Surface modified polymer thin films with enhanced sensitivity to a naphthenic acid model compound: A study by quartz crystal microbalance

X. Huang, A.L. Elias *

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2V4, Canada

ABSTRACT

A polymer coating was developed to enable the sensing of naphthenic acid (a hydrocarbon contaminant found in oil sands process affected water) using a quartz crystal microbalance (QCM). Previous research on QCM-based hydrocarbon sensors has focused on developing polymer coatings to sense non-polar hydrocarbons, rather than polar organic acids such as naphthenic acid. To detect a naphthenic acid model compound (4-methyl-cyclohexane acetic acid, MCAA), a polybutadiene thin film surface was modified with amine functional groups through a facile two-step process: hydroxides were generated on the surface of the polymer and subsequently used as sites for reaction with amino silanes. The attachment of amino groups was characterized by X-ray photoelectron spectroscopy. QCM measurements revealed that polybutadiene thin films modified with amino groups exhibited much higher sensitivity to MCAA than unmodified films. After amine modification, frequency shifts of 56 Hz were measured with exposure to 100 ppm MCAA, compared with only 8 Hz for an unmodified polybutadiene film. The QCM response was fast with stable readings achieved within 5 min of the sensor being exposed to a particular solution, and a linear relationship between frequency change and MCAA concentration was obtained. The responsivity of the system was also tested in various buffer solutions to determine how variations in both pH and salinity affected the measurements. To both investigate the applicability of this surface treatment and to elucidate the mechanism by which the amine group increased the responsivity of the film, the application of amine functional groups to other polymers and SiO_2 was examined. Both the modification with the amino group and the properties of the hydrophobic polymers themselves were found to impact the QCM sensor performance.

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1. Introduction

Hydrocarbon pollutants have been found in various natural environments, as a result of both natural seepage and spillage associated with the extraction, processing, and use of petroleum [1–3]. Due to the toxic and detrimental effects of these types of contaminants, sensitive and reliable chemical sensors that allow for fast, real-time screening and monitoring of environmental hydrocarbons are required in the field to monitor their dispersion [4,5]. Mass-based sensors that exploit the piezoelectric effect (such as quartz crystal microbalances (QCMs)) have been widely investigated to quantify the concentration of hydrocarbons in water [6,7]. QCMs oscillate at a given resonant frequency and, as described by the Sauerbrey equation, the adsorption of an analyte results in a frequency change proportional to the amount of mass adsorbed [8]. To increase the sensitivity and selectivity of these sensors to hydrocarbons, hydrophobic polymer coatings are often applied to the sensor surface to interact specifically with the molecules of interest. When thick polymer coatings (>200 nm) are utilized, the Sauerbrey equation must be modified to account for the viscoelastic properties of the layers [9,10].

Various polymer coatings have been studied for the detection of hydrocarbons (in QCM as well as other mass-based chemical sensors). It is generally accepted that rubbery polymers with low glass transition temperatures are more sensitive to hydrocarbons than glassy polymers [11]. However, most previous work has focused on the detection of *non-polar* hydrocarbons such as BTEX compounds (benzene, toluene, ethylbenzene, and xylene), while studies of the detection of *polar* hydrocarbons such as organic acids hasve been limited. Naphthenic acids (NAs), for example, are polar cyclic
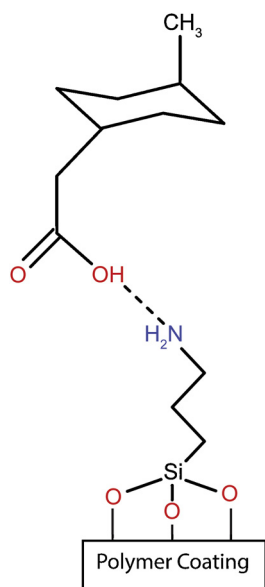
Fig. 1. Schematic illustrating the proposed interaction between the carboxylic acid group on MCAA and the amine group on APTMS.

Table 1
Characteristics of the sensing films.

Polymer	Concentration in THF for spin coating (wt%)	Frequency shift of crystal after spin-coating (kHz)	Thickness (nm) (as measured by ellipsometry)
PB	2	3.3	650
PIB	3	3.0	630
PAB	2.5	3.2	680

polymer coating due to its simple backbone containing only hydrogen and carbon (isolating the sensing effects to the added functional groups). Using a QCM technique, the effect of amines over MCAA sensitivity is investigated for concentrations from 0 to 100 ppm (0 to 100 mg/L), which encompasses typical concentrations in real water systems such as tailings ponds [13], and has been used in previous studies [18]. To investigate parameters that may affect the sensor during actual use, the effects of varying the pH and the concentration of inorganic salts in the solution are also examined. Finally, to better understand the role of amines in sensor response, several alternate polymers and SiO_2 are also functionalized with a range of silanes and the MCAA responses of these systems are analyzed.

2. Experimental

2.1. Materials and reagents

Polybutadiene (PB, CAS 9003-17-2), polyisobutylene (PIB, CAS 9003-27-4) and poly(acrylonitrile-co-butadiene) (PAB, CAS 9003-18-3), were purchased from Sigma Aldrich. Their properties are summarized in Table S1 of the supplementary information. 3-aminopropyltrimethoxysilane (APTMS, CAS 13822-56-5), 3-glycidyloxypropyltrimethoxysilane (GPTMS, CAS 2530-83-8), and 4-methylcyclohexaneacetic acid (MCAA, CAS 6603-71-0) were also purchased from Sigma–Aldrich and used as received.

To prepare buffer solutions, Na_2HPO_4 (CAS 7558-79-4) and NaH_2PO_4 (7558-80-7) were ordered from Sigma Aldrich. Stock solutions were prepared at 20 mM using deionized water. Solutions were mixed in ratios ranging from 1:3 (Na_2HPO_4:NaH_2PO_4) to pure NaH_2PO_4 to vary the final pH of MCAA solution from 7 to 4.5. Solutions at pH 3 were prepared by adding HCl to water. The pH of each solution was measured using pH meter.

2.2. Polymer coating and modification

Polymer thin films were prepared on QCM crystals by spin coating onto AT-cut gold-coated quartz crystals (supplied by Stanford Research Systems, USA). To clean the crystals, they were soaked in nitric acid (1:1 conc. nitric/deionized (DI) water) for ~15 min, and subsequently sonicated in ethanol for 10 min. They were then rinsed thoroughly with DI water and air dried in a ventilated environment. Casting solutions were prepared by dissolving the polymer of interest in tetrahydrofuran (THF, Sigma–Aldrich) at concentrations between 2 wt% and 3 wt% (as required to achieve film thicknesses close to 650 nm). A Laurell Technologies spin processor (model WS-400B-NPP-Lite) was used to coat the polymers onto the crystals. Approximately 200 μL of polymer solution was dispensed onto each sensor surface, which was then spun at 1000 rpm for 60 s. The resulting polymer thin films were dried overnight at room temperature to remove any remaining solvent. The characteristics of films prepared in this study are shown in Table 1.

To modify the polymer surfaces with amine groups, the polymer thin films were first exposed to a UV/ozone treatment for 10 min and then immersed in a 1 vol% APTMS aqueous solution for 1 h. Because the hydroxyl groups generated by UV/ozone

or acyclic aliphatic organic compounds with a carboxyl functional group, and compounds of this nature are the primary hydrocarbon contaminants found in the tailings ponds related to oil sands operations in Alberta and elsewhere [12,13]. NAs can partition easily into the water phase due to their carboxylic acid groups, especially at high pH values [12], and they are toxic to a wide range of organisms, leading to concern for the oil sands industry [14]. To enable sensing of these NA compounds, a polymer coating that can selectively adsorb NAs is desired. While the nonpolar (hydrophobic) polymers used for the sensing of BTEX compounds are not expected to undergo strong interactions with NAs due to their hydrophilic nature, polar polymers cannot be readily used as coatings as they are generally unstable or even soluble in aqueous environments [15]. Therefore, non-polar polymers tailored with functional groups designed to interact specifically with naphthenic acids are desirable.

Various strategies have been described in the literature to add functional groups to polymers to increase both the sensitivity and the selectivity for analytes of interest in sensor systems. To increase the responsivity of QCM sensors to BTEX compounds, Pejcic et al. [16] functionalized various types of polymer coatings with carbon nanotubes. They found that while thicker films exhibited higher responses to toluene, varying the loading of CNTs from 0% (w/w) to >20% (w/w) did not significantly affect the response. Silva et al. [17] investigated the effect of several plasticizers on the performance of a polyvinylchloride (PVC) sensing film utilized as a concentrator in FTIR-ATR studies and found that di-2-ethylhexylsebacate (DOS) improved the sensitivity of PVC to aromatic hydrocarbons. The modification of sensor surfaces to interact with polar hydrocarbons such as naphthenic acid, on the other hand, has not been well explored.

In this study, polymer thin films are modified with amino groups to increase their sensitivity to 4-methylcyclohexaneacetic acid (MCAA), a low molecular weight naphthenic acid which has been used frequently as a model compound in previous studies [18,19]. Amino groups are expected to interact favorably with the carboxylic acid groups present in NA complexes, including MCAA, as shown in Fig. 1. Amino groups are therefore attached to the surface of polymer thin films by modifying the films with a UV/ozone treatment, and subsequently reacting the modified surfaces with amine-terminated silanes. Polybutadiene (PB) is selected as the