

Research Article

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Effects of high polyamic acid content and curing process on properties of epoxy resins

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Abstract: Epoxy/polyamic acid (EP/PAA) adhesives with high polyimide precursor-PAA content have been synthesized and then cured. The structure, thermal, and adhesive properties were investigated by Fourier transform infrared spectroscopy, thermogravimetric analysis, and tensile shear test. The effects of PAA content and curing process on the tensile shear strength were also studied. The results showed that the addition of PAA improved the heat resistance and reduced the water absorption. EP/PAA adhesive kept good adhesion. A kind of EP/PAA composite adhesive with excellent comprehensive properties was prepared in this study.

Keywords: polyimide, polyamic acid, epoxy resin, tensile shear strength, heat resistance

1 Introduction

Flexible printed circuits (FPC) are widely used in telecommunication, computer, automobile, and electronic fields due to their excellent performance (1–4). With the rapid development of microelectronics industry, FPC are required to have lower dielectric constant, higher temperature resistance, and better processability (5). Flexible

copper clad laminate (FCCL) is an indispensable material for flexible printed circuit board (6,7). According to the presence or absence of adhesive, FCCL can be divided into three-layer FCCL (3L-FCCL) and double-layer FCCL (2L-FCCL) (8). 3L-FCCL is composed of copper foil, insulation substrate, and adhesive, which is the most widely used FCCL for its simple process and low cost (9). The adhesive bonding copper foil and insulating layer are the only products that have not achieved industrial standardization, which still directly determines the performance of 3L-FCCL.

At present, the adhesive used in 3L-FCCL mainly includes epoxy resins, acrylate, polyimide, polyester, and polyurethane (10), among which epoxy resin was widely investigated because of its excellent adhesion, moisture resistance, and chemical corrosion resistance (11–14). The studies on epoxy resins such as curing kinetics (15), flame retardant property (16), and toughness (17) of epoxy (EP) have become a hotspot. Moreover, the long-term use of epoxy resin cannot meet the application of 3L-FCCL at high temperature (18). Therefore, it is urgent for epoxy resin to be modified to adapt to the current development in the microelectronics industry. Gholipour-Mahmoudalilou et al. (19) improved the thermal properties of epoxy resin by preparing new curing agent of poly(amidoamine) dendrimer-grafted graphene oxide. Thermogravimetric analysis (TGA) results showed that decomposition temperature was improved compared to pure epoxy resin. Tao et al. (20) synthesized epoxy resin containing imine ring and siloxane. The results showed that the fully cured epoxy resin had good thermal stability and the 10% weight loss temperature was up to 365°C. Wang et al. (21) modified epoxy resin by bentonite. As the content of the bentonite increases, the heat resistance of the sample increases, and the 5% weight loss temperature of the system increases by 3.2% when the amount of the bentonite added is 10%.

Polyimide is also used as FCCL adhesive due to its low dielectric constant and high heat resistance (22–26). Tasaki et al. (27) developed soluble polyimides with good heat resistance and low dielectric constant/dissipation

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factor characteristics. The 10% weight loss temperature of polyimides was 455°C, which can be used as adhesive for 3L-FCCL. However, pure polyimide has the disadvantages of weaker adhesion with copper foil and higher cost than epoxy resin.

The combination of polyimide and epoxy resin is expected to balance the adhesive properties. However, it is difficult for polyimide to be directly melted and mixed with epoxy resin. Polyamide acid (PAA), as a precursor of polyimide, became a good candidate for mixing or even reacting with epoxy resin. At present, studies on PAA-modified epoxy resin mainly focused on thermal properties and curing kinetics. For instance, Yong *et al.* (28) investigated modification of epoxy resin with different contents of PAA varying from 1% to 10%. The onset temperature of thermal decomposition and the flexural properties of epoxy resin simultaneously increased after being modified by PAA. Armin Majd *et al.* (29) prepared PAAs through reaction between 4,4'-biphenolic dianhydride and 3,3'-dihydroxybenzidine and then mixed with epoxy resin. The results showed that the 10% weight loss temperature for EP with 5 wt% PAA improved by around 13°C. However, the mechanical properties of epoxy resins studied in these two works mentioned above did not include the tensile shear strength. Tensile shear strength of epoxy resin was one of the most important parameters for EP used as adhesive in 3L-FCCL. Besides, study on modifying epoxy resin with large polyimide content was rare.

In this study, the epoxy resin with EP equivalent of 170 was cured by self-made PAA without other curing agents. The effects of PAA content and curing process on the tensile shear strength and heat resistance of the epoxy resin were studied. Compared with the work of using PAA to modify epoxy resin (28,29), this study not only improved the heat resistance of epoxy resin, but also maintained good adhesive properties of epoxy resin. Besides, the optimum curing temperature and curing time of epoxy resin used as adhesive were found.

2 Materials and methods

2.1 Materials

4,4'-Oxydianiline (ODA), benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA), and *N*-methyl-2-pyrrolidone (NMP) were purchased from Shanghai Titan Technology Co., Ltd. The phenol A epoxy resin used in this study was

supplied by Shanghai Hummer Construction Technology Co., Ltd. All the reagents were utilized as supplied without further purification.

2.2 Preparation of PAA

The polymerization procedure for the synthesis of PAA was as follows. ODA (4.025 g, 0.0201 mol) was added into 250 mL three-necked flask and NMP (42 g) was used as a solvent. After ODA was completely dissolved, BTDA (6.445 g, 0.02 mol) was added, and the mixture was reacted for 6 h. The whole experiment was kept at 0°C under the protection of nitrogen atmosphere. The PAA solution was obtained and stored in the refrigerator at 0°C.

The reaction scheme for the EP/PAA is shown in Figure 1 and the synthesis equation of PAA is shown in Figure 2.

2.3 Blending and curing of epoxy resin modified by PAA

The epoxy resin was mixed with PAA solution in various weight ratios according to Table 1. The mixture (EP/PAA) was stirred at room temperature for 1 h. Then, it was put into the blast oven at 70°C for 3 h. EP/PAA was poured into the poly tetra fluoroethylene mold and cured according to the temperature program. The reaction equation during thermal curing is shown in Figure 3.

2.4 Characterization

Analysis using Fourier transform infrared spectroscopy (FTIR; Equinox 55) with a resolution of 0.5 cm^{-1} in the range of $500\text{--}4,000\text{ cm}^{-1}$ was performed. TGA (STA 449 C) was performed from room temperature to 800°C at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ in nitrogen environment. The tensile shear strength was evaluated at room temperature using universal testing machine (TES50T) according to ISO 4587:2003. The water absorption was tested according to ISO 62:2008. Scanning electron microscopy (SEM) images were obtained with a Quanta 200 FEG field emission microscope and all samples were brittle broken with liquid nitrogen and coated with gold by sputtering prior to observation.

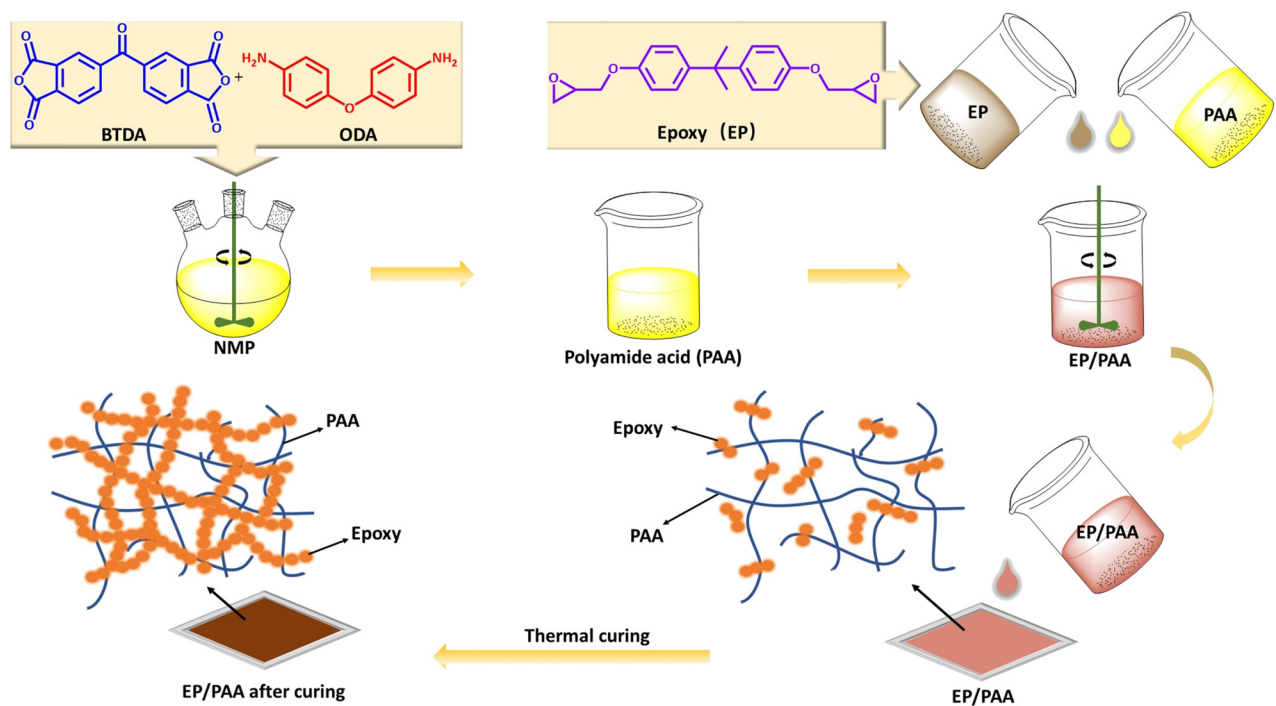


Figure 1: The reaction scheme for the epoxy resin modified by PAA.

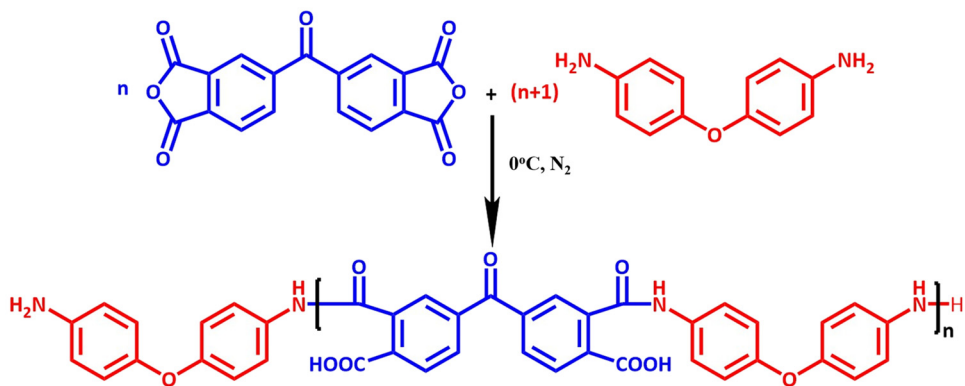


Figure 2: The reaction equation between BTDA and ODA.

3 Results and discussion

3.1 FTIR analysis

The FTIR spectra of EP, PAA, EP/PAA before and after curing are shown in Figure 4. There is no carbonyl $\text{C}=\text{O}$ absorption peak at 860, 800, 1,800, and $1,750\text{ cm}^{-1}$ in the infrared absorption of PAA (curve d), indicating that there is no anhydride group in PAA, and the PAA is successfully prepared.

The characteristic peak of EP group can be found at about 918 cm^{-1} in the EP (curve b) and EP/PAA before

curing (curve a), but it disappears in the EP/PAA after curing (curve c), which confirms that the epoxy resin has

Table 1: Component table of EP/PAA

| Items | PAA content (wt%) |
|-------|-------------------|
| E_1 | 20 |
| E_2 | 40 |
| E_3 | 60 |
| E_4 | 70 |
| E_5 | 80 |
| E_6 | 90 |

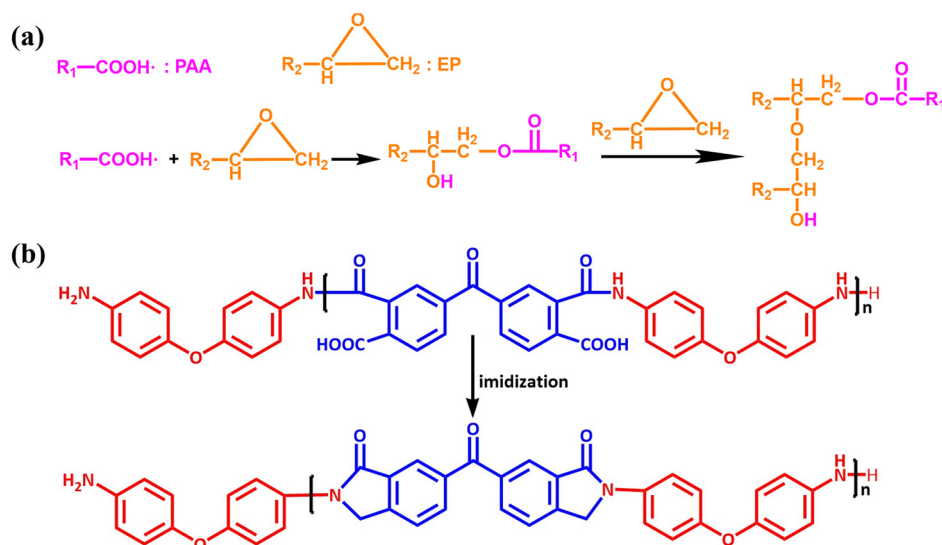


Figure 3: The reaction equation during thermal curing: (a) the reaction between PAA with EP and (b) the thermal imidization reaction of PAA.

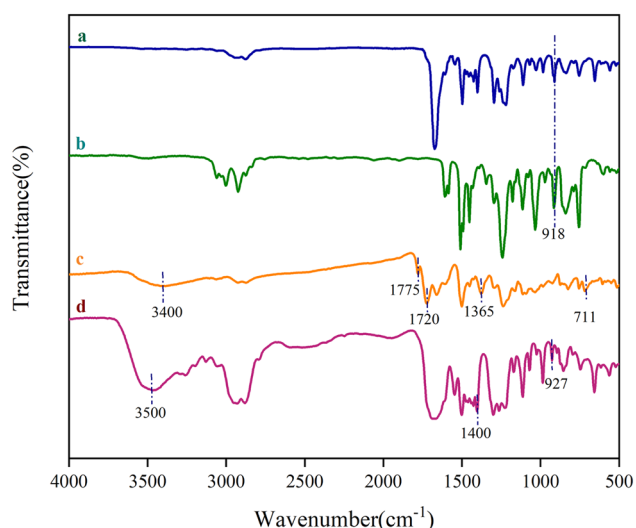


Figure 4: FTIR spectra of (a) EP/PAA before curing, (b) EP, (c) EP/PAA after curing, and (d) PAA.

been completely cured. The peak at $3,400\text{ cm}^{-1}$ in the EP/PAA after curing is assigned to the characteristic peak of hydroxyl due to the EP-ring opening reaction. The absorption peaks at $1,720\text{ cm}^{-1}$ (C=O symmetric stretching), $1,775\text{ cm}^{-1}$ (C=O asymmetric stretching), $1,365\text{ cm}^{-1}$ (imide C–N stretching), and 711 cm^{-1} (imide C=O bending) are believed to be the characteristic peaks of the imide architecture arising. In addition, the absence of peaks at $1,547$ and $3,464\text{ cm}^{-1}$ further confirms imidization ring closure.

3.2 Thermal properties

The TGA curves of EP/PAA after curing are depicted in Figure 5. There are two weight loss steps in all curves in Figure 5a. In the first stage, the weight loss between 200°C and 400°C is likely due to the decomposition of epoxy resin (30). The second decomposition step, the weight loss between 400°C and 600°C is maybe contributed to the decomposition of polyimide structure (31). All the EP/PAA after curing samples show good stability before 300°C .

The TGA data of EP/PAA after curing is shown in Table 2. The 5% weight loss temperature of all samples is above 300°C and the 10% weight loss temperature is above 330°C , which meets the use requirements of 3L-FCCL. With the increase in the content of PAA, the thermal decomposition temperature increases. For example, the 10% weight loss temperature increases about 20°C with the PAA content increasing from 40% to 80%. The residual weight also increases with the increase in PAA content. With the increase in PAA content, the semi-IPN structure is formed by the entanglement of PAA chains and EP during the curing reaction (28), which improves the heat resistance (32).

3.3 Water absorption analysis

The hydrophilic groups of epoxy resin will hydrolyze under high temperature and water vapor environment,

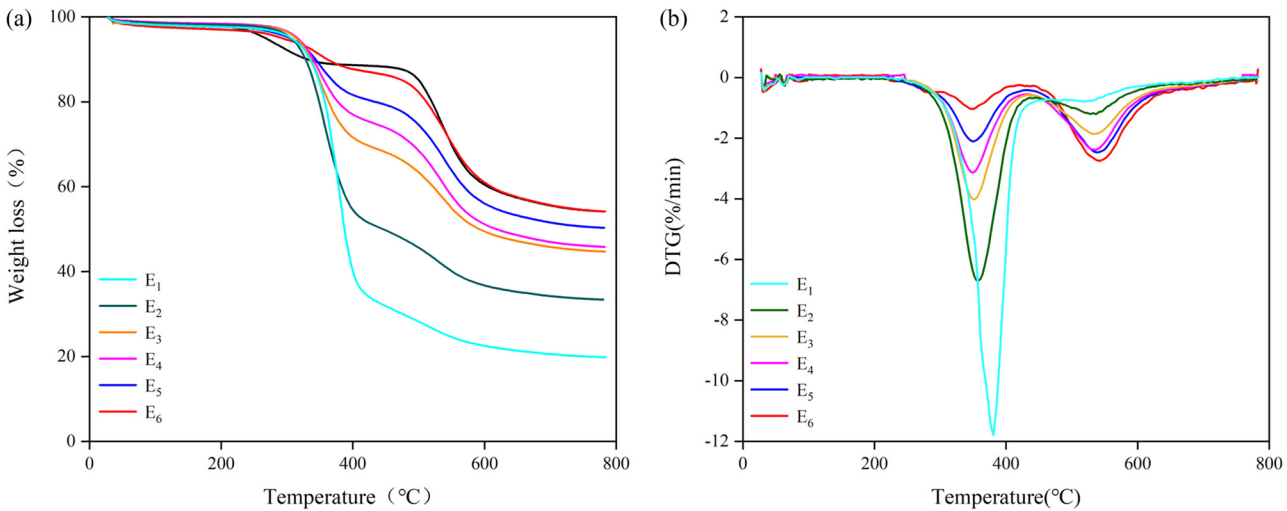


Figure 5: (a) TGA curves and (b) DTG curves of EP/PAA after curing.

Table 2: TGA data of EP/PAA

| Items | T_5 (°C) | T_{10} (°C) | Residual weight (%) |
|-------|------------|---------------|---------------------|
| E_1 | 306 | 327 | 34 |
| E_2 | 314 | 336 | 45 |
| E_3 | 316 | 337 | 46 |
| E_4 | 304 | 343 | 51 |
| E_5 | 342 | 357 | 52 |
| E_6 | 355 | 370 | 55 |

which lead to the reduction in molecular weight and the hygrothermal aging of epoxy resin. Therefore, it is important to reduce the water absorption of epoxy resin to avoid the failure of 3L-FCCL in humid and warm environment. Figure 6 shows the 24-hour water absorption of EP/PAA after curing. With the increase in PAA content, the water

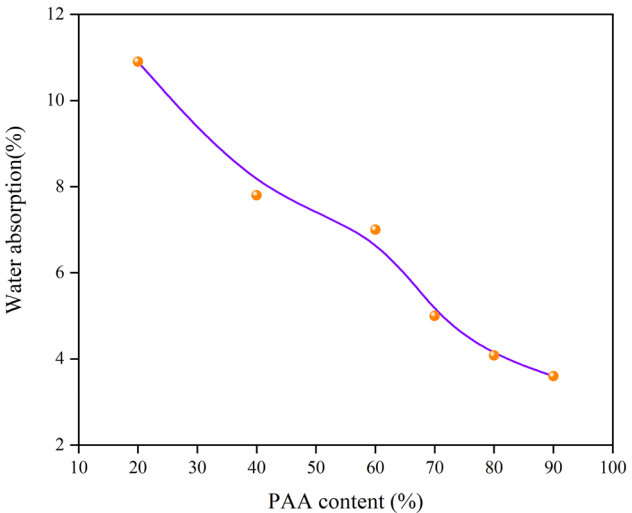


Figure 6: Water absorption of EP/PAA after curing.

absorption of EP/PAA after curing decreases. The water absorption of E_6 is only 3.6%, which is much lower than that of E_1 (10.9%). The number of polar imide rings for the EP/PAA after curing increases with the increase in the PAA content. The more imide rings created, the more molecular chains attract each other tightly and stack closely under polar action. Hence, it is more difficult for water to penetrate such compact structure.

3.4 Tensile shear analysis

Figure 7 shows the tensile shear strength of EP/PAA after curing. The tensile shear strength decreases gradually with the increase in PAA content, and the reasons can

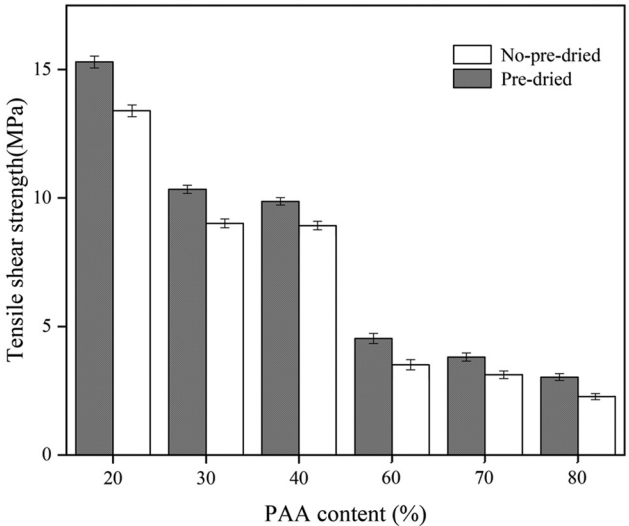


Figure 7: Effects of PAA content and curing treatment on tensile shear strength.

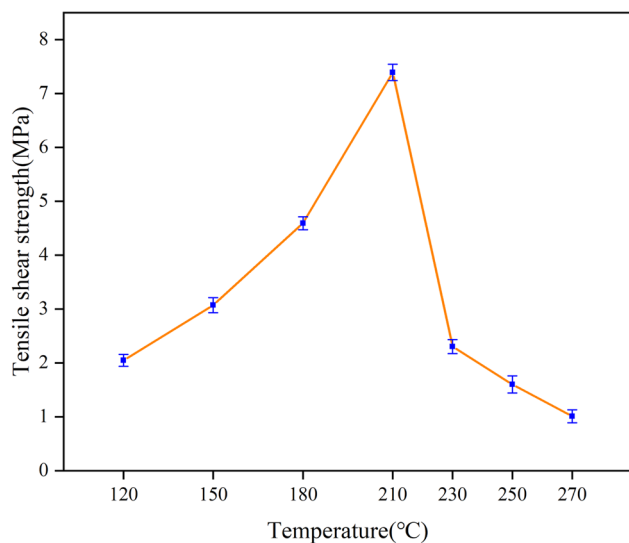


Figure 8: Tensile shear strength of E_2 with different curing temperatures.

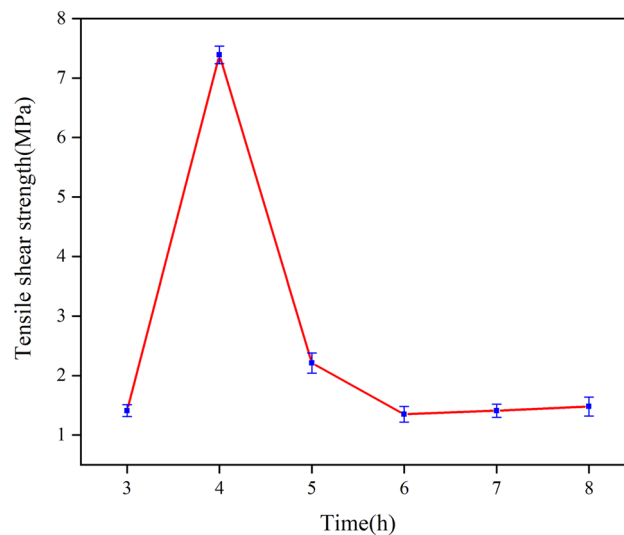


Figure 9: Tensile shear strength of E_2 with different curing time.

be given as follows. On the one hand, high PAA content requires more NMP solvent. NMP is not easy to remove in the process of thermal amination, and the following volatilization will produce bubbles. On the other hand, the increase in PAA content means the decrease in epoxy resin content. The bonding ability of epoxy resin is better than that of PAA due to the EP group, hydroxyl group, etc.

The tensile shear strength of EP/PAA after curing with or without pre-drying curing treatment is also shown in Figure 7. Comparing with that of EP/PAA without pre-drying treatment, the tensile shear strength of EP/PAA with pre-drying treatment is improved. For instance, the tensile shear strength of E_2 with pre-drying treatment (9.87 MPa) is 27% higher than that of EP/PAA without pre-drying treatment (8.93 MPa). The NMP solvent is

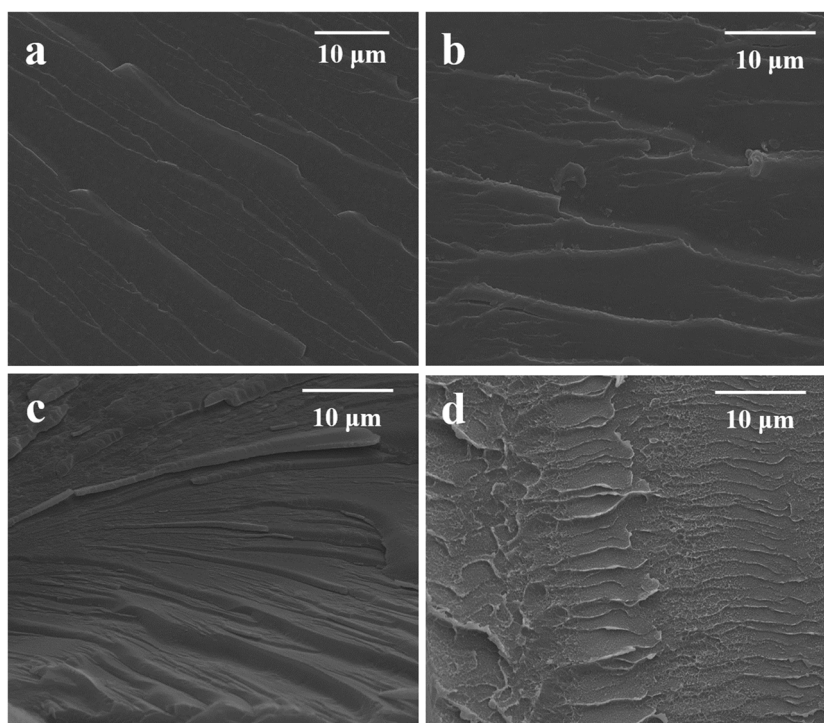


Figure 10: The SEM images of the fractured surfaces of EP/PAA after curing: (a) E_1 , (b) E_2 , (c) E_3 , and (d) E_6 .

removed during pre-drying process in the EP/PAA and the influence of solvent on the structure of the adhesive layer is avoided.

Figure 8 shows the tensile shear strength of E_2 cured at different curing temperatures. The tensile shear strength first increases and then decreases with the increase in temperature. The peak of tensile shear strength (7.39 MPa) is located at 210°C, which is about 6 times higher than the value at 270°C (1.01 MPa). Before 210°C, with the increase in temperature, both the reaction degree between PAA and EP and the polymer crosslinking density increase, which are beneficial for the increase in cohesion strength. However, epoxy resin is a thermosetting resin and the degree of intramolecular crosslinking increases with the increase in temperature. Therefore, excessive crosslinking makes the adhesive layer brittle and the cohesive strength decreases.

Figure 9 shows the tensile shear strength of E_2 cured at 210°C with different times. Tensile shear strength increases with increasing curing time up to 4 h and then reduces beyond 4 h. It is particularly noteworthy that the peak of tensile shear strength is 7.39 MPa when the curing time is 4 h, which is approximately 4 times higher than that cured for 8 h (1.58 MPa). The degree of reaction between PAA and EP increases with time, leading to first increase in the cohesive strength and then decrease.

3.5 SEM analysis

Figure 10 shows the SEM images of the fractured surfaces of E_1 , E_2 , E_3 , and E_6 . The fractured surface of E_1 shown in Figure 10a is smooth. The river line is shallow and its ability to prevent crack propagation is weak. With the increase in PAA content, the river line becomes thick and strong, as shown in Figure 10c and d. The propagation of cracks in the EP/PAA is limited by the semi-IPN structure and the fracture will absorb more energy.

4 Conclusion

PAA solution was prepared with BTDA and ODA as monomers and a new modified epoxy resin was prepared by blending epoxy resin with high PAA content. All the EP/PAA after curing samples showed good heat stability and the 10% weight loss temperature could arrive at around 340°C. The tensile shear strength of EP/PAA after curing samples improved after pre-dried curing process. Besides, the optimum curing time and temperature were

4 h and 210°C, respectively. The tensile shear strength reached 7.39 MPa under the optimum curing process. The water absorption decreased with the increase in PAA content. In this study, a new modified epoxy resin with good comprehensive properties was prepared, which meets the requirements of 3L-FCCL at the present stage and has broad application prospects.

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