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Material properties

The effect of thermo-oxidation on the mechanical behaviour of polymer epoxy materials

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ABSTRACT

This paper focuses on the employment of instrumented Ultra-Micro Indentation (UMI) and Confocal Interferometric Microscopy (CIM) for investigating the effect of thermo-oxidation on the local mechanical behaviour of two polymer materials. The UMI curves give good indication of the local short-time behaviour, while the CIM observation of the indentation prints and their recovery during time provides some information about the long-time behaviour. For both studied epoxy resins, this experimental approach reveals significant modification of the local mechanical behaviour with oxidation level.

1. Introduction

In aeronautics, the field of application of carbon fibre reinforced polymers (CFRP) is still increasing, due to their excellent specific properties and fatigue resistance. Specifically, the use of organic matrix composites (OMCs) is now considered for “warm” structural components, since they can withstand temperatures higher than 100 °C, but lower than their glass transition temperature. In such applications, polymer matrix composites are known to have limited life due to environmental degradation that results from complex interaction of time-dependent mechanical behaviour (creep and relaxation processes), temperature-dependent chemical degradation and thermo-oxidation. Evaluation of long-term durability of polymer matrix composites in “high” temperature environments requires deep understanding of the degradation phenomena occurring at these temperatures.

An experimental study of C/epoxy laminates subjected to thermal cycling (−50 °C/180 °C) under neutral (nitrogen) or oxidant (air or oxygen) environment has clearly demonstrated the significant role of thermal oxidation in the damage development of OMCs [1]. Other important contributions are provided by [2,3], showing that, during isothermal ageing, oxidation and damage growth are also influenced by the laminate lay-up. All damage in a composite lamina (thus at a “macroscopic” scale) is anticipated by degradation processes which have a tendency to develop at a very local scale (micrometric scale or lower), since the degradation mechanisms concern the macromolecular structure [4]. For instance, at a very local scale, matrix shrinkage and fibre/matrix debonding have been observed by Vu et al. [5] on the surfaces of aged epoxy matrix composites. Even at this local scale, composite degradation mechanisms are driven by the thermo-oxidative affected behaviour of three main items: carbon fibres, fibre/matrix interphase (/interface) and polymer matrix.

At “warm” temperatures – typically between 100 °C and the polymer glass transition temperature – the polymer matrix and the fibre/matrix interphase are affected by thermo-oxidative phenomena and a careful analysis of these elements is necessary. From a chemical point of view, some works [6,7] have pointed out that carbon atoms can

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have a stabilizing effect on polymer matrix ageing. Meanwhile, the fibre/matrix interphase seems to be a privileged path for oxygen diffusion by accelerating its penetration along the fibre direction [2,3,8,9]. However, some points, such as the effect of the fibre nature and of the fibre/matrix interphase on the thermo-oxidation (and degradation) mechanisms, need to be explored in more detail. A correct interpretation of all these unresolved questions requires a deeper analysis of the polymer matrix thermo-oxidative affected behaviour, since it is the heart of the chemical reactions. A model of polymer oxidation is a crucial issue as it represents the first element in modelling the composite oxidation-induced degradation (see for instance the architecture of the composite simulation framework proposed by Pochiraju and Tandon [9]).

Several studies have been carried out to properly model the various physical and chemical aspects of polymer degradation [10–15]. Isothermal ageing in oxidizing environments results in the growth of a thermo-oxidative layer [4,10–12,15] – developed over a length of few microns starting from the directly exposed surfaces to the core (less affected by oxygen reaction-diffusion) – and the elastic moduli change [11,16]. In the oxidized layer, material embrittlement is mainly due to modifications of atomic structure [4] (typically by chain scission) and leads to a local variation of density and mass [4,11,17]. This causes shrinkage strains in the oxidized layer, associated with tensile stresses, which can induce cracks [9,12,14,17]. Crack surfaces become new free surfaces directly exposed to the environment and, therefore, accelerate the oxidized layer growth [9,12,17].

Finally, an important remark concerns the use of oxygen pressure as an accelerating parameter. The effectiveness of pressure as an accelerating parameter of thermo-oxidation has been studied in [5,18–23], both at the lamina/laminate [18,19,22] and at the microscopic scale [5]: in particular, in [5], it has been demonstrated that “moderate” pressure values (around 2 bars) are appropriate for accelerating the thermo-oxidation phenomena without inducing additional parasite degradation mechanisms.

In order to model the amine crosslinked epoxy and bismaleimide degradation mechanisms, a mechanistic model, predicting the oxidized layer growth, has been proposed by [4]. At the same time, studying three resin systems (PMR-15, BMI and AFR-PE/4), Pochiraju and coworkers [9–11] have experimentally shown the interaction between damage and thickness of the oxidized layer, proposing a phenomenological damage/oxidation coupled model. Both models accurately predicted the regular increase of the oxidized layer thickness and the specimen weight evolution during isothermal ageing, without giving an exact link between the chemistry of oxidation reactions and mechanical polymer properties evolution. Some effort in this direction has been tackled in [16], in which a phenomenological law relating the elastic modulus changes to the concentration of oxidation products - resulting from the mechanistic model – has been proposed. Establishing a full link between the chemical processes taking place during thermo-oxidative diffusion-reaction and the material/structure properties is a complex issue which has never been completed.

In an oxidized specimen, the mechanical properties are functions of the distance from the exposed surface and the ageing duration [16,24]. Property gradients are located in a few microns starting from the exposed surface, depending on the oxidized layer thickness, which underlines the clearly local nature of the phenomenon. In such situations, classical tests – such as uniaxial traction/compression or DMA tests on “macroscopic” samples – are not conclusive.

On the other hand, local tests – such as Ultra-Micro Indentation (UMI) - can be successfully employed: by UMI, the matter can be tested locally, with low scatter, allowing the measurement of material inhomogeneities and property gradients. Significant research has been carried out with the purpose of modelling the polymer behaviour at this local scale by instrumented UMI tests. Depending on the studied polymer nature, many elastic-viscoplastic or viscoelastic numerical models [25–33] have been proposed. Moreover, in Olivier et al. [16] the UMI test has been used to evaluate the thickness of the oxidized layer from the measurements of the local indentation elastic modulus (EIT), suggesting that this tool is sensitive to the local mechanical properties variation engendered by thermal oxidation.

Summarizing the discussion, modelling the composite oxidative-induced degradation requires first a model of the matrix thermo-oxidative affected behaviour. Since material properties evolve during oxidation and along the specimen thickness, local tests must be used. In this regard, UMI test have already been used to develop local polymer models and to follow the elastic properties changes promoted by thermal oxidation. Therefore, in this way, a local polymer constitutive law – taking into account the thermo-oxidative inducted properties variation – can be effectively developed. However, some points in this research field need to be further explored. Firstly, numerical models are usually elaborated taking into account the load–displacement relationship only, which could be a great simplification due to the complex strain field produced by the indentation test. Then, polymers are time-dependent materials, hence viscous behaviour has to be considered also: a correct study must be founded on the observation of the material relaxation phenomena at short as well as at long timescales.

With this aim, Confocal Interferometric Microscopy (CIM) can be employed: by using this tool a high precision measure of the specimen surface (in this case the indentation surface) can be performed and a measurement of the indentation print recovery with time over the large timescales can then be carried out.

This paper presents a novel experimental technique indicating the thermal oxidation effects on the polymer mechanical behaviour at a local scale, where oxidation phenomena occur. The experimental approach aims at characterizing the time-dependent mechanical behaviour of virgin and aged epoxy polymers and is based on instrumented ultra-micro indentation and confocal interferometric microscopy tests:

- the UMI load vs. displacement curve is exploited to gain some information about the short-range timescales,