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An integrated photonic-diffusion model for holographic sensors in polymeric matrices

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ABSTRACT

Light–matter interactions are commonly described and studied in static systems for which molecular changes do not occur dynamically. Matter–matter interactions on the other hand are described independently from the light interaction phenomena. There is a need for a holistic approach that considers both. Holographic sensors are photonic structures built into polymer film composites that react to molecular interactions with analytes, showing changes in reflectivity and wavelength. These systems are attractive for sensor applications, not only because they easily read by color changes, but also because the light diffraction phenomena are directly related to intermolecular interactions. Here, we describe a theoretical model that couples photonic and molecular mixing phenomena, and demonstrate its experimental validation for holographic sensor systems.

1. Introduction

Hybrid nanomaterials and polymer composites have been proposed to improve the physical properties of future product building blocks [1–3]. Understanding the phenomena of molecular interactions, together with the improved physical properties, is paramount for designing novel product components. New hybrid nano-constructions in polymeric membranes are continuously reported in the scientific literature for applications in emerging technologies such as fuel-cells, membrane barriers, and sensor elements [4,2,5]. Sensor technologies, in particular, benefit from these hybrid polymer nano-composite materials because of their enhanced molecular selectivity. Recently, holographic sensors for gaseous hydrocarbons and volatile organic compounds (VOCs) have been demonstrated in poly(dimethylsiloxane) (PDMS)–silver nanoparticle composite films [5,6]. The fabrication of these sensors consists of in situ formation of silver nanoparticles by perfusion into the elastomer films, followed by laser ablation for patterning [5]. The sensor response is driven by the number of molecules in the sensor matrix at a certain point in time. Molecular interactions cause the physical deformation of the polymer chains, which ultimately leads to changes in geometry and optical properties of the patterned layers of material. All these chemical and physical interactions are governed by molecular surface interactions at the nanoscale, which can be modeled mathematically [1]. In the particular case of holographic sensors, the photonic phenomena are well understood and it has been theoretically described using various modeling methodologies [4,7–14]. However, a theoretical model that considers both, photonic effects and complex diffusion, has not been proposed for these systems until now.

Molecular transport into the polymer matrix is governed by diffusion, which becomes anomalous in the presence of nanoparticles. It has been shown that interactions between the diffusant, the polymer, and the nanoparticles affect this process [2]. Therefore, diffusion models coupled with rheology have been proposed for modeling these complex processes in polymeric membranes [3]. Extensions of these models account for swelling, consider microscopic (kinetic) and mesoscopic (thermodynamic) levels, energy of mixing, molecular polymer structure conformations, and interfacial interactions [1–3,15]. There are certainly other works that further extend these models to consider conformations and deformations [16,17], or even to molecular dynamics simulations for transport processes but in other type of systems [18]. In this work, diffusion, swelling, mixing, and changes in optical diffraction are discussed as elements of an integrated theoretical model.

Holographic sensor models: Empirical models that relate molecular interactions to wavelength changes in holographic sensors have been proposed previously [5]. These models attempt to explain analyte–sensor interactions via experimental observations of the diffracted light wavelength in relation to known physicochemical properties. For example, the cohesive energy density, δ^2, correlates to the total wavelength shift in holographic sensors for

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VOCs and gaseous hydrocarbons [5]. In this model the wavelength shift at equilibrium, $\Delta\lambda$, relates to δ as

$$\delta = \beta(\Delta\lambda)^{\alpha}. \tag{1}$$

where β is related to δ and to the type of penetrant, α is positive for penetrants with values of δ lower than that of the polymer, and negative for larger values. The cohesive energy density is related to the free energy of mixing (ΔG_m) via the Flory–Huggins interaction parameter ($\chi_{1,2}$), which accounts for polymer–solvent interactions and polymer molecular conformations (Ω)

$$\Delta G_m = k_B RT(\chi_{1,2} N_1 \upsilon_2 - \ln \Omega), \tag{2}$$

where k_B is Boltzmann's constant, N_1 the number of penetrant molecules, υ_2 the volume fraction of the polymer in the mixture, R the gas constant, and T the temperature. $\chi_{1,2}$ is related to δ as

$$\chi_{1,2} = \frac{V_t}{RT}(\delta_1 - \delta_2)^2, \tag{3}$$

where V_t is the total volume of the mixture and δ_1 and δ_2 indicate solvent and polymer values respectively. Therefore, the sensor response is related to the strength of the molecular interactions.

Changes in the photonic properties of the sensor are known as the *holographic response*, and are caused by the swelling of the films or by a change in the effective refractive index of the layer, which in turn cause light diffraction to change due to the increased separation between the layers [5]. Even though these conclusions hold true experimentally, ultimately a theoretical model that considers all underlying phenomena is required, i.e. molecular interactions, complex diffusion, and light diffraction. Here, we propose an integrated photonic-diffusion model for the holographic sensor response with applicability to any photonic multilayered sensor system.

2. Theoretical model

Diffusion: Liu and De Kee [2] proposed a mass transport model suitable for non-Fickian behavior in polymer nanocomposite membranes with complex interfaces. The model considers free energy of mixing and concentration changes, and describes the viscoelasticity of the system under moderate swelling. It consists of a set of equations that describe the time evolution of the solvent mass concentration and structural variables for the polymer internal structure and its complex interface. A set of variables are used to account for different phenomena: an area tensor $\mathbf{A}$, related to the rheological properties of immiscible blends, a conformation tensor $\mathbf{m}$, the mass flux of the solvent $\mathbf{J}_s$, the mass fraction of the solvent in the mixture c, and tensors $\mathbf{E}$ and $\boldsymbol{\Lambda}$ which relate the elastic part and interfacial interactions to the mixing part of the free energy [2]. In the model, the mass fraction is defined in terms of the apparent mass densities of the polymer and penetrant as

$$c = \rho_s/(\rho_s + \rho_N) = \rho_s/\rho, \tag{4}$$

where ρ_s and ρ_N are the apparent mass densities of the solvent and composite respectively. For a one-dimensional diffusion process for randomly oriented nanoparticles, and the time evolution of the $\mathbf{A}$ component in the direction of permeation (i.e. A_{11}, E_{11}, m_{11}, Λ_{11}), the model becomes

$$\frac{\partial C^*}{\partial \theta^*} = -\frac{1}{\sqrt{m_{11}^*}}\frac{\partial J_s^*}{\partial X^*}, \tag{5}$$

$$J_s^* = -\frac{1}{\sqrt{m_{11}^*}}\left(\frac{\partial C^*}{\partial X^*} + \Pi\frac{\partial m_{11}^*}{\partial X^*} + \Theta\frac{\partial A_{11}^*}{\partial X^*}\right), \tag{6}$$

$$\frac{\partial m_{11}^*}{\partial \theta^*} = \frac{c_{eq}}{1 - C^* c_{eq}}\frac{J_s^*}{\sqrt{m_{11}^*}}\frac{\partial m_{11}^*}{\partial X^*} - \sqrt{m_{11}^*}\frac{\partial}{\partial X^*}\left(\frac{c_{eq}}{1 - C^* c_{eq}}J_s^*\right) - \frac{1}{De_{\mathbf{m}}}(1 - C^* c_{eq})\{[1 - c_{eq}(2 - c_{eq})C^*]m_{11}^* - 1\}, \tag{7}$$

$$\frac{\partial A_{11}^*}{\partial \theta^*} = \frac{1}{\sqrt{m_{11}^*}}\frac{\partial}{\partial X^*}\left(\frac{c_{eq}J_s^*}{(1 - C^* c_{eq})}A_{11}^*\right) - \frac{1}{De_{\mathbf{A}}}C^*(C^* - 1), \tag{8}$$

where c_{eq} is the solvent concentration at equilibrium, and the dimensionless parameters are defined as

$$C^* = \frac{c}{c_{eq}}, \quad \theta^* = \frac{t}{(L_0^2/D)}, \quad J_s^* = \frac{J_s}{\rho D c_{eq}/L}, \quad X^* = \frac{x}{L_0}, \quad m_{11}^* = \frac{m_{11}}{k_B T/K}, \quad A_{11}^* = A_{11}\lambda_t,$$

$$\Pi = \frac{k_B T E_{11}}{K c_{eq}}, \quad \Theta = \frac{\Lambda_{11}}{\lambda_t c_{eq}}, \quad De_{\mathbf{m}} = \frac{\frac{k_B T}{G_0 \lambda^{\mathbf{m}} K}}{(L_0^2/D)} \quad \text{and} \quad De_{\mathbf{A}} = \frac{(1/\lambda_t \lambda_{1111}^{\mathbf{A}} c_{eq}^2 \Gamma_1)}{(L_0^2/D)};$$

for which L_0 is the membrane thickness at time zero, D the diffusion coefficient, t time, L the membrane thickness, x the Lagrangian coordinate, K a characteristic elastic constant, λ_t a characteristic length also used as a striation thickness, Γ_1 the interaction parameter between nanoparticles and solvent, $\lambda^{\mathbf{m}}$ and $\lambda_{1111}^{\mathbf{A}}$ are two non-negative parameters [2,1], and $G_0 = n_0 k_B T$ is the modulus of elasticity with n_0 being the elastic density of the dry composite.

Four dimensionless parameters Π, $De_{\mathbf{m}}$, Θ and $De_{\mathbf{A}}$ describe the system: Π relates the mixing properties of the components and the polymer elasticity, Θ relates the complex interface with the mixing properties, $De_{\mathbf{m}}$ is a Deborah number related to the polymer relaxation defined by the ratio of the elastic and diffusion times, and $De_{\mathbf{A}}$ a Deborah number for the time of interface relaxation defined by the ratio of the diffusion and interface relaxation times. $De_{\mathbf{A}}$ and $De_{\mathbf{m}}$ indicate how fast the polymer chains and complex interface react to changes. Overall, these four numbers determine how important are the polymer viscoelastic properties and the complex interface in the diffusion process, and describe whether the complex system deviates from Fickian diffusion [2,1,3].

Photonic: Holographic sensors are commonly polymer–nanoparticle composite films containing multilayered structures consisting of alternating refractive index values. There are, however, other non-nanoparticle based holographic sensors based on photosensitive polymer films. The photonic properties on either systems can be modeled using the Bloch theorem for the exact solution of Maxwell's equations in the periodic form [4], assuming the layers to be well-defined periodic structures with different refractive index values. A matrix formalism has been proposed by Yeh [19], in which the wavelength and the intensity of the diffracted light can be calculated by

$$\begin{pmatrix} I \\ R \end{pmatrix} = \begin{pmatrix} W & X \\ Y & Z \end{pmatrix}^q \begin{pmatrix} \tau \\ 0 \end{pmatrix}, \tag{9}$$

where q is the number of layers, I, R and τ are the amplitudes of the incident, reflected and transmitted waves respectively, and W, X, Y and Z take different forms for *TE* and *TM* waves as