In-line coated profiles: optimizing the pultrusion process

Nora Lardiés Miazza
Researcher
AIMPLAS Composites Department

The pultrusion process is an effective way to process composites, however several drawbacks that reduce the competitiveness of pultruded profiles in comparison to traditional materials still need to be addressed. On the one hand, the process is limited by the time required to polymerize the resin inside the die, which results in a low-speed process. On the other hand, when a coating is needed to improve surface properties, the surface of the profile must be carefully prepared off-line, requiring additional sanding and painting steps that are expensive, highly labour-intensive and polluting.

As part of the Coaline project, an in-line, clean one-stage process was developed to pultrude composites and at the same time coat the profile inside the die. This new process is free of VOC and small particle emissions. It can produce properly coated pultruded composite profiles by developing and integrating the advanced die design, sensing technology and microwave-aided curing needed to adjust the curing degree of the resin in each stage of the die. The process also fosters improved composite coating adhesion with reduced labour and process costs. Coaline profiles can be bonded to other materials by means of a primer-type coating, also incorporated in-line, with on-demand debonding properties for material repair or recyclability.

Two different moulds were manufactured: a rod for the building sector with a gelcoat applied in-line and a hollow profile for the automotive sector with an in-line coated primer in order to improve the adhesion of the parts using an adhesive.

The number of processing steps was reduced and the resulting process is cost effective for a minimum speed of 20 cm/min for a polyester matrix and 25 cm/min for an epoxy matrix. The quality of the coated pultruded profiles was also improved as the gelcoat and the primer are coated in-line when the resin is not fully cured, meaning there is a strong covalent bond between the resin and the coating.

To produce the coated profile in-line, several challenges had to be met, as described below.

Creating a specific microwave antenna for the pultrusion die

The profile was cured with microwaves (MWs) in order to increase the temperature of the resin and trigger its polymerization. It is important to cure the resin using MWs as it is heated from the inside of the profile to its surface and, when the coat is injected, the surface of the resin is still in the gel state, thus improving the adhesion between the coating and the resin. In addition, MW curing drastically reduces the resin curing time and makes it possible to shorten the mould. Figure 1 shows the MW system connected to the pultrusion mould. In the pultrusion process, it is important to ensure the safety of

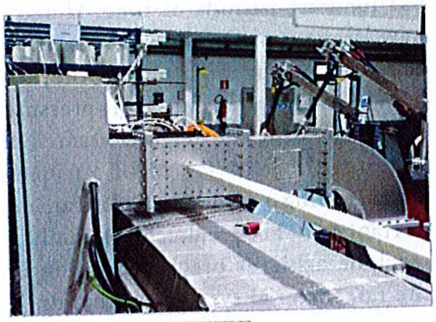

Fig. 1: Antenna MW design for the curing of the ALKÈ´s profile (automotive sector)

the microwave system by designing suitable radiation traps.

Formulating the resin with the necessary microwave susceptors

Some resins are not polar enough to be cured with MWs in seconds, so that susceptors (like metallic fillers, organic bipolar additives, etc.) need to be added to absorb the MWs and properly increase the resin temperature to accelerate polymerization during the pultrusion process. Three different susceptors were selected and evaluated for thermosetting resins. The microwave system employed for that purpose is composed of a 2000 W magnetron and a cylindrical antenna (Figure 2, above). The frequency of each antenna is 2.45 GHz and the wavelength 12 cm, similar to the conventional microwave devices used at home. The robot can be moved in the three directions using a remote control.

The evolution of the sample temperature (measured with an infrared sensor over the surface of the resin) versus time was recorded for each system at constant MW power. The graphs were compared in order to choose the most suitable susceptor in terms of interactions with the microwave radiation. Figure 2 (below) shows the evolution of the polyester resin's temperature without susceptor and with susceptor C. With the susceptor, polymerization time was reduced by more than 50%, which is a very good result.

Shore D hardness and tensile strength were measured for each sample in order to determine the influence of the susceptors on the mechanical properties of the resin. The conclusions revealed that the susceptors do not influence the mechanical properties.

Modelling the pultrusion process for die design

A model was developed to predict the curing degree of the resin and the coating as a function of the microwave generator parameters in order to properly design the length of each part of the modular die and the position of the injection chambers. The main objective was to achieve a covalent bonding between the composite and the coating (gelcoat or primer).
Good agreement between numerical and experimental results for the temperature and degree of cure distributions was obtained in both manufactured moulds.

Developing a specific sensor system to continuously monitor the curing degree of the resin and coating inside the pultrusion mould

An integrated data acquisition system was developed (and tested at the industrial level) in order to monitor in real time the most important parameters of the Coaline process: curing degree of the resin and coating (gelcoat and primer), pulling speed, temperature in each stage of the mould and MW power.

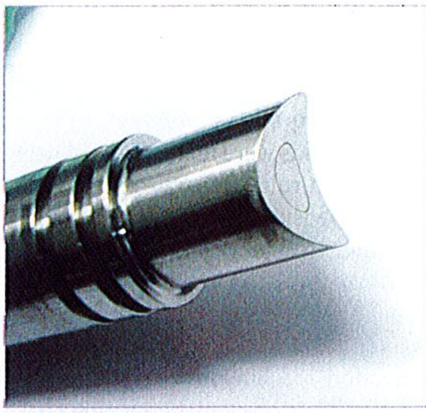

Fig.3: First curved sensor developed for an in-line process

The developed sensors were successfully integrated into the mould. The rod case demanded the manufacture of curved sensors (Figure 3), which were a world-first, and a challenging interpretation of the measurements for real-time predictions of the degree of cure for both the resin and gelcoat areas. The automotive profile application is challenging by itself (die, insert, microwaves). As can be seen in Figures 4 and 5, the set-up proved particularly robust and there was no interference

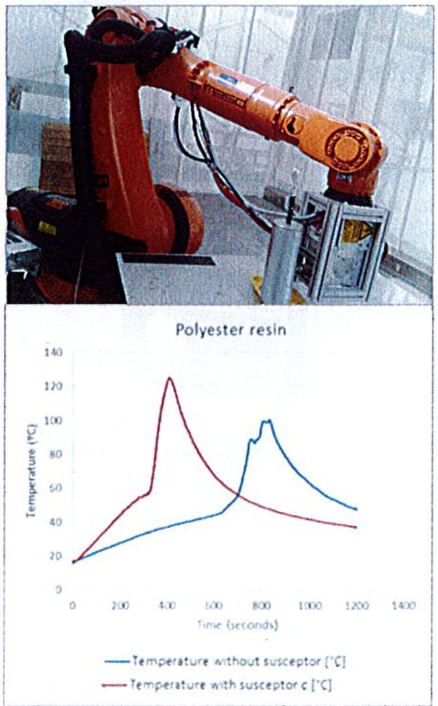

Fig. 2: Open antenna system available in AIMPLAS facilities (above) and temperature vs. time for the curing of the polyester resin with susceptor C (below)

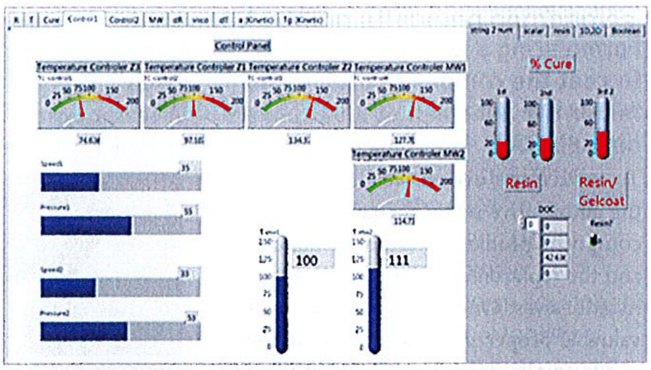

Fig.4: The real-time temperature measurements of the 4 heating zones together with the temperature at the Microwave heating area and the profile speed are displayed.

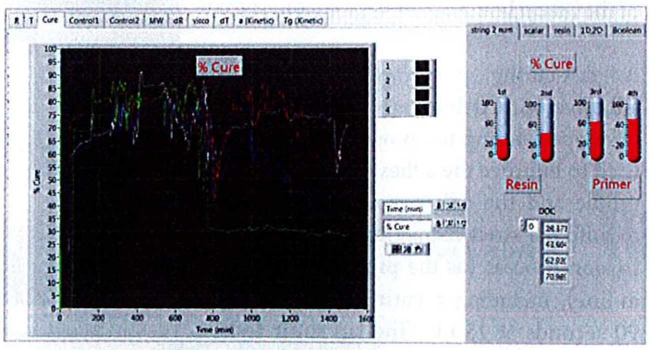

Fig.5: Online prediction of the degree of cure from the 4 cure sensors. At the top right-hand-side the real-time degree of cure are displayed for the 2 sensors in the resin region and the other 2 cure sensors at the primer area

with the microwave heating system.

Manufacturing the moulds and integrating all the subsystems

Both moulds were manufactured using the design rules (injection points, section dimensions and other parameters) in order to achieve the proper process performance. The integration of all the Coaline subsystems was developed and validated: each modular mould, two injection machines (one for the resin and another one for the coating), two microwave heating systems, a guidance fibre system and the sensing technology. Several trials were necessary for the integration and adjustment of all the parameters involved in the process. Finally, a properly coated rod was produced (Figure 6).

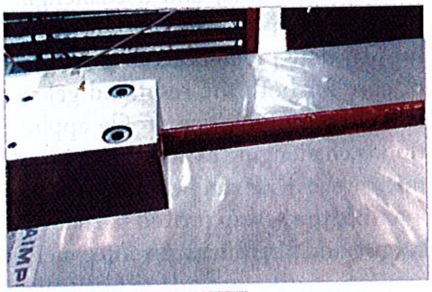

Fig.6: First coated pultrusion profile obtained in-line (with a red gelcoat)

Formulating a fast-curing primer to coat the composite profile and foster the adhesion of a debondable adhesive

To reduce the overall weight of vehicles, the automotive sector demands the use of composite profiles instead of metallic ones and the replacement of mechanical unions by adhesives. On-demand debonding is a valuable property of adhesives in order to allow simple repair or recycling at the end of the lifecycle.

A fast-curing two-component epoxy adhesive with debonding properties was developed during the project. The primer used to improve the adhesion between the profile and the adhesive was formulated to fulfil the strict requirements of the pultrusion process (as the primer is injected in-line), including a curing time of only 90 seconds at 150°C. The lap shear tests conducted on an isophthalic polyester resin profile bonded with the fast epoxy adhesive showed the following results:

- 4 MPa without surface preparation (adhesive failure, which is not desirable).
- 12 MPa with primer (cohesive failure in the substrate, which means the adhesion is very good). Similar values were obtained with a traditional surface treatment (degreasing and abrasion of the substrate and without primer).

These results clearly highlight the potential of the primer (composed of a bio-based solvent) as a substitute for the abrasion and degreasing steps usually implemented when bonding pultruded composites.
The heat-induced debondable adhesive was also tested, producing very good results: the debonding system allowed easy dismantling by induction heating the sleeve and using a mechanical tool for pull out with a strength around 30 kg (300 N). A full cargo bed chassis was manufactured using the primer-coated profiles and the adhesive developed (Figure 7).

Conclusions

An in-line coated profile with good adhesion properties was produced using MW technology. The susceptors reduced the curing time between 46-71% without affecting the mechanical properties of the resins.
A sensor system was developed to determine in real time the parameters that affect the pultrusion process and, especially, th the curing degree of the resin just before th coating injection.

A new primer for in-line injection wa formulated to replace the abrasion an degreasing steps. A full cargo bed was mar ufactured as a case study, using pultrusio profiles coated with the primer and joine with a two-component adhesive wit debonding properties. □

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Fig.7: Assemby of the full cargo bed by adhesive join and easy debonding picture