

Preparation and Properties of Epoxy Adhesives with Fast Curing at Room Temperature and Low-Temperature Resistance

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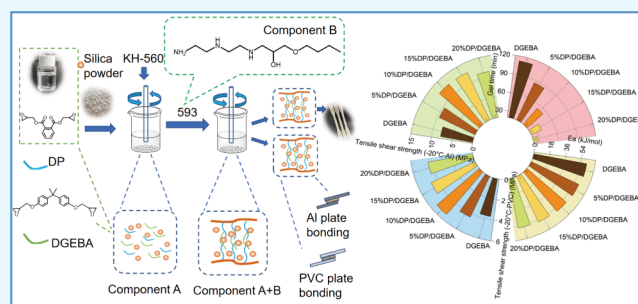
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ABSTRACT: Developing a highly efficient multifunctional epoxy adhesive is still an enormous challenge, which can rapidly cure at room temperature and has excellent low-temperature resistance performance and is crucial for the epoxy adhesive and electrical sealing fields during severe cold seasons. Herein, diglycidyl phthalate (DP) was synthesized with phthalic anhydride (PA) and epichlorohydrin (ECH) to enhance the curing rate and low-temperature resistance of bisphenol A diglycidyl ether (DGEBA) adhesive. The modified DP/DGEBA adhesives were systematically analyzed by gel time, mechanical properties, and aging resistance (time, temperature, and dry/wet treatment). The results showed that DP with highly active ester groups significantly accelerates the curing speed of DP/DGEBA. DP's rigid aromatic ring-benzene ring and flexible group-ester group gave the adhesive better low-temperature resistance. When the addition of DP was 10 wt % (based on the mass of DGEBA), the gel time of DP/DGEBA epoxy adhesives was reduced by 58 min compared to unmodified DGEBA epoxy adhesive, and after aging at low temperature ($-20\text{ }^{\circ}\text{C}$) for 7 days, the tensile shear strengths of polyvinyl chloride (PVC) and aluminum plate increased by 76.2 and 80.6%, respectively. The results of non-isothermal curing kinetics and dynamic mechanical analysis suggested that when the amount of DP was 10 wt %, the reaction activation energy of DP/DGEBA epoxy adhesive decreased by 4.0%, and the cross-linking density increased by 8.9%. Moreover, the toughness of the modified adhesive was also improved. This study opens up a feasible way for the development of a low temperature-resistant epoxy adhesive cured rapidly at room temperature in practical application.



1. INTRODUCTION

Epoxy adhesives have excellent mechanical properties,¹ thermal properties,^{2,3} adhesive properties,^{4–7} and electrical insulation properties,⁸ which have been widely used in packaging, construction, automotive, electronics,⁹ plastics, wood, and other fields. However, the slow curing rate of epoxy adhesives at room temperature¹⁰ and poor low-temperature resistance¹¹ still limits their application in the field of electronic and electrical sealing, especially during the winter season. Therefore, how to efficiently improve the curing rate and low-temperature resistance of epoxy adhesives has become an urgent problem in the electronic industry.

The development of epoxy adhesives that cure quickly at room temperature is essential to reduce the operation time, increase production efficiency, and reduce costs. Highly active curing accelerators can be used for shortening the curing time, such as 2,4,6-tris(dimethylaminomethyl) phenol (DMP-30) and 2-methylimidazole (2-MI).¹² Lakho et al.¹³ developed a curing system to quickly cure epoxy resins using triethylene-tetramine as a curing agent and 1-benzyl-2-methylimidazole as a catalyst. By calculation of the activation energy of the curing reaction, it was found that the addition of imidazole reduced the activation energy of the system curing reaction. Yang et

al.¹⁴ reported that the acidic hydroxyl and tertiary amine residues of DMP-30 had catalytic activity and could accelerate the initial reaction rate. The addition of accelerators can achieve the purpose of fast curing, but these accelerators have strong odor irritation and intense heat release, resulting in high residual thermal stress and reducing the thermal and mechanical properties of the adhesive.¹⁵ In addition, the curing concentrated heat released during curing can cause explosive polymerization.¹⁶ Therefore, developing a fast-curing epoxy system to minimize the utilization of accelerators is momentous.

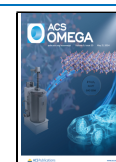
Electronic sealants demand maintaining good bonding properties in cold winter, so it is particularly important to study the effect of low-temperature aging on tensile and shear properties. Wang et al.¹⁷ modified the bisphenol A diglycidyl

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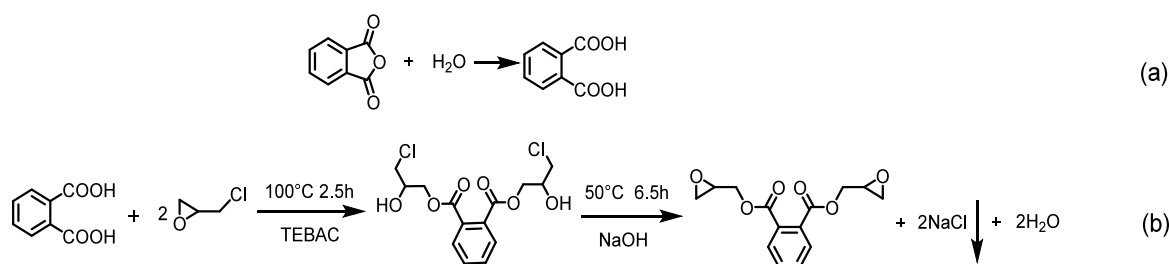


Figure 1. Synthesis of phthalic acid (a) and DP (b).

ether (DGEBA) adhesive with polystyrene-dimethyl methacrylate (PSiMMA) to prepare a low temperature-resistant adhesive for bonding aluminum alloy material. The shear strength of the modified adhesive was 18.75 MPa at $-70\text{ }^{\circ}\text{C}$, which was comparable to that at room temperature, while the shear strength of the unmodified DGEBA adhesive decreased by 28.7%. Rudawska et al.¹⁸ studied the effect of low-temperature aging on the strength of adhesive joints. Using aluminum alloy as a bonding substrate, three kinds of bisphenol A (Epidian 6, Epidian 62, and Epidian 57) as epoxy resin, and alicyclic polyamines (IDA) as curing agents, epoxy adhesives were prepared. Results indicated that the tensile shear strengths of the joints prepared by Epidian 6/IDA/100:50 epoxy resin adhesive after aging at -20 and $0\text{ }^{\circ}\text{C}$ were 1.14 and 3.48 MPa, respectively. However, the tensile and shear properties of the above low-temperature aging need to be further improved and the adhesive substrate is single. Therefore, developing an epoxy adhesive that can bond both metal and plastic plates and has excellent low-temperature resistance is still a popular topic.

Based on the adhesive market's demand for low-temperature resistance and the development trend of automated production lines, we use low-cost phthalic anhydride to prepare diglycidyl phthalate (DP). Because of its molecular structure with a benzene ring and glycidyl ester structure with strong polarity, it can play the role of rapid curing, good low-temperature resistance, high bonding strength, and excellent mechanical properties. This work proposes a new method to improve the room-temperature curing speed and low-temperature resistance of epoxy adhesives. Starting from the epoxy resin system, a fast-curing, low temperature-resistant epoxy resin was developed. Unlike adding accelerators to achieve rapid curing, modified adhesives avoid the pungent odor of accelerators and also have excellent mechanical properties. In addition, unlike epoxy adhesives on the market that have insufficient bonding strength under low-temperature aging and have a single bonding base material, the modified adhesive has better low-temperature resistance and versatility. Therefore, it provides a new strategy for the development of multifunctional modified epoxy adhesives with industrial potential.

2. EXPERIMENTS

2.1. Materials. Phthalic anhydride (PA; 99.7%) and γ -(2-propylene oxide) propyl trimethoxysilane (KH-560) were supplied by Shanghai McLean Biochemical Technology Co., Ltd. Epichlorohydrin (ECH), solid NaOH, benzyl triethylammonium chloride (TEBAC), bisphenol A diglycidyl ether (DGEBA), diethylenetriamine, and butyl glycidyl ether adduct (S93; industrial grade) were obtained from Anhui Hengyuan Technology Co., Ltd. Silicon powder was supplied by Shenzhen Haiyang Powder Technology Co., Ltd.

2.2. Synthesis of DP. Using a one-pot two-step preparation process, 37.0 g of PA, 4.5 g of distilled water, 231.1 g of ECH, and 2% of PA mass of TEBAC catalyst were added to a 500 mL four-port flask. After the reaction at $100\text{ }^{\circ}\text{C}$ for 2.5 h, the temperature was lowered to $50\text{ }^{\circ}\text{C}$, and 23 g of solid NaOH was added in batches and kept for 6.5 h. After the reaction was finished, the byproduct NaCl was removed and washed to neutral pH, and the excess ECH was recovered by vacuum distillation. The product DP was obtained. The epoxy value was 0.60 mol/100 g, the viscosity was 834 mPa·s, the content of inorganic chlorine was 0.0026%, and the content of hydrolyzable chlorine was 0.89%. The synthesis of DP is shown in Figure 1.

2.3. Preparation of Cured Products. The DP was mixed into DGEBA according to 0, 5, 10, 15, and 20 wt % DGEBA, and the metered silicon powder and KH-560 were added to mix evenly. Then, the S93 curing agent of theoretical demand was added to mix evenly, remove the air bubbles, and finally cast into the mold. The curing conditions were $25\text{ }^{\circ}\text{C}/12\text{ h} + 80\text{ }^{\circ}\text{C}/3\text{ h}$, and the properties were evaluated after aging at room temperature for 7 days. The specific formula is shown in Table 1, and the operation process is presented in Scheme 1.

Table 1. Formulation of Epoxy Resin Adhesives

sample	amount of DP added (wt % based on 100 g of DGEBA)				
	0	5	10	15	20
component A					
DGEBA	100	100	100	100	100
DP	0	5	10	15	20
KH-560	1	1.05	1.1	1.15	1.2
silicon powder	60	63	66	69	72
component B					
S93 curing agent	32.0	33.6	35.2	36.8	38.4

2.4. Preparation of DGEBA Epoxy Resin Adhesive Modified by DP. Polyvinyl chloride (PVC) (dimensions: $100 \times 25 \times 5\text{ mm}$) and aluminum (dimensions: $100 \times 25 \times 1.6\text{ mm}$) were selected as two types of substrates. PVC–PVC and aluminum–aluminum substrates were bonded separately by using a single-lap joint method. The specific formulation is presented in Table 1. The amount of DP was based on 100 g of DGEBA; the dosages of KH-560, silica powder, and S93 curing agent were 1, 60, and 32 wt % of the total mass of DP and DGEBA. The curing conditions were $25\text{ }^{\circ}\text{C}/12\text{ h} + 80\text{ }^{\circ}\text{C}/3\text{ h}$, followed by different aging treatments, and then performance evaluation was carried out. Five parallel samples were made for each group.

2.5. Characterization. Fourier transform infrared (FT-IR) spectroscopy was carried out using a Nicolet Nexus 670

Scheme 1. Preparation of the DP-Modified DGEBA Matrix Resin Sample (a) and Epoxy Adhesives (b)

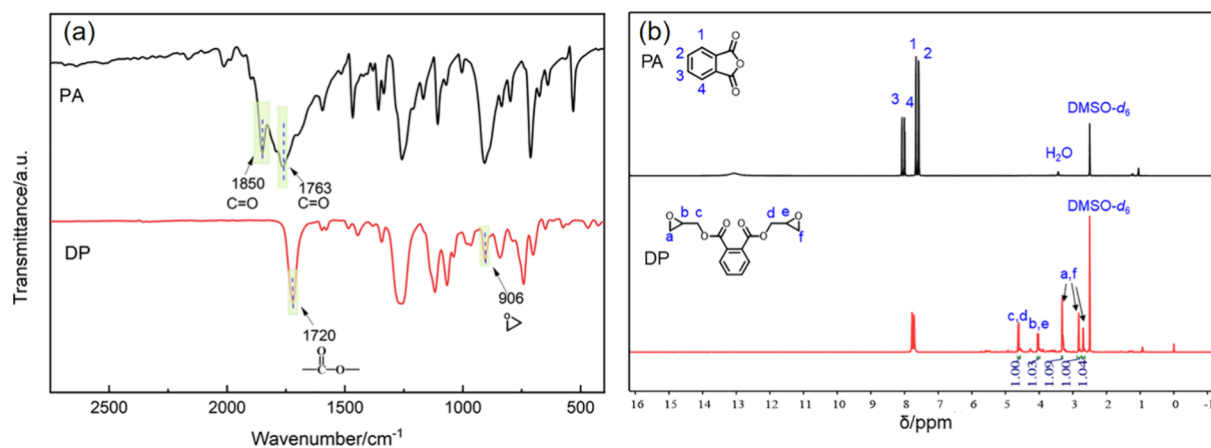
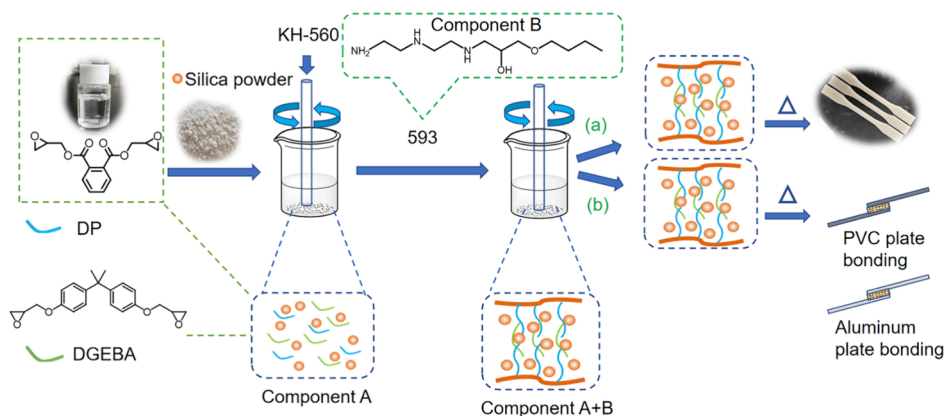


Figure 2. FT-IR (a) and ¹H NMR (b) diagrams of PA and DP.

infrared spectrometer with the resolution of 4 cm⁻¹, the scanning range was 400–4000 cm⁻¹, and the scanning times were 64 times. Nuclear magnetic resonance (¹H NMR) was performed with a Bruker spectrometer 112 (AVANCE III HD), with deuterated dimethyl sulfoxide (DMSO) as a solvent.

The epoxy value was tested by a Swiss Wantong 916 potentiometric titrator according to the national standard GB/T4612-2008, in which the test sample was about 0.2 g. Viscosity analysis was carried out according to the national standard GB/T22314-2008 by using an American Borefei DV2T viscometer. The gel time test was that a small amount of samples was placed in the centrifuge tube for 30 s from the beginning of sampling to wire drawing, in which the test temperature was 25 ± 2 °C.

The flexural properties, tensile properties, and elongation at break of the tested specimens were tested by an ETM504D universal testing machine (WANACE, Shenzhen, China) according to GB/T2567-2008. The impact resistance was tested by a PTM7000 impact tester. At least 5 samples were tested, and their average was taken. Tensile shear properties of the adhesive were tested by a universal testing machine (MTSE44.304, USA). A PVC plastic plate and aluminum plate were selected as bonding substrates, in which the PVC substrate does not need surface treatment, and the aluminum plate is polished with 600 mesh sandpaper. The length and width of the bonding surface were 25 ± 0.25 and 12.5 ± 0.25 mm, respectively. According to GB/T7124-2008 “adhesive

tensile shear strength”, the test rate was 5 mm/min. At least 5 samples were tested, and their average was taken.

The curing kinetics was measured by a Netzsch DSC 204 Polyma differential scanning calorimeter. In a N₂ atmosphere, the scavenging velocity was 40 mL/min, the protective gas velocity was 60 mL/min, the test temperature range was 50–200 °C, and the heating rates were 5, 10, 15, and 20 °C/min. The sample weight was 5–10 mg. Dynamic mechanical analysis (DMA) was carried out by a TA Q800 DMA analyzer in double cantilever mode and air atmosphere. The sample size was 60 mm × 10 mm × 3 mm, the test frequency was 1 Hz, the heating rate was 3 °C/min, and the test temperature was 30–180 °C. Thermogravimetric analysis (TGA) was performed by a NETZSCH TG 209 F3 Tarsus thermogravimetric analyzer. The temperature range was 50 to 800 °C (heating rate was 20 °C/min) at a N₂ atmosphere. The sample weight was 5–10 mg. Scanning electron microscopy (SEM) was carried out by a scanning electron microscope (QUANTA200, FEI Company, USA). The voltage was 20 kV, and the sample was sprayed with gold before the test.

3. RESULTS AND DISCUSSION

3.1. Structure of PA and DP. The infrared spectra of PA and DP are illustrated in Figure 2a. The C=O stretching vibration absorption peaks of PA are at 1850 and 1763 cm⁻¹, but in DP, the original C=O stretching vibration absorption peaks at 1850 and 1763 cm⁻¹ have disappeared, which depicted that the PA reaction was complete. The characteristic

Table 2. Gel Time and Component A Viscosity

sample	gel time (min)	component A viscosity (mPa·s)
DGEBA	112	40,600
5%DP/DGEBA	86	25,879
10%DP/DGEBA	54	13,761
15%DP/DGEBA	38	10,796
20%DP/DGEBA	27	8845

peak of the ester group appeared at 1720 cm^{-1} , and the absorption peak of the epoxy group appeared at 906 cm^{-1} . It can be seen that the epoxidation of PA was successfully carried out. Figure 2b shows the ^1H NMR spectrum of PA and DP. In the spectrum, DP shows the peaks of hydrogen in methylene linked to the epoxy group at $\delta = 4.04$ and $\delta = 4.61$ ppm. The peak of methyl hydrogen in the epoxy group appears at $\delta = 3.32$ ppm, and the peaks of hydrogen in the methylene group of the epoxy group appear at $\delta = 2.84$ ppm and $\delta = 2.83$ ppm. Through FT-IR and ^1H NMR spectral analysis, it is found that the product contains epoxy groups, which indicates that DP was successfully prepared.

3.2. Fast-Curing Performance Test of DP/DGEBA

Adhesive. As demonstrated in Table 2, the viscosity of the unmodified epoxy adhesive component A is large, with a measured value of $40600\text{ mPa}\cdot\text{s}$ at room temperature. High viscosity will lead to poor flowability, insufficient bonding, and difficulty in processing of the epoxy adhesive in practical applications. Therefore, diluents are added to improve fluidity and processability. With the addition of DP, the viscosity of epoxy adhesive component A gradually decreased gradually. When the addition of DP was 20% of the mass of DGEBA, the viscosity of the system decreased to $8845\text{ mPa}\cdot\text{s}$, and the viscosity reduction effect of DP was significant. When the addition of DP was 10% of the mass of DGEBA, the viscosity of epoxy adhesive was $13761\text{ mPa}\cdot\text{s}$, which decreased by 66.11%. The reason for this is that DP has good compatibility with DGEBA, thus achieving a viscosity reduction effect.

Table 3. Apparent Activation Energy

sample	β ($^{\circ}\text{C}/\text{min}$)	T_p ($^{\circ}\text{C}$)	E_a/R	E_a (kJ/mol)
DGEBA	5	84.5	7300.89	60.70
	10	96.7		
	15	102.9		
	20	108.1		
5%DP/DGEBA	5	85.1	7141.57	59.38
	10	97.8		
	15	102.9		
	20	109.7		
10%DP/DGEBA	5	83.4	7006.69	58.25
	10	95.4		
	15	101.3		
	20	108.2		
15%DP/DGEBA	5	84.3	6875.31	57.16
	10	96.2		
	15	103.2		
	20	109.2		
20%DP/DGEBA	5	85.0	6770.02	56.29
	10	96.7		
	15	103.7		
	20	110.3		

Gel time is the longest time that the system remains in a sufficient fluid state to apply to the substrate,¹⁹ reflecting the curing rate of the epoxy adhesive. Table 2 reveals that the gel time of the epoxy adhesive system becomes shorter with the increase in DP content at room temperature ($25\text{ }^{\circ}\text{C}$). The gel time of unmodified (pure DGEBA) epoxy adhesive was longer, and the result was 112 min at room temperature. When the content of DP was 20%, the gel time was 27 min, which shortened by about 85 min. The results suggest that DP has fast-curing characteristics, which can be attributed to the high activity of ester groups in DP. These groups promote the curing rate of the epoxy adhesive system.²⁰

The curing exothermic behavior of DP/DGEBA adhesive with DP contents of 0, 5, 10, 15, and 20% was investigated by

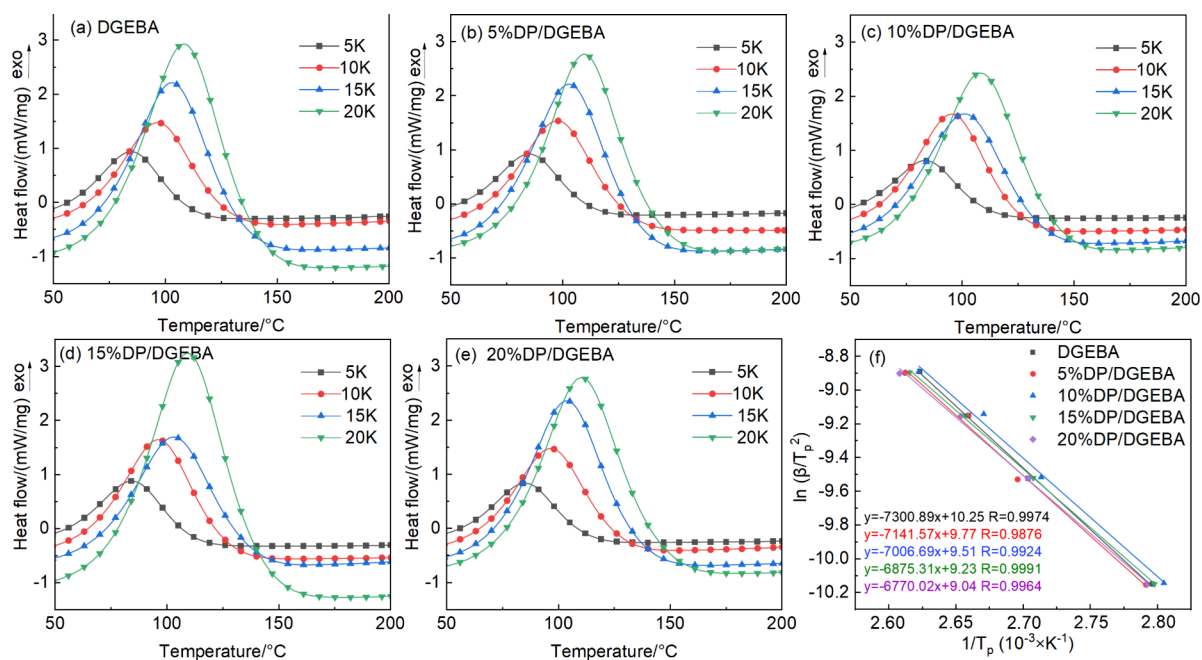


Figure 3. Linear regression graphs of DSC curves (a–e) and $\ln(\beta/T_p^2) - 1/T_p$ (K^{-1}) (f) of DP/DGEBA adhesives at different heating rates.

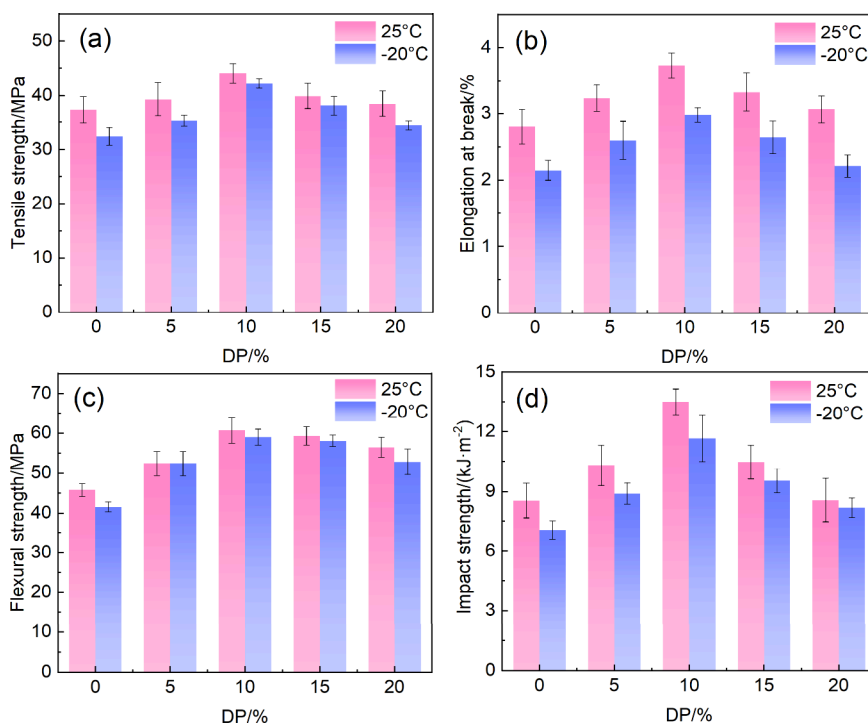


Figure 4. Mechanical properties of DP/DGEBA adhesive cured: (a) tensile strength; (b) elongation at break; (c) bending strength; (d) impact strength.

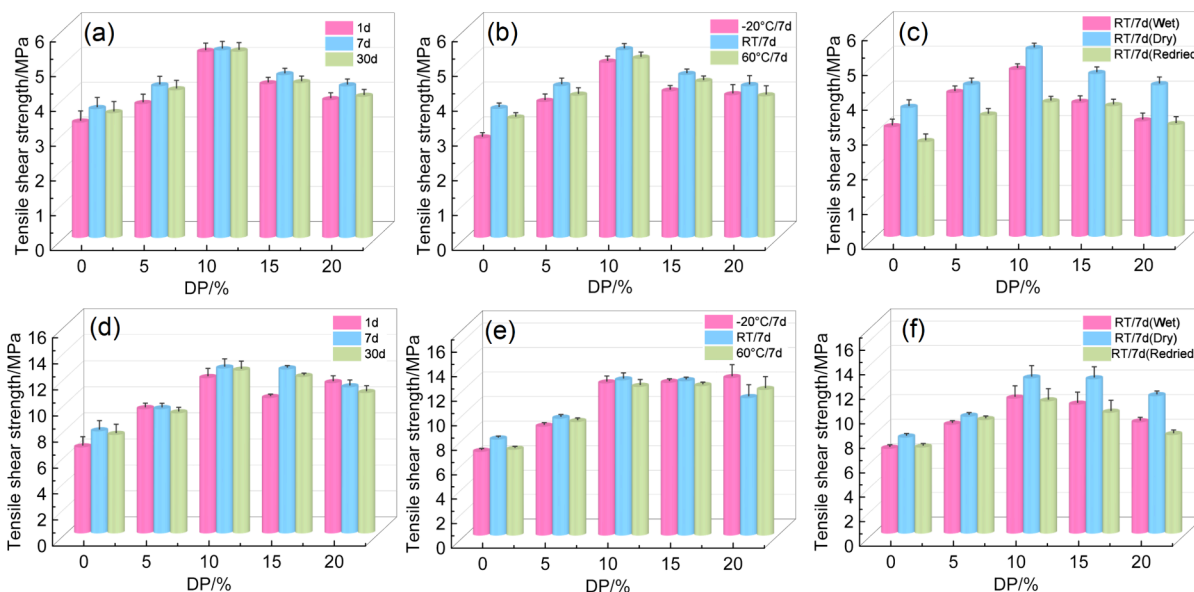


Figure 5. Effect of aging conditions on the tensile shear strength of DP/DGEBA epoxy adhesive: (a) aging time on the PVC substrate; (b) aging temperature on the PVC substrate; (c) wet and dry treatment on the PVC substrate; (d) aging time on the aluminum plate; (e) aging temperature on the aluminum sheet; (f) wet and dry treatment on the aluminum sheet.

DSC at heating rates of 5, 10, 15, and 20 °C/min. As illustrated in Figure 3a–e, all the DSC exothermic curves exhibited a single curing exothermic peak without shoulder peaks, indicating that the system followed a one-step reaction mechanism and had a uniform cross-linking structure.¹³ The exothermic peak shifted to higher temperatures with the increase in heating rate, because when the heating rate is higher, the curing system absorbs energy in a short time and does not have enough time to cure, resulting in a delay of the

curing reaction, and the curing exothermic peak moves to the range of higher temperatures.²¹

The value of E_{α} using the Kissinger equation is calculated, namely, eq 1.

$$\ln \frac{\beta}{T_p^2} = -\frac{E_{\alpha}}{R} \cdot \frac{1}{T_p} + \ln \frac{AR}{E_{\alpha}} \quad (1)$$

In the equation, β is the heating rate, and T_p is the peak temperature of the DSC curve at that heating rate. A linear regression of $\ln(\beta/T_p^2) - 1/T_p$ is plotted, as presented in

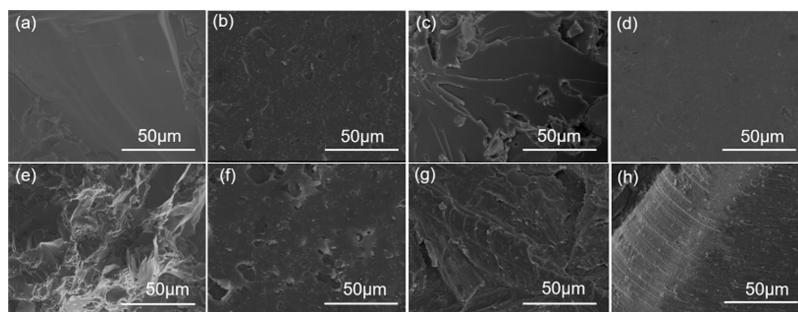


Figure 6. SEM images of the impact fracture surface and tensile shear fracture surface of epoxy adhesive-solidified material: (a) DGEBA-impact; (b) DGEBA-PVC; (c): DGEBA-aluminum; (d) pure PVC board; (e) 10%DP/DGEBA-impact; (f) 10%DP/DGEBA-PVC; (g) 10%DP/DGEBA-aluminum; (h) pure aluminum sheet.

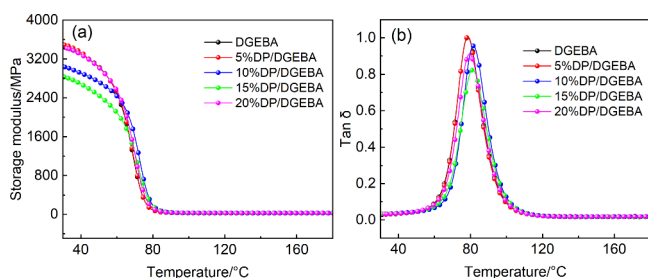


Figure 7. DMA diagram of the DP/DGEBA adhesive cured product: (a) storage modulus and (b) $\tan \delta$ curve.

Table 4. DMA and DSC Data Sheets for DP/DGEBA Adhesive Curables

sample	E' (MPa)	$\nu_e \times 10^3$ (mol/m ³)	$T_{g,DMA}$ (°C)	$T_{g,DSC}$ (°C)	$T_{g,DMA} + 30$ (°C)
DGEBA	23.39	2.46	78.59	82.40	108.59
5%DP/DGEBA	24.38	2.56	78.25	83.70	108.25
10%DP/DGEBA	25.71	2.68	81.72	85.50	111.72
15%DP/DGEBA	26.98	2.82	81.25	89.80	111.25
20%DP/DGEBA	28.24	2.96	79.34	92.80	109.34

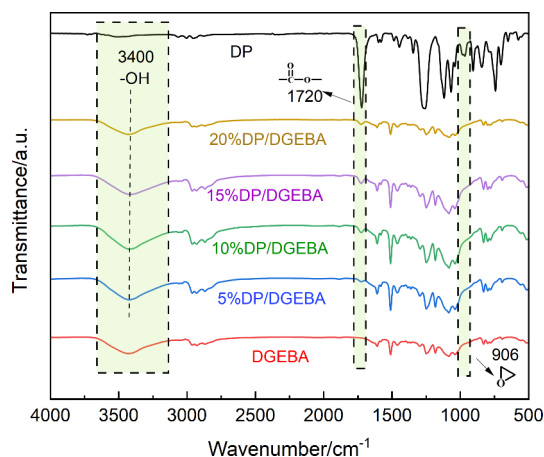


Figure 8. FT-IR spectra of DP, DGEBA, and DP/DGEBA adhesives cured.

Figure 3. Based on the linear fitting results of Figure 3, the slope of the line ($-E_a/R$) is calculated, and the E_a of pure DGEBA and DP/DGEBA adhesive with different DP contents

(5–20 wt %) is obtained. The results are shown in Table 3. The addition of DP reduces the reaction activation energy of the system, indicating that DP has a catalytic effect, thus increasing the reaction speed. More importantly, the increase in the strong electron-withdrawing group—ester group content can accelerate the ring-opening reaction, resulting in the decrease in the activation energy.²²

3.3. Mechanical Properties of DP/DGEBA Adhesive under Low-Temperature Conditions. 3.3.1. Analysis of Basic Mechanical Properties of DP/DGEBA Adhesive. Figure 4 presents the mechanical properties of DP/DGEBA adhesive after aging for 7 days at 25 and -20 °C. The tensile strength, elongation at break, flexural strength, and impact strength of the cured adhesive modified by DP were superior to those of the unmodified DGEBA adhesive and increased at first and then decreased with the increase in DP content. At room temperature, when the content of DP was 10% of the mass of DGEBA, the comprehensive mechanical performance was optimal.

As illustrated in Figure 4a,c, the tensile strength and flexural strength of 10%DP/DGEBA adhesive were 44.01 and 60.66 MPa, respectively, which were 18.12 and 32.68% higher than those of the unmodified adhesive. This can be due to the rigid benzene ring structure in DP playing a role of rigid support in the system, thus enhancing the tensile strength and flexural strength of the cured adhesive.^{23,24} As depicted in Figure 4b,d, the elongation at break and impact strength of 10%DP/DGEBA adhesive increased by 33.21 and 58.08%, respectively. After low-temperature aging, the brittleness of the epoxy adhesive increases, and hydrogen bonds are prone to breakage, resulting in poor mechanical properties. However, 10%DP/DGEBA adhesive had improved tensile strength, elongation at break, flexural strength, and impact strength by 30.15, 38.60, 42.10, and 65.5%, respectively, compared with the unmodified adhesives. This is because the addition of DP increases the degree of intermolecular cross-linking of the adhesive, making the structure more stable and making the chain segments less mobile and less prone to breakage. In addition, the modified glue contains flexible groups such as ester groups and ether bonds, which improves the toughness.²⁵ In addition, epoxy glue can easily form cavities at low temperatures, causing destructive cracks and leading to interface debonding and other phenomena. However, the modified DP/DGEBA adhesive system has a smaller viscosity, which makes it easier to eliminate bubbles and reduce the number of voids, giving the adhesive excellent strength.

3.3.2. Effect of Aging Conditions on the Bonding Properties of DP/DGEBA Adhesives. PVC and aluminum

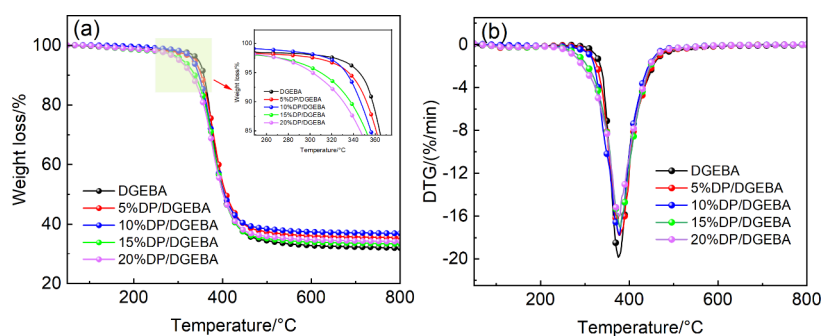


Figure 9. Thermogravimetric analysis diagram of the DP/DGEBA cured product: (a) TG and (b) DTG.

Table 5. Thermogravimetric Analysis Data of Cured Products

sample	$T_{10\%}/^{\circ}\text{C}$	$T_{\text{max}}/^{\circ}\text{C}$	char yield at 800 $^{\circ}\text{C}/\%$
DGEBA	357.4	375.7	32.0
5%DP/DGEBA	351.9	376.9	35.5
10%DP/DGEBA	346.6	376.1	37.0
15%DP/DGEBA	337.2	379.1	33.4
20%DP/DGEBA	330.6	378.2	34.2

plates were selected as the bonding substrates, and the tensile shear performance of DP/DGEBA epoxy adhesive specimens under different aging times, aging temperatures, and wet–dry treatments was tested. The result is illustrated in Figure 5.

The adhesive was treated with different aging times (1, 7, and 30 days) at room temperature to study the effect of aging time on the tensile shear strength. The results are indicated in Figure 5a,d. At the same DP content, the tensile shear strength of DP/DGEBA adhesive increases first and then stabilizes with aging time, because the curing process is a complex and long process including liquid stage, gel stage, and solid stage.²⁶ After aging for 1 day, the solid state stage has been carried out, but it does not mean that all the functional groups in the system that can participate in the reaction have participated in the reaction, and the curing process is still going on, so the strength is low.

With the extension of aging time, the tensile shear strength of PVC and aluminum samples increased gradually, which was attributed to the continuous improvement of the curing cross-linking degree of epoxy adhesive. When the aging time was 7 days, the tensile shear strengths of the PVC plate and aluminum plate of 10%DP/DGEBA adhesive were higher, which were 5.40 and 7.86 MPa, respectively. The viscosity of the modified epoxy adhesive was obviously reduced, which was beneficial for the adhesive to penetrate into the veneer surface, forming better mechanical interlock²⁷ and efficient interfacial contact. The presence of a moderate amount of ester groups promoted the fast curing of the adhesive and increased the cross-linking density of the cured product, thus enhancing the tensile shear strength of the adhesive. In addition, the increase in shear strength may be attributed to the cohesive fracture resistance provided by the silica microparticles in the matrix.²⁸ After aging for 30 days, the strength of the material did not decrease, indicating that the adhesive has excellent durability.

To evaluate the effect of different aging temperatures on the tensile shear strength of the adhesive, the samples with an aging time of 7 days were selected for testing. It is known from Figure 5b,e that the tensile shear strength of the unmodified DGEBA adhesive was lower after aging at -20°C . The addition of DP improved the performance of the adhesive at

low-temperature aging and made its tensile shear strength close to the level of room-temperature aging. When the aging temperature was -20°C , the tensile shear strengths of the PVC plate and aluminum plate of 10%DP/DGEBA adhesive were 76.2 and 80.6% higher than that of unmodified DGEBA adhesive, respectively. DP contains an ester group, and the introduction of an ester group makes the low-temperature resistance of the adhesive system better. After aging at 60°C , the tensile shear strength slightly decreased compared with room-temperature aging but still had a good level. 60°C did not reach the thermal failure temperature of the adhesive (according to Tg test), and the damage was mainly caused by strain-induced chemical bond breaking,²⁹ which did not affect the bonding performance of the modified adhesive.

When the aging time was 7 days and the aging temperature was room temperature, the untreated dry samples, wet samples boiled in hot water at 60°C for 3 h, and wet samples dried at 60°C for 1 h were evaluated, and the tensile shear strength tests are displayed in Figure 5c,f. Both wet and redried specimens demonstrated a trend of increasing first and then decreasing. The PVC tensile shear strength of 10%DP/DGEBA adhesive increased from 3.15 to 4.81 MPa, and the tensile shear strength of the aluminum plate increased from 6.95 to 11.04 MPa. This can be attributed to the fact that DP improves the surface wettability of the epoxy adhesive to the aluminum substrate, increases the adhesion area, and enhances the shear strength between the adhesive layer and aluminum.²⁷ When the addition of DP was constant, the tensile shear strength of wet and redried samples was lower than that of dry samples, because there were some free hydroxyl groups and amino groups in the epoxy adhesive system, which easily absorb water, thus reducing the shear strength of wet and redried samples.

In summary, 10%DP/DGEBA epoxy adhesive has superior tensile shear performance, especially in low-temperature aging resistance. The tensile shear strength of the PVC plate was 5.04 MPa, which was 76.2% higher than that of pure DGEBA epoxy resin. The tensile shear strength of the aluminum plate was 12.44 MPa, which was 80.6% higher than that of pure DGEBA epoxy resin. This provides a new idea for the practical production of a low temperature-resistant epoxy adhesive.

3.3.3. Fracture Surface Analysis of DP/DGEBA Adhesive. To further study the effect of DP on the mechanical properties of modified DGEBA epoxy adhesives, it was integral to conduct SEM tests on the impact fracture surface (Figure 6a,e) and tensile shear fracture surface (Figure 6b–d,f–h) of DGEBA and 10%DP/DGEBA adhesives cured for 7 days at low temperature.³⁰ The results are illustrated in Figure 6.

As the chart depicted in Figure 6a, the impact fracture surface of the unmodified DGEBA adhesive was smooth and flat, with only a few cracks, presenting many parallel river-like lines,³¹ which were typical characteristics of brittle fracture. This is due to the poor flexibility and impact strength of the unmodified DGEBA adhesive. As depicted in Figure 6e, the addition of DP makes the impact fracture surface of the adhesive cured product rough, showing distorted and wrinkled morphology³² and a large number of irregular fragments.³³ This is because the epoxy group of DP participates in the curing reaction. There are some flexible groups such as ester ether bonds in the system that have a synergistic toughening effect. In the meantime, there is good compatibility between DP and the matrix to form a homogeneous system.³⁴ In addition, the addition of the coupling agent KH-560 makes the silicon micropowder and epoxy resin produce weak intermolecular interactions (such as hydrogen bond and van der Waals forces),³⁵ which ensures that the structure of the adhesive is more stable, thus improving the toughness of the adhesive and increasing the roughness of the fracture surface.

PVC plastic itself has a smooth surface and a honeycomb mesh structure, but it was not easy to bond without surface treatment (Figure 7d). The physically treated aluminum plate surface indicated polished parallel hills and valleys (Figure 7h), and aluminum oxides were formed around the scratches.²⁵ The tensile shear crack surface of the unmodified pure DGEBA epoxy adhesive was relatively smooth, the damage area of the adhesive layer was small (Figure 7b), showing a "broom-like" morphology (Figure 7c), and the crack direction was a single linear propagation.³⁶ The fracture surface of the adhesive with 10 wt % DP was rough, and the tear of the adhesive layer demonstrated a large area of damage (Figure 7f), a large number of filaments, and a large number of irregular hills, ridges, and valleys³⁷ (Figure 7g). The toughness of the modified adhesive is improved, which can be attributed to the low viscosity of DP, which promotes the adhesive to penetrate the mesh structure of the PVC surface and increases the surface area of molecular binding. In addition, DMA analysis also displays that the addition of DP increases the curing cross-linking density of the adhesive layer, resulting in the roughness of the damaged area of PVC. There is an intermolecular force between the hydroxyl group and the amino group in the epoxy resin molecule and the oxide layer on the aluminum surface,³⁸ forming a chemical bond³⁹ and realizing the bonding.

3.4. Thermodynamic Properties of DP/DGEBA Adhesives. **3.4.1. Dynamic Mechanical Analysis of Cured Products of DP/DGEBA Adhesive.** Figure 7a,b illustrates the curves of the energy storage modulus (E') and loss factor ($\tan \delta$) of DP/DGEBA adhesive cured with the addition amount of DP, respectively. It is known from Figure 7a that the E' of the adhesive curing system increases continuously with the increase in the amount of DP added. The E' of 20 wt %DP/DGEBA adhesive was 28.24 MPa, which was 20.74% higher than that of unmodified DGEBA epoxy adhesive (23.39 MPa). E' reflects the stiffness and cohesive energy density of the cross-linked network.⁴⁰ The glass transition temperature (T_{gDMA} and T_{gDSC}) of the modified DP/DGEBA adhesive also increases, which helps to improve the adhesive performance of the adhesive.⁴¹ The increase in E' and T_{gDSC} is attributed to the enhanced intermolecular interactions by the ester groups in DP and the increased cross-linking density of the adhesive by the rigid aromatic group-benzene ring.⁴²

According to the rubber elasticity theory,⁴³ the cross-linking density (ν_e) of the cured product can be calculated by eq 2

$$\nu_e = \frac{E'}{3RT} \quad (2)$$

where T is the absolute temperature, E' is the storage modulus 30 °C higher than T_{gDMA} , and R is the gas constant.⁴⁴ The calculation results are depicted in Table 4. The cross-linking density of the adhesive increased with the increase in DP content, and the cross-linking density of 20%DP/DGEBA adhesive cured was $2.96 \times 10^3 \text{ mol}\cdot\text{m}^{-3}$, which was 20.33% higher than that of unmodified DGEBA ($2.46 \times 10^3 \text{ mol}\cdot\text{m}^{-3}$). This is attributable to the fact that the ester group of DP can accelerate the curing speed of the adhesive system, promote the formation of the cross-linking bond, and lead to the improvement of cross-linking density.

In addition, as illustrated in Figure 8, the infrared spectrum of the cured material of DP/DGEBA adhesive indicates that the absorption peak of the epoxy group at the original 906 cm^{-1} basically disappeared, and the hydroxyl absorption peak appeared at 3400 cm^{-1} , indicating that the epoxy group of DP participated in the curing cross-linking reaction after ring opening, and the reaction degree is relatively high.⁴⁵

3.4.2. Thermal Stability of Cured Products of DP/DGEBA Adhesive. The thermal stability of five kinds of DP/DGEBA adhesive cured products was analyzed under a N_2 atmosphere, and the TG and DTG curves are illustrated in Figure 9. Specific data are shown in Table 5. The $T_{10\%}$ of the unmodified DGEBA adhesive cured product was 357.4 °C, and T_{max} was 375.7 °C. The addition of DP caused a slight decrease in the $T_{10\%}$ of the adhesive system, which may be due to DP containing ester groups, and the ester groups were easily decomposed at high temperatures. However, the T_{max} of the modified adhesive cured products increased, char yield at 800 °C also increased from 32.0% of pure DGEBA to 37.0% of 10% DP/DGEBA adhesive, and DP reduced the mass loss rate of the system while increasing char yield.³⁶ The ester group of DP may have this effect because it can hasten the curing rate of the adhesive system, encourage the formation of cross-linking bonds, and lead to a higher cross-linking density. Therefore, after the addition of an appropriate amount of DP, the high-temperature resistance of the modified epoxy adhesive is slightly reduced, and the mechanical properties of the adhesive cured product are significantly improved.

4. CONCLUSIONS

DP was prepared from low-cost PA by a one-pot two-step method to modify the DGEBA epoxy adhesive. When DP was added to 10 wt % DGEBA, the adhesive formula was optimal. Due to the highly active ester group of the modified adhesive, the gel time of this formula is shortened by 51.8% to 54 min compared with DGEBA. After aging at room temperature for 7 days, the tensile shear strengths of the PVC and aluminum plates increased by 45.6 and 61.3%, respectively. Also, after aging at low temperature (−20 °C) for 7 days, the tensile shear strengths of the PVC and aluminum plates increased by 76.2 and 80.6%, respectively. SEM analysis showed that the modified epoxy adhesive has good toughness. In addition, DMA, DSC, and TG tests showed that although the thermal stability of the modified adhesive decreased slightly, the cross-linking density and glass transition temperature increased. Therefore, DP meets the demand for electronic and electrical

sealing adhesives in cold environments and achieves innovative technological breakthroughs in the adhesive field.

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Notes

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