Study on interfacial connecting properties of small molecule intervention repairable epoxy composites

Tianyu Zhao, Heshan Bai, Zhenkun Lei*, Ruixiang Bai*
State Key Laboratory of Structural Analysis for Industrial Equipment, Dalian University of Technology, Dalian, Liaoning, 116024, China
*Correspondent author’s e-mail: leizk@dlut.edu.cn and bairx@dlut.edu.cn

Abstract. The interfacial bonding method and mechanical properties of new repairable epoxy and its composites were studied. Ethylene glycol was used to connect the resin interface. The effects of temperature, time and resin content on the strength of interface bonding were systematically studied, and the optimal bonding scheme was determined. The results show that this connection method has significant advantages, and the tensile strength reaches 73% of the intact resin. Furthermore, the repairable resin matrix fiber-reinforced composite was prepared, and this method was successfully extended to the composite connecting. The interfacial shear strength of the fiber composites reached 21.88 MPa by single lap test, which has a good application prospect.

1. Introduction
Resin matrix carbon fiber reinforced composites are widely used in aerospace, automobile, sports and many other fields because of their light-weight, high specific strength and high specific modulus. However, the matrix is mostly thermosetting resin, which has stable properties after curing, but the highly cross-linked network makes it difficult to be processed. Therefore, the thermosetting resin and its composites have many problems, such as interface connection and damage repair.

In view of the above problems, scholars are keen to introduce bond exchange reaction into traditional resins to design new resins, which not only can be recycled and reshaped. Among them, vitrimers based on transesterification reaction is a new research hotspot [1-3]. In 2011, Ludvik Leiber team [4] published a paper on Science, introducing a new resin with transesterification reaction, named "vitrimer", which can realize the dynamic exchange of ester bond at a certain temperature. This kind of resin has the stability of non melting and non dissolving of thermosetting resin, but it can realize secondary processing. Based on the research of Ludvik Leiber team, Yu et al. [5] smashed the resin into powder, realized the repeated processing and recycling of the resin under a certain temperature and pressure, and explored the influence of temperature, time and pressure on the mechanical properties of the material.

In recent years, small molecules have been introduced into bond exchange reactions. Among them, Shi et al. [6] used ethylene glycol to realize non-pressure connecting of vitrimer, developed 3D printing of thermosetting resin [7], and recycling of carbon fiber composites [8]. Wang et al. [9] studied the influence of catalyst and curing agent content on resin structure, and recovered carbon fiber reinforced composites with ethylene glycol, and the recovery rate was nearly 100%.

At present, the research of new resin is mostly concentrated in the field of materials and the research of mechanics is still insufficient. However, there are few studies on the small molecules
involved in the transesterification reaction, which is still in the development stage. Most of them focus on the degradation of resin and the recycling of composites. There are few studies on the interface connecting and repair of vitrimer and its composites, and the evaluation of its bonding method and properties after bonding is not enough. This aspect has considerable research value and significance.

In this paper, bisphenol A diglycidyl ether was used as epoxy monomer, glutaric anhydride as curing agent and zinc acetylacetonate as catalyst to prepare repairable resin with dynamic ester bond. Based on the principle of glycol intervening in transesterification reaction, the method of resin interface connecting was studied and improved, and the properties of resin interface bonding were measured. Compared with the other two connection methods, the quality of interface connection is evaluated. Furthermore, the resin bonding method was successfully extended to resin based carbon fiber composites, and the shear properties of the composites were studied by single lap test.

2. Materials and methods

2.1. Experimental materials

Bisphenol A diglycidyl ether (epoxy monomer), glutaric anhydride (curing agent), zinc acetylacetonate (catalyst), Macklin Biochemical Technology Co., Ltd; ethylene glycol; T700 unidirectional carbon fiber cloth (12 K, 200 g/m²), Yituo composite materials Co., Ltd.

2.2. Resin preparation process

The drug was weighed according to the molar ratio of epoxy monomer: curing agent: catalyst 1: 1: 0.05. Stirring bisphenol A diglycidyl ether at 130 °C until transparent, adding zinc acetylacetonate stirring until uniform system. Cool to below 80 °C, add glutaric anhydride and continue to stir until a homogeneous system is formed. The mixed liquid is injected into the mold and vacuumized at 80 °C to remove bubbles. Curing at 130 °C/4 h+160 °C/2 h, then demoulding at 130 °C.

2.3. Interface bonding process of glycol intervention

Ethylene glycol / remediable resin degradation liquid was first prepared as an adjuvant. A certain amount of the curing resin and ethylene glycol were placed in the container, heated to 180 °C under a closed environment, the ester bonds of the resin were opened under the action of ethylene glycol, and gradually degraded in ethylene glycol.

For resin connection, pipet the degradant with a drop, apply evenly to the surface to be attached, let the surface touch and put into the mold for fixation. The mold and test piece were put into an oven and heated at an appropriate temperature until the resin interfacial re-crosslinking was complete.

For the connection of composites, similar to the resin connection method, but to ensure the consistency of the distance between the sheets of the composites, the whole process was carried out on a hot press, set the same temperature as the resin connection, and after the volatilization of ethylene glycol was complete (about 1.5 h), 1 MPa pressure was given to the connection.

2.4. Test and study methods

2.4.1. Study on influence factors of interface connection strength

The effect of temperature, time and content of resin in the degradation solution of ethylene glycol / resin on the strength of interfacial junctions was investigated. The connection experiments were carried out at 130 °C, 180 °C and 230 °C respectively. The connection time was 90 min, 120 min, 150 min, 180 min, 210 min and 240 min. The resin contents were 0%, 0.33%, 0.99%, 2.91%, 5.66% and 10.71% respectively. The connection test pieces under different conditions are made for research.

2.4.2. Evaluation method of interface connection quality

For the resin test pieces that were connected under different conditions mentioned above, the quality of their interfacial connection was evaluated by tensile testing using an Instron 3345 tester, and the
loading rate was set to 2 mm/min. Combined with tensile and single lap tests, the tensile and interfacial shear strength of the ethylene glycol/resin degradation solution bonding method in this paper were compared with the other two bonding methods such as traditional bonding.

For the connection of carbon fiber composite, the single lap test piece is made to test the shear strength of the connection. The test piece size and test method are in accordance with GB/T 33334-2016, and the test is carried out on WDW-300 electronic universal testing machine.

3. Results & Discussion

3.1. Study on influence factors of interface connection strength

The effects of temperature, time and resin concentration on the bonding strength were studied.

The results of 130 °C, 180 °C and 230 °C show that the best temperature is 180 °C, and the tensile strength reaches 25 MPa after heating for 4 hours; At 130 °C, the connection is not complete after 4 h. The load-displacement curve is shown in Fig. 1(a), and the tensile strength is only 0.0239 MPa. Further, after 6 h of heating, the tensile strength is improved, but only 4.704 MPa, as shown in Fig. 1(b). In the case of 230 °C, a large number of bubbles were generated in the interface due to the boiling of ethylene glycol, resulting in the failure of the connection.

![Fig. 1. Tensile load-displacement curves for (a) 130 °C/4 h connected specimen, and (b) 130 °C/6 h connected specimen](image)

For the specimens with different curing temperatures, the uniaxial tensile test is carried out, as shown in Fig. 2(a), and the curve of interface strength-heating time is obtained, as shown in Fig. 2(b). It can be seen that the interface strength increases with the increase of heating time, and the strength increases rapidly in the first 2 h, then increases steadily with time, and finally reaches 25.143 MPa.

![Fig. 2. (a) Connection strength test and (b) curve of interfacial tensile strength-heating time](image)
On the one hand, ethylene glycol undergoes transesterification reaction with resin under the action of catalyst to chain break the resin on both sides of the interface. On the other hand, the ethylene glycol at the end of the resin fragment was separated and the resin was re-crosslinked. During 0-1.5 h, free ethylene glycol volatilized a large amount; at 1.5 h, most of the ethylene glycol volatilized completely, and the reaction proceeded in the direction of focused crosslinking, at which time the linkage strength increased faster. After 2 h, the cross-linking degree of the interface steadily deepened as the curing time grew, but the speed somewhat slowed down, which is reflected by the steady growth of the connection strength, but the increasing rate decreased in the first 2 h. Therefore, properly increasing the curing time is helpful to improve the strength of the connection, and the curing time should be at least 4 h.

The influence of the resin content in the glycol/resin degradation solution on the connection strength was explored. The specific method is to degrade 0 g, 0.1 g, 0.3 g, 0.9 g, 1.8 g and 3.6 g resin in 30 g glycol respectively, that is, the mass fraction of resin is 0, 0.33%, 0.99%, 2.91%, 5.66% and 10.71% respectively. The degradation solution is shown in Fig. 3(a).

The interfacial strength of resin connected by degradation liquid with different resin contents was measured experimentally and shown in Fig. 3(b). It can be seen that the interfacial tensile strength increased from 10.146 MPa to 29.463 MPa with the increase of resin in the degradation liquid. It is worth noting that when the resin content is 0, the resin can connect although the strength is low, and the strength is greatly improved at the concentration of 0.33%, the visible connection liquid contains resin can obviously improve the connection strength. The resin in the degradation fluid is short chain resin fragments, which exist in the interface favoring the heavy cross-linking of the resin at both ends of the interface. In summary, 10.71% +180 °C + 4 h scheme was used to connect the best.

![Image](a)

![Image](b)

Fig. 3. (a) Degradation solutions with different resin contents of 0.33%, 0.99%, 2.91%, 5.66%, 10.71% from left to right and (b) curve of interfacial tensile strength-resin mass fraction

3.2 Test and comparison of connecting strength of resin interface

The connection method in this paper is compared with the other two methods, and the tensile strength and shear strength are compared respectively. One is called "curing connection", that is, the same resin before curing is applied on the surface to be connected, and then heated to cure (130 °C/ 4 h+160 °C/ 6 h) to make the two resins stick together. Another way is acrylate bonding. The tensile and shear test pieces of degradation solution connection method are shown in Fig. 4. Tensile test was used for tensile strength and single lap test for shear strength. The test was carried out on Instron 3345 with loading rate of 2 mm/min.

The interfacial tensile and shear strengths of the three connection methods are obtained, as shown in Fig. 5. It can be seen that the tensile strength of the connection method of glycol/resin degradation solution is much higher than that of the other two modes, with an average of 30.12 MPa. The tensile strength limit of intact resin is 41.46 MPa, which is 73% of intact resin strength. The average shear strength is 7.53 MPa, which is 26% higher than that of the cured bonding method and twice as high as that of the acrylate adhesive.
Fig. 4. (a) Tensile and (b) single lap test pieces for degradation solution connection method

Fig. 5. Comparison of (a) tensile strength and (b) shear strength for three connection methods

Compared with resin curing, the degradation solution is actually a mixture of resin short chain and glycol. The strength difference between the two is nearly two times due to the role of ethylene glycol. Ethylene glycol takes part in the transesterification reaction, which leads to the degradation of the resin surface on both sides of the interface. The resin short chains on both sides and in the degradation solution diffuse and cross link with each other, so that the interface is connected.

3.3. Study on interface connecting of repairable resin matrix fiber-reinforced composite

Carbon fiber composites based on repairable resin were prepared by hot-press, and the interface connection of the composites was realized by the method in Section 2.3. According to the influence of bonding time on the strength of resin interface, after the surface is coated with glycol/resin degradation solution, it is first placed at 180 °C under 0 MPa pressure for 1.5 h (The first 1.5 h is mainly due to the volatilization of glycol, while 0 MPa pressure can ensure that glycol volatilizes fully). After 1.5 h, the re-crosslinking of the interface began to have a significant effect, showing a rapid increase in strength. At this time, a pressure of 1 MPa was applied, which was the same as that of the composite plate preparation, to ensure that the interlayer distance was consistent. The temperature was still 180 °C for 4.5 h. As a result, the two composite plates were successfully connected.

Fig. 6. (a) Single lap specimen and (b) test device

In order to evaluate the connection quality, the single lap test was carried out to test the shear strength. The specimens and tests are shown in Fig. 6, and the average interfacial shear strength is
21.88 MPa. It can be seen that this connection method can be directly used in repairable resin matrix composites, and has reliable strength, so it has a broad application prospect.

4. Conclusion

Restorable resins with dynamic ester linkages were prepared using bisphenol A diglycidyl ether as the epoxy monomer, glutaric anhydride as the curing agent, and zinc acetylacetonate as the catalyst. Then the interfacial connecting of repairable resin was studied by using ethylene glycol involved in transesterification reaction.

The effects of temperature, time and resin content on the connecting strength were systematically studied. The interface strength increases with the increase of heating time. It increases rapidly in the first 1.5 - 2 h, and then increases steadily. The heating time should not be less than 4 h to get reliable connection quality. The connecting strength of the interface increases with the increase of resin content in the degradation solution, and the bonding quality can be significantly improved by adding resin into glycol. Finally, the optimized connection scheme of 10.71% + 180 °C + 4 h is selected.

In order to evaluate the connection quality, the tensile test and single lap test were used to detect the interface strength, and compared with adhesive bonding and curing bonding. The results show that the connection method in this paper has advantages in tensile and shear strength, and the average tensile strength reaches 30.12 MPa.

The repairable resin matrix fiber-reinforced composite was successfully prepared by hot press. And the resin connecting method was successfully applied to the connecting of composite board. The interfacial shear strength is 21.88 MPa, which is worthy of application.

The restorable resin and its composites, as well as the interface bonding process studied in this paper, have the application prospect. It can provide a reference for solving the problems of composite connection and repair, provide alternative solutions for traditional connection methods.

Acknowledgments

The authors thank the National Key Research and Development Program (No. 2019YFA0706803), the National Natural Science Foundation of China (No. 11972106) and the Fundamental Research Funds for the Central Universities of China (DUT2019TD37).

References

[1] Brutman, J.P., Delgado, P.A., Hillmyer, M.A. (2014) Polylactide Vitrimers. Acs Macro Letters, 3: 607-610.
[2] Liu, W., Schmidt, D.F., Reynaud, E. (2017) Catalyst Selection, Creep, and Stress Relaxation in High-Performance Epoxy Vitrimers. Industrial & Engineering Chemistry Research, 56: 2667-2672.
[3] Demongeot, A., Mougnier, S.J., Okada, S., et al. (2016) Coordination and catalysis of Zn2+ in epoxy-based vitrimers. Polymerchemistry, 7: 4486-4493.
[4] Montarnal, D., Capelot, M., Tournilhac, F., et al. (2011) Silica-like malleable materials from permanent organic networks. Science, 334: 965-968.
[5] Yu, K., Taynton, P., Zhang, W., et al. (2014) Reprocessing and recycling of thermosetting polymers based on bond exchange reactions. RSC advances, 4: 10108-10117.
[6] Shi, Q., Yu, K., Dunn, M.L., et al. (2016) Solvent Assisted Pressure-Free Surface Welding and Reprocessing of Malleable Epoxy Polymers. Macromolecules, 49: 5527-5537.
[7] Shi, Q., Yu, K., Kuang, X., et al. (2017) Recyclable 3D printing of vitrimer epoxy. Materials horizons, 4: 598-607.
[8] Yu, K., Shi, Q., Dunn, M.L., et al. (2016) Carbon Fiber Reinforced Thermoset Composite with Near 100% Recyclability. Advanced Functional Materials, 26: 6098-6106.
[9] Wang, D., Li, L.Y., Ke, H.J., et al. (2020) Preparation and Properties of Recyclable High-performance Epoxy Resins and Composites. Acta Polymerica Sinica, 51: 303-310. (in Chinese)