AUTOMATIC LAMINATION AND IN-SITU CONSOLIDATION: CONTROLLING THE PROCESS

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Abstract

The automatic lamination and in-situ consolidation process with thermoplastic composite materials consists on heating two layers of thermoplastic prepreg by using a heat source. After heating the parts, they are placed in contact by the pressure applied with an elastomeric roller. When the roller contacts with the layers they initiate a cooling stage. Semicrystalline thermoplastic materials are highly influenced by this cooling stage because of their inherent order development and densification while the temperature drops down. For that reason, it is necessary to predict the final degree of crystallization in order to modify the manufacturing variables, to reach optimal cooling profiles and to determine major conditionants in the final mechanical properties. The analysis of crystallization kinetics will provide not only information about the final degree of crystallization, also it provides essential information about the morphology of the crystals in the composite. The application of deconvolution and optimization methods to the exothermal peaks of crystallization shows the differences between the crystallization of pure PEEK (poly ether ether ketone) and the material reinforced with carbon fibers and so the differences imposed by the cooling rates.

1. Introduction

Based on the goal of scaling the use of thermoplastic materials to the same level reached with thermosets in the aeronautic industry, many research groups are working to understand the fundamentals of physics implied in the whole process. There are several studies of the heat transference during the in-situ consolidation process, the thermal degradation probable effects and the degree of bonding. Recent analysis are mainly focused on the thermal residual stresses generated in the set which are the cause of the geometrical distortions from draft specifications.

The final state in manufacturing processes with thermoplastic materials is the cooling stage. During cooling, semicrystalline thermoplastics evolve to partially ordered structure from the melt, this process is called crystallization [1].

The first step to analyze the evolution of conversion during crystallization is the equation of Avrami (Eq. 1) or the extention of Ozawa for non-isothermal cooling programs. With these methods n (which defines the reaction mechanism) appears directly. However they do not permit to obtain as easily the activation energy values. Additionally, at a macroscopic level, crystallization rate consists of two processes: nucleation and nucleus growth. It is improbable that both mechanisms have the same

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activation energy so it is not possible to associate k with one only Arrhenius dependence with temperature [2].

$$\alpha = 1 - \exp(-kt^{n}) \quad (1)$$

In the case of PEEK and CF/PEEK crystallization, most of the authors have accepted the model suggested by Velisaris and Seferis [1] which is based in the works of Lee and Springer. Their studies are based in the Avrami model which determines the presence of a parallel mechanism of nucleation and growth. The model is divided in two components, the first one takes into account the existence of nucleus ($\mathrm{F_{vc1}}$) and it is governed by mechanisms of kinetics of crystal growing, meanwhile the second one ($\mathrm{F_{vc2}}$) is related with an additional nucleation process with crystal growth, both processes give the final form to the equation (Eq. 2). The parameters have been determined conducting several crystallization test.

$$\frac{\hat{c}}{\hat{c}_\infty} = w\left[1 - exp\left\{-C_{11}\int_0^\tau T exp\left[-\frac{C_{21}}{T-T_g+51.6} - \frac{C_{31}}{T(T_{m1}-T)^2}\right] n_1\tau^{n_1-1}dt\right\}\right] + \quad (2)$$

$$(1-w)[1 - exp\left\{-C_{12}\int_0^\tau T exp\left[-\frac{C_{22}}{T-T_g+51.6} - \frac{C_{32}}{T(T_{m2}-T)^2}\right] n_2\tau^{n_2-1}dt\right\}]$$

With $\hat{c}_\infty$the equilibrium volumen fraction crystallinity, $\hat{c}$ the crystallinity based on volumen fraction, T_g the glass transition temperature, T_{mi} the crystallization onset temperatures for the two crystallization mechanisms and w the weight factor.

There are other models which try to explain the same processes, main differences among them are not only the parameter values but the form of equation, that is the case of Tierney's and Cebe's [3,4]. Some of them are shown in Table 1.

Table 1 Kinetic parameters for PEEK and CF/PEEK

	Velisaris		**Tierney**		**Cebe**					
					1°C/min		5°C/min		10°C/min	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
T_m	593	615	611		662					
n	2.5	1.5	2.5	1.5	3.45	2	3.45	2	3.45	2
C_{1i}	2.08e10 (s^{-n})	2.08e10 (s^{-n})	2.08e10 (s^{-n})	2.08e10 (s^{-n})	1.92 (s^{-1})	0.68 (s^{-1})	1.03 (s^{-1})	2.03 (s^{-1})	0.63 (s^{-1})	1.06 (s^{-1})
C_{2i} (K)	4050	7600	4050	7600	1500	1300	1540	1130	1700	1650
C_{3i}	1.80e7 (K3)	3.20e6 (K3)	1.80e7 (K3)	3.20e6 (K3)	1e6 (K2)	6.2e5 (K2)	8e5 (K2)	6.1e5 (K2)	6.3e5 (K2)	4e5 (K2)
C_∞	0.37		0.37							
w (↑cooling rates)	0.75 neat 0.61 prepreg		0.61 (prepreg)		0.79		0.76		0.72	

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2. Experimental work

Due to the previously shown situation, it has been decided to analyse the process using the general equation of kinetics. There have been performed cooling tests with a Q2000 DSC (Differential Scanning Calorimeter) from TA Instruments. The tests consist of three steps (heating ramp-cooling ramp-heating ramp), after the first heating ramp an isothermal condition was maintained to ensure a full melting of the polymer, that is not completely true when processes as insitu consolidation because of the high heating and cooling rates implied. Four different cooling rates were applied (2ºC/min, 5ºC/min, 10ºC/min and 15ºC/min). The material under study is PEEK 450G supplied by Victrex and APC2/AS4 from Cytec.

During cooling from melt, the material experiences a heat release which is monitored by the equipment. The relation between the measured heat flow and conversion is shown in (Eq. 3) [2].

$$\frac{dQ}{dt} = Q_c \frac{d\alpha}{dt} \rightarrow \alpha = \frac{1}{Q_c}\int_0^t \frac{dQ}{dt}dt \tag{3}$$

Where Q_c represents the crystallization heat flow (the result of crystallization peak integration).

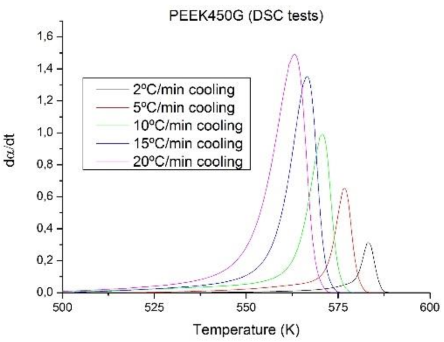

Figure 1 PEEK 450G DSC crystallization

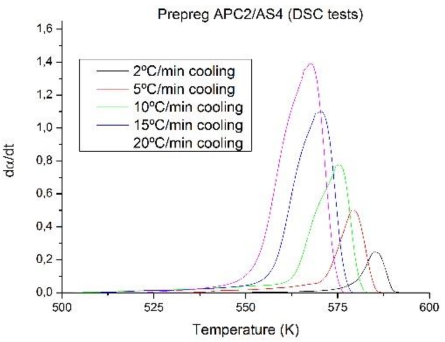

Figure 2 APC2/AS4 DSC crystallization

From these tests it is obvious that the higher the cooling rate the smaller the onset temperature of crystallization. APC2/AS4 materials shows advanced crystallization due to the presence of fiber which act as nucleation centre as is well know and referenced [5, 6]. Transcrystallization is one of the main effects caused by fibers, it consist of a perpendicular growth of crystals to the fiber. This growth appears until the impigment with bulk crystals happens. Nowadays the positive or negative effects of this crystal layer are not clear, but it is known that its creation is affected by fibre roughness, fibre treatments, thermal conductivity of fiber, manufacturing parameters, stresses on the surroundings of fibre and changes in molecular weight of matrix [6]. All of the aforementioned effects enforce the fact that kinetic parameters extracted by different authors for PEEK differ from the ones of others.

Also, when the melting is maintained during more time it is complex to develop bulk crystallinity. So, the areas that compose each process change its importance and that is relevant in processes as insitu consolidation.

To apply the kinetic study to the material the adopted procedure was the next one: firstly, the obtention of the activation energy of the process by using isoconvesional methods (cheking that the value is maintained with conversion. Based on [7], Eq. (4), correspons to differential Friedman isoconversional method can be applied to processes with $\beta<0$ (as crystallization). Reference [8] gives more information about the risks of using integral methods in this kind of analysis.

$$\ln(\frac{d\alpha}{dt})_{\alpha,i} = \ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \rightarrow \ln(\beta_i \frac{d\alpha}{dT})_{\alpha,i} = \ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{4}$$

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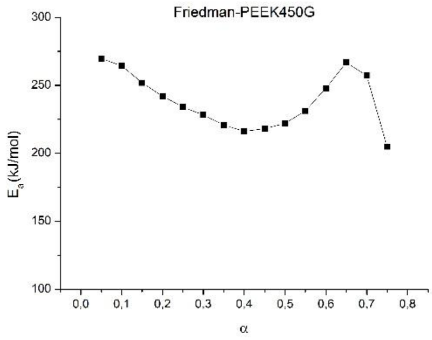
Straight lines are the result of plotting the left hand side of the above equation versus 1/T, its slopes permit to know the activation energy value for each conversion.



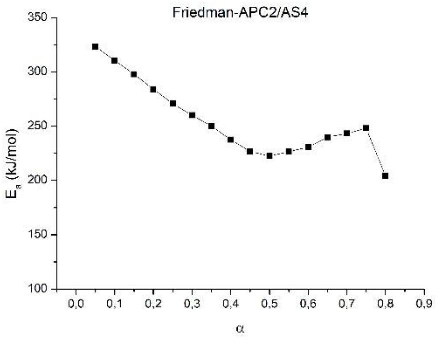


Figure 3 Activation Energy vs. conversion for PEEK 450G. Friedman method

Figure 4 Activation Energy vs. conversion for CF/PEEK. Friedman method

The variation in activation energy with conversion is higher than the 20% allowed to consider one only processes or reaction mechanism implied. Based on that evidence, it has been applied the procedure described in [9] and [10], dividing the whole curve in several ones by deconvolution. To determine the number of peaks in the deconvolution, the shape of the curve E_a vs. conversion is taken into account, in this case, there are an initial process with a high activation energy which evolves to at least two new processes with lower values of activation energy. The deconvolution was done with the software Fytik, employing Fraser-Suzuki functions and Levenber-Marquardt as the method for conducting the fitting.

For pure PEEK 450G, the best deconvolution is mainly reached with two Fraser-Suzuki functions, there are really three functions but the first one only represents the induction time and it would be possible to supress it by avoiding the use of first experimental data, in fact, the correspondent areas are minimal. Fig. (5) and (6) shows the results. The second and third fuctions represent an important contribution to the whole process. For each peak it has been developed the optimization showed in the previous added references to obtain the values of activation energy, pre-exponential factors and the orders of the reaction mechanisms. This optimization search the values of those parameters by forcing the representation of ${}^{d\alpha}/_{dt}\big/_{(1-\alpha)^n\alpha^m}$ vs $1/T$ to fit a straight line, Fig. (8).

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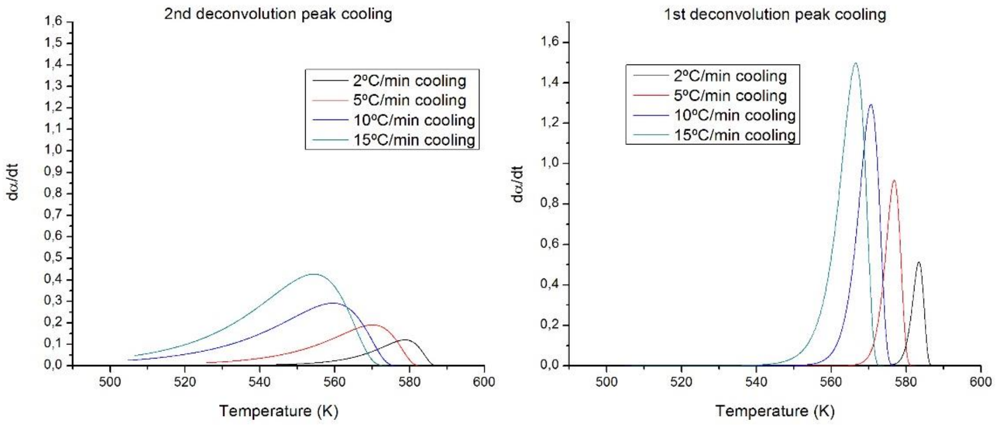

Figure 5 Deconvolution process for PEEK 450G

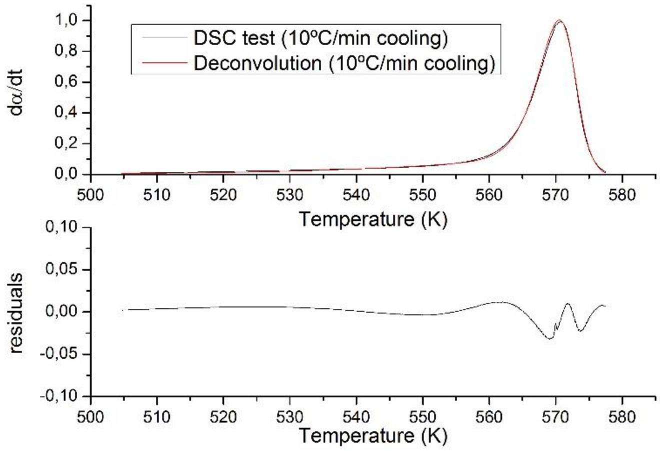

Figure 6 Residuals in deconvolution for 10ºC/min cooling program

For CF/PEEK the same procedure has been applied, Fig. (7). As it can be seen, it is not possible to obtain a good fit by using the same number of functions as there were used with neat PEEK.

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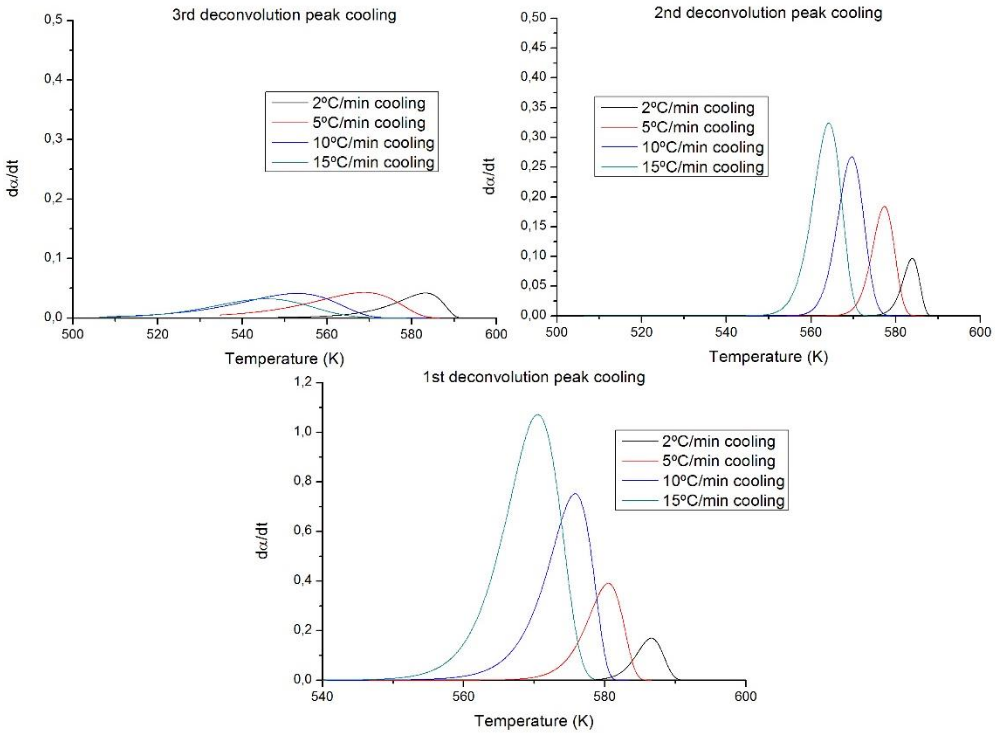

Figure 7 Deconvolution for CF/PEEK

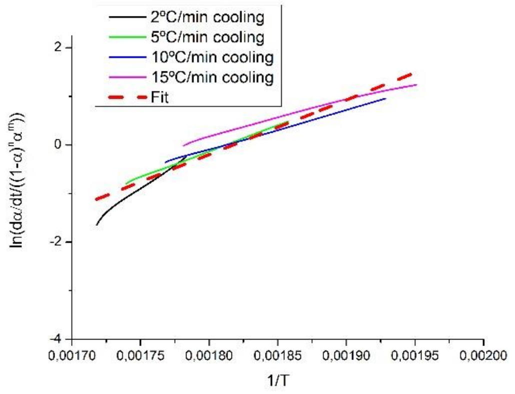

Figure 8 Optimization for secondary process (PEEK450G)

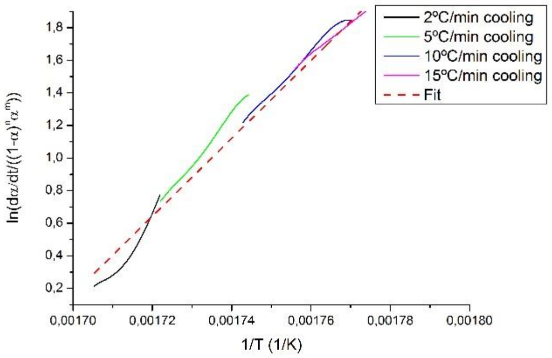

Figure 9 Optimization for secondary process (Prepreg APC2/AS4)

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2. Results

Table 2 contains the numerical results of these optimizations.Obtained values for activation energy are negative. Other studies conducted with PET [2] show a change in activation energy from negative to positive values, but positive values appear when conversion reaches 0.99 (out of our study range). This reference does not use this methodology to obtain a complete kinetic equation but to find clues about the general process experienced by the material.

Table 2 Resulting values after conducting isoconversional method and optimization

Parameter	**PEEK 450G**		**Prepreg ACP2/AS4**		
	1st process	**2nd process**	**1st process**	**2nd process**	**3rd process**
	α range (0.05-0.8)	**α range (0.1-0.9)**	**α range (0.05-0.8)**	**α range (0.05-0.8)**	**α range (0.05-0.8)**
n	1.269	1.703	1.479	1.287	1.541
m	0.658	0.394	0.64	0.672	0.514
E_a	-192.710	-93.319	-182.539	-184.987	-83.89
A	1.029e-17	1.3797e-9	1.266e-16	5.015e-17	1.295e-8
R^2	0.946	0.934	0.902	0.959	0.970
Pearson	0.973	0.966	0.950	0.979	0.985

Table 3 Resulting weight factors

Cooling speed (°C/min)	**PEEK 450G (w)**		**Prepreg ACP2/AS4 (w)**		
	1st process	2nd process	1st process	2nd process	3rd process
2	0.568	0.355	0.319	0.243	0.411
5	0.638	0.313	0.222	0.241	0.518
10	0.719	0.230	0.123	0.205	0.635
15	0.832	0.156	0.062	0.183	0.718

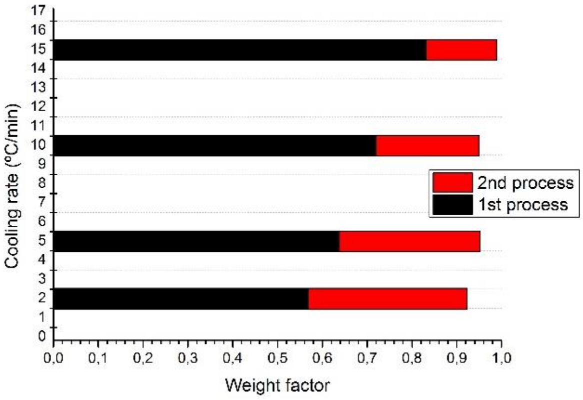

Figure 10 Weight factors evolution with cooling rate (PEEK 450G)

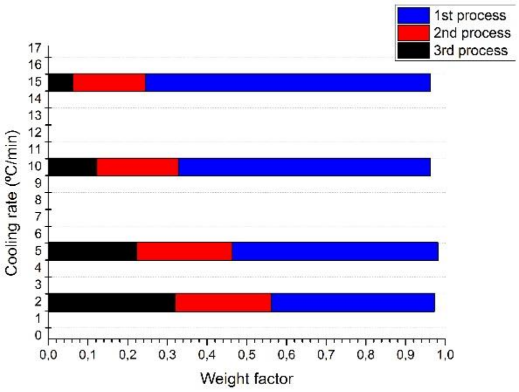

Figure 11 Weight factors evolution with cooling rate (APC2/AS4)

3. Conclusions

The studies over PEEK 450G show a similar tendency between conventional models including the contribution of nucleation and growth. The initial mechanism has a good correlation with A2 reaction model; random nucleation and growth of nuclei through different nucleation and nucleus growth models, and the secondary one has a good correlation with F1; random nucleation followed by an instantaneous growth of nuclei. The case of prepreg is quite different because it was not possible to fit the curve with only two processes but with three, A2 type. The differences can be associated with the

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fact that the matrix are not exactly the same in the neat material and in the composite. This analysis gives the possibility of detecting the existence of reaction mechanisms, necessary information about the crystallization processes and the magnitude of each independent mechanism, this additional process could be related with nucleation over fibers.

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