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Polymer 45 (2004) 2981–2984

polymer

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The use of AC potentials in electrospraying and electrospinning processes

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Received 19 August 2003; received in revised form 11 February 2004; accepted 16 February 2004

Abstract

The use of AC potentials in electrospraying and electrospinning processes was demonstrated. Carboxymethylcellulose (CMC) was electrosprayed onto semiconducting and insulating substrates using both DC and AC potentials. On the semiconducting substrate, both AC and DC methods were capable of producing significant CMC coverage. However, only the AC potential was capable of producing significant coverage on the insulating substrate, possibly due to a reduction in the amount of surface charging. In the electrospinning investigation, poly(ethylene oxide) (PEO) fibers were spun into mats using both DC and AC driving potentials. The AC potential resulted in a significant reduction in the amount of fiber 'whipping' and the resulting mats exhibited a higher degree of fiber alignment but were observed to contain more residual solvent. The average fiber diameter for both DC and AC-spun mats exhibited a strong dependence on solution concentration.

Keywords: Electrospinning; Electrospraying; Fibers

1. Introduction

Electrospray ionization (ESI) has become an essential component in the analysis of the molecular weight of large biomolecules [1]. In addition, ESI is finding applications in other fields such as propulsion, particle and aerosol development as well as thin film deposition [2–5]. Electrospinning is essentially an extension of the ESI process at higher solution concentrations where chain entanglement occurs and is capable of producing polymer fibers at submicron dimensions for various applications such as the creation of biocompatible scaffolds and semi-permeable membranes [6–9]. Both the electrospraying and electrospinning processes are driven by the application of a relatively large DC voltage applied to a polymer solution with respect to a grounded substrate (or vice versa). However, in some applications, this electrostatic configuration is problematic. For example, we have found it very difficult to deposit materials onto insulating substrates using the ESI method, most likely due to a build-up of surface charge. Electrostatic charging is also an inconvenience in ESI-based propulsion systems, which may need to incorporate a mechanism to compensate for the net charge loss. In electrospinning, fiber instability or 'whipping' has made it difficult to control the fiber location and the resulting microstructure of electrospun materials. We have found that some of these limitations can be overcome through the use of an AC potential as the driving force in both electrospraying and electrospinning. In this paper, we report on our initial investigations on the use, potential benefits and limitations of AC potentials in both the electrospraying and electrospinning processes.

2. Experimental

Carboxymethylcellulose (CMC) was chosen for the electrospraying work and was obtained commercially from Aldrich with an average molecular weight of 700,000 amu. A solution of 0.01% (w/v) in 50/50 MeOH/H_2O was used in the electrospraying experiments described below. The solution was sonicated for 1 h then set aside overnight, and then the solution was sonicated again before use. The solution was observed to be clear and without entrained air before every use.

Poly(ethylene oxide) (PEO) was chosen as a prototypical

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0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.02.056

material for the electrospinning work due to its propensity for spinning at moderate potentials in the DC mode. The PEO was obtained from Aldrich with an average molecular weight of 400,000 amu. A 7% (w/v) solution was prepared in water and all experiments were performed at room temperature.

The experimental configuration for both AC and DC electrospraying evaluations were similar. The source consisted of a syringe tip fit with a glass tip sleeve to reduce the inner diameter to approximately 20 μm. The counter electrode was a metal plate and the substrate to be coated was attached to the front surface. The needle-to-substrate distance was approximately 3 cm. A Fluke high voltage power supply, providing a maximum output of 10 kV, provided the DC potential, and the typical output current (as measured using a current meter on the output of the power supply) was measured to be between 300 and 400 nA during the spraying procedure. For the AC experiments, 60 Hz line voltage was used through a variable transformer with a maximum output of $7500V_{ac}$. The flow rate was controlled using a Harvard PHD 2000 Infusion syringe pump. Two substrates exhibiting very different electrical conductivity were tested: silicon and polycarbonate (PC). Both the silicon and PC substrates were plasma etched using argon gas to remove contaminants prior to deposition.

The electrospinning apparatus for both AC and DC evaluations was the same as above with the following modifications: the mounted 22-gauge syringe was used without the glass sleeve and the grounded target was a rotating aluminum drum, located from 10 to12 cm from the syringe tip. The mats collected on the drum were 2–3 cm wide and 5 cm long.

Characterization of the coatings and fibers was performed using an Olympus optical microscope.

3. Results and discussion

The ionization and fiber formation mechanisms in electrospraying and electrospinning processes have been the subject of numerous papers and will not be reviewed here [10–13]. In addition, no attempt will be made to provide a detailed description of the droplet or fiber formation mechanisms under the AC potentials. Rather, it is our goal to provide an empirical introduction to the use and potential benefits of AC potentials in the electrospraying and electrospinning processes.

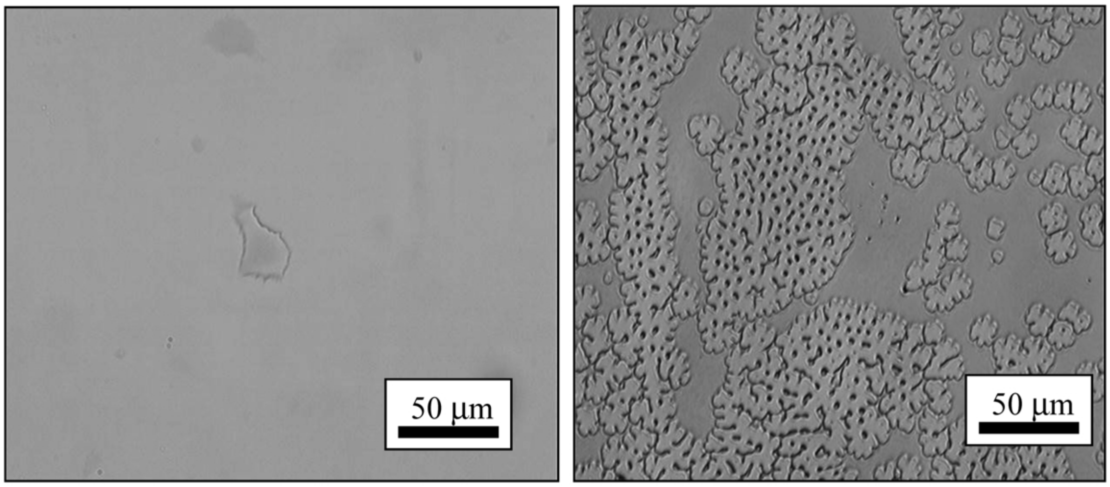
Fig. 1 shows two optical images of a CMC coating electrosprayed onto an insulating polycarbonate substrate from an identical solution, but under DC versus AC fields. Fig. 1(a) is an image of a coating developed using a DC potential and the coating shown in Fig. 1(b) was obtained from the same solution using an AC potential. For the DC coating of Fig. 1(a), very little CMC coverage could be obtained under DC fields of various magnitudes up to 10 kV and even at extremely long exposure times (several hours). However, significant CMC coverage could be obtained using AC driving potentials. For the AC case, the CMC surface coverage was observed to increase with exposure time and is approximately 50% for the image of Fig. 1(b). For this image, the flow rate was 2 μl/min, the AC potential was $5000V_{ac}$ and the exposure time was 60 min.

We believe that the lack of CMC coverage on the insulating PC substrate from the DC potential is due to electrostatic charging of the surface. For example, the surface charge density (σ) required to produce an electric field magnitude equivalent to the externally applied field can be determined using Gauss's law as $\sigma = 2\varepsilon_0 E$, where E is the electric field magnitude and ε_0 is the permittivity constant. From this equation we calculate that a surface charge density of about 10^{-10} C/cm^2 is necessary to produce an electric field magnitude in the order of 10^3 V/cm, which is equivalent to the magnitude of the field produced by the externally applied potential. Therefore, a DC electrospray current of 300 nA delivered to a 10 cm^2 surface area would produce sufficient surface charge density to overcome the external DC potential in less than 1 s. By contrast, the AC potential is expected to alternately deliver positively and negatively charged droplets onto the surface resulting in a significant reduction in surface charge accumulation and a corresponding increase in CMC surface coverage.

To investigate the influence of surface charging, a silicon substrate exhibiting much higher surface conductivity was also tested under both DC and AC potentials and it was found that significant surface coverage could be achieved for both AC and DC potentials. We surmise that the silicon substrate provides sufficient electrical conductivity for the deposited charge to flow to the grounded support electrode.

The PEO electrospinning process for both the DC and AC potentials showed fiber formation occurring at potential differences above 5 kV. The DC fiber formation process was found to be typical of what has been described in the literature and consisted of a stable region where the fiber emerges from the Taylor cone and travels for some distance followed by a region of instability. The region of instability is characterized by violent fiber oscillations or whipping that have been described and modeled in the literature [14–17].

The most obvious visual change that occurred when switching from the DC to the AC potential in the electrospinning investigation was a significant reduction in the amount of fiber whipping observed in comparison to the DC fiber formation process. In other words, the AC potential seems to reduce or eliminate the fiber instability. The fibers appear to form and then travel directly to the target. One explanation for this behavior is that, under AC potentials, the net charge on the fiber is reduced and, therefore, the electrostatic forces producing the fiber instability are also reduced. Due to the alternating polarity of the applied potential, the AC spun fiber should consist of short charge segments of alternating polarity, with the length of the



a) b)

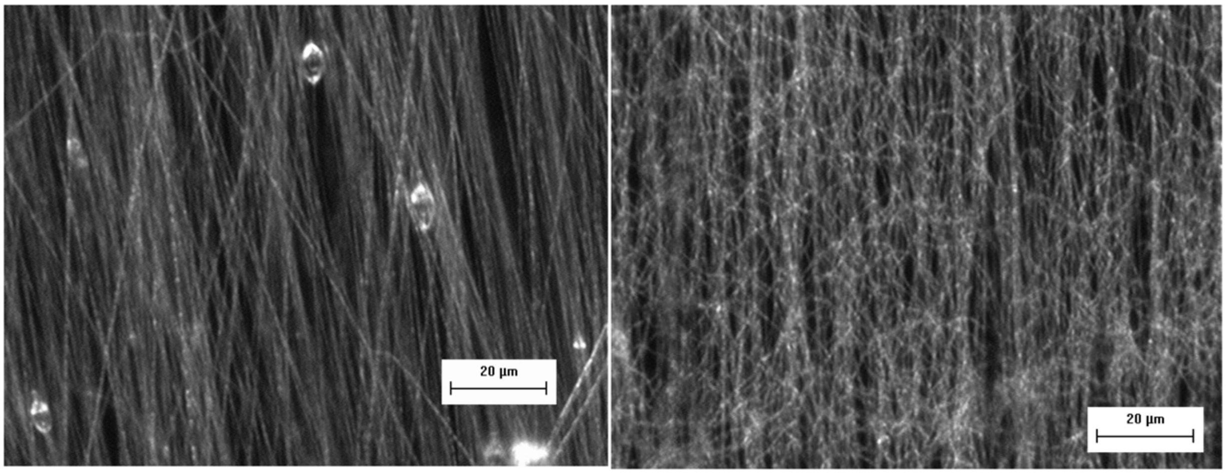
Fig. 1. Optical microscope images of CMC coatings deposited onto an insulating polycarbonate substrate from (a) DC electrospraying and (b) AC electrospraying.

charge segments depending on the fiber production rate as well as the frequency of the AC potential. Fig. 2 shows the microscope images of PEO mats produced from identical solutions but under both DC and AC conditions. Fig. 2(a) is an image of an electrospun PEO mat produced using an AC potential of $7500 V_{ac}$. The AC mat exhibits a high degree of fiber alignment and appears to contain residual solvent, which would be expected if the fiber oscillations observed in the DC case assist in solvent evaporation. Fig. 2(b) is an image of an electrospun PEO mat produced using a DC potential of $7000 V_{dc}$. The most striking visual difference in the AC versus DC mats is the much higher degree of fiber alignment in the AC-spun mat. In addition, the average fiber diameter is significantly smaller for the DC-spun mat, which supports the hypothesis that the fiber whipping is at least partially responsible for the small diameters of electrospun fibers.

We are currently modifying the apparatus to investigate the effect of the AC frequency on the resulting fiber morphology and are also developing a theoretical model for the AC spinning and spraying processes. The results of this work will be published in a separate paper.

4. Conclusions

In summary, electrospraying and electrospinning was performed using an AC potential and the resulting coatings and fibers were analyzed and compared to corresponding structures prepared under conventional DC potentials. It



a) b)

Fig. 2. Optical microscope images of a mat of PEO fibers produced by (a) AC and (b) DC electrospinning.

was demonstrated that AC driving potentials can result in a significant increase in surface coverage of electrosprayed materials deposited onto insulating substrates and can also reduce the amount of fiber whipping inherent to the DC electrospinning process. In addition, there may be several other important applications for AC potentials such as the reduction of charging in ESI-based propulsion systems as well as the introduction of 'built in' modulation in ESI-MS for improved signal-to-noise. Future work will include additional polymer/solvent systems as well as a more detailed investigation of important processing variables such as the AC frequency.

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