Food Hydrocolloids 39 (2014) 19–26

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Affecting parameters on electrospinning process and characterization of electrospun gelatin nanofibers

Nagihan Okutan, Pınar Terzi, Filiz Altay*

Istanbul Technical University, Faculty of Chemical and Metallurgical, Department of Food Engineering, Maslak, Istanbul 34469, Turkey

ARTICLE INFO

Article history:
Received 1 March 2013
Accepted 17 December 2013

Keywords:
Electrospinning
Gelatin
Electrospun nanofiber

ABSTRACT

Electrospinning has been one of the simple, versatile and promising processes to produce continuous nanofibers. Gelatin has been used widely at bulk state in foods for thickening and stabilizing purposes mostly. At nanoscale, electrospun gelatin nanofibers may be used in foods for the same purposes at smaller amounts giving more efficient results. In order to tailor properties of electrospun nanofibers in foods, the influence of affecting parameters on the functions of nanofibers should be known. Our aim was to investigate the influences of the affecting parameters during electrospinning on properties of electrospun gelatin. Gelatin concentrations at 7 and 20% (w/v) were electrospun under 28 or 35 kV of applied voltage. The feed rate was 1 or 0.1 mL/h. Before electrospinning, the electrical conductivity, surface tension and rheological properties of the feed solutions were determined. The morphological analysis showed that only gelatin solution at 20% produced nano-sized fibers. The electrical conductivity, the surface tension, the consistency index and flow behavior index of the gelatin solution at 20% were 4.77 mS/cm, 34.91 mN/m, 1.37 Pa s^n and 0.93, respectively. The range of nanofiber diameters increased with the applied voltage. The zeta potential and the diffusion coefficients of dispersions containing gelatin or electrospun gelatin were determined. Both values were higher for dispersions containing electrospun gelatin than for dispersions with gelatin at the same concentration. The zeta potential and diffusion coefficient values of dispersions containing electrospun gelatin decreased as the applied voltage during electrospinning increased. Lower applied voltage resulted in higher zeta potential and diffusion coefficient values for dispersions containing electrospun gelatin nanofibers, which may indicate that these nanofibers can be used for stabilizing food emulsions, whereas smooth nanofiber morphology without bead formation obtained at the highest voltage.

1. Introduction

Electrospinning has been one of the simple, versatile and promising processes to produce continuous nanofibers from synthetic and natural polymers because of structural integrity and specific fiber arrangements (Kulkarni, Bambole, & Mahanwar, 2010; Yördem, Papila, & Menceloğlu, 2008). It is not a new technique actually; A. Formhals had the first electrospinning patent in 1934 (Formhals, 1934). The history of electrospraying and electrospinning from 1745 to the recent day was well summarized by Bhardwaj and Kundu (2010), Kulkarni et al. (2010) and Reneker and Chun (1996). Electrospun nanofibers have been widely studied for various applications such as filtration (Agarwal, Wendorff, & Greiner, 2008; Veleirinho & Lopes-da-Silva, 2009), wound healing, scaffolds in tissue engineering (Agarwal, Wendorff, & Greiner, 2008; Li, Laurencin, Caterson, Tuan, & Ko, 2002), drug delivery (Loh, Peh, Liao, Sng, & Li, 2010), enzyme immobilization, biosensors, energy generation, protective clothing, affinity membrane and cosmetics (Bhardwaj & Kundu, 2010; Shen, Ng, Chow, & Tan, 2010, chap. 3). Nanofiber applications to the agriculture and food industries are relatively recent compared with their uses in other sectors.

In electrospinning process, an electrical potential is applied between a droplet of a polymer solution held at the end of the nozzle of the spinneret and a grounded collector plate. When the applied electric field overcomes the surface tension of the droplet, a charged jet of polymer solution, which is controlled by the electric field, is ejected. The ejected jet has bending instabilities caused by repulsive forces between the charges carried with the jet. The jet grows longer and thinner until it is collected on the collector plate as fibers (Ponhan & Maensiri, 2009). Electrospun nanofibers exhibit number of interesting characteristics such as high porosity, large surface area per unit mass, high gas permeability and small interfibrous pore size (Saeed & Park, 2010). Many parameters can influence electrospinning process, including solution properties

* Corresponding author. Tel.: +90 212 2856948; fax: +90 212 2857333.
E-mail address: lokumcu@itu.edu.tr (F. Altay).

0268-005X/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.foodhyd.2013.12.022

(e.g., concentration, viscosity, electrical conductivity, surface tension, dielectric properties), governing variables (e.g. electrical field strength, fluid flow rate, distance to the collector plate) and ambient parameters such as humidity and temperature (Bhardwaj & Kundu, 2010; Deitzel, Keinmeyer, Harris, & Tan, 2001; Liu et al., 2010; Theron, Zussman, & Yarin, 2004; Ying, Zhidong, Qiang, & Zhicheng, 2005).

The concentration of polymer in a solution determines if it can be electrospun into nanofibers and has an important effect on fiber morphology. In order to obtain fibers, a minimum feed solution is required, whereas there is an optimum concentration for fibers without beads (Bhardwaj & Kundu, 2010). Generally, an increase in solution concentration increases fiber diameter and uniformity (Deitzel et al., 2001). Electrospinning process requires the transfer of electric charges from the electrode to the spinning droplet. Therefore, a minimal electrical conductivity is essential for nanofiber formation. Solutions with zero conductivity cannot be electrospun into nanofibers. The electrical conductivity is affected by polymer and solvent type, polymer concentration and temperature. Where the polymer has ionic functionalities, the solution conductivity is concentration dependent (Andrady, 2008, chap. 4).

Surface tension is a function of composition and plays a critical role in electrospinning process (Bhardwaj & Kundu, 2010). It is the primary force opposing applied voltage during electrospinning process and determines electrospinnability (Andrady, 2008, chap. 4). The feed solutions with low surface tension produce fibers without beads. However, it does not mean all solutions with low surface tension can be electrospun (Bhardwaj & Kundu, 2010). The minimum voltage for producing nanofibers increases with the surface tension of solution but not always linearly. Surface tensions of polymer solutions change with concentration, chemical composition and temperature (Andrady, 2008, chap. 4).

Rheological properties, especially viscosity influences nanofiber formation process. The solutions with high viscosity cannot eject from the spinneret whereas the solutions with low viscosity do not produce fibers (Bhardwaj & Kundu, 2010). The viscoelastic force within the polymer charged jet is the key force acting against the Coulombic repulsion which is the main force leading elongation of the jet after from the Taylor cone apex. Numerous studies have shown the effect of feed solution viscosity on the size of the fiber, and generally greater viscosity means larger fiber size (Deitzel et al., 2001; Ratanavaraporn, Rangkupan, Jeerawatchai, Kanokpanont, & Damrongsakkul, 2010) and more uniform fiber formation (Deitzel et al., 2001).

The applied voltage is the critical element of electrospinning process because it provides surface charge on the electrospinning jet and affects nanofiber diameter. Generally increasing applied voltages lead to decreasing in nanofiber diameters with increasing electrostatic repulsive forces on the fluid jet (Andrady, 2008, chap. 4; Bhardwaj & Kundu, 2010). However, very high voltages may facilitate nanofibers at larger diameters due to more polymer ejection (Demir, Yilgor, Yilgor, & Erman, 2002; Zhang, Yuan, Wu, Han, & Sheng, 2005). In addition, bead formations can occur at high voltages (Deitzel et al., 2001; Demir et al., 2002). The rate of feed solution influences jet velocity and transfer rate of the solution. For evaporation of solvent and obtaining solid nanofibers lower feeding rates are desirable (Bhardwaj & Kundu, 2010). Ideally, feeding rate must match the solution removing rate from the tip. Lower feeding rates can inhibit electrospinning (Andrady, 2008, chap. 4) and high feeding rates result in beaded large diameter fibers due to unavailability of proper solvent evaporating time prior to reaching the collector (Bhardwaj & Kundu, 2010).

The characterization of electrospun fibers remains one of the difficult tasks as the chances of getting single fibers are rare (Bhardwaj & Kundu, 2010). Physical characterization of electrospun fibers is associated with structure and morphology of the sample. For morphological characterization, techniques such as scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) (Kriegel, Kit, McClements, & Weiss, 2009; Maretschek, Greiner, & Kissel, 2008) and atomic force microscopy (AFM) are used (Bhardwaj & Kundu, 2010; Demir et al., 2002; Li et al., 2002). For chemical characterization of nanofibers, Fourier transform infra red (FTIR), nuclear magnetic resonance (NMR), circular dichroism (CD), differential scanning calorimetry (DSC), X-ray diffraction and X-ray scattering can be used. In some studies AFM tips and nano tensile testing systems were used for mechanical characterization (Bhardwaj & Kundu, 2010). The characterization studies should also include behaviors of electrospun nanofibers in dispersions, which may affect their utilization in foods.

There has been growing interest in the synthesis of natural polymer based nanofiber. Advantageous attributes of natural polymers include biocompatibility, hydrophilicity and non-toxicity (Bhattarai, Li, Edmondson, & Zhang, 2006). Most natural polymers have limited applications due to the difficult handling of nanofiber (Moon & Farris, 2009). However, collagen, gelatin, chitosan and hyaluronic acid which have been successfully fabricated by electrospinning are the most commonly used natural polymers (Bhattarai et al., 2006; Songchotikunpan, Tattiyakul, & Supaphol, 2008). Gelatin is a biopolymer easily obtained from partial hydrolysis of collagen, which is the most abundant structural proteins found in the animal connective tissues such as skin, tendon, cartilage and bone (Zhang, Venugopal, Huang, Lim, & Ramakrishna, 2006). There are many studies related to the utilization of gelatin in various forms for many different applications such as cosmetics, pharmaceutical, and medical applications, including drug delivery (Vandervoort & Ludwig, 2004) because of commercial availability at low cost over the years (Moon & Farris, 2009; Songchotikunpan et al., 2008). In foods, gelatin is an ingredient generally used as an agent for enhancing elasticity, stability and consistency of food products due to its rheological properties (Giménez, Gómez-Guillén, & Montero, 2005). It has been electrospun from different solvents such as acetic acid, formic acid and ethyl acetate (Ki et al., 2005; Song, Kim, & Kim, 2008; Songchotikunpan et al., 2008). In addition, crosslinking of gelatin nanofibers were investigated to improve their water-resistant ability and thermomechanical properties for potential biomedical applications (Zhang et al., 2006). Due to applications in carrying/delivering and controlled release of drugs in medicine and pharmaceuticals (Kaasalainen et al., 2012; Loh et al., 2010; Maretschek et al., 2008), electrospun nanofibers appear to offer new applications such as encapsulation of functional components in foods (Fernandez, Torres-Giner, & Lagaron, 2009; Lopez-Rubio, Sanchez, Wilkanowicz, Sanz, & Lagaron, 2012; Wongsasulak, Patapeejumruswong, Weiss, Supaphol, & Yoovidhya, 2010). We think that electrospun nanofibers from biopolymers, especially gelatin, could be used for stabilizing food emulsions, inhibiting syneresis or oil separation in foods based on our preliminary studies. The zeta potential is used for predicting and controlling the stability of colloidal suspensions or emulsions (Cho, Lee, & Frey, 2012). According to Kaasalainen et al. (2012), zeta potential (ζ) has an important role in physical stability of nanosuspensions. A polymer spreads in the solution in time and this diffusion can be expressed by the Fick's law. The diffusion coefficient, D (also known as diffusivity), can be determined using dynamic light scattering. It is linearly correlated with the mobility of the