On-demand and Fast Recyclable Bio-epoxy

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Abstract

Thermoset applications that require high mechanical and chemical stability during service life, such as windmill blades and airplanes, do not allow for biodegradability that degrades naturally over time. In this study, we developed an eco-friendly epoxy resin that maintains high chemical and mechanical stability in normal times but can be chemically decomposed under certain conditions when we want. The new bio-based EP was prepared from vanillin and raspberry ketone via an L-proline-catalyzed aldol condensation reaction. The bio-based EP exhibited excellent tensile strength (58 MPa), flexural strength (183 MPa). In addition, CFRP prepared by using synthesized EP exhibited excellent tensile strength (957 MPa), Young's modulus (77 GPa), and interlaminar shear strength (49 MPa). Very interestingly, the synthesized EP and CFRP applicants were very rapidly degraded only under specific conditions. Therefore, this study is expected to give a great insight into solving the problems of eco-friendliness and recycling of thermoset resin applications.

1. Introduction

Epoxy resins are crosslinking cured polymers that are characterized by a wide range of desirable end properties, such as a good resistance to chemicals and high mechanical and thermal stabilities [1]. As such, they play a key role in the materials industry. For example, bisphenol A (BPA)-type epoxy resin is the most commercially used epoxy resin worldwide, accounting for > 75% of such materials [2]. However, due to its toxic nature, there are numerous global restrictions on BPA-containing products [3]. In addition, used epoxy products are commonly discarded in landfill sites or are thermally decomposed due to their inability to degrade naturally [4]. These treatments cause environmental pollution to both the soil and atmosphere [5]; thus, sustainable utilization and further development of BPA-type epoxy are hindered. To address these issues, preparation of eco-friendly degradable epoxy resins from bio-based monomers and oligomers has received increasing attention in recent years [6].

In general, degradable epoxy resins can be split into biodegradable resins and resins that are decomposed via a chemical route. Although biodegradable epoxy resins are completely decomposed into carbon dioxide (CO$_2$) and water by oxygen and microorganisms present in the soil [7, 8], they have relatively poor mechanical properties compared to the BPA-type epoxy,[7, 8] which limits their use in aeronautical industries. In addition, biodegradable epoxy resins can be decomposed by oxygen and microorganisms in the air; therefore, they are not suitable for replacing epoxy products that are frequently exposed to the natural environment. In contrast, chemically degradable epoxy resins tend to exhibit superior mechanical properties [9] and can be selectively decomposed as desired.

For the preparation of chemically degradable resins, a molecular structure or resin structure must be designed in which a reversible reaction can occur under selective conditions. Thus, systems based on Diels–Alder adducts [10], ester bonds [11], Schiff bases [12], and acetal linkages [13] are of particular interest and have been shown to exhibit high mechanical and thermal properties; thus, these systems could potentially replace BPA-type epoxy resins [12, 13]. However, the catalysts and materials employed
during their preparation can cause environmental pollution; therefore, it is desirable to employ eco-friendly catalytic approaches to prepare such resins. Furthermore, it is necessary to replace the petrochemical-based epoxy monomers with bio-based materials.

In terms of potential synthetic approaches, the aldol reaction, which is a reversible reaction that couples aldehydes and ketones, could be considered [14]. More specifically, the asymmetric aldol reaction is catalyzed using an eco-friendly asymmetric organic catalyst, namely L-proline [14, 15], and is one of the most useful eco-friendly carbon–carbon bond-forming reactions. For example, the cross-aldol reaction using L-proline has been used to couple heterogeneous aldehydes and ketones [16]. Furthermore, it has been used to induce the reversible aldol condensation reaction [17]. Therefore, this reaction–catalyst system has the potential to be applied in the preparation of a chemically degradable material via an eco-friendly synthetic route.

Herein, we report the preparation of a bio-based epoxy resin via an aldol condensation reaction using the eco-friendly L-proline catalyst to introduce a chemically cleavable unsaturated ketone moiety. More specifically, we employed vanillin (an aldehyde obtained from lignin) and raspberry ketone as the precursors (abbreviated as VR) for this cross-aldol condensation reaction. The key point in this strategy is the decomposition of the aforementioned unsaturated ketone moiety via a retro-aldol condensation reaction. Subsequently, epichlorohydrin is employed to promote an epoxy coupling reaction and yield the new chemically degradable bio-based epoxy resin (abbreviated as VREP). Finally, this novel bio-based epoxy resin and 4,4’-diamino diphenyl sulfone (DDS) which are commonly used as a curing agent are fabricated on carbon fiber-reinforced plastic (CFRP) with, and the unsaturated ketone is chemically decomposed via a retro-aldol condensation to enable recycling of the CFRP (Fig. 1).

2. Results And Discussion

2.1. Characterization of VR and VREP

The synthetic route employed to obtain the VREP via the eco-friendly L-proline-catalyzed approach is outlined in Scheme S1. Following the preparation of the solid VR and VREP samples, their chemical structures were confirmed by $^1$H nuclear magnetic resonance (NMR), $^{13}$C NMR (Fig. S1 and S2), and Fourier transform infrared (Ft-ir) spectroscopy (Fig. S3). As observed from the $^1$H NMR spectra of VR and VREP (Fig. S1a and S2a), doublets at 6.57 and 7.45 ppm confirmed the presence of alpha and beta protons of the unsaturated ketone moiety, while the peaks at 6.75, 6.91, 7.01, 7.06, and 7.09 ppm corresponded to protons of the aromatic benzene ring. However, upon comparison of the $^1$H NMR spectra of VR and VREP, the peaks at 4.54 and 5.88 ppm corresponding to the phenolic protons of VR disappeared, while eight new peaks derived from the epoxy group of VPEP appeared at 2.74, 2.89, 3.25, 3.38, 3.92, 4.04, 4.18, and 4.30 ppm, thereby confirming that the reaction was successful. In addition, the chemical shifts and carbon numbers in $^{13}$C NMR spectra matched the carbons of VR and VREP, respectively (Fig. S1b and S2b). Furthermore, from the Ft-ir results, peaks corresponding to unsaturated
ketone moieties (i.e., at 1650 and 1620 cm$^{-1}$) were confirmed for both compounds. As expected, the VR hydroxyl peak at 3300–3200 cm$^{-1}$ disappeared, while an oxirane peak (910 cm$^{-1}$) and ether peaks (1140 and 1210 cm$^{-1}$) corresponding to the epoxy group appeared in the spectrum of VREP, thus confirming the successfully coupling reaction.

2.2 Curing behavior analysis of the mixed VREP/DDS system

The reaction between VREP and DDS is outlined in Scheme S2. To determine the gelling time required to obtain the crosslink network, the complex viscosity and shear modulus of the VREP and DDS mixture were measured while increasing the temperature of the system at a rate of 2 °C min$^{-1}$. As shown in Fig. 2a, the complex viscosity tended to remain constant until the temperature increased rapidly at approximately 33 min (at 200 °C) due to curing. Subsequently, the viscosity increased at a slower rate as the viscosity inflection point was reached. Although the gelling time was close to this inflection point, it was difficult to precisely determine the exact gelling time. Thus, the shear storage and loss moduli ($G'$ and $G''$) was measured under the same conditions to obtain an accurate gelling time. In general, the crossover point where the $G'$ and $G''$ values intersect is defined as the gel time [18]. Thus, as shown in Fig. 2b, the crossover point was located at 33 min, which is consistent with the inflection point of the complex viscosity–time graph, and therefore reflects the gelling time of the VREP and DDS mixture.

To obtain a deeper understanding of this system, we investigated the curing behavior of the VREP and DDS mixture by differential scanning calorimetry (DSC). For comparison, DSC of VREP alone was also carried out (Fig. S4), and an endothermic peak was observed at 142.8 °C during the first heating, which corresponded to the melting point ($T_m$) of VREP. Figure 2c shows the DSC plot of the VREP and DDS mixture, wherein a slightly lower $T_m$ of 131 °C was recorded. In addition, an exothermic peak was observed between 175 and 245 °C, which represented the curing temperature range of the mixture. After the first heating, no endothermic or exothermic peaks were observed, indicating that complete curing had been achieved during the first cooling process. Thus, to explore the optimal curing temperature conditions in more detail, the enthalpy was calculated at each temperature point by dividing the temperature range into five equal stages between the starting onset point (175 °C) and the maximum peak (215 °C) in isothermal mode over 1 h (Fig. 2d). It was found that the highest enthalpy (305 J g$^{-1}$) correlated to a temperature of 185 °C, and no heat flow was detected after 1 h. These results indicate that a gelling time of 33 min and a curing temperature and time of 185 °C and 1 h, respectively, were optimal for the VREP and DDS mixture.

2.3 Mechanical and thermal properties of the cured epoxy resin based on VREP and DDS

Based on the above curing behavior analysis result, the mixture of VREP and DDS was pre-cured for 1 h at the onset point temperature (175 °C) prior to post-curing for 3 h at the optimal temperature (185 °C) to ensure complete curing. The specimens are shown in the insets of Fig. 3a and 3b, and the tensile and
flexural stress–strain curves of the cured epoxy resin based on VREP and DDS (abbreviated as VREP/DDS) are shown in Fig. 3a and 3b. From these plots, the tensile strength and Young’s modulus of VREP/DDS were determined to be 58 MPa and 2.9 GPa, respectively. The tensile strain gauge was recorded at 2.7%. Thus, our system exhibited a tensile strength similar to that of thermosetting plastics based on BPA-type epoxy resins (i.e., the diglycidyl ether of bisphenol A epoxy resin combined with DDS, DGEBA/DDS), with tensile strengths in the range of 57.2–59.4 MPa, in addition to a greater Young’s modulus (c.f., 0.56 GPa for DGEBA/DDS) [19]. Furthermore, the flexural strength and flexural modulus of VREP/DDS were 183 MPa and 3.6 GPa, respectively, and the flexural strain gauge was recorded at 4.8%. These results indicate a high flexural strength and flexural modulus compared with the DGEBA/DDS system (i.e., 79.5 MPa and 1.03 GPa, respectively), [19] thereby confirming the slightly superior mechanical strength of VREP/DDS compared to DGEBA/DDS.

Dynamic mechanical analysis (DMA) was then employed to evaluate the storage modulus, loss modulus, and tanδ. As shown in Fig. 3c, the storage modulus was 5351 MPa and the loss modulus was 432 MPa at the maximum peak located at 140 °C. Based on these data, it can be observed that the maximum peak from the calculated tanδ graph occurred at 151 °C, and this value corresponded to the glass transition temperature (T_g). Furthermore, the middle flexion point of the heat flow, which also indicates T_g, was detected at 148 °C in the DSC plot of VREP/DDS (Fig. 3d), thereby confirming similar T_g values obtained by both DMA and DSC analysis [19].

Furthermore, we investigated the crosslink density of the VREP/DDS system based on these DMA and DSC analysis data, as outlined in Eq. (1):

\[
\rho = \frac{E'}{3RT}(1)
\]

where \(\rho\), \(E'\), \(T\) and \(R\) are the crosslink density (mol cm\(^{-3}\)), tensile storage modulus (J cm\(^{-3}\)) at the rubbery plateau region, gas constant (8.314772 J K\(^{-1}\) mol\(^{-1}\)), and temperature (K) at determined \(E'\), respectively. The value of \(E'\) was selected based on the point at which it became constant at 191 °C; this temperature is higher 40 degree Celsius than \(T_g\) [20], thereby giving an \(E'\) value of 157.9 J cm\(^{-3}\) at 191 °C. Thus, the crosslink density of the VREP/DDS system was determined to be 0.0136 mol cm\(^{-3}\) based on the above equation. Since the crosslink density of DGEBA/DDS has been reported to be \(\sim 0.0118\) mol cm\(^{-3}\) [20], it is clear that the crosslink density of our VREP/DDS system is higher, exhibiting a higher storage modulus and superior mechanical properties compared to those of DGEBA/DDS. Thus, it can be inferred that the proposed VREP/DDS system is a potential replacement to the BPA-type epoxy.

2.4 Application of the VREP/DDS system to CFRP

Subsequently, to evaluate the potential application of the VREP/DDS system to CFRP, the interfacial shear strength (IFSS) was measured using the pull-out test method to determine the resistance to shear force between the cured epoxy resin and carbon fiber (CF). Figure 4a shows a photograph of the pull-out test setup and the obtained IFSS for the VREP/DDS and DGEBA/DDS systems, wherein values of 35.0 and
40.8 MPa were obtained, respectively. Although the IFSS of the VREP/DDS system was slightly lower than that of the DGEBA/DDS system, this was considered acceptable as the IFSS between BPA-type epoxy resins and CF typically ranges from 30 to 40 MPa [21].

During the fabrication of CFRP, it is necessary to evaluate how well the resin is impregnated into the CF, since a low degree of impregnation can create pores and voids, thereby resulting in inferior mechanical properties. It is therefore advantageous to impregnate into CF at a low complex viscosity; since VREP is a solid epoxy compound that cannot be impregnated at 25 °C, its impregnation must be carried out in the molten state, at which point the viscosity should be evaluated. Figure 4b shows a plot of the complex viscosity against temperature. As indicated, at a temperature of ≤ 170 °C, the complex viscosity was maintained below 110 mPa·s, although it increased rapidly beyond 170 °C. Thus, to reduce void formation, impregnation was carried out at 170 °C, i.e., before the sharp increase in the complex viscosity. The CFRP was prepared using the VREP and DDS mixture and a CF weave fabric (VREP/DDS-CFRP) as described previously under relatively low complex viscosity conditions for dwelling (i.e., 170 °C, 30 min.) and with curing at 185 °C for 4 h. Specimens for the tensile and ILSS tests were fabricated by laminating 3 and 10 piles of the CF fabric, respectively. Figure 4c shows photographs of the fabrication process and the prepared VREP/DDS-CFRP sample.

Figure 4d showed a scanning electron microscope image of how resin was impregnated in the CF. From the image, it can be seen that it was impregnated well without any empty space. Subsequently, to evaluate the number of voids, the cut cross-section (i) and the top surface (ii) were analyzed by X-ray microscopy (XRM). Figure 4e showed computed tomography (CT) images for x and y axis directions, and a 3D rendering reconstructed from the scanned CT images. Small voids marked with red arrows could be identified in the CT image (see Fig. 4e-i, ii), and we calculated the void volume fraction by summing the volumes of all voids present in the VREP/DDS-CFRP from the 3D rendering. Thus, a fiber volume fraction of 60% was obtained in addition to a void volume fraction of 0.36%. Importantly, this value is within the limit of ≤ 1% specified for CFRP materials exhibiting high mechanical properties [22]. Therefore, although VREP is a solid epoxy resin that cannot easily impregnate CF, our results indicated that no significant reduction in the mechanical properties took place following melting and impregnating.

The mechanical properties of the VREP/DDS-CFRP system were then evaluated as shown in Fig. 4f and 4g, and the tensile strength and ILSS results were obtained. The corresponding specimens are shown in the insets, and the obtained results are listed in Table S1. More specifically, the average tensile strength and Young's modulus were 957 MPa and 77 GPa, respectively, and the average ILSS was 49 MPa. These results are similar to those of the CFRP prepared using the DGEBA-type epoxy resin [23], which indicates the potential of VREP for application in CFRP products to replace BPA-type epoxy resins.

2.5 Chemical degradability of the cured VREP/DDS-containing epoxy resin

As described above, the molecular structure was designed considering the retro-aldol condensation reaction, which initially involves conversion of the alkene group of an unsaturated ketone into a
secondary alcohol. The resulting compound then reacts under heating and basic conditions in solvents such as sodium hydroxide (NaOH) solution, which promote retro-aldol reaction [24, 25]. Thus, we oxidized VREP/DDS using hydrochloric acid (HCl) solution and selected sodium hypochlorite (NaOCl) solution as the basic solvent due to its ability to generate NaOH at room temperature over a pH range of 12–15 [26].

Figure 5a shows the decomposition process and the resulting visible changes that occurred in the VREP/DDS sample. More specifically, following the oxidation process (step 1) that was carried out in a refluxing 1.0 M HCl solution (100 °C) over 12 h, the sample color was changed from yellow to brown. The brown VREP/DDS sample was then reacted in a 1.0 M NaOCl solution at 100 °C for 24 h (step 2), during which time the solution color changed to yellow, and the complete dissolution and decomposition of VREP/DDS was observed. To obtain a deeper understanding of the mechanism involved in this process, FT-IR spectroscopy was carried out (Fig. 5b). Following the oxidation process, the peak corresponding to the alkene group of the unsaturated ketone moiety (C = C, 1650 cm$^{-1}$) disappeared, and a new secondary alcohol peak was observed (C–O, 1168 cm$^{-1}$). In addition, after step 2, the secondary alcohol peak disappeared and new aldehyde peaks were observed (C–H, 2740 and 2789 cm$^{-1}$) [27].

Based on these FT-IR results, we propose a mechanism for the chemical degradation process of VREP/DDS (Fig. 5c). More specifically, in step 1, a proton (H$^+$) generated by HCl attacks the alpha site of the unsaturated ketone alkene moiety. Subsequently, a water molecule attacks the cation and H$^+$ is released to form a secondary alcohol. In step 2, an OH$^-$ ion generated from the NaOCl solution abstracts a proton from a secondary alcohol to form water, and the retro-aldol reaction is promoted by heating to decompose the structure of VREP/DDS into an aldehyde and a ketone, thereby confirming the chemical degradability of this system.

2.6 Chemical recycling of VREP/DDS-CFRP

Following the confirmation of the chemical degradability of VREP, we applied the same procedure to investigate the decomposition of VREP/DDS-CFRP, as outlined in Fig. 6a. As shown, in step 1, the color of the VREP/DDS-CFRP sample changed to brown caused by oxidation, while a yellow solution formed following step 2. After washing of the solid with water and subsequent drying, the reclaimed CF (r-CF) was obtained.

From the viewpoint of decomposition kinetics, the degrees of decomposition were investigated at 1 h intervals for VREP/DDS-CFRP and for the DGEBA/DDS-CFRP sample prepared according to the same procedure. Based on the obtained data, the degree of decomposition was calculated in each case, and the decomposition rate constant was determined as follows:
\[
\frac{d[EP]}{dt} = -k[EP][NaOCl]^m[H_2O]^n \quad \text{(2)}
\]

\[
\frac{d[EP]}{dt} = -k[EP] \quad \text{(3)}
\]

\[
\ln\left(\frac{\text{residue EP}}{\text{initial EP}}\right) = -k't \quad \text{(4)}
\]

In Eq. (2), \([NaOCl]\) and \([H_2O]\) can be considered constants because excess amounts of \(H_2O\) and \(NaOCl\) were used in the decomposition process. As a result, Eq. (3) is obtained, wherein \([EP]\) corresponds to a weight (g) rather than a concentration due to the fact that the EP specimen was a solid [28]. All results are presented in Table S2. Figure 6b and S5a show the degrees of decomposition of VREP/DDS-CFRP and DGEBA/DDS-CFRP, respectively, over time, wherein it can be seen that the decomposition degree of DGEBA/DDS-CFRP remained at almost 0% after 4 h, while 100% decomposition was observed after 4 h for VREP/DDS-CFRP. In addition, Fig. 6c and S5b were plotted to obtain the reaction rate constants (\(k\)) for VREP/DDS-CFRP and DGEBA/DDS-CFRP, which were determined to be \(1.4 \times 10^{-2}\) and \(0.064 \times 10^{-2}\) min\(^{-1}\), respectively; it was confirmed that the decomposition reactions of both specimens were of the first order with respect to the residual EP concentration. As expected, a rate constant of essentially zero was obtained for DGEBA/DDS-CFRP, while VREP/DDS-CFRP gave a rate constant ~ 20 times higher, thereby confirming the superior chemical degradability of the latter due to the retro-aldol reaction of VREP.

Finally, the insets of Fig. 6d and S6 show the FE-SEM images of the r-CF sample at 500× and 1000× magnification, respectively. From these images, it was observed that no epoxy resin remained on the r-CF surface, thereby confirming its successful decomposition. The tensile strength of the r-CF sample was then measured to determine whether mechanical properties of the r-CF were retained compared to those of the v-CF. More specifically, the tensile strength and Young’s modulus of the r-CF sample were 4.2 and 226.1 GPa, respectively, which represent at 13% loss compared to the corresponding values of the v-CF sample, i.e., 4.8 and 260.4 GPa, respectively (Fig. 6d), thereby confirming a good degree of mechanical performance retention following the decomposition process.

3. Conclusions

We successfully synthesized a new bio-based chemically degradable epoxy resin, VREP, from vanillin and raspberry ketone via an eco-friendly synthetic method, namely, an L-proline-catalyzed aldol condensation reaction and a subsequent epichlorohydrin coupling reaction. The optimal curing conditions for the VREP specimen were determined using DSC and rheometric analysis, and thermosetting plastics containing the curing agent DDS (i.e., VREP/DDS) were fabricated and evaluated. Further, DMA indicated a higher crosslink density in VREP/DDS compared to that in DGEBA/DDS, which resulted in similar or superior mechanical and thermal properties in the former, including the tensile strength and modulus (58 MPa and 2.9 GPa, respectively), flexural strength and modulus (183 MPa and 3.6 GPa, respectively), and \(T_g\) (150
°C). In addition, the IFSS was evaluated to determine the potential applicability of VREP in preparing CFRPs from CF. An IFSS of 35.9 MPa was determined, which is similar to the values reported for BPA-type epoxy resins. Furthermore, the void volume fraction (0.36%) was confirmed by SEM and XRM. Interestingly, despite the fact that VREP is a solid epoxy resin, the void volume fraction was < 1%, indicating that it is suitable for use in the production of CFRPs with excellent mechanical properties. It was also found that the tensile strength, tensile modulus, and ILSS of VREP/DDS-CFRP (i.e., 957 MPa, 77 GPa, and 49 MPa, respectively) were similar to those of the CFRP prepared using the BPA-type epoxy resin. We also examined the decomposition behaviors of the VREP/DDS and VREP/DDS-CFRP samples and proposed a decomposition mechanism based on Fourier transform infrared spectroscopy measurements. More specifically, based on a retro-aldol condensation reaction, in which a secondary alcohol was generated in HCl solution and then the retro-aldol reaction was performed under basic conditions (NaOCl solution), we confirmed the chemical degradability of VREP. In terms of the decomposition kinetics, DGEBA/DDS-CFRP exhibited a rate constant of almost zero, while that of VREP/DDS-CFRP (i.e., $1.4 \times 10^{-2}$ min$^{-1}$) was 20 times higher, with complete decomposition being observed over 4 h. Moreover, the reclaimed CF that was obtained following the decomposition process exhibited only 13% loss in tensile strength properties compared to the virgin CF. Overall, these results indicate the potential of VREP to replace DGEBA-type and BPA-type epoxy resins for the preparation of CFRP. Therefore, the findings of this study are expected to be of particular use to develop new practical applications of VREP in the field of industrial materials.

4. Experimental Section

4.1 Materials

Thin-layer chromatography (TLC) was performed on plastic plates coated with 0.25 mm silica gel containing a fluorescent indicator (Merck, #1.05715.0001). For silica-gel column chromatography, silica gel 60 (230–400 mesh) was used (Merck, #1.09385.9025). All reagents and solvents were of reagent grade and used as received. Vanillin, 4-(4-hydroxyphenyl) butan-2-one (raspberry ketone), epichlorohydrin, and tetrabutylammonium bromide (TBAB) were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). Sodium hydroxide (NaOH), hydrochloric acid (HCl), ammonium chloride (NH$_4$Cl), ethyl acetate (EA), dimethyl sulfoxide (DMSO), chloroform, and sodium sulfate anhydrous (Na$_2$SO$_4$) were purchased from Duksun Chemical Co., Ltd. (Seoul, Korea). L-proline and 4,4'-diamino diphenyl sulfone (DDS) were purchased from Sigma-Aldrich (USA). Diglycidyl ether of bis-phenol-A type of epoxy resin (DGEBA) was purchased from Kukdo Chemical Co. (South Korea). Sodium hypochlorite solution (NaOCl solution) was purchased from Daejung Chemical Co. (Korea). Carbon fiber and Carbon fiber 3k plain weave fabric from Toray’s T700 were purchased (Japan).

4.2 Instruments and Characterization Method
4.2.1 Proton nuclear magnetic resonance (\textsuperscript{1}H-NMR) spectroscopy: \textsuperscript{1}H-NMR analysis of synthesized molecules was carried out at 500 MHz on a JEOL 500 spectrometer (Japan) using CDCl\textsubscript{3} as the solvent. The pulse width was 1 \( \mu \)s, the delay time was 2 s, and 64 on each sample dissolved in CDCl\textsubscript{3} and packed into a glass sample tube were coadded.

4.2.2 Differential scanning calorimetry (DSC): The Discovery DSC 25 was used to perform DSC under a nitrogen atmosphere. 3–4 mg of VREP, a mixture of VREP and DDS, and VREP/DDS were encapsulated in an aluminum crucible and placed in the machine before the measurements. Each material was measured at a heating and cooling rate of 10°C min\textsuperscript{-1}. The mixture of VREP and DDS was measured at each temperature point dividing the temperature from the starting onset point to the maximum peak point into five equal parts in the isothermal mode for 1 hour.

4.2.3 Dynamic mechanical analyses (DMA): The DMA850 Dynamic Mechanical Analyzer (TA Instruments, New Castle, DE, USA) was used to measure the dynamic mechanical properties of VREP/DDS in this experiment. Measurements were uniformly 35 mm (length) \( \times \) 13 mm (width) \( \times \) 3 mm (thickness) in size. It was scanned with a heating rate of 3°Cmin\textsuperscript{-1} from 30°C to 200°C with an amplitude of 10 \( \mu \)m and a frequency of 1 Hz in a double cantilever mode.

4.2.4 Fourier-transform infrared (FT-IR) spectroscopy: FT-IR spectra were recorded on the FT-IR 4000 spectrometer (JASCO, Japan). The FT-IR spectra of VR, VREP, specimens before and after oxidation, and decomposition material were recorded at a resolution of 4 cm\textsuperscript{-1} using 32 coadded scans per sample, across the range of from 4000 to 600 cm\textsuperscript{-1} with the substances.

4.2.5 Rheometer measurement: The Discovery HR30 (TA Instrument, New Castle, DE, USA) was used to measure the complex viscosity, the storage modulus, and the loss modulus of the mixture of VREP and DDS as a function of time or temperature under nitrogen atmosphere. Measurement was taken with a heating rate of 2°Cmin\textsuperscript{-1} from 130°C to 200°C with the 25 mm parallel plate (Aluminum) in the 1 mm gap and a fixed frequency of 1 Hz with 5% strain gauge in the oscillation mode.

4.2.6 Field emission scanning electron microscopy (FE-SEM): Field emission scanning electron microscopy (FE-SEM) images of the r-CF were obtained using the SU-8010 instrument of Hitachi, Japan. (a voltage of 5.0 kV).

4.2.7 Tensile strength and Flexural strength of VREP/DDS: Tensile and flexural properties of VREP/DDS specimens were performed using a universal testing machine (Instron 4464, Instron Cop. USA). Speed of tensile test was 0.5 mm min\textsuperscript{-1} and strain was measured using a strain gauge (KFGS-5-120, KYOWA, Japan). The flexural properties of VREP/DDS specimens were obtained by 3-point bending tests. The dimensions of the specimens were 40 \( \times \) 9.5 mm\textsuperscript{2} and the span length of flexural test was 20 mm. Tests were conducted at a crosshead speed of 1.0 mm min\textsuperscript{-1}.

4.2.8 Tensile strength and ILSS test of VREP/DDS-CFRP: Tensile strength and ILSS test was performed using a universal testing machine (Instron 4469, Instron Cop. USA). Speed of tensile test was 2mm/min and strain was measured using a strain gauge (KFGS-5-120, KYOWA, Japan). The span length of the ILSS test was 12 mm and speed of test was 1 mm/min.

4.2.9 Tensile strength of v-CF and r-CF: The tensile strength and Young's modulus of v-CF and r-CF were measured using a single fiber tensile tester FAVIMAT\textsuperscript{+} (Textechno, Germany). A gauge length and a test
speed were 5 mm, 0.5 mm/min, respectively and a high-resolution load cell (1 µN at 210 cN full range) was used.

4.2.10 Pull-out test: Pull-out test was performed by the FIMATEST system (Textechno, Germany) to measure the IFSS of the single CF composites (DGEBA/DDS and VREP/DDS). The FIMATEST system consists of FIMABOND and FAVIMAT + with the pull-out device installed. The FIMABOND was used for embedding and curing a single CF into each resin to a depth of 300 µm. Thereafter, a pull-out test was performed at a test speed of 100 m/min using the FAVIMAT+.

4.2.11 Electron microscope: Cross-sectional images of the fabricated VREP/DDS-CFRP were obtained using Smartzoom 5 (Zeiss, Germany).

4.2.12 X-ray microscope (XRM): X-ray computed tomography (CT) images of VREP-based CFRP were obtained using an Xradia 510 Versa (Zeiss, Germany). The scanning parameters were an accelerating voltage of 60 kV, power of 5 W, spatial resolution of 0.7 µm, and exposure time of 2 s. 3D Image processing was performed using Dragonfly pro (Object Research Systems, Canada).

4.3 Synthesis of a new bio-based chemical degradable epoxy

4.3.1 1-(4-hydroxy-3-methoxyphenyl)-5-(4-hydroxyphenyl)pent-1-en-3-one (VR): In a 500 ml, round-bottom flask equipped with a magnetic bar, vanillin (10 g, 65.72 mmol) and raspberry ketone (10 g, 60 mmol) were added to DMSO solvent (300 mL). Then, the L-proline catalyst (2.1 g, 18.27 mmol) was added to the mixture and stirred at room temperature for 24 h. After the completion of the reaction, the color of the mixture was changed from yellow to brown. The mixture was quenched by saturated NH₄Cl solution (100 mL) and extracted by EA (100 mL × 3). The organic layer was collected and washed twice with brine, followed by drying with anhydrous Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure. The crude material was then purified by silica gel column chromatography using chloroform and EA as eluting solvent (chloroform : EA = 4 : 1). The compound was obtained as a yellow solid compound (10.73 g, 60% yield) after removing the solvent. $^1$H-NMR (500 MHz, CDCl₃, δ, ppm): 7.45 (d, J = 16.04 Hz, 1H), 7.09 (dd, J = 8.59 Hz, 2H), 7.06 (dd, J = 10.31 Hz, 1H), 7.01 (d, J = 1.72 Hz, 1H), 6.91 (d, J = 8.59 Hz, 1H), 6.75 (dd, J = 8.59 Hz, 2H), 6.57 (d, J = 16.04 Hz, 1H), 5.88 (s, 1H), 4.54 (s, 1H), 3.91 (s, 3H), 2.93 (m, J = 6.30 Hz 4H). $^{13}$C-NMR (125.76MHz, CDCl₃, δ, ppm): 199.0, 153.9, 148.3, 146.9, 143.1, 133.5, 129.6, 127.1, 124.1, 123.6, 115.4, 114.9, 109.5, 56.0, 42.5, 29.6 (refer to Fig. S1).

4.3.2 1-{3-methoxy-4-(oxiran-2-ylmethoxy)phenyl}-5-{4-(oxiran-2-ylmethoxy)phenyl}pent-1-en-3-one (VREP): In a 500 mL, round-bottom flask, VR (10 g, 33.54 mmol) was added to epichlorohydrin (160.17 g, 167.75 mmol) at 80°C for 30 minutes. After VR was completely dissolved in epichlorohydrin, TBAB catalyst (3.24 g, 10.06 mmol) was added to the mixture. Then, the mixture was stirred at 80°C for 3 hours. After the completion of the reaction, the mixture was cooled down in the ice bath. Thereafter, 30 wt% NaOH solution (9 mL) was added dropwise over 20 minutes, and then the mixture was reacted for 4 hours in the ice bath. After the completion of the reaction, the mixture was extracted by EA (80 mL × 3). The organic layer was collected and washed twice with brine, followed by drying with anhydrous Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure. The crude material was then purified...
by silica gel column chromatography using chloroform and EA as eluting solvent (chloroform : EA = 4 : 1). The compound was obtained as a white solid compound (12.38 g, 90% yield) after removing the solvent.

\[ ^1H-NMR \ (500 \text{ MHz, CDCl}_3, \delta, \text{ppm}): 7.45 \ (d, J = 16.04 \text{ Hz, 1H}), \ 7.09 \ (dd, J = 8.59 \text{ Hz, 2H}), \ 7.06 \ (dd, J = 10.31 \text{ Hz, 1H}), \ 7.01 \ (d, J = 1.72 \text{ Hz, 1H}), \ 6.91 \ (d, J = 8.59 \text{ Hz, 1H}), \ 6.75 \ (dd, J = 8.59 \text{ Hz, 2H}), \ 6.57 \ (d, J = 16.04 \text{ Hz, 1H}), \ 4.30 \ (dd, J = 14.32 \text{ Hz, 1H}), \ 4.18 \ (dd, J = 14.32 \text{ Hz, 1H}), \ 4.04 \ (q, J = 17.18 \text{ Hz, 1H}), \ 3.92 \ (q, J = 17.18 \text{ Hz, 1H}), \ 3.91 \ (s, 3H), \ 3.38 \ (m, J = 16.04 \text{ Hz, 1H}), \ 3.25 \ (m, J = 16.04 \text{ Hz, 1H}), \ 2.93 \ (m, J = 6.30 \text{ Hz, 4H}), \ 2.89 \ (m, J = 18.9 \text{ Hz, 2H}), \ 2.74 \ (m, J = 14.9 \text{ Hz, 2H}). \]  

\[ ^{13}C-NMR \ (125.76\text{MHz, CDCl}_3, \delta, \text{ppm}): 199.4, \ 157.0, \ 150.3, \ 149.8, \ 142.6, \ 134.0, \ 129.5, \ 128.3, \ 124.7, \ 122.8, \ 114.8, \ 113.5, \ 110.5, \ 70.1, \ 68.9, \ 56.0, \ 50.3, \ 50.1, \ 44.9, \ 42.5, \ 29.5 \ (\text{refer to Fig. S2}). \]

4.4 Fabrication of thermoset plastics (VREP/DDS)

\textit{VREP/DDS}: 3 g of VREP and 0.980 g of DDS (the molar ratio of the epoxy group to N–H was 1:1) were placed in a stainless steel cup, and mixed with a mixing machine. Afterward, the mixture was poured into a hot-press mold in which thickness was set to 3 to 4 mm. After pre-curing at 175°C for 1 hour, post-curing on hot-press at 185°C for 3 hours at 10 MPa pressure. Finally, the thermoset plastics (VREP/DDS) were obtained after natural cooling. The tensile strength and flexural strength of VREP/DDS specimens were fabricated according to the ISO 527 1BB and the ISO 178 standard, respectively.

4.5 Preparation of DGEBA/DDS-CFRP and VREP/DDS-CFRP

4.5.1 \textit{DGEBA/DDS-CFRP}. Carbon fiber plain weave fabric with three piles was placed into a hot-press mold. And 3 g of diglycidyl ether of bisphenol A epoxy (DGEBA) and 0.32 g of DDS (the molar ratio of the epoxy group to N–H was 1:1) were placed in a stainless steel cup and mixed with a mixing machine. Thereafter, the mixture was poured into a hot-press mold in which thickness was set to 0.93 mm (60% of fiber volume fraction). After dwelling and melting for 30 minutes at 190°C, curing on hot-press at 200°C for 4 hours at 10 MPa pressure. And then, obtained the specimen after natural cooling was cut to dimensions of 15 mm (width) \times 70 mm (length).

4.5.2 \textit{VREP/DDS-CFRP}. Carbon fiber plain weave fabric with three piles for tensile and ten plies for ILSS test specimens, was placed into a hot-press mold. And 20 g of VREP and 6.81 g of DDS (the molar ratio of the epoxy group to N–H was 1:1) were placed in a stainless steel cup and mixed with a mixing machine. Thereafter, the mixture was poured into a hot-press mold in which thickness was set to 0.93 mm and 3 mm for tensile and ILSS test specimens, respectively (60% of fiber volume fraction). After dwelling and melting for 30 minutes at 170°C, curing on hot-press at 185°C for 4 hours at 10 MPa pressure. And then, obtained the specimen after natural cooling was cut to dimensions of 15 mm (width) \times 120 mm (length) for tensile test and 6 mm (width) \times 12 mm (width) for ILSS test by a water jet cutting machine. The tensile strength and ILSS of VREP/DDS-CFRP specimens were fabricated according to the ASTM D3039 and the ASTM D2344 standard, respectively.

Declarations

Author contributions
Younggi Hong designed the study and idea, performed experiments, analyzed data, prepared figures, wrote the original draft, and visualization. Jisu Jeong also carried out experiments and analyzed data. Dongki Oh, Minkook Kim, and Min Wook Lee performed experiments and analyzed the mechanical properties of specimens. Munju Goh guided the work, designed the study and idea, analyzed data, directed visualization, wrote review & editing, supervised the work, and acquired the fund. All the authors contributed to the discussions of the results.

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**Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no conflict of interest.

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Figures
Figure 1

Schematic illustration of the synthetic route to the bio-based epoxy VREP from raspberry ketone and vanillin via an aldol condensation reaction using the eco-friendly organic catalyst L-proline, and its application to CFRP and to permit the chemical recycling of the template via a retro-aldol condensation reaction.
Figure 2

Rheological profiles of (a) the complex viscosity, and (b) storage and loss moduli as a function of time in the VREP and DDS mixture while increasing the temperature at a rate of 2 °C min\(^{-1}\). (c) DSC first heating and cooling curves for the VREP and DDS mixture under a nitrogen atmosphere at a heating rate of 10 °C min\(^{-1}\). (d) DSC curves for the VREP and DDS mixture under isothermal scanning conditions at different temperatures for 1 h. The inset shows the enthalpy calculations for the five temperature points.
Figure 3

(a) Representative tensile stress–strain and (b) flexural stress–strain curves and corresponding Young’s modulus of the VREP/DDS system. The insets show photographs of the VREP/DDS specimens. (c) Storage modulus, loss modulus, and tanδ curves of VREP/DDS as a function of temperature, as obtained by DMA analysis with a heating rate of 3 °C min⁻¹. The inset shows photographs of the VREP/DDS sample before and after analysis. (d) DSC heating and cooling curves for the VREP/DDS sample under dynamic scanning conditions at a heating rate of 10 °C min⁻¹ and under a nitrogen atmosphere.
Figure 4

(a) Photographs of the pull-out test setup, the force-displacement curve, and the calculated IFSS values following incorporation of the DGEBA/DDS and VREP/DDS systems with CF. (b) Rheological profile of the complex viscosity for the VREP/DDS mixture upon heating at a rate of 2 °C min⁻¹. (c) Photographs of the VREP/DDS-CFRP fabrication process and the obtained VREP/DDS-CFRP sample. (d) Scanning electron microscopy (SEM) image of the VREP/DDS-CFRP sample. (e) X-ray microscopy (XRM) images of (i) the
cross-section and (ii) the top surface, in addition to simulated images of the void volume fraction. (f) Tensile stress–strain and corresponding Young’s modulus results for the VREP/DDS-CFRP system and photographs of 5 VREP/DDS-CFRP specimens after analysis. (g) Force-displacement curve and average ILSS value of the VREP/DDS-CFRP system, and photographs of the VREP/DDS-CFRP sample before and after analysis.

Figure 5

(a) Photographs of the VREP/DDS oxidation and decomposition procedure. (b) Full-range FT-IR spectra of VREP/DDS before oxidation, after oxidation, and after decomposition. A magnification of the spectral line in the wavenumber range from 2000 to 600 cm\(^{-1}\) is also shown. (c) Mechanism of the two-step decomposition procedure based on the oxidation and degradation of VREP/DDS via a retro-aldol condensation reaction.
Figure 6

(a) Photographs of the VREP/DDS-CFRP oxidation and decomposition procedure. (b) Variation in the decomposition degree of VREP/DDS-CFRP with time, and (c) calculation of the decomposition rate constant ($k$) according to decomposition degree. (d) Tensile stress–strain curves and corresponding Young’s moduli of the virgin carbon fiber (v-CF) and r-CF samples, and an FE-SEM image of the r-CF at 500× magnification.

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