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Thin fluoropolymer films and nanoparticle coatings from the rapid expansion of supercritical carbon dioxide solutions with electrostatic collection

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Abstract

Application of nanometer thick fluoropolymer films onto metal and semiconducting substrates is described. In the first step, nanometer-sized polymer particles are generated by a process of homogeneous nucleation during the rapid expansion of supercritical fluid solutions. These gas-phase particles are then charged as they are being formed by application of a high voltage to the expansion nozzle. In this way the charged nanoparticles can be collected on a solid surface forming uniform coatings with thicknesses from tens of nanometers to several micrometers thick. Supercritical carbon dioxide solutions of three different fluoropolymers were used to generate different types of coatings. This represents a 'green' process for film deposition. A further unique aspect of this process is that the small charged nanoparticles can be deposited to electrically conducting microscopic regions with a spatial resolution better than 50 nm.

Keywords: Polymer science and technology; Polymer materials; Polymer composite materials

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1. Introduction

Densified CO_2 in either the supercritical or liquid state is an attractive delivery medium for the deposition of thin films in both fundamental and applied technologies because of its status as a 'green' solvent [1–9]. The low viscosity and surface tension of densified CO_2 coupled with the high solubility of performance coating materials such as fluorinated polymers enables a platform of processes for the deposition of thin, conformal coatings. Complete and even coverage of the surface is of paramount importance on demanding substrates such as biomedical implants and microelectronic devices. Such a coverage can be achieved through the uniform deposition of polymer particles that are orders of magnitude smaller than the features of the substrate and applied evenly across all dimensions.

In this communication we describe a method to use the expansion of a supercritical CO_2 solution to produce conformal films on surfaces. The rapid expansion of supercritical fluid solutions [1,2,10,11] through a small orifice (referred to as the RESS process) produces an abrupt decrease in dissolving capacity of the solvent as it is transferred from a supercritical fluid state, having near liquid density, to a very low density gas phase after the expansion. This abrupt transition in solvent characteristics results in the nucleation and growth of nanometer-sized particles from any low vapor pressure solute species that are dissolved in the solution prior to expansion. Because the solvent is transformed into a gas phase during the RESS expansion, RESS products are generated 'dry', without any residual liquids or solvents.

A difficulty with the RESS process for the last two decades has been that particles in the range from 10 to 500 nm are difficult or impossible to deposit on a surface [11] since their extremely low mass causes them to remain entrained in the expansion gas. In the work presented herein

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we describe a method to overcome this challenge by charging the particles with an electric field applied to the tip of the expansion nozzle. The charged particles can be forced to a solid surface in this field generating a uniform particle coating. With subsequent sintering of the surface-captured particles, we use this method to generate films of three different fluoropolymer materials from a carbon dioxide solution. We also compare the quality of these coatings to a coating that was generated by an in situ, cloud-point precipitation coating process. Generating coatings and films using CO_2 as a solvent completely circumvents the need to use environmentally detrimental organic solvents.

2. Experimental

Three different fluoropolymer compositions were investigated. The first was a copolymer of tetrafluoroethylene/-hexafluoropropylene (19.3%) (TFE/HFP) whose solubility in CO_2 has been previously reported by McHugh et al. [12, 13]. This TFE/HFP polymer has a reported weight-average molecular weight of 210,000, a glass transition temperature (T_g) of 57 °C and a melting point (T_m) of 150 °C. The second was a copolymer of tetrafluoroethylene/hexafluoropropylene/vinylidene fluoride (THV 220A) that was used as received from Dyneon. This polymer has a reported T_m of 120 °C. The third polymeric material, poly(1,1-dihydroperfluorooctylacrylate) or PFOA, was synthesized using methods previously described [14] and has a molecular weight of approximately 200,000. CO_2 solutions of these polymer compounds were at the following concentrations and conditions; for the THV material, 5 mg/ml, 110 °C, and 900 bar, for the TFE/HFP material, 5 mg/ml, 245 °C and 1000 bar and for the PFOA material, 0.06 mg/ml, 70 °C and 310 bar. A schematic of the RESS spray equipment is shown in Fig. 1. Polymer solutions were prepared in a 10 ml high-pressure view cell by first placing a weighed portion of the polymer in the cell. Then the vessel is heated to the set point temperature and allowed to fully equilibrate. The vessel is then rapidly filled with CO_2 to the desired pressure and allowed to equilibrate for about 3 min without stirring. The magnetic stir bar is then activated to vigorously stir the mixture which then becomes a clear homogeneous solution in about 15 s. The solutions are optically clear by the time the samples are collected but because the mixing times are relatively short, we do not know if complete dissolution or dis-entanglement of the polymer chains has occurred.

The RESS restrictor in all cases was a 10 cm long, 50 μm inside-diameter fused silica capillary. The capillary is attached directly to the mixing vessel wherein the inlet tip is immersed in the CO_2 solution. This approach avoids two potential complications for solutions at very high temperatures and pressure. First the absence of valves and long transfer lines provides a nearly adiabatic transfer of the solution (very short residence times, <1 ms) from the mixing vessel, through the insulated capillary restrictor to the expansion tip. Further this approach completely eliminates restrictor plugging that occurs from the precipitation of polymer in slight lower or higher temperature regions of the transfer lines. The duration of the spraying was about 2–3 min under an applied electric field of 2 kV/cm. One of the electrodes of the high-voltage power supply (15 kV) was attached to the exit tip of the RESS capillary. The other lead was attached to the targeted substrate to be coated. The targeted substrates are positioned away from the high velocity expanding jet at a position that is about 7 cm from exit tip of the capillary in a direction perpendicular to the central axis of the nozzle. The exit tip of the spray capillary and the coating substrate were contained within a 4 l, electrically-insulating bell jar. The coatings were applied to four different substrates including a fine stainless steel (SS) screen, a SS arterial stent, a Si wafer and a 200 MHz surface acoustic wave (SAW) device (Femtometrics, Irvine, CA). The 1.3 cm diameter, 304 SS screens had a mesh size of #150 (65 μm diameter wire). The 1 cm × 0.5 cm × 0.5 mm, high-purity Si wafer was highly polished on the coating side. Finally, the SAW device is a two port resonator fabricated on ST-cut quartz with aluminum interdigital electrodes and reflectors. The surface is covered with a thin overcoat of silicon dioxide. The interdigital fingers are designed as split fingers. These devices have been described previously [15,16].

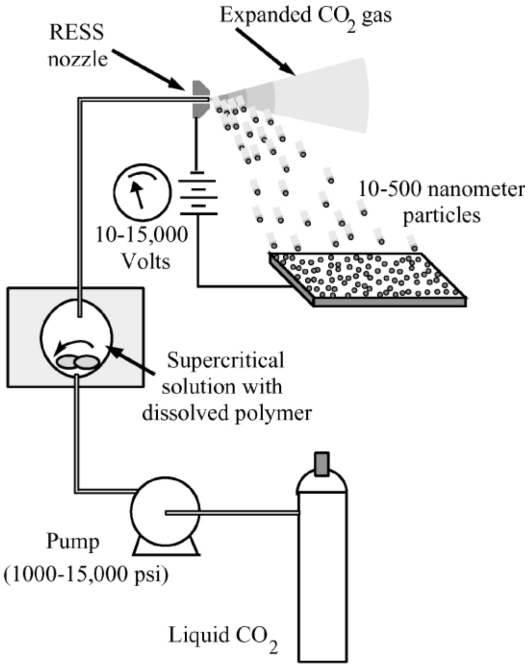

Fig. 1. Schematic of device for electrostatically charging particles in a RESS expansion and then depositing them onto a substrate in a strong electric field.

3. Results and discussion

3.1. Electrostatic RESS coating

A thin fluoropolymer coat was applied to a metal substrate by first dissolving a small amount of the THV polymer (5 mg THV/ml CO_2) in supercritical carbon dioxide at 110 °C and 900 bar. During the RESS expansion the applied electrostatic field of 2 kV/cm was then used to charge and drive the nanoparticles onto the screen substrates. Fig. 2 shows the optical micrograph of uncoated and coated wire screens using the electrostatic deposition method. In the absence of the applied field no particles are collected on the screen. Hence this ability to efficiently collect the gas-phase nanoparticles that are less than 500 nm in size overcomes a limitation of the RESS process. For the as-coated screen (center panel in Fig. 2), the coating appears as a uniform white mat rather than a clear film because the nanoparticles in the coating very efficiently scatter visible light. At the highest possible optical magnification (not shown), no individual particles can be resolved meaning that their size is below 500 nm.

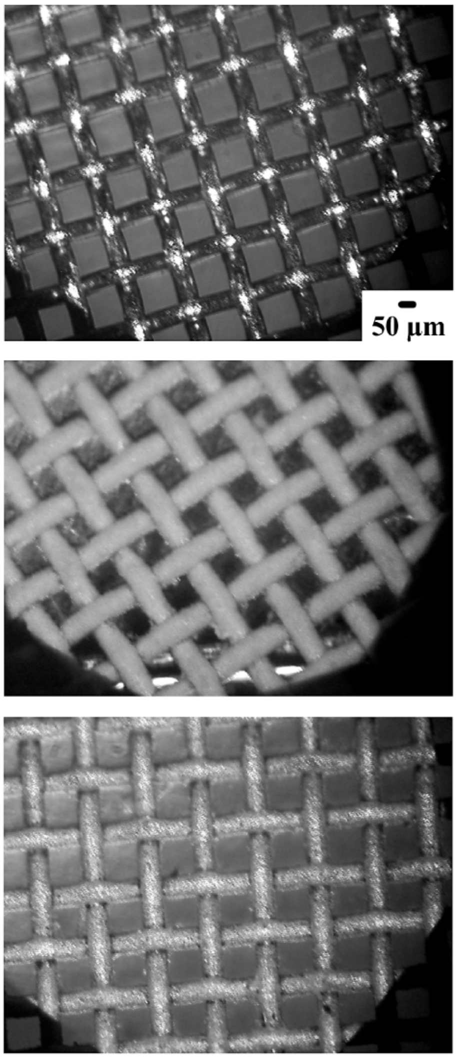

Fig. 2. Mesh screen coated with approximately 200 nm diameter particles of THV. The upper panel is the uncoated screen, the middle panel shows the particle coating on the screen and the lower panel is the appearance after sintering at 100 °C for 3 h under vacuum. The RESS pre-expansion conditions were 5 mg THV/ml CO_2, 110 °C, and 900 bar.

As shown in Fig. 2 (center), the particle layer partially occludes the opening of the screen and from this dimensional change we determine that the mat of particles has a thickness of about 8 μm. On the other hand, the coating thickness derived from a simple gravimetric measurement corresponds to a thickness of about 4 μm thick for a fully dense polymer layer ($\rho = 1.95$ g/cm^3). Thus the void volume of the as-sprayed coating is about 50%. The characteristics of extremely small particle size and the high uniformity of the coating on a macroscopic scale provide an interesting opportunity to sinter or coalesce the particles into a highly conformal film at temperatures far below T_m (120 °C for THV). In a subsequent processing step, the polymer particle coating was sintered in a vacuum oven at 100 °C for 3 h. As shown in the lower panel of Fig. 2, the individual polymeric particles can be coalesced into a film that uniformly coats all of the topographical features of the screen. An almost identical result was obtained by sintering at an even lower temperature in supercritical CO_2. In this latter method of sintering, the screen is immersed in lower-density supercritical CO_2 at 40 °C and 135 bar for 10 min. Under these conditions, CO_2 strongly plasticizes the polymer substantially lowering its glass transition temperature thereby allowing the individual nanoparticles to flow enough to form a film. The temperature and pressure conditions of this sintering step are well below the melting and dissolution point of the polymer in CO_2.

It is well known that the pre-expansion temperature, pressure and the solute concentration affect the particle sizes and morphology [11]. We thus explored the method of electrostatic deposition of RESS-generated nanoparticles under several other conditions. Polymeric THV nanoparticles were deposited onto a semiconducting surface (Si) using slightly higher RESS spray conditions (110 °C, 1 kbar) and lower concentrations (1.6 mg/ml). As shown in the SEM micrographs of Fig. 3(a) and (b), under these conditions a mixture of about 60% fibers and 40% particles are produced. The median fiber diameter is about 200 nm, as estimated by direct measurement of the SEM images, with some fibers as small as 20 nm. For more dilute polymer concentrations (0.6 mg/ml) in the starting solution, mostly spherical particles are formed having diameters of approximately 150 nm as shown in Fig. 3(c). The use of RESS for the production of polymeric fibers has been previously reported [1,8,17] although in the present case the collection efficiencies are much higher due to the electrostatic collection method and the mean fiber diameter appears to be substantially smaller.

A predominantly nanofiber coating was also produced while spraying TFE/HFP solutions onto the SS screens (not shown). In this case, we chose conditions where the pressure

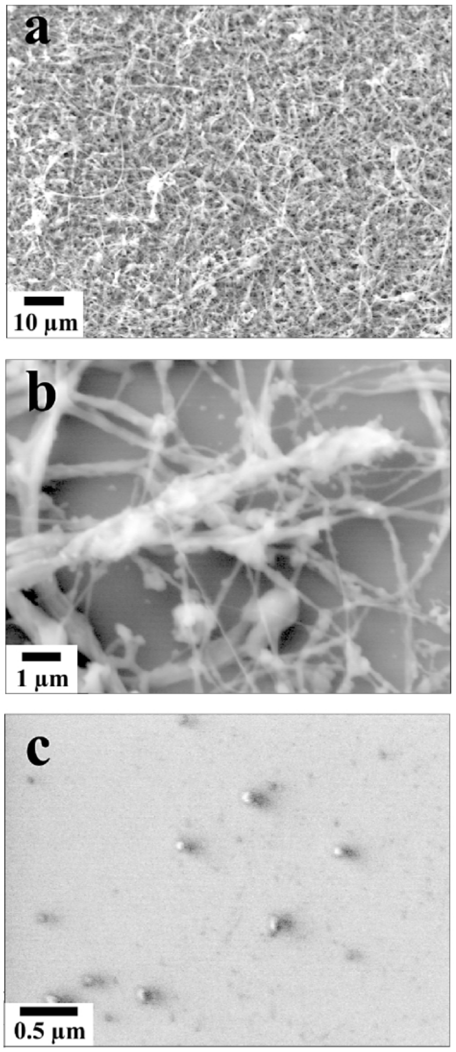

Fig. 3. SEM micrograph of THV coated Si wafer. In (a) and (b), conditions were selected to produce a mixture of filamentous and particulate coating. In (c), lower polymer concentrations were selected to produce particles. The RESS pre-expansion conditions were 1.6 mg THV/ml CO_2, and 0.6 mg THV/ml CO_2 at 110 °C, and 1000 bar, respectively.

of the supercritical solution in the mixing vessel upstream of the RESS capillary restrictor is just slightly above the cloud point pressure (5 mg/ml, 245 °C and 1000 bar). Under these conditions a phase separation occurs within the restrictor generating a polymer-rich liquid phase that wets the wall of the capillary. Upon exiting the capillary tip, this viscous liquid phase is drawn into ultra-small fibers [1,10]. Since the screen is positioned away from the high-velocity RESS jet, the fiber migration to this substrate is primarily driven by the electrostatic forces.

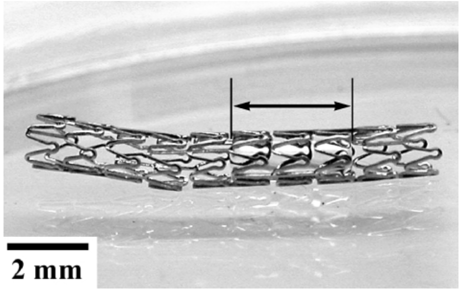

Fig. 4. Photograph showing the complex geometry of an arterial stent coated with PFOA. The region between the indicated lines contains a cylinder of water within the metal lattice of the stent that is held there by the highly repulsive effect of the very low surface energy of the fluoroacrylate coating. The conditions of the RESS solution were 70 °C, 350 bar and 0.2 mg/ml.

The electrostatic RESS technique was extended to explore coating of a complex substrate geometry on a device known as SS cardiovascular stent shown in Fig. 4. For this coating, a solution of poly(perfluorooctyl acrylate) copolymer (PFOA) was utilized to generate the RESS spray. Upon capture of the nanoparticles on the stent's surfaces, the agglomerated mat was initially opaque in the same manner as the THV coated wires in Fig. 2. After 30 min, at ambient conditions (substantially above the glass transition temperature of the PFOA copolymer), the particles flow into a clear film as seen in the photograph. As shown in Fig. 4, a uniform film approximately 1 μm thick coats the inner and outer surfaces of this biomedical device. In Fig. 4, an aliquot of water has been injected with a syringe into the inner portion of the stent. The strongly repulsive nature of the very low surface energy of the fluoroacrylate coating forces the water droplet to conform to the cylindrical shape inside the stent.

The final example demonstrates the high spatial specificity of the nanometer particle collection process. In this case a coating of a PFOA copolymer is applied to an electronic component known as a SAW device. The substrate electrode of the high voltage supply was connected to only one 'comb' of the aluminum interdigital transducers, such that the split fingers of one comb are charged and the split fingers of the other comb are not. The result is that the silicon dioxide surface above the electrodes is coated only directly above the aluminum electrodes that are connected to the voltage supply. In the optical micrograph of Fig. 5, one can see that every other pair of electrodes is coated, each such pair being a split finger, whereas the other electrodes are not coated. There is 100% selectivity for the

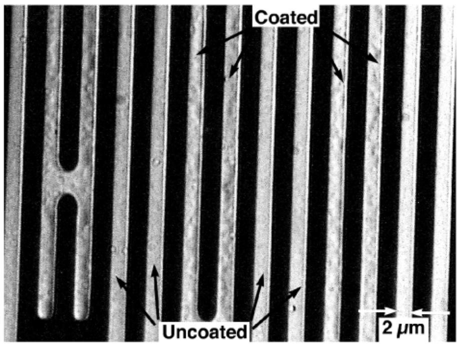

Fig. 5. PFOA-coated, surface-acoustic-wave device wherein the PFOA polymer only coats alternating pairs of parallel Al electrodes. The RESS pre-expansion conditions were 0.06 mg PFOA/ml CO_2, 70 °C and 310 bar.

charged electrodes. The polymer deposits only over the charged electrically conducting electrodes with a spatial resolution better than 50 nm. In this case the starting polymer concentration is about 100 times smaller than for the examples described above and this produces much smaller particles (estimated to be well below 100 nm in diameter). Furthermore, the surface of this electronic device is protected with a 50 nm thick layer of silica. Thus, the charge leakage through this coating is sufficient to maintain a highly specific local field. In a final step the SAW device can be used to accurately measure the coating thickness by measuring changes in the frequency of the surface wave. The observed frequency shift was −70 kHz, which would correspond to a film thickness of 7.7 nm if the material were evenly deposited over the surface ($\rho = 1.8$ g/cm^3). Since the material was only deposited on the charged electrodes, the actual film thickness on those electrodes will be higher by at least a factor of 4. These results differ significantly from those of Tepper et al. [18] who were the first to use a conventional RESS process to coat a SAW device. In this earlier work, 2 μm diameter poly(dimethylsiloxane) spheres were uniformly deposited over the entire SAW surface. We have shown that under the effect of a strong electrostatic field much smaller particles can be captured on the surface and they can be directed with very high specificity to the microscopic conducting regions of the SAW device.

3.2. Immersion coating

We also compared the quality of the film produced via the RESS process with a more conventional method of coating the substrate by immersing the screen in the supercritical fluid solution followed by controlled precipitation of the fluoropolymer solute onto the surface. The strategy here is to induce a slow cloud-point precipitation by applying a controlled temperature quench (100–30 °C in 30 min), then a pressure quench (850–400 bar in 15 min). The results of this coating strategy are shown in Fig. 6. The results can be compared directly to the RESS coatings shown in Fig. 2 (middle). For immersion coating, we find that coating quality is affected by differences in the surface topology and wettability. For instance there are larger polymer droplets at the intersection of the wires of the screen as would be expected for a minimum surface energy structure. There is, however, complete coverage of the screen with an average coating thickness of about 6 μm as determined from the gravimetric measurement. The coating on the major surface appears to be somewhat nodular which is possibly due to a wetting phenomenon. A much more uniform coating was achieved via the RESS method where there appears to be little dependency on the topology of the substrate.

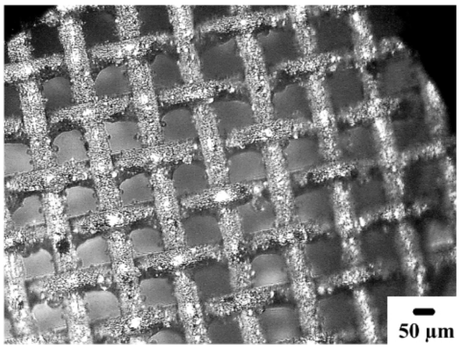

Fig. 6. THV coated screen using an in situ deposition from a cloud-point precipitation initiated with a temperature and pressure quench.

4. Conclusions

In summary, this methodology describes an essentially dry process for the application of nanoparticles to a wide range of conducting and semiconducting surfaces including high performance biomedical and microelectronic devices. The selective charging of discrete domains provides a new way to selectively pattern soft materials such as polymers onto specific regions of a microfabricated device, and could have application to a variety of sensors and actuators. The particles, once deposited, can be induced to flow into highly conformal films of thickness controlled between tens of nanometers to a few micrometers. In addition we have described a simple and effective method to harvest polymer nanoparticles from the rapid expansion of a supercritical fluid solution. Similar results could be obtained from a wide range of polymers and fluoropolymers soluble in supercritical CO_2 [13]. An even wider range of polymeric compounds could be processed using other types of supercritical solvents.

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