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Short Communication

Emulsion electrospinning: Composite fibers from drop breakup during electrospinning

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We evaluate the feasibility of electrospinning oil-in-water type emulsions. The emulsions had an aqueous solution of polyethylene oxide (PEO) as the continuous phase, and either mineral oil or a polystyrene (PS) in toluene solution as the drop phase. The Taylor cones and electrified liquid jets were stable even when the emulsion drops were as large as a few-ten microns in diameter. The resulting electrospun PEO fibers incorporated the dispersed phase of the emulsion in the form of drops (in case of mineral oil), or in the form of solid particles (in case of PS). Mineral oil drops appear to be completely encapsulated in the PEO fibers, whereas the PS particles are either incompletely encapsulated, or covered by only a very thin layer of PEO. Calculations show that in both cases, the initially large emulsion drops are broken during the electrospinning process. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: electrospinning; electrospun fibers; emulsion

INTRODUCTION

Numerous researchers have explored electrospinning of polymer solutions that have a solid phase, e.g., particles, carbon nanotubes, or proteins dispersed in them; several references to such ''suspension electrospinning'' are available in review articles.[1–3] In contrast, there has been little development of ''emulsion electrospinning'': cases in which an immiscible liquid phase is dispersed into a polymer solution. We are aware of only three reports of emulsion electrospinning, and will discuss them briefly. Sanders *et al.*[4] electrospun water-in-oil emulsions, where the water drops contained dissolved solutes (e.g., salt, protein, sugar), and the continuous organic phase was poly(ethylene-co-vinyl acetate) dissolved in dichloromethane. The resulting fibers were about 20 μm in diameter, much larger than typical for electrospinning, and contained droplets of the aqueous phase. Such fibers have obvious potential in biological applications that require controlled release of aqueous solutes. Similar research was reported by Xu *et al.*:[5] they electrospun water-in-oil emulsions where the water drops contained an anti-cancer drug, whereas the continuous organic phase was a poly(ethylene glycol)-poly(L-lactic acid) diblock copolymer dissolved in chloroform. Almost all the water from the drop phase evaporated during electrospin-

ning (unlike Sanders *et al.*[4]), and hence the anti-cancer drug was incorporated into the electrospun fibers in dry form. Finally, in a separate publication, Xu *et al.*[6] discussed a variation of the procedure in which the water drops incorporated a polymeric solute (polyethylene oxide, PEO), whereas the organic phase remained the diblock/chloroform solution as before.[5] Composite fibers of sub-micrometer diameter were realized, but remarkably, the fibers had a core-shell morphology with the PEO forming the core, and the diblock copolymer forming the annular shell. The authors suggested that during electrospinning, the aqueous drops move to the core of the fiber and coalesce, thus forming the PEO core.[6] This procedure appears to be an operationally simpler analog of core-shell electrospinning[6–12] which requires two concentric needles.

In this paper, we will show that the reverse case of oil-in-water emulsions can be electrospun as well, and can yield oil/polymer composite fibers, or polymer/polymer composite fibers. Furthermore, in the present case we will show that the emulsion drops break up into smaller droplets during the electrospinning process, in contrast to coalescence observed by Xu *et al.*[6]

EXPERIMENTAL

The continuous phase of all of the emulsions discussed here was a 7 wt% solution of PEO in water (Milli-Q). The PEO was Polyox WSR N-3000 supplied by Dow Chemicals, and a molecular weight of 400,000 g/mol has been quoted by the manufacturer. The drop phase of the emulsions was either

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mineral oil (Fisher), or a 15 wt% solution of polystyrene (PS) in toluene. The PS was grade 145D from BASF, and a melt flow index of 14 has been quoted by the manufacturer.

The appropriate amount of the drop phase and the aqueous phase (exact emulsion compositions specified later) were placed in a vial. Pluronic P105 (BASF) (0.5 wt%) was added as a surfactant to stabilize the drops against coalescence. This non-ionic surfactant is recommended by the manufacturer for stabilizing oil-in-water emulsions; indeed, the emulsions were stable against quiescent coalescence for at least several hours. Emulsions were prepared by two methods, either a high-speed homogenizer (TissueMiser), or by hand-shaking; these two methods will be compared in the Section ''Emulsions with PS/toluene drops.''

The emulsions were dispensed at the rate of 0.06 ml/min with a computer-controlled syringe pump. Electrospinning was conducted out of a 16 gauge needle at a voltage of 21 kV, with the substrate (a grounded aluminum wire mesh) being held 20 cm below the tip of the needle. Much of the imaging of this paper was done by optical microscopy, and the fibers collected on the wire mesh were not convenient for this purpose. Therefore, fibers were collected on glass slides by holding the slides (glued to a long polypropylene rod) over the substrate for a few seconds. These fibers collected on slides were used for optical imaging; the fibers collected on the grounded wire mesh were only used for dissolution/filtration experiments described in the Section ''Emulsions with PS/toluene drops.''

RESULTS AND DISCUSSION

Emulsions with mineral oil drops

Initial experiments were conducted using mineral oil as the drop phase. This may be regarded as a relatively simple case of emulsion electrospinning because mineral oil has a negligible evaporation rate at room temperature, thus, only the outer aqueous phase is expected to evaporate. Accordingly, the oil is expected to become incorporated into the fibers with no further changes; in the present case, the emulsion contained 2.5 wt% oil; thus, the final dry fibers contain 25.5 wt% oil, 5% surfactant, and the remainder PEO. The chief disadvantage of the mineral oil-based emulsions is that the resulting fibers cannot be studied by scanning electron microscopy since the oil does evaporate under high vacuum conditions. Therefore, optical microscopy was used for all the imaging in this section.

Fig. 1(a) shows an optical image of the mineral oil emulsion prepared by the high-speed homogenizer. This image does not refer to the as-prepared emulsion, but instead refers to a drop of emulsion collected from the electrospinning needle immediately before the voltage was turned on to initiate electrospinning. Thus, any structural changes such as coalescence occurring in the tubing connecting the electrospinning needle to the syringe can be ignored; Fig. 1(a) truly represents the emulsion being electrospun. While the drop size is too small to permit a quantitative measurement, it is clear that most drops are less than 5 µm in diameter, while very few are substantially larger.

Fig. 1(b) shows optical micrographs of fibers collected from oil-in-PEO electrospinning. Most fibers appear to be
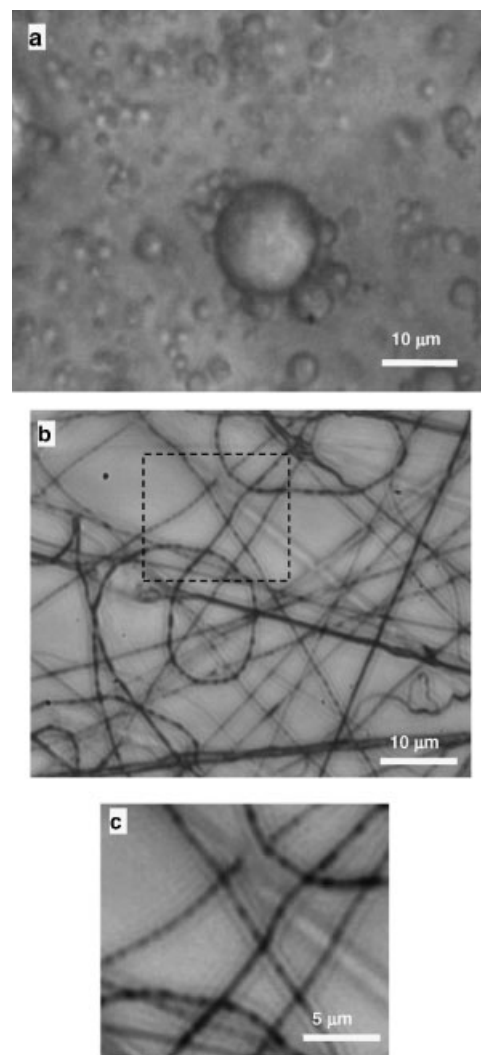

Figure 1. (a) Emulsion of mineral oil in aqueous solution of PEO. (b) Fibers electrospun from the emulsion. Dotted rectangle from (b) is magnified two-fold in the (c) to show the alternating dark and light regions more clearly.

less than 2 µm in diameter. In some places on the glass slide (not shown), occasional broad ''bands,'' about 10 µm in width, were evident. We believe that they result from fibers that occasionally reach the slide without drying fully, and therefore wet the slide.

The most interesting feature of Fig. 1(b) is the alternating bright and dark regions along the fiber length shown more clearly in Fig. 1(c), suggesting that each fiber has within it a string of oil drops. To verify that oil drops are indeed retained within the fibers, we placed a small drop of water on the fiber so as to dissolve the PEO. The kinetics of fiber dissolution are too fast to observe, but numerous small oil drops are visible in the water immediately after dissolution, thus confirming that oil drops are indeed incorporated into the fibers. This process is shown more clearly in the attached movie file, OilFiberDissolution.mpeg.

A visual comparison of Fig. 1(a) and 1(b) immediately suggests that the drops in Fig. 1(b) are far smaller than those in Fig. 1(a), i.e., the drops are broken during emulsion electrospinning. To our knowledge, this is the first report that shows such breakup of emulsion drops during emulsion

electrospinning; previous articles have either not compared the initial drop size with the final size at all,[4,5] or have reported coalescence of drops to form a continuous core.[6] That drops break up during electrospinning raises several questions: what is the effect of the emulsion drop size? Is electrospinning still possible as the emulsion drop size increases? If the initial emulsion has larger drops, will the size of the drops incorporated in the fibers change? Or is the size of the incorporated drops determined by the breakup process alone and hence independent of the emulsion drop size? We deemed mineral oil emulsions as inconvenient to address these questions since their volatility precludes electron microscopy. Therefore, further experiments were conducted with a PS/toluene solution as the dispersed phase. In this case the toluene evaporates completely during electrospinning, thus leaving the solid PS to be incorporated into the PEO fibers.

Emulsions with PS/toluene drops

Experiments were conducted on emulsions that contained 20% by weight of the PS/toluene solution, 0.5% surfactant, and remainder of the PEO/water solution. On a dry basis, this corresponds to 29% PS, 5% surfactant, and 66% PEO.

In order to test the effect of drop size, emulsions were prepared by two different methods. In the first case, the PS/toluene solution, the aqueous phase, and the surfactant were placed in a vial and shaken by hand. This yielded an emulsion with macroscopically visible drops; Fig. 2(a) shows that while the drops size distribution is broad, numerous drops have diameters well in excess of $20\,\mu m$. If the same emulsion is then subjected to high-speed homogenization (Fig. 2b), the drop size decreases substantially to less than $10\,\mu m$. As previously, both Fig. 2(a) and 2(b) were taken from emulsions collected from the electrospinning needle, and hence are representative of the emulsions actually electrospun.

Fig. 2(c) and 2(d) shows images of the Taylor cones taken during electrospinning. A corresponding movie, PSToluene-EmulsionElectrospinning.mpeg, of the Taylor cone of the hand-shaken emulsion has been provided as a movie file. The most obvious difference between the hand-shaken and the high-speed homogenized emulsions is that with the hand-shaken emulsion (Fig. 2c), the drops are clearly visible, whereas in Fig. 2(d), the cone appears to be uniformly white due to strong scattering from the drops. It is important to note from the movie that the cone remains stable (i.e., the fiber does not break) even when drops comparable to the cone dimensions pass through. Finally, Fig. 2(c) and the corresponding movie file clearly show the strong stretching of large drops as they exit the cone to form the fiber; such stretching is essential for drop breakup to occur.

Fig. 2(e) and 2(f) show SEM images of the fibers collected on glass slides during electrospinning; in both cases, the fibers have elongated bulbous regions along their length. Upon placing a water drop on the slide to dissolve the fiber under a microscope (not shown), the bulbous regions release insoluble elongated particles suggesting that the particles are the solid PS left after evaporation of toluene during electrospinning. Since the PS particles are insoluble in water, it is possible to separate them from the fibers and image them

more clearly. Accordingly, larger quantities of the electrospun fibers collected on the wire grid (see the ''Experimental'' section) were then dissolved in water. Drops of the solution were placed on filter paper (pore size $0.25\,\mu m$), dried, and the PS particles were examined under SEM; these images are shown in Fig. 2(g) and 2(h). The particles resulting from the hand-mixed emulsion appear to be elongated, whereas those from the homogenized emulsion are a mixture of some elongated and some round particles. Close examination of Fig. 2(g) and 2(h) reveals that many PS particles appear to be not simple elongated shapes, but flat disks that have curled up into elongated shapes. It is not clear how the emulsion electrospinning process produced such shapes. Finally, both sets of images, the electrospun fibers (Fig. 2e and 2f) as well as the PS particles collected on the filter paper (Fig. 2g and 2h), show a clear drop-size effect: the PS particles are substantially larger when the emulsion was hand-mixed. We will comment on this at the end of this section.

The SEM images show that in both the hand-mixed case as well as the high-speed homogeized case, the size of the PS particles is substantially larger than the fiber diameter. Thus, an immediate question is: are the particles completely encapsulated by the PEO? Fig. 3(a) shows higher magnification images of two PS particles, and it appears that at least some PS particles are not completely encapsulated. To test this in more detail, a glass slide covered with PS/PEO fibers (Fig. 3b) was exposed to toluene. PEO is insoluble in toluene and hence any PS that is completely encapsulated within the fibers should survive. Fig. 3(c) shows that virtually all of the bulbous regions appear to ''deflate'' suggesting that almost all of the PS particles are either incompletely encapsulated, or not centered in the fiber so that they are covered by only a very thin layer of PEO. In contrast, a similar experiment on the mineral oil-containing fibers showed no significant differences before and after exposing the fibers to toluene, indicating that oil drops were completely encapsulated.

Several comments about PS particle sizes are in order. First, we consider the issue of drop breakup during electrospinning for the PS/toluene emulsions by comparing the size of the final PS particles with the drop size in the initial emulsion. Knowing the PS concentration in the drop to be $15\,wt\%$, a typical drop (diameter $15\,\mu m$) in the hand-shaken emulsion has a PS volume of about $265\,\mu m^3$ While the PS particles recovered from the fibers have complex shapes, for the purposes of volume calculations, the largest PS particles may be assumed to be cylinders of $3\,\mu m$ diameter and $10\,\mu m$ length, which corresponds to a volume of $71\,\mu m^3$ This calculation clearly demonstrates that similar to the case of mineral oil drops, the hand-shaken PS/toluene drops are also broken up during electrospinning. A similar calculation can be performed for the high-speed homogeized emulsion. Although the emulsion drop size is smaller and harder to estimate with confidence, we estimate a typical drop diameter of size $6\,\mu m$, corresponding to a PS content of about $17\,\mu m^3$ The final PS particles are a mixture of roughly round shapes and highly elongated shapes. Assuming that the largest particles have a volume comparable to that of a $2\,\mu m$ diameter sphere, the corresponding volume of $4\,\mu m^3$ is still significantly smaller than of the PS in the emulsions, once
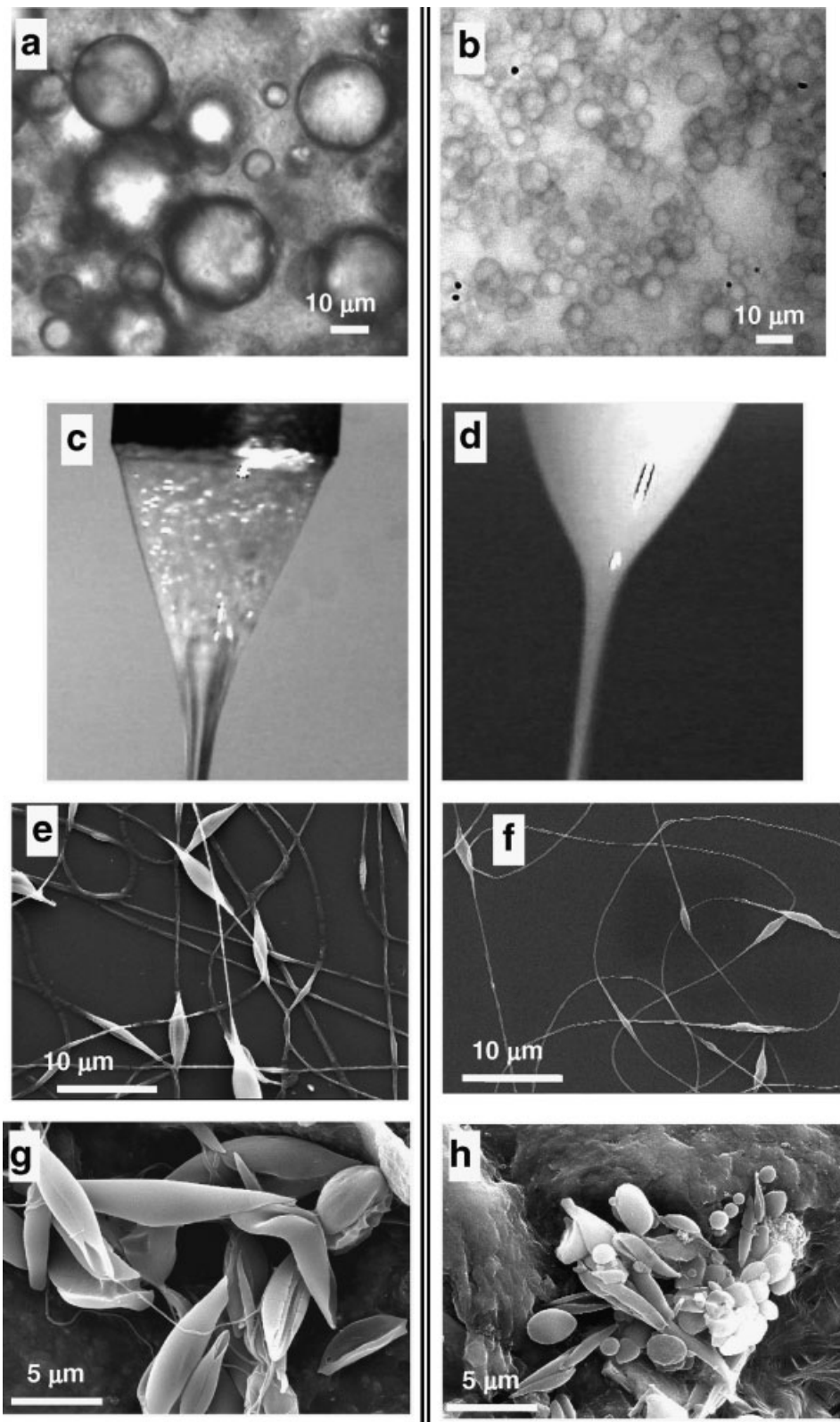
Figure 2. (a, b) Optical micrographs of PS/toluene in PEO/water emulsions. (c and d) Taylor cone of each emulsion during electrospinning. (e, f) SEM images of electrospun fibers collected on glass slides. (g, h) SEM images of PS inclusions obtained by dissolving fibers on water, and collecting the PS on a filter paper. All figures in the left column refer to the hand-mixed emulsion, whereas those on the right refer to the homogenized emulsion.

again suggesting breakup during electrospinning. The stress required for drop breakup can be crudely estimated: under steady flow conditions, drops breakup when the capillary number (stress × diameter)/(interfacial tension) exceeds a critical value.[13] The drops experience elongational flow in the present situation, and hence the capillary number is on the order 1. Interfacial tension between aqueous/oil interfaces with added surfactant are typically on the order of 10^{-2} N/m.
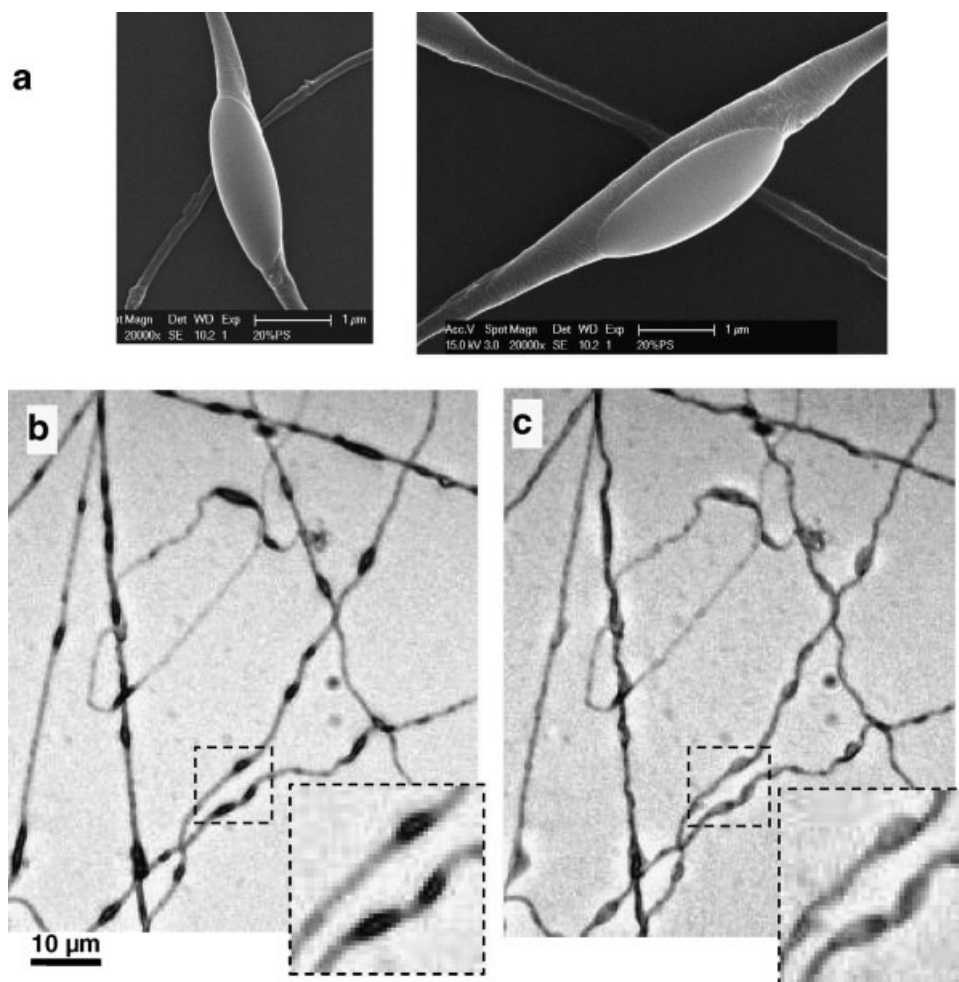
Figure 3. (a) Detailed images of PS inclusions that are not fully encapsulated by the fibers. (b) Optical micrograph of PS/PEO composite fibers collected on glass slides. (c) Same fibers after a toluene drop was placed on the fibers, and then allowed to evaporate. Insets to (b) and (c) show magnified versions of the dotted regions.

Thus, stresses on the order of 1000 Pa are required to break 10 μm diameter drops. The stress experienced by drops in the Taylor cone have been estimated to be about 500 Pa, thus it is possible that some of the largest drops break up in the Taylor cone itself,[14] whereas the smaller ones break downstream in the jet.

Second, in absolute terms, the mineral oil drops are substantially smaller than the PS particles. We speculate that during electrospinning, as water and toluene evaporate, the viscosity of the drop phase increases much more sharply than of the matrix phase. It is well-known that drops with a high viscosity relative to the continuous phase do not deform and breakup readily;[13,15] such decreased deformation of drops may then be responsible for the large size of the PS particles. Similar changes in viscosity of the drop phase do not occur when the drop phase is made of mineral oil, thus, those drops remain readily deformable and can be broken into much smaller sizes during electrospinning.

Finally, the PS particles resulting from electrospinning hand-mixed emulsions are larger than those resulting from electrospinning homogenized emulsions. This indicates that the final particle size incorporated into the fibers is not determined solely by the breakup process during electro-

spinning, and likely results from an interplay of initial emulsion drop size, evaporation kinetics (and the corresponding viscosity increases), as well as the electrospinning-induced breakup process.

SUMMARY

In summary, in this article we have shown that, similar to previous research on water-in-oil emulsions, the reverse case of oil-in-water emulsions can be also electrospun to produce micron-scale fibers. We show that the electrospinning process can deform and break up emulsion drops, thus, even emulsions with drop sizes on the order of tens of microns can be electrospun with the drop phase becoming incorporated into the fibers. In the case of mineral oil drops, the drops were completely incorporated into the fibers. With PS/toluene drops, the PS particles incorporated into the fibers were significantly larger than the fiber diameters, and hence the PS particles could be readily redissolved in toluene. We speculate that the sharp increase in the drop viscosity as toluene evaporates makes the drops less deformable, leading to relatively large PS particles, and hence incomplete encapsulation.

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