addition to impacting the solution viscosity, the type and amount of surfactant also determines the surface tension[22] and electrical conductivity[23] of the aqueous solution. Therefore, the polymer−micelle complex can be designed to manipulate the solution viscosity, surface tension, and conductivity so as to make the aqueous solution properties favorable for electrospinning.

To illustrate the use of a polymer−micelle complex as an aid to electrospinning, we demonstrate the electrospinning of the gel forming, silk-elastin protein polymers (SELP). These polymers combine the superior mechanical properties contributed by silk units and the controlled solubility and elastic properties contributed by elastin units. A wide range of biomedical applications of SELP including drug delivery, gene delivery, and as material for vascular grafting is currently being explored.[24] The protein polymers are water soluble, and they form irreversible gels due to physical interactions[25,26] even at ambient temperatures. The onset of gel formation is sufficient to cause problems with electrospinning. The gelation is avoided or at least the rate of gelation is retarded only when the biopolymer concentration in the aqueous phase is significantly decreased. But this causes the solution viscosity to also decrease below a level suitable for electrospinning.

Experimental Section

Materials. The biopolymer sample received from Genencor is a genetically engineered, repeat block copolymer, of protein sequences representative of silk and elastin. It has the structure $H_2N-(S_3E_4E_KE_3S_3)_{1-13}-COOH$, where S stands for the silk-like peptide block GAGAGS, E stands for the elastin-like peptide block GVGVP, and E_K stands for the modified elastin-like peptide block, GKGVP (one-letter amino acid abbreviations are used, G for glycine, A for alanine, S for serine, V for valine, P for praline, K for lysine). The molecular weight of the polymer is about 70 000 Da. All other chemicals including polyethylene oxide, sodium dodecyl sulfate, formic acid are commercial products and used as received.
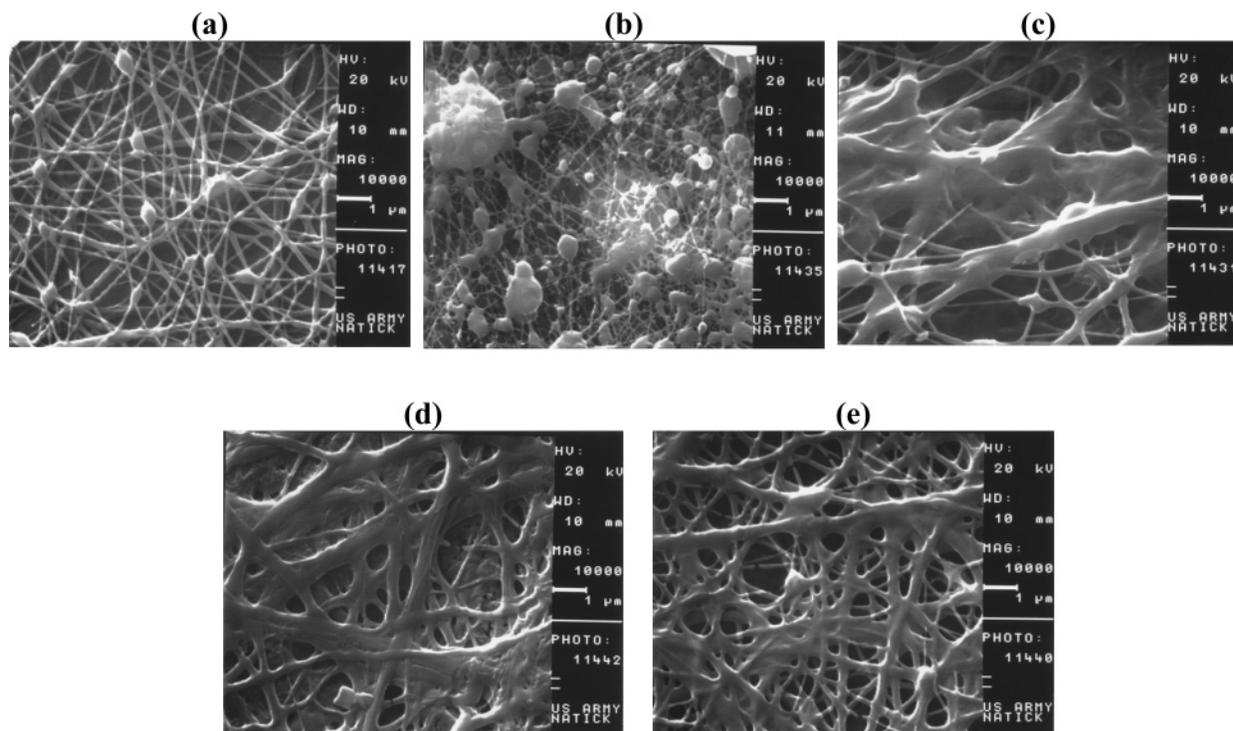
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Figure 4. SEM images of electrospun nanofibers of silk-elastin protein polymer, SELP67K prepared at an applied voltage of 20 kV and a polymer solution flow rate of 120 μL/h. (a) 15 wt % SELP67K in formic acid, (b) 8 wt % SELP67K in formic acid, (c) 6.7 wt % SELP67K, 2.1 wt % PEO (M_w = 900 000) and 1 wt % SDS in aqueous solution, (d) fibers from (c) were dried overnight in air and then exposed to air saturated with methanol at 25 °C for 1 h, (e) fibers from (c) were dried overnight in air and then thermally treated by incubation at 140 °C for 30 min.

Electrospinning Setup. A schematic of the electrospinning setup is shown in Figure 3. The polymer solution is placed in a syringe pump with a needle attached to the end. As the pump displaces the fluid, a droplet of the solution becomes suspended from the needle tip where it is held by surface tension forces. An electrode from a high voltage power supply is placed in contact with the needle tip, applying an electrical potential, which induces free charges in the polymer solution. These charged ions move in response to the applied electric field. This introduces a tensile force in the polymer solution. When the tensile force overcomes the surface tension force associated with the pendent drop of the liquid at the capillary tip, a jet of liquid is ejected from the tip. As the jet travels the short distance of about 10~20 cm between the nozzle tip and the collector, the contour length of the jet dramatically increases by orders of magnitude and the jet thins to nanometer scale. The solvent evaporates as the jet travels from the tip to the collector. The evaporation of the solvent leaves dry nanofibers at the collector surface. Aluminum foils or glass slides were used as collector surfaces.

SEM Imaging. The electrospun fibers were sputtered with a 15 nm layer of gold-palladium and imaged at 20 kV accelerating voltage using a Zeiss EVO 60 scanning electron microscope.

Results and Discussion

Electrospinning of SELP. SELP biopolymer is soluble in formic acid without the formation of any gels. The polymer was electrospun from a 15 wt % solution in formic acid at an applied voltage of 20 kV and a polymer solution flow rate of 120 μL/h. The distance between the nozzle end and the collector surface was approximately 15 cm and a grounded aluminum foil was used as the collector. Nanofibers of 200−300 nm diameter are produced as shown by the SEM image in Figure 4a. No bead formation is observed. What appear to be bead-like in the image are spots where fiber−fiber contact had occurred between not fully dry fibers. The same system was electrospun, but at a lower polymer concentration of about 8 wt %, corresponding to which the solution viscosity is lower. The resulting electrospun nanofibers are imaged in Figure 4b. One can see significant presence of beads forming in the system.

Aqueous solutions of SELP polymers undergo gelation and the fraction of polymer incorporated into the gel is a function of the polymer molecular weight, initial concentration of the polymer, temperature, and time.[26] Given adequate time, say 24 h, most of the polymer becomes part of the gel when the polymer molecular weight is as high as that of the product used in this study. We determined that an aqueous solution of SELP, up to about 7 wt %, did not lead to any gelation at room temperature for the duration of our experiments (2−3 h), whereas for higher concentrations, gelation was more rapid. However, for this concentration range of up to 7 wt % SELP, the solution viscosity is quite small, and therefore, the aqueous solution cannot be processed into fibers by electrospinning. The consequences of low solution viscosity could not be compensated by changes in other operational variables accessible for manipulation, such as the applied voltage (in the range 10−30 kV) or the solution flow rate (in the range 50 to 250 μL/hr).

Keeping SELP as the main polymer component, we added 2.1 wt % polyethylene oxide (M_w = 900 000) and 1 wt % sodium dodecyl sulfate (approximately 35 mM) to an aqueous solution of SELP at 6.7 wt % concentration. The polymer− micelle complex formation is spontaneous and the solution becomes significantly viscous. As mentioned before, the polymer PEO contributes to increasing the solution viscosity. The addition of the surfactant SDS further increases the solution viscosity by the formation of extended PEO−SDS micelle complexes, decreases the surface tension of the solution, increases the solution conductivity, and also increases the

clouding/gelation temperatures, thus retarding any possible gelation. Each one of these changes is conducive to the formation of fibers. Nanofibers of 200−300 nm diameter are formed as shown by the SEM image in Figure 4c. The fibers are more nonuniform in thickness compared to the fibers produced in formic acid (Figure 4a) and appear not to be fully dry.

Making Electrospun Nanofibers Water-Resistant. To make the dry nanofibers stable when contacted with water, the secondary structure of silk-like blocks can be modified to induce formation of a larger fraction of hydrogen-bonded beta sheets or beta strands. Such increased crystallinity in the silk-like blocks will make the nanofiber more stable when contacted with water vapor in practical applications and also impart improved mechanical properties. One approach to induce such structural changes in the silk-like blocks is by treatment with methanol.[27] From our experiments using liquid methanol, we found that the nanofiber morphology was compromised and liquid methanol transformed a part of the nanofibers into a thin polymer film with the remaining fibers incorporated into the film. This could be because the liquid methanol treatment was done on freshly spun nanofibers which were not completely dry. To avoid this result, the fibers were treated by contact with methanol vapor overnight. The resulting nanofiber morphology is shown in Figure 4d. The fibers are swollen compared to the untreated fibers (Figure 4c) and the fiber diameter is relatively larger.

An alternate approach to change the morphology of silk domains is though thermal annealing.[28] The fibers were annealed at 140 °C for 30 min. The thermal treatment also results in some fiber swelling (Figure 4e) but not as much as in the case with methanol vapor treatment. The fiber diameter is somewhat larger than that of the untreated fibers. In these exploratory experiments, no attempt has been made to optimize the polymer-micelle complex.

Choice of Polymer−Micelle Complex Systems. It is clear from Figure 2 that the polymer molecular weight, polymer concentration, and surfactant concentration are variables that can be manipulated to obtain any desired viscosity value. In general, when the polymer molecular weight is lower, higher polymer and surfactant concentrations are needed to attain the same viscosity level. A number of nonionic polymers including PEO, PVP, hydroxyl propyl cellulose (HPC), polypropylene oxide (PPO), and ethyl hydroxyethyl cellulose (EHEC) have been shown to form complexes with ionic micelles. The choice of the surfactant mainly controls the surface tension of the aqueous solution since the surface tension reduction with the surfactant is much larger than the reduction achieved with the polymer alone. Compared to the surface tension of ∼72 mN/m for water, surface tensions of 30−40 mN/m are attainable with hydrocarbon type surfactants, whereas for fluorinated surfactants, surface tensions in the range 17−24 mN/m can be achieved.[22] The conductivity of the aqueous solution depends on the concentration of the surfactant and has been measured[23] to be 33 mS/m at 5 mM SDS, 60 mS/m at 10 mM SDS, and 75 mS/m at 16 mM SDS. Similar values are achieved for various ionic surfactants, both of the hydrocarbon type and the fluorocarbon type. Thus, the solution containing polymer−micelle complex can be designed to have viscosity, surface tension, and conductivity properties covering a wide range, suitable for electrospinning, by the choice of the polymer−micelle complex system.

Conclusions

We propose and demonstrate the concept that the self-assembled polymer−micelle complex can be an aid to electro-spin nanofibers from aqueous solutions. The main contribution to the physical chemistry literature rests on the simple observation that the addition of a polymer-micelle complex simultaneously changes the solution viscosity, electrical conductivity, and surface tension, all in the direction favorable for electrospinning of nanofibers. An additional advantage that could result from the polymer−micelle complex is the reduction or delay in the gelation rate for gel-forming polymers. Further, since the polymer−micelle complex can act also as a colloidal dispersant, it may be possible to electrospin other polymer molecules, nanoparticles or enzymes in their dispersed state using polymer-micelle complex as an aid. The present approach is designed to keep the polymer-micelle complex as a secondary ingredient in the total solids that will form nanofibers. Although in the example presented here, the polymer-micelle complex accounts for a mass fraction of 0.32 based on total solids, this fraction can be significantly reduced to less than 0.10 by choosing a PEO of larger molecular weight.

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