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Electrospinning chitosan/poly(ethylene oxide) solutions with essential oils: Correlating solution rheology to nanofiber formation

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ABSTRACT

Electrospinning hydrophilic nanofiber mats that deliver hydrophobic agents would enable the development of new therapeutic wound dressings. However, the correlation between precursor solution properties and nanofiber morphology for polymer solutions electrospun with or without hydrophobic oils has not yet been demonstrated. Here, cinnamaldehyde (CIN) and hydrocinnamic alcohol (H-CIN) were electrospun in chitosan (CS)/poly(ethylene oxide) (PEO) nanofiber mats as a function of CS molecular weight and degree of acetylation (DA). Viscosity stress sweeps determined how the oils affected solution viscosity and chain entanglement (C_e) concentration. Experimentally, the maximum polymer:oil mass ratio electrospun was 1:3 and 1:6 for CS/PEO:CIN and:H-CIN, respectively; a higher chitosan DA increased the incorporation of H-CIN only. The correlations determined for electrospinning plant-derived oils could potentially be applied to other hydrophobic molecules, thus broadening the delivery of therapeutics from electrospun nanofiber mats.

1. Introduction

The electrospinning process fabricates non-woven mats composed of continuous nano- to micro- meter scale diameter fibers (Engel, Schiffman, Goddard, & Rotello, 2012; Reneker, Yarin, Fong, & Koombhongse, 2000). This well-established, scalable (Persano, Camposeo, Tekmen, & Pisignano, 2013) technique has been utilized to form fibers from over 100 different polymers including, polyelectrolytes (Ohkawa, Cha, Kim, Nishida, & Yamamoto, 2004; Pakravan, Heuzey, & Ajji, 2011), biopolymers (Chang, Lee, Wu, Yang, & Chien, 2012; Kong & Ziegler, 2012; Saquing et al., 2013), and synthetic polymers (Kai, Jin, Prabhakaran, & Ramakrishna, 2013; Luo et al., 2015). Additionally, researchers have further tailored the functionality of fibers by loading solid agents into the polymer precursor solutions, including TiO_2/graphene for increased electrical performance (Zhang et al., 2012), quantum dots for fluorescent detection (He et al., 2012), and single-walled carbon nanotubes for antibacterial activity (Schiffman, Wang, Giannelis, & Elimelech, 2011). In these cases, the solid agent was suspended in a concentrated polymer solution, which provided the chain entanglement necessary to "carry" the solid agent along the electrospinning process (Saquing et al., 2013). Alternatively, researchers have synthesized nanoparticles within a fiber mat post-electrospinning, thus avoiding the need to optimize precursor rheology (Persano et al., 2012). However, much less research has been conducted on electrospinning nanofibers from polymer solutions that contain immiscible phase liquids (Angeles, Cheng, & Velankar, 2008; Briggs & Arinzeh, 2014; Díaz, Barrero, Márquez, & Loscertales, 2006; Li, Ko, & Hamad, 2013; Qi, Hu, Xu, Wang, 2006; Rieger & Schiffman, 2014; Sanders, Kloefkorn, Bowlin, Simpson, & Wnek, 2003; Xu et al., 2005, 2006). A handful of reports used harsh organic solvents to emulsion electrospin specific polymers, by relying on a surfactant to carry the immiscible phase biological cargo — proteins (Briggs & Arinzeh, 2014; Yang et al., 2008), DNA (Yang et al., 2011), and water-soluble drugs (Xu et al., 2005; Xu, Chen, Ma, Wang, & Jing, 2008) — and protect them against coalescence (Angeles et al., 2008; Briggs & Arinzeh, 2014; Li et al., 2013; Qi et al., 2006; Sanders et al., 2003; Xu et al., 2005, 2006).

Another class of hydrophobic bioactive agents are essential oils. Due to the rise of antibiotic resistance, research into plant-derived agents has surged because they can inactivate microbes non-specifically (Bakkali, Averbeck, Averbeck, & Idaomar, 2008; Kavanaugh & Ribbeck, 2012). Within the past two years, a number of essential oils including *Cinnamomum* (Rieger & Schiffman, 2014), *Thymus vulgaris* (Karami, Rezaeian, Zahedi, & Abdollahi, 2013), *Chamomilla recutita* (Motealleh et al., 2014), *Cymbopogon* (Liakos et al., 2015), *Mentha piperita* (Liakos et al., 2015), *Acidum tannicum* (Xu, Weng, Gilkerson, Materon, & Lozano, 2015), *Eremanthus erythropappus* (de Oliveira Mori et al., 2015), and *Centella asiatica* (Yao, Yeh, Chen, Li, & Huang, 2015) have been electrospun

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