

Development and characterization of fast responding pressure sensitive microspheres

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The response times of pressure sensitive paint (PSP) and pressure sensitive microspheres to passing shockwaves were measured to investigate their ability to accurately determine pressure changes in unsteady flows. The PSPs tested used platinum tetra(pentafluorophenyl)porphine (PtTFPP), platinum octaethylporphine (PtOEP), and a novel set of osmium-based organometallic complexes as pressure sensitive luminophors incorporated into polymer matrices of dimethylsiloxane bisphenol A-polycarbonate block copolymer or polystyrene. Two types of pressure sensitive microspheres were used, the first being PtOEP-doped polystyrene microspheres (PSBeads) and the second being porous silicon dioxide microspheres containing the novel, pressure sensitive osmium complexes. Response times for the platinum-based PSPs ranged from 47.2 to 53.0 μs , while the osmium-based PSPs ranged between 37.6 and 58.9 μs . For the microspheres, 2.5 μm diameter PSBeads showed a response time of 3.15 ms, while the osmium-based silicon dioxide microspheres showed a response time ranging between 13.6 and 18.9 μs . © 2008 American Institute of Physics.

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I. INTRODUCTION

Pressure sensitive paint (PSP), developed by our laboratory in 1990,¹ provides a flexible method for continuous and nonintrusive global pressure mapping of aerodynamic surfaces,²⁻⁴ and offers an alternative to point measurement techniques that employ pressure taps and pressure transducers, which can be costly to implement and intrusive to the flow. PSP is made of an oxygen sensitive phosphorescent molecule that is incorporated into an oxygen-permeable polymer binder and dissolved in a volatile solvent to facilitate its application to surfaces. Exposing the phosphorescent molecule, or luminophor, to light of an appropriate wavelength places it in an excited state with a finite lifetime. The excited state can release its energy by giving off heat, emitting a photon, or by transferring its energy to a diatomic oxygen molecule. Consequently, the number of photons being emitted by the luminophor is inversely proportional to the amount of oxygen surrounding it. In other words, higher concentrations of oxygen cause the luminophor to emit less light, as more of its energy will be transferred to the oxygen molecules. This phenomenon, known as luminescence quenching, is the basis behind PSP. Because the oxygen concentration of air is proportional to pressure, quantitatively measuring luminophor emission intensity provides an accurate measure of pressure. By using a charge coupled device to measure the emission intensity, it is possible to obtain high resolution, two-dimensional pressure distributions over aerodynamic surfaces in wind tunnel environments.¹⁻⁵ The PSP approach has gained momentum and acceptance in the aerodynamic community and paint formulations, test equipment,

and software are now commercially available.⁶ The detailed theory of PSP measurements have been previously reported by¹⁻⁷ and will not be presented here.

While measuring surface pressures is important, it is also useful to be able to measure pressure fields within fluid flows. Such measurements would aid in understanding noise generation and its reduction, preventing damage due to large pressure fluctuations, and understanding the role of the velocity-pressure-gradient tensor within the Reynolds stress transport equation. Although PSP is well established for surface pressure measurements, little research has been done toward measuring pressure globally and nonintrusively within a fluid flow. Abe *et al.*⁸ used airborne pressure sensitive particles, which they refer to as PSParticles, for pressure measurements throughout a dynamic flow system. These particles are 0.5–25 μm in diameter, fumed silicon dioxide particles with porous outer shells that are loaded with a ruthenium-based pressure sensitive luminophor ($[\text{Ru}(\text{bpy})_3^{2+}]\text{Cl}_2$). The researchers injected the particles into a flow of N_2 gas that emptied from a jet into an ambient air chamber. The oxygen concentration within the emanating plume of N_2 was measured through rapid lifetime determination of the PSParticles. While this experiment demonstrates a proof of concept, the researchers could only make oxygen concentration measurements over a small dynamic range (0%–1% $[\text{O}_2]$), and the ruthenium luminophor's high temperature dependence required a careful monitoring of the temperature in the ambient air chamber. Furthermore, although the ability to provide simultaneous velocity measurements through particle imaging velocimetry (PIV) was stated, none were shown.

Our research groups have recently synthesized oxygen

sensitive polystyrene microspheres, which we refer to as PS-Beads (Ref. 9) that are doped with dual luminophors, thereby developing, for the first time, a self-referencing particle capable of measuring pressure fields within a gas phase flow. In this case, a pressure insensitive, reference luminophor (silicon octaethylporphine) was combined with platinum octaethylporphine (PtOEP) and incorporated into PSBeads. It was demonstrated that these PSBeads could be made with high uniformity

and high synthetic yield. In addition, the size of the microspheres could be easily varied between 1 and 5 μm by changing the concentration of polymerization initiator used in the synthesis. Kimura *et al.*¹⁰ demonstrated the potential of the PSBeads by measuring variations in their time-averaged emission intensity when exposed to gas phase flows with oxygen concentrations between 0% and 10%.

A. PSP and PSBeads response times

The response times of PSP to changes in pressure are dependent upon the luminescent lifetime of the oxygen sensitive luminophor used, the thickness of the matrix layer surrounding the luminophor, and the oxygen diffusivity of that layer. Generally, experimentally useful oxygen sensitive luminophors have lifetimes between 1 and 50 μs . This value serves as the ultimate time constant for PSPs as they cannot respond faster than the lifetime of the luminophor being used. However, these lifetimes are usually shorter than the time constants associated with oxygen diffusion through the matrix containing the luminophor.

The diffusion-limited, 99% rise time of a thin layer of PSP coating a surface can be estimated using

$$\tau_{99\%} = (12L^2)/(\pi^2D), \quad (1)$$

where L is the thickness of the sensor layer and D is the oxygen diffusion coefficient of the matrix being used.^{11,12} Therefore, a fast responding PSP would be a thin film made of a polymer with a relatively large oxygen diffusion coefficient. However, PSPs that are too thin may not provide enough emission intensity and will have a low signal-to-noise ratio. In addition, polymers with values of D that are too large will result in a large amount of luminescence quenching by oxygen near 1 atm of pressure. This will also lead to films that are too dim with a poor signal-to-noise ratio.

Much work has been done to develop fast responding PSP that is capable of measuring unsteady flow phenomena. To date, fast responding PSP has been used to study airflow over rotor blades^{13–16} and for measuring the unsteady pressure distribution on the side of a square cylinder during vortex shedding.¹⁷ Studies have shown that the fastest responding PSPs have used matrices that are not polymer based. Sakaue and Sullivan¹⁸ demonstrated that by using anodized aluminum as a supporting matrix, response times on the order of tens of microseconds are possible. Baron *et al.*¹⁹ showed that using silica gel thin-layer chromatography (TLC) plates as matrices can result in submillisecond response times and later, McGraw *et al.*²⁰ demonstrated that a

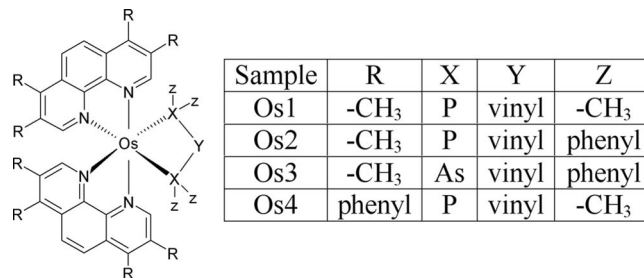


FIG. 1. Pressure sensitive osmium luminophors used in novel set of PSPs.

platinum-based porphyrin in a fluorinated copolymer, when pipetted onto TLC plates, can produce a sensor capable of detecting sound waves of up to 2370 Hz, which equates to a response time of 67 μs .²¹

Ultimately, the goal of this research is to develop a pressure sensitive particle that can accurately and simultaneously measure pressure and velocity in unsteady (i.e., turbulent) gas phase flow. Therefore, it is inherent that the response time of the existing PSBeads be established. The diffusion-limited response time of a spherical PSBead can be estimated using the following equation:

$$\tau_{99\%} = (3d^2)/(4\pi^2D), \quad (2)$$

where d is the diameter of the bead and D is the diffusion coefficient of the polystyrene microsphere.²² Depending on the value of $D_{\text{polystyrene}}$ used (literature values between 1.1×10^{-7} and 3.1×10^{-7} cm^2/s have been reported),²³ $\tau_{99\%}$ for a 2 μm diameter PSBead maybe anywhere between 9.8 and 27.6 ms. There was concern that this response time would be too slow to accurately measure pressure fluctuations in unsteady flow phenomena. Therefore, we elected to follow similar steps to those taken in the development of fast responding PSP by investigating the feasibility of synthesizing a new generation of PSBeads based upon a highly porous, silicon dioxide matrix.

B. Fast responding osmium-based pressure sensitive microspheres

A large amount of literature exists on the synthesis of porous silica microspheres. First developed to serve as highly uniform and highly porous solid phase packing in liquid chromatography columns, these microspheres have recently begun to demonstrate their versatility, showing promise as drug delivery agents^{24,25} and chemical sensors.²⁶ The synthesis of monodisperse microspheres of varying diameters is relatively straightforward, adding to their appeal.

Recently, a novel series of osmium-based, oxygen sensitive organometallic luminophors were synthesized at the University of Washington (Fig. 1).²⁷ These luminophors can be excited anywhere between 250 and 450 nm, and display oxygen sensitive phosphorescence at 550–670 nm. In addition, these luminophors exhibit short lifetimes (1–5 μs), good temperature stability ($\sim 0.5\%$ intensity loss per $^\circ\text{C}$), and limited photodegradation. As a result, they are excellent candidates to incorporate into porous silica microspheres for the development of a new generation of PSBeads.

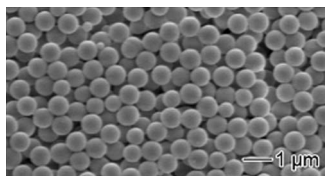


FIG. 2. SEM image of osmium-doped, porous silicon dioxide microspheres.

Therefore, the purpose of this paper is to investigate the response times of several PSPs as well as polystyrene and novel osmium-based silicon dioxide PSBeads in order to ascertain their applicability towards unsteady flow measurements. Toward this end, Sec. II will discuss the experimental procedures for fabricating the fast responding microspheres, the testing facility for measuring their response times, and the calibration procedure; Sec. III will discuss the results; and finally, Sec. IV will present the conclusions and future work.

II. EXPERIMENTAL PROCEDURE

A. Materials

Platinum tetra(pentafluorophenyl)porphine (PtTFPP) and PtOEP were purchased from Frontier Scientific, Logan, UT, USA. Dimethylsiloxane-bisphenol A-polycarbonate block copolymer (MAX), was purchased from General Electric LR 3320, New Jersey, USA. Polystyrene (molecular weight of 125 000–250 000) was purchased from Polysciences, Inc., Warrington, PA. Solvents utilized were dichloromethane (DCM) (Fisher Scientific Chemicals, Hampton, NH, USA) and acetonitrile (Fisher Scientific Chemicals, Hampton, NH, USA) and were used as received. The synthesis of the porous silica microspheres required the use of tetraethyl orthosilicate (TEOS) (Aldrich, St. Louis, MO, USA), ethanol (95%, Fisher Scientific, Hampton, NH, USA), and ammonium hydroxide (28%, J.T. Baker, Phillipsburg, NJ, USA). The osmium-based organometallic dyes were synthesized by the method similar to that in Ref. 27. PSBeads were provided by the Professor Younan Xia. The synthesis of PSBeads has been described previously.^{9,10}

B. Synthesis of pressure sensitive osmium-based silicon dioxide microspheres

Ethanol (66 ml), ammonium hydroxide (22 ml), and 18 mΩ de-ionized water (10 ml) were added to a 200 ml round-bottom flask under continual mixing with a magnetic stir bar. To this, 0.09 g of the osmium-based, pressure sensitive luminophor was added and allowed to dissolve into the solution. Finally, TEOS (5 ml) was added to the reaction mixture, which was allowed to stir for 8 h at room temperature. Once the formation of the microspheres was completed, the suspension was washed three times in warm ethanol via a centrifugation-decantation-sonication sequence to rinse away excess hydroxide. A scanning electron microscopy (SEM) image of these microspheres is shown in Fig. 2. For SEM

(FEI Sirion, Portland, Ore.) the samples were dried on a Si wafer under vacuum and sputtered with Au/Pd for 30 s.

C. Shock tube sample preparation

1. PSP thin film preparation

A typical film preparation is as follows. MAX (0.15 g) was dissolved in 15 ml of DCM. To this solution, 1.5 mg of PtTFPP was added. This solution (20 μL) was pipetted onto a polyethylene-backed TLC plate, resulting in a spot approximately 0.8 cm in diameter.

Osmium-based PSPs were also tested and they were made in an analogous manner to the platinum-based paints. However, when applied to the TLC plate, the dyes failed to travel far enough into the silica to be excited through the polyethylene backing. As a result, it was necessary to add 10 μL of acetonitrile to the paint spot to improve the mobility of the osmium dye through the silica layer.

2. PtOEP-based PSBeads monolayer preparation

Monolayers of 2.5 μm diameter PSBeads were formed by drop casting an ethanol suspension (~10% solids) of the microspheres onto the surface of a pool of water. The microspheres floated on the surface of the water and spontaneously formed a hexagonally packed monolayer upon addition of a small amount of surfactant. A glass cover slip was then carefully lifted from beneath the monolayer and out of the pool in such a way as to ensure a section of the monolayer was carried on its surface. The solvent was allowed to dry, leaving behind the monolayer of PSBeads electrostatically adhered to the glass cover slip. Verification that only a monolayer remained was performed via optical microscopy.

3. Os-based PSBead sample preparation

Originally, monolayers of the osmium-based PSBeads were made by drop casting an ethanolic solution of the microspheres on the surface of a glass cover slip and allowing the sample to dry. Then, a gloved finger that was carefully dragged across the surface of the sample collected any silica microspheres that were not in direct contact with the surface of the cover slip, thus leaving behind a monolayer of microspheres. Formation of the monolayer could be verified through optical microscopy.

However, it was observed that a monolayer of the osmium-based PSBeads did not provide enough emission intensity. It became necessary to use thicker layers of microspheres to obtain the necessary signal-to-noise ratio. The consequences of this will be discussed later in this publication.

D. Instrumentation

1. Shock tube

Shock tubes have been used to measure the response times of PSPs to fast pressure jumps.^{18,28} The schematic of the shock tube constructed in our laboratory is shown in Fig. 3. It is made from square aluminum tubing, with walls 0.64 cm thick and a cross-sectional area of 3.9 × 3.9 cm².

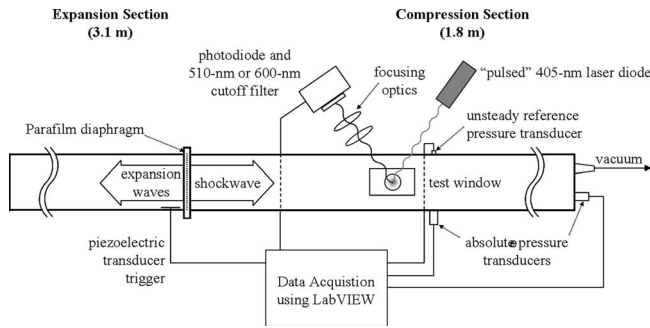


FIG. 3. Schematic of the shock tube facility constructed at the University of Washington.

The driver (expansion) and driven (compression) chambers are 3.1 and 1.8 m long, respectively. Parafilm® *M* (127 μm in thickness, Pechiney Plastic Packaging, Measha, WI) serves as the diaphragm material and is burst by the pressure difference between the expansion and compression chambers. The pressure difference is achieved by lowering the pressure in the compression chamber with a vacuum pump. The shock strength was varied by increasing or decreasing the number of Parafilm layers used. A 1.9 × 3.8 cm² test window made of polycarbonate is positioned 0.58 m downstream of the diaphragm. The pressure sensitive films and PSBead test samples were flush mounted directly onto this window. Unsteady and steady pressures were measured 0.64 m downstream of the diaphragm, 0.12 m past the location of the test samples. Unsteady pressure measurements were made using an ICP® dynamic pressure sensor (model 132A35, PCB Piezotronics, Depew, NY) coupled to a battery-powered ICP® sensor signal conditioner (model 480C02, PCB Piezotronics, Depew, NY). Steady pressure measurements were obtained by an Omega PX236 series pressure transducer (Omega Engineering, Inc., Stamford, CT). A second Omega PX236 series pressure transducer was mounted on the end wall of the test section. Both Omega pressure transducers were calibrated using a mercury barometer to provide absolute pressures. All pressure transducers

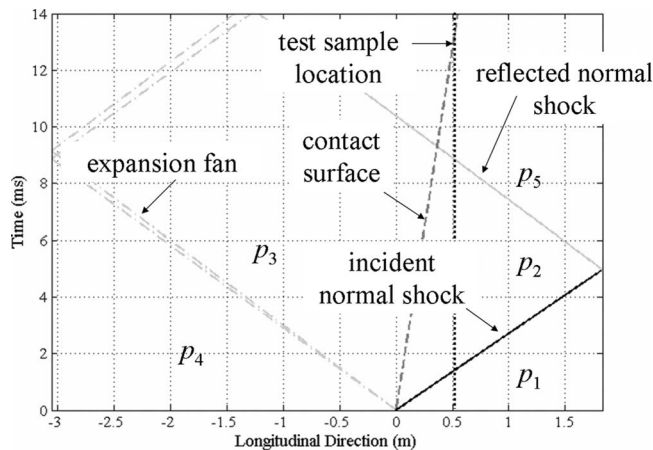


FIG. 4. *x-t* diagram of the theoretical shockwave behavior within the shock tube. Initial driven and driver pressures are 68.5 and 100 kPa, respectively. Samples are located 0.52 m from the diaphragm. Initial time, *t*=0 corresponds to the moment of diaphragm bursting.

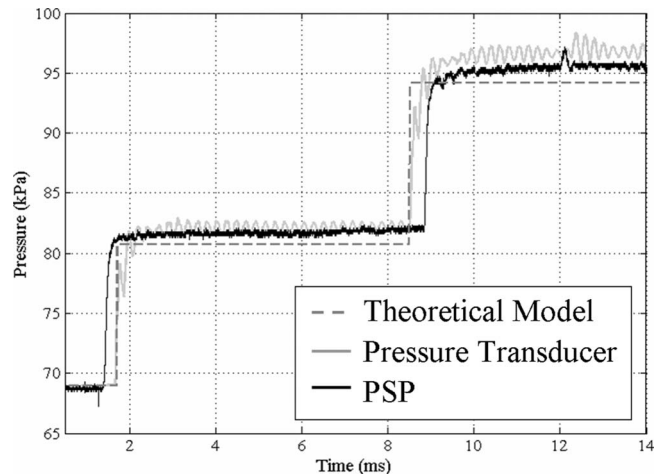


FIG. 5. Comparison of the theoretical model to pressure measurements from the pressure transducer and a 1%, 1:83 PtTFPP:MAX on TLC PSP.

were flush mounted on their respective walls. The stated accuracy of the steady pressure transducers are 0.25% of the full scale.

A theoretical model was developed to predict the behavior of the shockwave, contact surface, and expansion waves within the shock tube. For this model, initial driven and driver section pressures (*p*₁ and *p*₄) were 69.0 and 100. kPa respectively. This corresponds to the typical pressure ratio achieved when two pieces of Parafilm are used as a diaphragm. The *x-t* plot in Fig. 4 shows the results of this model. Here, the diaphragm is located at *x*=0 m. Negative *x* values represent the expansion section of the shock tube and positive *x* values represent the compression section. The location of the test sample is denoted at *x*=0.52 m with a dotted line. The initial time (*t*=0 ms) corresponds to the moment of diaphragm rupture. The aforementioned initial conditions result in an incident shockwave traveling at 369 m/s (*M*=1.07) with a pressure (*p*₂) of 80.7 kPa. This shockwave reflects off of the end of the driven section and returns with a velocity of 338 m/s and with a pressure (*p*₅) of 94.2 kPa. The duration of the incident shock is ~7 ms.

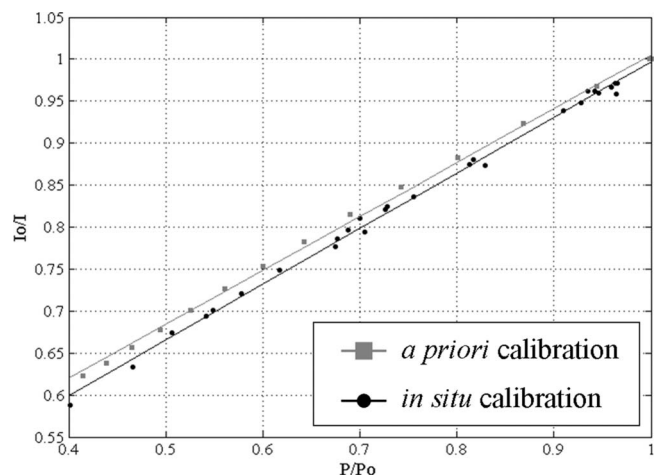


FIG. 6. *A priori* and *in situ* calibration curves of 1%, 1:83 PtTFPP:MAX on TLC. Stern–Volmer parameters of *A*=0.36 and 0.33 and *B*=0.64 and 0.66, respectively, were obtained from linear fits.

TABLE I. *A priori* and *in situ* Stern–Volmer parameters of various platinum-based PSPs, where *A* represents the intercept and *B* represents the slope (and thus sensitivity of the PSP) of a linear best fit.

Sample	<i>A priori</i>			<i>In situ</i>		
	<i>A</i>	<i>B</i>	r^2	<i>A</i>	<i>B</i>	r^2
1:83 PtTFPP:MAX, 1% w/v in DCM, 20 μ l on TLC	0.36	0.65	0.999	0.33	0.66	0.997
1:100 PtOEP:MAX, 1% w/v in DCM, 20 μ l on TLC	0.46	0.55	0.997	0.46	0.56	0.992
1:100 PtOEP:PS, 1% w/v in DCM, 20 μ l on TLC	0.52	0.50	0.991	0.46	0.55	0.990
ISSI UniFIB	0.21	0.80	0.998	0.22	0.78	0.991

Figure 5 shows how the theoretical model compares to both a pressure sensitive film and the absolute pressure transducer. It should be noted that the transducer is located ~ 10 cm downstream from the pressure sensitive film. This results in a delayed response to the incident shockwave and an early response to the reflected shock. The expected delays for the incident and reflected shocks are 0.27 and 0.30 ms, respectively. Experimentally, these delays were measured to be 0.27 and 0.32 ms.

2. Luminescence detection system

A 405 nm laser diode (LDCU12/5373, Power Technology, Inc., Little Rock, AR) was used to excite the PSBeads. The duty cycle of the laser diode is controlled via a pulse generator (BNC 565, Berkeley Nucleonics Corporation, San Rafael, CA) to reduce photodegradation of the pressure sensitive samples. In this way, the samples are only illuminated for the duration of a single experiment (~ 40 ms). The laser spot, being elliptical in shape, was oriented with its minor axis parallel to the flow direction, resulting in an excited region approximately 2 mm in length. Because the shock velocity is known (calculated through both time of flight and shock relations), a minimum pressure rise time (t_{limit}) of any phosphorescent pressure sensitive material can be calculated,

$$t_{\text{limit}} = d_{\text{spot}} / v_s, \quad (3)$$

where d_{spot} is the width of the spot and v_s is the shock strength. For our apparatus, t_{limit} was $5.5 \mu\text{s}$.

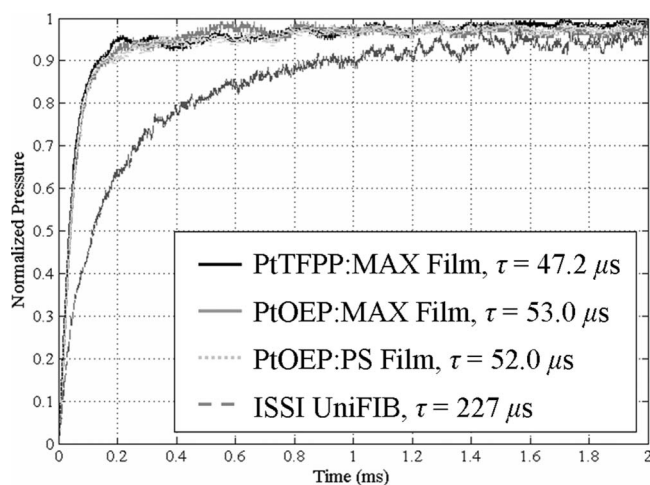


FIG. 7. Response times of various platinum-based PSPs to the passing shockwave.

As shown in Fig. 3, the samples are excited and their emission is detected through the same window. This was done to eliminate any variations in excitation intensity resulting from the refractive index change of the air as the shockwave passed the sample. The emission of the samples was collected by a photodiode fitted with a 610 nm cut-on filter. The photodiode had a time constant of $5 \mu\text{s}$ with a temporal bandwidth of 2.5 kHz. A piezoelectric transducer (Part No. 668-1008-ND, Digi-Key Corp., Thief River Falls, MN) placed within the expansion chamber next to the diaphragm served as a trigger for data acquisition. Data from all pressure transducers and the photodiode were captured with a PC equipped with a National Instruments data acquisition board (PCI-6110, Austin TX). LABVIEW was used to record the data, which consisted of 100 000 samples collected at 2.5 MHz.

3. *A priori* calibration

Each series of tests began with an *a priori* calibration of the pressure sensitive film and PSBead samples within the shock tube itself. Once each sample was secured to the test window, the pressure within the shock tube was gradually decreased from 100 to ~ 30 kPa. The subsequent emission intensity of the film to pulsed excitation was measured. The process is repeated after the testing is complete to determine whether any photobleaching of the sample has taken place. The temperature of the system is monitored during the calibration using a *T*-type thermocouple. Typically, the temperature varied by less than a degree centigrade during the process.

4. *In situ* calibration

A second *in situ* calibration was performed for each

TABLE II. $1/e$ and 90% rise times of various platinum-based PSPs.

Sample	$1/e$ time (μs)	90% rise time (μs)
1:83 PtTFPP:MAX, 1% w/v in DCM, 20 μ l on TLC	47.2	110
1:100 PtOEP:MAX, 1% w/v in DCM, 20 μ l on TLC	53.0	125
1:100 PtOEP:PS, 1% w/v in DCM, 20 μ l on TLC	52.0	122
ISSI UniFIB	227	485

TABLE III. $1/e$ and 90% rise times of Os-based PSPs.

Sample	$1/e$ time (μs)	90%rise time (μs)
1:100 Os1:MAX, 1% w/v in DCM, 20 μl on TLC	42.0	101
1:100 Os2:MAX, 1% w/v in DCM, 20 μl on TLC	58.9	134
1:100 Os3:MAX, 1% w/v in DCM, 20 μl on TLC	37.6	90.2
1:100 Os4:MAX, 1% w/v in DCM, 20 μl on TLC	48.5	109

pressure sensitive film and PSBead sample. This required the acquisition of two sets of data per experiment. The first set, obtained immediately before the compression chamber was evacuated, recorded the emission intensity of the pressure sensitive sample at atmospheric pressure, as well as the pressure measured by the absolute pressure transducer within the test section. These provided reference (I_0 and P_0) values for each experiment. The second set of data consisted of the emission intensity and pressure data as the shockwave passed by the PSBeads or PSP sample and pressure transducer. From this, pressures p_1 , p_2 , and p_5 , along with corresponding emission intensities could be determined. These were then ratioed with the reference values, providing three *in situ* points of calibration. A total of 27 *in situ* calibration points were calculated, as each sample was subjected to nine shocks (three runs for each of three shock strengths).

A typical series of Stern–Volmer plots for a 1:83 PtTFPP:MAX on TLC film is presented in Fig. 6. As the response of the majority of these samples were quite linear over the ranges of pressures measured, it was deemed sufficient to use the Kavandi equation¹ as a quantitative model,

$$I_0/I = A + B(P/P_0), \quad (4)$$

where I_0 is the intensity of the sample at a reference pressure, P_0 , which for these experiments was 760 torr. The Kavandi parameters, A and B , are determined from the intercept and slope that results from a linear fit of the calibration data. Once these parameters are obtained, I can directly be related to pressure, P . Tables I, IV, and V present Kavandi parameters for both the *a priori* and *in situ* calibrations, as well as r^2 values of the fit. While the *a priori* calibration compares well with the *in situ* calibration, the Kavandi parameters ob-

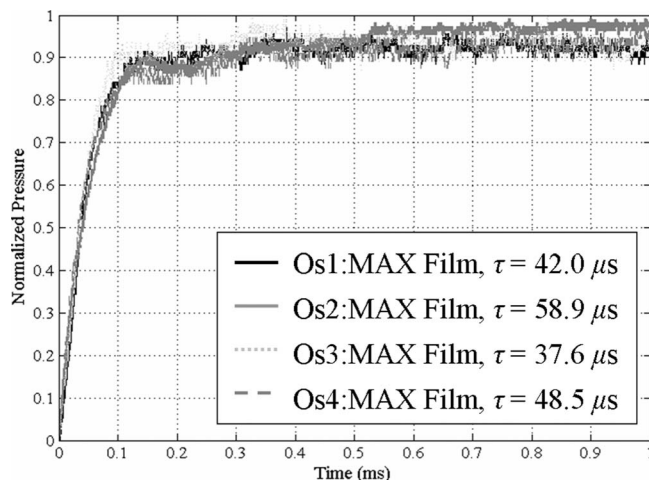


FIG. 8. Response of Os-based PSPs to the passing shockwave.

tained from the latter were used when converting emission intensities to pressure values, since the *in situ* calibration best replicated the testing environment and therefore provided the most accurate calibration constants.

III. RESULTS AND DISCUSSION

A. Step change of pressure

A series of PSP and PSBead samples described in Sec. II were prepared and sequentially tested within the shock tube facility. For pressure sensitive films that were drop cast on TLC plates, the plates were attached with their clear polyethylene backings against the polycarbonate test window. Excitation of the film and subsequent emission was performed through the polyethylene backing. This was done to ensure that no artifacts arose from the changes in index of refraction of the gas expected from the passing shockwave. Likewise, monolayers of PSBeads on glass cover slips were mounted in the same way so that excitation and emission detection occurred through the same window. Figure 5 shows the pressure response of a 1:83 PtTFPP:MAX, 1% paint solution on TLC as well as the signals from the pressure transducer and theoretical model prediction. The initial driven and driver pressures, p_1 and p_4 , were 68.5 and 100 kPa, respectively.

TABLE IV. *A priori* and *in situ* Stern–Volmer parameters of various osmium-based PSPs.

Sample	<i>A priori</i>			<i>In situ</i>		
	A	B	r^2	A	B	r^2
1:100 Os1:MAX, 2.5% w/v in DCM, 20 μl on TLC	0.74	0.27	0.985	0.74	0.27	0.979
1:100 Os2:MAX, 2.5% w/v in DCM, 20 μl on TLC	0.65	0.36	0.990	0.64	0.37	0.981
1:100 Os3:MAX, 2.5% w/v in DCM, 20 μl on TLC	0.79	0.22	0.982	0.84	0.17	0.966
1:100 Os4:MAX, 2.5% w/v in DCM, 20 μl on TLC	0.78	0.23	0.983	0.79	0.21	0.987

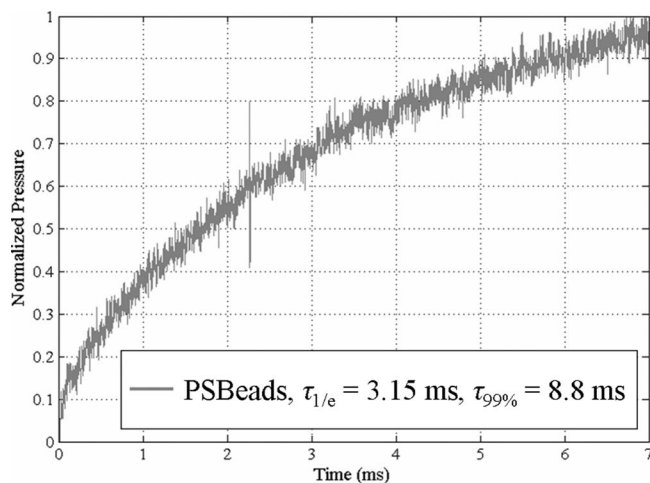


FIG. 9. Response of PSBeads (PtOEP in a polystyrene microsphere).

B. Response time measurements

1. Pressure sensitive paints

Figure 7 shows the step change response of a series of platinum-based PSPs to the reflected normal shock. PSP1 is a 1%, 1:83 PtTFPP:MAX paint on TLC, PSP2 is a 1%, 1:100 PtOEP:MAX paint on TLC, and PSP3 is a 1:100 PtOEP:polystyrene on TLC. As a comparison, the response time of PSP4, a commercially available, platinum-based PSP (UniFIB, ISSI, Dayton, OH, USA) is also presented. Because this paint has an opaque binder in its formulation, we elected to simply spin coat 100 μl of the PSP onto a glass cover slip.

The pressure signals were normalized to account for the small variations in shock strengths and the step responses of the PSPs to the reflected shock were fitted to a first-order exponential. The response times are reported in Table II. The PSP1, PSP2, and PSP3 exhibited response times of 47.2, 53.0, and 52.0 μs , respectively. These are all within a factor of 2 of being limited by the lifetimes of the platinum luminophors. This suggests that the highly porous silica TLC plate significantly increased the rate of oxygen diffusion through these PSPs as compared to the conventional ISSI PSP (227 μs) that uses a polymeric supporting matrix. This effect, and similar response times for PSPs of this nature, was observed by both McGraw *et al.*^{17,20} and Sakaue and Sullivan.¹⁸

The responses of the osmium-based PSPs are shown in Fig. 8 and the measured response times are presented in Table III. The table in Fig. 1 lists the functional groups of the four osmium complexes tested. These PSPs showed similar

response times to the platinum-based PSPs, which is somewhat surprising as the lifetimes of the osmium complexes are 6–15 times shorter than those of the platinum luminophors. This would suggest that the polymer matrix still has some effect on the oxygen diffusivity of PSP on TLC.

Table IV presents the Kavandi parameters for these osmium-based PSPs. The sensitivities of these PSPs, which can be ascertained from the parameter B , range from 17% to 37% over 1 atm, considerably less than the platinum-based PSPs. This is expected, as the lifetimes of the molecules are much shorter than those of the platinum-based luminophors. These sensitivities may improve with a change in the counterion associated with the osmium complexes. In addition, significant nonlinearity is displayed by these samples. This would suggest that the linear Kavandi model is insufficient to describe the pressure response of these new complexes. Improvements upon this model are in progress.

2. PtOEP-based polystyrene PSBeads

The response of a monolayer of 2.5 μm diameter, PtOEP-doped PSBeads to the step change in pressure is shown in Fig. 9. A $1/e$ response time of 3.15 ms and a 99% response time of 8.8 ms were measured. In Table V, it should be noted that only 9 *in situ* data points for these PSBeads could be obtained, as opposed to the 27 points collected for all other samples. It was found that the PSBeads were still responding to the onset of the first shockwave (p_2) by the time the reflected shockwave passed over the sample. As a result, intensities at p_2 and p_5 could not be accurately determined and only the intensity at p_1 could be measured.

The measured response time corresponds well to the estimated $\tau_{99\%}$ of a polystyrene-based PSBead. It could be argued that a contributing factor for the measured response time is the geometry of the PSBead monolayer. However, if the monolayer of PSBeads was behaving more like a 2.5 μm thick layer of PSP, a $\tau_{99\%}$ between 157 and 442 ms would be expected, much larger than the measured time. Furthermore, a hexagonally packed PSBead monolayer can only have a packing efficiency of 74%.²⁹ Large gaps will be present between each microsphere allowing them to be quickly surrounded by oxygen. Therefore, it is believed that monolayer should exhibit a diffusion-limited response time closer to that expected for a single PSBead.

3. Os-based silicon dioxide PSBeads

The response times of the osmium-based silicon dioxide microspheres, shown Fig. 10 and reported in Table VI, are

TABLE V. *A priori* and *in situ* Stern–Volmer parameters of PSBeads.

Sample	<i>A priori</i>			<i>in situ</i>		
	A	B	r^2	A	B	r^2
2.5 μm PSBeads	0.39	0.61	0.999	0.45	0.55	0.997
Os1 silica microspheres	0.74	0.27	0.978	0.73	0.29	0.983
Os2 silica microspheres	0.70	0.31	0.985	0.67	0.34	0.979
Os3 silica microspheres	0.70	0.31	0.991	0.71	0.31	0.975
Os4 silica microspheres	0.77	0.24	0.961	0.77	0.24	0.944

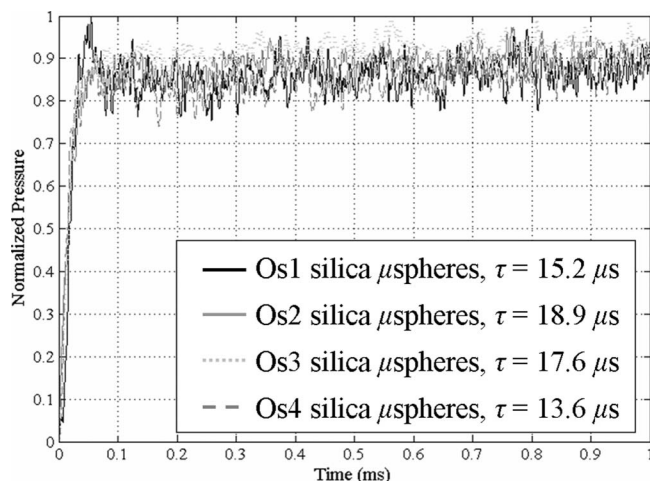


FIG. 10. Response of osmium-based silicon dioxide microspheres to the passing shockwave.

two orders of magnitude shorter than those of the polystyrene PSBeads, and are a factor of 3 shorter than PSP on TLC. However, a significant decrease in signal-to-noise ratio was observed. As noted previously, it was necessary to use a layer that was tens to hundreds of microspheres thick in order to obtain enough emission intensity for a response time measurement. Even with multiple layers of microspheres, response times of tens of microseconds were measured. These times are on the order of the time constant of the instrument ($5.5 \mu\text{s}$), as discussed previously. It appears that oxygen diffusion through the matrix is no longer the limiting factor.

Similar to the osmium-based PSP, a significant decrease in sensitivity (24%–34% over 1 atm) as well as significant nonlinearity was observed in their responses. Ways to improve upon these parameters are currently being investigated.

IV. CONCLUSION AND FUTURE WORK

The response times of different PSPs and microspheres to passing shockwaves were measured. The PtTFPP:MAX and PtOEP:MAX films showed response times between 47.2 and $53.0 \mu\text{s}$, while the four Os:MAX films showed response times ranging between 37.6 and $58.9 \mu\text{s}$. The PtOEP-doped polystyrene PSBeads exhibited a response time of 3.15 ms, while the more porous, Os-doped silicon dioxide PSBeads demonstrated response times between 13.6 and $18.9 \mu\text{s}$. This is a factor of 3 faster than all of the PSPs tested. In conclusion, all samples except for the PtOEP-doped polystyrene PSBeads can be used towards unsteady flow studies.

TABLE VI. $1/e$ and 90% rise times of osmium-based silicon dioxide microspheres.

Sample	$1/e$ time (μs)	90% rise time (μs)
Os1 silica microspheres	15.2	38.7
Os2 silica microspheres	18.9	43.4
Os3 silica microspheres	17.6	42.9
Os4 silica microspheres	13.6	33.4

The Os-based PSBeads also showed an overall lower signal-to-noise ratio and sensitivity. Future work will therefore include improvements upon the synthesis of the Os-based pressure sensitive microspheres in an effort to produce microspheres with higher signal-to-noise ratio and sensitivity while maintaining their fast response times.

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