

PROCESS OPTIMISATION FOR VACUUM INFUSED ANIONIC POLYAMIDE-6 COMPOSITES

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SUMMARY: An optimisation of the vacuum infusion process for glass fibre-reinforced anionic polyamide-6 composites is needed to obtain more homogeneous properties in flow direction. First of all, an alternative degassing procedure was investigated, which showed that degassing in a buffer vessel after mixing the resin decreased the void content significantly and therefore resulted in better mechanical and physical properties. After that, different process parameters during infusion and post-filling were varied in order to minimize the flow induced gradient and to find the optimal flow conditions. It was seen that the change in mechanical properties in flow direction is still significant for all conditions investigated: a minimum of 10% decrease in inter laminar shear strength was observed over a length of 25 cm. A thickness gradient as usually observed in a vacuum infusion process was not present within this research. A high infusion velocity caused a lower gradient in flow direction, but resulted in a lower overall quality compared to the lower infusion velocity. Applying a post-fill pressure after infusion proved to reduce the void content and therefore increasing the mechanical properties and reducing the flow induced gradient. Although the investigation of the infusion settings did not lead to the expected increase in homogeneity of the composites, a basic understanding was gained on the effect of these settings on the overall quality.

KEYWORDS: thermoplastic resin, vacuum infusion, optimisation, voids

INTRODUCTION

To explore the potential of fibre-reinforced thermoplastic anionic polyamide-6 composites for large structures, such as wind turbine blades, an optimisation of the infusion process is needed to obtain more homogeneous properties. Previous research on the isothermal infusion of the APA-6 composites [1] focused on the optimisation of the infusion temperature to study its effect on the composite properties and their homogeneity in flow direction. This infusion strategy was chosen because a non-isothermal infusion showed to induce thermal and chemical composition gradients in flow direction and hence a gradient in composite properties [2]. It was seen that at all infusion temperatures, there was still a gradient in composite properties in flow direction present, which

could be mainly attributed to the de-blocking equilibrium reaction and subsequent filtering of the activator, but also due to void formation in flow direction. An optimum for the mechanical properties was found at 130°C for the current heating rate, which indicates an optimum between the blocked and de-blocked state of the activator.

The presence of voids in composites is detrimental for several mechanical properties, especially for matrix-dominated properties, such as inter laminar shear strength, compressive strength and fatigue life [3]. Judd et al. [4] found experimental evidence that for each 1% increase in void content a 7% reduction in inter laminar shear strength of the composite is induced. This drop in inter laminar shear strength with void content is approximately linear up to a total void content of 4%. A void content of 1% is generally taken as the maximum acceptable void content for structural applications [5]. A void content of about 8% was observed for APA-6 composites and is therefore one of the major issues to address.

In this article, the degassing procedure will be investigated in order to decrease the void content, as well as the effect of the process parameters during infusion and post-filling in order to minimize the flow induced gradient. The effect of different infusion velocities and pressures will be investigated in order to find the optimal flow conditions.

EXPERIMENTAL

Materials

Resin Material

For the vacuum infusion of the anionic polyamide-6 thermoplastic laminates, a reactive resin mixture is used, which consists of three components: monomer, activator and initiator. The anionic polymerisation grade ϵ -caprolactam monomer (APCaprolactam) was supplied by Brüggemann Chemicals, Germany.

The combination of the activator and the initiator and their relative dose with respect to the monomer content was researched and determined by van Rijswijk et al. [6]. The resin mixture for this study consists of 1,2% mol of the difunctional toluene diisocyanate-caprolactam activator (TDCL) and 1,2% mol of the initiator caprolactam magnesium bromide, NYRIM[®] C1 (C1). Both the activator and the initiator were supplied by Brüggemann Chemicals, Germany and are stored in sealed glass containers. The TDCL activator is a blocked isocyanate, which can de-block above a certain temperature, its de-blocking temperature, 125°C [7], which is an equilibrium chemical reaction.

Glass Fibres

E-glass fibre mats are used to reinforce the APA-6 composites. The 8-harness satin weave E-glass fabrics (SS 0303 050, weave style 7781, 300 gram/m²) were supplied by Ten Cate Advanced Composites bv., Nijverdal, The Netherlands.

Processing Methods

Preparation of Resin Mixture

A special designed lab-scale mixing unit (Mini Mixing Unit 'MMU-TUDeft', Bronk Industrial b.v., The Netherlands), see Fig. 1., is used to prepare the resin mixture for infusion under a nitrogen atmosphere and at a temperature of 110°C. After dispensing the volume needed for the infusion of a laminate into a buffer vessel which is at a temperature of 130°C, the resin is degassed for 5 minutes to remove N₂ dissolved in the mixture during storage in the MMU tanks.

Infusion

A balanced, symmetric 12-ply laminate (25x29cm²) is prepared for vacuum infusion and is placed between two infrared panels, which is the heating device used, as can be seen in Fig. 2. The dry fibre perform is heated to 130°C prior to infusion, assuring an isothermal infusion. After degassing, the resin is allowed to flow through the inlet line-injection into the laminate. The resin injection and fibre compaction are achieved under vacuum, of which the pressure is varied in this research. When the resin reaches the line-injection outlet, the resin inlet tube is closed and the infused laminate is heated to the required processing temperature of 180°C. The vacuum is maintained during the cure cycle of one hour.

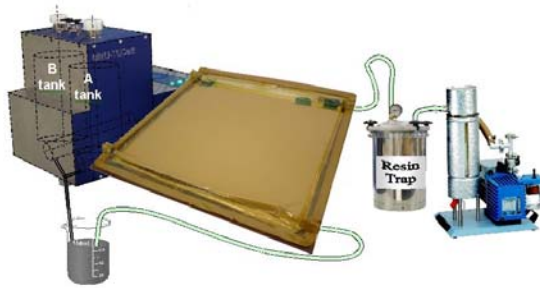


Fig. 1 Vacuum infusion set-up (from left to right: Mini Mixing Unit, buffer vessel, laminate and heating device, resin trap and vacuum pump).

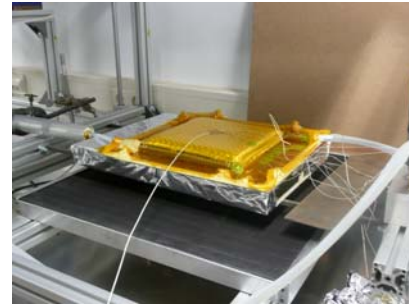


Fig. 2 Infrared panel as heating device for the laminate.

Analysis Methods

Degree of Conversion

To determine the degree of conversion (DOC) of the polymer, samples of the composite plate are taken at 5 cm from the resin inlet and outlet. After drying the samples at 50°C in a vacuum oven, they are weighed (m_{tot}). Next, the samples are refluxed overnight in demineralised water. After this process, the residue is dried and weighed again. As the monomer dissolves in the water, the mass loss can be attributed to the monomer (m_{mon}). Additionally the weight of the fibres needs to be measured. Therefore, the samples were burned off in a carbolite oven at 565°C for one hour; according to ASTM D 2584-02 [8] and the fibre weight (m_{fib}) was obtained. The degree of conversion can then be calculated as follows:

$$DOC = \left(1 - \frac{m_{mon}}{m_{tot} - m_{fib}} \right) \times 100\% \quad (1)$$

It should be taken into account that low molecular oligomers formed during polymerisation will also dissolve during the reflux process [9]. As these oligomers as well as the monomer do not have load carrying capabilities, Eq. 1 will give a good impression of the amount of non-load carrying substances in the composite but will thus not give the exact degree of conversion.

Degree of Crystallinity

The degree of crystallinity (X_c) and the melting temperature (T_m) of the polymer are determined by means of a Perkin Elmer Differential Scanning Calorimeter (DSC). Disc-shaped samples (m_{sp}) of approximately 5 mg are taken from the laminate at the same location as the degree of conversion samples and are dried overnight. In the DSC, the test sample is held at 25°C for two minutes and is then heated up to 240°C at a rate of 10°C per minute. The results had to be corrected for the fibre content of the sample. Therefore, the fibre content (m_{fib}) was determined by burning off the resin after the DSC test [8]. The degree of crystallinity can now be calculated as follows:

$$X_c = \frac{\Delta H_m}{\Delta H_{100}} \cdot \frac{m_{sp}}{m_{sp} - m_{fib}} \cdot \frac{1}{\text{DOC}/100} \times 100\% \quad (2)$$

In which: ΔH_m is the melting enthalpy of the specimen [J/g]; ΔH_{100} is the melting enthalpy of a fully crystalline polyamide-6 = 190 J/g [10]. The third term in Eq. 2 is a correction factor for the degree of conversion of the sample.

Ultrasonic Analysis

To check the homogeneity of the laminate, a high frequency (10 MHz) ultrasonic C-scan was used. A single through transmission mode was used to analyse the differences within the material, with water as a contact medium. Scans were performed at a speed of 352 mm/s to obtain images with a grid length of 0.5 mm and a width of 1 mm and were analyzed using ALIS software.

Short-Beam Strength

The short-beam strength tests were conducted on a Zwick Roell 2 ton force machine according to the ASTM D2344 norm. The test specimens for the short-beam strength test were rectangular shaped: 16.2 x 5.4 x 2.7 mm³. From the maximum force (P_{max}), the inter laminar shear strength (ILSS) can be calculated:

$$ILSS = 0.75 \times \frac{P_{max}}{b \times t} \quad (3)$$

in which b and t are the width and thickness of the specimen, respectively. A minimum of 5 specimens was tested. According to the ASTM Standard, the short-beam strength test is suited for comparative testing of composite materials, provided that failures occur consistently in the same mode [11].

RESULTS AND DISCUSSION

Degassing Procedure

In previous research, it was demonstrated that degassing of the MMU tanks for 15 minutes at 100 mbar was sufficient for infusing a void free polymer panel [12]. As shown in Table 1, for composites the same degassing procedure leads to a void content of approximately 8%. As a consequence, an alternative degassing procedure was investigated: degassing in the resin buffer for 5 minutes at 3 mbar. The void content was consequently reduced to about 5%. The resulting improvements were clearly visible in the ILSS data presented in Fig. 3.

Table 1 Effect of the degassing procedure on the composite properties

T_{mould} [°C]	Degassed in buffer vessel (3 mbar, 5 minutes)			Degassed in MMU (100 mbar, 15 minutes)		
	Conversion [%]	Crystallinity [%]	Void content [%]	Conversion [%]	Crystallinity [%]	Void content [%]
150	92	48	2	92	49	9
160	96	41	6	93	44	8
170	95	38	7	92	39	8
180	93	32	2	92	30	8

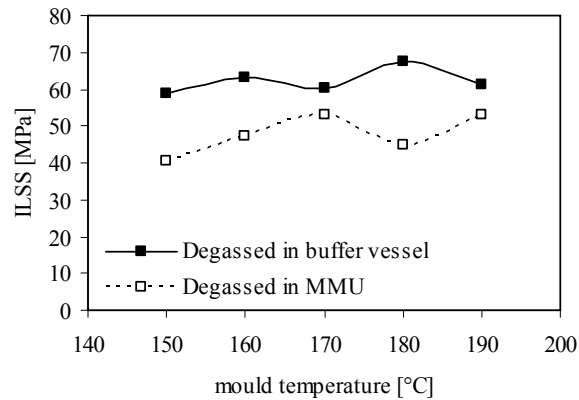


Fig. 3 The effect of the degassing procedure on the interlaminar shear strength (ILSS) of the composites.

Flow Conditions

To investigate the flow behaviour and identify the important parameters that influence the flow and quality of the composites, research was focused on different inlet tube cross-sections, infusion pressures as well as post-fill pressures. For all laminates, the flow front position was monitored by a video camera. The overall quality was assessed by a non-destructive technique, namely C-scan, after which the panel was tested for physical and mechanical properties. The baseline composites used in previous research were infused with an inlet tube cross-section of 20mm² and the infusion pressure and post-fill pressure are set to 250 mbar, to obtain the same fibre volume fraction as melt processed PA-6 composites. In this research a full-factorial design was established in which the following values were used:

- Inlet tube cross-section: 4 and 20 mm²
- Infusion pressure: 3 and 250 mbar
- Cure pressure: 3 and 250 mbar

Infusion

It was observed that the infusion time was mainly dependent on the infusion pressure and not as much on the inlet cross-section. For an infusion pressure of 250 mbar the infusion time was 55±11s while for an infusion pressure of 3 mbar the infusion time was only 35±4s. The flow front position and its flow rate through the fibre perform is shown in Fig. 4. As can be seen in this graph, the flow is stabilised and mostly pressure driven from approx. 7,5 cm in flow direction. It was shown that the infusion pressure also determines the thickness of the obtained laminate, regardless of the post-fill vacuum pressure, as can be seen in Table 2. A thickness gradient, usually observed when using vacuum infusion [13], was not present in our experiments.

Table 2 Thickness (t) and inter laminar shear strength (ILSS) near the inlet and outlet of the composites, and the infusion times at different infusion and post-fill pressures.

Infusion pressure [mbar]	Post-fill pressure [mbar]	t (inlet) [mm]	t (outlet) [mm]	ILSS (inlet) [MPa]	ILSS (outlet) [MPa]	Difference ILSS [%]	Infusion time [s]
3	3	2,69	2,72	48	43	10	34,5
3	250	2,71	2,73	47	37	19	36
250	3	2,75	2,78	48	42	12	58,5
250	250	2,76	2,78	55	38	31	51,5

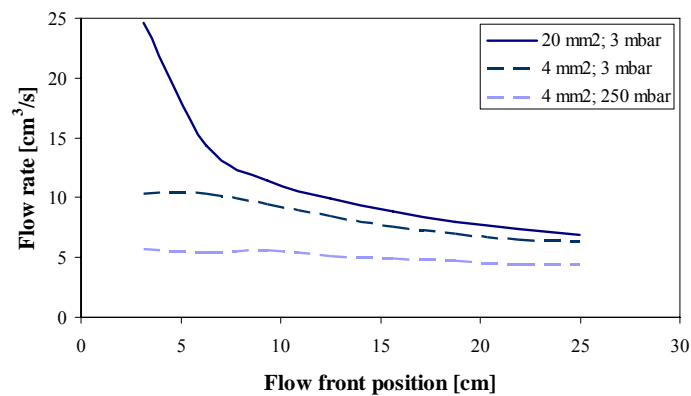


Fig. 4 Flow front position during infusion and their corresponding flow rate at different inlet tube cross-sections and infusion pressures.

Cure

After infusion the inlet tube is closed, the temperature is raised to the required curing temperature and the pressure is set to the post-fill pressure to be investigated. The difference in mechanical properties between inlet and outlet is significant: over a length of 25 cm a drop of 10 up to 31% in inter laminar shear strength was observed, as can be seen in Table 2. To assess the cause of this gradient, C-scan images were made (Fig. 5) and cross-sections in flow direction were investigated by the scanning electron microscope.

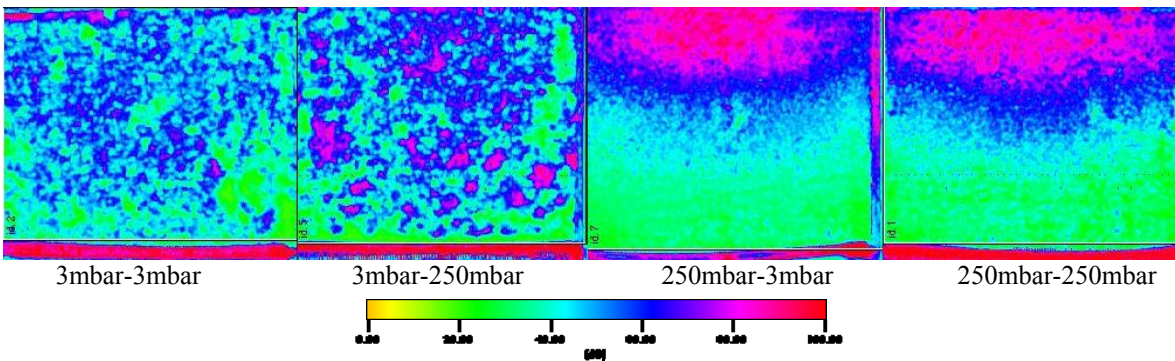


Fig. 5 C-scan results for different infusion pressures - post-fill pressures respectively, with an inlet tube cross-section of 20mm^2 .

From microscopy, it could be concluded that the drop in mechanical properties could be attributed to macro voids between the fibre bundles and that the voids were mostly located in the upper part when looking through the thickness. When looking at the C-scan images (Fig. 5), one can conclude that the higher infusion pressure (3 mbar) results in a more uniform damping but a lower overall quality, while the lower infusion velocity results in a clear transition in composite quality in flow direction. It was also shown that the ultrasonic attenuation of the laminates near the inlet had a good correspondence with the obtained ILSS data.

Barraza et al. [14] reported that, for a RTM process, applying a post-fill pressure reduced the void content significantly, independent of the infusion velocity, as is observed within this research. The higher post-fill pressure (3 mbar) led to an increase in mechanical properties of at least 14%, which can be attributed to a lower void content. When looking at the results for the ILSS in Table 2, it can be seen that the post-fill pressure influences the mechanical properties as well as reduces the gradient in flow direction.

Due to the low de-blocking temperature of the TDCL activator (125°C), the infusion temperature of 130°C used in this research may result in filtering of the activator during infusion, also inducing a chemical composition gradient in flow direction. Therefore, the degree of conversion was determined from the panels that showed the highest difference in quality and the results are shown in Fig. 6. It can be seen that the results for the outlet are higher than those near the inlet and have the same value for all infusion settings, which indicates that an optimum in resin constitution was found at the outlet. Near the inlet, more resin passed through the fibre bed ensuring a proper wet-out and a better fibre-to-matrix bond, therefore reducing the polymerisation as explained in [1]. It could be concluded that mainly the flow rate influences the

degree of conversion. Therefore, it is suggested that flushing the laminate with extra resin after full wet-out can be a solution to a better fibre-to-matrix bond in the whole laminate and may assure more homogeneous properties in flow direction. However it needs to be taken into account that this can lead to a lower overall degree of conversion.

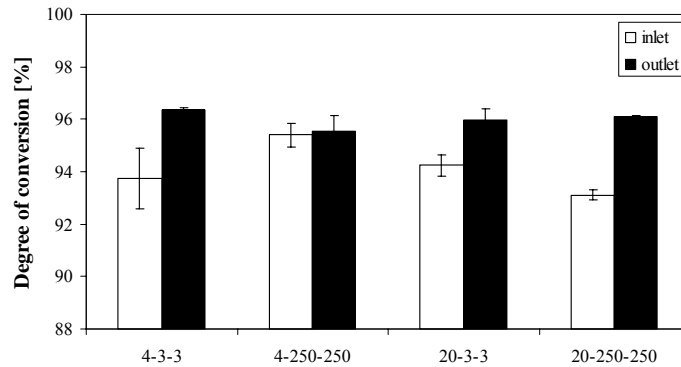


Fig. 6 Degree of conversion near the inlet and outlet of the laminates at different inlet tube cross-sections [mm^2] - infusion pressures [mbar] - cure pressures [mbar].

CONCLUSIONS

In order to increase the homogeneity of the APA-6 glass fibre reinforced composites, an alternative degassing method was investigated: after mixing the reactive resin, it was degassed in a buffer vessel. This decreased the void content significantly and therefore resulted in better mechanical and physical properties. To minimise the flow induced gradient, the effect of the several process parameters during infusion and curing were researched. Although the investigation of the infusion settings (inlet tube cross-section, infusion pressure and post-fill pressure) did not lead to the expected increase in homogeneity of the composites, a basic understanding was gained on the effect of these settings on the overall quality.

It was shown that with a fast infusion, which corresponds to a high infusion pressure (3 mbar), the flow gradient is less visible but that the overall quality of these laminates is lower than when infused slower. It is therefore recommended to investigate even lower infusion pressures (500 mbar) and to infuse longer panels to exclude possible edge effects from the research. It was shown that a high post-fill pressure (3 mbar) led to a reduction in the void content therefore resulting in an increase in the mechanical properties of the laminates. For the physical properties of the laminates, a flow induced gradient was also visible with a lower degree of conversion near the inlet. By flushing the laminate with extra resin after the wet-out of the fibre perform, this gradient may be resolved.

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