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# Experimental and numerical analyses of matrix shrinkage and compressive behavior of 3-D braided composite under thermo-oxidative ageing conditions

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ABSTRACT

Matrix shrinkage induced in thermo-oxidative ageing process of composites may lead to interfacial damage and thus significantly affect their mechanical properties. This work aims to characterize the oxidation-induced matrix shrinkage in three-dimensional (3-D) braided composite. Specimens were exposed at hot air (180 °C) for 4, 8, and 16 days respectively. Interferometric microscope was employed to determine the matrix shrinkage in composite surface under different ageing conditions. The resulting interfacial damage was observed by optical microscopic examination. Based on the experimental results, we propose a two-step numerical methodology to investigate the effect of thermo-oxidative ageing on compressive properties of braided composite. The established finite element model can effectively capture the deformed and degraded configuration of the aged material. Further simulation results reveal that the shrinkage-induced interfacial damage leads to a lower stress distribution in the exposed ends of braiding yarns. The ultimate deterioration in compressive properties of braided composite is attributed to both resin degradation and yarn-matrix interfacial damage.

## 1. Introduction

Three-dimensional (3-D) braided composite, due to its excellent through-thickness properties, high damage tolerance and outstanding designability, has been widely used in high temperature aerospace applications. For effective parts design of braided composites, the mechanism of property degradation induced in thermo-oxidative ageing environments is a critical issue.

The effects of thermo-oxidative ageing on polymers and polymer matrix composites have been investigated under different conditions [1–5]. Elevated temperature can efficiently accelerate the ageing process [6,7]. At the meantime, polymer matrix composites have shown to be dramatically sensitive to chemical degradation in presence of oxygen. Pochiraju et al. [3] even found that chemical and oxidative ageing was the primary life-limiting degradation process for high-temperature polymer matrix composites. It has been successfully proven that the oxygen pressure could be considered as a pertinent accelerating parameter for thermo-oxidative degradation [8–12].

Since carbon fibers are reasonably inert to oxidation at intermediate temperatures (at least below 200 °C), the thermo-oxidation of carbon fiber reinforced plastics (CFRP) can be generally interpreted by the polymer degradation [13]. Thermo-oxidative reaction within the polymer material promotes chain scission of the polymer system, accompanied with a departure of low-molecule volatiles. Both processes contribute to a density increase and a weight loss, then chemical shrinkage ensues [14,15]. It has been clearly demonstrated that oxidation is restricted to a superficial layer (few hundreds of microns, depending on the material) owing to its kinetic control by oxygen diffusion [16]. The generated oxidized layer effectively functions as a passive layer, arresting the diffusion of oxygen and protecting the polymer materials from further oxidation [17]. As a consequence, property gradients are located within the oxidative areas, and local tests – such as ultra-micro indentation (UMI) – have been successfully employed to estimate the material inhomogeneity and property gradients [3,18–20].

In the case of composites, material degradation can be expected to initiate from the embrittlement of superficial matrix layer. As the oxidized matrix strongly sticks to the non-degraded yarns, the resulting 'hindered' shrinkage induces a tensile stress within fiber-matrix interfacial phase. The stress accumulates and eventually generates interfacial cracks [21]. These cracks evolving in the oxidized regions exacerbate the thermo-oxidation by providing additional surfaces for

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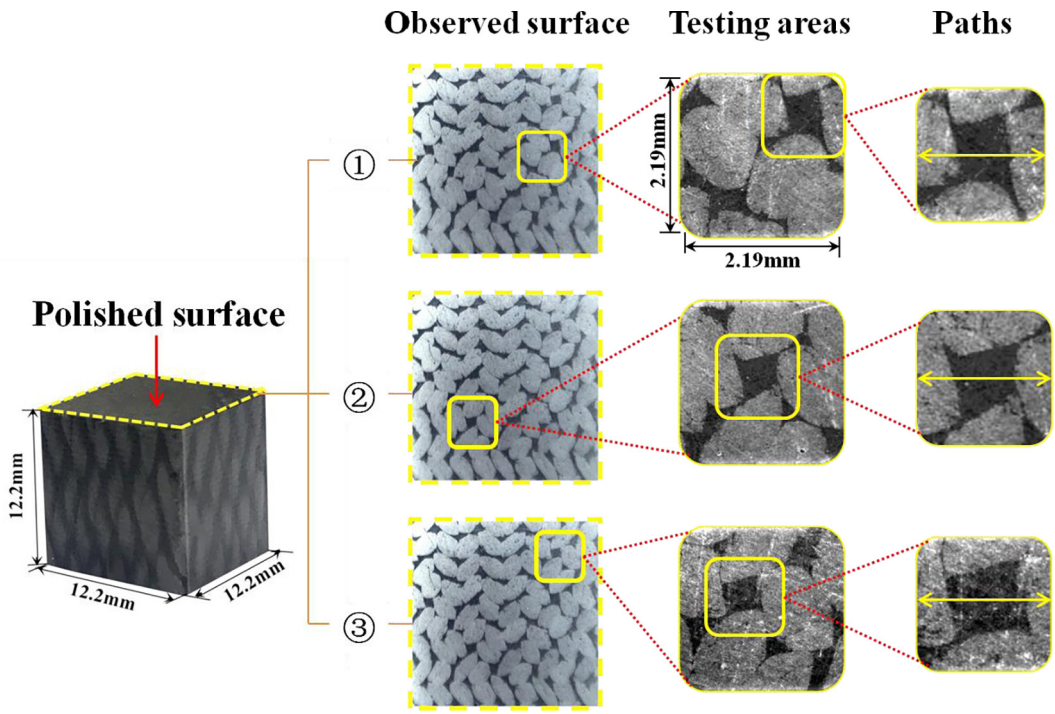


**Fig. 1.** 3-D braided composite specimen and the polished surface. Three areas of 2.19 × 2.19 mm were selected for microscopic observation.

oxygen diffusion. Therefore thermal oxidation growth and damage evolution are highly coupled [22]. Based on a positive correlation between crack initiation time and transverse failure strength, Liang and Pochiraju [23] proposed a methodology to determine the transverse failure strength of the oxidized regions. The mean transverse strength estimate can be quite useful for long-term life prediction of laminated composites. Moreover, the fiber/matrix interfacial layers contribute to preferred oxidation directions, hence architectural structures – such as fiber orientation [24], percentage of fiber end area [25], laminate lay-up [13,26], and three-dimensional structures [27,28] – will strongly affect the thermo-oxidative behavior of polymer composites.

In that context, the assessment of matrix shrinkage is a crucial issue as it represents the most important part in the oxidation-induced composite degradation. Gigliotti and co-workers [29–31] proved the interferometric microscopy was an effective experimental method to determine the thermo-oxidative induced chemical strain in composite surface. Colin et al. [32,33] proposed a coupled diffusion-reaction model for predicting the behavior of an epoxy-amine network when exposed to thermo-oxidative ageing. The model was developed by Tandon et al. [14,34,35] and currently it has been successfully applied to determine oxygen-concentration profiles and the thickness of oxidized matrix layer [12,36]. Furthermore, the applications of finite element analysis (FEA) on the predictive calculations of thermo-oxidation are also documented [3,21,37].

Following previous research work [38], in this paper, we propose a specific experimental/numerical protocol to characterize the thermo-oxidative degradation of 3-D braided composite. The focus lies on the assessment of oxidation-induced shrinkage and its effect on compressive behavior of braided composite. Here we use Interferometric Microtechnique to determine the matrix shrinkage in composite surface. More details and results will be presented in a first part. In a second part, based on the experimental results, we propose a two-step numerical methodology to illustrate matrix shrinkage and the consequent interfacial damage. The results obtained from both experimental and numerical, for different ageing conditions, will be presented and discussed.

## 2. Experimental

Based on our previous micro-FTIR analysis [6], oxidation was found in the exposed surface of materials. The surface oxidation facilitates chain scission and embrittlement of the resin system, accompanied with the generation of various oxidation products. The departure of some low-molecule volatiles contributes to a density increase and a weight loss. Both processes will induce chemical shrinkage within the skin layer of matrix. This oxidation-induced matrix shrinkage leads to the initiation of yarn-matrix debonding and thus accelerates material degradation. In this section, we report a micro-technique, i.e., interferometric microscopy, to measure the matrix shrinkage. The materials, ageing treatment process, and relevant characterization techniques are also reviewed.

### 2.1. Materials preparation and ageing

The material employed for this study was 3-D carbon fiber/epoxy braided composite. Carbon fiber was T700S-12K supplied by Toray Inc. (Japan) and the braided fabric was prepared with a four-step braiding technique. Epoxy resin (JA-02-type from Jiafa Chemical Inc., China) was injected into the preform with vacuum assisted resin transfer molding (VARTM) technique. Curing process was 90 °C/2hrs + 110 °C/1hr + 130 °C/4hrs. Then the composite was cut into testing coupons in size of 12.2 × 12.2 × 12.2 mm as shown in Fig. 1. The cut surfaces were polished to minimize initial mechanical damage.

Many literatures have demonstrated that matrix shrinkage is resulted from thermo-oxidative rather than other sources of degradation. The observations and measurements by Schoeppner [24] and Lafarie-Frenot [39] showed that matrix shrinkage was closely related to the presence of oxygen. The SEM micrographs in both non-oxidized and oxidized regions indicated that the matrix shrinkage only occurred in oxidative environment. Such phenomenon was not found when the ageing tests were performed in nitrogen or vacuum. Moreover, Vu [29] and Gigliotti [30] pointed out that matrix shrinkage development could be conveniently accelerated by increasing the oxygen pressure. All these findings can be regarded as evidences that matrix shrinkage is only caused by thermo-oxidation. Therefore, in the present work,