IMPACT OF PROCESSING PARAMETERS ON VOID CONTENT AND MECHANICAL PROPERTIES OF PEEK/CF THERMOPLASTIC COMPOSITES

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Abstract

Key parameters of different high performance thermoplastic manufacturing processes were modified in this work to obtain different levels of defectology in thermoplastic APC-2 AS4 (CF/PEEK) samples and to study the impact on the material behavior. Different laminates with a stacking sequence of $[+45/-45]_{4S}$ were manufactured by Out of Autoclave (OoA) with Vacuum Bag Only (VBO). Consolidation temperature was modified from the optimal cycle in order to obtain samples with different degrees of porosity and consolidation. PEEK is a high density resin and, therefore, consolidation temperature is directly related with the final consolidation degree of the specimens. All the samples were submitted to ultrasonic NDT, void content testing, optical microscopy analysis and shear mechanical testing to obtain the relation between manufacturing parameters and material integrity. Several methods for obtaining void content were explored and compared. Results show that shear properties are strongly dependent on the porosity in the matrix.

1. Introduction

High performance thermoplastic composite materials have been deeply studied in the last decades with the aim of being incorporated to the aeronautical and automotive industries. This fact is due to the advantages that thermoplastic matrix composites may offer, such as great mechanical properties, good corrosion resistance or reprocess ability, among others [1-2]. Despite its many advantages, high performance thermoplastic composites also have a counterpart mainly driven by high processing temperatures due to the high melting point of the polymers.

Even though they have been largely researched during many years, it is in the actual moment when the industry is about to incorporate them in aircraft structures due to the prompt evolution of the automatic lamination technologies during the last years [3]. Technologies such as in-situ consolidation assisted by different heat sources or fast lamination with ultrasonic welding [4] are being developed and optimized to offer high production and quality levels that the industry is demanding.

However, thermoplastic CFRP must overcome quality requirements and quality control to be incorporated in the aeronautical primary structures. For this reason, it is mandatory to characterize thermoplastic composite materials in terms of mechanical and physical-chemical properties in addition to ultrasonic response. Most of the works that can be found in the literature are related to thermoset composite materials characterization [5-6], which are the most broadly used in aeronautical industry. However, authors as Zhang *et al*. and Patou *et-al*. [7-8] characterize the void formation and distribution in thermoplastic pre-impregnates materials and their impact on properties, respectively.

Considering the consolidation process as the most critical point of formation of defects, several CF/PEEK (APC-2 AS4) laminates were produced in this work applying some deviations from the optimal parameters suggested by the product manufacturer [9]. Heat and pressure are the key parameters which drive the consolidation process of thermoplastic manufacturing and, consequently, these are the parameters which are mainly altered in the present work to obtain porosity in the laminates. Different levels of lack of consolidation and void content were achieved in order to study the impact of the porosity in mechanical and physical-chemical properties. Every laminate was subjected to C-Scan non-destructive testing in order to determine the attenuation level of each laminate and to determine the location of the coupon machining. A void context range including values between <1% and >10% were achieved and compared with the mechanical In-Plane Shear (IPS) strength and modulus, and physical-chemical behavior of the CF/PEEK composites.

2. Materials and experimental procedure

In order to obtain samples with different void content and to evaluate the impact of the porosity in the integrity of the specimens, six 300x300 mm thermoplastic composite laminates were manufactured. The material consists in a commercial APC2-AS4 carbon fiber/PEEK unidirectional tape, manufactured by Cytec®. All laminates were laid-up with the same stacking sequence [+45/-45]. Plies were hand laid-up and every ply was fixed with welding points. All laminates were consolidated in an IDEC oven by means of vacuum bag-only (VBO) with polyimide bags. The different levels of porosity were achieved by performing modifications from the optimal cycle given by the material supplier [9]. Consolidation cycle parameters for the modified cycles are shown in Table 1, where six different cycles are studied. All the consolidation cycles were monitored with several thermocouples and a vacuum gauge connected to the vacuum bag.

All specimens were inspected with automatic Tecnitest TRITON 8000 TT+ equipment. C-Scans for all the laminates were obtained and the machining of the coupons was defined according to the different attenuation levels to perform an indicative correlation between results.

Six coupons with 230x25x2.16mm were machined from each laminate for shear testing according to standard EN6031 [10]. At least six coupons 20x10x2.16mm were obtained in each thermoplastic laminate for void content testing and microscopy. The same samples were used for void content analysis and microscopy to compare the results between tests.

Table 1. Consolidation cycles of APC2-AS4 for porous samples manufacturing in the present study.

Consolidation cycle / Laminate	Consolidation temperature (°C)	Consolidation dwell (min)	Vacuum (mbar)	Ramp up (°C/min)	Cooling down (°C/min)
L1 (control)	400	15	2	2	2
L2	340	15	2	2	2
L3	350	15	2	2	2
L4	360	15	2	2	2
L5	370	15	2	2	2
L6	430	15	2	2	2

Void content level was measured by using different techniques: densities method, acid digestion and optical image analysis. Densities method was performed according to the international standard ISO 1183-1 [11] and acid digestion was performed in accordance to EN 2564 [12]. Void content values were calculated from density taking into account the Fiber Areal Weight (FAW) of the material, in addition to nominal values of fiber and matrix densities. In this way, void content could be calculated from the density value prior being polished for microscopy and degraded for acid digestion method. In relation to optical analysis, a Nikon Eclipse LV150 was used for the micrographs acquisition of coupons cross-section. Leika Application Suite software v4.9.0 was used for the image analysis in order to create binary images and obtaining void content measurements. The software allowed setting a color threshold and to create a binary image. In this way, voids, which are black in the original image, can be turned to red and quantified. An example of this procedure is shown in Figure 2

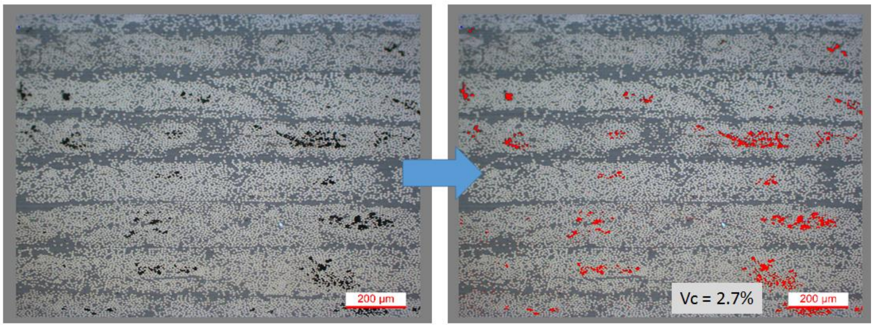

Figure 1. Binary image creation for void content value by image analysis.

3. Results and discussion

C-Scans obtained from every laminate are shown in Figure 1. Different levels of attenuation can be deducted from the images. Laminate 1 is stablished as the control. Laminates 2-4 show areas surpassing attenuation levels above 6dB. A 6dB attenuation level represents a threshold for the quality control in aerospace industry. The whole area of laminate 2 exceeds 18dB of sonic attenuation, involving a high porosity level. Laminate 3 was processed with a temperature slightly higher than the melting point of PEEK. Therefore, some areas with poor consolidation are observed. Laminate 4 shows less attenuation than laminates 1-2. However, the C-Scan is not perfectly homogeneous and some attenuated lattice is found in the image. Laminate 5 shows homogeneous attenuation levels and it appears to be similar to the control laminate. Even though laminate 6 was processed at a high temperature of 430ºC, no indications reaching the threshold level can be found in the C-Scan.

The void content values obtained by different techniques are compiled in Table 2. Laminate 2 shows the highest void content value, due to the fact that the consolidation temperature reached in the cycle was in the threshold of the melting point of PEEK, 342ºC. Laminates 3-5 show a decreasing in the porosity levels as the consolidation temperature is closer to the optimal consolidation temperature. However, all samples, except control laminate 1 and laminate 6 are still over the aeronautical composites requirements in terms of void content, considered less than 2%.
Void content was also acquired by image processing. Void content values obtained from the optical tests are also reported in Table 2.

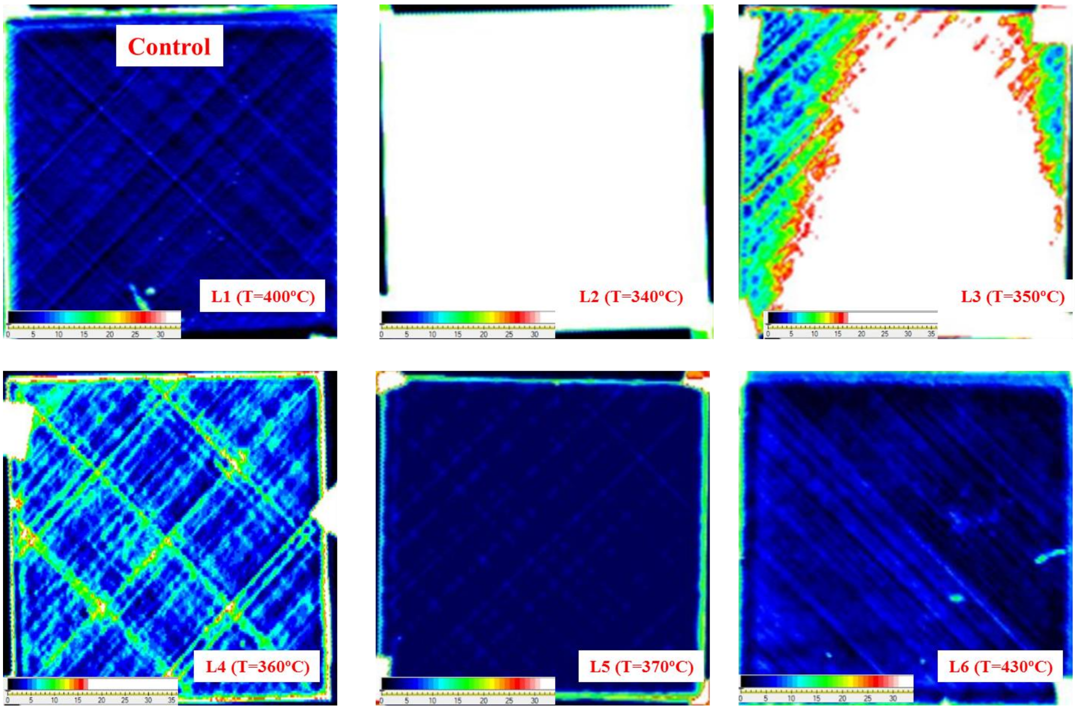

Figure 2. C-scans for laminates 1 to 6.

Table 2. Void content values obtained by three different techniques: densities, acid digestion and optical image.

	Densities method			Acid digestion			Optical image
Consolidation cycle / Laminate	Void content (%)	STDEV	COV (%)	Void content (%)	STDEV	COV (%)	Void content (%)
L1 (control)	1.4	0.2	16.9	1.1	0.3	29.0	0.4
L2	16.9	2.7	15.9	14.5	1.3	8.9	12.3
L3	3.6	0.9	25.0	3.8	1.9	49.8	4.4
L4	2.4	0.4	17.7	2.4	1.6	68.2	3.7
L5	2.7	0.4	15.7	2.2	0.1	5.9	3.7
L6	1.7	0.0	1.2	0.8	0.1	3.0	0.4

Micrographs were taken in order to carry out a correlation between void content and ultrasonic testing with optical images. Figure 3 shows cross section of samples from laminates 1 to 6. In this case, the optical images show how different consolidation temperatures can impact on the void distribution in thermoplastic laminates. As it may be expected from void content analysis in Table 2, laminate 2 shows the largest defectology including lack of consolidation between plies (similar to delamination in thermoset composites), intralaminar porosity, resin pockets and even matrix cracks. Since the consolidation temperature was elevated in the rest of the laminates, the defectology within the samples decreased. Less amount of porosity can be found in laminate 4, although interply void content observed in Figure 2 indicates bad consolidation between plies. Laminates 4-5, with consolidation temperatures closer to the optimal consolidation temperature, only show intralaminar voids, indicating that the high viscosity of the resin in the cycle blocked the removal of the trapped air from the panels.

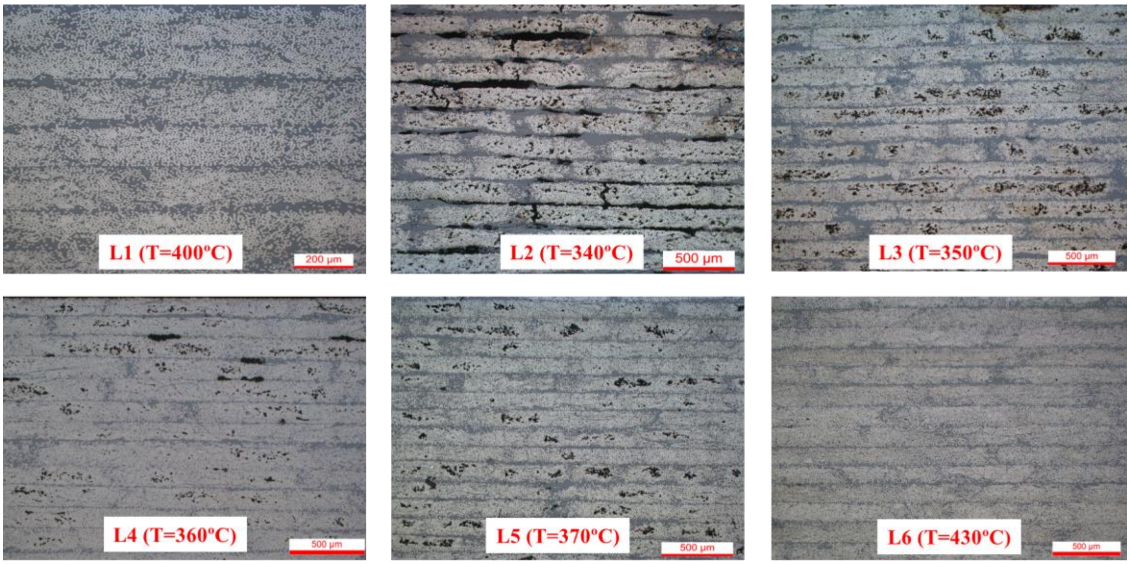

Figure 3. Cross-section micrographs for laminates L1 to L6.

Regarding the mechanical characterization, results from In-Plane Shear testing can be visualized in Table 3 including coefficient of variation and standard deviation. Results are also shown in Figure 4. Laminate 1 has been considered as the baseline because it was manufactured according to the material supplier recommended cycle. In-Plane shear strength is higher for temperatures closer to the optimal consolidation temperature. There is no significant difference between laminates 4 and 5 even though their consolidation temperature differs in 10ºC (from 360ºC to 370ºC). None of the laminates manufactured (with the exception of laminate 6) reached more than 70% of the shear strength value of the baseline laminate, which remarks the great importance of the temperature in the diffusion of the resin and the evacuation of trapped air. Even though it was expected to obtain a significant level of defects in laminate 6 due to the high processing temperature, void content and mechanical properties are similar to the baseline. Based on this, a higher temperature should be reached to obtain degradation effects in the APC2-AS4 laminates.

In terms of G_{12} modulus, all laminates reached at least 90% of the baseline modulus, with the exception of laminate 2, which was manufactured in the harshest conditions. Laminate 5 revealed a slightly higher modulus than the baseline.

Table 3. Mechanical IPSS results normalized in % in relation to the baseline (laminate 1).

In-Plane Shear testing				
Consolidation cycle / Laminate	Strength (% normalized to baseline)	COV (%)	G_{12} modulus (% normalized to baseline)	COV (%)
L1 (baseline)	100.0	2.0	100.0	2.0
L2	14.6	4.0	77.9	2.0
L3	39.9	36.0	90.8	6.0
L4	67.4	2.5	99.1	2.4
L5	68.6	1.7	103.7	1.9
L6	98.9	3.0	93.7	5.0

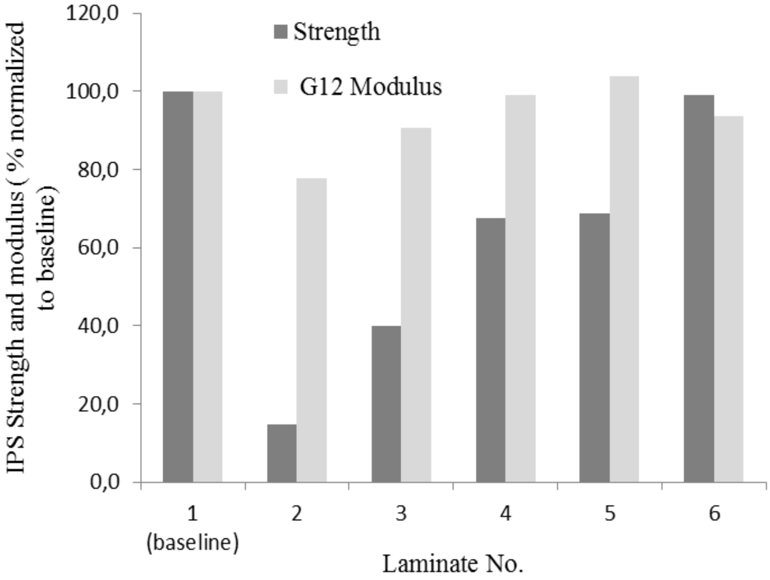

Figure 4. Results from In-Plane Shear testing, normalized to the laminate 1 (baseline)

A correlation between the mechanical values and the void content was performed as shown in Figure 5. Void content is presented in logarithmic scale. Trends observed show that higher void contents, and, therefore, lower consolidation temperatures, causes lower strengths and modulus in the laminates. A predictive trend lines have been included in the graph. According to the trending lines, reference values of in-plane shear strength could only be achieved with porosity levels less than approximately 1.75% in void content. The prediction curve for shear G_{12} modulus is not as restrictive as the case of strength; and acceptable values of 80% of the baseline could be achieved with higher porosity levels.

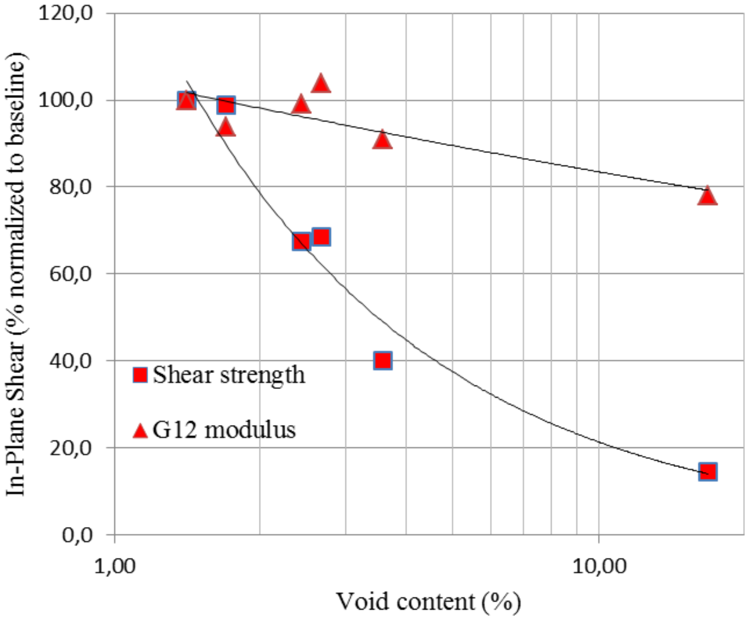

Figure 5. Correlation between In-Plane Shear (strength and modulus) and void content

4. Conclusions

CF/PEEK (APC-2 AS4 from Cytec®) laminates were manufactured with manufacturing parameters deviated from the optimal cycle recommended by the material supplier, in order to achieve different porosity levels. The recommended consolidation temperature is set at 400ºC. Mechanical and physical-chemical analyses were performed to the samples obtained from the laminates. Void content from each laminate was obtained via different methods including densities, acid digestion and image processing. A correlation between the mechanical properties and the consolidation temperature was carried out in relation to a baseline level. Laminates manufactured at 360ºC and 370ºC reached 70% of the strength reference value, meanwhile laminates processed at lower temperature reached less than 50% of the strength. The laminate processed at 430ºC presented similar mechanical values than the reference; therefore, no degradation was caused on the specimen. Higher consolidation temperatures are required to cause degradation damage. Trending lines of shear strength and modulus were obtained in relation with the void content of the samples. Strength values of 80% of the baseline could be achieved with porosity levels less than 1.75% approximately. Shear modulus values remained above 75% of the baseline even in specimens with a 16% of void content. If only a low void content range is considered (<4%), a linear correlation may be also performed to predict the material shear behavior.

To perform more accurate trending lines and to obtain an analytic expression to correlate mechanical properties in relation to void content, more laminates should be manufacture to validate the correlation by means of ensure repeatability in the results. In addition to that, a quantitative correlation should be performed with the sonic attenuation.

Further work will be performed following this study line and including a study of the crystallinity of the material at different temperatures and its influence in the material behavior. Higher processing temperatures will be reached to define the impact of the degradation in the mechanical properties. X-Ray computed tomography is highly recommended to study the inner defectology of the samples.

References

[1] M. Kutz. *Applied Plastics Engineering Handbook. 2nd edition. Processing, Materials and Applications*. Elsevier, 2016.

[2] M. Biron and O. Marichal. *Thermoplastics and Thermoplastic Composites*. Elsevier, 2013.

[3] Z. Qureshi, T. Swait, R. Scaife and H.M. El-Dessouky. In situ consolidation of thermoplastic prepreg tape using automated tape placement technology: Potential and possibilities. *Composites: Part B,* 66: 255-267, 2014.

[4] C. Modi. Thermoplastic composites: in-situ consolidation or in-situ welding?. *Proceedings of the 19th International Conference on Composite Materials. Montreal, Canada,* July 28 – August 2, 2013.

[5] M.L. Costa, M. Almeida and M.C. Rezende. The influence of porosity on the Interlaminar shear strength of carbon/epoxy and carbon/bismaleimide fabric laminates. *Composites Science and Technology,* 61: 2101–2108, 2001.

[6] L. Liu, B-M. Zhang, D.F. Wang and Z-J. Wu. Effects of cure cycles on void content and mechanical properties of composite laminates. *Composite Structures* 73 : 303–309, 2006.

[7] D. Zhang, A. Levy and J.W. Gillespie. On the Void Consolidation Mechanisms of Continuous Fiber Reinforced Thermoplastic Composites. *Proceeding of SAMPE 2012, Baltimore, MD,United States of America.* May 21-24, 2012.

[8] J. Patou and D. De Luycker. Influence of void content on the mechanical properties of Carbon/PPS laminates. *Proceedings of the 17th European Conference on Composite Materials Munich, Germany*, 26-30th June, 2016.

[9] APC2-AS4 Thermoplastic polymer. Technical data sheet https://www.cytec.com/sites/default/files/datasheets/APC-2_PEEK_031912-01.pdf

[10] EN 6031. European Standard. Aerospace series – Fiber reinforced plastics – test method - determination of in-plane shear properties (±45º tensile test), 1995.

[11] International Standard. Plastics – methods for determining the density of non-cellular plastics. *ISO1183-1, 2012*

[12] EN 2563. European Standard. Aerospace series - Carbon fiber laminates – determination of the fiber, resin and void contents, 1998.