Nanoscale

PAPER

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Cite this: Nanoscale, 2018, 10, 18857

Received 18th July 2018, Accepted 10th September 2018 DOI: 10.1039/c8nr05793a rsc.li/nanoscale

1. Introduction

Polymer micro/nanoparticles have attracted much attention recently because of their potential applications in many fields as controlled release agents, catalysts, scaffolds, selective separation agents, and chemical sensors.^{1–6} It is desirable for pores to be introduced into the surface of spheres because a porous structure possesses a higher specific surface area, a lower density, and better permeability, all of which are required in many demanding applications.^{7–9} Biocompatible and/or biodegradable polymer microspheres and onedimensional fibres are excellent candidates for biomedical, pharmaceutical, tissue engineering and degradable electronic applications due to their unique properties.^{10–15} Trials have been conducted with poly- ε -caprolactone (PCL) in many novel drug delivery systems and tissue engineering applications due

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Preparation of fluorinated PCL porous microspheres and a super-hydrophobic coating on fabrics *via* electrospraying[†]

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In this study, fluorinated polycaprolactone (PCL) block polymers with different fluorine contents were synthesized via atom transfer radical polymerization (ATRP). An electrospraying technique was used to prepare fluorinated PCL microspheres with different microstructures. In contrast to the golf ball shape of unmodified PCL microspheres displaying porous pits on the surface, block polymer PCL-PTFOA(2 h) and PCL-PTFOA(6 h) microsphere surfaces displayed regular honeycomb-like pore structures. Thermally induced and evaporation-induced phase separations are proposed as the main mechanisms involved in the formation of the porous microstructures. The micro-phase separation between the two blocks of the fluorinated PCL copolymer is another factor that promoted the uniform collapse on the microsphere surface and the formation of its rugged wall. The surface roughness of the porous microspheres significantly improved their hydrophobicity, generating coating contact angles on aluminium foil substrates that measured as high as $162.4 \pm 1.5^{\circ}$, which revealed that the surfaces were super-hydrophobic. Lastly, cotton fabric was directly coated with the fluorinated polymer microspheres *via* electrospraying, resulting in super-hydrophobic surfaces and CAs reaching $160.0 \pm 1.3^{\circ}$. The results demonstrate that electrospraying is a simple, innovative and cost-effective method for preparing polymer microspheres with controllable microstructures for fabric coating applications.

to its ease of fabrication, absorptive qualities, and tailorable properties.^{16–20} Many methods, such as emulsion,^{21–23} freeze drying,²⁴ nanoprecipitation and hydrolysis,²⁵ have been adopted to fabricate PCL microspheres with different morphologies, including solid, porous and hollow structures. The use of an emulsion (*e.g.*, oil in water (o/w) emulsion) and subsequent solvent evaporation is the most popular method to prepare PCL microspheres. However, these methods usually have limitations, such as complicated processes, extreme conditions, poor universal applicability, or uncontrollable microsphere morphology and size.

Electrospraying is a dispersion method in which high voltage is applied to a needle tip containing a conductive liquid to generate a spray. The electrostatic force overcomes the surface tension and produces near-monodisperse droplets with diameters varying from tens of nanometres to hundreds of micrometres.^{26–29} In principle, this method is essentially similar to that of electrospinning, with the most obvious difference between electrospraying and electrospinning being the solution concentrations used in the process and the chain entanglement density of the polymer solution.³⁰ Higher solution concentrations tend to form continuous fibres in the electrospinning process, while relatively lower concentrations will generate micro/nanoparticles in the electrospraying

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[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/ c8nr05793a

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process.³¹ Electrospraying has been experimentally demonstrated as a viable process for generating micro- or nanometre droplets that have a surface charge. The highly charged droplets consequently result in self-repelled particles without coalescence.³² It is conceptually easy to control the size of electrosprayed particles from the nanometre to micrometre range by varying the solution flow rate, the applied voltage, the spraying distance, and the physical properties of the solution.³³ In the micro- or nanometre range, the capability of producing polymer particles with controllable porous microstructures using electrospraying is unmatched by other aerosol processing methods. In general, compared with other methods for preparing porous polymer particles, there are several advantages of electrospraying, as follows:³⁴⁻³⁹ (1) relative ease of setup, (2) open-atmosphere operation without the use of a sophisticated chamber, (3) controllable particle sizes in a narrow distribution via a cone-jet spraying mode, (4) high production efficiency due to the direction of particles sprayed onto the collector under an electric field, and (5) welldispersed particles due to self-repellence resulting from the electrical charges on the particles. Given these advantages, we sought to use electrospraying as a means to fabricate porous fluorinated PCL microspheres.

To date, much work has been conducted to develop microand nanomaterials to achieve super-hydrophobic surfaces⁴⁰⁻⁴⁴ whose hydrophobicity is mainly determined by the chemical composition and the geometric architecture of the surface. Polymer coatings and inorganic colloid particulate coatings are popular approaches to obtain a rough surface by spherical protrusions,^{45–48} rendering an enhanced hydrophobic surface. Here, the particles are randomly stacked on a substrate, but the roughness obtained is not sufficient to acquire superhydrophobicity. These particles are often coated with a thin layer of hydrophobic fluoropolymer to decrease the surface free energy.⁴⁹⁻⁵¹ Moreover, raspberry-like particles have been developed for the fabrication of super-hydrophobic surfaces, whereby nano-sized guest particles are decorated onto much larger host particles.⁵²⁻⁵⁵ The hierarchical rough surface contributes to a dramatic increase in hydrophobicity. However, preparation of hierarchical micro/nanoparticles with high surface roughness is usually a complicated and multi-step process. Moreover, the particles are especially difficult to transfer onto substrates. The electrospraying technique has been proven to be a convenient and effective method for obtaining microscale to nanoscale particles from a range of materials, e.g., polymers⁵⁶⁻⁵⁹ and inorganic⁶⁰ and hybrid compounds.61,62 During the process of electrospraying, vapourinduced phase separation was responsible for the formation of the porous structure and thus the rough surface, which contributed to super-hydrophobicity.

In this study, fluorine-containing polyacrylate chains were introduced into PCL, and the fluorinated PCL microspheres formed cratered structures with honeycomb-like pores that were fabricated by electrospraying the copolymer solutions with a single solvent, instead of a blend containing a nonsolvent, directly onto substrates without using a

nonsolvent bath as the collector. Well-distributed coatings with hydrophobic properties were successfully prepared to obtain super-hydrophobic surfaces. Cotton fabrics were pretreated with a water-based polyacrylate emulsion adhesive and then coated with the microspheres via electrospraying. The electrosprayed fluorinated PCL microspheres with honeycomblike pore structures were randomly deposited on the surface of the cotton fabric, generating a microsphere deposition film with a micro/nanohierarchical structure. This structure endowed the surface of the cotton fabric with a higher surface roughness, leading to super-hydrophobic performance. Because the coated superhydrophobic cotton fabrics reject many naturally occurring pollutants and are not easily soiled, they can be used to make, for example, contamination free canvases, tents, table cloths and kitchen aprons. If the coating is thin enough and does not affect the feel and breathability of the fabric, superhydrophobic cotton can even be used to make garments such as jackets and shirts that require minimal cleaning.

2. Experiment

2.1 Materials

Poly(ε -caprolactone) (PCL) (average $M_n = 80\,000 \text{ g mol}^{-1}$) was purchased from Aldrich Chemistry (United Kingdom). 6-Amino-1-hexanol (97%) and 4-dimethylaminopyridine (DMAP, 99%) were obtained from Aladdin (Shanghai, China). Succinic anhydride (SA, 99%) was obtained from Sinopharm Chemical Reagent Co., Ltd. 1H,1H,2H,2H-Perfluorooctyl acrylate (TFOA) was supplied by Suzhou Zhongbo Chemical Technology Co., Ltd. Copper(1) bromide (CuBr, 99%) and N,N, N', N', N''-pentamethyldiethylenetriamine (PMDETA, 99%) were purchased from Aladdin (Shanghai, China). CuBr was stirred for 5 h in acetic acid, filtered, washed three successive times with ethanol and dried in a vacuum. 2-Hydroxyethyl 2-bromoisobutyrate (HEBiB, 95%) was obtained from Shanghai Bailingwei Chemical Technology Co., Ltd. Tetrahydrofuran (THF) and 1,4-dioxane were supplied by Qiangsheng Functional Chemicals Co., Ltd, and were purified by distillation. N,N'-Carbonyldiimidazole (CDI, 98%) was obtained from Energy Chemical (China). 2-Butanone was supplied by Sinopharm Chemical Co., Ltd. Ethyl alcohol, methanol, n-hexane and acetic acid were purchased from Qiangsheng Functional Chemicals Co., Ltd. 1,3-Bis(trifluoromethyl)benzene (98%) was obtained from Asic (Shanghai) Chemical Technology Co., Ltd. Aluminium oxide (200-300 mesh) was supplied by Aladdin (Shanghai, China).

Chloroform was purchased from Jiangsu Powerful Functional Chemical Co., Ltd. Adhesive (30% of polyacrylate emulsion) was made by our laboratory and diluted to 3‰ before use. Aluminium foil was purchased from Shanghai Klinlai Plastic Co., Ltd. Cotton woven fabric was purchased from Nantong Shengbaolu Textile Co., Ltd. Poly(tetrafluoroethylene) (PTFE) tubing (inner diameter, 1 mm) and 23 G stainless steel needles (inner diameter, 0.5 mm; outer diameter, 0.6 mm) were acquired from Changsha Nanometer Instrument Technology Co., Ltd. Polypropylene (PP) syringes of 10 mL volume were sourced from Jiangsu Kangyou Medical Equipment Co., Ltd.

2.2 Synthesis of fluorinated PCL block copolymer

2.2.1 Preparation of PCL-COOH.⁶³ Activation of PCL by aminolysis (PCL-OH). One gram of PCL was dissolved in 20 mL of re-distilled 1,4-dioxane in a three-necked flask under magnetic stirring at 37 °C. Subsequently, 1.1 g of 6-amino-1-hexanol was added to the mixture and the reaction took place under a N₂ atmosphere for 8 h. The resulting product was precipitated twice in *n*-hexane. Then, the precipitated PCL-OH was washed thoroughly in methanol, ethyl alcohol and doubly distilled water, yielding a pure product. The resulting PCL-OH was dried in an oven under vacuum at 37 °C for 24 h.

In a three-necked flask, 1.0 g of PCL-OH and 1.14 g of SA were dissolved in 20 mL of newly distilled 1,4-dioxane at room temperature. Subsequently, 0.4 g of K_2CO_3 and 0.35 g of DMAP were added to the flask. The mixture was stirred for 120 min at 70 °C-80 °C. After the reaction, the insoluble carbonate by-products were removed *via* filtration and the filtrate was washed with an aqueous solution containing acetic acid (0.2 g mL⁻¹). Subsequently, the product was precipitated twice in deionized water to remove all of the unreacted SA and DMAP. Finally, the product was washed with a large amount of deionized water and ethyl alcohol and dried under reduced pressure at 37 °C for 24 h, yielding activated PCL *via* carboxylation (PCL-COOH).

2.2.2 Synthesis of PTFOA polymer. The PTFOA was prepared via ATRP by using 1H,1H,2H,2H-perfluorooctyl acrylate (TFOA) as the monomer and 2-hydroxyethyl 2-bromoisobutyrate (HEBiB) as the initiator. A typical procedure is described below. In a three-necked flask, a solution of the initiator HEBiB (42 µL, 0.29 mmol) and PMDETA (64 µL, 0.32 mmol) in 6 mL dry 2-butanone was slowly stirred for 10 min. Then, CuBr (0.041 g, 0.29 mmol) was rapidly added to the flask and the solution was degassed with three freeze-pump-thaw cycles. After CuBr was thoroughly dissolved, the monomer TFOA (6.1 g, 14.5 mmol) dissolved in 2 mL dry 2-butanone was added to the flask. Then, the solution system was degassed and heated at 78 °C under N2. After the completion of the reaction, the reaction mixture was exposed to air to quench the reaction. The polymerization solution was then diluted with tetrahydrofuran (THF)/1,3-bis(trifluoromethyl)-benzene (3:1, total volume of solution was 40 mL) and filtered over aluminium oxide to remove the catalyst, and the resulting eluate solution was concentrated and then precipitated in methanol to obtain the light yellow gummy solid product. The product was redissolved in 2 mL 1,3-bis(trifluoromethyl)-benzene and precipitated in *n*-hexane again. This cycle was repeated three times to obtain a pure product. Lastly, the product was dried under reduced pressure at 55 °C for 24 h to constant weight. Polymerization was carried out for 2 h or 6 h to produce the fluoropolymer intermediates with different molecular weights: FT-IR ν (KBr): 3450.7 cm⁻¹ (-OH, from HEBiB initiator), 2920.7 cm⁻¹ and 2974.5 cm⁻¹ (-CH/-CH₂), 1636.4 cm⁻¹ (C=C), 1242.0 cm⁻¹, 1185.6 cm⁻¹, 1142.0 cm⁻¹ and

1083.2 cm⁻¹ (C–F), 1013.0 cm⁻¹ (C–Br). ¹H NMR (400 MHz, CDCl₃), δ (ppm). For TFOA monomer, δ 6.45 (d, J = 17.3 Hz, 1H), 6.13 (d, J = 17.3, 10.5, 2.0 Hz, 1H), 5.89 (d, J = 10.5 Hz, 1H), 4.53–4.40 (m, 2H), 2.63–2.42 (m, 2H). For PTFOA polymer, δ 4.36 (s, 2H), 3.80 (s, 2H), 2.47 (s, 2H), 2.11 (s, 1H), 1.27–2.01 (s, protons of the structural unit on the PTFOA main chain), 0.90 (s, 3H). (These results are shown in ESI S.1 and S.2.†)

2.2.3 Preparation of PCL-b-PTFOA copolymer. One gram of PCL-COOH was dissolved in 30 mL of dry THF in a threenecked flask under magnetic stirring at room temperature. Subsequently, 0.94 g of N,N'-carbonyldiimidazole was added to the mixture. After stirring for 2 h under a N₂ atmosphere, all PTFOA was dissolved in dry THF/1,3-bis(trifluoromethyl)benzene (3:1, total volume of solution was 24 mL) and was introduced into the mixture containing PCL-COOH. The reactants were stirred for 3 h at 50 °C. After the completion of the reaction, the product was precipitated twice in n-hexane. Then, the product was redissolved in THF and precipitated in deionized water to completely remove imidazole by-products again. The resulting product was washed with a large amount of ethyl alcohol and deionized water to obtain the pure modified product, PCL-b-PTFOA. Finally, the resulting PCL-PTFOA was dried under reduced pressure at 37 °C for 24 h to constant weight. According to the above procedure, PCL-PTFOA(2 h) and PCL-PTFOA(6 h) were prepared by modifying PCL with PTFOA(2 h) or PCL-PTFOA(6 h), respectively. The fluorinated PCL block copolymers were synthesized according to Scheme 1. FT-IR ν (KBr): 2950.4 cm⁻¹, 2866.8 cm⁻¹ (-CH/-CH₂), 1728.0 cm⁻¹ (C=O), 1242.0 cm⁻¹, 1185.6 cm⁻¹, 1142.0 cm⁻¹ and 1083.2 cm⁻¹ (C-F), 1241.5 cm⁻¹ (C(O)-O), 1178.2 cm⁻¹ (O–C(C)). ¹H NMR (400 MHz, CDCl₃): for PCL, δ 4.05 (t, J = 6.7 Hz, 2H), 2.31 (t, J = 7.6 Hz, 2H), 1.65 (d, J = 11.3, 6.8 Hz, 4H), 1.37 (d, J = 15.2, 6.8 Hz, 2H). For PCL-PTFOA copolymer, ¹H NMR (400 MHz, CDCl₃): δ 4.30 (s, 2H), 4.06 (s, 2H), 2.42 (s, 2H), 2.31 (s, 2H), 1.65 (s, 4H), 1.39 (d, J = 6.0 Hz, 2H). ¹⁹FNMR δ (376 MHz, CDCl₃): -79.84 (3F, CF₃), -111.99 (2F, CF₃CF₂), -120.20 (2F, CF₃CF₂CF₂), -121.29 (2F, CF₃(CF₂)₂CF₂), -121.91 $(2F, CF_3(CF_2)_3CF_2), -124.80$ (2F, $CF_3(CF_2)_4CF_2)$. (These results are discussed in ESI S.3-S.5.†)

2.3 Electrospraying

The electrospray apparatus consists of a digital syringe pump loaded with a syringe, a high-voltage generator and a grounded collector. PCL, PCL-PTFOA(2 h) and PCL-PTFOA(6 h) copolymers were dissolved in chloroform for at least 5 h at room temperature, generating a homogeneous and stable 3 wt% solution. In the electrospraying process, the solution was placed into a 10 mL syringe and continuously pushed by the syringe pump to a stainless steel nozzle bent at a right angle with an internal diameter of 0.5 mm, which was connected to a high-voltage power generator. The flow rates of the three copolymer solutions were 0.3 mL h⁻¹, 1 mL h⁻¹, and 1 mL h⁻¹, respectively. A direct-current high-voltage generator was used to provide a voltage of 12.5 kV of potential difference between the nozzle and the grounded collector. The spraying distance between the nozzle and the collector was maintained at 15 cm.



Scheme 1 Synthetic route of the fluorinated PCL block copolymer.

The working temperature was 20 ± 2 °C, and the relative humidity was controlled in the range of 50–60%. A flat sheet of aluminium foil (15×20 cm²) and a rotating cylinder collector covered by an immobilized piece of cotton woven fabric (10×23 cm²) were used as the collector apparatus. The cotton woven fabric was immersed in adhesive for 1 h and finished by a laboratory padder with an uptake of 115–120%. The electrospray deposition method was used to form a polymer particle deposit film. The thickness of the coating layer depended on the flow rate. Hence, the electrospraying time of the three copolymers was 180 min, 60 min, and 60 min. Furthermore, the fabrics coated by microspheres were immediately placed into an oven and baked at 50 °C for 24 h to crosslink the

microspheres on the fibre. A schematic of the electrospraying process is shown in Scheme 2.

2.4 Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra were obtained on a NICOLET 5700 spectrometer using KBr pellets. ¹H NMR spectra were recorded on an INOVA-400 spectrometer in CDCl₃ or CDCl₃/Freon-113 with tetramethylsilane (TMS) as an internal standard. All the chemical shifts were expressed in ppm. The molecular weight and molecular weight distributions of PCL, PCL-PTFOA(2 h) and PCL-PTFOA(6 h) were measured on gel permeation chromatography (GPC) columns (Waters Microstyragel) (guard, 105, 103, and 102 Å),



Scheme 2 Schematic diagram of the electrospraying apparatus.

THF eluent at 35 °C, flow rate = 1.00 mL min⁻¹. The detectors consisted of a differential refractometer (Waters 410, λ = 930 nm) and a multi-angle laser light scattering (MALLS) detector (Wyatt Technology DAWN EOS, 30 mW, λ = 690 nm). Absolute molecular weights were determined with the *dn/dc* values of PCL, PCL-PTFOA(2 h), PCL-PTFOA(4 h), PCL-PTFOA (6 h) and PCL-PTFOA(8 h) (5 mg mL⁻¹) using Wyatt ASTRA software.

The static contact angles (CAs) and sliding angles (SAs) of the PCL, PCL-PTFOA(2 h), and PCL-PTFOA(6 h) polymeric membranes were evaluated at room temperature and ambient humidity on a Krüss DSA100 instrument equipped with a video camera. For each test, a 6 μ L water and hexadecane droplet was used. The CA and SA values were the averages of three separate measurements made on different areas, which were estimated by the instrument software according to the fitting method employing the Young–Laplace equation.

The surface free energies of the PCL and PCL-PTFOA copolymer films were estimated according to the method proposed by Owens and Wendt.⁶⁴ Water and hexadecane were respectively adopted as the hydrophilic and oleophobic liquids for the analysis. The contents of the chemical elements on the film and microsphere surface were examined using energy-dispersive X-ray spectrometry (EDS).

Surface tension was examined with an OCAT21 surface tension detector *via* the du Nouy ring method in chloroform for 3 wt% polymer solutions. Viscosity was measured with a SNB-2 digital rotational viscometer at room temperature.

The surface morphology and size of electrospraying particles were studied under a Hitachi S4800 scanning electron microscope (SEM) with an accelerating voltage of 3–5 kV. The particle size and distribution were determined *via* SEM image analysis using image processing software (ImageJ). To investigate the internal structures, the microspheres were immersed in liquid nitrogen for 24 h and then slowly ground in liquid nitrogen. The powder was dried at 37 °C, and the cross-section morphology of the microspheres was observed using SEM.

The washing test was performed using a rotor washing machine (Wenzhou Fangyuan Instrument Co., Ltd, China) under the following conditions: 40 °C, 30 min, 30 cycles per min with 4 g L^{-1} of standard detergent. The mechanical properties of the coated fabrics were measured using a universal testing machine (WDW-200, Shenzhen SANS Test Machine Co., Ltd, Shenzhen, China).

3. Results and discussion

3.1 Fluorinated PCL block copolymer

Fluoropolymers, PTFOA, with terminal hydroxyl groups were synthesized *via* atom transfer radical polymerization (ATRP) using 1H, 1H, 2H, 2H-perfluorooctyl acrylate (TFOA) as the monomer, CuBr/(*N*,*N*,*N'*,*N''*-pentamethyldiethylenetriamine) (PMDETA) as a catalyst system and 2-hydroxyethyl 2-bromoisobutyrate (HEBiB) as the initiator.

The active hydroxyl groups were bonded at the end of PCL *via* aminolysis with 6-amino-1-hexanol. A terminal carboxyl was introduced by reacting with the ending hydroxyl of succinic anhydride (SA) to fabricate the reactive polymer PCL-COOH.

The PTFOA molecule was immobilized on PCL *via* esterification by using CDI as an activator under mild conditions to obtain hydrophobic copolymers (as shown in Scheme 1).

As shown in Table 1, the polydispersity of PCL, PCL-PTFOA (2 h) and PCL-PTFOA(6 h) was determined as 1.60, 1.53 and 1.55, respectively, indicating that the polydispersity of PCL only slightly changed after chemical modification. Our previous study reported that the fission of the PCL macromolecule chain led to a molecular weight decrease (the average $M_{\rm n}$ of PCL is 80 000 g mol⁻¹, and the $M_{\rm n}$ of PCL-OH is 77 414 g mol⁻¹ after modification) during the aminolysis process. While it can be observed that the molecular weight of PCL-PTFOA(2 h) was similar to that of PCL, the molecular weight of the PCL-PTFOA(6 h) copolymer was even higher than that of PCL because of the introduction of additional fluoropolymer block chains. The fluorine contents (atomic%) of PCL-PTFOA(2 h) and PCL-PTFOA(6 h) copolymer films were 1.31% and 4.02%, respectively. The fluorinated PCL block copolymer with longer fluoropolymer chains, and thus a higher molecular weight and higher fluorine content, possesses better hydrophobicity.

3.2 Electrosprayed fluorinated PCL microspheres with a honeycomb structure

Typical electrospraying equipment essentially consists of a syringe connected to a metallic needle, a high-voltage power supply, and a grounded collector. A digital pump is used for high-precision control of the flow rate of the polymer solution stored in the syringe. The setup is the same as that employed for electrospinning. Whether fibres or particles are produced depends on electrospray parameters, such as applied voltage,

Table 1	Molecular characteristics and surface properties of the copolymers

Polymers	$M_{ m n}{}^a$	$M_{ m w}{}^a$	$M_{ m w}/M_{ m n}^{\ a}$	Fluorine content ^b (%)	CA _{water} (°)	CA _{hexadecane} (°)	$\gamma_{\rm SV}^{\ c}$ (mN m ⁻¹)	Surface energy ^{d} (mN m ⁻¹)	Viscosity ^e (mPa s)
PCL	89 477	143 814	1.60		96.8 ± 1.0	$0\\102.2\pm0.6\\113.7\pm0.4$	28.72	29.9	27.5
PCL-PTFOA(2 h)	86 917	133 107	1.53	1.31	108.0 ± 0.8		8.99	21.7	20.6
PCL-PTFOA(6 h)	97 060	150 226	1.55	4.02	128.4 ± 1.3		3.29	19.2	17.5

^{*a*} Determined by GPC measurement. ^{*b*} Determined by EDS measurement. ^{*c*} Surface energy obtained indirectly from the contact angle (two fluid method). ^{*d*} Surface tension in chloroform for 3 wt% solutions *via* the du Nouy ring method. ^{*e*} Viscosity tested with a digital rotational viscometer.

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flow rate, collection distance, environmental conditions, and solution properties (solution viscosity, solution conductivity, surface tension, *etc.*). When a high voltage is applied to the metallic needle, the pendant polymer solution at the nozzle will be subjected to the electrical field and the induced charges are evenly distributed over the surface. Under the electrostatic repulsion and the coulombic force caused by the electrical field, the polymer solution droplet is stretched into a conical jet and further breaks into small droplets, provided that the applied electric field is sufficiently high. Polymer particles are finally obtained when the solvent is completely evaporated during the process.

Fig. 1 shows the SEM images and size distributions of PCL (a), PCL-PTFOA(2 h) (b) and PCL-PTFOA(6 h) (c) microspheres. The images clearly show that the three polymer microspheres were fabricated with uniform, dispersive and perfect spherical features *via* electrospraying technology using only a single solvent. The average particle size of the PCL, PCL-PTFOA(2 h) and PCL-PTFOA(6 h) microspheres is 6.69 μ m, 5.50 μ m, and 5.64 μ m, respectively. Compared to PCL, a faster flow rate was observed in producing PCL-PTFOA(2 h) and PCL-PTFOA(6 h) microspheres, as there was lower surface tension and lower vis-

cosity (as shown Table 1). Nevertheless, the fluorinated PCL microspheres have a lower average particle size than that of PCL. This size difference is due to the fluoropolymer solution droplets more easily breaking up into secondary droplets (or satellites) and producing smaller microspheres under electrostatic repulsion and the coulombic force exerted by the electrical field. Furthermore, the Wigner distribution maxima (WDM) of the three electrosprayed particles is $6.7 \ \mu m$, $5.25 \ \mu m$, and $5.75 \ \mu m$, respectively, and it can be clearly seen that their microsphere size distribution is uniform and narrow in Fig. 1.

The surface morphologies of the PCL (a), PCL-PTFOA(2 h) (b) and PCL-PTFOA(6 h) (c) microspheres are shown in Fig. 2. Electrospraying is a very convenient but complicated process during which solvent evaporation and polymer diffusion play important roles in determining the morphology of the final product. It can be observed that PCL formed a golf ball-shaped microsphere with many porous pits on the surface, while PCL-PTFOA(2 h) and PCL-PTFOA(6 h) displayed regular honey-comb-like pore structures on the microsphere surface. The rapid evaporation of chloroform due to less PCL and chloroform interaction early in the solution's ejection from the nozzle and passage to the collector account for these pore



Fig. 1 SEM images and size distributions of PCL (a), PCL-PTFOA(2 h) (b) and PCL-PTFOA(6 h) (c) microspheres.



Fig. 2 Magnified SEM images of PCL (a), PCL-PTFOA(2 h) (b) and PCL-PTFOA(6 h) microspheres (c).

structures. Chloroform molecules were expulsed rapidly from the electrosprayed droplets; thus, PCL polymer chains precipitated and linked in the final stage of the process, resulting in golf ball-shaped particles with closed pores on the surface. With respect to solvent evaporation, thermally induced and evaporation-induced phase separations are the pertinent phase separation processes for pore formation in electrosprayed PCL porous particles.^{65,66} Solvent evaporation and evaporative cooling result in a solution that is thermodynamically unstable, which is the driving force for phase separation. During the solvent evaporation and the resulting phase separation, the polymer solution develops into a polymer-rich and a polymer-poor phase.^{66,67} The polymer-rich phase begins to entangle and shrink, gradually forming the solidified shell. The polymer-poor phase, which mainly consists of chloroform, escapes the droplet surface and forms surface pores after complete evaporation.

Compared to PCL microspheres, the surface morphologies of fluorinated PCL microspheres have a notable difference of distinct honeycomb-like pore structures on their surface. The introduction of a fluoropolymer chain (PTFOA) into PCL lowered its surface tension and viscosity greatly, which facilitated the phase separation. During the electrospraying process, after the polymer solution formed the polymer-rich phase and the polymer-poor phase, the concentrated polymer phase solidified rapidly and formed the spherical matrix, whereas the polymer chain at the interface between the two phases tended to overcome the resistance of the solution and migrated to the interior of the droplet because of the concentration difference. This process favours the shrinking and surface collapse of the copolymer microsphere. However, the PTFOA component in the copolymer is poorly compatible with PCL due to the lower surface energy. After the PCL segment entangled and solidified to form the spherical shell, the incompatible PTFOA chain moved away from the PCL shell and migrated to the chloroform phase in the interior of the droplet. Consequently, microphase separation between the two blocks of the copolymer occurred, promoting the uniform collapse of the microspheres and the formation of a rugged wall surrounding the surface pores. As a result, the microspheres with honeycomb-like pores can be obtained after the solvent has completely evaporated.

Fig. 3 shows the fluorine content in the holes and on the wrinkles of PCL-PTFOA(2 h) (1) and PCL-PTFOA(6 h) (2) microsphere surfaces as captured by testing *via* energy-dispersive X-ray spectrometry (EDS). The SEM images reveal that the two copolymer microspheres have a porous and honeycomb-like morphology. Furthermore, it can be observed that all pores are surrounded by a furrowed wall and that the PCL-PTFOA(2 h) microsphere surface displays a smaller pore size and thicker wall than that of the PCL-PTFOA(6 h) microsphere. This difference can be attributed to the PCL-PTFOA(6 h) copolymer being equipped with a longer fluorinated chain segment and the copolymer solution having a lower surface tension and lower viscosity resulting from a higher fluorine content. The longer



Fig. 3 High-magnification SEM images of PCL-PTFOA(2 h) (1) and PCL-PTFOA(6 h) (2) microspheres obtained by electrospraying a solution directly onto the substrate and F element analysis of holes and wrinkles on the surface of the two copolymer microspheres.

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fluorinated polymer chain segment enhances the micro-phase separation between the two blocks in PCL-PTFOA(6 h). Lower surface tension and lower viscosity further facilitate the migration of the fluorinated segments and their shrinkage toward the interior of the droplet and generate the porous morphology with a larger pore size and thinner walls. The EDS analysis revealed that the fluorine content in the hole was higher than that on the surface wrinkle for both fluorinated copolymer microspheres. This finding confirmed that the fluorinated segment tended to move to the interior during the microsphere formation.

The internal structures of the microspheres were investigated by viewing cross sections, as shown in Fig. 4. The microsphere formation process could be considered as consisting of two steps. The first step is electrospraying, which is accompanied by rapid evaporation of the solvent, and the second step is the formation of microspheres. Macrovoids throughout the cross section of the microsphere that display a uniform cellular structure can be seen in Fig. 4a (PCL microsphere), while in Fig. 4b, only slight pits are observed on the cross section of the PCL-PTFOA(2 h) microspheres. Furthermore, the cross section of the PCL-PTFOA(6 h) microspheres becomes smooth and solid. The PCL polymer solution possesses a higher surface tension and viscosity, causing PCL polymer chains to precipitate rapidly and form links in the processing of solvent evaporation. Hence, the solvent cannot quickly escape from the electrosprayed droplets, thus forming inner cavities and producing a porous final structure. The intertwisting action of the fluorinated PCL copolymer chains is weaker because of lower intermolecular forces; therefore, the solvent is easily expulsed and evaporates from the electrosprayed droplets. In contrast, the fluorinated PCL copolymer molecules migrate more easily to the interior of the droplet, thus filling in the cavity and forming solid microspheres.

3.3 Microsphere coating and super-hydrophobicity

Surface wettability is a very important aspect of material properties and can affect the practical application of materials in many fields. In this work, the porous microstructure of the electrosprayed microsphere could significantly improve the surface roughness of coatings, increasing the surface hydrophobicity. The flat PCL film possesses a CA of only 96.8 \pm 1.0° (Table 1). However, the CA significantly increases to 150.7 \pm 1.6° for the electrosprayed PCL microspheres with a porous

golf ball shape. Furthermore, comparing the two fluorinated PCL copolymer microsphere coatings reveals that the CA of PCL-PTFOA(2 h) and PCL-PTFOA(6 h) microsphere coatings with honeycomb-like pore structures greatly increases to 162.4 \pm 1.5° and 158.2 \pm 1.0° respectively. This change occurs because the microspheres possess a porous surface morphology that forms a secondary roughness on the microsphere coatings. These micro/nanohierarchical structures create a larger surface roughness, allowing more air to be trapped in the pores on the coating surface, leading to a higher CA. Meanwhile, the fluorinated chains present play a role in enhancing the hydrophobicity of the coated substrate because of its low surface free energy. Although the fluorine content is lower for PCL-PTFOA (2 h), it is interesting that the CA of its microsphere coating is higher than that of PCL-PTFOA(6 h). This higher CA occurs because during the coating of PCL-PTFOA(2 h), denser and smaller pores formed on the microsphere surface, and these pores can capture more air and increase hydrophobicity. Additionally, the oil can wet the surface and spread over the coating surface more easily for PCL-PTFOA(2 h) microsphere coatings because of the capillary effect (Fig. 5).68

3.4 Direct coating of cotton fabrics

Cotton fabrics were coated with microspheres via electrospraying. To provide adhesion between the cotton fabric and the electrosprayed microspheres, the cotton fabrics were pretreated with a water-based polyacrylate emulsion adhesive and coated with one of the three polymers via electrospraying. The polymer microspheres firmly adhered to the cotton fabrics after crosslinking by drying. Fig. 6a-c show the morphology of the cotton fabrics coated with the electrosprayed microspheres of PCL, PCL-PTFOA(2 h) and PCL-PTFOA(6 h), respectively. It is clear that the polymer microspheres are evenly distributed on the surface of the cotton fabrics. Additionally, the thin membranes formed by the adhesive, which immobilized the spheres on the cotton fabrics and provided strong adhesion, are visible on the cotton fibre surface. Fig. 6a'-c' show that after a standard washing process with soap, the number of microspheres on the cotton fabric decreased slightly, but abundant microspheres still adhered to the fabric. This result indicates that electrosprayed microspheres adhere well to cotton fibres due to the adhesive force provided by polyacrylate. The water contact angle test shows that the cotton fabrics coated with PCL-PTFOA(2 h) or PCL-PTFOA(6 h) electrosprayed



Fig. 4 Cross-section SEM images of the copolymer microspheres: PCL (a), PCL-PTFOA(2 h) (b), and PCL-PTFOA(6 h) (c).



Fig. 5 SEM images of electrosprayed products with different copolymers: PCL (a), PCL-PTFOA(2 h) (b), and PCL-PTFOA(6 h) (c). Photo insets depict the contact angles of the aluminium foil substrate coated with the corresponding electrosprayed products.



Fig. 6 SEM images of electrosprayed microsphere coated different materials on cotton fabric: (a) PCL, (b) PCL-PTFOA(2 h), and (c) PCL-PTFOA(6 h); coated cotton fabrics after a soap wash: (a') PCL, (b') PCL-PTFOA(2 h), and (c') PCL-PTFOA(6 h).



Fig. 7 Photograph of the wettability and SEM image of the cotton fabric coated with the porous PCL-PTFOA(6 h) microspheres.

microspheres possess a CA of $159.5 \pm 1.8^{\circ}$ and $160.0 \pm 1.3^{\circ}$, respectively, and are thus super-hydrophobic surfaces (inset in Fig. 6b and c) as the micro/nanohierarchical structure endows the surface of the cotton fabric with a high surface roughness as well as very low surface free energy. To macroscopically display the super-hydrophobicity of the coated cotton fabric, Fig. 7a shows a photograph of the wettability of the cotton fabric coated with the porous PCL-PTFOA(6 h) microspheres. Clearly, the yellow potassium dichromate water solution droplets maintain their spherical shape and stand very well on the cotton fabric surface, indicating a hydrophobic coating performance.

We conduct linear abrasion tests to fully study the mechanical durability of the superhydrophobic fabric, and the method is illustrated in Fig. 8a. The cotton fabric weighing 200 g is placed facedown to 600 mesh sandpaper and moved for 100 mm along the ruler, and then pulled back when reaching the edge; this process was defined as 1 cycle. The water CAs and SAs after the abrasion test are shown in Fig. 8b. It is observed that CA values for water droplets placed on the fabric surface are varying from 159° in the initial state to 153° after 15 cycles of abrasion, whereas the corresponding SA values are ranging from 9° to 18°. Similarly, the PCL-PTFOA(2 h) micro-



Fig. 8 The abrasion and mechanical durability of PCL-PTFOA(2 h) microsphere coated cotton fabric. (a) Sandpaper abrasion tests. (b) CA and SA values of coated cotton fabrics.



Fig. 9 Magnified SEM images of the cotton fabric coated with (a) PCL, (b) PCL-PTFOA(2 h), and (c) PCL-PTFOA(6 h) microspheres.

sphere coated cotton fabric retains its water repellent property after other tests including washing and tape pressing, as shown in Fig. 8b. The above results indicate that the superhydrophobic property will not be destroyed by mechanical abrasion, tape adhesion and soaping.

Fig. 9 shows the magnified SEM images of the cotton fabric coated with microspheres. The microspheres are immobilized on the cotton fabric by the adhesive. The three copolymer microsphere preparations show poorer uniformity when comparing the deposition of microspheres using cotton fabric vs. aluminium foil as a collector. However, the microspheres still show good dispersal and maintain their spherical shape. In comparison with the coatings on the aluminium foil substrate, the PCL microspheres display a golf ball shape, and the two fluorinated PCL microspheres produce surface roughening and display a cage-like structure. This arrangement may be due to the kinetics that arise from the continually rotating cylinder collector and nozzle giving rise to an unstable electric field, resulting in a stronger whip effect.¹⁵ This phenomenon can create a greater roughness for the cotton fabric and thus produce a super-hydrophobic microsphere coating on the surface of cotton fabric.

4. Conclusions

In summary, fluorinated PCL copolymers with different fluorine contents were synthesized and characterized. PCL,

PCL-PTFOA(2 h) and PCL-PTFOA(6 h) copolymer microspheres possessing different microstructures were successfully produced by electrospraying with a single solvent. The average particle sizes of the PCL, PCL-PTFOA(2 h) and PCL-PTFOA(6 h) microspheres are 6.69 µm, 5.50 µm and 5.64 µm, respectively. Their microsphere size distribution is narrow, and the Wigner distribution maximum (WDM) is 6.70 µm, 5.25 µm and 5.75 µm, respectively. The SEM images show that the PCL microsphere surfaces appear to have many porous pits similar to the shape and texture of a golf ball, whereas the PCL-PTFOA (2 h) and PCL-PTFOA(6 h) microsphere surfaces display regular honeycomb-like pore structures. Thermally induced and evaporation-induced phase separations are considered to be the pertinent phase separation processes that promote pore formation in electrospraying microspheres with porous surfaces and/or even inner porosity. For the fluorinated PCL copolymer microsphere, the micro-phase separation between the two block chains is an additional factor promoting the uniform collapse of the copolymer microsphere surface and the formation of a rugged wall that surrounds the surface pores. Because of the high surface roughness, the CAs of coatings produced by the three electrosprayed microspheres with hierarchically porous surfaces are 150.7 \pm 1.6°, 162.4 \pm 1.5° and $158.2 \pm 1.0^{\circ}$, respectively. Furthermore, fluorinated segments enhance the hydrophobicity of the fluorinated PCL microsphere coating due to its low surface free energy and provide a super-hydrophobic coating surface. The cotton fabrics coated directly with the microspheres of the fluorinated polymers via

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a similar electrospraying technique become super-hydrophobic surfaces, with CAs as high as $160.0 \pm 1.3^{\circ}$, and after soaping, tape pressing and 15 cycles of sandpaper abrasion, the PCL-PTFOA(2 h) microsphere coated fabric still displays superhydrophobicity. According to the properties of the above fluorinated polymers, these materials can be considered as candidates for special textiles and for other protective coating applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge the financial support by the National Natural Science Foundation of China (No. 51673137) and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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