INFLUENCE OF OUT-TIME ON THE PROPERTIES OF OUT-OF-AUTOCLAVE AFP PREPREGS

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Keywords: AFP, Slit tapes, Volatiles, Automation, Carbon fiber

Abstract
In this study, the effect of out-time on the volatile content in the CYCOM® 5320-1 unidirectional prepreg tape is investigated by exposing prepregs to an elevated temperature for periods of 2 hours to 24 hours. In addition, samples based on a [0/±45/90]S stacking sequence were prepared for three exposure durations, these being 2, 24 and 48 hours. The laminates were laid using an in-house fiber placement rig and cured in an oven according to the manufacturer's recommended cure cycle. The glass transition temperature T_g and percentage of cure of the laminates were determined using dynamic mechanical analyzer in a single cantilever mode a differential scanning calorimeter, respectively. The mechanical properties of the laminates were also evaluated following manufacture. The results highlight a linear relationship between volatile uptake and out-time, with a maximum value of 0.6% being associated with an out-time of 24 hours. The exposure duration had a negligible effect on the tensile properties of the manufactured laminates, displaying a variation of ±8% from the mean values. The measured T_g values for the laminates manufactured in this study were similar to those quoted in the manufacturer's data sheet, with there being little change in T_g with prepreg out-time, within the intra-sample variations. The extent of cure of all the laminates manufactured in this work displayed cure values greater than the OEM acceptance criteria of 95%. Micrographs of laminates manufactured from tapes following an out-time of 2 hours show resin-rich areas between the plies, an observation that reduces with increased out-time. The void content in the laminates increased by more than 100% when the out-time was increased from 12 to 24 hours.

1. Introduction

Automated fiber placement (AFP) involves a fiber-processing head consisting of a guiding mechanism to layup the fiber tows and a compaction roller that aids in placing the tows along a pre-defined trajectory [1] The processing head is commonly attached to an end-effector of a robot and the fiber tows are laid on the tool by tacking them on the tool surface by applying pressure and heat, while the robot is in motion. The slit tape spools are either stored in a refrigerated cabinet provided by the machine manufacturer [2] or on the processing head of an AFP machine [3]. During layup on a tool, several tows are laid simultaneously and each tow may be driven independently in terms of being clamped, cut, and restarted, during manufacture [4], aiding layup over complex geometries easier. However, during instances of tow jam, spool replacement and under other catastrophic circumstances, several other spools in the processing head will be subjected to a longer period of out-time. This extended out-time in addition to long layup hours over large complex geometries may result in variability of inter-ply and/or intra-ply volatile uptake, that shows up as undesirable voids and porosities in the final part. Additionally, material manufacturers are constantly developing newer materials with the hindsight of manufacturing cost which again may have consequences on the out time. For example, the propensity of void formation in low temperature cure OOA towpregs may be higher than a high temperature pressure sensitive towpreg system because of lower T_{gel} values. This may in turn require the machine to adapt by either slowing or fastening the layup process, in effect requiring the equipment manufacturer to consider process-material interaction to adapt to the constantly changing material environment. For example, Coriolis have developed an AFP machine that is capable of using thermoset, thermoplastic and dry tapes on a single processing head, Electroimpact has incorporated the work of Cemenska et.al. [5] in the in-process inspection of the layup using AFP machines, in effect reducing the manual inspection duration during layup. Machine-independent off-line NC programming software developed by Hasenjaeger [6] is being provided with the machine in order to simulate the AFP layup beforehand to determine potential shortcomings. Works of other complex processing such as planning of trajectory, systems modelling, process parameter optimization [7-10] have been directly incorporated in the development phase of the machines, making them robust to handle complex processes. Complementing to development of machine hardware and software, several other literature relating to material science and material-process interactions are being developed to assist user to fine tune the machine to adapt to the new materials and hence processes. Typical analyses can be found in the works of Rao et.al. [11] where sem-empirical solutions for machine parameters such as the layup temperature, speed and roller compaction load for tacking on the tool surface was developed for OOA towpregs. The processing temperature and the compaction load range were primarily derived from stress relaxation experiments conducted on the towpregs at various temperatures [12]. In this work, the implications of extended out-time of AFP OOA towpregs on the laminate properties has been investigated by subjecting CYCOM® 5320-1 to different out-times, varying from 2 hours to 24 hours in 2 hour succession period, differing from literature [13] where the void content was correlated to the layup parameters

2. Materials and Experiments

2.1. Materials

CYCOM® 5320-1 carbon fiber towpreg from CYTEC Engineered Materials Inc. USA was used in this study. The nominal width and thickness of the tape are 6.35mm and 0.275 mm, respectively. The nominal fiber areal weight is 145 g/m^2 and the nominal resin content is 33% by weight [14]. Additional laboratory apparatus, such as the cutting blades, digital scales capable of measuring to 0.1 mg, a convection oven, a timer, a desiccator and a temperature and humidity indicator were used in the measurement of volatiles. An Instron universal testing machine, with a 50 kN load cell was used for tension tests and an extensometer with a gauge length 50mm was used to record the strain. A stereo microscope Zeiss AX10 was used to examine the cross-sections of the laminates.

2.2. Experiments

The specimens investigated in this study were manufactured from CYCOM® 5320-1 carbon fiber prepreg (also referred to as towpreg in this study). Prior to sample preparation, the rolls were conditioned in a sealed plastic bag for a 12h out-time in a laboratory environment at a temperature of 20.5°C and relative humidity of 44%. The roll of towpreg was initially stored in a sealed package at -18°C, as recommended by the manufacturer. The volatile content was measured as per standard ASTM D3530-97 for out-times varying from 2 hours to 24 hours. The specimens were weighed and subsequently exposed to elevated temperatures in a pre-heated convection oven maintained at the nominal cure temperature of the material (93 ±5 °C) [15]. The specimens were then re-weighed and the volatile content was determined from the percentage change in sample weight. Nine test runs were conducted and five specimens were used for each run. The volatile content was determining using:

$$V_c = \left(\frac{M_i - M_f}{M_i}\right) \times 100 \quad (1)$$

Where:
V_C – Volatile content in weight percent
M_i – Initial weight of the specimen (in grams)
M_f – Weight of the specimen after removal from the oven (in grams)

Quasi-isotropic laminates [0/±45/90]S were manufactured following exposure times of 2, 12 and 24 hours using an in-house fiber placement system that consisted of a roller and a 20kN load cell, (Omegadyne LCM202) housed between the roller and the tool arbour of a Bridgeport® milling machine. The lay-up temperature was monitored using an infrared camera, FLIR A655sc and a hot air gun from Bosch® was used as the heat source. Further details of the hardware set-up and the processing conditions for the automated lay-up, can be found in [11]. The bagging sequence used to cure the laminate in a convection oven cycle, is shown in Figure 1. The oven was programmed to heat to a temperature of 60±5 °C for 120±10 minutes, followed by a ramp at 2±1 °C per minute to 120±10° C and hold for 120±10 minutes. The second ramp was at 2±1 °C per minute to 180±5 °C with a hold time of 120±10 minutes. The set-up was then cooled to ambient temperature at 3±1 °C per minute.

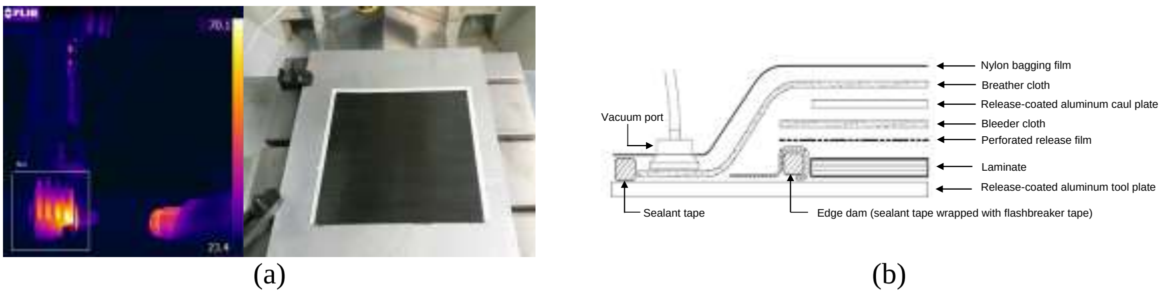


Figure 1 Composite manufacturing using an in-house AFP rig (a) Manufacturing set-up and a sample laminate on a Bridgeport® milling table (b) Bagging sequence used to cure the laminate after layup

The edges of the laminates were trimmed and tensile coupons per standard ASTM D3039 were cut using a diamond wheel cutter. Five specimens were tested from each manufactured laminate and the strength and the moduli were determined from their respective load vs. deflection traces. Polished cross-sections removed from the laminates were viewed under an optical microscope to examine the laminate quality, and the void content in the laminate was determined using Olympus stream image analysis software.

Dynamic mechanical analysis (DMA) experiments were carried out on the towpregs under a constant strain control mode in a single cantilever set-up, using a DMA8000 from Perkin Elmer. A single cantilever arrangement was chosen for characterizing the towpreg, as it generates data that are closer to the actual mechanical properties of the composite parts during curing [16, 17]. The tests were conducted according to the specifications listed in the ASTM D 7028-7 standard [18]. The T_g at onset was determined using the storage modulus whereas the maximum T_g of the samples was determined using the peak of the loss modulus trace. Variations in the viscosity were evaluated by comparing the transitions in the storage modulus trace in the thermogram.

The degree of cure was performed as per standard ISO 11357-1 [19] using a Perkin Elmer DSC8500 after conditioning the samples in the laboratory environment for 12h hours. The degree 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.

$$\propto = \frac{\Delta H_A - \Delta H_B}{\Delta H_A} 100\,[\%] \quad (2)$$

Where
ΔH_A is the reaction of enthalpy in Joules of the A curve which was heated at a rate of 10 °C/min an is the reaction of enthalpy in Joules of the B curve which was subjected to the cure cycle which und investigation.

2.3. Results

A monotonic increase in the volatile content is seen in the results of towpregs exposed from 2 to 24 hours (Tables 1 to 5), where a two-fold difference in volatile content is apparent between the two extremes. The laminates manufactured from the towpreg that had been exposed to an out-time of 2 hours showed reduced fiber nesting and distinct resin rich regions between adjacent plies. These effects decreased with an increase in out-time (see Figures 3 to 5). This phenomenon of reduced fiber nesting in the laminates could be attributed to lower strains during the layup process, where the fiber bed stress is relatively low with much of the compaction load being taken by the viscoelastic resin system [12]. The increase in fiber nesting with the duration of the exposure event suggests a link between the out-time and the viscosity of the resin in the towpreg system during the layup process. In essence, with reference to the previous work done [12], longer out-time seems to reduce the bulk factor, which has indeed improved the fiber nesting. It has to be noted that the reduction in bulk factor had no influence on the final thickness of the manufactured laminates, which can be attributed towards the use of universal cure cycle for all the samples.

Table 1 Out-time 2h and 4h

Out-time = 2 h				Out-time = 4 h			
Specimen	Initial Mass (g)	Final Mass (g)	Volatile Content (wt %)	Specimen	Initial Mass (g)	Final Mass (g)	Volatile Content (wt %)
1	0.0692	0.0692	0	1	0.0718	0.0718	0
2	0.0664	0.0664	0	2	0.0701	0.0700	0.143
3	0.0685	0.0685	0	3	0.0716	0.0716	0
4	0.0648	0.0648	0	4	0.0722	0.0721	0.139
5	0.0657	0.0657	0	5	0.0702	0.0702	0
		Average	0			Average	0.056

Table 2 Out-time 6h and 8h

Out-time = 6 h				Out-time = 8 h			
Specimen	Initial Mass (g)	Final Mass (g)	Volatile Content (wt %)	Specimen	Initial Mass (g)	Final Mass (g)	Volatile Content (wt %)
1	0.0667	0.0667	0	1	0.0439	0.0438	0.228
2	0.0719	0.0719	0	2	0.0448	0.0446	0.446
3	0.0703	0.0698	0.711	3	0.0439	0.0437	0.456
4	0.0703	0.0699	0.569	4	0.0442	0.0441	0.226
5	0.0687	0.0686	0.146	5	0.0431	0.043	0.232
		Average	0.285			Average	0.318

Table 3 Out-time 10h and 12h

Out-time = 10 h				Out-time = 12 h			
Specimen	Initial Mass (g)	Final Mass (g)	Volatile Content (wt %)	Specimen	Initial Mass (g)	Final Mass (g)	Volatile Content (wt %)
1	0.0697	0.0695	0.287	1	0.0692	0.0688	0.578
2	0.0700	0.0696	0.571	2	0.0702	0.0697	0.712
3	0.0708	0.0706	0.282	3	0.0762	0.0760	0.262
4	0.0686	0.0683	0.437	4	0.0725	0.0722	0.414
5	0.0709	0.0707	0.282	5	0.0711	0.0709	0.281
		Average	0.372			Average	0.449

Table 4 Out-time 14h and 16h

Out-time = 14 h				Out-time = 16 h			
Specimen	Initial Mass (g)	Final Mass (g)	Volatile Content (wt %)	Specimen	Initial Mass (g)	Final Mass (g)	Volatile Content (wt %)
1	0.0622	0.0619	0.482	1	0.0692	0.0687	0.723
2	0.0656	0.0652	0.610	2	0.0702	0.0697	0.712
3	0.0631	0.0629	0.317	3	0.0762	0.0759	0.394
4	0.0679	0.0674	0.736	4	0.0725	0.0722	0.414
5	0.0629	0.0626	0.477	5	0.0711	0.0707	0.563
		Average	0.524			Average	0.561

Table 5 Out-time 24h

Out-time = 24 hrs			
Specimen	Initial Mass (g)	Final Mass (g)	Volatile Content (wt %)
1	0.0697	0.0694	0.43
2	0.0698	0.0695	0.430
3	0.0663	0.0657	0.905
4	0.0745	0.0741	0.537
5	0.0731	0.0726	0.684
		Average	0.5972

Based on the experimental results, a simple curve-fitting procedure was applied to the experimental data yielding a relationship between the levels of volatiles and out-time in the form of an exponential function:

$$V_c = 0.67 - 0.88e^{-0.12T} \tag{3}$$

Where
where Vc is volatile content and T is the out-time.

Equation (3) provides a reasonable match with experimental data, within 10% deviations, as seen in Figure 2. This approach predicts a 0.7 wt% volatile content for towpregs exposed to an out-time of 48 hours, which is within 15% of the experimental value of 0.6 wt%, provided by the manufacturer [14]. The discrepancy may be due to other contributing factors, such as variations in room temperature and humidity, the age of the towpreg roll, variations in the resin content within the towpreg, etc.

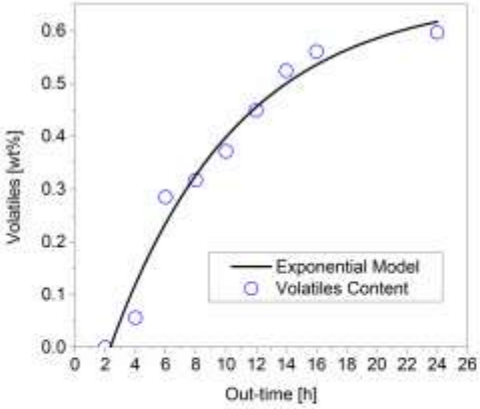
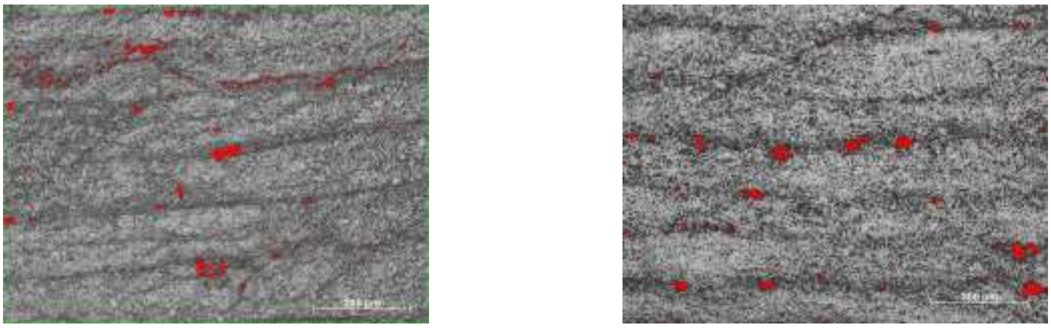
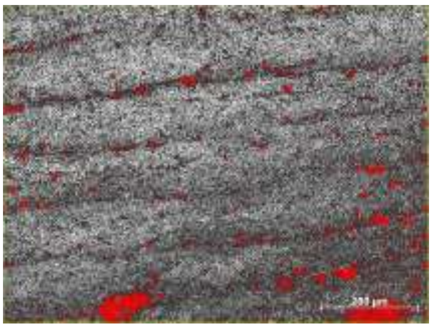


Figure 2 Volatile content modelled as a function of out-time using linear and exponential relations

Interestingly in Figures 3, the laminates manufactured from towpregs exposed to the three different exposure times show similar results, with void percentage increasing from 1.2% for an out-time of 2 hours to 2.5% at 24 hours. This indicates that the tapes subjected to longer out-times may require an additional devolatilization step before curing is initiated or alternatively an alteration of the cure cycle to accommodate the increase in the level of volatiles (a hold stage to vent out the volatiles).



(a) (b)



(c)

Figure 3 Micrograph of the cross-section of a $[0/\pm45/90]_S$ laminate manufactured from prepregs subjected to (a) 2h out-time with voids highlighted in red which is approximately 1.3% of the 0.576 mm^2 measured area (b) 12h out-time with voids highlighted in red which is approximately 1.5% of the 0.576 mm^2 measured area (c) 24h out-time with voids highlighted in red which is approximately 2.5% of 0.571 mm^2 measured area

Figure 4 shows DMA traces from towpreg samples exposed to out-times of 2, 12 and 24 hours, all samples irrespective of exposure time, show Tgel to be between 165 °C and 170 °C. Additionally, the variation in T_g values, seen in Figure 4 (a-c) as the peak of the loss moduli is also negligible with a maximum difference of 2 °C between all the samples tested, irrespective of their out-time. This is again replicated in the DMA results of the laminates manufactured from the tapes that have been subjected to different out-times, seen in Figure 5 as marginal shift in the peaks of loss modulus (T_g). The tensile strength and moduli values of the panels, Table 6, also exhibit a negligible change for panels with void contents of 1.2% and 2.5%. Therefore, in this work from the above experiments, it is evident that the volatile content increases with increasing out-time and the void content in the laminate also increases with towpreg volatile content. However, the mechanical properties and the DMA results show little evidence of the volatile content affecting the quality of the laminates. Additionally, the DSC results in Table 7 indicate levels of cure greater than 98%, indicating that the length of exposure has a negligible influence on the degree of resin cure in the laminate.

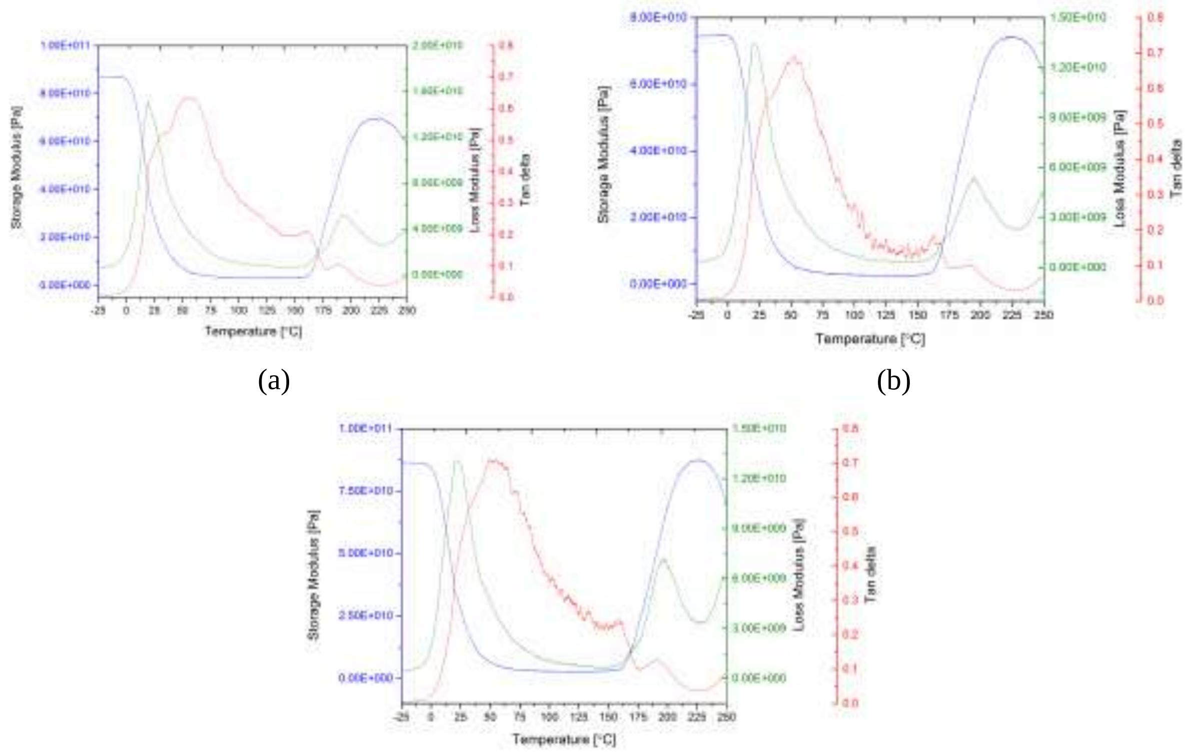


Figure 4 DMA test results of CYCOM 5320-1 tapes exposed to (a) 2h out-time (b) 12h out-time (c) 24h out-time

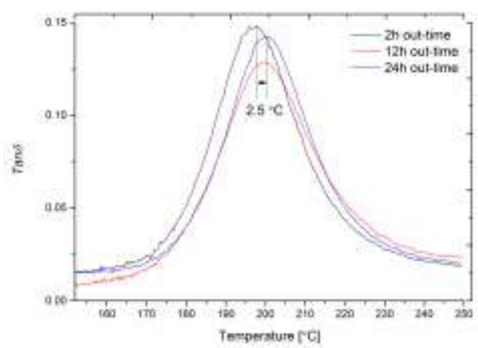


Figure 5 DMA tests of laminates manufactured from tapes exposed to out-time from 2h, 12h and 24h out-time, showing negligible change in T_g loss modulus peaks

Table 6 Tensile strength and Moduli values of [0/±45/90]S laminates manufactured from tapes of different out-time, tested per standard ASTM 3039

Out-time	Strength (MPa)	Modulus (GPa)
2h out-time	606	48
12h out-time	610	51
24h out-time	612	52

Table 7 Extent of cure of laminates manufactured from towpregs exposed to 2h, 12h and 24h out-time

Out-time time (min)	Weight (mg)	ΔH_{100} (J/g)	T_{onset} (°C)	T_{peak} (°C)	ΔH (J/g)	RC (%)	ΔH_{100} (J/g)	α_{100} (%)
2h	25.93	545.00	214.70	232.94	2.53	37.00	6.86	98.74
12h	30.02	545.00	215.38	231.83	3.06	37.00	8.29	98.48
24h	28.63	545.00	214.82	230.60	3.05	37.00	8.25	98.49

3. Conclusions

In this work, the effect of out-time on the volatile content in CYCOM® 5320-1 unidirectional prepreg tape is investigated by exposing the prepregs to room temperature conditions for 2 hours to 24 hours. Simple statistical curve-fitting of the experimental data yielded a negative exponential relation between the volatile content and out-time. The volatile content in the prepregs had no influence on the Tg of either the tapes or the resulting laminates. The void percentage increased from 1.2% to 2.5% in laminates manufactured from tapes subjected to 2 and 24 hours out-time, respectively. However, the tensile strength and modulus values exhibited little or no change in the samples tested, irrespective of out-time. Therefore, it may be concluded that out-times within specific bounds (2 to 24 hours) has a negligible effect on the Tg and mechanical properties of the manufactured composite laminates. However, in order to minimize the void level, it may be useful to devolatilize thicker laminates, that may have been subjected to extended out-times, either during the layup process or during any change of spools.

Acknowledgments

The authors thank Jerome Lozada Lacap at STRATA PJSC for his assistance in image analysis, Mubadala Aerospace for funding this work and the Department of Aerospace Engineering for the use of equipment.

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