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Sorption-induced static bending of microcantilevers coated with viscoelastic material

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Absorption of a chemical analyte into a polymer coating results in an expansion governed by the concentration and type of analyte that has diffused into the bulk of the coating. When the coating is attached to a microcantilever, this expansion results in bending of the device. Assuming that absorption (i.e., diffusion across the surface barrier into the bulk of the coating) is Fickian, with a rate of absorption that is proportional to the difference between the absorbed concentration and the equilibrium concentration, and the coating is elastic, the bending response of the coated device should exhibit a first-order behavior. However, for polymer coatings, complex behaviors exhibiting an overshoot that slowly decays to the steady-state value have been observed. A theoretical model of absorption-induced static bending of a microcantilever coated with a viscoelastic material is presented, starting from the general stress/strain relationship for a viscoelastic material. The model accounts for viscoelastic stress relaxation and possible coating plasticization. Calculated responses show that the model is capable of reproducing the same transient behavior exhibited in the experimental data. The theory presented can also be used for extracting viscoelastic properties of the coating from the measured bending data. © 2008 American Institute of Physics.

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I. INTRODUCTION

Chemical sensors have become an area of extensive research in the past few decades. Various devices including electrical, electrochemical, mechanical, and optical devices have been used as a sensor platform for chemical detection. In the early 1990s, microcantilevers utilized for atomic force microscopy were found to respond to various ambient effects, one of which was the adsorption of mercury vapor.¹⁻³ Microcantilever chemical sensors have since become a major area of research in the field of chemical sensing. This is partly due to the projected high sensitivity resulting from the large surface area to volume ratio, which greatly amplifies surface effects. Microcantilevers have been shown to detect certain chemical gases in the low ppt level⁴⁻⁶ and recently detect the presence of a few molecules.⁷ Furthermore, microcantilevers can inexpensively be manufactured into small arrays containing a very large number of sensors.⁸ These arrays can be deployed for the rapid detection of a wide variety of analytes.

In these systems, the cantilever is coated with a layer that either absorbs or adsorbs the analyte. In the static mode of operation, sorption results in cantilever bending, whereas in the dynamic mode, the result of sorption is a change in the resonant frequency. For the static mode of operation, sorption-induced bending of metal-coated microcantilevers has been extensively studied.^{9,10} In that research, it was

found that for bulk absorption, the bending of the microcantilever is dependent on the thickness of the metal film. However, for adsorption onto a thin metal film, the bending is usually independent of the thickness. In addition, responses from microcantilevers coated with metals were found to generally exhibit a first-order behavior resulting from Fickian diffusion into the bulk of the coating or adsorption rate limited by the surface coverage. The results of these studies can be used to accurately describe the transient response of a cantilever coated with an elastic material whose modulus does not change during absorption due to plasticization (softening). However, when different types of coatings, such as polymers, are used, the bending response during absorption is known to demonstrate a wide variety of behaviors, some of which include an overshoot followed with a decay to the steady state.^{11,12}

Viscoelastic coatings (which include polymers and monomers) are often used as the chemical recognition element in various sensor applications.¹²⁻¹⁴ These materials undergo a relaxation process in which a sudden strain will induce a stress that slowly relaxes over time until the asymptotic stress is reached. Similarly, a constant stress will result in a strain that slowly increases (i.e., creeps) until the asymptotic strain is reached. Previous studies of the sorption-induced stresses (or bending) of coated microcantilevers use models that rely on Young's modulus E to describe the stress/strain relationship in the coating material via Hooke's law. This presumes that the coating is a linear elastic material in which the stress is simply the strain multiplied by the modulus. This assumption can be used for metals, which in most

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cases can be assumed to be purely elastic. However, for viscoelastic materials, the stress is not only dependent on the strain at that specific instant in time but also dependent on the strain history. In the case of a viscoelastic material, the stress/strain relationship is given by the following heredity integral:

$$\sigma(t) = E_{\text{inst}}\varepsilon(t) + \int_0^t R(t-\tau)\varepsilon(\tau)d\tau, \quad (1)$$

where $\sigma(t)$ is the stress at time t , $\varepsilon(t)$ is the strain at time t , $R(\cdot)$ is the relaxation function, and E_{inst} is the instantaneous modulus, as observed in a relaxation experiment.¹⁵ Thus, there is no simple constant of proportionality between the stress and the strain. As in the development of the models for the elastic case, absorption of an analyte from the surrounding medium will create a tendency for the coating to expand. This sets up a stress in the coating, as well as stresses in the substrate, because the coating is attached to the substrate. However, unlike the elastic case, the stresses in the cantilever coated with a viscoelastic material will depend on time even if the absorbed analyte concentration remains constant. The coated cantilever's transient response will therefore exhibit more complex behaviors.

In most chemical sensor applications, only the equilibrium (steady-state) response is sought for analyte detection; however, the transient response may contain information relevant to the sorption process of an analyte/coating pair. This information could be used to optimize coatings such that the transient response is fast or has a desired signature. The information can also be used to improve processing of the cantilever sensor signal and analyte recognition in an array of sensors. Indeed, in sensor array data analysis, the transient information has been shown to improve analyte classification.^{13,16}

To effectively analyze the sensor response of a coated microcantilever, it is necessary to have good estimates of the material properties that contribute to the overall transient (and steady-state) response. These material properties, which include the viscoelastic properties of the coatings, are often not well known. Even those coatings that have been characterized and whose properties can be found in the literature have large uncertainties. Moreover, for relatively thin coatings, the material properties are dependent on the thickness of the coating, the method of applying the coating to the substrate, the coating/substrate interface, and the environmental conditions. For these reasons, one of the best ways to obtain the coating parameters is to directly extract them from the specific application and devices used. This idea has been previously demonstrated for surface stress measurements using microcantilevers.¹⁷ In that research, it was shown that using Young's modulus given in the literature results in large errors in the surface stress measurements. However, using an experimentally obtained spring constant for the device improved the accuracy of the stress measurements. In a similar manner, the model developed herein could permit one to accurately extract material property data from bending deflection measurements.

In this work, a theoretical model of absorption-induced

static bending of a microcantilever coated with a viscoelastic material is presented. The model accounts for viscoelastic stress relaxation and possible coating plasticization by assuming the general stress/strain relationship for a viscoelastic material. Classical beam theory is used as a foundation in developing the governing equations; thus, the mathematical model is subject to the same assumptions, such as small deflections and a linear strain profile through the thickness of the microcantilever. The theoretical model presented in this paper not only provides a means of predicting/understanding the time-dependent deformation of coated cantilevers but also a tool for extracting viscoelastic coating properties from sensor data.

II. THEORY

A. Elastic coating

When a coated microcantilever is exposed to a chemical analyte, absorption will create a tendency for the coating to expand. However, because the coating is attached to a substrate and is not free to expand, stress builds up in the coating. In order to partially relieve this internal force, the microcantilever bends so that the coating is expanded and a corresponding strain pattern is introduced into the substrate, thus resulting in curvature of the elastically coated beam. This phenomenon is very similar to that of the bimetallic thermostat. Assuming small deflections relative to the length of the cantilever, Timoshenko's original work relates the curvature, d^2Z/dx^2 [$Z(x)$ is the deflection dependent on the longitudinal coordinate x], of the bimetallic structure to the properties of the two metals as¹⁸

$$\frac{d^2Z}{dx^2} = 6(\alpha_2 - \alpha_1) \left(\frac{h_1 + h_2}{h_2^2 K} \right) \Delta T, \quad (2)$$

with

$$K = 4 + 6 \left(\frac{h_1}{h_2} \right) + 4 \left(\frac{h_1}{h_2} \right)^2 + \left(\frac{E_1}{E_2} \right) \left(\frac{h_1}{h_2} \right)^3 + \left(\frac{E_2}{E_1} \right) \left(\frac{h_2}{h_1} \right),$$

where $\alpha_{1,2}$ are the thermal expansion coefficients, $h_{1,2}$ are the thicknesses, and $E_{1,2}$ are the elastic moduli of the substrate and coating, respectively. This result can be used for the case of absorption-induced expansion assuming that the thicknesses, h_1 and h_2 , and the moduli, E_1 and E_2 , of the substrate and coating do not change significantly during absorption. In this case, the thermally induced mismatch strain, $(\alpha_2 - \alpha_1)\Delta T$, is replaced by the absorption-induced elongation of the coating (i.e., the relative elongation the coating would undergo if it were not attached to the substrate), ε^* , yielding

$$\frac{d^2Z}{dx^2} = 6 \left(\frac{h_1 + h_2}{h_2^2 K} \right) \varepsilon^*. \quad (3)$$

Equation (3) assumes that the substrate does not undergo any absorption-induced elongation. If $h_2 \ll h_1$, then Eq. (3) can be further simplified to yield Stoney's equation,¹⁹

$$\frac{d^2Z}{dx^2} = - \left[\frac{6(1-\nu_1)h_2}{E_1h_1^2} \right] \Delta\sigma, \quad (4)$$

where ν_1 is Poisson's ratio of the substrate and the term $(1 - \nu_1)$ has been added to account for the biaxial stress state of the substrate/coating interface.²⁰ The absorption-induced stress $\Delta\sigma$ is given by $\Delta\sigma = -E_2\varepsilon^*$.

In the gas phase, the volume of the coating, when not attached to the substrate, will change with the concentration C of the absorbed analyte (mol/ml of polymer) as²¹

$$V(C) = V_0(1 + CV_a), \quad (5)$$

where V_0 is the initial volume of the coating and V_a is the specific volume of the absorbed vapor (ml/mol). Assuming that the coating is isotropic and will expand the same in all directions, the absorption-induced elongation varies with concentration as

$$\varepsilon^*(C) = \sqrt[3]{1 + CV_a} - 1, \quad (6)$$

which has the linear approximation $\varepsilon^*(t) = \frac{1}{3}V_aC(t)$ for small volume expansions. The absorption-induced elongation can therefore be assumed directly proportional to the absorbed analyte concentration. Writing $\varepsilon^*(t) = \lambda C(t)$, where $\lambda = \frac{1}{3}V_a$, the deflection at the tip of the microcantilever, Z_L , for the general case described by Eq. (3) is then given by

$$Z_L(t) = 3L^2 \left(\frac{h_1 + h_2}{h_2^2K} \right) \lambda C(t), \quad (7)$$

where L is the length of the microcantilever. Stoney's equation [Eq. (4)] could similarly be used to develop a simpler expression for the deflection at the tip of the cantilever given that the assumption $h_2 \ll h_1$ is satisfied. These equations and those subsequently derived neglect the effect of the clamped end of the beam. This approximation has been shown to produce accurate results for long cantilevers with large aspect ratios ($L/w > 3$).²²

Equation (7) relates the microcantilever's response to the sorbed analyte concentration. The expression indicates that the elastic behavior of the beam causes the deflection to track the analyte concentration in the coating. Thus, it is necessary to know how the absorbed analyte concentration in the coating varies with time. This detail is extremely important to predict the transient response of a coated microcantilever during absorption.

The absorption process of an analyte into the bulk of a coating is generally rate limited by the diffusion of the analyte across the surface barrier and into the coating.⁹ If the diffusion is Fickian, then the rate of absorption will be proportional to the difference between the equilibrium concentration in the coating and the concentration already absorbed into the coating, $C(t)$. [The equilibrium concentration is defined by the ambient concentration $C_{\text{amb}}(t)$ multiplied by a proportionality factor γ . In the case of a polymer coating, the proportionality factor is known as the partition coefficient K_p .] This leads to a first-order absorption defined by a single decay rate $1/\tau_s$ (the constant of proportionality between the rate of absorption and the difference in the concentrations), which is dependent on the diffusivity across the surface bar-

rier. This first-order absorption model can be combined with Eq. (7) to form a set of state-space equations that use the absorbed analyte concentration as the state variable, the ambient analyte concentration as the input, and the deflection at the tip of the cantilever as the output. The equations model the sensor response when the modulus of the coating does not change upon absorption and are given by

$$\frac{dC}{dt} = \left(\frac{1}{\tau_s} \right) [\gamma C_{\text{amb}}(t) - C(t)], \quad (8a)$$

$$Z_L(t) = 3L^2 \left(\frac{h_1 + h_2}{h_2^2K} \right) \lambda C(t). \quad (8b)$$

Simulation of this model yields a typical first-order response, in which the deflection tracks the absorbed analyte concentration. As previously mentioned, the model described by Eqs. (8a) and (8b) is based on the assumptions that the coating is an elastic material, and the moduli of the coating and substrate do not change during analyte absorption. For metal coatings, as studied in Ref. 9, these assumptions are generally valid. However, polymer coatings may not act as purely elastic materials. These coatings are often viscoelastic and undergo stress relaxation. Furthermore, analyte absorption can cause a change in the material properties of the coating.

B. Viscoelastic coating

1. Viscoelastic materials

In a number of materials, viscoelasticity arises from the differences in the time required for the material to undergo local and wide-scale molecular readjustments.²³ When a stress is applied to a viscoelastic material, an instantaneous strain results due to local changes in the intermolecular spacing. In addition, the molecules have some freedom to rearrange themselves when the stress is applied (a slow diffusion of molecules within the material). This effect happens at a much slower rate. Macroscopically, this molecular rearrangement translates into an increasing strain under a constant applied stress (creep). Similarly, if a constant strain is applied, local stretching occurs, resulting in an initially large stress. Over time, the molecules are rearranged into a configuration of lower energy, resulting in a decrease in the stress (relaxation).

The simplest model describing the stress/strain relationship in a viscoelastic solid that exhibits both viscous and elastic properties is that of the three-parameter solid,^{15,24}

$$\tau_r E_U \frac{d\varepsilon}{dt} + E_R \varepsilon(t) = \tau_r \frac{d\sigma}{dt} + \sigma(t), \quad (9)$$

where E_U is the unrelaxed (instantaneous) modulus, E_R is the relaxed (asymptotic) modulus, and τ_r is the relaxation modulus time constant. Like a Maxwell fluid, the strain of a three-parameter solid will grow as a function of time when a constant stress is applied. However, the strain will converge to an asymptotic value, σ/E_R , demonstrating its solid properties. The behavior of the three-parameter solid model [governed by Eq. (9)] is indicated in Fig. 1. This figure shows the creep compliance $J(t)$ as a function of time, which is defined as the strain history for a unit step function applied stress,

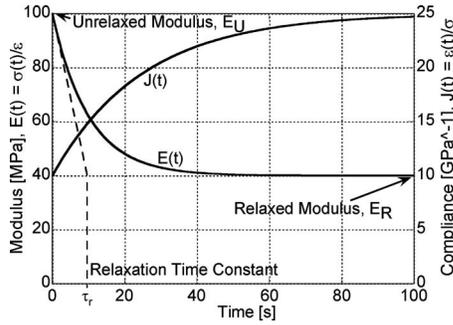


FIG. 1. Modulus $E(t)$ for a constant strain and compliance $J(t)$ for a constant stress in a viscoelastic material behaving as a three-parameter solid. [$E(t) = \sigma(t)/\epsilon$ and $J(t) = \epsilon(t)/\sigma$]. Parameters used: $\tau_r = 10$ s, $E_U = 100$ MPa, and $E_R = 40$ MPa.

and the relaxation modulus $E(t)$, which is defined as the stress history corresponding to a unit step function applied strain. The viscoelastic coatings for which the bending equations are derived in the present work are assumed to satisfy Eq. (9). However, it is possible to use a more general viscoelastic model (one that has higher-order derivatives) and perform a similar derivation.

2. Governing equations for bending of a polymer-coated cantilever

For the derivation of the equations governing the flexural deformation of a polymer coated cantilever, it is assumed that the viscoelastic coating is subjected to a volume expansion that depends on the concentration of the analyte absorbed into the coating. Vertical swelling has a negligible effect on the bending of the microcantilever; thus, only the longitudinal expansion due to the absorption of the analyte (i.e., the sorption-induced elongation, which is defined as the elongation the coating would undergo if it were not attached to the substrate) is considered. However, one may wish to account for the biaxial stress effects of plate geometry, in which case the biaxial modulus $E/(1-\nu)$ may be used in place of E . Again, it is assumed that the substrate does not undergo absorption-induced elongation.

Figure 2 shows the natural state of the coating elongated

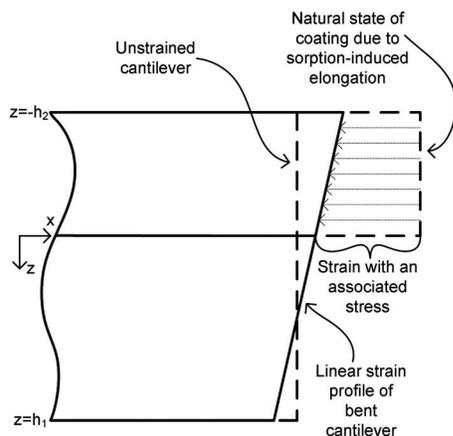


FIG. 2. Strain and resultant stress profiles in the coating and in the substrate during absorption-induced bending of a coated microcantilever (at an arbitrary cut along x).

due to analyte absorption. However, because the coating is attached to the substrate, it is not free to expand and the entire microcantilever (substrate and coating) bends. The total strain profile, including the effects of bending of the microcantilever, is assumed to be linear. Thus, as shown in Fig. 2, the strain with an associated stress denoted by ϵ_σ (which in the coating may be called the “viscoelastic strain”) at any time t is equal to the total strain less the absorption-induced elongation, $\epsilon^*(t)$,

$$\epsilon_\sigma(t, z) = \begin{cases} \kappa(t)[h_n(t) - z] - \epsilon^*(t), & -h_2 < z < 0 \\ \kappa(t)[h_n(t) - z], & 0 < z < h_1, \end{cases} \quad (10)$$

where z is the coordinate in the direction of the thickness of the coated cantilever with the origin at the interface between the two materials (positive z directed downward as shown in Fig. 2), $h_n(t)$ defines the position of the neutral axis at time t , and $\kappa(t)$ is the curvature of the cantilever at time t . The neutral axis is the locus of points on the cross section at which the extensional strain vanishes. Note that for a viscoelastic coating, the neutral axis position varies with time because of stress relaxation occurring in the coating.

The substrate of the coated microcantilever is assumed to be elastic; therefore, the stress profile at time t can be expressed as

$$\sigma(t, z) = \begin{cases} \sigma_2(t, z), & -h_2 < z < 0 \\ E_1 \kappa(t)[h_n(t) - z], & 0 < z < h_1, \end{cases} \quad (11)$$

where E_1 is the modulus of the substrate. Note that $\sigma_2(t, z)$ depends on the entire strain history of the coating, as described by the integral in Eq. (1) (tensile stresses positive). By substituting the expression for the coating’s strain from Eq. (10) into Eq. (1), it can be shown that (because the coating’s strain profile is linear in z and the integral is a linear operator) the stress profile in the coating is linear in z . Therefore, it is possible to define the coating stress profile using the stress at any two points through the thickness of the coating. If the coating stresses at the top ($z = -h_2$), $\sigma_{h_2}(t)$, and at the interface ($z = 0$), $\sigma_0(t)$, are used, then Eq. (11) can be rewritten as

$$\sigma(t, z) = \begin{cases} \{[\sigma_0(t) - \sigma_{h_2}(t)]/h_2\}z + \sigma_0(t), & -h_2 < z < 0 \\ E_1 \kappa(t)[h_n(t) - z], & 0 < z < h_1. \end{cases} \quad (12)$$

These stresses represent the internal forces (per unit area) in the cantilever. There are no applied external forces; therefore, to be in mechanical equilibrium, the net internal forces and moments must be zero. Solving the force and moment balance equations, assuming moments taken about the origin $z = 0$, yields the curvature and the neutral axis position, as functions of time, in terms of the two stresses as

$$\kappa(t) = \left(\frac{-3h_1h_2 - 2h_2^2}{E_1h_1^3} \right) \sigma_0(t) + \left(\frac{-3h_1h_2 - 4h_2^2}{E_1h_1^3} \right) \sigma_{h_2}(t) \quad (13)$$

and

$$h_n(t) = h_1 \left\{ \frac{[2h_1h_2 + h_2^2]\sigma_0(t) + [2h_1h_2 + 2h_2^2]\sigma_{h_2}(t)}{[3h_1h_2 + 2h_2^2]\sigma_0(t) + [3h_1h_2 + 4h_2^2]\sigma_{h_2}(t)} \right\}. \quad (14)$$

The three-parameter solid model in Eq. (9) relates the stress and strain at any point within the viscoelastic coating. As a result, the differential equations describing the time-dependent behavior of the stresses in the coating attached to the microcantilever can be expressed as

$$\begin{aligned} \tau_r E_U \frac{d\varepsilon_{\sigma_0}}{dt} + E_R \varepsilon_{\sigma_0}(t) &= \tau_r \frac{d\sigma_0}{dt} + \sigma_0(t), \\ \tau_r E_U \frac{d\varepsilon_{\sigma_{h_2}}}{dt} + E_R \varepsilon_{\sigma_{h_2}}(t) &= \tau_r \frac{d\sigma_{h_2}}{dt} + \sigma_{h_2}(t). \end{aligned} \quad (15)$$

However, it is desired to have the differential equations in terms of only the two stresses and the input to the system, that is, the absorption-induced elongation $\varepsilon^*(t)$. Using Eq. (10), Eq. (15) can be rewritten as

$$\begin{aligned} \tau_r E_U \frac{d}{dt} [\kappa(t)h_n(t) - \varepsilon^*(t)] + E_R [\kappa(t)h_n(t) - \varepsilon^*(t)] \\ = \tau_r \frac{d\sigma_0}{dt} + \sigma_0(t), \\ \tau_r E_U \frac{d}{dt} \{\kappa(t)[h_n(t) + h_2] - \varepsilon^*(t)\} + E_R \{\kappa(t)[h_n(t) + h_2] \\ - \varepsilon^*(t)\} = \tau_r \frac{d\sigma_{h_2}}{dt} + \sigma_{h_2}(t). \end{aligned} \quad (16)$$

Finally, substitution of Eqs. (13) and (14) for the curvature and the neutral axis location yields a set of coupled differential equations that relates the sorption-induced elongation and the coating stresses at the top and at the interface. Furthermore, Eq. (13) can be used to relate the deflection at the tip of the cantilever to the two stresses. The result is a model that relates the sorption-induced elongation, the stresses in the coating, and the deflection at the tip of the cantilever, $Z_L(t)$,

$$\begin{aligned} \tau_r \left(\frac{E_U}{E_1} a + 1 \right) \frac{d\sigma_0}{dt} + \tau_r \frac{E_U}{E_1} b \frac{d\sigma_{h_2}}{dt} &= - \left(1 + \frac{E_R}{E_1} a \right) \sigma_0(t) \\ &- \frac{E_R}{E_1} b \sigma_{h_2}(t) - E_R \varepsilon^*(t) - \tau_r E_U \frac{d(\varepsilon^*)}{dt}, \\ \tau_r \frac{E_U}{E_1} c \frac{d\sigma_0}{dt} + \tau_r \left(\frac{E_U}{E_1} d + 1 \right) \frac{d\sigma_{h_2}}{dt} &+ = - \frac{E_R}{E_1} c \sigma_0(t) \\ &- \left(1 + \frac{E_R}{E_1} d \right) \sigma_{h_2}(t) - E_R \varepsilon^*(t) - \tau_r E_U \frac{d(\varepsilon^*)}{dt}, \end{aligned} \quad (17a)$$

$$Z_L(t) = \frac{L^2}{2} \left[\left(\frac{-3h_1h_2 - 2h_2^2}{E_1 h_1^3} \right) \sigma_0(t) + \left(\frac{-3h_1h_2 - 4h_2^2}{E_1 h_1^3} \right) \sigma_{h_2}(t) \right], \quad (17b)$$

where

$$\begin{aligned} a &= 2 \left(\frac{h_2}{h_1} \right) + \left(\frac{h_2}{h_1} \right)^2, \quad b = 2 \left(\frac{h_2}{h_1} \right) + 2 \left(\frac{h_2}{h_1} \right)^2, \\ c &= 2 \left(\frac{h_2}{h_1} \right) + 4 \left(\frac{h_2}{h_1} \right)^2 + 2 \left(\frac{h_2}{h_1} \right)^3, \quad d = 2 \left(\frac{h_2}{h_1} \right) + 5 \left(\frac{h_2}{h_1} \right)^2 \\ &+ 4 \left(\frac{h_2}{h_1} \right)^3. \end{aligned}$$

In Eq. (17a) and (17b), if the sorption-induced strain is known, it is possible to solve for the two stresses (and, thus, the entire stress distribution) and the tip deflection as functions of time.

For the case in which the polymer-coated cantilever is subjected to a chemical analyte, the absorption-induced elongation is assumed proportional to the absorbed analyte concentration. Assuming that the analyte is absorbed into the coating in a first-order manner, as described in Sec. II A, then the model describing the bending response of a polymer-coated microcantilever under analyte absorption is given by

$$\begin{aligned} \frac{dC}{dt} &= \left(\frac{1}{\tau_s} \right) [K_p C_{\text{amb}}(t) - C(t)], \\ \tau_r \left(\frac{E_U}{E_1} a + 1 \right) \frac{d\sigma_0}{dt} + \tau_r \frac{E_U}{E_1} b \frac{d\sigma_{h_2}}{dt} \\ &= - \left(1 + \frac{E_R}{E_1} a \right) \sigma_0(t) - \frac{E_R}{E_1} b \sigma_{h_2}(t) - E_R \lambda C(t) \\ &- \tau_r E_U \lambda \frac{dC}{dt}, \\ \tau_r \frac{E_U}{E_1} c \frac{d\sigma_0}{dt} + \tau_r \left(\frac{E_U}{E_1} d + 1 \right) \frac{d\sigma_{h_2}}{dt} \\ &= - \frac{E_R}{E_1} c \sigma_0(t) - \left(1 + \frac{E_R}{E_1} d \right) \sigma_{h_2}(t) - E_R \lambda C(t) \\ &- \tau_r E_U \lambda \frac{dC}{dt}, \end{aligned} \quad (18a)$$

$$\begin{aligned} Z_L(t) &= \frac{L^2}{2} \left[\left(\frac{-3h_1h_2 - 2h_2^2}{E_1 h_1^3} \right) \sigma_0(t) \right. \\ &\left. + \left(\frac{-3h_1h_2 - 4h_2^2}{E_1 h_1^3} \right) \sigma_{h_2}(t) \right]. \end{aligned} \quad (18b)$$

The model given in Eqs. (18a) and (18b) does not include the effects of polymer plasticization. If the properties of the coating are known to change significantly with the sorbed analyte, then those properties (E_U , E_R , and τ_r) can be written as functions of the sorbed analyte concentration. Incorporation of this effect causes the differential equations [Eq. (18a)] in the model to become nonlinear.

C. Approximate models for a viscoelastic coating

The general differential equations [Eqs. (18a) and (18b)] derived in the previous section are useful for analyzing the

response of a microcantilever when all coating properties and the coating/analyte interactions are well known. In general, these polymer characteristics are not available in the literature. Therefore, one may wish to extract coating properties from the bending response using the presented theory. To determine the coating properties, it is advantageous to have a simple model, with few parameters, that completely describes the physics of the observed response of the coated microcantilever. The model of the polymer-coated cantilever given by Eqs. (18a) and (18b) can be greatly simplified when the coating is very soft or thin, or when stress relaxation in the coating occurs very rapidly or slowly.

1. Approximate model 1: The case of a soft or thin coating

In general, Young's modulus of the substrate material is much larger than that of the polymer coating. For example, silicon, with a Young's modulus of approximately 150 GPa, is much stiffer than the average polymer coating, which generally has an unrelaxed modulus in the range of 10 MPa to 5 GPa. For a soft or thin coating ($E_U \ll E_1$ or $h_2 \ll h_1$), the absorption-induced elongation must be large to produce significant curvature. Thus, the magnitude of the viscoelastic strain in the coating, which is defined in Eq. (10), may be approximated by the sorption-induced elongation. Neglecting the bending strain in the coating, Eq. (10) can be rewritten as

$$\varepsilon_{\sigma}(t, z) = \begin{cases} -\varepsilon^*(t), & -h_2 < z < 0 \\ \kappa(t)[h_n(t) - z], & 0 < z < h_1. \end{cases} \quad (19)$$

The strain (and thus the stress) in the coating is therefore taken as uniform. Thus, it is possible to express the stress profile in the coating in terms of the stress at any point in the coating. As a result, Eqs. (18a) and (18b) can be rewritten as

$$\begin{aligned} \frac{dC}{dt} &= \left(\frac{1}{\tau_s}\right)[K_p C_{\text{amb}}(t) - C(t)], \\ \frac{d\sigma}{dt} &= \left(1 - \frac{E_R \tau_s}{E_U \tau_r}\right) \left(\frac{E_U \lambda}{\tau_s}\right) C(t) - \left(\frac{1}{\tau_r}\right) \sigma(t) \\ &\quad - \left(\frac{E_U K_p \lambda}{\tau_s}\right) C_{\text{amb}}(t), \end{aligned} \quad (20a)$$

$$Z_L(t) = -\frac{3h_2(h_1 + h_2)L^2}{E_1 h_1^3} \sigma(t). \quad (20b)$$

As in the general model, these expressions can also be modified to take into account the case of plasticization by writing the material properties of the coating τ_r , E_U , and E_R as functions of the absorbed analyte concentration.

2. Approximate model 2: The case of fast or slow coating relaxation

Many polymer-coated microcantilevers exhibit the typical first-order response signature. It is therefore reasonable to expect that the general equations of the coated microcantilever will reduce to a first-order model under appropriate con-

ditions. These conditions occur when relaxation is either extremely slow or extremely fast compared to the sorption process.

For the case in which the relaxation process is extremely slow compared to absorption (i.e., $\tau_r \gg \tau_s$), the sorbed analyte in the coating will reach its equilibrium concentration before significant relaxation occurs. If the coated microcantilever is exposed to the chemical analyte for a length of time on the order of the relaxation time constant, then the effects of relaxation would be observed; however, it is possible that the analyte will be removed from the environment well before significant relaxation occurs. The time-varying modulus of the coating can then be considered constant and taken as the unrelaxed modulus ($E_2 = E_U$). On the other hand, if the relaxation process is extremely fast compared to the sorption process (i.e., $\tau_r \ll \tau_s$), then the time-varying modulus can also be considered constant and taken as the relaxed modulus ($E_2 = E_R$). Under either of the above conditions, the modulus can be assumed constant throughout absorption. Therefore, the bending equation and model for the case of an elastic coating [given by Eqs. (7), (8a), and (8b), respectively] can be used with the choice of E_2 depending on the limiting case considered.

3. Approximate model 3: The case of simple coating plasticization

A simple model, allowing one to evaluate the effect of varying degrees of plasticization on the microcantilever's absorption response, can be derived by combining both the fast (or slow) relaxation and the soft (or thin) coating approximations. If these assumptions hold, it is possible to use the model described by the absorption equation [in Eq. (8a)] and the deflection equation [in Eq. (20b) with $\sigma(t) = -E_2 \lambda C(t)$]. If the modulus is a linear function of the analyte concentration for the range of concentrations considered, then

$$E_2[C(t)] = E_{2,0} + \delta C(t), \quad (21)$$

and the model for this simple case of plasticization is given by

$$\frac{dC}{dt} = \left(\frac{1}{\tau_s}\right)[K_p C_{\text{amb}}(t) - C(t)], \quad (22a)$$

$$\begin{aligned} Z_L(t) &= 3L^2 h_2 \left(\frac{h_1 + h_2}{E_1 h_1^3}\right) E_{2,0} \lambda C(t) \\ &\quad + 3L^2 h_2 \left(\frac{h_1 + h_2}{E_1 h_1^3}\right) \delta \lambda C^2(t), \end{aligned} \quad (22b)$$

where $E_{2,0}$ is the modulus of the coating before the analyte is introduced (either E_U or E_R , which is dependent on the speed of relaxation process relative to the sorption process, as presented above) and δ is the change in modulus per sorbed analyte concentration. The parameter δ will be negative for the common case of polymer softening or positive for hardening. For this simple model of plasticization, it can be shown that the response described by Eqs. (22a) and (22b) will exhibit an overshoot if the coating softens and the condition

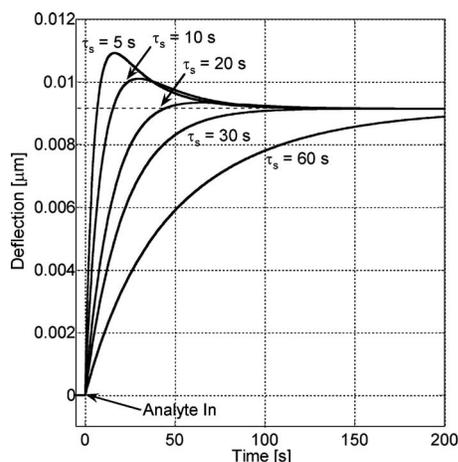


FIG. 3. Typical calculated bending responses for a PIB coated cantilever during the absorption of analytes for various sorption times but same steady-state sorption-induced elongation ($\varepsilon_{ss}^* = 0.01$). Parameters used for the PIB coating are $E_U = 0.72$ MPa, $E_R = 0.51$ MPa, and $\tau_r = 22$ s.

$$K_p C_{\text{amb}} > \frac{E_{2,0}}{-2\delta} \quad (23)$$

is satisfied. The above inequality indicates that, for this model, an overshoot due to plasticization occurs if analyte sorption causes more than a 50% decrease in the modulus (again, either E_U or E_R , which is dependent on the relaxation process) of the coating.

III. RESULTS AND DISCUSSION

A. Numerical calculations of polymer-coated microcantilever responses

In this section, the responses of polymer-coated microcantilevers upon exposure to chemical analytes will be numerically calculated using the models previously derived. An Euler approximation with a small step size is used to solve the differential equation. All calculations will be performed for a cantilever of the same geometry. The cantilever's substrate has a length of $400 \mu\text{m}$, a thickness of $1 \mu\text{m}$, and Young's modulus of 150 GPa (similar to that of silicon). The thickness of the coating is assumed to be $0.4 \mu\text{m}$ in all cases; however, the material properties (E_U , E_R , and τ_r) will be varied to represent different coatings. A rapid exposure of the analyte to the coated microcantilever, such that $C_{\text{amb}}(t)$ can be approximated as an ideal step function, will be assumed. Furthermore, the parameters of the absorption-induced elongation (the steady-state absorption-induced elongation, $\varepsilon_{ss}^* = \lambda K_p C_{\text{amb}}$, and τ_s), which are dependent on the analyte/coating pair, will also be varied to simulate different absorption processes.

The expressions in Eqs. (18a) and (18b) are used to simulate the response of a polymer-coated microcantilever upon exposure to a chemical analyte. Figure 3 shows typical responses that are possible when the same coating is exposed to different analytes. To calculate the responses in Fig. 3, the material properties of polyisobutylene (PIB) were used for the coating properties and the calculations were performed for exposure to various hypothetical analytes that result in

the same steady-state absorption-induced elongation ($\varepsilon_{ss}^* = 0.01$) but have different sorption time constants. It is noted that different values of the steady-state absorption-induced elongation with the same sorption time constant have the effect of scaling the responses. The coating properties of PIB ($E_U = 0.72$ MPa, $E_R = 0.51$ MPa, $\tau_r = 22$ s) were obtained by fitting the three-parameter solid model to data in the literature.²³

In a microcantilever coated with a viscoelastic material, there are two effects that contribute simultaneously to the bending response. Analyte is absorbed into the coating, causing the absorption-induced elongation to increase, which results in an increase in the stress and the curvature. However, because the coating is a viscoelastic material, the stress will also relax with time, resulting in decreasing stress and curvature. As shown in Fig. 3, a variety of response behaviors may occur depending on the value of the sorption time constant even when the coating is not changed. If sorption occurs slowly ($\tau_s \gg \tau_r$), then the stress from the absorption-induced elongation can be considered to be always at its relaxed state and the responses take a first-order shape, i.e., the deflection history simply tracks the absorption history. However, if absorption is faster than the relaxation process, there can be a buildup of unrelaxed stress, followed by a decrease due to the relaxation effects overtaking the increase from absorption. This occurs due to the slowing of the absorption process as the analyte in the coating approaches its equilibrium concentration; the net effect is that the bending response exhibits an overshoot characterized by a peak deflection followed by a decrease to the steady-state value.

In general, the time required to reach the cantilever's equilibrium response is governed by the slower of the two processes. If absorption is slower, then the steady-state will not occur until the equilibrium concentration is reached. Conversely, if relaxation is slower, then the steady-state will not occur until the coating has had enough time to fully relax. This could be long after the equilibrium concentration is realized. Furthermore, the amount of overshoot (if it occurs) is governed by the ratio of the two time constants τ_r/τ_s and the relaxation factor $1 - E_R/E_U$. The relaxation factor indicates the relative amount of stress relaxed at the steady state; a relaxation factor of 0 indicates that the steady-state stress is the same as the initial stress, whereas a relaxation factor of 1 indicates that the steady-state stress is zero. One would expect that greater relaxation would cause the stress to decrease more and thus contribute to a larger overshoot. The ratio of the time constants determines the percentage of the total relaxation that has occurred before absorption approaches the equilibrium concentration. If the relaxation time constant is much larger than the sorption time constant, very little relaxation occurs before absorption approaches equilibrium; thus, maximum stress is achieved before relaxation is significant and the peak is quite large. The relaxation factor and ratio of the two time constants also determine if an overshoot will occur. If approximate model 1 (case of a soft or thin coating) is used, then it is possible to arrive at a condition for which values of the sorption time constant will ex-

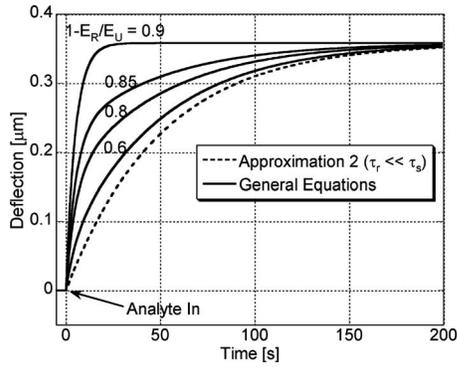


FIG. 4. Comparison of approximate model 2 (case of fast relaxation) and the general differential equations describing the absorption-induced bending of a coated microcantilever. A value of $\tau_r/\tau_s=0.1$ (ratio between the relaxation and sorption time constants) was used, and the calculations were performed for various relaxation factors.

hibit an overshoot. Using a closed form solution for Eq. (20a), it can be shown that an overshoot occurs if and only if $E_U > E_R$ and

$$\tau_s < \frac{E_U}{E_R} \tau_r. \quad (24)$$

The accuracy of the approximate models given in Sec. II C is next evaluated and compared to the results of the general formulation given by Eqs. (18a) and (18b). For approximate model 1 (the case of a soft or thin coating), it is the ratios E_U/E_1 , E_R/E_1 , and h_2/h_1 that govern the accuracy of the model. When approximate model 1 is compared to the general formulation, no significant discrepancies are observed for soft coatings on silicon ($E_1=150$ GPa and $E_U < 2.0$ GPa).

To illustrate the accuracy of approximate model 2 (the case of very slow sorption or very fast coating relaxation), calculations are performed using $\tau_r/\tau_s=0.1$ and compared to the general formulation for various relaxation factors, as shown in Fig. 4. The coating material was chosen to have $E_R=20$ MPa, $\tau_r=5$ s, and the absorption process described by the parameters $\varepsilon_{ss}^*=0.01$ and $\tau_s=50$ s. In this case, a discrepancy is observed between the results of the approximate and general model as absorption occurs, although both the approximation and the general equations converge to the same steady-state value. Agreement between the two improves as the time constant ratio τ_r/τ_s and/or the relaxation factor $1-E_R/E_U$ decreases. It is noted that the responses calculated by the general equations exhibit behaviors that are between an exponential rise to the steady state dictated by the sorption time constant and an exponential rise dictated by the relaxation time constant. This type of response has also been observed in experimental data.^{11,12}

In order to study the effects of plasticization, approximate model 3 given by Eqs. (22a) and (22b) is evaluated for various values of β , where $\beta=-K_p C_{amb} \delta/E_{2,0}$ (i.e., the fractional decrease in the modulus at full absorption) while keeping all other parameters constant. The results are shown in Fig. 5 and compared to responses calculated using the general model. In evaluating the general model, plasticization is assumed to cause coating softening and also causes relax-

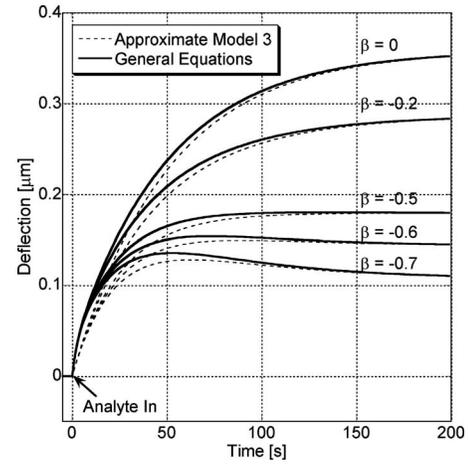


FIG. 5. Calculated bending responses using approximate model 3 (case of simple coating plasticization) during absorption for various degrees of plasticization. The parameter β is the percent change in modulus at the steady state.

ation to occur at a faster rate (E_U , E_R , and τ_r are linear functions of absorbed analyte concentration). The responses shown in Fig. 5 were calculated using $E_U=50$ MPa, $E_R=20$ MPa, and $\tau_r=2.5$ s for the coating parameters and $\varepsilon_{ss}^*=0.01$ and $\tau_s=50$ s for the absorption process. Note that an overshoot occurs when β is increased beyond its critical value of 0.5, as stated in Eq. (23). This overshoot occurs because the decrease in bending due to the softening of the coating is greater than the increase in bending due to the absorption-induced elongation. As seen in Figs. 3 and 5, two different effects (relaxation and plasticization) can cause the same type of response, i.e., an overshoot during analyte absorption. However, simulation of the two models indicate that the effects plasticization and relaxation have on the coated cantilever's response are very different during desorption.

B. Extraction of coating properties

Viscoelastic properties of coatings used in sensor applications are generally not well known. Using measured sorption-induced bending of the coated microcantilever, the theoretical models developed in this work can be used to extract the coating properties. Extraction of the coating properties will permit the analysis and/or prediction of the bending response in future experiments utilizing the same coating or a coating with similar properties on microcantilevers of different geometries.

The transient behavior of the microcantilever bending response demonstrated by the solution of the general equations [Eqs. (18a) and (18b)] is very similar to that of the observed experimental data. Thus, the effects of stress relaxation in a viscoelastic coating are able to account for the variety of behaviors that are observed in static-mode microcantilever responses. Since the behavior of the general mathematical model and the experimental bending responses are very similar, it is possible to correlate the theoretical solutions to the observed bending responses and thus extract the effective properties of each coating. In this section, coating properties will be extracted from experimental data by cor-

relating the physics-based model to the absorption portion of the experimental data. Ideally, the extracted values would then be compared to material properties for the coating available in the literature or the extraction would be performed several times on microcantilevers of various geometries and then tested for consistency. However, the material properties of the coatings used in the experimental data set are not well known and may be a function of the coating technique, molecular arrangement, thickness of the coating, and environmental conditions. Furthermore, at present, available experimental data for the coating/analyte pairs tested only utilize a single microcantilever geometry. Therefore, the coating properties, which are extracted from microcantilevers of the same geometry, coated with the same material, but exposed to different analytes, are compared for consistency. In addition, to provide an independent check, the coating properties extracted during absorption are used to predict the microcantilever's response during desorption and the predicted response is compared to the experimental data.

The experimental cantilever bending data used in this work were taken from a data set provided by the Oak Ridge National Laboratory and published in Ref. 12. This work utilized an array of polymer-coated microcantilevers on two silicon chips (five per chip). The microcantilevers were 400 μm long, 100 μm wide, and 1 μm thick, and the thickness of the coatings was approximately 0.4 μm . Each silicon microcantilever was coated with a different analyte recognition layer on a nanostructured gold surface. The nanostructured gold surface was used to prevent slippage of the coating when it begins to expand. All coated microcantilevers, which are placed in the same flow cell and, thus, under the same conditions, were simultaneously exposed to the same analyte and data were collected from each sensor. For the present analysis, several sensor responses were considered in order to characterize the delivery system, which consists of approximating the ambient analyte concentration as a function of time during the analyte injection and flush processes. The ambient concentration history was estimated by observing several responses that exhibited an exponential rise to the steady state (such that the coating relaxation effects are not essential to the general behavior of the response) and then using the previously developed elastic model [Eqs. (8a) and (8b)] to determine the input concentration that caused the response. Using this methodology, the ambient analyte concentration as a function of time was found to be a step function followed by a partial step down (50%) and then a slowly decaying exponential tail ($\tau=25$ s) for all experiments. The tested coatings and the analytes are summarized in Ref. 12, which contains a more detailed description of the work done to collect the bending data.

In order to extract coating properties from the experimental data, it is necessary to choose a model and a fitting algorithm. There are many least squares techniques available for fitting parameters to the experimental data. The method applied to obtain the results presented in this paper is the Gauss–Newton technique.²⁵ Generally, choosing the model with the fewest parameters that can fully explain the behavior yields the most consistent results. If the response seems to rise in a first-order fashion to the steady state, then ap-

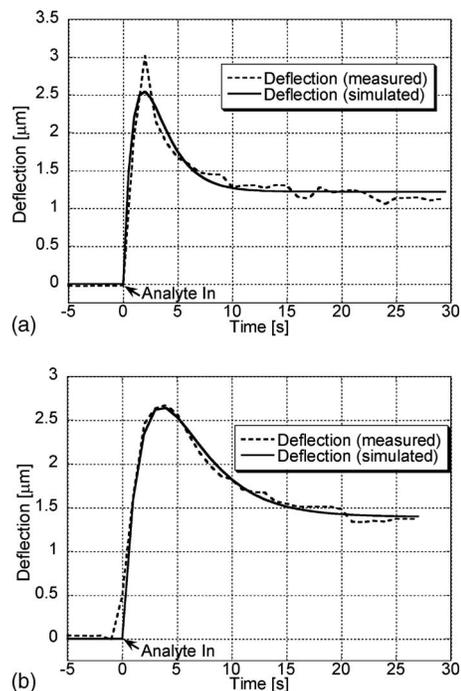


FIG. 6. Experimentally measured absorption-induced bending (Ref. 12) and numerically calculated responses using the extracted coating parameters for a CD-coated cantilever exposed to (a) dichloromethane and (b) trichloroethylene. The parameters extracted are $E_R \varepsilon_{ss}^* = 0.68$ MPa, $1 - E_R/E_U = 0.75$, $\tau_r = 1.9$ s, and $\tau_s = 1.2$ s for CD exposed to dichloromethane and $E_R \varepsilon_{ss}^* = 0.77$ MPa, $1 - E_R/E_U = 0.87$, $\tau_r = 1.7$ s, and $\tau_s = 4.3$ s for CD exposed to trichloroethylene.

proximate model 2 is more appropriate. If this model does not fit the data, then it may be necessary to use approximate model 1. The choice of model affects which coating parameters can be extracted. Approximate model 1 allows one to extract all the coating properties (some are scaled by the steady-state elongation) and the sorption time constant; however, approximate model 2 only contains the modulus (relaxed or unrelaxed, depending on the relaxation process) and the sorption time constant. The model choice should be governed by the transient behavior observed in the response.

Four typical responses were chosen to demonstrate the extraction of coating properties. The responses represent two different coatings, each exposed to two different analytes. In Fig. 6, the absorption portion of the experimental data is shown for a heptakis (6-*O*-*tert*-butyl dimethylsilyl)-2,3-di-*O*-acetyl)- β -CD (CD)-coated cantilever exposed to dichloromethane [Fig. 6(a)] and trichloroethylene [Fig. 6(b)]. The extracted parameters in each case are physically plausible and there is agreement between the extracted values (scaled by the steady-state elongation) from the responses of the microcantilevers using the same coating. Using approximate model 1, the extracted parameters for the data in Fig. 6(a) are $E_R \varepsilon_{ss}^* = 0.68$ MPa, $1 - E_R/E_U = 0.75$, $\tau_r = 1.9$ s, and $\tau_s = 1.2$ s and the extracted parameters for the data in Fig. 6(b) are $E_R \varepsilon_{ss}^* = 0.77$ MPa, $1 - E_R/E_U = 0.87$, $\tau_r = 1.7$ s, and $\tau_s = 4.3$ s. It is noted that the differences in the extracted material properties may be accounted for by the different effects of plasticization by the two analytes, as the contribution of plasticization to the material properties was neglected here in the

calculations. Furthermore, the difference in the steady-state response in Figs. 6(a) and 6(b) implies that the absorption-induced elongation is approximately 10% larger for the analyte in Fig. 6(b) compared to that of Fig. 6(a); this is approximately the same relative difference in the $E_R \varepsilon_{ss}^*$ values extracted from each response. Knowledge of the steady-state elongation ε_{ss}^* , which may be different for different analytes (as seen in the present data), allows the values of the unrelaxed and relaxed moduli to be calculated from the extracted parameters. The steady-state elongation can be calculated using the partition coefficient, which can be obtained from an independent experiment.^{21,26} If a steady-state elongation of 1.0% is assumed for the CD coating exposed to the dichloromethane and 1.1% is assumed for the CD coating exposed to the trichloroethylene (typical volume expansions for the absorption of analytes into chemically sensitive coatings vary between 1% and 5%),²⁶ the calculated unrelaxed and relaxed modulus for the CD coating are found to be around 350 and 70 MPa, respectively.

The extraction of coating properties was also performed for a poly(diphenoxyphosphazene) (PDPP)-coated microcantilever exposed to ethanol and diisopropylmethylphosphonate (DIMP). Using approximate model 2, the extracted PDPP coating parameters from the response exposed to ethanol and DIMP were found to be $E_R \varepsilon_{ss}^* = 0.077$ MPa with $\tau_s = 6.2$ s and $E_R \varepsilon_{ss}^* = 0.054$ MPa with $\tau_s = 3.4$ s, respectively. The steady-state response for PDPP exposed to ethanol is approximately 40% larger than that of PDPP exposed to DIMP. If a steady-state elongation of 1.4% is assumed for PDPP exposed to ethanol and 1.0% assumed for PDPP exposed to DIMP, then the calculated relaxed modulus for the PDPP coating is approximately 5.5 MPa. In this case, because stress relaxation in PDPP is fast, the first-order response implies $\tau_r \ll \tau_s$.

The results shown above demonstrate that it is possible to extract the coating parameters from experimental data using the developed models. Furthermore, it was shown that the coating parameters extracted from the response of a given coating material exposed to different analytes were in agreement. However, the comparison between the theory and experiment (as shown in Fig. 6) is obtained by using the four extracted parameters with the model. While this, by itself, does not prove predictive capability, it also does not guarantee the good fit shown in Fig. 6. The above analysis does allow one to conclude that the model including the viscoelastic properties of the coating can account for the different responses observed in experimental data.

A demonstration of the predictive potential of the model by comparing the theory (using material properties of the coating found in the literature) to the experimental data would strengthen the above conclusion. However, such thin coating properties are not well defined in many cases and may also depend on the actual coating process as well as the interfacial properties between the substrate and coating. Furthermore, the interaction between the coating and analyte (i.e., the sorption time and steady-state elongation) would have to be known.

In order to show the predictive potential of the models, the coating properties extracted from the absorption portion

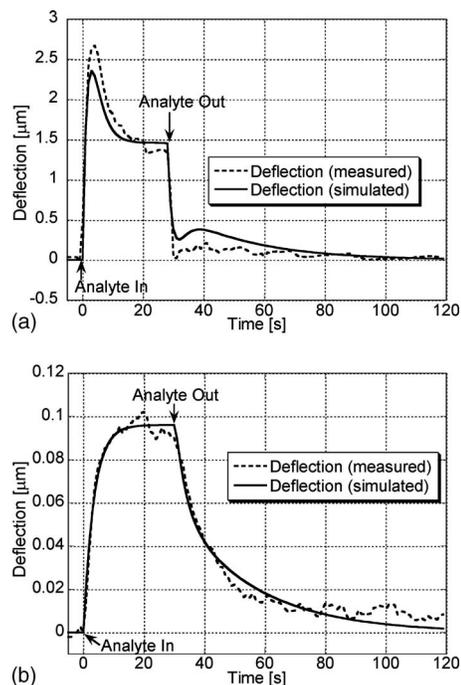


FIG. 7. Comparison of experimental data and calculated bending response during absorption and desorption for (a) a CD-coated cantilever exposed to trichloroethylene and (b) a PDPP-coated cantilever exposed to diisopropylmethylphosphonate. Coating properties used are those extracted from CD exposed to dichloromethane and PDPP exposed to ethanol. Analyte dependent absorption parameters (ε_{ss}^* and τ_s) are extracted during absorption only and used to calculate the entire response including desorption.

of the response of CD exposed to dichloromethane and PDPP exposed to ethanol were used to calculate the entire response (both absorption and desorption) of CD exposed to another analyte, trichloroethylene, and of PDPP exposed to DIMP. The comparison between the calculated responses and experimental results are shown in Fig. 7. In this case, the steady-state elongation and the sorption time are the only parameters that are used to fit the data. More importantly, these two parameters were extracted using only the absorption portion of the response; desorption was entirely predicted with no fitting parameters. The good agreement indicates that the predictive capabilities of the theoretical models are promising.

IV. CONCLUSIONS

A theory of the bending of a microcantilever coated with a viscoelastic material undergoing absorption/desorption is presented. The theory includes the effects of stress relaxation in a viscoelastic coating and is capable of accurately representing the observed response signatures of polymer-coated microcantilevers. The numerical calculations show very good agreement with the trend observed in the experimental data collected from microcantilevers coated with different viscoelastic materials and exposed to various analytes. The theoretical models can thus be utilized to extract values of the various coating parameters that may depend on the coating material, the thickness of the coating, the method of application, and the environmental conditions. Furthermore, the model can be used to predict/analyze the bending response of

a coated microcantilever during analyte absorption and desorption. By independently measuring or calculating the steady-state coating elongation, the actual values of the coating moduli can be extracted. The results will allow for the analysis/prediction of the bending response of microcantilevers coated with the same or similar coating.

Analysis of the transient response using the presented models could also be performed to greatly improve analyte recognition utilizing an array of coated microcantilevers. As demonstrated by the differential equations describing the bending response, both the equilibrium and transient behaviors of the coated microcantilever are dependent on the analyte/coating pair or class of analyte/coating pair and thus can be used to aid in the identification process.

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