



Controlling mass loss from RTM6 epoxy resin under simulated vacuum infusion conditions

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ARTICLE INFO

Keywords:

Thermosetting resin
Cure behaviour
Thermal analysis
Vacuum infusion

ABSTRACT

A certified aerospace resin (RTM 6) normally utilised for resin transfer moulding is considered for vacuum infusion. The resin was subjected to simulated vacuum infusion conditions by using a specialised thermogravimetric analysis that enables control of pressure as well as temperature. By varying conditions, it was possible to investigate the expected occurrence of volatile losses during infusion that could cause mechanical or cosmetic defects in a part. With particular reference to RTM6, it was determined that full vacuum could be used for infusion provided that the temperature was kept below ~130 °C. Higher temperatures could be used, but the applied vacuum should be significantly reduced. Of note is that the manufacturers datasheet recommends processing parameters that could result in volatile loss. As such, the pressure enhanced TGA method may be considered more widely for providing processing conditions supplemental to the manufacturers recommendation for any liquid resin used under vacuum conditions.

1. Introduction

Autoclave processing of polymer composites using prepreg materials is a favoured process in the aerospace sector as it provides high quality components with low void contents, which is essential to good mechanical performance [1,2]. However, this process is expensive and there is a drive to achieve cost savings by moving to so called out of autoclave (OOA) processing [3,4].

One OOA process is resin transfer moulding (RTM), whereby a liquid resin is forced under pressure into a dry fabric matrix within matched tooling. This produces components with the advantages of a fixed part thickness and a double-sided mould finish. Specific resins, such as HexFlow® RTM6, have been developed for this process. However, as air typically is not evacuated from the tool prior to injection, the potential arises for a higher void content compared to an autoclave processed component. Modified processes including vacuum assisted RTM,

injection compression techniques [5] and more recently high pressure (HP-)RTM [6] have improved part quality and speed of manufacture. Nevertheless, thermally controlled, matched tooling is required in each case, along with clamping to resist the positive pressures. These can be many 10s of bar for HP-RTM [7,8]. The required capital and tooling is expensive and with a desire for larger parts, RTM may become prohibitively expensive.

In many cases, composite products only require a high-quality finish on one surface and so single sided tooling techniques have been developed to limit both tooling and autoclave production costs. In particular, vacuum infusion using a flexible bagging [9] is a relatively inexpensive process that has been adopted widely and can be applied to very large parts without the limitation of press or autoclave size. Vacuum removal of air prior to infusion helps reduce voids [10] while maximising reinforcement compaction for an increased volume fraction. However, with a maximum of 1 bar of pressure the part quality is highly dependent on

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fabric compressibility and permeability of the reinforcement. As a result, precise dimensional control is lost [11,12].

While resins are available aimed specifically at vacuum infusion systems, the qualification of new aerospace materials can take many years and is extremely expensive [13]. Since Hexcel HexFlow® RTM6 is a widely utilised and aerospace certified resin system, having been in service for 20 years, it would be beneficial to apply it to vacuum infusion techniques. Indeed, Hexcel now promotes RTM6 for these negative pressure processes. However, negative pressure could potentially induce evaporation of resin components at the flow front, occurring due to a depression of the component boiling points according to the Clausius Clapeyron relationship [14]. This introduces the risk of entrapping gas bubbles generated at the flow front [15] or of incurring issues related to autophobic conditions (pre-wetting of the reinforcement in advance of the flow front by vapour from the resin) [16,17]. As an example, the boiling point of styrene drops from 145 °C at atmospheric pressure to 30 °C at 10 mbar [18]. Entrapped porosity can have a negative effect on mechanical properties [19] or surface quality depending on the location of the pores, while autophobic behaviour can lead to poor wet out and the occurrence of voids.

Conventionally, RTM6 is preheated from solid at ambient to viscous liquid at 80 °C to degas and is then infused (<5 mbar) into a mould at a constant temperature between 120 °C and 140 °C. Ramping to 180 °C is suggested for a minimum of 90 min to promote resin curing. Ongoing work in developing vacuum consolidated parts that include a typical panel stiffening component (such as an omega beam) have observed that at a mould temperature of 120 °C a degree of print through or dry surface is incurred in areas of compaction at the stiffener. Empirical evidence has suggested that increasing the infusion temperature can improve this result (see Fig. 1) and at least one other study indicates a benefit in using an increased mould temperature in VARTM, albeit for a different resin system [20]. Early use of higher temperatures also has potential benefit in process optimisation to reduce stress [21]. However, it is unknown whether any volatile loss is expected under these conditions, since it is outside manufacturer recommendations. Gel time is drastically reduced at 180 °C (to 15–20 min [22]) but infusion rates are increased and so a manufacturing route could remain viable.

This aim of this paper is to demonstrate a novel experimental technique for determining the resin infusion processing conditions

(temperature and pressure) under which volatile losses will be avoided. A high sensitivity thermogravimetric analysis (TGA) system is used that can be operated under a controlled pressure atmosphere. This enables a direct evaluation of volatile losses from RTM6 under simulated infusion conditions both at elevated pressure and at vacuum pressures. Measurements are combined with literature values describing the cure behaviour of RTM6 in order to gain an understanding of the observations and to offer suggestions on processing conditions. Such a study could be repeated for other resin systems in future, providing a means of determining their preferred processing conditions.

2. Material and methods

A XEMIS gravimetric sorption analyser (Hiden Isochema) was utilised to measure mass loss from the free surface of RTM6 resin. Unlike conventional thermogravimetric analysis, this equipment enabled the control of pressure as well as temperature. Twelve different conditions of pressure and temperature were selected as shown in Table 1. For all conditions, RTM6 resin was brought to room temperature and an amount of material (between 30 and 60 mg) was placed into an alumina pan (Almath Crucibles Ltd CC6 – 99.8% Alumina, 0.09 ml, 6 mm OD, 5 mm ID, 4 mm high), which was then suspended in the XEMIS equipment. As an illustration, condition 4 (highlighted in Table 1) is shown in Fig. 2

Table 1
Range of nominal temperature and pressure conditions used in the XEMIS.

Condition	Hold temperature (°C)	Pressure (mbar)
1	180	10
2	180	20
3	180	35
4	180	50
5	180	100
6	180	300
7	180	650
8	180	7000
9	150	10
10	150	50
11	120	10
12	120	50

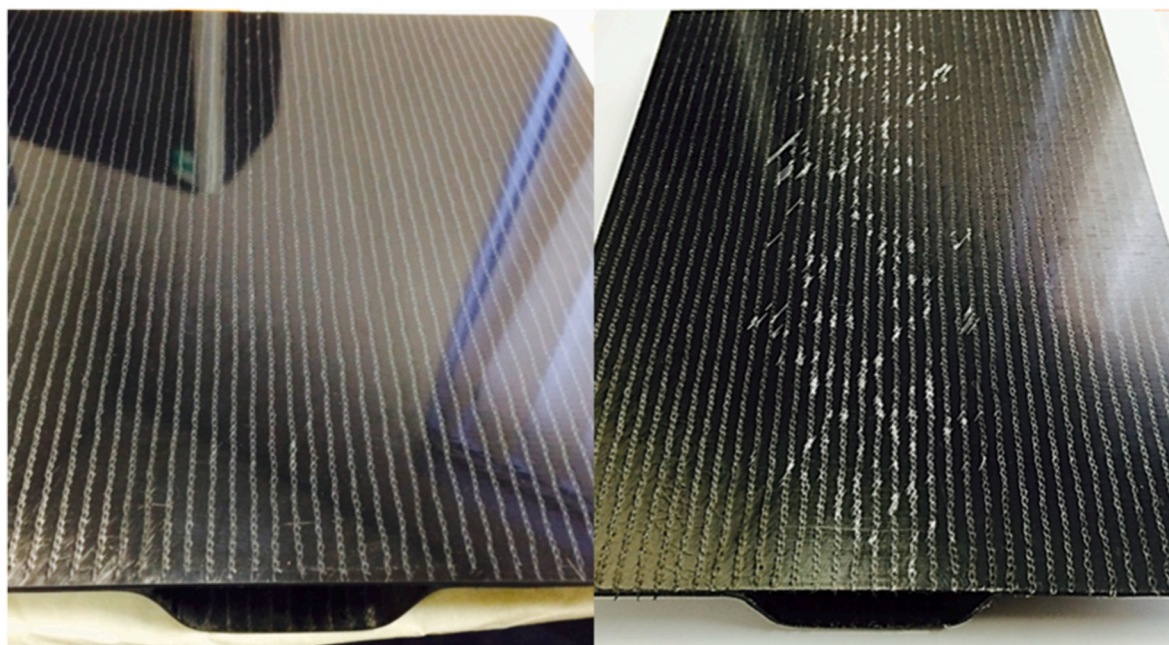


Fig. 1. Two carbon fibre/RTM6 panels produced with an omega beam stiffening element. The panel on the left was infused at 180 °C, while the panel on the right was infused at 120 °C. A reduction in print through was observed using a higher temperature infusion.

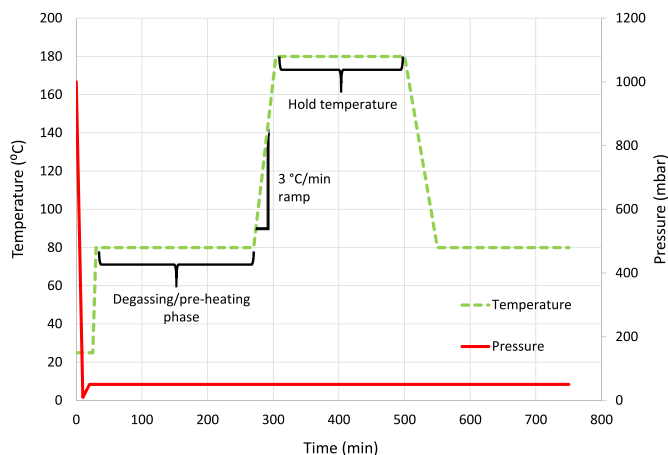


Fig. 2. Schematic showing the temperature and pressure cycle, illustrated for conditions of 180 °C and 50 mbar pressure (condition 4, Table 1).

where the sample was subjected to an ambient pressure of 50 mbar and a hold temperature of 180 °C. Temperature was measured using a thermocouple in close proximity to the alumina pan but not within the resin itself. Results are presented on the assumption that the resin temperature was equivalent.

The hold temperature was either 120, 150 or 180 °C, with a preheat/degassing phase at 80 °C based on the recommended processing method from the manufacturer. The resin was then heated to the hold temperature at the highest rate for which the manufacturer provided viscosity data (3 °C/min) and held for a period of ~200 min, after which it was allowed to cool back to 80 °C. The pressure was varied between 10 mbar and 7 bar. A value of 10 mbar was selected as representing a good bag seal for vacuum infusion, while 7 bar is representative of an RTM injection pressure. A control experiment using an empty alumina pan indicated an error level of ± 0.01 mg for the sample mass. Temperature variation at the hold temperature was ± 0.01 °C. Pressure was accurate to ± 0.5 mbar and once the desired pressure was achieved the system was sealed throughout the rest of the experiment.

Change in mass due to the heating cycle was taken to be the difference between the mass at 80 °C before the ramp and hold phase and the mass at 80 °C after the ramp and hold phase. In doing so, the sample would be at equivalent values of temperature and pressure and so buoyancy effects could be ignored. This assumed that the sample chamber volume was large in comparison to any evolved gas from the sample.

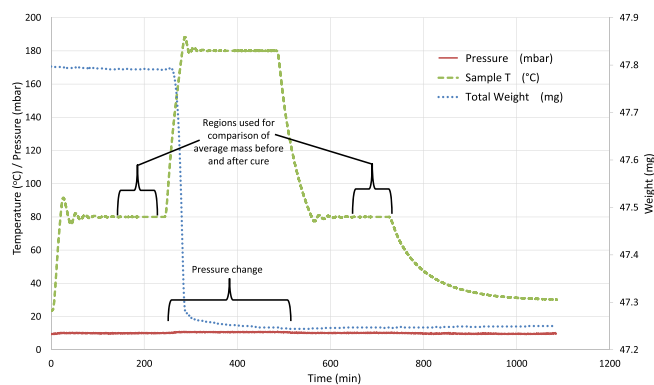


Fig. 3. Typical experimental result. Data shown for a sample at 10 mbar and a hold temperature of 180 °C. Brackets indicate the region used for average mass measurement, where the temperature is stable at 80 °C and pressure is constant.

3. Results

Fig. 3 shows an example of the real data obtained from the experiments (condition 1). There was a degree of temperature overshoot in the heating ramp, which was partially attributed to the low air pressure (and therefore limited heat transfer capability). It can also be seen that the pressure (P) changed with temperature (T), which is in accordance with Gay-Lussac's law since the system was sealed ($P_1/T_1 = P_2/T_2$ at constant volume (V)) [14]. Changes in pressure after the experiments were small (typically ± 0.2 mbar) and provided no systematic variation. A change in mass was clearly apparent, with the majority of the mass loss occurring within the heating ramp. Actual heating rates were back calculated from the data and were on average 2.8 ± 0.1 °C/min, with a range from 2.6 to 2.9 °C/min.

Fig. 4 provides the mass loss values for each of the conditions, plotted as a function of the pressure. The values are plotted as absolute and percentage values. There is a clear exponential trend indicating that a lower pressure atmosphere results in a greater mass loss. There is also a clear trend indicating that a greater mass loss occurs at higher temperatures.

Fig. 5 provides a plot of percentage mass loss vs temperature for two series of pressure, 50 mbar and 10 mbar (nominal). It is apparent that there is a linear trend between mass loss and hold temperature for a given pressure. The plot also demonstrates that both the magnitude and rate of mass loss are pressure dependent.

4. Discussion

Use of a TGA with combined temperature and pressure control has provided a clear trend in mass loss from a heated resin, with dependency both on temperature and pressure. It is readily apparent from Fig. 3 that the vast majority of mass loss occurs during the heating ramp. Although identification of what material was lost could not be made specifically, the long (~3 h) degassing at 80 °C at reduced pressure prior to the heating ramp suggests that it is unlikely to be water. However, additional verification would be desirable if the process could be combined with spectroscopic or chromatographic methods.

In Fig. 4 the effects of temperature and pressure on mass loss are apparent. The profile for percentage loss is reasonably consistent, while the absolute loss varies as sample mass varies. This suggests that the loss is volume limited rather than surface area limited, such that all nucleated gas bubbles are lost rapidly (i.e. no trapped material). If the process was surface area limited and gas was unable to escape (trapped material lower in the sample), a similar mass loss would be expected for samples with differing starting mass since they have the same surface area.

Table 2 provides an approximate extrapolated value of pressure for each temperature, above which no mass loss would be expected to occur. It is suggested that infusion pressures should be maintained at this level or higher. Subsequently, once the component is fully infused, pressure could be decreased (a greater vacuum applied) in order to suppress any voids prior to gelling [10,23].

The values from Table 2 fit well to a simple exponential (Fig. 6) to derive a region of conditions of temperature that can be used to avoid mass loss during infusion. However, this is based on a limited set of data and so should not be considered definitive. Of particular interest are the processing parameters within the Hexcel, HexFlow RTM6 datasheet [22]. These suggest, for example, that infusion of the resin into a mould at 140 °C under an infusion pressure of 5 mbar would be acceptable. However, referring to Fig. 6, at 140 °C mass loss is predicted to occur at any pressure less than approximately 100 mbar. While this may have no impact on component certification, if the mass loss is manifest as porosity a cosmetic defect may occur on the part surface. Further, the benefit of avoiding mass loss must be balanced against potential final void content, which can be affected significantly by the applied vacuum during infusion. Reduced vacuum provides less compaction pressure with which to re-dissolve the gas in small voids [10,20].

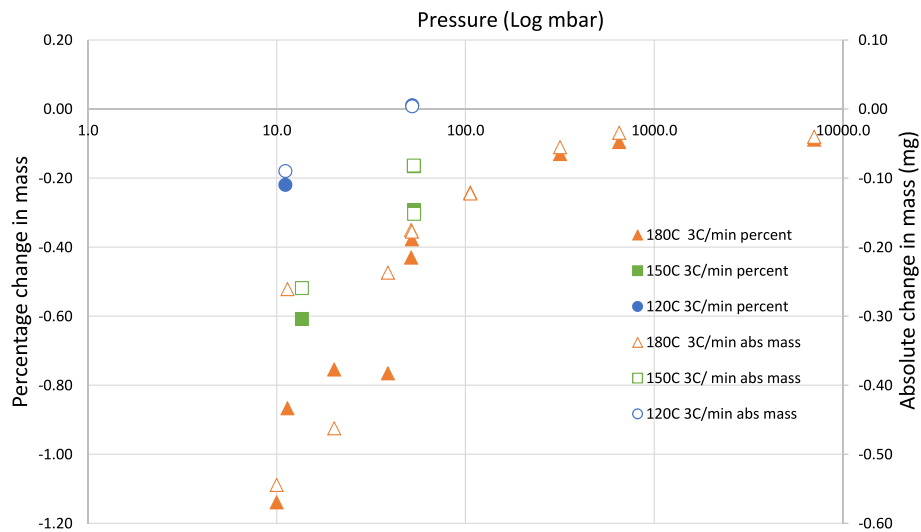


Fig. 4. Graph of mass change vs pressure for different hold temperatures, plotted both as an absolute mass loss and a percentage mass loss. Error values for measurements fall within the size of the markers.

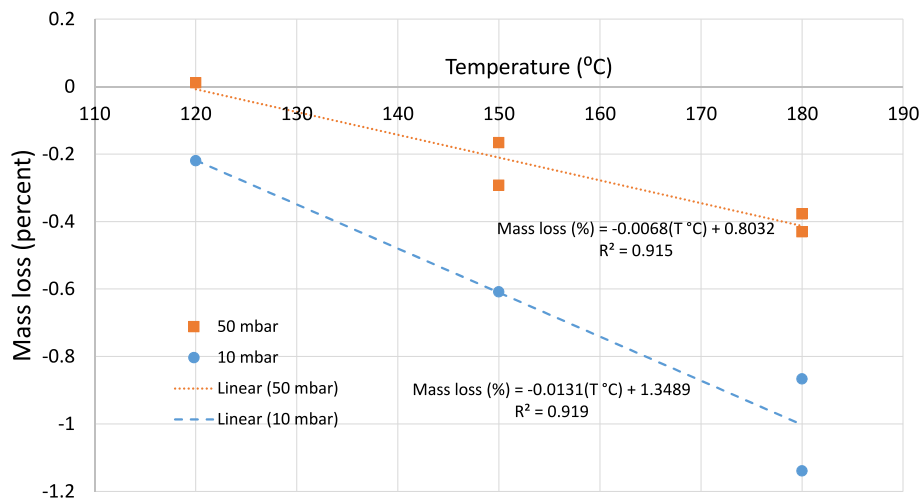


Fig. 5. Graph of percentage mass loss vs temperature for two series of pressure, 50 mbar and 10 mbar (nominal). Error values for measurements fall within the size of the markers.

Table 2

Approximate minimum pressure (maximum vacuum) required to avoid mass loss at a given temperature.

Hold temperature	Estimated pressure above which no mass loss would occur
120 °C	40 mbar
150 °C	140 mbar
180 °C	550 mbar

Fig. 5 provides further information on the relationship between temperature and pressure on mass loss. Diffusion rate is related to viscosity and both Zotti et al. [24] and the data sheet from the manufacturer [22] show a relatively linear decrease in viscosity for RTM6 resin between 80 and 180 °C when heated at 3 °C/min, which fits well with the linear change in mass loss with temperature seen in Fig. 5.

To gain more information from the region of the heating ramp, Fig. 7 shows examples of the data at 180 °C where the mass loss data has been normalised to the start of the heating ramp. It is apparent that irrespective of the pressure of the system, the point at which mass loss begins to occur is similar.

The point at which the first mass loss occurs was defined as being a

loss of >0.01 mg in comparison to the average value recorded at the end of the 80 °C plateau, prior to the heating ramp to hold temperature. This is in accordance with the error level determined by the blank run. Using this definition, the time and temperature at which mass loss began to occur was calculated for each specimen. An average of these values is provided in Table 3.

The values are within a small range, suggesting that the initiation of mass loss is a temperature dominated effect. It is of particular note that mass loss occurred at a minimum of 132 °C even for the nominally 120 °C run. This occurred due to the temperature overshoot on the heating ramp, which suggests that the small mass loss observed in the 120 °C sample may only be due to the occurrence of this overshoot. That the mass loss does not occur until >130 °C is further suggestive that the lost mass is not water. From Zotti et al. [24], the viscosity of the resin at 80 °C was on the order of 0.1 Pa s (in the sensible range for flow in liquid composite moulding processes), such that water should escape easily during the pre-ramp hold. However, aniline can form significant hydrated clusters [25] and so a higher temperature loss of bound water cannot be completely discounted.

That the total mass loss observed at a given temperature is different between the different pressures suggests that a distinct end condition

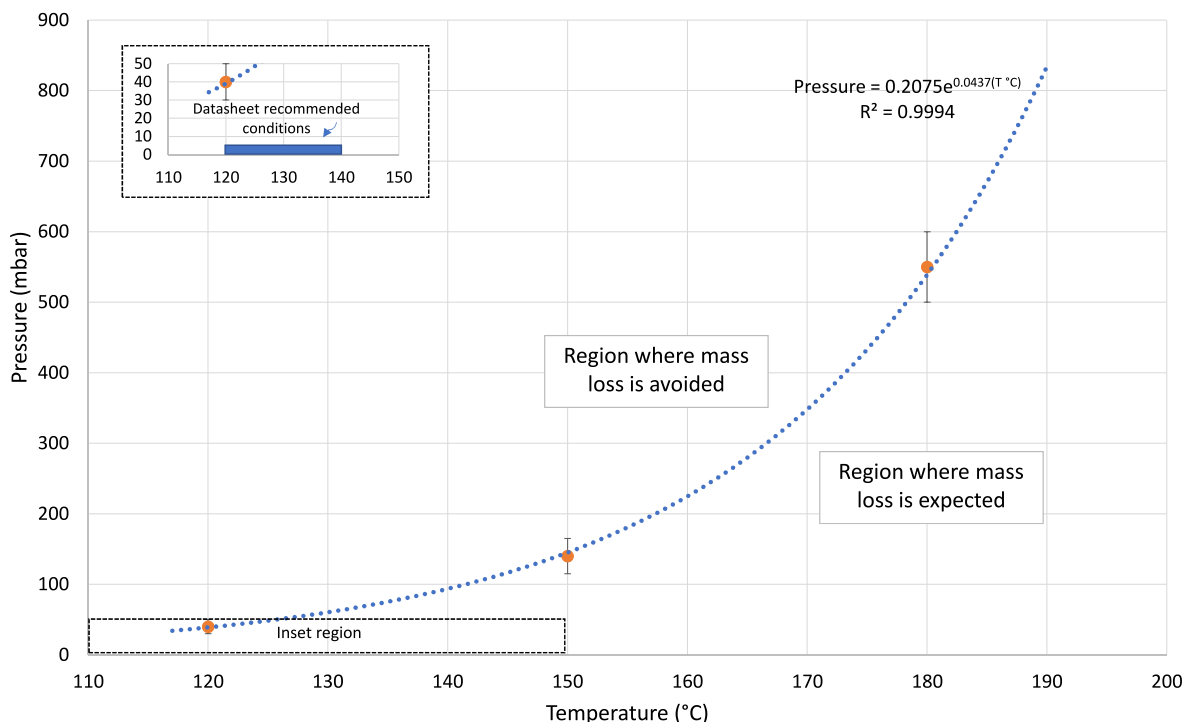


Fig. 6. Plot of temperature vs pressure indicating regions where mass loss would and would not be expected to occur during infusion.

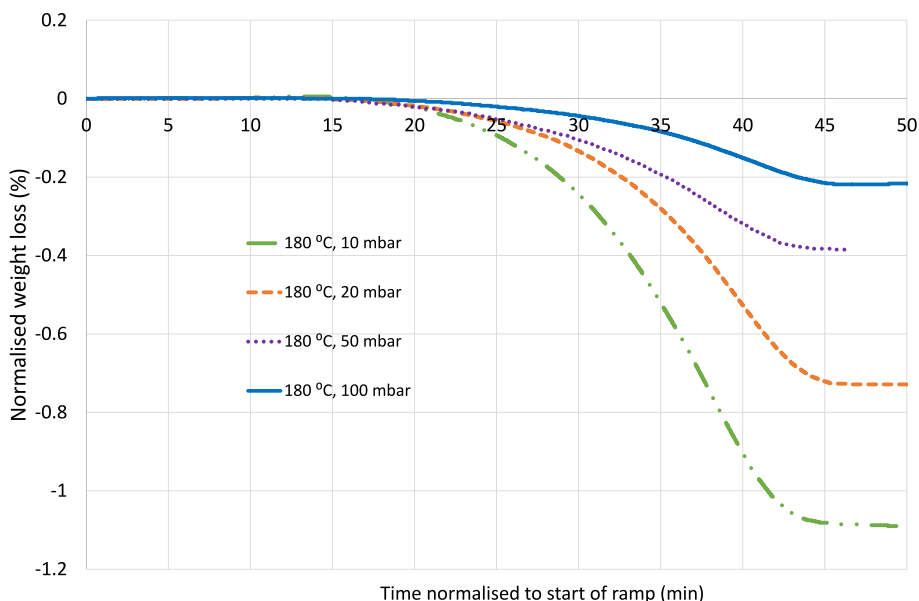


Fig. 7. Examples of loss percentage normalised to start of heating ramp, indicating similar times at which mass loss starts to occur.

Table 3
Average time and temperature at which mass loss (>0.01 mg) occurs.

	Time from start of heating ramp (min)	Temperature (°C)
Average	21	139
Stdev	2	5
Min	19	132
Max	25	148

ceases the loss. If not, then even at higher (sub-atmospheric) pressures the mass loss should be a factor of time, with total loss of the volatile component occurring eventually. This is not the case and, in fact, the

mass loss ceases at a relatively similar time irrespective of the pressure. In Fig. 7 for example, the mass loss ceases at around 45 min for all the 180 °C samples. An expectation could be that the occurrence of gelation in the resin, and the resultant extreme rise in viscosity (several decades within a few minutes), prevents further loss of mass.

Using the Kamal and Sourour kinetic equation (Equation (1)) [26] and values of k_1 and k_2 for RTM6 provided by Varley [27] (where $m = 1$, $n = 1$), an approximate cure conversion (α) profile was produced based on the heating profile for each hold temperature. Varley provides rate constants only for 110 °C and above, however based on the observations of Skordos [28] and the data provided by the manufacturer, virtually no reaction occurs for extended periods below this temperature and so the

contribution below 110 °C was ignored.

$$r = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (1)$$

The value of α considered to be the gel point varies slightly between studies, from 0.5 for Magniez [29] to the average 0.53 of Varley (range 0.45–0.57) [27] and the 0.59 of Karkanas [30]. Fig. 8 provides plots that include the temperature profile, approximate cure profile, gelation range and percentage mass loss profiles for each of the three hold temperatures. The gelation range is taken to be the period of time covering a change of α between 0.5 and 0.59 (Varley's value of 0.45 is for 110 °C and is anomalous compared to his other findings). For the 180 °C and the 150 °C samples the plateau of mass loss occurs very near to the gel region. For the 120 °C sample the plateau appears to fall somewhat after the gel region, though the beginning of the plateau is difficult to define. Gel times are broadly in line with expectation from the manufacturer's data sheet.

Overall, the extent of loss of mass is attributable to both temperature and pressure effects, with the region over which the mass loss occurs bounded at the start by a specific temperature and at the end apparently by viscosity limitation due to gelation. Since the viscosity of the resin is very low even at 80 °C (on the order of 0.1 Pa s), it is likely that the temperature at which the loss begins is related to the nature of the material that is lost. However, without the means to analyse the lost mass it cannot be confirmed at this stage and future work would benefit from developing this approach.

According to the manufacturer's safety data sheet (SDS), HexFlow

RTM6 contains 4,4'-Methylenebis[N,N-bis(2,3-epoxypropyl)aniline] (CAS 28768-32-3), 4,4'-Methylenebis(2,6-diethylaniline) (CAS 13680-35-8) and 4,4'-Methylenebis(2-isopropyl-6-methylaniline) (CAS 16298-38-7). These three components all have high boiling points under standard atmosphere (>400 °C [31]) but these would be depressed under vacuum. There is no side product evolved from the epoxy curing reaction. The purity of materials are not stated, so there is the possibility that a lower boiling point contaminant is being removed. A study on a prepreg material utilising mass spectrometry identified water, acetone and ethanol in HexPly 8552 [32]. They developed vapour maps indicating that at reduced pressure (less than ~300 mbar), all of these components would be evolved at 80 °C. This would suggest that the mass loss seen in the current study is not related to residual simple solvents, but this is not conclusive.

Ultimately, irrespective of the nature of the lost mass, there is the potential that it will present itself in the form of a gaseous entrapment, or porosity, within the resin. While no comment can be made as to the impact on the mechanical properties of the composite, even a superficial occurrence of porosity can produce an unacceptable cosmetic defect. This is a particular problem for components subject to oven baking as part of a painting process. In this case, the surface porosity can rupture leaving a pinhole in the painted surface of the component, leading to the requirement of reworking prior to customer acceptance. Although this study has been performed on small samples, the pathlength of evolved species through the resin is still on the order of millimetres and should be representative. In thicker parts, evolving material might become

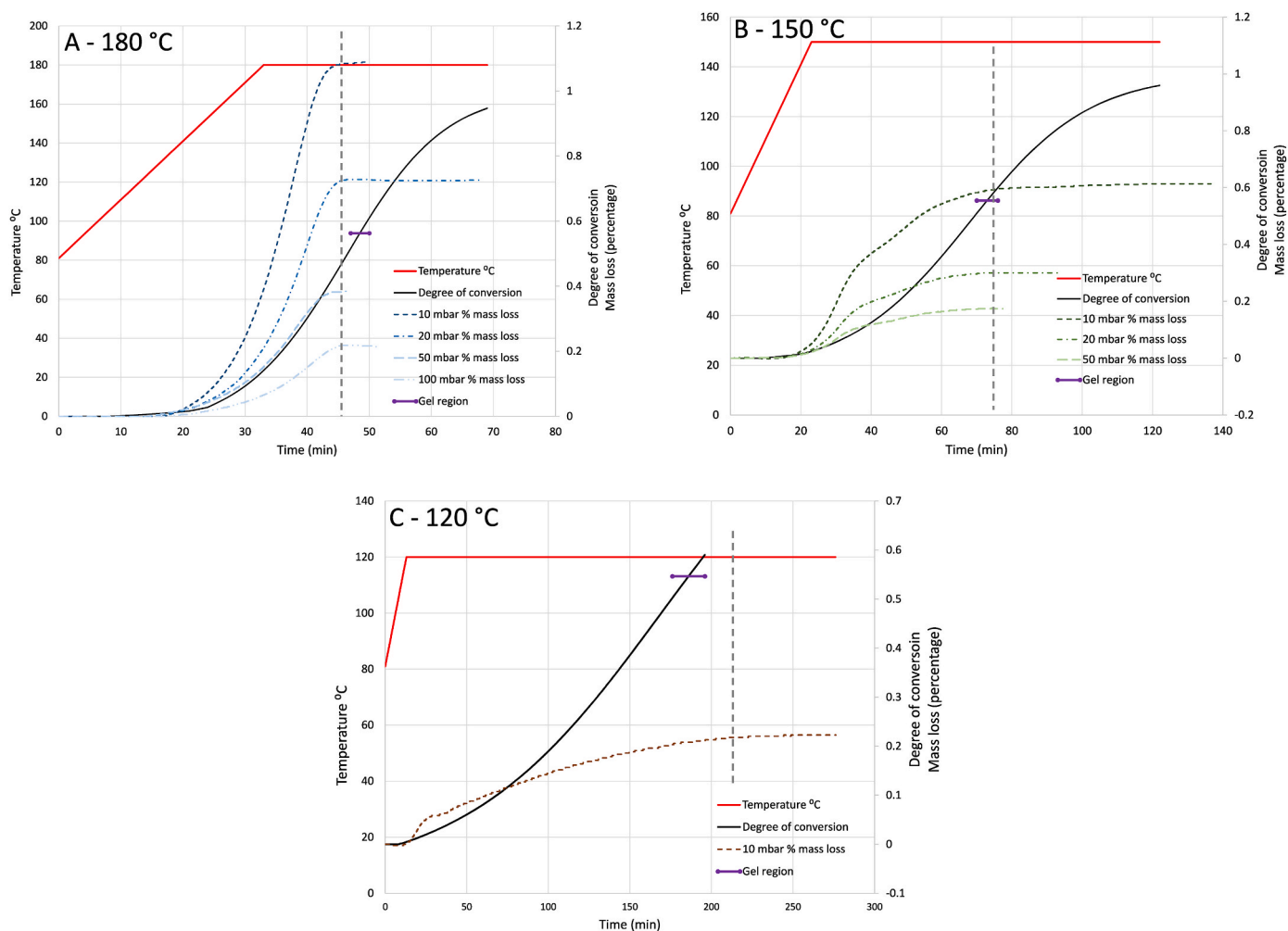


Fig. 8. Temperature ramp, estimated conversion profiles, approximated gelation region and mass loss profiles for (A) 180 °C hold, (B) 150 °C hold and (C) 120 °C hold. The vertical dotted lines provide the approximate position of the start of the plateau in weight loss.

entrapped before escaping (being much more difficult to quantify) but would still be lost to the resin in the form of a bubble.

5. Conclusions

This paper presents a novel experimental technique for determining the resin infusion processing conditions (temperature and pressure) under which volatile losses will be avoided. The method used is thermogravimetric analysis (TGA) that enables control of pressure as well as temperature and measures the amount of mass loss during a simulated processing cycle. The mass loss is associated with volatile evaporation which may become entrapped as porosity after resin gelation. While likely benign with respect to mechanical properties, these pores may become surface defects on the component. Cosmetic defects of this nature can result in component rework or rejection, particularly for Class A surfaces. In this regard, the constituent properties of the lost mass are of minor importance.

For Hexcel, HexFlow® RTM6, the degree of observed mass loss during the heating cycle appears to be a linear effect with temperature and an exponential effect with pressure. Mass loss begins to occur at > 130 °C, independent of pressure, and ceases approximately in line with the onset of gelation. The nature of the lost mass is not known but is unlikely to be water as this would boil off well below 130 °C, though the occurrence of bound water evolving at a higher temperature cannot be discounted.

Mass loss during the infusion of RTM6 can be avoided by two routes: (A) use full vacuum and maintain a temperature below 130 °C until gelation, subsequently ramping up to 180 °C to cure; (B) utilise a higher temperature of infusion but maintain sufficient pressure to prevent loss of volatiles (as per Fig. 6), then, once infusion is completed, subsequently increase vacuum to suppress any voids prior to gelation. Route (A) would require a much longer cycle time, while route (B) may incur a penalty to volume fraction (reduced compaction).

Of note is that the manufacturer's datasheet for RTM6 provides processing recommendations with pressure and temperature conditions that are likely to produce mass loss, hence porosity. As such, the information within this paper may be valuable as supplemental information to moulding practitioners using RTM6 under vacuum infusion conditions who are concerned with component surface quality. Furthermore, this method is applicable to other liquid moulding resin systems as a means of identifying processing conditions suitable for the avoidance of surface porosity.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

CRediT authorship contribution statement

Andrew J. Parsons: Conceptualization, Methodology, Validation, Formal analysis, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Aleksandra Gonciaruk:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – review & editing. **Xuesen Zeng:** Conceptualization, Methodology, Writing – review & editing. **Fernando Sarce Thomann:** Conceptualization, Methodology, Investigation, Writing – review & editing. **Peter Schubel:** Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Julien Lorrillard:** Resources, Writing – review & editing, Funding acquisition. **Michael S. Johnson:** Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

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 funded by Finance Birmingham, through the Advanced Manufacturing Supply Chain Initiative (AMSCI) funding stream (Reference Number 14029). The authors would also like to acknowledge the support of the Engineering and Physical Sciences Research Council, through the Future Composites Manufacturing Research Hub (Grant number: EP/P006701/1).

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