Research on wet-jet and wet-spun carbon fiber prepreg yarn for dry winding and its properties

Zhitao Li*, Guoqiang Yin, Ruijun Shan, Yan Shen, Mingxin Chen, Congcong Guo, Zihao Guo
Jiangsu Hengshen Co., Ltd., Zhenjiang, China
*Corresponding author: 915745954@qq.com

Abstract. Through the transformation of basic equipment, this paper realizes the control of the stable resin content of prepreg yarn while fully maintaining the impregnation. Through the research on the resin curing process, resin content, and aging degree of the resin system during the prepreg manufacturing process, the resin content and aging process of the prepreg corresponding to the optimal tensile performance of the NOL ring were determined, and a high-tension winding method was obtained. The prepreg yarn MP01/HF30F/28 prepreg yarn. During the manufacturing process of wound gas cylinders, through the research on the curing system and layup design, the burst strength of dry wound gas cylinders reached 68.5MPa, and the corresponding fiber performance conversion rate was 81.2%, which exceeded that of wet-sprayed wet-spun fibers. The blasting performance conversion rate of wound gas cylinders is 19.8%. Thus opening up a new application method of wet-jet wet-spun carbon fiber in the field of winding.

Keywords: prepreg yarn, burst strength, wet jet wet spinning carbon fiber, dry winding, NOL ring strength

1. Introduction

With the development of hydrogen fuel new energy vehicles, the field of carbon fiber composite wound gas cylinders [1-3] is quietly changing. Traditional carbon fiber composite wound gas cylinders are mostly realized by wet winding [4-7]. This method has disadvantages such as unstable resin content, poor operating environment, and difficult automation. With the deepening of the gas cylinder field, the wet winding method is facing severe challenges. However, a few foreign countries have been promoting dry winding [8-11]. Its advantages are stable and controllable resin content, clean and tidy operating environment, and easy automation. However, domestic research on dry winding is still in its infancy, and wet winding is still the main one that can be engineered. In the field of wet winding, most companies use dry-sprayed wet-spun carbon fiber as the fiber for winding gas cylinders, while few companies use wet-sprayed wet-spun carbon fiber. The manufacturability is better in the winding process, and the performance conversion rate of the fiber is high. In this paper, for wet spraying and wet spinning carbon fiber, combined with dry winding process, a dry winding prepreg yarn that can improve the performance conversion rate of wet spraying and wet spinning carbon fiber is exploratory developed [12-14], and through its related process parameters Research to explore optimal winding application parameters.

2. Experimental materials and methods

2.1. Raw materials

Resin: MP01 (Hengshen Co., Ltd.), AF4206 resin system (Huibai New Materials).
Fiber: PAN-based wet-jet wet-spun T700 grade carbon fiber HF30F-12K (Hengshen Co., Ltd.).

2.2. DSC test of resin

According to the GB/T19466.2 standard, the dynamic DSC analysis was carried out in a nitrogen atmosphere by using a Q20 differential calorimeter from TA Company of the United States.
2.3. DSC test of resin

According to the ASTM D4287 standard, the viscosity of the resin system was tested at different temperatures using a BROOKFIELD DVII cone-plate viscometer.

2.4. Resin gel time test

According to the ASTM D4217 standard, the standard heating plate is used to test the curing time of the resin system at different temperatures, and the temperature control accuracy of the tester is ±0.5°C.

2.5. Curing degree test of composite materials

According to GB/T2576 standard, the curing degree of fiber reinforced resin matrix composites was determined by extraction method.

2.6. Preparation of prepreg

The MP01 resin system made by Hengshen is vacuum defoamed and then added to the special equipment for prepreg as shown in Fig. 1. After the fixed-band glue treatment, the prepreg with precise resin content is obtained.

![Fig. 1 Schematic diagram of prepreg yarn preparation](image1)

2.7. Prepreg resin content test

Since there is no uniform standard for prepreg yarns for dry winding, the test is carried out by gravimetric method with reference to the commercial thermosetting prepreg standard, and the calculation formula is as follows:

\[ W = \frac{(m - lp)}{m} \]

In the formula: \( W \) is the glue content (%) of the prepreg yarn; \( m \) is the mass of the prepreg yarn (mg); \( l \) is the length of the prepreg yarn (mm); \( p \) is the linear density of the carbon fiber (g/m).

2.8. Preparation of NOL ring and unidirectional plate

The main difference between dry winding and wet winding is whether it is dipped synchronously in the process of manufacturing plates or parts, wet synchronous dipping, dry method does not need synchronous dipping. Fig. 2 is a basic schematic diagram of wet winding. Among them, the preparation of the plate and the preparation of the NOL ring are only different in the end mold, and the relevant test samples are obtained after oven curing.

![Fig. 2 Schematic diagram of wet winding](image2)

1--Carbon fiber spindle  2--drying oven  3--Dry yarn tension roller  4--tank  5--Squeezer roll  6--Tension device  7--Silk mouthpiece  8--loop model
2.9. Multifilament strength test

Adopt GB/T 26749 standard to test the strength of carbon fiber multifilament. The loading speed test of 2mm/min is used in the process, and the relevant strength calculation method is as follows:

\[
\sigma = \frac{P \times \rho_l}{t} \times 10^{-4}
\]

\(\sigma\) represents tensile strength (MPa),
\(P\) represents failure load (N);
\(\rho_l\) represents the density of multifilament (kg/m^3),
\(t\) represents the linear density of multifilament (kg/m).

2.10. Mechanical property test

Tensile strength and modulus performance test of unidirectional plate: according to ASTM D3039 standard, using AG-Xplus250KN universal testing machine, using a loading speed of 2mm/min, the tensile strength and modulus properties of composite materials are tested in a dry environment at room temperature. Test, tensile strength and modulus each test 5 valid data, get the average value.

Performance test of interlaminar shear strength of unidirectional slabs: According to ASTM D 2344 standard, the interlaminar shear strength of composite materials was characterized by three-point short-arm beam bending method on Instron 3382 universal testing machine. The loading speed of the indenter is 1 mm/min, and the test is performed at room temperature in a dry state. The interlaminar shear strength is measured for 5 valid data, and the average value is taken.

NOL ring strength test: according to GB/T1458 standard, using NOL special fixture, test on AG-Xplus250KN universal testing machine at a loading speed of 2mm/min, test 5 valid data, and take the average value.

Scanning electron microscope (SEM): The JSM-6460LV scanning electron microscope produced by JEOL Ltd. was used to characterize the cross-section of the composite material.

2.11. Preparation and blasting of filament-wound gas cylinders

Wet gas cylinder winding: After mixing AF4206 resin components A and B in a ratio of 1:1, add them to the dipping tank of the wet winding equipment, and set the temperature in the dipping tank to 30°C, so that The viscosity of its AF4206 resin is kept at 200~300cP, and Hengshen wet-jet wet-spun T700 grade fiber HF30F fiber is used for impregnation and winding to prepare a wound gas cylinder with a design nominal pressure of 30MPa.

Dry gas cylinder winding: use MP01/HF30F-12K/28 (resin content example) prepreg yarn to wind cylinders through dry winding equipment, and the winding method is consistent with the wet method. Cylinder blasting is carried out according to the requirements in the GBT35544-2007 standard.

3. Results and Discussion

3.1. Analysis of curing reaction process of MP01 resin

The matrix of carbon fiber composite materials is currently mainly thermosetting epoxy resin, and the mechanical properties of composite materials cannot be achieved without a reasonable molding and curing process. The establishment of molding and curing conditions is inseparable from the curing changes of the epoxy resin when heated. Therefore, the optimal process curing conditions can be determined by changing the characteristics of the DSC curve at different heating rates in the figure below. It can be seen from Fig. 3 that with the increase of the heating rate, the DSC curve correspondingly has the phenomenon that the initial reaction temperature, the peak reaction temperature and the termination reaction temperature shift backward. Table 1 specifically lists the relevant characteristic values. By using the extrapolation method, the heating rate is used as the
The abscissa, and the initial reaction temperature, peak reaction temperature and end reaction temperature are used as the ordinate respectively (Fig. 5), and linear fitting is performed to extrapolate the fitting curve. The corresponding intercepts when the heating rate of the resin is 0 are respectively the theoretical pre-curing temperature, theoretical curing temperature and theoretical post-curing temperature of MP01 resin. From Fig. 5 (the first three pictures), it can be seen that the pre-curing temperature, theoretical curing temperature and theoretical post-curing temperature of MP01 resin are 107.9°C, 127.6°C and 152.6°C, respectively. This lays a theoretical foundation for the subsequent selection of an appropriate curing temperature.

At the same time, on the DSC curve in Fig. 3, a rising weak endothermic peak can be clearly found in the range of 50-100 °C under different heating rates, which is partially enlarged as shown in Fig. 4. Also by extrapolation, the theoretical reaction initiation temperature in the range of 50~100°C is 48.8°C. The characteristic temperature shows that MP01 resin has low-temperature reactivity.

### Table 1. Eigenvalues of DSC curves at different heating rates

<table>
<thead>
<tr>
<th>MP01</th>
<th>Initial reaction temperature/°C</th>
<th>Peak reaction temperature/°C</th>
<th>Termination reaction temperature/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5℃/min</td>
<td>114.71</td>
<td>135.38</td>
<td>165.05</td>
</tr>
<tr>
<td>10℃/min</td>
<td>123.27</td>
<td>145.91</td>
<td>183.51</td>
</tr>
<tr>
<td>15℃/min</td>
<td>129.15</td>
<td>152.29</td>
<td>192.98</td>
</tr>
</tbody>
</table>

At the same time, on the DSC curve in Fig. 3, a rising weak endothermic peak can be clearly found in the range of 50-100 °C under different heating rates, which is partially enlarged as shown in Fig. 4. Also by extrapolation, the theoretical reaction initiation temperature in the range of 50~100°C is 48.8°C. The characteristic temperature shows that MP01 resin has low-temperature reactivity.

### Table 2. Amplified eigenvalues of DSC curves of MP01 below 110°C under different heating rates

<table>
<thead>
<tr>
<th>MP01</th>
<th>Initial reaction temperature/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5℃/min</td>
<td>56.21</td>
</tr>
<tr>
<td>10℃/min</td>
<td>68.18</td>
</tr>
<tr>
<td>15℃/min</td>
<td>73.19</td>
</tr>
</tbody>
</table>
3.2. Analysis of viscosity-temperature characteristics of MP01 resin system

During the wet winding process, the infiltration of the fiber by the resin is an important factor that determines the mechanical properties of the fiber. The traditional wet winding process generally requires the viscosity of the resin to be 200cP~800cP, which is beneficial for the resin to fully wet the fiber during high-speed transmission. Similarly, based on our prepreg preparation equipment, in order to ensure that the tow is fully infiltrated by the fiber during the high-speed impregnation process, the initial viscosity of the MP01 resin system we designed also needs to be low enough. Fig. 6 shows the viscosity-time characteristic curves of the MP01 resin system under different processing conditions. Among them, the square ■ line shows the change of the viscosity of the MP01 resin system with time at room temperature (25°C) after the mixing is completed. It can be seen from the figure that the MP01 resin system experienced a process of gradually increasing its own viscosity to a stable level at room temperature. On the 12th day, the viscosity began to be stable, and remained basically stable at 7300cP for the next 5 days. After the MP01 resin system was cured at 30°C, 40°C, and 50°C for 6 hours, the change of viscosity with time was tracked again, and it was found that the viscosity-time curve of the MP01 resin system cured at 30°C for 6 hours was basically the same as that of the uncured viscosity-time curve. The same, but the MP01 resin system cured at 40°C for 6 hours and the MP01 resin system aged at 50°C for 6 hours are obviously different. The viscosity change of the MP01 resin system cured at 40°C for 6 hours is basically stable after the 4th day, and can last for 12 days. However, the viscosity of the MP01 resin system cured at 50°C for 6 hours increases linearly with the passage of time, and there is no stable range of viscosity. This echoes the characteristics of the DSC curve of Fig. 4. When the curing temperature is higher than 48.8°C, the resin has been activated and reached its reaction initiation temperature, and the viscosity doubles linearly with time. However, when the curing temperature is lower than 48.8°C, the initial reaction temperature of MP01 resin at room temperature has not been reached. Therefore, after a short-term increase in viscosity, the resin stays in the B stage, forming a relatively stable system. However, considering that the arrival time of the too long resin stable period will affect the subsequent industrialization, 40°C is a reasonable curing temperature for the MP01 resin system. The tow prepregs prepared subsequently need to be aged at 40°C for 6h.
3.3. The effect of different curing systems of MP01 resin on the properties of NOL rings

Considering that AF4206 is an outsourced resin, the curing system of the resin has been fully matched and verified by most fibers in the market. Therefore, this part mainly investigates the effect of MP01 resin system on the performance of NOL ring under different curing systems\(^{[15-18]}\), to deduce the optimal curing system. Fig. 7 shows the change of NOL ring strength of MP01/HF30F-12K/28 prepreg yarn under different curing systems. The obtained NOL ring strength is optimal. Combined with the gel time of the MP01 resin system in Table 3, it can be seen that the gel time of the MP01 resin system is 21 minutes at 120°C, and the resin system can quickly transform from an opaque resin to a transparent resin at 120°C, which also shows that in At this temperature, the powder curing agent in the resin system quickly dissolves into the resin system, and the chemical crosslinking reaction begins to gradually occur. If the heat preservation platform is set before 120°C, the performance of the NOL ring in this system is not good. The main reason may be that at 80°C, the gel time of the resin is long, and the resin maintains a low viscosity (below 2000cps) state for a long time, resulting in the resin system The liquid part in the medium seeps down in the fiber, but the curing agent powder is filtered by the fiber in the interlaced environment of the carbon fiber tow, and stays in the interlayer part more, and enters the fiber less, so there is an uneven curing state, especially is inside the fiber bundle. Finally, during the stretching process, the resin in the fiber bundle is insufficiently cured due to the lack of curing agent, which affects the performance of the NOL ring. The degree of NOL curing under different curing systems shown in Table 5 can also be proved from the side. The performance of 100°C insulation is improved compared with 80°C. This is mainly because the medium temperature curing at 100°C has already started, and the resin viscosity has gradually begun to crosslink. The viscosity of the system increases, which reduces the problem of uneven curing caused by resin seepage. When the curing temperature is higher than 120°C, the strength of the NOL ring shows a downward trend again, which may be due to the fact that the temperature is too high, and the MP01 resin has not been given sufficient curing flow time, resulting in insufficient infiltration of the outer fiber bundle resin into the fibers, which in turn affects the final result of NOL ring performance.
Fig. 7 Performance changes of NOL rings under different curing systems of MP01 resin

Table 3. Gel time of MP01 resin system at different temperatures

<table>
<thead>
<tr>
<th>MP01 resin</th>
<th>80℃</th>
<th>100℃</th>
<th>120℃</th>
<th>130℃</th>
<th>140℃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>512min</td>
<td>115min</td>
<td>21min</td>
<td>9min15s</td>
<td>3min30s</td>
</tr>
</tbody>
</table>

Table 4. Viscosity changes of MP01 resin system at different temperatures and times

<table>
<thead>
<tr>
<th>MP01 resin</th>
<th>80℃@0h</th>
<th>80℃@2h</th>
<th>100℃@0h</th>
<th>100℃@2h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>562cP</td>
<td>1585cP</td>
<td>205cP</td>
<td>Cured</td>
</tr>
</tbody>
</table>

Table 5. The curing degree of MP01/HF30F-12K/28 prepreg yarn under different curing systems

<table>
<thead>
<tr>
<th>Solidification system</th>
<th>Curing degree of MP01/HF30F-12K/28 after curing (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80℃@2h+120℃@2h</td>
<td>89%</td>
</tr>
<tr>
<td>100℃@2h+120℃@2h</td>
<td>94%</td>
</tr>
<tr>
<td>120℃@2h</td>
<td>99.2%</td>
</tr>
<tr>
<td>120℃@3h</td>
<td>99.6%</td>
</tr>
<tr>
<td>130℃@2h</td>
<td>99.4%</td>
</tr>
<tr>
<td>140℃@1h</td>
<td>99.7%</td>
</tr>
</tbody>
</table>

3.4. The effect of different resin content of MP01/HF30F-12K prepreg yarn on the performance of NOL ring

Fig. 8 shows the tensile strength of the NOL rings of MP01/HF30F-12K prepreg yarns with different resin contents. It can be seen from the figure that when the resin content is stable at 28%, the corresponding NOL ring tensile strength reaches the maximum under the same environment. This rule is mainly due to the fact that after the prepreg is cured, the higher the fiber content per unit volume, the more fibers that can exert strength. At the same time, the appropriate resin content is used as the stress transfer matrix of the composite material, which can most effectively play the role of fiber performance. When the resin content is lower than 28%, the resin content between fibers is not enough to play the role of stress transmission or there are defects in the process of stress transmission. When the resin content is higher than 28%, the fiber volume content per unit volume is too low to maximize the fiber performance. Usually, the fiber resin content of wet winding is more than 37%, which is also an important reason why wet winding is not as good as dry winding in the industry. Table 6 shows the distribution of resin content in the linear long-distance of a single prepreg yarn randomly sampled. It can be clearly seen from the table that the long-distance distribution of resin content is stable, which ensures the uniformity and stability of resin content in the prepreg yarn production process.
3.5. Comparison of NOL ring strength under different winding methods and winding tension

Winding tension is a key factor affecting the performance of wound gas cylinders. Fig. 9 shows the influence of wet winding and dry winding on the tensile properties of NOL rings under different winding tensions. It can be seen from the figure that wet and dry winding have the same NOL ring with the increase of winding tension. Tendency to increase in tensile strength. But when the winding tension reaches a certain value, it continues to increase, and the tensile strength of the NOL ring tends to decrease. The difference between the two winding methods is that the optimal tension position is different. This is mainly because when the wet winding is under tension, the fiber is mainly under force, and the viscosity of the wet resin is low. When it is under tension, it cannot bear the tension together with the fiber. Friction also accelerates the wear of fibers, resulting in performance degradation. The performance degradation of wet NOL rings in the figure can support the above theory. In the dry winding process, the fiber and the resin are bonded together. When the tension is applied, the fiber and the resin are stressed at the same time, which can better transmit the force and withstand more winding tension. When the winding tension exceeds 62N, the performance of the NOL ring will appear. decline. This shows that the winding tension in this system is not easy to exceed 62N. In addition, in order to exclude the influence of the performance of the fiber itself, we conducted a long-distance test of the multifilament strength of carbon fiber. It can be seen from Table 7 that the multifilament strength of HF30F-12K fiber is basically stable. This ruled out the effect of poor NOL ring performance due to uneven fiber strength distribution.

At the same time, we conducted scanning electron microscope tests on the broken section of the wet-wound NOL ring under the winding tension of 24N and the broken section of the dry-wound NOL ring under the winding tension of 62N. From Fig. 10(B), it can be seen that the resin and fiber distribution of the dry-wound tow prepreg is more uniform after curing, and the fibers "loosen" during the stretching and breaking of the NOL ring. The fibers can better transmit the tensile stress. The cross-sectional view of the wet winding is shown in Fig. 10(A). From the scanning electron
microscope, it can be seen that the curing growth of the resin is unevenly distributed, which indirectly leads to the fact that the resin and the Where the fibers are weakly bonded, stress concentration is prone to occur, and it is difficult to realize the overall performance of the mechanical properties of the fibers. This also indirectly proves that MP01/HF30F-12K prepreg yarn has more advantages in fiber performance than AF4206/HF30F-12K wet winding.

![Fig. 9](image)

**Fig. 9** Strength comparison of wet and dry NOL rings under different winding tensions

**Table 7.** Multifilament strength of HF30F carbon fiber long-distance spot measurement

<table>
<thead>
<tr>
<th>Example</th>
<th>Tensile strength of multifilament (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200m</td>
</tr>
<tr>
<td>1</td>
<td>4926</td>
</tr>
</tbody>
</table>

![Fig. 10](image)

**Fig. 10** Cross-sectional view of wet (A) and dry (B) wound NOL rings

### 3.6. Bursting performance of gas cylinders under different winding methods and methods

In order to verify the burst pressure of MP01/HF30F-12K/28 prepreg yarn dry winding and AF4206/HF30F-12K wet winding parts. According to the design of the composite material gas cylinder winding process, a 9L aluminum liner is used. The relevant specifications of the liner are shown in the Fig. 11, where the radius of the liner is R=82mm, the length of the tube is L=531mm, the radius of the pole hole is r=15mm, and the diameter of the gas cylinder is The nominal working pressure P=30MPa, the minimum burst pressure Pb is set to 2.25 times of the nominal pressure or 67.5MPa. In order to ensure the consistency of the comparison between wet and dry winding, we set the winding angle α to 20° through experiments, which can meet the conditions of wet and dry winding at the same winding angle. According to grid theory\[19-20\], the thickness of filament winding is determined by formula (2):

\[
t_α = \frac{R P_b (2 \delta K K \cos 2 \alpha)}{2 \delta K}
\]  
\[
t_θ = \frac{R P_b (2 - \tan 2 \alpha)}{2 \delta K}
\]  

Among them, \(t_α\) is the thickness of the helically wound fiber, \(t_θ\) is the thickness of the hoop wound fiber, \(\delta\) is the tensile strength of the fiber multifilament 4918MPa (the average value of the
multifilament strength in Table 10), K is the fiber strength exertion rate, which is set to 0.8, and Ks is the stress balance coefficient which is set to 0.7, and Pb is the burst strength of the cylinder at 67.5MPa. Substituting the data, we can get: \( t_\alpha = 1.075 \text{mm} \), \( t_\theta = 1.241 \text{mm} \). Since the radius of the pole hole of the gas cylinder is only 15mm, the width of the winding yarn is not easy to be too wide in consideration of the possible fiber overhead problem at the pole hole of the gas cylinder. The gas cylinder has 8 layers of helical winding and 9 layers of hoop winding. In order to improve the overall performance of the gas cylinder, hoop winding and helical winding should be carried out alternately. The curing process of the cylinder is 120°C@2h. The wet winding adopts the same winding process design, and the curing process adopts 90°C@2h+130°C@3h.

According to the GB/T35544 standard, the hydraulic blasting test of the composite material gas cylinder is carried out. The burst pressure of the wet wound gas cylinder is 51.8 MPa, and the burst pressure of the dry wound gas cylinder is 68.5 MPa. The blasting positions of the wet and dry gas cylinders are both in the cylinder Fig. 12 belongs to the blasting in the normal working section, and Fig. 12 is a physical map of the blasting of the gas cylinder.

The wound gas cylinders prepared by the two methods burst due to insufficient hoop strength. The burst pressure of the wound gas cylinder is determined by the hoop strength, and the hoop strength Pb is determined by Equation 3.2. Through reverse derivation, the respective actual fiber conversion rates \( K_{\text{wet}} = 61.4\% \) and \( K_{\text{dry}} = 81.2\% \) can be calculated respectively. From the perspective of actual conversion rate, the conversion rate of prepreg yarn dry-wound gas cylinders is 19.8% higher than that of wet-wound gas cylinders.

4. Conclusion

In this paper, through the transformation and optimization of the basic equipment, the wet-jet wet-spun carbon fiber is used to realize the preparation of prepreg yarn with good manufacturability and excellent performance. In the prepreg preparation process, through the study of the DSC curve and viscosity-time characteristic curve of MP01 resin, the best resin aging process and curing process were determined, and the prepreg that can apply greater winding tension compared with wet winding was obtained. Impregnated yarn, and compared with the NOL ring performance and unidirectional board performance obtained by wet winding with AF4206 resin and HF30F fiber, the corresponding
performance of MP01/HF30F/28 prepreg yarn is better. The gas cylinder is wound under the same winding process design, and the blasting performance of the obtained gas cylinder is 68.5MPa in dry winding, which is higher than the theoretical design strength of 67.5MPa. The blasting strength of wet winding is 51.8MPa, and the performance conversion rate of the same fiber is increased from 61.4% to 81.2% for cylinders made of the same fiber in different application method.

Acknowledgements
The authors gratefully acknowledge the support from Jiangsu Hengshen Co., Ltd. funds.

References
