The Manufacture, Characterization and Aging of Novel High Temperature Carbon Fibre Composites.

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To Dr. David Brian Fox

Statement of Originality

The PhD research program has been conducted under the principal supervision of Dr. Adrian Lowe (ANU, Department of Engineering) and Dr. Jonathan Hodgkin (CSIRO, Division of Molecular Science).

I declare that the work presented in this thesis is to my belief original, except as acknowledged in the text, and that the material has not been submitted either in whole or in part, for a degree at this or any other university.

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ABSTRACT

High temperature composite materials used in aerospace applications are exposed to extremely harsh conditions and must be able to withstand moisture and extremes of temperature. For example, the surface of an aircraft flying at Mach 2.4 has been estimated to reach around 177°C as a result of aerodynamic heating. This thesis has examined the effect of isothermal aging on two high temperature composite materials, a novel CSIRO composite and a commercial composite, both based on bismaleimides. Changes in mechanical properties and resin chemistry at two different temperatures were measured in order to assess the validity of accelerated aging tests.

Delamination is a major cause of failure in materials, therefore, the Mode I interlaminar fracture toughness (G_{IC}) of both materials was measured using the double cantilever beam (DCB) test. After aging at 250°C, the CSIRO CBR 320/328 composites exhibited better retention of G_{IC} than the CIBA GEIGY Matrimid® 5292 composites. After 6 weeks of aging at this temperature, the CBR 320/328 material retained 100% of its initial interlaminar fracture toughness, however the Matrimid® 5292 material retained only 64% of its initial G_{IC}. This trend was reversed at the lower aging temperature, when after 30 weeks of aging at 204°C, G_{IC} was measured at 13% of its original value for the CSIRO composites, whereas it was measured at 64% in the case of the Matrimid® composites. When the fracture surfaces of these specimens were examined using scanning electron microscopy (SEM), the commercial material was observed to show an increasing degree of porosity with aging at 204°C. It was concluded that the good property retention at the temperature, despite this observed porosity, was a result of the excellent fibre/matrix adhesion exhibited by this material.

Chemical degradation of the matrix of the composites was monitored by Fourier Transform Infrared (FTIR) and Raman Spectroscopy. Chemical changes at the core of both of these materials were found to occur concurrently with the observed changes in interlaminar fracture toughness. FTIR analysis of both matrix materials revealed the predominant degradation mechanism to be oxidation, specifically the oxidation of the methylene group bridging two aromatic rings common to the structure of both resins, was substantiated by the ingrowth of a broad peak centred at 1600cm^{-1}. In addition to this, the pyromellitic anhydride unit present only in the CBR 320/328 composites was found to be highly resistant to the effects of aging, whereas the saturated imide, common to the cured structures of both materials, was observed to degrade.

Raman spectroscopy showed an increase in the intensity of a peak at 1646 cm^{-1} in the Matrimid® 5292 composites aged at 250°C towards the centre of the sample as a result of increased reaction of the allylic carbon-carbon double bond. At 204°C, the degree of reaction increased towards the surface of the material, possibly as a result of a reverse Diels-Alder reaction. The glass transition temperatures of both materials were found to decrease with aging, with the exception of the CSR 320/328 composites aged at 204°C, which initially increased due to continued crosslinking of the resin.

It is concluded that the degradation mechanisms at the two aging temperatures are very different. The reliability of results from accelerated (elevated temperature) aging tests has been drawn into doubt.

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