

Polymer Deposition from Supercritical Solutions for Sensing Applications

Gary Tepper* and Natalia Levit

Department of Chemical Engineering, Virginia Commonwealth University, 601 West Main Street, Richmond, Virginia 23284

Polymer surfaces are important in many applications including chemical sensing, corrosion protection, lubrication, and medicine. The growing demand for surfaces with specific and improved properties has catalyzed the development of new methods of polymer synthesis and processing that provide control of surface properties at the micro- and nanometer scales. Rapid expansion of supercritical solutions (RESS) is a technique that takes advantage of the enormous solubility change that occurs in a rapidly expanding supercritical solution in order to form precipitates with narrow and tunable size distributions. We have developed and tested a new RESS apparatus, incorporating a 340 cm³ extraction vessel and a capillary nozzle. The system provides the ability to independently control important expansion parameters including temperature, pressure, solute concentration, and nozzle geometry. Microspheres of high molecular weight poly(dimethylsiloxane) were deposited onto the sensing surface of a microfabricated transducer using the RESS technique. The siloxanes are excellent candidates for chemical sensing applications because of their affinity to particular organic vapors and other advantageous physical properties including low glass transition temperature, low crystallinity, and the potential for chemical modification for enhanced selectivity. The miniature chemical sensor was tested upon exposure to hexane vapor and exhibits a fast, reversible response.

Introduction

There is currently a need for small, portable chemical sensors for field applications including the identification of chemical warfare agents, industrial pollutants, and hazardous waste. Portable sensors have the potential to provide considerable cost and timesaving in comparison to conventional laboratory-based analytical instrumentation. Planar silicon technology has been successfully adapted to produce a variety of microfabricated devices with far-reaching applications including chemical sensing. A particularly promising approach toward miniaturization is the coupling of microelectronics technology with a chemically selective material (CSM).^{1–3} The CSM interacts with a particular analyte through a process such as selective absorption, and the transducer detects the physical or chemical change in the CSM and produces a detectable electrical signal. Much of the recent research has focused on the development of polymer CSMs which have proven to be particularly suitable for the detection of volatile organic compounds such as alcohols, hydrocarbons, and chlorinated solvents.^{4–7} However, although a variety of polymers have been investigated, the sensors produced to date are far inferior to laboratory-based analytical instrumentation, and fundamental improvements are required. In particular, although microfabricated devices are engineered at the microlevel, standard polymer coating methods such as solvent casting, spinning, or electrochemical deposition do not provide the same level of control over surface properties. Therefore, new coating methods are needed to produce microengineered polymer surfaces for applications in chemical sensing.

In this paper we present our initial results on the

development of polymer coatings for chemical sensing applications using the technique known as rapid expansion of supercritical solutions (RESS).⁸ Poly(dimethylsiloxane) (PDMS) microspheres were deposited onto the sensing surface of a surface acoustic wave (SAW) device using the RESS technique, and the sensor response was tested upon exposure to hexane vapor. The high surface area of the RESS-produced coating is expected to improve both the sensitivity and response time of the device. In addition, it may be possible to enhance the coating selectivity by incorporating molecular recognition centers into the polymer microspheres using RESS. For example, RESS has been previously used to perform microencapsulation of proteins for the pharmaceutical industry.^{9,10}

The RESS process takes advantage of the sudden change in solubility that occurs in a rapidly expanding supercritical solution to deposit coatings with a variety of morphologies including uniform films, fine powders, fibers, and particles with narrow size distributions. A solute with limited solubility under ordinary conditions is dissolved in a supercritical solvent at or above the critical point where the solution solubility is greatly enhanced.¹¹ Many different supercritical solvents including CO₂, water, propane, ammonia, and ethanol have been used to dissolve a wide variety of organic and inorganic solutes.^{8–16} The dilute, supercritical solution is then rapidly expanded through an aperture or capillary nozzle into a lower pressure region, resulting in the formation of a supersonic jet. Upon sudden expansion, the solution becomes supersaturated, which results in the nucleation and precipitation of solute particles. The size and shape of the particles are determined by expansion parameters such as the nozzle temperature (T_0), pressure (P_0), length-to-diameter ratio (L/D), and solute concentration.^{12,13,16}

* Corresponding author. E-mail: gcteppe@saturn.vcu.edu.
Fax: (804) 828-4269.

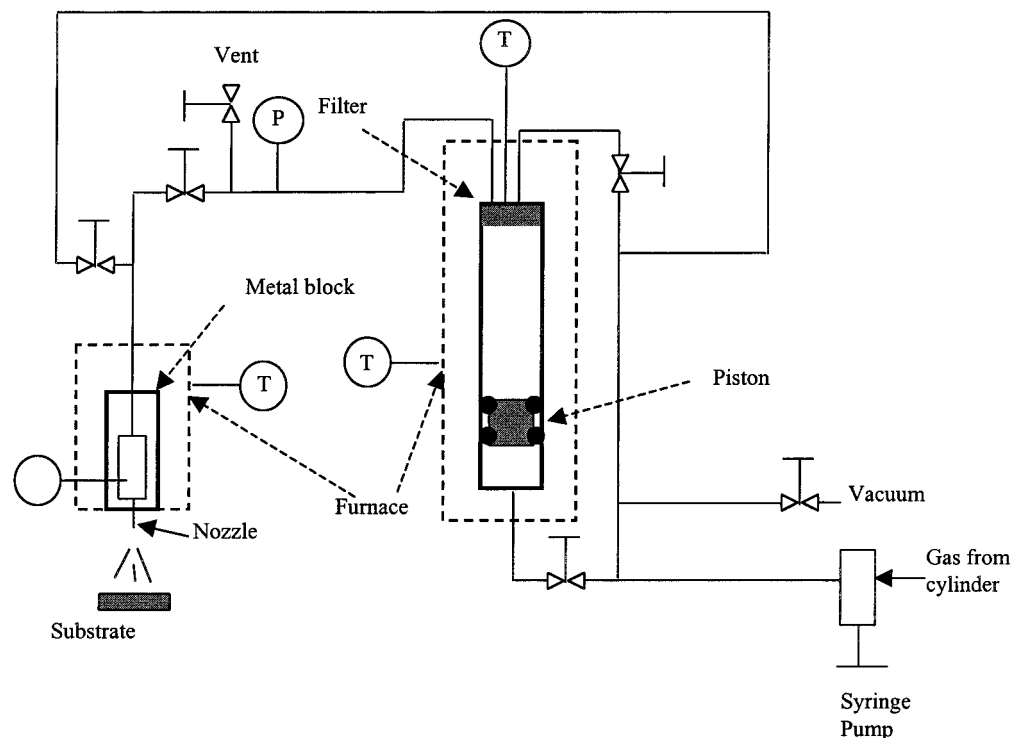


Figure 1. Schematic diagram of the RESS apparatus.

Surfaces are produced by placing a substrate in the path of the expanding, precipitating free jet. Surface properties are controlled by adjusting specific expansion parameters and substrate conditions, while the thickness is controlled by adjusting the nozzle-to-substrate distance and the exposure time.

Experimental Section

Materials. PDMS with an average molecular weight of 308 000 (viscosity of 1 000 000 sc.) was obtained from United Chemical Technologies, Inc. The polymer was used as received without any purification. Carbon dioxide was research purity from Matheson.

Phase Monitor. Solubility data were obtained using a modified phase monitor from Supercritical Fluid Technologies and consisted of a variable-volume view cell, camera, monitor, and pressure generator. The view-cell temperature and pressure could be varied to 200 °C and 750 bar. The cloud point was observed on the monitor visually during isothermal depressurization and defined as a point at which the screen turned fully turbid and a particular location within the cell was no longer visible. Each cloud-point measurement was repeated several times at 15–25 min intervals.

RESS Apparatus. Figure 1 is a schematic diagram of the RESS apparatus and includes a stainless steel variable-volume extraction chamber (Thar Designs) coupled to a capillary nozzle. The maximum volume of the extraction vessel is 340 cm³. The temperature and pressure of the vessel can be controlled to approximately 200 °C and 500 bar, respectively, using a tube furnace heater (International Thermoproducts) with a controller and a syringe pump (ISCO 260D). The extraction temperature was monitored using a J-type thermocouple inserted directly into the vessel through a HIP fitting. The pressure was monitored using a pressure transducer (PX945 Omega Engineering) with an accuracy of 1 bar. The mole fraction of the polymer was

kept constant by isolating the extraction chamber volume from the syringe pump using a floating piston. CO₂ gas was used both as the solvent and for movement of the piston to maintain constant pressure during RESS. A 5 μm filter placed between the extraction chamber and the nozzle assembly prevented physical entrainment of large undissolved particles. The expansion nozzle consisted of a polyimide-coated, fused-silica capillary incorporated in a poly(ether ether ketone) sleeve and fitting from Upchurch Scientific, Inc. Capillaries with inner diameters (*D*) of 50, 75, and 100 μm were tested. The nozzle length could be varied to investigate the effects of the nozzle length-to-diameter ratio *L/D* on the surface properties. However, for the experiments reported here, the nozzle length was kept constant at 5/8 in. The nozzle temperature was independently controlled using a separate tube furnace and monitored with a J-type thermocouple, fitted directly into the fluid stream just before the capillary entrance. The temperature of the transfer line between the extraction chamber furnace and the nozzle furnace was controlled using heating tape wrapped with metal foil.

The polymer was weighed and placed into the extraction vessel above the piston. The vessel was evacuated using a mechanical roughing pump to remove trapped air and was filled with liquid CO₂ from the syringe pump. The vessel was then isolated from the syringe pump and pressurized by reducing the vessel volume. The vessel temperature was increased to establish a single fluid phase and, after sufficient time for the PDMS to completely dissolve, the nozzle temperature was increased. Prior to each RESS experiment, pure CO₂ was expanded through the nozzle and the nozzle heater was adjusted to maintain a constant preexpansion temperature. The precipitates were collected on microscope slides and SEM stubs or deposited on the sensing surface of SAW transducers. The morphology

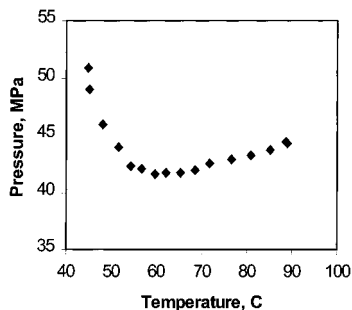


Figure 2. PDMS in CO₂ cloud-point data.

of the precipitates was determined using optical and scanning electron microscopy.

Sensors. SAW transducers (SAW PRO-250) with a resonant frequency of 250 MHz were obtained from the Microsensor Systems, Inc., and consisted of a differential pair of balanced oscillators, one for coating and one for reference. The differential configuration was chosen for this work because the output is less sensitive to common mode variables such as temperature. SAW oscillators use a delay line configuration that consists of a set of lithographically patterned interdigital electrodes deposited onto the surface of ST-cut quartz.

The sensor response was tested using a gold-plated flow cell from Microsensor Systems, Inc., with two compartments. One with gas inlet and outlet ports to the coated SAW oscillator and another isolated compartment for the reference device. The sensor response was tested upon repetitive exposure to hexane vapor using dry nitrogen as a carrier gas. The SAW device temperature was monitored using a J-type thermocouple. The flow rate and hexane concentration were controlled by means of mass-flow controllers (Cole Parmer), and the duty cycle of the solvent vapor introduction into the stream was controlled using a solenoid valve. The flow rate through the SAW chamber was 0.2 L/min at a pressure of 0.1 MPa (1 atm), and the exposure and purging time was approximately 100 s.

Results and Discussion

Phase Behavior. Figure 2 is a plot of pressure versus temperature illustrating the cloud-point data for 0.5 wt % concentration of PDMS in supercritical CO₂. The system exhibited both upper and lower critical solution temperature (UCST and LCST) behavior, as is expected for binary systems with a high degree of molecular asymmetry.¹¹ The transition region from UCST to LCST behavior occurred at a temperature of approximately 50 °C and a pressure near 41 MPa. The solubility data were used to determine suitable thermodynamic conditions for the RESS experiments. For example, it has been shown that by selecting preexpansion conditions well within the single-phase region it is possible to produce small, monodisperse particles.^{9,12} Also, it is prudent to avoid the UCST region because small thermal fluctuations can result in unwanted polymer precipitation.

Coating Development and Characterization. RESS was carried out for 0.5 wt % PDMS in CO₂ at nozzle *L/D* ratios of 160, 210, and 320. The temperature and pressure of the extraction vessel were kept constant at 75 °C and 50 MPa, respectively, during the experiments reported here, and the nozzle temperature was varied from 55 to 65 °C. Figure 3 is an optical micro-

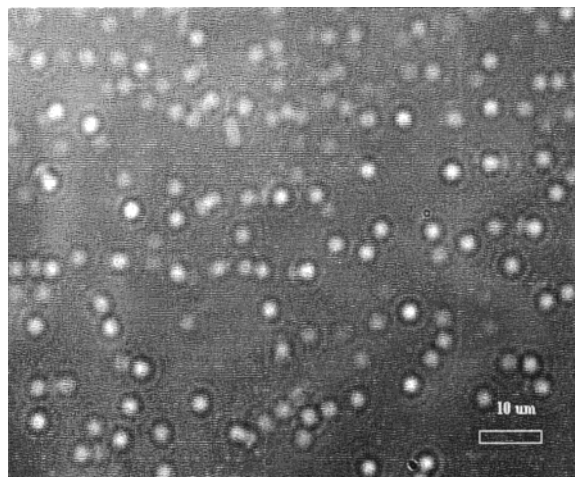


Figure 3. PDMS particles precipitated from RESS.

scope photograph of a typical PDMS coating received at a nozzle temperature of 65 °C and an *L/D* ratio of 160. As can be seen, uniform PDMS microspheres with a typical diameter of about 2–3 μm were obtained. We have varied the expansion conditions of the RESS process and have obtained surfaces consisting of a wide range of morphologies. In general, we have found that if the expansion conditions are adjusted so that nucleation begins upstream of the nozzle, larger, elongated particles are formed, while when nucleation takes place near the nozzle exit, small spherical particles are produced. SAW resonators were also coated at the same RESS conditions. The surfaces of the resonators as well as the microscope slides were cleaned prior to deposition. The cleaning process included a three-step solvent rinse followed by UV exposure (Boeckel model 135500) for 20 min. The cleaned surfaces were inspected prior to deposition using optical microscopy to verify the cleanliness. Wetting experiments were also performed by brushing the polymer onto microscope slides. No beading was observed for the high molecular weight polymer used in this paper.

Several groups have experimentally and theoretically investigated the influence of various expansion parameters on the morphology of the precipitates.^{9,12,13,16} However, although qualitative trends have been observed and reported, the predictive capabilities of the proposed models are still somewhat limited. Nevertheless, although additional experiments covering a broader range of RESS conditions are needed, the trends observed in these initial studies agree qualitatively with those of previous investigations.

Sensor Response. SAW devices use Rayleigh surface waves generated on a piezoelectric substrate. The Rayleigh waves are confined to a depth of only a few acoustic wavelengths, so the thickness of the coating in contact with the piezoelectric is a very important parameter for the sensor application (usually it is <0.2% of the acoustic wavelength¹). The frequency shift due to the applied coating is proportional in first approximation to the square of the resonant frequency of the device and mass per unit area of the coating. When vapors sorb into the coating, there is an additional frequency change proportional to the vapor mass. A dual SAW delay line with one coated oscillator and one uncoated oscillator helps to compensate the SAW frequency drift due to temperature changes and has a lower magnitude of detected signal (difference of frequency) than the fre-

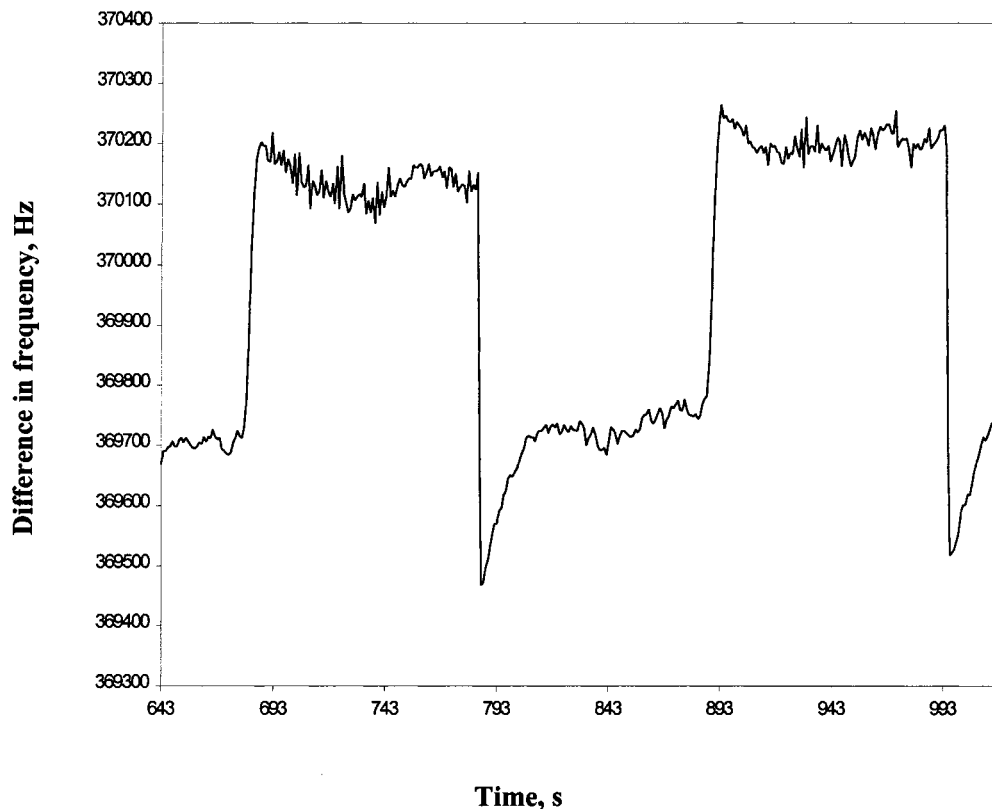


Figure 4. PDMS-coated SAW response to hexane vapor.

quency of the oscillators themselves.^{1,4} The frequency shift produced by the PDMS coating was typically 200–300 kHz. This frequency shift can be reduced by decreasing the coating time and/or lowering the polymer concentration. At this time we have not calculated an equivalent thickness of a uniformly distributed film producing the same frequency shift. This calculation is difficult because of the unknown effect of the morphology on the frequency response of the sensor. We are currently studying the effect of particle morphology on the sensor response and will report these results in a future paper.

Figure 4 shows a typical response of the PDMS-coated sensor upon repetitive exposure to hexane vapor. As the sensor is exposed to the vapor, hexane is absorbed into the PDMS microspheres. This increases the total mass loading on the polymer-coated SAW oscillator and produces an increase in the frequency difference between the coated and uncoated oscillators. When the vapor is removed, the process reverses and the frequency difference decreases to the original base-line value. The response time to the vapor is on the order of seconds.

Although uniform films have been the preferred coatings for SAW devices, we believe that coatings with morphology can provide additional flexibility for tailoring the performance parameters of the sensor, particularly for other transducers not relying on SAWs.

Conclusions

In this paper we demonstrated the feasibility and potential advantages of using supercritical fluid technology for the development of advanced coatings for chemical sensor applications. PDMS microspheres were deposited onto the sensing surface of a SAW device

using RESS. The sensor output was monitored during repetitive exposure to dilute hexane vapor and exhibited fast reversible behavior. Future investigations will be expanded to include additional polymers, surface morphologies, and transducers.

Acknowledgment

The authors acknowledge the advice and assistance of Dr. Anthony Guiseppi-Elie in performing the device characterization. This work was supported by grants from the Environmental Protection Agency and the American Chemical Society, Petroleum Research Fund.

Literature Cited

- (1) Ballantine, D. S.; White, R. M.; Martin, S. J.; Ricco, A. J.; Zellers, E. T.; Frye, G. C.; Wohltjen, H. *Acoustic Wave Sensors. Theory, design, and physicochemical applications*; Academic Press: New York, 1997; p 436.
- (2) Patrash, S. J.; Zellers, E. T. Investigation of Nematic Liquid-Crystals as Surface-Acoustic Wave Sensor Coatings for Discrimination between Isomeric Aromatic Organic Vapors. *Anal. Chim. Acta* **1994**, *288* (3), 167–177.
- (3) Gopel, W. Supramolecular and Polymeric Structures for Gas Sensors. *Sens. Actuators, B* **1995**, *24–25*, 17–32.
- (4) Wohltjen, H.; Ballantine, D. S.; Jarvis, N. L. Vapor Detection with Surface Acoustic Wave Microsensors. In *Chemical Sensors and Microinstrumentation*; Murray, R. W., Dessy, R., Heineman, W. R., Eds.; American Chemical Society: Washington, DC, 1989; pp 157–175.
- (5) Park, J.; Groves, W. A.; Zellers, E. T. Vapor recognition with small arrays of polymer-coated microsensors. A Comprehensive Analysis. *Anal. Chem.* **1999**, *71* (17), 3877–3886.
- (6) Snow, A.; Wohltjen, H. Poly(ethylene maleate)–Cyclopentadiene: a Model Reactive Polymer–Vapor System for Evaluation of a SAW Microsensor. *Anal. Chem.* **1984**, *56*, 1411–1416.
- (7) Grate, J. W.; Patrash, S. J.; Kaganove, S. N.; Wise, B. M. Hydrogen Bond Acidic Polymers for Surface Acoustic Wave Vapor Sensors and Arrays. *Anal. Chem.* **1999**, *71* (5), 1033–1040.

(8) Matson, K.; Norton, K. A.; Smith, R. D. Making Powders and Films from Supercritical Fluid Solutions. *CHEMTECH* **1989**, *19*, 480–486.

(9) Tom, J. W.; Debenedetti, P. G. J. Particle Formation with Supercritical Fluids—a Review. *Aerosol Sci.* **1991**, *22* (5), 555–584.

(10) Mishima, K.; Matsuyama, K.; Tanabe, D.; Yamauchi, S.; Young, T. J.; Johnston, K. P. Microencapsulation of Proteins by Rapid Expansion of Supercritical Solution with a Nonsolvent. *AIChE J.* **2000**, *46* (4), 857–865.

(11) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: principles and practice*, 2nd ed.; Butterworth-Heinemann: Boston, MA, 1994; p 512.

(12) Lele, A. K.; Shine, A. D. Morphology of Polymers Precipitated from a Supercritical Solvent. *AIChE J.* **1992**, *38* (8/5), 742–752.

(13) Mawson, S.; Johnston, K. P.; Combes, J. R.; DeSimone, J.

M. Formation of Poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) Submicron Fibers and Particles from Supercritical Carbon Dioxide Solutions. *Macromolecules* **1995**, *28*, 3182–3192

(14) Sun, Y. P.; Rollins, H. W.; Guduru, R. Preparations of Nickel, Cobalt, and Iron Nanoparticles through the Rapid Expansion of Supercritical Fluid Solutions (RESS) and Chemical Redaction. *Chem. Mater.* **1999**, *11*, 7–9.

(15) Turk, M. Formation of Small Organic Particles by RESS. *J. Supercrit. Fluids* **1999**, *15*, 79–89.

(16) Ksibi, H. Influence of the Nozzle Dimensions on the Formed Powder by RESS Process. *Chem. Biochem. Eng. Q.* **1999**, *13* (3), 139–144.

Received for review January 31, 2000
Revised manuscript received May 25, 2000
Accepted May 26, 2000

IE0001180