Composite Structures 134 (2015) 602–612

Contents lists available at ScienceDirect

Composite Structures

journal homepage: www.elsevier.com/locate/compstruct

Thermo-mechano-oxidative behavior at the ply's scale: The effect of oxidation on transverse cracking in carbon–epoxy composites

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ARTICLE INFO

Article history:
Available online 2 September 2015

Keywords:
Environmental degradation
Transverse cracking
Experimental testing
Finite fracture mechanics

ABSTRACT

The use of polymer matrix composites at relatively high temperatures (150–300°C) requires accounting for the oxidation of the polymer and its coupling with mechanical degradation. A vast body of literature investigates these phenomena at very small scales, from the chemistry of the polymer to the mechanical behavior at the fiber's scale. The aim of this work is to apprehend the effect of oxidation on the transverse composite properties directly at the ply's scale, and in particular to examine its effect on the evolution of transverse cracking during aging and mechanical loading. Experimental results demonstrated the appearance of a new cracking scenario with respect to unaged composites, and a model based on finite fracture mechanics enabled us to explore the competition between the two different mechanisms. This work is a first step towards a damage mesomodel which incorporates the effects of oxidation aging.

1. Introduction

In the last few decades, the use of polymer matrix composites in aeronautical applications has increased, due to their excellent specific properties. A further development of their use in civil aviation, and in particular in 'warm' areas of the aircraft (that is, at temperatures ranging between 150 °C and 300 °C), requires designers to account for their response to coupled environmental and mechanical loadings.

In this range of temperatures, oxygen diffuses within the composite and it reacts with the polymer matrix, leading to the appearance of a thin oxidized layer along the laminate's external surfaces. In this layer, oxidation causes local modifications of the physical and mechanical properties of the matrix and of the fiber/matrix interphase. All of these phenomena interact with the composite's microstructure and with the external mechanical loading in complex ways: in particular, oxidation-related and mechanical-related cracks can develop, thus providing further pathways for oxygen diffusion within the structure and leading to anisotropy of the oxidized/degraded zone. The characteristic times associated to these phenomena are generally long, thus an in-depth understanding of the coupled oxidation-cracking behavior is required to develop predictive structural models and to design representative accelerated experimental tests.

A number of literature studies explored the phenomena occurring during oxidation at very small scales, ranging from the bulk polymer chemistry to the composite at the fiber's scale. These works enabled the researchers to observe, to understand and to model the competition between diffusion and reaction in the definition of the thickness of the oxidized layer [1–3] as well as the link between oxidation and the modification of the polymer's mechanical properties [4–6]. Although the understanding of the physicochemical phenomena at these scales is quite rich, the transition towards the scales of the ply and of the laminate is still not completely achieved [7]. The main difficulty resides in the characterization and the modeling of the interphase between fibers and matrix, which appears as a preferred zone for oxygen diffusion and crack creation [8], but which is extremely difficult to characterize since it cannot be isolated from the other constituents. Structural scale studies on the effect of oxidation, on the other hand, often focus on the application of standard test methods on oxidized specimens [9,10]: this gives access to the global loss of properties associated to a given aging protocol, however this information can hardly be extrapolated to different aging conditions and durations, since the evolution of the different mechanisms leading to failure is not analyzed.

An alternative approach, proposed in this work, is to apprehend the effect of oxidation on the mechanical behavior directly at the

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http://dx.doi.org/10.1016/j.compstruct.2015.08.103
0263-8223/

ply's scale. This is the characteristic scale of a number of models which have been successfully used for the simulation of the mechanical degradation of composite structures (see [11–17] for a few examples). However, it is rarely chosen as the scale of observation when oxidation phenomena are involved; an exception, albeit different from the present work, is [18]. Here, the ply's scale was chosen as the pertinent scale of observation, since the ultimate aim of this work is to introduce the effects of oxidation on the mesoscale modeling strategy developed at the LMT-Cachan [11,16]. A first, promising example of the integration of the effect of oxidation into a ply-scale, micromechanical modeling strategy is given in [19].

For the relatively short aging durations considered in this study, oxidation essentially affects a thin layer along the laminate's external surfaces, therefore only the behavior of the external plies is modified with respect to unaged specimens. Since the fibers' properties are not affected by aging at these temperatures, we chose here to focus on the effect of oxidation on the transverse behavior of the elementary ply and, in particular, on the kinetics of transverse matrix cracking. To this aim, an experimental investigation was carried out on aged and unaged $[90/0]_s$ specimens, where the 0° direction corresponds to the direction of the mechanical loading. Both global and local experimental indicators enabled us to gather information on the evolution of the degradation of the external 90° plies due to oxidation and subsequent mechanical loading. The kinetics of transverse cracking was shown to be significantly modified by oxidation, and high levels of oxidation even led to the appearance of two different cracking scenarios.

A finite fracture mechanics approach was then developed, based on the information available at smaller scales and on some pragmatic assumptions, which enabled us to explain the appearance of the two different cracking scenarios and to describe their competition in the development of the kinetics of transverse cracking. A comprehensive understanding and modeling of the physical phenomena occurring during oxidation and mechanical loading is essential for the construction of a physical-based mesoscale model, which can then be used to predict the behavior of more complex stacking sequences.

The experimental study and the associated results are presented in Section 2. The model construction and its use for the interpretation of the different cracking scenarios is presented in Section 3. Finally, some conclusions and perspectives are given in Section 4.

2. Experimental investigation of the transverse behavior of aged composite specimens

The experimental study presented here was designed to investigate the transverse behavior of an elementary ply exposed to environmental and mechanical loadings. For the short aging durations considered in this study, only the external plies are affected by oxidation. For this reason, different experimental methods were used in order to access both global and local indicators of the evolution of their degradation.

A first key point is the choice of the specimens' stacking sequence. Since the aim is to characterize the transverse behavior of the external, oxidized plies, a $[90/0]_s$ laminate was considered, where the 0° direction corresponds to the direction of the mechanical loading. The laminate's thickness is small in order to amplify the role of the oxidized layer on the overall response. A previous work [18] considered the evolution of transverse cracking of oxidized $[0_n/90_m]_s$ specimens: in that case, the transverse 90° plies were only oxidized along their edges, while in the present case a thin oxidized-degraded layer developed along the whole external surface of the transverse plies.

After oxidation, the specimens were subjected to different tests. Some specimens were observed under an optical microscope in order to evaluate the thickness of the oxidized-degraded zone and to detect the eventual presence of transverse cracks prior to mechanical testing. Free vibration tests in a bending configuration were used as a non destructive way to assess the variation of stiffness in the external layers. The same specimens were then loaded in tension and the kinetics of transverse cracking in the surface plies was characterized by Digital Image Correlation (DIC).

2.1. Material specimens and aging protocol

This study was carried out within the framework of the joint academic and industrial project Comptinn. A carbon–epoxy unidirectional tape was considered (see Ref. [20] for more details on the material system). The composite plates were manufactured by Airbus Group Innovation. The average ply thickness as measured on the manufactured plates was 0.14 mm.

Two types of specimens were extracted from the plates: $20 \times 20\ \text{mm}^2$ specimens were cut from the $[90/0]_s$ plate and from a unidirectional $[0]_8$ plate and used for optical microscopy observations of the oxidized/degraded layer, while $180 \times 20\ \text{mm}^2$ specimens were cut from the $[90/0]_s$ plate and used to characterize the transverse behavior of the oxidized layer via free vibration and tensile tests.

All of the specimens were dried in an oven at 70 °C for 7 days, then they were aged for 0, 1, 3 and 6 weeks at 180 °C under dry air. At the end of the aging period and prior to testing, they were kept in a vacuum desiccator in order to prevent water absorption. Composite tabs, whose dimensions were $40 \times 20\ \text{mm}^2$, were manufactured and bonded to the ends of the $180 \times 20\ \text{mm}^2$ specimens, leaving 100 mm of gage length.

2.2. Microscopic observations of the oxidized/degraded layer

After aging, the $20 \times 20\ \text{mm}^2$ specimens were cut in order to reveal the internal surfaces. They were embedded in acrylic resin for polishing and optical microscopy observations. The polishing protocol was similar to the one proposed by Vu et al. [21].

Optical microscopy observations were carried out in both light-field and dark-field modes. The light field enabled us to observe the details of the specimen section, while the dark field highlighted the oxidized/degraded region: indeed, this region is generally more textured due to the embrittlement of the matrix and of the fiber/matrix interphase, which leads to degradation of the surface state during polishing. As an example, the external surface of a 90° ply in a specimen aged for 6 weeks observed in both light-field and dark-field modes is given in Fig. 1.

The dark-field observations provide an indication of the presence of an oxidized/degraded zone on the surface of the specimen, however they do not give any quantitative information on the oxidation level as a function of depth. Nevertheless, they enabled us to observe the anisotropic nature of the propagation of the oxidized/degraded zone: at 6 weeks of aging, its average thickness was evaluated at 33 μm from the surface parallel to the fibers' direction and at 315 μm from the surface perpendicular to the fibers' direction. While surfaces perpendicular to the fibers' directions and exposed to the environment can only be found on the specimens' edges, the two faces of the specimen are parallel to the fibers' direction, and thus the whole of the external plies is impacted by the presence of a fine oxidized/degraded layer.

The light-field observations of the specimens aged for 6 weeks, furthermore, revealed the presence of multiple cracks traversing a small portion of the external 90° ply (see Fig. 2). These cracks, which will be called 'partial cracks' hereafter, developed in the