



Interaction parameters for the uptake of sulfur mustard mimics into polyurethane films



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ABSTRACT

Chemical warfare agent (CWA) sorption into polymeric coatings is an important consideration for preventing human exposure to CWAs. The specific nature of CWA–polymer interactions greatly influences the degree of gas uptake into a polymeric coating. By uncovering the role the various functional groups in CWAs play during gas sorption, better films and coatings can be engineered. This study utilized a quartz crystal microbalance to measure sulfur mustard (HD) analog (simulant) and hexane vapor uptake into polyurethane films. Analysis of the uptake data with Flory–Huggins theory yielded interaction parameter values (χ) between 0.24 and 0.40 for each HD simulant–polyurethane system compared to 0.97 for hexane, revealing the importance of the chlorine and sulfur groups in gas uptake at the thin film interface. We predict similar uptake behavior for HD in polyurethane coatings due to structural similarities between HD and the simulants.

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1. Introduction

The chemical warfare agent (CWA) bis(2-chloroethyl)sulfide (sulfur mustard, HD) readily infiltrates polymeric coatings and other materials, which prolongs the risk of human exposure [1–4]. Willis et al. [1] found that HD slowly off-gasses from polymeric coatings into the environment, further increasing the potential for human exposure. The presence of chlorine and sulfur groups in HD suggest HD is capable of having strong dipole and dispersive interactions with many polymeric coatings, which may facilitate gas uptake into the polymer. To date, little is understood about the relationship between CWA structure and polymeric coating properties that affect initial uptake, diffusion into the material, and residence times.

The work presented here utilized a quartz crystal microbalance with dissipation monitoring (QCM–D) to measure gas uptake of HD chemical analogs into polyurethanes, commonly used coating materials. Gas uptake measurements of less toxic, but structurally similar compounds to HD, referred to as simulants, provided the

advantage of being able to systematically probe the effect specific functional groups have on gas uptake. In addition to studying HD simulants, the commonly used solvent, hexane was also examined. While QCM–D gas uptake experiments involving chemical warfare agents and other volatile organic compounds are not novel, QCM–D use has seen limited application in probing fundamental interactions in gas–polymer systems [5–8].

2. Experimental methods

2.1. Materials

Poly(tetramethylene oxide) (PTMO) oligomer (Terathane, Du Pont) with a number average molecular weight of 2000 g/mol and 1,4-butanediol were purchased from Aldrich and dried *in vacuo* at 40 °C for 24 h prior to use. Bis(4-isocyanatocyclohexyl)methane (HMDI) was graciously donated by Covestro with purity greater than 99.5%. Chloroform (CHCl₃, Fisher Scientific, HPLC grade), tetrahydrofuran (THF, EMD Science, HPLC grade), and diethyl ether (Fisher Scientific, 99.9%, anhydrous) were used as received. *N,N*-Dimethylformamide (DMF, Fisher Scientific, HPLC grade) was dried with a PureSolv[®] solvent purification system prior to use. Dibutyltindilaurate (DBTDL, 99%) was dissolved in THF as a 1 wt% solution. Sulfur mustard simulants: 1-chloropropane (99%), 1-chlorobutane (anhydrous, 99.5%), 1-chloropentane (99%), 1,5-dichloropentane (99%), diethyl sulfide (98%), 2-chloroethyl ethyl sulfide (98%), and hexane (Spectrum, HPLC grade) were purchased

Abbreviations: CWA, chemical warfare agent; HD, sulfur mustard or mustard gas; QCM–D, quartz crystal microbalance with dissipation monitoring; 2-CEES, 2-chloroethyl ethyl sulfide; PTMO, poly(tetramethylene oxide); HMDI, Bis(4 isocyanatocyclohexyl)methane; BDO, 1,4-butanediol; ¹NMR, proton nuclear magnetic resonance; DSC, differential scanning calorimetry; TGA, thermogravimetric analysis.

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from Sigma Aldrich and unless otherwise noted used as received. Gold (QSX-301) QCM–D sensors were purchased from Q-sense AB. The gold sensors are 14 mm in diameter with a 0.3 mm quartz thickness. The quartz is plated with a thin layer of chromium (~2 nm), followed by a thin layer of gold (~100 nm).

2.2. Synthesis of 43 wt% hard segment content polyurethane

The model polymeric coating examined in this work was a segmented polyurethane prepared from a 2000 g/mol poly(tetramethylene oxide) (PTMO), hydrogenated methylene diphenyl diisocyanate (HMDI), and 1,4-butanediol (BDO) with 43 wt% hard segments. The synthesis was adapted from Williams et al. [9]. Briefly, HMDI (66.8 mmol, 17.536 g) was added dropwise to the reaction flask containing PTMO (15.0 mmol, 29.990 g) and 50 ppm DBTDL at 80 °C. Dry DMF (100 mL) was then introduced, followed with dropwise addition of 1,4-butanediol (51.8 mmol, 4.672 g) which was allowed to react for 24 h. The resulting reaction solution was twice purified via precipitation into diethyl ether. The resulting white, elastomeric product was subsequently dried *in vacuo* at 50 °C for 12 h.

2.3. Preparation of polyurethane films

QCM–D sensors were cleaned prior to use by exposure to UV/ozone for 45 min (BioForce Nanoscience Inc. ProCleaner™ 110), immersion into a 1:1:5 v/v solution of ammonium hydroxide/hydrogen peroxide/ultrapure water at 80 °C for 2 h, followed by a rinse with ultrapure water and drying with nitrogen. The polyurethane was dissolved in chloroform to make 0.5–1.0 wt% polymer solutions. The polyurethane solution was spin-coated onto the top of the cleaned QCM–D sensors at a spinning speed of 2000 rpm for 1 min. The bottom of each crystal was cleaned with acetone for the removal of residual polymeric material.

2.4. Polyurethane characterization

Proton nuclear magnetic resonance (¹H NMR) spectroscopy was performed in a Varian 400 MHz spectrometer in CDCl₃ at 23 °C. The polyurethane sample was stored in a desiccator after synthesis and was dried *in vacuo* at 50 °C for 12 h before analysis. Differential scanning calorimetry (DSC) was accomplished using a TA Instruments DSC Q1000 under a N₂ atmosphere with a heat/cool/heat cycle performed at 10 °C min⁻¹. Prior to performing DSC, the sample was annealed *in vacuo* at 100 °C for 12 h. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA Q500 under N₂ from 25 °C to 600 °C at a heating rate of 10 °C min⁻¹. Characterization results can be found in Supporting information.

2.5. QCM–D sorption experiments

In order to measure gas uptake into the polyurethane films, the vapor of interest was entrained in nitrogen gas bubbled through a gas saturator cell. The polyurethane films were continuously exposed to the vapor of interest inside flow cell modules of a Q-Sense E4 QCM–D system, where changes in resonant frequencies and dissipation of the oscillating polyurethane-coated quartz crystals were measured. Vapor exposure continued until maximum gas uptake was achieved and the system reached equilibrium. Gas uptake was measured at controlled activity shown by Eq. (1):

$$a_1 = \frac{p_1}{p_1^*} \quad (1)$$

where p_1 is the vapor pressure of the simulant or solvent gas flowing above the sensor and p_1^* is the vapor pressure of the pure condensed vapor at the temperature of the polymer film. Activity

was controlled over the range of 0.1–0.9 by independently varying the temperatures of the gas saturator cell and the coated quartz crystal (Table S1). See Supporting information for a more detailed description of the QCM–D method.

3. Results and discussion

The measured changes in frequency at equilibrium during QCM–D sorption experiments were used in the Sauerbrey relationship (Eq. (2)) to calculate mass uptake of the chemical of interest in the polymeric films [10]:

$$\frac{\Delta f}{n} = -C_f \Delta m \quad (2)$$

where Δf is the change in resonant frequency after an applied load (Hz), C_f is the sensitivity factor which is equal to 56.6 Hz cm² μg⁻¹, n is the overtone number, which can take on only odd integer values, and Δm is the change in mass per unit area due to the applied load. As dissipation in these systems was negligible (<0.5% of $\Delta f/n \times 10^{-6}$) and the frequency values for multiple overtone values overlapped, criteria for use of the Sauerbrey equation were met.

Assuming additive volumes, measured changes in frequency values collected during gas exposure were used to calculate simulant and hexane volume fractions, ϕ_1 , at equilibrium in the swollen polyurethane films:

$$\phi_1 = \frac{\frac{(\Delta f_s/n)}{\rho_s}}{\frac{(\Delta f_s/n)}{\rho_s} + \frac{(\Delta f_p/n)}{\rho_p}} \quad (3)$$

where Δf_s is the change in frequency due to simulant or hexane uptake, Δf_p is the change in frequency due to the polyurethane film, and ρ_s and ρ_p are the densities of the condensed simulant or hexane and polyurethane, respectively. Calculated volume fractions reveal each simulant and hexane readily penetrated and absorbed into the polyurethane films across the entire activity range studied. A swelling plot containing volume fraction versus activity is shown in Fig. 1. All systems exhibit a rise in the volume fraction with increasing simulant activity, which indicates greater gas uptake into the polyurethane films at higher activities. At high activities, volume fraction values approach 0.5 for HD simulants, denoting a large degree of swelling of the polyurethane film. Gas uptake was not found to be significantly different between any of the HD simulants across the entire activity range; however, our results show notably lower swelling for hexane.

The nearly indistinguishable ϕ_1 values between HD simulants as a function of a_1 provides insight into the role each functional group plays in gas uptake. For example, similar volume fraction values between chloropropane, chlorobutane, and chloropentane for a given a_1 signify that the additional dispersion forces from the methylene units have a limited effect on the overall polymer swelling within this chain length regime.

While the additional dispersive forces due to added methylene units in the n -chloroalkane simulants did not result in changes in ϕ_1 vs a_1 , replacement of the chlorine with a CH₃ group, as is the case for hexane, reduced swelling by nearly 50%. The lack of a highly electronegative chlorine atom in hexane results in a non-polar molecule capable of only weak dispersive interactions with the polyurethane film. The polar, chlorine containing simulants interact with the polymer through both dipole–dipole and dispersive interactions which enhance polymer swelling. Volume fractions for diethyl sulfide at similar activity matched the n -chloroalkanes, further supporting the idea that the ability to have dispersive and dipole–dipole interactions opposed to only weak dispersive interactions greatly increased the degree of swelling in these polymer films.

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