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Cure state detection for pre-cured carbon-fibre epoxy prepreg (CFC) using Temperature-Modulated Differential Scanning Calorimetry (TMDSC)

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ABSTRACT

Carbon-fibre prepregs have found widespread use in lightweight applications. They are based on a carbon-fibre fabric impregnated with reactive epoxy resin. Prepreg materials are generally pre-cured so that they have a higher molecular weight than typical resins in order to reduce resin flow, which facilitates storage and later processing properties.
The measurements were carried out using commercially available materials and follow the published DMA investigations of the same material [1]. TMDSC was used to find the correlation between curing conditions, the degree of cure and glass transition temperature. TMDSC has the advantage over standard DSC that it enables better determination of the glass transition temperature, which is often accompanied by an exothermic curing reaction, and thus overshadowed. The influence of the amplitude of temperature modulation was tested in preliminary experiments. For non-cured material a glass transition temperature of approximately 0 °C was determined; whereas for the totally cured material it was approximately 230 °C. The changes in degree of cure, temperature of actual glass transition and post-reaction are given as a function of curing time at 180 °C. The correlation between actual glass transition temperature and degree of cure is derived.

1. Introduction

Glass and carbon-fibre composite parts are based on the combination of fibres, often as woven fabric impregnated with polymer matrix. Traditionally, reactive casting resins are used for impregnation, although thermoplastic composites also find application due to their positive recycling properties. Typical reactive resins are epoxy, unsaturated polyester and polyurethane. For curing, they contain a reactive species as hardener. Hardeners are mainly amines, anhydrides or peroxides. In epoxy materials, a polyaddition reaction leads to a cross-linked network. During cross-linking at sufficiently high temperatures the material changes from a liquid via a gel into a glass-like solid.

Knowledge of the curing state reached during the technical process is of enormous importance for the application of composite parts. For safety-relevant parts, the degree of cure (α) must be controlled and documented. Trappe et al. [2] published that the crack propagation rate in epoxy resin was reduced by a factor of 10 when the isothermal curing temperature was increased by 10 K. The increase in temperature caused a change in the degree of cure from 92.8 to 94.8 %, along with a shift in the onset temperature of glass transition from 65 to 71 °C. Jaunich et al. [3] found that for melamine moulding compounds, the maximum impact resistance was not reached until the degree of cure was 100%.

In order to predefine optimal manufacturing conditions, the glass transition temperature as a function of the degree

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of cure must be known, especially for full cure ($T_{g\infty}$). Only if the manufacturing temperature approaches or exceeds $T_{g\infty}$ can the reaction be completed within reasonable cure times. Otherwise the reduction in the reaction rate when the glass transition temperature reaches the curing temperature, also called vitrification, prevents or delays full curing. Knowledge of the correlation between glass transition temperature and degree of cure is also needed for the kinetic modelling of curing reactions to incorporate vitrification by diffusion control [4].

To characterise thermosetting resin, control incoming goods and optimise manufacturing parameters, thermoanalytic methods like Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA) are typically used [5,6].

DSC evaluates the change in temperature difference between a sample crucible and a reference crucible during continuous temperature change or under isothermal conditions. The temperature difference is used to calculate the heat flow into or out of the sample. Characteristic changes in heat flow indicate melting, evaporation of volatiles, glass transition and also chemical reactions by the release or uptake of heat [5–7]. An advantage of DSC is that it can also provide results on the glass transition and the degree of cure in a single measurement.

DMA methods are usually favoured to detect the glass transition temperature, often with higher resolution due to the significant changes in mechanical parameters [8–11]. DMA is also well suited to follow the cross-linking process [1].

To determine the correlation between glass transition temperature and degree of cure it is common practice to pre-cure samples for different lengths of time and to investigate their cure state in a subsequent non-isothermal DSC experiment [12–14]. These experiments work well when the reaction temperature is higher than the maximal glass transition temperature $T_{g\infty}$, because only under these conditions can full curing be achieved.

The situation is more complicated when the actual glass transition temperature is in the same temperature range as the post-curing reaction. The term actual glass transition temperature (T_{gact}) will be used for the value achieved by partial curing, which is situated between T_{g0} of the neat resin and $T_{g\infty}$. In many cases, vitrification occurs during partial curing, as the cure temperature is lower than $T_{g\infty}$.

In the non-isothermal DSC run following the partial curing process, an initial or actual glass transition is reached. In the vicinity of the glass transition, devitrification starts and the mobility of the reaction partners is recovered. Therefore, the post-curing reaction should immediately follow the glass transition, and the endothermic step caused by T_{gact} is followed directly by an exothermic reaction peak. This can obstruct the detection of T_{gact} and make accurate determination difficult. Additionally, the heat of reaction, which is needed to calculate the degree of cure, may be distorted.

Examples where the actual glass transition temperature is always lower than the start temperature of post-curing reaction are also found in the literature [13,15].

In other publications, examples for the close correlation between devitrification when the temperature reaches T_{gact} and the start of the post-curing reaction are seen. Alig et al. [12,16] pre-cured DGEBA/DDM epoxy samples at 373 K for 0 to 200 min. In the 2nd 10 K/min DSC run the devitrification phenomenon is obvious. Hutchinson et al. [14] showed a 10 K/min DSC for epoxy (TGASP/DDS) pre-cured at 150 °C for times between 0.5 to 6 h. Here, for the higher curing times T_{gact} is immediately followed by the post-curing reaction and the two effects interfere with each other.

Glass transition and cross-linking reaction phenomena can be separated by temperature-modulated DSC. In this work, the abbreviation TMDSC is used, although the other terms TM-DSC and ADSC are also common. The measurement principle from TMDSC is to superimpose on the usual temperature program an oscillating temperature component with defined amplitude and period. For non-isothermal DSC, three parameters must be selected: the underlying heating rate, amplitude and period. By analysing the oscillating heat flow the signal can be separated into a reversing and a non-reversing part [5–7]. From the reversing part, the change in specific heat at glass transition is clearly apparent. The information on the exothermic curing reaction is deducible from the non-reversing signal. Another form of data evaluation is to also measure the phase between excitation temperature and heat flow. In this case, the modulus of c_p ($|c_p^*|$) is ascertained to be proportional to the reversing signal [17]. Besides sinusoidal temperature modulation, in the method called TOPEM® the temperature is varied in the form of stochastic temperature pulses [14,18,19]. The advantage here is that various modulation frequencies in the mHz range can be evaluated and gives the influence of frequency on the glass transition [18,19].

TMDSC results for epoxy used under non-isothermal and isothermal conditions are found, for example, in [12,14,16–18,20–30]. Hutchinson et al. [14] showed for a sample pre-cured for 3 h at 150 °C in a temperature-modulated DSC (heating rate 2 K/min) that the actual glass transition can be determined at approximately 175 °C. The post-curing reaction also starts at this temperature. Swier and van Mele [28] investigated non-cured samples and samples pre-cured at 100 °C (100 to 400 min) using TMDSC with a heating rate of 2.5 K/min. For samples pre-cured for 100 and 200 min, post-curing reactions are seen to follow the actual glass transition. For samples pre-cured for 400 min the final glass transition temperature was reached. In [5], using TMDSC (heating rate 2 K/min, modulation amplitude 0.5 K, period 60 s) it is demonstrated that the overlaid glass transition can clearly be detected at 73 °C.

Flammersheim and Opfermann [4] used non-isothermal TMDSC for pre-cured samples ($\alpha = 0.248$ and 0.598) and found that post-curing starts just at the actual glass transition (53 °C and 98 °C). Especially for the sample with a high degree of cure, the change in heat flow at the actual glass transition is small and close to the exothermic peak. Ersoy and Tugutlu [31] published TMDSC measurements for carbon-fibre epoxy prepreg pre-cured at 140 °C. The underlying heating rate was 5 K/min, the amplitude 0.5 K. The actual glass transition just at the onset of the post-curing reaction was clearly seen in the reversing heat flow signal.