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Microscopic polymer cups by electrospinning

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Abstract

Polymer solution above a critical concentration is generally required for making a uniform diameter nano fiber by electrospinning. Below this critical concentration, nanofibers are accompanied with bead formation and, therefore, this concentration region has not received much attention. A systematic investigation reveals that unique particle shapes can be obtained by electroprocessing within this lower concentration range. Several micrometer diameter poly(methyl methacrylate) PMMA cups with wall thickness in the 200–800 nm range and 50–300 nm size pores have been obtained by electroprocessing in high dielectric constant solvents.

Keywords: Electrospinning; Electrospray; PMMA

1. Introduction

Electrospinning [1–4], first reported in 1934 [5], can now be used for processing aligned nanofibers from polymer solutions or melts [6–8], continuous ceramic nanofibers [9], continuous core/shell nanofibers [10], continuous hollow nanofibers [11], as well as fibers with diameter less than 100 nm [12]. The presence of beads in electrospun fibers is a common problem [13] and if beads are the main product, electrospinning becomes electrospray. Electrospraying is also practiced for a number of metal oxides [14]. From Rayleigh instability, surface tension tends to convert the liquid jet into spherical droplets [15]; on the other hand, electrostatic repulsion between charges on the jet surface and viscoelastic force favour the formation of a thin jet rather than beads [2]. Structure of the electrosprayed particle depends on the dielectric constant, surface tension, viscosity, evaporation rate and the solvent power.

2. Experimental details

PMMA ($\bar{M}_w = 95,000 - 150,000$ g/mol) was obtained from Cyro industries and used as received. All solvents were purchased from Aldrich and also used as received. Electroprocessing was done in the horizontal mode in a chemical hood with a syringe pump at 2 ml/h via a 18 gauge stainless steel needle at 22,000 V and the distance between the needle and the grounded aluminum foil target was 10 cm. Scanning electron microscopy was done on gold coated samples in LEO 1530 thermally-assisted FEG scanning electron microscope at 15 kV.

3. Results and discussion

PMMA was electroprocessed from solutions in various solvents listed in Table 1. At a given polymer concentration and electroprocessing parameters, different morphology particles were obtained using different solvents. At 1.5 wt% concentration, large (typical dimension ~10 μm) porous polygonal particles were obtained from methylene chloride (Fig. 1(a)). Particle size generally increased with concentration and at 8 wt% concentration in methylene chloride, particles of ~25 μm dimension were obtained. Dielectric constant of methylene chloride is quite low and the evaporation rate is the highest among the solvents used in this study. Solvents with intermediate dielectric constants (acetone, DMF, acrylonitrile or nitromethane) at 8 wt% polymer concentration resulted in particles of 2–6 μm dimensions. Acetone yielded somewhat odd shaped particles (dimension ~3 μm, Fig. 1(b)), while DMF resulted in

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Table 1
Properties of various solvents and PMMA at room temperature

	Dielectric constant	Viscosity (10^{-3} Pa s)	Surface tension (mN/m)	Evaporation rate (butyl acetate = 1)	R_{ij}^2 (MPa)	Particle size and shape at 8 wt% polymer content
Methylene chloride	9.1	0.44	28.1	14.5	20	~25 μm, porous polygonal
Acetone	20.7	0.30	25.2	5.6	39	~3 μm, solid polygonal
DMF	38.3	3.80	37.1	0.2	30	~2 μm, solid polygonal
Acrylonitrile	38.0	0.34	26.6	4.5	66	~5 μm, cup
Nitromethane	39.4	0.63	36.8	1.4	106	~3 μm, cup
Formic acid	58.0	1.80	58.2	2.1	159	~0.5–1 μm, solid polygonal with fibrous tails
PMMA	4.0		43.0			

$R_{ij}^2 = (\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2$, where δ_{d1}, δ_{p1} and δ_{h1} are three dimensional solubility parameter values for the solvent and δ_{d2}, δ_{p2} and δ_{h2} for PMMA.

somewhat round featureless particles with dimensions closer to 2 μm (not shown). A high dielectric constant value of DMF is somewhat offset by its low evaporation rate. In addition, DMF itself has high viscosity and it is also a good solvent for PMMA (low R_{ij}^2 value). Thus, the PMMA/DMF system is characterized by high viscosity and low evaporation rate. Formic acid, the highest dielectric constant solvent, yielded particles (not shown, dimension 500 nm to 1 μm) with fibrous tails at 8 wt% concentration. As can be seen from the large R_{ij}^2 value, formic acid is the poorest PMMA solvent used in this study. At a given concentration, poor solvents result in lower viscosity, thereby allowing for jet break up into smaller particles.

In the concentration range of 1–5 wt% PMMA/nitromethane, ladle type structures (Fig. 1(c)) were observed, while concentrations higher than 12 wt% resulted in fibers with beads and above 20 wt%, uniform fibers without beads were obtained. The beaded fibers also result in the formation of the hammock type of structures (Fig. 1(d)). For acrylonitrile and nitromethane, cup shaped particles were obtained in the 6–10 wt% polymer concentration range (Fig. 2) and, therefore, this concentration range is of special

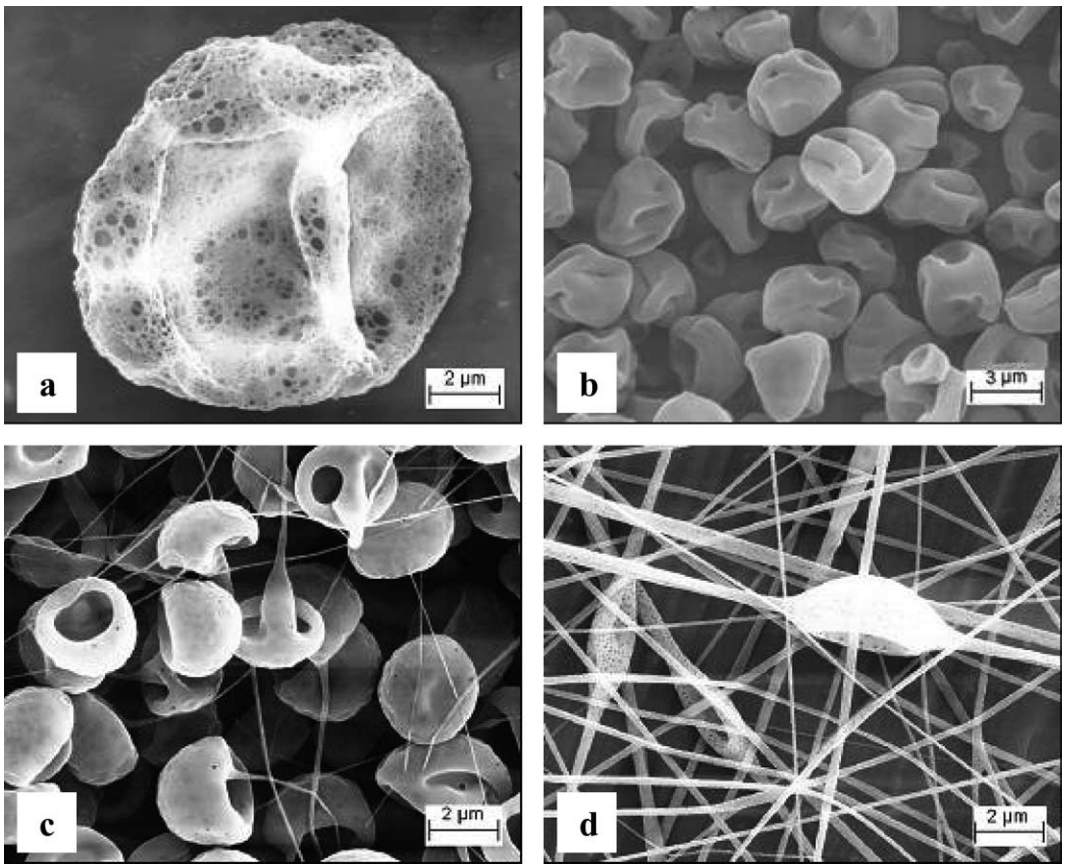

Fig. 1. Electroprocessed structures from (a) 1.5 wt% PMMA in methylene chloride, (b) 8 wt% PMMA in acetone, (c) 4 wt% PMMA in nitromethane, (d) 16 wt% PMMA in nitromethane.

interest here. At a given concentration and electro-processing condition, the diameter of these microscopic cups was highly uniform. At 8 wt% concentration, the cup diameter from acrylonitrile was about 50% larger and less porous than that obtained from nitromethane (Fig. 2(a) and (b)). The dielectric constants of acrylonitrile and nitromethane are very comparable, however, based on their R_{ij}^2 values, acrylonitrile is a much better solvent for PMMA than nitromethane. Therefore, at the same weight concentration, acrylonitrile solution will have higher viscosity than the nitromethane solution. Larger diameter of the cups obtained from acrylonitrile is attributed to this difference in viscosity. The cup diameter (D) to the cup height (H) ratio (Fig. 2(b)) decreased from ~1.5 to about ~1.2 when the polymer concentration increased from 6 to 10 wt%. A scanning electron micrograph (Fig. 2(d)) of the razor cut cross-sections of the cup wall shows that the walls are highly rounded at the tip of the cup and for cups processed in nitromethane at 8 wt% concentration, the wall thickness is ~800 nm near the cup tip and close to 200 nm at the bottom of the cup. The nitromethane-processed cups also exhibited porosity, with pore dimensions in the 50–300 nm range. The BET specific surface area, of microscopic cups processed from nitromethane at 8 wt% concentration, measured by nitrogen gas adsorption was 13.7 m^2/g.

As many polymer solutions, melts and ceramics can be electrospun into continuous nanofibers, similarly with appropriate control of solution viscosity, surface tension, dielectric constant, solvent power and solvent evaporation rate, formation of cup like geometries will be possible from homopolymers, block copolymers, polymer blends, as well as composites containing nanoparticles and ceramics. Semi-spherical hollow structures (diameter 20–30 μm) have already been reported from electroprocessing of polystyrene [13]. Potential applications for the microscopic cups made from various materials with and without nanostructure control include controlled drug release, protective layer on fabrics and other substrates, electrochemical supercapacitor electrode and parts for microscopic devices including shock absorbers in miniature devices, as well as vascular grafts, surgical dressings and tissue engineering scaffolds.

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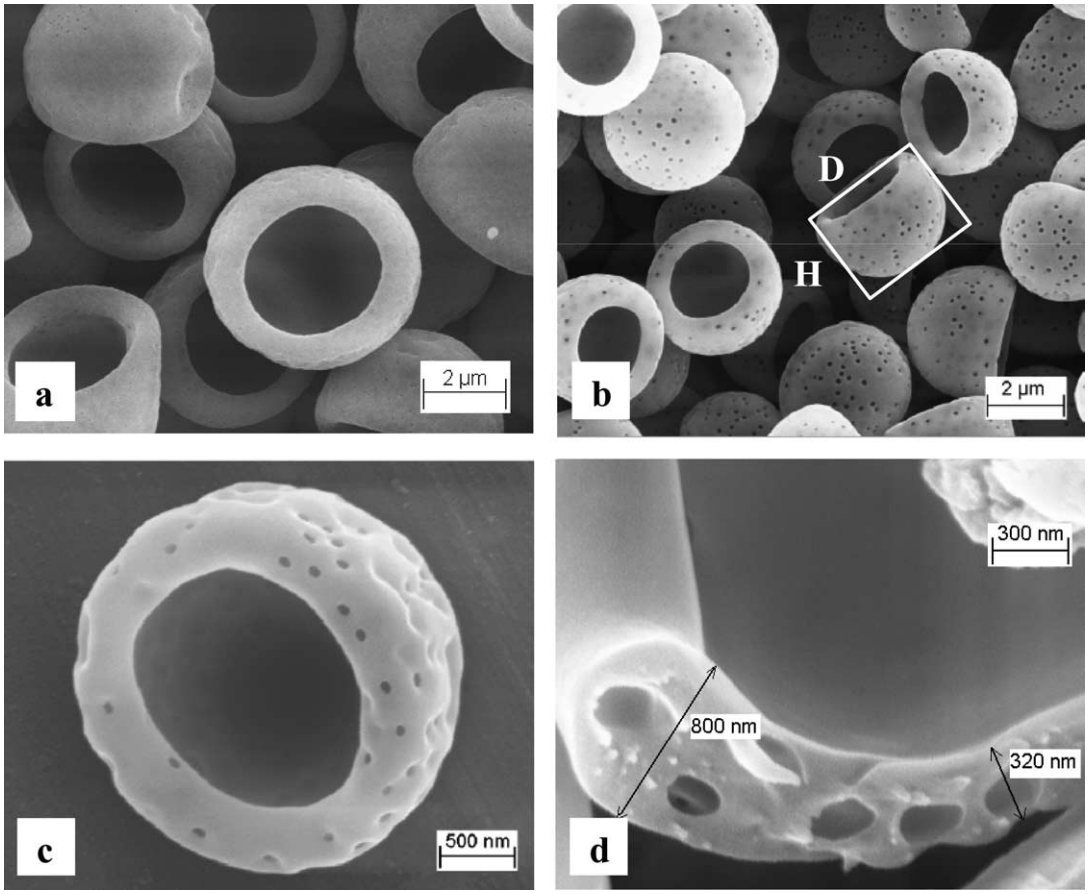

Fig. 2. Electroprocessed structures from (a) 8 wt% PMMA in acrylonitrile. (b), (c) and (d) 8 wt% PMMA in nitromethane, (d) is the razor cut wall cross-section of the cup.

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References

[1] Dzenis Y. Science 2004;304:1917–9.
[2] Li D, Xia Y. Adv Mater 2004;16:1151–70.
[3] Yu JH, Fridrikh SV, Rutledge GC. Adv Mater 2004;16:1562–6.
[4] Zarkoob S, Eby RK, Reneker DH, Hudson SD, Ertley D, Adams WW. Polymer 2004;45:3973–7.
[5] Formhals A. US Patent 1, 975, 5042;1934.
[6] Dersch R, Liu T, Schaper AK, Greiner A, Wendoref JH. J Polym Sci, Part A: Polym Chem 2003;41:545–53.
[7] Li D, Wang Y, Xia Y. Nano Lett 2003;3:1167–71.
[8] Kameoka J, Craighead HG. Appl Phys Lett 2003;83:371–3.
[9] Dai H, Gong J, Kim H, Lee D. Nanotechnology 2002;13:674–7.
[10] Liu J, Wang T, Uchida T, Kumar S. J Appl Polym Sci [in press].
[11] Li D, Xia Y. Nano Lett 2004;4:933–8.
[12] Zhou YX, Freitag M, Hone J, Staii C, Johnson AT, Pinto NJ, MacDiarmid AG, et al. Appl Phys Lett 2003;83:3800–2.
[13] Lee KH, Kim HY, Bang HJ, Jung YH, Lee SG. Polymer 2003;44:4029–34.
[14] Chen CH, Emond MHJ, Kelder EM, Meester B, Schoonman J. J Aerosol Sci 1999;30:959–67.
[15] Woosley J, Turnbull R, Kim K. J Appl Phys 1988;64:4278–84.