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Carbon Fiber Reinforced Epoxy Resin Matrix Composites

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ABSTRACT

Carbon fiber reinforced polymer matrix composites have been the focus of research. As the most widely used epoxy resin in all matrix materials, it is also the most studied. In this paper, the modification of TDE-85 epoxy resin, the curing properties of curing agent and the preparation method of prepreg were reviewed. The progress and application of carbon fiber reinforced epoxy resin composites at home and abroad were reviewed, made carbon fiber / epoxy resin composite materials in the automotive fuel cell application prospects.

KEYWORDS: Carbon fiber, epoxy resin, matrix, composite material

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Preface

Among the many composites (metal matrix composites, ceramic matrix composites and carbon-based composites), carbon fiber reinforced polymer composites (CFRP) have high specific strength, specific stiffness, fatigue resistance , Dimensional stability and good corrosion resistance and other excellent performance in the aerospace, defense industry, building materials, automotive industry and sports and leisure equipment and other fields have been widely used [1].

In the field of aerospace, foreign advanced composite materials in the aircraft structure of the application has been developed to the wing, fuselage and other main bearing structure [2]. In order to meet the design requirements of the damage tolerance of the aircraft, the composite bearing structure of the composite material adopts the composite material with high performance carbon fiber as the reinforcement and high temperature curing high toughness epoxy resin. In recent years, with the expansion of domestic carbon fiber production scale, the cost reduction and the development of production technology, carbon fiber reinforced polymer composite materials from the initial military defense field is limited to the use of military aircraft to the current dual-use dual- In the field of energy power generation, sports equipment, transportation and biomedical tools are widely used.

Carbon fiber reinforced epoxy resin matrix composite material is carbon fiber reinforced, epoxy resin as the matrix. As the carbon fiber is a brittle material [3], it can be compounded with epoxy resin to improve the toughness of composite materials, and carbon fiber excellent mechanical properties can also give the composite good strength and stiffness. In the process of preparing the carbon fiber reinforced epoxy resin composite material, the carbon fiber and the epoxy resin matrix are preliminarily prepared by prepreg, and then the prepreg is made into composite material by the molding process The

1. Carbon fiber reinforced epoxy resin prepreg

1.1. Epoxy resin matrix

Currently used for high-grade composite resin mainly epoxy resin. In order to further improve the heat resistance, strength and stiffness (i.e. modulus) of the composites, scientists at home and abroad have developed a number of new epoxy resins with better performance than the common bisphenol a type epoxy resin, domestic industrial varieties Also a lot. The following describes the TDE-85 epoxy resin is developed in recent years in China and first put into the industrial production of a better performance of a new type of epoxy resin.

TDE-85 epoxy resin, scientific name: 4, 5-epoxy cyclohexane-1, 2-dicarboxylate (4, 5-epoxy cyclohexane-1, 2-dicarboxylate diglycidyl). It is a trifunctional epoxy resin, is the development of epoxy resin at home and abroad the only molecule contains both active glycidyl esters, but also alicyclic epoxy resin. It comes with two characteristics which are glycidyl ester and ester ring epoxy. TDE-85 epoxy resin can be made of high temperature adhesives, filling materials, coatings and excellent performance of the composite material. Especially in the production of fiber composite materials, its performance is even more prominent. It not only has excellent mechanical properties at room temperature, and at 100 °C high temperature many mechanical properties are basically unchanged, so it is a very practical the value of the composite matrix resin.

However, epoxy resin also has a high cross-linking density after curing, crisp, fatigue resistance and temperature level is not high enough shortcomings, restricting the epoxy resin cannot be used for structural materials and other types of composite materials, so change Epoxy resin toughness and heat resistance has been one of the important issues at home and abroad. In recent years at home and abroad have done a lot for TDE-85 epoxy resin toughening and improve the heat resistance of the modified study.

Polypropylene glycol (PPG), 4,5-epoxy cyclohexane-1,2-dicarboxylic acid diglycidyl ester (TDE-85), acrylic acid (PUA) prepolymer and TDE-85 epoxy acrylate (EA) prepolymer were synthesized by using AA and glycidyl as raw materials. The results show that, in the PUA / EA system, the compatibility of the PUA / EA is better. The possible reason is that both of them have the same hydroxyl group in the main chain, thereby increasing the compatibility of the two. When the ratio of the two is 50/50, the overall performance is the best, 25 °C tensile shear strength of 13.4MPa, -196 °C when the 12.9MPa.

Wu Guanglei et al. [5] used 4, 4'-diphenyl methane bismaleimide (BMI), bisphenol a dicyanate (BADCy) and 4, 5-epoxy cyclohexane- (TDE-85) epoxy resin was used to prepare bismaleamide-triazine / epoxy resin interpenetrating polymer. The results showed that when the content of TDE-85 epoxy resin was 20wt %, The polymer TDE-85 / BMI / BADCy showed very good mechanical and thermal properties, impact strength and bending strength reached a maximum of 13.5kJ / m2 and 148MPa, respectively, polymer BMI / BADCy 1.41 times, dielectric The performance is 0.9 times the polymer BMI / BADCy.

Guo et al. [6] conducted a non-isothermal DSC experiment on TDE-85 and AG-80 epoxy resins. The activation energy of TDE-85 resin system was higher than that of AG-80 resin system. TDE-85 resin the flexural modulus of AG-80 resin system reached 1804.32MPa and the flexural strength was 42.64MPa. The flexural modulus of AG-80 resin was 1880.03MPa and the flexural strength was 61.08MPa. The surface of AG-80 resin casting is very smooth, while the TDE-85 resin casting section has a large number of water-like cracks in line with the toughness of the fracture after the morphological characteristics.

1.2. Curing agent

Pure epoxy resin is only a thermoplastic low molecular weight prepolymer, not much use value, so the need to join the curing agent to form a three-dimensional epoxy resin network structure to play its maximum use.

Epoxy resin variety, different types have different curing temperature, generally divided into: low temperature curing (room temperature below), room temperature curing (room temperature 50 °C), medium temperature curing (50 - 130 °C) and high temperature curing (130 °C the above). Low temperature curing has always been pro-gaze, mainly because it can greatly reduce the cost of output, compared to low-temperature curing, high-temperature curing of the equipment will certainly put stringent requirements, but can get excellent heat resistance curing products. Therefore, it is necessary to select the appropriate curing agent according to the curing temperature of the epoxy resin to fully reflect the effect of the curing agent, while giving the best performance of the cured product.

The most widely used curing agents are mainly polyamine and acid anhydride type, because they can provide very active groups, only a small amount of the need to participate in the system curing and curing the system completely, they are able to Directly through the addition principle directly involved in the entire process of curing to go.

1.3 Prepreg

The prepreg is a prepreg product which is made of resin impregnated with resin and is an intermediate product of composite material. Depending on the properties of the desired composite material and the intended use, there are various differences in the preparation of the prepreg.

Wet preparation of prepreg, not only easy to operate, simple equipment, but also has the characteristics of versatility, most of the prepreg can be prepared by wet method, but due to wet preparation process to enhance the proportion of fiber and resin Difficult to control, it is difficult to prepare uniform performance of the prepreg, and thus affect the overall performance of composite materials. Compared with the wet method, dry method can be a good way to overcome the shortcomings of the wet method, while the dry method can also avoid the volatile content of the wet, further control the performance of the prepreg to optimize.

Whether it is wet or dry or dry and wet method, are more suitable for thermosetting prepreg, for thermoplastic prepreg, the main use of powder, such as powder electrostatic powder and powder suspension.

At present, the focus of domestic research is still thermosetting prepreg. (6) The T800 carbon fiber / epoxy prepreg was prepared by differential scanning calorimetry (MDSC). The results showed that the prepared prepreg had good thermal conductivity, the thermal conductivity in the direction of the fiber is 1.15 to 1.40 W / (m.k), and the thermal conductivity in the vertical fiber direction is 0.85 to 1.25 W / (m.k). Thermal conductivity is a manifestation of the thermal properties of the prepreg and is a function of heat.

For the overall performance of the prepreg, we also need to focus on its mechanical properties. Sun Zhanhong et al. [8] prepared CF / BA9918 prepreg with phase migration toughening technology with a volatile content of only 0.7%, a resin flow of 10.7% and a resin content of 36.2%, and the composite The flexural strength of the material is 1216MPa, the interlaminar shear strength is 107MPa, and the tensile strength is 2837MPa. It can be seen that the performance of the prepared prepreg can achieve a very high level even among foreign products. Sui Yuemei [9] the epoxy resin prepreg with stable performance was prepared by synthesizing B-stage resin. Further, under the influence of B-stage epoxy resin, the flexural strength is improved by 36.56MPa, the flexural deflection is improved by 0.843mm, the tensile strength is increased by 20.78MPa, and the elongation is increased by 2.35%.

In recent years, with the development and widespread use of carbon fiber reinforced resin matrix composites, the development of prepreg for specified uses has also developed rapidly, especially in foreign countries, which have begun to study carbon fiber thermoplastic prepregs [10] and develop rapidly. At the same time there have been prepregs for different applications, such as automotive fields, rapid curing of the prepreg for short-term molding of the parts; structure and function of the combination of prepreg, that is, in the resin mixed with carbon nanotubes or chopped Carbon fiber to obtain a prepreg having a heat absorbing function.

2. Carbon fiber reinforced epoxy resin matrix composites

With the increasing scale of production of carbon fiber, production equipment technology is more and more advanced, and the use of more and more widely, for the carbon fiber research is also endless, followed by the promotion of carbon fiber in the composite materials, especially the Carbon fiber and epoxy resin composite, the composite material not only in the mechanical properties have improved, in toughness and thermal stability have been greatly enhanced.

2.1. Status of domestic research

2.1.1 Molding method and its effect on the properties of composite materials

Different molding methods for the resin matrix requirements will be different, mainly in the resin viscosity and curing properties, the appropriate viscosity is conducive to the coating of resin glue, and good curing properties are conducive to long-term storage of resin. WJ-3 / T-700S composites were prepared by WOP-3 epoxy resin as the matrix and by hand-paste molding. Low viscosity WBS-3 resin matrix is conducive to the operation of hand laying, in addition WSB-3 resin toughness and good storage performance can give the composite material excellent mechanical properties and high temperature performance. The tensile strength, tensile strength and shear strength of WBS-3 / T-700S composites were 1434MPa, 76.1MPa, 1972MPa, and the glass transition temperature (Tg) exceeded 210 ℃, which belonged to high temperature curing. While at the same time, the composite material has a good interface bonding performance.

The brittleness of the carbon fiber itself needs to be improved by the toughness of the substrate by recombination with the substrate, so that the resin used as the substrate must have good toughness. Yang Xiao-ping of Chemical Engineering University [12] by the first carbon fiber and epoxy resin made of prepreg, and then use the electrospinning device to polysulfone (PSF) nanofibers directly deposited on the prepreg, the resulting composite The toughness to improve the effect is more obvious. Chen Zhenhua, Hunan University [13] uses phenol, resorcinol and acrylic acid as raw materials, through the voltammetry, electrochemical deposition, to the carbon fiber surface into the active group, thereby enhancing the carbon fiber and epoxy resin interface adhesion, by the transverse strength, longitudinal strength and interlaminar shear strength of the composites were increased by 50%, 64% and 135%, respectively.

2.1.2 Carbon fiber surface roughness on the performance of composite materials

The use of water and oxygen in supercritical water to modify the surface of carbon fiber makes the carbon fiber surface roughness and oxygen-containing functional groups effectively increased, thereby enhancing the carbon fiber and epoxy resin binding capacity, research shows that supercritical water The maximum interlaminar shear strength of the composites was 58.3MPa and 92.8MPa, respectively, which increased by 10% and 75% respectively on the basis of 52.9MPa without any treatment.

The results show that the surface roughness of the treated carbon fiber is significantly higher than that of the untreated carbon fiber, and further studies show that the increase of the surface roughness is beneficial to the carbon fiber and the ring The shear strength of the CF / EP composites prepared by the wetting of the epoxy resin was improved remarkably.

2.2. Status of foreign research

Due to the inertia of the carbon fiber itself, it is necessary to use some means to modify the surface of the carbon fiber to improve the activity of the carbon fiber and thereby be better used for the composite material. Compared with the traditional graft modification, electrochemical modification has relatively simple operation and stability. In addition, some nanoscale materials, such as carbon nanotubes and nanoclays, can be added to improve the inertness of carbon fibers to improve the compatibility of carbon fibers with epoxy resins, and to improve the mechanical properties of composites. Smrutisikha Bal [16] uses carbon nanofibers and epoxy resins to make composite materials and study their mechanical properties and electrical properties. The carbon fiber / epoxy resin composites were analyzed by electron microscopy, and the composites at room temperature had good conductivity, and the carbon nanofibers were reinforced by carbon nanofibers. , So that the mechanical strength and flexural modulus of the composite material are greatly increased.

2.2.1 Carbon nanotube doping modified composites

A. Godara et al. [17] put carbon nanotubes into the epoxy resin matrix and disperse them in a unidirectional prepreg to obtain a composite material with improved mechanical properties. The addition of carbon nanotubes can effectively enhance the mechanical properties of the composites by effectively combining the interface between the epoxy resin and the carbon fiber, and can also play a role in the interface between the epoxy resin and the carbon fiber, reinforce the toughness of the composite.

Daniel C. Davis et al. [18] studied the use of carbon nanotubes to improve the mechanical properties of carbon fiber / epoxy composites. The results show that the mechanical properties of the composites are significantly improved with the addition of carbon nanotubes.

J. Rams et al. [19] studied the prepared carbon nanofibers / epoxies, and the stiffness and modulus of the composites obtained by Nano indentation were higher than those obtained by dynamic thermomechanical analysis. The Due to the use of carbon nanofibers and their ability to disperse and distribute in the resin, the interfacial bonding properties of carbon fibers and epoxy resins are enhanced. M. Sánchez et al. [20] added carbon nanotubes of different content (mass ratio) to the carbon fiber composites of the epoxy resin matrix, which were uniformly dispersed in the resin matrix by calendering and then vacuum-assisted resin Forming a composite material. The results show that the addition of carbon nanotubes is beneficial to the transfer of stress and the strengthening of the system, which makes the mechanical properties of composite materials, especially the bending strength and interlaminar shear strength are significantly improved.

Similarly, MT Kim et al. [21] prepared carbon nanotubes / carbon fiber / epoxy composites with excellent mechanical properties by adding carbon nanotubes. In addition, due to the addition of carbon nanotubes, the carbon fiber composites treated with acid, Performance has been significantly improved, while giving the composite better wear properties and interface bonding performance.

Farhana Pervin et al. [22] used a high-intensity ultrasonic treatment to obtain a homogeneous carbon nanotube / epoxy resin mixture, and then the mixture and carbon fiber composite through the vacuum assisted resin transfer molding method to prepare the strength and fracture toughness were significant Improved CF / EP composites.

2.2.2 Nano-clay Doping Toughening Composites

Shafi Ullah Khan et al. [23] conducted a cyclic fatigue test on carbon fiber / epoxy resin with nano-clay. The results show that the addition of Nano clay improves the mechanical strength and static load of the composites, while not only extending the composite the fatigue life of the composites is also reduced and the interfacial bonding properties of the composites are enhanced by the inhibition and retardation of the Nano clay.

2.3. Carbon fiber / epoxy resin composite materials

Carbon fiber reinforced epoxy resin composites can be used not only in aerospace and defense industry, but also for civil use, such as sports and leisure, bridge construction, and even can be used in fuel cells. However, due to the weak conductivity of CF / EP composites, it is necessary to take some means to conduct conductive treatment on the surface of composite materials. Ha Na Yua et al. [24] studied the conductivity of composites by coating a thin layer of graphite on the surface of CF / EP composites, and the results show that CF / EP composites coated with graphite layers are excellent When the thickness of the graphite coating is 50μm, the total electrical interface and the resistance of the contact interface are reduced by 90% and 96%, respectively, compared with the conventional CF / EP composites.

3. Application Prospect of Carbon Fiber Reinforced Epoxy Resin Matrix Composites

Carbon fiber reinforced epoxy resin composites for automotive fuel cells can not only provide high power [25], but also can reduce the weight of the car, and CF / EP composite materials, high strength, high modulus can give the battery bipolar Board good wear resistance, extend the battery life.

In addition, compared with the traditional fuel cell, by using CF / EP composite material as a fuel cell bipolar plate need to consider its thickness. Since the conductivity of the CF / EP composites is weak, it is necessary to coat the surface with a layer of conductive film, which affects the thickness of the electrode plate.

Therefore, the overall performance of CF / EP composites, as long as the control of the thickness of the conductive coating and thermal conductivity, CF / EP composite materials in the automotive fuel cell applications will be possible, and then at a faster rate Development, and even other areas.

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