

Efficient Toughening of DGEBA with a Bio-Based Protocatechuic Acid Derivative

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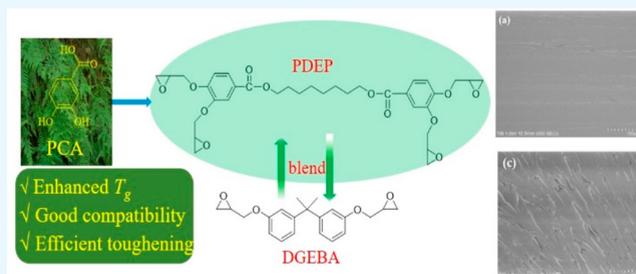
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ABSTRACT: In this work, a bio-based epoxy resin, protocatechuic acid diester epoxy resin, (PDEP), was synthesized using protocatechuic acid. The structure and properties of PDEP have been characterized by ^1H NMR, ^{13}C NMR, and Fourier transform infrared. After different contents of PDEP were added to diglycidyl ether of bisphenol A (DGEBA), the modified epoxy resins were cured by 4,4'-diaminodiphenylmethane (DDM). With the addition of a flexible long-chain bio-based monomer to improve toughness, the impact strength was $50 \text{ kJ}\cdot\text{m}^{-2}$ with only 5.0 wt % PDEP; compared with pure DGEBA, the impact strength was $27 \text{ kJ}\cdot\text{m}^{-2}$. Further, an increase in T_g should be confirmed from the mechanical cross-linking density and rigidity group content. The single T_g proved the homogeneous phase structure of the PDEP-cured resin. Morphology exhibiting the ductile fracture of the cured resin was confirmed by scanning electron microscopy. Overall, this work demonstrates the utilization of renewable protocatechuic acid as an effective modifier for epoxy resin, which reflects its potential application.



1. INTRODUCTION

Epoxy resins are among the most important thermosets widely used as matrix materials in advanced composites, coatings, adhesives, and electronic packaging due to their outstanding integrated properties.^{1,2} Currently, most epoxy resins (~90% market share) are synthesized from bisphenol A (BPA) and epichlorohydrin via an O-glycidylation reaction.³ Because the diglycidyl ether of BPA (DGEBA) epoxy resin exhibits rigid and brittle behavior and poor resistance to crack propagation due to its high cross-linking,⁴ its brittleness or lack of crack growth resistance reduces its extensive exploitation.⁵ Therefore, to broaden the application of DGEBA, it is necessary to create DGEBA applications.

To date, there are many methods for toughening epoxy resin, such as using rubber particles,^{6,7} thermoplastics toughening,⁸ and using liquid crystal polymers.^{9,10} However, the nonmiscibility between the matrix and modifier results in high viscosity, opaqueness, and low flowability, limiting the advanced applications of electronic packaging, wind-power insulation coatings, etc.¹¹ An increasing number of researchers are interested in how to effectively toughen epoxy resins. In addition, sustainable bio-based materials are of importance to toughen epoxy resin, including vegetable oil and its derivatives, cashew phenol,^{12–14} and tannic acid.^{15,16} But, there are still some problems such as uneven dispersion and performance degradation. Wang et al.¹³ used cashew phenol to synthesize a flame retardant toughening agent, the amount of addition is 30%, the limiting oxygen index is 30.5%, but the impact strength only increased by $4.29 \text{ kJ}\cdot\text{m}^{-2}$. Fei et al.¹⁵ used tannic

acid to toughen the epoxy resin, the amount of addition is 0.5%, the impact strength to $38.8 \text{ kJ}\cdot\text{m}^{-2}$. All in all, the toughening effect is not ideal, and there are not enough bio-based varieties at present.

However, protocatechuic acid (PCA, 3,4-dihydroxybenzoic acid) is a natural hydrophilic phenolic compound. It has a number of pharmacological properties and benefits to human health.¹⁷ It has similar chemical structure with lignin-based compounds such as vanillin; the structure of carboxyl group, phenol hydroxyl group, and benzene ring can give it better modifiers. PCA can be extracted from plants or fermented by glucose inorganic salt medium.^{18,19} With the breakthrough of biotechnology, the cost of PCA will be expected to be greatly reduced. PCA can be used in a bio-based platform chemical with unique chemical structure and function, but there are few reports on PCA bio-based polymers. Therefore, in addition to guaranteeing the amount of medicine, if the use of protocatechuic acid can be expanded, it will undoubtedly have good social benefits and greater academic value. Chen et al.²⁰ synthesized PA-EP epoxy resin, with T_g exceeding $250 \text{ }^\circ\text{C}$ and a coefficient of thermal expansion of $66 \text{ ppm}/^\circ\text{C}$,

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providing a new way for converting bio-based PCA. Wu et al.²¹ modified PMMA with PCA, obtaining high T_g and excellent ultraviolet-shielding efficiency. This shows that PCA is an ideal raw material for preparing high-performance materials.

As a result, in this work, a rigid-and-flexible and biosourced building block with a symmetrical structure was designed to produce high-performance and toughened epoxy resins. The synthetic compounds contain both flexible carbon chains and rigid benzene rings; second, structure similar to DGEBA, good dispersion, and compatibility with DGEBA. Considering that PCA can be produced on a large scale by fermenting bio-based glucose,¹⁹ this study also provides a new method for converting bio-based glucose to high-performance polymers. Here, we report the details.

2. EXPERIMENTAL SECTION

2.1. Materials. Protocatechuic acid was provided by Qinhong Wang's group. Tetrabutylammonium bromide (TBAB; 98%), *p*-toluenesulfonic acid (PTSA; 99%), epichlorohydrin (ECH), 4,4'-diaminodiphenylsulfone (DDM, 98%), and 1,8-octanediol were purchased from Shanghai Aladdin Biochemical Technology Co.; 1,4-diethylene dioxide and NaOH were provided from Damao Chemical Reagent.

2.2. Instruments. ¹H NMR and ¹³C NMR spectra were recorded on a Quantum-I 400 MHz NMR spectrometer at room temperature, CDCl₃ or DMSO-*d*₆ and tetramethylsilane (TMS) are served as the solvent and the internal standard, respectively. Fourier transform infrared (FTIR) spectra were measured on a Bruker TENSOR II FTIR spectrometer with KBr crystal over the wavenumber range of 400–4000 cm⁻¹. Differential scanning calorimetry (DSC) was run on a TA Instrument DSC 250 at a heating rate of 20 °C/min under a N₂ atmosphere (50 mL min⁻¹). A thermogravimetric analyzer (model Q50, TA Instruments) was used to study the thermal decomposition of the cured epoxy. About 10 mg of the cured epoxy resin was subjected to thermogravimetric analysis (TGA) with 10 °C/min increments from 50 to 600 °C under a nitrogen flow. Dynamic Mechanical Analysis (DMA) was performed using a TA Instrument Q 850 under a N₂ atmosphere with a 3 °C/min increment from 50 to 300 °C at a frequency of 1 Hz. The Hitachi SU8010 scanning electron microscopy (Hitachi, Japan) was adopted to observe the fracture surface of specimens after the impact test.

The impact testing was carried out according to China National Standards GB/T 1043–2008 using a instron 9250HV impact test machine.

2.3. Synthesis of the Protocatechuic Acid Diester (PDES). Under mechanical stirring, PCA (123.3 g, 80 mmol) and 1,8-octanediol (36 g, 40 mmol) and a catalytic amount of PTSA were dissolved in dioxane (50 mL) in a distillation system. The mixture was heated at 120 °C distilling the solvent which is continuously refilled until the reaction was completed. Afterward it was cooled to room temperature and then cooled by a water–ice bath to give a precipitate that was filtered five times with water. The product was a white solid (80% yield). ¹H NMR (400 MHz, DMSO) δ 7.38 (d, J = 2.2 Hz, 5H), 7.32 (dd, J = 8.3, 2.2 Hz, 4H), 6.82 (d, J = 8.3 Hz, 4H), 4.19 (t, J = 6.5 Hz, 8H), 1.68 (p, J = 6.9 Hz, 8H), 1.46–1.27 (m, 21H).

¹³C NMR (101 MHz, DMSO) δ 166.20, 150.81, 145.51, 122.22, 121.29, 116.72, 115.80, 64.50, 61.20, 33.01, 29.38, 28.79, 26.02.

2.4. Synthesis of Protocatechuic Acid Diester Epoxy Resin (PDEP). Under mechanical stirring, PDES (36.2 g, 100

mmol) and epichlorohydrin (148 g, 1600 mmol) were charged into a 500 mL reactor and heated to 100 °C under a N₂ atmosphere. After PDES was completely dissolved, TBAB was added. The mixture was allowed to react for 1 h at 100 °C. When the mixture was cooled to 30 °C, a water/NaOH solution (32 g of NaOH and 128 g of water) was then added dropwise within 30 min. After cooling to room temperature, the mixture was washed with water three times to remove residual salts. Most unreacted ECH was removed and recycled through vacuum using distillation. The crude product was purified three times with EA and filtered. The final product, PDEP, is a white solid. ¹H NMR (400 MHz, CDCl₃, δ): 8.02 (d, 1H), 7.97 (s, 1H), 7.39 (d, 1H), 6.65 (d, 2H), 6.34–6.27 (t, 2H), 6.08 (d, 2H), 3.95 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.24, 151.66, 146.60, 123.91, 115.29, 112.57, 77.88, 68.33, 63.27, 51.36, 44.77, 30.30, 27.53.

2.5. Kinetic Experiments. The non-isothermal DSC measurement has been used to investigate the kinetic behaviors of current DEGBA/10 wt %PDEP system with heating rate of 5, 10, 15, 20 °C/min. According to Kissinger and refs 18 and 22, the apparent activation energy (E_a) and were calculated by using the kinetic data from DSC curves under different heating rate.

2.6. Preparation of the PDEP/DGEBA Curing System. Under mechanical stirring, PDEP and DGEBA were mixed at different mass ratios at 100 °C. After homogeneous mixtures were obtained, stoichiometric amounts of DDM were added at 100 °C under mechanical stirring (the molar ration of epoxy group to N–H was 1:1). When DDM was fully dissolved, the mixture was poured into Teflon rubber molds and cured in a air-circulating oven. All samples were cured using a four-step cure scheme: 100 °C for 1 h, 130 °C for 1 h, 160 °C for 3 h, and 190 °C for 1 h. After curing, samples were cooled naturally to room temperature.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of PDES and PDEP. The chemical structure of PDES and PDEP were characterized with ¹H NMR, ¹³C NMR, and FT-IR spectroscopy. The ¹H NMR and ¹³C NMR spectra of PDES were shown in Figure 1. These ¹H NMR spectra confirmed the presence of the benzene ring and methylene group, showing at 7.37, 7.33, 6.82, 4.26, and 2.78 ppm, respectively. The ¹³C NMR spectra shown the characteristic signal of the C=O group appears at 166.67 ppm. ¹H NMR and ¹³C NMR spectra of PDEP was shown in Figure 2. For the ¹H NMR spectrum, the peaks at 4.5 and 4.0 ppm belong to the protons of the methane e, f, g, and h, directly connecting with hydroxyl and carboxyl of PCA.²⁰ It was seen that the characteristic peaks at 2.5–3.5 ppm belong to the protons of epoxy ethyl groups. The ¹³C NMR spectra shown the characteristic signal of the C=O group and C=C bonds appeared at 163.20, 133.62, and 126.90 ppm, respectively. All data are in accord with the proposed chemical structure, suggesting the confirmation of the structure of PDES and PDEP.

The FT-IR spectra of Protocatechuic acid, PDES, and PDEP are shown in Figure 3. For PCA, the observed broadband peak at 3500 cm⁻¹ is attributed to the O–H stretching vibration of carboxylic acid, the carboxyl absorption peak is at 3200–2500 cm⁻¹. The hydroxyl and carboxyl absorption peaks of PDEP near 3300 cm⁻¹ basically disappear, and a new epoxy absorption peak appears at 910 cm⁻¹.²³

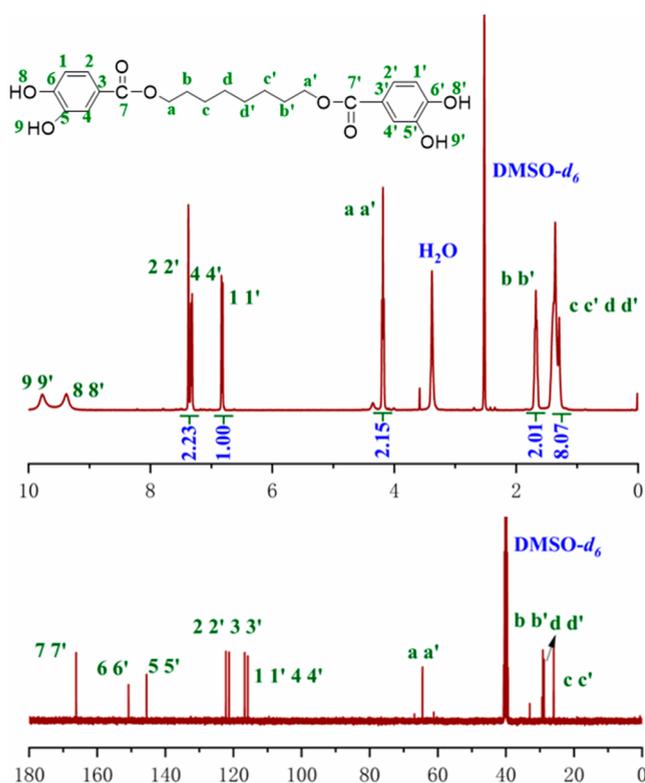


Figure 1. ^1H NMR and ^{13}C NMR spectra of PDES.

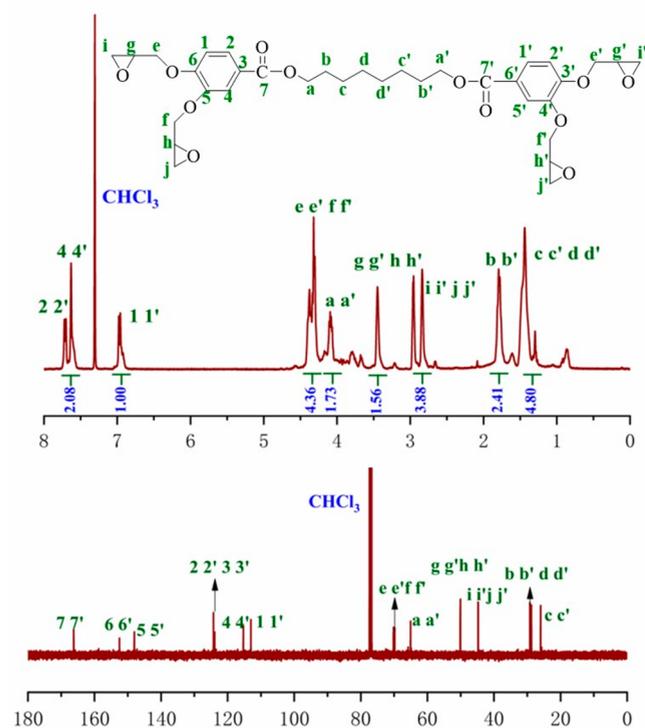


Figure 2. ^1H NMR and ^{13}C NMR spectra of PDEP.

3.2. Curing Behavior and Kinetic Evaluation. Non-isothermal DSC measurement was used to study the curing reaction behavior of DGEBA/10 wt % PDEP and DGEBA/DDM. Figure 4 displays the registered DSC thermal analytical curves. With 10 wt % PDEP curing systems displayed a single

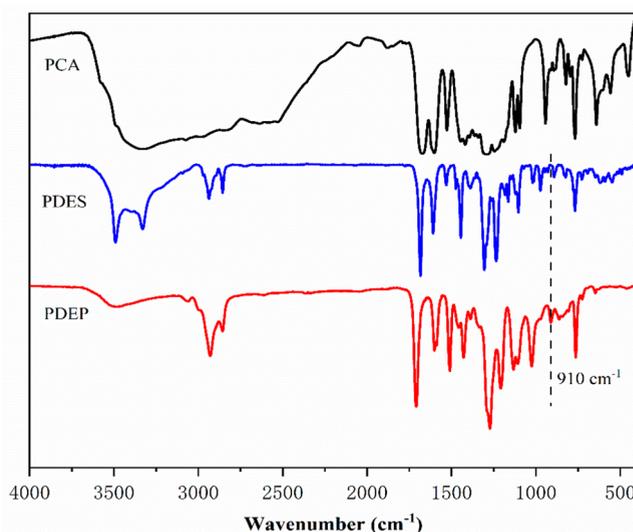


Figure 3. FT-IR spectra of PDES and PDEP.

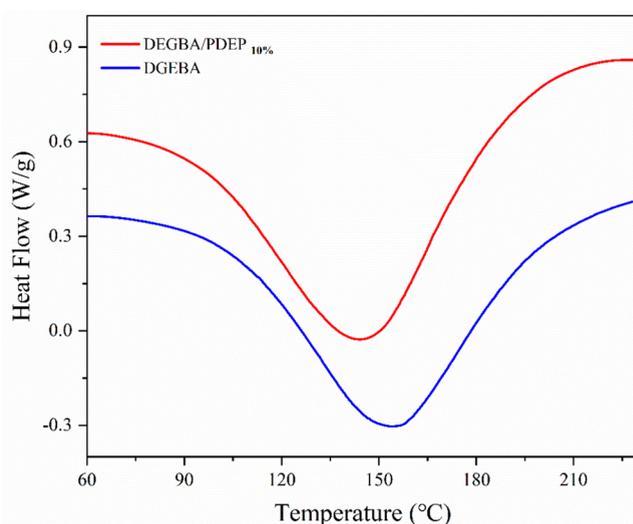


Figure 4. Thermal analytical curves of DGEBA/DDM and DGEBA/PDEP_{10%} with a heating rate of 10 °C/min.

exothermic peak corresponding to the curing reactions of DGEBA/DDM, which implies that the thermal curing has performed completely for with 10 wt % PDEP curing system without any postcuring as a result of homopolymerization. However, as shown in Figure 4, the thermal curing reaction of with 10 wt % PDEP occurs initially at a lower temperature than DGEBA/DDM curing systems. This indicates that the chemical reactivity of the blend system with 10 wt % PDEP is much higher than that of the pure DGEBA system. It is well-known that activation of the oxirane ring opening is achieved by proton donors such as the generated hydroxyl groups during the course of curing reaction.²⁴

Figure 5 displays DSC profiles of DGEBA/PDEP_{10%} for heat flow against temperature with heating rates of 5, 10, 15, and 20 °C/min. As the heating rate increases, DGEBA/PDEP_{10%} shows a consistent increase in the exothermic peak corresponding to the temperature Figure 5, which is typical for non-isothermal curing methodology. The non-isothermal curing characteristic parameters of DGEBA/PDEP_{10%} are listed in Table 1.

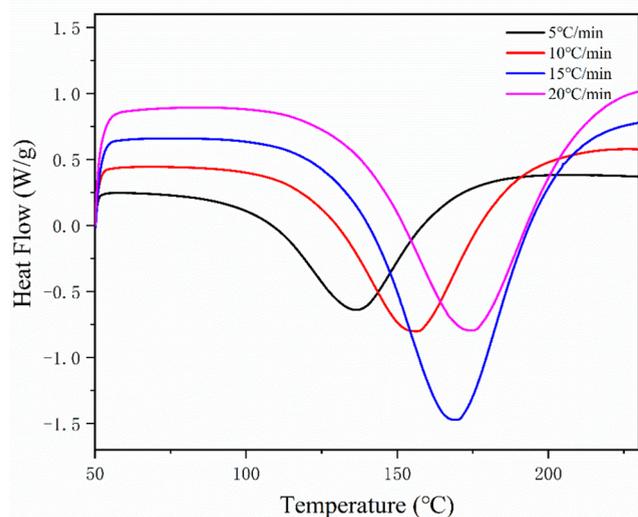


Figure 5. DSC curves of DGEBA/PDEP_{10%} system at different heating rate in N₂.

Table 1. Non-Isothermal Curing Characteristic Parameters of DGEBA/PDEP_{10%}

β	T_s	T_p	T_c	H_t (J/g)
5	105.55	136.33	173.57	403.74
10	122.90	153.84	192.85	284.82
15	134.41	167.80	214.55	356.76
20	135.46	175.34	219.83	225.75

By using the data listed in Table 1, the curing reaction E_a of DGEBA/PDEP_{10%} can be calculated according to the Kissinger equation, as shown below

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_a}{RT_p} - \left(\ln \frac{AR}{E_a}\right) \quad (1)$$

Here, T_p is exothermic peak temperature at a corresponding heating rate (β), R is the gas constant with a value of 8.314 J/mol. The curing reaction E_a of PA-EP/DDM system is finally calculated as 33.63 kJ/mol according to Figure 6. In

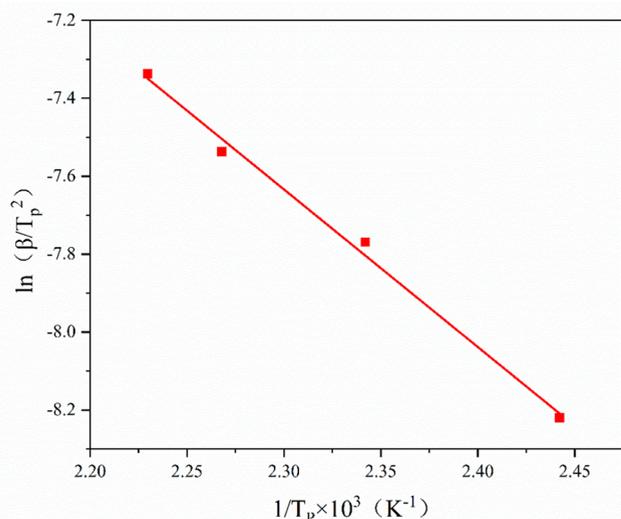


Figure 6. $\ln(\beta/T_p^2) - (1/T_p)$ fit of epoxy resin curing systems.

comparison with the E_a of DGEBA/DDM that was reported as 58.8 kJ/mol.²⁵ This indicates that the curing reaction of the blend system is easier to carry out and the curing rate is faster.

3.3. Thermogravimetric Analysis. Thermogravimetric analysis (TGA) curves of cured hybrids are shown in Figure 7,

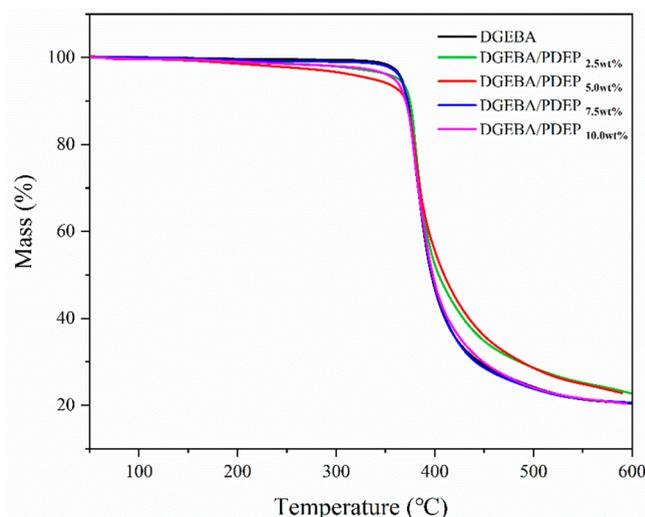


Figure 7. TGA curves of the DGEBA and DGEBA/PDEP in N₂ with a heating rate of 10 °C/min.

and the temperature corresponding to 5% weight loss (T_{d5}) are tabulated in Table 2. The addition of PDEP decreased

Table 2. Thermal Stability Data of the DGEBA and DGEBA/PDEP

Samples	T_{d5}	Residue
DGEBA	366.6	24.2%
PDEP 2.5 wt %	363.6	28.6%
PDEP 5.0 wt %	338.2	28.6%
PDEP 7.5 wt %	366.0	24.1%
PDEP 10.0 wt %	358.1	23.8%

DGEBA/DDM. Because PDEP contains softer $-C_4H_8-$, it will reduce heat resistance. More impressively, the addition of 2.5% and 5% PDEP increased the residual carbon rate at 500 °C by 4% compared with pure DGEBA. This is mainly due to an increase in the rigid benzene ring content of PDEP, which increases residual carbon. Generally, increasing the cross-linked density for the thermosetting systems is beneficial for enhancing their thermal stability.²⁶

3.4. Dynamic Thermomechanical Analysis. Dynamic mechanical behaviors of neat DGEBA and DGEBA/PDEP resins were investigated, as shown in Figure 8; accurate parameters are presented in Table 3. T_g is taken from peak temperature of $\tan \delta$ curve, E is the storage modulus at $T_g + 50$ °C, and cross-linking density (V_c) is calculated from the following formula:

$$V_c = E/3RT \quad (2)$$

where R is the gas constant and T is the absolute temperature at $T_g + 50$ °C. As shown in Figure 8a, the storage modulus of the cured resin was affected by the addition of PDEP. It is well-known that the storage modulus in the glassy state is affected synthetically by chemical structure and chain packing.^{27,28} For each composition, only one single step is observed the storage

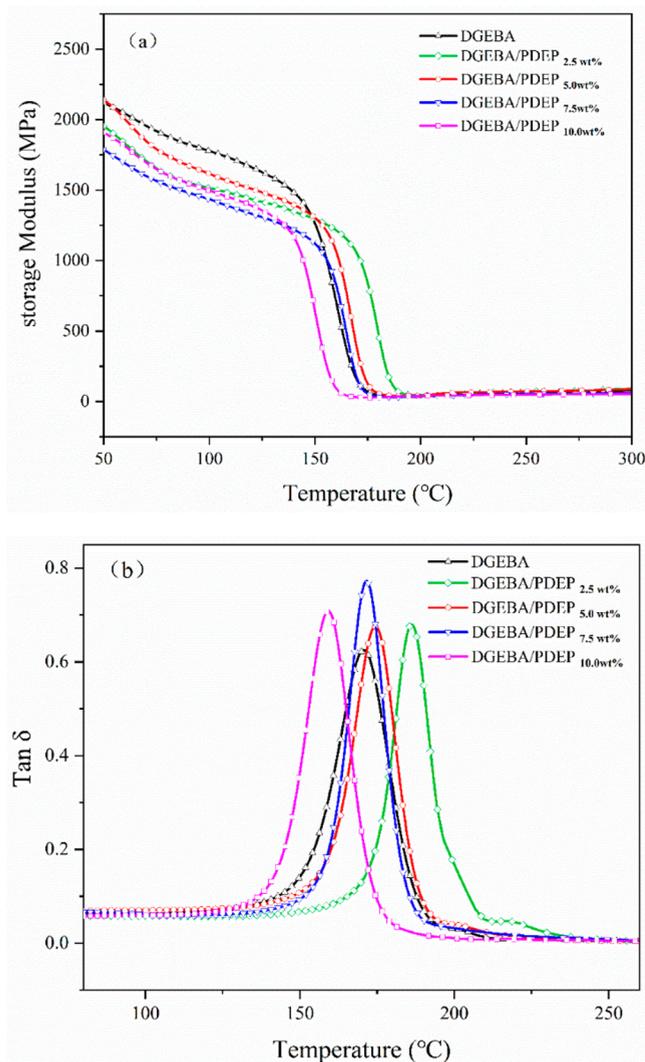


Figure 8. DMA cures of (a) storage modulus and (b) $\tan \delta$ for epoxy resin blends.

Table 3. DMA Parameters of the Neat and Toughened Epoxy Resin Thermosets

DGEBA/ PDEP	E' (MPa)		V (mol/cm ³) 10 ⁻³	T_g (°C)	
	50 °C	T_g + 50 °C		DSC	DMA
100:0	2120.5	55.3	10.0	161.2	170.1
100:2.5	1951.7	67.4	11.4	170.9	186.5
100:5	2134.4	64.6	11.5	165.6	174.6
100:7.5	1785.3	46.7	8.4	158.5	172.1
100:10	1907.0	40.8	7.8	144.4	159.7

modulus and only one peak is observed in $\tan \delta$, suggesting that no phase separation occurs.²⁹ It can be observed that the storage modulus decreased first and then increased with the incorporation of PDEP. Figure 8b shows that each sample had one narrow and smooth α -relaxation peak. The peak of the $\tan \delta$ versus temperature is taken as glass-transition temperature (T_g). As shown in Figure 8b, when the amount of PDEP increased to 5%, T_g and storage modulus increased slightly. On one hand, PDEP with soft long alkyl chain could decrease the stiffness of the resins. On the other hand, PDEP could increase the distance of resin chains and make the resin segment easy to

move. However, there was a gap of T_g between dynamic mechanical analysis (DMA) and DSC analysis results because of the difference test principle and mechanism of these two equipment.³⁰

3.5. Mechanical Properties. The reinforcing and toughening effects of the incorporated SCNER into this curing system were investigated by impact tests. The results are shown in Figure 9. It can be observed that the impact strength

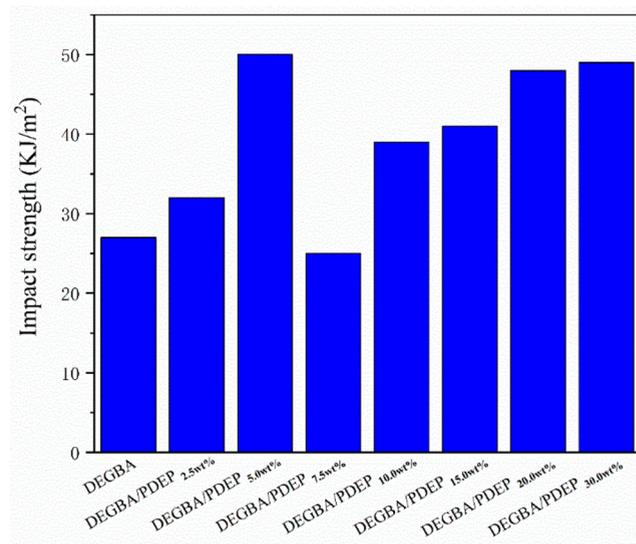


Figure 9. Impact strength properties of cured resins with PDEP.

increased first and then decreased with the incorporation of PDEP. A thermoset with 5 wt % PDEP loadings shows the best toughening effect and the impact strength of the cured resin reaches 50 kJ·m⁻², which is almost twice as high as that of neat epoxy (27 kJ·m⁻²).

3.6. Fracture Surface Morphology. Fracture morphologies of all samples were observed by SEM, as shown in Figure 10. The cured neat DGEBA exhibited a characteristic smooth fracture surface without deformation, which was consistent with the low impact strength.³⁰ After the addition of PDEP, the original smooth surfaces of the cured resin became rougher and appeared to have many ridges. This change meant energy dissipation and improved toughness of the epoxy-PDEP resins. 5% is the best amount of PDEP loading. The cured resin has the best impact strength, less addition, and good compatibility. This toughening effect can be explained by in situ toughening mechanism. Because PDEP has multiple epoxy groups and symmetric structure, similar in structure to DGEBA, it can be evenly dispersed in the system after blending. PDEP epoxy groups participating in the reaction caused an uneven cross-linking network. Formation of the microscopic structure generated stress when yielding to the filar strips which absorb the impact energy; in addition, there are some unclosed hydroxyl branch chains in the blending system, which plays a synergistic toughening effect.^{31–33}

4. CONCLUSIONS

The synthesis of a new toughening agent based on PCA. Due to the synergistic effect of the rigid benzene ring and cross-linking, the PCA diester epoxy resin (PDEP)-cured resin exhibited higher glass transition temperatures (T_g) than pure DGEBA epoxy-cured resin. PDEP was liquid at room

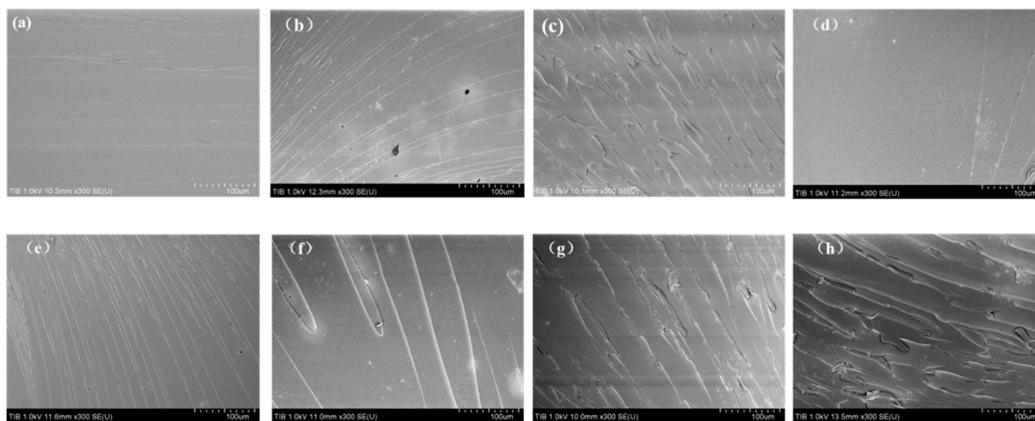


Figure 10. SEM images of frozen fracture morphology: (a) neat epoxy; (b) DGEBA/PDEP_{2.5} wt %; (c) DGEBA/PDEP_{5.0} wt %; (d) DGEBA/PDEP_{7.5} wt %; (e) DGEBA/PDEP_{10.0} wt %; (f) DGEBA/PDEP_{15.0} wt %; (g) DGEBA/PDEP_{20.0} wt %; (h) DGEBA/PDEP_{30.0} wt %.

temperature, easily dispersed in DGEBA epoxy resin, and efficiently toughened the cured resin because of its longer alkyl chains. The results showed that the impact strength of the cured resin with 5 wt % PDEP reached $50 \text{ kJ}\cdot\text{m}^{-2}$, which was almost two times higher than that of pure DGEBA ($27 \text{ kJ}\cdot\text{m}^{-2}$). At $500 \text{ }^\circ\text{C}$, the residual carbon of the blending system with 5 wt % PDEP was slightly higher than that of pure DGEBA. These results demonstrated that PDEP could be used as a potential toughening agent.

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Notes

The authors declare no competing financial interest.

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