



Synthesis and degradable property of novel sulfite-containing cycloaliphatic epoxy resins



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ABSTRACT

Liquid cycloaliphatic diepoxide containing sulfite group (**Epoxyde-S**) was designed and synthesized through the two-step reactions: the nucleophilic substitution between thionyl chloride and cyclohex-3-1-methanol, and the subsequent epoxidation. The chemical structures of the epoxidized product and its olefin precursor were confirmed by FTIR and ^1H NMR spectra. Different from conventional thermosetting epoxy resins, the cured **Epoxyde-S** started to decompose at 185 °C. The apparently lower degradable temperature is desirable for reworkable electronic packaging materials because the dismantlement of waste electronic products or the replacement and repair of faulty chips become convenient. Moreover, after co-curing between **Epoxyde-S** and the commercial cycloaliphatic diepoxide **ERL-4221**, the thermal degradation temperatures of the copolymers were tunable in the range from 185 to 323 °C by varying the ratio of two monomers. The unique degradation behaviors were investigated by means of computer calculation, thermogravimetric analysis, and FTIR spectra.

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1. Introduction

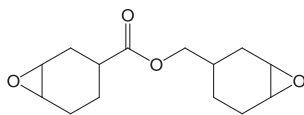
Conventional epoxy resins are high performance thermosetting materials that have been widely applied in the field of microelectronic packaging due to their excellent chemical and heat resistance [1–6]. The above advantages are mainly contributed to the three-dimensional network of the cured epoxy resins. Nevertheless, with the rapid development of microelectronic industry, the large amount of electronic wastes annually generated brings about an ever-increasing pressure on environment since, once an electronic product has been encapsulated by epoxy resin, the highly cross-linked structure makes it extremely difficult to be dismantled in the event that the repair, replacement and recycle of the defective electronic component are needed [7–9]. Based on the economic and environmental considerations, and because of the strict regulation of the Waste Electrical and Electronic Equipment directives (WEEE Directives), it is urgent to develop new epoxy packaging materials with reworkable function [10–13].

A key point to reworkable epoxy resin is that the three-dimensional network can be decrosslinked in a controlled way. To address this issue, Buchwalter et al. reported that the incorporation of acetal and ketal linkages in the epoxy network led to an easy

dissolution in acid-containing solvents [14]. Ober et al. synthesized a series of epoxies containing heat-cleavable groups and found that the cured products decomposed at temperature ranging from 200 to 300 °C [15,16]. Wong et al. introduced thermally degradable carbamate and carbonate linkages into epoxies which showed that the cross-linked network pyrolyzes at temperature between 200 and 300 °C [17,18]. Shirai et al. created a series of photo-cross-linkable epoxies containing thermally cleavable sulfonate ester groups. These cross-linked polymers could become soluble in organic solvents or water after heating at 120–200 °C [19–21]. We previously reported the synthesis of liquid cycloaliphatic diepoxides bearing secondary and tertiary carbon–ether linkages, and the cured epoxies displayed the thermal decomposition at around 220 °C [22]. Recently, two liquid di- and tri-functional cycloaliphatic epoxy resins containing thermally degradable phosphate groups which underwent a quickly thermal cleavage in the 255–280 °C range were also synthesized [23].

The above reworkable epoxies can decompose at the temperature range from 200 to 300 °C. However, the degradation temperature is still slightly higher for the practical reworking operation. Our previous study [23] has demonstrated that the C–O bond in O=P–O–C– is less stable than that in the O=C–O–C– linkage, which suggests that the stability of C–O bond is strongly affected by the electron-withdrawing effect of the neighboring group. Therefore, the replacement of O=P with O=S in the diepoxide is expected to further reduce the decomposing temperature of the cured

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Scheme 1. Chemical structure of commercial diepoxide **ERL-4221**.

network. Based on the above consideration, in this paper, we designed and synthesized a sulfite-containing cycloaliphatic diepoxide (**Epoxide-S**). The focus of the present work is to (i) synthesize and well characterize a novel diepoxide **Epoxide-S**, (ii) study the thermal degradation mechanism of the cured **Epoxide-S**, and (iii) tune the thermal degradation temperature by co-curing between **Epoxide-S** and **ERL-4221** through varying the ratios of two monomers.

2. Experimental

2.1. Materials

Thionyl chloride, cyclohex-3-enyl-1-methanol and OXONE (a monopersulfate compound: $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) were purchased from Shanghai Regent Company and used without further purification. Commercial epoxy resin **ERL-4221** was obtained from Xinjin Chemicals Company; its chemical structure is shown in [Scheme 1](#). Latent thermal cationic initiator KWM-753 (a triarylsulfonium salt) was provided by Beijing Kewei Materials Co., Ltd. Other chemical reagents were of analytical reagent grade and used as received.

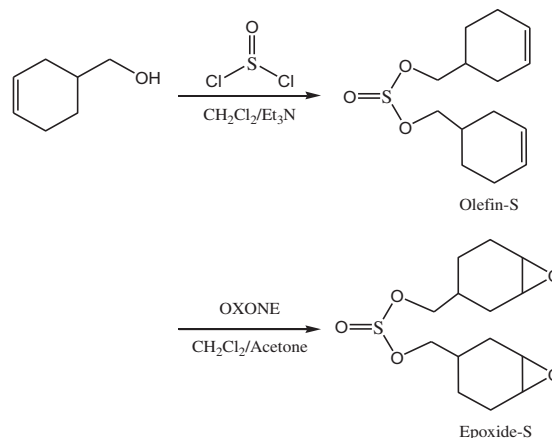
2.2. Synthesis

2.2.1. Synthesis of bis(cyclohex-3-enylmethyl) sulfite (Olefin-S)

Cyclohex-3-enyl-1-methanol (20.2 g, 0.18 mol) and triethylamine (20 mL, 0.144 mol) were dissolved in anhydrous dichloromethane (70 mL) in a 250 mL four-necked flask equipped with a mechanical stirrer, a thermometer and a dropping funnel with a drying tube. Thionyl chloride (7.14 g, 0.06 mol) was added dropwise from the dropping funnel while maintaining the mixture at 0°C with an ice bath. After reaction, the mixture was washed with 10% of dilute HCl aqueous solution, 10% of Na_2CO_3 aqueous solution, and deionized water to neutrality. The organic phase was dried over anhydrous MgSO_4 . After filtration and concentration under reduced pressure, there was obtained 12.6 g bis(cyclohex-3-enylmethyl) sulfite as a colorless liquid having a bp of 138°C at 5 mmHg. Yield: 78%. FTIR (cm^{-1}): 3024, 2917, 2839, 1652, 1435, 1389, 1206, 1089, 1045, 982, 933, 806, 729, 658. ^1H NMR (CDCl_3/TMS , ppm): 5.61–5.73 (m, 4H, =CH–), 3.75–4.01 (m, 4H, $-\text{CH}_2-\text{O}$), 1.23–2.22 (m, 14H, $-\text{CH}_2-$, $-\text{CH}-$).

2.2.2. Synthesis of bis(3,4-epoxycyclohexylmethyl) sulfite (**Epoxide-S**)

Olefin-S (8.1 g, 30 mmol) was dissolved in dichloromethane (90 mL) and acetone (90 mL) in a 1000 mL three-necked flask equipped with a mechanical stirrer and two dropping funnels. Then a phosphate buffer (pH 7.5, 60 mL) and 18-crown-6 ether (0.9 g, 3.0 mmol) as a phase transfer catalyst were added into the mixture. At 0°C , OXONE and ethylenediaminetetraacetic acid (0.06 g, 0.2 mmol) dissolved in 240 mL deionized water were added dropwise to the stirred mixture. The obtained mixture was allowed to react for 3.5 h. The organic phase was then isolated, and the aqueous phase was extracted with dichloromethane. The organic portions were combined, washed with deionized water, and dried over anhydrous MgSO_4 . After filtration and concentration, there



Scheme 2. Synthetic route to the sulfite-containing **Epoxide-S**.

was obtained 7.7 g bis(3,4-epoxycyclohexylmethyl) sulfite as a colorless liquid. Yield: 85%. FTIR (cm^{-1}): 2933, 1437, 1386, 1196, 1083, 1029, 973, 940, 920, 844, 808, 793, 739. ^1H NMR (CDCl_3/TMS , ppm): 3.59–3.92 (m, 4H, $-\text{CH}_2-\text{O}$), 3.12–3.25 (m, 4H, C–H on epoxide ring), 1.00–2.27 (m, 14H, $-\text{CH}_2-$, $-\text{CH}-$).

2.3. Curing of the epoxides

The homopolymer network of **Epoxide-S** was prepared via cationic polymerization using KWM-753 as an initiator with a molar stoichiometric ratio of 1:0.005. The curing reaction took place at 70°C for 2 h, then at 80°C for 4 h, and finally at 90°C for 2 h. The copolymers of **Epoxide-S/ERL-4221** with the **Epoxide-S** content of 25 wt%, 50 wt% and 75 wt% were prepared under the same curing condition as **Epoxide-S**.

2.4. Measurements

Fourier-transform infrared spectra (FTIR) were recorded on a Nicolet 5700 spectrometer. ^1H NMR spectra were recorded on an INOVA-400 NMR spectrometer (Varian) in CDCl_3 using tetramethylsilane (TMS) as an internal standard. TGA measurements were performed with a NETZSCH TG 209 thermal analyzer from 25 to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Differential scanning calorimetry (DSC) was recorded on a NETZCH DSC 204 thermal analyzer using N_2 as a purge gas (20 mL/min) at a heating rate of $10^\circ\text{C}/\text{min}$. About 5–10 mg sample was put into the aluminum pan for DSC measurement. Computational calculations were conducted with Gaussian 03W program package. The optimized geometries and energies were calculated with the 6-31G (d)-level calculations based on the restricted Hartree–Fock calculation method. Viscosities of epoxides were measured with a rotary viscometer (NDJ-1) in the temperature range of 25– 85°C .

3. Results and discussion

3.1. Synthesis and characterization of the diepoxide **Epoxide-S**

The synthetic route of cycloaliphatic diepoxide containing sulfite linkage is presented in [Scheme 2](#). The synthesis of Olefin-S was achieved via the nucleophilic substitution reaction of thionyl chloride with cyclohex-3-enyl-1-methanol in good yield (78%). Subsequently, through the moderate epoxidation by OXONE oxidant, **Epoxide-S** was readily obtained with yield of 85%.

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