

# INTEGRAL DESIGN OF COMPOSITE STRUCTURES USING A MODIFIED CO-CURING PROCESS

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## ABSTRACT

Due to their high specific stiffness and strength, fiber-reinforced polymers (FRP) are increasingly utilized for the production of lightweight parts in various industries, among them aviation, automotive and sports equipment.

FRP structures feature either differential design, in which case the structure is assembled from different parts, or integral construction, i.e. the part is produced in one step. Depending on geometry of the structure, integral design can lead to complex and expensive toolings. Differential design, however, leads to a demand for joints which can form initiation sites for failure. To overcome this problem, the basics of a novel method for production of complex composite parts in integral construction are analyzed in this paper. This method employs pre-produced parts made from FRP which bond to the surrounding structure during the curing cycle to form the final part.

To investigate the feasibility of this approach, the curing behavior and the mechanical properties of laminates produced in this method are studied. The material used is a prepreg with epoxy-based resin and unidirectional carbon fiber reinforcement. Temperature-modulated Differential Scanning Calorimetry is used to investigate the curing behavior of the prepreg. Stack-ups of the prepreg are partly cured to different degrees in an autoclave using a modified curing cycle. Subsequently, a stack of uncured prepreg is laid up onto the partly cured laminate and then completely cured together using the manufacturer recommended curing cycle. The laminate properties are examined using measurements of the critical energy release rate  $G_{1C}$  and the interlaminar shear strength.

## 1 INTRODUCTION

With the widespread application of fiber-reinforced polymers, a need for optimization of the production methods arises. Traditionally, complex structures have been produced using elaborate and costly toolings, as the uncured composite material needs to be stabilized until polymerization has progressed in the curing cycle.

For instance, the production of hollow structures poses challenges. Several techniques have been developed and applied to achieve this goal, among them removable foldable cores made from metallic materials or soluble cores that can be removed by dissolution of the core material and cores that remain in the part throughout the lifetime. Most of these techniques, however, are associated with problems. Foldable cores are costly during handling and restrict features like undercuts in the part design. Soluble cores induce high handling effort to ensure complete removal of the core material. Remaining cores form dead weight and therefore increase part weight.

In order to overcome these constraints, the production of complex parts using partly cured cores is studied. The structure to be manufactured is divided into sub-parts, some of which are pre-cured separately from the surrounding structure using a specifically defined curing cycle, to attain a defined state of cure. After pre-cure, the sub-parts are assembled with the uncured parts and subjected to a curing cycle to achieve full cure and bonding of the part. The degree of cure is optimized such that the stability of the pre-cured parts is sufficient to support the uncured parts during cure, but at the same time a high bond quality is attained.

To find a suitable curing cycle and the optimum state of cure, the progression of cure has to be characterized. The polymerization of the epoxy resin can be measured using various techniques.

Hardis et al. showed the possibilities of monitoring epoxy resin cure by Differential Scanning Calorimetry (DSC), Raman spectroscopy and Dielectric Analysis (DEA) and showed the methods to be in good agreement [1]. The applicability of DSC to measure the degree of cure of carbon-fiber epoxy prepreg was demonstrated by Stark et al. [2]. Due to the possibility of measuring reversing and non-reversing heat flow and heat capacity simultaneously, temperature-modulated DSC is beneficial for this kind of application [2, 3]. In the present study, TOPEM® temperature modulation technique was employed. TOPEM® is a temperature-modulated DSC (TMDSC) method in which the underlying temperature profile is overlaid with a series of stochastic temperature pulses of varying pulse duration. For an example of the application of TOPEM® to curing analysis of epoxy, see [4].

Several researchers have investigated the joining of partly cured FRP structures. Corbett et al. and Adamson et al. have analyzed joining of composite structures using areas with low degree of cure after the first curing step, which are then fully cured in a second step [5, 6]. Using epoxy resin prepreg, Corbett et al. showed that for a certain temperature profile the flexural and shear properties of samples cured in two steps match those of samples cured in the manufacturer recommended autoclave curing cycle.

Studer et al. investigated b-stage curing and subsequent co-curing of carbon fiber-reinforced polymers CFRP [7]. They used biaxial non-crimp fabric and spread tow fabric in RTM process with epoxy resin system (HexFlow® RTM6, Hexcel Corporation) to produce CFRP parts with local reinforcement patches. The results show that joining of b-staged sub-parts with a void-free bond is possible by free-standing cure of the part with local pressure. Joining of partly cured laminates with RTM6 resin system was also examined by Moosburger-Will et al., who tested partly cured laminates joined with uncured laminates in a Vacuum Assisted Process (VAP) and showed that the fracture toughness of joined samples with one partly cured laminate equals or exceeds the value of a conventionally produced laminate for certain states of pre-cure [10].

## 2 EXPERIMENTAL

The experiments were carried out using an epoxy intermediate modulus carbon unidirectional prepreg with a toughened epoxy matrix. The resin content is 34% by weight and the reinforcement is intermediate modulus carbon fiber with an areal weight of 268 g/m<sup>2</sup>.

The peel ply used is a PA66 plain weave type fabric with a thickness of 0.12 mm and an areal weight of 83 g/m<sup>2</sup>.

### 2.1 Thermal Characterization using TMDSC

The Differential Scanning Calorimetry measurements were carried out on a DSC1 by Mettler Toledo GmbH. Samples of approximately 7 mg were cut from the prepreg and placed in aluminum crucibles with manually perforated lids for testing. For the temperature modulation, a pulse height of 1 K and a pulse duration of 15 to 30 seconds were defined. One influence to be considered is the state of cure of the resin in the prepreg. During the production of the prepreg, the cure of the resin is started to provide properties suitable for handling of the prepreg (e.g. the right tack). As this degree of cure could not be determined, all measurements are relative to the state of cure of the prepreg as delivered.

In order to measure the total heat, dynamic TMDSC measurements were performed from room temperature to 300 °C with a heating rate of 2 K/min, which matches the heating rate of the autoclave curing cycle. The ultimate heat of reaction was calculated by integration over the dynamic measurement as:

$$\Delta H_{ult} = \int_0^t \frac{dH}{dt} dt \quad (1)$$

For the measurement of the heat of reaction of an isothermal curing process, the heating rate at the start of experiment was set to 2 K/min in accordance with the dynamic measurements. After reaching the isothermal temperature, an isothermal step was incorporated. The length of the isothermal step was set to 10 h so that the exothermic reaction was finished within the isothermal step. The heat of reaction for a defined isothermal hold time  $t_h$  at a temperature  $T$  was determined as follows:

$$\Delta H_{T,t_h} = \int_0^{t_h} \frac{dH}{dt} dt \quad (2)$$

The degree of cure  $\alpha$  for a hold time  $t_c$  at temperature  $T$  is given by the ratio of the heat of reaction to the ultimate heat:

$$\alpha = \frac{\Delta H_{T,t_c}}{\Delta H_{ult}} \quad (3)$$

Several authors have shown the progression of the degree of cure and the achievable degree of cure to be dependent on cure temperature [1, 7, 11]. Higher curing temperatures induce a faster progression of cure. For this study, a curing cycle with an isothermal step at 140 C was examined as shown in Figure 1. This temperature profile was chosen for experimental testing, as the slower progression of cure allows for a realization of the process for heavier parts with thermal inertia. Furthermore, the progression of cure depends on the heating rate. Higher heating rates lead to an increase of the exothermic peak and a decrease of reaction duration [7]. To ensure optimum viscosity of the resin in the curing cycle, the heating rate was affixed to 2 K/min.

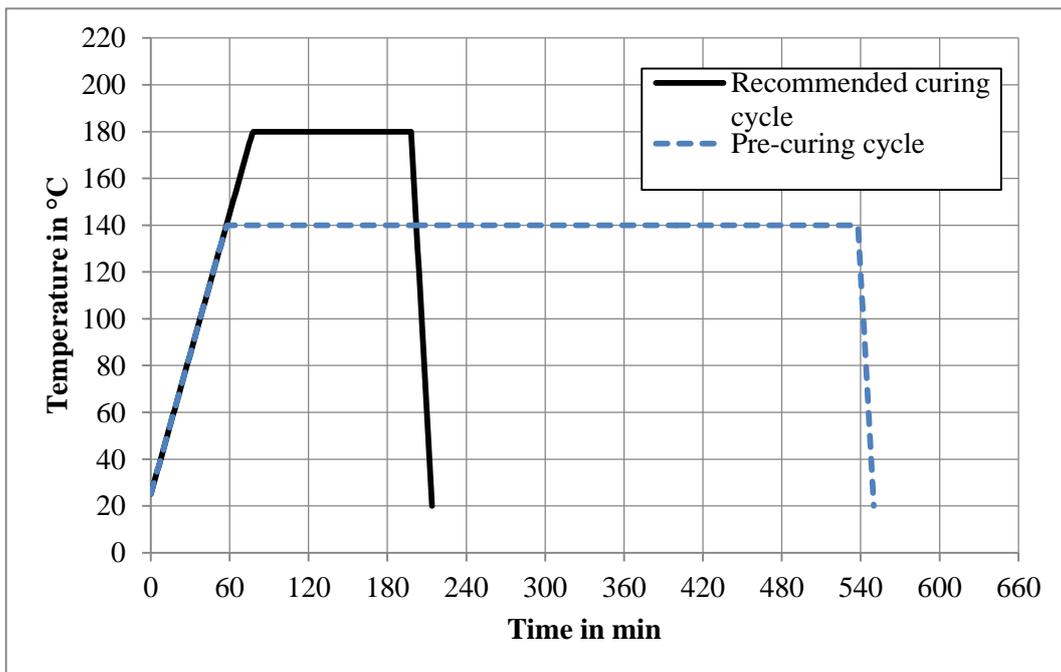


Figure 1: Recommended curing cycle and isothermal cycle for pre-cure

## 2.2 Mechanical characterization

The quality of the bond formed between partly cured and uncured laminates was tested mechanically on coupon level in tests of interlaminar shear strength (ILSS) referring to ISO 14130 [8] and mode I interlaminar fracture toughness energy referring to EN 6033 [9].

The ILSS specimen geometry was 20 mm x 10 mm x 2 mm (width x depth x thickness). For specimen preparation, a unidirectional stack-up (called 'stack A' from here on) of thickness 1 mm was laid up and cured partly in an autoclave. The curing cycle is based on the DSC experiments and features a ramp to 140 °C with a heating rate of 2 K/min and a subsequent isothermal step of varying length of 150 min, 240 min or 330 min to achieve different degrees of cure. For reference, uncured and completely cured stacks were included as well. The stack-ups were wrapped in unreleased peel ply to ensure a clean bonding surface to the second stack. After partial cure, the peel ply was removed and an uncured stack-up (called 'stack B') of identical thickness and orientation was laid up onto the partly

cured stack A. The two stacks were then exposed to the standard curing cycle (see Figure 1) to reach full cure of both constituents. Table 1 summarizes the state of cure of the stacks prior to the second curing step.

Configuration	Curing Cycle Stack A	Curing Cycle Stack B
$C_1$	uncured	uncured
$C_2$	140 °C 150 min	uncured
$C_3$	140 °C 240 min	uncured
$C_4$	140 °C 330 min	uncured
$C_5$	fully cured	uncured

Table 1: Curing state of the stacks at assembly before final cure

After curing, the specimens were cut from the plates using a diamond saw. Testing was performed at room temperature on a standard testing machine Zwick 1474 with a 10 kN load cell and a displacement rate at the loading nose of 1 mm/min. In accordance with ISO 14130, the loading nose had a radius of 5 mm and the support rollers had a radius of 3 mm. To decrease the chance of compressive failure, a 0.1 mm polypropylene interply was placed under the loading nose. The tests were filmed using a camera to allow for observation of onset and progression of failure in the specimens.

The specimens for  $G_{IC}$  testing were prepared similarly to the ILSS specimens with minor changes due to specimen geometry of 250 mm x 25 mm x 3 mm (width x depth x thickness). The stacks had a thickness of 1.5 mm each to achieve the total specimen thickness of 3 mm. A PTFE film was inserted at the edge of the specimens at the interface of the stacks to start the crack. The specimen design given in EN 6033 was modified in the design of the load introduction blocks. A design based on the loading blocks specified in ASTM 5528 was used instead of piano hinges. After cutting and adhesive bonding of the loading blocks by 2K epoxy adhesive, the sides of the specimens were stamped to apply a scale for the observation of crack propagation.

The experiments were carried out on a testing cylinder with a 1 kN load cell at room temperature with a displacement rate of 10 mm/min. The propagation was observed using a camera with a magnification device. The crack was started by loading the specimen until a similar crack length for all specimens was attained, then loading was stopped and the test was started.

The results were evaluated using the area method by integration of the area under the load-displacement curve to a crack length of 100 mm.

### 3 RESULTS

The TMDSC measurements of the pre-curing cycle depicted in Figure 1 were used to calculate the degree of cure from the growth of the heat of reaction using equations (2) and (3). Comparison to the ultimate heat of reaction obtained from the dynamic measurements using equation (1) showed that the isothermal step at 140 °C leads to a degree of cure of 0.6 as compared to state of delivery for long holding times. The evolution of the cure is depicted in Figure 2, with the phases I and II marking the heating and isothermal segments.

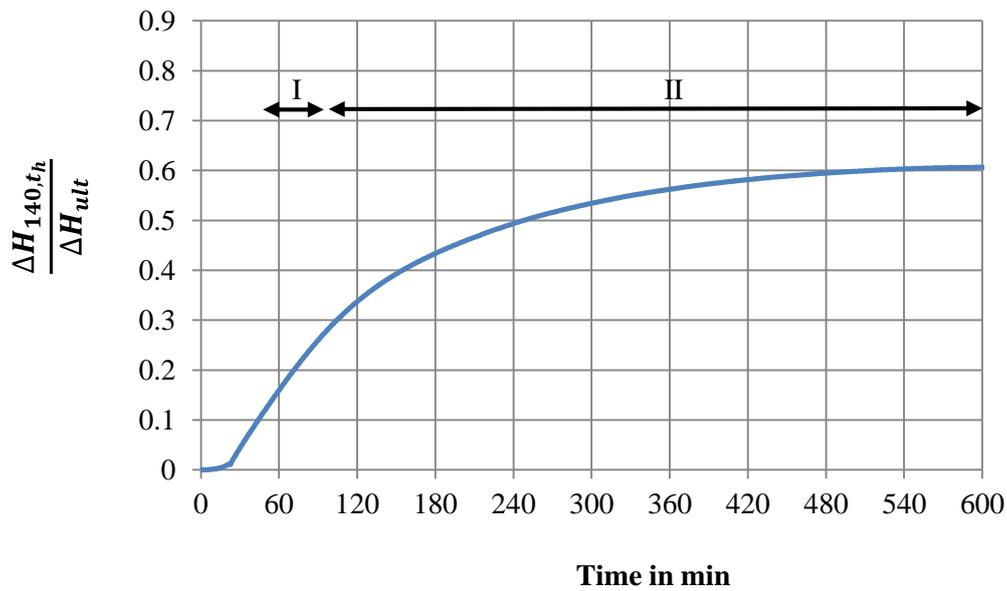


Figure 2: Evolution of the state of cure during the pre-curing cycle

The results of ILSS testing are summarized in Figure 3. All results were normalized to the specimens of reference configuration  $C_1$  to show the performance of the manufacturing process relative to a conventional co-curing process. The partly cured specimens of configurations  $C_2$  to  $C_4$  show apparent interlaminar shear strength values reduced by 1 %, 2 % and 8 % ( $C_2$ ,  $C_3$ ,  $C_4$ , respectively), while the fully cured configuration  $C_5$  exhibits a 24 % lower value.

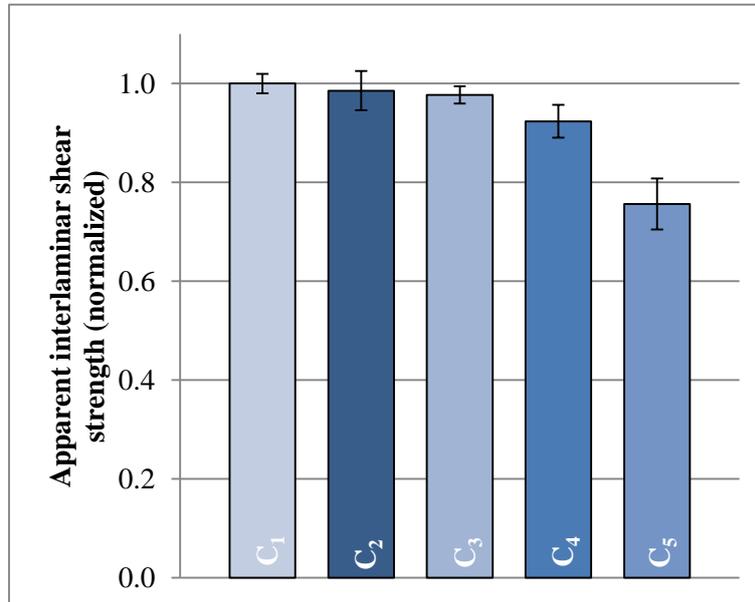


Figure 3: ILSS testing results normalized to reference

The interlaminar fracture toughness energy measurements shown in Figure 4 are also normalized to the results of the reference configuration  $C_1$ . With a reduction of 3 % and an increase by 10 %, the partly cured specimens of configurations  $C_3$  and  $C_4$  perform better than those of configuration  $C_5$  with a decrease by 12 %, though the raised variation coefficient is to be considered. Configuration  $C_2$  was not included for this experiment.

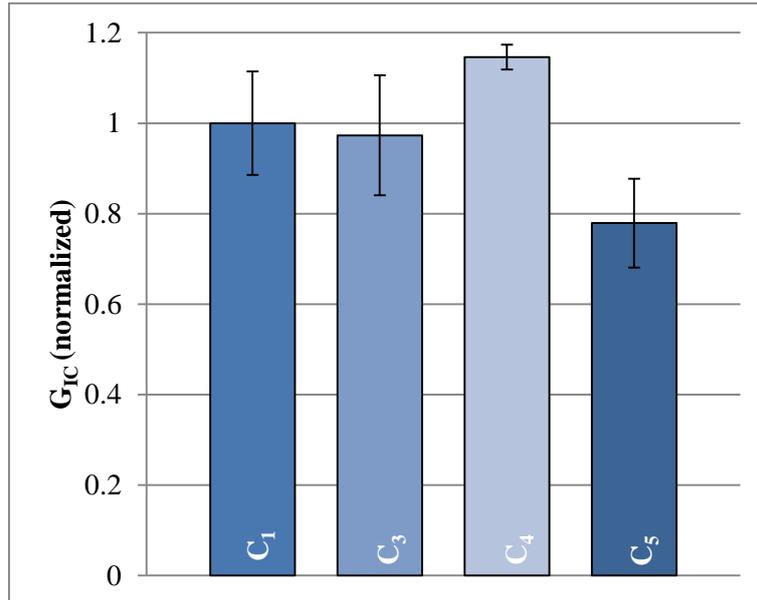


Figure 4: Interlaminar fracture toughness energy  $G_{IC}$  normalized to reference

Judging from these results, the mechanical bonding properties between the two stacks for the partly cured specimens are close to those produced in co-curing process and is significantly better than those produced in co-bonding.

#### 4 CONCLUSION

Basic investigations for a novel method for producing complex parts from FRP materials have been undertaken. TMDSC measurements have been performed in order to characterize the cure behavior of carbon fiber reinforced epoxy prepreg during an isothermal step at lowered temperature and the evolution of cure has been examined.

Based on the TMDSC results, specimens made from partly cured stacks joined with uncured stacks have been manufactured and the bonding between the constituting stacks has been analyzed in ILSS and  $G_{IC}$  measurements. The performance of the partly cured and then joined specimens is superior to specimens produced by co-bonding and is slightly inferior to co-cured specimens.

The results presented in this paper show the basic properties of the novel production process. For a thorough evaluation, further studies are necessary. For a deeper insight, influencing factors like peel ply type, mechanical properties of the material after pre-curing, surface preparation and reinforcement architecture are possibly relevant and will be investigated in subsequent studies.

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