Manufacturing curing cycles influence on local fracture toughness properties at micro and macro scale

F Lahuerta and S Rajmaekers
Knowledge Centre WMC. Kluisgat 5, 1771 MV Wieringerwerf, The Netherlands
E-mail: f.lahuerta@wmc.eu

Abstract. Ultimate strengths and fatigue properties (S-N curves) of thick laminates vary through the thickness showing unexpected values in comparison with thin laminate. This is related to curing cycles, residual strains and manufacturing thermal history. These observations were reported using the sub-laminate technique where thick laminates through-thickness mechanical properties can be described according to a prescribed curing cycle. A similar behaviour might be also expected at a micro level for the fibre/matrix interface properties. In the present work, the curing cycles influence is studied for fracture toughness properties at a macro and micro level. For this purpose, standard test coupons are obtained with the sub-laminate technique and single fibre fragmentation tests are carried out at different curing cycles.

1. Introduction
Epoxy glass fibre reinforced plastics (GFRP) are widely used in the manufacturing of large-scale structures such as wind turbine blades. The manufacturing process consists of an open mould vacuum assisted resin transfer moulding (VARTM). Once the resin infusion is finalized, a thermal curing cycle is applied to solidify the resin and fibre forming the composite structure. During this process, the epoxy resin is transformed into a thermoset plastic by a cross-linking reaction which shows an exothermal behaviour.

Curing cycle design aims to achieve the shortest manufacturing times and avoid excessive manufacturing temperatures driven by the exothermic reaction above the resin degradation temperature. In particular, GFRP present a big challenge from the manufacturing process design point of view. Due to the small thermal conductivities of GFRP and the resin exothermal reaction, large temperature gradients can be observed during the thick laminate manufacturing through the thickness [1, 2, 3, 4]. This can lead to strong temperature peaks above the resin degradation temperatures hampering the resin and composite mechanical properties. Below the resin degradation temperatures, the variability of the GFRP mechanical properties with the manufacturing history has been reported due to the curing influence [5, 6, 7, 8] or the thermal residual strains [9, 10, 11, 12]. The sub-laminate technique consists on extracting sub-laminates plates from a thick laminate with the help of peel ply layers at different thickness positions. The sub-laminates plates are extracted with a smaller thickness than the thick laminate. This allows manufacturing coupons with standard dimensions which have equal properties as the ones of a thick laminate at a given thickness position [13]. The use of the sub-laminate technique to
study thick laminates showed a dependence of static and fatigue properties with the curing rates thermal history. Compression, tension and shear properties were studied. [13, 14, 15, 16].

In this regard, two complementary causes have been hypothesized to describe the variation of the mechanical properties with the manufacturing thermal history and thermal gradients. On one hand, the residual strains which drive a micro-damage mechanism by which interface fractures diminish the macro-mechanical properties. And on the other, the resin and interface adhesion properties depend on the curing path, which leads to a gradient of mechanical strengths related to the thermal history [17].

The sub-laminate technique offers the possibility to study the static and fatigue mechanical properties at a coupon level and relate those properties to the curing thermal history and residual strains measurements. At a micro-mechanical level single fibre fragmentation tests allow studying the mechanical properties of the fibre / matrix interface for composite materials as well as residual strains measurements when combined with the shear lag model [18, 19]. In the present work, the curing cycle influence on fracture toughness properties is studied for a GFRP at the macro and micro levels. For this purpose, the sub-laminate technique is used with standard coupon tests and the single fibre fragmentation tests are used to study the fibre/matrix interface properties.

2. Materials and methods

As reinforcements, unidirectional (UD) glass fiber type E 948 [g/m^2] non-crimp fabric and biaxial (biax) (±45°) glass fiber type E 812 [g/m^2] fabric were used as base material for this study. A commonly used wind energy epoxy resin Hexion RIM 135 epoxy with Hexion RIM 137 hardener was used. The research was divided into four steps:

- The manufacturing of a thick laminate and extraction of sub-laminates
- Static mechanical tests of the fracture toughness of sub-laminates coupons
- Manufacturing of the single fragmentation test coupon at two different curing cycles
- Single fibre fragmentation tests

2.1. Standard coupons, sub-laminates technique

An 84 layer 600x600 [mm] thick laminate was manufactured. Peel ply layers were used to define sub-laminates to study the lamina properties at different thickness positions (see reference [15] for more details). Sub-laminates for interlaminar fracture toughness (Glc) tests consisted of plates of 6 plies UD fabric with a thin (62 [mum]) Teflon strip placed between each third and fourth layer, which served as delamination initiator for fracture toughness tests. A polytetrafluoroethylene (PTFE) peel ply was used to allow the extraction of the sub-laminates after the laminate was cured. Eight thermocouples (type K) and strain gauges (5 [mm] gauge section TML FLA-10-11) were embedded in the laminates at different thickness positions to monitor the temperatures and strains through the thickness during the infusion and curing process. Both were placed in the middle of the 600x600 [mm] laminate at different Z positions between the fabrics and oriented with the UD fibre direction, as figure 1 shows. Temperature deviations were corrected on strain gauges based on thermocouples temperatures and the temperature deviation curve supplied by the strain gauges manufacturer. The sensors were connected to a data acquisition system and data was recorded every second during the manufacturing process. Heating rates were computed from the thermocouples temperature recordings as max(dT/dt).

The laminate was infused using a vacuum bagging technique on a single-sided mould. The mould and resin were heated to 25 [°C] before infusion. A two-stage cure cycle was used after two hours of infusion. The hardening of the resin took place in soak 1 (380 minutes) with a mould set temperature of 35 [°C]. Soak 2 had a duration of 800 minutes with a temperature of 80 [°C]. The long post-curing duration promoted the temperatures stabilization through the
thickness, with each layer experiencing an 80 °C uniform post curing cycle temperature. The mould was setup with temperature ramps of 1 °C/min. Full vacuum (0.9 bars) was applied during the infusion and curing process.

The fibre weight ratio and void content were calculated by a calcination method according to ISO 1172. Glass transition temperatures were determined with a differential scanning calorimeter (DSC) according to ISO 1357. Moreover, UD G\textsubscript{IC} coupons were milled from the sub-laminates and tested in static loading. Six coupons per sub-laminate were tested. Interlaminar fracture toughness was tested in Mode I using DCB coupons according to ASTM D5528-13. One side of the coupons was painted with brittle white paint and the crack initiation distances were marked. Static tests were carried out using an MTS 10 kN hydraulic test frame with a 1 kN load cell (see figure 2). A black background was used and illumination was controlled to avoid shadows and glare to maximize contrast between the coupon and background. The coupons were pre-cracked with an initial cycle and then loaded with 3 mm/min until maximum machine displacement was reached. An HD camera was placed perpendicular to the coupon and using a video image processing technique [20], crack propagation was determined. G\textsubscript{IC} fracture toughness values were computed by means of deviation from linearity (NL) and 5% offset according to the three calculation methods contained in the standard: modified beam theory (MTB), compliance calibration (CC) and modified compliance calibration (MCC). For each DCB sub-laminate tests, batches of six coupons were carried out.

![Figure 1. Laminate before infusion (left) and detail of embedding thermocouple and strain gauge (right).](image)

### 2.2. Single fiber fragmentation tests

Eleven fibre fragmentation coupons were tested with an MTS 10 kN test frame equipped with a 1 kN load cell. The coupons were manufactured using type E glass fibres obtained from the fabrics described in section 2.1 and the same epoxy resin. Coupons dimensions are shown in figure 8. For this purpose, latex moulds were used to manufacture the single fibre fragmentation coupons. The moulds were instrumented with type K thermocouples to measure the coupons manufacturing curing cycles temperatures (see figure 3). Due to the coupons small size in comparison with the thermocouples and the latex mould large thermal inertia, the exothermal peaks were not visible in this setup. Half of the coupons were manufactured at a low curing cycle divided in a first soak at 50 ° for 500 min and the second soak at 70 ° for 700 min. The other half of coupons was manufactured at a high curing cycle with a single curing soak at 90 ° during 800 min. In both cases, the heating rates of the mould were setup at 1 °/min.
Fibre diameters were measured with a 100x magnification microscope prior the manufacturing with average values of 18 [µm]. The fibre fragmentation coupons were positioned in the test frame between two polarized films and recorded with a digital USB microscope with an HD resolution (see figure 2 right). The videos were image processed to obtain the strain $\sigma_c/E_c$ at the gauge section and the fibre debonded length $l_d$ temporal signal for each fragment appeared during the test (see figure 4). Figure 4 shows an example of fibre fragments that were discarded due to having an unclear broken fibre zone or because some fragments were too close to others. In addition, fragments which did not show a linear dependence between the strain $\sigma_c/E_c$ and the debonded length $l_d$ were also discarded. Since it was not possible to directly measure the broken fibre gap $2 \cdot \delta$ with the image processing automated system, the dimension $2 \cdot \delta$ was measured at the beginning of the fibre failure and the end of the test. It was then assumed to show a linear behaviour with the measured strain. Based on the measured average values of $2 \cdot \delta$ a value $\delta \approx 0.8 \cdot r$ was obtained. The residual strain $\Delta \epsilon^T$, the sliding shear stress $\tau_s$ and the interfacial fracture energy $G_i$ were computed from the temporal signals [18]. For these computations, a matrix modulus $E_m = 3.13$ [GPa], fibre modulus $E_f = 73$ [GPa] and a fibre radius $r = 9$ [µm] were considered. The fibre fragmentation tests were run at a speed of 1 [mm/min].

![Figure 2. Test setup interlaminar fracture toughness test (left) and single fiber fragmentation (right).](image1)

![Figure 3. Single fiber fragmentation coupons manufacturing setup.](image2)
3. Results and discussion

The sub-laminate technique was successfully applied and allowed to sub-divide the thick laminates into plates of reduced thicknesses which could be tested as standard fracture toughness coupons. The fibre weight ratio (FWR), void content and glass transition temperatures of each sub-laminate were measured to study the evolution of those manufacturing indicators through the thick laminate thickness. FWRs varied from 72.4% to 74.7% through the thickness showing no correlation with the thickness position. Sub-laminate void contents were below 0.1%, for sub-laminates 01 and 02 void contents were 0.4% and 0.2% respectively. The DSC glass transition temperatures varied from 91 °C in the lower sub-laminate to 85 °C in the upper sub-laminate. Fibre weight ratios, void contents and glass transition temperatures showed uniform values through the laminate thickness, indicating uniform levels of fabrics impregnation and curing degrees.

Large temperature gradients were observed through the thickness (Z positions) during the curing process of the laminate. Figure 6 shows the evolution of temperature of the embedded thermocouples. During thick laminate soak 1, the mould set temperature of 35 °C was exceeded due to the exothermic reaction of the resin to maximum temperatures of 85 °C in the middle sub-laminates. Temperature differences were up to 35 °C within the laminates and up to 50 °C with the mould set temperature. Based on these temperature measurements it can be stated that each thickness position followed a local curing cycle, and each sub-laminate was cured according to those local curing cycles. For each local curing cycle, the maximum heating rates $\max(dT/dt)$ were computed.

The maximum strains recorded through the thickness during the process were up to 600 [µε]. However, once the plate cooled down, the residual strains between plates reduced to up to 200 [µε] (0.02% elongation). Since each corresponding sub-laminate experienced a different local
The influence of the manufacturing process on the sub-laminates which experienced the highest curing temperature peaks showed the highest contractions during the manufacturing process. A residual strain gradient could be observed through the thickness between the outer layers and the inner layers (see figure 5).

The evolution of the manufacturing process on the $G_{lc}$ fracture toughness was evaluated for sub-laminates with UD lay-up using DCB tests. Fracture toughness was evaluated according to the MCC and MBT methods described in the standard ASTM D5528-13. The results showed an evolution of the fracture toughness for both analytical methods within the thickness position, where larger values can be observed in the positions with the larger maximum temperatures and heating rates. The average fracture toughnnesses varied from 718 to 1200 [J/m²] through the thickness. Figure 9 shows a cross-correlation between sub-laminate fracture toughnnesses and maximum heating rates monitored for each sub-laminate with the embedded thermocouples. Cross-correlation R coefficients vary with the $G_{lc}$ calculation methods chosen between 0.84 and 0.87. In the case of the residual strains measurements, it was not possible to state a similar correlation between the measured fracture toughnnesses and the residual strains. This fact and
the lower relative residual strains magnitudes in comparison with the maximum resin strain strengths (around 5 to 7%) suggest a weaker dependence of the residual strains in comparison with the maximum heating rate indicators.

Single fibre fragmentation tests were carried for coupons manufactured at two different curing cycles. Due to the small dimensions of the single fragmentation coupons (see figure 8) and the low sensitivity of the thermocouples it was not possible to record the exothermic peaks during manufacturing. However, as shown in figure 7 the coupons were manufactured with two different curing cycles, a low one and high one, resulting in two different curing states. Temporal signals of
normalized debonded length $l_d/r$ and applied strain $\sigma/E_c$ for different coupons were aggregated and grouped in a low curing cycle and high curing cycle group. Figure 10 shows the single fragmentation test results divided into two different groups by curing cycle conditions. Single fragmentation coupons manufactured at low curing cycles show lower residual strain $\Delta e^T$ sliding shear stress $\tau_s$ and interfacial fracture energy $G_i^c$ when compared to coupons manufactured at a higher curing cycle. This trend agrees with ones observed in the fracture toughness sub-laminates test. The residual strain $\Delta e^T$ showed a difference of 0.06 [%] between both curing cycles, which implies that the resin gelification and solidification temperatures occurred at different temperatures. It should be mentioned that the magnitude of the residual strains $\Delta e^T$ is rather low in comparison with the maximum strains, and of the same order of magnitude of the residual strains measured during the thick laminate manufacturing. In addition, an increase of the interfacial fracture energy $G_i^c$ with the curing cycles was observed. Despite the thick laminates tests $G_{lc}$ (in mode I), fracture toughness is not comparable with the measured interfacial fracture energy $G_i^c$ (mainly in mode II). Both show a dependence with the curing conditions, suggesting a strength gradient dependent on the thermal history.

One can hypothesize on which are the mechanisms behind the relation between the thermal history and the changes in the residual strain, shear stress and interface fracture energy. In the case of the residual strains, the variation with the curing cycles is related with the gel and solidification matrix temperatures. To vary the curing cycles modifies at which temperature occurs the matrix solidification or hardening. Therefore at which temperature are the resultant residual strains locked. On the other hand, the shear stress and interface fracture energy are related to the adhesion mechanisms of the fibre to the matrix. The adhesion mechanisms also appear to be dependent on the thermal history according to the experimental data reported in the present work. This dependence of the interface cohesive properties with the thermal gradient is also observable at a macro level. Where $G_{lc}$ fracture toughness shows a relation with the thickness position of a thick laminate and the curing speeds during or temperature profiles through the thickness.

4. Conclusions
The influence of curing cycle in fracture toughness properties was studied at a macro and micro levels. Using the sub-laminate technique, a dependence on the mode I fracture toughness $G_{lc}$ with the heating curing rate was observed. In addition, a weak variation on the residual strains through the thickness was observed. In a similar manner, single fragmentation tests were performed for coupons manufactured at two different curing cycles. High curing cycles coupons showed higher residual strain $\Delta e^T$ in comparison with lower curing cycles. The order of magnitude of the residual strains was similar to the one measured during the sub-laminate test, showing in both cases values below 1000 [µε]. As observed for sub-laminate coupons, single fibre fragmentation test showed higher interfacial fracture energy $G_i^c$ values for the high curing cycles than for the low curing cycles.

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