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Methodology for optimization of the curing cycle of paste adhesives

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ABSTRACT

This contribution, carried out in the frame of the European Joint Technology Initiative 'Clean Sky', presents the results of a research program investigating the influence of fast curing on the quality of epoxy based paste adhesives. Today, the curing of paste adhesives is typically carried out following the supplier's recommendations. In order to reduce cycle time, save costs and energy resources, paste adhesives could be cured at higher temperature. To ensure a bonded joint quality with maximum mechanical performance, the limitation of this temperature increase is studied. This study shows the effects of the use of high temperatures in the curing process, which can lead to a degradation of the adhesive system due to the increase of void content, decreasing the mechanical performance in the paste adhesive as well as in the bonded joint. The goal of this research is to find fast and robust processing of paste adhesives and to develop a methodology to determine the maximum curing temperature possible. Different properties of the adhesive are investigated, including different thermal analysis techniques, optical and mechanical testing of the pure adhesive. Additionally, state of the art qualification of paste adhesives, single lap shear testing, is considered. In this study, a novel method to control the quality of the cured paste adhesives is defined based on the analysis of the pure cured paste adhesive, not influenced by the adherent quality, by measuring the void content and its effects on the bonded joint.

1. Introduction

In this research contribution, a methodology to control the quality of paste adhesives with a high temperature curing process is investigated. The background of this research is to accelerate the curing cycle of the paste adhesive by increasing the temperature of the process without affecting the mechanical performance of the joint. The paste adhesive system used is the LMB 6687-1/LME 10049-3 from Huntsman Advanced Materials. The curing process is performed without pressure [1]. Samples are cured under different curing cycles, obtaining products with different properties that are analyzed.

An acceleration of the supplier's recommended curing cycle is possible without decreasing mechanical performance. For industrial applications, acceleration of the curing process is usually not applied as the mechanical performance of the joint can be affected if too high temperatures are applied [2]. For this reason, effects of an accelerated curing process are not considered [3]. The goal of this research is to investigate a methodology to control the quality of the paste adhesive when high temperatures are used in the accelerated curing process. This quality control is established through the analysis of different properties of the adhesive in a range of samples with different degrees of degradation.

One of the main indicators of degradation of paste adhesives is an increase of the void content. An increased void content leads to a reduction of the mechanical performance of the paste adhesive. During the mixing process some air is entrapped [4]. If the paste adhesive is cured at higher temperature, the air inside expands, increasing the volume of the voids thus affecting the mechanical properties of the joints [5,6]. The quality of adhesives is mechanically tested by strength tests such as shear and peel tests [7]. Non-Destructive Inspection (NDI) techniques such as ultrasonic testing are also used to detect defects such as voids [8].

Maximum void content can be found in literature for composite panels and limitations about positioning of voids in the edge in order to avoid delamination problems [9]. However, there are no explicit considerations for bonding systems [10]. The detection of void content in paste adhesives is limited by the minimum defect size detected by NDI techniques. If the voids are small enough they may not be detected by NDI [11]. Today, there are no reliable methods to assess quality of a bonded joint [12]. This contribution focuses on the experimental analysis of this effect, observing how the increment of curing temperature affects the void content and how this increment of porosity affects different mechanical properties of the paste adhesive, and to find a methodology to assess the quality of the adhesive.

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The samples produced in this research are completely cured applying different curing cycles, with temperatures from 80 °C (as recommended by the supplier) to 200 °C (which causes a clear thermal degradation on the adhesive). Physical and mechanical properties of these samples are then measured.

The tests considered in this study include thermal analysis techniques, e.g. Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA), as well as optical microscopy to observe the evolution of different physical properties of cured epoxy paste adhesive when the curing temperature is changed. Additionally, mechanical testing is considered by the measurement of flexural properties of the pure adhesive in three point bending test and Dynamic mechanical analysis (DMA) and single lap shear test with Carbon fiber Reinforced Polymers (CFRP) bonded systems. All the testing is firstly considered by separate in order to analyze the benefits and inconveniences of each test. From the information obtained from each test, recommendations for suitable qualification of paste adhesives are defined.

The acceleration of the curing process of a paste adhesive is considered and a methodology to control the quality considering thermal degradation is established

2. Curing kinetics modeling theory

Firstly, the curing cycles used to produce the samples are defined. The reference curing cycle from the supplier is composed of a gelling stage of 2 h at room temperature, followed by a curing process at 80 °C for 4 h. The rest of the curing profiles chosen have shorter cycle times but higher temperatures with a risk of thermal degradation. The definition of the curing temperatures is carried out by using the kinetics model of the paste adhesive, which gives the relation between temperature, time and curing degree for this paste adhesive system.

The theoretical model of the chemical reaction is measured following Arrhenius relation, based on the n-th order kinetics [13], in the Eq. (1)

$$f(\alpha)=(1-\alpha)^n \tag{1}$$

This reaction can be written in the following form by combining an Arrhenius relation [14]

$$\frac{d\alpha}{dt}=k_0\exp\left(\frac{-E}{RT}\right)(1-\alpha)^n \tag{2}$$

The model depends on three variables: the degree of cure α [-], temperature T [K] and time t [s], and three parameters which characterize the reaction: k_0 [-], which is the specific rate constant at temperature T [K], the activation energy E [KJ/mol] and the reaction order n [-].

Once the parameters of the chemical reaction are defined, it is possible to predict which will be the degree of cure for a certain temperature applied for a given time. The equation with the degree of cure depending on temperature and time is shown in Eq. (3).

$$\alpha=1-\left[1-(1-n)\,z\,t\,\exp\left(\frac{-E}{RT}\right)\right]^{\frac{1}{1-n}} \tag{3}$$

Eq. (3) can be solved by using multiple linear regression of the general form: $z=a+bx+cy$ where the two basic parameters on Eq. (2), the reaction rate $\frac{d\alpha}{dt}$ [1/s], and the curing degree α, are determined from the DSC measurements. Three parameters (z, which is the Arrhenius frequency factor [1/s], E and n) are calculated by the software of the DSC, Pyris. Material obeying n-th order has the maximum rate of heat evolution at the beginning of the reaction [15].

This theoretical modeling for the kinetics characterization is carried out by a single dynamic heating measurement in the DSC of a non-cured sample of the paste adhesive. To minimize errors, this measurement is done 8 times and the average is used to measure the relation between temperature, time and degree of cure. Results are shown in Fig. 1.

The curing times are chosen following the theoretic model, having always more than 90% theoretical degree of cure. It must be considered that samples will have an extra gelling stage not considered in the theoretical model. Therefore, the real degree of cure will be slightly higher than the theoretical one. This should reach more than 95%, as recommended by supplier. The curing profiles for the samples are summarized in Table 1.

Table 1
Summary of curing conditions for tested samples.

Temperature (°C)	Time (min)	Theoretical curing degree (%)
80	240	93.2
100	60	91.3
120	60	95.6
140	45	97.1
160	30	97.8
180	15	97.8
200	10	98.2

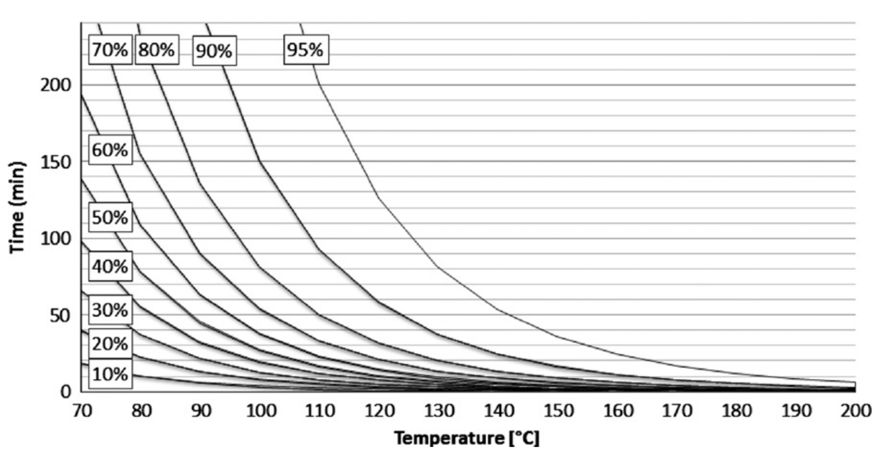

Fig. 1. Kinetics of curing reaction of LMB 6687-1/LME 10049-3 from Huntsman Advanced Materials.