Synthesis of a Degradable High-Performance Epoxy-Ended Hyperbranched Polyester

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ABSTRACT: Degradation and recycling of cured thermosetting epoxy resins are major challenges to the industry. Here, a low-viscosity, degradable epoxy-ended hyperbranched polyester (DEHP) is synthesized by a reaction between epichlorohydrin and a carboxyl-ended hyperbranched polyester (DCHP) obtained from an esterification between citric acid and maleic anhydride. The chemical structures of DCHP and DEHP were characterized by Fourier transform infrared and 1H NMR. DEHP has a positive effect on reinforcing and toughening of the diglycidyl ether of bisphenol-A (DGEBA). With an increase in the content and molecular weight of DEHP, the mechanical performances of the cured DEHP/DGEBA composites, including the tensile, flexural, and impact strengths, increase first and then decrease. The improvements on the tensile, flexural, and impact strengths were 34.2−43.4%, 35.6−48.1%, and 117.9−137.8%, respectively. Moreover, the DEHP also promotes degradation of the cured DEHP/DGEBA composites. The degree of degradation of the cured DEHP/DGEBA composites increases with an increase of the DEHP content and molecular weight. The composites containing 12 wt % DEHP can be degraded completely in only about 2 h at about 90 °C, compared with the degradation degree (35%) of cured DGEBA, indicating good degradation and recycling properties of the DEHP.

INTRODUCTION

Epoxy resins (EPs) are thermosets for a wide range of applications, including coatings, paintings, adhesives, laminates, and composite materials due to their high adhesion, mechanical strength, chemical resistance, and process ability. However, the high cross-linking density of EPs causes brittleness, low impact strength and fatigue resistance, and environmental concerns due to poor degradability. The high viscosity of EPs is another disadvantage, requiring large amounts of organic solvents to dilute them. Solid tougheners, such as blending rubbers and polyesters, have been incorporated into EPs to improve their toughness. On the other hand, organic solvents, often poisonous, are used to improve their process ability. Recently, hyperbranched epoxy resins (HERs) with low viscosity, high solubility, and high toughness have been developed. The HERs with a large number of functional terminal groups as thermosetting polymers have been proved to be the best additive for toughening commercial diglycidyl ether of bisphenol-A (DGEBA). It is reported that the toughness of DGEBA increases several folds with the use of about only 10 wt % HERs. HERs have now become an important class of toughening additive for DGEBA. Many synthetic methods of HERs have been explored, including proton transfer polymerization, end group modification of hyperbranched polymers, and atom transfer polymerization. However, the HERs obtained from these synthetic techniques are in the form of a solid or a high-viscosity liquid, which need to be diluted with thinners or organic solvents for application. In addition, the mechanical strength is also impaired to some extent by the addition of HERs. In 2006, our group synthesized a low-viscosity aromatic hyperbranched polyester EP from epichlorohydrin, trimellitic anhydride, and diethylene glycol, which increased not only the toughness but also the tensile strength and flexural strength of DGEBA because of a novel in situ reinforcing and toughening mechanism. HERs with a silicone skeleton at low viscosities of 103.5−697.4 mPa s were obtained by our group through an environmentally friendly synthetic method, improving a comprehensive range of performances. Although HERs offer improved reinforcement, especially toughness, and process ability due to their low viscosity,
degradation and recycling of DGEBA are still a significant challenge. The traditional EPs are usually difficult to break down or recycle due to their three-dimensional network structure, producing solid waste which is a heavy burden to the environment. The main methods for decomposing EPs include mechanical recycling, pyrolysis process, supercritical fluid process, and biodegradation. In mechanical recycling, cured EPs were ground into fine powders and then used as filler in new composites. The cured epoxy powder from the mechanical recycling showed poor compatibility with DGEBA due to the lack of reactive groups, resulting in poor mechanical performance. El Gersi reported a chemical recycling process by solvolysis of EPs at 245 °C. Dang reported a 19 h long process to degrade EPs cured with amine using nitric acid. These pyrolysis processes could effectively degrade cured EPs at a high temperature of about 245 °C or a long degradation time of about 19 h. Liu studied the degradation behaviors of an anhydride-cured DGEBA in near-critical water at 270 °C for 30 min. The supercritical fluid process is not effective for recycling EPs because the solutions are not always feasible for all composites. Biodegradation of cured EPs takes about 48 h, and the degraded products are difficult to recycle because of usage of many mineral salts. With the increase of EP consumption, finding an effective method to deal with the thermo-setting resin waste has become an important research subject.

In this article, we select a degradable citric acid as a monomer to synthesize HERs and investigate the effect of the HER content and molecular weight on the performances of HER/DGEBA composites. The mechanisms for reinforcing, toughening, and degradation of HERs are discussed in detail.

## RESULTS AND DISCUSSION

### Structure Characterization of the Carboxyl-Ended Hyperbranched Polyester (DCHP) and Degradable Epoxy-Ended Hyperbranched Polyester (DEHP)

Fourier transform infrared (FT-IR) spectra of DCHP-1, DCHP-2, and DCHP-3 are shown in Figure S1. The wide absorption peak at around 3473 cm⁻¹ is attributed to the vibration of the —OH group. The strong absorption peak at 1729 cm⁻¹ (Figure S1) belongs to the C=O bond. The peak at 1216 cm⁻¹ corresponds to the vibration of the C—O—C group. The absorption peak at 1631 cm⁻¹ belongs to the C=C group. The appearance of the absorption peak at 1729 cm⁻¹ and the disappearance of the peak at 1800–1880 cm⁻¹ show that the anhydride group has reacted completely and the ester group has been generated. The 1H NMR spectra of DCHP-1, DCHP-2, and DCHP-3 are shown in Figure S2. The signals of protons of —CH=CH— are obtained at δ 6.27 ppm (H_a). The peaks of the protons of —CH_2— appear at δ 2.69–2.93 ppm (H_b, H_c). There is almost no change of the chemical environment of methylene protons after esterification. So the peak of —CH_2— attached with the ester group appear at the same position as that of —CH_2— attached with carboxyl. The peak at δ 6.27 ppm becomes weaker with an increase of the molecular weight of DCHP.

The properties of DCHP-1, DCHP-2, and DCHP-3 are shown in Table S1. According to the polycondensation between the hydroxyl group and carboxyl group, the acid value of the DCHP can calculate the degree of polymerization and further the number-average molecular weight. Explicit relationships between theoretical average degrees of polymerization and average molecular weights are established in the AB_f + B_g monomer polymerization case by "Recursive Probability Approach", and \( X_n \), \( \delta_n \), \( A_v \), \( p_B \), and \( X_a \) satisfy the following relationships:

\[
\delta_n = M_0 + 18 + \delta (M_{AB3} - 18) \tag{1}
\]

\[
A_v = \frac{56100(2 + 2\delta_n)}{98.06 + 192.14\delta_n - 18\delta_n - 1} \tag{2}
\]

\[
p_B = \frac{\delta_n}{3\delta_n + 2} \tag{3}
\]

\[
X_a = 1 + \frac{2p_y(f + g)[f(1 - p) + gx + p_y^2[(f - 1) + gx(g - 1)]]}{(1 + x)f(1 - p) + gx} \tag{4}
\]

Here, \( X_n \) refers to the number-average degree of polymerization; \( \delta_n \) refers to the number-average molar mass; \( M_0 \) and \( M_{AB3} \) refer to the molar masses of the \( B_f \) and \( AB_f \) monomers, respectively; the acid value \( A_v \) refers to the number of milligrams of the KOH, which neutralizes resin per gram; and \( p_B \) refers to the fraction of \( B_f \) groups that reacted.

Therefore, \( A_v \) and \( p_B \) satisfy the following relationship:

\[
p_B = \frac{112200 - 116.06A_v}{112200 + 0.1A_v} \tag{5}
\]

From eq 1 to eq 5, \( p_y = f, p_B = 2, g = 3, \) the molecular weight can be calculated and is shown in Table S1. Table S1 illustrates that the \( M_0 \) values of DCHP by the "Recursive Probability Approach" are very close to their theoretical molecular weights.

The FT-IR and 1H NMR spectra of DEHP-1, DEHP-2, and DEHP-3 are shown in Figures S3 and S4. The peak at 1739 cm⁻¹ (Figure S3) is attributed to the absorption peak of the C=O group. The appearance of the peaks at 1240, 910, and 844 cm⁻¹...
suggests the formation of the epoxy group. $^1$H NMR spectral data of DEHP in DMSO-$d_6$: $\delta$ 6.1 ppm (a), 2.79 ppm (b, c), 3.81–4.21 ppm (d, e), 3.17 ppm (f), and 2.5–2.63 ppm (g, h). The strong peaks at 2.10 (n) and 3.30 (m) ppm belong to the solvent peak of DMSO-$d_6$. After epoxidation, the positions of $H_a$ and $H_b$, $H_c$ change to 6.1 and 2.79 ppm, respectively. The presence of the epoxy group is confirmed by the signals 3.17 and 2.5–2.63 ppm. The chemical shifts at 3.81–4.21 ppm are attributable to $=\text{CH}_2=$ attached with the epoxy unit.

The properties of DEHP-1, DEHP-2, and DEHP-3 are shown in Table S2. The main characteristics of the DEHP are the low epoxy equivalent weight and low viscosity, from Table S2. The low epoxy equivalent weight can increase their curing rate and cross-linking density. The viscosity is measured by the discovery hybrid rheometer (TA Instruments) at 25°C. The viscosity of DEHP-2 is only 44 cp, suggesting a potential application in solvent-free resins.

**Mechanical Performance.** DEHP has a remarkable effect to increase the impact, tensile, and flexural strengths of DGEBA. The effects of the content and molecular weight of DEHP on these mechanical properties are shown in Figure 1.

With an increase of the molecular weight of DEHP, the mechanical performance of the DEHP/DGEBA composites increased first and then decreased. The impact strength of cured 12 wt % DEHP-1/DGEBA, 12 wt % DEHP-2/DGEBA, and 12 wt % DEHP-3/DGEBA increased about 117.9, 137.8, and 126.1% compared to that (17.1 kJ/m²) of the cured DGEBA, in Figure 1. Also, their tensile strengths increased about 34.2, 43.4, and 40.0%, respectively, and their flexural strengths increased about 35.6, 48.1, and 40.7%, respectively.

The mechanical performances of the DEHP/DGEBA composites increased first and then decreased with an increase of the DEHP content. The best mechanical performance was achieved by the composite with 12 wt % DEHP-2, which demonstrated 137.8, 43.4, and 48.1% increases in the impact, tensile, and flexural strengths of DGEBA, respectively. DEHP-1 and DEHP-3 are expected to have similar effects on toughening and reinforcing of DGEBA as that of DEHP-2.

The improvement of the mechanical performance of the DEHP/DGEBA composites can be explained as follows. The intramolecular cavities formed from the non-cross-linkable hyperbranched structure of DEHP would be responsible for the improved toughness, but the intramolecular cavities would have a negative effect on the tensile and flexural strengths of the composites. The increase of the cross-linking density in the composites would improve the tensile and flexural strengths. In other words, intramolecular cavities and high cross-linking density have opposite effects on the mechanical properties of the composites. The incorporation of 12 wt % DEHP and medium molecular weight of DEHP provided the right balance to achieve outstanding toughness as well as excellent tensile and flexural strengths.

**Thermal Performance.** The glass-transition temperatures ($T_g$) of the composites are shown in Figure 2a,b. The effects of the DEHP content and molecular weight on the thermal degradation temperature of the DEHP/DGEBA composites are shown in Figure 2c,d. The relative mass loss is shown in Table S3. The results in Figure 2a show that $T_g$ decreased with the increase of both the DEHP-2 content and the molecular weight. A possible explanation for the decrease of $T_g$ may be that the aliphatic flexible chains increased by the introduction of DEHP. With the increase of the molecular weight and content of DEHP in the composites, both the starting thermal degradation temperature and the rate of degradation decreased. This decrease...
in turn may be caused by the decrease of rigid benzene in the composites due to the introduction of DEHP.

**Reinforcing and Toughening Mechanism.** The scanning electron micrographs of the fracture surfaces of the DGEBA and DEHP/DGEBA composites are shown in Figure 3.

The obvious smooth fracture surface of DGEBA in Figure 3 shows that it is a brittle material. The striations on the fracture surface of the DEHP/DGEBA composites suggest good toughness. As shown in Figure 3, the density of the stripes increased with an increase of the DEHP content and molecular weight. The mechanism can be explained with an “in situ” reinforcing and toughening mechanism. The non-cross-linkable hyperbranched structure in DEHP forms intramolecular cavities, which would distort and form the stripes upon impacting. Thus, the amount of stripes increases with the increase of the non-cross-linkable hyperbranched structure, which improves the toughness of the DEHP/DGEBA composites over DGEBA.

The dynamic mechanical analysis (DMA) curves of the cured DGEBA and DEHP/DGEBA composites are shown in Figure 4.

The $\alpha$-relaxation peak measured from DMA in Figure 4a,b is related to the $T_g$. It can be seen that the $\alpha$-relaxation peak for the cured DEHP/DGEBA composites shifts toward a lower temperature with the increase in the content and molecular weight of DEHP. The change of $T_g$ agrees with the results from

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**Figure 3.** Scanning electron microscopy (SEM) micrographs of the impact fracture surface of the cured composites for (a) pure DGEBA, (b) 3 wt % DEHP-2/DGEBA, (c) 6 wt % DEHP-2/DGEBA, (d) 9 wt % DEHP-2/DGEBA, (e) 12 wt % DEHP-2/DGEBA, (f) 15 wt % DEHP-2/DGEBA, (g) 12 wt % DEHP-1/DGEBA, and (h) 12 wt % DEHP-3/DGEBA.
the DSC curves in Figure 1. The increase of aliphatic flexible chains caused by the increase in the content and molecular weight of DEHP leads to the decrease in $T_g$. The $\beta$-relaxation peak measured from DMA indicated the toughness of the composites. The higher the $\beta$-relaxation peak, the better the toughness. With the increase of the content and molecular weight of DEHP, the height of the $\beta$-relaxation peak of the composites increased and then decreased. The results agree with the change of mechanical performance of the composites.

From Figure 4c,d, it could be found that the storage modulus of cured DEHP/DGEBA increased first and then decreased with the increase of the molecular weight and content of DEHP, which is also reflected in the mechanical performance (Figure 1). The trend can also be explained by the balance of intramolecular cavities and cross-linking density.

The cross-linking density of these cured DEHP/DGEBA composites can be calculated by the rubber elasticity model, as in eq 6

$$V_c = \frac{E_r}{3\varphi RT}$$

(6)

where $V_c$ is the cross-linking density, $E_r$ is the storage modulus, $\varphi$ is the front factor, $R$ is the gas constant, and $T$ is the absolute temperature. The storage modulus at $T_g + 50$ °C is taken as the rubbery modulus to calculate the cross-linking density. As shown in Figure 5, the cross-linking density increases with the increase of molecular weight and content of DEHP.

Degradation Mechanism. The chemical structure of EPs, cure agent, and cured resins are shown in Scheme 1. The degrees of degradation of the cured DEHP/DGEBA composite films with different DEHP contents from 0 to 15 wt % are presented in Figure 6.
The degradation result in Figure 6 showed that the degree of degradation of the cured epoxy films increased constantly with the increase of the DEHP content and molecular weight. This is due to the presence of hydrolyzable ester linkages of DEHP in the structure that are more easily attacked than the ether linkages of DGEBA. At the same time, the amount of ester linkages increases with the increase in the DEHP content and molecular weight, causing the degree of degradation to increase.

The gas chromatography–mass spectrometry (GC–MS) spectra of the degradation solutions after extraction are shown in Figures S5 and S6. From GC–MS, the degradation products of the cured 12 wt % DEHP/DGEBA composites and the cured DGEBA were obtained and are presented in Tables 1 and 2. The degradation mechanism of the cured DEHP-2/DGEBA is shown in Scheme 2.

As shown in Table 1 and Figure S5, the main degradation product (3) was about 16 wt %, being from the main molecular chain of the reacted diethylene triamine acrylonitrile (DETA–AN). The formation of product (3) is owing to the cleavage of the ester and ether bonds and partial cleavage of the C–N bond. The formation of (4) is similar to that of (3) except for the cleavage of the C–N bond. Products (1) and (2) are the results of DGEBA after degradation. Product (5), citric acid, was once again proved to be due to the cleavage of the ester bond. In Table 2, the main products are (6) and (7), which are about 15.91% of the total. The molecular structures of these products show that the ester and ether bonds are broken but the C–N bonds are intact. Thus, the degradation degree of cured DGEBA is less than that of 12 wt % DEHP/DGEBA, agreeing with the experiments. The above analysis indicates that the introduction of DEHP can promote effectively the degradation of cured DEHP/DGEBA composites.

**CONCLUSIONS**

In this study, a low-viscosity DEHP was prepared by an esterification method. DEHP could improve distinctly the tensile, flexural, and impact strengths of the DGEBA/DEHP composites of about 34.2–43.4, 35.6–48.1, and 117.9–137.8%, respectively. With the increase of the DEHP molecular weight, the mechanical performance of the DEHP/DGEBA composites increased first and then decreased. The DEHP-2/DGEBA composites have a better performance than that of the DEHP-1/DGEBA and DEHP-3/DGEBA composites. It is important that the DEHP can promote the degradation ability of the composites. The cured DGEBA/DEHP-n composites containing 12 wt % DEHP-n can be degraded completely in only about 2 h at about 90 °C; however, the degradation degree of cured DGEBA is only 35% under the same degradation conditions, suggesting the good degradation and recycling properties of the DEHP.
Table 1. Degradation Products of the Cured 12 wt % DEHP-2/DGEBA Composites from Scheme 2

| RT(min) | m/z | Degradation products | Area(%) |
|---------|-----|----------------------|---------|
| 10.68   | 226 | (12wt% DEHP/DGEBA)   | 2.07    |
| 10.848  | 136 | (2)                  | 1.83    |
| 12.402  | 232 | (3)                  | 16.00   |
| 13.34   | 422 | (4)                  | 1.61    |
| 13.574  | 192 | (5)                  | 0.74    |

Table 2. Degradation Products of the Cured DGEBA from Scheme 2

| RT(min) | m/z | Degradation products | Area(%) |
|---------|-----|----------------------|---------|
| 10.68   | 226 | (DGEBA)              | 1.07    |
| 10.848  | 136 | (2)                  | 1.83    |
| 15.351  | 348 | (6)                  | 15.91   |
| 388     |     | (7)                  |         |

**EXPERIMENTAL SECTION**

**Materials.** Citric acid (CA), maleic anhydride (MA), toluene, 1,4-dioxane, p-toluenesulfonic acid, epichlorohydrin (ECH), ethyl acetate (EtOAc), NaOH, Na$_2$SO$_4$, hydrogen peroxide (H$_2$O$_2$), and N,N-dimethylformamide (DMF) were commercially supplied by Shanghai Chemical Reagent Co., Ltd. All reagents were of analytical grade. The diglycidyl ether of bisphenol-A (DGEBA) containing 5.1 mmol epoxy group per gram of resin was purchased from Yueyang Baling Petrochemical Co., Ltd. DETA-AN, as a curing agent, was prepared by an addition reaction between acrylonitrile (AN) and diethylene triamine (DETA)$^{32}$ at equal molar ratio.

**Synthesis of DCHP.** DCHP was synthesized by an esterification reaction between CA and MA according to Scheme 3. The typical process for the synthesis of DCHP-1 carrying 6
mol carboxyl groups was followed. CA (15.37 g, 0.08 mol), MA (3.92 g, 0.04 mol), toluene (30 mL), 1,4-dioxane (20 mL), and p-toluenesulfonic acid (0.20 g) were added into a three-necked round-bottomed flask equipped with a mechanical stirrer, cooler, nitrogen inlet, and water trap. The reaction was carried out for 6 h at 100 °C and then for 5 h at 125 °C. After 1,4-dioxane was
removed under reduced pressure, 16.9 g of a light yellow solid with a yield of 91% was obtained, which proved to be a DCHP (DCHP-1). DCHP-2 with a yield of 92% and DCHP-3 with a yield of 92% were synthesized by a similar process as that for DCHP-1 using the molar ratios between CA and MA of 8:1 and 26:1, respectively.

**Synthesis of DEHP.** DEHP was synthesized by a two-step method according to Scheme 3. The typical process for the synthesis of DEHP-1 was followed. First, DCHP-1 (3.75 g) and ECH (33.31 g) were taken in a three-necked round-bottomed flask equipped with a mechanical stirrer, cooler, and thermometer. The temperature was raised to 115–120 °C, and the mixture was stirred for 3 h. The excess ECH was removed under a pressure of 3–5 mm Hg at 120°C. After the compound cooled to ambient temperature, 50 mL of EtOAc was introduced to dissolve it completely. Then, 18.0 g of NaOH was added into the flask and the reaction was allowed to continue for 5 h. After the mixture was washed by 50 mL of water once and 10 mL of water three times, 5.0 g of Na2SO4 was added to remove water. The remaining solvent was removed under a pressure of 3–5 mm Hg at 90 °C. A yellowish-brown low-viscosity transparent liquid (2.32 g) with a yield of 43% was obtained, which proved to be DEHP-1. Both DEHP-2 with a yield of 45% and DEHP-3 with a yield of 40% were synthesized by a similar process as that for DEHP-1.

**Preparation of DEHP/DGEBA Composites.** The DEHP/DGEBA blends containing 0–15 wt % DEHP were prepared by mixing DEHP with DGEBA in a glass cup at 25 °C. A stoichiometric amount of DETA–AN was added into the cup and stirred for 5 min. After the bubbles in the DEHP/DGEBA blend were removed under vacuum for 10 min, the blend was put into a silicone rubber mold and cured at 25 °C for 12 h and then at 80 °C for 4 h. After that, the samples were cooled gradually to room temperature and stored for about 12 h. The mechanical performances of the product were then assessed using standard methods.

**Degradation of Grafted DEHP/DGEBA Composites.** The cured DEHP/DGEBA composite films with DEHP contents between 3 and 15 wt % were prepared by a similar process as described in the above section. The pure cured DGEBA film was obtained and used as comparison. These films (0.5 g) were cut into small pieces of about 1 mm × 2 mm × 2 mm and put into a 100 mL stainless hermetic autoclave with 7.5 g of H2O2 and 7.5 g of AN was added into the cup and stirred for 5 min. The autoclave was heated to 90 °C and maintained for 2 h and then cooled to room temperature. After this process, the remaining solid was filtered out and washed with water several times and then dried in vacuum at 80 °C for 3 h. The degradation degree (D0) of the composites was calculated using eq 7

$$D_0 = \frac{W_0 - W}{W_0} \times 100\%$$

where $W_0$ is the mass of composites before degradation and $W$ is the mass of solid residues after degradation.

The degradation liquid was extracted by EtOAc and H2O for GC–MS analysis.

**Characterization.** FT-IR studies were performed using a Nicolet Nexus 470 FT-IR spectrometer. 1H NMR measurements were conducted using a Bruker Avance III-400 NMR spectrometer with tetramethylsilane as an internal standard and D2O and DMSO-d6 as solvents.

The measurements of impact strength were conducted on a GOTECH GT-7045-MDL impact tester according to GB/T 2567-2008. The tensile and flexural strengths were measured on a GOTECH AI-700M universal materials tester according to the same standard method.

Tg measurements were carried out using a NETZSCH TG209F3 system. Samples weighing 5–10 mg were heated from 40 to 600 °C under a nitrogen atmosphere at a heating rate of 10 °C/min. DSC study was carried out using a NETZSCH DSC200F3 instrument in a nitrogen atmosphere. The samples were first heated to 200 °C at a rate of 10 °C/min to remove thermal history, then cooled to room temperature, and finally re-heated to 150 °C at a rate of 10 °C/min. The glass-transition temperature ($T_g$) was obtained from the second heating scan.

The morphology of the fractured surface was examined on a SEM (SU8010, Hitachi). A thin section of the fractured surface was cut and sputter-coated with gold prior to fractographic examination. SEM micrographs were obtained under conventional secondary electron imaging conditions, with an accelerating voltage of 20 kV.

Dynamic mechanical thermal analysis was performed on cured samples (30 mm × 10 mm × 4 mm) using a Q800 dynamic mechanical analyzer (TA Instruments) in the temperature range from 298 to 473 K at the rate of 10 K/min.

**ASSOCIATED CONTENT**

 Supporting Information
 The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00132.

 Properties of DCHP and DEHP, FT-IR and 1H NMR spectra, TGA data, and the GC–MS of the degradation products (PDF)

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