LONG-TERM AGING AND DURABILITY OF HIGH TEMPERATURE POLYMER COMPOSITES

G. A. Schoeppner¹, K.V. Pochiraju², and G. P. Tandon³

¹Air Force Research Laboratory, Wright Patterson AFB, OH, USA
²Steven’s Institute of Technology, Hoboken, NJ, USA
³University of Dayton Research Institute, Dayton, OH, USA

ABSTRACT

Durability and degradation mechanisms in composites are fundamentally influenced by the fiber, matrix, and interphase regions that constitute the composite domain. The thermo-oxidative behavior of the composite is significantly different from that of the fiber and matrix constituents as the composite microstructure, including the fiber-matrix interphases/interfaces, introduces anisotropy in the diffusion behavior. In this work, neat resin PMR-15 high temperature resin and unidirectional G30-500/PMR-15 composite specimens were aged at elevated temperatures. PMR-15 has been used in the aeronautical industry for over 20 years due to its high glass transition temperature and thermo-oxidative stability [1]. It is well known that the free surfaces of high-temperature Polymer Matrix Composites (PMCs) are susceptible to oxidation that leads to the development of surface and ply cracking and accelerated degradation when in the presence of thermo-mechanical loading. Once ply cracking has initiated, new free surfaces are introduced into the composite providing pathways for oxidants that inevitably lead to degradation of the fiber matrix interfaces, reducing the lifetime and durability of these material systems [2]. Therefore, it is essential to fully characterize these high-temperature composites on a constituent level so that their physical and chemical responses from the oxidation process are fully understood.

A primary measure of the thermal oxidative stability of PMR-15 and other high temperature composite materials is the percentage weight loss as a function of isothermal aging time and temperature. In general, the relationship between weight loss and property changes can be highly nonlinear and does not provide any measure of the spatial variability of degradation within the specimen. The reliability of predictive methods based on weight loss in which small changes in weight can result in significant declines in mechanical properties, is highly questionable. However, in the absence of methods to predict end of life properties, weight loss is an accepted screening tool to compare the thermal oxidative stability (TOS) of different materials. To accurately predict the performance of polymer matrix composite (PMC) components and structures subjected to thermo-mechanical loading, knowledge of the individual aging mechanisms, their synergistic effects, and the spatial variability of the thermo-oxidative degradation is critical. The findings of the present investigation along with the results of ongoing work to characterize the influence of the fiber-matrix interface on thermal oxidation will provide the necessary basis for predicting the thermo-oxidative micromechanical response of PMR-15 laminates [3].

In this work, unidirectional G30-500/PMR-15 composite specimens were aged at elevated temperatures in air resulting in oxidation propagation parallel and perpendicular to the fibers. Four different specimen geometries were chosen such that different surface area ratios (i.e., ratios of surface area perpendicular to the fibers to surface area parallel to the fibers) were obtained. Weight loss and volumetric changes were monitored as a function of aging time to study the high temperature anisotropic oxidation process. A new weight loss model has been developed. Optical micrographs were taken on polished internal sections and viewed in the dark-field mode to measure the degree, depth and distribution of thermal oxidation development from external surfaces perpendicular and parallel to the fibers as shown in Figure 1. Additionally in this work, thermo-oxidative aging is simulated with a diffusion/reaction model in which temperature, oxygen concentration and weight loss effects are considered [4,5]. A parametric reaction model based on a mechanistic view of the reaction is used for simulating reaction rate dependence on the oxygen availability in the polymer. Macroscopic weight-loss measurements are used to determine the reaction and polymer consumption parameters. As a first approximation, it is assumed that the transport of oxygen within the polymer is controlled by Fickian diffusion. The oxygen reacts with the polymer followed by degradation of the material. With $C(x,y,z;t)$ denoting the concentration field at any time within a
domain with a diffusivity of $D_{ij}$ and consumptive reaction with a rate $R(C)$, the diffusion reaction with orthotropic diffusivity is given by Eq. (54)

$$\frac{\partial C}{\partial t} = \left( D_{11} \frac{\partial^2 C}{\partial x^2} + D_{22} \frac{\partial^2 C}{\partial y^2} + D_{33} \frac{\partial^2 C}{\partial z^2} \right) - R(C)$$

subjected to the boundary conditions: $C = C^s$ on the exposed boundaries and $dC/dt = 0$ on symmetry boundaries. The boundary sorption on the exposed boundaries is given by Henry’s equation

$$C^s = S P$$

where $S$ is the solubility and $P$ is the partial pressure of the oxygen in the environment. The diffusivities are temperature dependent typically given in Arrhenius form:

$$D_{ij} = D_0 \exp(-E_a/RT)$$

and determined using permeability tests at lower temperatures to determine the pre-exponent $(D_0)$ and the activation energy parameters $(E_a)$. The reaction rate term, $R(C)$, is modeled with the Arrhenius-type kinetics model [6,7] for capturing the temperature dependence of the reaction rates or using mechanistic reaction models such as Abdeljaoued [8] for capturing the oxygen concentration dependence.

REFERENCES

Figure 1. Oxidation of unidirectional G30-500/PMR-15 composites at 288°C