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Online measurement of thermal diffusivity during cure of an epoxy composite

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Abstract

Thermal diffusivity was measured online during cure of an epoxy composite using a method somewhat similar to the Ångström Method. It is shown that a simple experimental setup can be used, thus avoiding expensive instrumentation. The experimental instrumentation is explained in detail. The measurements show an increase of thermal diffusivity during the cure of composite material. Using modulated differential scanning calorimetry (MDSC), heat capacity was measured online during the cure of an epoxy composite. Combining thermal diffusivity measurements with MDSC measurements, the thermal conductivity was found to change during the cure process, similar to the measurements of heat capacity. These changes are referred to vitrification at the end of the cure process.

Keywords: Cure processes; Composite material; Epoxy composite; Thermal diffusivity; Modulated differential scanning calorimetry (MDSC); Ångström method

1. Introduction

Epoxy composite materials are often used in the industry as a structural component or as adhesive coatings [1].

Thermal diffusivity is important in electronic applications. The development of heat during the application of electronic devices may cause large temperature gradients which could lead to failure of the component. Estimation of these temperature gradients may then become important and requires knowledge of thermal diffusivity.

The thermal conductivity is in some cases acquired with the measurement of thermal diffusivity [2]. Using known values of heat capacity and density, thermal conductivity can be calculated. Accordingly, many references reporting methods to measure thermal conductivity actually measure thermal diffusivity from which thermal conductivity is calculated. This is in particular true for dynamic methods of measuring thermal conductivity.

Refs. [2,3] contain detailed descriptions of many different methods for measuring thermal conductivity. The classical reference of heat conduction [4] also includes many methods for thermal conductivity based upon a more mathematical background. A more recent review of measuring thermal conductivity using the guarded hot plate is available in [5].

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If heat capacity measurements are available, thermal conductivity may also be measured assuming known density. In many cases, relatively accurate online heat capacity measurements are available using modulated differential scanning calorimetry (MDSC). As MDSC measurements are both readily available at many universities and measurements of thermal diffusivity do not require advanced and expensive instrumentation, measurement of thermal conductivity may readily be performed using thermal diffusivity and heat capacity data.

The direct measurement of thermal conductivity requires measurement of heat flow, see [2,3]. Calculating thermal conductivity from measurements of thermal diffusivity and heat capacity may therefore become an attractive method as these measurements are easier to perform and readily available. Furthermore, heat capacity and thermal diffusivity may both be measured online and continuously which allows covering a large temperature range from just a few measurements.

The principle of the measurement of thermal diffusivity used in this article is that, if one end of a long bar or cylindrical-shaped sample is heated periodically, then the temperature along the sample also varies with the same period, but with an amplitude that decays exponentially to zero towards the free end. Moreover, as the temperature wave travels along the sample with finite velocity, there is a varying phase relationship [6]. The measurement of phase can be directly related to thermal diffusivity using only the phase, length of material and frequency of the periodically varying temperature.

The original reference for this method of measuring thermal diffusivity was proposed in 1863 in [7]. A modification of this method, designated the modified Ångströem method, is often used in the literature in which the heat convection moving away along the sample is taken into account using a coefficient of heat convection. An adjustment is used in those cases for calculating thermal diffusivity, see [6,8–12].

This original Ångström measurement principle has been utilised by [13] to measure thermal diffusivity of an epoxy during cure; however, they use very specialised and expensive instrumentation in order to measure the temperature and phase lag. In the present work, simple thermocouples are used to measure the temperature and computer software is used to calculate the phase difference. This reduces the costs for instrumentation considerably.

In the present work, thermo-physical parameters are measured in terms of heat capacity, thermal diffusivity and heat generation during cure of the epoxy composite material. Online measurement of thermal diffusivity and heat capacity using MDSC during the cure of epoxy prepreg at different quasi-isothermal temperatures has been performed.

2. Measuring principle

A solution of the unsteady-state heat conduction equation (1) with boundary conditions stated in Eqs. (2) and (3) should be solved:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}, \tag{1}$$

where T is the temperature (°C), x is the distance (m), t is time (s) and α is the thermal diffusivity (m^2/s).

The boundary conditions are stated as

$$T(0,t) = A\cos(2\pi f\, t), \tag{2}$$

$$\underset{x\to\infty}{T(x,t)} = 0, \tag{3}$$

where A is the amplitude (°C) and f is the frequency (s^{-1}).

The solution is given as [4,14]

$$T(x,t) = A\exp\left(-\sqrt{\frac{\pi f}{\alpha}}\right)\cos\left(2\pi f t - x\sqrt{\frac{\pi f}{\alpha}}\right). \tag{4}$$

From Eq. (4), it can be observed that the phase shift of the periodic temperature variation is linear and proportional to the distance x. Thus, it can be derived that the phase difference of the periodic temperature variation measured at a length, L, apart is given by

$$\phi = L\sqrt{\frac{\pi f}{\alpha}}. \tag{5}$$

From (4) it can be derived that

$$\alpha = \frac{\pi f L^2}{\phi^2}. \tag{6}$$

Using only the measured phase difference, ϕ, in Eq. (6), and using known values of the length, L, and the frequency, f, we can calculate the thermal diffusivity. It should be noted that the measurement is available during the entire cure process as the measurement of phase is independent of the developed heat of reaction.

Performing a linear regression analysis with $\sqrt{f}$ as independent variable and φ as the dependent