Experimental study on process of carbon fiber composites based on high temperature epoxy system curing

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Abstract. The carbon fiber reinforced composite materials used in sliding friction pairs was studied in the paper. A type resin matrix of epoxy CYD-128 with 4-4’ Diamond dipheny methane(DDM) was prepared, and the curing dynamics parameters under different heating rates were studied by DSC thermal analysis, the curing step as 100°C/2h+160°C/2h was assured according to the β extrapolation method; The exsistance and the content change of the characteristic functional groups in the cured epoxy resin were analysed by the Infrared spectrum of the cured epoxy resin; The carbon fibers were processed with vacuum impregnation technology after glued, and the tensile fracture of the sample was observed as well as the micro morphology by SEM. The tests showed that the tensile strength of carbon fiber composite had grown 18.9% and the compression strength increased 25.9% by vacuum impregnation, and the carbon fibers were closely combined with the epoxy resin.

1. Introduction
Sliding friction pairs are important parts of mechanical equipments, Conventional friction pairs materials have the disadvantages of high manufacturing cost, high friction coefficient, insufficient bearing capacity and low efficiency [1]. Polymeric composites are frequently used in applications where traditional fluid lubrication cannot be used. These composites usually consist of a reinforcement, resin matrix, one or more solid lubricant added for binding components together, for environmental stabilization, etc. . Carbon fiber (CF) has the advantages of high strength, excellent chemical stability and low price. It was the good choice for reinforcement materials. Epoxy resin (EP) materials are the most commonly used resin matrix. Solid lubricants often use MoS2 and graphite, etc. [2]

Excellent properties of CF composite materials are closely related to resin matrix. The high-temperature curing agents for EP commonly used in the preparation of CF composites are: acid anhydrides and aromatic amines [3]. Compared with the acid anhydride curing agent, the aromatic
amine curing agent has the characteristics of low viscosity, short curing time, easy control of the reaction process, and excellent mechanical properties of the cured product. However, the EP of the room temperature curing system has a short storage period, a high viscosity, and a poor wettability of the glue, thereby weakening the interface bonding strength between the fiber and the substrate. Moreover, its low glass transition temperature is not suitable for sliding friction transmission applications. Therefore, it is very urgent to study a suitable high temperature curing preparation process.

In the published paper, special research on DDM (4-4'diaminodiphenylmethane) is less, and it is often necessary to blend with m-phenylenediamine to lower the melting point. In this paper, preparation process of CF composites based on high temperature epoxy system curing was experimented primarily.

2. Fabrication of samples
2.1. Experimental materials
The resin-based fiber reinforced composite materials used in the experiment are mainly composed of CF and EP, and others are added to improve the properties of the composite. CF reinforcement material: CF plain weave cloth, T300-1K, produced by Toray Co. Japan(Table 1). EP (Table 2), industrial grade, produced by Yueyang Baling Petrochemical Co., Ltd., Curing materials: 4-4' diamino Diphenylmethane (DDM) (Table 3), analytical grade, Light yellow crystalline flake at room temperature; produced by Aladdin Reagent Co.. Other materials: Epoxy reactive diluent 501 ; dibutyl phthalat; Amine. The detailed Composite material formula are shown in Table 4.

| Table 1. The product specification of Japan Toray 1K CF. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| **Warp yarn**                  | **Weft yarn**   | **Weaving type**| **Thickness**   | **Width(cm)**   | **Densit(g/m²)**|
| T300-1K                        | T300-1K         | Plain           | 0.15            | 100             | 119             |

| Table 2. The essential parameter of EP CYD-128. |
|---------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| **Type**                                    | **epoxy value** | **Epox equivalent** | **Viscosity(25°C)** | **mPa·s** |
| CYD-128                                     | 0.53mol/g       | 184–194         | 11000–14000     |

| Table 3. The essential parameter of DDM. |
|-----------------------------------------|-----------------|-----------------|-----------------|
| **Type**                                 | **molecular formula** | **Active hydrogen equivalent** | **Melting point** |
| DDM                                      | C13H14N2        | 49.57           | 89–91°C         |

| Table 4. Composite material formula. |
|--------------------------------------|-----------------|-----------------|-----------------|-----------------|
| **Epoxy**                            | **DDM**         | **Active diluent** | **Plasticizer** | **Graphite**   | **MoS₂** | **French chalk** | **Chopped Fiber** | **Plain weave carbon fabric** |
| 50                                    | 12.5            | 2.5             | 5              | 3.25           | 5       | 8.25            | 13.5            | Several layers based on the sample |

2.2. Fabrication of samples
2.2.1 Preparation of resin samples. DDM has poor compatibility with EP. Before being used,
Weighed the EP, curing agent, modified components, etc. according to the specific formula ratio. The EP and the modified component are mixed and stirred uniformly at room temperature, and the DDM curing agent is heated to 120℃ to melt, in order to prevent the liquid DDM from cold crystallization again, the other components are pre-baked at low temperature for 20 min, and then DDM is evenly mixed. Finally, the vacuum defoaming treatment is carried out at room temperature for 30 min.

2.2.2. Preparation of resin matrix samples. Slowly pouring the prepared colloid into the self-made mold, and heating and keeping warm according to a certain curing step; after cooling, it is naturally cooled to room temperature, and after demolding, it is processed to stretch and compress the sample.

2.2.3. Preparation of resin-based fiber reinforced composite materials samples. The CF cloth is cut into a certain size, and pre-treated according to the sequence of: acetone cleaning,nitric acid heating oxidative, coupling treatment. Using hand lay-up method, uniformly coating the glue on the surface of the CF cloth, stacking and placing it in the mold, pressing to the required thickness, the mold is placed in an oven and heated in accordance with the same curing step of the resin body. After the curing, it is naturally cooled. then demolding, processing and polishing to the stretching and compressive samples.

2.3. Experimental equipment
Q2000 DSC, American TA Co.; Nicolet 6700 Fourier Infrared Spectrometer, American Thermo Fisher Co.; CMT5504 Microcomputer Control Electronic Universal Tensile Machine, Shenzhen Xinsansi Material Co.; NDJ-1E Rotating Viscometer, Shanghai Changji Co.; S-3400N SEM, Japan Hitachi Co.; vacuum drying oven, Shenzhen Kuaike Co..

2.4. Performance test methods
2.4.1. DSC test. About 10 mg sample was taken, nitrogen flow rate was 50.0 ml/min, temperature rise interval: 20℃ to 300℃, and heating rates were 5 K/min, 10 K/min, 20 K/min, respectively.

2.4.2. Fourier infrared spectroscopy test. Take a little epoxy cured product, grind it into powder, sample according to KBr tableting method, wave frequency interval 500-4000cm⁻¹;

2.4.3. Colloid viscosity test. Select 4# rotor, 12r/min, Take appropriate amount of colloid and immerse the rotor in the glue;

2.4.4. Mechanical properties. Tensile strength and compressive strength of the resin matrix samples are tested on the test machine according to GB/T2568-1995 and GB/T2569-1995 test requirements. The Tensile and compressive strength of CFRP were tested on the test machine according to the test requirements of GB/T1447-2005 and GB/T1448-2005, respectively, wherein the compressive sample pressure was perpendicular to the direction in which the CF cloth was laid.

3. Experiment results and analysis
3.1. Epoxy curing process by DSC test
The curing process of the resin and the degree of curing directly determine the properties of the composite material. For a certain resin and curing agent system, it is especially important to select suitable curing process. In this study, based on a set of heat flow curves at different heating rates, the extrapolation T-β method was used to determine the gelation temperature, peak temperature, cure termination temperature and reaction heat ΔH at the heating rate β=0, thus determining the best curing process[6]. The DSC test results of the colloid system are as follows:

Figure 1 is the heat flow curve when the heating rate is β = 5, 10, 20K/min, The result can be seen : the reaction process is an exothermic reaction, with the increase of the heating rate, The curing initiation temperature Ti, The peak temperature Tp and the termination temperature Te also increase, the heat flow curve continuously moves toward the high temperature direction, and the curing exothermic peak becomes high and wide, and the reaction exotherm is also generally increased. This is because, with the increase of the heating rate, the thermal inertia of the system becomes larger, and the resulting measurement temperature difference is larger, resulting in the movement of the curve[7].

Figure 1. The DSC curves at different heating rate.

Figure 2. The linear regression relationship of temperature and heating rate.

Table 5. The thermo dynamic parameters at different heating rate.

| β/(K/min) | Ti (℃) | Tp (℃) | Te (℃) | ΔH (J/g) |
|-----------|--------|--------|--------|----------|
| 5         | 73.8   | 146.4  | 182.9  | 385.6    |
| 10        | 75.3   | 163.7  | 241.3  | 402.2    |
| 20        | 78.4   | 182.5  | 274.2  | 448.0    |

In Table 5, the thermodynamic parameters of the curing system at different heating rates are listed according to the DSC heat flow curve. Using the data in Table 5, Ti, Tp, and Te curve (Figure 2) can be obtained by linear fitting. It can be seen from Fig.2 that when β=0, the initial solidification temperature Ti0=72.2℃, the peak temperature Tp0=137℃, and the termination temperature Te0=166.5℃. It is concluded that the resin system begins to crosslink between 72.2℃ and 137℃. Due to the explosion of EP, it can not be raised to high temperature in a short time. It should be heated slowly and kept for a period of time. Related literature[8], considering the cycle of the curing reaction and the regularity of the data, the curing step is determined to be: 100℃ / 2h + 160℃ / 2h. According to the calculation, the degree of solidification of the product is over 95% on this curing system, which satisfies for the use of the resin matrix for the CF composite material.
3.2. Glass transition temperature of Resin cured product

Due to the poor thermal conductivity of polymer composites, it is important to increase the glass transition temperature Tg of composites as much as possible for composites used in sliding friction pairs. In order to reflect the effect of curing conditions on Tg of the cured EP, the DDM/CYD-128 epoxy system was cured according to three different heating steps, and the vitrification temperature of each system was tested. Among them, system1 is cured at 100°C/2h+150°C/2h, system2 is cured at 100°C/2h+160°C/2h, system3 is 100°C/2h+160°C/2h+180°C/1h. Tg of the cured product were measured to be 107.8 °C, 147.82 °C, and 148.45 °C, respectively.

The effect of the curing process on Tg of the cured product is: The increase of the curing step temperature can further promote the reaction of the EP with the curing agent molecule, so that the degree of curing is higher, and the cross-linking density of the EP is increased. For tighter cross-linked networks, more energy is needed to trigger large-scale coordinated segmental motion at the glass transition [7]. Therefore, in the system2, Tg of the resin is improved as compared with the system1. After the system3 was subjected to 100°C/2h+160°C/2h, the degree of reaction was consistent with that of the system 2, and the curing was complete. Therefore, after the 180°C/1h curing process, the Tg of the cured product did not change significantly.

3.3. Infrared spectroscopy

It was known that the molecular structure determines the characteristic wavelength of its infrared spectrum. In this paper, infrared spectroscopy is used to analyze and identify the existence of characteristic functional groups such as epoxy, amine and hydroxyl, and quantity based on the position and shape of the characteristic peak.

![Figure 3](image1.png) ![Figure 4](image2.png)

Figure 3. The Infrared spectrum of EP.

Figure 4. The Infrared spectrum of DDM.

It can be seen from Fig. 3 that in the region around 913 cm⁻¹, the appearance of the characteristic peak of the epoxy group corresponds to the CYD-128 spectrum. On the infrared spectrum of the curing agent DDM in Figure 4 Symmetrical and antisymmetric stretching vibration peaks (double peaks) of nN-H appear at 3407 cm⁻¹ and 3446 cm⁻¹, and there are spikes on the low side of the nN-H absorption band, This phenomenon is consistent with the characteristics of aromatic diamines [11]. In Fig. 5, there are infrared spectra of cured products of three different degrees of cure, respectively. It can be seen that as the curing reaction proceeds, the epoxy group is gradually opened, the amine group is continuously consumed, and the corresponding band intensity is correspondingly weakened.
Compared with Figures 4 and 5, Figure 5 shows a hydroxyl peak at around 3500 cm\(^{-1}\). This indicates that the epoxy group undergoes a ring opening reaction with an amine group, and a hydroxyl group is continuously formed. In terms of quantity, System 1 > System 3. Comparing the ratio of the ratio of the epoxy group to the hydroxyl group, it can be inferred that the degree of cure \(\alpha_1 > \alpha_3\).

### 3.4. Viscosity curve

Figure 6 is a plot of viscosity versus time for DDM/epoxy system (high temperature cure) and amine/epoxy system (room temperature cure). It can be seen from the Figure 3 that the viscosity of the room temperature curing system is 12000 mPa.s, slowly rises to 20000 mPa.s within 60 min, but then its viscosity increased sharply. This indicates that the EP begins to carry out the crosslinking reaction. It can also be seen that the viscosity of the high-temperature curing system tends to increase linearly with time from 0 to 140 min. After this time, the viscosity change rate becomes slower and is basically stable at about 35000 mPa.s, indicating that the gelation process of the system is basically completed at this time, and because the aromatic amine curing agent has low reactivity at room temperature, its viscosity does not change much. This shows that the DDM/epoxy system not only has low viscosity, but also has a relatively long storage period at room temperature.

### 3.5. Mechanical properties of resin-based fiber reinforced composite materials

#### 3.5.1. Effect of vacuum dipping on mechanical properties

It can be seen from the data in Table 6 that the CF reinforced epoxy composite material is superior to the resin matrix itself by 4 to 5 times. After resin coating, the tensile strength and compressive strength of the composite were increased by 18.9% and 25.9%, respectively, under the condition of pressure of -101 KPa for 1 h.

| Sample                  | Tensile Strength / MPa | Compressive strength / MPa |
|-------------------------|------------------------|-----------------------------|
| Epoxy Body              | 88.7                   | 106.3                       |
| CFRP                    | 474.3                  | 407.2                       |
| CFRP (vacuum dipping)   | 563.6                  | 512.5                       |

After vacuum treatment, the bubbles generated by the glue and the small molecule gas generated by the reaction are easily discharged, which facilitates further penetration of the colloid into the CF tow,
strengthens the bonding of the EP, and thereby improves the mechanical properties of the composite.

3.5.2. Macroscopic fracture morphology observation. In Fig. 7, the left and right sides are respectively the fracture portions of the tensile specimen of the composite which has not been vacuum treated and subjected to vacuum treatment. Careful observation of the fracture of the left side of the sample, the length of the fiber break is different, the CF tow is exposed to the air, and the layer peeling phenomenon occurs at the fracture; while the fracture of the right side of the sample is relatively flat, and the fiber cloth layer is firmly bonded. The left side of Fig. 8 is a compressed sample of the composite after vacuum treatment. The fracture surface is at an angle to the direction of compression. It is known that the fracture occurs between the fibers; the right side is a composite sample compressed without vacuum treatment, and the surface is flat. The fracture occurs between the CF layers during the failure.

![Figure 7. The fractures of CFRP tensile samples.](image)

![Figure 8. The fractures of CFRP compression samples.](image)

![Figure 9. The SEM photographs of CFRP tensile sample fracture.](image)

3.5.3. SEM analysis of tensile fracture. As can be seen from Figure 9, after the vacuum treatment, the CF tow is filled with EP, the fibers are very tightly bonded, and the fracture is neat; and the CF without vacuum treatment is scattered and detached from the resin matrix. It is inferred that the cohesive force formed between the vacuum-treated composite fibers is large, the fibers are broken at one place during the break, and the fractures are flat; while the untreated CFs are insufficiently combined with the resin body, and the fibers are pulled out.
4. Conclusion
The optimal curing process of DDM/epoxy system is 100°C/2h+160°C/2h by DSC extrapolation method, and the ratio of CYD-128:DDM=4:1 is suitable by test. At the same time, the glass transition temperature of the resin matrix is greatly affected by the curing process, and the Tg reaches 147.82°C.

Vacuum treatment can improve the wetting effect of fiber and glue, and further improve the bonding strength between CF and epoxy. When the pressure is -101KPa, the tensile strength of CF composite increases by 18.9%, its compression strength increased by 25.9%.

Compared with the room temperature curing system, the high temperature curing system has the characteristics of low viscosity and long storage period, and its effective use period is more than 2 hours, which improves the practical operability of the hand lay-up method and is beneficial to the fiber reinforced composite material.

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