

Article

# Synthesis and Characterization of a Polyurethane Phase Separated to Nano Size in an Epoxy Polymer

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**Abstract:** Epoxy resins are widely applicable in the aircraft, automobile, coating, and adhesive industries because of their good chemical resistance and excellent mechanical and thermal properties. However, upon external impact, the crack propagation of epoxy polymers weakens the overall impact resistance of these materials. Therefore, many impact modifiers have been developed to reduce the brittleness of epoxy polymers. Polyurethanes, as impact modifiers, can improve the toughness of polymers. Although it is well known that polyurethanes (PUs) are phase-separated in the polymer matrix after curing, connecting PUs to the polymer matrix for enhancing the mechanical properties of polymers has proven to be challenging. In this study, we introduced epoxy functional groups into polyol backbones, which is different from other studies that focused on modifying capping agents to achieve a network structure between the polymer matrix and PU. We confirmed the molecular weight of the prepared PU via gel permeation chromatography. Moreover, the prepared material was added to the epoxies and the resulting mechanical and thermal properties of the materials were evaluated. Furthermore, we conducted tensile, flexural strength, and impact resistance measurements. The addition of PU to the epoxy compositions enhanced their impact strength and maintained their mechanical strength up to 10 phr of PU. Furthermore, the morphologies observed with field emission scanning electron microscopy and transmission electron microscopy proved that the PU was phase separated in the epoxy matrix.

**Keywords:** epoxy resin; polyurethane; physical properties

## 1. Introduction

Epoxy resins are thermosetting polymers that form 3D network structures after exothermic reactions with amine or acidic anhydride hardeners [1,2]. Epoxy resins are interesting materials due to their excellent mechanical and thermal properties as well as chemical resistance [3–6]. A main disadvantage of the resins is their brittleness, which allows crack propagation upon outside impact.

Therefore, many studies have been conducted to overcome this weakness by adding toughening agents that enhance impact resistance. In general, rubbery resins, such as carboxyl-terminated butadiene (CTBN) [7] and amine-terminated butadiene (ATBN) [8] have been used as toughening agents, whereas thermoplastic polyethersulfone [9] and polyetherimide [10] have also been applied. Elastomeric polyurethanes (PUs) are representative tougheners for thermosetting polymers. PUs are composed of a soft segment of polyol and a hard segment of diisocyanate [11], which are not compatible with each other and lead to phase separation.

Upon addition of PUs to other polymers, the mechanical properties are enhanced because of the networking of the two polymers. The interaction between PU and the epoxy matrix is usually achieved

by mixing PU, which contains –NCO functional groups, with epoxy, which contains a hydroxyl group [12,13], or reacting polyol with diisocyanate in the presence of fillers [14,15].

On the other hand, the interaction between epoxy matrix and PU can be achieved by introducing glycidyl ethers in the polyol backbones of PUs instead of reacting epoxy groups with terminal NCO groups. Once the prepared polyols react with diisocyanate (DIC), the resulting PUs are furnished with epoxy functional groups. Therefore, the interaction between PU with the polyols and epoxy matrix can be enhanced by chemical reaction.

In this study, dimeric fatty acids were reacted with two equivalents of epoxy groups to provide both polyols and epoxy functional groups. When the polyols were reacted with DIC, the obtained PU contained epoxy groups designed to react with an amine curer or epoxy groups in the epoxy matrix. Therefore, a fatty acid-modified epoxy polyol was reacted with diisocyanate to synthesize PU to increase the impact resistance and maintain the mechanical properties. Furthermore, the toughening properties of PU on the epoxy compositions were tested. Different amounts of PU were poured into the epoxy materials and cured to form thermosetting polymers, and their mechanical and viscoelastic properties were evaluated using a universal testing machine (UTM) and dynamic mechanical analysis (DMA), respectively. Furthermore, the fracture surfaces of the test specimens were observed by using field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM).

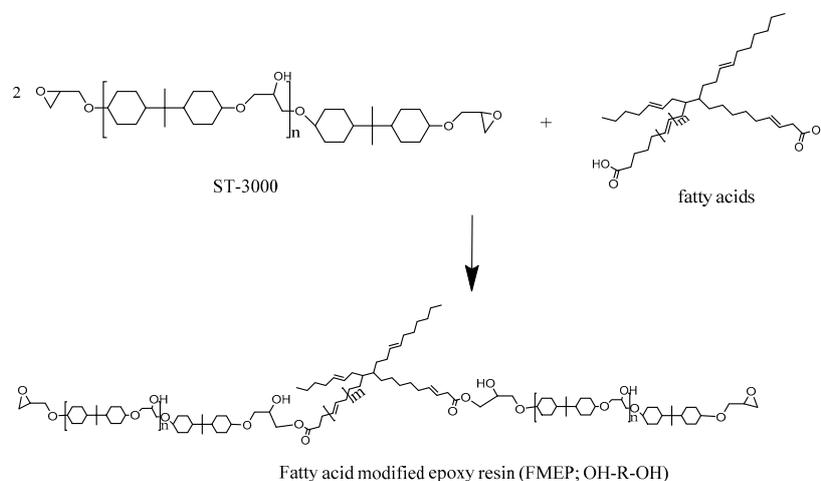
## 2. Experiments

### 2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA, YD-128, epoxy equivalent weight (EEW, g/eq unit), 187 g/eq) and a hydrogenated epoxy resin (ST-3000, EEW, 228.6 g/eq) were obtained from Kukdo Chemical (Seoul, Korea). D-230 (polyether diamine,  $M_w$  230 g/mol) was also purchased from Kukdo Chemical. A dimeric fatty acid (pripol 1013-LQ,  $M_w$  560 g/mol) was obtained from Croda Europe (Gouda, The Netherlands), LTD (Korea branch, Incheon, Korea). Polypropylene glycol (PPG,  $M_w$  2000 g/mol), dibutyltin dilaurate (DBTDL), 2-hydroxyethyl methacrylate (HEMA), and isophorone diisocyanate (IPDI) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

### 2.2. Synthesis of Polyol: Modification of Hydrogenated Epoxy Resin with Fatty Acids

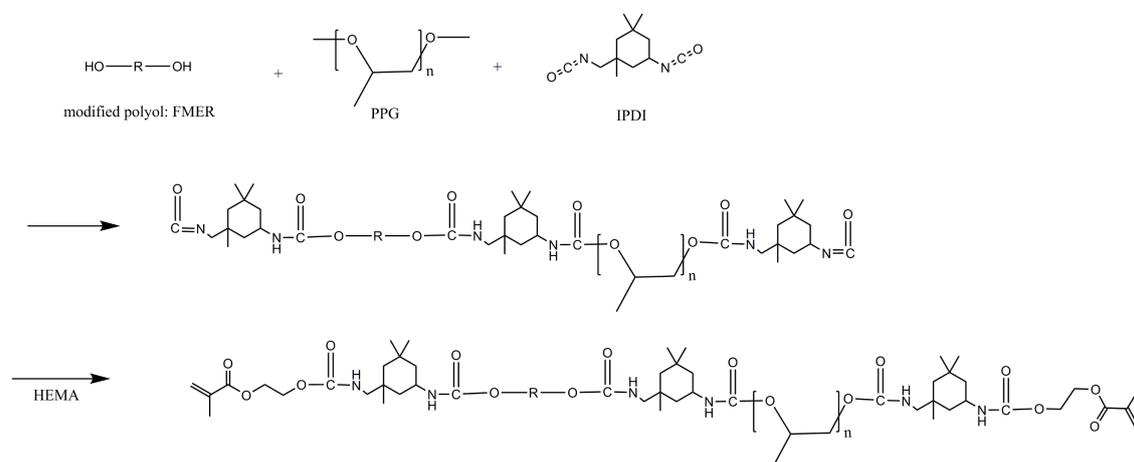
A dimeric fatty acid (45 g, 0.08 mol) was reacted with ST-3000 (73 g, 0.16 mol) in a 200-mL reactor at 100 °C for 40 min while triphenyl phosphine (0.3 g) was added as a catalyst (Figure 1). The product was cooled to room temperature followed by analysis via  $^1\text{H-NMR}$  and FT-IR to confirm that the reaction was completed to produce the fatty-acid-modified hydrogenated epoxy polyol (FMEP).



**Figure 1.** Reaction scheme of the fatty acid-modified epoxy resin to synthesize the polyol.

### 2.3. Synthesis of Polyurethane using FMEP (FMEP-PU)

FMEP (60 g, 0.04 mol), polypropylene glycol (20 g, 0.04 mol), and IPDI (9.8 g, 0.16 mol) were added to a reactor and stirred for 40 min at 80 °C under nitrogen and a DBTDL catalyst was added. Subsequently, 2-hydroxyethyl methacrylate (HEMA, 21 g, 0.16 mol) was added to cap the terminal NCO group and the solution was stirred for 3 h at 80 °C. The reaction scheme is displayed in Figure 2.



**Figure 2.** Reaction scheme for PU by reacting the fatty acid-modified hydrogenated epoxy polyol with isophorone diisocyanate (FMEP-PU).

### 2.4. Preparation of the Epoxy Compositions and Cured Thermosetting Plastics

The epoxy resin and D-230 were stoichiometrically mixed based on the equivalent molar ratio (Equation (1)). The amount of FMEP-PU in the epoxy resin was varied from 5 to 15 parts by weight per 100 parts of epoxy resin (phr). The formulation information for the epoxy compositions is summarized in Table 1.

$$\{100 \text{ g (of epoxy resin)}\} / \{187 \text{ (g/epoxy resin)}\} \times 60 \text{ (amine hydrogen equivalent wt.)} \quad (1)$$

**Table 1.** Formulation information for the epoxy compositions.

Compositions (g)	YD-128	D-230	FMEP-PU
Binder	100	32.1	–
PU-5	100	32.1	5
PU-10	100	32.1	10
PU-15	100	32.1	15

The epoxy resin and FMEP-PU were mixed and stirred for 20 min at 40 °C followed by the addition of D-230 for 20 min. The prepared paste was poured into a metal mold. The metal mold was placed in an oven and heated for 1 h at 80 °C to polymerize the epoxy resin and amine hardener.

### 2.5. Measurements and Analyses

The synthesized FMEP and FMEP-PU were analyzed by Fourier transform-infrared spectrometry (FT-IR, Nicolet 6700/Nicolet Continuum; Thermo Fisher Scientific Inc., Waltham, MA, USA) and gel permeation chromatography (GPC, 1260 series, Agilent Technologies, New York, NY, USA, calibrated using polystyrene standards).

The cured epoxy polymers in the metal mold were processed to achieve a 60 mm × 25 mm × 3 mm test specimen and used to measure the flexural strength based on the ASTM D790M standard [16] with a grinding machine (BESTPOL P2b2; SSAUL Bestech Co., Seoul, Korea) and diamond cutter

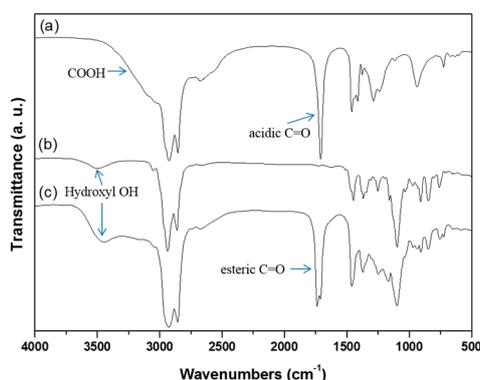
(Manix, MBS 500/E; Woosung E&I Co., Sungnam, Korea). Additionally, the test specimen for the tensile strength measurement was processed to a size of 150 mm × 13 mm × 3 mm. The tensile strengths were tested with 10 specimens per condition with the UTM (UTM 5982, Instron, Norwood, MA, USA) following the ASTM D638-14 method [17], and the mean value (excluding the maximum and minimum values) was used. The impact strength was measured using an Izod impact tester (JJHBT-6501, JJ-test, Chengde, China) based on the ASTM D256-10 method [18].

The viscoelastic properties of the cured polymers were evaluated by subjecting a 60 mm × 12 mm × 3 mm sample to dynamic mechanical analysis (DMA, Q800, TA Instruments, Inc., New Castle, DE, USA). The test sample was mounted on a dual cantilever probe and tested at a heating rate of 5 °C/min from 25 to 200 °C at a frequency of 1 Hz to measure both the storage moduli and tanδ values. The fractured surface obtained during the impact test was observed by FE-SEM (MIRA 3, TESCAN, Brno, Czech Republic) and FE-TEM (JEM-2010, JEOL, Tokyo, Japan).

### 3. Results and Discussion

#### 3.1. Modification of the Epoxy Resin (FMPEP)

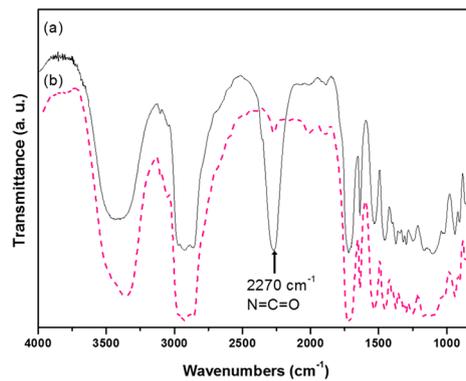
The prepared FMPEP was analyzed via FT-IR, as shown in Figure 3. The FT-IR results showed that the fatty acid carbonyl (C=O) peak at 1708 cm<sup>-1</sup> shifted to 1740 cm<sup>-1</sup> upon reaction between the hydroxyl group of the fatty acid and the epoxy group of ST-3000 (Figure 1). A chemical shift in the hydroxyl group of ST-3000 was observed from 3413 to 3472 cm<sup>-1</sup> upon the reaction, along with an intensity increase. The EEW of FMPEP that was measured using the ASTM D1652-11e1 method [19] was 722 EEW, which is similar to the theoretical value (736 EEW) for the complete reaction.



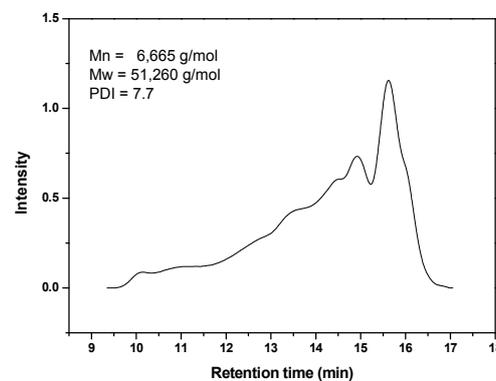
**Figure 3.** FT-IR spectrum of (a) the fatty acid, (b) ST-3000, and (c) the fatty acid-modified hydrogenated epoxy polyol (FMPEP).

#### 3.2. Synthesis of PU

The prepared polyol, FMPEP, was mixed with PPG in a 1:1 molar ratio before the mixed polyol was reacted with IPDI to form the PU. The ratio of the mixed polyol to IPDI was 1:2, and the terminal isocyanate group was observed at 2270 cm<sup>-1</sup> (–N=C=O) in the FT-IR spectrum, as shown in Figure 4a. In contrast, the isocyanate peak was minimal (in terms of –NCO content, Figure 4b) after the reaction with HEMA. The molecular weights of the PU obtained via GPC analyses were as follows: the number average molecular weight ( $M_n$ ) = 6,665 g/mol and the weight molecular weight ( $M_w$ ) = 51,260 g/mol with a 7.7 polydispersity index (PDI; Figure 5).



**Figure 4.** IR spectrum of polyurethane (FMEP-PU) (a) before mixing with the capping agent and (b) after 3 h of mixing with the capping agent.



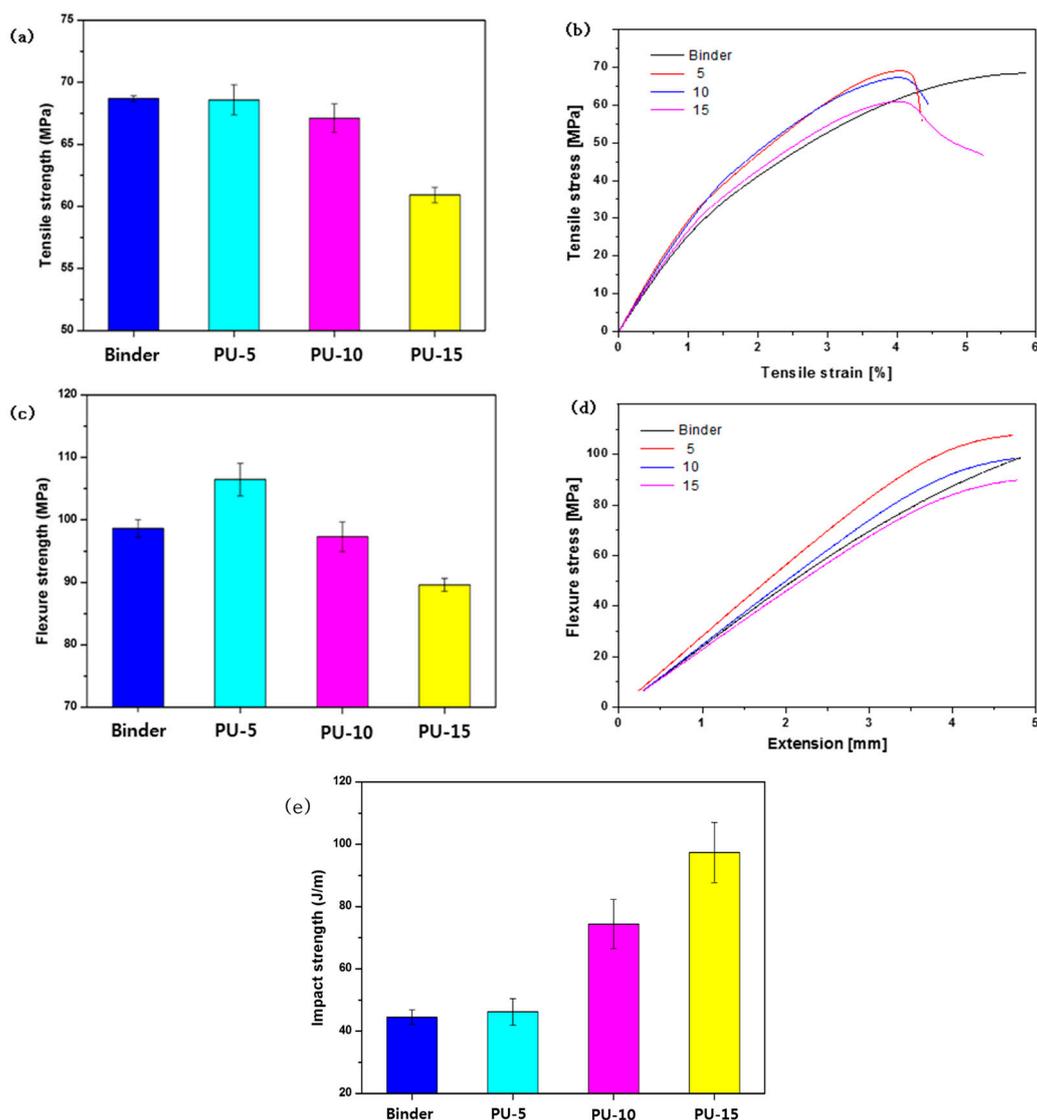
**Figure 5.** Gel permeation chromatogram of FMEP-PU.

### 3.3. Mechanical Properties of the Cured Epoxy Polymer

The mechanical properties, including tensile, flexural, and impact strengths, of the cured epoxy polymers were measured using an UTM, as shown in Figure 6. Epoxy polymers have excellent mechanical properties but are brittle and suffer from severe crack propagation. Therefore, the synthesized PU was added to the epoxy compositions as a toughening agent to minimize cracking. The viscous liquid PU was thoroughly mixed with the compositions and phase-separated when the pastes formed a solid polymer after the high-temperature curing reaction. However, when the PU phase-separated, it lowered the cross-linking density of the polymer and reduced the mechanical properties. The cross-linking density of the compositions was calculated using data obtained from the DMA experiments in Table 2 by Equation (2). The data shows that the cross-linking density decreased upon addition of PU to the epoxy compositions.

$$\nu_e = E'/3RT \quad (2)$$

where  $\nu_e$  is the cross-link density,  $E'$  is the tensile storage modulus (MPa),  $R$  is the gas constant ( $8.314 \text{ m}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ),  $T$  is temperature in K corresponding to the storage modulus value [20].



**Figure 6.** Characterization of the cured epoxy polymers: (a) tensile strength, (b) stress-strain curves of tensile test, (c) flexural strength (d) stress-strain curves of flexural test, and (e) impact strength.

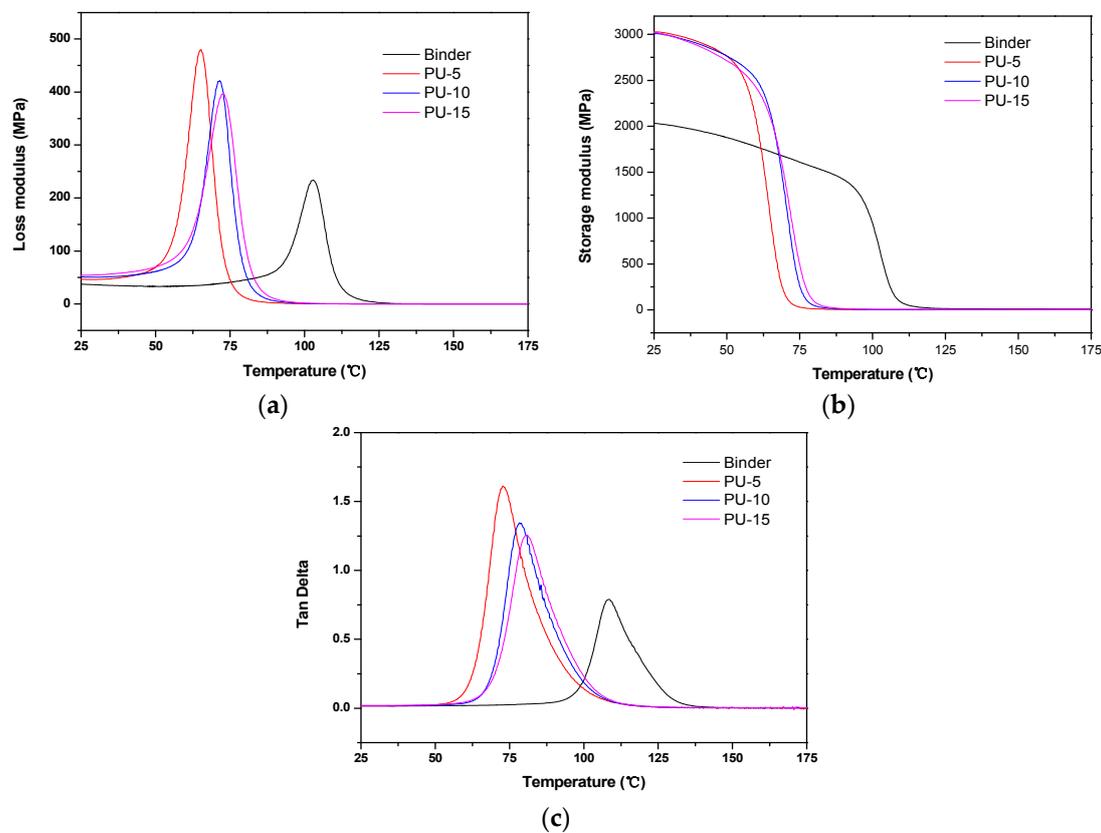
**Table 2.** Calculation of cross-linking density of the cured epoxy compositions with DMA.

Compositions	Storage Modulus at $T_g + 40\text{ }^\circ\text{C}$ (MPa)	$T_g$ ( $^\circ\text{C}$ , with DMA)	Cross-Linking Density (moles/ $\text{cm}^{-3}$ )
Binder	10.78	108	$1.03 \times 10^{-3}$
PU-5	3.17	72	$0.33 \times 10^{-3}$
PU-10	4.75	78	$0.49 \times 10^{-3}$
PU-15	5.45	82	$0.55 \times 10^{-3}$

Typically, decreases in tensile or flexural strength are proportional to the amount of PU added to the epoxy. To increase strength, the synthesized PU was designed to contain glycidyl groups to bridge the epoxy polymer via a reaction between the PU glycidyl groups and hardener amines. As shown in Table 2, though the cross-linking density of the epoxy compositions decreased upon addition of PU (PU-5), it increased with increasing PU content (PU-10 or PU-15), indicating the formation of cross-linking bonds between the PU and epoxy polymers. As shown in Figure 6a, the tensile strength increased when 5 phr of PU was added, but decreased when 10 phr of PU was added. In terms of flexural strength (Figure 6b), even a 5 phr addition of PU increased the strength, which was maintained

at 10 phr PU, but decreased at 15 phr PU. The impact strength data (Figure 6c) show that the impact strength of the epoxy polymers increased from 46.3 to 76.4 J/m when 10 phr PU was added. At 15 phr of PU, the impact strength increased to 96.4 J/m, more than twice the increase of the binder. The results show that the synthesized FMEP-PU increased the impact strength, while the well-known toughening agent CTBN enhanced tensile strength [21].

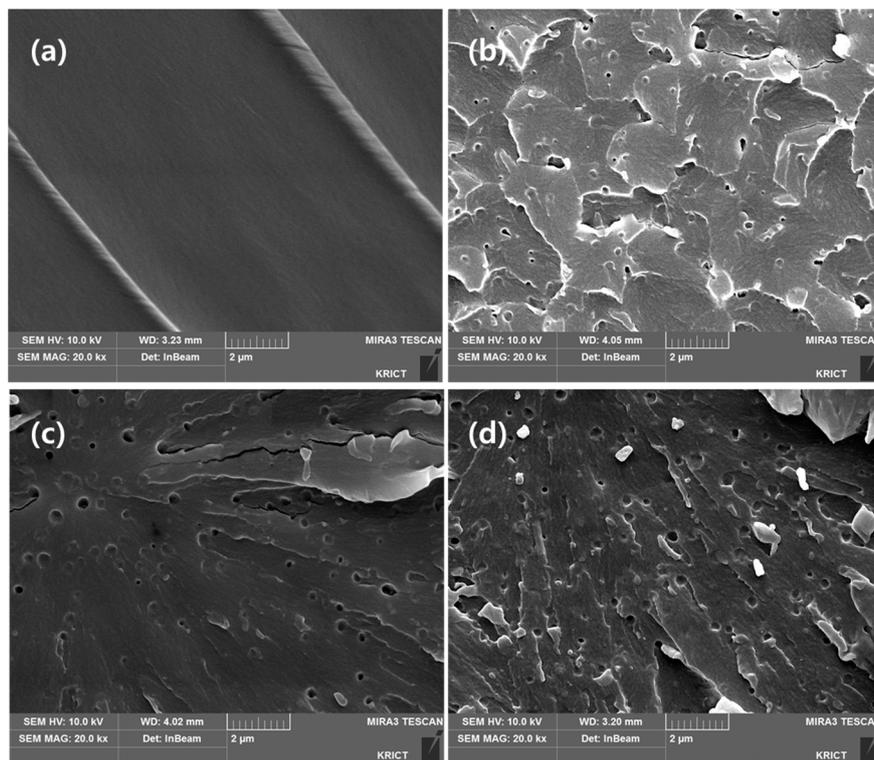
The viscoelastic properties of the cured epoxy polymers were subjected to DMA. The obtained storage modulus, loss modulus, and  $\tan\delta$  data are shown in Figure 7. The initial storage modulus at 25 °C for the epoxy polymers increased from 2,035 to 3,000 MPa upon addition of PU, while the storage modulus of the polymers decreased with increasing temperature.  $\tan\delta$  provides a measure of the viscous to elastic portion ratio. As shown in Figure 7c, the glass transition temperature ( $\tan\delta$ ) of PU-5 abruptly decreased, as the  $\tan\delta$  of PU-10 and PU-15 showed a higher temperature than that of PU-5. This indicates that the cyclohexyl groups of the modified polyol imparted rigidity to PU.



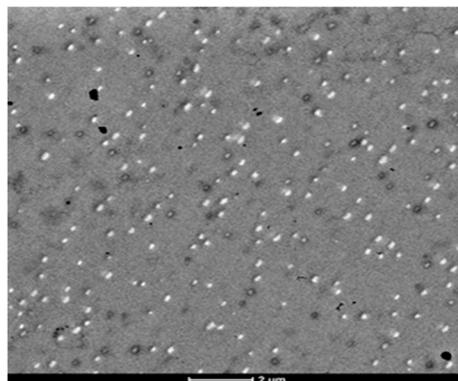
**Figure 7.** DMA data of the cured epoxy polymers: (a) storage modulus, (b) loss modulus, and (c)  $\tan\delta$ .

### 3.4. FE-SEM and TEM Images of the Fractured Epoxy Polymers Obtained after Impact Tests

Both FE-SEM (Figure 8) and TEM (Figure 9) images of the fractured cured epoxy matrix were obtained and are shown in Figure 8. The surface of the neat resin was smooth, whereas the fractured surfaces of the epoxy polymers, including PU, contained small holes approximately 100 nm in size. The holes were left from the phase-separated PU particles bouncing off due to the impact. In addition, similar sized protruding parts were observed, indicating that a strong interaction between the epoxy matrix and PU particles occurred upon curing of the system.



**Figure 8.** FE-SEM images of the fractured surfaces: (a) binder, (b) PU-5, (c) PU-10, and (d) PU-15.



**Figure 9.** TEM image of PU-15.

#### 4. Conclusions

In this study, a bisphenol A epoxy resin was modified with a dimeric fatty acid, both of which contained polyol and diglycidyl groups. The prepared polyol was mixed with PPG and reacted with IPDI followed by the addition of HEMA to form a stable elastomeric PU (FMEP-PU). The synthesized FMEP-PU was used as a toughener for the epoxy system to compensate for the brittleness of the epoxy polymer formed by curing. Various amounts of FMEP-PU were added to the epoxy compositions and were cured at high temperature to form the epoxy polymer. The tensile strength measurements showed that the epoxy compositions with FMEP-PU decreased in proportion to the contents of FMEP-PU while flexural strength increased up to 5 phr of FMEP-PU. However, the impact strength of the compositions proportionally increases from 46.3 J/m with the binder to 96.4 J/m of PU-15. Thus, FMEP-PU enhanced the toughness of the epoxy compositions. Viscoelastic properties obtained from DMA experiments showed that the  $T_g$  decreases upon the addition of 5 phr PU from 108 to 72 °C, but increases along with the increasing PU content to 82 °C. The calculated cross-linking density indicated that the glycidyl groups of PU reacted with the amine curer to form a cross-linked structure. Therefore, PU-5 with a

cross-linking density of  $1.03 \times 10^{-3}$  moles/cm<sup>-3</sup> increased to  $0.55 \times 10^{-3}$  moles/cm<sup>-3</sup> when 15 phr of PU was added to the epoxy composition.

**Author Contributions:** Conceptualization, B.S. and C.-S.L.; Methodology, W.L. and H.-G.K.; Formal Analysis, M.K.; Investigation, T.H.K.; Writing—Original Draft Preparation, T.H.K.; Writing—Review & Editing, B.S. and C.-S.L.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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