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Accelerated thermal ageing of epoxy resin and 3-D carbon fiber/epoxy braided composites

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ABSTRACT

This paper reports the accelerated thermal ageing behaviors of pure epoxy resin and 3-D carbon fiber/epoxy braided composites. Specimens have been aged in air at 90 °C, 110 °C, 120 °C, 130 °C and 180 °C. Microscopy observations and attenuated total reflectance Fourier transform infrared spectrometry analyses revealed that the epoxy resin oxidative degradation only occurred within the surface regions. The surface oxidized layer protects inner resin from further oxidation. Both the resin degradation and resin stiffening caused by post-curing effects will influence the compression behaviors. For the braided composite, the matrix ageing is the main ageing mode at temperatures lower than glass transition temperatures (T_g) of the pure epoxy resin, while the fiber/matrix interface debonding could be observed at the temperatures higher than T_g, such as the temperature of 180 °C. The combination of matrix degradation and fiber/resin interface cracking leads to the continuous reduction of compressive behaviors.

1. Introduction

In the design of the new generation of aircraft structures, three-dimensional (3-D) braided composite is currently widely used due to its excellent through-thickness properties, high damage tolerance and fatigue resistance [1]. The aerospace applications require a long service life of materials, in particularly in harsh environments (temperature, oxidizing environment, etc.). Hence, the effects of thermal ageing on the mechanical properties of the 3-D braided composites are considered vitally important for aircraft design.

Currently, the studies have mainly concentrated on characterizing degradation and damage initiation. Tsotsis [2–5] found that the weight loss during thermo-gravimetric test could not be used as criteria for material acceptance. The properties' changes, such as mechanical properties [6–12], physical properties [13], thermal conductivity [14] and the development of microcracks [15–17] caused by thermal treatment have been extensively studied and documented. Compared with isothermal ageing, thermal cycling can accelerate the damage processes and especially the matrix crack propagation from the surfaces to the core of the laminate [18].

It was found that there are two step changes in the mechanical properties under thermal ageing [19]. In the first consolidation stage, owing to the post-curing reaction, there are improvements in the mechanical properties. In the second degradation stage, the mechanical properties decreased significantly. For pure epoxy, the thermo-oxidative ageing can be characterized by three phases [20]. The first phase is dominated by the polymer viscoelastic behavior and by stress relaxation at high temperature. The second phase is characterized by thermo-oxidative matrix shrinkage and change of the instantaneous matrix elastic modulus with time. The third phase is attributed to the development of microcracks.

In the thermal degradation of composite materials, the oxygen pressure is an accelerating factor [21–23]. The thermal ageing process was controlled by the oxygen diffusion and the thickness of oxidized layer [24–26]. Instrumented ultra-micro indentation was used to characterize the mechanical property of an oxidized epoxy polymer. And the experimental measures agreed well with the predicted values of an oxidation model [27,28].

The degradation mechanism also strongly depends on the specimen geometry and anisotropy [29,30]. Nam and Seferis [31] found that the property degradation was significantly dependent on the fiber orientation pertaining to the composite anisotropy. The work of Mlyniec et al. [32], similarly, concluded that the alignment of the reinforcing fibers would affect long term damping performance of the carbon/epoxy composites. Stability of the modal damping of unidirectional carbon/epoxy laminates is affected mainly by the properties of the fiber–matrix interface, while the quasi-isotropic laminates depends mainly on long-term properties of the matrix. Surfaces with different microstructural characteristics, on the

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other hand, could be expected to exhibit different oxidation behavior [11,33].

The degradation is often investigated under accelerated conditions at elevated temperatures. As described above, the mechanical properties of composite are more dependent on the matrix and thus more sensitive to thermal ageing. In this paper, both pure epoxy resin and three-dimensional carbon/epoxy braided composites were exposed to an isothermal high-temperature environment. Their micro-morphologies and compressive behaviors after thermal ageing were presented. From the experimental results, we also investigated the influence of the temperature on the thermal ageing mechanisms.

2. Experimental

2.1. Materials and specimens

The materials used in this study were T700S-12K carbon fiber supplied by Toray Inc. (Japan) and JA-02 epoxy resin supplied by Changshu Jiafa Chemical Inc. (China). The 3-D braided preform (shown in Fig. 1) with square cross section of 11 × 11 braiding yarn arrays, was manufactured with a four-step 1 × 1 braiding technique. Epoxy resin was injected into the braided preform with vacuum assisted resin transfer molding (VARTM) technique. Curing process followed a stepwise program of 90 °C for 2 h, 110 °C for 1 h, and 130 °C for 4 h. For comparison, an epoxy cube was also prepared at the same conditions. Ageing is not considered during curing process. The surface braiding angle for the braided composite is 20°. The fiber volume fraction is 38%. The braided composite was cut into about 12.2 mm along longitudinal direction which equals to the size of the braided cross section, i.e., the size of the braided composite cube is 12.2 mm × 12.2 mm × 12.2 mm. The epoxy cube has the same size with the braided composite coupon.

2.2. Thermal ageing

The isothermal ageing was accomplished in an air-circulating oven which provided a continuous replenishment of oxygen in the ambient air. The glass transition temperatures (T_g) of pure epoxy resin and the 3-D braided composite, measured by the dynamic mechanical analyses (DMA), were equal to 110 °C and 130 °C, respectively. Based on the values of T_g, five temperature points (90 °C, 110 °C, 120 °C, 130 °C, and 180 °C) were selected to explore the temperature effects on thermal ageing. Before ageing, all specimens were dried in oven at 80 °C for 1 h. Moisture effects were not considered in this study. With a short drying time and low temperature, ageing can be ignored during the drying process. Then all testing coupons were isothermally aged at prescribed temperatures for 1, 2, 4, 8, and 16 days. At specified time intervals, specimens were removed from the oven and cooled down to ambient temperature.

2.3. Characterization

2.3.1. Microscopy observation

Optical microscopy was used to observe the morphology of epoxy cube aged at different ageing conditions. A thin layer of the specimen, as shown in Fig. 2, was taken out for micro examination. The color change observed in the micrographs illustrated the formation of the oxidized surface layer. The damage generated on the free surfaces of the composites was observed with scanning electron microscopy (SEM). At a microscopic scale, matrix shrinkage and fiber–matrix debonding were observed to illustrate the thermal aging effect on composite coupons.

2.3.2. ATR-FTIR spectroscopy

To explore the chemical ageing effects, especially the thermal-oxidation reaction, microscope-infrared spectroscopy (Micro-FTIR) analysis was conducted on the epoxy cube with a Nicolet 6700 FTIR spectrometer. Both the surface and the center of each specimen were tested and analyzed.

2.3.3. Compression test

To investigate the effect of thermal ageing on mechanical behaviors, compression tests were conducted on both epoxy cube and composite coupons at different stages of ageing. The tests were performed on MTS 810 material test system at room temperature (20 °C). The compressive speed was set as 2 mm/min. Each test was duplicated three times and the average compressive behaviors were obtained. Note that the loading mode for the braided composites was out-of-plane compression, as shown in Fig. 3.

The specimen deformation, which was considered equal to the displacement of load cell, was recorded during the compression tests. A built-in loading sensor of MTS tester was used to measure the compressive load. The engineering stress–strain curve could be derived from these measurements. Compressive properties such as modulus, strength and yield strength were obtained to investigate the change of compressive behaviors after ageing.

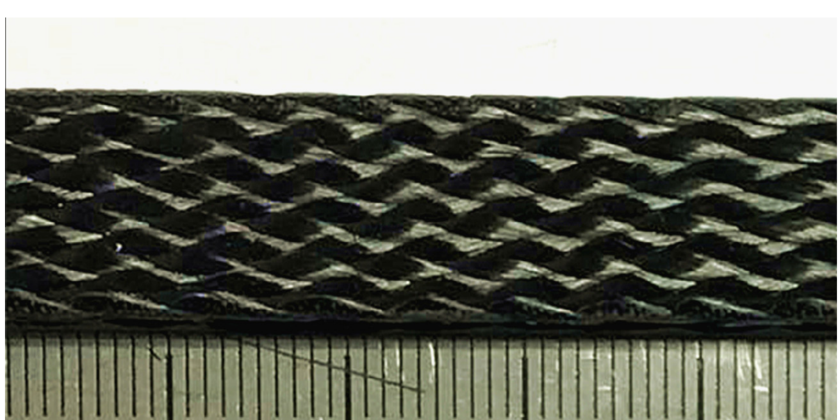

Fig. 1. 3-D carbon fiber rectangular braided preform in 11 × 11 arrays. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)