

Synthesis of polyfunctional amines as curing agents and its effect on mechanical property of epoxy polymers

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Abstract

A curing agent is required to cure an epoxy resin, but a few curing agents also improve the mechanical properties of the resin. In addition, it is rare to find hardeners containing multiple amines, which can be used to form high cross-link densities. In this study, two different curing agents with six amine functional groups each were synthesized via a two-step reaction. In the first step, isophorone diamine (IPDI) was reacted with two equivalents of pentaerythritol triacrylate (PETA). The resulting IPDI-PETA2 was reacted with ethylene diamine and 4,4'-diaminodiphenyl sulfone to form two amine curers with six amines each—IPDI-PETA2-ED (ED) and IPDI-PETA2-DDS (DDS). Both amines were added in varying amounts to an epoxy composition consisting of dicyandiamide and 2-methylimidazole to improve the mechanical properties compared with a reference epoxy composition. Mechanical studies showed that an epoxy composition containing 5% IPDI-PETA2-DDS improved the flexural strength by 34% and impact strength by 36.7%. Furthermore, adding 5% IPDI-PETA2-ED to the epoxy composition increased the flexural strength by 39.7%, to 197 MPa and the impact strength by 38.8% to 68 J/m. These results highlight the potential of curing agents containing multiple amines for improving the mechanical properties of epoxy resins.

KEYWORDS

adhesive, curing agent, epoxy resin, impact resistance, Michael addition

1 | INTRODUCTION

Epoxy resins have excellent solvent resistance and mechanical and electrical properties and are used in various applications, such as adhesives, paints, electronics, and civil engineering/construction.^{1–12} Epoxy resin is mixed with a curing agent and cured into a three-dimensional thermosetting

material; thus, its performance is significantly influenced by the selection of the epoxy and curing agent, the mixing ratio, and curing conditions.¹³ Curing agents are essential for tuning low-molecular-weight epoxy oligomers into highly cross-linked networks and imparting high mechanical strength.

Representative curing agents include isophorone diamine (IPDA), polyamines, polyamides, anhydrides,

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phenol-formaldehyde resins, and polysulfides, which are toxic before hardening and cause environmental and health problems.^{14–18} Isophorone diamine is a cycloaliphatic amine with low viscosity and moderate reactivity. However, it has disadvantages, including hygroscopicity, high cost compared to aliphatic amines, and carbamate formation by interaction with atmospheric carbon dioxide, which imposes certain restrictions on transportation and storage.¹⁹ Aliphatic polyamines have low cost and low viscosity and cure at ambient temperature. However, unmodified amines present certain handling risks owing to their high basicity and relatively high vapor pressure.^{20–24} Polyamides are convenient for curing at room temperature; however, they have high formulation costs, possess high viscosity, and have low heat resistance. Anhydrides exhibit good thermal, mechanical, and electrical properties, but require long curing times at elevated temperatures.^{25,26} Phenol-formaldehyde resins have good chemical resistance, shelf stability, compatibility with epoxies, and high-temperature resistance. However, they require a high-temperature cure and high-melting solids.²⁶ Polysulfides have advantages such as moisture insensitivity, quick set-time, and flexibility, but perform poorly at elevated temperatures.^{25,26}

Among these, the most commonly used curing agents are amine-based. Banthia et al. synthesized new curing agents, including amine-functionalized aniline formaldehyde condensates (AFAFC) and amine-functionalized chloroaniline formaldehyde condensates (AFCFC).²⁷ The AFAFC and AFCFC cured epoxies showed tensile strengths of 15.17 and 10.09 MPa, low flexural strengths of 59.76 and 47.63 MPa, and high-impact strengths of 290 and 210 J/m, respectively. However, AFAFC and AFCFC contain formaldehyde, a highly toxic systemic poison. Li et al. prepared a silicon-containing aliphatic polyamine, 1,3-bis(2-aminoethylaminomethyl) tetramethyl disiloxane (SFA).²⁴ SFA has the advantages of lower viscosity and increased thermal stability, corrosion resistance, and flame-retardant properties. However, mechanical properties, such as tensile strength, flexural strength, and impact strength, were not reported. Gu et al. synthesized polyaminopropylmethylsiloxane (PAPMS) oligomer/N-(2-hydroxyethyl)ethylenediamine as a curing agent.²⁸ The curing agent had improved compatibility with the epoxy matrix and corrosion resistance. However, the mechanical properties were not reported. Li et al. prepared a silicone-phenyl-containing aliphatic polyamine (PSPA),²⁹ which showed excellent curing behavior and thermal behavior. However, its mechanical strength was not reported. Alam et al. synthesized a diamine derivative of ferrocene, 1,1'-bis(α -aminoethyl)ferrocene (FcDA), as a curing agent.³⁰ The ferrocene-based curing agent exhibited an enhanced stress relaxation behavior above its T_g . FcDA exhibited a tensile strength of approximately 62 MPa, which was

lower than that of Jeffamine D-230, methylene dianiline, and isophorone diamine (IPD). Multifunctional curing agents, such as triethylene tetraamine and diethyl triamine, with three or more NH_2 groups, are highly brittle because of the linear alkyl structure.^{31,32}

In this study, two different amine curing agents, Isophorone diisocyanate-pentaerythritol triacrylate 2-diaminodiphenyl sulfone (IPDI-PETA2-DDS) (DDS), and Isophorone diisocyanate-pentaerythritol triacrylate 2-ethylene diamine (IPDI-PETA2-ED) (ED), were synthesized. We investigated the effects of the curing agents on the mechanical properties of epoxy, including tensile strength, flexural strength, and impact strength.

2 | EXPERIMENTAL SECTION AND METHODS

2.1 | Materials

The diglycidyl ether of bisphenol-A (DGEBA, Epikote 828, epoxy equivalent weight [EEW], 187 g/eq) was obtained from Momentive Co. Ltd. Dicyandiamide (DICY) was obtained from Alzchem Co. Ltd. Isophorone diisocyanate (98%), 4-methoxyphenol (99%), catalyst dibutyltin dilaurate (DBTDL) (95%), 2-methylimidazole (2-MI) (99%), 4,4'-diaminodiphenyl sulfone (97%), and ethylene diamine ($\geq 99\%$) were purchased from Sigma-Aldrich Co. Ltd. Pentaerythritol triacrylate (PETA) was purchased from Thermo Scientific Co. Ltd. Hexane and methanol were purchased from Daejung Chemical Co. Ltd. All the chemicals were used without further purification.

2.2 | Synthesis of multifunctional amine curing agents

2.2.1 | Synthesis of IPDI-PETA2

Isophorone diisocyanate (20.0 g, 0.09 mol), 4-methoxyphenol (0.9 g, 0.007 mol), DBTDL (0.25 g, 0.0003 mol), and hexane (30 mL) were charged into a 250-mL three-neck flask equipped with a mechanical stirrer and nitrogen inlet. After stirring under a nitrogen atmosphere at 45°C, PETA (59.59 g, 0.1998 mol) was added slowly into the reactor using a dropping funnel. The mixture was stirred at 60°C for 6 h. The hexane was evaporated using a rotary evaporator, and IPDI-PETA2 was obtained as a clear liquid. ^1H NMR (300 MHz, CDCl_3) (Figure 3a): δ (ppm) = 6.41 (H, m), 6.17 (H, m), 5.89 (H, m), 4.23 (16H, m), 3.68 (H, m), 3.02 (2H, m), 1.22 (4H, m), 1.07 (5H, m), 0.90 (6H, m).

TABLE 1 Epoxy compositions.

Sample	DGEBA (g)	DICY (g)	Prepared curing agent (g)	2-MI (g)
Reference	100	11.24	–	0.21
DDS 5%	100	10.68	3.42	0.21
DDS 10%	100	10.12	6.85	0.21
ED 5%	100	10.68	1.75	0.21
ED 10%	100	10.12	3.51	0.21

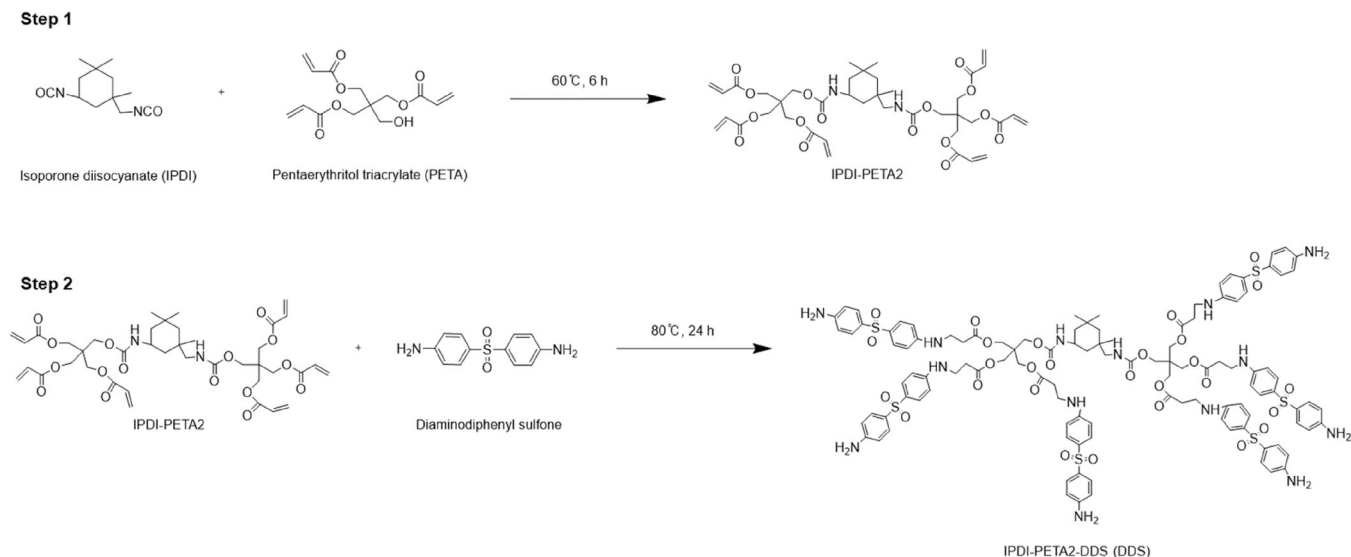


FIGURE 1 Synthesis of DDS.

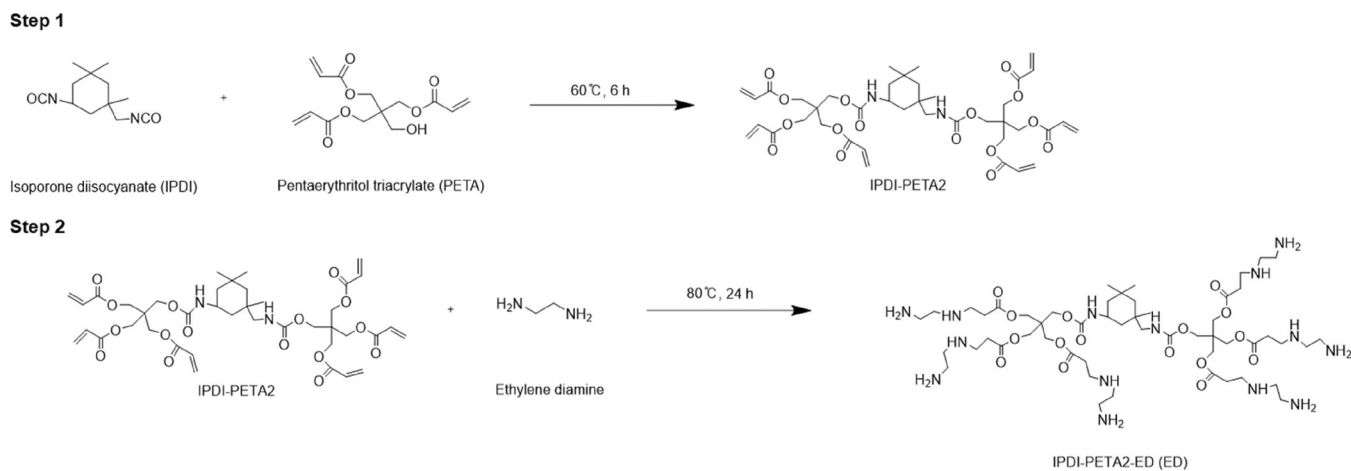


FIGURE 2 Synthesis of ED.

Elemental analysis (EA):% (calculated.%): C: 60.28 (58.67), H: 7.4 (6.65), N: 4.15 (3.42), O: 26.88 (31.26).

2.2.2 | Synthesis of IPDI-PETA2-DDS (DDS)

4,4'-Diaminodiphenyl sulfone (6.36 g, 0.025 mol), IPDI-PETA2 (3 g, 0.003 mol), and methanol (20 mL) were

added to a 250-mL three-neck flask equipped with a reflux condenser and nitrogen inlet. The mixture was agitated at 80°C for 24 h. Finally, the solvent was removed using a rotary evaporator, and the IPDI-PETA2-DDS was obtained as a white solid. ^1H NMR (300 MHz, DMSO- d_6) (Figure 3b): δ (ppm) = 7.46 (24H, m), 6.59 (24H, m), 5.99 (18H, m), 4.14–4.12 (16H, m), 3.36 (13H, m), 1.45 (4H, m), 0.99 (5H, m), 0.97 (6H, m).

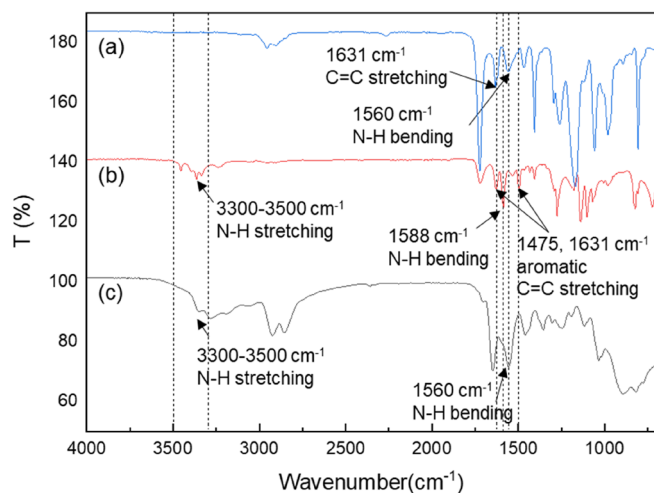


FIGURE 3 FT-IR spectra of (a) IPDI-PETA2, (b) DDS, and (c) ED. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.53806)]

Elemental analysis (EA):% (calculated %): C: 58.09 (58.27), H: 5.55 (5.50), N: 8.55 (8.49), O: 19.82 (19.40) S: 7.78 (8.33).

2.2.3 | Synthesis of IPDI-PETA2-ED (ED)

Ethylene diamine (1.54 g, 0.025 mol), IPDI-PETA2 (3 g, 0.003 mol), and methanol (20 mL) were added to a 250 mL three-neck flask equipped with a reflux condenser and nitrogen inlet. The mixture was stirred at 80°C for 24 h. Finally, the solvent was removed using a rotary evaporator and IPDI-PETA2-ED was obtained as a viscous yellow liquid. ^1H NMR (300 MHz, CDCl_3) (Figure 3c): δ (ppm) = 3.39 (16H, s), 3.26 (12H, m), 3.09–2.64 (24H, m), 2.36 (12H, m), 1.49 (22H, s), 1.03 (5H, m), 0.81 (6H, m). Elemental analysis (EA):% (calculated %): C: 52.52 (52.95), H: 10.87 (8.72), N: 16.69 (16.63), O: 19.87 (21.70).

2.3 | Preparation of epoxy blends

Epoxy blends with different DDS and ED contents were prepared according to the following procedure. First, the reference composition was prepared in the ratio [DGEBA]: [DICY]: [2-MI] = 1: 0.112: 0.002, according to the amine hydrogen equivalent weight (AHEW). The DDS and ED contents of the epoxy composition were 5% and 10%, respectively, based on the synthesized multifunctional amine curing agent. The epoxy compositions are listed in Table 1. Each epoxy composition, with different amounts of the curing agent, was mixed using a planetary mixer. Epoxy compositions were cast into a metal mold and subsequently cured in an oven for 2 h at 150°C.

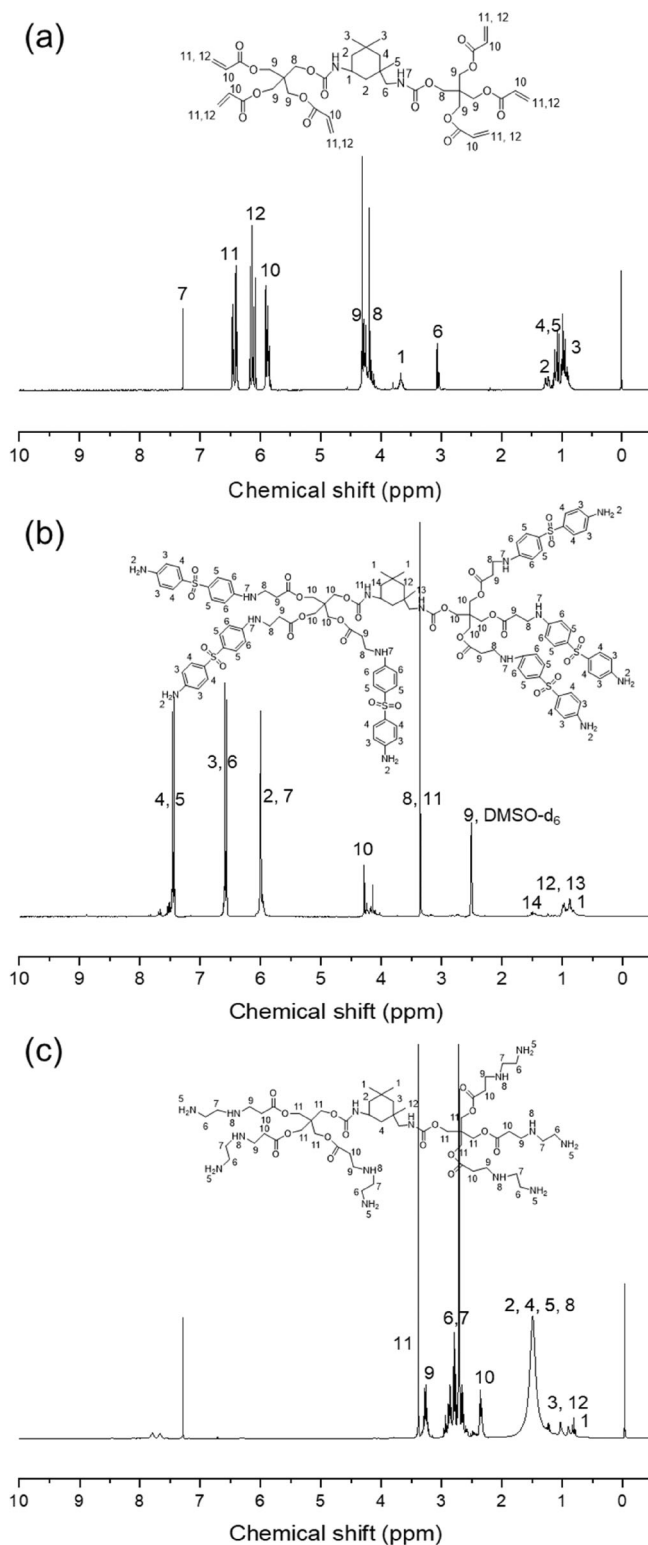


FIGURE 4 ^1H NMR spectra of (a) IPDI-PETA2, (b) DDS, and (c) ED.

2.4 | Characterization

The synthesized DDS and ED were analyzed by proton nuclear magnetic resonance (^1H NMR, Bruker Advance

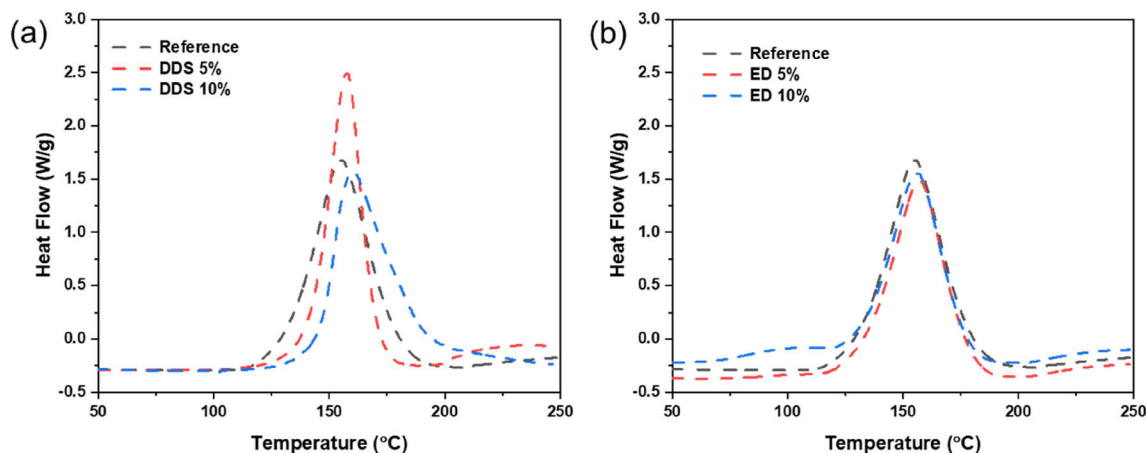


FIGURE 5 DSC curves of the different epoxy compositions. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

TABLE 2 DSC data of various epoxy compositions.

Sample	T_{peak} (°C)	T_{onset} (°C)
Reference	155.1	121.7
DDS 5%	157.3	122.7
DDS 10%	160.2	136.9
ED 5%	157.9	119.5
ED 10%	156.3	122.7

300 MHz spectrometer, Bruker, MA). DMSO- d_6 and chloroform- d were used for the measurements. The synthesized DDS and ED were characterized using Fourier-transform infrared spectroscopy (FT-IR, Nicolet 6700, Nicolet Continuum; Thermo Fisher Scientific Inc., Waltham, MA). Quantitative elemental analysis (EA, Flash 2000 series, Thermo Fisher Scientific Inc., Waltham, MA) was performed to measure the atomic composition of the synthesized DDS and ED.

Differential scanning calorimetry (DSC, Q 2000, TA Instruments Inc., New Castle, DE) was conducted to investigate the curing behavior of epoxy compositions from -80°C to 250°C at a scanning rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen purging. Approximately 5 mg of each sample was placed in a hermetically sealed aluminum pan.

The viscoelastic properties of the cured epoxy compositions were determined by dynamic mechanical analysis (DMA, Q 800, TA Instruments Inc., New Castle, DE). The test samples ($60\text{ mm} \times 12\text{ mm} \times 3\text{ mm}$) (length \times width \times thickness) were installed on a dual cantilever probe and measured from 30°C to 200°C at a heating rate of $5^{\circ}\text{C}/\text{min}$ at a frequency of 1 Hz under nitrogen gas to measure both the storage modulus and $\tan \delta$ values. The cross-linking density was calculated using the following equation and the storage modulus value of each sample, according to the rubber elasticity theory.^{33–35}

$$\nu = \frac{E_r}{3RT}$$

where ν is the cross-linking density, R is the gas constant ($8.314\text{ cm}^3 \cdot \text{MPa} / \text{mol} \cdot \text{K}$), T is the temperature at which E_r is evaluated, and E_r is the elastic modulus in the rubbery elastic region $T = T_g + 40$.

The tensile and flexural strengths of the cured epoxy compositions were determined using a universal testing machine (UTM 5982; Instron, Norwood, MA). The tensile strength was evaluated using the ASTM D 638 method, and the specimens were prepared with dimensions of $150\text{ mm} \times 13\text{ mm} \times 3\text{ mm}$ (length \times width \times thickness), according to the specifications. The flexural strength was tested according to the ASTM D 790 method, and the specimen dimensions were $60\text{ mm} \times 25\text{ mm} \times 3\text{ mm}$ according to the standard. The length of the specimen support was 48 mm, and the test was performed at a speed of 1.2 mm/min. The tensile and flexural tests were repeated five times to get the average values. The impact strengths were obtained using an Izod impact tester (JJHBT-6501, Chengde, China) according to ASTM D 256 standards. The specimen samples were $63.5\text{ mm} \times 12.7\text{ mm} \times 3\text{ mm}$, and a notch of 2.54 mm was applied. Surface fractures of the tensile strength test specimen were examined by field-emission scanning electron microscopy (FE-SEM; MIRA 3, TESCAN, Brno, Czech Republic) at an appropriate magnification. The specimen surfaces were coated with Pt using a sputter coater.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of synthesized DDS and ED

As shown in Figures 1 and 2, IPDI-PETA2 is synthesized via a urethane reaction between the isocyanate (NCO) of

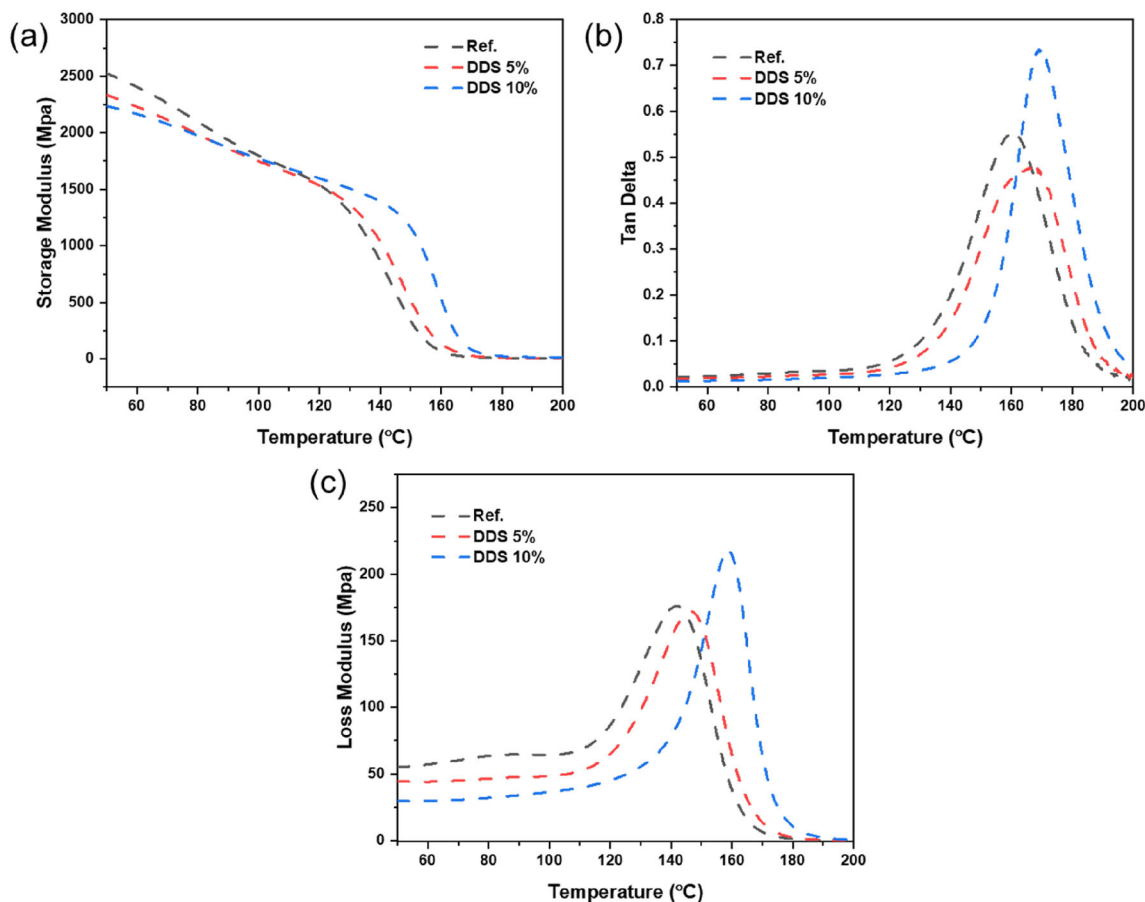


FIGURE 6 DMA for various epoxy compositions including DDS (a) Storage moduli of epoxy compositions, (b) Tan δ values, and (c) Loss moduli of epoxy compositions. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.53806)]

IPDI and the hydroxyl (OH) group of PETA. The novel curing agents DDS and ED are synthesized via Michael addition between the double bonds of IPDI-PETA2 and the amine group of diaminodiphenyl sulfone or ethylene diamine. FT-IR and ^1H NMR spectroscopy confirmed the successful synthesis of the DDS and ED.

Figure 3 shows the FT-IR spectra of IPDI-PETA2 (Figure 3a), DDS (Figure 3b), and ED (Figure 3c). A strong band at $3300\text{--}3500\text{ cm}^{-1}$ in the FT-IR spectrum reveals the formation of the —NH— bond between IPDI-PETA2 and diaminodiphenyl sulfone or ethylene diamine (Figure 3b,c). The aromatic C=C stretching bonds in DDS appear at 1475 and 1631 cm^{-1} (Figure 3b). The —NH bending vibration in the DDS is also observed at 1588 cm^{-1} (Figure 3b). In the ED spectrum, the —NH bending vibration is observed at 1560 cm^{-1} (Figure 3c). The characteristic peaks of IPDI-PETA2 ($6.41\text{--}5.89\text{ ppm}$, Figure 4a) in the ^1H NMR spectrum disappear after reaction to DDS or ED. In the ^1H NMR spectrum of DDS (Figure 4b), peaks at $7.5\text{--}5.99\text{ ppm}$ corresponding to the phenylsulfonyl aniline protons of DDS can be observed. Figure 4c shows the

^1H NMR spectrum of ED, where peaks at $3.09\text{--}2.64\text{ ppm}$ is because of the ethylene protons ($\text{—CH}_2\text{CH}_2\text{—}$) of ethylene diamine.

3.2 | Characterization of epoxy compositions

Differential scanning calorimetry (DSC) was performed on the epoxy compositions with DDS and ED. As shown in Figure 5 and Table 2, all epoxy compositions exhibit a similar onset temperature (T_{onset}) of $119\text{--}137^\circ\text{C}$ and peak temperature (T_{peak}) of $155\text{--}160^\circ\text{C}$. The increase in T_{onset} shows relatively high-thermal stability. T_{onset} increased gradually with the increase in the number of amino groups in the curing agent (an increase in the amount of DDS and ED). The increase in T_{onset} is caused by the formation of a cross-linking network in the epoxy compositions.^{36,37} Even when the amount of the curing agent increases, the curve appears at a constant temperature, showing that the curing time does not increase for the same energy area, and a constant temperature is

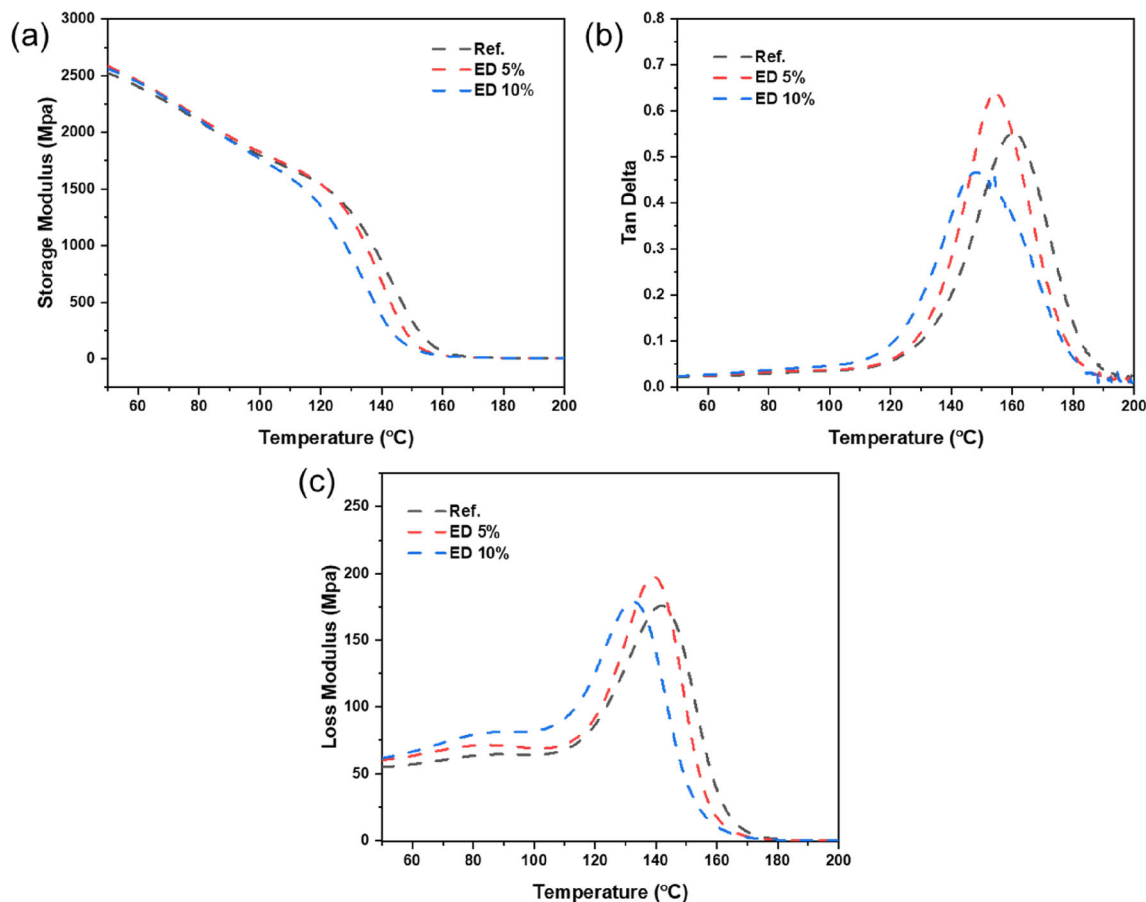


FIGURE 7 DMA for various epoxy compositions including ED (a) Storage moduli of epoxy compositions, (b) Tan δ values, and (c) Loss moduli of epoxy compositions. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 DMA results of epoxy compositions.

Sample	T_g ($^{\circ}\text{C}$)	Storage modulus at $T_g + 40^{\circ}\text{C}$	Cross-linking density ρ ($\times 10^{-3}$ mol/cm 3)
Reference	162.0	4.61	0.39
DDS 5%	167.5	4.77	0.40
DDS 10%	169.9	11.28	0.94
ED 5%	154.1	5.70	0.49
ED 10%	148.2	6.88	0.60

required. All epoxy compositions were therefore cured for 2 h at 150°C , higher than T_{onset} , to provide sufficient energy for the curing process.

A dynamic mechanical analysis (DMA) was performed to investigate the dynamic thermal properties of the cured epoxy compositions. The storage modulus (E'), $\tan \delta$, and loss modulus (E'') are shown in Figures 6 and 7. The storage modulus reveals important information regarding the stiffness of the epoxy compositions, interfacial bonding, and cross-linking degree.³⁸ Figures 6 and 7 show the effects of different DDS or ED contents, respectively. In the glassy region, the reference sample and the

DDS-treated samples show high-storage modulus values (2250–2560 MPa, Figure 6a). The addition of DDS decreases the storage modulus from 2560 to 2250 MPa. After the glass transition region, the storage modulus of the reference and DDS-treated compositions decreases considerably because the mobility of the polymer chains increases above the T_g . As the temperature increases, the storage modulus of the DDS-treated epoxy compositions increases, indicating that the mechanical properties are enhanced by the addition of DDS. However, as the ED content increases, the storage modulus decreases (Figure 7a). The flexibility of the ED decreases the

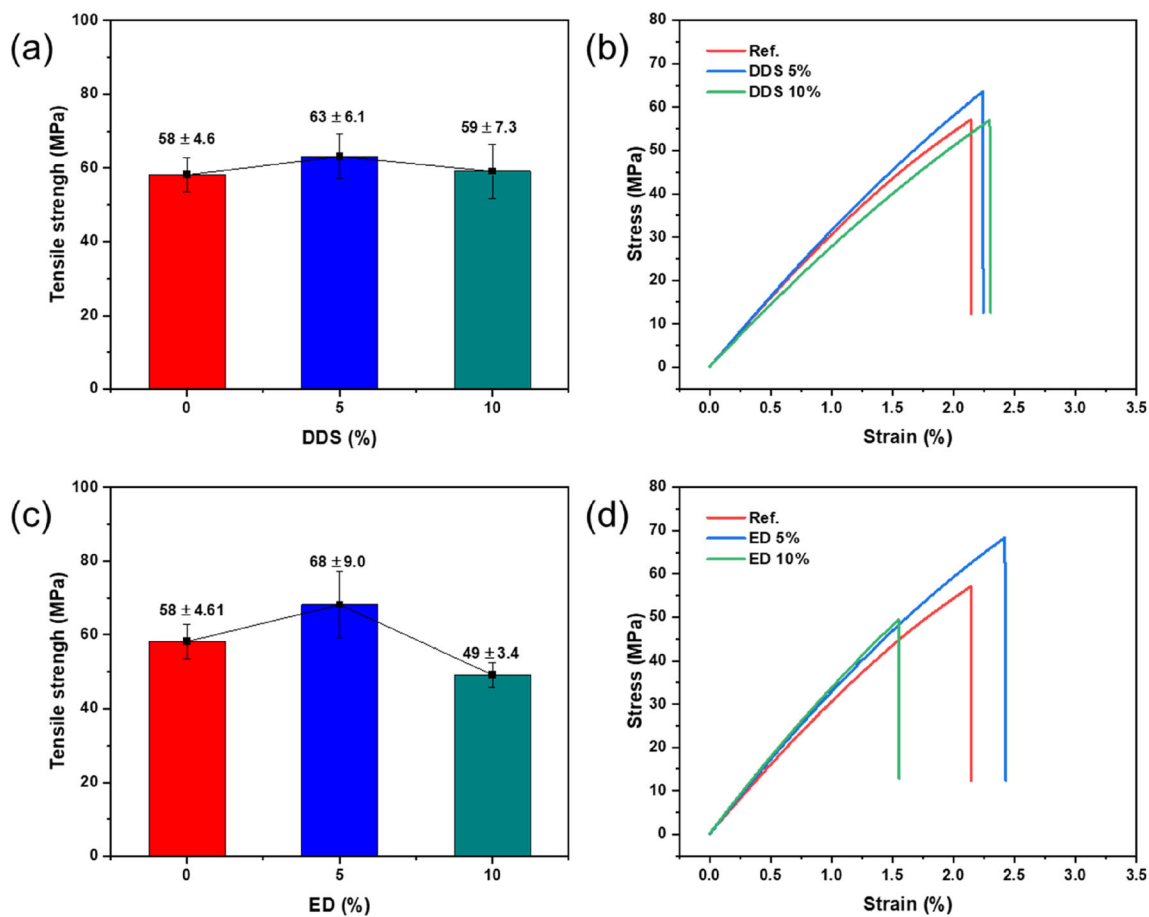


FIGURE 8 (a) Tensile strength and (b) stress–strain curve of DDS and (c) tensile strength and (d) stress–strain curve of ED. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.53806)]

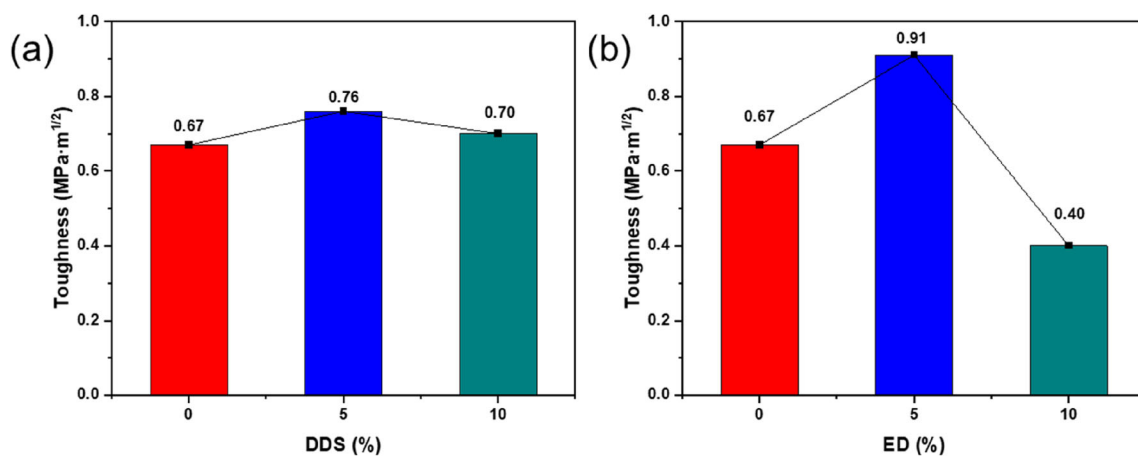


FIGURE 9 Tensile toughness of (a) DDS and (b) ED. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.53806)]

storage modulus.^{39,40} $\tan(\delta)$ is calculated as the ratio of the loss modulus (E'') to the storage modulus (E' ; Figures 6b and 7b). It represents the relative amount of dissipated energy versus that stored elastically in the material. In this study, the measured peak of the tan curve was used to identify T_g , listed in Table 3. The

mobility of polymer chains is closely related to the crosslinking density. Generally, as the crosslinking density increases, the polymer chain mobility decreases; thus, a higher crosslinking density results in a relatively higher glass transition temperature. For the DDS-treated samples, T_g increases with the crosslinking density, whereas

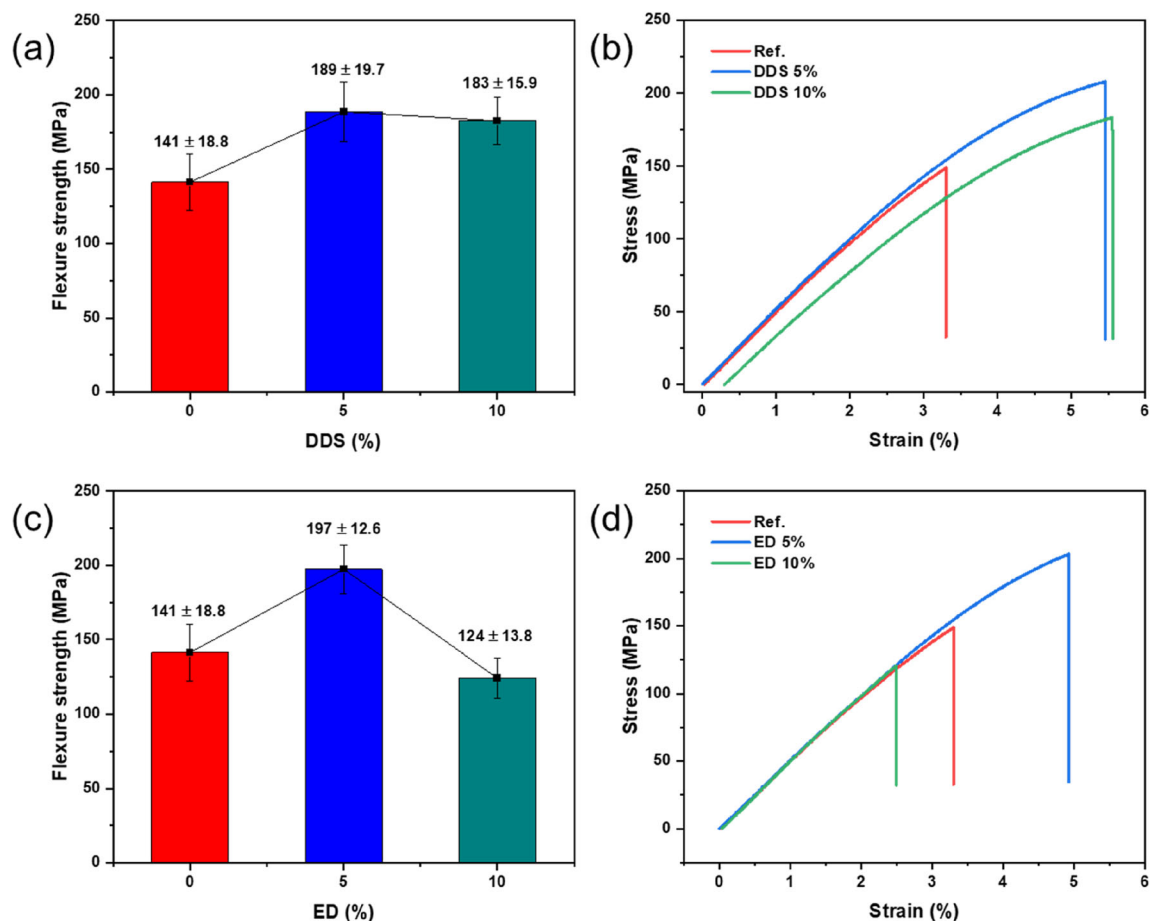


FIGURE 10 (a) Flexure strength and (b) stress–strain curve of DDS and (c) flexure strength and (d) stress–strain curve of ED. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.53806)]

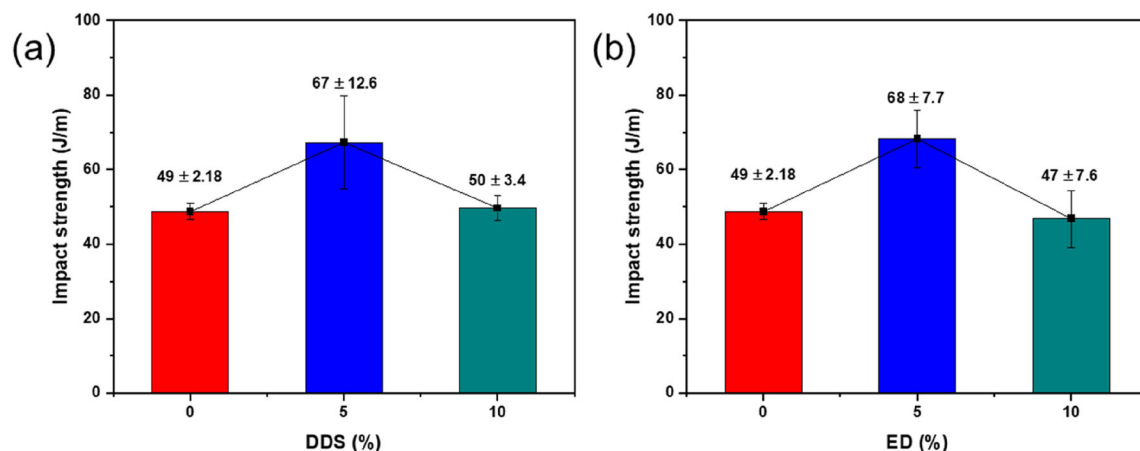


FIGURE 11 Impact strength for (a) DDS and (b) ED. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.53806)]

for the ED-treated samples, T_g decreases. This is owing to the more flexible main-chain structure of the ED-treated sample.^{41–45} The loss modulus represents the viscous characteristics or the amount of energy dissipated. The loss modulus and $\tan \delta$ graph showed a similar tendency.

3.3 | Mechanical properties of epoxy compositions

Figure 8 shows the tensile strength and stress–strain curves of the epoxy compositions as a function of the DDS or ED content. The reference epoxy composition

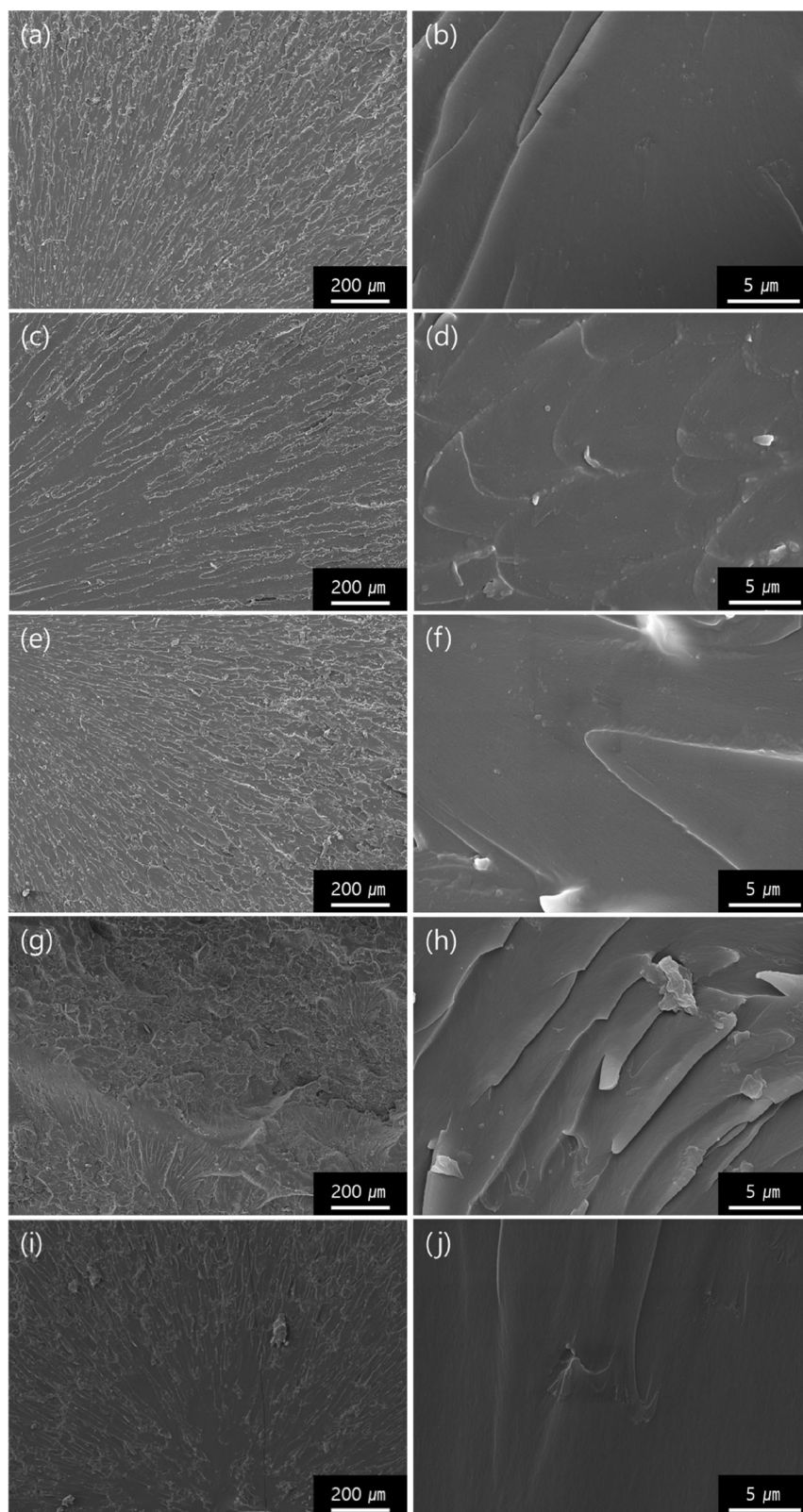


FIGURE 12 Field-emission scanning electron microscopy (FE-SEM) images of the fractured surface after tensile strength tests. Images show the reference (a and b), 5% DDS (c and d), 10% DDS (e and f), 5% ED (g, h), and 10% ED (i, j).

has a tensile strength of 58 MPa. The tensile strength of the cured epoxy composition, including 5% DDS, is 63 MPa, approximately 8.6% higher than the reference (Figure 8a,b). For the cured epoxy composition, including 5% ED, the tensile strength is 68 MPa, approximately

17.2% higher than the reference (Figure 8c,d). The increased tensile strength is because of cross-linking network formation between the epoxy compositions and the DDS or ED.^{46,47} However, the cured epoxy compositions including 10% DDS or ED exhibit decreased tensile

strength. This result shows that the tensile strength initially increases, but after reaching a maximum value, it decreases with the crosslinking density. These observations are attributed to the embrittlement of the polymer owing to decreased chain mobility.⁴⁸ As seen from Figure 8b,d, the trend of the curves is like linear right up to the fracture breaking point without plastic deformation. The changes in tensile toughness (integrated area under the stress–strain curve during the tensile strength test)^{49,50} as a function of the DDS and ED contents are shown in Figure 9. The tensile toughness was proportional to the tensile strength. 5% ED had the highest tensile strength (68 MPa) and the maximum toughness (0.91 MPa·m^{1/2}).

Figure 10 shows that the flexural strength of epoxy compositions is enhanced upon the inclusion of 5% DDS or ED. The reference epoxy composition has a flexural strength of approximately 141 MPa. The flexural strength of the cured epoxy composition, including 5% DDS, is 189 MPa, an increase of 34.0% compared to the reference (Figure 10a,b). In the case of the cured epoxy composition including 5% ED, the flexural strength is 197 MPa, which is approximately 39.7% higher than the reference (Figure 10c,d). The mechanical properties of the epoxy compositions were enhanced by the formation of the cross-linking network between the epoxy compositions and the DDS or ED. The flexural strength decreases for samples containing 10% DDS or ED (Figures 10a,c). The reason for the lower flexural properties with higher proportions of DDS or ED is likely the embrittlement of the polymer owing to decreased chain mobility. Figure 10b,d show that the stress–strain curves are in an almost linear fashion right up to the fracture breaking point.

Figure 11 shows the variation in the impact strength of the epoxy compositions with the addition of the DDS or ED. The maximum impact strength is observed for samples containing 5% DDS or ED (Figure 11a,b). For these samples, the impact strength for DDS and ED reaches the highest values of 67 and 68 J/m, respectively, which is an improvement of 36.73% or 38.77% compared to the reference. The formed network structure can tolerate more mechanical loading under stress. With the addition of 10% DDS or ED, embrittlement of the polymer leads to a reduction in the impact strength of the epoxy compositions. A prominent steric hindrance effect could suppress hydrogen bonding, resulting in reduced impact strength.⁵¹

3.4 | Morphology of fracture surface

Figure 12a–j shows the FE-SEM images of the fractured specimen after the tensile strength measurements. The

fracture surface of the reference (Figure 12a,b) looks smooth, with a slight line pattern caused by the brittleness of the epoxy compositions. The fractured surfaces of 5% DDS and 10% DDS (Figure 12c–f) were as smooth as that of the reference. In the case of 5% ED (Figure 12g,h), the fractured surface with the highest tensile strength (~68 MPa) was rough. In the case of 10% ED (Figure 12i,j), the fractured surface appeared smoother than the reference, which correlated with a low tensile strength to 49 MPa.

4 | CONCLUSIONS

In this study, IPDI-PETA2-DDS (DDS) and IPDI-PETA2-ED (ED) were synthesized via a Michael addition reaction between IPDI-PETA2 and diaminodiphenyl sulfone or ethylene diamine and added to epoxy compositions to improve their mechanical properties. The chemical synthesis was verified using FT-IR, EA, and ¹H NMR. Synthesized DDS or ED was added to epoxy compositions to examine their effects on polymer properties. From the DSC data results, all the epoxy compositions exhibited a similar onset temperature (T_{onset}) of 119–137°C and peak temperature (T_{peak}) of 155–160°C. This shows that the curing time did not increase for the same energy area, and a constant temperature was required. From the DMA, it was found that, as the temperature increased, the storage modulus of the epoxy compositions, including DDS, increased, showing that the addition of the DDS enhanced the mechanical properties of the epoxy compositions. However, as the content of ED increased, the storage modulus values decreased owing to the flexibility of the ED.^{39,40} Furthermore, the cross-linking density increased linearly with DDS or ED content and reached a maximum value of 0.94×10^{-3} mol/cm³ or 0.60×10^{-3} mol/cm³, at a DDS or ED content of 10%, respectively. The highest impact, flexural, and tensile strengths were achieved at 5% DDS and 5% ED because of cross-linking network formation between the epoxy compositions and the DDS or ED. However, for epoxy compositions of 10% DDS or ED, the impact, flexural, and tensile strengths were decreased owing to the embrittlement of the polymer by the decreased chain mobility. FE-SEM analysis showed that the fracture surface of the 5% ED specimen with the highest tensile strength (~68 MPa) was rough and irregular.

AUTHOR CONTRIBUTIONS

Seoyoon Yu: Investigation (lead); writing – original draft (equal). **Hye Jin Kim:** Investigation (supporting). **Sugyeong Jeon:** Formal analysis (supporting). **Choong-**

Sun Lim: Investigation (supporting); writing – review and editing (equal). **Bongkuk Seo:** Project administration (lead); supervision (lead); writing – review and editing (equal).


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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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