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Optimization of Curing Process for Polymer-matrix Composites Based on Orthogonal Experimental Method

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Abstract: In this paper, the orthogonal experimental method was carried out to optimize the curing process of aeronautical composite X850/T800 in autoclave process. Four important curing parameters including curing pressure, heating rate, curing temperature and heat preservation time were taken into account, and sixteen samples were fabricated to study the effects of the four parameters mentioned above on the curing quality by interlaminar properties test and microstructure analysis. The interlaminar properties and the interfacial bonding quality of these samples were studied by the short-beam three points bending test and scanning electron microscopy, respectively. Results revealed that the optimal curing process of X850/T800 composite laminate should be as follows: curing pressure of 0.6 MPa, heating rate of 1.5 ^{o}C/min, curing temperature of 160 ^{o}C, and heat preservation time of 120 min.

Keywords: Orthogonal method, Polymer-matrix composites, Curing process, Optimization

Introduction

Advanced polymer-matrix composites consist of continuous fibers and resin, are widely used in the main load-bearing or secondary load-bearing components for large aircraft due to their excellent performance, such as light weight, high specific strength and stiffness [1,2]. Various of methods are usually employed to fabricate the composite components, such as autoclave process [3], resin transfer molding process [4], vacuum film infusion [5] and electron beam curing process [6]. At present, autoclave process has become the major way for manufacturing the high-performance composite components. In which the semi-finished composite prepreg laminas are stacked on mold and squeezed closely at a vacuum state, and undergoing the technological process of heating, pressurization, heat-preservation, cooling, the aerospace-level components are ultimately fabricated. Many complex physical and chemical reactions exist in the curing process, such as the curing reaction of resin, resin flow and fiber compaction, which influence the fiber/matrix interfacial bonding behavior [7-9]. The distribution of forming pressure and curing temperature are the two important factors for the quality of component in autoclave process, and the uniformity of them makes it possible to obtain the optimal curing quality. Therefore, the curing parameters of autoclave process have a critical impact on the stability and reliability of internal quality for composite components.

Most scholars have studied the influences of curing parameters on curing quality and mechanical properties of advanced composite component and have gotten lots of achievements. Aifred *et al.* reported the relationship between curing temperature and the resin flow for advanced composites [10]. Je *et al.* simulated the pressure field and temperature field in the curing process of advanced composites [11]. Jung *et al.* studied the effect of heating process on deformation of composite laminates, and found that the deformation of composite laminates increased as the curing temperature increased [12]. Olivier and Costa analyzed the mechanism of curing pressure on pore defects of advanced composites and established the quantitative relationship between the void content and the mechanical properties [13,14]. However, relative researches mentioned above mostly focused on the single parameter, which were lack of certain systemic. Effect of single curing parameter on forming quality of composite component is difficult to guide reasonably formation in curing process. While other drawbacks such as high capital investment and low efficiency, are also the major reason to restraint the development of autoclave process. Therefore, the optimization of curing process is the necessary, which can enhance the competitive advantage of autoclave process.

Orthogonal experimental method is an effective way to solve the experimental problems of double factors or multi-factors tests. In which this method can reasonably arrange the experiment and reduce the test times. The full experimental results can be obtained by analyzing of the fractional experiment, and the working efficiency can be improved [15]. However, few researches have explored the application of orthogonal experimental method to optimize the curing process for polymer-matrix composites. This paper mainly aims to determine an optimal curing process conditions including curing pressure, heating rate, curing temperature, and heat preservation time for aeronautical composites X850/T800 based on the orthogonal experimental method. The short-beam three points bending test and scanning

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electron microscopy method were employed to analyze the curing quality of composite laminate with various parameters, and all of these can assist in optimizing the curing process by orthogonal experimental method.

Orthogonal Experimental Method

Some analysis steps are included in the orthogonal experiment, such as the determination of experimental factors and levels, the choice of experimental scheme, and the mathematical analysis on test results *et al.* By which the impact of various factors on the significance of the experimental index can be analyzed, the importance of various factors can be clarified, and ultimately the optimum factors conditions can be obtained.

The Basic Principle

This method is mainly based on the orthogonal array. The orthogonal array could be used to the overall design, comprehensive comparison, and statistical analysis. An orthogonal array of n trials with k number of t level factors, it will be denoted as $L_n(t^k)$ [15]. Take the orthogonal array L_9 (3^3) for an example, the full experiment would be arranged twenty-seven times, but nine experimental times is carried out in the orthogonal array. It can be seen in Figure 1 that, each intersection point in cube represents an experiment, and the selected tests are marked by red points. If every plane represents a level, it has nine planes in total. In this cube, every plane has three red points, and every segment has one red point. The red points selected are distributed evenly among these intersection points. Therefore, nine tests selected have a strongly representativeness in orthogonal array, and could reflect results of the full experiment, which is the unique characteristic of orthogonal experimental design. This characteristic can be used to design and arrange as little as possible the number of trials in order to find out the optimum process conditions.

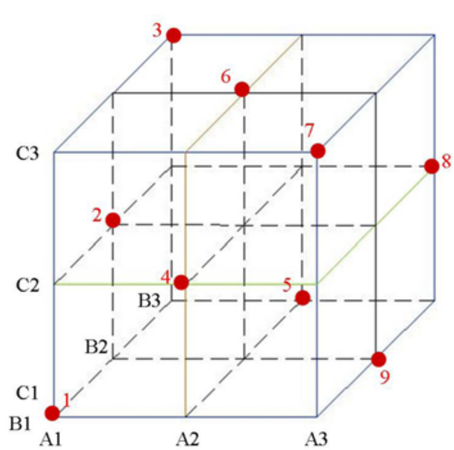

Figure 1. Nine test points in the three-dimensional space.

Table 1. Factors and levels of the orthogonal experiment

Factors and levels	A (MPa)	B (°C/min)	C (°C)	D (min)
1	0	2.5	160	90
2	0.2	3.5	170	120
3	0.4	4.5	180	150
4	0.6	1.5	190	180

Where A is cure pressure, B is heat rate, C is cure temperature, and D is heat preservation time.

Orthogonal Experimental Design

The autoclave process for the composite components needs to undergo a long process of heating, pressurization, heat preservation, and cooling in the autoclave tank, in which the internal resin would react with the cross-linking reaction and their states would be changed from the liquid to the rubber state until it was changed into a three-dimensional network structures. The resin states significantly influence the forming quality of composite components and determine the fiber/matrix interfacial bonding behaviors. Therefore, four important curing parameters including curing pressure, heating rate, curing temperature, and heat preservation time were selected in the orthogonal test. An orthogonal experimental design L_{16} (4^4) was designed to evaluate the effect of curing parameters on interlaminar shear strength (ILSS) for cured composite laminates. The composite laminates were fabricated by manual paving in autoclave process. The designed laminates dimension was 150 mm (length)×100 mm (width)×2 mm (thickness), and the final thickness was approximately 1.8-2.2 mm. The range value of each cure parameters has been obtained according to the actual engineering practice, as is shown in Table 1.

Difference Analysis Method

The difference analysis plays an important role for orthogonal experimental results analysis. Firstly, it can be used to analyze the experimental results directly. Secondly, the influence of every factor on results can be shown. In the orthogonal tests, sixteen composite laminates were fabricated by different cure cycles and their ILSS results were used for the difference analysis.

Assuming the ILSS result of i level in j factors is represented by y_{ij}, and thus the sum of the ILSS results in i level can be expressed as follows:

$$T_{ij} = \Sigma_{k=1}^{m} y_{ij}^{k} \quad (1)$$

where, m is the number of factors in orthogonal experiment.

The mean value (M_{ij}) of the sum of the ILSS results in i level can be expressed as follows:

$$M_{ij} = \frac{p}{n} T_{ij} \quad (2)$$

where, n is the total number of orthogonal test, and p is the number of levels in orthogonal test.

The difference value of j factor is defined by R_j, and the mathematical model is as follows:

$$R_j = \max M_{ij} - \min M_{kj} \quad (3)$$

Variance Analysis Method

In order to assess the influence of each factor on the ILSS accurately, the variance analysis was employed. This method can assist to analyze the actual effect of each factor through the F-test, if the F value is higher than the maximum critical value, the effect is significant. If the F value is less than the minimum critical value, the effect can be neglected. The fluctuations of the ILSS results obtained by orthogonal experiments can be expressed by the following equation:

$$S_T = \sum_{i=1}^{n}(x_i - \bar{x})^2 \quad (4)$$

where, S_T is the square sum of total deviation, x_i is the mean value of ILSS for the i group, and $\bar{x}$ is the mean value of all ILSS results in the orthogonal test.

Let, $T = \sum_{i=1}^{n} x_i$, and so $\bar{x}$ can be expressed:

$$\bar{x} = \frac{T}{n} \quad (5)$$

If square sum of the j factor deviation is represented by S_j, and the equation of S_j is as follows:

$$S_j = \sum_{i=1}^{p}(\bar{T}_{ij} - \bar{x})^2 \quad (6)$$

The square sum of the experiment errors deviation represented by S_e is the difference between square sum of the total deviation and square sum of deviation of all factors, which is caused by random errors. The mathematical model can be expressed as follows:

$$S_e = S_T - \sum_{j=1}^{m} S_j \quad (7)$$

According to the statistical principle, the homogeneity test of variance, which is known by F-test, can be obtained as follows:

$$F = \frac{S_j}{f_j} \Big/ \frac{S_e}{f_e} \quad (8)$$

where F is inspection value of the j factor, f_j is degree freedom of the j factor, and f_e is degree freedom of the experimental errors.

Experimental

Material

The composite material used in this study was manufactured by unidirectional carbon fiber (T800) reinforced/ epoxy (X850) prepregs. Pre-impregnated sheets were supplied by Commercial Aircraft Co., Ltd., China with fiber volume fraction of 65 % and area density of 190 g/m^2. Cytec's CYCOM X850 resin system, as the next generation epoxy resin for aerospace industry, is formulated with the most advanced epoxy chemistry available to provide good heat resistance, high specific strength and adhesion properties.

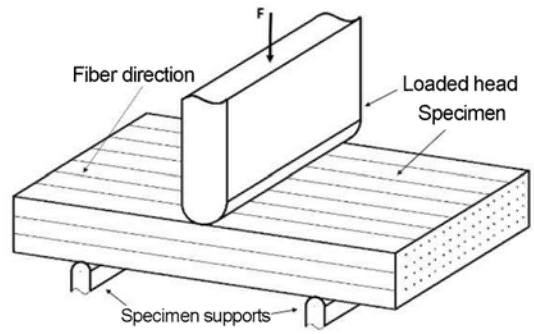

Figure 2. Schematic diagram of the short-beam three points bending experiment.

Tested Methods

Mechanical Properties Test

The interlaminar shear strength were determined according to Chinese standard JC/T 773-2010 using the short-beam three points bending test method, which put the sample on the two bearing, and applies the bending load at the center of the bearing, the Schematic diagram of the short-beam three points bending experiment as is shown in Figure 2. The sample was taken of the mechanics performance test that was conducted on CMT5105 tensile testing apparatus (produced by Sansi Taijie Co., Ltd., China) and five tests for each group of samples were performed under stroke control at a crosshead speed of 1 mm/min. The specimens were cut by diamond saw to nominal dimensional of 20 mm×10 mm (length×width). The interlaminar shear strength of the composite samples was determined according to equation:

$$\tau_{ILSS} = \frac{3}{4} \times \frac{F}{bh} \quad (9)$$

where F is the maximum load (N), b is the sample width (mm) and h is the sample thickness (mm).

Microstructure Observation

In order to explore the influence of curing parameters on the forming quality of the laminates, the interface bonding state of the tested samples should be need to further observe. The scanning electron microscopy (SEM, model: TESCAN MIRA3 LMU) was employed to examine the fracture surfaces of tested samples.

Results and Discussion

Tested Results Analysis

The effects of curing pressure, heating rate, curing

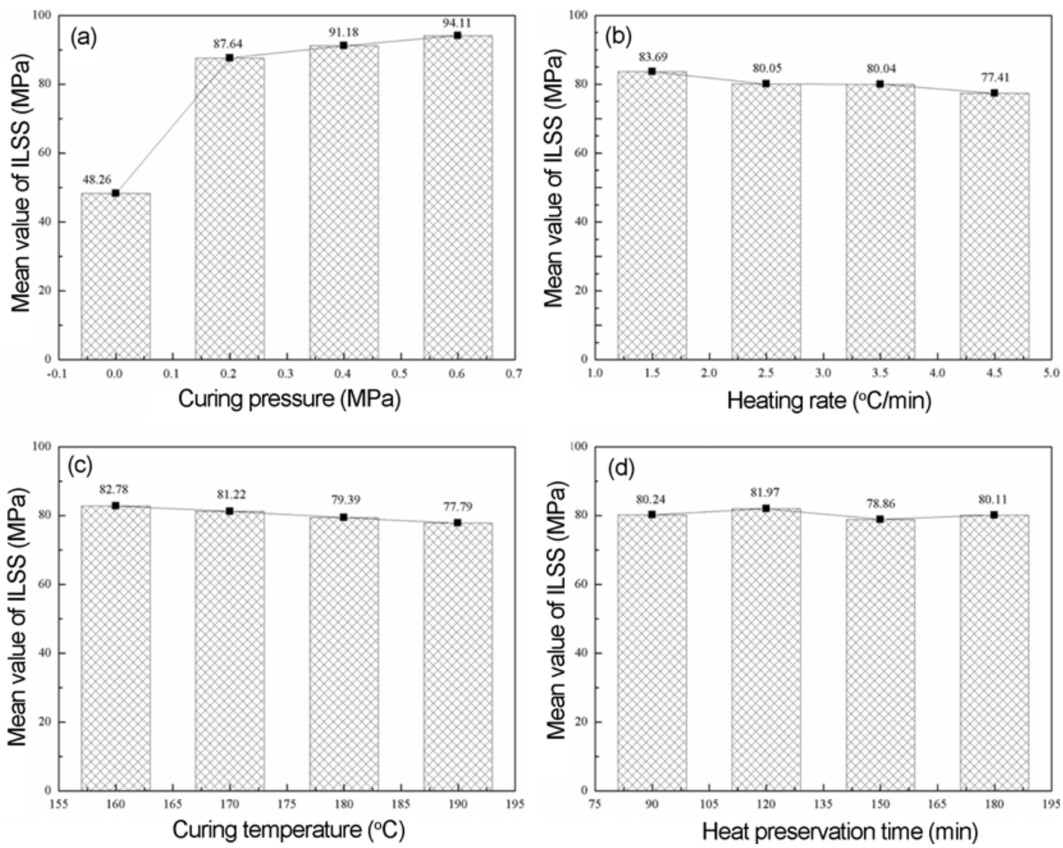

Figure 3. Plot of curing parameters on the ILSS results; (a) curing pressure, (b) heating rate, (c) curing temperature, and (d) heat preservation time.

temperature, and heat preservation time on the ILSS results were shown in Figure 3. Figure 3(a) showed the results of curing pressure on the ILSS, where the ILSS increased from 48.26 MPa to 94.11 MPa as the value of curing pressure increased from 0.0 MPa up to 0.6 MPa, while the ILSS increased by 48.72 %. The increment of ILSS accelerated as the value of curing pressure was below 0.2 MPa and when curing pressure was higher than 0.2 MPa, the increment of ILSS increased slowly. The ILSS decreased as the heating rate and curing temperature increased, as can be seen in Figure 3(b) and Figure 3(c) respectively. When the value of heating rate increased from 1.5 ^{o}C/min to 4.5 ^{o}C/min, the ILSS decreased from 83.69 MPa to 77.41 MPa, and the ILSS decreased by 7.50 %. When the value of curing temperature increased from 160 ^{o}C to 190 ^{o}C, the ILSS decreased from 82.78 MPa to 77.79 MPa, and the ILSS decreased by 6.03 %. Their amplitude of decrease was small comparatively. It can be seen in Figure 3(d) that the variation of ILSS results was small and irregular as the value of heat preservation time increased from 90 min to 180 min. This can be illustrated that heat preservation time has no effect on the ILSS, and the effects of heating rate and curing temperature on the ILSS are small slightly. However, the effect of curing pressure on ILSS is the most significant of all.

In order to study the influence of curing pressure on the ILSS of cured laminates, the fracture surfaces of tested samples under different curing pressure were observed by the SEM analysis, as is shown in Figure 4. Figure 4(a) shows the fracture surface cured under curing pressure of 0.0 MPa, where the surface of fibers is smooth and the gap between the fibers is evident. Some fibers are even inclined and rotated due to the lack of support from the resin matrix. The resin rich pocket is frequently observed, which means impregnation of resin is poor and inhomogeneous, leading to accelerate the decrement of ILSS. SEM image in Figure 4(b) illustrates the typical interface debonding under the shear loads. Fibers from the upper layer are debonded from the matrix in the adjacent lower layer along the fiber direction. There is some resin remained on the surface of fibers after debonding, while the gaps are still presented in this sample due to inadequate curing pressure. The fracture surfaces in Figure 4(c) and Figure 4(d) is showing no distinguish difference with resin cusps and interface deboning. Increasing external pressure will lead to more resin cusps areas. Upon the application of the external pressure, most of the load was transferred through a continuous skeleton of fiber-rich regions. The higher curing pressure in these regions led to the migration of resin. These SEM images confirm the curing

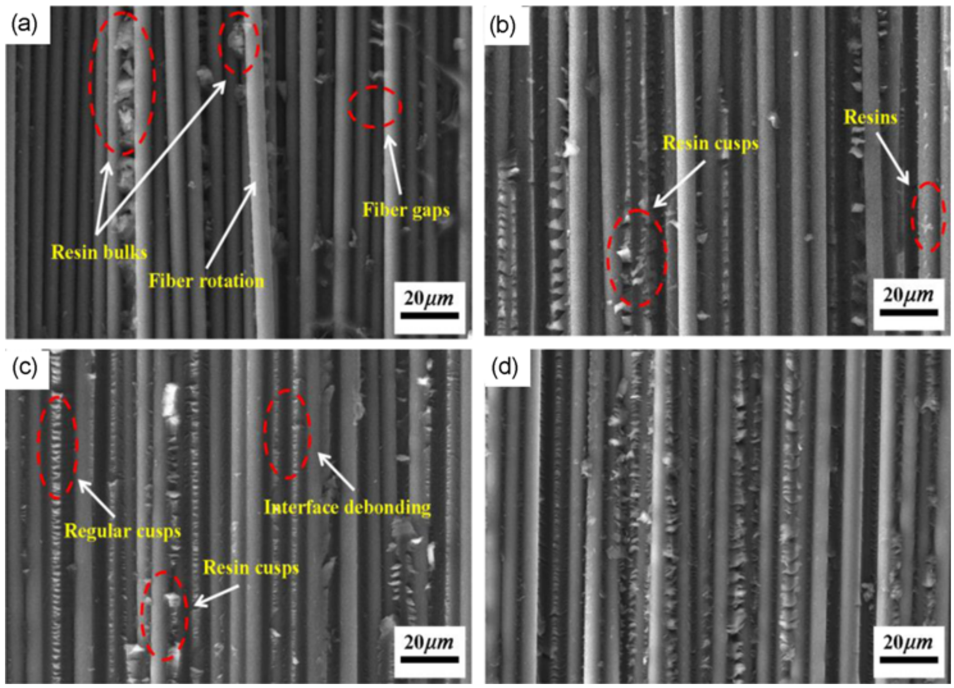

Figure 4. SEM morphology of the failure surface with different curing pressure; (a) 0.0 MPa, (b) 0.2 MPa, (c) 0.4 MPa, and (d) 0.6 MPa.

pressures drive the resin flow to impregnate the fibers. The higher curing pressure will lead to better impregnation bonding. Therefore, the ILSS has been improved correspondingly.

Difference Analysis

The difference between the maximum and minimum tested results each factor could have is called difference value, which is represented by *R*. If the value of *R* is larger, this indicates the effect of tested factor on experimental results is more significant. The ILSS results of every test were showed in Table 2, the *R* value of curing pressure was 45.86, which was the maximum value in all tested parameters. The *R* values of heating rate, curing temperature, and heat preservation time were 6.28, 5.00, and 6.75 respectively, and there were no obvious differences among them. This reported that curing pressure was an important influencing cure parameter on ILSS of the composite laminates, while the effects of other cure parameters on ILSS were small comparatively, which was agreement with the analysis results of Figure 3. According to the varied tendency of ILSS results in different levels of each factor, as shown in Table 2, it was found that the optimum curing cycle conditions were as follows: $A_4B_4C_1D_2$, that was, curing pressure of 0.6 MPa, heating rate of 1.5 °C/min, curing temperature of 160 °C, and heat preservation time of 120 min.

Variance Analysis

The variance analysis of different cure parameters was shown in Table 3, clearly indicating that curing pressure had

Table 2. Tested results of ILSS in orthogonal experiment

Text number	Factor				Tested results of the ILSS (MPa)
	A	B	C	D	
1	1	1	1	1	53.24
2	1	2	2	2	46.65
3	1	3	3	3	41.96
4	1	4	4	4	51.17
5	2	1	2	3	89.09
6	2	2	1	4	88.62
7	2	3	4	1	78.23
8	2	4	3	2	94.60
9	3	1	3	4	85.89
10	3	2	4	3	89.77
11	3	3	1	2	94.67
12	3	4	2	1	94.37
13	4	1	4	2	91.97
14	4	2	3	1	95.12
15	4	3	2	4	94.76
16	4	4	1	3	94.60
Mean value I	48.26	80.05	82.78	80.24	
Mean value II	87.64	80.04	81.22	81.97	
Mean value III	91.18	77.41	79.39	78.86	
Mean value V	94.11	83.69	77.79	80.11	
Range R	45.86	6.28	5.00	6.75	

Where A is curing pressure, B is heating rate, C is curing temperature, and D is heat preservation time.

Table 3. Analysis of variance of curing pressure, heating rate, curing temperature, and heat preservation time

Factor	Sum of squares	Degree freedom	F value	Significance
A	5558.94	3	47.11	Significant
B	79.88	3	0.68	Very low
S	56.61	3	0.48	Very low
D	19.70	3	0.17	Very low
Error	117.99	3		

[a]Fisher's F-test, $F_{0.10}(3,3)=5.36$, $F_{0.05}(3,3)=9.28$, and $F_{0.01}(3,3)=29.28$.

a significant effect on the ILSS of the laminates, and other cure parameters like heating rate, curing temperature, and heat preservation time had a very low effect. This major reason may be that the curing pressure can determine the flow rate and the direction of resin, in which the resin would be filled uniformly between the fibers as the increase of curing pressure. If the fiber-matrix interfacial bonding behavior had been improved, the ILSS of the samples would be increased corresponding. However, all other cure parameters are heat treatment conditions. For this reason, these cure parameters only enhance the impregnation of resin between the fibers, but could not offer the external load on the compaction of the resin. And so, the effects on the ILSS are not obvious.

Based on the orthogonal experiment analysis mentioned above, it can be identified that the optimum curing cycle in X850/T800 composites was as follows: curing pressure of 0.6 MPa, heating rate of 1.5 °C/min, curing temperature of 160 °C, and heat preservation time of 120 min. By which the energy-saving and efficiency maximization can be realized for the autoclave process. In order to verify the rationality of this optimum curing cycle conditions, the tests should be further in progress.

Verification Test

According to the optimal curing cycle conditions, the composite laminates were fabricated in autoclave to prepare for the experimental tests. The fracture surface of tested sample was shown in Figure 5. The SEM image showed that the typical resin cusp structures by debonding under the shear loads. Cusps were formed as successive and some resin was remained on the surface of fibers, indicating that the impregnation of resin on the fibers was better. The phenomenon of that the resin filled uniformly between the fibers was observed frequently, which meant the fiber-matrix interface bonding behavior was excellent. The cured quality of composite laminates can be determined.

The results of ILSS measurements were shown in Figure 6. As can be seen from it, the maximum value of ILSS was 105.35 MPa, and the minimum result was 97.88 MPa. There weere no difference in every measurement result, which illustrated that the measurements had a good repeatability.

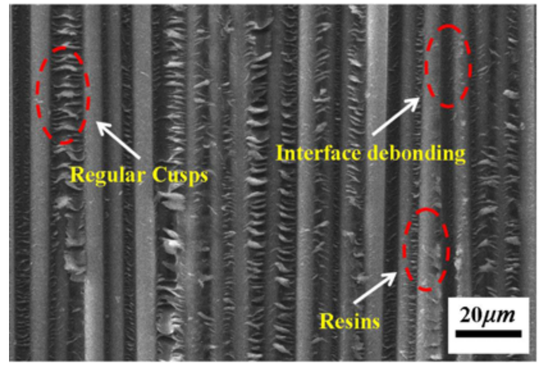

Figure 5. Fracture surface of the cured sample under the optimized condition.

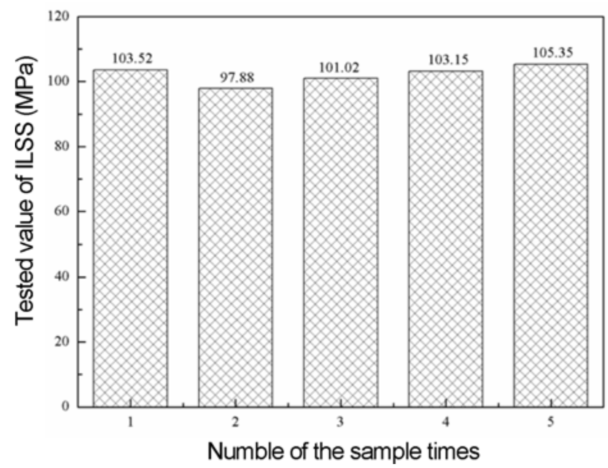

Figure 6. Tested results of ILSS.

Based on calculations, the average value of all tested ILSS was 102.18 MPa. Compared the maximum ILSS result in the orthogonal experiment, as shown in Table 2, the ILSS had increased by 7.42 %.

Conclusion

This paper had optimized the curing process conditions of X850/T800 polymer matrix composites based on orthogonal experimental method. Four influence factors including curing pressure, heating rate, curing temperature, and heat preservation time were selected, and sixteen composite laminates were fabricated in autoclave process by orthogonal experimental design. The influence of the four curing parameters mentioned above on the curing quality of composite laminates was assessed by interlaminar properties test and microstructure analysis. The interlaminar shear strength (ILSS) of samples was calculated by the short-beam three points bending test. The interfacial bonding behavior of tested samples was studied using scanning electron microscopy.

Results showed that the ILSS increased by 48.72 % as the curing pressure increased from 0.0 MPa to 0.6 MPa; The ILSS decreased by 7.50 % as the heating rate increased from 1.5 ^{o}C/min to 4.5 ^{o}C/min; The ILSS decreased by 6.03 % as the curing temperature increased from 160 ^{o}C to 190 ^{o}C; The ILSS was relatively insensitive to the heat preservation time. According to the analysis results obtained by the orthogonal experiment, the optimal curing process conditions for X850/T800 composites can be drawn as follows: the curing pressure was 0.6 MPa, the heating rate was 1.5 ^{o}C/min, the curing temperature was 160 ^{o}C, and the heat preservation time was 120 min. By this process, the laminates can possess a good interfacial bonding property. And the ILSS can reach to 102.18 MPa, which can increase by 7.42 % compared with the maximum value obtained by the orthogonal experiments.

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