Development of polymer coatings with high surface-to-volume ratio for chemical sensor application

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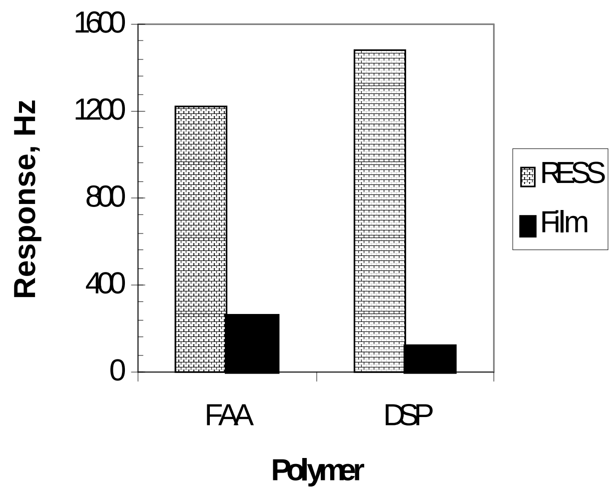
Many glassy and crystalline polymers, though not normally suitable as sensor coatings because of low vapor permeability, exhibit favorable selectivity to certain analyte molecules. For non-glassy polymers with good permeability, functionalization has been used to improve selectivity, but these special, chemically modified polymers are not commercially available and are limited to a narrow group of parent polymer. Our results show that increasing the surface to volume ratio of glassy polymer coatings enhances the adsorption step in the polymer-analyte interaction and reduces the permeation length within the coating. Therefore, practically any polymer, even those with low permeability, can be utilized as a sensor coating. High surface area coatings were deposited using a technique known as Rapid Expansion of Supercritical Solutions. RESS has been previously applied to a wide range of polymer - supercritical fluid systems and it has been demonstrated that, by appropriate selection of the supercritical solvent, a wide range of polymers can be processed.

We deposited high surface area coatings form fluoroalkyl acrylate (FAA) and 2,5-distyrylpyrazine (DSP) over a 250 MHz SAW device using the RESS technique. For comparison, airbrushing was used to deposit polymer films with matching thickness, expressed as a shift in the SAW frequency. DSP monomer was deposited by RESS, airbrushing and vapor-deposition followed by solid state UV photopolymerization. According to the microscopy study, the RESS coatings consist of monodisperse particles and exhibit greater overall uniformity than the airbrush and vapor deposition coatings. The RESS FAA particles range in diameter from 100-500 nm and are highly porous agglomerates with a pore size ranging from tens to hundreds of nm. The origin of the porous structure is not clear at the moment, but one possible explanation is the escape of trapped solvent during particle formation. The photopolymerization of DSP occurs by direct rearrangement of molecules from the monomer to the polymer crystal. The resultant polymer is highly crystalline and is linked by cyclobutane rings. Unfortunately, during photopolymerization DSP films usually undergo two-directional fracturing resulting in the formation of small fragments with a range of critical dimensions depending on the monomer history and irradiation parameters. This property apriory excludes the DSP polymer from any film-based applications, including sensor coatings. Our results show that DSP monomer particles developed by RESS range in size of 50-100 nm, which is smaller than critical dimensions, and can be polymerized without physical disintegration.

The FAA and DSP coated SAW were tested to different analyte vapors. RESS coatings provide 3 to 5 times higher frequency change relative to the film response due to the toluene vapor in wide range of concentration. SAW sensor response time is nearly independent of the coating morphology. Therefore, the enhanced surface to volume ratio of the RESS coating results in a greater sensor response. The response time, determined by the adsorption kinetics, is approximately the same due to the low permeability of the material. Surprisingly, the vapor deposited film exhibited the same response to toluene as an airbrushed film. The same trends were observed for other vapors of different concentrations, excluding very low concentrations. At low vapor concentrations the SAW response is difficult to interpret at the moment, because of a lack of information on other sensor parameters such as attenuation. The polymer coated SAW sensor response to methanol vapor is shown in figure below.

SAW sensor response to a methanol vapor concentration of 20800 mg/m^3

In this paper high surface to volume ratio polymer morphologies have been developed from supercritical fluid expansions. The RESS technique can be applied to many classes of polymers, including those that have proven difficult to deposit using conventional techniques and polymers with low permeability. Increasing the surface to volume ratio of polymer coatings enhances the adsorption step in the polymer-analyte interaction and reduces the permeation length within the coating.



Therefore, the impact of low vapor permeability can be minimized by developing coatings with high surface-to-volume ratio. Polymer coatings consisting of nanoscale particles act as an acoustically continuous film and do not degrade the sensor performance. The RESS polymer deposition technique may provide a unique way to develop sensors based on glassy and even crystalline polymers that have been previously overlooked as sensor coatings.

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