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Compression RTM of reactive thermoplastic composites using microwaves and cure monitoring

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Abstract

Thermoplastic-matrix composites are ideal to improve recyclability of composites not to mention easier assembly and repairability. The EC-funded project Recotrans aims in combining the advantages of the Elium acrylic reactive-thermoplastic resin from Arkema with microwave curing and intelligent process monitoring towards sustainable mass production for the European transport industry.

Both the microwave heating and the online process monitoring technologies have been successfully used in thermoset-matrix composites, while the new carbon-fibre proof sensors were introduced successfully in a compression high pressure RTM facility. In the present application a microwave heating device has been developed to preheat the liquid resin either after injection and before mould compression or before resin injection in order to decrease resin's viscosity and improve impregnation as well as to accelerate the reaction. Furthermore, through a durable cure sensor installed in the tool, the Optimold cure monitoring system measures the electrical resistivity and temperature of the resin which are directly correlated to the degree of conversion. The use of a preform from recycled carbon fibres makes the implementation of both technologies more challenging as both technologies are prone to carbon fibres so special techniques were used to circumvent the effect of carbon fibres. The first lab-scale trials showed that both technologies can improve performance ensuring the high potential of the Elium resin for high quality thermoplastic CFRPs.

Keywords: Thermoplastic Composites; Monitoring; Process control; microwave curing

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1. Introduction

Nowadays, polymer matrix composites with continuous fibers are widely used in aerospace, automotive, railway and sport industries. For equivalent properties, these materials are very attractive since they are 30 to 40% lighter than metallic counterparts. In a current context of environmental development issues, thermoplastic-matrix composites, more precisely acrylic, can be easily recycled as opposed to thermoset polymers. Furthermore, they exhibit good mechanical properties in terms of stiffness, strength and toughness, making them serious candidates for many modern applications.

Manufacturing structural composites requires to produce good quality parts with complex geometries while maintaining short processing cycle times for cost-effectiveness. For this purpose, Resin Transfer Molding (RTM) or vacuum assisted resin infusion (VARI) have been selected in many cases to manufacture these composites. Indeed, a relatively low temperature closed mold process allows for manufacturing complex continuous fibre-reinforced parts. However, liquid composite moulding requires resins with very low viscosity (well below 1Pa.s) to ensure a good impregnation of the dry preform therefore conventional thermoplastic polymers cannot be used.

Within the Recotrans project which aims to enhance the processing of reactive thermoplastic composites for transport applications, the target is to use an acrylic-based reactive formulation, which exhibits a very low viscosity (≈100 mPa.s) and is subsequently polymerised via a radical mechanism in the mould. Therefore, our main objective is to optimize and enhance the filling and curing conditions, especially the

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thermal initiator ratios and temperature of RTM-compatible acrylic-based reactive formulations, to yield satisfying composite parts with high conversion rate, low residual monomers content, low VOC and optimal process cycles. Indeed, an incomplete polymerization or too high temperatures can lead to difficulties in demoulding the part and may deteriorate part's final properties (residual stresses, porosity, etc.). Furthermore, within the Recotrans project, advanced technologies such as microwave heating and intelligent reaction monitoring are employed to enhance processability at industrial level.

2. Low viscosity reactive thermoplastic resin

Unlike most thermoplastic resin systems, the Elium® acrylic resins [1,2] are injectable at room temperature and are engineered for reactive closed-mold processes, including Resin Transfer Moulding (RTM), Compression Resin Transfer Moulding (CRTM), infusion (VARI) and Flex-Molding. Further, through their activation by peroxide, this acrylic resin reacts in the mould to create a fully thermoplastic polymer via in-situ radical polymerization. Elium® resins are available in a range of viscosities between 100 and 500 cps at 25°C. Reactivity varies as well, depending on the selected grade and the initiator. Some grades have been optimized for elevated temperature curing in a matter of minutes, while others polymerize at room temperature with cycle times ranging from half hour to several hours depending on the processing conditions.

Due to their thermoplastic nature, the Elium® resins can be used to manufacture composite parts that can be easily formed and are recyclable with mechanical properties comparable to epoxy resins. Parts made from Elium® can be also assembled by welding and/or gluing especially with methacrylic structural adhesives. Overall Elium® is a thermoplastic resin that can be processed like polyesters and has the mechanical properties of toughened epoxies.

3. Microwave assisted CRTM in a metal mould

Microwave (MW) heating has been proposed for curing composite parts with mixed results. In principle microwave curing can cure thermosets faster with mechanical properties which are similar to conventional curing [3]. However, the application of the microwaves during moulding is quite challenging either because of the metal tools or because of the inhomogeneous field that the composite tools and the fibre preforms generate.

The integration of microwaves in closed moulding with metal moulds has not been successful yet. The main reason is that microwaves do not penetrate metals but are reflected on their surfaces preventing the heating of the resin in the mould [4]. However, microwaves can be irradiated into a metal mould to heat the resin but in a closed metal mould, microwaves form temporally constant field patterns. For microwave frequency of 2.45 GHz, the distance between minima and maxima of this field pattern is at least 6 cm which inevitably leads to inhomogeneous heating i.e. hot and cold spots. However, in the present project a variant of the RTM process with resin injection in a semi-closed mould is being used. In the so-called CRTM, the resin is injected in a temporary gap formed between the not-completely closed upper tool and the preform inside the mould which is compressed into the preform when the mould closes completely. Taking advantage of the resin injection into this gap and over the preform, the microwaves can heat the resin in the gap just before compression as can be seen in fig.1. In this way, the resin flows under the minima and maxima of the standing MW field resulting in a timely homogeneous heating of the injected resin front. The concept is modular and more than one microwave slot can be integrated in the mould.

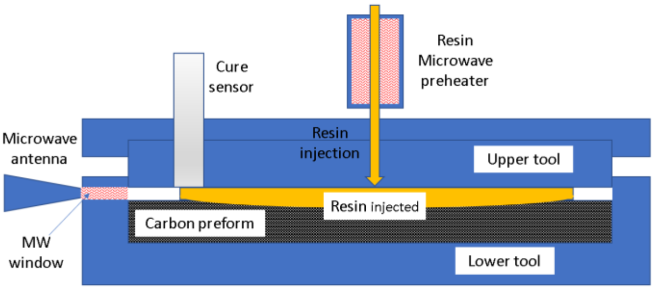

Fig.1. Graphical cross section of the MW-heated CRTM lab-scale facility at Fraunhofer ICT with both heating options.

As a second option, the direct preheating of the resin before entering the mould cavity has been also studied. This concept has been already applied in a RTM application [5] with quite good results and has been also developed within the Recotrans project. In both heating options, a magnetron of 2.45 GHz was employed with a maximum power of 2 kW. The microwaves either are connected to the wave guide WR340 which is tapered in height and width to the slot in the mould to 5 mm height and 260 mm length as can be seen at the left of fig.1or heat directly the resin in the resin pot as can be seen in top of fig.1.

4. Intelligent in-situ reaction monitoring

In dielectric cure monitoring, a range of sinusoidal electrical excitations is applied to the two electrodes of a sensor which are in contact with the material under investigation so that its post-processed feedback provides information about the material state. Although significant effort has been devoted in this technology for more than 30 years, only limited industrial applications exist. On the other hand, the DC-measured conductivity was studied in lab-scale [6, 7] but only in 2009 a new DC-based process monitoring system, the Optimold system by Synthesites [8], was presented with a clear focus on industrial manufacturing. The Optimold system measures the resin's electrical resistance and temperature through suitable electronic systems in combination with specially designed durable or disposable sensors with two co-planar electrodes in a comp or concentric configuration. The Optimold system is capable for the in-situ monitoring of the full transformation of a reactive resin i.e. from very low viscosities at high temperatures to fully cured resins at room temperature with the measured resistance ranging from 10^5 Ohm up to 10^{14} Ohm. Comparison between the DC cure monitoring and commercial dielectric systems demonstrated the superiority of the DC sensing particularly with carbon fibres and after gelation where conductivity measured by the DC-based system is more reliable and accurate. Furthermore, the DC-based monitoring is cheaper and requires simpler sensors which can be more flexible in geometry and more robust. Last but not least, in contrast to the through-thickness measuring nature of the dielectric systems, the DC sensing is significantly less vulnerable to carbon fibres in the cavity due to its inherited "surface" measuring nature so it may be used easier in the industrial production of carbon fibre parts even without protection. The durable sensor used in this study has an outer diameter of 16 mm, two concentric electrodes on the surface of the sensor and was flush mounted into the mould's cavity. The sensor has an integrated temperature sensor measuring the temperature close to the resin which is absolutely necessary in conjunction with its conductivity for the calculation of the resin state.

It has been shown ([9], [10]) that the electrical resistance of a resin is directly related to the resin's viscosity and T_g. Based on this observation and experimenting with several resins, Synthesites developed a proprietary technology for the online estimation of the development of the Glass Transition temperature and/or of the degree of cure valid not only in the laboratory but also during composites production. This technology has been already applied successfully to thermoset-based composites manufacturing in automotive [9], wind turbine blades [10], and aerospace [11] while in reactive thermoplastics it was used only in lab-scale trials [12]. Following this well-established theory that has been widely proven in practice, the resistivity of a resin was directly related to its viscosity while the Glass Transition temperature (T_g) can be estimated online using Synthesites proprietary algorithms via the Online Resin State (ORS) module ([9], [10]).

This online estimation technique was extended successfully for the specific acrylic resin that is being used in the Recotrans project. The ORS module was initially developed for isothermal cure cycles and was further extended to deal with highly non-isothermal conditions i.e. high exotherms with long cooling stages. Similarly to the resistance correlation to the T_g in thermoset resins, for the reactive thermoplastic resin the correlation is with the residual of the monomer which corresponds to the degree of conversion as can be seen in fig.2 for three different processing temperatures.

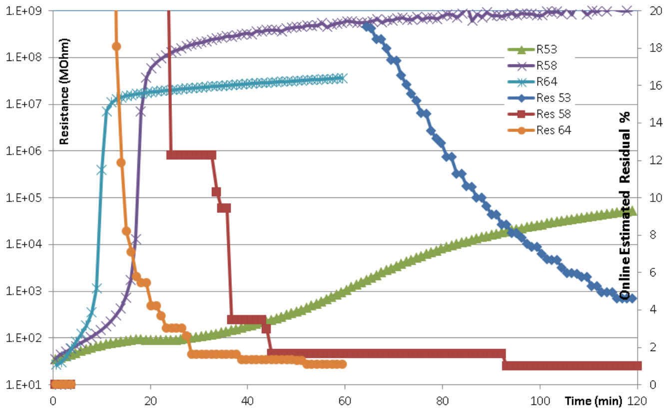

Fig. 2. Resistance vs. online estimation of the residual of monomer during the transformation of the Elium® resin at 40 ºC (R and Res 53), 60ºC (R and Res 58) and 80ºC (R and Res 68).

This online estimation technique was verified by measuring the remaining monomer level of a neat thermoplastic part by a gas chromatography apparatus (Series II 5890 Hewlett Packard Co.) following an internal Arkema standard. The preliminary results show the good correlation between the estimated and the measured residual monomer (Table 1) but further studies are necessary to establish this correlation for composites.

Table 1. Comparison of the online estimated residual of monomer and the corresponding measured one in the laboratory for the three isothermal cases.

		Residual Monomer (%)	
case	Temp (ºC)	Estimated online	Measured
53	40	4.7	5.2
58	60	1.6	4.5
64	80	1.7	1.9

5. Results

Within the framework of the R&D project, an extensive characterisation of the Elium® 150 grade was performed towards developing an online intelligent process monitoring system that can be used in production to optimise and to ensure the part quality of this innovative resin.

Initially, extensive trials were performed at isothermal conditions in a small closed metal mould (50x50x2 mm) without any fibres by pouring a few ml of resin over a durable cure sensor. In this way, the self-heating of the Elium® resin sample was kept at a minimum level and didn't affect the polymerisation rate. However, in general the exotherm of the Elium® during curing may play an important role just as it happens in the processing of polyester/ vinylester resins. As can be seen in fig.3 only a low exotherm was encountered during the transformation of the Elium® resin even at higher temperatures where the reaction is quite faster.

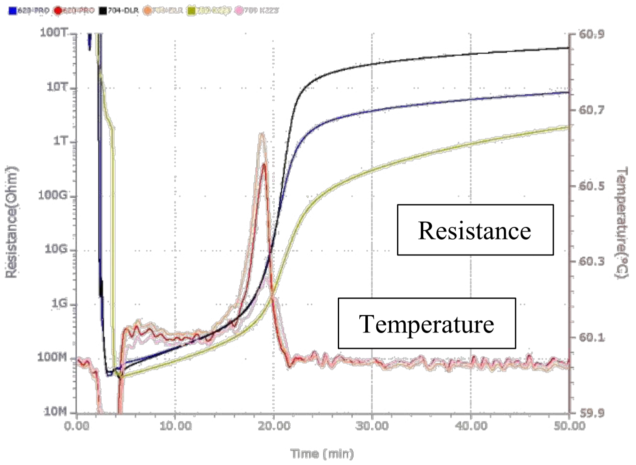

Fig. 3. Resistance and temperature during the transformation of the Elium® resin in a heated mould at 60ºC with three durable cure sensors.

A first series of lab-scale trials with this specific Elium® resin revealed the qualitative advantages of using the specific cure monitoring technology. As can be seen in fig.4 for two isothermal trials at 25ºC, the increase of the initiator percentage from 1.5% to 3.0% accelerated significantly the polymerisation as can be assumed from the faster increase of the electrical resistance.

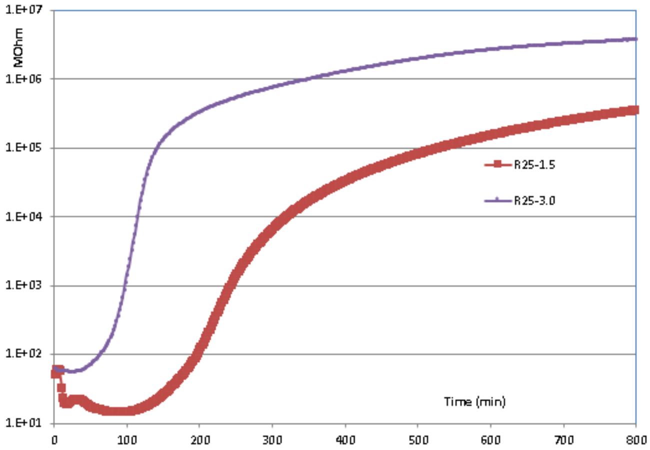

Fig. 4. Resistance history during low temperature (25ºC) curing of Elium® resin with initiator 1,5% (R25-1.5) and 3,0% (R25-3.0).

For the same percentage of initiator (1,5%), the reaction speed was significantly increased when raising the processing temperature as depicted in fig.5 from 25ºC to 80ºC. This series of trials shows that the cure monitoring system can track closely the significant speed-up of the reaction of the Elium® resin no matter how slow or fast the reaction speed is.

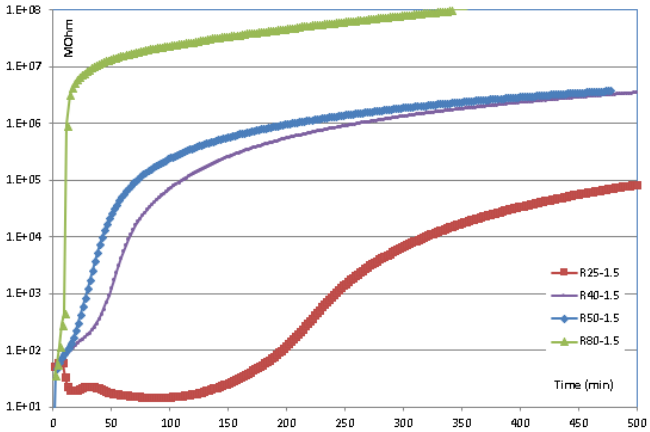

Fig. 5. Resistance history of isothermal polymerisation of Elium® resin with 1,5% initiator at 25ºC (R25-1.5), 40ºC (R40-1.5), 50ºC (R50-1.5) and 60ºC (R60-1.5).

In order to validate the performance of the monitoring system with Elium® resin with carbon fibres some preliminary trials were also performed. At first, a lay-up of 10 plies of 30x20 cm carbon-fibre plain-weave fabric was infused under vacuum and cured at room temperature. A disposable film cure sensor was embedded in the middle of the stacking and both the resistance and temperature were recorded and shown in fig.6. Without external heat there was a constant but slow increase both in temperature and resistance followed by a mild exothermal peak up to 45ºC. During the peak of the exotherm, the resistance was sharply increased as depicted in fig. 6.

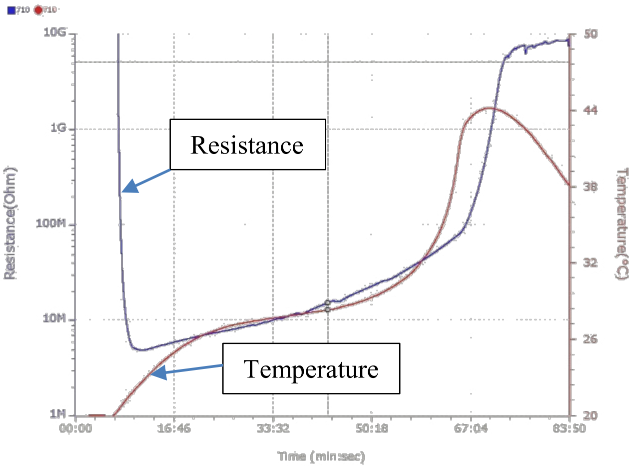

Fig. 6. Monitoring the transformation of the Elium resin infused for the manufacturing of a cfrp without external heating the evolution of resistance and temperature.

Regarding the trials with microwave heating, a realistic CRTM facility already described in section 3, was developed, constructed and operated by Fraunhofer ICT to prove the concept which will then be extended to the tooling for the manufacturing of an automotive door panel demonstrator.

The mould was made of aluminum with dimensions 280 mm wide and 380 mm long (fig.7). As prescribed by the automotive use case, carbon fiber mats of density 400 g/cm^2 and Elium resin with benzoyl peroxide hardener were used. Two mats were inserted into the mould (pre-heated either at 80°C or 90°C) and the mould was closed except for a small gap of about 5 mm. Through this gap the microwaves are radiated and the resin during injection is heated. This slit is covered with a ceramic plate to prevent resin entering into the waveguide. As soon as the mould is filled, the microwave is switched off and the mould is closed and pressure is raised to 8 bar for the curing of the composite part.

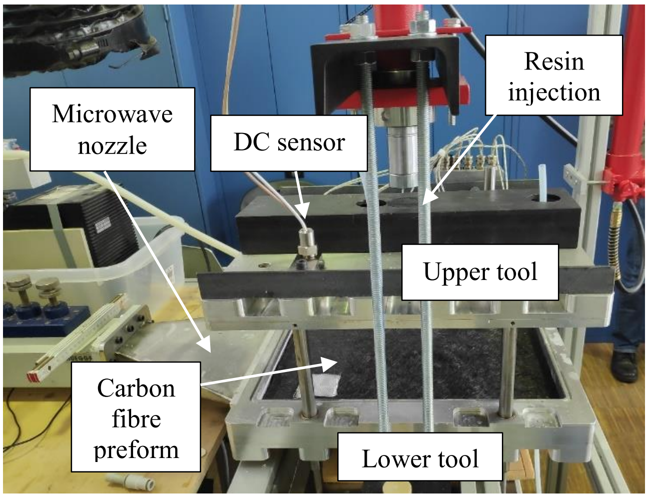

Fig.7. The CRTM lab-scale facility at Fraunhofer ICT with the 2nd option of the microwave resin pre-heating device.

In the top tool, a durable sensor (DC sensor in fig.7) was installed, flush mounted in the cavity to measure online the electrical resistance and temperature. The sensor was connected to the Optimold cure monitoring system as provided by Synthesites and the measurements were recorded in a PC through the Optiview data acquisition software.

A first series of trials was performed in order to study the effect of Carbon Fibres mats (CFM) plies and the different microwave heating in the CRTM process and the most successful ones are summarised in Table 2. In the first option (cases 2, 4 and 5) the microwaves are radiated during the injection of the resin in the gap which at the present case was approx. 15s. For the heating, a maximum pulsed microwave power of 1 kW was applied with a pulse pause ratio of 40/60. In the second option (cases 6 and 7), the resin pot is directly heated with microwaves just before the injection. In the present paper, the effect of the microwaves on the reaction speed was related only to the measured electrical resistance and temperature through the cure monitoring system. Further analysis of the mechanical properties of the matrix and the composites will follow.

Table 2. Configuration of the trials performed.

Trial	CFM plies	Curing temperature	MW & type
2	1	98-92°C	No
4	2	98-87°C	No
5	2	96-87°C	Gap heating (1st option)
ref6	2	80°C	No
mw6	2	80°C	Preheating (2nd option)
ref7	2	90°C	No
mw7	2	90°C	Preheating (2nd option)

Comparing the resistance of trials 4 and 5 depicted in fig. 8 that have the same number of CF plies, the introduction of the microwaves (trial 5) speeds up the curing by approx.1 minute.

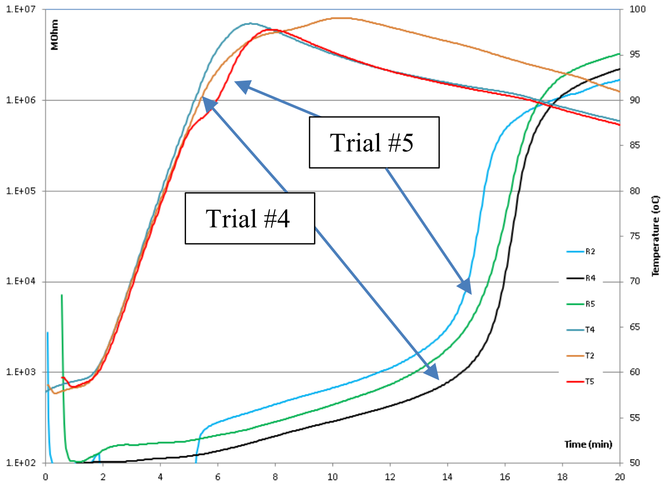

Fig.8. 1st MW heating option: Temperature and resistance histories for trials with and without microwave heating.

Following this first set of trials of the first heating option, a second round of trials to validate the 2nd MW heating option was executed. As can be seen in fig.9 four trials at two mould temperatures (80°C and 90°C) with or without MW heating were executed.

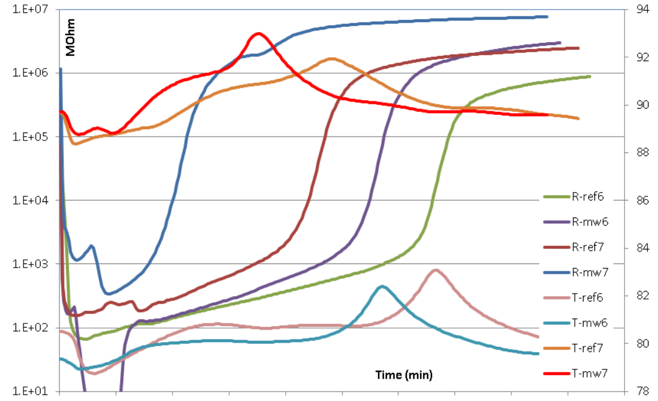

Fig.9. Resistance (R) and Temperature (T) of the injections 6 and 7 with (mw6 and mw7) and without (ref6 and ref7) MW resin preheating.

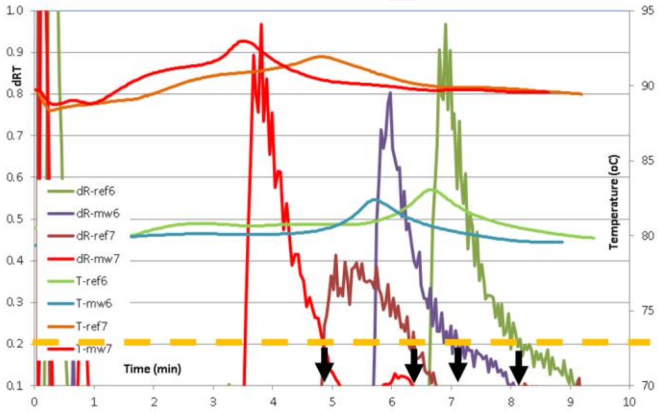

Fig.10. 2nd MW heating option: Resistance rate (dR) and Temperature (T) of the injections 6 and 7 with (mw6 and mw7) and without (ref6 and ref7) MW preheating.

It has been shown in section 4 that the resistance rate can be used to define the end of the reaction so if this threshold is set to 0.2 as denoted by the yellow dashed line in the fig.10 the required curing times are shown for each case. The clear advantage of using the MW preheating is shown in table 2 with a speed-up of 25% with respect to the specific temperature and 41% overall has been achieved.

Table 2. Processing times and corresponding speed-up factors with respect to reference cases without MW (ref6 and ref7) and with MW preheating (mw6 and mw7), resp.

Case	Processing time (min)	Speed-up (wrt ref6)	Speed-up (wrt ref)
ref6	8.1		
mw6	7.2	11%	11%
ref7	6.4	21%	
mw7	4.8	41%	25%

6. Conclusions

An advanced cure monitoring system and a microwave system were developed and applied successfully for the acceleration of the reaction and the intelligent process monitoring of the manufacturing of composites using a liquid reactive thermoplastic resin.

Two microwave heating options were realised and tested in a lab-scale facility. The first option heats the resin in the gap inside the mould cavity while the second option directly preheats the resin before its injection. During the trials it was shown that the resin MW preheating (second option) clearly outscores the first option by achieving 25% speed-up of the Elium reaction at the same mould temperature. Furthermore, since the second option is considerably easier to implement in production of real parts it was chosen for the door panel demonstrator.

The DC-based cure monitoring system can provide in real-time the evolution of the reaction and as a result it allows for real-time quality and process control purposes during manufacturing. Its combination with microwave curing proved efficient and without any effect of microwaves in the electric field of the sensor.

The next challenge in the Recotrans project is to extent and demonstrate these advantages in the manufacturing of an automotive door panel which is currently under construction. Furthermore, there is an on-going study to validate the correlation between the online resistivity measurements to the resin properties such as viscosity and Tg, so that a real-time process control can be used in production ensuring optimal part quality and minimum cycle times.

Acknowledgements

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