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An Acid-/Base-Degradable Epoxy Resin Cured by 1,3,5-Triacroyl-amino-hexahydro-s-triazine Derivative

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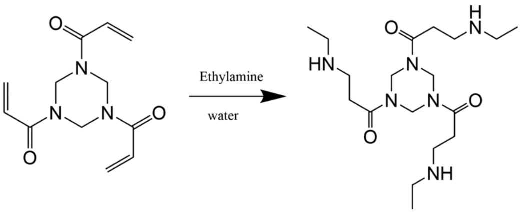

Abstract: The degradation and recycling of waste epoxy resin products is an urgent environmental problem. To solve this issue, we use acid-/base-degradable 1,1',1"-(1,3,5-hexahydro-s-triazine-1,3,5-triyl) tris(3-ethylamino-propan-1-one) (TAHT-EA) as curing agent to introduce the hexahydro-s-triazine (HT) ring structure into the cross-linking network to prepare degradable epoxy resin. Specifically, 1,3,5-triacryloyl-hexahydro-1,3,5-triazine (TAHT) and ethylamine quickly complete the Aza-Michael addition reaction at the interface of chloroform and water droplets under the catalysis of water. The FTIR spectra, NMR spectrum and mass spectrum show that mono- and bis-addition products of ethylamine coexist in the product in which the content of the primary addition product reaches 97%. TAHT-EA can be decomposed by acid and base solutions. Through NMR analysis of the degradation products, it can be explained that the degradation mechanisms are different. The breaking of amide bonds and HT rings in acid solution and the cracking of amide bonds in base solution are speculated to be the main mechanisms under these two different circumstances, respectively. We tested the mechanical, thermal and degradation properties of the epoxy resin cured by TAHT-EA, and compared it with the epoxy resin cured by 4,4'-diamino-diphenylmethane and triethylenetetramine. TAHT-EA-cured epoxy resin shows comparable mechanical properties with Young's modulus up to 2.05 GPa and tensile strength up to 70.9 MPa. What is more, it degrades completely by 1 M H^+/OH^- solution at 60 ℃ within 36 h. Nevertheless, it exhibited a relatively low crosslinked density (633 mol/m^3) and low heat resistance (the initial decomposition temperature is lower than 205 ℃). Overall, TAHT-EA cured epoxy resin has the potential to gradually replace traditional thermosetting resin, thereby solving the environmental problems caused by discarded epoxy resin products.

Keywords: degradable epoxy resin, hexahydro-s-triazine derivative, degradation property, degradation mechanism.

1. Introduction

Since its first synthesis, epoxy resins have been studied for one hundred years and has become an important polymer because of its excellent properties. However, traditional epoxy resins are difficult to be recycled or degraded by natural process, making it hard to meet the environment protection requirements. Therefore, degradable epoxy resins are of great interests to researchers. In last decade, researchers have reported several degradable resins containing dynamic covalent bonds, such as disulfide,[1-3] ketal[4] or acetal,[5,6] imine,[7,8] ester[9,10] Diels-Alder reaction products,[11,12] and hexahydro-s-triazine ring (HT ring).[13,14]

The HT derivatives can be decomposed to amines and formaldehyde when the environment pH is less than 2.[15] Base on this feature, the acid-degradable epoxy resins could be prepared by using HT derivatives as curing agent[16] or introducing the reversible HT ring into epoxy prepolymer.[17] However, in previous works, the synthesis of degradable epoxy resins is complicated and has many by-products. Therefore, it is necessary to study a simpler and more economical way to introduce HT ring into degradable epoxy resin.

1,3,5-Triacryloyl-hexahydro-1,3,5-triazine (TAHT) is a kind of acid-/base-degradable HT derivatives.[15] It can self-polymerize to prepare PTAHT[18] or produce block copolymers.[19,20] It also can be used as crosslinker in polymer electrolyte fuel cells.[21] Meanwhile, it can react with amines,[22-24] thioethers[25,26] and phosphites[27] by Aza-Michael addition reaction. However, the addition reaction of primary amines and TAHT in organic solvents usually takes long time (~24 h) and produce bis-addition by-products.[23]

Brindaban C. Ranu and Subhash Banerjee[28] provided a very simple and green procedure for the Aza-Michael addition in water without the use of any catalyst or organic solvent, which produces mono-addition products only. Inspired by this work, we chose water to promote the Aza-Michael addition reaction to synthesize 1,1',1"-(1,3,5-hexahydro-s-triazine-1,3,5-triyl)-tris(3-ethylamino-propan-1-one) (TAHT-EA) and used it as curing agent in recyclable epoxy resins. It is a simple and effective method with less

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by-products to introducing reversible HT rings into epoxy resins. In this work, we fully investigated the mechanical, thermal, degradable properties of cured epoxy resins, especially the mechanisms of degradation in both acid and base solution. The result shows that the TAHT-EA cured epoxy can be used for the recovery and degradation of waste epoxy resin.

2. Experimental

2.1. Materials

1,3,5-Triacroylamino-hexahydro-s-triazine (TAHT), triethylenetetramine (TETA), and 4,4'-diaminodiphenylmethane (DDM) were purchased from Aladdin (China) without further purification. Ethylamine was supplied by Macklin (China). Chloroform and acetone were purchased from Guangzhou Chemical Reagent Factory (China). Diglycidyl ether of bisphenol F (DGEBF, epoxy equivalent is 162 g/eq) was supplied by Nanya Plastics Corp. (China).

2.2. Instrument and test method

Nuclear magnetic resonance (NMR) spectra of TAHT-EA were recorded on a Bruker 400 MHz spectrometer, using $CDCl_3$ or D_2O as a solvent at room temperature.

The infrared spectra were measured with a Nicolet iS10, spectrophotometer and scanning wave number interval was between 4000 cm^{-1} to 400 cm^{-1}.

Mass spectra of the products were obtained with a Waters Xevo G2-XS QTof.

The mechanical properties of the cured resins were tested by Mtssans CMT4204 universal mechanical testing machine with a steady movement speed of 5 mm/min, in accordance with GB/T2567-2008. All test samples were prepared as dumbbell with the thin neck dimensions of 50 mm × 6 mm × 2 mm.

Differential scanning calorimetry (DSC) was performed on a Netzsch Model TAQ2000 instrument (Bavaria, Germany) from 30 ℃ to 200 ℃ under a flowing nitrogen atmosphere at a scan rate of 5 ℃/min.

Thermogravimetric analysis (TGA) was performed on a Netzsch STA409PC instrument (Bavaria, Germany) under a flowing nitrogen atmosphere at a scan rate of 10 ℃/min from 30 ℃ to 600 ℃.

Dynamic mechanical analysis (DMA) was carried out on a TA Q800 system using a tensile fixture. All the samples with a dimension of 40 mm × 6 mm × 0.25 mm were tested from 30 ℃ to 180 ℃ at a heating rate of 3 ℃/min and a frequency of 1 Hz.

Degradation properties test: all the test samples were prepared with the dimensions of 10 mm × 6 mm × 2 mm. The test samples were immersed in 0.5 mol/L H_2SO_4 ethanol-water solution or 1 mol/L NaOH ethanol-water solution. The original weight of the test sample was recorded as W_0. At a given moment, the test samples were removed from the solution and immersed in deionized water to remove the residual acid or base on the surfaces. Then filter paper was used to wiped off the water on the surface of samples. To this end, the weight was recorded as W_{wet}. At last, the samples were dried at 60 ℃ until there was no obvious weight loss. This weight of dry samples was recorded as W_{dry}.

The weight changes ratios (W_d) of wet or dry samples were calculated according to the Eq. (1):

$$W_d = 100\ \% \times W/W_0. \tag{1}$$

where W is W_{wet} or W_{dry}.

2.3. Synthesis of TAHT-EA

TAHT (1 g, 4.016 mmol), chloroform (10 mL) was added into a 50 mL flask and stirred at room temperature. After TAHT was dissolved, 70 wt% ethylamine aqueous solution (0.7745 g, 12.048 mmol) was added into the solution. After 2 h, the excess chloroform and water were removed by rotary evaporation. The residue was redissolved in acetone and filtered. Then, acetone was removed under reduced pressure. The filtrate was dried under vacuum at 50 ℃ overnight. TAHT-EA was obtained as a yellow viscous fluid.

2.4. Preparation of cured epoxy resin

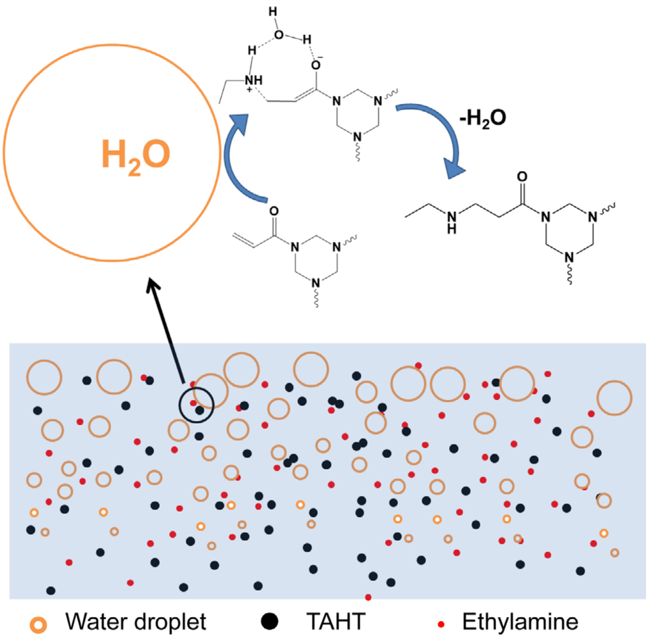
The molar ratio of N-H of TAHT-EA or DDM or TETA to epoxy group of DGEBA was 1:1. A small amount of acetone was added into the mixture and stirred at room temperature for 10 min to form a homogeneous solution. Then, the mixture was vacuumed at 40 ℃ for 30 min to remove air bubbles and acetone. After that, it was transferred into a Teflon mold and cured in an oven. The curing procedure were set according to the DSC thermogram (Figures S4, S6, and S7 in the Supporting information). The mixture of DEGBF and TAHT-EA was curing at 90 ℃ for 2 h, 140 ℃ for 2 h, and 160 ℃ for 1 h. The epoxy resins cured by DDM was curing at 80 ℃ for 2 h, 150 ℃ for 2 h and 180 ℃ for 1 h. The epoxy resins cured by TETA was curing at 50 ℃ for 2 h, 80 ℃ for 2 h, 110 ℃ for 1 h.

3. Results and discussion

3.1. Synthesis and characterizations of TAHT-EA

According to Brindaban C. Ranu and Subhash Banerjee's work,[28] we think water can be used as a catalyst to accelerate the Aza-Michael addition of amines and TAHT. However, TAHT is insoluble in water and unstable in basic solution, so the water cannot be used as reaction medium (the detailed demonstrated shows in supporting information). We chose chloroform as reaction medium and water in ethylamine aqueous solution as the catalyst. As shown in Scheme 1, TAHT dissolved in chloroform, and ethylamine diffused to chloroform from water. Water promotes the Aza-Michael addition reaction through forming an unstable intermediate state by hydrogen bonds.[28] Chloroform reduces the hydrolysis reaction of ethylamine and controls the decomposition of amide bond during the reaction. All of these make most of Aza-Michael addition reaction concentrate at the interface of chloroform and water droplets, and the whole reaction is complete within 3 h.

The characterization of the Aza-Michael reaction product is shown in Figure 1. We can see the peak of HT ring is located at



Scheme 1. Mechanism: the catalysis of water during the Aza-Michael reaction in chloroform.

5.44 ppm and the peaks at 5.83, 6.36, 6.79 ppm are assigned to vinyl group. After the reaction with ethylamine, the peak of HT ring moved from 5.44 to 5.29 ppm and the peak of vinyl group disappeared. Meanwhile, a peak at 1.88 ppm appeared, which is attributed to $\text{-CH}_2\text{-}NH\text{-CH}_2\text{-}$ (Hc). From the FTIR spectra of products (shows in Figure 1(C)), we can see the 3300 cm^{-1} which point to -NH-, 2966 cm^{-1} is belonged to $\text{-CH}_2\text{-}$, 1645 cm^{-1} is belonged to -CO- and 1429 cm^{-1} is assigned to the $\text{-CH}_2\text{-}$ in HT ring.

The ^{1}H NMR spectrum and ^{13}C NMR spectra of products illustrate that the Aza-Michael addition of amines and TAHT in CHCl_3/H_2O is difficult to stop at mono-addition step. In Figure 1(A), it is found that there are peaks located at 1.02 ppm, which is obviously assigned to the structure -CH_2CH_3 (Ha') from the bis-addition byproducts. The simultaneous presence of different carbon peaks of mono-addition and bis-addition products in ^{13}C NMR spectra (Figure 1(B)) further verifies that speculation. The Mass spectra of TAHT-EA (Figure 1(D)) further proved the bis-addition products were obtained. The m/z = 385 peak is assigned to the mono-addition and the m/z = 724 peak is assigned to the bis-addition products. From the ^{1}H NMR spectrum of addition products, the integral ratio of $\text{-CH}_2\text{-}NH\text{-CH}_2\text{-}$ (Hc) peak and $\text{-N-}CH_2\text{-N-}$ (Hf) peak is calculated to be 0.47, to which we can estimate that only about 3% mono-addition products reacted with olefin groups to generate bis-addition products.

In order to detect the degradation of TAHT-EA, we use 0.5 mol/L H_2SO_4 solution or 1mol/L NaOH solution for treatment, followed by neutralization and purification. The 3-(ethyl-

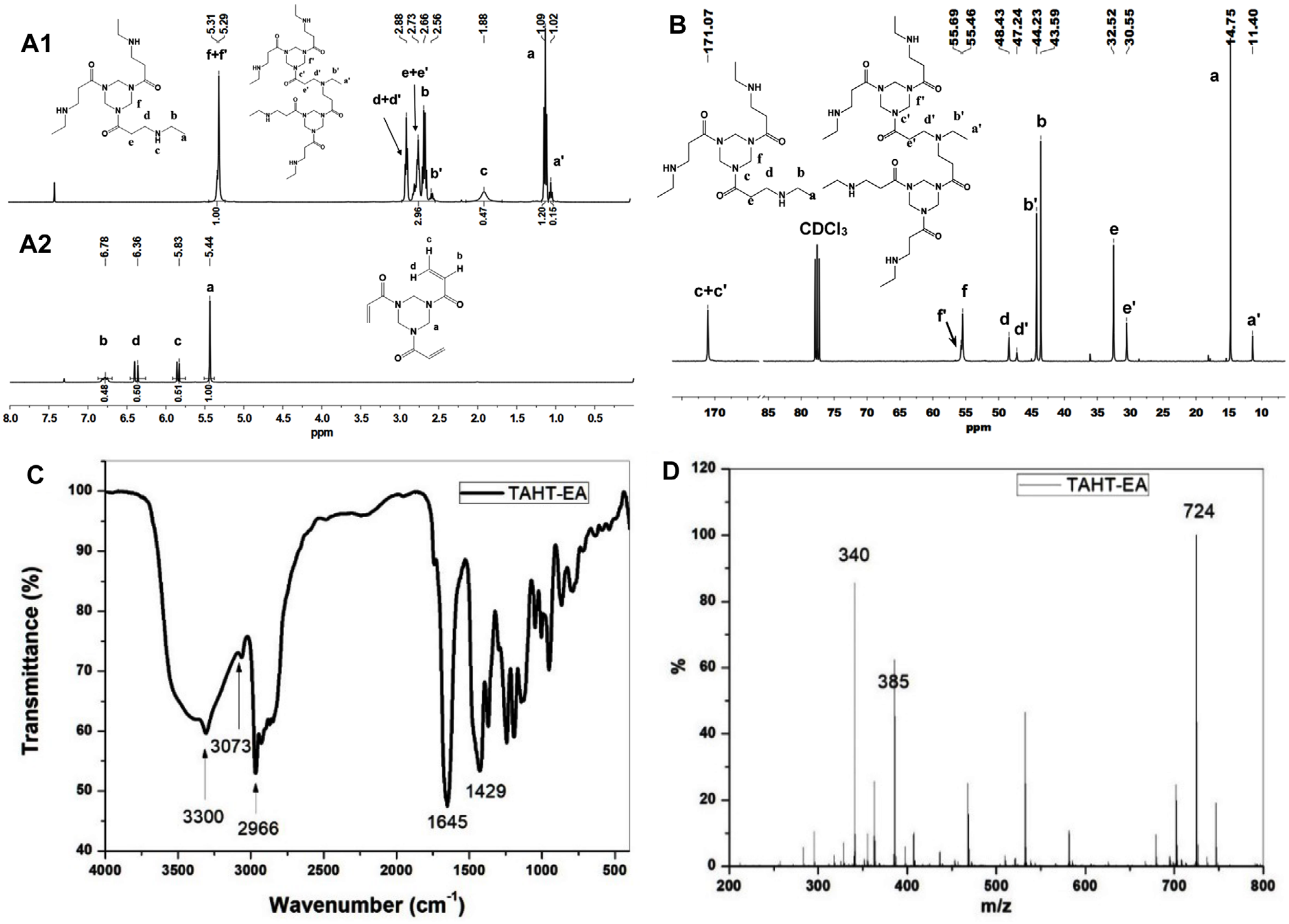


Figure 1. ^{1}H NMR spectra of TAHT-EA (A1) and TAHT (A2); ^{13}C NMR spectra (B), FTIR spectra (C), and Mass spectra (D) of TAHT-EA.

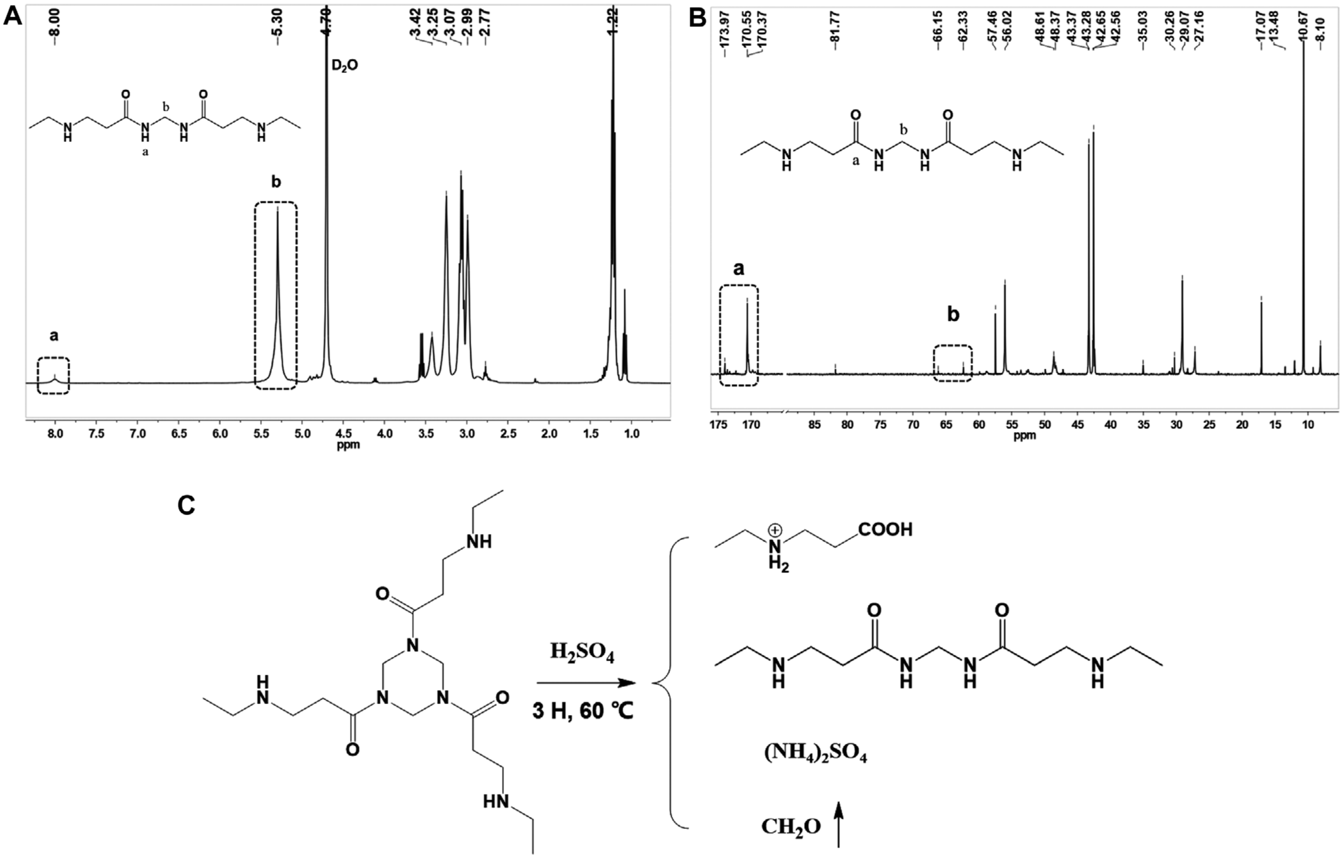


Figure 2. ^{1}H NMR spectra (A) and ^{13}C NMR spectra (B) of TAHT-EA acid-degradation products, treated with 0.5 mol/L H_2SO_4 solution and followed by neutralization and purification; (C) The degradation reaction of TAHT-EA (mono-addition) treated with 0.5 mol/L H_2SO_4 solution at 60 ℃.

amino) propanoic acid was the final degradation product of these two methods. However, the degradation processes are different.

In 0.5 mol/L H_2SO_4 solution, the HT rings and amide of TAHT-EA were broken and produced four main degradation products. The ^{1}H NMR spectra and ^{13}C NMR spectra of degradation product proved this degradation mechanism (shows in Figure 2). The peak at 8.0 ppm (-CO-N*H*-CH$_2$-N*H*-CO-) and 5.3 ppm (-NH-C*H*$_2$-NH-) in ^{1}H NMR spectra is assigned to HT rings degradation residue. In Figure 6(B), the peaks at 62.33 and 66.15 in ^{13}C NMR spectra are assigned to -NH-*C*H$_2$-NH-; the peaks at 170.3~173.97 indicate four different -*C*O-.

In 1 mol/L NaOH solution, the amide bonds were broken, and the HT rings were still intact. The ^{1}H NMR spectra and ^{13}C NMR spectra of degradation products are shown in Figure 7. In Figure 3(A), the peaks at 1.12, 2.44, 3.07, 3.15 belong to the 3-(ethylamino) propionyl groups and the peaks of HT rings were at 4.60, 4.69, 4.90, 4.93. In Figure 3B, the peaks at 70.00, 71.48, 77.57 and 81.59 in ^{13}C NMR spectra are from HT rings; the peaks at 177.73 and 177.54 indicates two different -*C*O- which belong to 3-(ethylamino) propionyl group and 3-(ethylamino) propanoic acid.

3.2. Properties of the epoxy networks

The aliphatic secondary amine groups have a high reactivity making the TAHT-EA could cure BAF at a lower temperature (shows in Figure S4). We prepared the cured epoxy and investigated its mechanical, thermal and degradable properties.

3.2.1. Thermal properties

Figure 4 and Figure 5 show the DMA and DSC curves of the cured epoxy resins. Data are listed in Table 1. The DSC test results showed the glass-transition temperature (T_g) of TAHT-EA-cured epoxy, DDM-cured epoxy and TETA-cured epoxy are 61, 142, and 75 ℃, respectively. The T_g test by DMA showed the same tendency with T_g of 83, 160, and 107 ℃.

According the Eq. (2),[16] we can get the cross-link density (υ_e) of the cured epoxy resins.

$$E' = 3\upsilon_e RT \tag{2}$$

where E' is the storage modulus of the epoxy at T_g + 30 ℃, R is the gas constant, and T is the absolute temperature.

The results of DSC and DMA test show that TAHT-EA has the lowest υ_e value and T_g. The reason may be related to the amine hydrogen number of the curing agent. Secondary amine forms a lower crosslink density than primary amine. One mole of DDM can react with 2 mole BAF, TETA is 3 mole BAF and TAHT-EA is 1.5 mole BAF. Moreover, TAHT-EA has a higher molecule weight and molecular volume, causing the TAHT-EA-cured epoxy form a lowest number of cross-linking bonds per unit volume. Therefore, the TAHT-EA-cured epoxy has the lowest υ_e value.

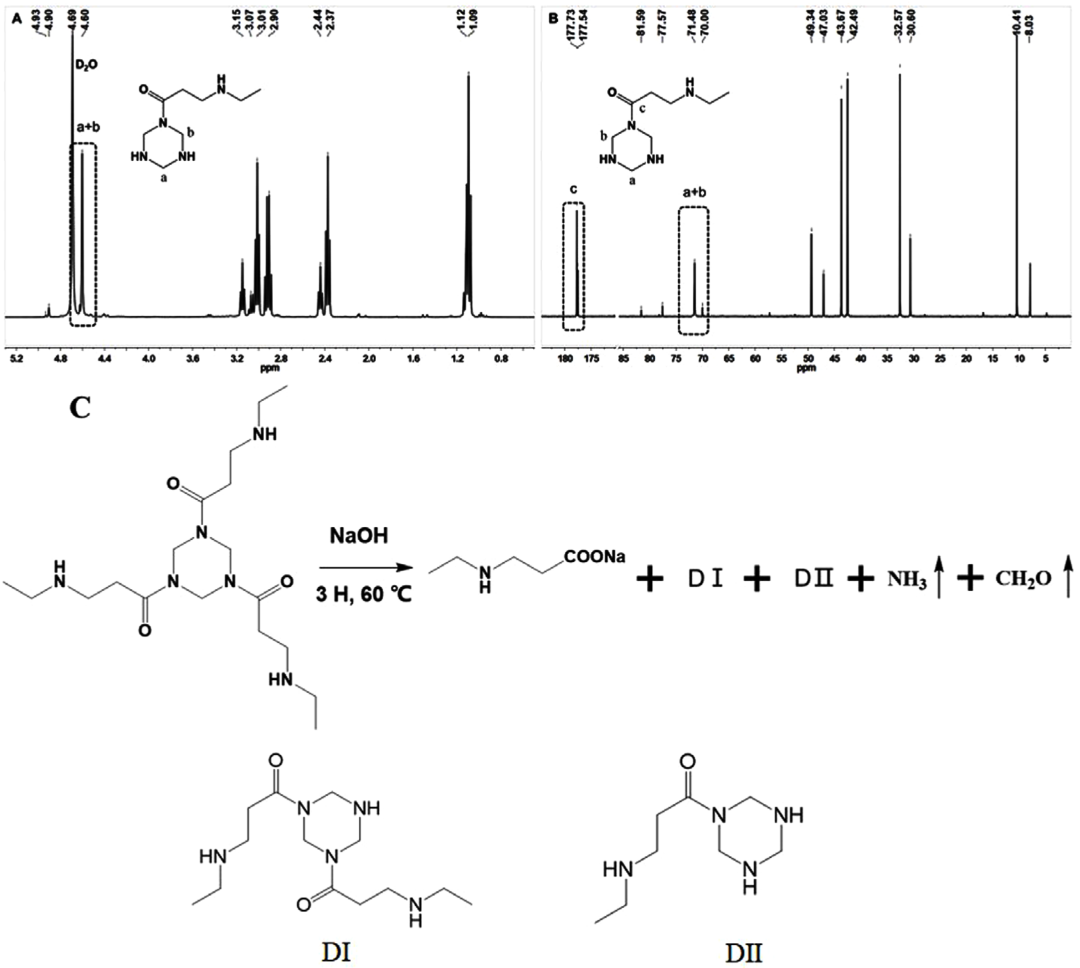


Figure 3. ^{1}H NMR spectra (A) and ^{13}C NMR spectra (B) of TAHT-EA base-degradation products, treated with 1 mol/L NaOH solution at 60 ℃ and followed by neutralization and purification; (C) The degradation reaction of TAHT-EA (mono-addition) treated with 1 mol/L NaOH solution at 60 ℃.

Table 1. Thermal properties of the cured epoxy resins

Property		TAHT-EA-cured epoxy	DDM-cured epoxy	TETA-cured epoxy
E' at $T_g + 30$ ℃ (MPa)		6.1	11.5	20.3
υ_e (mol/m^3)		633	996	1,985
T_g (℃)	DMA	83	160	107
	DSC	61	142	75

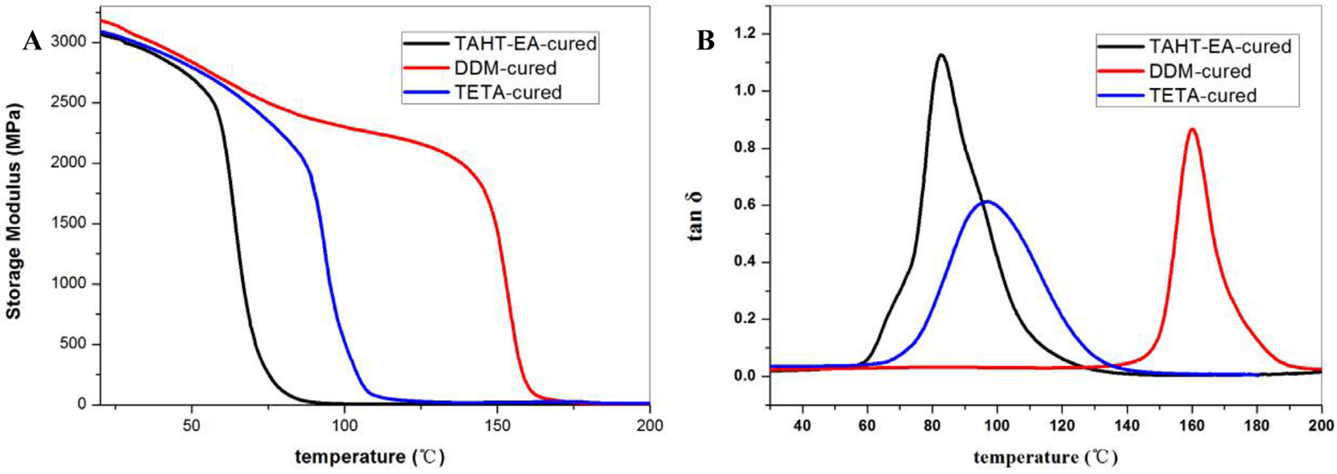


Figure 4. (A) Storage modulus *vs*. temperature and (B) tan δ *vs*. temperature for the cured epoxy resins.

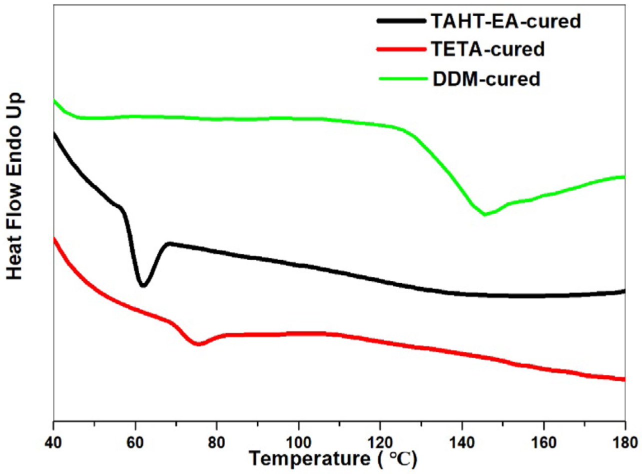


Figure 5. DSC curves of the cured epoxy resins.

The chemical structure of chain segment and cross-link density have a great effect on the storage modulus at room temperature and T_g. The flexible aliphatic secondary amine groups and relatively rigid HT ring structure endow the TAHT-EA cured epoxy resins network an intermediate flexibility. The flexible ethylene structures and the lowest υ_e value made the T_g of TETA-cured epoxy obviously lower than those of DDM-cured epoxy and TETA-cured epoxy. And the relatively rigid HT ring structure enhance the storage modulus at room temperature, making TAHT-EA cured epoxy resins has a comparable modulus at room temperature.

Figure 6 shows the TG and DTG cure of TAHT-EA-cured epoxy, TETA-cured epoxy and DDM-cured epoxy. The value of initial decomposition temperature (T_i), degradation temperature for 5% weight loss (T_{d5}) and temperature of the maximum decompose rate (T_{max}) are shown in Table 2. We can see TETA-cured epoxy and DDM-cured epoxy has a single T_{max}, which is at 353 ℃ and 376 ℃, respectively. In contrast, the TAHT-EA-cured epoxy has two T_{max} at 330 ℃ and 410 ℃. Meanwhile, The T_i and T_{d5} of TAHT-EA-cured epoxy are lower than those of TETA-cured epoxy and DDM-cured epoxy. All of these explain that the TAHT-EA-cured epoxy has a poorer thermal stability.

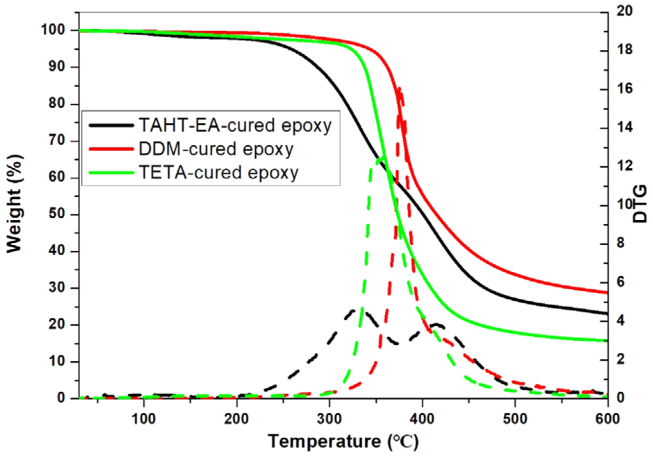


Figure 6. The TG (solid line) and DTG (dash line) curves of cured epoxy resins.

Table 2. Thermal properties of the cured resins

Properties	Value		
	TAHT-EA-cured epoxy	TETA-cured epoxy	DDM-cured epoxy
T_i	205 ± 3	301 ± 7	314 ± 3
T_{d5}	258 ± 4	323 ± 3	345 ± 3
T_{max}	330 ± 4 & 410 ± 5	353 ± 5	372 ± 4

3.2.2. Mechanical properties

The mechanical properties of TAHT-EA-, TETA-, and DDM-cured epoxies were listed in Table 3. TAHT-EA-cured epoxy shows comparable mechanical properties to DDM-cured epoxy and TETA-cured epoxy. We have discussed the effect factors of modulus at storage room temperature. The relatively rigid HT rings, flexible ethylene structures and the lowest υ_e value make the TAHT-EA-cured epoxy shows the lowest Young's modulus (down to 2.05 GPa), the relatively higher elongation at break (up to 5.6%) and the tensile strength can up to 70.9 MPa. From the aspect of mechanics properties, the TAHT-EA-cured epoxy has the potential to replace traditional thermosetting resin applying at ambient temperature.

3.2.3. Degradation properties

Figure 7 shows the degradability of all cured epoxy resins. We can see that the TAHT-EA cured epoxy resins degraded completely at 60 ℃ in 0.5 mol/L H_2SO_4 ethanol-water solution or 1 mol/L NaOH ethanol-water solution. While DDM-cured epoxy resins and TETA-cured epoxy did not have obviously dimensional change in acid/base solutions, but DDM-cured epoxy resin has a color change in H_2SO_4 solution.

To further study the degradation process, we monitored the weight change of TAHT-EA cured epoxy resin. Due to the differences in the degradation process of TAHT-EA in acid solution and basic solution, the TAHT-EA cured epoxy resin exhibits different degradation phenomena in acidic solution and basic solution.

According to the degradation mechanism of TAHT-EA, combined with the degradation process of sample, we believe that the degradation of the cured product can be divided into two

Table 3. Mechanical properties of the cured resins

Property	Value		
	TAHT-EA-cured epoxy	TETA-cured epoxy	DDM-cured epoxy
Young's modulus, E (GPa)	2.05 ± 0.12	2.71 ± 0.22	2.65 ± 0.32
Elongation at break, ε (%)	5.5 ± 0.2	5.6 ± 0.4	4.8 ± 0.2
Tensile strength, σ (MPa)	70.9 ± 2.1	73.1 ± 3.6	75.0 ± 2.6

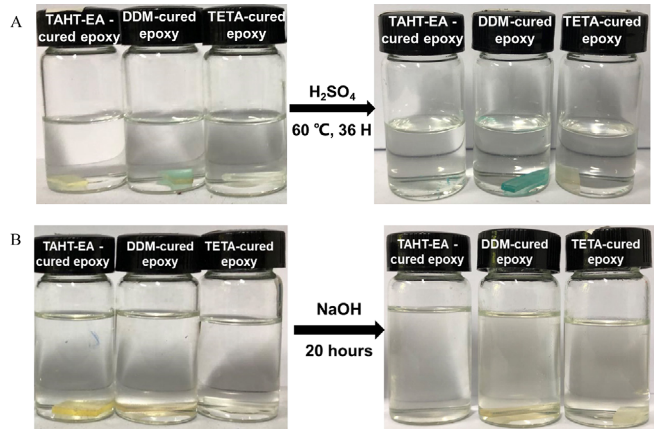


Figure 7. The photographs of the cured resins initial (left) and complete degradation (right) in 0.5 mol/L H_2SO_4 ethanol-water solution (A) or 1 mol/L NaOH ethanol-water solution (B) at 60 ℃.

stages. In the first stage, the degradable structure in the cross-linking network is degraded to form soluble segments. In the second stage, amide bonds on the soluble segments were hydrolyzed to produce soluble small molecules.

In 0.5 mol/L H_2SO_4 ethanol-water solution, the W_d change of dry samples and wet samples are shown in Figure 8. The detailed degradation process and mechanism can be as follows:

Within the first 5 h, the cross-linking network on the surface of the sample began the first stage of degradation, generating carboxyl, amino and aliphatic segments. Then, the solvent and sulfuric acid were absorbed into the surface cross-linking network, so that the W_d of sample was increased in both dry and wet states.

In 5~20 h, the W_d of wet sample gradually increased, while the W_d of dry sample slowly decreased. It indicates that sulfuric acid penetrates the deep cross-linking network, causing the internal cross-linking points to begin the first stage of degrada-

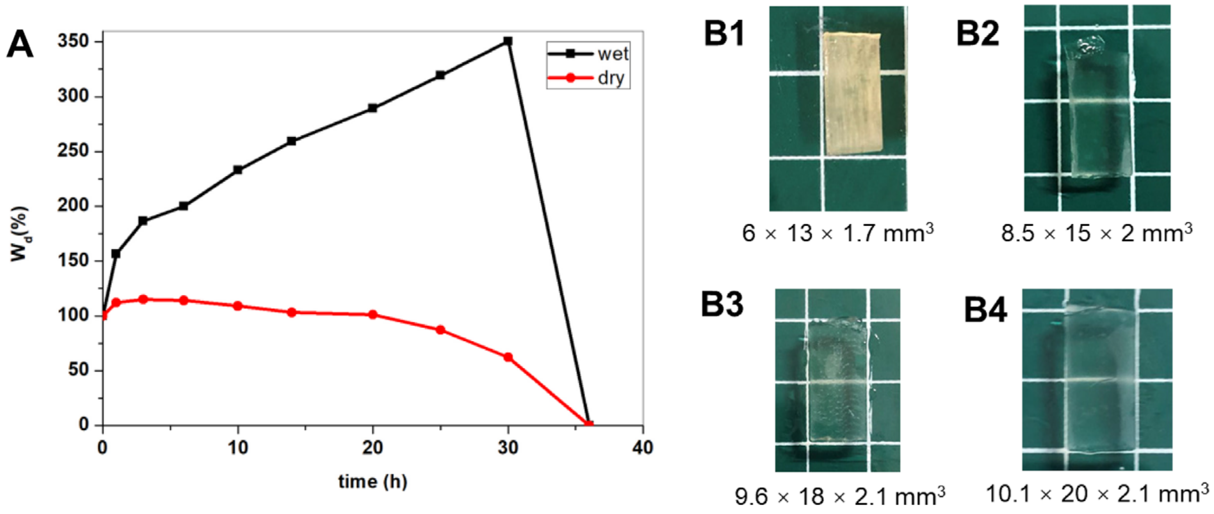


Figure 8. The W_d *vs*. time of TAHT-EA cured epoxy resin immersed in 0.5 mol/L H_2SO_4 ethanol-water solution at 60 ℃ (A) and the dimensional changes for (B1) 0 h, (B2) 8 h, (B3) 20 h, and (B4) 30 h.

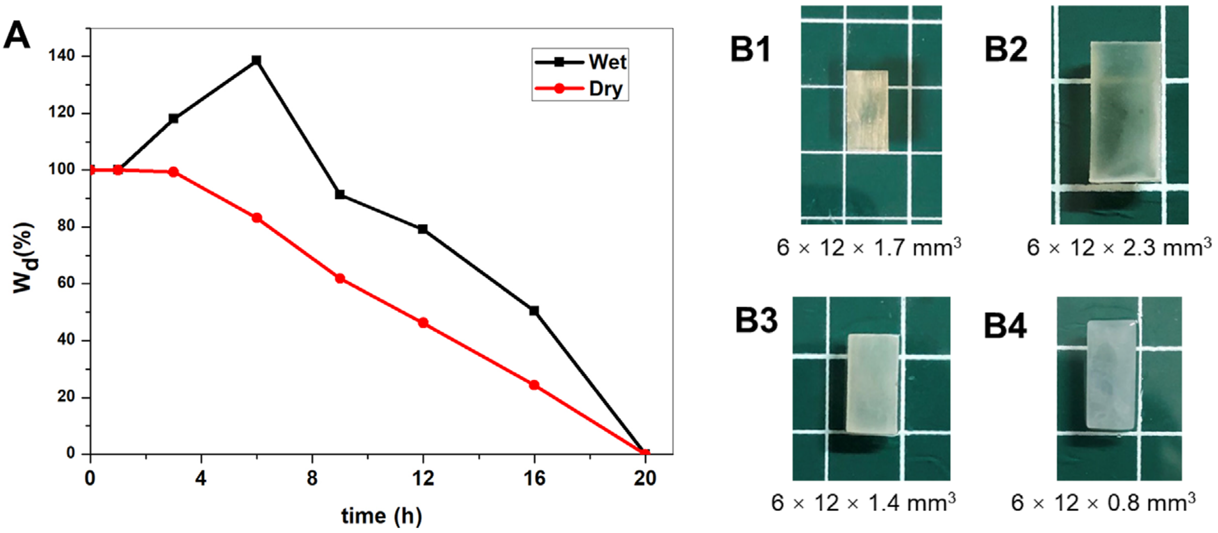


Figure 9. The W_d *vs*. time of TAHT-EA cured epoxy resin immersed in 1 mol/L NaOH ethanol-water solution at 60 ℃ (A) and the dimensional changes for (B1) 0 h, (B2) 6 h, (B3) 12 h, and (B4) 16 h.

tion. At the same time, some of residual segments began the second stage of degradation, causing a small amount of mass loss.

In 20~36 h, the W_d of wet sample continued to increase until the network was disintegrated. At the same time, the W_d of dry sample dropped rapidly. It means that more and more HT structures were destroyed, and many residual segments began the second stage degradation process.

In 1 mol/L NaOH ethanol-water solution, the W_d change of dry samples and wet samples are shown in Figure 9. Throughout the degradation process, the sample became thinner and thinner. Finally, it disappeared completely at 20 h. The W_d of wet sample did not show a constant increasing trend. It started to increase after 1 h, reached 138% at 6 h, then dropped to 0. At the same time, the W_d of dry sample did not change significantly in the first 3 hours, then it decreased continuously to 0.

It illustrates that after the first stage of degradation process on the surface of the sample, the generated soluble segments and hydrophilic groups absorbed solvent and sodium hydroxide into the surface cross-linking network. However, due to the presence of $-COO^-$, it is difficult for OH^- to penetrate deeper into the internal crosslinking network. Therefore, the internal crosslinking point cannot begin degradation process until the surface cross-linking network of the sample is completely degraded into small molecules and dissolved in solvent.

4. Conclusions

In summary, TAHT can react with ethylamine by aza-Michael addition to obtain TAHT-EA. The TAHT-EA cured epoxy has the potential to gradually replace traditional thermosetting resin. It shows a lower thermo properties, the glass-transition temperature (T_g) is 61 ℃, the initial decomposition temperature lower to 205 ℃, and a relatively low crosslinked density (633 mol/m^3). However, the TAHT-EA cured epoxy shows comparable mechanical properties, the Young's modulus can be up to 2.05 GPa and tensile strength can be up to 70.9 MPa. Particularly, it can be degraded completely by 1 M H^+/OH^- solution at 60 ℃ in 36 h. It provides a research direction for solving the environmental problems caused by discarded epoxy resin products.

Supporting information: Information is available regarding the original data of the Aza-Michael addition reaction in water, and the determination of curing procedure. The materials are available *via* Internet at http://www.springer.com/13233.

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