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# Material selection in electrospinning microparticles

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## HIGHLIGHTS

- 10 μm particles can be electrospun when suspended in polymer solutions, with loadings of up to 66 wt% particles in fibers.
- The factors that influence electrospinnability and morphology are the particle density, aggregation, and fiber:particle size.
- This study provides a platform for product design for new electrospun materials with high loadings of functional particles.

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## ABSTRACT

Electrospinning is a valuable production method for nanoscale polymeric fibers. A major limitation of the technology is the requirement for high molecular weight polymers as a major part of the matrix. Many applications would benefit from flexibility in the materials for electrospinning, including pharmaceuticals, wearable devices and diagnostics, and structured fibers with particles included that are larger than the fiber size. To realize these more advanced functional composites, a strong understanding of how particle inclusion affects the electrospinning process and mat properties is essential. In this work, we examine materials systems containing polymers and microparticles, focusing on how inclusion of particles affects the electrospinnability and morphology of the fiber. The primary factors that influence electrospinnability and morphology are the particle density, particle aggregation, and size ratio of the fibers to the particles. These results provide a platform for product design for new electrospun materials with high loadings of functional particles.

## 1. Introduction

Solution processing methods such as roll-to-roll coating, 3D printing and electrospinning are common ways to transform polymers into complex functional products. Electrospinning, which produces nano-to-microscale fiber mats, provides significant advantages over other production methods, including high surface area and readily tunable surface chemistry and morphology. Electrospinning has made great progress recently with an increase in publications and patents [1] including major leaps in biomedical applications, such the encapsulation of bacteria and viruses in nanofibers [2–4], and the inclusion of drugs into nanofibers for oral delivery [5–7], and in technological applications such as water and air filtration [8,9] and wearable electronic devices [10–12].

In single needle solution electrospinning, a polymer solution is pumped through a needle, forming a drop at the tip of the needle. When a high voltage is applied to the polymer solution, electrostatic forces on the droplet compete with the surface tension, leading to formation of a Taylor cone. When the electrostatic forces overcome the surface tension, a jet extends from the Taylor cone, with the fluid moving in the electric field towards the grounded plate. The jet thins and dries as it travels to the grounded plate resulting in solid nano-to-microscale fibers [13]. From this simple process, electrospinning has grown as a technology for polymer processing, with at least 55 companies focusing on production of nanofibers to commercialize products for applications such as air filtration, protein purification, cell culture and composite reinforcements, and large companies such as Samsung, Toray, and Boeing incorporating it into their R&D programs [1].

Despite these exciting improvements, progress is slowed by materials currently considered electrospinnable, which are limited to high molecular weight polymers in solution mixed with limited quantities of small molecules and particles. This holds back technology for many applications including structural materials, electronic devices, and drug delivery systems and limits the production rate due to poor solubility of the polymers, inhibiting widespread commercial development [1]. In order to expand the use of the processing technique, electrospinning

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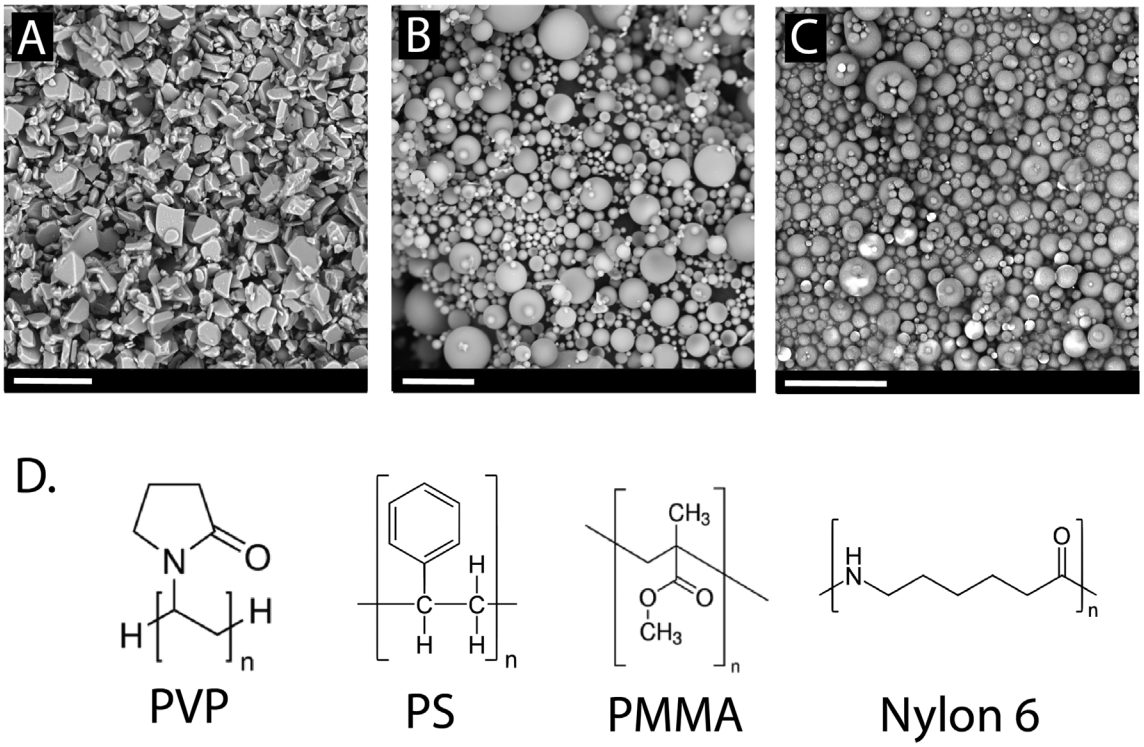


**Fig. 1.** A) $Al_2O_3$ particles, B) Glass particles, C) PMMA-co-EGDMA particles and D) Chemical structures of PVP, PS, PMMA and nylon 6. Scale bars indicate 30 μm.

**Table 1**
Properties of optimized polymer solutions and the resulting average fiber diameter.

| Solution | Average fiber diameter (μm) | Viscosity (Pa-s) | Solvent dielectric constant | Solution conductivity (μS/cm) |
|---|---|---|---|---|
| 9 wt% PVP in MeOH | 1.60 ± 0.26 | 0.12 ± 0.02 | 32.6 | 4.29 |
| 20 wt% PS in DMF | 0.81 ± 0.27 | 0.49 ± 0.07 | 36.7 | 1.49 |
| 25 wt% PMMA in DMF | 1.50 ± 0.30 | 0.88 ± 0.08 | 36.7 | 4.48 |
| 20 wt% Nylon in FA | 0.24 ± 0.06 | n/a | 57.2 | 1170 |

must allow for inclusion of additional functional materials, such as metals, ceramics, pharmaceuticals, etc. A particularly exciting future application is wearable devices [10,12], but this is not currently feasible in a scalable manner with the limits on materials considered "electrospinnable". High molecular weight conducting polymers are expensive and the most common one, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), is a dispersion of polymeric particles. One way to increase conductivity is by adding high loadings of PEDOT:PSS or other less expensive conducting particles such as silver to the polymer solution [12]. A few attempts have been made to electrospin PEDOT:PSS using other polymers as matrix materials, including polyethylene oxide (PEO) [14] and polyvinyl alcohol (PVA) [15]. However these works primarily demonstrate the ability to make functional nanofibers containing PEDOT:PSS; they do not examine methods to maximize the PEDOT:PSS content of the resulting material. The capability to prepare advanced composites by adding functional particles to electrospun fibers is exciting for expanding the application space, but requires significant development to be reliable and widely used.

In addition to expansion of composites, the inclusion of particles can also introduce new surface and morphological properties to the electrospun mats. Wang et al. demonstrated that air filtration properties could be tuned by the morphology of the fibers, including the beads-on-string morphology [16]. Additionally, the contact angle has been shown to be sensitive to morphology, with the beads-on-string morphology capable of producing superhydrophobic surfaces [17]. The hydrophilic/hydrophobic nature of included particles has also been shown to impact the wettability of the fiber mats, providing an additional tuning parameter [18]. With large particle sizes, the fibers resemble the beads-on-string morphology, but are not as sensitive to processing conditions and the "bead" size is readily tunable using particle size. Thus, a thorough understanding of particle electrospinning is necessary for greater applicability in controlling surface morphology of electrospun mats.

Particle or suspension electrospinning refers to dispersing particles in the polymer solution and electrospinning the mixture. Various nanoparticles have been electrospun at low loadings including magnetite [19], $TiO_2$ [20], $CaCO_3$ [21], fumed silica [18], carbon black [22], iron and nickel [23], with average particle diameters of less than 100 nm and fiber sizes on the order of 200–2000 nm. Particles of approximately the same size as the fibers, including clays [24] and bacteria and viruses [2–4] have also been electrospun, but electrospinning of particles with average diameters larger than the fibers was first shown by Brettmann et al. using polyvinyl pyrrolidone (PVP) mixed with polystyrene (PS) beads of varying sizes [25]. Later, Armstrong et al. was able to fully entrap 12.5 μm ZIF-8 particles at a loading of 10 wt%. In examining the mechanism of particle inclusion, they determined that the particles localize to the center of the fibers due to the minimization of surface tension [26]. While these studies demonstrate the feasibility of electrospinning particles, including those with diameters much larger than the fiber diameter, they are limited in scope and do not examine how the properties of the polymer and particle impact spinnability.

The intent of this study is to perform a systematic study of microparticle inclusion on electrospun nanofibers. In this work, we examine four different polymer types and three different particle types to