

Assessment of the influence of curing parameters on fibre reinforced epoxy composite properties using guided ultrasonic waves

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Abstract: The degree of crosslinking in unidirectional prepreg materials was investigated using differential scanning calorimetry to assess their curing behavior and thermal characteristics. To complement these measurements with a non-destructive, in-situ method, the propagation properties of guided acoustic waves in cured carbon fibre-reinforced epoxy plates were analysed. Correlations between the degree of crosslinking and acoustically determined mechanical properties were drawn to enable a future non-destructive evaluation approach.

Keywords: fibre-reinforced polymers, differential scanning calorimetry, degree of crosslinking, guided waves, ultrasound.

Introduction

In the automotive industry, reducing weight through lightweight design is a significant approach for conserving resources and improving vehicle dynamics. In this context, hybrid structures combining metal and fibre-reinforced plastic offer significant potential [1]. Fibre-reinforced polymers (FRP) are widely used in sectors such as automotive and aerospace due to their low mass and high tensile strength [1, 2]. Epoxy-based composites, a common type of FRP, require thermal curing during the manufacturing of components, as process parameters such as curing temperature and duration significantly influence the final component properties. The microscopic and macroscopic properties of these FRP material can be assessed through destructive methods, such as Differential Scanning Calorimetry (DSC). This technique is based on the principle that physical and chemical transformations are associated with changes in heat flow. Investigating the pre-impregnated semi-finished products (prepregs) under DSC provides valuable insights into its curing behavior and offers a fast, reliable method for determining the degree of cure (DOC) [3, 4, 5, 6].

Aiming to complement these measurement with a non-destructive, in-situ method, the properties of guided acoustic waves in cured carbon fibre-reinforced epoxy plates are analysed. Broadband, guided acoustic waves are excited using pulsed laser radiation and detected using a custom piezoelectric transducer. Varying the distance between excitation and detection of the guided waves enables the acquisition of spatiotemporal measurement data, from which the frequencies and wavenumbers of the excited modes can be ex-

tracted. These measurement results are matched by the output of a waveguide simulation tool, allowing for the identification of elastic material parameter.

Samples cured under different conditions are analysed with respect to their elastic properties. Similarly, equally conditioned samples are analysed using DSC measurements to infer the degree of crosslinking of the polymers molecules. Relations between the degree of crosslinking and the acoustically determined mechanical properties are drawn in an effort to determine the quantity non-destructively in a future measurement procedure.

Material

In this study, the specimens are fabricated from stacked unidirectional (UD) prepreg composed of carbon fibers and the thermosetting matrix resin E320 from SGL Carbon SE, Germany. The matrix content in the current prepreg is approximately 39 % by weight. The specimens used in this study consist of a single unidirectionally oriented layer with a defined thickness of 0.23 mm. The fibre orientation is aligned along the 0° axis, with a fibre volume fraction of 60 % [7, 8].

DSC cure characterization

DSC measurements were carried out using a DSC 214 (Netzsch, Germany). For each test, approximately 10 mg of uncured prepreg material was placed into an aluminium crucible with a pierced lid. Dynamic DSC scans were performed at a constant heating rate of 20 °C min⁻¹, up to a final temperature of 250 °C. Additionally, isothermal DSC measurements

were conducted at two curing temperatures T_c of 80 °C and 150 °C, under a continuous nitrogen purge.

The objective of these measurements was to evaluate the degree of cure of the prepreg under varying thermal conditions. Upon applying a defined temperature profile, the exothermic curing reaction is triggered. The degree of cure, α , is calculated based on the specific heat released over time, $H(t)$, relative to the total heat of reaction, H , as follows:

$$\alpha = \frac{H(t)}{H} \quad (1)$$

The curing or crosslinking behavior is then described in the form of a rate equation:

$$\frac{d\alpha(t)}{dt} = f(T, \alpha) \quad (2)$$

where $\alpha = 0$ and $\alpha = 1$ represent the uncured and fully cured states, respectively. Fig. 1 and Fig. 2 illustrate the characteristic progression of the degree of cure at 80 °C and 150 °C under isothermal conditions.

The results of the isothermal DSC analysis provide discrete data points of the recorded heat flow at defined intervals (in this case, every six seconds). Based on the respective sample mass, the corresponding specific heat flow values can be calculated. It is important to consider that, in the case of prepreg materials, only the matrix contributes to the reactive portion of the sample, meaning that approximately 40 % of the total sample mass is involved in the curing reaction. The reaction enthalpy of the curing process is determined by the area between the measured heat flow curve and the corresponding baseline, which is obtained from a second heating run of the fully cured sample. Consequently, the baseline values are subtracted from the measured heat flow. The reaction enthalpy is then calculated by summing and integrating the resulting values over time. Complementary data on temperature, curing time, and degree of cure are provided in Tab. 1. Specifically, at 80 °C, 80 % and complete cure (100 %) are achieved after 5.3 h and 10 h, respectively, while at 150 °C, the same levels of cure are reached within only 7 min and 1 h respectively.

Acoustic material characterisation

In an effort to non-destructively quantify the mechanical behaviour of the samples, the assumption is made that the cured sample constitute acoustic waveguides. Aiming to realise a material characterisation procedure based on the properties of guided waves in the samples, acoustic waves are excited using pulsed laser radiation via the thermoelastic effect (Fig. 3) [9]. A short pulse duration (1 ns) and small focus result in excitation of broadband acoustic waves in frequency and wavenumber regime, i.e. spatial and temporal

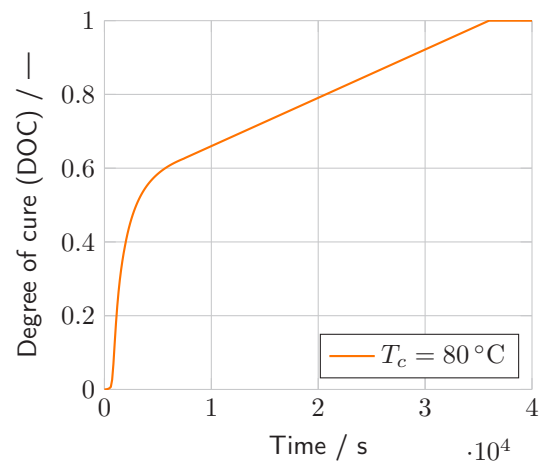


Fig. 1: Progression of the degree of curing of prepreg at $T_c = 80\text{ °C}$ under isothermal curing.

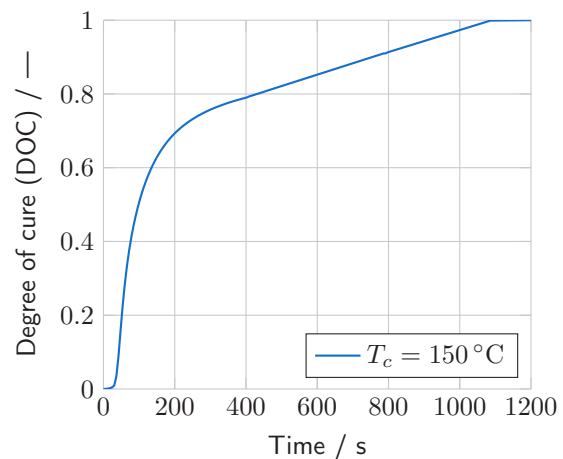


Fig. 2: Progression of the degree of curing of prepreg at $T_c = 150\text{ °C}$ under isothermal curing.

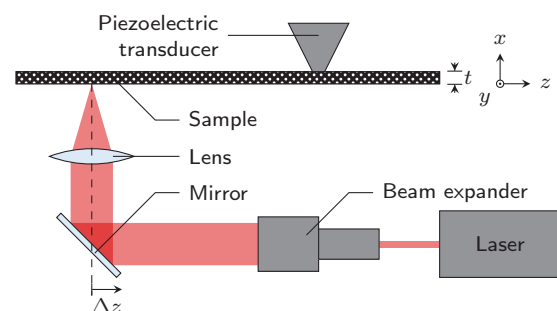


Fig. 3: Experimental setup for the excitation and detection of acoustic waves in plate-like samples with adjustable propagation distance.

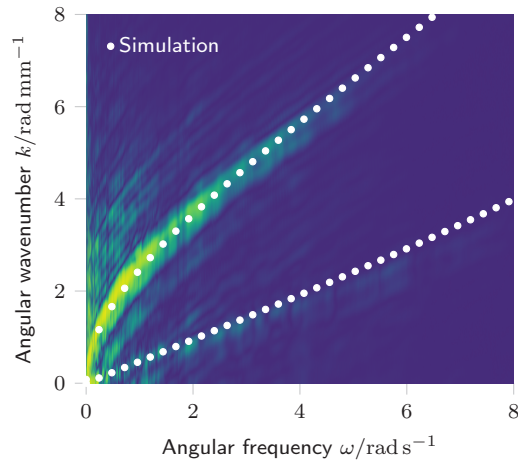


Fig. 4: Processed spectral measurement data for the sample cured at 80 °C for 10 h superimposed with waveguide simulation data for the determined wave velocities.

frequency. The focus is line-shaped in y -direction for a directed emission of acoustic waves and movable in z -direction. The acoustic waves are detected by an equally broadband piezoelectric transducer with an active area also resembling a line [10].

Measurements are performed moving the excitation position in equidistant steps along the z -direction and recording a signal at each step. The resulting spatio-temporal matrix of measurement data is processed by applying a two-dimensional Fourier transformation, transforming the time to frequency and the spatial axis to wavenumber. In the resulting matrix, modes propagating in the sample and thus present in the measurement data are visible as ridges [11]. In previous work on metallic and homogenous samples [10, 9], large numbers of modes are visible in such depictions. However, due to the complex structure and high absorption of the samples examined in this study, only few ridges are pronounced in the data (Fig. 4). These correspond to the basic asymmetric and symmetric modes of the plate.

To identify the an quantitative material model for the samples, the inverse problem of fitting the output of a numerical waveguide model to the measurement data is solved. For this study only the behaviour of the sample perpendicular to the fibre-direction is quantified. Based on the assumption, that the overall material behaviour follows transversely-isotropic symmetry, with the strong axis being aligned with the fibres, the properties of the sample in the observed plane can be assumed isotropic. When parametrising the acoustic behaviour using the longitudinal and transversal wave velocities c_l and c_t only two param-

Tab. 1: Identified acoustic wave velocities for differently processed samples.

Curing			Measurement	
Temp.	Time	DOC	$c_l/\text{m s}^{-1}$	$c_t/\text{m s}^{-1}$
80 °C	5.3 h	80 %	5995	1169
80 °C	10 h	100 %	6000	1074
150 °C	7 min	80 %	6000	1162
150 °C	1 h	100 %	6568	1079

eters need to be identified, which greatly simplifies the underlying optimisation problem. This especially advantageous given the limited information carried by the measurement data. The simulation model is based on a semi-analytical finite element method [12], assuming harmonic function in propagation direction z and infinite dimensions in y . For efficiency, a single high-order (16th) element is used, which, due to the assumptions is one-dimensional. Solving for the eigenfrequencies of the system for a given frequency yields the wavenumber of the modes that are able to propagate that frequency.

The objective function for the subsequent optimisation procedure is formulated by sampling the measurement data at the points yielded by the simulation model. The resulting values are maximised by gradient based optimisation using a trust region algorithm [13], in which the parameters of the simulation model (c_l and c_t) are adapted until measurement and simulation are in agreement. Fig. 4 shows the measurement data for the 80 °C for 10 h superimposed with the simulation result for the determined wave velocities after the optimisation process showing good agreement. The remaining deviation can be explained by small anisotropic effects still being present, a cause for which may be a possible misalignment between the fibres and the measurement axis.

The results for the wave velocities of the four sample examined in this study are summarised in Tab. 1. The results for the longitudinal wave velocity c_l show now clear indication of influence with respect to the curing parameters. This observation may be due to the fact that the primary sensitivity of the determination of c_l comes from the symmetric mode (the lower wavenumber mode in Fig. 4), which is only present with low intensity in the measurement data. This results in low gradients in the objective function and thus an increased uncertainty of c_l . The determination of the transversal wave velocity c_t , however, is primarily based on the shape of the asymmetric mode, which is more pronounced in the measurement data. Accordingly, the determined transversal wave velocity of the samples show a clear dependence on

the degree of curing, with higher curing degrees yielding lower values for c_t . Within the limited scope of this study, the mode with which the degree of curing is achieved appears to have little influence. The fact that primarily the transverse wave velocity c_t has a high sensitivity with regard to the degree of curing can be considered advantageous for future applications, as acoustic characterisation methods show equally high sensitivity with respect to c_t .

Conclusions

The present study indicates that the degree of cure of epoxy composite can be assessed by the analysis of guided ultrasonic wave properties, in particular the transversal wave velocity c_t perpendicular to the fibre direction. This opens the possibility of a non-destructive testing method, as measurement of c_t are possible excitation of surface acoustic waves. Future research will include the analysis of the complete, anisotropic, viscoelastic material behaviour of the sample, with the aim to find other dependencies between acoustic behaviour and parameters of the curing process, especially the curing time.

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