The effect of photodegradation on effective properties of polymeric thin films:

A micromechanical homogenization approach

Chao Zhang^{1*}, Natalie Waksanski², Vincent Wheeler¹, Ernian Pan², Ross Larsen¹

1. Computational Science Center, National Renewable Energy Laboratory, Golden, CO 80401

2. Department of Civil Engineering, The University of Akron, Akron, OH 44325

Abstract

An analytical model is developed to study the impact of photodegradation on the elastic properties of polymeric thin films. The multi-phase heterogeneous aged polymer material is considered as a two-phase functionally graded material with varying volume ratios as functions of both time and depth. The concentration gradations are obtained using a three-species chemical kinetic model with the kinetics being driven by light that is absorbed as it passes through the film. Concentration gradations are connected to the elastic stiffness through volume averaging and a micromechanics approach is employed to find effective properties of functionally graded composites. Concise matrix expressions of the effective properties are presented. The derived formulas are applied to study the effective responses of an aged simply-supported polymer film under surface loads. The obtained results are then compared with and validated by those from a multi-layer analytical model. The present formulas are also applied to predict the evolution of effective properties of a polymer thin film under photodegradation, and the variation of effective responses under surface loads. The present solution could be useful in studying the relation between polymer molecular structure and mechanical properties, and in the evaluation of long-term mechanical responses of polymeric structures.

Keywords: Effective properties, Photodegradation, Polymer film, Functionally graded material, Homogenization

The effect of photodegradation on effective properties of polymeric thin films:

A micromechanical homogenization approach

Abstract

An analytical model is developed to study the impact of photodegradation on the elastic properties of polymeric thin films. The multi-phase heterogeneous aged polymer material is considered as a two-phase functionally graded material with varying volume ratios as functions of both time and depth. The concentration gradations are obtained using a three-species chemical kinetic model with the kinetics being driven by light that is absorbed as it passes through the film. Concentration gradations are connected to the elastic stiffness through volume averaging and a micromechanics approach is employed to find effective properties of functionally graded composites. Concise matrix expressions of the effective properties are presented. The derived formulas are applied to study the effective responses of an aged simply-supported polymer film under surface loads. The obtained results are then compared with and validated by those from a multi-layer analytical model. The present formulas are also applied to predict the evolution of effective properties of a polymer thin film under photodegradation, and the variation of effective responses under surface loads. The present solution could be useful in studying the relation between polymer molecular structure and mechanical properties, and in the evaluation of long-term mechanical responses of polymeric structures.

Keywords: Effective properties, Photodegradation, Polymer film, Functionally graded material, Homogenization

1. Introduction

Due to their unique electronic, thermal, and mechanical properties, polymeric thin films are used increasingly in technological applications such as flexible electronics [1-3], optical reflectors [4-6], and transistors [7-9]. The chemical structure of polymers has a strong influence

on physical and mechanical properties of the film structure [10]. Mechanical properties can limit the application for which a polymer can be used, and the mechanical properties of polymers could change over time due to various environment conditions, such as radiation, temperature, and humidity [10]. Such change can, as a consequence, lead to mechanical failures as the material ages. Ultraviolet (UV) irradiation is one of the most destructive factors for polymers and it can cause main chain scission, oxidation, crosslinking, and side-group abstraction in a polymer. The intrinsic evolution of chemical structures will then result in evolution of the mechanical performance of the macro-scale polymer structure that may lead to failure earlier than would be expected from the mechanical properties of un-aged films. Hence, the study of UV aging on the mechanical properties of polymer film is of great important for the design of polymer thin film structures, and for forecasting the limit of their use.

The quantitative evaluation of the effects of UV aging on the mechanical properties of polymers has been extensively discussed [10-15]. Nowicki et al. [10] investigated the influence of ultraviolet irradiation on the elastic indentation modulus of three commercial polymers—polyvinyl chloride, polyethylene oxide, and polyacrylic acid—using depth-sensing nanoindentation technology. An increase of elastic modulus and hardness was observed in all samples, and this was attributed to the domination of crosslinking reaction. Tavares et al. [11] conducted UV irradiance-thermal-humidity acceleration tests on low-density polyethylene for up to 1600 hours, measured the mechanical properties using nanoindentation and observed a continuous variation of elastic modulus with depth. The elastic modulus tended to increase with aging time and it was correlated with the carbonyl index history from infrared spectroscopy. Barany et al. [13] and Aglan et al. [14] also observed an increase of elastic modulus against UV exposure time as well as a decreasing of tensile failure strain and tensile strength for syndiotactic polypropylenes and polyurethane, respectively. Fernandes et al. [15] examined photodegradation of several polypropylene and polystyrene blends, and found the modulus of elasticity, tensile

strength, strain, and impact strength decreased upon UV exposure for all of pure materials and blends.

The presented previous work was limited to the experimental quantification level. To the best of our knowledge there is no literature on analytically predicting the effect of aging on mechanical properties of polymers. Since photodegradation of solid polymers is a continuous process, it is of interest to develop a general methodology that can use models of photodegradation kinetics to predict the evolution of mechanical properties during the aging process. In this work, we introduce a general methodology to predict the time-dependent effective mechanical properties of polymer thin film. Assuming the case of UV irradiation on the top of the polymer film, the optical properties may change as a consequence of UV aging. This is shown in Figure 1 for a polyethylene terephthalate (PET) film that was aged over 300 hours under approximately ten times the solar UVA/UVB I light intensity. The PET film yellows as it ages due to the absorption tail in the blue part (around wavelength 400 nm) of the spectrum that grows with time. Because of the strong absorption in the UV, leading to an optical density of greater than 1.5, more of the UV light is absorbed at the top of the film than at the bottom, so we expect the polymer to be more damaged at the top than at the bottom of the film. Thus, based on Figure 1, we can consider the UV aged polymer as a composite material comprised of un-damaged chromophores and degraded polymer, with gradually changing volume ratios of two types as a function of depth and time. Henceforth, we will refer to the un-damaged polymer as “chromophores” and to the degraded polymer as “oxidized,” without loss of generality as to the actual degradation mechanism that might apply for any given material. The chromophores and oxidized chromophores have different mechanical properties, so it is expected that the aged polymer film has continuously varying properties through the thickness direction, as identified in [11]. The UV aged film at each specific time could be considered as a kind of functionally graded material (FGM) so being able to predict mechanical properties of a material that becomes

an FGM over time is of interest. A general solution is developed in this study to obtain the overall effective properties of functionally graded plates with consideration of time dependency.

Numerous researchers have attempted variety of analytical, numerical methods for studying the mechanical responses of FGM structures. Jha et al. [17] and Birman and Byrd [18] have published very detailed literature reviews of FGMs addressing the recent progress in modeling and analysis of FGM structures. In order to analyze the heterogeneous structure in an efficient manner, it is necessary to have a homogenization scheme, which enables understanding of relationship between the effective properties of the FGMs and the microstructure (or distribution of volume fractions of constituent phases). Many models have been developed to predict the effective properties of FGMs in two-dimensional domains for a specific volume fraction, including micromechanical models [19-21], finite element methods [22-25] and multi-scale approaches [26,27]. Recently, Wu et al. [28] developed a homogenization method for random heterogeneous materials using Richardson extrapolation technique. Wu et al. [29] proposed a semi-analytical, state-space method for surface instability study of elastic layers with varying properties in thickness direction. In these models [19-29], the material properties of each sub-layer need to be calculated and integrated into the model individually, which limits the computational efficiency and requires a convergence study to determine the minimum number of sub-layers that gives the required accuracy. Recently, Wang et al. [30] proposed an efficient micromechanics approach, through which explicit expressions of the effective properties of magnetoelectric multiferroic multilayer composites can be obtained.

In this work, we develop a general analytical model to obtain effective properties of FGMs. We extended the model by Wang et al. [30] to a general integration formulation, which is fully consistent with the continuous varying properties of a functionally graded material. The present model provides explicit expressions of the effective properties of a functionally graded material with the known of base stiffness constants and grading function. More importantly, the

model we will introduce can predict the evolution of mechanical properties due to the change of molecular structures or chemical components, especially suitable for studying the degradation of polymers under UV aging. Finding direct relationships between molecular characteristics and macroscopic mechanical properties of polymeric materials has attracted a vast number of academic and industrial research studies [31-35]. In the present work, considering the UV aged film as a multi-phase composite with varying volume fractions through the thickness direction, a simple optically-driven chemical kinetic model is presented to calculate the thickness-dependent and time-dependent volume fractions, through correlating experimental measured absorption data. A simple volume-average method is applied to represent the macro-scale effective properties of heterogeneous intrinsic molecular structure for each specific two-dimensional plane. Using the homogenization process of this work, we are able to predict the chemical degradation induced evolution of effective mechanical properties from degradation that is far from homogeneous.

The remainder of this paper is organized as follows. Section 2 presents governing equations of our chosen chemical kinetic models and numerical predictions of chromophore concentration for a simplified kinetic model of photodegradation. The derivation of effective properties of functionally graded material and solutions for simply supported plate is presented in Section 3. The results, are presented in Section 4, consist of verifying the derived model of Section 3 by comparing to analytical solutions for multilayered models, predicting the time-dependent effective properties of UV aged polymer thin film and illustrating mechanical responses for a simply supported film. Section 5 concludes the contribution of this work and introduces potential applications of the developed model.

2. Photodegradation kinetics of polymer films

One main object of this work is to predict effective properties of UV aged polymer film. As stated in the previous section, the UV aged polymer film can be considered as a functionally

graded composite with varying concentrations against both time and thickness. We propose developing a micromechanical model to predict the effective properties of the UV aged polymer film. To achieve this goal, the first step is to obtain the thickness-dependent concentrations of each component during the aging. In this section, a one-dimensional simplified optically-driven chemical kinetic model is developed to calculate concentration profiles of each component through correlating experimental measured absorption histories. The obtained concentration profiles are then fitting using two-variable (thickness and time) exponential equations, which are ready to implement into the micromechanical model.

During polymer photodegradation, there are two types of processes: primary photochemical reactions due to absorbed radiation and secondary reactions in which radicals formed initiate a number of reactions which are independent of the light [36]. In this work, we consider the problem of an irradiated, reacting solid film made up of three chemical species. The problem is assumed to be transient and one-dimensional. Each species, i , has a concentration $n_i = n_i(z, t)$ that depends on depth z and time t . For $t > 0$ the surface of the film is subject to a uniform radiative intensity. The species experience optically-driven excitation at a rate $\alpha_i I$ where α_i is the absorption cross-section of the i th species and $I = I(z, t)$ is the intensity of the light. For simplicity we ignore the wavelength dependence of the absorption. The concentration of the i -th excited species is denoted by a new concentration n_i^* . From the excited state, the species will either drop down to the ground state at a rate of γ_i or react and become a new species n_{i+1} with a rate $\kappa_{i,i+1}$. The reaction scheme governing this behavior and the corresponding mathematical model can be found in Table 1. An over dot on n_i or n_i^* denotes a time derivative of the concentration. The intensity $I = I(z, t)$ is assumed to obey the Beer-Lambert law [37]. This approximation is subject to numerous assumptions. Most notably, we have assumed thin film interference effects are negligible and absorption is the dominant process of attenuation [38].

The model in Table 1 is represented by a set of seven coupled, non-linear partial differential equations. It may be represented using fewer unknowns by first assuming the populations of excited states are in their stationary states such that $\dot{n}_i^* \approx 0$. This approximation is justifiable under the safe assumption that excitation ($\alpha_i I$ and de-excitation γ_i) happens far more rapidly than reactions to form new species. The number of unknown concentrations is then reduced by half after expressing the excited state concentration of each species in terms of its ground state concentration. Further, we integrate the optical model to a depth z in the film giving the solution, $\overline{I(z, t)} = I \exp(-\sum_k \alpha_k \int_0^z n_k(\xi, t) d\xi)$. The opto-kinetic can now be rewritten as a system of just three non-linear integro-partial-differential equations. The resulting simplified reaction scheme and mathematical model are given in Table 2.

The simplified model represented in Table 2 has been numerically solved by discretizing the film into layers (elements). Concentrations were calculated first within the top discretized layer for all times using an implicit second-order accurate time integration scheme [39]. The solution was then determined at each element for all times at increasing depth utilizing the fact that the spatial dependence of the solution can be determined at a depth z_n using only the solution at $z < z_n$. The integral appearing in the intensity factor is calculated by a simple rectangle rule.

The simplified opto-kinetic model was solved with varying absorption cross-sections and effective reaction rates. These parameters were varied until, at a given wavelength, a good qualitative agreement was found between the predicted UV/vis absorption of the film over time agreed with a time-trace of the measured data for a PET film shown in Figure 1. It was assumed at time $t = 0$ that the only species in the film is n_0 . The total concentration of species was normalized to 1. It was found that the absorption cross-section of the n_1 component had to be

very high relative to the others in order to fit the dramatic temporal changes in experimental data. The resulting parameters, which are used in the remainder of this study, can be found in Table 3.

Figure 2 (a)-(c) shows the concentration histories of the three components. Light intensity decays roughly exponentially after it enters the surface of the film, which causes dynamic spatial variations in species; species n_0 reacts into species n_1 more quickly near the surface. Because of the high absorption cross-section of species n_1 , it rapidly reacts and never attains a high concentration in the film creating a system that is effectively made up of two components.

The smooth shapes of the concentration curves prompted us to fit a simple functional form to obtain expressions of the predicted concentration histories. Since the total concentration $\sum_{i=1}^3 n_i(z, t) = 1$, we only need to obtain expressions for two of the three components. Based on the shapes of the curves, we presume $n_0(z, t)$ has the following form:

$$n_0(z, t) = d(t)e^{g(z, t)} \quad (2-1)$$

where we assume $g(1, t) = 0$ and $d(t)$ is determined by fitting $n_0(1, t)$. The function $g(z, t)$ is then obtained in a sequential fashion. First, for each time, we fit $\ln(n_0(z, t)/d(t))$ to a form $\alpha + \beta z + \gamma z^2$. Second, we fit α , β and γ versus time to linear functions of time. Similarly, we obtain an expression for $n_1(z, t)$. The resultant fitted value are shown below

$$n_0(z, t) = e^{-0.0014t - 0.0012tz - 0.0013tz^2} \quad (2-2)$$

$$n_1(z, t) = \begin{cases} e^{-4.0078 - 0.0014t - 0.0012tz - 0.0013tz^2} = 0.01818n_0(z, t) & t > 0 \\ 0 & t = 0 \end{cases} \quad (2-3)$$

$$n_2(z, t) = 1 - n_0(z, t) - n_1(z, t) \quad (2-4)$$

where units of length were chosen so that z varies from 0 to 1. It is interesting that $n_1(z, t)$ is proportional to $n_0(z, t)$, which means their reactions follow the same kinetics. This is a consequence of the rapid reaction converting component 1 to component 2. Note that the fitted form in Eq. (2-3) implies that there is an instantaneous development of n_1 when light is turned on. This is a consequence of the rapid kinetics that makes this approximately true, and simple

fitting form we have chosen, which does not accommodate the rapid turn on. To simplify the problem, in this work, we shall assume that the mechanical properties of components n_1 and n_2 are the same, in other words, in mechanical aspect we consider the aged material as a two-phase composite material. Because of the very low concentrations of component n_1 this assumption should introduce negligible error in the analysis.

3. Basic equations of the mechanical model

In previous section, we obtained the concentration grading equations for the two components (n_0 and n_1) of aged polymer film. In this part, we present the development of a micromechanical homogenization method for a functionally graded material. The present model provides explicit expressions of effective properties and is able to implement directly the concentration grading equations (Eqs (2-3) and (2-4)). The propagate matrix solution is presented to verify the accuracy of the homogenization method and predict the evolution of mechanical response of aged film under simply-supported boundary condition.

3.1 Effective properties of functionally graded materials

In this part, a general homogenization methodology is introduced to obtain the effective properties of a functionally graded plate. Let us consider an anisotropic, linear elastic and rectangular FGM plate with varying material properties through the thickness directions (z -direction). A Cartesian coordinate system (x, y, z) is attached to the plate in such a way that the its origin is at one of the four corners on the top surface and the plate is in the positive z -region. The linear constitutive equations of a homogeneous elastic material can be written as

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \quad (3-1)$$

where σ_{ij} and ε_{kl} are the stress and strain components, C_{ijkl} the elastic stiffness matrix. It is noted that the Voigt expression C_{ij} ($i, j=1-6$) of the elastic stiffness will be also used in this paper.

The stress and strain components can be partitioned into in-plane and out-plane vectors, with the subscript $\parallel$ and $\perp$ being associated to them respectively.

$$\begin{aligned}\boldsymbol{\sigma}_{\perp} &= \{\sigma_{33}, \sigma_{23}, \sigma_{13}\}^T & \boldsymbol{\sigma}_{\parallel} &= \{\sigma_{11}, \sigma_{22}, \sigma_{12}\}^T \\ \boldsymbol{\varepsilon}_{\perp} &= \{\varepsilon_{33}, 2\varepsilon_{23}, 2\varepsilon_{13}\}^T & \boldsymbol{\varepsilon}_{\parallel} &= \{\varepsilon_{11}, \varepsilon_{22}, 2\varepsilon_{12}\}^T\end{aligned}\quad (3-2)$$

In Eq. (3-2), T denotes matrix transpose, and 1, 2 and 3 indicates the in-plane x , y and out-of-plane z directions, respectively. Then, the constitutive equation Eq. (3-1) can be equivalently written in the following concise matrix form:

$$\boldsymbol{\sigma}_{\parallel} = \mathbf{C}_{\parallel}\boldsymbol{\varepsilon}_{\parallel} + \mathbf{C}_{\times}^T\boldsymbol{\varepsilon}_{\perp} \quad (3-3)$$

$$\boldsymbol{\sigma}_{\perp} = \mathbf{C}_{\times}\boldsymbol{\varepsilon}_{\parallel} + \mathbf{C}_{\perp}\boldsymbol{\varepsilon}_{\perp} \quad (3-4)$$

where $\mathbf{C}_{\perp}$, $\mathbf{C}_{\parallel}$, $\mathbf{C}_{\times}$ and $\mathbf{C}_{\times}^T$ are the generalized Voigt matrices given by

$$\mathbf{C}_{\parallel} = \begin{bmatrix} C_{11} & C_{12} & C_{16} \\ C_{12} & C_{22} & C_{26} \\ C_{16} & C_{26} & C_{66} \end{bmatrix} \quad (3-5)$$

$$\mathbf{C}_{\perp} = \begin{bmatrix} C_{33} & C_{34} & C_{35} \\ C_{34} & C_{44} & C_{45} \\ C_{35} & C_{45} & C_{55} \end{bmatrix} \quad (3-6)$$

$$\mathbf{C}_{\times} = \begin{bmatrix} C_{13} & C_{23} & C_{36} \\ C_{14} & C_{24} & C_{46} \\ C_{15} & C_{25} & C_{56} \end{bmatrix} \quad (3-7)$$

It is observed that $\mathbf{C}_{\perp}, \mathbf{C}_{\parallel}$ are symmetric but not positive definite. Now we consider an FGM plate consisting of N layers with each being homogeneous material as shown in Fig.3. In the following, we will attach a superscript (i) to the quantities associated with layer i ($i=1,2,\dots,N$). To help with the derivation, some assumptions are made. First, we assume the layers are perfectly bonded, which means the displacements and tractions are continuous across each layer interface, and second, that the total thickness of the plate (H) is much lower than the in-plane dimensions (L_x, L_y). Then the in-plane strain in each layer can be assumed to be the same and equal to the effective strain.

$$\bar{\boldsymbol{\varepsilon}}_{\parallel} = \boldsymbol{\varepsilon}_{\parallel}^{(1)} = \boldsymbol{\varepsilon}_{\parallel}^{(2)} = \dots = \boldsymbol{\varepsilon}_{\parallel}^{(N)} \quad (3-8)$$

where the overbar denotes effective properties. The effective out-of-plane strain is taken to be the volume (thickness) average of the strain in layers

$$\bar{\boldsymbol{\varepsilon}}_{\perp} = v^{(1)} \boldsymbol{\varepsilon}_{\perp}^{(1)} + v^{(2)} \boldsymbol{\varepsilon}_{\perp}^{(2)} + \dots + v^{(N)} \boldsymbol{\varepsilon}_{\perp}^{(N)} \quad (3-9)$$

where $v^{(i)} = h^{(i)}/H$ is the volume fraction of the i -th layer and $H = h^{(1)} + h^{(2)} + \dots + h^{(N)}$ is the total height. The in-plane stress also assumes a volume average of the stress in layers

$$\bar{\boldsymbol{\sigma}}_{\parallel} = v^{(1)} \boldsymbol{\sigma}_{\parallel}^{(1)} + v^{(2)} \boldsymbol{\sigma}_{\parallel}^{(2)} + \dots + v^{(N)} \boldsymbol{\sigma}_{\parallel}^{(N)} \quad (3-10)$$

and the out-of-plane stress in each layer is the same and equal to the effective out-of-plane stress

$$\bar{\boldsymbol{\sigma}}_{\perp} = \boldsymbol{\sigma}_{\perp}^{(1)} = \boldsymbol{\sigma}_{\perp}^{(2)} = \dots = \boldsymbol{\sigma}_{\perp}^{(N)} \quad (3-11)$$

Substituting Eqs. (3-8) and (3-11) into Eq. (3-4), we solve $\boldsymbol{\varepsilon}_{\perp}^{(i)}$ as

$$\boldsymbol{\varepsilon}_{\perp}^{(i)} = \left(\mathbf{C}_{\perp}^{(i)} \right)^{-1} \bar{\boldsymbol{\sigma}}_{\perp} - \left(\mathbf{C}_{\perp}^{(i)} \right)^{-1} \mathbf{C}_{\times}^{(i)} \bar{\boldsymbol{\varepsilon}}_{\parallel} \quad (3-12)$$

Taking Eq. (3-9) into consideration and rearranging the involved terms, we arrive at

$$\bar{\boldsymbol{\sigma}}_{\perp} = \bar{\mathbf{C}}_{\perp} \bar{\boldsymbol{\varepsilon}}_{\perp} + \bar{\mathbf{C}}_{\times} \bar{\boldsymbol{\varepsilon}}_{\parallel} \quad (3-13)$$

where

$$\bar{\mathbf{C}}_{\perp} = \left[\sum_{i=1}^N v^{(i)} \left(\mathbf{C}_{\perp}^{(i)} \right)^{-1} \right]^{-1} \quad (3-14)$$

$$\bar{\mathbf{C}}_{\times} = \bar{\mathbf{C}}_{\perp} \left[\sum_{i=1}^N v^{(i)} \left(\mathbf{C}_{\perp}^{(i)} \right)^{-1} \mathbf{C}_{\times}^{(i)} \right] \quad (3-15)$$

Similarly, substituting Eqs. (3-8) and (3-12) into Eq. (3-3) yields

$$\boldsymbol{\sigma}_{\parallel}^{(i)} = \left[\mathbf{C}_{\times}^{(i)T} \left(\mathbf{C}_{\perp}^{(i)} \right)^{-1} \right] \bar{\boldsymbol{\sigma}}_{\perp} + \left[\mathbf{C}_{\parallel}^{(i)} - \mathbf{C}_{\times}^{(i)T} \left(\mathbf{C}_{\perp}^{(i)} \right)^{-1} \mathbf{C}_{\times}^{(i)} \right] \bar{\boldsymbol{\varepsilon}}_{\parallel} \quad (3-16)$$

Taking Eq. (3-10) into consideration, Eq. (3-16) becomes

$$\bar{\boldsymbol{\sigma}}_{\parallel} = \sum_{i=1}^N v^{(i)} \left[\mathbf{C}_{\times}^{(i)T} \left(\mathbf{C}_{\perp}^{(i)} \right)^{-1} \right] \bar{\boldsymbol{\sigma}}_{\perp} + \sum_{i=1}^N v^{(i)} \left[\mathbf{C}_{\parallel}^{(i)} - \mathbf{C}_{\times}^{(i)T} \left(\mathbf{C}_{\perp}^{(i)} \right)^{-1} \mathbf{C}_{\times}^{(i)} \right] \bar{\boldsymbol{\varepsilon}}_{\parallel} \quad (3-17)$$

Substituting Eq. (3-13) into Eq. (3-17) and rearranging the involved terms, we then obtain

$$\bar{\sigma}_{\parallel} = \bar{\mathbf{C}}_{\times}^T \bar{\epsilon}_{\perp} + \bar{\mathbf{C}}_{\parallel} \bar{\epsilon}_{\parallel} \quad (3-18)$$

where

$$\bar{\mathbf{C}}_{\times}^T = \left[\sum_{i=1}^N v^{(i)} \mathbf{C}_{\times}^{(i)T} \left(\mathbf{C}_{\perp}^{(i)} \right)^{-1} \right] \bar{\mathbf{C}}_{\perp} \quad (3-19)$$

$$\bar{\mathbf{C}}_{\parallel} = \sum_{i=1}^N v^{(i)} \mathbf{C}_{\parallel} + \sum_{i=1}^N v^{(i)} \mathbf{C}_{\times}^{(i)T} \left(\mathbf{C}_{\perp}^{(i)} \right)^{-1} \left(\bar{\mathbf{C}}_{\times} - \mathbf{C}_{\times}^{(i)} \right) \quad (3-20)$$

Thus, we finally obtain the effective properties in the form as

$$\begin{Bmatrix} \bar{\sigma}_{\parallel} \\ \bar{\sigma}_{\perp} \end{Bmatrix} = \begin{bmatrix} \bar{\mathbf{C}}_{\parallel} & \bar{\mathbf{C}}_{\times}^T \\ \bar{\mathbf{C}}_{\times} & \bar{\mathbf{C}}_{\perp} \end{bmatrix} \begin{Bmatrix} \bar{\epsilon}_{\parallel} \\ \bar{\epsilon}_{\perp} \end{Bmatrix} \quad (3-21)$$

for perfectly bonded layers in a thin film. For an FGM plate with varying material properties as functions of the thickness and time, the elastic stiffness matrix in Equation (3-1) can be expressed most simply as

$$C_{ijkl}(z, t) = f(z, t) C_{ijkl}^0 \quad (3-22)$$

where $f(z, t)$ is the grading function describing the time-dependency and thickness-dependency of elastic stiffness matrix. The superscript 0 corresponds to the stiffness matrix of un-aged material in this study.

Eqs. (3-14, 3-15, 3-19 and 3-20) can be also applied to derive the effective properties of a functionally graded material by discretizing it into multiple layers. For such formulations one generally must perform a convergence study as the number of layers in the discretization increases to verify the accuracy of results. Instead, in this work, the expressions are further simplified and extended with an integration formulation that takes the limit of an infinite number of layers. The integration formulation provides guaranteed accuracy and saves computational efforts. We normalize the total thickness so that the FGM plate varies in the thickness direction from $z=0$ to $z=1$. Then for an infinite number of equal-thickness layers the average terms can be expressed in an integration formation as, for example,

$$\lim_{n \rightarrow \infty} \sum_{i=1}^N v^{(i)} \mathbf{C}_{\perp}^{(i)} = \int_0^1 f(z, t) \mathbf{C}_{\perp}^0 dz \quad (3-23)$$

so that Eqs. (3-14) and (3-15) can be expressed as

$$\bar{\mathbf{C}}_{\perp} = \left[\int_0^1 \frac{1}{f(z,t)} (\mathbf{C}_{\perp}^0)^{-1} dz \right]^{-1} = \frac{1}{\int_0^1 \frac{1}{f(z,t)} dz} \mathbf{C}_{\perp}^0 \quad (3-24)$$

$$\bar{\mathbf{C}}_{\times} = \bar{\mathbf{C}}_{\perp} \left[\int_0^1 \frac{1}{f(z,t)} (\mathbf{C}_{\perp}^0)^{-1} f(z,t) \mathbf{C}_{\times}^0 dz \right] = \frac{1}{\int_0^1 \frac{1}{f(z,t)} dz} \mathbf{C}_{\times}^0 \quad (3-25)$$

Similarly Eqs. (3-19) and (3-20) become

$$\bar{\mathbf{C}}_{\times}^T = \left[\int_0^1 f(z,t) \mathbf{C}_{\times}^{0T} \frac{1}{f(z,t)} (\mathbf{C}_{\perp}^0)^{-1} dz \right] \bar{\mathbf{C}}_{\perp} = \frac{1}{\int_0^1 \frac{1}{f(z,t)} dz} \mathbf{C}_{\times}^{0T} \quad (3-26)$$

$$\begin{aligned} \bar{\mathbf{C}}_{\parallel} &= \int_0^1 f(z,t) \mathbf{C}_{\parallel}^0 dz + \int_0^1 f(z,t) \mathbf{C}_{\times}^{0T} \frac{1}{f(z,t)} (\mathbf{C}_{\perp}^0)^{-1} \bar{\mathbf{C}}_{\times} dz \\ &\quad - \int_0^1 f(z,t) \mathbf{C}_{\times}^{0T} \frac{1}{f(z,t)} (\mathbf{C}_{\perp}^0)^{-1} f(z,t) \mathbf{C}_{\times}^0 dz \\ &= \int_0^1 f(z,t) dz \mathbf{C}_{\parallel}^0 + \left[\frac{1}{\int_0^1 \frac{1}{f(z,t)} dz} - \int_0^1 f(z,t) dz \right] \mathbf{C}_{\times}^{0T} (\mathbf{C}_{\perp}^0)^{-1} \mathbf{C}_{\times}^0 \end{aligned} \quad (3-27)$$

To further simplify the expressions, we can define the average values

$$f_1 = \frac{1}{\int_0^1 \frac{1}{f(z,t)} dz}, f_2 = \int_0^1 f(z,t) dz, \quad (3-28)$$

with which we obtain

$$\begin{bmatrix} \bar{\mathbf{C}}_{\parallel} & \bar{\mathbf{C}}_{\times}^T \\ \bar{\mathbf{C}}_{\times} & \bar{\mathbf{C}}_{\perp} \end{bmatrix} = \begin{bmatrix} f_1 \mathbf{C}_{\parallel}^0 + (f_1 - f_2) \mathbf{C}_{\times}^{0T} (\mathbf{C}_{\perp}^0)^{-1} \mathbf{C}_{\times}^0 & f_1 \mathbf{C}_{\times}^{0T} \\ f_1 \mathbf{C}_{\times}^0 & f_1 \mathbf{C}_{\perp}^0 \end{bmatrix} \quad (3-29)$$

The above equation provides a straightforward method for obtaining the effective properties of a functionally graded plate with known reference stiffness matrix and grading function $f(z,t)$. For the photodegraded polymer film structure, based on the chemical kinetic model and volume-average principle, the elastic stiffness matrix can be expressed as

$$\mathbf{C}_{ijkl}(z,t) = n_0(z,t) \mathbf{C}_{ijkl}^0 + (1 - n_0(z,t)) \mathbf{C}_{ijkl}^1 \quad (3-30)$$

where $\mathbf{C}_{ijkl}^0$ and $\mathbf{C}_{ijkl}^1$ are the stiffness matrix of un-aged component (n_0) and aged components (here taken to comprise both n_1 and n_2), respectively. Since for most applications, there

probably will be no fully aged material available, C_{ijkl}^1 is actually an *in-situ* material property that is not measureable. It must be fitted in some fashion to experimental results. In this work, we assume $C_{ijkl}^1 = gC_{ijkl}^0$, where $g \geq 0$. It should be noted that $g = 1$ corresponds to the homogeneous case, which means the material properties do not change over time, $0 \leq g < 1$ indicates the material stiffness gradually decreases under the aging. when $g > 1$, we have the aged material stiffens. The coefficient g provides a simple way to estimate the mechanical property degradation during material aging, it can be inversely calculated from a kinetic model that gives a known chromophore concentration $n_0(z, t)$, effective properties $C_{ijkl}(z, t)$ and initial un-aged properties C_{ijkl}^0 . We note that Eq. (3-30) is simple volume-average estimation of elastic stiffness matrix for a two-phase composite. The effective properties of an inhomogeneous material are actually functions of geometry (shape, orientation and boundary) parameters [40]. Kachanov and Sevostianov [40, 41] presented a micromechanical approach to evaluate the effective properties of heterogeneous solids with quantitative characterization of microstructure and individual analysis of inhomogeneous contribution. The implementing of Kachanov and Sevostianov's approach into the current micromechanical model could more accurately represent the evolution of effective properties for aged polymer film. This is subjected to future research.

3.2 Propagator matrix solution of a simply supported plate

In order to verify the derived analytical model of effective properties, numerical examples for the simply supported FGM plate under surface loads are studied using the derived effective properties (Homogenized Model) of the previous section. There are several analytical models [42, 43] available in the literature solving the elastic response of multi-layer composites or functionally graded materials. In this work, the results obtained using the homogenized model will be compared with previously published analytical solution [43]. Both models are solved using the propagator matrix method [43, 44]. Here, the FGM is considered to be isotropic in

plane with varying properties through the thickness. As from Eq. (3-29), the effective stiffness components $\bar{\mathbf{C}}_x^T$, $\bar{\mathbf{C}}_x$, and $\bar{\mathbf{C}}_\perp$ have the same scaling factors, f_I , so the homogenized effective properties should be transversely isotropic. In the derivation using the propagator matrix method, we assume that each sub-layer has the linear constitutive relations given by Eq. (3.1) and strain-displacement relations given by

$$\varepsilon_{ij} = 0.5(u_{i,j} + u_{j,i}) \quad (4-1)$$

where u_i represents the elastic displacement.

In the absence of body forces, the equations of equilibrium are governed by

$$\sigma_{ij,j} = 0 \quad (4-2)$$

For a homogenous simply supported plate, the general solution of the displacement vector $\mathbf{u}$ is expected to take the following form [43]:

$$\mathbf{u} = \begin{Bmatrix} u_1 \\ u_2 \\ u_3 \end{Bmatrix} = e^{sz} \begin{Bmatrix} a_1 \cos px \sin qy \\ a_2 \sin px \cos qy \\ a_3 \sin px \sin qy \end{Bmatrix} \quad (4-3)$$

where

$$p = \frac{m\pi}{L_x}, \quad q = \frac{n\pi}{L_y} \quad (4-4)$$

m and n are positive integers, s is the eigenvalue, and $(a_1, a_2, a_3)^T$ is the corresponding eigenvector to be determined. It should be noted that Eq. (4-3) is actually part of a double Fourier series expansion with summations for m and n over suitable ranges.

Substituting Eq. (4-3) into the strain-displacement relations in Eq. (4-1) and constitutive equations in Eq. (3-1), the z -direction traction vector $\mathbf{t}$ is found to be

$$\mathbf{t} = \begin{Bmatrix} \sigma_{13} \\ \sigma_{23} \\ \sigma_{33} \end{Bmatrix} = e^{sz} \begin{Bmatrix} b_1 \cos px \sin qy \\ b_2 \sin px \cos qy \\ b_3 \sin px \sin qy \end{Bmatrix} \quad (4-5)$$

where b_1, b_2, b_3 are determined by the eigenvector $(a_1, a_2, a_3)^T$ as will be presented below.

The two vectors,

$$\mathbf{a} = \{a_1, a_2, a_3\}^T, \mathbf{b} = \{b_1, b_2, b_3\}^T \quad (4-6)$$

are introduced to represent the coefficients in Eqs. (4-3) and (4-5), respectively. It can be shown that the coefficient vector $\mathbf{b}$ can be expressed in terms of the coefficient vector $\mathbf{a}$ by substituting the displacement components in Eq. (4-3) into Eq. (4-1) and Eq. (3-1). The relation is obtained as

$$\mathbf{b} = (s\mathbf{T} - \mathbf{R}^T)\mathbf{a} \quad (4-7)$$

where

$$\mathbf{R} = \begin{bmatrix} 0 & 0 & C_{13}p \\ 0 & 0 & C_{13}q \\ -C_{44}p & -C_{44}q & 0 \end{bmatrix} \quad (4-8)$$

$$\mathbf{T} = \begin{bmatrix} C_{44} & 0 & 0 \\ 0 & C_{44} & 0 \\ 0 & 0 & C_{33} \end{bmatrix} \quad (4-9)$$

Similarly, in-plane stress components in Eq. (3-1) are obtained as

$$\begin{Bmatrix} \sigma_{11} \\ \sigma_{12} \\ \sigma_{22} \end{Bmatrix} = e^{sz} \begin{Bmatrix} c_1 \sin px \sin qy \\ c_2 \cos px \cos qy \\ c_3 \sin px \sin qy \end{Bmatrix} \quad (4-10)$$

where

$$\begin{Bmatrix} c_1 \\ c_2 \\ c_3 \end{Bmatrix} = \begin{bmatrix} -C_{11}p & -C_{12}q & C_{13}s \\ C_{66}q & C_{66}p & 0 \\ -C_{12}p & -C_{11}q & C_{13}s \end{bmatrix} \begin{Bmatrix} a_1 \\ a_2 \\ a_3 \end{Bmatrix} \quad (4-11)$$

Substituting the displacement vector given by Eq. (4-3) into the equilibrium equations given by Eq. (4-2) yields the eigenproblem for the eigenvalue s and eigenvector $\mathbf{a}$ as

$$(\mathbf{Q} + s(\mathbf{R} - \mathbf{R}^T) + s^2\mathbf{T})\mathbf{a} = \mathbf{0} \quad (4-12)$$

where

$$\mathbf{Q} = \begin{bmatrix} -(C_{11}p^2 + C_{66}q^2) & -pq(C_{12} + C_{66}) & 0 \\ -pq(C_{12} + C_{66}) & -(C_{66}p^2 + C_{11}q^2) & 0 \\ 0 & 0 & -C_{44}(p^2 + q^2) \end{bmatrix} \quad (4-13)$$

The formulation in Eq. (4-13) is similar to the Stroh formalism [45]. Thus, it can be appropriately called the pseudo-Stroh formalism [43].

The eigenproblem in Eq. (4-12) can be recast into the following 6×6 linear eigenproblem by making use of the relation between vectors $\mathbf{a}$ and $\mathbf{b}$ as indicated by Eq. (4-7):

$$\mathbf{N} \begin{Bmatrix} \mathbf{a} \\ \mathbf{b} \end{Bmatrix} = s \begin{Bmatrix} \mathbf{a} \\ \mathbf{b} \end{Bmatrix} \quad (4-14)$$

where

$$\mathbf{N} = \begin{bmatrix} \mathbf{T}^{-1}\mathbf{R}^T & \mathbf{T}^{-1} \\ -\mathbf{Q} - \mathbf{R}\mathbf{T}^{-1}\mathbf{R}^T & -\mathbf{R}\mathbf{T}^{-1} \end{bmatrix} \quad (4-15)$$

Solving the eigenproblem in Eq. (4-14) yields six eigenvalues s_j (for $j=1,2,\dots,6$). For each eigenvalue s_j , there is a corresponding eigenvector where the first three components make up the vector $\mathbf{a}_j$ and the next three components make up the vector $\mathbf{b}_j$. Thus, the general solution for the displacement vector in Eq. (4-3) and traction vector in Eq. (4-5) are obtained as

$$\begin{Bmatrix} \mathbf{u} \\ \mathbf{t} \end{Bmatrix} = \begin{bmatrix} \mathbf{A}_1 & \mathbf{A}_2 \\ \mathbf{B}_1 & \mathbf{B}_2 \end{bmatrix} \langle e^{s^*z} \rangle \begin{Bmatrix} \mathbf{K}_1 \\ \mathbf{K}_2 \end{Bmatrix} \quad (4-16)$$

where

$$\begin{aligned} \mathbf{A}_1 &= [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3], \mathbf{A}_2 = [\mathbf{a}_4, \mathbf{a}_5, \mathbf{a}_6] \\ \mathbf{B}_1 &= [\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3], \mathbf{B}_2 = [\mathbf{b}_4, \mathbf{b}_5, \mathbf{b}_6] \\ \langle e^{s^*z} \rangle &= \text{diag}[e^{s_1z}, e^{s_2z}, e^{s_3z}, e^{-s_1z}, e^{-s_2z}, e^{-s_3z}] \end{aligned} \quad (4-17)$$

$\mathbf{K}_1$ and $\mathbf{K}_2$ are two 3×1 constant column matrices determined from boundary conditions of the plate, and s^* includes all six eigenvalues of layer i obtained from $\mathbf{N}$. Note that if s is an eigenvalue of $\mathbf{N}$ so is $-s$.

Considering layer i of the discretized FGM plate shown in Fig.3, the lower and upper interfaces are at $z = z^{(i)}$ and $z = z^{(i+1)}$, respectively. It follows that $z^{(1)} = 0$ and $z^{(N+1)} = H$. Accordingly, the thickness of layer i also can be written as

$$h^{(i)} = z^{(i+1)} - z^{(i)} \quad (4-18)$$

From Eq. (4-16), the constant column matrices, $\mathbf{K}_1$ and $\mathbf{K}_2$, can be found for any point within layer i as follows:

$$\begin{Bmatrix} \mathbf{K}_1 \\ \mathbf{K}_2 \end{Bmatrix} = \langle e^{s^*(z-z^{(i)})} \rangle^{-1} \begin{bmatrix} \mathbf{A}_1 & \mathbf{A}_2 \\ \mathbf{B}_1 & \mathbf{B}_2 \end{bmatrix}^{-1} \begin{Bmatrix} \mathbf{u}(z) \\ \mathbf{t}(z) \end{Bmatrix} \quad (4-19)$$

Letting $z = z^{(i)}$ and $z = z^{(i+1)}$ in Eq. (4-19) we find that the column matrices can be expressed in terms of those on the lower and upper interface of layer i as

$$\begin{Bmatrix} \mathbf{K}_1 \\ \mathbf{K}_2 \end{Bmatrix} = \begin{bmatrix} \mathbf{A}_1 & \mathbf{A}_2 \\ \mathbf{B}_1 & \mathbf{B}_2 \end{bmatrix}^{-1} \begin{Bmatrix} \mathbf{u}(z^{(i)}) \\ \mathbf{t}(z^{(i)}) \end{Bmatrix} = \langle e^{s^*h^{(i)}} \rangle^{-1} \begin{bmatrix} \mathbf{A}_1 & \mathbf{A}_2 \\ \mathbf{B}_1 & \mathbf{B}_2 \end{bmatrix}^{-1} \begin{Bmatrix} \mathbf{u}(z^{(i+1)}) \\ \mathbf{t}(z^{(i+1)}) \end{Bmatrix} \quad (4-20)$$

Solving for the displacement vector $\mathbf{u}$ and traction vector $\mathbf{t}$ on the upper surface at $z = z^{(i+1)}$ in Eq. (4-20) yields

$$\begin{Bmatrix} \mathbf{u}(z^{(i+1)}) \\ \mathbf{t}(z^{(i+1)}) \end{Bmatrix} = \begin{bmatrix} \mathbf{A}_1 & \mathbf{A}_2 \\ \mathbf{B}_1 & \mathbf{B}_2 \end{bmatrix} \langle e^{s^*h^{(i)}} \rangle \begin{bmatrix} \mathbf{A}_1 & \mathbf{A}_2 \\ \mathbf{B}_1 & \mathbf{B}_2 \end{bmatrix}^{-1} \begin{Bmatrix} \mathbf{u}(z^{(i)}) \\ \mathbf{t}(z^{(i)}) \end{Bmatrix} \quad (4-21)$$

Using the assumption that displacement $\mathbf{u}$ and traction $\mathbf{t}$ are continuous along the interface, Eq. (4-21) can be applied repeatedly allowing the physical quantities to propagate from the bottom surface $z = 0$ to the top surface $z = H$ of the multilayered plate. Therefore,

$$\begin{Bmatrix} \mathbf{u}(H) \\ \mathbf{t}(H) \end{Bmatrix} = \mathbf{P}^{(N)}(h^{(N)}) \mathbf{P}^{(N-1)}(h^{(N-1)}) \dots \mathbf{P}^{(2)}(h^{(2)}) \mathbf{P}^{(1)}(h^{(1)}) \begin{Bmatrix} \mathbf{u}(0) \\ \mathbf{t}(0) \end{Bmatrix} \quad (4-22)$$

where

$$\mathbf{P}^{(i)}(h^{(i)}) = \begin{bmatrix} \mathbf{A}_1 & \mathbf{A}_2 \\ \mathbf{B}_1 & \mathbf{B}_2 \end{bmatrix} \langle e^{s^*h^{(i)}} \rangle \begin{bmatrix} \mathbf{A}_1 & \mathbf{A}_2 \\ \mathbf{B}_1 & \mathbf{B}_2 \end{bmatrix}^{-1} \text{ for } i = 1, 2, \dots, N \quad (4-23)$$

is defined as the propagator matrix of layer i .

We consider the simply supported multilayered plate subjected to a loading over the entire area at the top surface of the plate where $z = H$. All other traction boundary conditions at the top and bottom surfaces of the plate are zero. Applying these boundary conditions to Eq. (4-22), the general solution is simplified to

$$\begin{Bmatrix} \mathbf{u}(H) \\ \mathbf{t}(H) \end{Bmatrix} = \begin{bmatrix} \mathbf{G}_1 & \mathbf{G}_2 \\ \mathbf{G}_3 & \mathbf{G}_4 \end{bmatrix} \begin{Bmatrix} \mathbf{u}(0) \\ \mathbf{0} \end{Bmatrix} \quad (4-24)$$

where

$$\begin{Bmatrix} \mathbf{u}(H) \\ \mathbf{t}(H) \end{Bmatrix} = \{u_x, u_y, u_z, t_{x0} \cos px \sin qy, t_{y0} \sin px \cos qy, t_{z0} \sin px \sin qy\}^T \quad (4-25)$$

and $\mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3$ and $\mathbf{G}_4$ are the submatrices of the product of the propagator matrices of multiple layers, t_{x0} is the amplitude of shear stress applied in the x -direction, t_{y0} is the amplitude of shear stress applied in the y -direction, and t_{z0} is the amplitude of normal stress applied in the z -direction. Several boundary conditions at the top surface of the plate where $z = H$ can be considered by modifying Eq. (4-25). For instance, the shear stress σ_{yz} loading over the entire area at the top surface can be obtained by setting t_{x0} and t_{z0} in Eq. (4-25) equal to zero. From Eq. (4-24), the unknown displacement on the bottom and top surface of the layered plate is respectively computed as

$$\mathbf{u}(0) = \mathbf{G}_3^{-1} \mathbf{t}(H), \quad \mathbf{u}(H) = \mathbf{G}_1 \mathbf{G}_3^{-1} \mathbf{t}(H) \quad (4-26)$$

Thus, for the displacement and traction vectors at any depth in layer i bounded by $z^{(i)} \leq z \leq z^{(i+1)}$ the solution is

$$\begin{Bmatrix} \mathbf{u}(z) \\ \mathbf{t}(z) \end{Bmatrix} = \mathbf{P}^{(i)}(z - z^{(i+1)}) \mathbf{P}^{(i-1)}(h^{(i-1)}) \dots \mathbf{P}^{(2)}(h^{(2)}) \mathbf{P}^{(1)}(h^{(1)}) \begin{Bmatrix} \mathbf{u}(0) \\ \mathbf{0} \end{Bmatrix} \quad (4-27)$$

By solving the displacement and traction vectors at any depth, the in-plane stresses can also be readily obtained. To obtain the effective response of the FGM plate with homogenized effective stiffness matrix, the propagator matrix method can be also utilized. It follows that the displacement and traction vectors at any depth $0 \leq z \leq H$ will be

$$\begin{Bmatrix} \mathbf{u}(z) \\ \mathbf{t}(z) \end{Bmatrix} = \bar{\mathbf{P}}^{(1)}(z) \begin{Bmatrix} \mathbf{u}(0) \\ \mathbf{0} \end{Bmatrix} \quad (4-28)$$

where $\bar{\mathbf{P}}^{(1)}(z)$ represents the propagator matrix of the single-layer homogenized plate from the bottom of the surface to the z -level. In the next section, the exact solution (Analytical Model) of a simply supported FGM plate subjected to surface loadings is compared with predicted response (Homogenized Model) of single-layer homogenized FGM plate to validate the derived effective properties.

4. Results and discussion

Having derived the expressions for the effective properties of FGM and introduced the propagator matrix solution for simply supported plate, we now present numerical examples to validate the proposed homogenization method and to show the application of the derived formulas.

4.1 Model validation

As the first example, the polymer film under simply supported conditions is analyzed for both the presented homogenized model and the discretized model. Under the present model, the effective stiffness matrix is first obtained based on Eq. (3-29) derived in Section 3.1, and then the global responses are predicted using the propagator matrix method. The analytical model has no homogenization process but considers the structure as multiple layers (Figure 3) where each individual layer has a propagator matrix defined.

Let us consider an isotropic polymer film (nominally polyethylene terephthalate (PET)) with initial elastic modulus $E=1.8$ GPa, Poisson's ratio $\nu=0.4$. For this film, the reference stiffness matrix in Equation (3-22) in the (x,y,z) -coordinate can be expressed as

$$C_{ij}^0 = \begin{bmatrix} 3.8571 & 2.5714 & 2.5714 & 0 & 0 & 0 \\ & 3.8571 & 2.5714 & 0 & 0 & 0 \\ & & 3.8571 & 0 & 0 & 0 \\ & & & 1.26 & 0 & 0 \\ & Sym & & & 1.26 & 0 \\ & & & & & 1.26 \end{bmatrix} \times 10^9 (\text{Pa}) \quad (5-1)$$

Model validation is conducted on the PET film with 300 hours UV aging, assuming the chromophore concentration follows Eqs. (2-2)-(2-4). Using the two-phase model (Eq. (3-29)), and taking $g=0.2$, we will have the stiffness matrix of PET film aged 300 hours as

$$C_{ij}(z, 300) = (0.2 + 0.525637e^{-0.36z - 0.39z^2}) C_{ij}^0 \quad (5-2)$$

As noted in Section 2, in this work the thickness is normalized to be consistent with the chemical kinetic modeling result and fitted grading equations. The normalized dimension of the plate is

$L_x \times L_y \times H = 100 \times 100 \times 1$. For model validation, two cases are studied: (1) A z -direction normal surface load is applied on the top surface of the plate $z=1$. That is, the extended traction given by Eq. (4-25) is considered with $m=n=1$ (i.e. $p=\pi/L_x$, $q=\pi/L_y$) and an amplitude $t_{z0}=1$ Pa. The bottom surface is assumed to be traction-free. (2) A shear load is applied on the top surface along x -direction with $t_{x0}=1$ Pa. For all cases shown, responses are calculated in the thickness direction, with fixed horizontal coordinates $(x, y)=(0.75L_x, 0.75L_y)$.

Figures 4, and 5 show the variation of displacement, stress and strain components along the thickness direction of the plate calculated utilizing both homogenized and exact analytical models. For both given loading conditions, the variations of the deformation, stress and strain predicted by the homogenized model agree, in a reasonable manner, with those from the analytical model. For the normal loading case, the homogenized model gives very close prediction of through-thickness normal stress σ_{zz} (Figure 4(c)) when comparing to the analytical model. For both homogenized and analytical models, the displacements evolve linearly across the thickness, with the z -displacement being constant. This linear variation is attributed to the thin thickness of the plate reflected in the exponential term of the displacement vector $\mathbf{u}$ general solution given by Eq. (4-3). Stresses, on the contrary, will exhibit a higher-order variation because the constitutive relations take into account derivatives of the displacement. Although the z -displacements predicted by two models differ, the values are very close to each other with a variation of 2.39%. The displacement in x -direction u_x (Figure 4(a)), normal strain ε_{xx} (Figure 4(g)) and in-plane shear strain ε_{xy} (Figure 4(h)) are exactly antisymmetric for the homogenized model and approximately antisymmetric for the analytical model about the middle plane, with top surface being extended and the bottom surface being compressed, similar to the results reported by Pan and Han [43]. Due to the homogenization, the u_x , ε_{xx} and ε_{xy} are exactly zero at position $z=0.5$ (neutral plane of the plate) while the analytical model presents zero values at

thickness around 0.46 due to the varying material properties through the thickness. For the shear stress σ_{yz} (Figure 4(d)), the responses at the top and bottom surfaces match closely as does the maximum shear stress value. As for the shear stress σ_{yz} , the homogenized model presents strictly symmetric response while the maximum value of the analytical model goes slightly below the neutral plane as the bottom half of the layered composite is stiffer than the top. On the other hand, the in-plane stresses (Figures 4(e) and 4(f)) of the two models vary differently. This feature is consistent with the in-plane strain plots (Figures 4(g) and 4(h)) which show linear variation through the thickness. Since the analytical model has varying stiffness from the top surface to the bottom, the variation of the in-plane stresses through the thickness will manifest as a curvature because stress is the product of stiffness and strain. However, the variation of the in-plane stresses through the thickness of homogenized model will be linear as the stiffness is uniformly distributed.

The discrepancy of the two models is relatively larger for the shear loading case, as compared with the normal loading case. This is because the effective stiffness is derived under the assumption the FGM plate subjected to the through-thickness loading condition on the top and bottom of the plate ignoring the effects from the sides. The displacement in the x - and z -directions (Figures 5(a) and 5(b)) are still linear across the thickness. Similar to the normal loading case, the in-plane stresses (Figures 5(c), 5(d) and 5(g)) predicted by homogenized model change linearly through the thickness while the curves predicted by analytical model show gradually changing slopes. On the other hand, the homogenized model also captures the shape of out-of-plane stress curves (Figures 5 (e), 5(f) and 5(h)) well. Table 3 summarizes percentage errors of the responses predicted by the homogenized model compared with results from the analytical model. Here, the percentage error is the ratio of root-mean-square deviation of curves predicted by homogenized and analytical models to root mean square of analytical model data. It can be observed from the table that most of the errors are less than 14% and the out-of-plane

responses under surface normal load are all lower than 7%. Overall, the homogenized model predicts the responses of this FGM plate with acceptable error range for both studied cases. It is also observed that the percentage errors of the three different aspect ratios are the same, indicating that the accuracy of the model is insensitive to aspect ratio. So the present homogenized model is not limited to thin films but can be utilized to study FGM plates of any size.

Based on these results, we conclude that the homogenization model provides reasonable accuracy in predicting the global responses of a functionally graded structure, indicating that the derivation of effective properties is accurate. The simple formula (Eq. (3-29)) is a general expression to conduct through-thickness homogenization. The homogenization derived here provides a simple approach for studying the effective responses and optimization design of a multilayered structure, functional graded plate and any structure with varying elastic properties through the thickness of the plate.

4.2 Polymer films under photodegradation

The main goal of this work is to develop an analytical tool to investigate the effect of non-spatially uniform photodegradation on the effective properties of polymer films. In the previous section, the accuracy of the derived effective property formulas was validated. Here, the evolution of effective properties and effective responses under simply supported surface-loading conditions are studied using the homogenized model.

We consider a PET film with initial stiffness properties as Eq. (5-1). Assuming the chromophore concentrations follow Eqs. (2-4)-(2-6), the grading function can be expressed as

$$f(z, t) = g + (1 - g)e^{-0.0014t - 0.0012tz - 0.0013tz^2} \quad (5-3)$$

Figure 6 shows the evolution of effective modulus against time for different g factor values. It is observed that the effective modulus gradually decreases with increasing time when

$g < 1$, increases with increasing time when $g > 1$ and is constant for $g = 1$. For a fixed time, the resultant modulus increases with increasing value of factor g . After 500 hours of aging, the in-plane modulus will decrease from 1.8 GPa to 0.792 GPa (56% lower) if $g = 0.2$ or increase to 3.06 GPa (70% higher) if $g = 2.0$. According to these results, the impact of photodegradation on the effective elastic properties of the polymer film is significant for a material aged under high-intensity ultraviolet light. The effective stiffness matrix after 300 hours aging with $g = 0.2$ is shown below

$$\begin{bmatrix} 2.2289 & 1.4794 & 1.4697 & 0 & 0 & 0 \\ & 2.2289 & 1.4697 & 0 & 0 & 0 \\ & & 2.2046 & 0 & 0 & 0 \\ & & & 0.72 & 0 & 0 \\ \text{Sym} & & & & 0.72 & 0 \\ & & & & & 0.73 \end{bmatrix} \times 10^9 (\text{Pa}) \quad (5-4)$$

Consistent with our expectation, the structure changes from isotropic to transversely isotropic after aging, and the degradation percentages of in-plane components are the same as the out-of-plane stiffness components. It is also noticed that the difference of in-plane stiffness and through-thickness stiffness is very small. According to (3-29), the difference of effective stiffness components C_{11} and C_{33} of an isotropic material can be expressed as

$$\frac{C_{11} - C_{33}}{C_{33}} = \left(\frac{f_2}{f_1} - 1 \right) \frac{\nu^2}{(1 - \nu)^2} \quad (5-5)$$

The above equation suggests that the variation of effective in-plane stiffness and out-of-plane stiffness components is mainly controlled by the gradation function. In our case, since the concentration variation (between the top surface ($z=1$) and bottom surface ($z=0$)) is small and the variation somewhat linear as shown in Figure 2, then the ratio f_2/f_1 will be close to one, resulting in a negligible difference between in-plane stiffness and through-thickness stiffness. Assuming a larger variation of concentration (a faster or more intensive photo degradation process, or a thicker film), the anisotropy feature of aged film will be more significant.

The effect of factor g is further investigated by studying the effective responses of simply supported polymer film (aging time $t=500$ hours) under surface normal load as shown in Figures 7, 8 and 9. Figure 7(a) and 7(b) show the variation of displacement components (u_x and u_z) along the thickness direction of the polymer film. The value of g does not alter displacement behavior since u_x shows linear decreasing behavior from the top to bottom and u_z shows constant values through the thickness of the plate. It is observed that the magnitude of the displacements decreases with increasing g . This is what we expected considering that a stiffer (larger g) material will be harder to deform than a less stiff (smaller g) material. In Figure 7(a), because of the antisymmetric feature, at the thickness of $z=0$ where the horizontal displacements are zero, curves intersect each other. Figures 8(a) and 8(b) show the variation of stress components (σ_{xz} and σ_{zz}) along the thickness direction of the polymer film. It is observed that the curves with different g values all develop the same stress values. This is attributed to the effective propagator matrices $\bar{\mathbf{P}}^{(1)}(z)$ being the same for different g values. Similarly, for different aging times, the effective propagator matrices $\bar{\mathbf{P}}^{(1)}(z)$ will be the same as well. However, if the responses are obtained using the analytical model (such that each sub-layer has substantially different stiffness properties), the stress curves of different g values will show some difference, as discussed in previous work by Pan [46]. As we saw in the previous section, the shortcoming of the current homogenized model is in predicting the stress distribution through the thickness direction. This disadvantage is also the origin of the errors listed in Table 3.

Although the factor g and time t have no influence on the stress components, the corresponding strains change significantly as shown in Figure 9 and 10. In Figure 9(a) and 9(b), the maximum strains when $g=0$ are about 10 times larger than the strains when $g=4.0$. As shown in Figure 10, the effective strain increases as the aging time increases. For the case of $g=0.2$, after 500 hours of aging, the maximum strains increase to more than 2 times the initial response.

The numerical examples suggest that the parameter g is a critical factor quantifying the impact of photodegradation. The derived effective property formulas in this work provide an easy way to evaluate g values through correlation with experimental measurements of the effective modulus for different UV aging time. The correlated model can be further used to evaluate the long-term mechanical behavior of the material and assist the lifetime design of polymer-based structures.

5. Conclusion

In this paper, we have developed a chemical-mechanical model to study the evolution of effective properties of polymer thin films under photodegradation. We first presented a three-species chemical kinetic model for prediction of chromophore concentrations of the heterogeneous aged-polymer structure. By considering the aged polymer as a functionally graded material, we obtained the time- and depth-dependent gradation equations of stiffness properties based on a volume-average principle for how the stiffness matrix evolves. Concise and general formulas have been derived to obtain the effective properties of functionally graded materials.

We presented numerical analysis for an initially isotropic polymer film under surface loading with laterally simply supported conditions. The results predicted by the homogenization model were validated against an exact multi-layer analytical model, with relative errors being 15% or less. We consider this level of error acceptable for providing reasonable estimates on how mechanical properties evolve in time for materials subject to spatially inhomogeneous degradation. The developed model was also successfully applied to investigate the evolution effective properties of the polymer film under photodegradation and the resulting time variation in, for example, predicted displacements suggests an approach for estimating effective parameters of FGM produced via optical aging.

To the best of our knowledge, this work is the first attempt to analytically model the impact of spatially non-uniform photodegradation on the effective properties of polymer. The

presented methodology is simple and straightforward. Future work will include further refinement and correlation of the chemical-kinetic model, inclusion of the effect of light intensity on degradation rates and experimental estimation of the value of factor g for aged polymer films.

References

- [1] Alzoubi, K., Lu, S., Sammakia, B., & Poliks, M. (2011). Experimental and analytical studies on the high cycle fatigue of thin film metal on PET substrate for flexible electronics applications. *Components, Packaging and Manufacturing Technology, IEEE Transactions on*, 1(1), 43-51.
- [2] Ulrich, R. K., & Brown, W. D. (2006). *Advanced Electronic Packaging* (Vol. 9). Wiley-IEEE Press.
- [3] Jiang, T., Huang, R., & Zhu, Y. (2014). Interfacial Sliding and Buckling of Monolayer Graphene on a Stretchable Substrate. *Advanced Functional Materials*, 24(3), 396-402.
- [4] Sun, Y. C., Ng, A., Fung, M. K., Djurišić, A. B., & Chan, W. K. (2012). Enhancement of polymer solar cell performance using spin-coated reflector structure. *Materials Chemistry and Physics*, 135(2), 1044-1047.
- [5] Yu, W., Shen, L., Shen, P., Long, Y., Sun, H., Chen, W., & Ruan, S. (2013). Semitransparent polymer solar cells with 5% power conversion efficiency using photonic crystal reflector. *ACS Applied Materials & Interfaces*, 6(1), 599-605.
- [6] Stafford, C. M., Harrison, C., Beers, K. L., Karim, A., Amis, E. J., Vanlandingham, M. R., Kim H. C, Volksen, W., Miller, R. D. & Simonyi, E. E. (2004). A buckling-based metrology for measuring the elastic moduli of polymeric thin films. *Nature Materials*, 3(8), 545-550.
- [7] Salleo, A., Chabinyc, M. L., Yang, M. S., & Street, R. A. (2002). Polymer thin-film transistors with chemically modified dielectric interfaces. *Applied Physics Letters*, 81(23), 4383-4385.
- [8] Dimitrakopoulos, C. D., & Mascaro, D. J. (2001). Organic thin-film transistors: A review of recent advances. *IBM Journal of Research and Development*, 45(1), 11-27.
- [9] Lee, J., Panzer, M. J., He, Y., Lodge, T. P., & Frisbie, C. D. (2007). Ion gel gated polymer thin-film transistors. *Journal of the American Chemical Society*, 129(15), 4532-4533.

- [10] Nowicki, M., Richter, A., Wolf, B., & Kaczmarek, H. (2003). Nanoscale mechanical properties of polymers irradiated by UV. *Polymer*, 44(21), 6599-6606.
- [11] Tavares, A. C., Gulmine, J. V., Lepienski, C. M., & Akcelrud, L. (2003). The effect of accelerated aging on the surface mechanical properties of polyethylene. *Polymer Degradation and Stability*, 81(2), 367-373.
- [12] Fernandes, L. L., Freitas, C. A., Demarquette, N. R., & Fechine, G. J. M. (2011). Photodegradation of thermodegraded polypropylene/high- impact polystyrene blends: Mechanical properties. *Journal of Applied Polymer Science*, 120(2), 770-779.
- [13] Barany, T., Földes, E., Czigany, T., & Karger-Kocsis, J. (2004). Effect of UV aging on the tensile and fracture mechanical response of syndiotactic polypropylenes of various crystallinity. *Journal of Applied Polymer Science*, 91(6), 3462-3469.
- [14] Aglan, H., Calhoun, M., & Allie, L. (2008). Effect of UV and hygrothermal aging on the mechanical performance of polyurethane elastomers. *Journal of Applied Polymer Science*, 108(1), 558-564.
- [15] Fechine, G. J. M., & Demarquette, N. R. (2008). Cracking formation on the surface of extruded photodegraded polypropylene plates. *Polymer Engineering & Science*, 48(2), 365-372.
- [16] Sutter, F., Meyen, S., Heller, P., & Pitz-Paal, R. (2013). Development of a spatially resolved reflectometer to monitor corrosion of solar reflectors. *Optical Materials*, 35(8), 1600-1608.
- [17] Jha, D. K., Kant, T., & Singh, R. K. (2013). A critical review of recent research on functionally graded plates. *Composite Structures*, 96, 833-849.
- [18] Birman, V., & Byrd, L. W. (2007). Modeling and analysis of functionally graded materials and structures. *Applied Mechanics Reviews*, 60(5), 195-216.
- [19] Reiter, T., Dvorak, G. J., & Tvergaard, V. (1997). Micromechanical models for graded composite materials. *Journal of the Mechanics and Physics of Solids*, 45(8), 1281-1302.

- [20] Zuiker, J. R. (1995). Functionally graded materials: choice of micromechanics model and limitations in property variation. *Composites Engineering*, 5(7), 807-819.
- [21] Yin, H. M., Sun, L. Z., & Paulino, G. H. (2004). Micromechanics-based elastic model for functionally graded materials with particle interactions. *Acta Materialia*, 52(12), 3535-3543.
- [22] Cho, J. R., & Ha, D. Y. (2001). Averaging and finite-element discretization approaches in the numerical analysis of functionally graded materials. *Materials Science and Engineering: A*, 302(2), 187-196.
- [23] Grujicic, M., & Zhang, Y. (1998). Determination of effective elastic properties of functionally graded materials using Voronoi cell finite element method. *Materials Science and Engineering: A*, 251(1), 64-76.
- [24] Kim, J. H., & Paulino, G. H. (2002). Finite element evaluation of mixed mode stress intensity factors in functionally graded materials. *International Journal for Numerical Methods in Engineering*, 53(8), 1903-1935.
- [25] Chakraborty, A., & Gopalakrishnan, S. (2003). A spectrally formulated finite element for wave propagation analysis in functionally graded beams. *International Journal of Solids and Structures*, 40(10), 2421-2448.
- [26] Khan, K. A., & Muliana, A. H. (2009). A multi-scale model for coupled heat conduction and deformations of viscoelastic functionally graded materials. *Composites Part B: Engineering*, 40(6), 511-521.
- [27] Tan, T., Rahbar, N., Allameh, S. M., Kwofie, S., Dissmore, D., Ghavami, K., & Soboyejo, W. O. (2011). Mechanical properties of functionally graded hierarchical bamboo structures. *Acta Biomaterialia*, 7(10), 3796-3803.
- [28] Wu, Z., Meng, J., Liu, Y., Li, H., & Huang, R. (2014). A State Space Method for Surface Instability of Elastic Layers With Material Properties Varying in Thickness Direction. *Journal of Applied Mechanics*, 81(8), 081003.

- [29] Wu, Y., Nie, Y., & Yang, Z. (2014). Prediction of effective properties for random heterogeneous materials with extrapolation. *Archive of Applied Mechanics*, 84(2), 247-261.
- [30] Wang, X., Pan, E., Albrecht, J. D., & Feng, W. J. (2009). Effective properties of multilayered functionally graded multiferroic composites. *Composite Structures*, 87(3), 206-214.
- [31] Meijer, H. E., & Govaert, L. E. (2005). Mechanical performance of polymer systems: the relation between structure and properties. *Progress in Polymer Science*, 30(8), 915-938.
- [32] Oleinik, E. T. F., Rudnev, S. N., Salamatina, O. B., & Kotelyanskii, M. I. (2008). Mechanisms of anelastic deformation in solid polymers: Solidlike and liquidlike processes. *Polymer Science Series A*, 50(5), 494-506.
- [33] Arruda, E. M., & Boyce, M. C. (1993). Evolution of plastic anisotropy in amorphous polymers during finite straining. *International Journal of Plasticity*, 9(6), 697-720.
- [34] Wu, J. J., & Buckley, C. P. (2004). Plastic deformation of glassy polystyrene: a unified model of yield and the role of chain length. *Journal of Polymer Science Part B: Polymer Physics*, 42(11), 2027-2040.
- [35] Engels, T. A., Govaert, L. E., Peters, G. W., & Meijer, H. E. (2006). Processing- induced properties in glassy polymers: Application of structural relaxation to yield stress development. *Journal of Polymer Science Part B: Polymer Physics*, 44(8), 1212-1225.
- [36] Rabek, J. F. (1995). *Polymer Photodegradation: Mechanisms and Experimental Methods*. Springer.
- [37] Swinehart, D.F. (1962) The Beer-Lambert Law. *Journal of Chemical Education*, 39: 333-335.
- [38] Modest, M. F. (2013). *Radiative Heat Transfer*. Academic Press.

- [39] Masuri, S. U., Sellier, M., Zhou, X., & Tamma, K. K. (2011). Design of order-preserving algorithms for transient first- order systems with controllable numerical dissipation. *International Journal for Numerical Methods in Engineering*, 88(13), 1411-1448.
- [40] Kachanov, M., & Sevostianov, I. (2013). *Effective Properties of Heterogeneous Materials*. Springer Science & Business Media.
- [41] Kachanov, M., & Sevostianov, I. (2005). On quantitative characterization of microstructures and effective properties. *International Journal of Solids and Structures*, 42(2), 309-336.
- [42] Şimşek, M., & Reddy, J. N. (2013). Bending and vibration of functionally graded microbeams using a new higher order beam theory and the modified couple stress theory. *International Journal of Engineering Science*, 64, 37-53.
- [43] Pan, E., & Han, F. (2005). Exact solution for functionally graded and layered magneto-electro-elastic plates. *International Journal of Engineering Science*, 43(3), 321-339.
- [44] Pan, E. (1997). Static Green's functions in multilayered half spaces. *Applied Math Modeling*, 21, 509-521.
- [45] Stroh, A. N. (1958). Dislocations and cracks in anisotropic elasticity. *Philosophical Magazine*, 3(30), 625-646.
- [46] Pan, E. (2003). Exact solution for functionally graded anisotropic elastic composite laminates. *Journal of Composite Materials* 37(21), 1903-1920.

Acknowledgements

This work was supported by U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy under award number DE-FOA-0000861. We also thank Dr. Matthew Gray and Katelyn Kessinger for supplying UV/Vis spectra of un-aged and aged PET films.

Table 1: A three-component optically-driven reaction scheme.

Reaction Scheme	Model
$ \begin{array}{c} \xrightarrow{\alpha_0 I} \\ n_0 \rightleftharpoons n_0^* \\ \xleftarrow{\gamma_0} \\ n_0^* \xrightarrow{\kappa_{0,1}} n_1 \\ \xleftarrow{\alpha_1 I} \\ n_1 \rightleftharpoons n_1^* \\ \xleftarrow{\gamma_1} \\ n_1^* \xrightarrow{\kappa_{1,2}} n_2 \\ \xleftarrow{\alpha_2 I} \\ n_2 \rightleftharpoons n_2^* \\ \xleftarrow{\gamma_2} \end{array} $	<p>Kinetic Model:</p> $ \begin{aligned} \dot{n}_0 &= -\alpha_0 I n_0 + \gamma_0 n_0^*, \\ \dot{n}_0^* &= \alpha_0 I n_0 - \gamma_0 n_0^* - \kappa_{0,1} n_0^*, \\ \dot{n}_1 &= -\alpha_1 I n_1 + \gamma_1 n_1^* + \kappa_{0,1} n_0^*, \\ \dot{n}_1^* &= \alpha_1 I n_1 - \gamma_1 n_1^* - \kappa_{1,2} n_1^*, \\ \dot{n}_2 &= -\alpha_2 I n_2 + \gamma_2 n_2^* + \kappa_{1,2} n_1^*, \\ \dot{n}_2^* &= \alpha_2 I n_2 - \gamma_2 n_2^*, \end{aligned} $ <p>Initial Conditions:</p> $ \begin{aligned} n_0(z, 0) &= \bar{n}_0, \\ n_1(z, 0) &= \bar{n}_1, \\ n_2(z, 0) &= \bar{n}_2, \\ n_0^*(z, 0) &= n_1^*(z, 0) = n_2^*(z, 0) = 0. \end{aligned} $ <p>Optical Model:</p> $ \frac{\partial I}{\partial z} = - \sum_k \alpha_k n_k I, $ <p>Boundary Condition:</p> $ I(0, t) = \bar{I}, $

Table 2: A simplified three-component optically-driven reaction scheme. An absorption cross section scaled by a dimensionless reaction rate for secondary reactions appears in this simplified model denoted by $\delta_{i,i+1} = \alpha_i \kappa_{i,i+1} (\gamma_i + \kappa_{i,i+1})^{-1}$.

Simplified Reaction Scheme	Simplified Model
$ \begin{array}{c} \xrightarrow{\delta_{0,1} I} \\ n_0 \longleftrightarrow n_1 \\ \xleftarrow{\delta_{0,1} I} \\ \xrightarrow{\delta_{1,2} I} \\ n_1 \longleftrightarrow n_2 \\ \xleftarrow{\delta_{1,2} I} \end{array} $	<p>Opto-kinetic Model:</p> $ \begin{bmatrix} \dot{n}_0 \\ \dot{n}_1 \\ \dot{n}_2 \end{bmatrix} = \begin{pmatrix} -\delta_{0,1} & 0 & 0 \\ \delta_{0,1} & -\delta_{1,2} & 0 \\ 0 & \delta_{1,2} & 0 \end{pmatrix} \begin{bmatrix} n_0 \\ n_1 \\ n_2 \end{bmatrix} \times \bar{I} \exp \left(- \sum_k \alpha_k \int_0^z n_k(\xi, t) d\xi \right) $ <p>Initial Conditions:</p> $ \begin{aligned} n_0(z, 0) &= \bar{n}_0, \\ n_1(z, 0) &= \bar{n}_1, \\ n_2(z, 0) &= \bar{n}_2. \end{aligned} $

Table 3: Parameters used to solve Model 2.

α_0 [m ²]	α_1 [m ²]	α_3 [m ²]	$\delta_{0,1}$ [s ⁻¹]	$\delta_{1,2}$ [s ⁻¹]
0.0081	0.24	0.0075	0.5	0.952

Table 4: Root-mean-square percentage errors (%) of responses of a FGM plate under surface normal load (aspect ratio $L/H= 10, 100$ and 1000) and surface shear load (aspect ratio $L/H= 100$) along the whole thickness direction predicted by the homogenized model compared with results of the analytical model.

L/H	Surface normal load			Surface shear load
	10	100	1000	100
u_x	12.79	12.79	12.79	9.07
u_y	12.79	12.79	12.79	5.61
u_z	2.40	2.40	2.39	9.82
σ_{xx}	13.39	13.39	13.39	16.25
σ_{yy}	13.39	13.39	13.39	12.69
σ_{zz}	2.92	2.92	2.92	10.03
σ_{yz}	6.12	6.12	6.12	6.13
σ_{xz}	6.12	6.12	6.12	9.69
σ_{xy}	13.40	13.40	13.40	13.25
ε_{xx}	12.79	12.79	12.79	9.06
ε_{yy}	12.79	12.79	12.79	5.64
ε_{zz}	12.79	12.79	12.79	13.61
ε_{yz}	3.56	3.56	3.56	21.69
ε_{xz}	3.56	3.56	3.56	6.68
ε_{xy}	12.79	12.79	12.79	13.60

Figure 1: Evolution of UV/Vis absorption spectra for Melinex® ST504 Poly(ethylene terephthalate) (PET) film aged for ~300 hours under approximately 10X enhanced UVA/UVB light.

Figure 2: Variation of concentration against time and thickness predicted by three-component reaction model: (a) $n_0(z,t)$, (b) $n_I(z,t)$ and (c) $n_2(z,t)$. Note the different scale for concentration in (b).

Figure 3: Sketch of a multilayered plate.

Figure 4: Variation of displacement, stress and strain components along the thickness direction in an aged polymer film caused by a surface normal load on the top surface predicted by the homogenized model and analytical model: (a) displacement u_x , (b) displacement u_z , (c) normal stress σ_{zz} , (d) shear stress σ_{yz} (e) normal stress σ_{xx} , (f) shear stress σ_{xy} , (g) normal strain ϵ_{xx} and (h) shear strain ϵ_{xy} .

Figure 5: Variation of displacement, stress and strain components along the thickness direction in an aged polymer film caused by a surface shear load on the top surface predicted by the homogenized model and analytical model: (a) displacement u_x , (b) displacement u_z , (c) normal stress σ_{zz} , (d) shear stress σ_{yz} (e) normal stress σ_{xx} , (f) shear stress σ_{xy} , (g) normal strain ϵ_{xx} and (h) shear strain ϵ_{xy} .

(a)

(b)

Figure 6: Evolution of effective modulus of a polymer film under aging for factor $g = 0, 0.2, 0.5, 1.0, 2.0$ and 4.0 : (a) in-plane elastic modulus and (b) out-of-plane shear modulus.

Figure 7: Variation of the displacement components along the thickness direction in an aged polymer film ($t=500$ hours) caused by surface normal load on top surface for factor $g=0, 0.2, 0.5, 1.0, 2.0$ and 4.0 : (a) u_x and (b) u_z .

(a)

(b)

Figure 8: Variation of the stress components (unit in Pa) along the thickness direction in an aged polymer film ($t=500$ hours) caused by surface normal load on top surface for factor $g=0, 0.2, 0.5, 1.0, 2.0$ and 4.0 : (a) σ_{xz} and (b) σ_{zz} .

(a)

(b)

Figure 9: Variation of the strain components along the thickness direction in an aged polymer film ($t=500$ hours) caused by surface normal load on top surface for factor $g=0, 0.2, 0.5, 1.0, 2.0$ and 4.0 : (a) ε_{xz} and (b) ε_{zz} .

(a)

(b)

Figure 10: Variation of the strain components along the thickness direction in polymer film ($g=0.2$) caused by surface normal load on top surface under different aging time $t=0, 100, 200, 300, 400$ and 500 hours: (a) ε_{xz} and (b) ε_{zz} .