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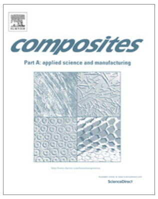

A methodology for the estimation of transverse failure strength of an oxidized lamina from isothermal aging studies

Jianyong Liang, Kishore V. Pochiraju *

Department of Mechanical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030, United States

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ABSTRACT

Surface oxidation and ensuing damage substantially decrease the service life of High Temperature Polymer Matrix Composite (HTPMC) structures. Oxidative degradation behavior of composites is strongly dependent on the coupling between chemical and mechanical responses of the material. In a composite lamina, the onset of damage and subsequent coupled acceleration of both damage and oxidation are controlled by the transverse failure strength of the oxidized regions. The direct measurement of this strength from experimentation is challenging and cumbersome. A model-based methodology for estimating the mean transverse failure strength of the oxidized regions of a unidirectional composite is described in this paper. As the strength of the oxidized region is expected to show a high-degree of spatial variability, the estimated mean is shown to be relatively insensitive to the effect of strength variance. The developed methodology is illustrated with isothermal aging data available for a typical high-temperature composite system.

1. Introduction

High Temperature Polymer Matrix Composites (HTPMCs) with durability are desired for aerospace structures and propulsion applications. At elevated temperatures, oxidative degradation and oxidation-induced cracks substantially reduce the service life of HTPMCs [1]. Weight loss characterization has been used for many years [2–4] to assess the thermo-oxidative stability of the polymers. Since the weight loss is a gross response of several underlying degradation mechanisms, the measurements are not translatable to composites with same constituents but with different fiber volume or morphologies. The utility of these measurements for life prediction or establishing material property allowables needed for design is minimal. A mechanism driven approach is desired for predicting the service life of composite structures operating under thermo-oxidative conditions [5–7]. Various mechanisms of polymer degradation due to oxidation reactions, constitutive relationships for chemically transforming solids, oxidation-induced strain fields, and damage development are of interest to both chemistry and mechanics communities. The reactions of various polymers have been studied with mechanistic chemistry models [8,9], which provided considerable insight into the chemical transformation rates during oxidative aging of several polymers. Recently several groups began simulating the oxidation degradation of polymers by incorporating the mechanistic chemistry models into structural mechanics [10–13]. In a polymeric composite, the reinforcing fibers are generally assumed to be oxidatively stable at operating temperatures (applications under 300 °C). Although the fibers enhance stiffness of the composite at high temperatures, the presence of oxygen diffusing fibers and the fiber/matrix interface introduces directional dependence of oxidative degradation [14–16]. Experiments show that oxidative degradation in a lamina is substantially higher along fiber axis direction [14,15]. The dependence is attributed partly to the orthotropy of oxygen diffusivity in the lamina and to the low fracture resistance of the matrix and the fiber–matrix interfaces.

Material oxidation is accompanied by volume changes (polymer shrinkage) and the shrinkage strain depends upon the oxidation state [16]. As the matrix undergoes oxidative shrinkage and even if the fibers remain dimensionally stable, oxidation-induced stress and damage develop in the composite [16,17]. Matrix and interface cracking occurs along the axis of the composite lamina [14,18]. The newly created crack surfaces connect the oxygen-starved material inside the structure with the oxidizing environment at the boundaries, thus accelerating the oxidation growth. Experiments on several composite systems show that the oxidation-induced cracks always remain within the oxidized layer indicating the oxidation process and associated weakening of the material are necessary for continued damage evolution [14]. While oxidation reduces

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* Corresponding author.
E-mail address: kishore.pochiraju@stevens.edu (K.V. Pochiraju).

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the fracture resistance of the material and creates the stress fields necessary for the crack formation, oxygen adsorbing crack surfaces increase the dissolved oxygen concentration available for oxidation. Oxidation growth and crack propagation are strongly coupled, with one mechanism accelerating the other.

Despite substantial amount of work on predicting the service life of polymer composites using mechanistic chemistry models and structural mechanics models [5–13], relatively little progress has been made on predicting the oxidation-induced stress and the coupling between oxidation and crack growth. Without incorporating the effect of cracks on accelerating the oxidation growth, the numerical models are applicable only to short time aging (<200 h for polymer composites) before the crack initiation. Oxidation-induced damage state in polymer composites after certain hours of aging has been predicted by Wang and Chen [10] using coupled physic-chemical and damage models. Oxidation-induced damage growth has been considered as evolution of diffuse damage [19] or as debonding of cohesive zones along a predetermined path [12]. The effect of cracks on facilitating oxygen diffusion has been studied using a numerical oxidation model by incorporating a predefined crack growth rate [21]. The temperature, pressure and the substrate stress dependence [20] on the oxidation growth has also been investigated. Recently we considered the mutual dependence of oxidation layer growth and crack propagation using a coupled framework [13]. First, we determined the morphological changes due to oxidation reaction chemistry, followed by the evolution of the stress during oxidation with a mechanics model and the development of discrete cracks within the oxidized material. Using this framework, detailed crack initiation and propagation due to oxidation of materials were predicted without any assumptions about the crack locations or propagation paths. However, several assumptions had to be made for the strength and toughness of the oxidized lamina and experimental methods for determining these parameters were impractical, time consuming and expensive. From this effort, we determined that the transverse failure strength (F_T^t) and mixed-mode fracture energy of oxidized lamina are necessary for high quality prediction of the damage growth and damage-induced acceleration of oxidation. This paper focuses on developing an indirect but original method for estimating the mean strength of the oxidized lamina.

The resin toughness and fiber/matrix interface adhesion determine the transverse failure strength and the mixed-mode fracture energy of the material, and degrade substantially during thermal oxidation [22–24]. Due to the fragility of the oxidized composite lamina and the impracticality of oxidizing the entire thickness of a specimen without surface erosion, direct experimental measurements of the transverse failure strength is infeasible. However, isothermal aging experiments can reliably provide both the oxidation layer size and crack length measurements with optical, nano-indentation and elemental analysis [14]. In addition, the time at which discrete cracks initiate due to aging in oxidizing environments is directly related to the transverse failure strength F_T^t of the oxidized lamina. This paper describes a methodology for extracting the transverse failure strength of an oxidized lamina using the first observations of a discrete crack in an isothermal aging experiment.

2. Oxidative degradation mechanisms

Using a coupled oxidation–damage evolution model developed earlier [13], the relationship between the crack initiation time and the transverse strength can be established for a composite system with known oxidation and stiffness behavior of the fiber and matrix constituents. Fig. 1 shows the representative volume element (RVE) [25,26] that has been used to study the coupled oxidation and damage growth in a high temperature composite lamina. The reference coordinates in the RVE (L-, T-, Z-) indicate fiber axis (L-), transverse (T-) and the through-the-thickness (Z-) directions. Typical dimensions of the RVE required to analyze the oxidation problem are also indicated. One or more surfaces of the RVE are exposed to an oxidizing environment. The figure depicts typical oxidation layer growth when the left (T–Z) plane is exposed to oxygen and oxidation grows along the fiber axis. At any given time during the aging, a fully oxidized region, an actively oxidizing region and the unoxidized region can be delineated from the surface and the size of these zones can be measured using optical microscopy, nano-indentation and X-ray scanning techniques.

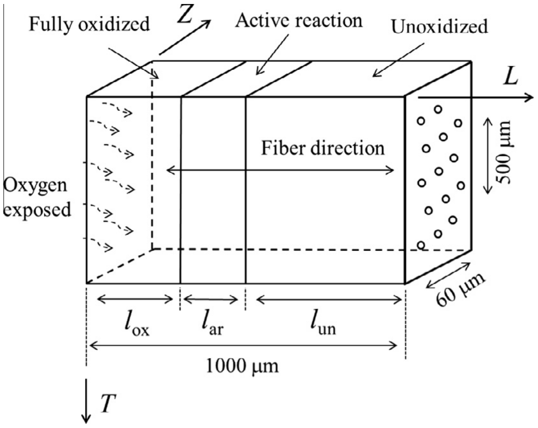

Fig. 1. Representative volume element model for a composite lamina.

2.1. Growth of surface oxidation layers

The surface of polymer composites exposed to oxidizing environment adsorbs oxygen and the saturation value for the dissolved oxygen concentration (C_s) can be determined according to Henry's law [27]. $C(x, y, z; t, T; V_f)$ is the oxygen concentration (molar volume) field inside the material. The concentration gradient drives diffusive flow of oxygen into the interior of the material. Oxidizing reactions are activated in the polymer due to the presence of the dissolved oxygen at a substantial rate due to the elevated aging temperatures. An oxidation state variable ($\emptyset$) is defined to indicate the total extent of the oxidation reaction [28]. The oxygen diffusivity of composite lamina $D_{L,T,Z}^{\emptyset}$ is dependent on fiber volume fraction (V_f), oxidation state ($\emptyset$) and the fiber orientation. The chemical reaction rate, $R(\emptyset, T, C, V_f)$, defines the net rate of oxygen consumed for oxidation, which is controlled by the chemistry of oxidation reaction and availability of oxygen and polymer resin[6,29]. The oxidation model [16] computes the oxidation state $\emptyset(x, y, z, t)$ using physics-based simulation of oxygen diffusion, its reaction with the polymer and conversion of the polymer into oxidized regions. The diffusion–reaction equation with orthotropic oxygen diffusivity for homogenized material is given by Eq. (1).

$$\frac{\partial C}{\partial t} = \left(D_L \frac{\partial^2 C}{\partial x^2} + D_T \frac{\partial^2 C}{\partial y^2} + D_Z \frac{\partial^2 C}{\partial z^2} \right) - R(\emptyset, T, C, V_f) \qquad (1)$$

where D_L, D_T and D_Z are oxygen diffusivities along axial (L-) and transverse directions (T- and Z-) respectively. The oxygen diffusivity for a G30/PMR-15 lamina is shown in Table 1. The diffusivities and the reaction rates are dependent on the aging temperature and stress-state in the substrate materials [20]. The solubility of oxygen in the material, which determines the saturation molar volume adsorbed at the surface is also temperature dependent. Since only