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Synthesis of urethane-modified aliphatic epoxy using a greenhouse gas for epoxy composites with tunable properties: Toughened polymer, elastomer, and pressure-sensitive adhesive



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ABSTRACT

Epoxy, which exhibits tunable mechanical properties, has been investigated to overcome its inherent brittleness and extend its application range. Herein, various epoxy composites, including a toughened polymer, elastomer, and pressure-sensitive adhesive (PSA), with tunable mechanical properties were prepared by adjusting the ratio of a rigid aromatic epoxy and flexible aliphatic epoxy. A flexible aliphatic epoxy that incorporated urethane linkages was used to extend the tuning range; it was synthesized via an eco-friendly route utilizing CO_2 without isocyanate. The prepared toughened polymer-like and elastomeric epoxy composites can be used in structural epoxy adhesive (lap shear strength = 27.8 MPa) and flexible electronics (plastic strain < 10%), as confirmed through single lap shear, cyclic tensile, and Izod impact tests, respectively. The most flexible among the prepared epoxy composites exhibited PSA properties (peel strength = $6.8 \text{ N}\cdot\text{cm}^{-1}$) that were comparable to those of conventional tapes. A viscoelastic window also supported that the prepared PSA can be utilized as a generalpurpose PSA and a removable PSA. This work proposes a new application of eco-friendly epoxies and a strategy to facilitate the wide tuning range of epoxy materials, including PSAs.

1. Introduction

Epoxy resins are some of the most useful polymers and exhibit excellent properties, including mechanical strength, chemical resistance, heat resistance, and bonding capability [1–7]. These resins are utilized in various forms such as coatings, composite matrices, and adhesives but have limitations includinginherent brittleness and poor elongation [1,4]. To overcome the limitations, several strategies have been employed to improve elongation with minimal loss of strength, i.e., toughening of the epoxy, using reactive additives (e.g., rubber-modified epoxy, epoxy-functionalized particles, and epoxy-terminated resin) [8–16], and non-reactive additives (e.g., nanoparticles, elastomers, and block copolymers) [17–25]. In some cases, both elongation and strength are freely adjusted at the same time to prepare versatile epoxies. Until now, the mechanical properties of versatile

epoxies have been tuned between brittleness and elastomerism, which enabled the epoxy to be utilized in various applications [26-31].

Epoxies exhibiting tunable mechanical properties are generally prepared via the following methods: 1) employing an epoxy with different functionalities [26,27], 2) varying the stoichiometry between the epoxy and hardener [28,29], and 3) changing the ratio of rigid moiety to flexible moiety [30,31]. The key strategy for achieving tunable properties is to control the ratio between the flexibility and rigidity of epoxies, which is prevalent in all of the aforementioned methods. The fraction of rigidity increases upon incorporating high-functionality epoxy or aromatic epoxy resin, e.g., bisphenol A diglycidyl ether (DGEBA), which makes the epoxy more brittle. Meanwhile, the flexibility fraction increases upon employing mono-functional epoxy or aliphatic epoxy resin, which grants an elastomeric nature to an epoxy.

Aliphatic epoxy resins, e.g., poly(propylene glycol) diglycidyl ether

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Scheme 1. a) Synthesis of urethane-modified epoxy through an eco-friendly route using CO_2 (left) and a conventional route using isocyanate (right-up). b) Preparation of epoxy composites with tunable properties by adjusting ratio of aromatic/aliphatic epoxy and possible application of prepared epoxy composites. c) Schematic illustration of possible hydrogen bonding of CO_2 -derived urethane modified epoxy.

(PPGDGE), are generally utilized to improve the flexibility of epoxies, but their concentrations are typically limited (< 30 wt%) [1,13,14,32]. As the amounts of aliphatic epoxies exceed the limit, elongation and impact resistance deteriorate, preventing extensive tuning of the mechanical properties of the epoxies. To address this limitation of aliphatic epoxy resins and expand the tuning range, additional intermolecular interactions such as hydrogen bonding should be added. It was previously found that mechanical properties of epoxies were extensively adjusted when aliphatic pre-polymers incorporating urethane linkages were employed, rather than aliphatic epoxies without urethane linkages were employed [32].

The most promising way to incorporate urethane linkages into the aliphatic epoxy might be the ring-opening reaction of cyclic carbonates with aliphatic primary amines owing to the use of CO_2 and an isocyanate-free system. First, cyclic carbonates can be synthesized from the reaction between CO_2 and epoxides, which exhibits environmental benefits because of its use of CO_2 , a greenhouse gas [33]. Second, urethane linkages can be prepared without isocyanates, which are key materials for the conventional synthesis of urethane linkages (Scheme 1a). The use of isocyanates usually raises some problems, including storage stability (e.g., water sensitivity), human health hazards (e.g., asthma) [34], and environmental hazards (e. g., using toxic phosgene for production) [35].

In this study, flexible aliphatic epoxy incorporating urethane linkages was synthesized through an eco-friendly non-isocyanate route utilizing CO_2 (Scheme 1a). The synthesized aliphatic epoxy was crosslinked with rigid aromatic epoxy (DGEBA) to tune the mechanical properties. The mechanical properties were widely tuned by simply adjusting the ratio of two epoxies, and the resulting epoxy composites exhibited three different natures, i.e., a toughened polymer, elastomer, and pressure-sensitive adhesive (PSA), as shown in Scheme 1b. Single lap shear, cyclic tensile, and Izod impact tests were conducted for toughened or elastomeric epoxy composites, and the viscoelastic window and adhesive performances of the PSA epoxy were assessed. It was confirmed that toughened, elastomeric, PSA-like epoxy composites can be utilized as conventional structural adhesives, elastomers, and PSA tapes, respectively.

2. Experimental

2.1. Synthesis

2.1.1. General considerations

All manipulations were performed under an ambient atmosphere unless otherwise noted. Epichlorohydrin (Sigma aldrich), polyoxypropylenediamine (Jeffamine® D-400, Huntsman), anhydrous magnesium sulfate (MgSO4, Samchun chemical), and tetrabutylammonium bromide (Alfa aesor) were used as received. Sodium hydroxide and dichloromethane (DCM, HPLC grade) were purchased from Samchun Chemicals. CDCl₃ (D 99.8%, ¹H: 7.26 ppm, ¹³C: 77.16 ppm, Cambridge Isotope Laboratories) was used as the NMR solvent, and Bruker 300 MHz and 75 MHz spectrometers were used for ¹H NMR and ¹³C NMR, respectively. The NMR spectra are presented in Fig. S1, and the splitting patterns are denoted as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

2.1.2. Propylene carbonate

A 100 mL stainless steel autoclave reactor was charged with propylene oxide (29.0 g, 0.50 mol), 2.0 g of polymer-supported Zn-containing imidazolium salts (PS-(Im)ZnI₂) catalyst, and a stir bar. The reactor was purged with 1 bar of CO₂ five times at 0 °C, followed by pressurization with 10 bar of CO₂. The reactants were stirred for 8 h at 80 °C and then cooled to 0 °C. The remaining CO₂ in the product was ventilated, and the propylene carbonate was obtained as a colorless liquid (49.01 g, 95%). ¹H NMR spectra showed that propylene carbonate was successfully synthesized as reported in reference [33]. ¹H NMR (300 MHz, 23 $^{\circ}\text{C},$ CDCl_3): 4.85 (m, 1H), 4.54 (t, 1H), 4.01 (t, 1H), 1.47 (d, 3H).

2.1.3. Hydroxyurethane-terminated aliphatic diol

A 1 L flask was charged with propylene carbonate (100 g, 0.980 mol) and Jeffamine® D-400 (200.7 g, 0.467 mol). The reactants were mechanically stirred for 4 days under an ambient atmosphere at 100 °C. The obtained mixture was directly diluted with water (1 L) and DCM (1 L) and extracted three times with water. The desired product dissolved in DCM was obtained, and water was removed using anhydrous MgSO₄. After drying in a vacuum oven, a deep brown-colored liquid was obtained (349.1 g, 93%). ¹H NMR (300 MHz, 23 °C, CDCl₃): δ 5.73–5.33 (br, -NH in urethane; 2H), 4.86 with 4.07–3.40 (br, 27.3H) and 1.23–1.10 (br, 27.3H). ¹³C NMR (75 MHz, 23 °C, CDCl₃): δ 156.29, 75.25, 75.15, 74.98, 73.26, 73.02, 72.26, 72.04, 69.97, 66.06, 65.95, 47.22, 47.06, 19.09, 17.92, 17.77, 17.16, 17.08, and 16.61.

2.1.4. CO₂-derived urethane-modified epoxy

A 1 L vessel was charged with diol (130 g, 0.21 mol), sodium hydroxide pellets (82 g, 2.10 mol), and epichlorohydrin (190 g, 2.10 mol). After stirring the reactants for 15 min at room temperature, tetrabutylammonium bromide (2.15 g, 1.03 mmol) was added. After stirring at 50 °C for 4 h, a pale brownish mixture was obtained, and the residual solid was filtered. The filtrate was diluted with water and DCM and extracted three times with water. After extraction, water was removed using anhydrous MgSO₄, and the remaining solvent and epichlorohydrin were distilled out under reduced pressure. The desired final product, C-UME, was obtained as a brown-colored viscous liquid (108 g, 71%). ¹H NMR (300 MHz, 23 °C, CDCl₃): δ 5.38–4.96 (br, -NH in urethane; 2H), 4.97 with 4.04-3.44 (br, 31.3H), 3.13 (m, 2H), 2.78 (pseudo t, 2H), 2.61 (m, 2H), and 1.25–1.09 (br, 27.3H) 13 C NMR (75 MHz, 23 °C, CDCl₃): δ 155.96, 155.66, 75.58, 75.42, 75.21, 75.07, 74.06, 73.44, 72.97, 72.53, 72.25, 71.86, 50.91, 47.23, 45.90, 44.20, 18.12, 17.39, and 17.29. The epoxy equivalent weight of C-UME was obtained as 378.14 g·eq⁻¹ according to ASTM D1652-11.

2.2. Characterization

2.2.1. Dynamic mechanical analysis

DMA (Q800, TA Instruments) was used to assess the viscoelasticity of the cured epoxies. For C-UME content from 0 to 50 mol%, specimens were prepared using a rectangular-shaped steel mold (length, width, thickness = 80 mm, 10 mm, 4 mm), and a dual cantilever clamp with a fixed length of 35 mm was employed. The temperature was increased from 30 to 200 °C at a constant temperature increasing rate (5 °C·min⁻¹), strain (0.1%–35 mm fixed length), and frequency (1 Hz).

For C-UME 100, exhibiting PSA nature, a shear sandwich clamp was employed, and the specimen was prepared as follows: epoxy resin was cured in a rectangular-shaped Teflon mold (length, width, and thickness = 80 mm, 12 mm, and 1.7 mm), and the cured epoxy was cut to a length and width of 10 mm. The frequency was increased from 0.01 to 100 Hz with constant strain (2% to thickness) and temperature (23 °C). All DMA observations were made in a single experiment.

2.2.2. Tensile test

Test specimens of the tensile test in a range of C-UME contents from 0 to 50 mol% were prepared using dumbbell-shaped steel molds, and the size of the specimens satisfied the 1BA type in ISO 527-2. UTM (5982, Instron) was used, and the strain rate was fixed at 5 mm·min⁻¹. The strain was calculated by dividing the moved distance by the grip-to-grip distance (30 mm), and stress was obtained by dividing the applied force by the cross-sectional area (5 mm × 2 mm). Tensile strength, elastic modulus, and strain at break represented the maximum stress, initial slope in the strain-stress curve, and maximum elongation for fracture of the specimen, respectively. The tensile test was conducted at room temperature (23 °C) and repeated four times.

2.2.3. Single lap shear test

Epoxy resin was applied to a steel substrate (type: CR340, length: 100 mm, width: 25 mm, thickness: 1.6 mm) in an adhesion area of 12.5 mm \times 25 mm, followed by curing. The thickness of the adhesive layer was maintained at 0.18 mm using a Teflon tape spacer (AGF-100FR, Chukoh Chemical Industries, Ltd). The lap shear strength represented the maximum stress required to destroy the bonded specimen. Stress was calculated by dividing the applied force by the adhesion area (12.5 mm \times 25 mm) and was evaluated using a UTM (5982, Instron). Lap shear strength was repeated five times, and all experiments were conducted at room temperature (23 °C).

2.2.4. Cyclic tensile test and Izod impact test

Test specimens of the cyclic tensile test were prepared as specimens of the aforementioned tensile test. Grip-to-grip distance and testing speed were 50 mm and 100 mm·min⁻¹, respectively. Loading and unloading were repeated 10 times at a constant temperature (23 °C). Cyclic tensile tests were performed in a single experiment.

Test specimens for the Izod impact test were prepared using a rectangular-shaped steel mold (length, width, thickness = 80 mm, 10 mm, 4 mm). All specimens had a notch with a fixed depth of 2 mm in the middle of the specimens. The impact strength represented the absorbed energy under impact conditions, and the test capacity was 750 J·m⁻¹. Five specimens for each sample were assessed at 23 °C.

2.2.5. 90° peel test and loop tack test

To assess peel strength, a 90° peel test was conducted at room temperature (23 °C). C-UME 100 was cured in a rectangular-shaped Teflon mold (length, width, thickness = 80 mm, 12 mm, 1.7 mm) because the epoxy resin, which was used to coat the polyethylene terephthalate (PET) film, appeared uneven after curing (Fig. S3). A PET film with a thickness of 50 μ m was used as the backing film, and the prepared tape was attached to the stainless steel 304 using a 2 kg roller twice. Four types of specimens (C-UME 100, acrylic PSA, Scotch tape, and Masking tape) were assessed, as presented in Fig. S7a. Peel strength (N·cm⁻¹) was obtained using a UTM (LS 1, Lloyd Instruments) with a fixed crosshead speed of 300 mm min⁻¹ and calculated by dividing the average force (N) of the middle region (20%–80% of the working range) by the width of the specimen (cm). The peel test was repeated three times for each specimen, and all specimens exhibited interfacial failure being fractured at the interface between the PSA and substrate.

For the same specimens of the peel test, the loop tack test was performed at 23 °C. All specimens were cut to a length of 100 mm and bent to form a string, as shown in Fig. S7b. The crosshead speed was set at $300 \text{ mm} \cdot \text{min}^{-1}$, and the loop tack (N·cm⁻¹) was obtained by dividing the maximum force (N) by the width of the specimen (cm). The loop tack test was repeated three times for each specimen.

3. Results and discussion

3.1. Strategy

Two types of epoxies, aromatic and aliphatic, were used to facilitate tunable mechanical properties. Aliphatic epoxy incorporating urethane linkage (C-UME) was prepared through an eco-friendly route (Scheme 1a). First, propylene carbonate was synthesized using CO₂. There are several ways to synthesize propylene carbonate using CO₂ [36–38]. We employed polymer-supported Zn-containing imidazolium salts, which presented excellent catalytic performance and reusability [33]. The propylene carbonate was allowed to react with polyoxypropylenediamine (Jeffamine® D-400, Huntsman), and a brown-colored hydroxyurethane-terminated aliphatic diol, which incorporated urethane linkage, was quantitatively obtained. Hydroxyurethane-terminated aliphatic diol was treated with epichlorohydrin in the presence of sodium hydroxide (NaOH) and a catalytic amount of tetrabutylammonium bromide (TBAB) to obtain the desired product, i.e., CO₂-derived urethane-modified epoxy (C-UME). The final

Table 1

Characterization of epoxy composites with a different ratio of CO₂-derived urethane-modified epoxy and bisphenol A diglycidyl ether. Dicyandiamide was used as the curing agent and 3,3'-(4-methyl-1,3-phenylene) bis (1,1-dimethylurea) was used as the accelerator. T_g , Max. tan δ , and E' at 40 °C represent the glass transition temperature, maximum value of tan δ , and storage modulus at 40 °C, respectively. Storage modulus-temperature and tan δ -temperature curves are shown in Fig. S4.



Entry ^a	[DGEBA]:[C-UME] Mole ratio ^b	$T_{g}^{c,d}$ (°C)	Max. tan δ^c	E' at 40 °C (GPa) ^c
DGEBA	100:0	172.4	0.752	2.23
C-UME 10	90:10	121.6	0.846	2.34
C-UME 20	80:20	96.0	0.888	2.55
C-UME 30	70:30	76.9	0.986	1.92
C-UME 40	60:40	61.7	1.046	0.80
C-UME 50	50:50	42.0	1.265	0.03

^a C-UME #: # represents the mole fraction of C-UME.

^b Mole ratio was set as follows; [Epoxy resin]:[Curing agent]:[Accelerator] = 100:28.6:1.43.

^c Characterized through dynamic mechanical analysis.

^d T_o was reported as the temperature at maximum of tan δ .

product was isolated through extraction and drying, and brown-colored viscous C-UME was obtained. All chemical structures were identified using 1 H NMR and 13 C NMR (Fig. S1).

Bisphenol A diglycidyl ether (DGEBA, YD-128, KUKDO Chemical), dicyandiamide (Dyhard® 100S, AlzChem), and 3,3'-(4-methyl-1,3phenylene) bis (1,1-dimethylurea) (Dyhard® UR500, AlzChem) are commonly used materials in epoxy resins as the aromatic epoxy, curing agent, and accelerator, respectively. The ratio of C-UME and DGEBA content was controlled to balance flexibility and rigidity, maintaining a constant mole ratio of di-functional epoxy resin, curing agent, and accelerator at 100:28.6:1.43 (Table 1). This composition is generally utilized in conventional epoxy curing [39]. All epoxy resins, except DGEBA in Table 1, were cured at 160 °C for 2 h, and the curing conditions were determined from pre-experimentation using differential scanning calorimetry analysis (Fig. S2). Only DGEBA was cured in two steps, i.e., 130 °C for 1 h and 160 °C for 1 h, to avoid charring (Fig. S3).



Fig. 1. Strain-stress curve of the cured epoxy composites consisting of a) DGEBA/C-UME and b) DGEBA/PPGDGE. c) Tensile strength, d) elastic modulus, and e) strain at break according to C-UME and PPGDGE content. PPGDGE represents poly(propylene glycol) diglycidyl ether ($M_n = 640 \text{ g} \cdot \text{mol}^{-1}$) and the characterization table of the cured DGEBA/PPGDGE is presented in Table S1. Single lap shear test for toughened epoxy.



Fig. 2. a) Lap shear strength of the DGEBA/C-UME in the range of C-UME content from 0 to 30 mol%. b) Fractured surface after single lap shear test. Interfacial failure; test specimen was fractured at the interface between adhesive layer and substrate. Cohesive failure; test specimen was fractured at the inside of adhesive layer.

3.2. Mechanical properties

The viscoelasticity and tensile strength of the cured epoxy composites were evaluated to confirm that the mechanical properties could be tuned by varying the ratio of the two epoxies, DGEBA and C-UME. Viscoelasticity was evaluated through dynamic mechanical analysis (DMA) with a dual cantilever clamp and increasing temperature (5 °C·min⁻¹ from 30 °C to 200 °C). Tensile strength was assessed using a universal testing machine (UTM) with a constant strain rate (5 $mm \cdot min^{-1}$). The C-UME content was controlled from 0 to 50 mol% to prepare freestanding specimens (Fig. S3). As the amount of C-UME increased, the storage modulus decreased, but the maximum value of tan δ increased, suggesting that a higher fraction of C-UME led to low rigidity but high flexibility (Table 1). The tensile test results also indicated that the mechanical properties of the cured epoxies were widely tuned in the range of C-UME content from 0 to 50 mol% (Fig. 1a). Three types of deformation behaviors were observed in the tensile test: brittle deformation for C-UME 0, deformation of toughened polymer for C-UME 10, 20, and 30, and deformation of elastomer for C-UME 40 and 50.

Poly(propylene glycol) diglycidyl ether (PPGDGE, $M_n = 640 \text{ g} \cdot \text{mol}^{-1}$), a urethane-linkage-free aliphatic epoxy exhibiting a molecular weight similar to that of C-UME ($M_n \approx 744.72 \text{ g} \cdot \text{mol}^{-1}$), was employed to investigate the effect of urethane linkages on the tuning of mechanical property range. The deformation behavior of the cured DGEBA/PPGDGE was transformed from brittle to elastomeric deformation, but the elongation and tan δ values were significantly lower than those of DGEBA/C-UME (Fig. 1b and Table S1). The maximum strain at break of DGEBA/ PPGDGE was also lower (118.2%) than that of DGEBA/C-UME (196.2%). Drastic decrease in the strain at break of PPGDGE 50 was supposedly resulted from phase separation and agglomeration, which was confirmed by tan δ in DMA curves (Fig. S4d) and scanning electron microscope images of fracture surface (Fig. S8). It suggested that the content of PPGDGE should be lower than 50 mol% to tune the mechanical properties (Fig. 1e). In addition, the tensile strength and elastic modulus of DGEBA/PPGDGE were widely tuned but much lower than those of DGEBA/C-UME at the same aliphatic epoxy content (Fig. 1c and d). Our results strongly supported that additional hydrogen bonding of the urethane linkage in C-UME enhanced inter- or intramolecular interactions, and it facilitated wider tuning range than DGEBA/PPGDGE. The hydrogen bonding of the urethane linkage in C-UME was confirmed by shift of glass transition temperature [40] and Fourier-transform infrared spectroscopy [41] (Fig. S10). Enhanced interaction, induced from urethane linkage, resulted in widening tuning range by It was demonstrated that incorporating urethane linkages into flexible aliphatic epoxy can significantly expand the tuning range of elongation and tensile strength, compared to general aliphatic epoxy without urethane

linkages.

Epoxy resins are used in various forms, including coatings, composite matrices, and structural adhesives. We conducted a single lap shear test to determine whether the prepared epoxies could be utilized as a structural adhesive. Adhesion area and testing speed were fixed as 25 mm \times 12.5 mm and 1.3 mm·min⁻¹, respectively, and the lap shear strength represents the maximum force required to destroy the adhesive layer. The lap shear strength of the DGEBA/C-UME epoxies exhibiting brittle or toughened deformation behavior in the tensile test, i.e., DGEBA, C-UME 10, 20, and 30, was assessed as presented in Fig. 2.

As the amount of C-UME increased, lap shear strength increased from 19.8 MPa for C-UME 0 to27.8 MPa for C-UME 20, which was similar to or higher than that of conventional epoxy structural adhesives [3, 42-44]. This increase in lap shear strength was attributed to the improvement in interfacial adhesion between the adhesive layer and steel substrate. Urethane linkage in the C-UME generated additional intramolecular interactions, i.e., hydrogen bonding, between the adhesive layer and surface of the steel substrate, which could improve interfacial adhesion [3]. It was supported by 1) the change in the fracture behavior from interfacial failure to partially cohesive failure with increasing C- UME content (Fig. 2b) and 2) gap of lap shear strength between DGEBA/C-UME and DGEBA/PPGDGE (Fig. S5). However, with increasing C-UME content, although interfacial adhesion was improved, the internal cohesive strength of the epoxy adhesive layer decreased simultaneously, and thus the lap shear strength decreased at 30 mol% of C-UME.

3.3. Cyclic tensile test and Izod impact test for elastomers

Elastomeric epoxies exhibit superior flexibility and impact resistance compared to conventional brittle epoxies and can be utilized in medical applications [45,46], dampers [47,48], and electronic devices [49,50]. In the range of C-UME content from 40 to 50 mol%, the cured epoxy composites exhibited an elastomeric nature, and cyclic tensile tests and Izod impact tests were conducted on the elastomeric epoxy composites. Loading–unloading was repeated for 10 cycles at a constant rate of 100 $mm \cdot min^{-1}$ in the cyclic tensile test. The impact strength was assessed by measuring absorbed energy under impact conditions in the Izod impact test.

In the cyclic tensile test, both C-UME 40 and 50 were fractured at the second cycle with an applied strain of 100% (Fig. S6), but they exhibited elastomeric nature under strain 50% for 10 repeated cycles (Fig. 3). For C-UME 50, although the tensile strength was relatively weak, the decrease in the tensile strength with repeated cycles was lower than that of C-UME 40. Importantly, the plastic strain that was not recovered after



Fig. 3. Strain-stress curves according to repeated cycle with 50% of applied strain for a) C-UME 40 and b) C-UME 50. $\varepsilon_{\text{plastic}}$ represents the plastic strain which was not recovered after unloading. c) Izod impact test results of DGEBA/C-UME in the range of C-UME content from 0 to 50 mol%. Test capacity was below 750 J m⁻¹ and C-UME 50, data point marked with star exceeded test limits.



Fig. 4. a) Storage modulus (G') and loss modulus (G'') as a function of frequency at room temperature (23 °C). b) Viscoelastic window of C-UME 100 (left) and conventional PSA (right, E. P. Chang, *J. Adhes.*, 1991, **34**, 189–200). Dahlquist criterion (<0.3 MPa) is a standard of maximum G' for sufficient wetting of PSA.

unloading, $\varepsilon_{\text{plastic}}$, was smaller for C-UME 50 (< 10%) than C-UME 40 (> 20%). It is suggested that C-UME 50 was elastic enough for use as an elastomer for a flexible electronics matrix [49]. Furthermore, impact strength was significantly enhanced with increasing C-UME content (Fig. 3c), and C-UME 50 exhibited excellent impact strength that exceeded test limits (> 750 J·m⁻¹). The low $\varepsilon_{\text{plastic}}$ and high impact strength of C-UME 50 could have resulted from the low T_{g} , similar to the testing temperature (23 °C), facilitating fast relaxation of the polymer chain [51].

3.4. Viscoelastic window and adhesion performances of pressure-sensitive adhesives

Epoxies exhibiting tunable mechanical properties have been investigated, but their tuning range has been limited to toughened polymers and elastomers, and not as a PSA [26–31]. However, in this study, we successfully prepared various epoxy composites exhibiting tunable mechanical properties, including a PSA. The epoxy with 100 mol% C-UME was too soft to be freestanding, but it was viscous at room temperature, exhibiting a PSA nature. The viscoelasticity of C-UME 100 was assessed through DMA with a shear sandwich clamp in a frequency range from 0.01 to 100 Hz. A 90° peel test and loop tack test were conducted to evaluate the peel strength and loop tack of C-UME 100, respectively. Adhesion performances were assessed by UTM and stainless steel as the adherend.

The storage modulus (G') increased as the frequency increased, but it satisfied the Dahlquist criterion (< 0.3 MPa), which is the maximum G' of PSA for sufficient wetting of the substrate (Fig. 4a). A viscoelastic window was constructed using G' and G" at the bonding frequency (0.01 Hz) and de-bonding frequency (100 Hz), as depicted in Fig. 4b. The viscoelastic window was divided into five regions, and the possible applications can be predicted according to the region covered by the PSA; regions 1, 2, 3, 4, and 5 represent release non-PSA, high shear PSA, removable PSA, low-temperature PSA, and general-purpose PSA,



Fig. 5. Adhesion performance of C-UME 100, acrylic PSA, Scotch tape, and masking tape. Acrylic PSA was prepared as presented in Fig. S7. Scotch tape and masking tape were commercially available tapes.

respectively [52]. The constructed viscoelastic window of C-UME 100 mainly covered regions 5 and 3; therefore, it can be possibly utilized as a general-purpose PSA or removable PSA. For adhesion performance, although the loop tack was slightly inferior to other tapes, its peel strength was significantly higher than that of commercially available tapes (Scotch tape and Masking tape) and similar to that of acrylic PSA (Fig. 5). Additionally, the peel strength of C-UME 100 was much higher than that of previously reported PSAs prepared from epoxy (< $5 \text{ N} \cdot \text{cm}^{-1}$) [53–57].

4. Conclusions

In this study, the mechanical properties of epoxy composites were tuned over a wide range, including toughened polymer, elastomer, and PSA. Tuning was accomplished by adjusting the ratio of a rigid aromatic epoxy and a flexible aliphatic epoxy, i.e., DGEBA and C-UME, respectively. A flexible aliphatic epoxy that incorporated urethane linkages was synthesized through an environmentally benign route that utilized CO2 rather than isocyanates. From the tensile test results, it was demonstrated that the deformation behavior changed from brittle deformation to deformation of toughened polymers and elastomers, and the urethane linkages facilitated a wider tuning range of mechanical properties. Epoxy composites exhibiting a toughened polymer or elastomeric nature were expected to be utilized in structural adhesive (lap shear strength = 27.8 MPa) or flexible electronic devices (plastic strain < 10%), and this was confirmed through single lap shear, cyclic tensile, and Izod impact tests. Among the prepared epoxy composites, the most flexible epoxy exhibited PSA properties, and its adhesion performance (peel strength = $6.8 \text{ N} \cdot \text{cm}^{-1}$) was comparable to that of conventional PSAs. The viscoelastic window of the prepared PSA suggested that it could be utilized as a general-purpose PSA or removable PSA. We believe that this work suggests a new field of eco-friendly epoxies, which could be utilized as a powerful strategy to extend the tuning range of epoxy materials to the PSA area.

CRediT authorship contribution statement

Jong-Ho Back: Conceptualization, Methodology, Investigation, Writing – original draft. Chiwon Hwang: Investigation, Writing – original draft. Dooyoung Baek: Investigation, Validation. Dongwoo Kim: Resources. Youngchang Yu: Methodology, Writing – review & editing. Wonjoo Lee: Conceptualization, Funding acquisition. Hyun-Joong Kim: Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesb.2021.109058.

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