A MULTI-PHYSIC AND MULTI-SCALE APPROACH TO MODEL THE CONTINUOUS WELDING OF THERMOPLASTIC MATRIX COMPOSITES

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Abstract

This article deals with a new processing method for continuous fibre-thermoplastic composites, named "Drapcocot". The mean characteristic of this method is to perform simultaneously the prepreg tape placement and its thermal welding. The experimentally observed effects of temperature and lay-down velocity on interfacial strength indicate the existence of two thermally activated antagonist effects: chain diffusion through the interface and polymer thermal ageing. On the basis on simple rheometrical experiments, it was tried to establish the kinetic laws of these process. A careful thermal mapping of the process served as a basis for a thermokinetic model to which diffusion and ageing kinetics were coupled. The results of this model were expressed in terms of "isodiffusion" and "isoageing" curves in temperature/lay-down velocity maps. These maps allow explaining why, in the case of APC-2 (carbon/PEEK) composites, welding in optimal conditions is not possible. They allow also imagining trends for the design of new welding systems.

1 Introduction

Thermoplastic matrix composites are more and more used in the aircraft industry for structural parts. In the case of continuous fiber-reinforced materials, a common way of processing consists to weld elementary tapes one to another to constitute the desired part. A two steps procedure was needed in the past: first a manual or automated tape placement, then a consolidation in autoclave. The aim of this study is to investigate a new process, named "Drapcocot" [1], developed by EADS, Dassault Aviation and Eurocopter, in which placement and consolidation are performed simultaneously in order to increase the productivity.

The process principle can be briefly described as follows (Fig. 1): the first layers are supposed to be already laid down. Then the tape under consideration is placed in its position using the tow guide. Two torches blow hot nitrogen in order to melt the material at the interface between the plies to weld. A roller applies a normal force on the tape in order to improve the adhesion between the plies. The process parameters that can be controlled are: torches temperature, head velocity, roller temperature and roller force.

The chosen material was the well known APC-2 pre-impregnated UD carbon-PEEK composite supplied by Cytec.
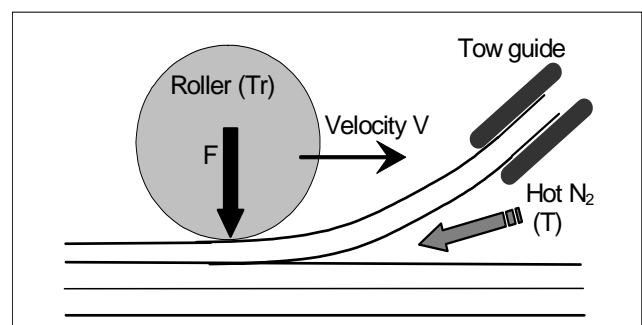

Fig. 1. Schematic principle of "Drapcocot" process

2 Influence of processing conditions on interfacial strength

The weld quality was characterized using peel tests on two layers samples. These latter differed by their processing conditions: torches temperature and lay-down velocity. The applied roller force was kept constant and high enough to make the intimate contact time [2] negligible, compared to the welding time. The peel energy was plotted in Fig. 2 against temperature, for several values of the head velocity.
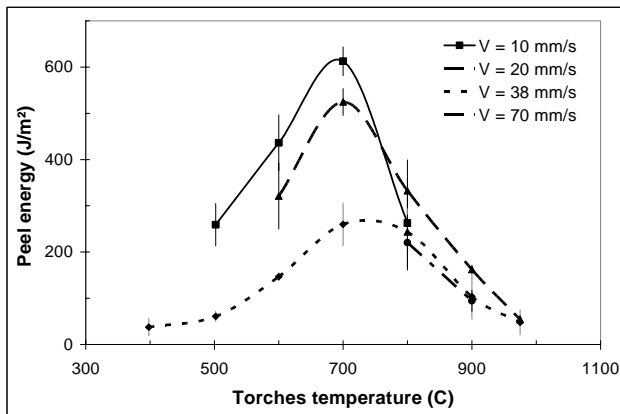

Fig. 2: Influence of parameters on interfacial adhesion

The curves display a maximum of which the amplitude is a decreasing function of the head velocity. It appears thus that adhesion is under the dependence of two antagonists, thermally activated processes: the role of velocity puts in evidence the importance of kinetics aspects.

The fact that, in the low temperature domain (typically $T_{torches} \leq 700$ C), adhesion is an increasing function of temperature and a decreasing function of velocity e.g. an increasing function of the time spent at high temperature, suggests that it results from a thermally activated diffusional process. To explain the decrease of adhesion at high temperature, the simplest hypothesis is, no doubt, that the polymer undergoes thermal ageing and that this latter affects adversely the welding quality. Other phenomena, for instance crystallization, could also affect the mechanical performance of welded joints. Their eventual influence has been studied [3] and will be reported elsewhere.

According to this choice, the model elaboration must involve three steps: i) Determination of kinetic laws for chain diffusion. ii) Identification of thermal ageing processes susceptible to influence welding and determination of their kinetic parameters. iii) Thermokinetic mapping of the process in order to determine the material thermal history at every point, every time, in order to apply the above established kinetic models to each volume element.

3 Macromolecules diffusion

Once the intimate contact between plies is established, the interdiffusion of macromolecular chains at the interface occurs as long as the matrix is melt, i.e before crystallization quenches long range chain motions. The interfacial strength depends of the degree of chain interpenetration. Beyond a certain state, the interfacial zone becomes indistinguishable from the bulk polymer, the interface healing can be considered perfect. The (temperature dependant) time tw to reach this state is, indeed, a key quantity of the process modeling.

The chain motion in the melt is modeled by the reptation theory introduced by De Gennes [4] and Doi and Edwards [5]. An important characteristic of the chain diffusion kinetics is the reptation time *tr*, e.g. the time for the chain to loose its initial configuration and to move over a distance equal to its end-to-end distance. In the frame of a welding experiment, *tr* is the time beyond which interface healing must be perfect. In order words the optimal time for welding *tw* must be of the order of the reptation time *tr*. This latter can be determined from rheological experiments.

Unfortunately, the PEEK grade used for APC-2 was not available so that rheometric measurements were made on a pure PEEK grade (G450) which was supposed to be the highest boundary of the APC-2 matrix in terms of molecular weight. The measurements were performed on an Ares Rheometric Scientific rheometer using a parallel plates geometry. Several isothermal tests were made under nitrogen in the 310-410 C temperature range, at 2% strain amplitude, with angular frequency ranging from 0.01 to 100 rad.s^{-1}. It can be recalled that the main transition temperature of PEEK are: glass transition temperature *Tg* = 140 C, melting point *Tm*= 330 C. In a programmed temperature decreasing experiment, crystallization begins at about 280 C.

The modulus of the complex viscosity η* was recorded against angular frequency ω. The transition between the newtonian regime, corresponding to the horizontal asymptote, and the rheo-thinning regime, corresponding to the oblique asymptote, is characterized by an angular frequency of the order of 1.1 rad.s-1 and thus the characteristic time

$\lambda = \omega - 1$ of the order of 0.9s (at 360 C). At every temperature, this characteristic time, called also terminal relaxation time, and the newtonian viscosity η_0 were determined using the Carreau law [6]:

$$\eta^* = \eta_0 \left[1 + (\lambda\omega)^\alpha \right]^{(m-1)/\alpha} \qquad (1)$$

It has been shown that λ obeys Arrhenius law (Fig. 3), that allows to extrapolate its value at higher temperatures, inaccessible to experiments:

$$\lambda = \lambda_0 \exp\frac{E_\lambda}{RT} \qquad (2)$$

with E_λ equal to 59.7 KJ.mol^{-1}. In the following, it will be considered that $\lambda = t_w$, i.e. that the optimal welding time is the terminal relaxation time of the polymer.
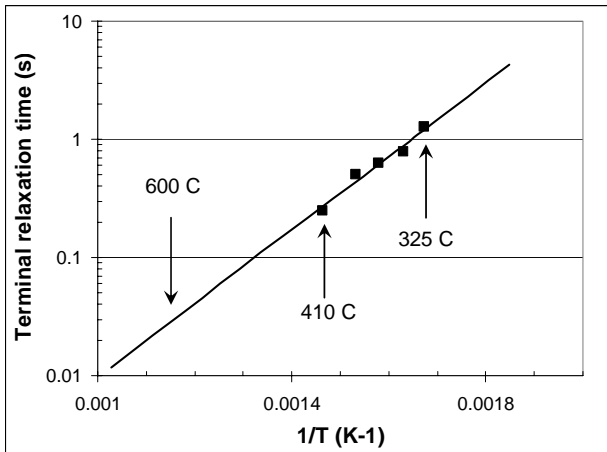

Fig. 3. Variation of the terminal relaxation time versus temperature

4 Thermal ageing

According to the literature [7,8,9] crosslinking is resulting apparently from radical processes and predominates during PEEK thermal ageing. It is expected to disfavour welding because it increases the melt viscosity.

To study crosslinking kinetics, it was chosen to perform isothermal experiments in the 360-460 C temperature range. The records of the real viscosity η' changes at low frequency, e.g. in the newtonian regime were done. Very small changes were observed, after 6 hours, at 360 C, whereas the viscosity increases by almost two orders of magnitude after about 2 hours at 460 C.

At low conversion (far from the gel point), the number of crosslinking events per mass unit r is given by:

$$r = \frac{1}{M_{n_0}} - \frac{1}{M_n} = \frac{I_{P_0}}{M_{W_0}} - \frac{I_P}{M_W} \qquad (3)$$

where M_n and M_w are the number and weight average of molar mass and I_P is the polydispersity index. It will be assumed that $I_P \sim I_{P0}$ and that the viscosity obeys the power law established for linear chains:

$$\eta_0' = K\, M_W^{\,3,4} \qquad (4)$$

where K is a temperature dependant material's property. More sophisticated relationships, taking into account the specific effect of branched architecture of crosslinked polymers on their viscosity are available, but it seems to us that the above equations are sufficient, in a first approach, to predict the trends of viscosity variations. Then, the crosslink concentration is thus given by:

$$r = \frac{I_{P_0}}{M_{W_0}} \left[1 - \left(\frac{\eta_0'}{\eta'}\right)^{1/3,4} \right] \qquad (5)$$

and r was plotted against exposure time in Fig. 4. It varies quasi linearly with time, even at 460 C, in the first hour of exposure.
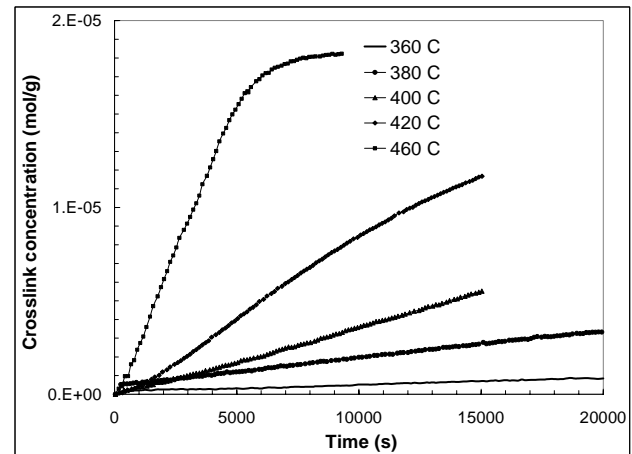

Fig. 4. Evolution of r with time for different temperatures

The slope of the linear part gives the crosslinking rate K$_{app}$. The crosslinking kinetics of this latter can be approximated by a zero order process:

$$r = K_{app} t \qquad (6)$$

where the kinetic constant obeys to Arrhenius law (Fig. 5):

$$K_{app} = A \exp\left(\frac{-E_a}{RT}\right) \qquad (7)$$

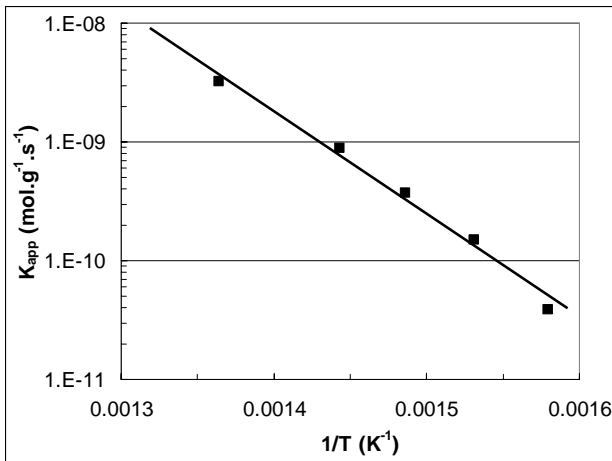with $A = 3384$ mol.g^{-1}.s^{-1} and $E_a = 168$ KJ.mol^{-1}.

Fig.5. Variation of the kinetic constant of crosslinking

Indeed, the knowledge of the initial characteristics I_{P0} and M_{W0}, and this initial newtonian viscosity at the temperature under consideration, allow determining the viscosity η' from r at any time and temperature.

5. Thermokinetic mapping of the process

A time dependant bidimensional model has been build to predict temperature maps. The assumption that temperature is constant along the ply width is justified by the fact that the thermal conductivity is ten times higher in the fibre direction than in the transverse direction. The 2D model uses a finite volume formulation with an explicit scheme. The program was written with Matlab®.

The principle of modelling is schematised in Fig. 6. The heat transfer from hot nitrogen to the material is characterized by a heat transfer coefficient htor over a length ltor. Indeed, before the roller applies the pressure, both plies are not yet welded. The boundary condition is then convection with atmosphere. The interface is considered inexistent in the welded zone so that, thermal exchanges are due only to conduction. The roller imposes a local surface heat flow characterized by its heat transfer coefficient h_{rol} and the contact length l_{rol}.
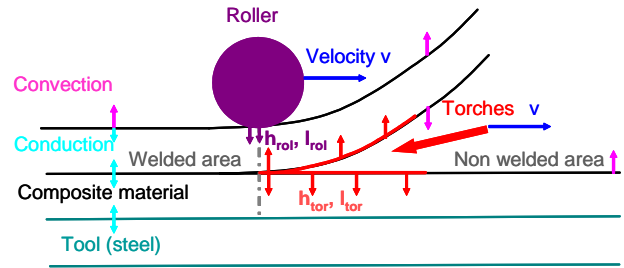

Fig. 6. Principle of the 2D modeling of the Drapcocot process

The global heat equation must thus contain two source terms relative to crystallization and melting. Both source terms can be identified from DSC characterizations [3].

The experimental temperature mapping was made using small thermocouples inserted between the plies. Once a thermocouple is covered by the upper layer, one can be confident that it gives reliable data and thus that realistic boundary conditions for the torches can be determined.

The thermal simulations can predict the thermal history seen by the material. For example, we can see on Fig. 7 that the ply being welded has a higher temperature than the welded plaque.
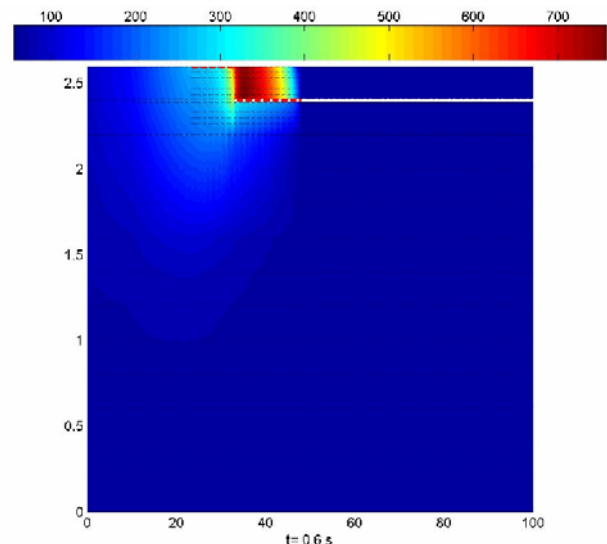

Fig. 7. Moving temperature field.

6 Weldability predictions

It is now possible to predict, using the above models, the local extent of macromolecular diffusion and thermal ageing, and thus to appreciate, with pertinent criteria, the welding quality.

6.1 Macromolecular diffusion

To quantify the extent of reptation in the direction normal to the interface, it is possible to solve the diffusion equation in the nonisothermal case [10]. An alternative approach consists to consider the quantity N defined by:

$$N = \int_{t_{contact}}^{t_{crystallisation}} \frac{dt}{tr(T(t))} \qquad (8)$$

where N, that depends of the composite thermal history and on the reptation time, describes the probability for a chain to cross the interface. When $N = 1$, this means that the processing time is equivalent to the reptation time in an isothermal experiment e.g. that the interface healing must theoretically be achieved.

N has been calculated, taking the origin of time when the interface reaches the melting point, for various sets of processing parameters. It was thus possible to plot the envelope of points where $N = 1$ in the Temperature-time diagram.

6.2 Thermal ageing

As for diffusion, it is possible to define a quantity R representing the extent of thermal ageing in a given point:

$$R = A \int_{t_{contact}}^{t_{crystallisation}} \exp\left[\frac{-E_a}{R[T(t)]} \right] dt \qquad (9)$$

Knowing that it is the new ply which is being laid down that will the more suffer thermal ageing, we will focus for this calculation at the lower surface of the layer n°13. This calculation was also implemented in the model so that it was possible to plot iso-ageing curves in the Temperature-velocity diagram.

6.3 Weldability predictions

Let us now consider a temperature-velocity diagram (Fig. 8) in which the curve corresponding to N=1 represents the "perfect welding". In fact, from our mechanical measurements, it was found that thermal ageing begins to hinder adhesion for R =10-7 mol.g-1. The envelope of the points corresponding to this value was also plotted in the diagram.

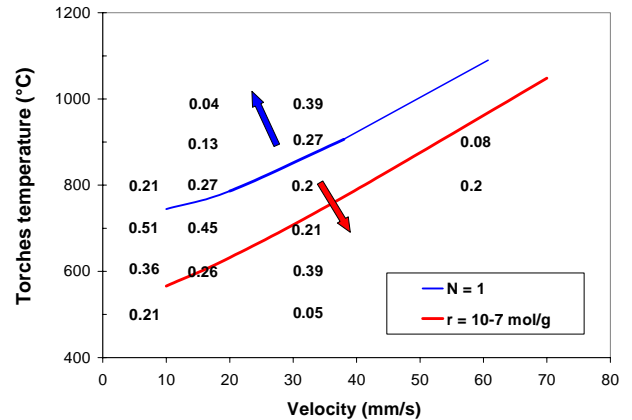Fig. 8: time-temperature diagram process

The conditions for perfect welding would be thus: $N \geq 1$ and $r \leq 10^{-7}$ g.mol-1. According to Fig. 8, these conditions cannot be realized in the experimentally accessible temperature range ($T \leq 1000$ C). In other words, there is no way to obtain, with the system under study, the theoretically maximum interfacial strength. This is confirmed by the results of peel tests: in the best case ($T_{torches} = 700$ C, V= 10 mm.s-1), the peel energy is twice smaller than for autoclave consolidated samples.

It is however possible to define an "admissible welding domain" using a less severe endlife criterion for thermal ageing, for instance r = 10^-6 mol.g^-1, but bonding values are not acceptable.

Fig. 8 shows that technological improvements are necessary to reach ideal conditions in the high temperature/high velocity zone. Thus, the proposed model could be an interesting tool for the design of new processing systems.

The (T, t) diagram shows also that there is no acceptable solution in the domain of low temperature, low velocities, because the curves "isodiffusion" and "isoageing" diverge in the unfavourable sense.

A possible way towards better welding could consist to have a nonsymetric heating, the upper ply being less heated than the lower one, in order to shift the "isodiffusion" curve under the "isoageing" one. Here, also, the thermokinetic analysis suggests an interesting way for machine design.

7. Conclusion

The "Drapcocot" process is a new in-situ consolidation process for thermoplastic composites. As any polymer processing method in the molten state, it is characterized by a "thermal stability ceiling" which can be represented by a curve in the (time-temperature) space. Since consolidation results from chain diffusion through the interface, iso-diffusion (e.g. iso-welding quality) conditions can also be represented by a curve in the (t, T) space. This curve can be called the "rheological floor". Using simple kinetic laws for diffusion and for thermal ageing and combining these laws with a thermal model, we have made temperature-head velocity maps in which boundaries corresponding to the "rheological floor" and to the "thermal stability ceiling" were plotted for the case of APC-2 (carbon/PEEK composites). This analysis showed that in the case under study, there is no "perfect welding window" because the "floor" is above the "ceiling". However a domain of "admissible welding" can be defined and corresponds well to experimental results. This model could be interesting to define technological objectives for the design of new welding systems.

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