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Acceleration of the curing process of a paste adhesive for aerospace applications considering cure dependent void formations

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ABSTRACT

In this publication, the acceleration of the curing process of a paste adhesive used for bonding aerospace components is investigated. Previous investigations have proven that the use of high temperatures not only reduces the curing time but also increases the void formation. This phenomenon takes place due to evaporation of volatiles at high temperatures and affects the mechanical performance of the bonded joint. In this study a dual step cure process is investigated, where the curing temperature is increased depending on the degree of cure of the paste adhesive. In this context, the impact of increasing the temperature at different stages of the curing reaction is analyzed, determining a strategy to accelerate the curing reaction without major void formation. By this approach, the curing time of the paste adhesive used for this investigation could be reduced from 4 h to 30 min without decreasing the mechanical performance of the bonded joint.

1. Introduction

This publication presents the results of a research investigating the acceleration of the curing process of a paste adhesive by means of using a cure dependent heating process. This program is part of the Eco Design ITD of the European Joint Technology Initiative 'Clean Sky', aiming to reduce emissions during manufacturing and fuel consumption of aircrafts by applying a more efficient design.

Today, bonding of composite structures in aerospace industry is mainly carried out by heating the complete assembly in forced convection ovens [1]. The applied curing cycles are typically recommended by the adhesive suppliers, which use low curing temperatures leading to long curing cycles.

In this paper, the paste adhesive LME 10049-4/LMB 6687-2 from Huntsman Advanced Materials is investigated. The recommended curing process is typically 4 h at room temperature followed by 80 °C for 4 h. In a previous study with the same paste adhesive, the curing process could be accelerated with a single isothermal heating stage at 100 °C for 1 h [2]. Curing the paste adhesive with a higher temperature significantly increased the void formation.

This phenomenon is caused by the expansion of the air entrapped during the mixing process, the evaporation of moisture absorbed by the adhesive components and the evaporation of some chemical components during the heating process [3–5]. A high void content caused by high temperatures applied leads to a decrease of the mechanical performance of the joint [6]. For this paste adhesive system, it was proven that a porosity lower than 2% is required to maintain the mechanical performance of the paste adhesive [2].

In this context, the objective of this paper is the investigation of a non-isothermal curing strategy in order to accelerate the cure ensuring a low void formation of the paste adhesive. This approach would be of interest in terms of ecological and economical aspects because the acceleration of the curing processes is beneficial for saving energy resources and processing time. However, investigating this approach requires the use of a fast heating method in order to exploit the potential of cure acceleration by non-isothermal processes.

For this reason, this investigation uses induction heating to vary the temperature and thus to accelerate the curing process of the paste adhesive under study. This technique, widely used in industry for brazing operations, allows a faster temperature increase compared to traditional ovens and presses [7,8]. It heats electrical conductive materials by Joule effect due to the induction of Eddy currents [9,10]. As the paste adhesive investigated is non-electrical conductive, for bonding operations, Carbon Fiber Reinforced Polymer (CFRP) adherents can be used to induce the energy, curing the paste adhesive by conduction [11–14]. One of the benefits of induction heating is that the technique can be applied locally, i.e. just heating the bondline area to cure the adhesive, thus saving energy compared to ovens that typically heat the entire assembly.

In this paper, a dual step heating process is selected to accelerate the curing process of the paste adhesive, i.e. a process to cure a paste adhesive consisting of two temperature steps. This approach is based on the hypothesis that paste adhesives are more vulnerable to void

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formation at the early stages of curing. For this reason, low temperatures are initially applied and, as soon as a certain degree of cure is reached, the temperature might be raised without increasing the void formation of the paste adhesive. The dual step heating process represents a first step towards optimization of curing cycles of paste adhesives by variable temperature cycles. In this context, the impact of increasing the temperature at different stages of the curing reaction must be evaluated in order to determine the best strategy to accelerate the curing reaction without major void formation.

In the experimental part of this investigation, different paste adhesive samples are produced by induction heating, applying different dual step heating processes. The energy is generated in CFRP plates used as susceptors. Then, the heat is transferred to the paste adhesive placed on top of them, curing it afterwards. As a result, samples with different physical and mechanical properties, due to the different degree of thermal degradation, are produced and analyzed.

Differential Scanning Calorimetry (DSC) is used to define the cure kinetics model of the paste adhesive. This model permits to calculate the degree of cure of the samples heated for a certain curing cycle. Additionally, Thermogravimetric Analysis (TGA) is carried out with pure adhesive samples in order to analyze the impact of the initial curing temperature on the evaporation of volatiles and thus to define the range of temperatures under study. Then, paste adhesive samples cured with different cycles are produced by induction and analyzed by microscopy. The aim of this test is to assess the impact of the heating cycles on the degree of cure and on the related void formation of the paste adhesive. Finally, single lap shear tests (SLS), today's state of the art for mechanical testing of bonded samples, are carried out to measure the effect of applied curing cycles on the mechanical performance of the joint.

2. Approach

The approach to accelerate the curing process of paste adhesives consists of a cure dependent heating process, increasing the curing temperature when the degree of cure is high enough to ensure a low void formation. The ideal curing process is expected to be a ramp with a variable slope, starting at a low temperature and increasing it when the paste adhesive becomes more resistant to void formation due to the higher degree of cure: When the degree of cure exceeds the gelation point, typically with a degree of cure between 55 and 80%, the solidification occurs [15–16], therefore the formation of voids is hindered. As a consequence, such a curing strategy would ensure a low void formation and thus maintaining a good mechanical performance.

As a first approach towards an optimum curing cycle with regards to low final void content, this publication considers a dual stage heating process consisting of two isothermal heating stages, as it is shown in Fig. 1. The heating rates applied in this study for reaching the two isothermal stages are set to 25 °C/min. For the used setup this is the maximum heating rate which can be applied accurately in order to ensure a reproducible quality of the samples. Lower heating rates are not considered because they would unnecessarily increase the overall heating time.

In this publication, the dual step heating process is applied to the paste adhesive LME 10049-4/LMB 6687-2 from Huntsman Advanced Materials, having a T_g [°C] of the fully cured adhesive equal to 126 °C. The range of the parameters affecting the void formation and the degree of cure to be studied are:

- Initial temperatures T_1 [°C] in the range of 80–160 °C. Previous research has shown that higher temperatures degrade the paste adhesive too much and lower temperatures do not improve the quality of the paste adhesive but require longer curing cycles [2].

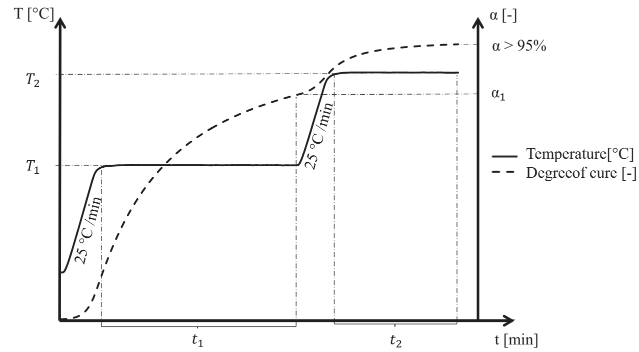

Fig. 1. Two step heating process.

- The duration of the first heating step t_1 [min] is defined in steps of 5 min between 5 and 20 min in order to get samples with a wide range of degree of cure after the first heating stage and thus to analyze the influence of the gelation in the void formation.
- The second stage at T_2 [°C] is carried out in the range of 140 °C to 180 °C in order to reach a degree of cure of 95%, which is the minimum considered for aerospace applications. Lower temperatures are already considered for the first step (T_1 [°C]). Higher temperatures are not considered because the maximum achievable T_g [°C] of the adherents is around 190 °C [2], and the bonded joint could be damaged.
- The duration of the second step, t_2, is varied in steps of 5 min in such a manner that samples with a degree of cure higher and lower than 95% are available. This allows calculating the necessary heating time at the second step to achieve a degree of cure of exactly 95%, and to estimate the void content at this point by linear regression.

The aforementioned processing parameters of the curing process affect the degree of cure and the void formation. In order to assess its influence, the following steps are conducted:

- A cure kinetics model for this paste adhesive, which was validated in previous work [17], is applied in order to calculate the resulting degree of cure in the sample.
- TGA is used to analyze the impact of the initial curing temperature on the evaporation of volatiles in the paste adhesive by measuring the mass change due to evaporation.
- Induction heating is used to produce samples of pure paste adhesive applying different curing cycles. Then, the void content of these samples is measured by microscopy techniques.

Finally following information about the curing cycles applied is obtained:

- Calculated degree of cure after the first heating step (α_1).
- Total curing time considering t_1, t_2 and the time of the heating ramps (t_{total}).
- Calculated degree of cure after the curing process (α).
- Measured void content (V_c).
- Assessment of t_2 [min] necessary to achieve 95% of degree of cure ($t_{2\alpha=95}$).
- Total curing time to get a degree of cure of 95% ($t_{total\ \alpha=95}$).
- Estimation of the void content of samples with a degree of cure of 95% ($V_{c\ 95\%}$).

These results are used to study the impact of the processing parameters of the curing cycle (T_1, t_1, T_2, and t_2) on the degree of cure and on the void formation of the paste adhesive.