

Chemically Sensitive Polymer Coatings For SH-Surface Acoustic Wave Sensors for the Detection of Benzene in Water

Robert Lenisa
Marquette University

Recommended Citation

Lenisa, Robert, "Chemically Sensitive Polymer Coatings For SH-Surface Acoustic Wave Sensors for the Detection of Benzene in Water" (2013). *Master's Theses (2009 -)*. Paper 213.
http://epublications.marquette.edu/theses_open/213

CHEMICALLY SENSITIVE POLYMER COATINGS FOR SH-SURFACE
ACOUSTIC WAVE SENSORS FOR THE DETECTION OF BENZENE IN
WATER

by

Robert Lenisa, B.S.

A Thesis submitted to the Faculty of the Graduate School,
Marquette University,
In Partial Fulfillment of the Requirements for
the Degree of Master of Science

Milwaukee, Wisconsin

August 2013

ABSTRACT
CHEMICALLY SENSITIVE POLYMER COATINGS FOR SH-SURFACE
ACOUSTIC WAVE SENSORS FOR THE DETECTION OF BENZENE IN
WATER

Robert Lenisa, B.S.

Marquette University, 2013

Polymer-coated shear horizontal surface acoustic wave (SH-SAW) sensors are investigated for the detection of benzene in aqueous samples. The SH-SAW sensors using three-layer geometry have a single polymer sensing layer which absorbs the analyte and interacts with the surface wave. Several polymers are identified as potential improvements over current sensing films based on glass transition temperature and Hildebrand solubility parameter. The polymers investigated in this work include poly (methyl acrylate) (PMA), poly (butyl acrylate) (PBA), poly (ethylene co-vinyl acetate) (PEVA), bisphenol-A poly (dimethylsiloxane) (BPA PDMS), and bisphenol-A poly (hexamethyltrisiloxane) (BPA HMTS).

The polymers are spin coated on a lithium tantalate (LiTaO_3) SH-SAW dual delay-line device at thicknesses between $0.3 \mu\text{m}$ and $1.0 \mu\text{m}$. Each film's thickness is measured and the film is exposed to multiple concentrations of the aromatic hydrocarbons benzene, ethylbenzene, toluene, and xylenes (BTEX). The added mass and viscoelastic changes in the sensing layer result in a change in center frequency and acoustic loss of the device. The frequency change is measured and used to determine sensitivity of the coated sensor to each analyte.

BPA PDMS and BPA HMTS show larger sensitivities to each of the BTEX analytes than PBA, PMA, or PEVA. However, both BPA PDMS and BPA HMTS were observed to lose sensitivity during the aging process. It is shown that the aging effect on BPA HMTS can be mitigated by baking the film after it is applied to the device.

ACKNOWLEDGEMENTS

Robert Lenisa, B.S.

I would like to thank my family for their constant love and support throughout my educational journey. Your support has brought me to where I am, and I am grateful for all that you have given me.

I would also like to thank Dr. Fabien Josse and Dr. Florian Bender for the time and effort they have both invested in me. The direction, instruction, and guidance provided by these advisors have helped me along the path to completing this thesis. I would also like to thank Dr. Chung-Hoon Lee for his input and guidance throughout my time here at Marquette. Finally, I would like to thank Tian Newman for her support and for training me so effectively in the use of the Microsensor Research Lab.

Table of Contents

1	INTRODUCTION	1
1.1	Problem Statement	1
1.2	Background	2
1.3	Overview of Chemical Sensors	3
1.4	Overview of Acoustic Wave-Based Chemical Sensors	5
1.5	Overview of SH-SAW Sensors	7
1.6	Polymer Characteristics.....	9
1.7	Thesis Organization.....	11
2	THEORETICAL DISCUSSION	13
2.1	Introduction	13
2.2	SH-SAW Sensing Mechanism and Parameters.....	13
2.2.1	SH-SAW sensing mechanism.....	16
2.2.2	Polymer Viscoelasticity Effect	20
2.3	Relevant Polymer Properties.....	23
2.3.1	Polymer Viscoelastic States	23
2.3.2	Hildebrand Solubility Parameter.....	25
2.4	Sorption Process.....	26
2.5	Selection of Polymers.....	28
2.5.1	Glass transition temperature	28
2.5.2	Solubility parameter.....	30
2.6	Analysis of Polymers of Interest	31
2.6.1	Selected polymers	31
2.6.2	BPA co-polymers.....	31
3	EXPERIMENTAL PROCEDURE.....	33
3.1	Introduction	33
3.2	Equipment Used	33
3.3	Materials Used.....	39

3.4	Procedures	40
3.4.1	Introduction.....	40
3.4.2	Polymer Solution Preparation.....	40
3.4.3	BPA PDMS Synthesis.....	41
3.4.4	Device Cleaning and Preparation.....	42
3.4.5	Film Deposition	43
3.4.6	Thickness Measurement.....	44
3.4.7	Analyte Preparation	47
3.4.8	Response Measurement	49
3.4.9	Data Preparation.....	50
4	RESULTS AND DISCUSSION.....	51
4.1	Introduction	51
4.2	Results	53
4.2.1	Introduction.....	53
4.2.2	PMA, PBA, and PEVA.....	55
4.2.3	BPA PDMS, BPA HMTS.....	59
4.3	Conclusion.....	67
5	SUMMARY, CONCLUSION, AND FUTURE WORK	69
5.1	Summary	69
5.2	Conclusion.....	70
5.3	Future Work	72
	Bibliography	75

1 INTRODUCTION

1.1 Problem Statement

The goal of this thesis is to help develop an improved sensor for detecting benzene in water samples. Benzene is a chemical that occurs in nature and as a result of several industrial processes, and is a known carcinogen to humans. Current EPA limits for drinking wells require benzene concentration to not exceed 5 parts per billion (ppb) [1]. Methods in place for measuring benzene concentration in water in drinking wells, which require transporting a sample to a laboratory for analysis, are expensive and time consuming. This process can be improved by using an on-site chemical sensor. This sensor would be able to determine the concentration of benzene in the water without the cost and time of transporting the sample away from the source. Such a chemical sensor can be made by using a shear horizontal surface acoustic wave (SH-SAW) device with a thin chemically selective coating [2]. The sensors made with the current sensing polymer layers respond quickly but have a limit of detection of 200 ppb [3]. This thesis investigates several sensor coatings for the detection of smaller concentrations of benzene using SH-SAW device platforms.

1.2 Background

Benzene is a naturally occurring organic chemical. It is clear, colorless, volatile, and aromatic. According to the United States Department of Health and Human Services (HHS), benzene is mainly produced from petroleum. Benzene exists in crude oil, gasoline, cigarette smoke and is naturally produced by volcanoes and forest fires. [4]

The harmful effects of benzene on human health are well known. Benzene is potentially harmful through inhalation, consumption, and exposure to skin [1] [5]. Its volatility will cause it to be present in the air and therefore skin contact may also result in inhalation [4]. HHS has labeled benzene as a carcinogen which can increase the risk of leukemia.

There are several sources of benzene in our environment such as cigarette smoke and car exhaust, but the one of greatest concern is underground gasoline storage. Gasoline is stored underground in large tanks. These storage tanks may fail and leak gasoline into the environment [6]. Leaks are a great concern because benzene is a component of gasoline (up to 5% [7]), and a leak can cause benzene to enter the soil and groundwater. It is therefore necessary to monitor the area around gasoline storage tanks for benzene pollution. The EPA requires that the concentration of drinking water not exceed 5ppb (five parts of benzene per billion parts water) [1] [5]. This affects the water directly, but also accounts for the amount of benzene that can evaporate from the water during other uses such as cleaning or boiling water for cooking. A chemical sensor can be used to identify benzene contamination before it causes a health risk. [4]

1.3 Overview of Chemical Sensors

A chemical sensor is a device which measures the presence or concentration of a substance and converts that information into an electrical signal. Different sensor platforms receive a stimulus from the measured substance or parameter in different ways, such as measuring the change in a capacitance or resonant frequency. To detect benzene, a chemical sensor must measure a response based on the concentration of benzene present. [2]

A chemical sensor consists of a sensor platform, a sensing medium, and a data output system. The sensing medium interacts with the targeted chemical, or analyte, and changes in a manner that perturbs a physical parameter of the sensing platform [8]. For example, the sensing medium may change its electrical properties, such as dielectric constant or conductivity, in the presence of the analyte. The sensor platform is a device or system which responds to a change in the sensing medium. In some examples, the sensor platform applies a swept voltage to the sensing medium to measure the current. The data output system converts the measured property of the sensing platform into an output readable by an end user. This may be a computer system which records the input voltage and output current, and saves it to a hard disk in the form of a table and I-V curve. [8]

Important parameters used to characterize or classify a sensor include its sensitivity, selectivity, linearity, and environmental stability. To properly interpret the output of the sensor, a calibration curve is used [8]. The calibration curve is typically

plotted as an output parameter as a function of the input parameter. The calibration curve is used to determine the sensitivity and partial selectivity of a sensor. Sensitivity is described as how much the measured quantity changes for a given change in input perturbation. The sensitivity of a device is measured as the slope of the calibration curve [8]. A large sensitivity is beneficial because it results in an increased signal to noise ratio and reduces the limit of detection [8]. Selectivity refers to how much of the response is caused by the specifically targeted measured quantity. For chemical (e.g. benzene) sensing, it is more useful to discuss the partial selectivity of a sensor [9]. Partial selectivity in a chemical sensor refers to the relative magnitude of the sensor's response (and therefore sensitivity) for a particular analyte compared to that of a different analyte [10] [11].

The linearity of a sensor describes the closeness between the calibration curve and a straight line [8]. A sensor is linear if the sensitivity is constant within the measurement range of interest. In some cases, a non-linear sensor may exhibit hysteresis which prevents the system from accurately determining the measured quantity because the output depends on the values of the previous input [8]. One of the qualities investigated in this project is the reusability of a polymer film. A film may exhibit hysteresis if it does not fully release the absorbed analyte between exposures.

Environmental stability is particularly important because the environment in which this sensor will be used cannot be accurately controlled. For example, temperature is an environmental factor which affects chemical sensors, and the temperature cannot accurately be controlled on site. As will be discussed later, the viscoelastic properties of the polymer film are influenced by the temperature of the film [12]. A dual delay line

configuration is used in these experiments to compensate for changes in temperature by having a second film which does not respond to the analyte [11]. This film undergoes the same changes in temperature as the sensing layer and can be used to determine if changes in the sensing polymer are due to analyte absorption or temperature drift. [8]

1.4 Overview of Acoustic Wave-Based Chemical Sensors

Chemical sensors may use acoustic wave (AW) - based sensor platforms. In these devices, a wave is generated and transmitted through a medium. A chemically sensitive element alters the wave properties, and these changes are measured. Information about the wave can then be used to find the concentration of the target substance because the changes in the wave depend on the analyte concentration. Some AW sensors can operate in both gas (typically air) and liquid (typically aqueous solutions) environments. This work focuses on the use of a liquid phase sensor in an aqueous solution. Measuring the concentration of benzene in the headspace of a water sample requires additional energy to evaporate the benzene, or is potentially inaccurate. A liquid phase sensor is able to operate in direct contact with the sample and does not require evaporation, although it may have its own drawbacks which must be accommodated [13]. [2] [8]

There are many variations of AW sensors which involve different types of waves. The most common configurations used for sensor applications are the thickness-shear mode (TSM), surface acoustic wave (SAW), acoustic plate mode (APM), and flexural plate wave (FPW) device [2] [10]. Each configuration is different from the others in either the type of the wave or the method in which the wave is generated.

These different device configurations can be divided into configurations that use bulk waves and configurations that use surface waves. A bulk wave will not be as sensitive to the changes in the film because the wave energy is distributed throughout the substrate. TSM, FPW, APM, and SAW devices are all acoustic wave devices, but the SAW device is the most promising for this work. This is because the SAW energy is largely confined at the surface of the crystal and the operating frequency is high. This will be further explained in chapter 2. [2]

The acoustic wave sensor platforms require a piezoelectric substrate in order to function. Piezoelectric materials exhibit the piezoelectric effect, which is a transduction of electrical potential and mechanical stress. A wave is excited when an electrical field inside the substrate is oscillated. The wave is then measured at the output where the stress is converted back into an alternating voltage [2]. Commonly used piezoelectric materials are quartz (SiO_2), lithium niobate (LiNbO_3), and lithium tantalate (LiTaO_3) [2] [10].

Surface waves used in a SAW device can have particle displacement in three directions – shear horizontal, shear vertical, and longitudinal. Shear horizontal motion is perpendicular to the direction of propagation of the wave and in the plane of the surface. Shear vertical motion is perpendicular to the direction of propagation, but is normal to the surface on which the wave travels. Longitudinal motion is in the direction of propagation, and is also known as compression. Shear vertical motion is not effective for liquid phase sensors because the surface particles lose energy when they displace the liquid, so it is important to minimize the amount of shear vertical motion the wave has.

1.5 Overview of SH-SAW Sensors

Shear horizontal surface acoustic wave (SH-SAW) sensors are a specific type of sensor platform which can be used in a chemical sensor. SAW sensors, sometimes called Rayleigh wave sensors, operate largely with shear vertical displacement with a small longitudinal component, but SH-SAW sensors are made with a specific crystal structure that is rotated so that it does not support the shear vertical component of the surface wave. The wave in this crystal will have both longitudinal and shear horizontal components, but the longitudinal motion will be negligible compared to the shear horizontal component. An SH-SAW device will therefore be preferred over devices which use shear vertical surface waves for sensors which operate in liquid phase and use a chemically sensitive film. [2] [10]

The wave's velocity and amplitude are affected by the mechanical properties of the medium in which the wave travels. If the mechanical properties change, the velocity (which is related to the frequency) and amplitude (which is related to the loss) of the wave will also be altered. By measuring the change in center frequency and loss, information regarding changes in the medium probed by the wave can be gathered [10] [11]. In an SH-SAW sensor there is a chemically sensitive film on the surface of the device. As this film interacts with the target analyte, its physical properties change and this change causes a shift in loss and the wave's center frequency. The amount of analyte present in the environment can be determined by using the calculated changes in physical properties. [2]

Most SH-SAW devices are comprised of a piezoelectric substrate with input and output interdigitated transducers (IDTs) arranged in a delay line configuration. The IDTs are electrode patterns on the surface of the piezoelectric substrate. When a voltage is applied between the two sides of the IDTs, an electric field is coupled between the neighboring digits. This field creates a mechanical strain in the piezoelectric substrate. Alternating the applied voltage excites a shear horizontal wave which propagates from the IDTs. The shear horizontal wave penetrates deeper into the substrate than a shear vertical wave, but the chemically sensitive film acts as a guiding layer which traps the energy of the wave close to the surface. A thin gold layer is also used to guide the wave to the device surface. This is beneficial because more wave energy will be confined within the sensing layer [11] [14]. The frequency is defined by the velocity of the wave and spacing of the IDT fingers using equation (1).

$$f = \frac{v}{P} \quad (1)$$

In equation (1), f is the frequency of the wave, v is the velocity of the wave, and P is the periodicity of the electrode fingers of the IDTs. The wave travels along the delay line and then is received by the opposite IDT, and is converted back to an alternating voltage. At first approximation, any changes in frequency can be attributed to a change in wave velocity due to the sensing layer, and change in amplitude can also be attributed to changes in the elastic properties of the sensing layer. [10] [11]

1.6 Polymer Characteristics

The sensing layer in the SH-SAW devices discussed in this thesis is made of a thin film of polymer material. A polymer has a chain-like structure on an atomic scale where several repeating groups of material are attached to form one large molecule [11]. The polymer material has several important characteristics which must be considered when using it as a sensing layer on an SH-SAW device. [10] [11] A polymer which undergoes shear deformation can be characterized by its complex shear modulus, G [15] [12]. The shear modulus is affected by both the intramolecular and intermolecular forces holding the material together (such as covalent bonding or hydrogen bonding) and the molecular mass of the polymer. [11] G is defined mathematically as the sum of the storage and loss moduli, G' and G'' respectively, in the material by equation (2).

$$G = G' + jG'' \quad (2)$$

A polymer is categorized as glassy, rubbery (viscoelastic), or liquid (amorphous, or viscous) depending on the relative values of G' and G'' . A polymer is glassy when $G' \approx 10^9 \text{ Pa}$ and $G'' \ll G'$ and rubbery if $G' \leq 10^7 \text{ Pa}$ and $G'' < G'$ [16]. A glassy polymer is hard and has a high storage and low loss. As heat is applied to raise the temperature of the polymer above its glass transition temperature, T_g , it undergoes a change into a rubbery state. A rubbery polymer has more loss and less storage than a glassy one. As temperature exceeds the melting temperature, the polymer becomes liquid and G' tends to 0, and G is entirely defined by G'' [11] [12]. Fig. 1.1 shows G' as it changes with temperature.

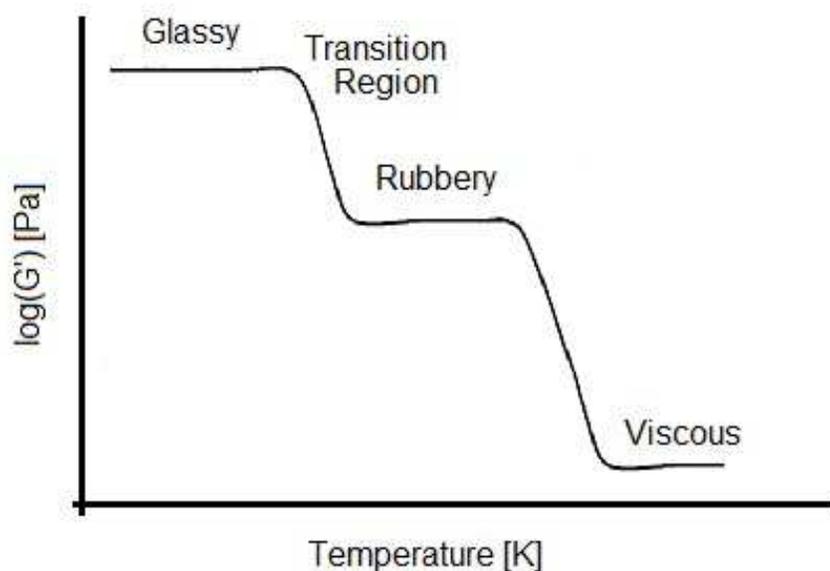


Figure 1.1 G' as a function of temperature

A sensing layer film made with polymer will ideally operate within that polymer's glassy transition region because the film will be relaxed enough to allow the analyte to penetrate without damping the acoustic wave. When the polymer is glassy, the molecular chains are closely locked together and there is no excess space for analyte. As it enters the transition region, the chains separate and there is space for the absorption of analyte. If the polymer becomes rubbery, however, it will damp the surface wave too heavily because of the relatively large loss modulus. Experimental testing and previous work have demonstrated that the glass transition temperature should be approximately -20°C so that the film is in or slightly above the transition region at room temperature. [11]

Another characteristic of a polymer – and any molecule – is its solubility. In this application, it is desirable to have a sensing polymer which is miscible with benzene. The Hildebrand Solubility Parameter is a value defined by the cohesive energy density of a molecule [17]. The value of this parameter is influenced by many properties of the molecule such as polarity and molecular mass, and materials with similar values will be miscible. This relationship will be discussed in Chapter 2. For this sensing application, it is important that the sensing layer have a solubility parameter which is close to that of benzene. If the solubility parameter of a polymer is close to that of benzene and the polymer is not glassy, the benzene molecules can be absorbed into the film. [17]

1.7 Thesis Organization

This thesis is presented in 5 chapters and includes an abstract. Chapter 1 is an introduction to the problem and the current state of sensors. The motivation is provided along with a qualitative description of the current methods of measuring benzene. Chapter 2 gives a review of how the SH-SAW device functions and how it interacts with the polymer coating. This chapter also discusses the sorption process which the film undergoes when it is exposed to analyte. The changes which result from this exposure are used to explain how the polymers of interest to this project were selected and to introduce which coatings were investigated. Chapter 3 presents the experimental procedure. It includes a description of the devices and materials used along with a description of how the devices were prepared and tested. Chapter 4 presents the results of the research. The results of the measurements are presented along with a discussion of

their significance. The discussion evaluates the sensitivity and limit of detection of the polymer coatings of interest. Chapter 5 summarizes the results of the work done for this thesis. Some particular polymers are identified for their sensitivity and limit of detection, and potential future work is discussed.

2 THEORETICAL DISCUSSION

2.1 Introduction

This chapter discusses the physical processes which dictate the function of an SH-SAW device coated with a chemical sensing layer and explains the selection of the polymers investigated in this work. The surface acoustic wave sensing platform is theoretically described with an emphasis on the shear horizontal wave. Important parameters of polymer coatings are defined here, and their relevance to the sensing application is discussed. The process of analyte sorption by a chemically sensitive film is also explained and used to define criteria for the selection of the polymers.

2.2 SH-SAW Sensing Mechanism and Parameters

Guided shear horizontal surface acoustic wave sensors with a chemically sensitive layer are effective chemical sensors in the liquid phase [11] [15] [16]. A SAW with shear vertical particle displacement will lose energy by radiating compressional waves into the liquid environment, but SH-SAW devices do not have this disadvantage [2]. SH-SAW particle displacement is mostly in the plane of the device surface and not perpendicular to the surface. This leaves viscous loss as the sole significant mechanism of attenuation of the acoustic wave by the liquid environment. A shear horizontal wave penetrates deeper

into the substrate than a shear vertical wave [2], but the chemically sensitive polymer layer acts as a waveguide to trap the acoustic energy closer to the surface, making the guided wave more sensitive to surface perturbations [18]. The wave is also confined to the surface of the device by the metalized delay line. The gold layer has a much slower wave velocity than the LiTaO_3 substrate, and will therefore cause the acoustic wave to be confined to the surface of the substrate-polymer interface [19].

The profile of an SH-SAW device is shown in Fig. 2.1. The polymer has thickness h and the substrate and liquid layers are considered to be semi-infinite. The applications discussed in this thesis only include the detection of benzene and similar compounds dissolved in water, so the liquid layer is assumed to be a low viscosity Newtonian fluid. The analyte which is dissolved in the liquid layer will absorb into the polymer layer and cause the film to swell. SH-SAW devices have previously used a four-layer geometry; the four-layer model uses a rigid waveguide layer between the chemically sensitive polymer and the piezoelectric substrate. This system has less loss and is more stable than a 3-layer model, but it also has a smaller sensitivity [20].

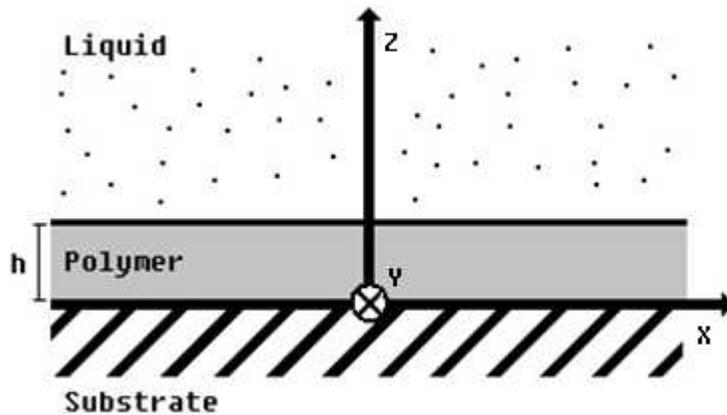


Figure 2.1 SH-SAW Device profile with three layer geometry

SH-SAW devices function through the use of a piezoelectric substrate, or the piezoelectric effect [2]. The piezoelectric effect is a reversible process by which a material converts mechanical stress into electric potential. Commonly used piezoelectric materials are quartz (SiO_2), lithium tantalate (LiTaO_3), and lithium niobate (LiNbO_3). All of the devices in this work are made using a lithium tantalate substrate because it has larger piezoelectric and dielectric constants than quartz and a smaller temperature coefficient of delay than lithium niobate [21]. More of the energy of the electric fields will exist within the lithium tantalate substrate because of the difference in dielectric constant between the lithium tantalate substrate and polymer and liquid layers. [10] [11] The substrate used is 36° rotated Y-cut LiTaO_3 . The anisotropic structure of the crystal allows the surface wave to propagate in the X direction with particle motion in the Y direction.

Interdigitated transducers are used to create the electric field which can excite the SAW. A voltage applied across the transducer will create an electric field which penetrates the substrate and causes the piezoelectric material to become stressed. The voltage can be alternated to excite an acoustic wave on the substrate's surface. [2] [16]

2.2.1 SH-SAW sensing mechanism

The 3-layer model for the SH-SAW sensor depicted in Fig. 2.1 shows that the sensing polymer layer has contact with both the substrate and the liquid environment. Because the sensing layer traps the wave energy at the surface of the substrate, the acoustic wave is influenced by the properties of both the polymer and substrate. The liquid carries the analyte molecules which are absorbed into the bulk of the sensing layer through a diffusion process. The properties of the sensing layer change with the addition of the analyte and this in turn alters the acoustic wave's velocity and attenuation. Velocity can be related to center frequency and attenuation can be related to loss, which can both be directly measured to detect analyte sorption by the sensor. [16] [11]

In general, an acoustic wave can have particle displacement in any direction. The particle displacement for a shear horizontal surface acoustic wave, however, is only in the y direction. The particle displacement for such a wave is a function only of x , z , and time, given by [2]

$$u_y(x, z, t) = u_y(z, t)e^{j\omega t - \gamma x} \quad (3)$$

where ω is the angular frequency ($2\pi f$) and γ is the complex propagation coefficient comprised of attenuation and wave number (α and k) defined as [2]

$$\gamma = \alpha + jk = \alpha + j \frac{\omega}{v}. \quad (4)$$

Measured changes in wave propagation characteristics at a given frequency are therefore only a function of the change in the propagation coefficient, γ . Written normalized to the starting frequency and velocity, this is

$$\frac{\Delta\gamma}{k_0} = \frac{\Delta\alpha}{k_0} - j \frac{\Delta v}{v_0}. \quad (5)$$

A network analyzer can be used to measure the frequency spectrum of the SH-SAW device. The relationship

$$f = \frac{v}{P}, \quad (6)$$

where P is the periodicity of the IDT, is used to find the operating frequency of the SH-SAW device. If we assume that the phase velocity is equal to the group velocity and that P is constant for a given device, the normalized change in frequency is equal to the normalized change in wave velocity as

$$\frac{\Delta f}{f} = \frac{\Delta v}{v}. \quad (7)$$

This relationship means that any change in velocity due to changes in the film will also result in a change in frequency.

Changes in phase velocity and attenuation for an SH-SAW device are due to changes in mass (m), viscoelastic constant (c), dielectric constant (ϵ), conductivity (σ), temperature (T), and pressure (P). For small perturbations, the total change in velocity

and attenuation can therefore be written as a sum of partial derivatives with respect to these parameters as [2] [11]

$$\Delta v = \frac{\delta v}{\delta m} \Delta m + \frac{\delta v}{\delta c} \Delta c + \frac{\delta v}{\delta \varepsilon} \Delta \varepsilon + \frac{\delta v}{\delta \sigma} \Delta \sigma + \frac{\delta v}{\delta T} \Delta T + \frac{\delta v}{\delta P} \Delta P, \quad (8)$$

$$\Delta \alpha = \frac{\delta \alpha}{\delta c} \Delta c + \frac{\delta \alpha}{\delta \varepsilon} \Delta \varepsilon + \frac{\delta \alpha}{\delta \sigma} \Delta \sigma + \frac{\delta \alpha}{\delta T} \Delta T + \frac{\delta \alpha}{\delta P} \Delta P. \quad (9)$$

Note that in equation (9) the change in attenuation is not a function of mass accumulation. [10] [16]

The experimental setup used in this thesis was selected such that the effects of dielectric constant, conductivity, temperature, and pressure are all reduced or removed [11]. A metalized delay line removes acoustoelectric interactions so that $\Delta \varepsilon$ and $\Delta \sigma$ are zero [11]. By controlling the ambient temperature to limit variations in temperature and using a dual delay line device, a differential measurement can be established to eliminate the effects of Δt and ΔP [11]. By removing these terms from equations (8) and (9), we can simplify them to

$$\Delta v = \frac{\delta v}{\delta c} \Delta c + \frac{\delta v}{\delta m} \Delta m, \quad (10)$$

$$\Delta \alpha = \frac{\delta \alpha}{\delta c} \Delta c. \quad (11)$$

This means that the change in attenuation is due only to change in the viscoelastic properties of the sensing film. The change in wave velocity depends on changes in both viscoelastic constant and mass loading. As the film is deformed by the wave, energy is

stored and dissipated causing the attenuation and velocity of the wave to change. Mass loading is the result of mass entering the sensing film and changing the density and thickness. The SAW velocity changes proportionally to the mass density of the film [2]. The mass loading does not change the attenuation, as seen in equations (9) and (11). [10]

Changes in the viscoelastic properties of the polymer film (written previously as Δc) are the result of the material's modulus changing. A modulus in this context is the amount of stress caused by one unit of strain (expressed in dyn/cm^2). The particle motion of an SH-SAW is primarily in the shear direction, and the shear modulus, G , is what defines how a material behaves under shear deformation. G is a complex term written as [10] [12]

$$G = G' + jG'', \quad (12)$$

where G' is the storage modulus and G'' is the loss modulus. The storage modulus relates to energy stored and released as the film displacement changes with the oscillation of the acoustic wave. The loss modulus relates to energy that is lost, usually to heat, by the deformation of the material.

Assuming that the shear modulus is the only component of the viscoelastic changes, it is possible to substitute G' and G'' into equations (10) and (11) so that they can be rewritten as functions of the parameters that are changing – the mass loading and moduli – as [11] [16]

$$\Delta f = f(\Delta m, \Delta G', \Delta G''), \quad (13)$$

$$\Delta\alpha = f(\Delta G', \Delta G'').$$

(14)

The network analyzer used in this experimental work measures insertion loss instead of attenuation. Insertion loss is the amount of energy lost when a wave is sent across the entire device, as opposed to the attenuation which is loss per unit length. The insertion loss is directly proportional to the attenuation by [11]

$$\frac{\Delta\alpha}{k} = \frac{\Delta L}{54.6} N,$$

(15)

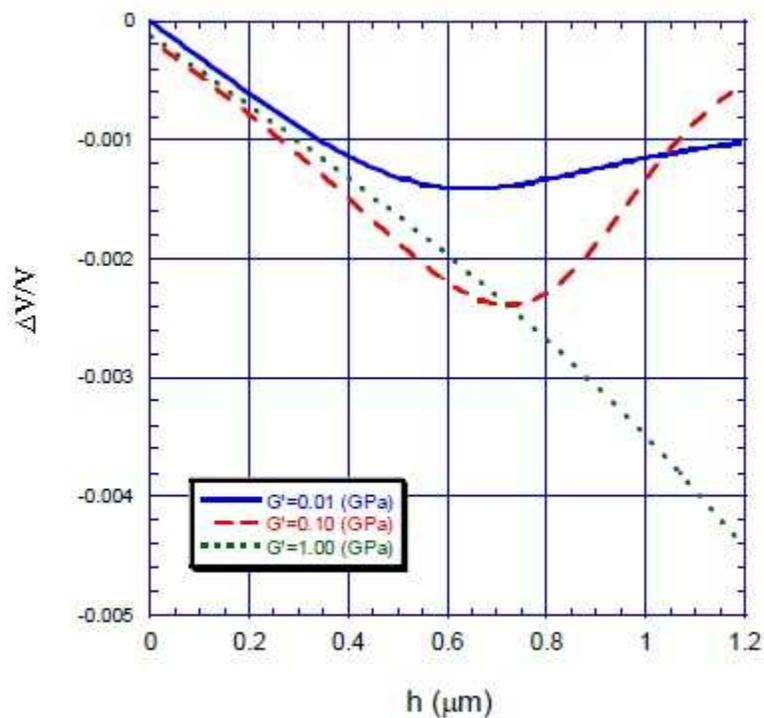
where L is the insertion loss and N is the length of the transmission line in units of wavelengths. Because all of the testing done uses the same size device and wavelength (and the change in insertion loss can be directly related to a change in attenuation as shown in (15)), the measured insertion loss can be used interchangeably with the calculated attenuation.

2.2.2 Polymer Viscoelasticity Effect

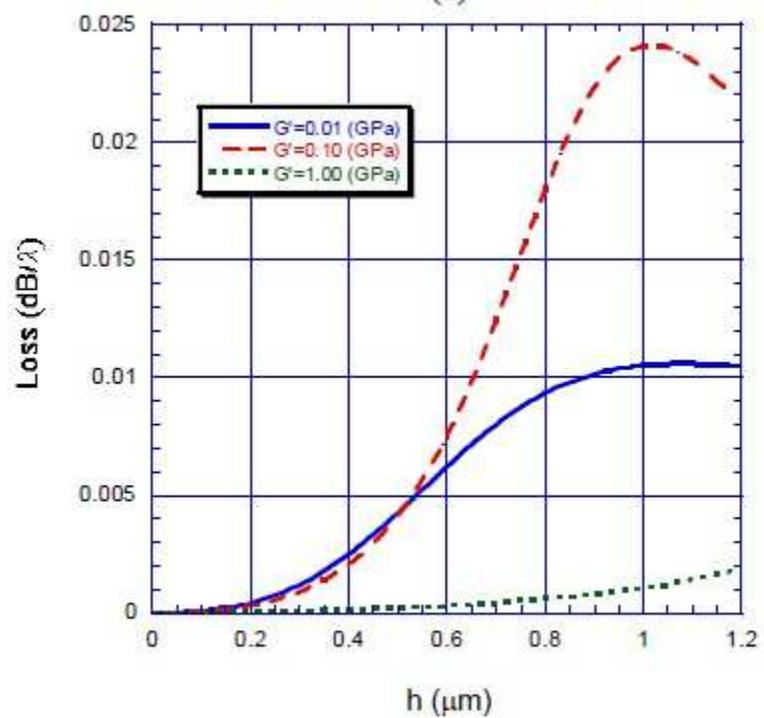
The polymer-substrate interface is assumed to show no slip, but the particle displacement may vary across the thickness of the polymer. The polymer near the substrate will move synchronously with the substrate, but there may be a phase lag in the part of polymer that is farther away from the substrate. This phase lag increases if the polymer is more rubbery (or viscous). If the polymer/liquid interface moves in phase, or less than $\pi/2$ out of phase, with the substrate then the film is acoustically thin. As the

film thickness increases, the phase lag increases. A film with a phase lag equal to or greater than $\pi/2$ is acoustically thick [22]. The film will resonate constructively with a phase lag of exactly $\pi/2$, and it will experience destructive interference if the phase lags by more than $\pi/2$. The exact thickness range where the film behaves as acoustically thin is dependent on the shear modulus of the film and the temperature [22]. [16] [23]

Typical SH-SAW sensor responses will be dominated by the changes in mass loading and viscoelastic properties [2]. As the sensing film absorbs analyte, however, its thickness and viscoelastic properties change [24]. This will alter the amount of phase lag at the liquid-polymer interface and will therefore alter the fractional change in velocity, which results in a frequency shift, and loss. It has been shown that some films may exhibit such a pronounced resonance effect that the observed frequency shift due to the absorption of analyte will be a positive change [23]. This is demonstrated in chapter 4 where PBA and BPA PDMS are observed to give a positive frequency shift.



(a)



(b)

Figure 2.2 The fractional change in velocity and change in loss as a function of film thickness for several different values of G' , with $G''=0.1\text{GPa}$ [16]

Figs. 2.2 (a) and (b) show how the fractional change in velocity and change in loss is affected by film thickness for several different values of storage modulus, G' . These figures demonstrate how a sensor's frequency may experience a positive frequency shift under certain conditions. The film's thickness and shear modulus both change during analyte sorption, and the loss and velocity will both change. For a G' of 0.10 GPa, the fractional change in velocity has a positive slope as film thickness increases from 0.8 μm to 1.0 μm . G' is decreased as the polymer absorbs analyte, which also increases the fractional change in velocity. Both of these effects combined may cause a positive frequency shift instead of the negative frequency shift expected for pure mass loading in acoustically thin films.

2.3 Relevant Polymer Properties

2.3.1 *Polymer Viscoelastic States*

As discussed earlier, the shear-horizontal particle displacement of the sensing layer of an SH-SAW sensor is influenced by the sensing polymer's shear modulus, G . Shear modulus varies with temperature and material. There are three states in which a polymer may exist – glassy, rubbery, and viscous. A glassy polymer has a storage modulus (G') which is much larger than its loss modulus (G'') which means that the material is rigid and an acoustic wave travelling through it will not lose as much energy as in a rubbery polymer. A rubbery polymer has a G' which is smaller than that of a glassy polymer, meaning that the same amount of stress will produce a larger strain in a rubbery polymer than it would in a glassy one. The trend of G' vs. temperature was

shown in Fig. 1.1. A viscous polymer is generally not a useful sensing material because it does not support the propagation of acoustic shear waves and will therefore strongly attenuate the wave. [23]

The G' and G'' of a polymer change slightly with small variations in temperature when in the glassy or rubbery state, and the change is even larger in the transition region. In the bounds of this transition region is a specific temperature known as the glass transition temperature, T_g . One way to determine the value of the glass transition temperature is by using its relationship with a polymer's thermal coefficient of expansion. The specific volume of a polymer varies linearly with respect to temperature at a rate known as the thermal coefficient of expansion. This coefficient changes with a discontinuity at the glass transition temperature. An experiment can be conducted using the measured volume of a polymer to determine the value of that polymer's T_g . For the polymers used in this thesis, T_g has been determined by either the manufacturer or previous research at Marquette University's Microsensor Laboratory. [12]

The state of a polymer affects its use as a sensing layer of an SH-SAW sensor in three ways: the temperature stability of the sensor varies with the polymer state, the insertion loss depends on the value of G'' , and the absorption of the analyte into the polymer film is affected by G' . As mentioned in section 2.2, the measured change in attenuation and velocity are influenced by the change in G' and G'' . If the polymer is used at a temperature in the transition region between glassy and rubbery states, G' and G'' vary rapidly with temperature. It is therefore important that the temperature be held constant, even with a dual delay line setup. The polymer state at room temperature influences the amount of insertion loss which is caused by the sensing film. A rubbery

polymer will have a relatively large G'' value and will dissipate energy through friction as heat. A device with high insertion loss will have a smaller measured signal and this leads to a smaller signal to noise ratio. A glassy polymer will have a large G' and be rigid. During the sorption process, the target analyte is absorbed into the polymer film. A polymer with a large G' will require more energy to move (because a large G' indicates more stress required per unit of strain) to make room on a molecular level for the analyte. A polymer's ability to absorb analyte is therefore dependent on the value of G' and a rubbery polymer will absorb more analyte than a glassy one. Because the state of a polymer affects its use as a sensing layer in so many ways, it is important to consider the polymer's T_g when selecting a film for a sensing application. Section 2.5 looks at these considerations in more detail. [12]

2.3.2 Hildebrand Solubility Parameter

A solubility parameter can be used to make predictions about the solubility of one substance in another. Two different materials with similar values will often be miscible or soluble. The Hildebrand solubility parameter is one such parameter defined by the square root of the cohesive energy density [17]. The cohesive energy density is defined as the amount of energy needed to separate the molecules of one mole of a substance by an infinite distance. The cohesive energy density can be written as the amount of energy needed to boil the liquid to a gas (heat of vaporization, or $\Delta H_v - RT$) divided by its molecular volume (V_m). Equation (16) defines the Hildebrand solubility parameter, (δ). [17]

$$\delta = \sqrt{\frac{\Delta H_v - RT}{V_m}} \quad (16)$$

The solubility is affected by the inter- and intra-molecular forces present in the material, including dipole-dipole interaction and hydrogen bonding. Different molecules with similar polarity will usually have similar solubility parameters.

The solubility parameter is important when discussing sensing polymers for SAW-based sensors because the sensing layer must absorb the target analyte. When dealing with the specific application of benzene sensing in an aqueous environment, the sensing layer should be miscible with benzene and should not dissolve in water. Part of the intent of this thesis is determining the significance of the solubility parameter when selecting a polymer for benzene sensing.

2.4 Sorption Process

During analyte detection, the analyte is absorbed into the sensing polymer. The sensing polymer has a finite volume, with a finite amount of free space which the absorbed analyte can occupy. The concentration of analyte in the polymer at equilibrium (C_p) is the mass of sorbed analyte at equilibrium (m_a) divided by the volume of the polymer film (V_s). The amount of absorption of the analyte into the film can be expressed by a partition coefficient (K_p), the ratio of the concentration of analyte in the environment (C_a) and concentration of analyte in the polymer at equilibrium, and it can be written as: [11] [24]

$$K_p = \frac{C_p}{C_a} = \frac{m_a/V_s}{C_a} . \quad (17)$$

Different combinations of sensing polymer and analyte will have different partition coefficients, and it is therefore beneficial to select a polymer which shows a large partition coefficient for benzene. A sensing polymer layer with a large K_p will experience greater sorption than a different sensing layer with the same volume and a smaller K_p [7]. For weakly interacting polymer/analyte combinations (physisorption), the kinetics of the sorption process is dominated by the diffusion of the analyte into the sensing polymer [25]. The rate of absorption decreases as the concentration of analyte in the polymer approaches saturation, until equilibrium is reached. This means that the concentration of the analyte in the sensing film will show exponential behavior as it approaches equilibrium. Note that previous work in this field utilizes the partition coefficient to determine the concentration of one or more analytes with a gas sensor [13] [26]. The partition coefficient is presented here as an explanation for the exponential response observed by the sensor, and not as a method for determining concentration. [10] [23]

As discussed in section 2.2, the experimental procedure used in this work will measure the insertion loss and resonant frequency of the SH-SAW device. The insertion loss and frequency of the device will also follow an exponential curve in response to a step change in ambient concentration because these values, for small concentrations, both relate linearly to the concentration of analyte in the film. The trend of the device response contains information about both time constant and magnitude, and these two

parameters can be used to identify analyte species as well as concentration. The work presented in this thesis focuses primarily on the concentration of benzene present, so the species identification is not evaluated. Therefore, the magnitude of the response at saturation is evaluated in greater detail than the response time.

2.5 Selection of Polymers

2.5.1 *Glass transition temperature*

The relative values of G' and G'' determine both a polymer's ability to absorb analyte and the amount of energy dissipated by an acoustic wave. The polymer state (i.e. glassy, rubbery) is therefore important when selecting a polymer for the sensing layer of an SH-SAW device because it indicates the relative values of G' and G'' . A rubbery sensing polymer will have a smaller G' than a glassy polymer, causing it to deform more easily and accept analyte molecules into its free volume. A rubbery sensing polymer will have a larger G'' than a glassy one, so it will dissipate more acoustic energy and thus increase the insertion loss of the sensor. An ideal sensing layer will be rubbery enough to absorb the analyte, yet glassy enough to support the acoustic wave with minimum acoustic attenuation. A polymer in the transition state may have these properties, and some rubbery polymers may have a small enough loss to be usable as well.

The state of a single polymer will change with temperature, so a single temperature (or a small range) must be chosen. The selected polymers should be compared based on their state in the temperature range of 0° to 25° C because the practical use intended for these films is benzene detection in ground water supplies [27].

The transition temperature, T_g , is approximately the middle of the transition region, so the polymer will always be in the transition or rubbery region if T_g is below 0°C . Reference [28] also explains that the operating frequency of a SAW sensor will affect the observed T_g . A lower T_g means that the polymer is more rubbery at the tested temperature. Table 2.1 shows the T_g values of some polymers which are known to be effective sensing layers for the detection of benzene, and includes the polymers tested in this work.

Table 2.1 Polymer Solubility and Transition Temperature Values [29] [11]

Polymer	Hildebrand Solubility Parameter, δ [$\text{MPa}^{1/2}$]	Glass Transition Temperature, T_g [$^\circ\text{C}$]
Poly (epichlorohydrin) (PECH)	21.6	-22
Poly (isobutylene) (PIB)	18	-64
Poly (ethyl acrylate) (PEA)	18.6	-23
Polystyrene	18.5	100
Poly (methyl acrylate) (PMA)	19.1	9
Poly (butyl acrylate) (PBA)	19.8	-49
Poly (ethylene co-vinyl acetate) (PEVA, Elvax 40W)	18.6	-28.8
Bisphenol-A poly (dimethylsiloxane) (BPA PDMS)		-54
Bisphenol-A poly (hexamethyltrisiloxane) (BPA HMTS)		4.95

A polymer like poly (isobutylene) (PIB) is rubbery at room temperature because the polymer is far from the glassy state. Poly (ethyl acetate) (PEA) shows lower acoustic attenuation than PIB at room temperature because at this temperature, PEA is just slightly above its glass transition temperature. These polymers are known to be effective for sensing benzene in water [30]. The T_g values for these two polymers is used to establish a range for acceptable T_g values – only polymers which are more glassy than PIB but not

substantially more glassy than PEA at room temperature will be considered for this thesis. The optimal film thickness will depend on the shear modulus (which, as discussed previously, is a function of T_g and temperature) of the polymer [16] [31]. A rubbery polymer (one with a low T_g) will become acoustically thick at a smaller thickness than a glassy polymer [22].

2.5.2 Solubility parameter

The effect of the solubility parameter is investigated by this work. In order for the sensing layer to function, it must absorb the target analyte. Sensing polymers which are miscible with benzene will be able to absorb more of the benzene in their free volume, so polymers with a solubility parameter close to that of benzene were chosen for this work. Table 2.1 also shows the Hildebrand solubility parameters of the selected polymers as well as some other polymers which are known to absorb benzene. Benzene itself has a value of $18.5 \text{ MPa}^{1/2}$ [29]. Some polymers which are known to be effective at benzene detection have a solubility value which is not equal to that of benzene. This shows that the value does not need to be met exactly, but it is expected to have strong influence on the performance of the sensing layer.

The acceptable range of values for the solubility parameter is difficult to quantify because there are other properties which must be considered. Some materials have the same solubility parameter as benzene but would never function as a sensing layer for an SH-SAW device because they are too rubbery or glassy at the operating temperature. Polystyrene, for example, has the same solubility parameter as benzene, but it has a T_g value of 100°C and will not absorb enough analyte to be an effective sensing layer. The

selected polymers were first chosen from those whose transition temperature is in the acceptable range, and then a subset of three polymers which all have solubility parameters within a small range of benzene were selected for investigation.

2.6 Analysis of Polymers of Interest

2.6.1 Selected polymers

Previous studies have shown that PIB, PECH, and PEA are all effective sensing layers for the detection of benzene in liquid form. PMA, PBA, and PEVA were all selected because they have similar or better qualities to these known materials. Table 2.1 shows the values of T_g and solubility parameter for each of these polymers. PMA, PBA, and PEA are all polymers made from similar monomers, with each monomer having either a methyl, butyl, or ethyl group but sharing similar functional (acrylate) groups. Because PEA can make an effective sensing layer for an SH-SAW sensor, PBA and PMA may give greater results because they also have transition temperatures slightly below the operating temperature and a δ value close to benzene. PEVA was selected because it has a solubility parameter of $18.6 \text{ MPa}^{1/2}$, which is almost equal to that of benzene, and a glass transition temperature which is in the range of the known sensing polymers.

2.6.2 BPA co-polymers

Two additional polymers were also selected for this work. The BPA co-polymers bisphenol-A poly (dimethylsiloxane) (BPA PDMS) and bisphenol-A

poly (hexamethyltrisiloxane) (BPA HMTS) have been used in other work at Marquette University and it has been shown that these materials make for effective sensing layers for SH-SAW sensors for the detection of organophosphates [32] [11] [23]. Because it is known that these sensing layers can support acoustic waves with acceptable loss and are able to absorb analyte molecules, they are of interest to this work with benzene detection. These co-polymers have a porous inorganic backbone (the PDMS or HMTS) with functional organic sites (the BPA). Grate et al. uses BSP3, a polymer similar to BPA HMTS, for gas-phase detection of toluene as well as other gases [33]. For toluene, he observed high sensitivity as well as a fast response. Toluene, which is one of the BTEX analytes, contains a benzene ring and has a solubility parameter similar to that of benzene. It is therefore reasonable to expect BSP3, and therefore BPA PDMS and BPA HMTS, to also absorb benzene. Because this study has shown that polymers similar to BPA PDMS and BPA HMTS can absorb toluene, it is expected that BPA PDMS and BPA HMTS can be used to make effective sensing layers for the detection of benzene. PDMS and HMTS by themselves are too rubbery at room temperature and will not support the acoustic wave. It is necessary to combine these polymers with BPA through the hydrosilylation process to make the sensing layer glassier and reduce the insertion loss of the sensor [11]. [32]

3 EXPERIMENTAL PROCEDURE

3.1 Introduction

This chapter contains a description of the materials, equipment, and procedures used when gathering the data for this project. Information about the selected polymers was gathered through a specific procedure which measures the relative changes in mass uptake and viscoelastic properties due to exposure to select analytes. The polymer film is first prepared by dissolving the polymer in a solvent for a known concentration. This solution is used to spin coat a thin film on an SH-SAW device. The device is exposed to both deionized water and solutions of benzene and other aromatic analytes while being measured periodically by a network analyzer.

3.2 Equipment Used

The spin coater used is a Specialty Coating System Model P6024. The spin coater functions by applying a vacuum to the back side of a device to hold it in place, and then spinning it rapidly following a preset routine. The routine can be configured to select spin speed, ramp time, spin time, and ramp down time. This device is used to create a reproducible film thickness. The thickness of a film deposited through spin coating will vary based on the parameters of the solution (viscosity, molecular mass,

solvent evaporation rate) and the spin process (spin time, spin speed) [34] [11]. Having a spin coater with configurable routines allows convenient and accurate control over the final film thickness.

The profilometer used is a KLA-Tencor Alpha-Step IQ. A profilometer uses a microscopic tip to measure the height of a surface step. The profilometer moves the sample and probes the surface to record the profile of a sample [35]. This method of direct measurement is potentially destructive to the film because the probe may scratch the surface of the sample. Because of this restriction, the samples must be prepared on a glass slide and not an SH-SAW device. Additional consideration must be taken for particularly soft films which may be damaged by the profilometer probe tip. This will be explained in section 3.4.6.

An ellipsometer can measure the thickness of a film without making physical contact with the surface. This removes the risk of damaging the film with a probe. The ellipsometer used is a Gaertner Scientific Corporation L2WLSE544. An ellipsometer functions by shining a laser of particular wavelength at the surface of the sample at an oblique angle. The laser is transmitted through the film and substrate and is reflected into a receiver. The interface between the thin film and substrate, and the boundary between the film and air, will both reflect part of the incident laser beam. For thin films, the two reflected beams will overlap and the ellipsometer records the effective polarity of the reflected laser beam [36]. The receiver records information about the transmitted light and uses software to analyze the sample. This ellipsometer uses two wavelengths of light to get enough independent variables to determine both the refractive index and thickness of the thin polymer film [36].

A vector network analyzer is used to measure the signal that is transmitted through an SH-SAW device at multiple frequencies. The network analyzers used in this investigation are Agilent 8753 ES and E5061B. This instrument is used to measure both the real-time response of the device in the presence of analyte as well as characterizing the device in a steady state. For experiments that occur over time, the network analyzer is connected to a switch control unit that changes between the two delay lines on the SH-SAW device. Software on an attached computer is used to read the output from the network analyzer and periodically change the delay line being read by the switch control unit. This provides a differential measurement between the lines when the separate sets of data are compared.

The pumps used to deliver the analyte solutions are manufactured by ISMATEC and Eppendorf. The aromatic analytes are volatile and may evaporate from the solution. These solutions are stored in closed containers and a pump is used to pull the liquid through a fitted brass flow cell which contains the sensor device. The flow cell holds a single device and connects the device to the network analyzer with coaxial cables that are shielded to prevent signal loss or distortion. The flow cell holds approximately 0.134 mL [11] of liquid at a time when fully assembled as shown in Fig. 3.1.

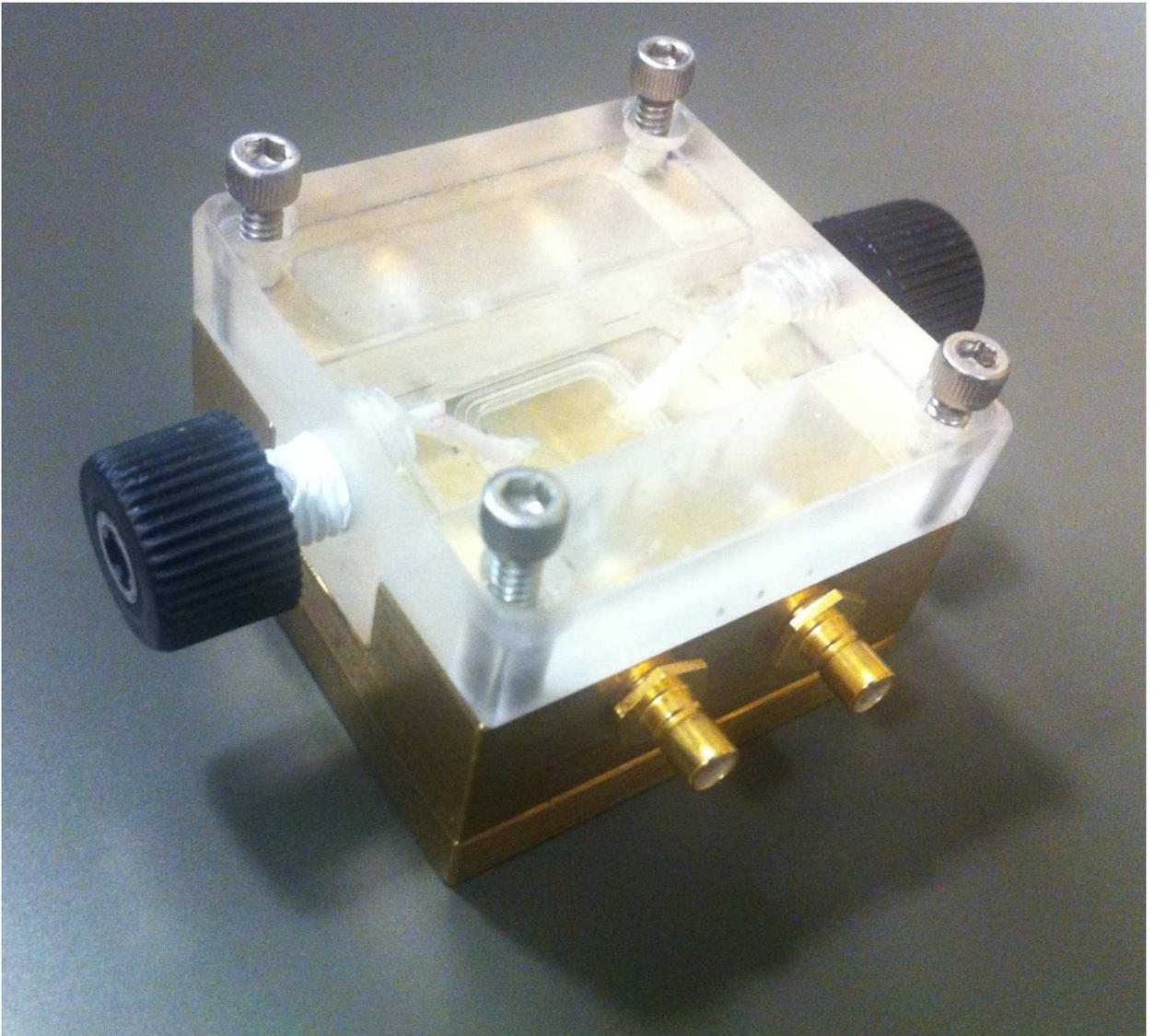


Figure 3.1 An assembled flow cell, designed by the Marquette Microsensor Research Laboratory

The SH-SAW devices used in this experiment were designed at the Marquette Microsensor Laboratory. The device is a lithium tantalate substrate with gold metalized regions patterned to make the IDT fingers and delay line. The devices used in these experiments have a pass band between 102.7 MHz and 103.9 MHz and the center

frequency which is tracked in the measurement procedure varies based on many parameters including ambient temperature and film thickness.

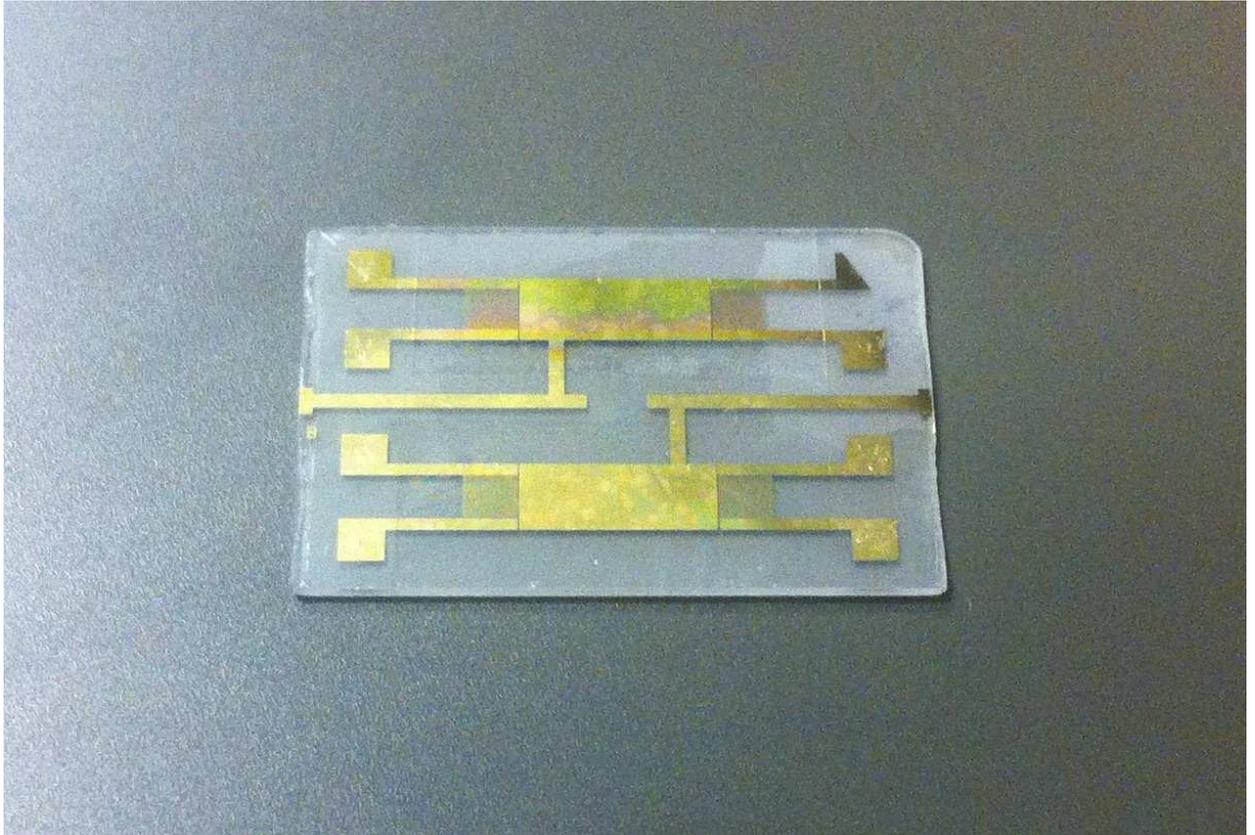


Figure 3.2 A coated SH-SAW device, designed and coated by the Marquette Microsensor Research Laboratory

Fig. 3.2 shows a coated device. The film is placed so that it covers the IDTs and metalized delay line without insulating the contact pads. The bottom edge on the width of the device is beveled and the corners are rounded to reduce reflections. The top edge

on the width of the device is scratched only on the segment which is in line with the nearest IDT pairs.

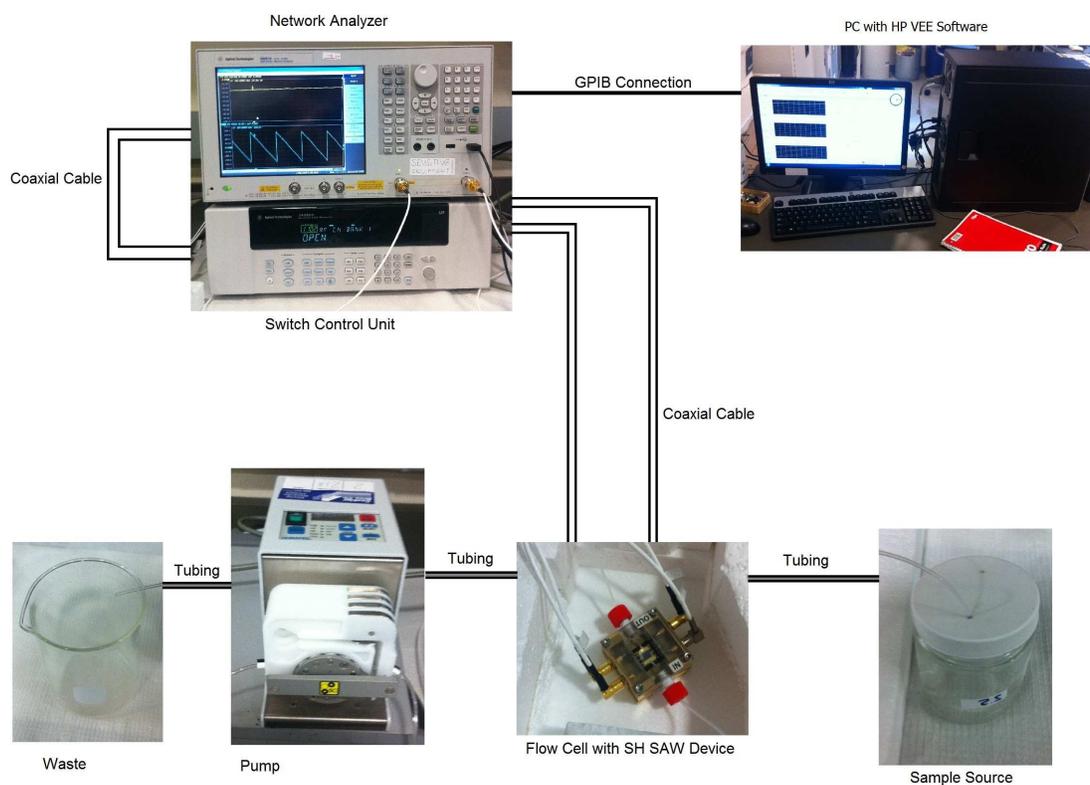


Figure 3.3 Diagram of the experimental setup used to measure sensor response to an analyte

The entire setup of equipment used to measure the frequency response of a device is shown in the diagram of fig. 3.3. The network analyzer is connected to the switch control unit which can select between its two connections to the flow cell. A computer

program operates both the network analyzer and switch control unit. The switch control unit is controlled by the computer to periodically change between the two delay lines of the device, and the program records the information from the network analyzer output and saves it to a file after each cycle. The flow cell is connected to a jar and a pump which pulls liquid from the jar through the flow cell. The waste liquid is stored in a temporary container until disposal. An operator must stop the pump to exchange samples when needed.

3.3 Materials Used

The sensing layers are made from polymer solutions which are spin coated on the device. These solutions are made by dissolving the polymer in toluene. The solid polymer material used to make these solutions was either purchased from a commercial supplier or produced at Marquette University from components which are commercially available. Poly (methyl acrylate) and poly (butyl acrylate) are purchased from Sigma Aldrich and dissolved in toluene. Poly (ethylene co-vinyl acetate), also known as Elvax-40W, was purchased from Sigma Aldrich as a solution in toluene. Bisphenol-A poly (dimethylsiloxane) and bisphenol-A poly (hexamethyltrisiloxane) are copolymers that were synthesized at Marquette University from components purchased from Sigma Aldrich. BPA HMTS was produced previously and stored in a solid state until it is dissolved in toluene. BPA PDMS has a short shelf life and is made immediately prior to its use.

The analytes tested in this thesis are benzene, ethyl benzene, toluene, and xylenes. These are collectively referred to as the BTEX analytes. All of these chemicals are purchased from Sigma Aldrich. The analytes are diluted in water to make solutions of specific concentration. The water is deionized and filtered with a Milli-Q system. This water is then heated to a boil to remove any dissolved gasses.

3.4 Procedures

3.4.1 Introduction

The procedures which are used in this work are largely based on previous work done in the Microsensor Laboratory. These have been developed by combining known procedures to prepare and test the polymers of interest.

3.4.2 Polymer Solution Preparation

In order to apply a polymer film using a spin coating process, the polymer must be dissolved in a solvent. The film thickness as a result of spin coating depends on spin time and speed as well as the viscosity of the polymer and how rapidly the solvent evaporates. Two solutions of the same polymer and solvent will have different viscosities if the ratio of solvent to polymer is different and the same viscosity if both solutions are the same [11] [37]. It is important to accurately control the concentration of the polymer solution to have reproducible results from the spin coating process.

Concentrations are represented using percent weight. The percent weight (or weight by weight) of a solution is calculated in equation (18). Some solutions are also

prepared using a weight by volume percent weight, and because the density of water is 1.0 g/mL the values of percent weight per weight and per volume are the same if the solvent is water.

$$\frac{\text{Mass of polymer}}{\text{Total mass of solution}} \times 100 = \text{Percent weight} \quad (18)$$

Solutions are made by placing a measured mass of polymer into a container and adding solvent until the total mass is such that the desired percent weight is obtained. The solution is then stirred to completely dissolve the polymer. Because the solvents evaporate in air, the container must be sealed completely. As the solvent evaporates, the percent weight increases slowly. Polymer solutions are kept tightly sealed and are not stored for more than three months in order to prevent inaccuracy due to this evaporation [11].

3.4.3 BPA PDMS Synthesis

The copolymer bisphenol-A poly (dimethylsiloxane) (BPA PDMS) used in these experiments was synthesized at the Marquette University chemistry laboratory for this project. The final BPA PDMS polymer is formed from a reaction of the component parts bisphenol-A and poly (dimethylsiloxane). The polymers are dissolved in toluene, and a platinum catalyst is added. The solution is then stirred with a magnetic stir bar in a hot oil bath. Fourier transform infrared spectroscopy (FTIR) is used to verify the completion of the reaction. The PDMS polymer has a siloxane group which has a wave number of 2120 cm^{-1} . This siloxane group is changed through a reaction between the (Si-H) bond and the (-C=C-) bond in the presence of the platinum catalyst. The 2120 cm^{-1} peak is

removed from the FTIR spectrum as the reaction completes. Once the reaction is complete, activated charcoal is added to the solution. The charcoal absorbs the excess platinum catalyst, and is then filtered out. The final solution has a concentration which depends on the ratio of the mass of the reactants and the total solution mass – including the mass of the toluene used as a solvent. [23] [11]

3.4.4 Device Cleaning and Preparation

Before coating a device, it must be prepared through several steps. A new device must first be reshaped with rougher edges to improve its performance. In order to promote film adhesion and to improve consistency between films, the device must be thoroughly cleaned.

The substrates of the devices used in this experiment are cut from a larger wafer on which the devices are laid out in a grid pattern. The flat edges of a new device will cause the surface and bulk waves to reflect directly back at the transducer, which will cause noise in the measured signal. Sanding the edges of the device to a beveled shape by rounding the rear edge will cause the wave to scatter in more directions and this will disperse the energy to reduce the magnitude of the reflected noise.

Cleaning the device must be done through the use of chemicals and solvents because physical contact may damage the metal pattern and ruin the IDT fingers. The device is submerged in a solvent in a sealed jar and the jar is placed in an ultrasonic bath for 3 minutes. The device is then removed from that solvent and rinsed with deionized water or blown dry with nitrogen gas before being placed in another solvent. The solvents used are, in order: trichloroethylene, chloroform, acetone, and 2-propanol.

These solvents are chosen because they will dissolve the polymers of interest, and then the acetone and 2-propanol will remove any partially dissolved residue from the stronger solvents. The final blow-drying step leaves the surface of the device 'wet' to the solvents used in the polymer solution. This helps the polymer film adhere to the surface of the device and reduces delamination of the film. [23]

3.4.5 Film Deposition

The polymer films are deposited using a spin coater. The SH-SAW device is covered with low-residue tape that exposes only the portion of the surface to be coated and placed on a vacuum chuck inside the spin coater. Polymer solution is deposited on the surface of the device and the spin coater is activated immediately. Variations in time spent idle can cause significant changes to the viscosity of the solution because the solvents used are volatile. The film thickness is a function of the polymer solution (viscosity, drying rate, etc.) and the spin conditions (speed, ramp time, duration) [16] [34]. After the spin coater has completed the programmed routine, the tape can be removed but the film will still contain some solvent.

In order to remove the solvent, the film must be subjected to a drying process. To ensure that all of the solvent is removed, the film should be heated to a temperature above the boiling point of the solvent. The properties of a polymer film are affected by the arrangement of the polymer chains, and the addition of energy from heating the film may cause significant changes in the conformation of the polymer chains. In general, polymers with a high T_g can be safely heated without altering their properties, but some polymers cannot be subjected to heat. The alternative is to place the device in a

contained desiccator for a period greater than 12 hours to ensure that the solvent is completely evaporated.

3.4.6 Thickness Measurement

The film thickness, as discussed previously, influences the function of a chemical sensor. Thicker films will absorb more of the acoustic energy and can cause higher insertion loss and greater sensitivity than a thinner film of the same material. Two methods of measuring film thickness are used in this research.

A profilometer is used to measure the thickness of a film that is deposited on a glass slide. The surface of the slide is prepared the same as that of an SH-SAW device, and then the film is applied using the same spin coating technique. Glass slides are used instead of the actual device because the metallization on the surface of the device would interfere with the reading from the profilometer. It is also possible for the probe in the profilometer to damage the device, or the profilometer stylus, if it scratches the metalized region. This measurement identifies the thickness of the film which results from spin coating a given solution with specific spin time and speed. That same spin-coating procedure can then be applied to a device to produce a film with similar thickness.

In some cases, the polymer being measured is too soft and the profilometer will scratch or penetrate the film. This will result in an inaccurate measurement of step height and may damage the probe. A thin metal layer can be deposited by evaporation to allow the profilometer to function properly. The metal will be of equal thickness in all regions of the coated slide, because the evaporation process coats the target sample evenly, and the step in height where the film was originally deposited will remain the same. The

Marquette University lab uses zinc to make the metal layer because a thin zinc layer is hard enough to allow accurate measurements without being so hard as to risk damaging the probe tip. [23]

The process for using the profilometer is as follows:

1. Clean a glass slide as described in section 3.4.4.
2. Place tape such that only a strip of glass between 1mm and 5mm thick is exposed across the width of the slide.
3. Coat the desired film thickness using spin coating techniques.
4. Remove the tape, and complete any necessary spin coating steps.
5. If the film is too soft to be used with the profilometer, follow these sub steps:
 - a. Using heat-resistant tape, secure the coated slide to a metal plate.
 - b. Place a small piece of zinc in a joule-heating basket.
 - c. Secure the wire basket and metal plate inside a vacuum chamber and pump the pressure down to approximately 10-6atm.
 - d. Apply voltage to the wire basket such that a current of 50A is maintained to heat (and evaporate) the zinc for 5 minutes.
 - e. Carefully repressurize the chamber and allow the devices to cool before continuing.
6. Place the device in the profilometer and position the probe above the device, so that it will touch outside of the film.
7. Run the profilometer program so that the probe travels completely across the film and measures the change in height from both edges.

8. Use smoothing and averaging functions within the profilometer program to determine the actual film thickness in the center of the strip.

Measurements using an ellipsometer do not require physical contact and thus can be used on a film which is applied to a metalized device. The refractive index of the lithium tantalate is measured using the same system that will measure the film [36]. The software used to operate the ellipsometer can determine film thickness and refractive index simultaneously, but must have an initial value. In order to calibrate the approximate initial value for refractive index and film thickness for a given polymer solution spun at a particular speed, the film must be deposited on a glass slide and measured with both the profilometer and ellipsometer. This is needed because the ellipsometer, as discussed previously, can produce inconsistent results due to the nature of the method used. Once approximate values are input, the device is aligned within the ellipsometer and measured to get a measurement of the actual film thickness [36].

The process for using the ellipsometer is as follows:

1. Prepare a device for testing by cleaning and spin coating it as described previously.
2. Complete all film preparation (i.e. baking) so that the film is ready to be tested.
3. Place the device within the path of the lasers of the ellipsometer such that the entire laser beam shines on either the metalized region of the device or none of it does.
4. Load the appropriate settings for measuring the reflected light from either the substrate or the gold metallization, depending on where the device is placed.

5. Align the ellipsometer by using the software and fine tuning knobs on the device.
6. Using the provided software, determine the approximate refractive index of the polymer and use that to find the thickness.
7. Repeat steps 3-5 for at least 3 points on the film, and calculate the mean thickness.
 - a. Note that the two wavelengths may give slightly different values for a single measurement. These values should be averaged to find the true thickness.

3.4.7 Analyte Preparation

The analytes tested must be prepared as a solution of analyte in water with a specific concentration. Concentrations used in this experiment are on the order of 1 ppm, and these solutions are prepared with the use of equation (19).

$$ppm = \frac{v_{solute} * d_{solute}}{v_{solute} * d_{solute} + v_{solvent} * d_{solvent}} * 10^6 \quad (19)$$

This can be further simplified for practical lab use. Because the solvent is water, its density is assumed to be 1.0 g/mL. The volume of solvent is significantly larger than the volume of solute, and the denominator is dominated by the solvent terms. Equation (20) is then used as a simplified form of (19).

$$ppm = \frac{v_{solute} * d_{solute}}{v_{solvent}} * 10^6 \quad (20)$$

The solutions are prepared in 250mL jars with sealing lids, which are filled to 260 mL to minimize headspace. According to their respective material safety data sheets, benzene, toluene, ethylbenzene, and the xylenes all have approximately the same density – 0.88 g/mL. Using equation (5), each 1 ppm of analyte solution in 260 mL of water requires approximately 0.30 μ L of analyte. Table 1 shows some examples of this calculation using equation (19) and an approximated 0.88 g/mL density of BTEX analytes [38].

Table 3.1 Sample volumes used to prepare analyte solution

Volume of DI Water (mL)	Volume of Solute(μ L)	Mass of Solute (mg)	Concentration (ppm)
260	3.0	2.64	10.15
260	1.2	1.056	4.062
260	2.4	2.112	8.123
260	6.0	5.28	20.31

It is important that the solutions be prepared immediately before use because the aromatic analytes will evaporate in air, reducing the actual concentration of the solution. The jars which store the solutions must be tightly sealed with the appropriate lids, and it is important that the volume of air in the sealed jar is minimal. After placing the appropriate volumes of solute and solvent into the jar, it is sealed and mixed. The mixing is done with a magnetic stir bar and stir plate for one hour in the same location that the device will be tested in so that the temperature may reach equilibrium.

3.4.8 Response Measurement

The sensing layer is tested by using the previously described SH-SAW device with a polymer film, analyte solutions, flow cell, pump, and network analyzer. The device is placed in the flow cell and degassed Milli-Q water is pumped through the cell at approximately 200 μ L/min. This will bring the cell and device to the same temperature as the water and analyte solutions. The network analyzer is attached to the flow cell and the software which records the data from the network analyzer is initiated. Once the device has reached temperature equilibrium in the water, the center frequency is determined. The center frequency is set by the operator and is tracked by the software as the device parameters change throughout the experiment. It is selected such that the phase is near 0° for both delay lines and the insertion loss is minimized. Then, the liquid source is switched to the first sample. The pump is stopped whenever a sample is changed and the sample is changed as rapidly as possible to limit the amount of exposure the samples have to air. If a sample is left open or not properly sealed, it can evaporate and is no longer the same concentration as what was prepared. The current frequency shift can be seen by watching the display of the data recording software. The response time for each analyte and film will be different so the operator must determine when the device, and therefore the sensing layer, has reached equilibrium. This process is repeated by alternating an analyte solution and water, to expose the sensing layer to an analyte and then remove the analyte by flushing the device with clean water, until the response to each analyte of interest has been recorded. If a film is reused for additional measurements, it is not removed from the flow cell. The difference in pressure causes a suction to hold the device to the gasket of the flow cell, and the screws used to tightly

hold the parts of the flow cell together will also press the gasket into the film. Removing the gasket may damage the surface of the film because the gasket may peel the film off from the device. [23]

3.4.9 Data Preparation

Once the data is collected from the network analyzer, it is stored in a comma-separated value (.csv) file. This format can be imported into Microsoft Excel and manipulated as a spreadsheet there. Because the baseline will drift due to temperature changes over the length of a single experiment, the graphs use corrected fits which remove the effect of the baseline drift. This fit is done using a piecewise linear function which sets an initial baseline value and determines the slope of the drift between the two times at which two consecutive analyte solutions are switched into the flow system. The data is then shown as a plot of frequency shift over time where the frequency returns to baseline between samples.

4 RESULTS AND DISCUSSION

4.1 Introduction

This work investigates a selection of polymers (PBA, PMA, PEVA, BPA PDMS, and BPA HMTS) as sensing layers for a shear horizontal surface acoustic wave sensor for their potential in the detection of benzene in liquid environment. The polymer-coated sensor is exposed to aqueous solutions of BTEX analytes at concentrations ranging from 1ppm to 20 ppm. As the coated device is exposed to the analyte samples, the resulting perturbation in the SH-SAW is measured using a network analyzer. Specifically, the network analyzer records changes in attenuation, frequency and phase of the acoustic wave. The change in frequency at constant phase is measured to determine the device's sensitivity, and the change in attenuation is recorded to observe the viscoelastic behavior of the coating. This chapter presents the results of the experimental work and discusses their significance.

From equations (13) and (14) in chapter 2, both the frequency and loss change as a function of the viscoelastic properties of the sensing layer. The frequency change is also a function of mass accumulation. The change in frequency as a function of time is plotted to show both the response time and response magnitude in Figs. 4.1 to 4.5. Response time can be used to distinguish between benzene and the other BTEX compounds tested [16]. Because this work focuses on the comparison of different

polymer films in the detection of benzene rather than the comparison of responses to different analytes, the magnitude of the frequency shift is the more important parameter in the characterization of a given film. Changes in loss are also monitored to track film aging and to ensure reproducible polymer synthesis and film deposition. The sensitivity of a film is calculated from the slope of the calibration curve. The calibration curve for a particular analyte/coating combination can be found by measuring the steady-state frequency shift of the sensor as a function of benzene concentration and modeling the results using a linear fit. It is reasonable to expect the selected polymer films to have a linear sensitivity to BTEX analytes in the investigated concentration range based on the observations of references [16] [39].

The frequency response data is corrected for linear baseline drift to compensate for changes in the film and environmental conditions (including local temperature) over the course of the experiment. When the film is initially exposed to water, it absorbs a small amount of water and swells. The swelling will change both the viscoelastic properties and thickness of the film, causing a change in the resonant frequency [2]. The device must be given sufficient time for the water to fully absorb into the film and reach equilibrium before applying the analyte sample. Variations in temperature will also cause a change in the frequency [2]. The ambient environment temperature and sample temperatures are controlled as described in chapter 3, but there will be small unavoidable changes in temperature due to the movement of personnel in the laboratory or differences in the temperatures of the samples. A change in the device temperature due to a change in the ambient temperature, like the one caused by a person entering or leaving the room, will happen on a longer time scale than the response to any of the analytes. It is therefore

possible to correct the baseline drift by subtracting a linear function from the response curve to compensate for the frequency shift caused by the temperature change.

Variations in sample temperature may cause abrupt changes in film temperature when samples are exchanged. The dual delay line configuration is used to account for these changes. The temperature coefficient of delay for the reference line – coated with poly (methyl methacrylate) (PMMA) – can be made approximately equal to that of the sensing film by selecting a proper PMMA film thickness [21]. This change in temperature can be accounted for by subtracting the frequency shift on the reference line from the shift on the sensing line. The results shown in this chapter are already modified to include all of these baseline and temperature corrections.

4.2 Results

4.2.1 Introduction

The film materials and thicknesses tested are listed in table 4.1. The polymers were tested at multiple thicknesses because the optimal thickness of the polymer will depend on its loss modulus, and each of the selected polymers has different physical properties (including the loss modulus) [10] [15] [40] [41]. The loss shear modulus of a polymer affects the propagation of the shear horizontal surface acoustic wave. At a constant thickness, a rubbery polymer will absorb more of the energy of the wave than a glassy polymer. Therefore, the polymers of interest will all have different optimal film thicknesses for a given application. The thicknesses used in this work were selected by comparing the loss of the polymer-coated sensor in the liquid environment to similar

known sensing layers which had performed well. Multiple thicknesses were then tested for each polymer to identify a range of suitable values. Some of the cells in table 4.1 are labeled “n/a” to identify cases where the film thickness was inconsistent or the response could not be successfully measured with the setup as described in chapter 3. The results, with a discussion of any specific difficulties encountered, of each polymer will be presented below. Table 4.1 also presents the measured sensitivity of the selected polymers to the BTEX analytes. This value is represented here as the frequency shift (in Hz) per analyte concentration (in ppm). As discussed in chapter 2, the frequency shift may be either positive or negative depending on the resonance conditions of the film [16].

Table 4.1 Polymer thicknesses which were tested, and the measured sensitivity to BTEX

Polymer	Thickness [μm]	Sensitivity [Hz/ppm]			
		Benzene	Ethyl Benzene	Toluene	Xylenes
PMA	0.3	n/a	n/a	n/a	n/a
	0.75	-8	-110	-94	-114
PBA	0.3	22	430	167	490
	0.6	n/a	n/a	n/a	n/a
PEVA	0.3	n/a	n/a	n/a	n/a
	0.85	-20	-35	-10	-20
BPA PDMS	0.29	68	664	299	908
	0.5	330	4000	750	3750
BPA HMTS	0.4	-46	-460	-190	-558
	0.4, Baked	-187	-2320	-630	-1735

4.2.2 PMA, PBA, and PEVA

Poly (methyl acrylate) (PMA) and poly (butyl acrylate) (PBA) are similar in structure because of the acrylate functional group. Poly (ethyl acrylate) (PEA), which also has a similar structure, has been shown to be effective at sensing benzene at a thickness of 1.0 μm when used as the sensing layer on an SH-SAW platform with a sensitivity of 240 Hz/ppm [30]. Fig. 4.1 shows the frequency response of a 0.75 μm PMA film when exposed sequentially to 10 ppm each of benzene, ethylbenzene, toluene, and xylenes (BTEX). Thin films, such as 0.30 μm , of PMA do not exhibit measurable responses to 10 ppm of any BTEX analyte. The sensitivity of the thicker film is greater as expected, because a thicker film will absorb more analyte, and it might also act as a more efficient waveguide (confining the SH-SAW closer to the surface) and/or show more pronounced viscoelastic effects. The signal-to-noise ratio of the response in Fig. 4.1 is small because the sensitivity of the film is relatively low compared to that of other films such as PEA. PMA films such as the one shown here are not effective sensing layers for the detection of benzene because the response magnitude is very small. The sensitivity is not sufficient to effectively measure sub-ppm concentrations. The small frequency response indicates that PMA might not be rubbery enough, as opposed to PBA or PEA, because PMA will absorb less of the analyte, and because its glass transition temperature is just slightly below room temperature as stated above. This is also consistent with the low attenuation found for PMA films.

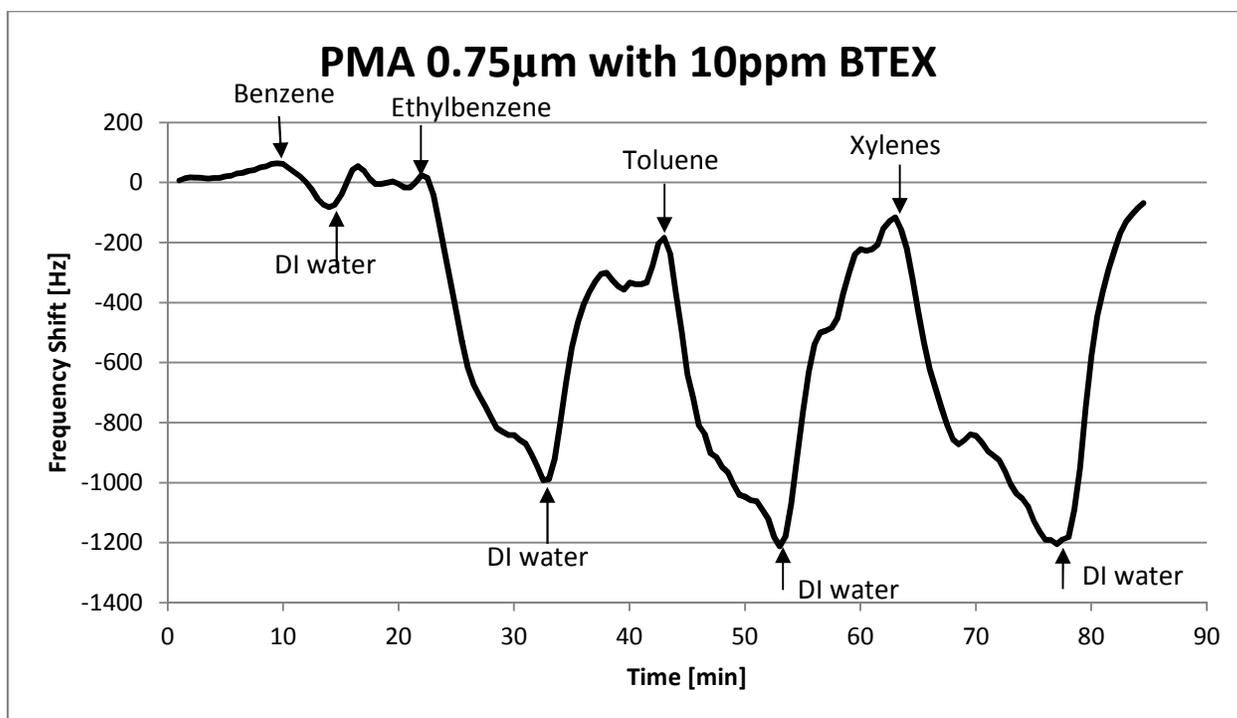


Figure 4.1 Frequency response of an SH-SAW device with a 0.75 μ m thick PMA sensing film to BTEX analytes

PBA has a much lower glass transition temperature than either PMA or PEA. A PBA film will be more rubbery than films of the other acrylate sensing polymers at room temperature, and the PBA film will have a larger loss modulus. PBA films within the tested thickness range have a large insertion loss because of the relatively large loss modulus. The observed insertion loss of a PBA film with a thickness of 0.6 μ m is greater than 40dB in air. A sensor with such a PBA film would not perform well because the surface wave is heavily attenuated by the film, leading to poor signal-to-noise ratios. Thinner films lead to smaller attenuation, as was observed with a 0.3 μ m thick PBA film. This film thickness had an insertion loss of 29 dB in air, which is large but still acceptable. The measured change in frequency of a sensor with a 0.30 μ m PBA sensing

layer is shown in Fig. 4.2. The response to ethylbenzene was interrupted in the measurement, but the remainder of the response was estimated using a fitting process incorporating an extended Kalman filter technique [42] to determine the steady-state frequency shift magnitude of 4.3 kHz [43]. The results shown in Fig. 4.2 also demonstrate a positive frequency shift. The positive frequency shift is a result of the resonance condition discussed in section 2.2.2 and provides further evidence for the rubbery nature of this polymer. The phase lag between the polymer-substrate and polymer-liquid interface changes as the PBA film absorbs analyte and swells. In this case, the resulting change in frequency is positive instead of the negative frequency shift expected for pure mass loading. As previously discussed, this PBA film is able to absorb more analyte than the 0.75 μm PMA film. This increased absorption causes the observed sensitivity of the PBA film to be greater than that of the PMA film. PBA is a promising candidate for sensing aromatic analytes of approximately 1 ppm, but it has already been shown that PEA is more sensitive to benzene than PBA. This is due to the lower acoustic attenuation of PEA and the correspondingly larger thickness that can be used (up to 1.0 μm), leading to larger analyte absorption. This may potentially be caused in part by the difference in solubility parameter as well. The solubility parameter of PEA ($18.6 \text{ MPa}^{1/2}$) is much closer to that of benzene ($18.5 \text{ MPa}^{1/2}$) than PBA ($19.8 \text{ MPa}^{1/2}$) [29]. To further investigate the importance of solubility parameter, poly (ethylene co-vinyl acetate) (PEVA) was selected because it has the same solubility parameter as PEA. [17]

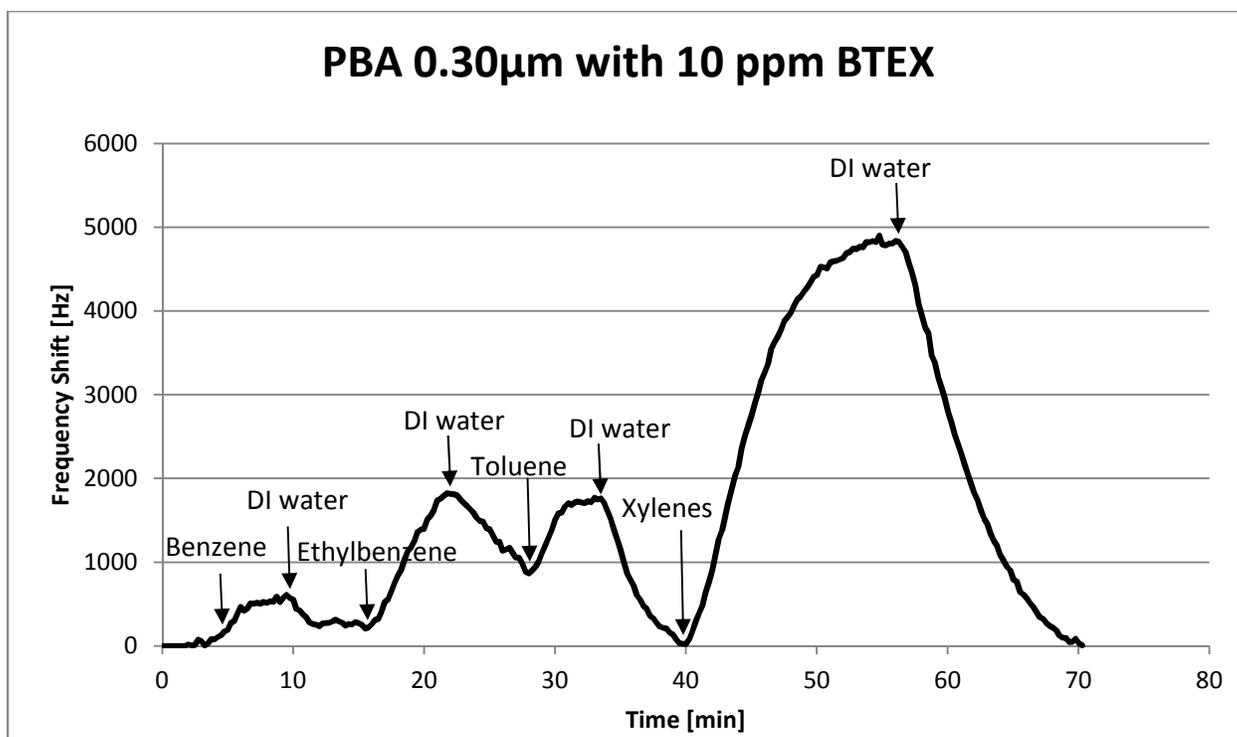


Figure 4.2 Frequency response of an SH-SAW device with a 0.30 μm thick PBA sensing film to BTEX analytes

PEVA is a co-polymer which has a solubility parameter of $18.6 \text{ MPa}^{1/2}$ and a glass transition temperature of $-28.8 \text{ }^\circ\text{C}$. PEVA is expected to be very miscible with benzene and also to be rubbery enough to readily absorb analyte at room temperature. However, this film presented challenges in the coating procedure. Unlike other sensing polymers discussed here, PEVA does not adhere properly to the LiTaO_3 substrate. The lack of adhesion causes large variations in the film across the delay line. This also prevents the film from performing in a reproducible manner, because films which adhere to the substrate differently will have substantially different interactions with the acoustic wave. Thicker films of PEVA were more consistent when coated on the SH-SAW device, but were still not effective sensing layers for this application. The signal did not

return to baseline after switching back from the analyte sample to the reference (water), and thus might not be reusable for more than one measurement. Approximate values for the sensitivity were measured for a 0.85 μm thick PEVA film, but the lack of reusability and the low sensitivity render it obsolete for on-line sensing applications. It is possible that PEVA could still be used for BTEX sensing if a suitable adhesion layer could be found, but that is beyond the scope of this investigation.

4.2.3 BPA PDMS, BPA HMTS

The BPA co-polymers, bisphenol-A poly (dimethylsiloxane) (BPA PDMS) and bisphenol-A poly (hexamethyltrisiloxane) (BPA HMTS), have been previously shown to be good sorbents for organophosphates. These films have been used previously at thicknesses of both 0.25 μm and 0.5 μm for the detection of organophosphates [10] [11] [23]. BPA, the chemically sensitive component of these co-polymers, has shown promise in the absorption of toluene as well [33]. All of these previous experiments and results have been applied here by testing films of BPA HMTS and BPA PDMS which are approximately 0.25 μm and 0.50 μm thick. These films have demonstrated the greatest potential and have been covered in greater detail than the other selected polymers.

BPA PDMS films were deposited at both 0.29 μm and 0.50 μm thickness. Both of these films experience the resonance condition (see section 2.2.2) which causes a positive frequency shift, as was also seen in the response of PBA. The BPA PDMS layer with a thickness of 0.50 μm was much more sensitive to benzene than any of the other selected polymers in this discussion. Fig. 4.3 shows the frequency response of the 0.50 μm thick BPA PDMS film to the BTEX analytes. The response to each of the

analytes is much greater than the noise, which suggests that this sensor has a very low limit of detection. The detection limit is defined as the analyte concentration which produces a frequency shift three times the RMS noise, and an approximation for RMS noise is the standard deviation of the signal when no systematic change is present [31]. The observed RMS noise of this polymer is approximately 95 Hz, which means the limit of detection for benzene is 863 ppb (producing a frequency shift of 385 Hz).

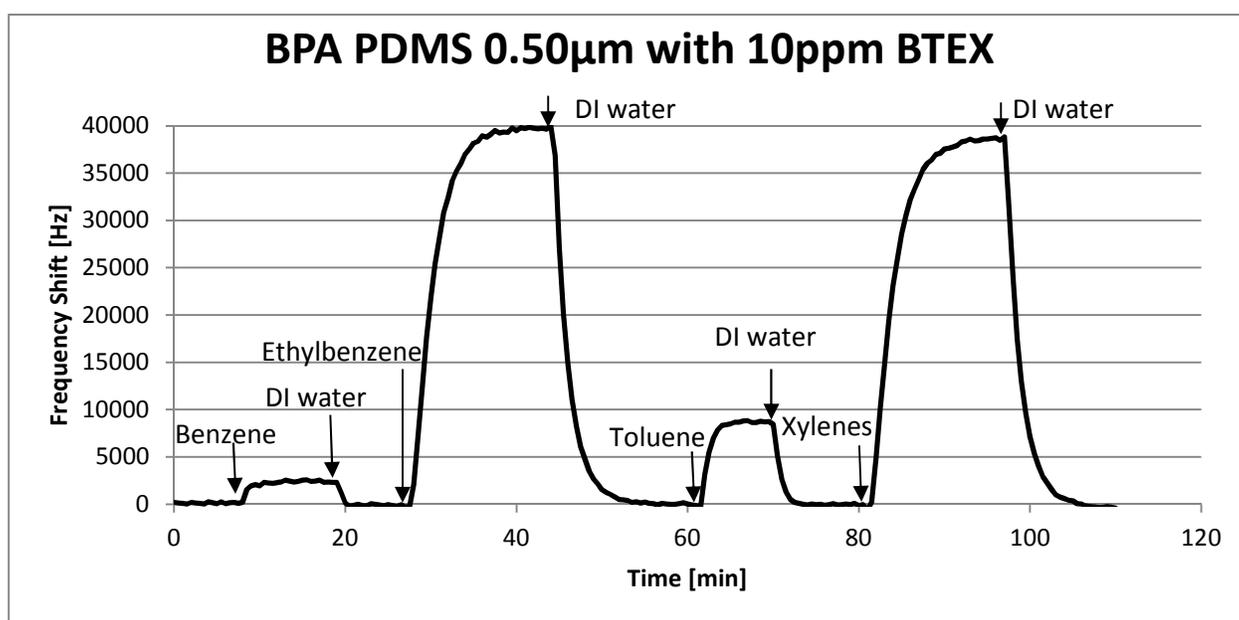


Figure 4.3 Frequency response of an SH-SAW device with a 0.50 μm thick BPA PDMS sensing film to BTEX analytes

BPA PDMS does not give very consistent results. The sensitivity can vary between films and a given film does not have a constant sensitivity over time, indicating film aging. Fig. 4.4 shows the sensitivity of a different BPA PDMS film, of thickness 0.30 μm , as it changes over several weeks. The initial sensitivity is different from that

presented in Fig. 4.3 because of the difference in thickness. After three weeks, the sensitivity has decreased by more than 40%. Other polymers can be cured to remove or stabilize some aging effects, but baking BPA PDMS did not alter the rate at which its sensitivity changed. Because of both its inconsistency and aging, BPA PDMS is not as useful as other established sensing polymers despite its potentially large sensitivity. It is pointed out that several experiments were conducted with BPA PDMS and the same observations were noted.

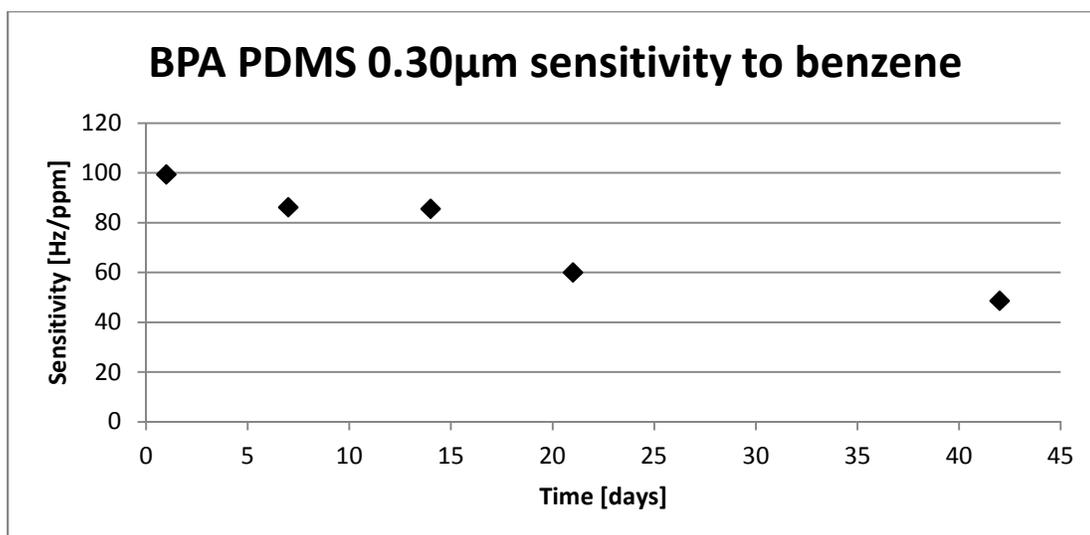


Figure 4.4 Sensitivity of an SH-SAW device with a 0.30 µm thick BPA PDMS sensing film to benzene as it changes over time

BPA HMTS was deposited at a thickness of 0.40 µm. Like BPA PDMS, the film was observed to rapidly age. The insertion loss increased by 10 dB in air (from 30 dB to 40 dB) within 3 days after the film was deposited. To cure the film and prevent the aging, a different film of the same initial thickness was baked in an oven at 55°C for 30

minutes immediately after spin coating. The baking process removed any excess solvent and cured the film, leading to a more stable conformation of the polymer chains. The film thickness was $0.40\ \mu\text{m}$ before baking, but the final film thickness for the baked film was measured at $0.29\ \mu\text{m}$. Responses for both the baked and unbaked films are shown in Figs. 4.5 and 4.6 for comparison; note that the scale is not the same for each film. The baked film has a longer time constant for the response of all of the BTEX analytes, but also has a larger sensitivity. The increase in sensitivity and response time occur because the polymer is absorbing a greater mass of analyte, causing a larger amount of mass loading and requiring additional time to reach equilibrium. The baked film has an observable RMS noise of 42 Hz, which results in a benzene detection limit of approximately 680 ppb (with a frequency shift of 125 Hz). This is less than the detection limit of BPA PDMS because of the lower noise level of the BPA HMTS film.

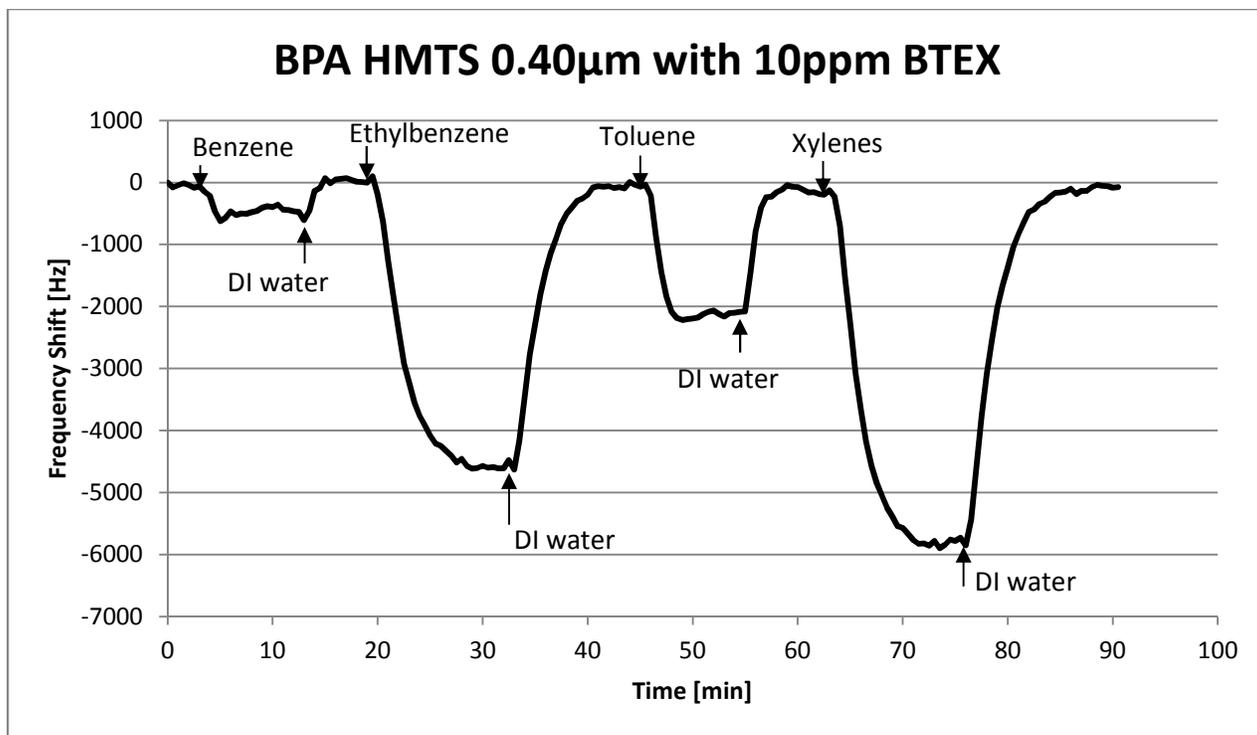


Figure 4.5 Frequency response of an SH-SAW device with a 0.40 μ m thick BPA HMTS sensing film to BTEX analytes

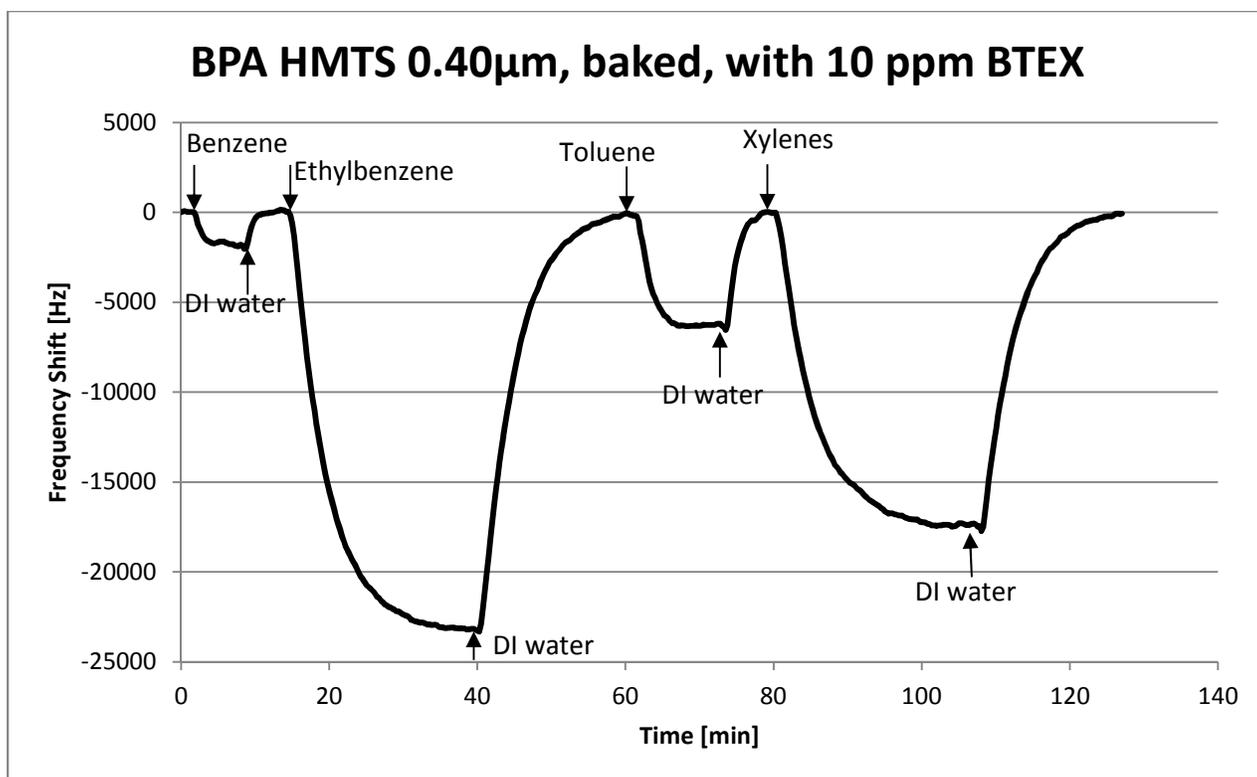


Figure 4.6 Frequency response of an SH-SAW device with a 0.40 μ m thick BPA HMTS sensing film, which was baked and had a new thickness of 0.29 μ m, to BTEX analytes

Both BPA PDMS and BPA HMTS show promising sensitivities for benzene when exposed to 10 ppm concentrations of benzene in water. To demonstrate the films' linearity and repeatability, these films were further tested by exposing them to various concentrations of benzene between 1 ppm and 20 ppm. Fig. 4.7 shows the frequency shift of a 0.50 μ m thick BPA PDMS film when exposed to several concentrations of benzene. The response is fairly linear, but not all of the responses fall onto the same slope. This is likely due to small deviations in sample concentration due to the manual sample mixing procedure and analyte volatility. The sensitivity of this film is lower than the one recorded in Fig. 4.3 because this test was performed several days after the film

had been deposited. This time allowed the film to undergo further aging compared to the one used in the results shown in Fig. 4.3 and caused a decrease in sensitivity as described above (see Fig. 4.4).

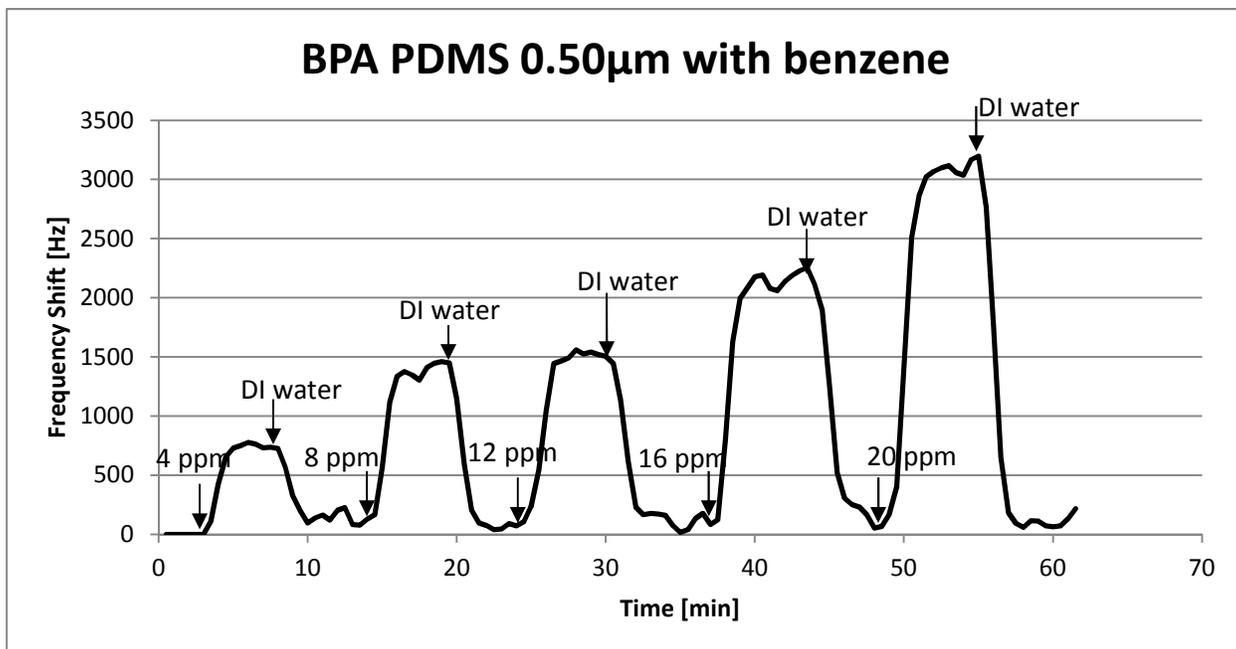


Figure 4.7 Frequency response of an SH-SAW device with a 0.50 μm thick BPA PDMS sensing film to different concentrations of benzene

A BPA HMTS film of thickness 0.40 μm , prepared with the additional baking steps described earlier in this section, was tested with several low concentrations of benzene. The results of this test are shown in Fig. 4.8. The sensor response is linear with concentration except for the frequency shift for exposure to 4ppm benzene, which was found to be slightly outside of the trend. As was the case with the BPA PDMS tests, this is likely the result of the inaccuracies in sample preparation resulting in a concentration

slightly greater than 4 ppm. In addition, the pump must be stopped and restarted when changing samples, and this causes the pressure inside the flow cell to spike when the pump is restarted. Equation (8) in chapter 2 shows that a change in pressure does influence the change in frequency of a surface acoustic wave sensor. However, this pressure change is brief and does not result in a permanent effect. Several visible spikes in frequency change which were caused by this change in pressure were removed from Fig. 4.8 because they obscured the response to the analyte. The increased response time of the baked film is of no concern because the baked film still reaches equilibrium within only two minutes of exposure for concentrations of benzene below 10 ppm.

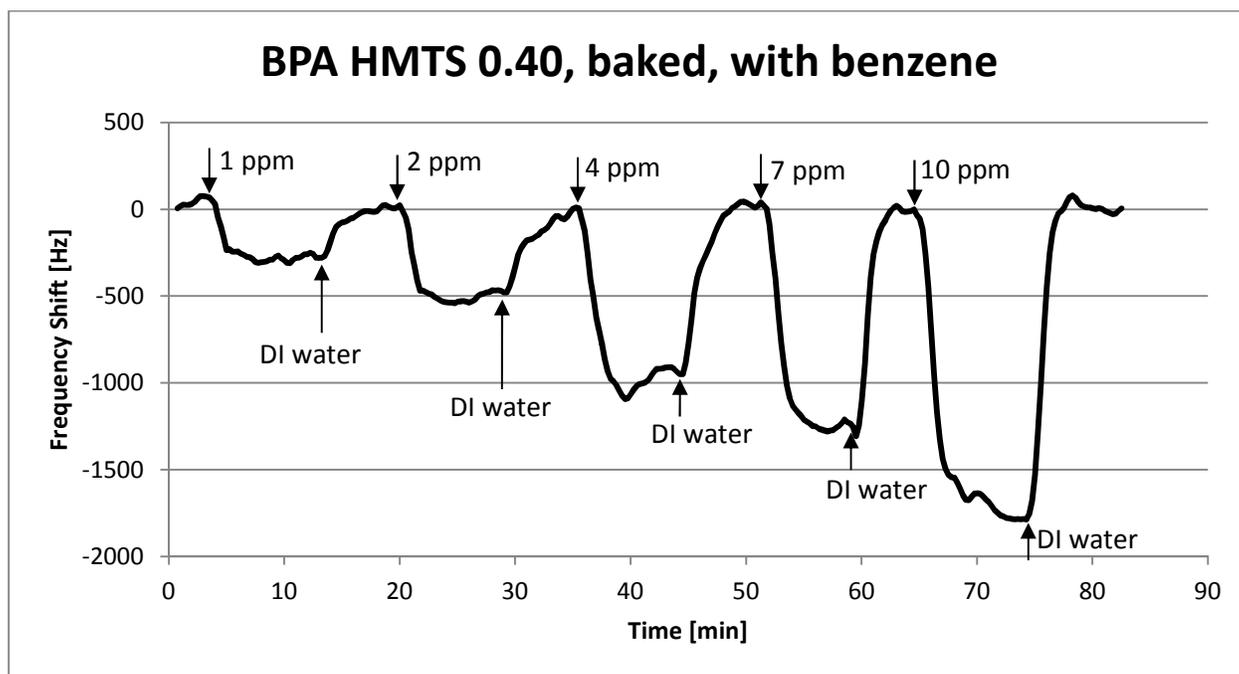


Figure 4.8 Frequency response of an SH-SAW device with a 0.40 μm thick BPA HMTS sensing film, which was baked, to different concentrations of benzene

4.3 Conclusion

The polymers selected for this investigation (PBA, PMA, PEVA, BPA PDMS, and BPA HMTS) were prepared at multiple thicknesses and exposed to BTEX analytes. Polymer films which were effective for sensing benzene were exposed to additional concentrations of benzene to show both the linearity with concentration and the repeatability in the responses for that polymer. The polymer's aging was investigated in some cases. PMA and PEVA both had small frequency shifts to BTEX analytes, and have a small signal-to-noise ratio as a result. The performance of PEVA as a sensing layer was inadequate because the sensor did not return to baseline when the analyte was removed and its response was not repeatable due to poor adhesion of the film to the substrate. PBA strongly attenuates the wave even at low thicknesses, causing a large insertion loss. BPA PDMS and BPA HMTS were both shown to be effective sensing layers for the detection of benzene, with detection limits below 1 ppm, but they both undergo an aging process which requires additional processing steps. BPA HMTS can be baked to reduce the effect of aging, and this also increases the film's sensitivity and response time for BTEX analytes. This makes BPA HMTS the most promising of the polymers investigated for benzene detection. Baking BPA PDMS did not affect its response to the BTEX analytes and also did not prevent it from losing sensitivity over time. BPA PDMS and BPA HMTS show the highest sensitivities of the polymers tested, and they can be used in a sensor array. However, more research into film pretreatment might be advisable, particularly for BPA PDMS. Moreover, additional steps need to be

taken in coating synthesis, coating preparation and storage to ensure coating stability and reproducibility.

5 SUMMARY, CONCLUSION, AND FUTURE WORK

5.1 Summary

This work presents an investigation into several selected polymers for their potential use as sensing layers in a shear horizontal surface acoustic wave sensor array for the detection of benzene in water. The SH-SAW device can operate in liquid environments and uses a sensing polymer which absorbs the analyte [2] [3]. The polymers of interest for this work were selected based on their glass transition temperature, solubility parameter, and previous studies which use these polymers under similar conditions. The polymers were tested to measure sensitivity to benzene, and some of the polymers were monitored over time to show how aging affects repeatability. The objective of this work is to improve sensors which measure benzene in water by finding a sensing polymer which is able to detect smaller concentrations of benzene than what can currently be measured with one or several sensor elements in a sensor array.

A description of benzene and its uses was presented and it was shown that there is a need for accurate sensing equipment to monitor groundwater for contamination [44]. Several acoustic wave sensor designs were discussed and the SH-SAW sensor was chosen as the sensing platform for these tests because of its ability to function in a liquid environment. The relevant physical and chemical properties of sensing polymers were introduced.

The SH-SAW sensor parameters were introduced and examined. The theory behind SH-SAW liquid phase sensors was reviewed to show the role played by the sensing polymer in the function of the entire sensor. It was shown that, by controlling the environment of the tests as well as using particular testing equipment, the sensor response can be modeled as a change in viscoelastic properties and mass loading. The polymer glass transition temperature and solubility parameter were described in details. This provided the rationale for the selection of the polymers of interest. The selected polymers (PMA, PBA, PEVA, BPA PDMS, and BPA HMTS) were identified as potential sensing polymers for the detection of benzene.

The polymers of interest were tested by applying them at multiple thicknesses on SH-SAW devices, and then measuring the frequency response of the sensor when the device is exposed to several concentrations of BTEX analytes in water. The film thickness was varied for each polymer to find a suitable thickness. The sensitivity to benzene for each polymer was found using various concentrations of benzene between 1 ppm and 20 ppm. The limit of detection was calculated using the RMS noise and sensitivity. BPA PDMS was investigated over several weeks to determine the effects of aging. The polymer was repeatedly tested to determine the sensitivity to benzene at weekly intervals.

5.2 Conclusion

This work measured the sensitivity of several polymers (PMA, PBA, PEVA, BPA PDMS, and BPA HMTS) to benzene in water when used as the sensing layer of an SH-

SAW sensor. The films were prepared by spin coating to produce a reproducible thickness. The thicknesses used were chosen to be effective for sensing BTEX analytes. The sensor response was measured by recording the shift in frequency, and the change in insertion loss was also monitored to observe the viscoelastic behavior of the polymer during analyte sorption. Some of the polymers showed either less sensitivity than that for known polymers, or were not stable and could not produce repeatable results. BPA HMTS had a large sensitivity and can be baked to reduce the effects of aging.

Several of these polymers of interest did not have suitable properties for sensing benzene. PMA had a frequency response which was one order of magnitude less than that of the previously documented polymer PEA. One potential reason for this is because the film may be too glassy at room temperature, and therefore will not absorb enough benzene. PBA had a large insertion loss when prepared at a film thickness of 0.30 μm . PBA also experienced a positive frequency shift when exposed to BTEX analytes, suggesting that the film is acoustically thick. This indicates that the film was too rubbery ($G'' \gg G'$) to be used at that thickness. Reducing the thickness further will result in a smaller frequency shift, which would reduce the film's sensitivity to benzene to a value lower than that of PEA. A PEVA film was observed to have a large amount of system noise, and the film was observed to delaminate easily during preparation. The noise is likely caused by a loss of adhesion between the film and substrate during measurement. PEVA also did not return to baseline conditions after removing the analyte from the environment, which prevents PEVA from making repeatable measurements.

The BPA co-polymers both had large sensitivity to benzene. A 0.50 μm thick BPA PDMS film was shown to have a positive frequency shift due to the resonance

condition caused by being acoustically thick. This BPA PDMS film had a sensitivity of 330 Hz/ppm of benzene and a limit of detection of approximately 860 ppb. BPA PDMS was further investigated to determine how much it is affected by aging. A film of thickness 0.30 μm exhibited a sensitivity consistently decaying over several weeks. The sensitivity of the film was reduced by more than 50% in 6 weeks, and baking the film during its preparation did not reduce this aging effect. Unbaked BPA HMTS also experienced a rapid aging process. The insertion loss of a BPA HMTS film was observed to increase rapidly, but baking the film immediately after spin coating reduced this effect and also increased the film's sensitivity. The baked BPA HMTS film with a thickness of 0.40 μm (before baking) had a sensitivity of -187 Hz/ppm of benzene and a limit of detection of approximately 680 ppb. The sensitivity of this 0.40 μm thick baked BPA HMTS film was less than that of the 0.50 μm thick BPA PDMS film, but the smaller RMS noise allows for a lower limit of detection.

5.3 Future Work

Identifying potential sensing layers is only a part of the goal of this project. The coated sensor device will eventually be incorporated into a sensor array which uses multiple devices with different sensing films that all have unique responses to the different analytes being measured. The use of an array with multiple independent variables allows the identification and measurement of multiple species of analyte in an unknown sample [23] [30] [45]. Based on the conclusions of this thesis, several additional steps should be taken to prepare an optimized array for sensing benzene in

water. The polymers in this work each have different partial selectivity and sensitivity to each of the BTEX analytes. This can be used to build a sensor array which uses different films to identify an unknown analyte and determine its concentration. An array should be assembled using BPA PDMS and/or BPA HMTS because of their high sensitivity and low limit of detection. PMA and PEVA need additional consideration before being used in such an array, but PBA should not be considered.

Each of the polymers should be prepared at additional thicknesses to determine one optimal thickness for each polymer [41]. The thickest PMA film tested did not have a large sensitivity but it also did not heavily damp the wave. Relatively glassy polymer films, such as PMA, may function on an SH-SAW device at much greater thicknesses; thus PMA should also be investigated to find an optimal thickness. The other polymers may require some small changes to determine an optimal thickness, but the thicknesses tested in this work are already within an adequate range for sensing benzene and can be used for future measurements. PBA had a large insertion loss when prepared at a relatively low thickness of 0.30 μm . As discussed previously, a PBA film which had a thickness smaller than 0.30 μm would have a small sensitivity and likely not be applicable to the measurement of benzene at concentrations below 1 ppm. PEVA was expected to have a larger response to benzene than the actual observed data, due to its excellent glass transition temperature and solubility parameter. Additional tests should be performed to determine an effective process for preparing the PEVA film to prevent it from delaminating from the surface of the device. This can be done by preparing the surface of the device by first coating it with a different polymer such as PMMA.

Like BPA PDMS, BPA HMTS should also be investigated to determine the effects of aging. Baking was shown to reduce the rapid initial change in sensitivity, but the sensor response was not repeatable when tested over a longer period of time. This aging test should be redone to determine how the baked and unbaked BPA HMTS films change over a longer time than what was previously observed. Additional work should also be done to determine an optimal method for storing the film both before and after it is coated on the device. Determining an optimal procedure for preparing and storing BPA HMTS can increase its stability and reproducibility when used as a sensing layer on an SH-SAW device.

Once the polymer film thickness is optimized to achieve the best sensitivity and limit of detection, the response time of the response to BTEX analytes should be found for each film in addition to the sensitivity. Adding another linearly independent parameter to the sensor array data (multi-variable sensors) will allow for a better level of confidence and will improve species identification [23]. The response time is a function of the sensing film thickness, but should not be considered when optimizing the film. The response time for the BTEX analytes is not prohibitively long, even if the film is extremely thick, and it is more beneficial to improve the sensitivity and limit of detection to identify smaller concentrations of analyte.

Bibliography

- [1] U.S. Environmental Protection Agency, "Basic Information about Benzene in Drinking Water," 21 5 2012. [Online]. Available: <http://water.epa.gov/drink/contaminants/basicinformation/benzene.cfm>. [Accessed 10 7 2012].
- [2] D. Ballantine, *Acoustic Wave Sensors: Theory, Design, and Physico-Chemical Applications*, San Diego: Academic Press, 1997.
- [3] F. Josse, "Quantification of benzene in ground water using SH-shear acoustic wave sensors," in *The 14th International Meeting on Chemical Sensors*, Nuremberg, Germany, 2012.
- [4] U.S. Department of Health and Human Services, "Toxicological Profile for Benzene," 2007.
- [5] U.S. Environmental Protection Agency, "Benzene," 3 2 2012. [Online]. Available: <http://www.epa.gov/ttn/atw/hlthef/benzene.html>. [Accessed 10 7 2012].
- [6] U.S. Environmental Protection Agency, "FY 2011 Annual Report On The Underground Storage Tank Program," 2012.
- [7] J. S. Arey and P. M. Gschwend, "Estimating Partition Coefficients for Fuel-Water Systems: Developing Linear Solvation Energy Relationships Using Linear Solvent Strength Theory To Handle Mixtures," *Environmental Science & Technology*, vol. 39, pp. 2702-2710, 2005.
- [8] R. Pallàs-Areny and J. G. Webster, *Sensors and Signal Conditioning*, New York: John Wiley & Sons, Inc., 2001.
- [9] B. Pejic, P. Eadington and A. Ross, "Environmental Monitoring of Hydrocarbons: A Chemical Sensor Perspective," *Environmental Science & Technology*, vol. 41, no. 18, pp. 6333-6342, 2007.
- [10] A. Mensah-Brown, "Detection of organophosphates in the liquid-phase using guided SH-SAW sensors," Thesis (M.S.) -- Marquette University, 2007.

- [11] A. K. Mensah-Brown, "Analysis of the Detection of Organophosphate Pesticides in Aqueous Solutions Using Polymer-Coated SH-SAW Devices," Dissertation -- Marquette University, 2010.
- [12] J. Aklonis, W. MacKnight and M. Shen, Introduction to Polymer Viscoelasticity, New York: Wiley-Interscience, 1983.
- [13] Y. K. Jones, Z. Li, M. M. Johnson, F. Josse and J. M. Hossenlopp, "ATR-FTIR Spectroscopic Analysis of Sorption of Aqueous Analytes Into Polymer Coatings Used With Guided SH-SAW Sensors," *IEEE Sensors Journal*, vol. 5, no. 6, pp. 1175-1184, 2005.
- [14] E. Gizeli, "Design considerations for the acoustic waveguide biosensor," *Smart Materials and Structures*, vol. 6, pp. 700-706, 1997.
- [15] Y. Jones, "Spectroscopic and Computational Investigation of Polymer Coatings and Analyte Systems for use with Guided Shear Horizontal Surface Acoustic Wave (SH-SAW) Sensors for Liquid Phase Detection," Marquette University, 2005.
- [16] Z. Li, "Guided Shear-Horizontal Surface Acoustic Wave (SH-SAW) Chemical Sensors for Detection of Organic Contaminants in Aqueous Environments," Dissertation -- Marquette University, Milwaukee, 2005.
- [17] A. F. Barton, Handbook of Polymer Liquid Interaction Parameters and Other Solubility Parameters, CRC Press, 1993.
- [18] L. Rayleigh, "On Waves Propagated along the Plane Surface of an Elastic Solid," *Proceedings of the London Mathematical Society*, vol. 17, pp. 4-11, 1885.
- [19] Y. V. Gulyaev, "Review of Shear Surface Acoustic Waves in Solids," *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, vol. 45, no. 4, pp. 935-938, 1998.
- [20] Z. Li, Y. Jones, J. Hossenlopp, R. Cernosek and F. Josse, "Analysis of Liquid-Phase Chemical Detection Using Guided Shear Horizontal-Surface Acoustic Wave Sensors," *Analytical Chemistry*, vol. 77, pp. 4595-4603, 2005.
- [21] B. Drafts, "Acoustic Wave Technology Sensors," *IEEE Transactions on Microwave Theory and Techniques*, vol. 49, no. 4, pp. 795-802, 2001.
- [22] S. J. Martin, G. C. Frye and S. D. Senturia, "Dynamics and Response of Polymer-Coated Surface Acoustic Wave Devices: Effect of Viscoelastic Properties and Film

- Response," *Analytical Chemistry*, vol. 66, pp. 2201-2219, 1994.
- [23] T. Newman, "Analysis of the Detection of Organophosphate Pesticides In Aqueous Solutions Using Polymer-Coated SH-SAW Sensor Arrays," Thesis (M.S.) -- Marquette University, 2012.
- [24] J. W. Grate, R. Klusty, R. A. McGill, M. H. Abraham, G. Whiting and J. Andonian-Haftvan, "The Predominant Role of Swelling-Induced Modulus Changes of the Sorbent Phase in Determining the Responses of Polymer-Coated Surface Acoustic Wave Vapor Sensors," *Analytical Chemistry*, vol. 64, pp. 610-624, 1992.
- [25] J. W. Grate, S. N. Kaganove and V. R. Bhethanabotla, "Comparisons of Polymer/Gas Partition Coefficients Calculated from Responses of Thickness Shear Mode and Surface Acoustic Wave Vapor Sensors," *Analytical Chemistry*, vol. 70, pp. 199-203, 1998.
- [26] W. A. Groves, A. B. Grey and P. T. O'Shaughnessy, "Surface acoustic wave (SAW) microsensor array for measuring VOCs in drinking water," *Journal of Environmental Monitoring*, vol. 8, pp. 932-941, 2006.
- [27] T. Gass, "Geothermal Heat Pumps," *Geothermal Resources Council Bulletin*, vol. 11, pp. 3-8, 1982.
- [28] K. Bodenhoefer, A. Hierlemann, G. Noetzel, U. Weimar and W. Gopel, "Performances of Mass-Sensitive Devices for Gas Sensing: Thickness Shear Mode and Surface Acoustic Wave Transducers," *Analytical Chemistry*, vol. 68, pp. 2210-2218, 1996.
- [29] W. L. Archer, *Industrial Solvents Handbook*, New York: Marcel Dekker, Inc., 1996.
- [30] F. Bender, R. Mohler, A. Ricco and F. Josse, "Quantification of Benzene in Groundwater Using SH-Surface Acoustic Wave Sensors," in *14th International Meeting on Chemical Sensors - IMCS 2012*, Nuremberg, Germany, 2012.
- [31] F. Josse, F. Bender and R. W. Cernosek, "Guided Shear Horizontal Surface Acoustic Wave Sensors for Chemical and Biochemical Detection in Liquids," *Analytical Chemistry*, vol. 73, pp. 5937-5944, 2001.
- [32] A. K. Mensah-Brown, D. Mlambo, F. Josse and J. Hossenlopp, "Rapid Detection of Organophosphates in Aqueous Solution Using a Hybrid Organic/Inorganic Coating on SH-SAW Devices," in *2010 IEEE International Frequency Control Symposium*

(FCS), 2010.

- [33] J. W. Grate and D. A. Nelson, "Sorbptive Polymeric Materials and Photopatterned Films for Gas Phase Chemical Microsensors," *Proceedings of the IEEE*, vol. 91, no. 6, pp. 881-889, 2003.
- [34] Brewer Science, "Spin Coater Theory," [Online]. Available: <http://www.brewerscience.com/products/cee-benchtop-products/cee-technical-information/spin-coater-theory/#scpt1>. [Accessed 19 10 2012].
- [35] KLA Tencor, Alpha-Step IQ Surface Profiler User Manual, 2003.
- [36] Gaertner Scientific, Ellipsometer User Manual.
- [37] Columbia University, "Spin Coat Theory," [Online]. Available: <http://www.clean.cise.columbia.edu/process/spintheory.pdf>. [Accessed 10 10 2012].
- [38] Sigma Aldrich, "Material Safety Data Sheet - Toluene," 24 04 2012. [Online]. Available: <http://www.sigmaaldrich.com/united-states.html>. [Accessed 19 10 2012].
- [39] F. Bender, F. Josse and A. J. Ricco, "Influence of ambient parameters on the response of polymer-coated SH-surface acoustic wave sensors to aromatic analytes in liquid-phase detection," *Frequency Control and the European Frequency and Time Forum (FCS), 2011 Joint Conference of the IEEE International*, pp. 1-6, 2011.
- [40] F. Bender, R. W. Cernosek and F. Josse, "Love-wave biosensors using cross-linked polymer waveguides on LiTaO₃ substrates," *Electronics Letters*, vol. 19, no. 1672-1673, p. 36, 2000.
- [41] K. Zinszer, R. Zhou, F. Josse, F. Bender and R. W. Cernosek, "Optimization of SH-SAW liquid sensor platforms for (bio-)chemical detection using polymer," in *Acoustic Wave-Based Sensors Symp*, 2000.
- [42] A. Mensah-Brown, M. Wenzel, F. Josse and E. Yaz, "Near Real-Time Monitoring of Organophosphate Pesticides in the Aqueous-Phase Using SH-SAW Sensors Including Estimation-Based Signal Analysis," *IEEE Sensors Journal*, vol. 9, no. 12, pp. 1817-1825, 2009.
- [43] M. J. Wenzel, A. Mensah-Brown, F. Josse and E. E. Yaz, "Online Drift Compensation for Chemical Sensors Using Estimation Theory," *IEEE Sensors Journal*, vol. 11, no. 1, pp. 225-232, 2011.

- [44] C. K. Ho., A. Robinson, D. R. Miller and M. J. Davis, "Overview of Sensors and Needs for Environmental Monitoring," *Sensors*, vol. 5, pp. 4-37, 2005.
- [45] J. W. Grate, "Acoustic Wave Microsensor Arrays for Vapor Sensing," *Chemical Reviews*, vol. 100, no. 7, pp. 2627-2648, 2000.