



Manufacturing thick laminates using a layer by layer curing approach

Xiaochuan Sun^a, Lawrence Cook^b, Jonathan P-H. Belnoue^a, Kostas I. Tifkitis^b, James Kratz^a, Alex A Skordos^{b,*}

^a The Bristol Composites Institute, University of Bristol, Queen's Building, BS8 1TR, Bristol UK

^b Composites and Advanced Materials Centre, School of Aerospace, Transport and Manufacturing, Cranfield University, Cranfield MK43 0AL, UK

ARTICLE INFO

Keywords:

Cure
Additive manufacturing
Layer-by-Layer
Simulation

ABSTRACT

The work presented in this paper puts forward a manufacturing strategy for the processing of thermosetting composites based on Layer by Layer (LbL) curing. The process operates additively with sublaminate placed in a heated press, partially cured while consolidating, followed by loading of the next sublaminate and repeating the cycle until part completion. Coupled consolidation-cure simulation was utilised to design the process and establish its capabilities showing that halving the cure time is possible for thick parts. Mechanical testing showed that for pre-cure of placed layers below the gelation degree of cure, interlaminar properties are equivalent to those of conventionally manufactured material. A trial was carried out demonstrating successfully the LbL process. On-line measurements of temperature and compaction matched the predictions of the simulation, whilst the quality of the material produced is equivalent to that of conventionally produced composites.

1. Introduction

Placement, consolidation, and curing have historically remained separate and sequential steps carried out to manufacture composites structures. Carrying out placement and consolidation at relatively low temperatures to avoid curing implies slower material response and longer time scales required for consolidation. Furthermore, curing the material in bulk costs more in time as thermal lags in the low thermal conductivity thickness direction need to be equilibrated. The inefficiencies of the current processing philosophy are exaggerated as component dimensions – especially thickness – increase. Placement/forming and consolidation often need to be carried out in stages, while thermal lags increase non-linearly with thickness. For the largest structures, there is a significant challenge to lay up the part within the out-life of the prepreg. In the case of thick and ultra-thick components, thermal profiles need to be conservative and long to eliminate detrimental temperature overshoots [1].

Efforts to combine processes into a single Layer-by-Layer (LbL) process have been investigated for thermoplastic composite materials. The main obstacle is still matching the interlaminar properties achieved through LbL to those when a subsequent autoclave consolidation step is used [2]. In this regard, lower viscosity thermosetting materials may allow combining all three steps if final fibre volume fraction is retained, while advancing the degree-of-cure to the appropriate level where

adhesion is retained across subsequent ply interfaces. White and Kim [3] proposed a curing technique to process thick composites in stages without exothermic overshoots; sublaminate stacks were consolidated individually at low temperature to build up thickness, followed by a final curing step. Staged curing advances the degree-of-cure to a point where both temperature overshoot is reduced and interlaminar properties are retained because the polymer remains only partially cured until the final cure stage. As a result, adhesion and consolidation are possible with this approach, but the total process time is much longer than a conventional curing cycle. Modelling of an additive processing strategy that relies on partial curing of 3D printed tows/tapes has shown that benefits in the order of 50 % in processing time and more than 85 % in temperature overshoot are possible for thick components, with the strong non-linearity in the dependence of overshoot on thickness eliminated by the additive character of the process [4]. A process that combines printing with in-situ curing of prepreg layers during deposition using Joule heating has been implemented successfully to manufacture composites in a free form printing process [5]. Success of an additive process based on this type of strategy depends on the integrity of the interface between successively deposited layers, which is essentially governed by the ability of partially cured layers to bond. A similar situation arises in variations of co-curing in which one of the two laminates has been previously partially cured [6,7]. In this case, it has been reported that the highest interfacial fracture toughness is obtained at a

* Corresponding author.

E-mail address: a.a.skordos@cranfield.ac.uk (A.A. Skordos).

<https://doi.org/10.1016/j.compositesa.2024.108489>

Received 4 July 2024; Received in revised form 12 September 2024; Accepted 21 September 2024

Available online 22 September 2024

1359-835X/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

high partial degree of pre-cure between 70 % and 80 % [7]. Partially cured assemblies in the form of a part and its reinforcement patch have been successfully joined by a similar process [8], removing the need for adhesive bonding [9]. The partially cured assembly does not need to be joined to an uncured laminate. Examples of two partially cured parts have been joined in a process termed melding [10]. Recent studies have taken co-curing further by applying it to liquid composite moulding [11] and core materials [12].

Frontal polymerisation has been investigated as a means of achieving gradual progression of the curing reaction within the composite accomplished by achieving an appropriate balance between heat generation and transfer [13,14]. Additive strategies based on frontal polymerisation applied to thermosets and their non-continuous reinforcement composites enable free-form production printing to be carried out with significant efficiency benefits [15,16]. Combination of UV initiation with frontal polymerisation in composites curing offers additional cure process acceleration and tailoring of the thermal field [17,18], that could potentially lead to additive processing strategies. However, potential property knockdowns observed when multiple polymerisation fronts are utilised within a processing strategy [19] would need to be addressed.

An LbL process aims to provide sufficient consolidation quality in each placement stage. Experimental definition of conditions with which placement, consolidation, and cure are delivered without compromising adhesion might be possible. Modelling tools are sufficiently well advanced and capable of defining the optimal conditions. Cure and consolidation models are available in the literature [20–24], alongside appropriate methods for material property characterisation [22,25,26].

The work presented here addresses the main developments for demonstrating the benefits of LbL processing for thermosetting composites. The process concept is defined and simulation tools are adapted to model the coupled cure-consolidation behaviour. The mechanical behaviour of interfaces produced from material with different states of pre-cure is established and an instrumented process trial of the LbL process is carried out using a setup adapted for this purpose.

2. Process concept

The concept proposed in this work addresses the limitations and inefficiencies of current strategies through layer by layer cure of prepreg during placement/consolidation. The proposed process takes place in steps of consolidation and partial curing on a heated tool, with the upper layer heated through contact in a press. The process is illustrated schematically in Fig. 1. The process starts with a layer or sublaminar placed on the heated lower tool. The upper tool, which is also heated, is brought in contact and held in place to consolidate the material until the cure has progressed sufficiently. Subsequently, the tool is raised and the next layer or sublaminar is placed on top of the partially cured material. Press application follows, to achieve consolidation and partial cure of the new layer or sublaminar. This sequence is repeated until the whole

of the thickness in built up. This processing strategy results in periodic heating and compaction of the layers already placed in the stack.

The main advantage of the LbL processing strategy is that it allows fast processing of a fraction of the thickness of the laminate. The fact that the process operates in a fraction of the thickness permits use of aggressive thermal profiles. This can achieve significant acceleration of the overall process. Consolidation under higher than usual temperature can achieve faster compaction and void removal for the relatively thin layer of material in contact with the top tool. Similarly, the low thickness of the active layer or sublaminar allows acceleration of the cure as heat transfer is faster and heat dissipation more effective when required to ameliorate the effects of exothermicity of the curing reaction. The latter is of high importance in thick and ultrathick laminates, in which the potential of uncontrollable temperature overshoots makes necessary the use of highly conservative and long cure profiles.

Successful implementation of the proposed concept involves challenges in controlling the cure process to achieve sufficient progress without compromising the adhesion of adjacent layers and in the selection of processing rates ensuring adequate consolidation quality and void removal. The former can be achieved by investigating the mechanical behaviour of interfaces produced between partially pre-cured material and uncured material upon cure of the whole laminate to identify the level of partial pre-cure that allows sufficient interfacial bonding. The latter can be accomplished by exploring the interplay between acceleration of the cure reaction and acceleration of the consolidation process with increasing temperature, with the aim of establishing processing conditions that allow a high level of prepreg compaction before cure progresses sufficiently to increase the viscosity resin beyond processable levels. The processing characteristics of high performance epoxy prepreps, which are based on the autocatalytic nature of epoxy cure, lend themselves to this type of strategy.

3. Methodology

3.1. Materials and manufacturing

Composite specimens were manufactured using glass reinforced 913 epoxy matrix unidirectional (UD) prepreg supplied by Hexcel (913G-E-5–30 %). The prepreg contains 30 wt% resin and has a fibre areal density of 192 g/m² corresponding to a cured thickness of 125 µm for a fibre volume fraction of approximately 60 %. HexPly® 913 is a modified epoxy with a density of 1.23 g/cm³. The fibres are E-glass with a diameter of 5 µm. For thin laminates, below 3 mm, the matrix system can be cured in a single dwell in the 125–160 °C range. For greater thicknesses the exothermicity of the resin system necessitates the utilisation of a low temperature dwell, below 100 °C, before the final isothermal cure step.

Composite plates with an interface at mid-plane comprising one side of partially pre-cured material at prescribed levels and one side with fully uncured material prior to final cure were manufactured using a Fontijne Grotnes LabPro 1000 two column press. The plates were used to characterise the influence on interfacial mechanical properties of partially pre-curing the material on one side before the final step of processing. The procedure, which is illustrated schematically in Fig. 2.a, comprises three steps. Initially, two halves of 15 layers of UD prepreg with 300 mm × 300 mm in-plane dimensions were laid up. One half was placed in the press between PTFE coated steel plates and a fixed height spacer with a thickness of 2.15 mm and cured under 20 kN following a thermal profile appropriate for reaching the prescribed level of pre-cure. The top surface of the laminate was covered with a layer of nylon peel ply (PeelPlyN85 VAC Innovation Ltd.) aiming at generating a controlled level of roughness on the pre-cured surface. A PTFE coated k-type thermocouple was placed in the centre of the assembly in contact with the steel platen to allow measurement of the actual cure profile and subsequent calculation of the degree of pre-cure. After completion of curing and cooling down, the peel ply was removed and the uncured half

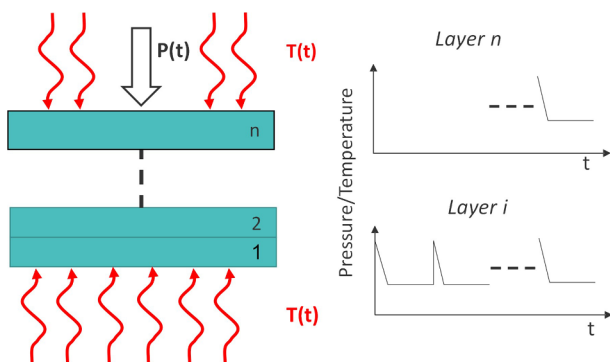


Fig. 1. LbL process concept.

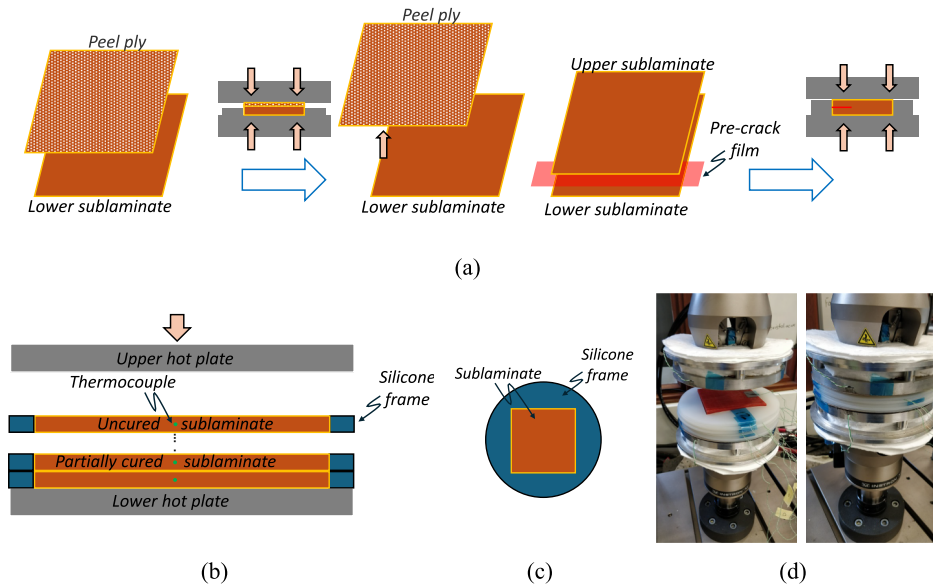


Fig. 2. (a) Procedure used for the production of partially pre-cured interface specimens. LbL process setup: (b) section of setup; (c) top view of silicone frame with sublaminate; (d) experimental setup.

was placed on top of the pre-cured sublaminate. An 80 mm wide strip of 10 μm thick FEP crack starting film was inserted between the two halves aligned to one edge of the plate. The stack was placed in the press between the two PTFE coated plates adding a 2.35 mm fixed height spacer to reach a total thickness of 4.5 mm. Curing was carried out under a pressure of 20 kN using a ramp rate of 2 $^{\circ}\text{C}/\text{min}$ to 100 $^{\circ}\text{C}$, a 10 min isothermal dwell followed by a 2 $^{\circ}\text{C}/\text{min}$ ramp to 160 $^{\circ}\text{C}$ and a second 10 min dwell. The plates were cut to the appropriate dimensions for subsequent testing using a diamond impregnated saw blade (Crandon 60/85).

A 40 mm thick 913 epoxy/glass laminate was manufactured using the LbL process. The manufacturing was carried out using an Instron servo-hydraulic 8801 universal testing machine equipped with two temperature controlled heated plates clamped by the grips of the testing machine. The process and geometry are illustrated schematically in Fig. 2.b and 2.c. and the setup is shown in Fig. 2.d. Three hundred 100 mm $\times$ 100 mm prepreg sheets were cut and laid up to produce 6 sublaminate each with a $[[0/90]_{25}]_6$ layup sequence. A k-type thermocouple was placed at the mid-plane of each sublaminate as well as on its top surface. Circular 2.5 mm thick silicone sheets with a diameter of 180 mm and a 102 mm square centre cut-out (Fig. 2.c) were prepared to constrain the sublaminate and to prevent excessive resin bleeding from the prepreg during compaction. Each sublaminate was positioned in the cavity formed by two silicone sheets. During the process, both heated plates were kept at 130 $^{\circ}\text{C}$. The first sublaminate was placed on the lower heated plate and a compressive force of 1 kN was applied at a rate of 100 N/s. After 10 min, the upper plate was raised and the next sublaminate was placed in the assembly. The duration of the material loading step, during which the underlying sublaminate was cooling down, was 30–60 sec. This sequence was repeated 6 times to produce the 40 mm thick laminate. A diamond impregnated saw blade was used to cut the laminate, followed by grinding using 1200 and 2400 grit silicon carbide paper and polishing with 9 μm diamond spray to prepare microscopy samples.

3.2. Simulation

The compaction and cure of the material were simulated using an 1-D model. During consolidation, two types of flow are observed; (i) percolation, in which the fluid can be squeezed and bled out and (ii) shear flow, in which the composite behaves like a viscous fluid with

inextensible fibres. The model, which is based on [21], allows to capture these two flows and has been enhanced with the use of analytical physics-based expressions linking the thickness evolution with time to the applied temperature and pressure cycles, the viscosity and meso- and micro- geometrical characteristics of the reinforcement [27]. The deformation through the ply thickness is averaged whilst the ply undergoes through-thickness compaction and in-plane spreading. A criterion for the transition between the flow modes is based on the assumption that fibre convection is impeded once the shear deformation at ply edges reaches a critical level. At the meso-scale, this gives rise to the existence of a compaction limit over which the fibres are so tightly packed that the material cannot compact anymore. Before locking, the squeezing flow is incompressible i.e. the strain in the transverse direction is considered equal and opposite to the strain in the compaction direction. After locking, the ply is assumed to be fully compressible i.e. no transverse expansion occurs and the volume is lost in bleeding flow.

The consolidation stress (σ) is linked to the strain rate in the thickness direction ($\dot{\epsilon}$) as follows:

$$\sigma = \eta_{\text{strain}}(\epsilon) \eta_{\text{rate}}(\dot{\epsilon}) \dot{\epsilon} \quad (1)$$

where η_{strain} and η_{rate} represent the elastic and viscous behaviour of the overall apparent viscosity of the prepreg.

The viscous term follows a power law:

$$\eta_{\text{rate}}(\dot{\epsilon}) = \bar{e}^{\bar{b}} (-\dot{\epsilon})^a \quad (2)$$

where a and $\bar{b}$ are resin material and temperature dependent parameters estimated experimentally.

The elastic term incorporates the transition between squeezing and bleeding flow that occurs when shear deformation at the edges of the prepreg reaches a critical locking strain (ϵ^l). The strain dependent term in Eq. (1) is decomposed into a term expressing effects at ply level (η_{ply}) and a term representing microscale phenomena (η_{micro}):

$$\eta_{\text{strain}}(\epsilon) = \eta_{\text{micro}}(\epsilon) \eta_{\text{ply}}(\epsilon) \quad (3)$$

The ply term depends on the size of the prepreg layer and is expressed as follows:

$$\eta_{ply} = 2 \left(\frac{w_0}{h_0} \right)^2 e^{-4\varepsilon}, \varepsilon < \varepsilon^l$$

$$\eta_{ply} = 2 \left(\frac{w_0}{h_0} \right)^2 e^{-2(\varepsilon + \varepsilon^l)}, \varepsilon \geq \varepsilon^l$$
(4)

Here w_0 and h_0 are the initial width and thickness of the ply respectively, whilst the locking strain (ε^l) is computed based on geometrical considerations [21].

The microscale term is:

$$\eta_{micro} = 2\eta_{resin} \sqrt{\chi_l} e^k \left[\left(\frac{k}{\sqrt{\chi_f} e^e - k} \right)^2 + 3 \right], \varepsilon < \varepsilon^l$$

$$\eta_{micro} = 2\eta_{resin} \left(\frac{l_0}{d} \right)^2 k \left(\frac{k}{\sqrt{\chi_f} e^e - k} \right)^2, \varepsilon \geq \varepsilon^l$$
(5)

where l_0 is the fibre length, d is the edge length of the fibres in the direction perpendicular to their orientation, k is a phenomenological parameter estimated experimentally, η_{resin} is the resin viscosity and χ_l and χ_f are the aspect ratios of a unit cell at locking and at the compaction limit respectively. The aspect ratio at locking can be computed directly from the true locking strain as:

$$\chi_l = e^{-2\varepsilon^l}$$
(6)

The aspect ratio at the compaction limit can be approximated as $\chi_f \approx 1.4\chi_l$ [21].

The ordinary differential equation system expressed by Eqs. (1)–(6), which constitute the consolidation model, is solved using MATLAB ODE® Solver15s. The three empirical parameters of the model (a , b , k) are estimated using the result of compaction experiments and curve fitting to be discussed later.

The cure solution is based on the 1-D energy balance with heat conduction and generation terms:

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} K \frac{\partial T}{\partial x} + (1 - v_f) \rho_r H_{tot} \frac{d\alpha}{dt}$$
(7)

Here K is the thermal conductivity of the composite in the through thickness direction, ρ and c_p the density and specific heat capacity of the composite respectively, v_f the fibre volume fraction, ρ_r the density of the resin, H_{tot} the total enthalpy of the curing reaction of the resin, whilst α denotes the degree of cure of the resin, T the temperature, t the time and x the spatial coordinate in the thickness direction.

The heat generation term calculation is based on the assumption that heat release rate is proportional to the rate of reaction. The rate of reaction is expressed as a function of the instantaneous temperature and degree of cure, with the following expression selected for the 913 epoxy resin system:

$$\frac{d\alpha}{dt} = k_1 (1 - \alpha)^{n_1} + k_2 (1 - \alpha)^{n_2} \alpha^m$$
(8)

Exponents n_1 , n_2 and m are phenomenological parameters corresponding to reaction orders and k_1 , k_2 are rate constants following an Arrhenius dependence on temperature:

$$k_i = \frac{A_i e^{\frac{E_i}{RT}}}{1 + e^{C[a - \alpha_r(T - 273.15) - \alpha_c]}}, i = 1, 2$$
(9)

where E_1 and E_2 are activation energies, A_1 and A_2 are pre-exponential factors and R is the universal gas constant. The denominator in Eq. (9) incorporates diffusion limitations to the kinetics model, which are of significance when the glass transition temperature of the curing resin approaches the curing temperature. This is achieved through use of a critical degree of cure value, which is a function of temperature and is

controlled by parameters α_r and α_c , whilst the breadth of the transition to diffusion controlled reaction is governed by parameter C . Eq. (9) uses absolute temperature.

Solution of the differential equation expressed by Eq. (7) coupled with the cure kinetics model expressed by Eqs. (8) and (9), comprising the cure model, is carried out using a finite element modelling solution of the problem implemented and validated in [20]. The thermal properties are assumed to be constant, whilst the cure kinetics parameters are estimated using differential scanning calorimetry results and curve fitting. The model does not take into account volumetric and dimensional changes due to shrinkage and thermal expansion/contraction. The assumptions of constant volume and thermal properties are expected to have a small influence in the quality of simulation results as dimensional changes in the composite are in the order of a few percent, whilst significant changes in the order of 10–15 % in thermal properties happen around the latter stages of the cure during vitrification, with the model presented here used predominantly to assess transient effects in the early and intermediate stages of the process.

The two models are coupled in a weak scheme, which is illustrated in Fig. 3. The simulation starts with the first sublaminate and the execution of the cure model. This generates a temperature distribution which is fed into the compaction simulation to compute the thickness of the sublaminate. This is fed back to the cure model, which using the updated thickness, computes a new temperature distribution. This is first checked for convergence by comparing with the previous iteration and if convergence is not reached the consolidation model is executed again with the updated temperature distribution. This procedure is repeated until convergence. Subsequently, the next sublaminate is added and the simulation starts using the temperature and degree of cure of the existing sublaminate as initial conditions of the cure model solution for the corresponding part of the finite element mesh. The iterations with the consolidation model are executed by using the temperature distribution since the beginning of the process and updating only the new increments corresponding to the new sublaminate. This procedure is repeated until all sublaminate are placed and the process is complete. In the simulation for the material system of this investigation the solution converges within the second iteration as a result of the full dominance of bleeding flow resulting in very fast approach to the final thickness of the layers.

3.3. Characterisation and mechanical testing

The parameters of the consolidation model were derived from ramp-dwell compaction tests under isothermal conditions. Rectangular sheets of the prepreg, with in-plane dimensions of 25 mm × 50 mm, were laid up to form a crucifix geometry with a stacking sequence of [0/90]₈. This arrangement results in an effective 25 mm × 25 mm square region in the centre of the specimen with a mean thickness of 2.4 mm. This geometry minimises lateral loss of material from the edges of the central square area as the plies are squeezed in the through-thickness direction. The tests were carried out using an Instron servo-hydraulic 8801 universal testing machine and the same heated plates and camera setup as the one utilised in LbL process trials. The tests were performed at 30, 60 and 90 °C. The compaction load was 80 N initially and was increased in 4 steps of 40 N each, with the load kept constant at each force level for 240 s. The highest load was 240 N and the overall duration of the experiment 1200 s. The loading rate was 65 N/s. In terms of pressure levels, these conditions correspond to pressure levels of 0.13 to 0.38 MPa with a step of about 0.06 MPa and a loading rate of 0.1 MPa/s. Three specimens were used for each test case.

Differential scanning calorimetry (DSC) was utilised to identify the parameters of the cure kinetics model. The experiments were carried out using a TA Instruments DSC Q200. Nitrogen purge gas with a flow rate of 50 ml/min was used. Samples of the prepreg of 4–8 mg weight were encapsulated in Tzero™ pans and lids. Isothermal experiments were carried out at 90, 110, 130 °C and dynamic tests at 1, 2, 5 and 10 °C/

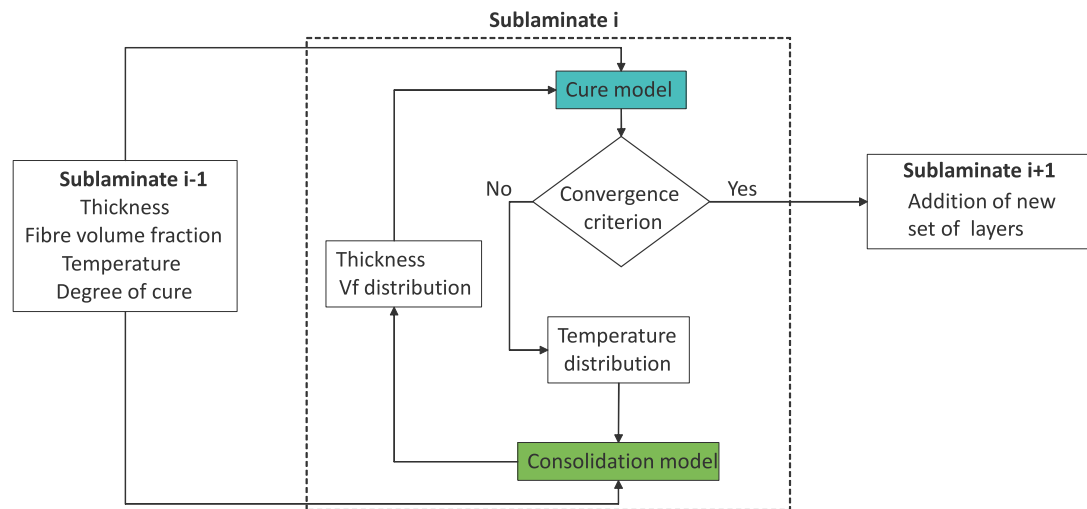


Fig. 3. Simulation flow.

min. The material was cured fully after the end of isothermal experiments in a heating ramp at $10\text{ }^{\circ}\text{C}/\text{min}$ to allow measurement of residual heat, which was subsequently used to estimate the total reaction enthalpy per sample. This is necessary in prepreg samples as the variability in resin content does not allow calculation of reaction rates based on total enthalpies measured in independent dynamic tests. The DSC data were integrated to calculate the degree of cure and reaction rate evolution using a horizontal baseline for isothermal conditions and sigmoidal for dynamic conditions. All DSC tests were duplicated. The specific heat capacity of the prepreg was measured using the DSC apparatus in modulated mode. Tests were performed at 90, 110 and $130\text{ }^{\circ}\text{C}$. The period and amplitude of the modulation were 60 s and $1\text{ }^{\circ}\text{C}$ respectively. An average specific heat capacity was calculated over all tests and data points to use in the simulation.

Interlaminar shear strength (ILSS) short beam tests were carried out to measure the dependence of ILSS on the degree of pre-cure of one side of the interface. The testing procedure followed British Standard BS ISO 14130. The 3-point bending tests were performed using an Instron 5500R testing machine with a 30 kN load cell using specimens of 23 mm in width, 4.5 mm in thickness and 22.5 mm in span length, resulting in a 5:1 span to thickness ratio. The loading rate was 1 mm/min. Five specimens were tested for each case. After each test, the failure mode of the specimen was inspected to ensure the occurrence of shear failure mode without any presence of compressive and tensile failure in specimens used for subsequent analysis.

Mode I double cantilever beam tests were carried out on an electro-mechanical Zwick Z010 test machine with a 2 kN load cell. The test procedure followed the British Standard BS ISO 15024. The specimens dimensions were $140\text{ mm} \times 20\text{ mm} \times 4.5\text{ mm}$. Aluminium loading blocks ($15.5\text{ mm} \times 20\text{ mm} \times 8\text{ mm}$) were bonded on the specimens using Huntsman Araldite® 420 A/B. Two specimens were tested for each case. The specimens were painted and marked every millimetre on both sides in order to record the crack length. The crosshead speed was 1 mm/min. The applied load and crosshead displacement were recorded automatically and the crack length was determined visually and recorded alongside the corresponding load and displacement regularly. The initiation fracture toughness was determined using the 5 %/max point. The corrected beam theory (CBT) was used to analyse the data. Correction factors were taken into account to compensate for the rotation at the delamination front due to asymmetrical specimen clamping, stiffening and rotation due to loading blocks and reduction of the lever arm at large displacements due to rotation at the end of the specimen. Average strain release rates were computed using the propagation toughness values for crack lengths greater than 80 mm.

Polished cross sections of the material produced in LbL trials and conventional press curing were analysed using scanning electron microscopy (SEM, Philips, XL 30 SFEG) and optical microscopy (Olympus BH50). Scanning Electron Microscopy samples were coated by sputter deposition (Polaron Equipment Ltd., E5100) of a thin layer of conductive gold alloy.

Data underlying this study can be accessed through the Figshare repository at <https://doi.org/10.6084/m9.figshare.26165311> [28].

4. Results and discussion

4.1. Constitutive models

The results of compaction experiments are illustrated in Fig. 4. The response for all cases shows a very fast compaction in the first dwell at 0.13 MPa completed within about 10 s. This is indicative of dominance of bleeding flow as the squeezing part of the response takes place almost instantaneously. The compaction increases with increasing temperature. Similarly, the rate of compaction is also greater at higher temperatures. The compaction step at each dwell is reduced as the pressure increases. The fitting of the empirical model parameters of Eqs. (1)–(6) was carried out using the procedure detailed in [21] and the results are reported in

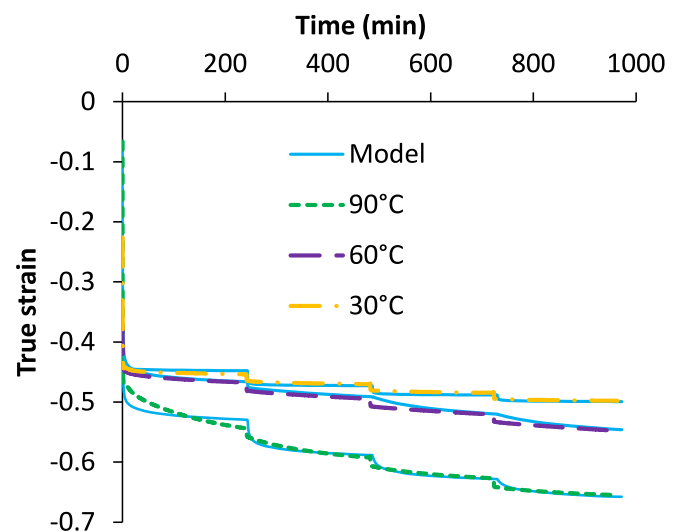


Fig. 4. Consolidation of 913/glass prepreg: evolution of compaction and model fitting for isothermal experiments.

Table 1

Fitting parameters of the consolidation model over the 30–150 °C temperature range.

T (°C)	30	60	90	120	150
$a(-)$	-0.92	-0.92	-0.92	-0.92	-0.92
$b(-)$	-37.9	-36.6	-35.1	-34.4	-33.8
$k(-)$	0.79	0.68	0.62	0.58	0.54

Table 1 for the 30–150 °C temperature range. The rest of the parameters of the consolidation model are reported in **Table 2**. It can be observed that the model reproduces the experimental data very closely.

The results of isothermal and dynamic DSC experiments are illustrated in **Fig. 5**. The isothermal data show the typical autocatalytic behaviour of epoxies. The reaction is accelerated by increasing temperature, whilst diffusion limitations result in partial curing under isothermal conditions. The maximum degree of cure reached at 90 °C is around 70 %, at 110 °C 80 % and at 130 °C over 90 %. This justifies the use of a diffusion term in the cure kinetics model expressed by Eqs. (8)–(9) to capture this behaviour. Dynamic data are consistent with the positive effect of temperature on the reaction rate. The reaction occurs at higher temperatures as the rate increases with the earlier onset being about 100 °C for the 1 °C/min experiment. The cure kinetics model using the parameters reported in **Table 2** follows the experimental results very closely. The model represents successfully the temperature dependence of the evolution of cure under both isothermal and dynamic conditions. Furthermore, the model reproduces successfully diffusion limitations manifested at the latest stages of isothermal cure experiments. **Table 2** also summarises the rest of the parameters of the cure model.

4.2. Mechanical behaviour

Quantification of the degree of pre-cure of one side of the interface of mechanical testing specimens was carried out using the cure kinetics model expressed in Eqs. (8) and (9) with the parameter values reported in **Table 2**. The results alongside the corresponding thermal profiles are reported in **Table 3**. It should be noted that for all partial cure profiles the ramp rate was 2 °C/min.

The results of mechanical testing are summarised in **Fig. 6**. It can be observed that both ILSS and strain energy release rate are relatively constant up to a degree of pre-cure of 60 % with plateau values of about 60 MPa and 480 J/m² respectively. Beyond this level of pre-cure, both interfacial properties deteriorate, with a gradual reduction to about 35 MPa for ILSS and a step drop to about 130 J/m² for a fully pre-cured side

Table 2

Parameters of constitutive models and material properties.

Parameter	Value	Units
A_1	$4.46 \cdot 10^9$	1/min
A_2	$1.67 \cdot 10^{10}$	1/min
E_1	90,350	J/mol
E_2	79,520	J/mol
n_1	4.96	–
n_2	1.88	–
m	0.98	–
C	34.5	–
α_T	0.00573	1/°C
α_c	0.150	–
H_{tot}	538.7	J/g
ρ	1.55	g/cm ³
ρ_r	1.23	g/cm ³
c_p	1.4	J/g/°C
K	0.28	W/m/°C
ϵ^I	0.010	–
l_0	100	mm
d	0.017	mm
h_0	0.18	mm
w_0	100	mm

of interface. The transition point occurs at a degree of pre-cure which coincides with the degree of cure at which gelation is expected to happen for an epoxy of this type. Therefore, it can be inferred that the critical degree of pre-cure of the interface is dictated by the formation of a three dimensional cross linking network between the pre-cured and uncured sides of the interface as well as the ability of the material to flow for pre-cure levels below the gelation region. Beyond this level, the pre-cured side of the interface is already cross linked sufficiently and allows only partial bonding with the material of the uncured side, whilst the infinite viscosity of the material inhibits mechanical keying between the two sides of the interface. Consequently, reaching a pre-cured state just below the gelation degree of cure of the resin system appears as an optimal choice to achieve minimisation of process time and maximisation of mechanical integrity of the interface.

4.3. Simulation and process design

The coupled consolidation-cure model was utilised to investigate different scenarios of the LbL process. The processing of a 40 mm thick 913/glass laminate was investigated using the models expressed by Eqs. (1)–(9) and the material parameter values reported in **Tables 1 and 2**. The LbL process simulated was carried out in six steps following the setup utilised for manufacturing trials. Two different cure temperatures were investigated, 110 and 130 °C, aiming at a moderate (low temperature overshoot) and an aggressive (high temperature overshoot) cure profile respectively. The duration of the dwell was determined using the simulation to identify the duration of the heating step that would be sufficient to achieve full cure by the end of the six sublaminate cycle. A duration of 10 min was chosen for the 130 °C case and 15 min for the 110 °C case. It should be noted that according to the simulation the high temperature case results in degree of pre-cure higher than the critical conversion; however, the choice was made to allow additional pre-cure to proceed so that excessive overshoot (over 50 °C) did not occur in subsequent steps. The cooling/material loading step was set to 2 min in accordance with experimental trials of the LbL process.

The results of the coupled simulation for the two cases are illustrated in **Fig. 7**. It can be observed that in both cases the temperature follows a periodic behaviour. In the cycle at which a sublaminate is loaded its temperature is maximised, reaching overshoots of approximately 50 °C and 15 °C for the aggressive and moderate cure profile cases respectively. The temperature in the sublaminate goes through subsequent local maxima in subsequent steps. These correspond to lower overshoots (around 20 °C and 10 °C for the aggressive and moderate cure profile cases respectively) in the second cycle. This behaviour is explained by the exothermic character of the curing reaction and its diminishing role as the reaction progresses through the different cycles. The maximisation of temperature occurs with a time lag in sublaminate that are already placed. The lag for the sublaminate immediately under the one deposited is about 2 °C and 1.5 min for the aggressive and moderate profiles respectively, with this lag increasing for lower sublaminate. This is accompanied by broadening of the peak of temperature overshoot for sublaminate that are already placed. This behaviour is caused by the slow heat conduction through the thickness of the curing composite, whilst the greater lag for the aggressive scenario can be explained by the greater value of the peak temperature. The degree of cure evolution curves shows that in both cases the cure of a sublaminate is complete after completion of two placement/consolidation-cure cycles. The degree of pre-cure upon placement of a sublaminate for the aggressive scenario is about 0.75 for the first placement and about 0.85 for subsequent layers. In the case of the moderate scenario, the degree of pre-cure is about 0.6 for the first layer and 0.65 for subsequent layers. The overall cure, defined as the time at which all of the laminate reaches 90 %, is 70 min for the aggressive scenario and 135 min for the moderate curing scenario. The consolidation results (**Fig. 7.a and 7.b**) show that full compaction is achieved within a very short time in each step. The time needed is less than 1 min, which is within the time limit before the

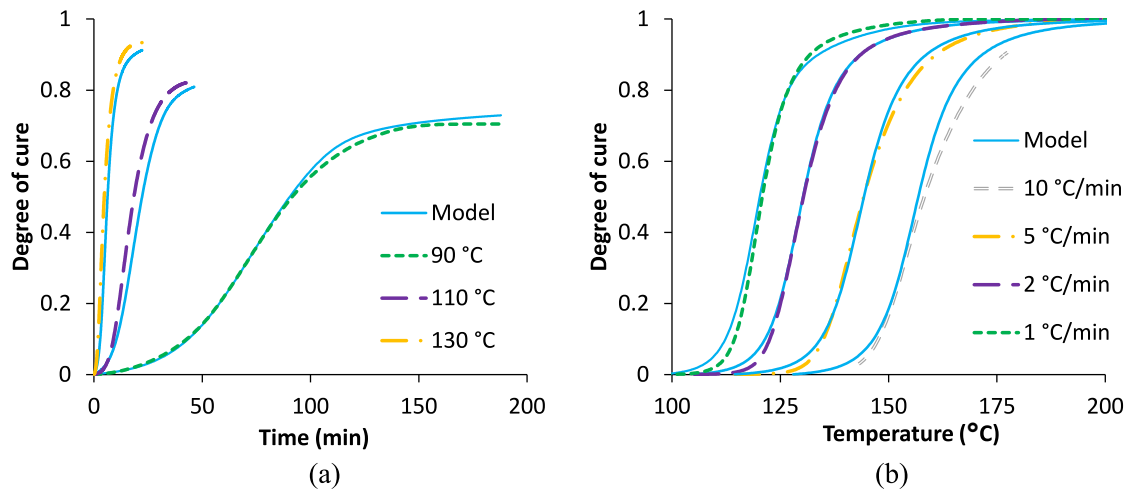


Fig. 5. Cure kinetics of 913/glass prepreg: (a) evolution of degree of cure and model fitting for isothermal experiments; (b) evolution of degree of cure and model fitting for dynamic experiments.

Table 3

Cure profiles used for cure of lower half sublaminae.

Dwell temperature (°C)	Dwell duration (min)	Final degree of cure
—	—	0.0
100	8	0.15
100	12	0.30
100	18	0.50
100	23	0.64
100	30	0.72
110	30	0.85
125	30	0.94
180	30	1.0

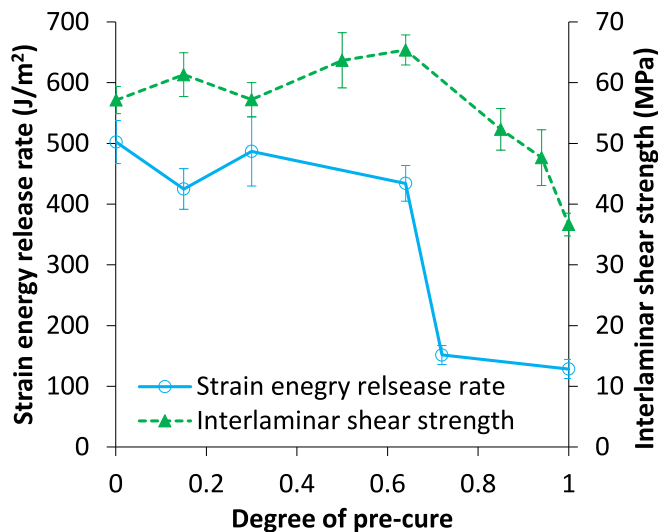


Fig. 6. Dependence of interfacial properties on degree of pre-cure of one side of the interface.

onset of the curing reaction. The level of thickness reached (about 6 mm for each sublaminate) corresponds to full compaction, which implies that the process under both scenarios shown here achieves the level of fibre volume fraction and consolidation quality required.

Assessment of the efficiency of the LbL process was carried by comparing its performance with that of conventional processing. As conventional cure profiles tend to be conservative, the comparison was carried out against optimised profiles for the cure of 913 epoxy/glass

laminates. This was carried out by evaluating the temperature overshoots and cure duration using the model described by Eqs. (7)–(9) for a 40 mm laminate cured conventionally by direct contact heating on both of its external surfaces. This is the most efficient scenario in the context of conventional processing. The cure profile was considered to comprise two dwells and heating ramps set at a constant rate (2 °C/min). The first dwell duration was in the 70–95 °C range, the second dwell duration in the 95–135 °C range and the duration of the first dwell in the 60–240 min range. The duration of the second dwell was considered to be equal to the time required for reaching a minimum degree of cure of 90 % throughout the whole thickness of the laminate. An exhaustive search was carried out using a step of 2.5 °C for the first dwell temperature, 5 °C for the second dwell temperature and 15 min for the first dwell duration resulting in 891 conventional process designs. The results are illustrated in Fig. 8 alongside the outcomes of the aggressive and moderate LbL process scenarios. The set of feasible solutions illustrated is limited in the range of temperature overshoot below 120 °C and of first dwell duration below 250 min. A set of efficient solutions (Pareto set) can be identified. These solutions have the property that no improvements with respect to both objectives can be achieved by another solution in the set.

Comparison of the LbL process performance with conventional solutions in the Pareto set provides the most conservative assessment of the efficiency of the new process. Both LbL scenarios examined result in significant improvement with respect to the two objectives compared to efficient conventional process designs. An overshoot similar to the one occurring in the aggressive LbL process can only be achieved with a process duration greater than about 130 min using conventional curing. This compared to the 70 min required for completion of the LbL process represents an improvement of about 50 %. Similarly, a process duration similar to the one achieved using the moderate LbL scenario can only be accomplished with an overshoot of about 45 °C for the conventional process. This represents a reduction of overshoot of about 70 % with the LbL process. Most importantly, a cure time of 70 min, such as the one achieved with the aggressive LbL profile, is not feasible with conventional processing. Similarly, a temperature overshoot of 17 °C, such as the one occurring in the moderate LbL process design, is not feasible with the conventional process. These results show that the conventional process has some hard limits in terms of what can be achieved for the minimisation of cure time or temperature overshoot which for the 40 mm 913/glass laminate considered here are about 90 min and 20 °C respectively. Improvements beyond these limits cannot be achieved irrespective of how large the value of the other objective is. In contrast, the LbL process can operate in areas of the objective space inaccessible by conventional processing, allowing processing of thick laminates

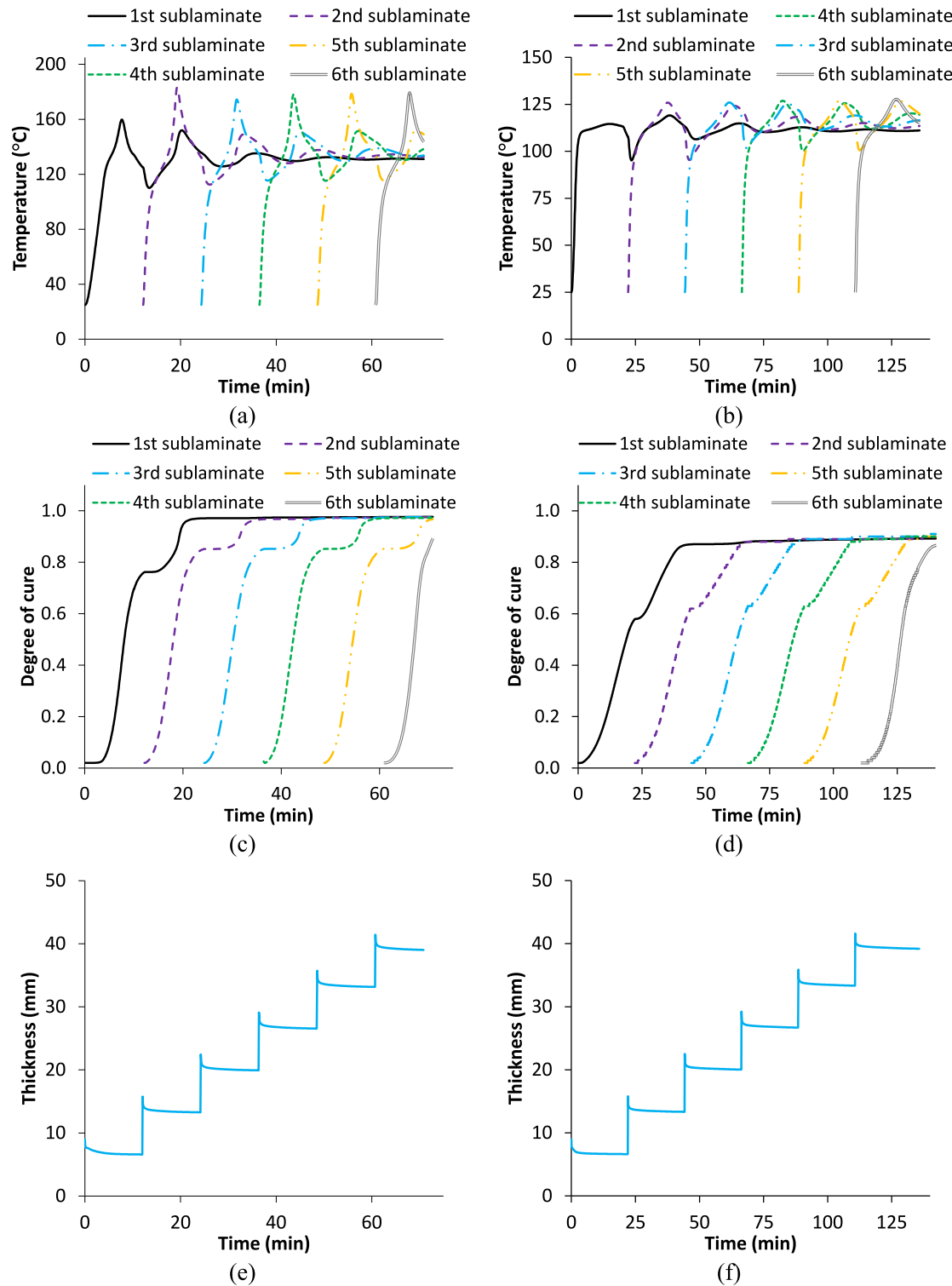


Fig. 7. Simulation of LbL process: (a) 130 °C, (b) 110 °C temperature at mid-thickness of sublaminate; (c) 130 °C, (d) 110 °C degree of cure on top layer of sublaminate; (e) 130 °C, (f) 110 °C thickness evolution.

under conditions not feasible otherwise. Furthermore, the additive character of the LbL process means that increasing the thickness by increasing the number of sublaminate results in the same temperature overshoot and a process duration increasing linearly. This is in contrast to conventional processing in which both process time and overshoot increase non-linearly, making the set of feasible solution smaller and eventually making processing beyond a thickness impossible. This limitation is lifted completely by the LbL process. Adoption of the LbL

processing strategy can also results in potential energy consumption benefits and enhancement of sustainability. Reduction of curing times as well as merging consolidation with cure decreases significantly the time during which the processing assembly needs to be heated, reducing overall consumption. Furthermore, the LbL process is associated with two-sided heating which has a greater potential of reducing heating loss due to convection losses occurring in one sided tooling configurations.

Further insight on how the conventional process achieves the cure of

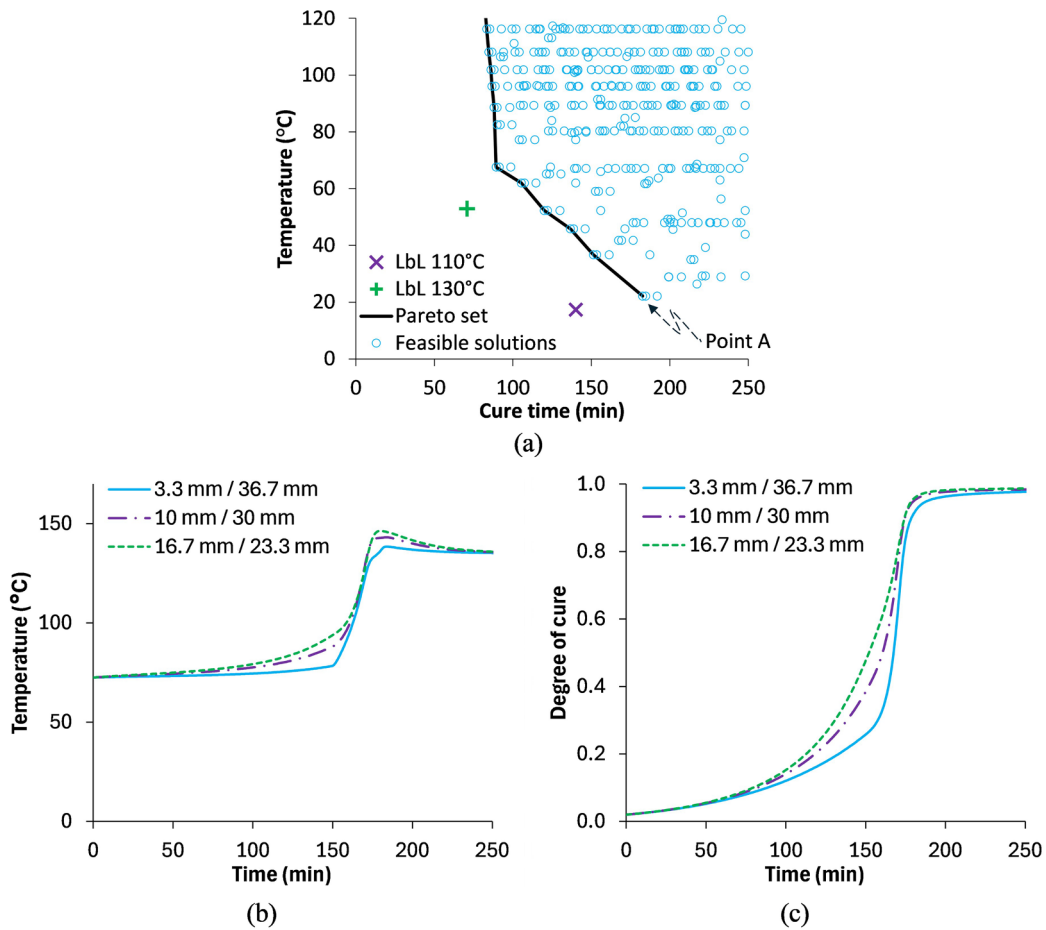


Fig. 8. (a) Overshoot-cure duration feasible set in conventional cure of 40 mm glass/epoxy prepreg and comparison with LbL. Simulation of conventional cure using optimised conditions (point A); (b) temperature and; (c) degree of cure at different positions across the thickness of the laminate.

the laminate in contrast to the LbL process and why the latter has inherent efficiency benefits can be gained by examining the evolution of temperature and degree of cure as predicted by simulation. The solution illustrated in Fig. 8 corresponds to the process design with the lowest overshoot feasible using conventional processing (point A in Fig. 8.a). The specific process design involves a 150 min long 75° C first dwell and a 135° C second dwell. The role of the first dwell is to progress the reaction as much as possible before an overshoot occurs. Once this point

has been reached, the temperature is raised to carry out the rest of the reaction during the dynamic ramp and the second dwell resulting in a moderate overshoot level. This strategy is limited in terms of further improvements, as lowering the temperature of the first dwell or reducing its duration results in more energy release during the ramp and the second dwell increasing the overshoot further, whilst increasing the temperature or duration of the first dwell results in manifestation of a higher overshoot at its end. Modification of the second dwell

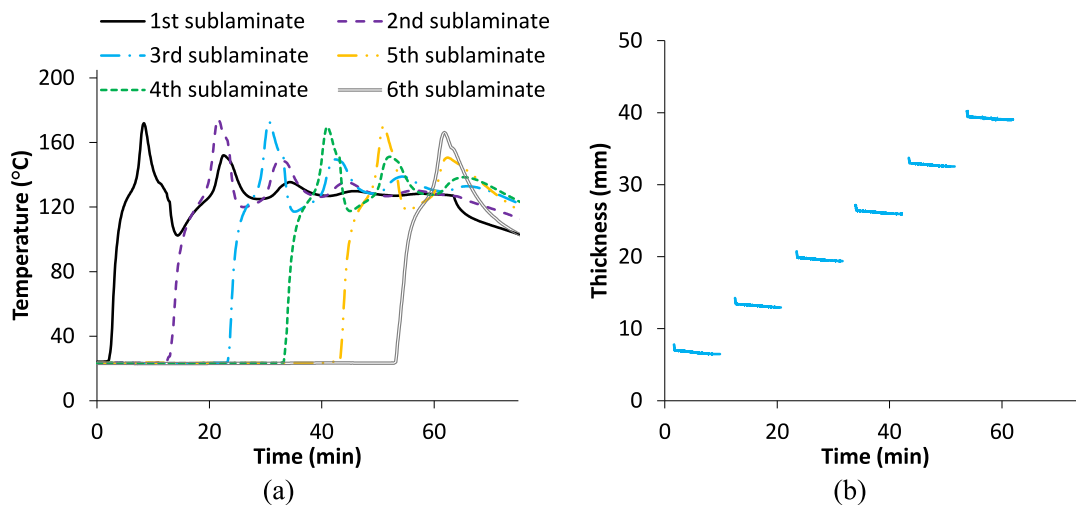


Fig. 9. LbL process trial: (a) temperature at mid-thickness of sublaminate; (b) thickness evolution.

temperature also has a negative effect as reducing it results in manifestation of the overshoot at a lower tool temperature and increasing it in its occurrence during the ramp.

4.4. LbL process trial

The results of monitoring of temperature and compaction during the LbL process trial are illustrated in Fig. 9. The temperature evolution has the periodic characteristics predicted by the simulation (Fig. 7). The level of temperature overshoot at sublamine mid-plane is 45 °C, which is very close to the value predicted by simulation (50 °C). The cyclical heating of each layer after its placement goes through lower local maxima (about 20 °C in the second cycle) and a slight lag is observed for lower sublaminates accompanied by broadening of the overshoot peak. These results show that the cure simulation is valid and the results obtained with respect to process efficiency as reported in Fig. 8.a hold true. The time to completion of the cure in the trial is slightly lower than that predicted by the simulation (67 instead of 70 min) as a result of variations of the cooling stage duration in the trials. The compaction monitoring results presented in Fig. 9.b also confirm the outcomes of the simulation. Compaction occurs quickly upon application of pressure on each sublamine, whilst a final thickness of around 6 mm is reached in each layer corresponding to a fibre volume fraction of about 60 %. The final geometry of the laminate produced in the trial indicates the absence of macroscopic distortion that could have been caused by the gradient in progress of cure across the thickness of the component. This could be potentially attributed to fast relaxation of stresses developed across the new interface at each step due to the low degree of cure that facilitates uniformity in the development of process strain and deformation.

The quality of the material produced (Fig. 10.a) using the LbL process was investigated by microscopy. The micrographs in Fig. 10.b-10.e compare the morphologies of the LbL material with material produced conventionally in the press. In both cases the matrix has a dual phase morphology. Domains appearing dark in optical micrographs (Fig. 10.b and 10.d) correspond to a modifier rich phase. This is shown clearly in the SEM micrographs in Fig. 10.c and 10.e, where the dark regions of optical micrographs appear as light coloured particles that deform during sample preparation. These domains are elongated, possibly as a result of consolidation, whilst their aspect ratio and size are greater in conventionally processed material possibly as a result of the UD layup of this material and the moderate temperature history. Microscopy does not reveal any significant levels of porosity in the LbL material; the overall picture is very similar to that of the conventionally processed composite. These results show that the quality of the LbL material is similar to that obtained in conventional processing. The consolidation levels achieved are appropriate and voids have been removed. Small changes and potential refinement of the dual phase morphology of the epoxy matrix can be explained by the difference in thermal history and layup and are not expected to cause significant variations in resin dominated properties of the material.

5. Conclusion

The simulation and experimental results of this study showed that the LbL process concept put forward in this investigation is successful. The process can deliver thick and ultrathick laminates produced in an additive manner. The quality of laminates obtained with the LbL process matches that produced by conventional processing whilst the degree of pre-cure reached in a sublamine after its placement and consolidation can be adjusted to a level around the gelation degree of cure of the matrix to achieve interfacial properties equivalent to those of standard material. The LbL process brings about significant efficiency benefits as cure process duration can be halved for equivalent temperature overshoot, whereas temperature overshoots can be reduced by 75 % for equivalent process duration. The process duration benefits are enhanced

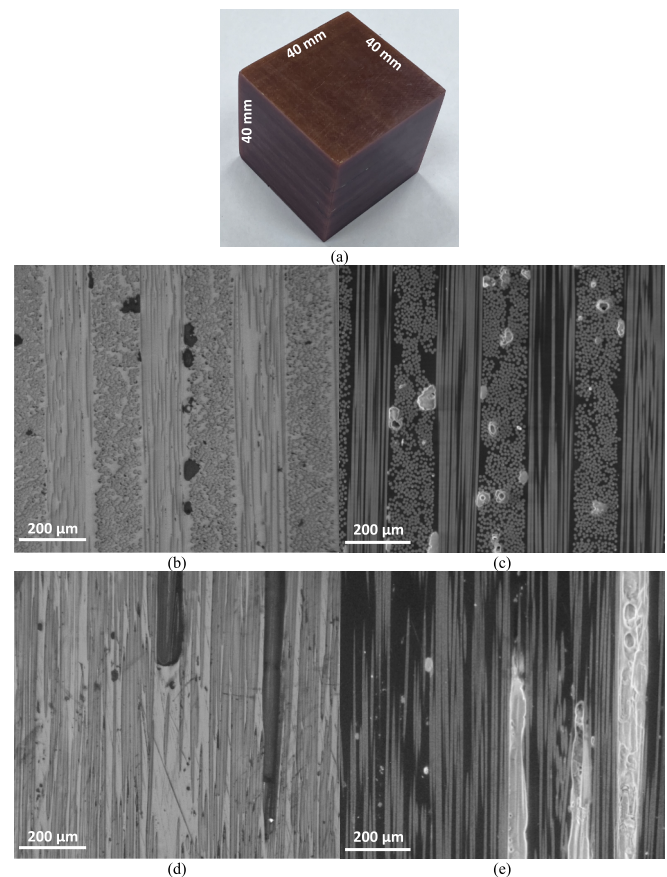


Fig. 10. Product of the LbL process and comparison with conventional curing: (a) 40 mm LbL laminate; (b) optical micrograph of LbL laminate; (c) SEM micrograph of LbL laminate; (d) optical micrograph of conventional UD laminate; (e) SEM micrograph of conventional UD laminate.

by the fact that in the LbL process the consolidation stage is merged with cure, which for cases where deposition/consolidation needs a similar amount of time as cure, implies an overall process duration benefit of about 75 %. Furthermore, the LbL process can operate in conditions that are not feasible in conventional processing and can be used for the production of thicknesses that are impossible to manufacture using standard methods.

The potential of the LbL process stretches well beyond thick and ultrathick structures. Its capability for fast curing and for merging the consolidation with cure can find uses in the context of automated fibre placement (AFP), automated tape laying (ATL), especially for small to mid-sized components [4], and filament winding (FW). The opportunities offered by designing a tailored LbL process with sublamine thickness, temperature and cycle duration treated as optimisation variables can increase efficiency and enhance the feasibility of processing of extra-large structures. The methodologies developed here require expansion for simulation to address three dimensional complexity and additional process physics around the build-up of process stress and for manufacturing to incorporate integration with robotic placement heads aiming at using the LbL process for complex curved geometries.

CRediT authorship contribution statement

Xiaochuan Sun: Writing – original draft, Validation, Investigation, Formal analysis. **Lawrence Cook:** Writing – original draft, Methodology, Investigation, Formal analysis. **Jonathan P-H. Belnoue:** Validation, Methodology, Investigation, Formal analysis. **Kostas I. Tifkitis:** Validation, Methodology, Investigation, Formal analysis. **James Kratz:** Writing – review & editing, Supervision, Methodology, Funding

acquisition, Conceptualization. **Alex A Skordos**: Writing – review & editing, Supervision, Methodology, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Engineering and Physical Sciences Research Council (grant number EP/P006701/1) through the EPSRC Future Composites Manufacturing Research Hub.

References

- [1] Bogetti TA, Gillespie JW. Two-dimensional cure simulation of thick thermosetting composites. *J Compos Mater* 1991;25(3):239–73.
- [2] Pitchumani R, Gillespie Jr J, Lamontia M. Design and optimization of a thermoplastic tow-placement process with in-situ consolidation. *J Compos Mater* 1997;31(3):244–75.
- [3] White SR, Kim YK. Staged curing of composite materials. *Compos A Appl Sci Manuf* 1996;27(3):219–27.
- [4] Struzziero G, Barbezat M, Skordos AA. Assessment of the benefits of 3D printing of advanced thermosetting composites using process simulation and numerical optimisation. *Addit Manuf* 2023;63:103417.
- [5] Dasari SS, Wright AJK, Carroll JM, Sarmah A, Carey DG, Nagabandi N, et al. Freeform additive manufacturing of carbon fiber reinforced composites using dielectric barrier discharge-assisted Joule heating. *Compos A Appl Sci Manuf* 2024; 179:108047.
- [6] Moosburger-Will J, Greisel M, Sause MGR, Horny R, Horn S. Influence of partial cross-linking degree on basic physical properties of RTM6 epoxy resin. *J Appl Polym Sci* 2013;130(6):4338–46.
- [7] Moosburger-Will J, Sause MGR, Horny R, Horn S, Scholler J, Llopard PL. Joining of carbon fiber reinforced polymer laminates by a novel partial cross-linking process. *J Appl Polym Sci* 2015;132(27):42159.
- [8] Studer J, Dransfeld C, Masania K. An analytical model for B-stage joining and co-curing of carbon fibre epoxy composites. *Compos A Appl Sci Manuf* 2016;87: 282–9.
- [9] Corbett T, Forrest M, Gac PL, Fox BL. Characterization of melded carbon fibre/ epoxy laminates. *Compos A Appl Sci Manuf* 2007;38(8):1860–71.
- [10] Adamson BP, Fox BL. An evaluation of the performance of advanced melded composite joints. *Compos Struct* 2010;92(9):2071–6.
- [11] Motsch-Eichmann N, Rieger F, Rief T, Hausmann J. Experimental investigation of modified co-curing process for carbon fiber/epoxy-laminates. *J Micromech Mol Phys* 2021;06(03):1–12.
- [12] Rief T, Motsch-Eichmann N, May D, Hausmann J. Development of a new method for manufacturing hollow fibre-reinforced plastic structures for aeronautical applications using structural CFRP cores. *Plast, Rubber Compos* 2022;51(8): 407–17.
- [13] Vyas S, Goli E, Zhang X, Geubelle PH. Manufacturing of unidirectional glass-fiber-reinforced composites via frontal polymerization: A numerical study. *Compos Sci Technol* 2019;184:107832.
- [14] Luo T, Fu K, Zhu H, Chen Y, Yang B, Li Y. In-plane and in-depth frontal polymerization behaviors of continuous fiber-reinforced epoxy composites. *Polym Compos* 2024;45:3604–16.
- [15] Robertson ID, Yourdkhani M, Centellas PJ, Aw JE, Ivanoff DG, Goli E, et al. Rapid energy-efficient manufacturing of polymers and composites via frontal polymerization. *Nature* 2018;557:223–7.
- [16] Zhang Z, Gao C, Liu R, Li W, Qiu J, Wang S. Catalyzed frontal polymerization-aided 3D printing of epoxy thermosets. *Additive Manufacturing Letters* 2022;2:100030.
- [17] Sangermano M, Antonazzo I, Sisca L, Carello M. Photoinduced cationic frontal polymerization of epoxy-carbon fibre composites. *Polym Int* 2019;68:1662–5.
- [18] Sangermano M, D'Anna A, Marro C, Klikovits N, Liska R. UV-activated frontal polymerization of glass fibre reinforced epoxy composites. *Compos B Eng* 2018; 143:168–71.
- [19] Centellas PJ, Yourdkhani M, Vyas S, Koohbor B, Geubelle PH, Sottos NR. Rapid multiple-front polymerization of fiber-reinforced polymer composites. *Compos A Appl Sci Manuf* 2022;158:106931.
- [20] Skordos AA, Partridge IK. Inverse heat transfer for optimization and on-line thermal properties estimation in composites curing. *Inverse Prob Sci Eng* 2004;12 (2):157–72.
- [21] Belnoue JPH, Nixon-Pearson OJ, Ivanov D, Hallett SR. A novel hyper-viscoelastic model for consolidation of toughened prepregs under processing conditions. *Mech Mater* 2016;97:118–34.
- [22] Skordos AA, Partridge IK. Cure kinetics modeling of epoxy resins using a non-parametric numerical procedure. *Polym Eng Sci* 2001;41(5):793–805.
- [23] Antonucci V, Giordano M, Imparato SI, Nicolais L. Analysis of heat transfer in autoclave technology. *Polym Compos* 2001;22(5):613–20.
- [24] Zimmermann K, Van Den Broucke B. Assessment of process-induced deformations and stresses in ultra thick laminates using isoparametric 3D elements. *J Reinf Plast Compos* 2011;31(3):163–78.
- [25] Karkanas PI, Partridge IK. Cure modeling and monitoring of epoxy/amine resin systems. I. Cure kinetics modeling. *J Appl Polym Sci* 2000;77(7):1419–31.
- [26] Farmer J, Covert E. Thermal conductivity of a thermosetting advanced composite during its cure. *J Thermophys Heat Transfer* 1996;10(3):467–75.
- [27] Belnoue JPH, Valverde MA, Onoufriou M, Sun X, Ivanov DS, Hallett SR. On the physical relevance of power law-based equations to describe the compaction behaviour of resin infused fibrous materials. *Int J Mech Sci* 2021;199:106425.
- [28] Sun X, Cook L, Belnoue JPH, Tifkisis KI, Kratz J, Skordos AA. Dataset supporting Manufacturing thick laminates using a layer by layer curing approach, Dataset. Figshare Repository 2024. <https://doi.org/10.6084/m9.figshare.26165311>.



DSPACE

<https://dspace.org/>

Manufacturing thick laminates using a layer by layer curing approach

Sun, Xiaochuan; Cook, Lawrence; Belnoue, Jonathan P-H.; Tifkitsis, Kostas I.; Kratz, James ...

2024-12-01

Elsevier

<https://doi.org/10.1016/j.compositesa.2024.108489>

Sun X, Cook L, Belnoue JP-H, et al., (2024) Manufacturing thick laminates using a layer by layer curing approach. Composites Part A: Applied Science and Manufacturing, Volume 187, December 2024, Article number 108489