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The effect of photodegradation on effective properties of polymeric thin films: A micromechanical homogenization approach

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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.

1. Introduction

Due to their unique electronic, thermal, and mechanical properties, polymeric thin films are used increasingly in technological applications such as flexible electronics (Alzoubi, Lu, Sammakia, & Poliks, 2011; Jiang, Huang, & Zhu, 2014; Ulrich & Brown, 2006), optical reflectors (Stafford et al., 2004; Sun, Ng, Fung, Djurišić, & Chan, 2012; Yu et al., 2013), and transistors (Dimitrakopoulos & Mascaro, 2001; Lee, Panzer, He, Lodge, & Frisbie, 2007; Salleo, Chabinyc, Yang, & Street, 2002). The chemical structure of polymers has a strong influence on the physical and mechanical properties of the film structure (Nowicki, Richter, Wolf, & Kaczmarek, 2003). Mechanical properties can limit the applications 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 (Nowicki et al., 2003). 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,

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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 importance 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 (Aglan, Calhoun, & Allie, 2008; Barany, Földes, Czigany, & Karger-Kocsis, 2004; Fernandes, Freitas, Demarquette, & Fechine, 2011; Fechine & Demarquette, 2008; Nowicki et al., 2003; Tavares, Gulmine, Lepienski, & Akcelrud, 2003). Nowicki et al. (2003) 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. (2003) conducted UV irradiance-thermal-humidity acceleration tests on low-density polyethylene for up to 1600 h, 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. (2004) and Aglan et al. (2008) 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. Fechine and Demarquette (2008) 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 Fig. 1 for a polyethylene terephthalate (PET) film that was aged over 300 h 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 Fig. 1, we can consider the UV aged polymer as a composite material comprised of un-damaged polymer and degraded polymer, with gradually changing volume ratios of

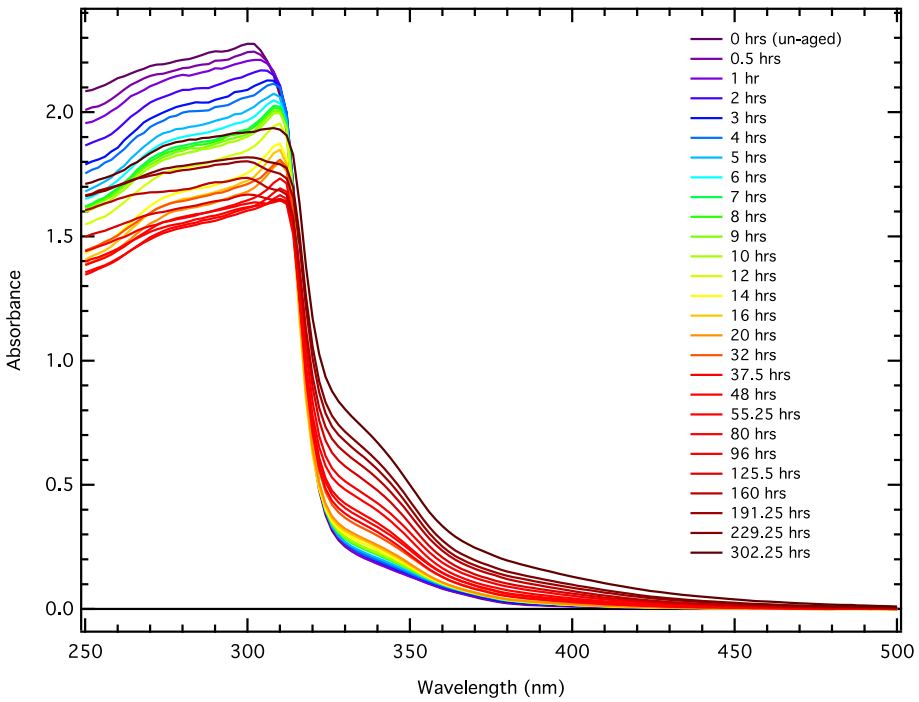

Fig. 1. Evolution of UV/Vis absorption spectra for Melinex® ST504 Poly(ethylene terephthalate) (PET) film aged for ~300 h under approximately 10X enhanced UVA/UVB light.