CURE MONITORING OF HIGHLY REACTIVE RESIN DURING HIGH-PRESSURE COMPRESSION RESIN TRANSFER MOULDING

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Abstract

Manufacturing high-volume structural automotive components using high-pressure compression resin transfer moulding (HP-CRTM) requires resin cure behavior to be well understood. An understanding of cure behaviour enables process optimization leading to more robust and predictable processing, with reduced cycle time and scrap rate. Although cure models allow resin behaviour to be predicted, validating expected behaviour under real process conditions is essential. As cure evolution is heavily dependent on process parameters including tool temperature, on-line cure monitoring provides opportunities for quality assurance and adaptive process control.

The Optimold DC monitoring system from Synthesites was demonstrated for real time flow and cure monitoring during high-pressure compression resin transfer moulding (HP-CRTM) on industrial equipment at the National Composites Centre (NCC) (Bristol, UK) using a new durable in-mould sensor developed by Synthesites.

Lab measured viscosity showed good agreement with viscosity estimated by the Optimold system during HP-CRTM trials. Glass transition temperature (T_g) estimated by the Optimold system was also compared with T_g measured from the cured panels using DSC. Estimated T_g showed good agreement with measured values, particularly after fine tuning the software calibration with real trial results; after which T_g values estimated by the Optimold system were within DSC accuracy for all cases tested.

1. Introduction

Manufacturing composite components to meet the volume requirements of the automotive industry (>80 000 per annum) requires robust, repeatable and predictable processing, with short cycle times of less than 180 seconds. High-pressure compression resin transfer moulding (HP-CRTM) provides the opportunity to meet these requirements and is currently used to manufacture composite components for a number of automotive OEM's.

The HP-CRTM process uses closed cavity, matched metal tooling mounted in a hydraulic press. Resin is impingement mixed and injected at high pressure using a self-cleaning mix head, connected directly to the mould cavity. In HP-CRTM, the mould is not fully closed during injection. Although the preform contacts both upper and lower tool surfaces, the fibre volume fraction in the cavity is reduced, compared with the final fibre volume fraction achieved once the mould is fully closed. This increases permeability, allowing the resin to flow more easily in-plane. A pre-defined weight of resin is injected into the mould, before the press is fully closed at an assigned speed. Closing the tool completes mould

filling and compresses the preform to the final fibre volume fraction, before the full press force is applied.

In order for short cycle times to be achieved, HP-CRTM uses highly reactive resins, with viscosity increasing rapidly during impregnation. High injection flow rates are therefore required to ensure the preform is completely wet out before the resin viscosity increases to the point where it can no longer flow. Understanding resin's reaction behaviour is therefore critical for robust processing and enables process optimisation, reducing cycle time and scrap rate.

Mechanical performance and glass transition temperature (T_g) are also highly dependent on degree of cure. Although cure behaviour can be predicted using kinetic models, validating expected behaviour under real process conditions is essential. Cure evolution can also be significantly affected by process variability, particularly tool temperature, therefore the ability to monitor cure in real time provides opportunities for on-line quality assurance and adaptive process control, further reducing scrap rate and ensuring all components have the mechanical performance and T_g required for intended use.

In this paper, ongoing work at the National Composite Centre is presented, aiming to adapt the capabilities of the Optimold direct current (DC) monitoring system from Synthesites for real time monitoring of flow and cure during HP-CRTM production.

2. Previous Work

Direct current (DC) methods for cure monitoring of thermoset resins have been studied [1-3], allowing in-situ monitoring of viscosity, glass transition temperature (T_g) and degree of cure, through measurement of electrical resistance and temperature. The Optimold flow and cure DC monitoring system from Synthesites has been demonstrated for low pressure RTM processes by several researchers e.g. [5, 6, 7], with process optimization, online quality assurance and adaptive process control demonstrated based on sensor output [6, 7]. Although the Optimold system has previously been applied to fast curing prepregs resins [4], it has not previously been used in HP-CRTM with online evolution of resin properties.

Di-electric cure monitoring (DEA) has also been studied and has been demonstrated for cure monitoring of epoxy resin in low pressure RTM processes [e.g 5, 8]. Dielectric cure monitoring is based on a similar principle, however sinusoidal excitations are applied across a range of frequencies using an alternating (AC) current. The measured response requires significant post-processing to allow viscosity, glass transition temperature (T_g) and degree of cure to be determined [5]. Recently DEA has been demonstrated for cure monitoring of fast-curing resin in prepreg compression moulding [9] and for cure monitoring of highly reactive HP-CRTM resin at lab scale [10]. However, in these studies the dielectric properties were linked either qualitatively [9] or offline quantitatively [10] with the resin properties.

3. Cure Monitoring System

The Optimold system from Synthesites allows real time estimation of viscosity, glass transition temperature (T_g) and degree of cure, using Synthesites Online Resin State (ORS) software. This is achieved through excitation of the resin using a constant current (DC) for the measurement of electrical resistance and temperature.

During the early stages of cure, measured electrical resistance can be directly correlated to viscosity [1-3]. Approaching gelation, viscosity increases rapidly and correlation with electrical resistance begins to diverge. After this point, measured electrical resistance can be directly correlated with T_g development [4].

In order for the Optimold system to be used for HP-CRTM (resin pressure over 100 bar), a new durable, in-mould high-pressure sensor was developed by Synthesites. The new sensor, shown in Figure 1, is well suited to integration with a range of high-volume processes, with an outer diameter of 16 mm and integrated Pt100 RTD temperature sensor.

Figure 1. Synthesites Optimold sensor

4. Online Resin State (ORS) Software Calibration

The Optimold system allows resin arrival to be determined and flow to be monitored without calibration. However, for cure monitoring, calibration of the ORS software for a specific resin is required to correlate sensor response with viscosity, T_g and cure progression.

In this study, the software was calibrated for Araldite 3585 epoxy resin, with an experimental hardener LME10996 (Huntsman international LLC) and EWOmould 3733 internal release agent (KVS Eckert & Woelk GmbH), allowing viscosity and T_g to be estimated in real time during manufacture.

4.1. Viscosity

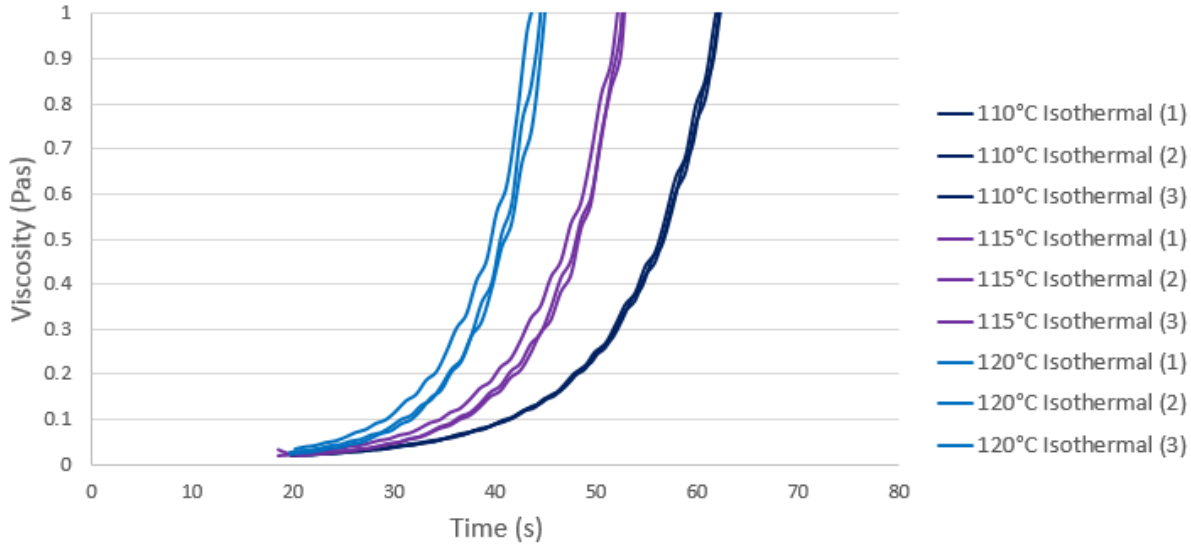

Figure 2. Measured viscosity progression

Viscosity development during cure was characterised at three isothermal temperatures 110, 115 and 120 °C, selected to be representative of processing conditions. Testing was performed using a TA

instruments AR-G2 rheometer, with the furnace preheated to the required temperature. Disposable, parallel aluminium plates were used, with 25 mm upper diameter and 45 mm lower diameter to prevent resin overspill. All tests were performed using steady shear (continuous rotation), with a gap of 500 microns and shear rate of 10 $rads^{-1}$.

As the selected resin system is highly reactive, fresh resin samples were prepared at room temperature for each test. To minimize stoichiometric error, 10 grams of resin were mixed with 2.1 grams of hardener, at a mix ratio of 100:21 by weight. Sample weights were measured using a Mettler Toledo XS105 precision scale, with a tolerance of ±6 mg used for each component. All samples were mixed by hand for 2 minutes.

A syringe was used to dispense approximately 5 ml of mixed resin onto the centre of the lower plate and the measurement started immediately. As some measurement time was lost due to the closing of the plates, the time to the first data point was recorded and the data offset to account for this. 3 repeats were performed at each temperature, showing good repeatability, as can be seen in Figure 2.

4.2. Glass Transition Temperature (T_g)

Development of glass transition temperature (T_g) during cure was characterised using a TA Instruments Q2000 DSC, with the furnace preheated to the required temperature. A sample mass of 2 mg was used following the same preparation methodology detailed in the previous section. Samples were cured for the required time (Table 1), before being cooled to 50 °C at the fastest rate possible by the DSC (40 °C min^{-1}). A dynamic scan was then performed from 50 - 250 °C at a heating rate of 10 °C min^{-1}, with modulation frequency of ±0.30 °C every 15 s, based on the method presented in [11]. All measurements were conducted using a nitrogen purge flow, with T_g measured directly from the reversible heat flow.

Table 1. DSC test matrix

Tool Temperature (°C)	Cure Time (s)	Repeats
110	180, 240, 480	2
115	120, 180, 240, 360, 480	2
120	180, 240, 480	2

Isothermal temperatures and cure times tested are shown in Table 1. Measured T_g values were slightly higher than expected, due to the resin continuing cure as it is cooled, even at the fastest cooling rates possible in the DSC. The observed discrepancy may also be increased due to data lost at the beginning of the isothermal stage and temperature overshoot, due to furnace temperature control, during closing. Similar challenges are described in [11] and [12] and the resin used in this study is even more reactive. T_g values provided by Huntsman, as shown in Table 2, were therefore used for the initial software calibration, which was fine-tuned based on real trial results.

Table 2. Glass transition temperatures used for calibration

Tool Temperature (°C)	Cure Time (s)	T_g (°C)
110	180, 240, 480	100, 113, 123
115	120, 180, 240, 360, 480	89, 110, 120, 126, 127
120	180, 240, 480	118, 125, 131

5. HP-CRTM Trials

In order to test the performance of the new durable in-mould sensors and validate the software calibration under real process conditions, HP-CRTM trials were performed at the National Composites Centre (NCC) (Bristol, UK) using a Pinette Emidecau Industries (PEI) press (Figure 3) and Krauss Maffei (RimStar Compact) high-pressure injection equipment.

Figure 3. PEI press at the National Composites Centre (NCC)

Trials were carried out using a 600 gsm 50k carbon non-crimp fabric (HPT610 C090, SGL Kümpers GmbH) with 14 gsm LT3366 binder (Huntsman international LLC). Plies were cut using a computer numerically controlled (CNC) ply cutter and preforms assembled as a balanced stack of 4 plies oriented at 0/90°. The binder was activated by placing preforms in an oven for 5 minutes at 180 °C under 800 mbar vacuum. The Huntsman recommended mass production cycle of: 20 sec (+/-10 s) at 180 °C ± 20 °C followed by cold stamping could not be achieved due to the small size of the preforms and minimum press force limit.

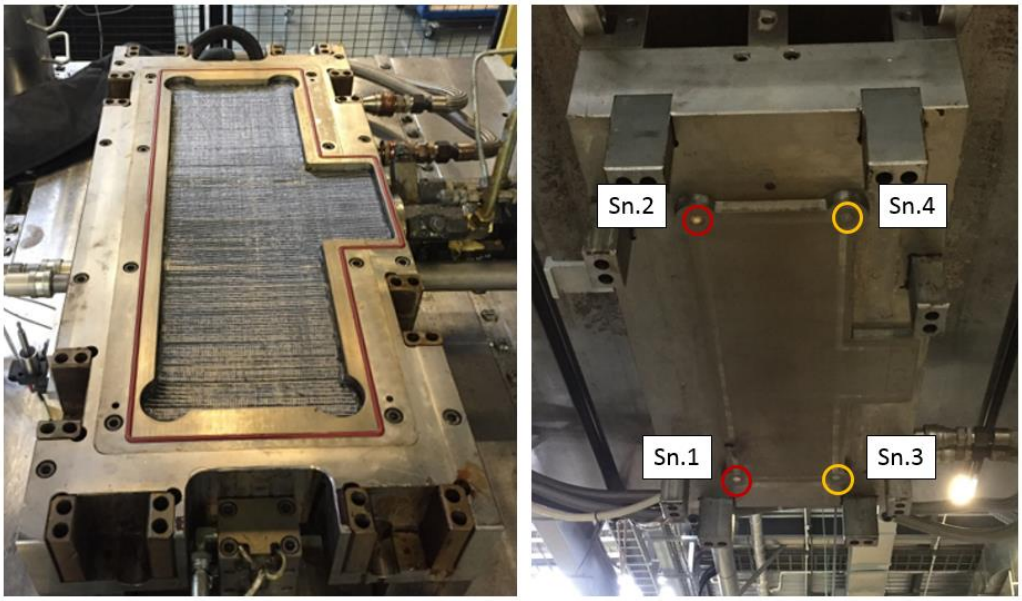

Figure 4. Left: HP-CRTM development tool with loaded preform, Right: upper tool sensor positions

All trials were carried out on the HP-CRTM development tooling shown in Figure 4. The tool has a nominal cavity thickness of 2.5 mm and manufactured panels have approximate dimensions of 644 x 288 mm**.**

Electrical resistance and temperature were recorded using two Optimold sensors, located in the upper mould half (Sn.1 and Sn.2, Figure 4). Cavity pressure was recorded using two Kistler 6162A pressure sensors (Sn.3 and Sn.4, Figure 4). An LVDT gap sensor was also used to monitor the mould gap, during press closure. All data recorded by the tool mounted sensors, as well as the press and injection equipment can be collated into a single log file, allowing a detailed image of the manufacturing process of each component to be created.

HP-CRTM trials were carried out based on the test matrix given in Table 3. Before each injection, both Optimold sensors were covered with an adhesive glass fibre pad, in order to electrically isolate the sensors from the carbon fibres in the preform. Once the closed tool reached the required temperature setpoint (± 1 °C) measured by Optimold sensors, the tool was opened and preform loaded. The automatic press cycle was then started. During this cycle, the press closes to a gap of 0.5 mm, a hydraulic vacuum valve opens and vacuum is drawn for 50 seconds. The press then closes to an injection gap of 0.3 mm and 207 grams of resin is injected at a constant flow rate of 85 gs^{-1}. The mixing ratio was set to 100:21 and 2% internal release agent used. Once complete the mould closed fully at a speed of 0.1 mms^{-1} before a press force of 1700 kN was applied. After a defined cure time, the press opens and components are de-moulded automatically using hydraulic ejectors in the lower tool. This process was repeated until all panels were manufactured, with data recorded for each trial.

Table 3. HP-CRTM trial test matrix

Tool Temperature (°C)	Cure Time (s)	Repeats
110	600	2
115	180, 240, 600	2
120	600	2

6. Results

The Optimold output from two representative trials are shown below in Figure 5, 110 °C results are shown in the left hand column, with 120 °C results shown on the right. The top row shows real-time values of electrical resistance and temperature measured by the Optimold system, with the bottom row showing online estimation of viscosity and T_g based on these measurements.

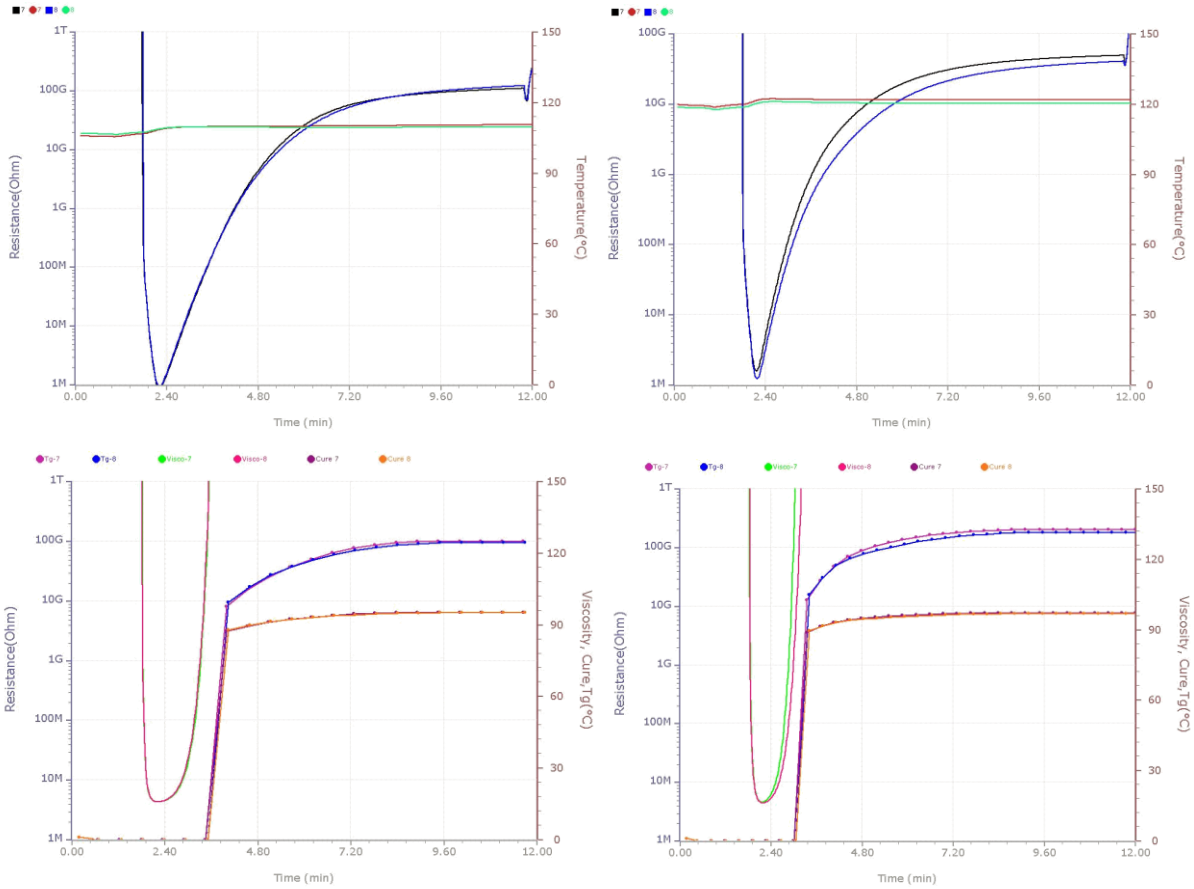

Figure 5. Typical Optimold graphs a) Top Left - Temperature and Resistance 110°C, b) Top Right - Temperature and Resistance 120°C, c) Bottom Left - Viscosity and T_g 110°C and d) Bottom Right - Viscosity and T_g 120°C

Viscosity estimated by the Optimold system from a single 600 s run at each temperature (110, 115 and 120 °C) was compared with the viscosity measured in the lab, via rheology (Section 4.1). As can be seen in Figure 6, measured viscosity shows very good agreement with the viscosity estimated by the Optimold system based on electrical resistance (visco110, visco115, visco120).

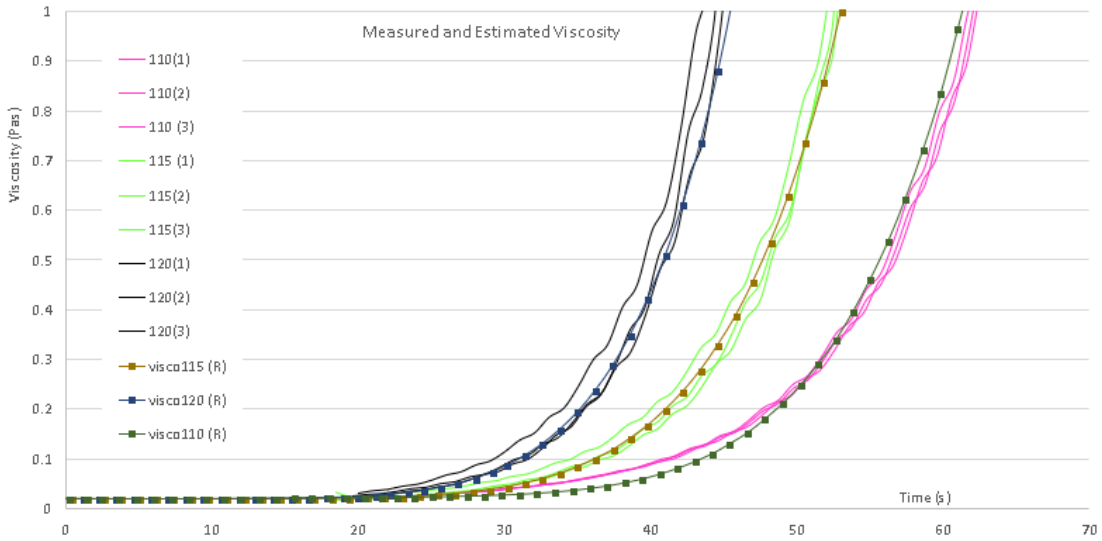

Figure 6. Comparison between the measured viscosity development at three different curing temperatures (110, 115 and 120°C) and the viscosity estimated by the Optimold system.

T_g estimated by the Optimold system for each of the panels manufactured (Table 2), was also compared with T_g measured using DSC. T_g of the cured panels was measured using the same TA Instruments Q2000 DSC used for initial software calibration. 10-15 mg composite samples were taken from the centre of the two sensor positions on each cured panel. Dynamic scans were performed from 50 - 250 °C, at a heating rate of 10 °Cmin^{-1}, with a modulation frequency of ±0.30 °C every 15 s and T_g determined from the reversible heat flow. Averaged results are presented for each trial in Table 4, together with a comparison between measured T_g and the real-time estimated T_g from the Optimold system, based on the original software calibration, prior to fine tuning with real trial results.

Table 4. Overview of the various cure cycles and the difference between T_g estimated online by the Optimold system (Original Calibration) and T_g measured using DSC after demoulding.

Tool Temperature (°C)	Cure Time (s)	DSC T_g (°C)	DC T_g (°C)	Error Compared with DSC Values (%)
110	600	124	122	1.6
115	180	114	113	< 1
115	240	115	121	5.2
115	600	126	125	< 1
120	600	129	128	< 1

Based on the DSC results, the software calibration was fine-tuned to include additional T_g datapoints from the HP-CRTM trials. This is a standard step in the calibration procedure, accounting for any differences between T_g used for calibration, measured under laboratory conditions and T_g obtained under real process conditions. Results from the fine-tuned software are shown in Table 5, as can be seen in the right-hand column the difference between these two values is within the DSC accuracy for all cases tested.

Table 5. Overview of the various cure cycles and the difference between T_g estimated by the Optimold system with fine tuned calibration and T_g measured using DSC after demoulding.

Tool Temperature (°C)	Cure Time (s)	DSC T_g (°C)	DC T_g (°C)	Error Compared with DSC Values (%)
110	600	124	122	< 1
115	180	114	112	1.5
115	240	115	116	< 1
115	600	126	125	< 1
120	600	129	128	< 1

7. Conclusions

The Optimold flow and cure DC monitoring system from Synthesites was demonstrated for real time flow and cure monitoring during high-pressure compression resin transfer moulding (HP-CRTM), using a new durable in-mould sensor developed by Synthesites.

Synthesites Online Resin State (ORS) software was calibrated for Araldite 3585 epoxy resin, with experimental hardener LME 10996 (Huntsman international LLC) and EWOmould 3733 internal release agent (KVS Eckert & Woelk GmbH); allowing real time estimation of viscosity and glass transition temperature (T_g) during manufacture. Some challenges in accurate T_g measurement of the partially cured resin using DSC were experienced, requiring further work to improve the characterisation methodology.

The software calibration and performance of the new in-mould sensors were validated under real process conditions, through HP-CRTM trials, using industrial equipment at the National Composites Centre (NCC) (Bristol, UK).

Viscosity measured in the lab, via rheology showed good agreement with viscosity estimated by the Optimold system during HP-CRTM trials. T_g estimated by the Optimold system was also compared with T_g measured from cured panels after de-moulding using DSC. Estimated T_g showed good agreement with measured values, particularly after fine tuning of the software calibration with real trial results, after which estimated values were within DSC accuracy for all cases tested.

The next steps are to continue use of the Optimold system in development trials to improve process understanding and plan how the system can be optimally integrated for online quality assurance and adaptive process control in a high-volume production environment.

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