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THE EFFECT OF AUTOCLAVE PROCESSING ON THE PERFORMANCE OF CF/PPS COMPOSITE LAMINATES

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ABSTRACT

Carbon fiber-reinforced polyphenylene sulfide (CF/PPS) thermoplastic composite laminates were formed by autoclave under high temperature and high pressure. The phase transition parameters were determined by differential scanning calorimetry (DSC) analysis, and the thermodynamic properties of PPS were evaluated by thermogravimetric analysis (TGA) and rheological testing, which provided theoretical guidance for the establishment of autoclave molding of CF/PPS. According to the principle of response surface methodology, the experiment was designed to analyze the effects of temperature, pressure, and time on the mechanical properties of the laminate with interlaminar shear strength (ILSS) as the evaluation index. The results indicate that the influence of parameters on the mechanical properties of CF/PPS laminates is in the order of temperature, time, and pressure. Finally, the optimal parameters of the autoclave were obtained: 332°C, 23min, and 1.75Mpa. The interlaminar shear strength of the CF/PPS laminated plate prepared under these parameters reached 66.25Mpa.

1 INTRODUCTION

Thermoplastic composite materials are composed of reinforced phases such as carbon fiber and glass fiber, as well as various thermoplastic resin matrices. They have advantages such as excellent impact and corrosion resistance, high material utilization rate, unlimited storage environment and time for prepregs, and recyclability. These advantages have received widespread attention from the aviation manufacturing industry[1-2]. As the matrix of thermoplastic composite material, polyetheretherketone (PEEK), polyphenylenesulfide (PPS), and polyetherimide (PEI) have higher specific strength and specific stiffness, good flame retardancy, low smoke, and non-toxicity. Due to these advantages, they are ideal materials for lightweight, low-cost aviation structural components and have enormous potential in the field of civil aviation[3-4].

In thermoplastic resins, the molecular chains of PPS material are composed of benzene rings and sulfur atoms, which give the molecular chains high rigidity and good regularity, making them crystalline polymers. PPS material has extremely high fatigue resistance, good flame retardancy, and low moisture absorption. Especially under high temperature and humidity conditions, PPS material will not deform and can maintain excellent electrical insulation. Due to the presence of lone pair electrons of sulfur atoms in the molecular chain, PPS resin has a good affinity with fibers. Therefore, PPS material is suitable for manufacturing composite structural components and has been widely used in the aerospace field[5-7]. For example, Fokker uses CF/PPS thermoplastic composites for the tail section, rudder, and elevator of Gulf-stream G650 aircraft (Figure 1). As shown in Figure 2, Airbus A380 uses GF/PPS thermoplastic composites provided by TenCate to prepare the fixed-wing leading edge[8].

Figure 1. The thermoplastic composite rudder for Gulf-stream 650

Figure 2. The fixed wing leading edge for A380

Continuous fiber-reinforced thermoplastic resin composites have different molding processes, such as compression molding, pultrusion, automatic placement technology, and autoclave molding. Compression molding can manufacture complex structural components quickly, but due to the high viscosity of the resin matrix during melting, this method has drawbacks such as poor fiber wettability, difficulty in eliminating pores, and uneven resin flow. These problems limit the application of compression molding [9-10]. Pultrusion is one of the most effective methods for manufacturing structured components with regular shapes, but this method generally difficult to shape structural components with varying cross-sectional shapes [11]. Automatic placement is an in-situ forming technology that is not limited by the processing site, part size, and shape, which has high processing efficiency. Therefore, the automatic placement technology of thermoplastic composite materials will be an important technology for the production of aerospace composite components in the future [12-14]. But this method also has some drawbacks, such as insufficient molecular chain diffusion, hard to control cooling rate, high porosity, and low strength of molded components. To improve the strength, the components usually need to be post-treated by autoclave, which restricts the use of automatic placement technology for thermoplastic composite in production [15]. Autoclave molding is a widely used method for molding composite structures. It has some advantages over other methods, such as low porosity and stable mechanical properties of components due to the uniform temperature and pressure in the autoclave and enough heating and pressing time [16-18].

Composite materials are widely used in civil aircraft, and their usage is an important indicator of the technological advancement and market competitiveness of aircraft. The molding process of composite components is also a critical technology in aircraft manufacturing. In this paper, the autoclave molding process of continuous carbon fiber-reinforced PPS resin composites was investigated. The effects of process parameters like temperature, autoclave pressure, and holding time ware explored. The optimal autoclave molding process parameters ware optimized, and the best mechanical performance values of laminates ware obtained.

2 Equipment and Method

2.1 Equipment

CF/PPS composite laminates were prepared by autoclave and the indicator of mechanical performance was the interlaminar shear strength (ILSS). The ILSS of laminates was measured according to ASTM D 2344/D 2344M-00 and the size of specimens was 18×6×3mm [19]. The ILSS test was performed by the universal testing machine. The phase transition parameters of PPS were determined by differential scanning calorimetry (DSC). The thermodynamic properties of PPS were tested by the thermogravimetric analyzer (TGA) and rheometer.

2.2 Preparation of test pieces

The high-temperature and high-pressure autoclave used in this experiment is shown in Figure 3. The effective working size of the autoclave was ϕ1m×2m and the maximum working temperature was 400℃. The temperature uniformity of the autoclave was as follows: ≤±2℃ below 250℃ and ≤±3℃ between 250-400℃. It could also applied a maximum pressure of 3.5MPa, with a heating rate of 0.1-5℃/min and a cooling rate of 0.5-6℃/min.

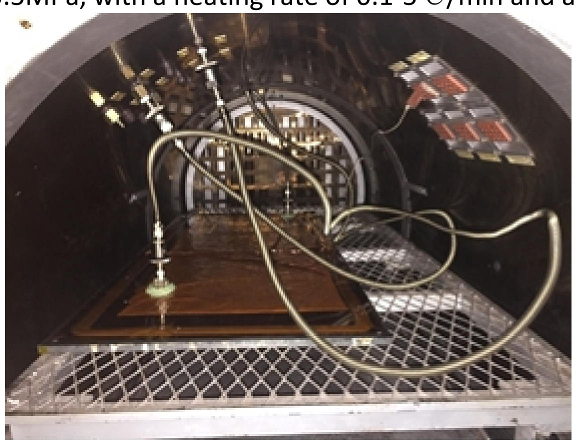

Figure 3. High-temperature and high-pressure autoclave

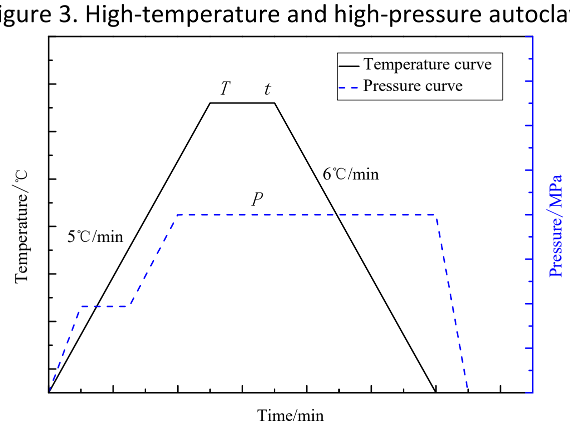

Figure 4. Autoclave forming process for the CF/PPS composite material

The autoclave preparation process of CF/PPS composite materials is shown in Figure 4. The sample was vacuumed throughout the process. The temperature in the autoclave was increased from room temperature to the experimental temperature T at a rate of 5℃/min, the pressure in the autoclave was increased from atmospheric pressure to the experimental pressure P, and the holding time was t. The cooling down speed was 6℃/min. Test pieces with a size of 220×220×3mm (Figure 5) were prepared, and then they were cut and polished into specimens.

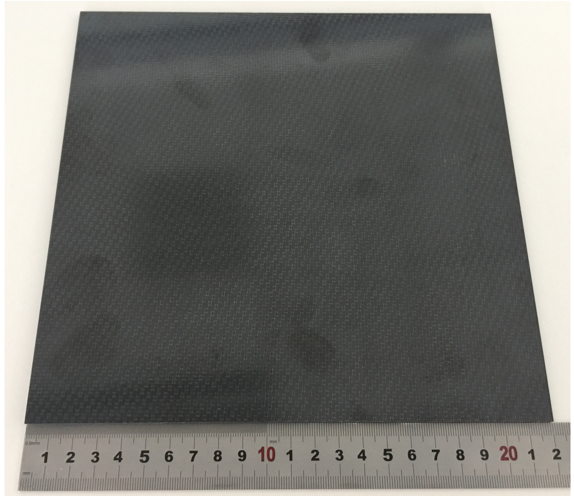

Figure 5. The CF/PPS composite laminate made by autoclave

2.3 Results and discussion

The resin matrix has a high melting point and melt viscosity, which makes it difficult to achieve uniform and complete impregnation. Therefore, the thermodynamic analysis of the resin was conduct firstly to obtain the range of process parameters. The PPS considered in this study has a melting point range of 265-300℃ and a thermal decomposition temperature of around 400℃. Figure 6 shows the DSC curve of the CF/PPS used in this study composite material melting process obtained by dynamic scanning. It can be observed that the PPS resin matrix has an initial melting temperature of 270.6℃, reaches a peak at 293.4℃, and completes the phase transition at 304.7℃

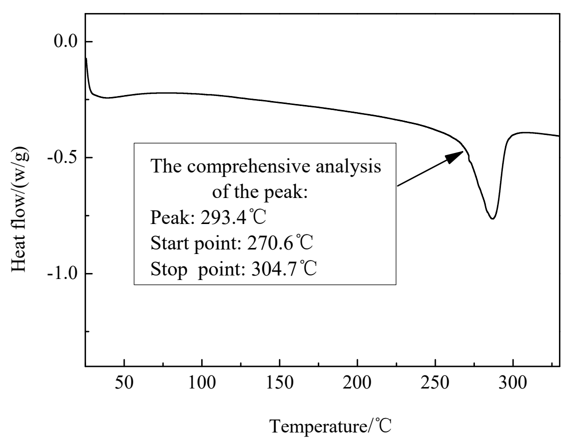

Figure 6. Curve of the melting process dynamic scanning DSC for CF/PPS

Figure 7 depicts the TGA curve of the CF/PPS composite material. It can be inferred from the figure that the onset temperature of thermal degradation for the PPS resin matrix is around 440℃.

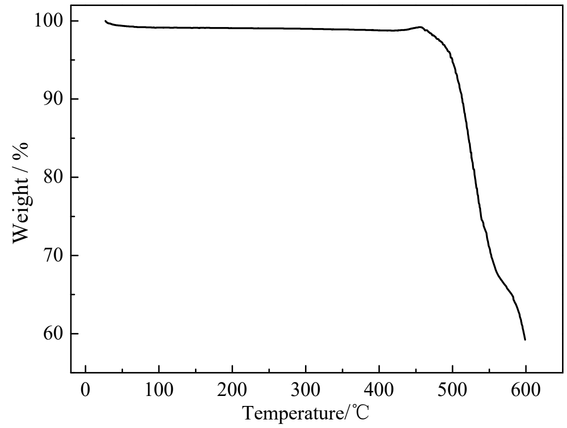

Figure 7. Curve of the TGA for CF/PPS composite

Figure 8 illustrates the viscosity-temperature curve of the PPS resin matrix. It can be observed from the figure that the PPS resin matrix has a relatively low melt viscosity at 320-340℃. When the temperature exceeds 340℃, the viscosity of the resin increases due to the cross-linking reaction.

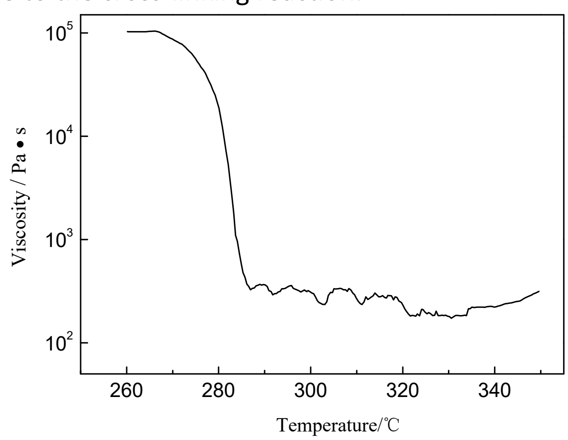

Figure 8. Curve of the viscosity-temperature for PPS matrix

The impact of autoclave parameters on the mechanical properties of CF/PPS composite laminates was investigated using response surface methodology. The experimental design utilized the Central Composite Design (CCD) method for response surface analysis, and a second-order response model was used for data fitting [20-21]. The mechanical properties of the formed specimens were explored in different temperatures, pressure, and holding times of the autoclave. The processing factors and design levels are presented in Table 2. The heat temperature was 320°C, 330°C, and 340°C, respectively. The heat preservation pressure was 1.5 MPa, 2 MPa, and 2.5 MPa, respectively. The heat preservation time was chosen at three levels: 10 minutes, 20 minutes, and 30 minutes. The following transformations were made for the heat temperature, heat preservation pressure, and heat preservation time:

$$A = \frac{T - 330}{10} \#(1)$$

$$B = \frac{P - 2}{0.5} \#(2)$$

$$C = \frac{t - 20}{10} \#(3)$$

The experimental results are shown in Table 2, with the level values calibrated using ILSS.

Table 1. Table of the processing factors and design levels

Factors	Levels		
	-1	0	1
A : Heat temperature(T/℃)	320	330	340
B : Heat preservation pressure (P/MPa)	1.5	2	2.5
C : Heat preservation time(t/min)	10	20	30

Table 2. Autoclave forming table of the response surface program and the result for CF/PPS composite

NO.	A	B	C	ILSS X / MPa
1	1	1	-1	65.12
2	1	0	0	69.19
3	0	0	0	67.12
4	0	0	1	67.09
5	1	1	1	67.12
6	0	1	0	66.02
7	0	1	0	64.78
8	-1	1	1	64.35
9	0	0	0	66.82
10	0	0	0	65.97
11	-1	1	-1	61.27
12	-1	-1	-1	59.63
13	-1	1	1	67.19
14	0	0	0	66.37
15	1	-1	-1	66.4
16	-1	-1	1	66.58
17	0	0	0	68.04
18	0	0	1	59.91

19	0	0	0	65.98
20	-1	0	0	63.94

The experimental data were subjected to regression analysis using Design Expert 8 software, as shown in Table 3. In Table 3, the significance of the variables' impact on the response values was determined through the p-value (P). From Table 3, it can be observed that the p-value of the model for the ILSS is less than 0.0001, indicating the high significance of the experimental model. Therefore, this model is suitable for analyzing the influence of autoclave parameters on the mechanical properties of CF/PPS. The influence of the linear terms (A,B,C) and interaction terms (AB,AC,BC) on the response is significant, indicating that a simple linear model cannot describe the mechanical performance of the specimens. At the same time, the effects of the factors on the response from high to low in turn are heat temperature, heat preservation time, and heat preservation pressure.

Table 3. Autoclave forming table of the significance for the regression equation coefficient for CF/PPS composite

Model item	X	
	Coefficients	P
Model	-	<0.0001
Constant	67.79	-
A	1.35	0.0043
B	1.28	0.0159
C	0.32	0.0082
AB	1.05	0.0391
AC	-0.32	0.0173
BC	-0.98	0.0125
A^2	1.57	0.2514
B^2	0.3	0.4394
C^2	-3.59	0.2137

The quadratic polynomial regression model can be obtained from the regression equation coefficients in Table 3:

$$X = 6.83 + 13.5A + 1.28B + 0.32C + 1.05AB - 0.32AC - 0.98BC + 1.57A^2 + 0.3B^2 - 3.59C^2 \#(4)$$

In the autoclave forming process, it is sufficient to heat the material to the melting point of the PPS resin matrix theoretically. However, as shown in Figure 8, the PPS used in this study exhibits poor flowability when heated to the melting temperature due to its high viscosity. As illustrated in Figure 9, it is difficult to enhance the mechanical properties of specimens by increasing the pressure or employing other methods at lower temperatures. When the temperature increases, there is an improvement in the ILSS of the test specimens. This is primarily due to the gradual reduction in viscosity of the PPS resin matrix, leading to enhanced resin flowability. As a result, a stronger interface bonding between the matrix and fibers is established. When the temperature is appropriate, an increase in the applied pressure during the curing stage results in a gradual improvement in the ILSS of specimens. This can be attributed to two key factors. Firstly, higher pressure encourages the flow of the PPS resin matrix, enhancing its impregnation capability and promoting better wetting of the reinforcing fibers. Secondly, it aids in the removal of internal porosity and consequently enhances the ILSS of specimens after the curing process. However, when the pressure exceeds 1.75 MPa, there is a tendency for the ILSS of specimens to decrease. Moreover, this tendency of decrease becomes more pronounced at higher temperatures. This is due to the improved flowability of the resin matrix at high temperatures. When higher pressure is applied, the molten PPS resin matrix tends to flow towards areas of lower pressure, such as the vacuum port on the vacuum bag. This uneven resin distribution leads to a decrease in the ILSS of specimens. Based on Figure 9, it can be inferred that the specimens achieve their optimal ILSS) when the heat temperature is set at 332℃ and heat preservation pressure is maintained at 1.75 MPa.

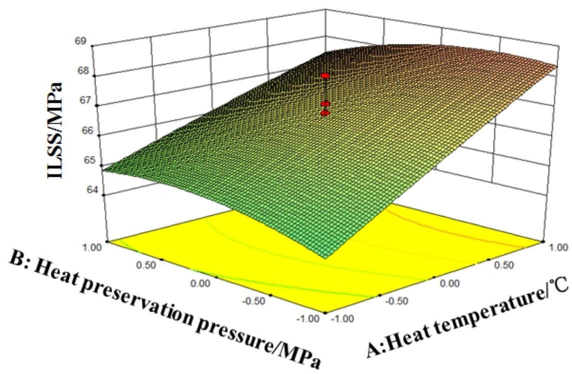

Figure 9. The interaction effect of heat temperature (A) and heat preservation pressure (B) with different values on the ILSS for CF/PPS composite

Figure 10 illustrates the impact of the coupling between the heat temperature and the heat preservation time on the ILSS of specimens. The viscosity of the PPS resin matrix decreases continuously as the heating temperature increases, this helps to increase the ISLL of the specimen. However, when the temperature exceeds 332°C and the heat preservation time exceeds 23 minutes, the ILSS of the specimen decreases with the extension of the heat preservation time. This is due to the increase of the crosslinking degree of PPS resin under long-term high temperature, which causes the resin matrix to become brittle. When the temperature is below 332°C, the molecular chains diffuse more fully as the heat preservation time increases. This improves the wetting of the reinforcing fibers by the PPS matrix and thus increases the ILSS of the specimen. However, the ILSS of the specimen does not vary much when the temperature surpasses 23 minutes, as the molecular chains have already diffused enough. It can be concluded from Figure 10 that the ILSS performance of the specimen is optimal when the heating temperature is 332°C and the heat preservation time is 23 minutes.

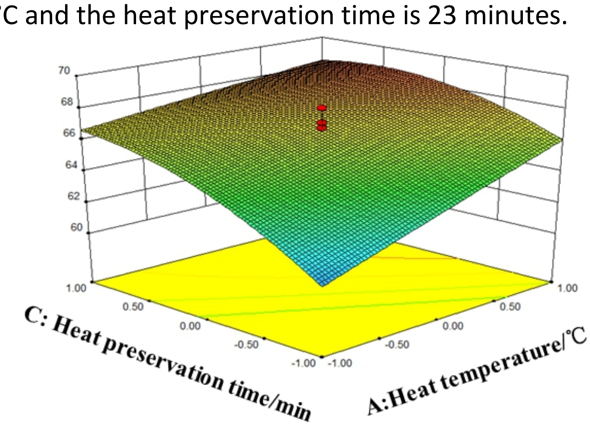

Figure 10. The interaction effect of heat temperature (A) and heat preservation time (C) with different values on the ILSS for CF/PPS composite

Figure 11 illustrates the impact of the coupling between the heat preservation pressure and the heat preservation time on the ILSS of specimens. As shown in Figure 11, the ILSS of the specimen gradually increases with the increase of pressure and the heat preservation time. But when the pressure exceeds 1.75 MPa or the heat preservation time exceeds 23 min, the ILSS of the specimen decreases rapidly with the increase of pressure, due to the uneven distribution of resin in the specimen under high pressure. Therefore, when the pressure of the autoclave is 1.75 MPa and the heat preservation time is 23 min, the ILSS of the specimen reaches its maximum value.

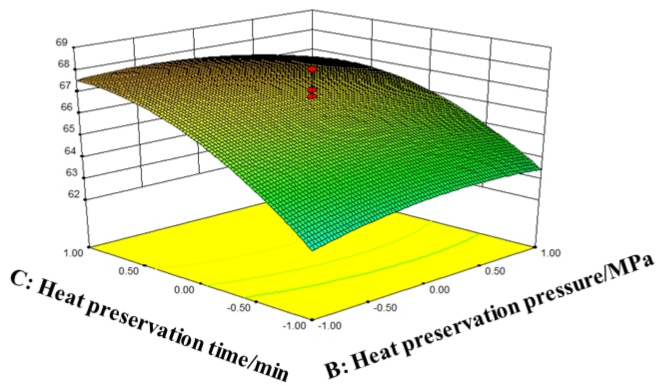

Figure 11. The interaction effect of heat preservation pressure (B) and heat preservation time (C) with different values on the ILSS for CF/PPS composite

According to the above analysis, the optimal process parameter combination for autoclave curing CF/PPS composite laminate is 332°C, 23 min, and 1.75 MPa. The parameters A, B, and C can be calculated by equations (1), (2), and (3), which are 0.2, -0.5, and 0.3 respectively. Substitute them into equation (4) and obtain the optimal predicted value of ILSS for the laminate as 68.32 MPa. The laminate prepared under this optimal parameter combination has an actual measured ILSS of 66.25 MPa. The actual measured value corresponds to the predicted value, which demonstrates that the model can predict the relationship between various parameters and ILSS.

3 Conclusion

(1) The optimal parameters for preparing CF/PPS composite laminates by an autoclave were obtained. Specifically, the heating temperature was 332 °C, the heat preservation time was 23 minutes, and the heat preservation pressure was 1.75 MPa. The ILSS of the laminate is 66.25 MPa under these parameters.

(2) The response surface method was used to explore the effect of the parameters of the autoclave on the ILSS of the CF/PPS composite laminates. The influence-degree of the autoclave parameters on the ILSS is in order of heating temperature, the heat preservation time, and the heat preservation pressure.

(3) There are no standards for the mechanical properties of CF/PPS formed by automatic placement. This paper prepared CF/PPS composite laminates by optimizing the process parameters, obtained the optimal mechanical performance values of the laminates, and established the prediction model for the mechanical performance, which laid a foundation for the CF/PPS automatic placement process.

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