

# Characterization of Plasticizer-Polymer Coatings for the Detection of Benzene in Water Using Sh-Saw Devices

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CHARACTERIZATION OF PLASTICIZER-POLYMER COATINGS  
FOR THE DETECTION OF BENZENE IN WATER  
USING SH-SAW DEVICES

by

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Marquette University,  
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Milwaukee, WI

# CHARACTERIZATION OF PLASTICIZER-POLYMER COATINGS FOR THE DETECTION OF BENZENE IN WATER USING SH-SAW DEVICES

## ABSTRACT

Jude K. Coompson, B.S.

Marquette University, 2014

Benzene is a constituent component of crude oil that has been classified as a carcinogen by the EPA with a maximum contamination level (MCL) of 5ppb in drinking water. However, of the aromatic compounds, benzene has one of the lowest polymer-water partition coefficients using commercially available polymers as sensor coatings, resulting in poor limits of detection. This work investigates new coating materials based on polymer/plasticizer mixtures coated onto a shear horizontal surface acoustic wave (SH-SAW) sensor to detect benzene in water. There are many polymers which are unavailable for use as a sensing polymer due to their glassy nature. The use of plasticizers allows the polymer properties to be modified to give a more sensitive polymer by reducing the glass transition temperature,  $T_g$ , and increasing the free volume creating a more rubbery polymer which will absorb benzene.

Three polymers, polystyrene (PS), poly (ethyl acrylate) and poly (methyl acrylate) were chosen to be plasticized with dioctyl phthalate (DOP). Polystyrene, which also possesses benzene rings, was chosen as its glass transition temperature is 100°C making it glassy. PEA was chosen because it has previously been used as a sensing polymer for benzene and has a  $T_g$  of -21°C. PMA was chosen because it has a  $T_g$  of 9°C and has previously been shown to have a low sensitivity to benzene. Dioctyl phthalate was chosen as the plasticizer because it possesses a benzene ring and had previously been used as a plasticizer in industry and research for polystyrene and acrylate polymers.

The plasticizer-polymer mixtures are spin coated on a lithium tantalate ( $\text{LiTaO}_3$ ) SH-SAW dual delay-line device at various thicknesses. Each coating was exposed to multiple concentrations of benzene and frequency shifts were measured. Plasticization led to increased sensitivity for all polymers to benzene.

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## 1 INTRODUCTION

### 1.1 Problem Statement

Benzene ( $C_6H_6$ ) is an organic compound found as a constituent of crude oil and its refined products. Benzene is an aromatic hydrocarbon. Benzene is also derived from many industrial processes and is used as a precursor in forming other organic compounds and chemicals. Benzene has been found to be a cause of cancer in humans, particularly leukemia and cancers of other blood cells [1]. Due to benzene carcinogenic properties, the Environmental Protection Agency (EPA) set a benzene concentration limit of 5 parts per billion (ppb) or  $5\mu\text{g/L}$  in drinking water sources [10].

The EPA currently requires owners of Underground Storage Tanks (UST) to perform monthly monitoring for possible releases. In the case of USTs which are younger than 10 years, only monthly inventory control and structural test of the tanks are required.

In December of 2013, the EPA reported that there were 577,981 active UST regulated by the EPA. Approximately 1.8 million USTs have been closed down since 1984. While 514,123 releases have been reported, 436,406 have been cleaned up. During the 2013 fiscal year, there were 6,128 confirmed releases from USTs and 11,582 confirmed cleanups [11]. These numbers illustrate the need for a way to monitor groundwater for potential leaks, involving a minimum of manpower and cost while providing maximum protection of the public and the environment.



## 1.2 Overview of Chemical Sensors

Chemical sensors are defined as devices capable of detecting and converting chemical quantity into a signal. The chemical quantity usually measured is concentration of a specific compound, atom or ion [6]. Chemical sensors require ruggedness and fast response times [4]. The biggest challenge to chemical sensors is the selectivity of the chemical sensor to a target analyte, in a background of various interferents [3].

Chemical sensors consist of a sensor platform and sensing medium along with a system to display the data. The sensing medium interacts with the analyte and the interferents in the ambient environment; this interaction perturbs a physical parameter of the sensor platform. A common analogy to a sensor is the banana skin which changes colors to portray how ripe the banana is; this change is caused by the release of chlorophyll and ethylene gas. However, in most chemical sensors a computer system is needed to interpret and display the data.

Sensitivity, selectivity, linearity and environmental stability are important parameters used to characterize a sensor. A calibration curve is used to interpret the output of the sensor. The calibration curve is plotted as an output parameter as a function of an input parameter. Sensitivity is defined by how much a measured output changes for a given input perturbation, whereas selectivity is defined as how much of the output response is caused by the specifically targeted measured quantity [5]. However, for chemical sensing, single analyte selectivity is difficult to achieve as there are various interactions that take place

between chemicals. For chemical sensing, the term partial selectivity is often used. Partial selectivity in a chemical sensor refers to the relative magnitude of the sensors response for a particular analyte compared to the interferents in the environment [3].

Current measurement techniques for benzene concentrations in water require the transportation of samples to a laboratory for analysis. This process is usually expensive and time consuming. The most common lab measurement technique is the combination of gas chromatography and one of various types of detectors to extract the amount of benzene and other analytes that have passed through the gas chromatography stage.

Apart from gas chromatography based detection, optical based detection systems are also employed. One such detection system is that of laser induced molecular fluorescence. Laser induced molecular fluorescence has been shown to have a limit of detection of around 19 ppb for benzene. Despite its high sensitivity, it requires the need to collect and take samples to a lab for testing [7].

Current polymers utilized commercially and for research to detect benzene are classified as rubbery polymers, i.e. polymers which are soft, and have the ability to absorb analytes on a short time scale (minutes or seconds). Two examples are poly (ethyl acrylate) (PEA) and poly (epichlorohydrin) (PECH). These polymers have glass transition temperatures below room temperature. A detection limit of 100ppb for benzene has been found for these polymers when used with an SH-SAW delay line [8]. For many commercially available polymers

benzene has a low polymer-water partition-coefficient in comparison to other aromatic hydrocarbon compounds [33][34]. There are other polymers which theoretically could be used to detect benzene and achieve lower detection limits. However, these polymers are glassy and absorb benzene very slowly. If these polymers could be modified to facilitate rapid and efficient absorption of the target analyte, a whole range of polymers could be made available for inclusion into a sensor array for benzene detection at ppb concentrations.

### **1.3 Acoustic Wave Sensors**

Acoustic wave devices have been in commercial use for over 70 years primarily in the telecommunication industry for use as filters. However, acoustic wave devices are being applied as sensors outside the telecommunications industry. A few applications are in the automotive industry as torque and tire pressure sensors, in medical sciences as biosensors and other commercial applications to measure physical and chemical quantities.

Acoustic wave sensors acquire their name from the mechanical or acoustic wave which is used as the sensing mechanism. As this wave propagates through or on the surface of substrate, any perturbation from the environment of the propagation path will affect the velocity and/or amplitude of the wave. Changes in amplitude can be monitored by measuring the loss spectrum of the sensor, where changes in velocity can be monitored by measuring frequency and phase properties. The responding frequency and phase shift can be associated with the desired quantity that is being measuring.

Piezoelectric materials are used to generate acoustic waves in virtually all acoustic wave devices and sensors. Piezoelectricity is the phenomenon where the imposition of an electrical field on a material produces a mechanical stress and the converse holds true. To generate an acoustic wave an oscillating electrical field has to be applied. After the acoustic wave has interacted with the environment, it is then converted back into an electric field to measure any perturbations to the system. The most common piezoelectric materials are quartz ( $\alpha$ -SiO<sub>2</sub>), lithium tantalate (LiTaO<sub>3</sub>) and lithium niobate (LiNbO<sub>3</sub>).

The mode of wave propagation through or on a piezoelectric substrate is used to describe an acoustic wave device. If the acoustic wave generated propagates through the bulk it is called a bulk wave. The most common bulk wave device is the thickness shear mode (TSM) resonator also known as quartz crystal microbalance. If the wave propagates on the surface it is known as a surface wave device. The two most common are the surface acoustic wave (SAW) and the shear horizontal-surface acoustic wave (SH-SAW) devices.

#### **1.4 Thesis Organization**

This thesis is organized into 4 chapters. Chapter 1 is a brief introduction to the application and chemical sensors. In addition, examples of chemical sensor systems used to detect benzene are given. Chapter 1 also includes a brief overview of acoustic wave devices. In chapter 2, the theories of the mechanism of plasticizers are examined. Principles of surface acoustic wave devices are further explored and explained. The guided SH-SAW sensor is then explained.

Chapter 2 also discusses the sorption process a polymer undertakes and how the state of the polymer affects the polymer sorption process. Chapter 3 contains a brief description of the polymer and plasticizer materials chosen for the experiments in this thesis. Chapter 3 provides a list of the equipment, experimental setup and procedures undertaken. Chapter 4 presents the results and analysis of the study. Sample results of the measurements are presented along with an interpretation of the phenomena which affected the results. Chapter 5 provides a summary of the findings from this study followed by a proposal for further options to explore.

## 2 REVIEW OF ACOUSTIC-WAVE AND PLASTICIZER THEORIES

### 2.1 Introduction

Acoustic wave devices can be used for chemical and biological sensing in both gas and liquid environments depending on the acoustic mode. Surface acoustic wave devices have been shown to be more sensitive to perturbation occurring in the ambient environment because the acoustic energy of the wave is highly confined to the sensing surface. The particle displacement of conventional surface acoustic wave devices has a longitudinal component and a vertical component that can couple energy into compressional waves radiated into a fluid medium in contact with the substrate's surface [13]. The loss of energy into the liquid medium can be reduced by suitable rotation of the cut of the piezoelectric substrate until a wave with predominant particle displacement parallel to the surface, but perpendicular to the direction of wave propagation is obtained transforming the vertical component of the wave into a horizontal component. This type of wave is referred to as the shear horizontal wave and does not radiate energy into a fluid medium.

The guided SH-SAW sensor device consists of a piezoelectric material ( $\text{LiTaO}_3$ ) cut at an angle to support a shear-horizontal surface acoustic wave, a thin-film coating acting both as a sensing layer and a wave guide layer, and the electrode structures to generate and receive the acoustic wave. In comparison to bulk acoustic wave devices, SH-SAW sensors are more sensitive as they confine the acoustic energy primarily on the surface in contact with the medium

containing the analyte; whereas in the case of bulk acoustic wave devices, the acoustic energy is distributed throughout the entire substrate. However, depending on the substrate material and cut, SH-SAWs often propagate slightly at an angle into the substrate and as a result have reduced sensitivity to surface perturbations. By depositing a thin guiding layer on the device surface, the SH-SAW gets properly confined to the surface, increasing its sensitivity to mass and viscoelastic loading [14].

## 2.2 SAW Sensing Principles

As the acoustic wave propagates along the surface of the substrate, any surface perturbations will affect the wave's characteristics, i.e. phase velocity,  $v$ , and attenuation,  $\alpha$ . By tracking the changes in wave characteristics a sensor can be built. The particle motion caused by an SH-SAW is parallel to the surface and perpendicular to the direction of propagation. If  $x_1$  represents the direction of wave propagation,  $x_3$  the direction normal to direction of the wave but in plane with the surface and  $x_2$  the direction normal to the surface, then the particle displacement can be written as

$$u(x_1, x_2, x_3, t) = u(x_2, t)e^{j\omega t - \gamma x_1} \quad (2.1)$$

where  $\omega$  is the angular frequency of the wave ( $\omega=2\pi f$ , where  $f$  is frequency), and  $\gamma$  is a complex propagation factor representing both attenuation,  $\alpha$ , and wave number, ( $k=\omega/v$ ) and is given by [15]

$$\gamma = \alpha + jk = \alpha + j \frac{\omega}{v} \quad (2.2)$$

If frequency is constant then changes in wave propagation can be represented by [15]

$$\Delta\gamma = \Delta\alpha + j\Delta k = \alpha - jk_0 \frac{\Delta v}{v_0} \quad (2.3)$$

which can then be normalized to

In the above equation,  $k_0$  and  $v_0$  are the unperturbed wave number and phase velocity [16]. Deposition of a film on the surface of the acoustic substrate will affect the acoustic wave. The mechanical deformation and electrical potential associated with the propagating wave are coupled to the surface film. The mechanical coupling takes place in the form of mass loading caused by the translation of surface mass and elastic/viscoelastic effects [15][16]. The electrical coupling of the film and wave results in acoustoelectric interactions between the electric field generated by the SH-SAW and charge carriers in the film [15]. The film is selected such that the acoustic phase velocity in the film is lower than the acoustic wave velocity in the substrate in order to confine the wave to the surface.



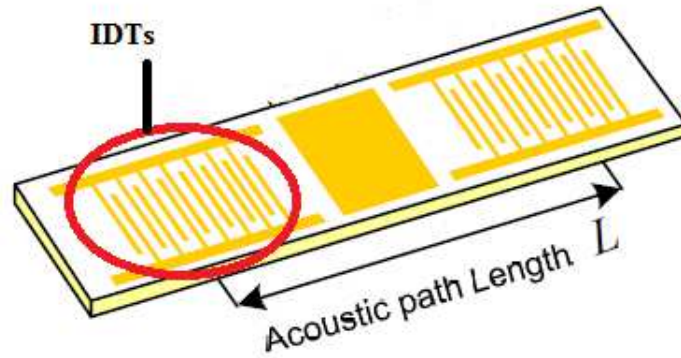


Figure 2.1 Schematic of a single delay line SH-SAW sensor

A single delay line sensor is shown in Figure 2.1, where  $L$  represents both the acoustic path length and the sensing length. The two parameters are identical here because in the configuration used both the inter-digital transducers and the metalized paths are coated with the sensing polymer and are exposed to the analytes. Therefore, the entire wave path is perturbed and the fractional change in frequency is given by the equation

$$\frac{\Delta f}{f} = \frac{\Delta v}{v} \quad (2.5)$$

It should be noted that in deriving eq. 2.5, it is assumed that there is no dispersion of the propagating wave, i.e. phase velocity,  $v$ , equals the group velocity,  $v_g$  [15].

The changes in phase velocity and attenuation due to perturbation are functions of the change in mass accumulation,  $\Delta m$ ; the viscoelastic change,  $\Delta c$ ; the change in dielectric constant,  $\Delta \epsilon$ ; the change in conductivity,  $\Delta \sigma$ ; the change

in temperature,  $\Delta T$ ; and the change in pressure,  $\Delta P$ . This is expressed as a sum of the partial derivatives of the phase velocity and/or attenuation with respect to each factor. The resultant responses are represented by the equation [16]

$$\Delta v = \frac{\partial v}{\partial m} \Delta m + \frac{\partial v}{\partial c} \Delta c + \frac{\partial v}{\partial \varepsilon} \Delta \varepsilon + \frac{\partial v}{\partial \sigma} \Delta \sigma + \frac{\partial v}{\partial T} \Delta T + \frac{\partial v}{\partial P} \Delta P \quad (2.6)$$

$$\Delta \alpha = \frac{\partial \alpha}{\partial m} \Delta m + \frac{\partial \alpha}{\partial c} \Delta c + \frac{\partial \alpha}{\partial \varepsilon} \Delta \varepsilon + \frac{\partial \alpha}{\partial \sigma} \Delta \sigma + \frac{\partial \alpha}{\partial T} \Delta T + \frac{\partial \alpha}{\partial P} \Delta P \quad (2.7)$$

Due to the use of a reference line polymer and differential measurements, temperature and pressure effects on our measurements are negligible. Pressure effects can also be neglected because SH-SAW devices used are not sensitive to pressure fluctuations unless the density of the medium changes or the substrate deforms as a result of pressure variations. In addition, the use of a measurement chamber to house the experimental setup reduces temperature fluctuations. In addition, the use of metalized delay lines also eliminates acoustoelectric interactions [15].

The surface mass of the film is translated by the traveling wave. While under the influence of the SH-SAW the film undergoes deformation. Mass loading produces a change in SAW velocity proportional to the areal mass

density ( $\rho$ ) contributed by the film. Additionally, the deformation produces energy storage and power dissipation in the film, resulting in a change in phase velocity and attenuation, respectively [15] [16]. Thus, changes in phase velocity and attenuation result from a combination of viscoelastic and mass-loading effects. Thus equation 2.6 and 2.7 can be further reduced to

$$\Delta v = \frac{\partial v}{\partial m} \Delta m + \frac{\partial v}{\partial c} \Delta c \quad (2.8)$$

$$\Delta \alpha = \frac{\partial \alpha}{\partial m} \Delta m + \frac{\partial \alpha}{\partial c} \Delta c \quad (2.9)$$

The viscoelastic properties of a polymer are described by its moduli: bulk modulus,  $K$ , and shear modulus,  $G$ . Under linear or sinusoidal deformation, the mechanical properties of a viscoelastic material are complex quantities:  $K = K' + jK''$  and  $G = G' + jG''$ . The real part represents the component of stress in phase with strain. This leads to energy storage in the film and thus the real parts of  $K$  and  $G$ ,  $K'$  and  $G'$  are referred to as storage moduli. The imaginary parts represent the component of stress 90° out of phase with strain which leads to power dissipation in the film thus the complex parts,  $K''$  and  $G''$  are called loss moduli. However, for this study  $G'$  and  $G''$  are used as the wave being perturbed is a shear horizontal wave.

Over a temperature range, a polymers can have different regions of storage and loss modulus behaviors. These regions are referred to as glassy, transition, rubbery and viscous regions. A glassy film exists when  $G' \cong 10^9$  Pa

and  $G'' \ll G'$ . The polymer is hard and brittle because the thermal energy of the polymer cannot overcome the potential energy barriers for molecule rotation and translation motion in the glassy region [32]. Therefore it is difficult for glassy polymers to absorb analytes. In the transition region, the polymer becomes softer by changing from a glassy state to a rubbery state. In this region, the storage modulus  $G'$  decreases rapidly with increasing temperature while the loss modulus  $G''$  increases due to the polymer softening. The glass transition temperature,  $T_g$  is the center temperature of the transition region and also the temperature at which the peak dynamic thermal loss occurs [32]. In the rubbery region, the polymer is soft and is able to absorb compatible analytes. A rubbery polymer has storage modulus  $G' \leq 10^7$  Pa and  $G''$  comparable to or less than  $G'$  [32]. In the viscous region,  $G'$  for a Newtonian liquid tends to zero and  $G'' = \omega\eta$ , where  $\eta$  is the liquid viscosity [32]. In figure 2.2 the various regions are presented.

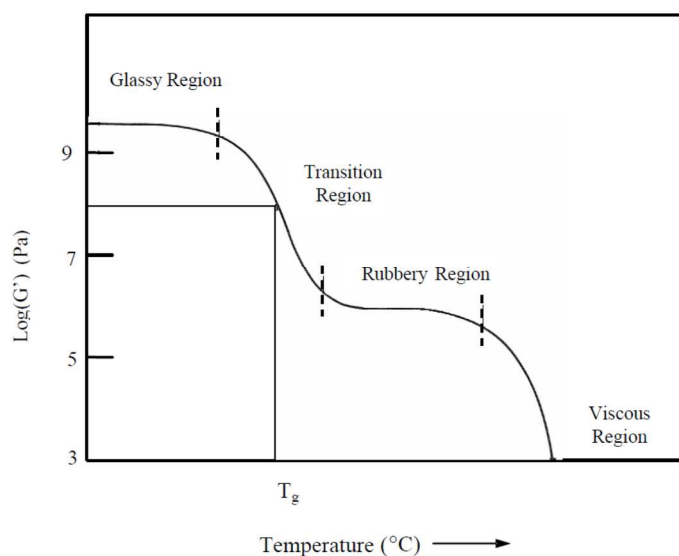


Figure 2.2 Modulus-Temperature curve showing the regions of viscoelastic behavior

## **2.3 Plasticizers**

### **2.3.1 Introduction**

Plasticizers have two purposes to aid in processing polymers and modify the properties of the final product. Plasticizers lower the processing temperature, reduce sticking in molds, and enhance wetting. Plasticizers increase the temperature range of usage, flexibility, elongation, and toughness and lower the glass transition temperature [17]. There are two kinds of plasticizers, internal and external plasticizers. Internal plasticization occurs when two polymers are co-polymerized, e.g. [bisphenol A-hexamethyltrisiloxane (BPA-HMTS)]. In the case of BPA-HMTS, The HMTS acts as a porous backbone increasing free volume [18]. External plasticizers are low volatile substances which do not chemically react when added to polymers. For this study, any reference to plasticizers will relate to external plasticizers.

### **2.3.2 The Lubricity Theory**

The lubricity theory states that a plasticizer facilitates the movement of polymer chains over each other. It takes into account the resistance of a polymer to deformation as a result of intermolecular friction. The lubricity theory assumes that there is very weak bonding between the plasticizer and the polymer

molecules. It also assumes there is no bonding between macromolecules of the polymer beyond that of surface irregularities [19].

### 2.3.3 The Gel Theory

According to the gel theory the rigidity of a polymer is the result of an internal three dimensional honeycomb-like structure. This gel is formed by the loose attachments which occur at intervals along the polymer chains. In glassier polymers the cells are small because the centers of attachments are close together. The plasticizer acts by masking the centers of attachments that hold the polymer chains together. This reduces the number of centers of attachments increasing flexibility. Free molecules of plasticizers serve to swell the polymer up into a gel and enable movement of the polymer chains. However, the gel theory is not sufficient in explaining the entire increase in flexibility [19].

### 2.3.4 The Free Volume Theory

The free volume or free space of a polymer is defined as the difference between the volume observed at absolute zero temperature and the volume measured at a given operating temperature. This is represented by the equation [20]:

$$V_f = V_t - V^0 \quad (2.10)$$

where  $V_f$  is the free volume,  $V_t$  is the volume at temperature  $t$  and  $V^0$  is the specific volume at the reference point at absolute zero [22].

## 2.4 External Plasticizer Requirements

When selecting a plasticizer one must consider three criteria: its compatibility with the polymer, its efficiency in plasticizing the polymer, and its permanence in the polymer.

### 2.4.1 Compatibility

It is necessary to use a plasticizer that is compatible with the intended polymer. Compatibility depends on polarity, structural configuration (shape), and molecular size (Mw) of plasticizer. Good compatibility results from the plasticizer and polymer having a similar chemical structure and close Hansen solubility parameters (see below). Plasticizers should have low volatility, as well as being non-toxic and aroma free (have a low vapor pressure) [19]. If compatibility is not established, syneresis occurs. Syneresis is the exudation (leaching out) of plasticizer out of the polymer matrix.

One method to determine compatibility is by looking at the solubility parameter ( $\delta$ ) of both polymer and plasticizer. The rule “like dissolves like” was one of the earliest rules to determine compatibility. There are two solubility parameters commonly used to determine compatibility, the Hildebrand solubility parameter and the Hansen solubility parameter [20].

The Hildebrand solubility parameter is related to the cohesion energy which characterizes the intermolecular interactions between molecules of the same polymer/solvent and is given by the equation [25]:

$$\delta = \left( \frac{\Delta E_i}{V_i} \right)^{1/2} \quad (2.11)$$

where  $E_i$  is the cohesive energy and  $V_i$  is the molar volume.  $\delta$  varies from 12 (MJ/m<sup>3</sup>)<sup>0.5</sup> for non-polar substances to 32 (MJ/m<sup>3</sup>)<sup>0.5</sup> for water and 36.7 (MJ/m<sup>3</sup>)<sup>0.5</sup> for triethanolamine [25]. Using  $\delta$  values, it is possible to predict which solvents are not able to dissolve a solute. However, if a polymer and a plasticizer have the same or similar  $\delta$  value they might still be incompatible as solubility depends on having similar functional group with mutual levels of interactions between polymers and plasticizers. This also holds true for polymers and analytes as well.

Hansen's solubility parameter takes the Hildebrand's solubility parameter and breaks it down into the contributions by the individual molecular interactions [20]. Hansen assumed the cohesive energy was a result of contributions of dispersion such as van der Waals, polar and hydrogen bond interactions portraying the relationship in the equation [20]

$$E = E_d + E_p + E_h \quad (2.12)$$

where  $E_d$ ,  $E_p$  and  $E_h$  represent the cohesive energy due to dispersion, polar and hydrogen bond interactions, respectively. By applying equation 2.11 to 2.12 Hansen obtained the following equation [20]



$$\delta = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2.13)$$

where  $\delta_d$ ,  $\delta_p$ ,  $\delta_h$  represent the solubility parameters due dispersion, polar and hydrogen bond interactions, respectively. [20].

#### 2.4.2 Efficiency

Good plasticizers provide high plasticization at low concentration and show rapid polymer diffusion and interaction. Plasticizer efficiency is defined as the amount of plasticizer required to yield the desired film mechanical properties. One method to evaluate plasticizer efficiency is the amount of plasticizer required to lower the glass transition temperature ( $T_g$ ). However, there is no established system to determine the efficiency of each plasticizer, because it depends on the polymer properties. The size or molecular weight ( $M_w$ ) and the rate of plasticizer diffusion into the polymer matrix can also be used to define plasticizer efficiency. Higher plasticizer diffusion rates result in higher plasticizer efficiency. Small molecules have high diffusion rates but they possess higher volatility. Higher volatility leads to plasticizer leaching out of the polymer [17].

#### 2.4.3 Permanence

Plasticizer permanence is defined as the measure of the likelihood that the plasticizer would not leach out of a polymer. The plasticizer permanence in polymers depends on the size of the plasticizer molecule and on the rate of diffusion in polymers. Larger plasticizer molecules are less volatile. Large alkyl

moieties in plasticizers such as the larger phthalates have increased hydrophobicity [20]. Polarity and hydrogen bonding capabilities between the plasticizer and polymer, and plasticizer and the ambient environment will influence the volatility/solubility of plasticizers. If greater plasticizer efficiency is defined by rapid diffusion into the polymer, then this may result in lesser plasticizer permanence due to diffusion out of the polymer matrix [17].

#### **2.4.4 Antiplasticization**

If a small amount of plasticizer is added to a polymer, the polymer tends to become more ordered and compact. This is a result from the creation of new crystallites or the growth of existing crystallites at the expense of more fluid parts. Intermolecular forces between the plasticizer and the polymers tend to trap the few plasticizer molecules in place. This prevents the movement of side chains and segments of the polymer which absorb mechanical energy. This results in a more rigid polymer increasing the storage modulus of the polymer [19].

Antiplasticization does not always occur at low concentrations of plasticizers but can occur at higher concentrations as well. Further crystallite formation can occur when a large amount of plasticizer is added to a polymer and is mixed and heated up together. In certain polymers like Poly vinyl chloride, the degree of crystallinity increases, but the amorphous regions are swollen and the polymer becomes softer. This plasticized polymer is more flexible, has better elongation, higher impact resistance, but lower tensile strength and modulus than the base polymer. However, the crystallites can be eliminated if more plasticizer is added [19].

### 2.4.5 Calculating Glass Transition Temperature using the Gordon and Taylor Equation

As earlier stated, one method to determine how effective a plasticizer would be is to measure the glass transition temperature. However, it is not always possible to measure the glass transition temperature due to lack of equipment. Due to this fact, there are multiple plasticization methods used to predict the glass transition temperature of a system. The most commonly used is the Gordon and Taylor equation [21][20].

It is assumed that energetic effects of plasticizers interactions are caused by binary heterocontacts which cause conformational redistribution of polymer chains in the neighborhood of these contacts. This assumption is modeled by the following power equation [21][20]

$$\frac{T_g - T_{g1}}{T_{g2} - T_{g1}} = (1 + K_1)w_{2c} - (K_1 + K_2)w_{2c}^2 + K_2w_{2c}^3 \quad (2.14)$$

where  $T_g$  is the glass transition temperature of the system,  $T_{gi}$  are the glass transition temperatures of individual components, and  $i=2$  represents component with higher  $T_g$ ,  $K_1$  is the parameter of power equation, which depends on the difference between the interaction energies of the binary hetero- and homo-contacts between the polymers and plasticizers, and  $K_2$  is the parameter of power equation, which depends on additional energetic contributions due to conformational entropy changes during binary contact formation [37].  $W_{2c}$  is the weight fraction of the component with higher  $T_{g2}$ , corrected for the different volume expansivity of the blend components and is given by the formula [20]

$$w_{2c} = \frac{K_{GT}w_2}{w_1 + K_{GT}w_2} \quad (2.15)$$

where  $w_i$  represents the weight fraction of a component, and  $K_{GT}$  is the Gordon Taylor Parameter defined as [21][20]:

$$K_{GT} = \left( \frac{\rho_1}{\rho_2} \right) \left( \frac{\Delta\alpha_2}{\Delta\alpha_1} \right) \quad (2.16)$$

where  $\rho_i$  represents the density of the component and  $\Delta\alpha_i$  is the increment of expansion coefficients at the glass transition temperature. Using the Simha-Boyer rule  $\Delta\alpha T_g = \text{constant}$ , the Gordon Taylor parameter is simplified to:

$$K_{GT} = \left( \frac{\rho_1}{\rho_2} \right) \left( \frac{T_{g1}}{T_{g2}} \right) \quad (2.17)$$

The Gordon Taylor equation is further simplified if we assume there are no interactions ( $K_1=K_2=0$ ) then it becomes:

$$T_g = \frac{w_1T_{g1} + K_{GT}w_2T_{g2}}{w_1 + K_{GT}w_2} \quad (2.18)$$

However, several mixtures have been found to deviate from the Gordon and Taylor model at high plasticizer content. The Gordon Taylor Parameter  $K_{GT}$  assumes ideal volume mixing and no interactions between the components. This deviation was theorized to be a result of interactions between components; one example being hydrogen bonding. Key accounted for these interactions by

modifying the Gordon and Taylor equation through the introduction of a second parameter,  $q$ . Kwei's equation states [21]:

$$T_g = \frac{w_1 T_{g1} + K_{GT} w_2 T_{g2}}{w_1 + K_{GT} w_2} + q w_1 w_2 \quad (2.19)$$

Plasticizers not only lower the glass transition temperature but also spread the loss peak over a larger range of temperatures, widening the glass transition region. In addition, plasticizers ensure that resultant coating has a lower degree of stiffness than the base polymer for a given temperature due to the addition of the plasticizer with its lower molecular weight [35]. This is evident in Figure 2.3 which shows modulus-temperature curves of plasticized poly (vinyl chloride) (PVC). Addition of 30% DOP reduces the stiffness modulus of PVC to 1% of its value at 23°C whereas for polymers with  $T_g$  slightly above room temperature such as poly (vinyl acetate) (PVA) addition of only 10% DOP is required to have the same effect [35].

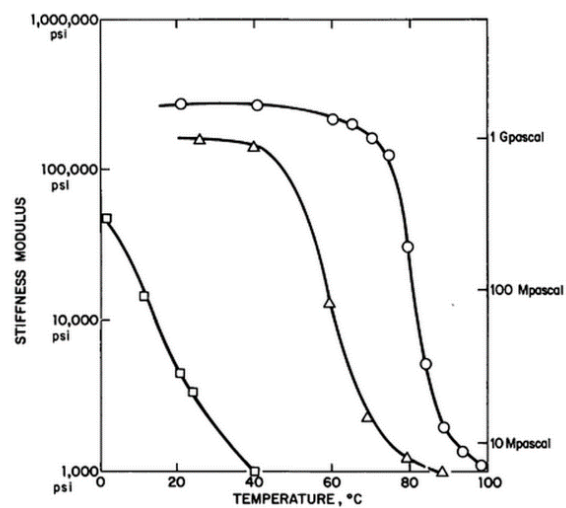


Figure 2.4 Modulus-Temperature curves of plasticized poly (vinyl chloride): (○) no plasticizer; (Δ) 10% DOP; (□) 30% DOP. Tg of (○) 80°C; (Δ) 59°C; (□) 16°C [35]

### **3 EXPERIMENTAL PROCEDURE**

#### **3.1 Introduction**

This chapter provides a list and description of the materials, equipment, and procedures used for the experimental work of this project. Polymer-plasticizer blends of various compositions were used to make the sorbent coatings of the SH-SAW sensors. The coated sensor devices were then characterized by measuring the mass uptake and changes in viscoelastic properties through changes in the device characteristics (frequency and attenuation loss) due to exposure to target analyte solutions. The device was successively exposed to Milli-Q-deionized water and aqueous solutions of benzene in various concentrations while being monitored periodically by a network analyzer.

#### **3.2 Materials Used**

##### **3.2.1 Polymers**

##### **Polystyrene**

Polystyrene was chosen for this experiment because it has a Hildebrand solubility parameter of 18.3, close to that of benzene [25]. Having close solubility parameters is a prerequisite for good miscibility and high sensitivity in chemical sensing. However, polystyrene has a glass transition temperature of about 100°C [29], necessitating the addition of a plasticizer to facilitate analyte sorption.

Polystyrene of average molecular weight of 35,000 measured using gel permeation chromatography (GPC) was purchased from Sigma Aldrich.

### **Poly (Ethyl Acrylate)**

Poly (Ethyl Acrylate) (PEA) was chosen for this study as it had previously been used as a sensing layer for benzene [8]. A 20% PEA solution in toluene with an average molecular weight of 90,000 GPC was purchased from Sigma Aldrich.

### **Poly (Methyl Acrylate)**

Poly (Methyl Acrylate) (PMA) was chosen for this study because Poly (Methyl Methyl Acrylate) (PMMA), a member of the acrylate family, had been shown to absorb benzene with the addition of various plasticizers including DOP [22] [23]. PMA has glass transition temperature below room temperature at 9°C [28] which places the polymer in the viscoelastic transition region at room temperature and ground water temperature. A 40% PMA solution in toluene with an average molecular weight of 40,000 GPC was purchased from Sigma Aldrich.

### **3.2.2 Dioctyl Phthalate (DOP)**

Dioctyl phthalate ( $C_{24}H_{38}O_4$ ) is a commonly used plasticizer in various polymers for many applications. Dioctyl phthalate has been used in concentration of 5-25 wt.% for optical sensing in polystyrene Dioctyl phthalate is not to be confused with di-n-octyl phthalate (DNOP) ( $C_6H_4(COOC_8H_{17})_2$ ) an isomer of



dioctyl phthalate. Due to this isomer dioctyl phthalate is often referred to as di (2-ethylhexyl) phthalate (DEHP) [20].

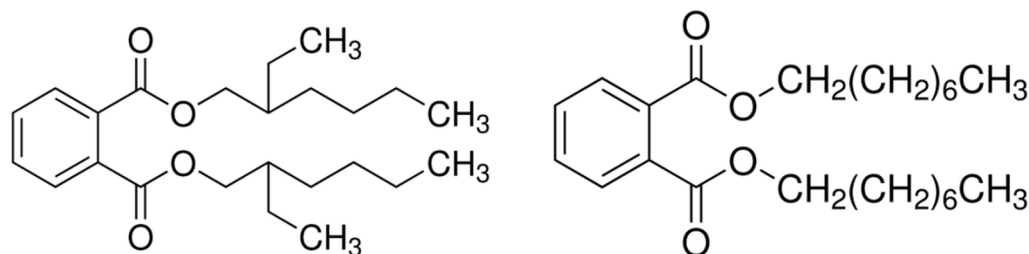


Figure 3.1: Chemical structure of DOP (left) and DNOP (right)

DOP has a boiling temperature point of 384°C and a freezing temperature point of -50°C which ensures that a phase change will not occur in groundwater monitoring wells [20]. DOP is highly hydrophobic due to its aliphatic chain and has a water solubility of 0.285mg/l at 24°C. Hence it is considered insoluble [30]. DOP is highly toxic and the EPA has set a limit of 5ppb in drinking water [10].

### 3.3 Equipment Used

The spin coater used was a Specialty Coating System Model P6024. The spin coater functions by applying a vacuum to the back side of the SH-SAW device holding it in place, and then spinning the device with the polymer solution on it using a preset program. The program is configured to select the spin speed, ramp time, spin time, and ramp down time desired. The spin coater is used to recreate reproducible film thickness for a given polymer solution. The

thickness of a film deposited through spin coating will vary based on the properties of the polymer solution (concentration, viscosity, molecular mass, solvent evaporation rate) and the spin process (spin time, spin speed) [26].

The profilometer used to determine the thin coating thickness was a KLA-Tencor Alpha-Step IQ. A profilometer drags a microscopic tip over the surface of a substrate to measure variations in height across a profile of the surface. The profilometer moves the sample and probes the surface to record the profile of a sample [26]. In this work, the profilometer was used to measure the height of the edge of a polymer coating. The profilometer tip can scratch a polymer surface if the polymer is soft. This could give false readings or even damage the profilometer tip or the device underneath the polymer. In order not to damage the device, glass slides cut in the shape of the SH-SAW devices are used to initially characterize the coating thickness. However, when the polymer coating is too soft, an ellipsometer was used.

The ellipsometer used was a Gaertner Scientific Corporation L2WLSE544. This ellipsometer measures the thickness of a film by using two lasers at 633nm and 544nm at oblique angle [27]. The lasers are then fired without making physical contact with the surface. This removes the risk of damaging the film with a probe. The laser beams propagate through both the film and substrate on a black surface and are reflected into a receiver off the film-air boundary, film-substrate boundary and substrate-black surface boundary. Measurements can also be taken on the gold delay lines, eliminating the reflection from the bottom of the substrate. Part of the incident laser beams is reflected at the boundary of the

thin film and substrate and the boundary between the film and air, respectively. For thin films, the two reflected beams will overlap and the ellipsometer records the effective polarity of the reflected laser beam [28]. The receiver records information about the transmitted light and uses an appropriate 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 [28].

Electrical characterization of the uncoated and coated devices was accomplished using a vector network analyzer. The vector network analyzer used was the Agilent E5061B. A vector network analyzer measures the signal transmitted through an SH-SAW device at multiple frequencies. The vector network analyzer is also used to monitor the response of the coated device in the presence of a given analyte. A switch control unit is used in conjunction with the network analyzer to allow the network analyzer to monitor two delay lines alternately. A program based on Agilent VEE software is used on an attached computer to process the data and display changes in frequency, loss and phase of both delay lines. This can be used to conduct a differential measurement between a reference line and a sensing line.

A pump used to deliver the analyte solution to the device surface. The pump was manufactured by ISMATEC, model Reglo Digital MS. The pump is used to transfer the benzene samples or the reference solution from a sealed container via a tube through a 3-way valve to a flow cell and then finally into a sealed waste container. The flow cell used to maintain a constant volume of the

analyte solution on the device surface was a fitted brass/polycarbonate flow cell capable of holding one dual delay line SH-SAW Device. Shielded coaxial cables connect the flow cell to the network analyzer. The flow cell and samples are stored in a chest cooler to shield the device and samples from sources of heat, and to simulate the environment of a groundwater monitoring well. Note that changes in temperature will result in signal baseline drift.

### 3.4 Experimental Procedures

#### 3.4.1 Plasticizer Polymer Solution Preparation

The procedure for preparing plasticizer-polymer blends was largely based on previous work done at the Microsensor laboratory group and work done by Pejic et al. [23][22]. Listed below are the steps used in preparing the plasticizer-polymer blend.

1. List targeted mass of polymer mixture and target plasticization percentage
2. Measure polystyrene initially
  - a. List your target mass of polystyrene
  - b. Record actual mass of polystyrene
3. Calculate total mass of di(2-ethylhexyl) phthalate (DOP) and polystyrene needed

$$\text{a. } \text{Mass}_{DOP-PS} = \frac{\text{Mass}_{PS}}{1 - \text{PlasticizerPercentage}} \quad (3.1)$$

4. Measure mass of DOP
5. Record new total mass

6. Calculate plasticizer percentage

$$\text{a. } PlasticizerPercentage = \frac{Mass_{DOP+PS} - Mass_{PS}}{Mass_{DOP+PS}} \quad (3.2)$$

7. Calculate mass/volume of solvent needed to achieve desired concentration

8. Wear gas mask

9. Add required mass/volume of solvent and record measurement

10. Calculate mass percentage of the plasticizer-polymer blend in the solution

11. Mildly sonicate the plasticizer-polymer solution for 4 hours at least.

(Sonication was employed instead of stirring as sonication led to more reproducible results and evenly distributed plasticizers in the blend)

12. Spin coat device.

13. Bake for 60 minutes at 60°C

### 3.4.2 Benzene Solution Preparation

The benzene solutions are prepared as a solution of benzene in Milli-Q deionized water. Concentrations in ppm are prepared using the following formula.

$$ppm = \frac{v_{benzene} \times \rho_{benzene}}{v_{benzene} \times \rho_{benzene} + v_{water} \times \rho_{water}} \times 10^6 \quad (3.3)$$

Where  $v$  represents volume and  $\rho$  represents density.

However, the volume of water is considerably greater than that of benzene and the density of water is 1.0g/mL. The denominator of equation (3.3) becomes dominated by terms associated with water. As a result, equation (3.3) is simplified into

$$ppm = \frac{v_{benzene} \times \rho_{benzene}}{v_{water}} \times 10^6 \quad (3.4)$$

The solutions are prepared in 240mL graduated glass jars with Teflon® lined cap. The Glass jars are filled with 260mL of water to minimize headspace and reduce the possibility of benzene evaporating. Benzene has a density of approximately 0.88g/mL. Using equation (3.4), 0.30 µL of benzene is required to make 1ppm of benzene solution in 260mL of water. After filling the jar with water, a stir bar is added and then the appropriate amount of benzene is added to make the desired concentration. Immediately after adding the benzene, a Teflon® line cap is tightly screwed onto the jar. Then samples are stirred for an hour and a half on a stir plate.

### 3.4.3 Chemical Sensing Measurements

Electrical tape is applied closely to the back of the coated device to act as an acoustic absorber for bulk waves which travel through the substrate. The reflected bulk waves could be detected by the output transducer, thus resulting in

the main signal distortion. Then the contact pads of the SH-SAW dual delay lines are coated with a conductive silver paint. It is noted that this step is not needed, but is done to prevent the contact pads from being scratched. After the paint dries, the coated device is placed in a flow cell and the space above the acoustic delay lines is tightly sealed with a gasket to prevent air bubbles from forming. Then degassed Milli-Q water and a pre-conditioning solution are flown through two separate tubes into the three-way valve. Once both tubes are filled the three-way valve is filled while tapping it to remove air from the interior of the three-way valve. Then water is flown through to the flow cell. Once the flow cell is filled and no air bubbles are present, the flow cell is connected to the vector network analyzer. Then the flow cell is left for approximately an hour allowing the temperature in the cooler to stabilize and the pump is set to a flow rate of  $7\mu\text{l/s}$ . Afterwards, the Agilent VEE program is started and measures a baseline for 10 minutes as Milli-Q water is continuously pumped over the SH-SAW device. The device is exposed to the highest concentrated benzene sample as a preconditioning step until the sensor response reaches steady state, then it is exposed to water until all of the benzene has been desorbed from the plasticizer-polymer coating. Then the same procedure is repeated with individual concentrations of benzene while alternating with Milli-Q water. After benzene samples are changed, their lids must be tightened to ensure that benzene does not evaporate. If the device is to be reused with a particular coating at a later occasion, it must remain in the flow cell; otherwise the removal of the flow cell gasket may result in damage to the polymer coating.

#### **3.4.4 Data Preparation**

Software based on Agilent VEE collects the data from the network analyzer and stores them in a data file (.DAT). The stored data is in a data file (.DAT). The data file can be imported into any spreadsheet program such as Microsoft Excel. Then a linear piecewise baseline correction is performed where each linear section extends from the time the device is exposed to a benzene sample until the moment the sample has been completely flushed out. The piecewise linear baseline correction is done because, as the experiment takes place, temperature changes, water swelling of the plasticizer polymer coating and other environmental factors will cause the baseline to drift.



## **4 RESULTS**

### **4.1 Introduction**

The performance of the SH-SAW device each coated with one of three polymers (PS, PMA and PEA) mixed with varying concentrations of dioctyl phthalate (DOP), a plasticizer, for detection of benzene is investigated. The investigation is undertaken to characterize the effect of DOP on the response of the polymer-coated sensors to benzene and to create additional coatings for the implementation of a sensor array. Two or more plasticizer-polymer ratios are investigated at different coating thicknesses. Data collected consisting of frequency shifts as a function of time and ambient benzene concentration are used to compare the effects of the plasticizer concentration on performance of various thin film coated SH-SAW devices. Three polymers within three different glass transition temperature regions are utilized to show the efficacy of the plasticizer-polymer composite coatings.

### **4.2 Measurement**

#### **4.2.1 Polystyrene**

Polystyrene presents itself as a suitable candidate for a polymer coating for the detection of benzene due to its Hildebrand's solubility parameter being

18.3MPa<sup>1/2</sup>, which matches the solubility parameter of benzene. However, Polystyrene is a rigid polymer and has a glass transition temperature greater than 100°C which does not allow benzene to diffuse into the polymer; thus the need to plasticize polystyrene with DOP to improve the absorption of benzene by polystyrene.

#### 4.2.1.1 Higher Concentrations of Benzene

To initially test the efficacy of plasticizer polymer composite coatings, benzene concentrations ranging from 2-20 parts per million (ppm) were tested over various composite ratios of DOP and polymer. Initially, 25% DOP-PS and 30% DOP-PS were tested at thicknesses of 1.0 µm, 1.1 µm and 1.3 µm, with 1.1 µm and 1.3 µm showing the highest sensitivity.

Figure 4.1 shows the frequency response of sensors with 1.1 µm thick coatings of polystyrene and 30% DOP-PS, respectively, being exposed to concentrations of 2, 5, 10 and 20 ppm of benzene. As predicted, the frequency response of the polystyrene-coated device does not show much perturbation in the presence of benzene. In addition, it is noticed that for 30% DOP-PS, frequency shift is not linear with concentration as the concentration approaches 20ppm. This is most likely due to viscoelastic effects as higher concentrations of benzene further plasticizes the polymer. Figure. 4.2 shows the response of a 1.1 µm thick 25% DOP-PS polymer coated device being exposed to 2, 5, 10 and 20ppm of benzene. In comparison, the 30% DOP-PS polymer coated device had an insertion loss of -27dB and a sensitivity of 210Hz/ppm whereas the 25% DOP-

PS polymer coated device had an insertion loss of -23dB in water and a sensitivity of 200Hz/ppm.

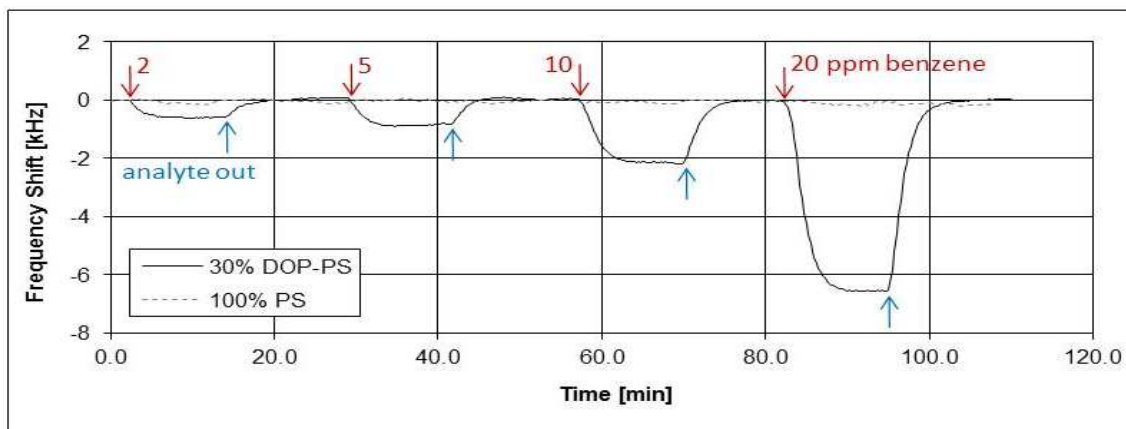


Figure 4.1 Frequency responses of SH-SAW devices with 1.1  $\mu\text{m}$  thick 30% DOP-PS and 100% PS sensing films.

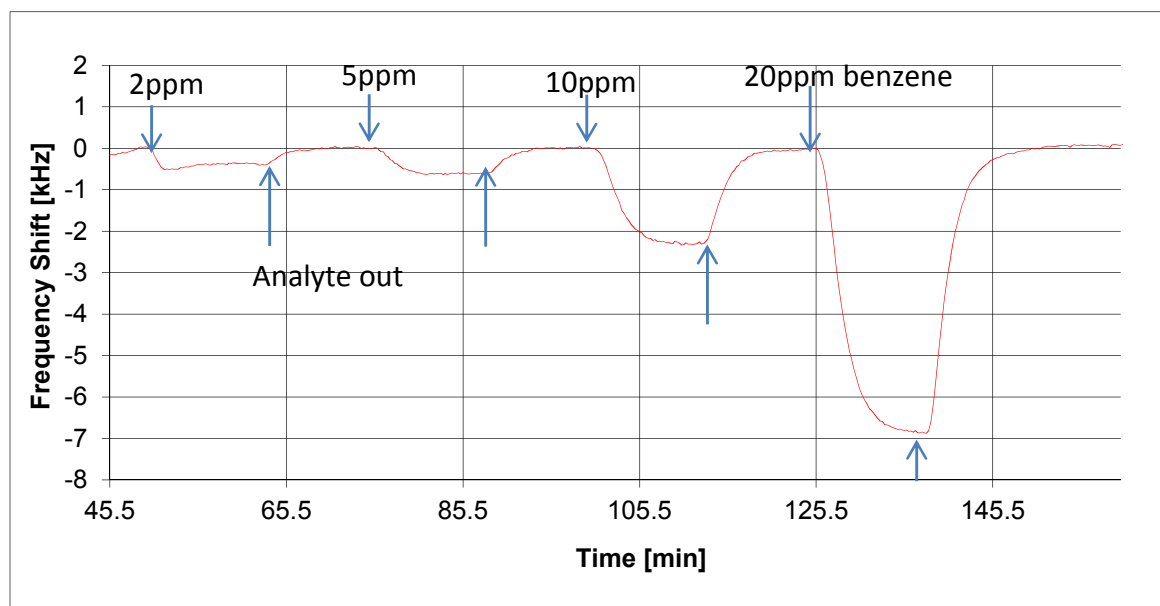


Figure 4.2 Frequency response of an SH-SAW device with a 1.1  $\mu\text{m}$  thick 25% DOP-PS sensing film.

After testing 1.1  $\mu\text{m}$  thicknesses, 1.3  $\mu\text{m}$  thick 25% DOP-PS and 1.3  $\mu\text{m}$  30% DOP-PS were tested. However, the respective devices had insertion losses of -37dB and -40dB. Figure 4.3 And Figure 4.4 show the frequency responses in the presence of 2, 5, 10 and 20 ppm of benzene. As can be seen, as the signal increases, the noise also rises. On the one hand, sensitivity increases from 200Hz/ppm to 300Hz/ppm for 25% DOP-PS and from 210Hz/ppm to 400Hz/ppm for 30% DOP-PS. However, due to the initial high insertion loss, it is not recommended to use a sensor with 1.3  $\mu\text{m}$  thick coating of any ratio of DOP-PS because this would result in increased baseline noise and/or reduced longevity for this sensor.

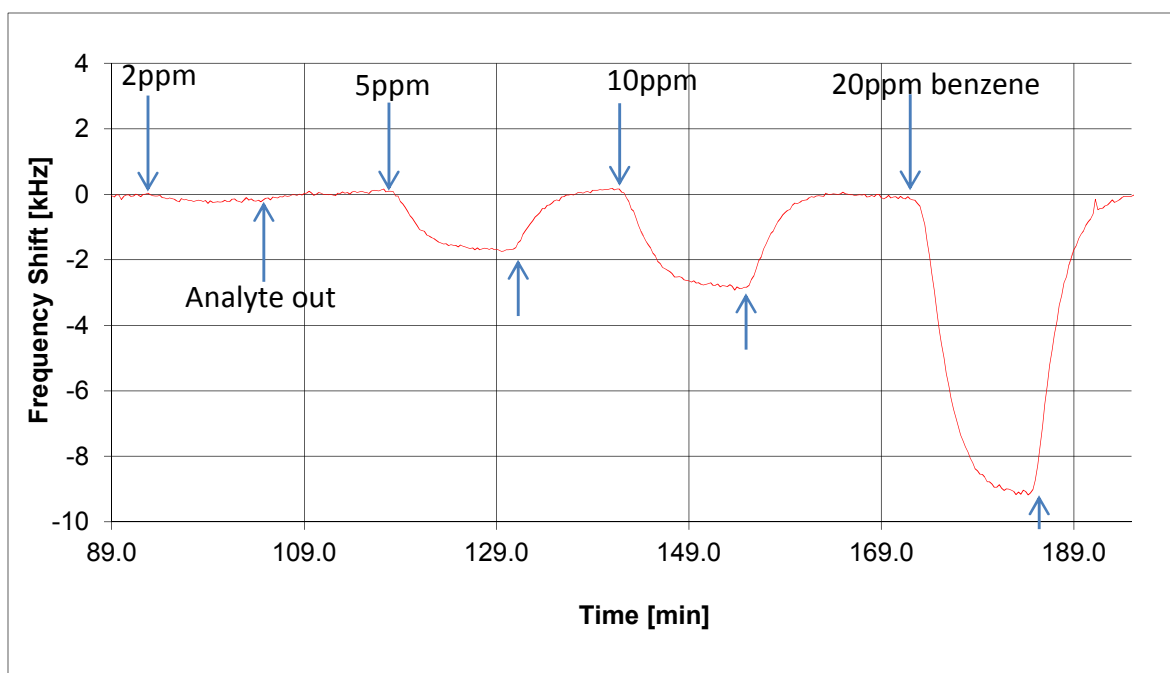


Figure 4.3 Frequency response of an SH-SAW device with a 1.3  $\mu\text{m}$  thick 25% DOP-PS sensing film.

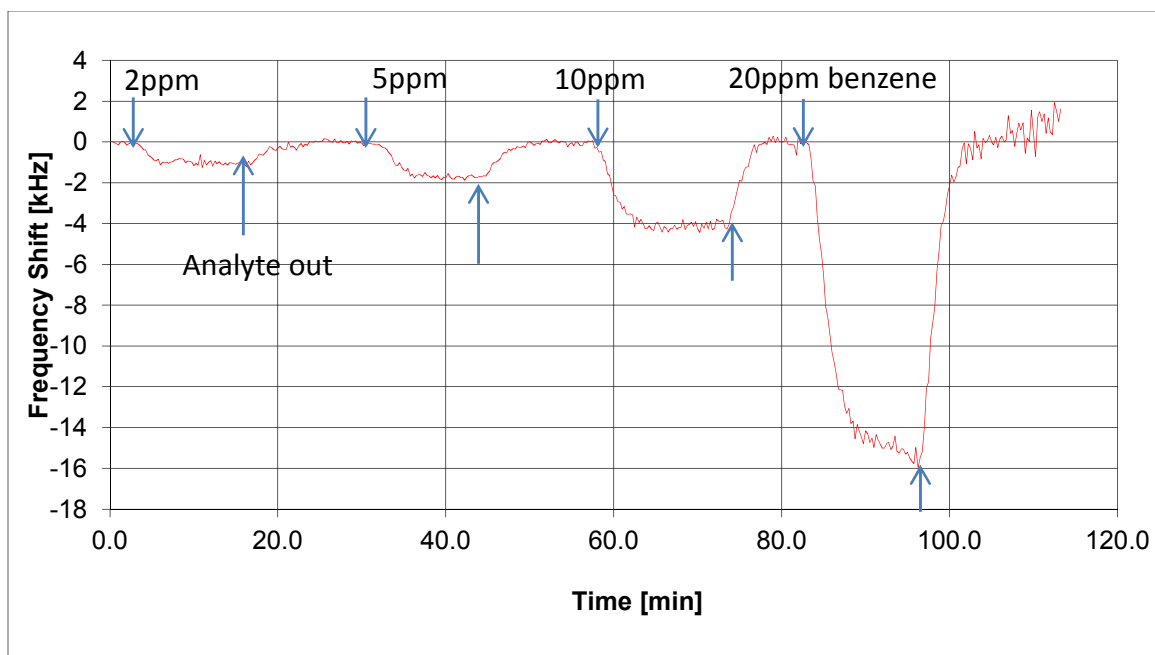


Figure 4.4 Frequency response of a SH-SAW device with a 1.3  $\mu\text{m}$  thick 30% DOP-PS sensing film.

#### 4.2.1.2 Lower Concentrations of Benzene

As stated earlier, the maximum acceptable contamination limit for benzene is 5 ppb. As such there is a need to test the DOP-PS polymers in the presence of lower concentrations of benzene. At lower concentrations of benzene, viscoelastic effects due to plasticization through absorption of benzene would be less pronounced, resulting in a linear relation between frequency shift and benzene concentration. Concentrations of 0.2, 0.5, 0.8, 1.0 and 2.0 ppm were selected to conduct the lower concentration test. In addition, due to the proximity of sensitivity between 25% DOP-PS and 30% DOP-PS, it was decided to look at lower concentrations of DOP in the DOP-PS polymer coatings. Originally, 22.5% DOP-PS and 20% DOP-PS were intended to be used as test

polymer coatings. However during the preparation of the polymer-plasticizer blend, 23% DOP-PS and 20% DOP-PS were obtained.

Upon conducting tests on 1.1 $\mu$ m 23% DOP-PS and 1.1 $\mu$ m 20% DOP-PS, it is noticed that their sensitivities are higher than those of 30% DOP-PS and 25% DOP-PS. However, the sensitivity for 1.1 $\mu$ m 23% DOP-PS is 940Hz/ppm and the sensitivity of 20% DOP-PS is 560Hz/ppm as shown in figures 4.5 and 4.6 respectively. The lower sensitivities at 25% DOP-PS and 30% DOP-PS are caused by anti-plasticization beyond the optimal concentration of plasticizer in a polymer, as extra plasticizer occupies existing free volume.

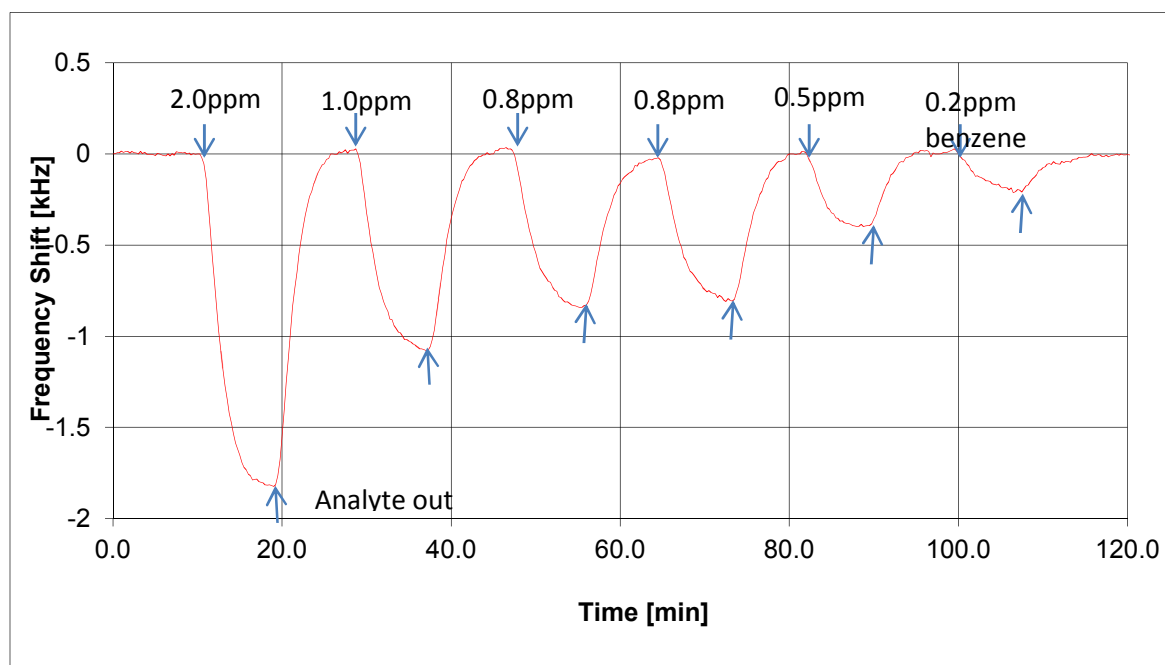


Figure 4.5 Frequency response of a SH-SAW device with a 1.1  $\mu$ m thick 23% DOP-PS sensing film.

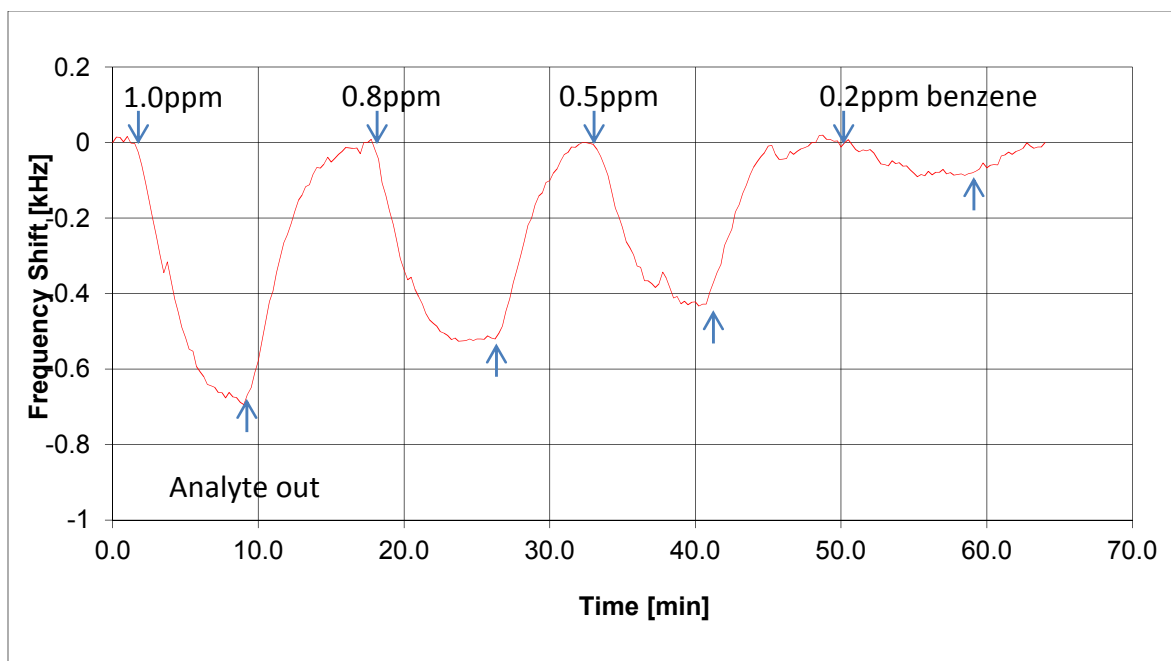


Figure 4.6 Frequency response of a SH-SAW device with a 1.1  $\mu\text{m}$  thick 20% DOP-PS sensing film.

#### 4.2.2 Poly (Ethyl Acrylate)

Poly (ethyl acrylate) (PEA) has previously been used as a sensing polymer for BTEX compounds. In addition, another polymer with an acrylate functional group, poly (methyl methyl acrylate) (PMMA) has previously been plasticized with DOP to improve its physical properties to enable it to sense BTEX compounds [22]. PEA with a  $1\mu\text{m}$  thickness on a SH-SAW platform has been shown to have a sensitivity of 300Hz/ppm and a detection limit of approximately 100 ppb [8]. Figure 4.7 shows the frequency response of  $1\mu\text{m}$  thick 1% DOP-PEA polymer exposed to 2, 5, 8 and 10 ppm samples of benzene in Milli-Q deionized water.

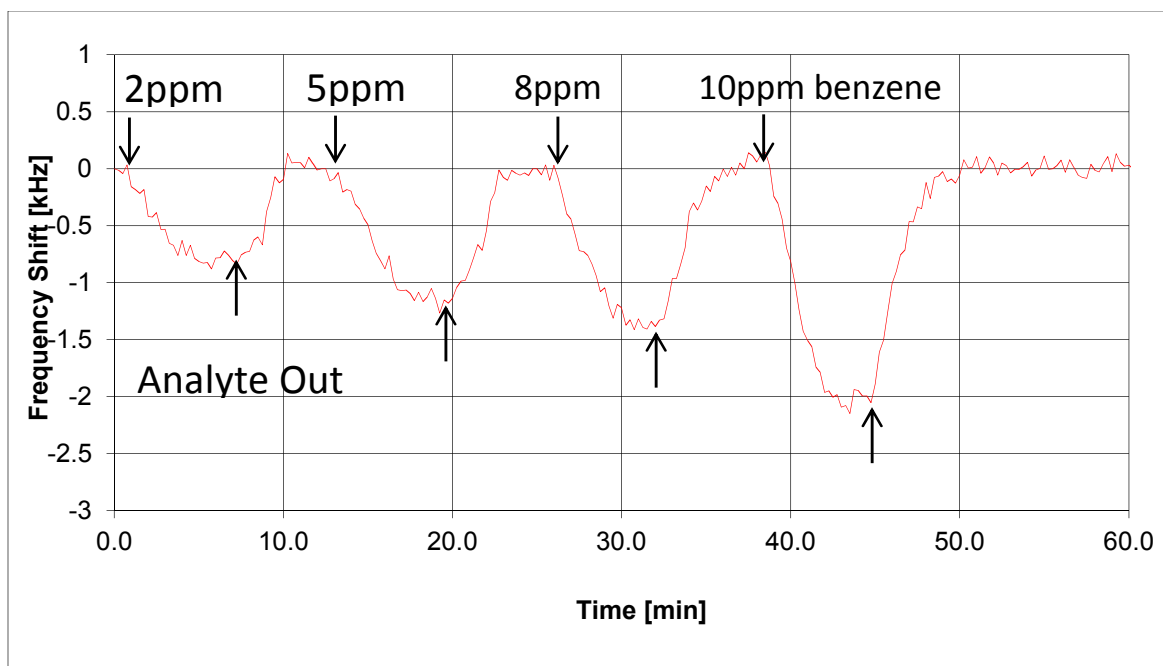


Figure 4.7 Frequency response of a SH-SAW device with a 1  $\mu\text{m}$  thick 1% DOP-PEA sensing film.

However, upon testing, the 1  $\mu\text{m}$  thick 1% DOP-PEA coating shows a sensitivity of 240 Hz/ppm, and an rms noise level of 55Hz. The reduced sensitivity is evidence that anti-plasticization occurred whereby less free volume was created, as the plasticizer occupied the existing free volume.

After anti-plasticization effects were observed, the DOP concentration in the mixture was increased to 2%. Figure 4.8 shows the frequency response of 1  $\mu\text{m}$  2% DOP-PEA thick polymer exposed to 2, 5, 8 and 10 ppm samples of benzene in Milli-Q deionized water. However, the measured initial insertion loss was -53dB, which signifies that the response would have a poor signal-to-noise ratio.



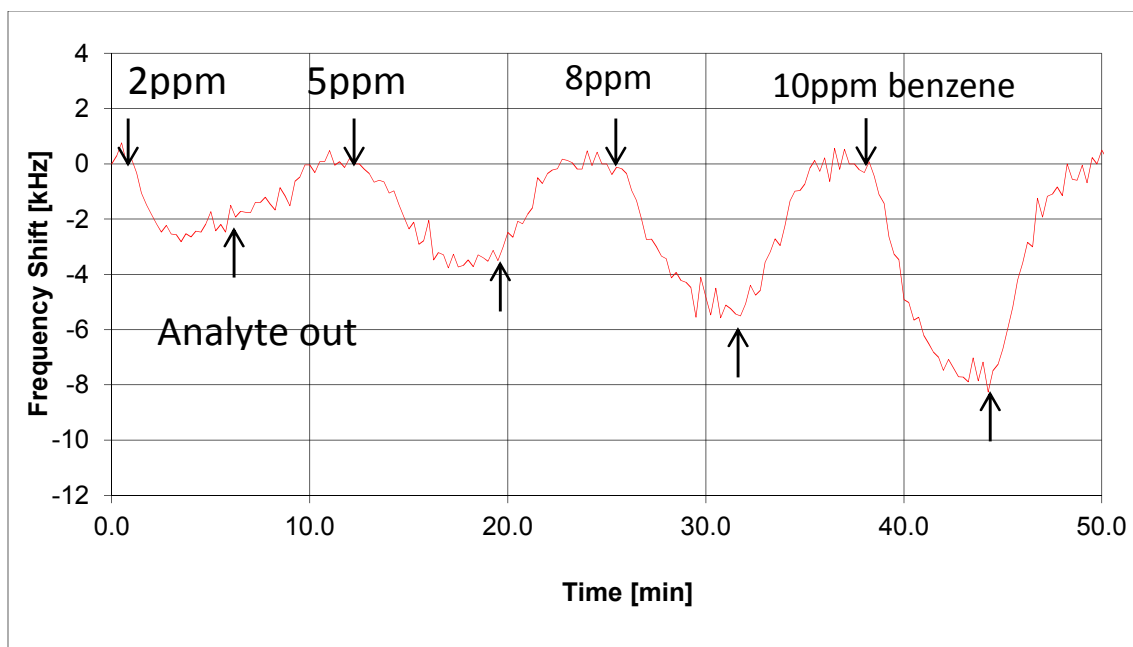


Figure 4.8 Frequency response of a SH-SAW device with a 1  $\mu\text{m}$  thick 2% DOP- PEA sensing film.

However, upon testing, the 1  $\mu\text{m}$  thick 2% DOP-PEA coating has a sensitivity of 750 Hz/ppm, and a detection limit of 2700ppb. Due to the increased insertion loss and decreased signal-to-noise ratio, the detection limit obtained was not as good as that of 100% PEA, signifying that for soft polymers, plasticization might not be helpful to improve sensor quality.

#### 4.2.3 Poly (Methyl Acrylate)

Poly (methyl acrylate) (PMA) is similar in structure to PEA and PMMA which have previously been plasticized with DOP. However, a thin film of 100% PMA with a thickness of 0.75  $\mu\text{m}$  has previously been shown to exhibit a lower sensitivity to BTEX compounds when compared to PEA [31]. The small

frequency response suggests that the polymer is not rubbery enough to detect sub ppm concentrations of benzene. PMA can potentially be made rubbery by adding a plasticizer such as DOP to it. Through the addition of plasticizers the glass transition temperature of PMA can be further reduced from 9°C to below freezing point to improve the sensitivity of a PMA coated SH-SAW device and to ensure the coating will be in the rubbery state over the entire temperature range relevant for groundwater monitoring applications.

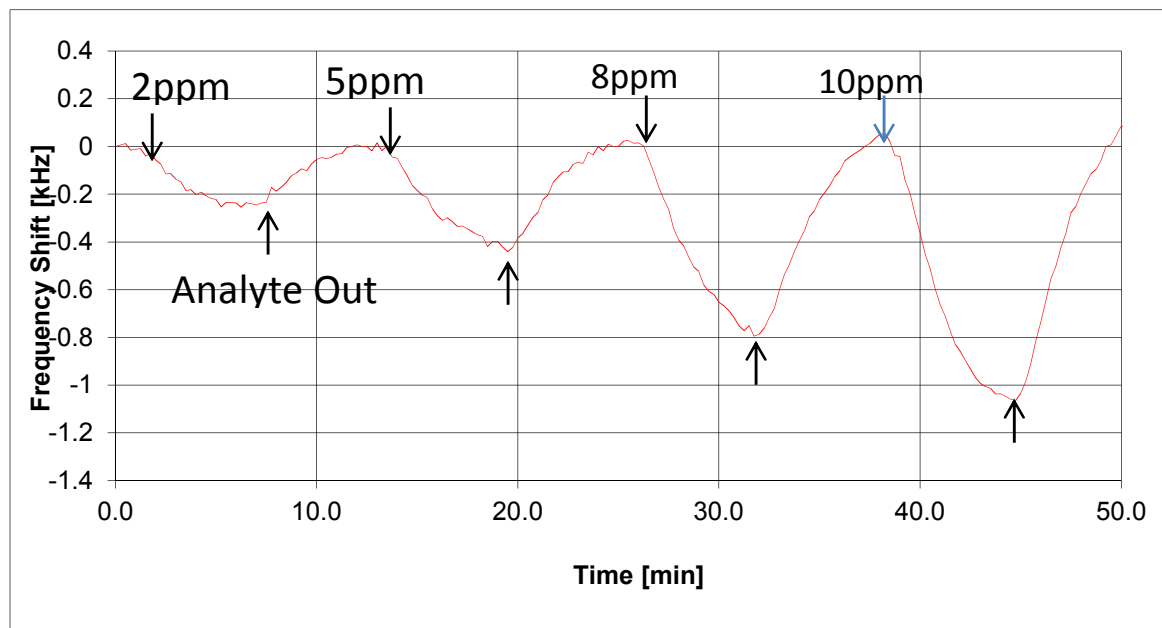


Figure 4.9 Frequency response of a SH-SAW device with a 0.56  $\mu\text{m}$  thick PMA sensing film.

Figure 4.9 shows that a 0.56  $\mu\text{m}$  thick layer of PMA on a SH-SAW device leads to a sensitivity of 70Hz/ppm. Although it has a lower sensitivity to benzene than a 1  $\mu\text{m}$  thick PEA coated device, its insertion loss is -19dB whereas the PEA coated device has an insertion loss of -33dB. This signifies that upon low plasticization, the insertion loss would not be detrimental to the detection limit.

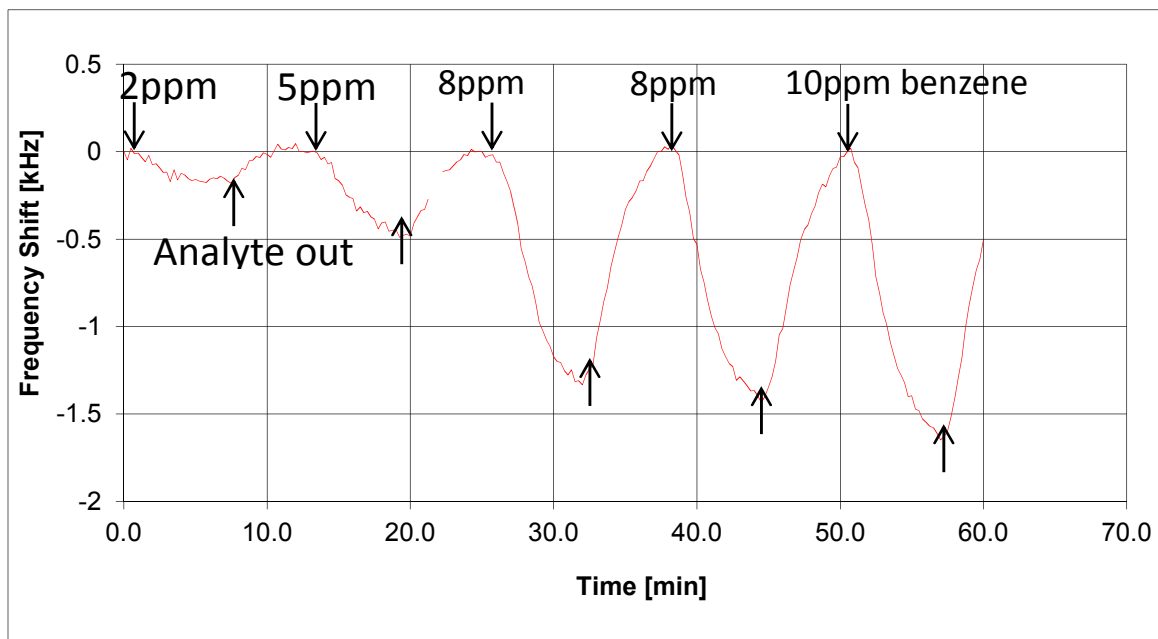


Figure 4.10 Frequency response of a SH-SAW device with a 0.56  $\mu\text{m}$  thick 3% DOP-PMA sensing film. Note that at  $t = 22$  min, an outlier that was due to a measurement perturbation (probably a bubble) has been removed.

Figure 4.10 shows the frequency response of a device coated with a 0.56 $\mu\text{m}$  thick 3% DOP-PMA layer exposed to 2, 5, 8 and 10 ppm samples of benzene in Milli-Q deionized water. The sensitivity of the polymer increased to 145Hz/ppm.

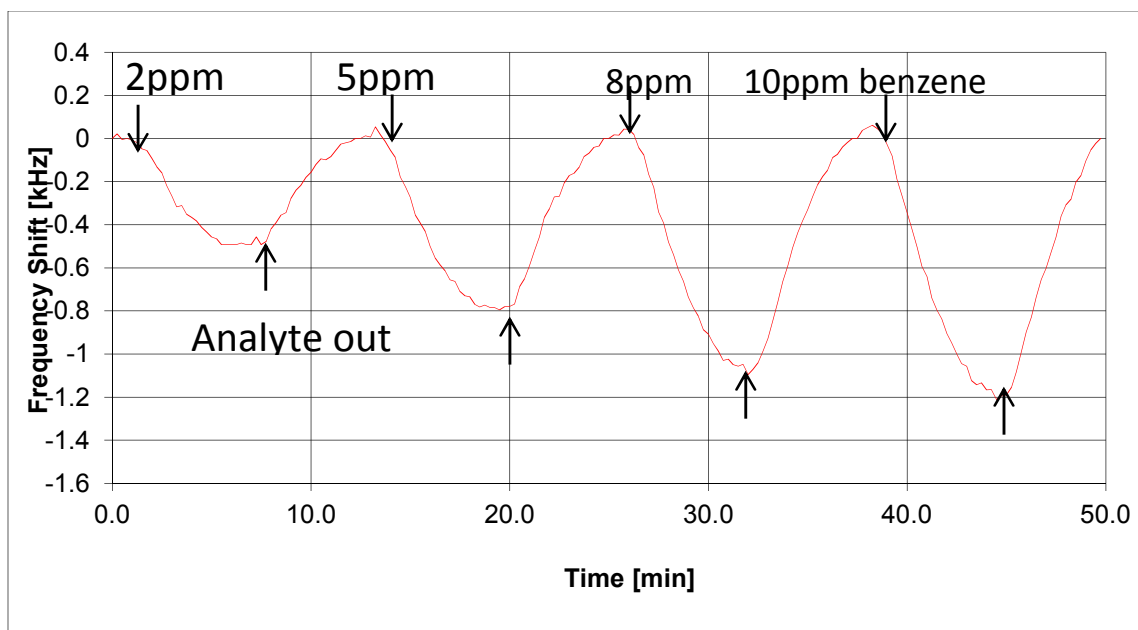


Figure 4.11 Frequency response of a SH-SAW device with a 0.56  $\mu\text{m}$  thick 5% DOP-PMA sensing film.

Figure 4.11 shows the frequency response of 0.56 $\mu\text{m}$  5% DOP-PMA thick polymer exposed to 2, 5, 8 and 10 ppm samples of benzene in Milli-Q deionized water. The sensitivity of the 5% DOP Polymer was 150Hz/ppm upon further plasticization of the polymer. In addition, a detection limit of 55 ppb was calculated. However, during the course of testing 5% DOP-PMA, issues with reproducibility were encountered at low concentrations.

### 4.3 Discussion

Upon plasticization of the base polymer, an increase in sensitivity is generally noticed. However as noticed with polystyrene increased plasticization does not always result in an increase in sensitivity over the entire range of plasticizer concentrations. After initial tests with 1 $\mu\text{m}$  thick coatings and mixing ratios of 25% DOP-PS and 30% DOP-PS, attempts were made to develop

thinner coatings. However, upon preparations of diluted 20% DOP-PS, 25% DOP-PS and 30% DOP-PS solutions and spin coating on to the device and confirmation of thickness by the ellipsometer of 0.9  $\mu\text{m}$ , the frequency response was less than half that of the 1  $\mu\text{m}$  thick DOP-PS polymers. The 20% DOP-PS polymer was unresponsive to 2ppm and 5ppm concentrations of benzene. This discovery led to a visual inspection of the coating surface by a microscope, where it was noticed that the plasticizer was pooled in regions and not evenly distributed throughout the coating surface. These pooled regions of plasticizers altered the path of the lasers, thus providing an inappropriate estimation of the coating thickness. This led to the switch from using a stirring bar and heating to using mild sonication in sonic bath to prepare the plasticizer-polymer solution. The use of the sonication resulted more homogeneous distribution of plasticizer, thus improving the verification of the polymer coating thickness.

After initially testing various thicknesses of 25% and 30% DOP-PS to detect benzene, it was noticed that with higher concentrations of plasticizers there was an increased insertion loss of 2-3 dB after a few hours of testing. This increased loss was more pronounced in measurements conducted using 30% DOP-PS polymers. This led to the initial assumption that the polymers might have undergone syneresis, leaching out excess plasticizer or the polymer coating was absorbing water and swelling up. This led to an intermediary test of 27.5% DOP-PS which showed less pronounced device loss increase than the 30% DOP-PS did.

To mitigate fears of syneresis, it was decided to test 20% DOP-PS and 22.5% DOP-PS polymer coatings. The reduction was intended to reduce the contribution of  $\delta_p$ , the dipolar intermolecular force associated with the oxygen atoms in DOP. Not only was the drift in insertion loss reduced upon the reduction of DOP in the DOP-PS blend, but in addition an increase in sensitivity was observed while maintaining the thickness at 1.1  $\mu\text{m}$  verified using the ellipsometer. The increase in sensitivity is assumed to be a result of an increase in free volume as it is assumed that excess plasticizer occupied the free volume in the coating as a certain optimum mixing ratio was exceeded.

Tests conducted on DOP-PEA were cut short because the 1  $\mu\text{m}$  thick polymers had insertion losses in water in excess of 35dB. At this point, preliminary test were conducted to portray the increased sensitivity upon addition of plasticizer as well as the transition further into the rubbery region of the viscoelastic properties of the composite polymer coating. Along with the high insertion loss, high RMS noise in the sensor response was observed as well. This is to be expected as for polymers with  $T_g$  just above room temperature the modulus to 1% of its original value for 10% plasticization. However, since PEA has a glass transition temperature lower than room temperature, the necessary amount of plasticizer to drop to 1% of its modulus is minute. This results in a polymer where  $G'$  is extremely low increasing the inserting loss as the polymer has little energy storage capacity for the wave. Any further plasticization by analytes lowers the modulus to a greater degree.

After plasticizing both a glassy polymer (polystyrene) and a rubbery polymer (PEA), it was decided to plasticize a polymer which was within or at the edge of the transition region, PMA. The glass transition temperature of 9°C for PMA means at room temperature of 22°C the polymer lies at the edge of the transition region close to the rubbery region. Through plasticization, a composite coating that fell closer to or in the rubbery region was achieved. This resulted in an increase in sensitivity from 70 Hz/ppm for 0.56µm pure PMA to 150Hz/ppm for 0.56µm 5% DOP-PMA. Beyond this point there were issues with the reproducibility of the composite coatings and further plasticization of PMA could not have been investigated.

To effectively determine the efficacy of the plasticized polymers, one would need to determine their detection limit. The limit of detection (LOD) is given by the formula [8][31]:

$$LOD = \frac{3 \times RMS_{noise}}{S} \quad (4.1)$$

where  $S$  is sensitivity and  $RMS_{noise}$  is the root mean square noise measured during the experiment.

In table 4.1, a selected list of plasticized polymers is presented alongside the calculated limit of detection and measured sensitivity for benzene in water.

Polymer	Plasticizer	Thickness ( $\mu\text{m}$ )	Detection Limit (ppb)	Sensitivity (Hz/ppm)
PS	0%	1.1	NA	NA
PS	23% DOP	1.1	20	940
PS	20% DOP	1.1	40	800
PS	25% DOP	1	50	300
PS	30% DOP	1.1	230	210
PS	30% DOP	1.3	329	400
PMA	0%	0.56	400	70
PMA	5% DOP	0.58	210	150
PEA	0%	1	100	330
PEA	2% DOP	1	2700	750

Table 4.1: Limit of detection and sensitivity of selected polymers

As can be seen, 23% DOP-PS and 20% DOP-PS achieved the highest sensitivities as well as the lowest detection limits.



## 5 SUMMARY, CONCLUSION AND FUTURE WORK

### 5.1 Summary

This work presents a study of various plasticized polymers for use as a sensing layer on a SH-SAW sensor for the detection of benzene in water. The polymers were selected based on their solubility parameters and relation to previous polymers investigated for the detection of benzene in water. The polymers were plasticized in various ratios to tailor their chemical and mechanical properties to improve their sensitivity to benzene and were then tested to confirm their sensitivity to benzene.

An analysis of the plasticizer was reviewed and presented. These theories were used to explain the observed results of the experiments. It also provided information on what methods were needed to choose the right plasticizer for a given polymer. The significant physical and chemical properties of the plasticizer and selected polymer were also provided.

The polymers of interest (PS, PMA and PEA) were plasticized at various ratios, and then applied at multiple thicknesses on an SH-SAW device, and then the frequency responses of the sensor to various concentrations of benzene in Milli-Q deionized water were recorded to find optimum conditions for sensing benzene. The device was exposed to concentrations ranging from 0.2 ppm to 20.0 ppm of benzene and the resulting frequency shift was used to calculate the

plasticized polymer coated device' s sensitivity to benzene. The limit of detection was calculated using the observed RMS noise and the recorded sensitivity.

## 5.2 Conclusion

This work measured the sensitivity of three polymer coated SH-SAW devices (PS, PMA and PEA) plasticized with DOP to benzene in Milli-Q deionized water. The plasticized polymer solutions were first prepared through the use of mild sonication to evenly disperse the plasticizer in the polymer solution. Then the films were spin coated onto the SH-SAW device to produce a desired thickness. Frequency shift was measured to observe the sensor's response to the ambient benzene concentration. Most plasticizer-polymer coatings were more sensitive than their base polymer as the plasticized polymers tend to have a lower glass transition temperature and at room temperature the plasticized composites are more rubbery in comparison with their base polymer. A more rubbery coating has a higher shear loss modulus,  $G''$ , resulting in decreased wave velocity and in some cases increased insertion loss. The additional free volume resulting from plasticization also provides more sites for analytes to further plasticize the polymer resulting in larger reduction of wave velocity and therefore a larger frequency shift. A 1.1 $\mu$ m thick 23% DOP-PS polymer showed the highest sensitivity to benzene as well as the lowest limit of detection, indicating a good balance between effective plasticization and still moderate acoustic loss was achieved for this coating.

For PEA, whose glass transition temperature was well below room temperature and groundwater testing conditions, it was noticed that, although an increase in sensitivity was observed after anti-plasticization had been overcome, its signal-to-noise ratio was poor. The signal-to-noise ratio was poor because upon further plasticization the coating was more rubbery than its base polymer. In addition both 1% DOP-PEA and 2% DOP-PEA have insertion losses higher than -35dB, which signifies the polymer coating is not suitable to test. The high insertion loss is a result of plasticization causing the composite polymer to have a higher shear loss modulus  $G''$  resulting in energy from the acoustic wave dissipating to heat in the plasticizer-polymer composite coating. In addition, the extra free volume created resulted in further plasticization by benzene compounds which results in larger frequency shifts.

Like PEA, PMA also saw an increase in sensitivity from 70 Hz/ppm for 0.56 $\mu$ m pure PMA to 145 Hz/ppm for 3% DOP-PMA and further on to 150Hz/ppm for 0.56 $\mu$ m 5% DOP-PMA. Upon the addition of DOP to PMA, the glass transition temperature is reduced. At room temperature, this will move the resulting blend from close to the transition region to well within the rubbery region. The increase in free volume allows PMA to absorb more benzene resulting in greater perturbation to the SH-SAW, and a lower wave velocity. In addition, the limit of detection for 5% DOP-PMA was improved to 210ppb. Although the limit of detection is higher than the value of 100ppb for a 1 $\mu$ m thick polymer of PEA, 210 ppb is a better limit of detection in comparison with polymers such as BPA-HMTS which has a detection limit of 680ppb for a 0.4 $\mu$ m coating [31]. Experiments with

plasticization of PMA and PEA indicate that the plasticization of polymers with glass transition temperatures below room temperature is not likely to result in improved detection limits or sensing characteristics of the coating. This is a result of the base polymer being either in its rubbery region or at the boundary, where the capacity of the coating for analyte sorption is already at or near optimum; the main effect of plasticization will be to create more free volume and a higher shear loss modulus,  $G''$ , increasing the insertion loss and the rms noise level. The latter will offset any potential gains in analyte sorption capacity that can still be made.

Polystyrene showed the most improvement upon plasticization. As noted, polystyrene is glassy and therefore does not effectively absorb benzene. Upon plasticization it is able to absorb benzene and other analytes. However, when plasticized over the optimum mixing ratio, its detection limit rises due to increased RMS noise and a decrease in sensitivity brought by a reduction in free volume. For naturally rigid polymers below the optimum mixing ratio, a low RMS noise is observed and increasing sensitivity to benzene was observed. The two highest sensitivities and lowest limits of detection were found for 23% DOP-PS and 20% DOP-PS, both with a thickness of 1.1  $\mu\text{m}$ . This suggests that the optimum plasticization ratio lies between 20% and 24% DOP. It should be noted that if the plasticizer-polymer mixing ratio was properly selected, it was possible to use coatings of larger thicknesses and, thus, higher sensitivities than for the commercially available polymer coatings (PEA, PECH, and PIB) were achieved. This illustrates the advantage of using plasticizer-polymer blends to tailor the mechanical characteristics of the coating until an optimum compromise between

high analyte sorption and low acoustic loss is achieved. In addition, for the example of polystyrene, it was demonstrated that the use of plasticizers allows to make additional polymer materials available for use in a sensor array. This will be achieved by selecting and designing different plasticizer-polymer mixtures at various mixing ratios. The result will eventually lead to the design of sensor arrays with increased selectivity.

### **5.3 Future work**

Based on the conclusion in this thesis, further investigation needs to be undertaken for the viability of plasticized polymers for the use in a sensor array for the detection of benzene. There is a need to conduct further measurements with other aromatic analytes, in particular, the other BTEX compounds (toluene, ethylbenzene and the xylene isomers). In addition, long term systematic measurements are needed to test the permanence of DOP in polystyrene and other polymers, i.e. to determine the leaching rate of the plasticizer.

In addition, other glassy polymers such as polyethylene terephthalate (PET) and polycarbonate of bisphenol-A (PC) which have glass transition temperatures of 70°C for PET and 147°C for PC could be plasticized. Both polymers contain benzene rings which allow for pi-interaction with benzene. Both polymers contain oxygen atoms which will provide polar properties and will improve the retention of DOP reducing the chance of syneresis (leaching out) of DOP.

There is also a need to investigate other plasticizers to aid polymers detect benzene. One alternative to DOP could be di-n-octyl phthalate (DNOP) which is 10 times less soluble in water than DOP. Larger plasticizers could be used to improve permanence in polymers to prevent plasticizers leaching out and extend the coatings life, especially in liquid environments. A smaller but more hydrophobic plasticizer could be utilized to increase miscibility between the polymer and coating. A smaller plasticizer will be more effective in reducing the glass transition temperature, while its hydrophobic nature will prevent it from leaching out into the water environment. Currently, 1, 2-Cyclohexane dicarboxylic acid diisononyl ester trademarked as Hexamoll DINCH by BASF is being used as a DOP substitute in another study. DINCH is promoted as being more stable in aqueous environment and has a shown to have an extremely low leach rate in PVC [36].

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