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Influence of laminate lay-up on oxidation and damage growth: Isothermal aging

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ABSTRACT

The thermo-oxidative behavior of a composite is significantly different from that of the constituents as the composite microstructure, including the fiber/matrix interphase/interface, architecture and ply lay-up introduce anisotropy in the diffusion and oxidation behavior. In this work, light microscopy and scanning electron microscopy techniques are used to characterize the oxidative process in laminated carbon fiber-reinforced polyimide composites. Four different composites are considered, namely, unidirectional $[0]_{16T}$, quasi-isotropic $[0/\pm45/90]_{2S}$, cross-ply $[0/90]_{4S}$, and angle-ply $[\pm45]_{2S}$ laminates. The observed anisotropy in composite oxidation is explained by carefully monitoring the development and growth of damage through the use of fluorescence imaging using dye impregnation. It is shown that the oxidation behavior of a laminate is strongly dependent on the ply stacking sequence, while alternative pathways for transport of oxygen into the interior of the composite are fiber–matrix debonds and matrix cracks that propagate with the oxidation front.

1. Introduction

Polymer matrix composites (PMCs) used in aerospace high-temperature applications, such as turbine engines and engine-exhaust-washed structures, are known to have limited life due to environmental degradation. Evaluating the extended service life of composite structures subjected to mechanical loading, high temperature, moisture, and corrosive conditions is challenging [1,2] due to the complex physical, chemical, and thermo-mechanical mechanisms involved. While the time-dependent physical, chemical, and damage-induced degradation mechanisms have been studied for some resin systems, polymer composite thermal oxidation studies from a mechanistic perspective are nascent. Notable exceptions to this are the works of Colin and Verdu [3], Colin et al. [4], Tandon et al. [5], Tandon and Pochiraju [6] and Wang et al. [7]. Equally important are the experimental characterization efforts by such groups as Bowles and Nowak [8], Bowles et al. [9], Wong et al. [10], Tsotsis and Lee [11], Tsotsis et al. [12], Abdeljaoued [13], Bellenger et al. [14], and Whitley and Collins [15]. However, most literature is confined to thermal oxidation of unidirectional polymer systems and there are limited studies on laminated composite materials.

Nelson [16] was the first to document the anisotropy of oxidation in PMCs and that the oxidation process was sensitive to the surface area of the test specimens. He found that the dominant degradation mechanism for the graphite/polyimides was oxidation of the matrix at the laminate edges. Additionally, the materials degraded preferentially at the specimen surface perpendicular to the fiber (axial surface) and the rate of oxidation was hastened by microcracks opening on the axial surface increasing the surface area for oxidation. Subsequently, numerous other investigators (e.g., Bowles and Meyers [17], Bowles [18], Nam and Seferis [19], Salin and Seferis [20], Schoeppner et al. [21], and Tandon et al. [22]) also observed the anisotropic nature of oxidation in high-temperature unidirectional PMCs. In these composites, the diffusion-limited oxidation behavior is predominantly controlled by the properties of the resin and the fiber–matrix interface and the total surface area through which the oxygen can diffuse. Various factors such as resin cure shrinkage, localized micromechanical residual stresses in the fiber–matrix interphase region, and the presence of the sizing [23,24] can affect the local diffusivity and/or thermal oxidative stability. In addition, severe surface oxidation degradation results in the formation of fiber–matrix disbonds coalescing with transverse surface cracks. These cracks not only reduce strength, but also create enhanced pathways [25–30] for oxygen to penetrate deeper into the composite.

In laminated systems, interlaminar residual stresses (besides the fiber–matrix micromechanical stresses at the ply level) further play an important role in the degradation process. For example, Bowles et al. [9] observed greater weight loss in cross-ply PMR-15 laminates in comparison to unidirectional laminates because the free-edge cracks, resulting from interlaminar residual stresses, were much more prominent in cross-ply laminates causing

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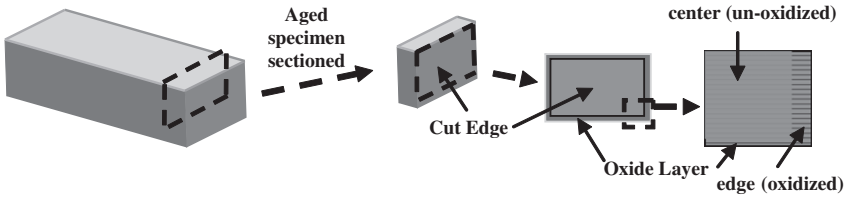

Fig. 1. Oxidation measurement procedures.

extensive advancement of oxidation into the interior of the composite. Similarly, Tsotsis and Lee [11] observed that residual stresses arising from aging-induced differential resin shrinkage and interaction between plies of different orientations were found to have a strong effect on the degradation process for plies close to the surface and, especially, near free edges in carbon fiber-reinforced epoxy composites. Recently, Lafarie-Frenot and Rouquie [31] and Rouquie et al. [32] performed thermal cycling tests on four different carbon/epoxy laminates: $[0]_8$, $[0_3/90_3]_S$, $[45_3/-45_3]_S$ and $[45/0/-45/90]_S$ in nitrogen and air. Microscopic observations and X-radiographs showed an acceleration of matrix cracking and matrix shrinkage due to coupling between oxidation and cyclic thermal stresses. Moreover, damage observations on the polished edges of the samples were highly dependent on the laminate stacking sequence. In their study of thermo-oxidative aging of multi-hole carbon/epoxy laminates, Ammar-Khodja et al. [33] have shown that oxidation and cracking progresses faster on the hole edges than on the mold surfaces resulting in damage of the multi-hole panels bulk, and greater diminution of the perforated laminate properties compared to the plain panels. Obviously, increasing the surface in contact with the aging environment leads to enhancement in oxygen action and resulting degradation. An analytical model has been developed by McManus and Chamis [25] that links matrix material degradation and shrinkage to the ply and laminate behavior that result. Using a coupled model [30,34] that tracks oxygen diffusion, oxidation reaction and mechanical behavior changes in the resin, a hierarchical modeling methodology has recently been developed by Tandon and Pochiraju [6] to simulate oxidation growth patterns in laminated composites. Oxidation simulations were performed for some selected lamina stacking sequences, and the oxidation growth profiles within individual plies and across the ply interfaces were correlated with experimental observations.

While these limited studies demonstrated coupling between material degradation [35,36] and damage development [25–30] associated with thermo-oxidation aging, very little work has been reported on quantifying the oxidation growth behavior in multidirectional laminated composite systems. In this work, we investigate the influence of laminate architecture, ply lay-up and the neighboring ply effects on oxidation growth within high-temperature PMCs. Light microscopy techniques are used to characterize the oxidative process in laminated carbon fiber-reinforced polyimide composites. Several different laminates are considered, namely, unidirectional $[0]_{16T}$, quasi-isotropic $[0/\pm45/90]_{2S}$, cross-ply $[0/90]_{4S}$ and angle-ply $[\pm45]_{2S}$ composites. The laminates were fabricated using unidirectional prepreg manufactured by Cytec following their recommended cure cycle. The nominal fiber volume fraction of the panels is 63%. Prior to aging, the panels were post-cured in air for 6 h at 227 °C. Isothermal aging was conducted at 177 °C. In addition to oxidation growth behavior, we also examine the oxidation-induced damage development and the associated coupling through fluorescence imaging using dye impregnation in conjunction with optical and scanning electron microscopy techniques. Oxidation and damage growth measurements are made as a function of ply orientation in both axial and transverse directions to illustrate the anisotropic oxidation process in composite laminates.

2. Isothermal aging and characterization of test specimens

Rectangular specimens measuring approximately 125 mm × 12.5 mm were used to monitor oxidation propagation and damage development in laminated composites. The isothermal aging was accomplished in an air-circulating oven that provided a continuous replenishment of oxygen in the ambient air by convection through the oven inlet. At specified sparse time intervals, specimens were removed from the ovens and samples were dry-sectioned from the aged larger specimen, potted in epoxy and polished as illustrated in Fig. 1. The cross-section was cut at a minimum of 6 mm from the exposed surface. This allowed monitoring of four of the exposed edges (left, right, top and bottom) in the interior of the large specimen. The remainder of the large sample was subsequently placed back in the oven to continue the aging process. Additional details on specimen handling, aging and vacuum impregnation procedure are included in Tandon et al. [22].

Dark-field microscopy was utilized to monitor the oxidation propagation in $[0]_{16T}$, $[0/\pm45/90]_{2S}$, $[0/90]_{4S}$ and $[\pm45]_{2S}$ composites. Note that each observation of extent of oxidation is for a unique cross section of the sample since the specimen preparation process, which includes sectioning, impregnating, and polishing specimens at each discrete aging time, precludes tracking oxidation growth on a unique cross-section. The oxidation layer formation near the exposed specimen edges changes the optical characteristics of the material, and the oxidized layer is observed by light microscopy. Specifically, the oxidation layer appears as a frame around the composite cross-section, and is clearly seen as the lighter oxidized material using standard light microscopy in the grayscale mode. Nanoindentation measurements have shown [37] that modulus changes occur mainly over the oxidized zone thickness (measured using optical microscopy), while the relative oxygen content is higher in the oxidized region, and reduces to the average value in the unoxidized region beyond the zone boundary. Thus, both nanoindentation and chemical mapping techniques have validated the extent of the oxidized region determined using optical methods. The dye-impregnated potted specimens were also viewed under fluorescent light to document the growth and development of damage.

Quantification of the oxidation growth and damage propagation history is complicated by the fact that the optical microscopy techniques utilized preclude tracking individual oxidation zones and cracks as a function of aging time. Each observation on a polished cross-section represents oxidation and damage growth measurements within a unique specimen cross-section. Alternately, X-ray micro Computed Tomography (CT) enables one to examine the details of the microstructure of a material in a non-destructive fashion. In a recent study [6], fluorescence and X-ray imaging of cracks were compared in a $[0/90]_{4S}$ laminate aged for 4996 h. There was a general agreement between the observed crack lengths, the crack distribution and the density of crack growth between the fluorescence and X-ray images (randomly selected from the interior of the laminate) demonstrating that the damage observations made on a polished discrete section are generally representative of the damage behavior inside the laminate. Similar comparisons, although not shown here, have also been observed