OPTIMIZATION OF MECHANICAL PROPERTIES OF BASALT WOVEN/APA-6 COMPOSITE PARTS BY MEANS OF VELOCITY CONTROL

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1 General Introduction

Nowadays the use of liquid composite molding (LCM) processes for the development of composite parts for both structural and non-structural applications has become of increasing interest. Carbon fiber has been traditionally used as reinforcement for its outstanding properties (chemically inert and very stiff), but it has the disadvantage of its high cost. Glass fiber is susceptible to undergo surface damage and to be sensitive to alkaline environment. Additionally, the current environmental requirements promote the use of natural fibers as reinforcement, in order to achieve more sustainable *GreenComposites*. In this context, basalt fibers are an alternative to current reinforcements. They are obtained directly from the molten single material, thus being biologically inactive, non-toxic, good electric insulator, and resistant to high temperature. Moreover they exhibit mechanical properties comparable with those of E-glass [1].

These new *Greencomposites* also assume the use of a thermoplastic matrix (*Thermoplastic Composites*, TpC's). The matrix determines most of the mechanical and chemical properties. Unlike thermoset-based matrices, their thermoplastic counterparts can be recycled or reprocessed. In addition, TpC's do also offer higher mechanical properties [2].

Polyamide-6 (PA-6) currently used in industry is hydrolytically polymerized and delivers pellets, which are further thermoformed into parts. But the molten viscosity of thermoplastic resins is very high, which makes it difficult to impregnate thermoplastic resin into fiber bundles. To overcome this problem, *anionic reactive processing* is used as an alternative way to obtain PA-6: initial low viscosity raw reactants (Monomer (ϵ-caprolactam) + Activator + Initiator) are injected through the reinforcement, being it a low energy consumption process. It is followed by a catalyzed ring opening reaction, which take place at temperatures between 130 and 190 degrees and completed within 2 to 50 minutes, depending on the amount and the type of activator and initiator. The result is a high molecular weight linear polymer (*anionic* PA-6, APA-6) [2]. In this process, it is also to remark that the void content, together with the fiber volume fraction, the microstructure of the preform, will affect the mechanical performance of LCM obtained parts.

The main objective of this paper is to validate the use of APA-6 as matrix material of basalt fibers. It studies the dependency between injection flow rate and void content, which affects final mechanicals properties o the part. FEM simulation is suggested to optimize the filling process, opposed to commonly used trial and error methods at shop floor.

2 Overview on the anionic polymerization of ε-caprolactam

In the APA-6, the most important intermolecular force is hydrogen bonding. The nitrogen-bonded hydrogens of one chain will bond very strongly with the carbonyl oxygens of another chain, resulting in great physical properties [2]. These interactions are obtained via a classical ring-opening anionic polymerization. This reaction is a polyaddition reaction, that is, in ideal conditions (free-moisture environment), no byproducts are produced. It requires an *activator* and an *initiator* that will ensure both initiation and propagation of the reaction. Reactants are shown in Fig. 1.

The *initiator* has to be a very strong base to break the N-H bond of the ε-caprolactam, in order to form a reactive amide. Introducing an *activator* will lead

us to have very reactive imides, allowing, after an *induction time*, a very fast chain growth polymerization. This reaction time is due to the difference of reactivity between amides and imides. This difference simply relies on the number of reactive carbonyl carbons, two for the imides against one for the initial amide. One can modify the induction time (from 2 to 50 minutes [2]), using the different reactivity of the common activators and initiators. The reaction will end when any proton donating species neutralizes all anionically-charged polymeric chains.
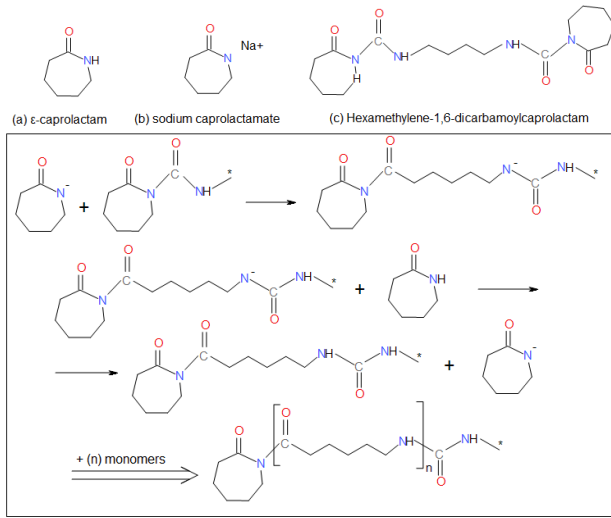

Fig. 1. Up, reactants used; (a) monomer, (b) initiator, (c) activator; down, reaction mechanism for APA-6 polymerization

3 Governing Equations

3.1 Darcy's Law

Flow through porous media is usually treated as a flow Newtonian governed by Darcy's Law and the continuity equation. In such considerations, the process is modeled either as a flow through fully saturated or as a flow through unsaturated porous media. Modeling and measurements through saturated porous media is much easier since it practically involves only unidirectional Darcy's flows and corresponding simple theoretical models [1]. However, in a wide range of application of porous media such as in LCM processes, unsaturated permeability is more important for the analysis of initial fabric wet out, which requires more sophisticated models and an in-depth analysis of two or three-dimensional theoretical models. In its

original form, Darcy's Law is not very useful because the permeability term (K_h) term is dependent on the properties of both the fluid and porous medium:

$$Q = -K_h \cdot A \cdot \frac{\partial P}{\partial x} \quad (1)$$

where Q is the volumetric flow rate, A is cross sectional area of the flow, dP/dx is the pressure gradient and K_h is a constant of proportionality known as the hydraulic permeability. In order to separate the influences of the two constituents, K_h was defined in terms of fluid viscosity μ and permeability K, which is dependent on the structure of the porous medium only :

$$K_h = \frac{K}{\mu} \quad (2)$$

This concept was popularized by Wyckoff et al. in 1933 and has been validated by many successful determinations of permeability. The practice has converged on the use of the tensorial form of Darcy's Law for anisotropic media:

$$\overline{v}_i = -\frac{\left[K_{ij} \right]}{\mu} \cdot \nabla P_i \quad (3)$$

where $\left[K_{ij} \right]$ is the second order symmetric permeability tensor (its value depends on the direction of the flow), $\overline{v}_i$ is the volume averaged "Darcy velocity", μ is the viscosity of the resin, and ∇P_i is the pressure gradient. For non-isothermal mold filling, the resin is a function of temperature and degree-of-cure.

The continuity equation for the flow in RTM process of an incompressible resin through a porous medium can be expressed as:

$$\nabla v = 0 \quad (4)$$

Inserting eq. (3) into (4) lead to the following simplified form:

$$\nabla \left(\frac{\left[K_{ij} \right]}{\mu} \cdot \nabla P_i \right) = 0 \quad (5)$$

3.2 Cure and rheology modeling

The prediction of polymer viscosity as a function of temperature and time can help to find the acceptable temperature and velocity range to successfully accomplish impregnation of the fabric without thermal degradation of the resin. For the non-isothermal filling analysis, a model relating the viscosity and the resin conversion is needed. Moreover, due to the low viscosity of the precursors, the most important parameter is the *induction* time [2] prior to the *in situ* polymerization.

The heat balance of a composite part can be expressed as one-dimensional heat conduction in the thickness direction as:

$$\rho_c c_p \frac{\partial T}{\partial z} = \frac{\partial}{\partial z}\left(k_z \frac{\partial T}{\partial z}\right) + \rho_r \varepsilon_r H_r \frac{\partial \beta}{\partial t} \qquad (6)$$

where ρ_c, c_p, k_z are respectively the density, specific heat capacity, and the thermal conductivity in the thickness direction of the part. During mold filling, the viscosity of the resin may vary due to the polymerization reaction. The heat generation rate due to the resin cure is described by the resin density ρ_r, the porosity ε_r, the enthalpy of reaction H_r, and the resin rate of reaction $\partial \beta / \partial t$.

Opposed to *mechanistic* kinetic models, *overall* ones consider all reactions as a single reaction step, losing some influence of intermediate reactants on the kinetic of the reaction. As detailed by Teuwen and Bersee [3], let's consider the fractional degree of conversion (β) obtained by means of adiabatic temperature measurements:

$$\beta = \left(T - T_0\right) / \left(T_f - T_0\right) \qquad (7)$$

Here, T is the temperature at time t, T_0 and T_f are respectively the initial and maximum temperature of the reaction. We can get to the point that an autocatalytic model as proposed by Kim et al. [4] and Lee et al. [5] would be valid:

$$\frac{\partial \beta}{\partial t} = k \cdot \exp\left(-\frac{E}{RT}\right)\left(1 - \beta\right)^n \left(1 + B_0 \beta\right) \qquad (8)$$

where k is the front factor, E is the activation energy, and B_0 is the autocatalytic term. The front factor allows comparing the efficiency of various initiators, while the autocatalytic term describes the self-acceleration effect of the chain growth.

3.3 Filling stage optimization

In composite parts produced using RTM processes; voids are to be avoided to improve the mechanical properties. Researchers have published several investigations on micro and macrovoids formation and have shown that macrovoids tend to form during injection at low flow rates, due to capillary dominant effects whereas high injection rates lead to microvoids formation. It has been also shown that the formation of voids can be related to the modified capillary number C_a^*:

$$C_a^* = \frac{\mu v}{\gamma \cos(\theta)} \qquad (9)$$

where μ is the viscosity of the fluid, γ the surface tension at the interface air/resin, v is the fluid velocity and θ is the contact angle between the resin and the fibers. The method proposed by E. Ruiz et al. [6] to optimize the macro/microvoids content is then controlled by the injection velocity, which can be expressed by:

$$V_{imp}^{opt} = \frac{C_a^* \gamma \cos(\theta)}{\mu} \qquad (10)$$
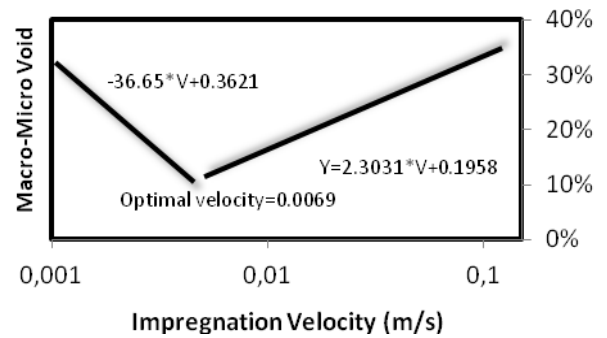

Fig. 2. Macro-Micro void function [7].

Fig. 2 shows an LSQ-estimated relationship between macro/microvoid content and impregnation velocity. The curve with the negative slope is the macrovoid function, and the other one is the microvoid function. In order to analyze the formation of voids during the resin impregnation process, a one-dimensional solution based on two-phase flow through a porous medium, was proposed in [7]. This

model leads to the introduction of *relative permeability* as a function of saturation and a *modified equation* for the saturation, as a non-linear advection-diffusion equation with viscous and capillary phenomena. The resulting equation for the saturation in its most general form gives

$$\phi \frac{\partial S}{\partial t} + \nabla \cdot \left(v f(S) \right) = -\nabla \cdot \left(D_{cf}(S) \nabla S \right) \quad (11)$$

where

$$f(S) = \frac{\lambda_R(S)}{\lambda_R(S) + \lambda_A(S)} \quad (12)$$

$$D_{cf}(S) = f(S) \lambda_A(S) \frac{\partial P_C}{\partial S} \quad (13)$$

$D_{cf}(S)$ is the nonlinear diffusivity coefficient due to capillary pressure P_c, defined as $P_c = P_A - P_R$; v is the total velocity, S is the degree of saturation of the reinforcement by the liquid resin, $\lambda_j(S) = K_{Rj}(S) \cdot K / \mu_j$ is the phase mobility, with $K_{Rj}(S)$ the relative permeability of the phase j, μ_j the viscosity of phase j and K the permeability tensor.

4 Numerical Simulations

Finite Element Method (FEM) simulation packages are very helpful work tools in industrial field. They have gained importance in the last few years by allowing any process or product`s behaviour to be quantified and tested, or just to compare alternative designs, thus saving on costs and lead times. In the context of filling processes, a numerical simulation will involve the following operations at each time step:

1. Calculate the pressure distribution by applying a standard finite element discretization to equation

$$\nabla \cdot \left(K_R(S) \nabla p \right) = \frac{\phi \mu}{K_{sat}} \frac{\partial S}{\partial t} \quad (13)$$

where the relative permeability and the term on the right side depend on the saturation degree (see [7]).

2. Calculate the velocity field from Darcy's law for the resin.

3. Update the saturation distribution by integrating eq. (11) using a flux limiter technique described in [7].

The boundary conditions are given by: the pressure gradient in the normal direction to the mold walls vanishes, the pressure or the flow rate is specified on the inflow boundary, and the pressure is zero in the empty part of mold.

4.1 Numerical Case Study

Commercially available packages such as ANSYS™, NASTRAN™, ABAQUS™, etc., cannot directly support LCM process simulation but only mould filling simulations by homogenization techniques with limitations of heat transfer and cure kinetics analysis. Some research groups have developed their own codes such as LIMS, LIMS3D, and RTMSIM etc., to achieve their requirements [8][9][10]. Moreover, in the last five to ten years, there has been considerable interest in developing easier-to-use commercial simulation software products, such as PAM-RTM™ (Esi-group™) [11], Moldflow™ (Autodesk™), RTM-Workx™ (Polyworx™). In addition, the major manufacturing-oriented simulators have introduced programming into their software in one or both of the following ways:

- The facility to use "programming-like" constructs (e.g., setting global variables, if-then-else logic, etc.) at certain points in the simulation-building process
- The facility to call external programmed routines at certain points in the simulation-building process
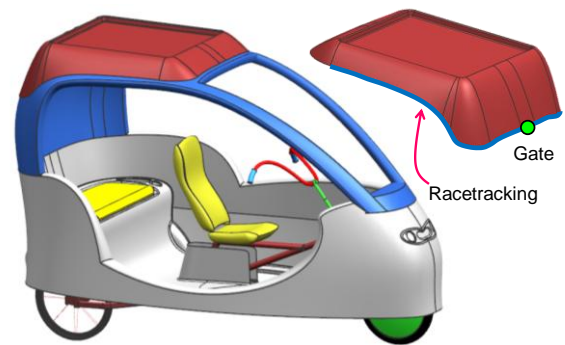

Fig. 3. Part geometry (Sunroof) designed at the Universidad Politécnica de Valencia

In this work a complex optimization study has been carried out on a three dimensional geometry under PAM-RTM software. It consists of the filling of a sunroof for a touristic man powered vehicle, as shown in Fig. 3. It involves non-isothermal flow of

resin (APA-6) through a basalt fibre preform. Thus, the routines solve simultaneously the following 3D equations:

- Darcy
- Mass transfer
- Heat transfer
- Cure kinetics
- Reactive injection of APA6
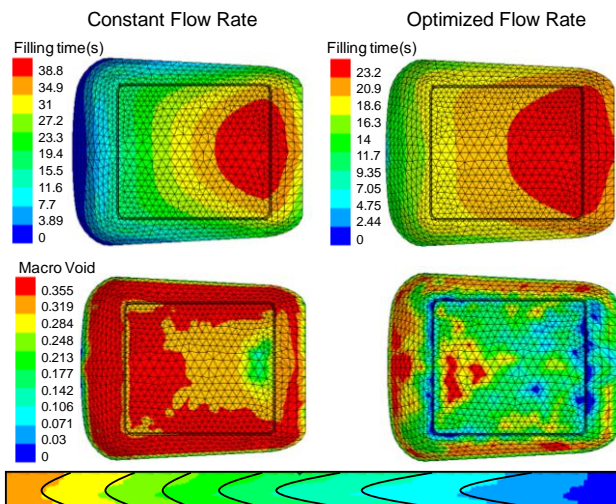- Void content and optimization

Fig. 4. Filling times (top) and void contents (bottom) before (left) and after (right) numerical optimization of the injection rate. Below, simulation of the flow front through-the-thickness.

The material properties and parameters of cure kinetics used in this case study are listed in Table 1. The following values of physical parameters have been considered for the mold filling optimization:

- Macro Voids function: $-36.65\,v + 0.3621$
- Micro Voids function: $2.3032\,v + 0.1958$
- Resin capillary coefficient: 0.02
- Optimal capillary number: 0.0069

The inlet gate is located on the back border, looking for a racetracking effect along this border, see Fig. 3. Fig. 4 shows the filling times (reduced from 38.8s to 23.2s) and void contents (zones up to 0.35%, in red) for a constant injection pressure of 1bar (left) and with optimized injection velocity (right). As observed in the comparison at the bottom of Fig. 4, the void content in the second simulation has been reduced to a minimum.

Parameters of cure kinetics			
H_r	310,484 Kj/Kg	A	533000 s^{-1}
R	8,314 J/molK	E/R	8432 K
		B_0	11
		n	1.04
Thermal Properties of composites and Resin			
ρ_r	1130 Kg/m3	ρ_a	1000 Kg/m3
ε_r	0,5	C_p	700 J/(Kg*K)
		k_a	0.3 W(m*K)

Table 1. Parameters of cure kinetics and thermal properties for the Basalt/APA-6 composites used in this numerical study
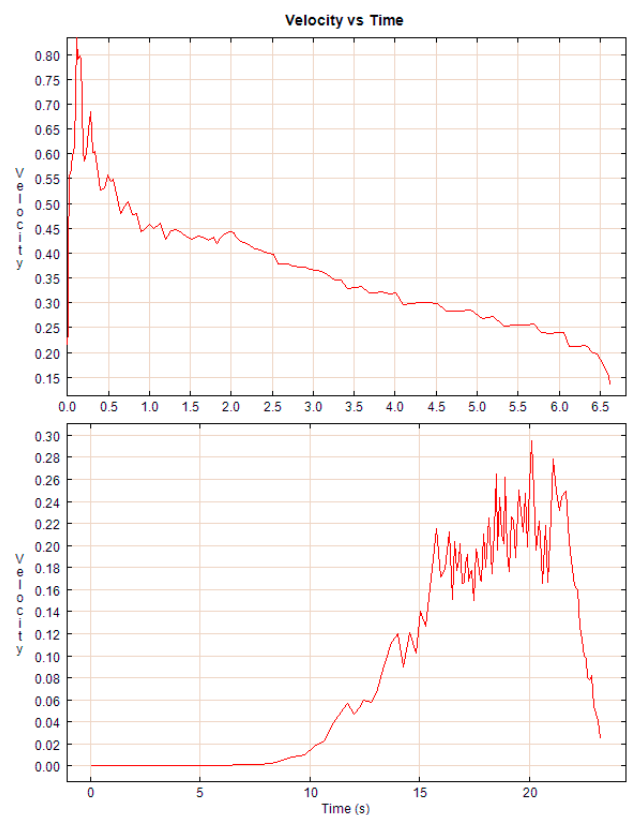

Fig. 5. Injection rate for a constrant inlet pressure of 1 bar (top) versus the optimized injection velocity reducing void content (bottom).

As can be seen in Fig. 4, the flow front through-the-thickness reproduces the three dimensional behaviour. The different impregnation velocity also affects on the macro and micro void content.

5 Conclusions

This work has shown the latest tendencies on the manufacturing of composites, namely

GreenComposites. In this study, they are made of more sustainable basalt fabrics and thermoplastic matrices.

As it involves an anionic in situ polymerization, new considerations on the injection methods have been studied. With the low viscosity of the precursors, almost like-water, one of the main effects of varying the flow rate in LCM is that the void occurrence will be affected. It has been shown a numerical approach to estimate the flow control, thus reducing void contents. With a constant inlet pressure, and meantime the impregnation of the reinforcement, the flow rate will decrease with the increasing distance from the injection port. Nevertheless, with the exposed approach, an optimal injection rate can be programmed in a numerically controlled injection machine.

Numerical approach by FEM methods also demonstrate its validity to determine the effective injection strategy including the position of vents and gates, and the most effective values of parameters for minimum mould filling time without formation of voids.

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