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Abstract

We report the first-ever direct detection of benzene in water at concentrations below 100 ppb (parts per billion) using acoustic wave (specifically, shear-horizontal surface acoustic wave, SH-SAW) sensors with plasticized polymer coatings. Two polymers and two plasticizers were studied as materials for sensor coatings. For each polymer–plasticizer combination, the influence of the mixing ratio of the blend on the sensitivity to benzene was measured and compared to commercially available polymers that were used for BTEX (benzene, toluene, ethylbenzene, and xylene) detection in previous work. After optimizing the coating parameters, the highest sensitivity and lowest detection limit for benzene were found for a 1.25 μm thick sensor coating of 17.5%-by-weight diisooctyl azelate-polystyrene on the tested acoustic wave device. The calculated detection limit was 45 ppb, with actual sensor responses to concentrations down to 65 ppb measured directly. Among the sensor coatings that showed good sensitivity to benzene, the best long-term stability was found for a 1.0 μm thick coating of 23% diisononyl cyclohexane-1,2-dicarboxylate-polystyrene, which was studied here because it is known to show no detectable leaching in water. The present work demonstrates that, by varying type of plasticizer, mixing ratio, and coating thickness, the mechanical and chemical properties of the coatings can be conveniently tailored to maximize analyte sorption and partial chemical selectivity for a given class of analytes as well as to minimize acoustic-wave attenuation in contact with an aqueous phase at the operating frequency of the sensor device.

KEYWORDS:
plasticized polymer coatings, SH-SAW sensor, hydrocarbon sensor

The BTEX compounds (benzene, toluene, ethylbenzene, and xylene) are among the most common target analytes in water monitoring and are regulated in drinking water and public waterways in many countries to protect public health.(1, 2) The BTEX compounds are constituents of crude oil, gasoline, and other refined products. Accidental releases from underground storage tanks or hazardous waste sites can introduce BTEX into nearby groundwater, affecting public health. It is important to detect the presence of BTEX in groundwater as early as possible, and to monitor concentrations periodically throughout cleanup processes, in order to minimize the impact on public health and the cost for site remediation. Of the BTEX compounds, benzene is considered the most hazardous. Exposure to benzene for a prolonged period of time above the specified MCL (maximum contaminant level) can cause anemia, blood platelet decrease and an increased risk of cancer.(3) For these reasons, the MCL for benzene in drinking water is 5–10 ppb in many countries.(2, 3) Because of its low MCL and high hazard potential for human health, this work focuses on benzene detection and quantification using new chemically sensitive coatings based on plasticizer–polymer blends. The ultimate objective beyond this work will be a complete characterization of the coatings in detection of all BTEX compounds in the presence of various interferents.

At present, the standard procedure for analyzing a groundwater sample is to collect the sample on site, pretreat it for preservation, and transport it to an off-site laboratory where the sample can be analyzed.(4) This procedure is time-consuming and costly and can lead to potential sample deterioration or adulteration of concentrations during transport due to evaporation and chemical or biological degradation. Because of the large number of sites(5) and the cost of collection and time needed for monitoring each site, not all locations are checked frequently enough to detect a possible release before
extensive contamination occurs. Therefore, an urgent need exists to develop an in situ BTEX measurement technique to analyze groundwater and to protect the environment from possible hazardous impacts. An on-site chemical sensor system would allow for early, accurate monitoring for the presence and concentration of benzene in groundwater supplies as well as an increase in the number of sites tested each year. It would also provide a convenient means to monitor the progress of site remediation once a contaminated site has been identified.

To address this problem, a sensor system based on a polymer-coated SH-SAW (shear-horizontal surface acoustic wave) sensor platform has been investigated and shown to be a promising tool for in situ detection of BTEX compounds directly in the aqueous phase. In this SH-SAW sensor system, sensitivity and (partial) selectivity of the SH-SAW sensor for chemical detection depend on the sorption properties of the coating. In the selection of the coating material, one has to take into account its physical properties and the chemical interaction between coating material and analyte of interest. The highest sensitivity for chemical sensors results from the formation of covalent bonds between coating and analyte. Though high sensitivity is desired, formation of covalent bonds makes the sensor response irreversible, which is to be avoided if the sensor is to be deployed for an extended period of time. For a reversible sensor response, the interactions between coating material and analyte are limited to dispersion, dipolar and hydrogen-bonding interactions.

Commercially available polymers that can be used as suitable coatings for BTEX detection directly in the aqueous phase are limited in sensitivity and long-term stability. Many apparently promising polymers, e.g., those having a solubility parameter very close of that of benzene, are glassy at ambient temperatures, which results in very low sensitivity; specifically, this is the case for many polymers containing phenyl rings—such as the ubiquitous thermoplastic polystyrene—which might otherwise be suitable for BTEX detection due to π-stacking interactions with aromatic compounds. To improve the sensitivity of a suitable polymer, the addition of a plasticizer is a convenient means to lower the glass transition temperature and thus increase sensitivity, as explained below. In this paper, various polymer–plasticizer blends are studied for their application as sensor coatings in BTEX detection in liquid phase. The following section will serve as a guideline for the selection of suitable polymer–plasticizer blends.

Theory

The use of plasticizers can increase significantly the number of suitable polymers available for use in a sensor array. In this section, we describe how, by adding a plasticizer to a polymer and adjusting the coating thickness, the mechanical properties of the coating can be tuned in order to optimize its characteristics for a sensor application, i.e., to achieve the best combination of large analyte sorption capacity and low acoustic wave attenuation.

A plasticizer is usually added to a polymer in order to increase its fluidity, plasticity, flexibility, or resiliency. The plasticizer interacts with the chains of the polymer to increase chain mobility and free volume in the polymer, offering the potential of increased as well as accelerated analyte sorption. Plasticizers typically change both the thermal and mechanical properties of a polymer. Therefore, in order to optimize analyte absorption in the coating and minimize acoustic-wave attenuation, the viscoelastic properties of the coating must be considered.

The viscoelastic properties of polymers depend on both temperature and frequency, $f$. In general, there is a characteristic relaxation time, $\tau_r$, which describes the time scale for segmental chain motions in the polymer. If the polymer is deformed on a much shorter time scale than the relaxation time ($\omega \tau_r \gg 1$, where $\omega = 2\pi f$), the polymer chains do not have time to move with respect to each other, strain is accommodated elastically, and the polymer behaves in a “glassy” manner. For $\omega \tau_r \ll 1$, strain is accommodated inelastically, and the polymer behaves in a “rubbery” manner.
absorption, the polymer has to be in its rubbery regime at long time scales, i.e., over the typical minutes-long duration of the sorption and desorption transients. This is necessary so the polymer chains can move and the polymer can swell at the time scale of analyte absorption and desorption. For the shear modulus of the coating, \( G = G' + jG'' \), this means that the storage modulus, \( G' \), will be \( 10^7 \) Pa or less, and the loss modulus, \( G'' \), will be comparable to or less than \( G' \).\(^{(13)}\)

It should be noted that a polymer’s behavior can be strongly impacted by the time scale of the phenomenon or perturbation and, furthermore, a single polymer can exhibit rubbery properties at one time scale while simultaneously exhibiting glassy properties at a different time scale.\(^{(13, 15)}\) For example, the perturbation caused by absorption of an organic compound occurs on a time scale of seconds to minutes for the sensor films used in this work; on this time scale, these polymer films do exhibit rubbery behavior. This means there is time for the polymer chains to move in order to accommodate the motion of the organic molecules being absorbed into the polymer; this chain movement allows relatively rapid and reversible responses to changes in organic analyte concentration on a time scale of seconds. At the same time that the absorption is occurring, the same polymer film is also being perturbed by an acoustic wave with a frequency of 103 MHz, corresponding to a time scale of about 9.7 ns per cycle. On this very rapid time scale, the polymer chains are not able to move significantly in response to the perturbation, and the polymer therefore responds in a predominantly elastic way like a rigid, glassy material. For one of the polymers used for comparison in this work, poly(isobutylene) (PIB), this was previously reported in the literature.\(^{(13, 15)}\) In the present work, all investigated coatings behave as glassy at the operating frequency of the SH-SAW device (103 MHz), resulting in low acoustic wave loss and a good signal-to-noise ratio; however, the same coatings simultaneously behave as rubbery at the time scale of analyte sorption, resulting in high analyte sorption and high sensitivity.

In addition, the thickness of the coating must be selected for optimum sensor performance. Making the coating thicker increases its sorption capacity but results in higher acoustic wave attenuation. From experimental observation, with the sensor design used in this work, polymer thicknesses in the range of about \( h = 0.02 \lambda - 0.03 \lambda \) (\( \lambda \) = acoustic wavelength, here 40 \( \mu \)m) can be tolerated before the wave attenuation becomes too high. At this thickness, a rubbery coating is slightly in the acoustically thick regime,\(^{(13, 16)}\) i.e. there will be a phase lag across the thickness of the vibrating coating; however, as long as this phase lag is small, the resulting increase in wave attenuation will not be prohibitive for the sensor signal.

The state of the polymer material at ambient temperatures depends on its (static) glass transition temperature. Many polymers that would otherwise be chemically suitable for BTEX absorption—because they are chemically quite similar to those compounds as indicated, for example, by their solubility parameters\(^{(17)}\) (see below)—have high glass transition temperatures and are glassy at ambient temperatures. The addition of a plasticizer lowers the glass transition temperature of such a polymer,\(^{(10)}\) potentially making it a good sorbent material for BTEX compounds at ambient temperatures. The amount of plasticizer added should be adjusted to make the polymer rubbery in the low frequency range while keeping it glassy at the operating frequency of the sensor device.

Properly choosing the polymer and plasticizer for a sensor coating is dependent on their chemical structure, compatibility and solubility. One method to determine compatibility between a polymer and a plasticizer is by looking at their solubility parameters (\( \delta \)). Using the Hansen solubility parameters is the best method to predict the miscibility of two materials.\(^{(17)}\)\(\text{Equation 1} \) was developed by Skaarup\(^{(17)}\) using the partial solubility parameter components (Hansen solubility parameters) to calculate a solubility parameter “distance,” \( R_a \), between two materials:

\[
(R_a)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2
\]
\[(Ra)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2\]

In this equation, the subscripts d, p, and h refer to dispersion forces, dipolar intermolecular forces, and hydrogen bonds, respectively. The relative energy difference (RED) can be calculated using eq 2.

\[\text{RED} = \frac{R_a}{R_0}\]

Here, \(R_a\) is the distance in Hansen parameters between two materials in Hansen space and \(R_0\) is the radius of a sphere in Hansen space that contains all the solvents capable of dissolving those two materials (\(R_0 = 8.6\)). The condition for solubility isRED < 1. A value around 1.0 is a borderline case, and values exceeding 1.0 indicate a decrease in affinity between the two materials.

Using Hansen solubility parameters for all materials discussed in this work, the RED values were calculated for various material combinations and are listed in Table 1. Note that the best match by far for benzene is polystyrene, PS, for which RED = 0.54.

Table 1. Summary of RED Values for Various Combinations of the Materials Studied in this Work

<table>
<thead>
<tr>
<th></th>
<th>DINCH</th>
<th>DIOA</th>
<th>PS</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>DINCH</td>
<td>N/A</td>
<td>N/A</td>
<td>0.82</td>
<td>0.94</td>
</tr>
<tr>
<td>DIOA</td>
<td>N/A</td>
<td>N/A</td>
<td>0.85</td>
<td>0.88</td>
</tr>
<tr>
<td>PS</td>
<td>0.82</td>
<td>0.85</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.94</td>
<td>0.88</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>THF</td>
<td>0.46</td>
<td>0.19</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TCE</td>
<td>0.46</td>
<td>N/A</td>
<td>N/A</td>
<td>0.91</td>
</tr>
<tr>
<td>chloroform</td>
<td>0.67</td>
<td>0.52</td>
<td>N/A</td>
<td>0.90</td>
</tr>
<tr>
<td>benzene</td>
<td>1.07</td>
<td>1.06</td>
<td>0.54</td>
<td>1.38</td>
</tr>
</tbody>
</table>

N/A, not applicable; italic, miscible; bold, borderline case; bold-italic, poor miscibility. Abbreviations for materials and chemicals are defined in the Materials and Methods section.

Materials and Methods

In this investigation, two polymers, polystyrene (PS) and poly(methyl methacrylate) (PMMA), and two plasticizers, diisooctyl azelate (DIOA) and diisononyl cyclohexane-1,2-dicarboxylate (DINCH), were studied for their use in sensor coatings. Blends of DIOA-PS, DINCH-PS, DIOA-PMMA, and DINCH-PMMA were investigated to find suitable SH-SAW sensor coatings and to optimize mixing ratios and coating thicknesses for BTEX detection. These polymers and plasticizers are commercially available; PS (35 000 g/mol) was purchased from Sigma-Aldrich, PMMA (35 000 g/mol) and DIOA (413 g/mol) were purchased from Scientific Polymer Products, and DINCH (425 g/mol) was kindly provided by BASF Corporation. Note that plasticizers with higher molecular weight were selected as they are expected to show good permanence in the coatings. Benzene was purchased from Sigma-Aldrich with purity ≥ 98.5%. All the solvents,
tetrahydrofuran (THF), chloroform, and trichloroethylene (TCE) were purchased from Sigma-Aldrich with purity ≥ 99%.

The sensor platform used in this work was a SH-SAW device previously described elsewhere.(6, 20) Briefly, a 36° YX-LiTaO₃ piezoelectric crystal serves as a substrate for the sensor design. The interdigital transducers (IDTs) have a periodicity of λ = 40 μm, generating a 103 MHz SH-SAW. The center-to-center IDT separation is 8 mm (200 λ). The surface between the IDTs was metalized to eliminate or minimize acoustoelectric interaction with the surrounding aqueous environment; this is important for groundwater monitoring since groundwater samples can vary widely in salinity and conductivity, potentially leading to spurious responses or nonreproducibility. A multielectrode transducer design was used to minimize phase distortion and improve the signal-to-noise ratio.(20)

Mixing ratios of polymer–plasticizer blends are given as weight/weight percentage values (mass of plasticizer over total mass of blend). Plasticizer-polymer blends were dissolved in a suitable solvent in various weight/weight percentages (mass of polymer and plasticizer divided by total mass of solution) to produce different coating thicknesses by spin coating. For example, for the DIOA-PS blend, tetrahydrofuran (THF) was used as a solvent. Coating solution was stirred overnight and sonicated for at least 4 h to obtain a homogeneous solution. Sensor coatings were deposited from solution by spin coating (Specialty Coating Systems SCS 6800 spin coater). Coated devices were baked for 1 h at 60 °C to evaporate the remaining solvent and remove internal stresses from the coating.

A glass slide was used in place of a sensor device to reproduce an identical coating for thickness characterization. Thicknesses were measured using a surface profilometer (KLA Tencor Alpha-Step IQ) with a low stylus force to prevent coating damage and to obtain an accurate representation of the surface profile. Investigated thicknesses ranged from 0.5 to 1.5 μm. The coating surface was studied under a microscope for imperfections created during deposition and use.

The investigated range of benzene concentrations in water was 50 to 2000 ppb. Samples were prepared by dispensing benzene in deionized degassed water using a micropipette. The sample was stirred for more than 1 h. Headspace in the sample vials was kept to a minimum to decrease possible analyte evaporation. In order to account for any remaining inaccuracies in sample concentration, analyte concentration was independently measured by gas chromatography using a photoionization detector (GC-PID) (FROG-4000, Defiant Technologies, Albuquerque, NM) immediately after each sensor experiment using the same analyte sample.

A schematic diagram of the experimental setup can be seen in Figure 1. A three-way valve allows for switching between analyte solution and reference solution without interrupting sample flow in order to minimize any baseline distortion. A peristaltic pump (IDEX Ismatec Reglo Digital MS, Oak Harbor, WA) draws the solution through the flow cell and into the waste container. The flow cell was made in-house; the flow rate of the pump was set to 7 μL/s for all experiments. Flow rate must be constant throughout experiments to ensure response times can be compared, if desired. Coaxial cables connect the flow cell containing the SH-SAW sensor device to the vector network analyzer (Agilent E5061B, Santa Clara, CA) used to collect sensor data. Data were collected every 12 s using Agilent VEE software on the connected computer.
Fluctuations in temperature affect the frequency response of the sensor. The device within the flow cell, the three-way valve, and the samples were kept within a measurement chamber to maintain a stable temperature throughout experimentation. Remaining effects of temperature on the sensor signal can then be accounted for with a reference measurement using the two delay lines of the sensor and/or by a linear baseline drift correction. Once data were collected, correction for linear baseline drift was performed using an automated procedure. Frequency shift and response time constant were extracted using eq 3:

\[ y(t) = y_0 \left( 1 - e^{-t/\tau} \right) \]  

(3)

where \( y(t) \) is the frequency shift at time \( t \), \( y_0 \) is the equilibrium frequency shift, and \( \tau \) is the response time constant, defined as the time it takes the sensor to respond (to the introduction of the analyte, represented as a step input), and reach \( \left( 1 - \frac{1}{e} \right) \) 63% of the final, asymptotic value for the sensor response. Frequency shift (for a response to 1 ppm benzene) and time constant are the two main parameters used to characterize the response of each plasticizer–polymer blend coating.

A plot of the shift in frequency as a function of analyte concentration is used to determine the sensitivity from the corresponding slope of a linear fit as defined by

\[ S = \frac{\Delta f}{C_0} \]  

(4)

Here, \( \Delta f \) is the frequency shift measured for analyte concentration \( C_0 \). Once sensitivity is determined, the limit of detection (LOD) can be calculated. The RMS noise is extracted from the baseline data over a duration of 5–6 min and the detection limit for the coated device to the specific analyte is calculated as the analyte concentration required to produce a frequency shift of three times the RMS noise.
Results and Discussion
In previously reported work,(21, 22) a range of mixing ratios from around 10% to 30% was investigated for various plasticizers in poly(methyl methacrylate) sensor coatings. These references provide a starting point for the selection of molecular size and chemical structure of plasticizers for liquid-phase hydrocarbon sensing.

Another aspect that is important for the present work is the long-term stability of the coating, which depends on the rate of plasticizer leaching from the coating.(23) Ideal plasticizer percentage is unique for each plasticizer–polymer blend due to the chemical nature of the materials, and was determined in this work based on an analysis of experimental results. Plasticizer concentration was adjusted to determine the best plasticizer:polymer ratio for high sensitivity while maintaining long-term stability. In the following section, results on each plasticizer–polymer blend (DIOA-PS, DINCH-PS, DIOA-PMMA, and DINCH-PMMA) are reported and discussed for different plasticizer concentrations. Responses to benzene were recorded for coatings obtained from each plasticizer–polymer blend over extended periods of time to investigate the repeatability of the sensor response. Frequency shift was extracted from the raw experimental data and was plotted as a function of the corresponding benzene concentration for each plasticizer–polymer blend. Initial insertion loss (which includes acoustic wave attenuation) at the operating frequency was recorded before each experiment to track changes in the viscoelastic properties of the coating over time.

DIOA-PS
Experiments were conducted to optimize the DIOA percentage in the plasticizer–polymer blend. The plasticizer–polymer mixing ratio is known to affect the long-term stability of the coating. For the DIOA-PS blends, it was observed that the stability of the coating also depends on the thickness of the coating. Coating thickness was varied by spin coating solutions with different concentrations of DIOA-PS in THF onto the sensors. Initially, various combinations of coating thickness (0.0175 \( \lambda \) to 0.035 \( \lambda \)) and DIOA-PS mixing ratio (10–30%) were tested to map the range of stability of the coating and repeatability of the sensor response (frequency shift). Based on the initial results, a 1.0 \( \mu \)m-thick (0.025 \( \lambda \)) sensor coating was prepared from 17% DIOA-PS blend. Experiments were conducted to determine the sensor response to benzene over the course of several weeks of sensor operation. Figure 2 shows the average of nine responses with error bars, representing ± one standard deviation, of a sensor coated with 1.0 \( \mu \)m thick 17% DIOA-PS. Responses were normalized to 1 ppm benzene using the independent concentration measurements by GC-PID. Experiments were conducted over the course of 36 days. The observed standard deviation in the equilibrium frequency shift is about ±9%. Note that the measurement error of the GC-PID is about ±7%.(24) The insertion loss of the coated sensor device at the operating frequency was tracked to determine any long-term changes in the viscoelastic properties of the coating (due to coating degradation) and is shown as an inset in Figure 2. For the device used in this investigation (center-to-center IDT separation: 200 \( \lambda \)), the insertion loss was 24 dB and remained stable within ±1 dB for 1 month for the plasticizer–polymer-coated device in water, indicating physical stability of the coating throughout the time of experiment. (Note that insertion loss includes acoustic wave attenuation in the coating as well as transducer losses.) Appropriate comparison of the mechanical and chemical absorption properties of the plasticizer–polymer coatings with those of commercially available polymer coatings will be given in the Sensitivity Comparison subsection.
Percentage of DIOA and thickness of the coating can be further adjusted to change the sensing characteristics of the coating. It was observed that reducing the percentage of plasticizer increases the rigidity of the coating, making it glassier. The percentage was reduced to 16.0% DIOA-PS at 1.0 μm thickness, giving slightly reduced sensitivity and an increase in response time constant as expected. Increasing the percentage of plasticizer with higher thickness (more than 1.0 μm) showed a trend toward reduced coating stability. To find the optimal balance between sensitivity and stability, the plasticizer percentage and coating thickness were increased slightly. As described in the Theory section, a slightly acoustically thick coating can be accepted as long as the phase lag across the thickness of the vibrating polymer is not too large. It was determined that a 1.25 μm thick (0.031 λ) 17.5% DIOA-PS coating gave the highest sensitivity, as well as lowest detection limit, among all the investigated DIOA-PS coatings while maintaining stability for over 1 month. Figure 3 shows the frequency response to benzene in the concentration range of 65–990 ppb. From Figure 3, it can be seen that low concentrations of benzene (around 50 ppb) can be measured. The figure also shows linearity between frequency shift and concentration for the concentration range investigated. The insertion loss at the operating frequency was tracked over the course of the experiments (1 month), and the coating was found to be stable throughout the experiments.

Equations 3 and 4 were used to extract equilibrium frequency shifts from the sensor responses and to calculate the sensitivities, respectively. The sensitivity of the 1.25 μm thick 17.5% DIOA-PS sensor coating was found to be 480 Hz/ppm, with a calculated limit of detection of 45 ppb. Concentrations of benzene down to 65 ppb were actually measured. The 1.0 μm thick 17.0% DIOA-PS sensor coating was found to have a sensitivity of 380 Hz/ppm with a calculated limit of detection of 60 ppb. Another coating with high
plasticizer percentage and low thickness was also investigated; this 0.7 μm thick (0.0175 λ) 22.9% DIOA-PS coating was found to be stable for 100 days. But the sensitivity of the coating was 220 Hz/ppm which is relatively low compared to the other coatings. These results demonstrate that, by varying plasticizer percentage and coating thickness, the plasticizer–polymer coatings can be tailored to a specific application, maximizing either the long-term stability or sensitivity to a given compound.

**DINCH-PS**

DINCH was selected for this investigation because of its reported negligible rate of leaching from polymers into water.\(^{(23)}\) Various plasticizer–polymer blends for DINCH-PS were investigated. Based on previously reported results,\(^{(21-23)}\) an initial plasticizer percentage of around 20% was selected. A 0.8 μm thick (0.020 λ) 20.9% DINCH-PS coating was prepared for the measurements. An initial insertion loss, shown in Figure 4, of 19.8 dB in water suggests the coating is near the glassy regime. The low initial insertion loss in water suggests it is possible to increase the coating thickness and/or the plasticizer percentage. Therefore, the plasticizer concentration and thickness were increased to produce a 1.3 μm thick (0.0325 λ) 24.4% DINCH-PS coating. The initial insertion loss of this coating, shown in Figure 4, was 28.4 dB which indicates a thick, rubbery coating. The 24.4% DINCH-PS sensor coating was investigated for 20 days before the loss increased beyond the 35 dB limit. This was due to polymer creep and formation of defects as confirmed by microscopic observation. Note that from experimental observation it is known that the signal-to-noise ratio of the device deteriorates significantly if the device insertion loss exceeds about 35 dB.

![Figure 4. Plots of insertion loss versus time, indicating the changes in the viscoelastic properties of various DINCH-PS coatings. The device used in this investigation has a center-to-center IDT separation of 200λ with λ = 40 μm.](image)

Next, the plasticizer percentage and thickness were reduced to 23.0% and 1.0 μm (0.025 λ), respectively, to increase the long-term stability of the DINCH-PS coating. Initial insertion loss from Figure 4 was 21.9 dB, and the coating was investigated for 57 days. The average of eight frequency shift responses along with error bars to 1 ppm benzene is shown for this device in Figure 5. Over this period of time, the device was determined to be stable and the frequency response to benzene was found to be repeatable.
The sensitivity of the 23.0% DINCH-PS sensor coating to benzene was found from Figure 5 to be 304 Hz/ppm. RMS noise levels were extracted (8.9 Hz) and the calculated detection limit for benzene was 85 ppb. The 23.0% DINCH-PS sensor coating offered a good compromise between long-term stability and high sensitivity to benzene. A second 1.0 μm thick 23.0% DINCH-PS sensor coating gave similar sensitivity to benzene and showed long-term stability for around three months; see Figure 4.

**DINCH-PMMA and DIOA-PMMA**

A second polymer, PMMA, was investigated for plasticizer–polymer coatings. This polymer has already been combined with some plasticizers for the purpose of liquid-phase hydrocarbon sensing. However, the long-term stability was not studied, and DINCH-PMMA blends were not investigated. PMMA has a similar glass transition temperature to PS; however, RED values in Table 1 indicate that PS is likely to be a far more effective coating for benzene sorption.

DINCH-PMMA and DIOA-PMMA were studied for benzene detection using a SH-SAW sensor. Various plasticizer percentages (23% to 35%) and coating thicknesses (0.5–1.5 μm, 0.0125λ–0.0375λ) were investigated. In addition, three different solvents (THF, TCE, and chloroform) were used to dissolve the plasticizer–polymer blends for spin coating. However, no significant sensitivity to benzene was found for any of these coatings. For DIOA-PMMA, this finding is in agreement with other results reported in the literature. Sensitivity to benzene is generally lower than to the other aromatic compounds for polymer-coated SH-SAW devices, due to the higher aqueous solubility of benzene. Response of the DINCH-PMMA coating (e.g., 0.6 μm-thick 30.0%) to ethylbenzene was also investigated, and significant sensitivity was found, ruling out the possibility that the coating is glassy. The observed low sensitivity of PMMA-plasticizer blends to BTEX analytes may instead be related to the slightly high RED value listed in Table 1 for miscibility of PMMA and benzene. It is concluded that polystyrene is a better choice for this application due to its chemical composition and structure.

**Sensitivity Comparison**

The sensitivities of the plasticizer–polymer blend sensor coatings, DIOA-PS and DINCH-PS, were compared to those of commercially available polymers previously identified as suitable SH-SAW sensor coatings for the detection of benzene. Note that, for the plasticizer–polymer blends, the type of plasticizer and the mixing ratio will affect the glass transition temperature, the free volume, and the viscoelastic properties of the coating, and ultimately its long-term stability. Therefore, the optimum coating thickness that can be used will be different for each coating material. Based on sensitivity and repeatability considerations, the optimum coating thicknesses for each polymer and plasticizer–polymer blend were determined for this comparison as follows: 1.25 μm (h = 0.031 λ) for DIOA-PS; 1.0 μm (h = 0.025 λ) for DINCH-PS; 0.8 μm (h = 0.020 λ) for poly(isobutylene) (PIB); and 0.6 μm (h = 0.015 λ) for poly(epichlorohydrin) (PECH).
The difference in these values is related to differences in shear modulus, surface smoothness, and physical stability of the coating materials. The commercially available polymer coatings are either not sensitive to benzene (i.e., unplasticized PS), or they are relatively soft and show high acoustic-wave attenuation (i.e., PIB and PECH), thus limiting the maximum coating thickness that can be used. On the other hand, the plasticizer–polymer blends allow adjustment of the shear modulus of the coating by varying the plasticizer–polymer mixing ratio; this enables the use of thicker coatings with larger analyte sorption capacity and, ultimately, higher sensitivity. Note that the thicker polymer is not necessarily acoustically thicker, because the criterion for separating acoustically thin and thick coatings depends not on the absolute coating thickness but on the ratio of coating thickness divided by the shear modulus of the polymer. A thicker coating also leads to better electric shielding of the IDTs from the analyte sample, which is particularly important if the sample is electrically conducting (e.g., groundwater, brackish water). For these reasons, the plasticizer–polymer coatings can be used at larger thicknesses than the commercially available polymer coatings and, therefore, can achieve higher sensitivities.

Sensitivity was compared by plotting the frequency shift as a function of benzene concentration in Figure 6. The figure shows that the plasticizer–polymer blends produce sensor coatings with increased sensitivities compared to that of commercially available polymers. Even taking into account differences in coating thickness, the plasticizer–polymer blends show greater analyte sorption capacities than the commercially available polymers, indicating they are rubbery in the low-frequency range as desired (see the Theory section). The shear moduli of the coatings produced from plasticizer–polymer blends have not been measured, as this would be beyond the scope of this investigation. However, tracking the insertion loss of the devices led to the conclusion that the plasticizer–polymer blends can be used with greater coating thicknesses, indicating that they have a lower loss modulus, $G''$, than the commercially available polymers ($\sim 3 \times 10^8$ Pa for PIB(13)) and are glassy at the operating frequency of the sensor device. PIB and PECH show good long-term stability, but the sensitivity of PIB to benzene is not very high, as indicated in Figure 6. Among the commercially available sensor coatings, this leaves only PECH as an excellent candidate for detection of benzene in groundwater. Therefore, if an array of sensors with different coatings is desired, the plasticizer–polymer blends represent valuable alternatives for such an array, permitting increased partial selectivity and accuracy.

Figure 6. Comparison of equilibrium frequency shift as a function of benzene concentration for SH-SAW devices with plasticized polymer coatings and commercially available polymer coatings. The thickness of each coating is given in parentheses in units of $\lambda$ with $\lambda = 40 \mu$m for the present device. The sensitivity of a given polymer-coated device is the slope of the respective response line.

Among the coatings investigated, the 1.25 \( \mu \)m-thick (0.031 $\lambda$) 17.5% DIOA-PS coating showed the lowest detection limit (45 ppb) for benzene and stability up to about 1 month. The 1.0 \( \mu \)m thick (0.025 $\lambda$) 23.0% DINCH-PS coating is the best choice for long-term stability (3 months). The results presented here indicate that both DINCH-PS and DIOA-PS would be excellent candidate members for a sensor array. This is particularly important because of the very limited number of commercially available polymers identified as suitable for benzene detection in long-term aqueous-phase measurements.
It should be mentioned that the results shown on the long-term stability of the plasticizer–polymer blends should not be regarded as final. Polymers and plasticizer–polymer blends may show various forms of coating degradation in the form of pinhole formation, polymer creep, and aging of the film. In this study, plasticizer type and percentage and coating thickness were observed to play a role in the rate of coating degradation. It is also known that an increase in molecular weight of a polymer tends to promote secondary bonding between polymer chains, thus making the polymer more creep resistant. In the future, coating degradation could be further addressed by increasing polymer molecular weight or by addition of an adhesion promoter.

**Conclusion**

Plasticizer–polymer blends can be employed as sensitive coatings for SH-SAW sensors to detect organic compounds and, in particular, benzene in water. It was determined both theoretically and experimentally that polystyrene is a better polymer choice than PMMA for detection of benzene using plasticized polymer coatings. Plasticized PMMA blends showed no significant sensitivity to benzene whereas the sensitivity to benzene of plasticized polystyrene was found to be excellent. The affinity for polystyrene to benzene can be explained by the high miscibility of polystyrene and benzene as well as the structure of PS that contains phenyl rings.

Generally, the mixing ratio and coating thickness have been adjusted to obtain a coating that is rubbery at low frequencies, enabling large analyte sorption capacity, but glassy at the operating frequency of the sensor device, ensuring low acoustic-wave attenuation, with the former condition given greater importance for short-term measurement applications and the latter given greater importance for long-term measurements. The ability to tune the sensitivity and stability characteristics by adjustment of the plasticizer percentage and coating thickness is an attractive choice over commercially available polymers where only coating thickness can be adjusted; this increases the number of suitable coatings available for a sensor array. The possibility of using the coated sensor responses together with suitable signal processing will permit the design of sensor systems showing good selectivity to a specific analyte or class of analytes. Preliminary work indicates good partial selectivity of plasticized PS to other BTEX compounds (i.e., toluene, ethylbenzene, and xylene). For these listed compounds, the response times were also found to be significantly longer than that of benzene. To further evaluate the selectivity of the new coatings, the detection of BTEX compounds in the presence of various interferents (ethanol, MTBE, sediments, salt, humic acid, etc.) will be investigated.

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