MULTISTEP HEATING TO OPTIMIZE THE CURING PROCESS OF A PASTE ADHESIVE

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Keywords: Pate adhesive, induction curing.

Abstract
In this contribution, the optimization of the curing process of a paste adhesive used for bonding carbon fiber reinforced polymer structures is investigated. Today in industry this process is typically carried out at low temperatures in order to ensure low void content in the bondline, leading to long curing cycles. In this study, the use of a multistep curing process is considered to accelerate the process. Firstly, a curing process at low temperature is applied and, when the paste adhesive is partially cured, the temperature is increased in a second stage, reducing the overall processing time. To define the optimal processing conditions, several curing cycles are tested, analyzing how the different curing temperatures and times of both stages influence the performance of the bonded joint. In this study the curing time of the paste adhesive used in this investigation is reduced from 4 hours to less than 30 minutes.

1 Introduction

This contribution presents the results of a research investigating the optimization of the curing process of a paste adhesive. This program is part of the European Joint Technology Initiative 'Clean Sky', inside the Eco Design ITD, investigating a more efficient design in aerospace industry in order to reduce energy consumption and emissions.

Today in aerospace industry, bonding of composites structures is mainly carried out by heating the complete assembly in forced convection ovens or autoclaves. The adhesive suppliers recommend the use of low temperatures for the curing of paste adhesives in order to achieve good quality in the bondline, leading to long processes which ensure the robustness of the process. Higher temperatures are today not considered because they lead to a higher void content in the bondline, decreasing the mechanical performance of the joint. Void formation in paste adhesives is caused mainly by the expansion of the air entrapped during the mixing process, the moisture absorbed by the adhesive components and the evaporation of some chemical components during the heating process [1].

The goal of this research is to accelerate the curing process of a paste adhesive by increasing the temperature applied. The challenge in this study is to reduce the overall curing time without decreasing the mechanical performance of the bonded joint, having a low void

formation [2]. The main hypothesis of this research is that the adhesive generates more voids at earlier curing stages, being more resistant to this effect after certain curing time when the paste adhesive is partially cured. For this reason, a first isothermal curing step is carried out at lower temperature and then, after certain time, the curing temperature is increased. Then, a second isothermal curing step is reached and the temperature is maintained until the process is finished, accelerating the final part of the curing process, when the reaction kinetics is slower. To carry out this novel curing process, a fast increase of temperatures is needed in order to accelerate the process. Today's state of the art for curing of paste adhesives, oven heating, shows a slow response to the change of temperatures. For this reason, induction heating is used in this research, allowing a faster temperature increase compared to traditional heating methods.

Induction heating is today widely used in industry for brazing operations. This technique is based in the physical effect of induction of Eddy currents in electrical conductive materials, which are heated due to Joule effect [3]. Induction heating has been previously validated for bonding Carbon Fiber Reinforced Polymer (CFRP) structures, heating the electrical conductive CFRP adherents and then curing the non-electrical conductive paste adhesive by transferring the heat generated by conduction [4]. One of the advantages of induction heating compared to traditional heating methods is the high efficiency of the process, around 90%. The reason is that this technique permits to heat locally the materials instead of heating the entire assembly, having lower energy losses. Additionally, this method permits to heat up faster than traditional heating methods permitting, for instance, a fast increase of the curing temperature in CFRP bonded systems.

In this research, different experiments are considered. Thermo Gravimetric Analysis (TGA) used to analyze the effect of the initial temperature in the degradation of the adhesive. Then, paste adhesive samples are cured by induction heating, combining different processing temperatures and times on both heating steps. Afterwards, these samples are analyzed by microscopy techniques, measuring the void content caused by the different curing cycles applied. Finally, after a selection of different curing cycles, single lap shear (SLS) samples are produced and tested studying the effects of void formation on the mechanical performance.

2 Testing methodology

The acceleration of the curing process considered in this study consists on applying two isothermal heating steps consecutively. The heating ramps before each isothermal are set to 25 ºC /min in order to simplify the study. The first isothermal curing step is carried out at temperature T_1 [ºC] for certain time t_1 [min]. This step must not degrade the paste adhesive in order to generate low void content. The reason is that this study is based on the hypothesis that the paste adhesive is more sensible to void formation at an earlier curing stage. Hence, low temperatures must be used to ensure good quality in the bondline. The acceleration of the curing process is carried out after certain time curing at low temperature, when the paste adhesive has achieved certain degree of cure allowing higher temperatures without major additional void generation. At this point, the curing temperature is increased to T_2 [ºC] with a heating rate of 25 ºC /min and is maintained until the curing degree is higher than 95%.

The initial temperature applied, T_1, is selected by analyzing the thermal degradation of the paste adhesive by TGA, using a Perkin-Elmer TGA 1. Samples of non-cured adhesive with a mass of 20 ± 5 mg are analyzed in the TGA applying curing cycles with one single isothermal step after an initial heating from 30 ºC with 25 ºC/min. 7 samples are analyzed heating them isothermally with temperatures from 40 ºC to 160 ºC for 60 minutes. For these measurements, the oxygen flow rate used is 50 ml/min.

After defining the optimal T_1 *by TGA*, samples of adhesive with a size of 20x15x2 mm are cured by induction heating following different curing cycles combining different processing parameters, T_1 [ºC], t_1 [min], T_2 [ºC] and t_2 [min]. For manufacturing these samples, the paste adhesive is placed on CFRP plates that are then heated by induction, curing the adhesive. Afterwards, the void content of these samples is measured by microscopy techniques. 3 images are taken from each sample with the microscope Leica DMRXA, and then they are analyzed by dark field microscopy (DFM) with the microscope software Leica QWin.

Finally, SLS samples are produced bonding CFRP plates with different curing cycles thus causing different thermal degradation in the bondline. The selection of the curing cycles used to manufacture the samples for mechanical testing is based in two criteria:

- A maximum of 20 minutes at isothermal temperatures, having an overall curing process shorter than 30 minutes if considering the heating ramps.
- A minimum degree of cure of 95%, necessary to consider the curing reaction completed.

Additionally, 5 more samples for SLS test are produced, curing them with one single heating step. These samples are produced isothermally applying temperatures from 80 ºC to 160 ºC, and are used as reference to assess the acceleration of the process analyzed in this research.

SLS tests are performed following the International standard EN-2243-1. The CFRP bonded plates are made of prepreg supplied by UMECO (resin system MTM® 44-1, fibers Sigmatex CF 5804A). The plates are cured in autoclave following recommendations from the supplier (180ºC for 2 hours with 4 bars of pressure). The surface treatment is applied to the plates before bonding them [5] and the processing conditions used by the induction heating equipment [6] have been validated in previous research.

The degree of cure is calculated in this study using a kinetics model, briefly described in the Appendix A. This model permits to calculate the degree of cure of the samples for a given temperature and time. It is defined for the paste adhesive of this study by fitting the parameters of the theoretical model with data of the curing of the paste adhesive. This data is obtained by Dynamic Scanning Calorimetry (DSC), a well-known technique for cure kinetics characterization.

The adhesive used in this investigation is a bi-component paste adhesive amino based (LME 10049-4 / LMB 6687-2) from Huntsman Advanced Materials [7]. The mixing process is

carried out in a centrifugal laboratory mixer (Speedmixer DAC 150.1 FV) in three stages of one minute: two of them at 1500 rpm and the last one at 2500 rpm.

3 Results and discussion

TGA measurements to analyze the thermal degradation caused by different temperatures applied in the curing process of the paste adhesive are shown in Figure 1.

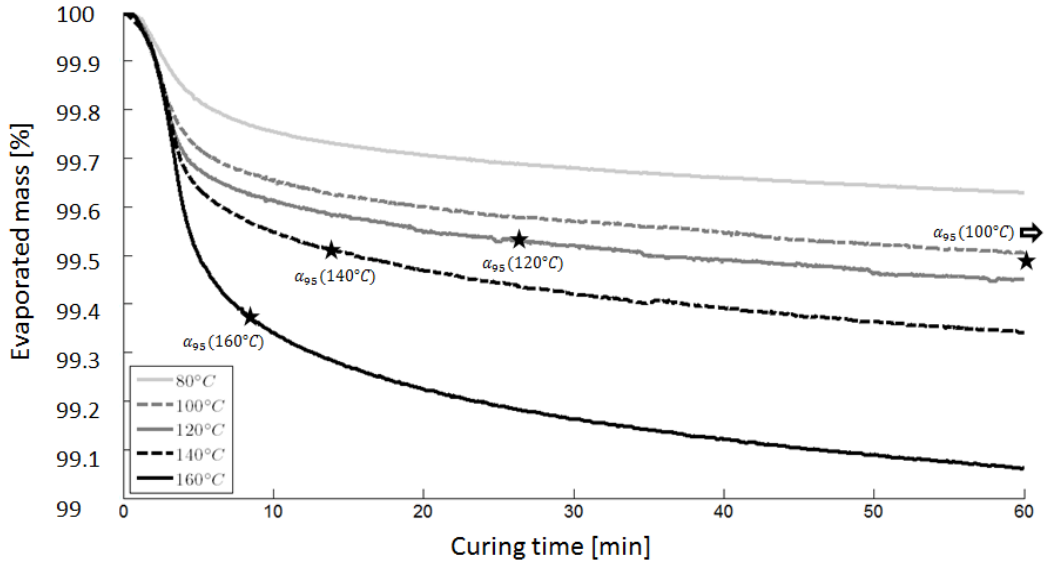

Figure 1. TGA carried out for different temperatures.

Observing the results form TGA, it can be stated that the adhesive degrades more when a higher temperature is applied:

- Curing at 80 ºC needs at least 4 hours to complete the process. This temperature is not considered as initial curing temperature T_1 [ºC] because the process is too slow.
- Curing at 100 ºC, 120 ºC and 140 ºC produce a similar degradation on the paste adhesive under study. The results show that these samples have a similar evaporated mass, around 0.5%, when they achieve 95% of degree of cure. For this reason, none these temperatures can be discarded as optimal T_1 [ºC] and they are considered in further experiments.
- Curing at 160 ºC causes a higher thermal degradation than the rest of temperatures analyzed, having more than 0.65% of mass evaporated in the paste adhesive cured 95%. This higher mass evaporated leads to a higher void content, and therefore to a lower mechanical performance. For this reason, this temperature is not considered in further experiments as initial curing temperature T_1 [ºC].

Afterwards, samples for the analysis of the effect of different temperatures on the void generation are manufactured applying different multistep curing cycles. The processing parameters are defined as follows:

- T_1 [ºC] between 100 ºC and 140 ºC, as defined by TGA.
- t_1 [min] between 5 and 20 minutes: Longer times are not considered hence the goal is to accelerate the process.

- T_2 [ºC] in the range of 140 ºC to 180 ºC to accelerate the process. Higher temperatures are not considered because the glass transition temperature of the CFRP used as adherent is around 190 ºC and the bonded joint could be damaged.
- t_2 [min] until the degree of cure of the sample is at least 95%.

Results for the analysis of the void generation caused by the application of curing cycles combining different processing parameters: T_1 [ºC], t_1 [min] T_2 [ºC] and t_2 [min] are shown in Table 1.

Curing process	Volumetric void content [%]	Degree of cure [-]	Curing process	Volumetric void content [%]	Degree of cure [-]
80 °C 240 min*	**1.3**	**86.77**	100 °C 20 min + 160 °C 10 min	1.4	98.9
100 °C 5 min + 140 °C 5 min	3.9	92.8	**100 °C 60 min***	**1.4**	**94.9**
100 °C 5 min + 140 °C 15 min	5.2	97.8	**120 °C 5 min + 140 °C 10 min**	**4.4**	**96.9**
100 °C 5 min + 180 °C 5 min	6.8	98.8	**120 °C 5 min + 160 °C 10 min**	**4.6**	**98.8**
100 °C 7.5 min + 160 °C 15 min	5.3	99.3	120 °C 5 min + 180 °C 5 min	8.0	98.9
100 °C 10 min + 140 °C 15 min	3.2	98.0	**120 °C 10 min + 140 °C 5 min**	**4.3**	**95.7**
100 °C 10 min + 140 °C 20 min	3.4	98.6	**120 °C 10 min + 160 °C 10 min**	**4.1**	**98.9**
100 °C 10 min + 160 °C 10 min	**3.8**	**98.8**	120 °C 10 min + 180 °C 5 min	5.4	99.0
100 °C 10 min + 160 °C 15 min	4.2	99.3	120 °C 12.5 min + 160 °C 5 min	3.9	98.0
100°C 10 min + 180 °C 5 min	4.0	98.9	120 °C 15 min + 140 °C 5 min	3.9	96.6
100 °C 15 min + 140 °C 15 min	1.5	98.1	**120 °C 15 min + 160 °C 5 min**	**3.7**	**98.2**
100 °C 15 min + 140 °C 20 min	1.4	98.6	120 °C 15 min + 180 °C 5 min	4.4	99.1
100 °C 15 min + 140 °C 5 min	1.3	94.6	120 °C 20 min + 160 °C 20 min	3.5	99.6
100 °C 15 min + 160 °C 5 min	**2.9**	**97.5**	**120 °C 60 min***	**3.9**	**98.7**
100 °C 15 min + 160 °C 10 min	3.3	98.8	**140 °C 5 min + 180 °C 5 min**	**13.4**	**99.0**
100 °C 15 min + 180 °C 5 min	**3.1**	**98.9**	140 °C 10 min + 180 °C 5 min	9.9	99.2
100 °C 17.5 min + 160 °C 15 min	2.4	99.3	**140 °C 15 min***	**6.1**	**97.9**
100 °C 20 min + 140 °C 10 min	1.2	98.3	**160 °C 10 min***	**15.6**	**98.6**
100 °C 20 min + 140 °C 15 min	1.2	98.2			

Table 1. Summary of void content analysis. * refers to samples cured isothermally [8]

As initially predicted, the paste adhesive is more sensible to void formation at a lower degree of cure. The initial temperature T_1 [ºC] is the curing parameter which affects most the void formation. Samples cured at 100 ºC in a first step show a lower void content than the samples initially cured at higher temperatures. A higher T_2 [ºC] will also produce more voids, but in this case the difference is lower if compared to the effect of an increase of T_1 [ºC]. This fact can be explained by advanced state of the chemical reaction, proving the main hypothesis of this research. Most of the samples produced show a degree of cure much higher than 95%, so the second step could still be shortened.

A selection of the samples is carried out, considering curing cycles shorter than 30 minutes in total with a degree of cure higher than 95%. The selected samples are highlighted in bold in Table 1. Then, samples for SLS test are bonded by induction heating under the curing cycles selected. Results of these tests are summarized in Table 2.

Sample	Curing process	Shear strength [MPa]	Failure mode	Void content [%]
1	100 °C 10 min + 160 °C 10 min	21.7 ± 1.9	Cohesive	3.8
2	100 °C 15 min + 180 °C 5 min	21.3 ± 8.3	Cohesive	3.1
3	100 °C 15 min + 160 °C 5 min	26.4 ± 1.3	Adherent	2.9
4	120 °C 5 min + 140 °C 10 min	19.4 ± 12.8	Cohesive	4.4
5	120 °C 5 min + 160 °C 10 min	14.6 ± 2.7	Cohesive	4.6
6	120 °C 10 min + 140 °C 5 min	20.9 ± 4.2	25% Adherent 75% Cohesive	4.3
7	120 °C 10 min + 160 °C 10 min	19.5 ± 2.5	25% Adherent 75% Cohesive	4.1
8	120 °C 15 min + 160 °C 5 min	22.9 ± 1.8	Adherent	3.7
9	140 °C 5 min + 180 °C 5 min	11.3 ± 7.9	Cohesive	13.4
R80	80 °C 240 min	24.4 ± 1.5	Adherent	1.3
R100	100 °C 60 min	22.1 ± 2.1	Adherent	1.4
R120	120 °C 60 min	15.2 ± 2.1	50% Adherent 50% Adhesive	3.9
R140	140 °C 45 min	9.6 ± 3.4	Adhesive	6.1
R160	160 °C 10 min	8.1 ± 7.8	Adhesive	15.6

Table 2. Summary of SLS test.

Observing the results, it can be stated that:

- Curing with T_1 = 140 ºC degrades the adhesive, showing a cohesive failure mode, which indicates degradation in the adhesive, leading to a decrease in the mechanical performance of the joint.
- Samples cured with T_1 = 120 ºC mostly show a cohesive failure, indicating certain degradation on the adhesive. In this case, a longer first heating stage will increase the mechanical performance but still showing relative high void content, as in sample 8.
- Curing with T_1 = 100 ºC improves the shear performance. In general can be stated that mechanical performance is higher when the first heating stage t_1 [min] is longer and T_2 [ºC] is lower.

- Thermal degradation appears for T_2 = 180 ºC, as shown in sample 2. In this sample, despite having a similar curing cycle as sample number 3, cohesive fracture indicates degradation.

The best curing cycle analyzed in this study consists on a first heating step of 15 minutes at 100 ºC followed by a second stage of 5 minutes at 160 ºC, using heating rates of 25 ºC /min. With this process, the curing time can be shortened from 4 hours to 27 minutes without affecting the mechanical performance.

4 Conclusions

Induction heating is used in this research to investigate the acceleration of the curing process of a paste adhesive by applying a multistep heating strategy. The results prove that it is possible to accelerate the curing process of a paste adhesive by this approach without affecting the mechanical performance of the joint. The hypothesis of this research is proved, showing that the paste adhesive is more affected by thermal degradation at an earlier curing stage. Thermal degradation leads to a higher void generation, mainly from the evaporation of moisture and chemicals during the curing process, decreasing the mechanical performance of the bonded joint. The results of this investigation show that a higher void content is generated in the paste adhesive when higher temperatures are initially applied in the process. It is observed that a lower temperature in the first curing step for a longer time will improve the mechanical performance of the joint showing a lower void generation. The second heating step will accelerate the curing process, shortening the final part of the curing reaction, where the curing rate is slower. This second stage is limited to 160 ºC for the paste adhesive tested in order to avoid major void formation caused by higher temperatures. In this study, a reduction of the curing time from 4 hours to 27 minutes is achieved, while maintaining unaltered the mechanical performance of the bonded joint.

APPENDIX A: Cure kinetics modeling

To model the curing process of the paste adhesive, a kinetics characterization is carried out. The chemical reaction is modeled by a modified *n*-th order model shown in Equation (1). The modification considers a chemically controlled part and a diffusion controlled part in order to consider the effect of vitrification of the adhesive in the curing process [9].

$$\frac{d\alpha}{dt} = k \cdot (1-\alpha)^n = \frac{1}{\frac{1}{k_T} + \frac{1}{k_D}} \cdot (1-\alpha)^n \qquad (1)$$

α [-] is the degree of cure, k [-] the overall reaction rate, n [-] is the reaction order. k_T [-] is the rate constant of the chemical controlled region, which is valid in the early curing stage of the reaction until vitrification occurs. k_D [-] is the diffusion controlled part, used at the rest of the curing reaction. This model is composed of 11 fitting parameters [10]. To calculate them, 15 samples, with a mass of 10 ± 2 mg, are analysed by DSC curing them at 5 different temperatures from 70 ºC to 110 ºC for 2 hours with the Perkin Elmer DSC 1 using nitrogen flowing at 40 ml/min. Results of a baseline consisting of empty sample pans are subtracted from the original measurements to account for instabilities of the measurements. The data from the measurements (heat flow, time and temperature) is introduced in the mathematical

software Matlab, in the least-squares-routes curve fitting algorithm called 'lsqcurvefit', calculating the fitting parameters summarized in Table A1.

Fitting parameter	Value	Fitting parameter	Value
A	112280 1/s	T_{g0}	252 K
E	53795 J/mol	$k_{D_{onset}}$	$0.1677 \cdot 10^{-3}$ 1/s
n	1.63	$T_{g\infty}$	399 K
C_1	9.1 K	p_1	889 K
C_2	51.6 K	T_1	265 K
λ	0.3746		

Table A1. Summary of parameter used for the modeling of the chemical reaction.

Finally, to calculate partially cured samples, the total energy from the reaction ΔH [J/Kg] must be measured. For this measurement, a non-cured sample of adhesive is completely cured by DSC, measuring the energy generated in the curing process. The measurement is carried out 7 times and the average measured is 262 ± 6.9 J/g. This value is used as reference for measuring the degree of cure in partially cured samples.

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