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Degradation behavior of glass fiber reinforced cyanate ester composites under hydrothermal ageing

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ABSTRACT

This work investigates the effect of hydrothermal ageing on the mechanical and thermo-mechanical properties of glass fiber reinforced cyanate ester composites. A large test campaign was realized to this direction. Coupons from in-house autoclave manufactured plates were immersed in distilled water at four different temperatures 40, 60, 75 and 90 °C for up to 61 days. Moisture absorption measurements followed by dynamic mechanical analysis as well as a series of mechanical tests were conducted at regular intervals during the ageing process. In addition, scanning electron microscopy was utilized in order to identify the exact degradation mechanisms that are active and dominant in the different ageing scenarios. The analysis of the results outlines the degradation behavior of the material properties and the accelerating effect of temperature elevation on the activation and acceleration of certain degradation mechanisms. Based on the existing literature this is probably the first thorough experimental study regarding the hydrothermal ageing of cyanate ester glass fiber reinforced composites.

1. Introduction

Cyanate esters (CEs) form a family of thermosetting resins whose performance characteristics, make them attractive competitors to many current commercial polymer materials for many applications. CEs are characterized by many attractive physical, electrical, thermal and processing properties required of an ideal matrix resin. Moreover, they generally exhibit high glass transition temperature (Tg), good fracture toughness, excellent substrate adhesion, low shrinkage, low dielectric loss and low moisture uptake [1]. Their high temperature service ceiling (due to their high Tg) and low shrinkage render CEs an excellent candidate for lightweight composite rocket nozzles and other high temperature applications in aerospace and elsewhere [2,3]. The low out-gassing, microcracking properties, and resistance to ionizing radiation and thermal cycling make them suited for satellite applications. The minimal dimensional changes during thermal cycling, good long term stability, self adherent properties to honeycomb and foam cores, good electrical properties, and high service temperature are the key advantages of CEs over state-of-the-art epoxy resins [4,5]. Generally, this type of thermoset resin encompasses the process ability of epoxy resins, thermal characteristics of bismaleimides and heat and fire resistance of phenolic resins.

In a wide range of applications, CEs are utilized as the matrix system for the development of composite materials. The conventional composite processing techniques including prepregging [6,7], filament winding [8] and sheet molding [9] are applicable to cyanate systems. Curing of cyanate ester is catalyzed by heat or a combination of heat and catalyst [1].

Although CE systems absorb significantly less moisture than epoxies do, the time to blister is less than that of epoxy and they are prone to undergo hydrolysis-mediated degradation. Kasehagen et al. [10] consider that hydrolysis lowers the Tg and pressure from either vaporized water or products of the hydrolysis reaction can expand to form a blister. This suggests that blistering is caused by hydrolysis which produces gaseous products. Studies have shown the presence of phenols, carbon dioxide and cyanuric acid as hydrolysis products [11].

Prolonged exposure in moisture, resulted in extensive matrix microcracking and moisture gain, leading to interface degradation, delamination and intralaminar cracking in the ply [12].

Marella et al. [13] link the environmental moisture conditioning time to phenol formation and Tg reduction due to hydrolytic degradation for a cyanate ester resin system exposed to moisture at 100 °C.Yeh et al. [14] report water uptake, hydrolysis

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and Tg reduction for cyanate esters conditioned at 60 °C/100% RH. They found that hydrolysis affects the triazine ring rather than the cyanate ester crosslink with a reverse polymerization reaction that produces an aminated isocyanate. Conclusively, the main degradation mechanisms that may activate under hydrothermal environment are plasticization, hydrolysis and osmotic cracking. Kotrotsos et al. [15] studied the effect of CNTs matrix modification of cyanate ester CFRPs on the hydrothermal behavior of the composite material. It was shown that the presence of CNTs into the cyanate matrix affects the water absorption mechanism, since an important amount of additional interfaces has been introduced.

The main purpose of this study is to evaluate the degradation behaviors which occur under hydrothermal ageing of glass fiber reinforced cyanate ester composites and their effect on moisture absorption/desorption, thermo-mechanical and mechanical properties. The cyanate ester matrix composites are finding increasing applications in operational environments of high temperature in combination with moisture presence but the relevant literature is quite limited if non-existent. Consequently, the ageing response of cyanate-ester based composite materials to these harsh environmental conditions needs further study and deeper understanding. To the authors' knowledge, this is the first extensive experimental study on the behavior of glass fiber reinforced cyanate ester composites under hydrothermal conditions. This study contributes to this field by characterizing the mechanical and thermo-mechanical properties of this class of composite materials through an exhaustive carefully designed test campaign.

2. Materials, experimental procedure and test methods

2.1. Material system

The composite material system investigated, in the current study is the commercial PN901-G201-45 obtained from Gurit (Switzerland). It has a reinforcement phase of woven fabric of E-glass filament yarn 390 g/m^2, 2/2 twill pre-impregnated with phenylene (C_6H_4) cyanate ester resin PN901. Laminated composites were prepared in-house using autoclave technique. The curing cycle followed is the one suggested by the manufacturer and a post curing treatment of the plates for 24 h at 120 °C was also applied. Each plate consists of 8 plies stacked in an orientation so that the plate's length coincided with the weft direction of the 2/2 twill weave. The resulted plate thickness was on average 2.6 mm. Various specimens were cut in standard sizes in order to execute a thorough test plan detailed in the following.

2.2. Test procedure

The test plan summarized in Fig. 1 consists of weight measurements, glass transition temperature (Tg) determination via Dynamic Mechanical Analysis (DMA) tests, Interlaminar Shear Strength (ILSS) tests and Transverse Flexural Stress (TFS) tests at several exposure periods to four ageing processes of hydrothermal ageing. A plethora of mechanical and thermo-mechanical properties are calculated in this test campaign and their degradation pattern over different ageing durations and processes is revealed.

Initially and prior to any ageing plan, all specimens were dried at 80 °C overnight in order to remove moisture. Once these samples had reached a constant dry weight they were immersed in baths of distilled water. The oven dry specimen mass was recorded as the baseline mass M_b. To examine the effect of moisture absorption on the aforementioned specimens, water immersion tests were conducted in the temperature range of 40°–90 °C (Ageing Processes AP1, AP2, AP3 and AP4: immersion in water at 40 °C, 60 °C, 75 °C, 90 °C respectively). The accelerating factor is obviously the bath temperature. At this point, it should be noted that the aforementioned temperatures are well below the glass transition temperature of the material which was experimentally determined at 340 °C.

ASTM D 5229/2004 was used for the moisture absorption tests. All samples were placed in perforated holding trays in order to expose all surfaces to the aqueous environment. The distilled water was renewed weekly, so the pH variation can be considered as negligible. The rates at which water was absorbed were determined by periodic weighting. Gravimetric measurements were performed by removing the samples from the bath rapidly dried with tissue paper to remove excess water and immediately weighed using an electronic balance with ±0.001 gr accuracy. The time periods for the weighing experiments were assumed to be sufficiently short so as not to influence the values of the mass measured. A constant measurement procedure was used throughout.

The percent weight gain was calculated according to the following equation:

$$\text{Absorbed moisture } (\%) = \left(\frac{W_w - W_d}{W_d}\right) * 100 \quad (1)$$

where:

W_w: the weight of the wet sample
W_d: the weight of the dry sample.

To identify the effect of hydrothermal ageing, on the glass

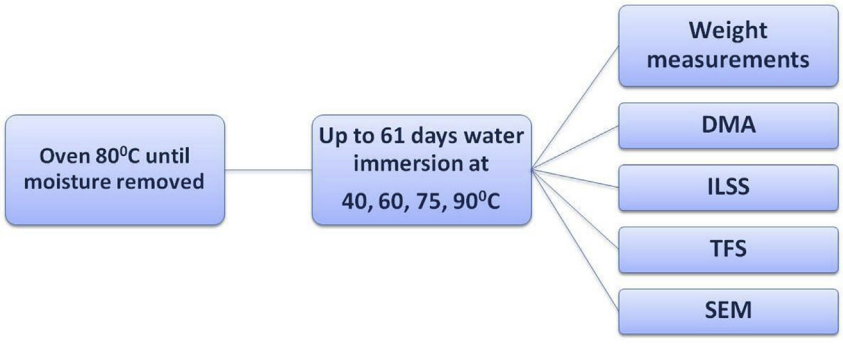

Fig. 1. An overview of the total test campaign of the GFRP samples.