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Test method

# Investigation of the curing behaviour of carbon fibre epoxy prepreg by Dynamic Mechanical Analysis DMA

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ABSTRACT

Carbon fibre prepregs have found widespread application in lightweight constructions. They are based on a carbon fibre fabric impregnated with reactive epoxy resin. Measurements were carried out using commercially available prepreg material. For Dynamic Mechanical Analysis (DMA), a single cantilever measuring device was applied. The DMA results were refined by additional DSC measurements. The measurements were carried out with dynamic heating in the temperature range −90 to 280 °C. The heating rates were 1 and 2 K/min, respectively. A glass transition of the uncured material ($T_{g0}$) near 1 °C, and crosslinking-induced vitrification and devitrification at the maximal glass transition temperature of the cured material ($T_{gmax}$) in the temperature range 220 to 230 °C were found. The activation energies for the glass transitions were determined using an Arrhenius plot. By detailed consideration of the influence of the frequency on the DMA data, indications for gelation were deduced.



## 1. Introduction

Glass and carbon fibre composite parts are based on the combination of fibres, mainly as fabric, with a polymer matrix. For fibre impregnation, the polymer material must be in the liquid state. For application the matrix must be a stiff solid. Traditionally, reactive casting resins have been used for impregnation. Typical reactive resins include epoxy, unsaturated polyester and polyurethane. For curing, a second reactive species must be added as a hardener. Hardeners are mainly amines or peroxides. During crosslinking, the material changes from a liquid via a gel and, finally, to a glass-like solid. Some resin-hardener combinations already start curing reactions at room temperature, but for resins with higher technical standards curing temperatures can be as high as 200 °C. The aim of this work was to demonstrate the possibilities of classical Dynamic Mechanical Analysis (DMA) with a cantilever sample to investigate the curing behaviour of a carbon fibre prepreg. Typically, thermoanalytical methods such as Differential Scanning Calorimetry (DSC) are used [1,2] in the development of resins to closely monitor the material that arrives at prepreg processors and to develop manufacturing parameters. DSC can provide two interesting data: the glass transition temperature and the progression of the crosslinking process. DMA methods are favoured to detect the glass transition temperature through the typical changes in mechanical parameters. DMA is also well suited to follow the crosslinking process [3,4].

Oscillating rheometers are a special form of DMA. They offer advantages for liquid resins where a plate-plate measuring device can be applied. For prepregs with low resin content, this assembly is more difficult to use.

To obtain results that characterize the curing behaviour of prepreg by classical DMA, samples are placed in a torsional or a single cantilever arrangement [5–9]. In a special case, DMA is combined with dielectric analysis [10,11]. Theriault et al. [12] measured the curing behaviour

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of a prepreg resin by a rotating rheometer. Oscillating plate-plate rheometers are often used [13–19]. Numerous DMA-based investigations of crosslinking process have been performed using what is known as Torsional Braid Analysis (TBA) [20]. Glass and carbon fibre braid were found to be nearly neutral in terms of the relation between temperature and rigidity and their logarithmic decrement, and thus suitable for this application [21]. From many relevant articles, the following may be highlighted [22–28].

## 2. Experimental

### 2.1. Material

A commercially available carbon fibre prepreg from Hexcel type HexPly® 6376C-HTS was used for the experiments [29]. The resin system 6376 from Hexcel (formerly Ciba–Geigy) has found application in carbon-epoxy composite manufacturing for aircraft structures [30]. Curing conditions of 2 h at 175 °C at a heating rate of 2-5 K/min to the oven temperature are proposed. The guaranteed shelf life at −18 °C is a minimum of 6 months; at 23 °C the service life is 10 d [29].

### 2.2. Thermal analysis methods

#### 2.2.1. Dynamic mechanical analysis (DMA)

DMA is a widely used method in polymer characterisation [3,4]. In DMA, a sinusoidal mechanical excitation is executed whereby the force, elongation and phase shift between force and elongation are measured as a function of temperature.

The equipment used was a DMA 242C, Netzsch, Germany [31] with a Netzsch single cantilever holder and sample length of 5 mm. The arrangement is drawn schematically in Fig. 1.

One clamp is fixed, the other oscillates sinusoidally. The sample holder is located in a temperature chamber regulated by liquid nitrogen cooling in combination with electrical heating elements in the wall of the chamber, and is brought to temperature via heat conduction of the air in the chamber. The air temperature is measured by a small thermocouple in the vicinity of the sample.

The complex modulus E* is calculated from the measured data and the sample geometry:

$$E^*_{cantilever} = \frac{l^3}{16 \cdot b \cdot h^3} \cdot \frac{F^*}{A^*}$$

l – sample length
b – sample width
h – sample thickness
F* – complex force
A* – complex deflection

The samples were cut from the prepreg film and had the geometry l = 5 mm, b = 5 mm, h = 0.275 mm.

With the measured phase shift δ, the complex modulus E* can be split into two components:

$$E' = \frac{\sigma_0}{\varepsilon_0}\cos\delta$$

E′ – storage modulus

$$E'' = \frac{\sigma_0}{\varepsilon_0}\sin\delta$$

E″ – loss modulus
$\sigma_0$ – stress amplitude
$\varepsilon_0$ – strain amplitude

The mechanical parameters indicate the macroscopic consequences of molecular movements. In polymers, molecular mobility is a function of temperature. Typical heating rates lie between 1 and 5 K/min and a compromise rate must be found. The higher the heating rate, the more the real sample temperature deviates from the temperature registered by the thermocouple in the chamber. For low heating rates, the measurements becomes more and more time consuming. Hence, the heating rate was selected at first to be 2 K/min, a value found in the literature as an upper limit [32]. The amplitude was held constant at 40 μm. During the measurement run, the DMA device was switched between five frequencies – 1; 3.33; 10, 16.6 and 33.3 Hz – continuously in a polling mode.

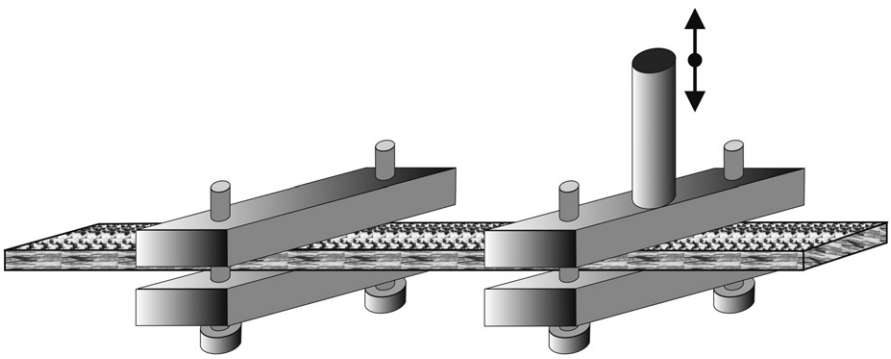

**Fig. 1.** Prepreg clamped in single cantilever DMA device, fixed wedge on left, oscillating wedge on right.