EFFECT OF DWELL TIME ON THE PROPERTIES OF COMPOSITE MATERIALS

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Abstract
Material manufacturers often specify maximum duration a prepreg is allowed to dwell in an autoclave at the higher isothermal cure temperatures preceding which, their acceptance is usually questioned, due to possible structural damage owing to the overexposure. As the cure specifications for the material are usually designed considering ideal temperature conditions, it may indeed not be satisfied in real manufacturing situations. The discrepancies in the leading and lagging thermocouples, presence of different tools in the autoclave for example may lead to over exposure and may be rejected in the first instance according to specifications. In such examples, not only the productivity is hindered but also the cost of production increases dramatically. Therefore, in view of improving productivity, investigations have been carried out on composite parts manufactured using Cycom 977-2 prepregs. Test coupons were manufactured using standard 120 minutes and two extended postcure cycles, 200 and 300 minutes. ILSS tests were conducted to examine any change in laminate shear strength, DMA was used to measure the variation in T_g, DSC was used to determine the extent of cure and flatwise tensile tests were conducted to determine any change in the core-to-facings bonding, with respect to postcure durations.
The results from ILSS show negligible changes in the laminate shear strength (average 74 MPa), exhibiting standard deviation of 2 MPa. DMA test results show 6-10 °C shift in Tg when the postcure duration is changed from standard 120 minutes to 300 minutes, flatwise tensile tests reveal consistent core failure exhibiting strengths of 2.5 ±0.2 MPa for all the samples and the DSC confirms a consistent cure of greater than 97% for all the specimens. In conclusion, there is negligible changes in mechanical and material properties of the parts that are subjected to extended postcure, upto 90 minutes from the maximum allowable 210 minutes.

1. Introduction

Autoclave processing remains the backbone of continuous fibre reinforced thermoset composite fabrication. They can accommodate a single large composite part or numerous smaller parts loaded onto racks and cured as a batch. Once the parts are laid, bagged and loaded in an autoclave, a pre-programed cure cycle which is a combination of pressure, temperature and vacuum is applied. A typical cure cycle used to process many thermoset epoxy composite parts consists of two ramps and two isothermal hold periods, where the first ramp and isothermal hold is used to allow the resin to

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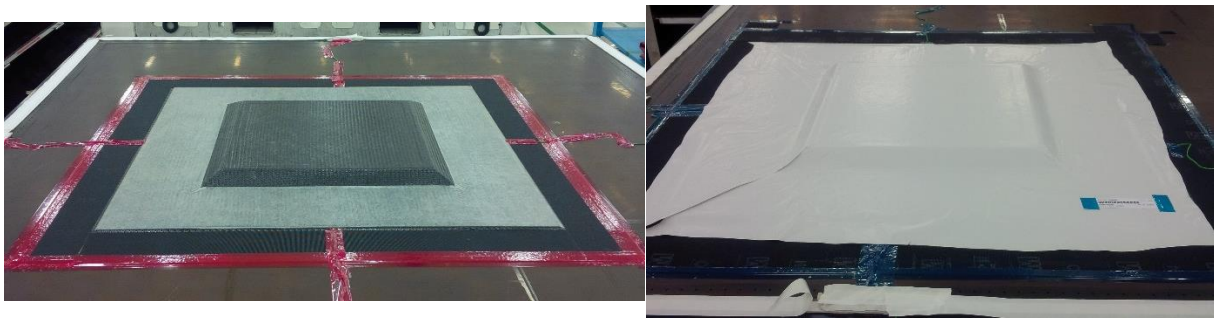
flow and volatiles to escape. The applied autoclave pressure for a monolithic part is typically 5-6 bar, and a full vacuum is applied underneath the bag. The second ramp and hold is the polymerization portion of the cure cycle. During this stage, the viscosity rises dramatically to gel and additional crosslinking occurs. Thermal integrity and structural strength are developed during this portion of the cycle. At some point during this portion, normally at less than 100% as measured by residual cure energy in the DSC, the T_g slows substantially or stops increasing and the material would have acquired its full mechanical strength. After this point, any increase in postcuring provides no advantage, adding cost and time to the production, on contrary. In some resin/prepreg systems, this occurs as early as 94% of complete cure (measured by the residue enthalpy of cure in the DSC), and with this information in hindsight, several material manufacturers design an optimum cure cycle and define safe operation limits for that system, in order to shrink production costs.

However, in an ideal factory environment where various parts are manufactured for several customers, following the customer specified cure cycle as may indeed not be satisfied; either due to accidents or as a virtue of the process by itself. For example, the discrepancy in the leading and the lagging thermocouple may lead to a longer postcure dwells, subjecting the parts to further scrutiny and quality checks. However, if this information was available beforehand, it would make it easier for the Q&C department to accept or reject the part without having to go through further enquiries.

Therefore, in order to provide justification to disposition overexposed parts, investigations have been carried out on composite laminates by subjecting them to prolonged postcure dwells in an autoclave and examine if the effect was truly detrimental to the material and mechanical properties of the manufactured part. Interlaminar shear stress (ILSS) tests were conducted to examine any change in laminate shear strength, dynamic mechanical analysis (DMA) was used to measure the variation in T_g and resin degradation, differential scanning calorimetry (DSC) was used to determine the extent of cure and flatwise tensile tests on sandwich panels were conducted to determine any change in the core-to-facings bonding, with respect to postcure durations.

2. Materials and manufacturing

Cycom 977-2 twill carbon fabric was used as prepregs for the composite laminate, over-expanded Nomex™ honeycombs with a taper angle of ~35° was used for as core material for the sandwiched areas. Grit strips from Gurit was used to stop the core from slipping, and adhesive film Cytec FM300 was used to bond the core to the laminates. Figure 1 (a). Finally a layer of Tedlar was used for waterproofing, similar to the standard production parts, Figure 1 (b). Standard K-type thermocouples were used to monitor the temperature within the laminates during the cure cycle.



(a) (b)

Figure 1 Test coupons (a) being laidup before using protective tedlar layer and showing the regions of embeded thermocouples in red (b) with the final layer of protective Tedlar just before being bagged for the autoclave cure cycle

Six flat test laminates of 800mm x 800mm were manufactured on an Invar flat tool; two of each representing parts subjected 120 minutes, 210 minutes and 300 minutes of the postcure isotherm, respectively. The layup sequence shown in Figure 2. The cure profile for all samples was similar to that of the production parts except, the postcure dwell segment at 180 °C was extended from the standard 120 minutes dwell time to 210 minutes and 300 minutes for the extended postcure samples..

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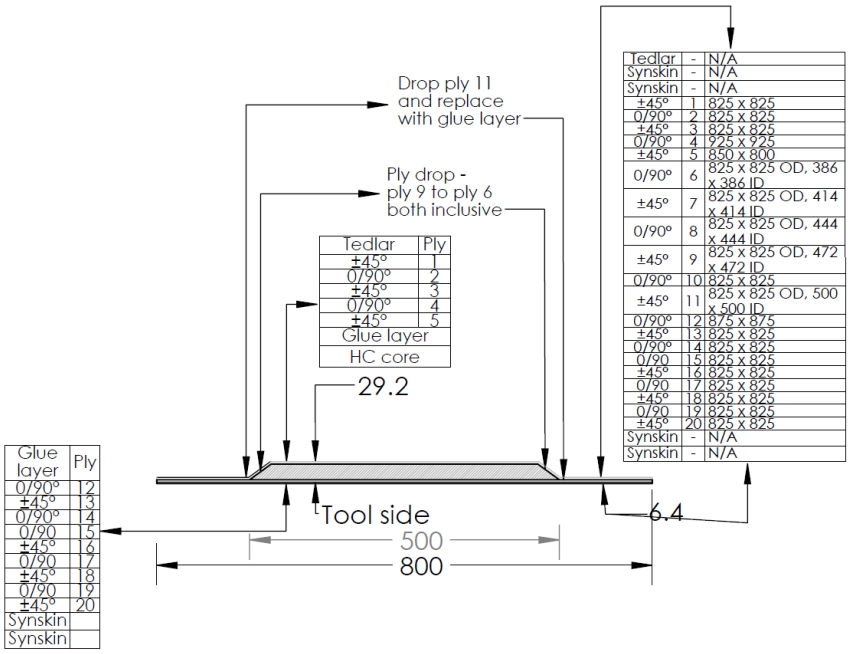

Figure 2 Test piece dimensions and layup sequencing

3. Testing

Interlaminar shear strength (ILSS) tests were conducted as per standard EN 2563, the test specimens were prepared as per standard EN 2655 having average thickness of 5.85 mm (SD 0.05 mm) and an average width of 10.10 mm (SD 0.02 mm). The span length of the specimen was 26mm. The test was conducted in a 10 kN load cell, C101104002 in Zwic/Roell Z010 UTM at a crosshead displacement of 1 mm/min and the shear strength was calculated as per Eq. (1).

$$\tau = \frac{3P_R}{4\,b\,h} \tag{1}$$

Where τ is the apparent interlaminar shear strength in MPa
P_R is the maximum load at the moment of first failure in N
b *and* h are breadth and height of the sample respectively in mm.

The extent of cure was performed as per standard AITM 3-0008 using Perkin Elmer DSC8500 after conditioning the samples, per EN2743. The extent of cure was calculated using Eq. (2) and a correction of 100% resin content was done by using EN 2559 in order to determine the actual resin content in the system.

$$\propto = \frac{\Delta H_A - \Delta H_B}{\Delta H_A} 100[\%] \tag{2}$$

Where ΔH_A is the reaction of enthalpy in Joules of the A curve which is heated at a rate of 10 °C/min and ΔH_B is the reaction of enthalpy in Joules of the B curve which is subjected to the curing cycle which is being investigated.

To determine the glass transition temperature, dynamic mechanical analysis (DMA) experiments were carried out on the cured samples according to standard EN 256. The test specimens were prepared as per standard EN 2655, having average thickness and width of 5.85 mm (SD 0.05 mm) and 10.10 mm (SD 0.02 mm), respectively. The test was conducted under a constant strain control mode in a single cantilever set-up, using a DMA8000 from Perkin Elmer. The DMA continuously measures force (F), displacement (D) and phase angle (δ) between the stress and strain vectors during tests. The

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storage modulus E′, loss modulus E″ is calculated using Eq. (3) [1].

$$E' = \frac{l^3}{wt^3}\frac{F}{D} g\ sin\delta$$
$$E'' = \frac{l^3}{wt^3}\frac{F}{D} g\ cos\delta \quad (3)$$

where l is the sample length, w, t are the width, thickness of the sample respectively and g is the gravitational constant.

A single cantilever arrangement was chosen since it generates data that are closer to the actual mechanical properties of the composite parts during curing [1, 2]. The glass transition temperature was determined using loss modulus traces and tan δ peaks. The thermal degradation was evaluated by comparing the magnitude and transitions of tan δ traces.

Flatwise tensile tests for the sandwich panels were performed as per standard ASTM C297-94 using 100 kN load cell, 55408 in a Zwic/Roell Z100 UTM. The top and bottom surfaces of the sandwich sample were well sanded using a sand blaster and cleaned to assure a good bond to the blocks. The bonding pressure was less than the original sandwich bonding pressure (3.20 bar), and the curing temperature was 50 °F (28 °C) less than the original bonding temperature (180 °C).

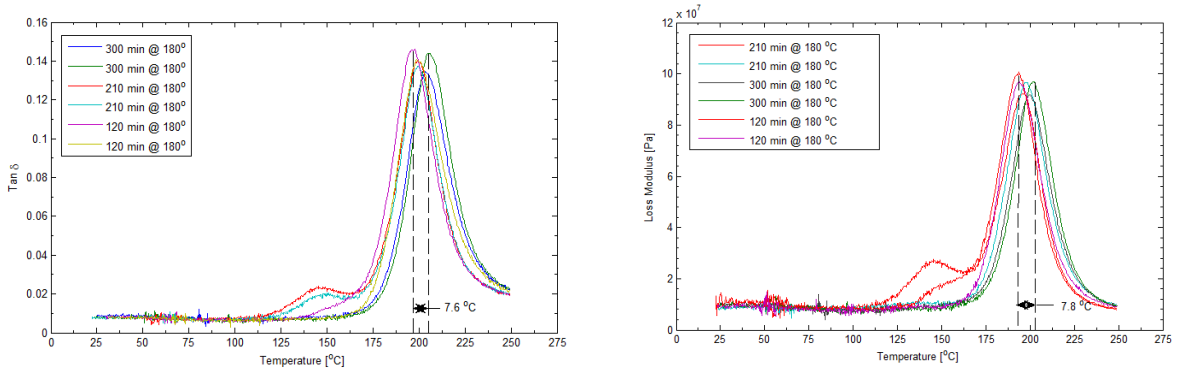
4. Results and discussion

4.1 Dynamic Mechanical Analyser

The glass transition temperature Tg for all the samples lie between 198 °C and 205 °C in the *tan δ* traces and between 194 °C and 202 °C in the loss modulus traces. Three samples for each cure were tested and the variation in the magnitude of their peaks were compared.

In Figure 3 and

Table 1, the slight shift in the peaks of *tan δ* and the loss modulus traces is seen which accounts to ~8 °C. However, this marginal increase is within the variations exhibited by the specimens of the same sample set; therefore, indicating negligible increase in the T_g with the increase in the postcure duration. Furthermore, as the magnitudes and transitions of all traces are similar, it can be concluded that no thermal degradation has occurred due to increased postcure soaking.



(a) (b)

Figure 3 DMA results used to determine the glass transition temperatures using (a) Tan delta traces (b) Loss Modulus traces

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Table 1 T_g values from the DMA tests

Postcure time (min)	Sample Num	*T_g (°C)
120	1	195
	2	199
210	1	197
	2	201
300	1	204
	2	205
* Rounded value		

4.2 Differential Scanning Calorimetry

The results of the extent of cure from DSC tests are listed in Table 2. It is obvious that all the samples have achieved cure over 95% as specified by the OEMs. However, it is noteworthy that the degree of cure reaches over 99% at extended postcure soaking but mechanical tests confirms that marginal increase has negligible effect on the mechanical properties of the composite material. Therefore, it can be concluded that the extended postcure soaking has negligible effect on the extent of cure.

Table 2 Results of the extent of cure from the DSC tests

Postcure time (min)	Sample Num	Weight (mg)	ΔH_{100} (J/g)	T_{onset} (°C)	T_{peak} (°C)	ΔH (J/g)	RC (%)	ΔH_{100} (J/g)	α_{100} (%)
120	1	31.52	370.00	190.68	250.25	2.13	42.00	5.07	98.63
	2	22.43	370.00	179.15	235.54	3.23	42.00	7.71	97.92
210	1	28.47	370.00	199.16	235.95	1.28	42.00	3.07	99.17
	2	23.79	370.00	198.42	235.91	2.46	42.00	5.86	98.42
300	1	32.49	370.00	202.79	235.22	1.76	42.00	4.21	98.86
	2	30.65	370.00	204.65	236.00	1.32	42.00	3.16	99.14

4.3 Interlaminar shear stress

ILSS depends primarily on the matrix properties and fiber–matrix interfacial shear strengths rather than the fiber properties. Therefore, the ILSS is higher for composites with higher matrix volume fraction. The ILSS decreases linearly with increasing void content, fabrication defects, such as internal microcracks and dry strands. In this work, the ILSS of all the samples are within ±3 MPa from the average of 73 MPa (Table 3), confirming no change in the ILSS values with increasing postcure soaking upto 300 minutes.

Table 3 ILSS test results of all the post cure soak time

Postcure time (min)	Sample Num	ILSS (MPa)
120	1	71.90
	2	73.75
210	1	72.88
	2	70.39
300	1	75.59
	2	70.76

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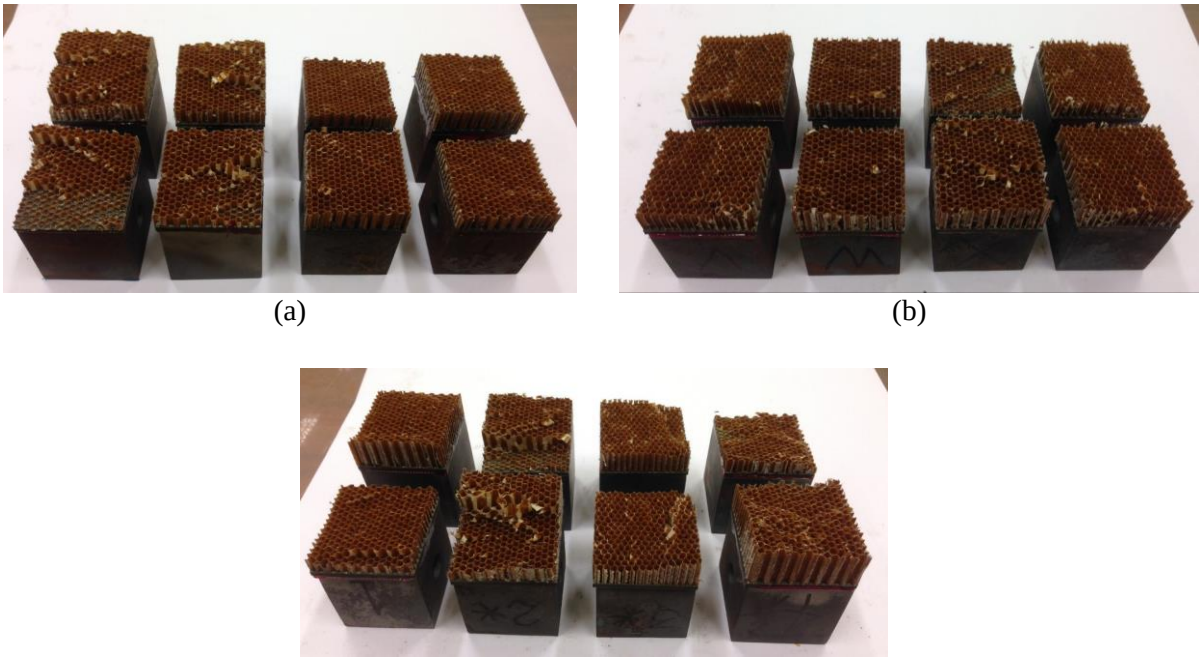
4.4 Flatwise tensile testing

During flatwise testing, three common failure modes occur; core tearing (the middle of the core or at the core edges); adhesion to the honeycomb or to the loading blocks (could be the facing if a sandwich sample is being tested); and cohesion (a cohesive failure of the adhesive itself). The desired failure mode is a uniform core tearing at the core thickness mid plane which produces the highest strength and is typical in cores having deep fillets. However, if the core fails at the cell edges the flatwise tension values are usually lower. In Figure 4, core tearing mode of failure is seen predominantly with a few samples exhibiting mixed mode of tearing and adhesion failure to the core. However, all specimens exhibited similar tensile strengths (Table 4) and none failed due to adhesive failure singly. Therefore, it can be concluded that the extended postcure has no effect detrimental effect on the adhesive film properties.



(a) (b)

(c)

Figure 4 Pictures depicting the core failure mode during a flatwise tensile test of samples post cured for (a) 120 min (b) 210m (c) 300 min

Table 4 Flatwise tensile test strength of specimens exposed to different postcure dwell time

Postcure time (min)	Sample Num	FWT (MPa)
120	1	2.44
	2	2.42
210	1	2.36
	2	2.58
300	1	2.62
	2	2.51

5. Conclusion

In this work, test coupons were manufactured using the cure profile provided by the material manufacturer and extended postcure isotherm at 180 °C to examine the effect of longer soak time on the mechanical and material properties of the matrix and the composite part. OEM standard material and mechanical tests have been performed on the coupons to affirm the consequences of the extended postcure on the composite parts. The T_g which is a material property that has been determined using DMA in this work reveals negligible change in the values, roughly 6-10 °C increase in samples

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exposed to 300 minutes postcure duration (204-205 °C) when compared to those at 120 minutes (195-199 °C), the magnitudes and transitions of all traces are similar, exhibiting no thermal degradation due to increased postcure soaking. The DSC results show all the specimens to have achieved cure greater than the OEM specified acceptance limit (95%), and there is no conclusive evidence elucidating any additional cure due to the overexposure. The ILSS results show no change in the strength values with similar variations among samples of a single sample set and the flatwise test confirms no degradation in adhesive properties of the adhesive film used in between the laminates and the honeycomb core. Therefore, in conclusion, composite parts that are subjected to extended postcure soaking at 180 °C upto 300 minutes show no signs of degradation in terms of mechanical or material properties when subjected to the above cited tests.

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