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Synthesis and properties of novel liquid ester-free reworkable cycloaliphatic diepoxides for electronic packaging application

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Abstract

Four novel liquid cycloaliphatic diepoxides, with two epoxycyclohexyl moieties linked via –O– (EpoI), $-OCH_2CH_2O-$ (EpoII), $-OCH(CH_3)CH_2O-$ (EpoIII), $-OCH(CH_3)CH_2CH(CH_3)O-$ (EpoIV), respectively, and their diene precursors were synthesized and characterized. These diepoxides could be readily cured with hexahydro-4-methylphthalic anhydride (HMPA) using Iron (III) acetylacetonate as curing accelerator. The thermal and mechanical properties of cured products were examined by differential scanning calorimetry (DSC), thermal mechanical analysis (TMA) and dynamic mechanical analysis (DMA). The thermogravimetric analysis (TGA) data revealed that, the cured EpoI and EpoII had similar thermal decomposition onset temperature to the commercial ERL-4221™ (> 300 °C), whereas the cured EopIII and EpoIV, having secondary or tertiary carbon–ether linkages, started to decompose at obviously lower temperature (around 220 °C), which just lay in the desired reworkability temperature range (200–300 °C). The higher glass transition temperature (> 120 °C) and moderately low thermal decomposition temperature made EpoIII and EpoIV suitable candidates for future reworkable flip chip electronic packaging application.

Keywords: Cycloaliphatic diepoxide; Reworkability; Electronic packaging

1. Introduction

Currently, the trend of developing semiconductor devices is the miniaturization and complex functionality of the electronic products [1]. In recent years, flip chip technology is attracting attention for integrated circuit (IC) packaging because of its higher inputs/outputs (I/O) count, smaller packaging area, high reliability and low cost. In flip chip packaging process, the faced-down IC chip is directly mounted onto the circuit board, and the space between chip and circuit board is filled with a liquid epoxy (often referred as underfill resin), and then cured. The underfill resin serves to evenly distribute stress caused by thermal cycling, improve heat shock properties, and enhance the reliability of structure [2,3].

Cycloaliphatic epoxy resins have long been used in a variety of industrial applications, such as coatings, reactive diluents, molded compounds, vacuum pressure impregnation of coils, encapsulation of electronic circuit elements, and printed circuit board coatings, due to their low viscosity prior to curing, and good heat and chemical resistance, superior mechanical and electrical properties after curing [4–6]. Unlike the aromatic epoxides, the cycloaliphatic epoxides do not have strong UV chromophore groups, and therefore are highly resistant to ultraviolet light and more durable for outdoor applications such as electrical insulators. Moreover, the synthesis of cycloaliphatic epoxides involves the peracid epoxidation of olefins rather than the condensation of epichlorohydrin with phenols so that the cycloaliphatic epoxides are essentially free of chloride. For these reasons, the cycloaliphatic epoxides have been widely used in microelectronic packaging applications [7].

After curing, the insoluble and infusible crosslinking network endows thermosetting epoxy resins with excellent long-term use reliability. However, this intractability also brings about severe problems in the practical flip chip process where unknown bad die often needs to be removed and replaced to reduce cost. Especially for the multi chip module (MCM) packaging, in which several chips are mounted onto one high-density board, if one chip is

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damaged, the whole MCM integrated circuit will become useless. To solve this problem, the effective way is to adopt thermally reworkable underfill epoxies. In this way, the cured epoxy network can break down by locally heating to a desired temperature and the faulty chip could be replaced. This type of approach was proposed by S. Yang [8], who synthesized several epoxides containing secondary or tertiary ester bonds and which started to decompose at temperature between 200 and 300 °C. Thereafter, L. Wang reported a series of diepoxides containing carbamate and carbonate groups [9,10] that also degraded between 200 and 300 °C.

Generally speaking, as thermally reworkable underfill materials, epoxides should meet four primary requirements: (i) epoxides should be liquid at room temperature prior to curing; (ii) epoxides should not decompose during the curing reaction; (iii) the cured epoxy resin should retain thermal stability before 200 °C; (iv) the cured epoxy network could rapidly decompose in the temperature region of 200–300 °C, which is the desirable reworkability temperature range for the electronic packages based on organic printed circuit board substrates.

A review of epoxides reported in the literature revealed that, most of conventional and reworkable cycloaliphatic epoxides are ester bonds-containing compounds [11–13] in which the epoxycyclohexyl moiety are linked via ester bonds (e.g. ERL-4221). Under the high temperature and moist environment, the ester bonds can hydrolyze and yield large amount of carboxylic acid groups, which may cause severe erosion to metal wire on integrated circuit and shorten the working life of electronic device.

The purpose of this research is to synthesize a series of ester-free cycloaliphatic epoxides. The cycloaliphatic structure increases the likelihood that the synthesized epoxides will be liquid at ambient temperature. Different aliphatic groups were incorporated between two epoxycyclohexyl moieties to adjust the thermal decomposition temperature, whereas the epoxycyclohexyl linkage via ether bonds instead of ester bonds is expected to greatly improve its moist resistance. This paper describes their syntheses and characterizations, as well as the thermal and mechanical properties of cured epoxides.

2. Experimental

2.1. Materials

Cyclohexene and tetrahydrofuran were refluxed with sodium and distilled before use. Carbon tetrachloride was dried with phosphorus pentoxide. Glycol, 1,2-propanediol, 2-methyl-2, 4-pentanediol, *m*-chloroperoxybenzoic acid, and 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexane carboxylate (trade name ERL-4221) were used as purchased from Aldrich Chemical Company. 3-Bromocyclohexene was prepared from cyclohexene and *N*-bromosuccinimide according to the literature [14]. 3-Hydroxycyclohexene was obtained by the hydrolysis of 3-bromocyclohexene [15]. Hexahydro-4-methylphthalic anhydride (HMPA) and Iron (III) acetylacetonate (Acros organics) was used as curing agent and curing accelerator, respectively.

2.2. Characterizations

Fourier transform infrared (FTIR) spectra were recorded on a Perkin–Elmer Model 7 FTIR spectrometer. ^{1}H NMR spectra were measured on a DMX-300 NMR Spectrometer (Bruker) in chloroform-d$_1$ using tetramethylsilane as an internal standard. Elemental analyses (EA) were carried out on a Heraeus CHN-O Rapid Analyzer. Dynamic mechanical analyses (DMA) were performed using a Perkin–Elmer 7 Series Thermal Analysis System at the frequency of 1 Hz and the heating rate of 5 °C/min under nitrogen atmosphere. Differential scanning calorimeter (DSC) thermograms were obtained by using a Perkin-Elmer 7 Series Thermal Analysis System at the heating rate of 10 °C/min under nitrogen atmosphere. Thermogravimetric analyses (TGA) were also performed on a Perkin–Elmer 7 Series Thermal Analysis System in the temperature of 50–600 °C at the heating rate of 20 °C/min under nitrogen atmosphere. Thermal expansion plots were recorded on a DuPont TMA 2940 Thermomechanical Analyzer at the heating rate of 5 °C/min under nitrogen atmosphere, from which the coefficient of thermal expansion (CTE) were calculated according to the slopes of curves. The epoxy equivalent weights (EEW) of diepoxide were measured according to the titration procedure as described in the literature [16].

2.3. Syntheses

Four cycloaliphatic diepoxides, EpoI–EpoIV, were designed and synthesized. Their structures are shown in Fig. 1.

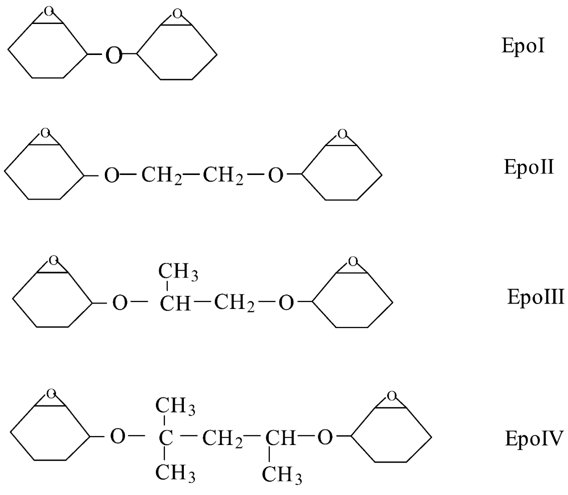


Fig. 1. Structures of synthesized diepoxides EpoI–EpoIV.

2.3.1. Cyclohexenyl ethers syntheses (*I–IV*)

Bis (2-*cyclohexenyl*) *ether* (**I**). Into a 500 ml three-necked round-bottom flask equipped with a thermometer, a water separator with refluxing condenser, and a magnetic stirring bar were added 96.3 g (0.98 mol) of 3-hydroxycyclohexene, 1.1 g (0.006 mol) of *p*-toluenesulfonic acid, and 250 ml of benzene. The mixture was heated to 80 °C and refluxed for 2 h. After cooling, the reaction mixture was washed twice with 1.0% solution of sodium hydroxide (2 × 100 ml) and finally was washed with deionized water to neutrality. The organic layer was dried over anhydrous sodium sulfate, and then the solvent was stripped off and the crude product was purified by fractional distillation under reduced pressure. There was obtained 66.0 g (0.37 mol, yield 76%) of bis (2-cyclohexenyl) ether (**I**), as a colorless liquid having a bp of 104–105 °C at 12 mm Hg. Elemental analysis for $C_{12}H_{18}O$: calcd C, 80.90; H, 10.11. Found C, 80.74; H, 9.74; IR (cm^{-1}): 3026, 2936, 2864, 1650, 1437, 1393, 1311, 1162, 1138, 1077, 1015, 941, 724, 659, 581. ^1H NMR ($CDCl_3$, ppm): 5.78–5.80 (d; 4H, =CH), 3.98 (s; 2H, CHO), 1.65–2.00 (m; 12H, CH_2).

1,2-*Bis* (2-*cyclohexenyloxy*) *ethane* (**II**). 27.0 g (1.12 mol) of sodium hydride, 1.0 g of 18-crown-6-ether (phase transfer catalyst), and 240 ml of tetrahydrofuran were added into a 1000 ml four-necked round-bottom flask equipped with a thermometer, a nitrogen inlet, a addition funnel, and a mechanical stirrer. The mixture was stirred at room temperature for 0.5 h and then a solution of 11.7 g (0.19 mol) glycol in 40 ml of tetrahydrofuran was added dropwise over 1 h under nitrogen atmosphere and maintained at this temperature for 1 h. The reaction mixture was then heated to 45 °C, and a solution of 106 g (0.66 mol) 3-bromocyclohexene in 60 ml of tetrahydrofuran was added dropwise to the above mixture with vigorous stirring over a period of 2 h and the stirring was continued for 36 h at 45 °C. After cooling, the reaction mixture was filtered and washed twice with tetrahydrofuran (2 × 50 ml). The light yellowish filtrate was concentrated using a rotary evaporator. The crude product was purified by fractional distillation under reduced pressure. There was obtained 24.5 g (0.11 mol, yield 58%) of 1,2-bis (2-cyclohexenyloxy) ethane (**II**), as a colorless liquid having a bp of 138–140 °C at 7 mm Hg. Elemental analysis for $C_{14}H_{22}O_2$: calcd C, 75.63; H, 9.97. Found C, 75.44; H, 10.01; IR (cm^{-1}): 3026, 2934, 2862, 1650, 1451, 1395, 1317, 1163, 1101, 939, 725, 672, 572. ^1H NMR ($CDCl_3$, ppm): 5.79–5.83 (d; 4H, =CH), 3.90 (s; 2H, CHO), 3.60–3.65 (m; 4H, CH_2O), 1.52–2.02 (m; 12H, CH_2).

1,2-*Bis* (2-*cyclohexenyloxy*) *propane* (**III**). The similar etherification procedure to that used for 1,2-bis (2-cyclohexenyloxy) ethane was followed, except that the binary alcohol used was 1,2-propanediol instead of glycol. The yield was 52% and the product, 1,2-bis (2-cyclohexenyloxy) propane (**III**), was a colorless liquid having a bp of 142–144 °C at 5 mm Hg. Elemental analysis for $C_{15}H_{24}O_2$: calcd C, 76.22; H, 10.24. Found C, 76.09; H, 10.17; IR (cm^{-1}): 3026, 2934, 2863, 1650, 1451, 1395, 1316, 1101, 1014, 947, 725, 673, 569. ^1H NMR ($CDCl_3$, ppm): 5.72–5.86 (d; 4H, =CH), 3.88–4.05 and 3.48–3.54 (m, m; 3H, CHO), 3.67–3.71 (d; 2H, CH_2O), 1.51–2.01 (m; 12H, CH_2), 1.16–1.18 (d; 3H, CH_3).

2-*Methyl*-2,4-*bis* (2-*cyclohexenyloxy*) *pentane* (**IV**). A similar etherification procedure to that used for 1,2-bis (2-cyclohexenyloxy) ethane was followed, except that the binary alcohol used was 2-methyl-2,4-pentanediol instead of glycol. A colorless liquid, 2-methyl-2,4-bis (2-cyclohexenyloxy) pentane (**IV**), was obtained with 38% yield, having a bp of 154–156 °C at 2 mm Hg. Elemental analysis for $C_{18}H_{30}O_2$: calcd C, 77.65; H, 10.86. Found C, 77.48; H, 10.87; IR (cm^{-1}): 3026, 2933, 2864, 1651, 1449, 1366, 1317, 1231, 1157, 1067, 1015, 988, 931, 904, 723, 669. ^1H NMR ($CDCl_3$, ppm): 5.58–5.79 (d; 4H, =CH), 3.78–4.03 (m; 3H, CHO), 1.55–1.98 (m; 14H, CH_2), 1.17–1.25 (t; 9H, CH_3).

2.3.2. Diepoxides syntheses (EpoI–EpoIV)

Bis (2,3-*epoxycyclohexyl*) *ether* (EpoI). A 2000 ml three-necked round-bottom flask equipped with a thermometer, addition funnel and a mechanical stirrer was first cooled with a ice bath for 10 min. It was then charged with 139 g (0.803 mol) of *m*-chloroperoxybenzoic acid (*m*-CPBA) and 800 ml of methylene chloride, and this mixture was cooled to 0 °C with stirring. Into this mixture was added dropwise a solution of 65 g (0.365 mol) bis (2-cyclohexenyl) ether (**I**) in 60 ml of methylene chloride over 2 h while the reaction mixture was maintained at 0 °C. After further stirring for a period of 10 h at 0 °C, the reaction mixture was filtered. The filtrate was washed with a solution of sodium sulfite, and then a solution of saturated sodium bicarbonate, and finally, deionized water to neutrality. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator and distilled under reduced pressure to give final product. There was obtained 68 g (90% yield) of the pure product, bis (2,3-epoxycyclohexyl) ether (EpoI), as a colorless liquid having a bp of 148–149 °C at 15 mm Hg. Elemental analysis for $C_{12}H_{18}O_3$: calcd C, 68.57; H, 8.57. Found C, 68.53; H, 8.30; IR (cm^{-1}): 2994, 2940, 2865, 1457, 1376, 1353, 1311, 1248, 1176, 1091, 1033, 978, 934, 857, 828, 801, 774. ^1H NMR ($CDCl_3$, ppm): 3.79–3.83 (s; 2H, CHO), 3.06–3.27 (m; 4H, CH on epoxide ring), 1.21–2.04 (m; 12H, CH_2).

1,2-*Bis* (2,3-*epoxycyclohexyloxy*) *ethane* (EpoII). The similar epoxidation procedure to that for bis (2,3-epoxycyclohexyl) ether was carried out, except that the etheric compound used was 1,2-bis (2-cyclohexenyloxy) ethane instead of bis (2-cyclohexenyl) ether. A liquid product, 1,2-bis (2,3-epoxycyclohexyloxy) ethane (EpoII), was obtained with 88% yield and having a bp of 160–162 °C at 3 mm Hg. Elemental analysis for $C_{14}H_{22}O_4$: calcd C, 66.12; H, 8.72. Found C, 66.15; H, 8.69; IR (cm^{-1}): 2987, 2940, 2866, 1457, 1372, 1345, 1317, 1253, 1102, 977, 891, 860, 825, 796, 776. ^1H NMR ($CDCl_3$, ppm): 3.61–3.77 (d, s; 6H, CHO + CH_2O), 3.12–3.24 (d; 4H, CH on epoxide ring), 1.19–2.01 (m; 12H, CH_2).

1,2-*Bis* (2,3-*epoxycyclohexyloxy*) *propane* (EpoIII). The similar epoxidation procedure to that used for bis (2,3-epoxycyclohexyl) ether was carried out, except that the etheric compound used was 1,2-bis (2-cyclohexenyloxy) propane instead of bis (2-cyclohexenyl) ether. A liquid product, 1,2-bis (2,3-epoxycyclohexyloxy) propane (EpoIII), was obtained with 83% yield and having a bp of 167–169°C at 2 mm Hg. Elemental analysis for $C_{15}H_{24}O_4$: calcd C, 67.14; H, 9.01. Found C, 67.02; H, 8.96; IR (cm^{-1}): 2939, 2867, 1455, 1374, 1316, 1255, 1102, 978, 919, 856, 827, 796. ^1H NMR ($CDCl_3$, ppm): 3.58–3.78 (m, m; 5H, CHO + CH_2O), 3.08–3.18 (m; 4H, CH on epoxide ring), 1.09–1.99 (m; 15H, CH_2 + CH_3).

2-*Methyl*-2,4-*bis* (2,3-*epoxycyclohexyloxy*) *pentane* (EpoIV). The similar epoxidation procedure to that used for bis (2,3-epoxycyclohexyl) ether was carried out, except that the etheric compound used was 2-methyl-2,4-bis (2-cyclohexenyloxy) pentane instead of bis (2-cyclohexenyl) ether. A viscous liquid product, 2-methyl-2,4-bis (2,3-epoxycyclohexyloxy) pentane (EpoIV), was obtained with 80% yield and having a bp of 177–178 °C at 1 mm Hg. Elemental analysis for $C_{18}H_{30}O_4$: calcd C, 69.64; H, 9.74. Found C, 69.55; H, 9.63; IR (cm^{-1}): 2939, 2865, 1456, 1369, 1250, 1164, 1128, 1073, 1007, 977, 893, 861, 798, 776. ^1H NMR ($CDCl_3$, ppm): 3.66–3.78 (m; 3H, CHO), 2.99–3.18 (m; 4H, CH on epoxide ring), 1.16–1.95 (m; 23H, CH_2 + CH_3).

2.3.3. Curing of diepoxides

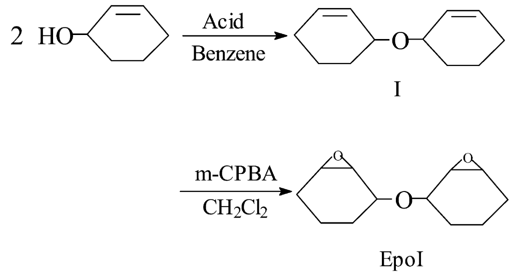
Diepoxides (EpoI–EpoIV) and hexahydro-4-methylphthalic anhydride (HMPA) as hardener were mixed with 1:1 molar ratio at room temperature. Into this homogeneous mixture was added 1.0 wt% of iron (III) acetylacetonate as curing accelerator and mixed. The mixture was cured first at 120 °C for 2 h, then at 140 °C for 8 h, and finally at 170 °C for 4 h.

As a comparison, commercial diepoxide ERL-4221™ was also mixed with HMPA and iron (III) acetylacetonate in the same ratio and cured under the same conditions as above.

3. Results and discussion

3.1. Synthesis and characterization

As shown in Schemes 1 and 2, four cycloaliphatic diepoxides containing ether linkages were synthesized by the following two steps: syntheses of dienes (**I**–**V**) and then epoxidation of dienes via peracid to give the epoxides (EpoI–EpoIV). EpoI is a cycloaliphatic diepoxide containing two symmetrical epoxycyclohexyl groups linked with an oxygen atom (an ether bond). EpoII, EpoIII, and EpoIV are cycloaliphatic diepoxides containing two primary carbon–ether groups, one primary and one secondary carbon–ether groups, and one secondary and one tertiary carbon–ether groups, respectively.

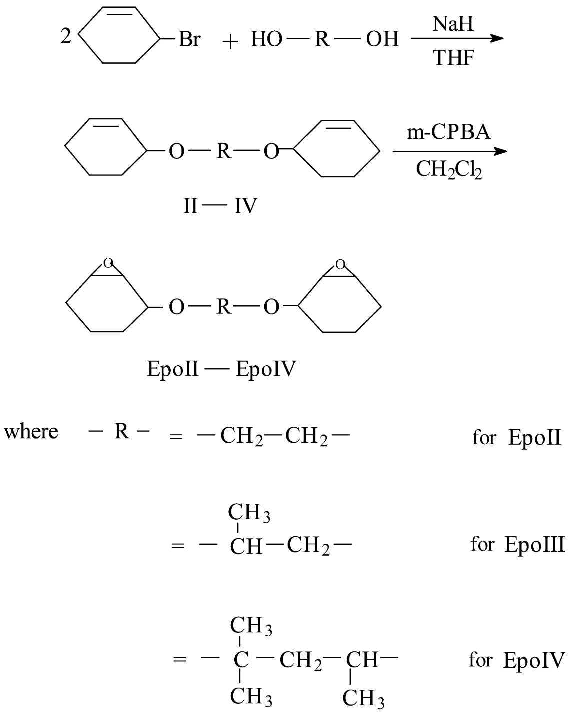


Scheme 1.

According to the literature [15], **I** could be easily obtained with high yield (over 75%) via the dehydration of 3-hydroxycyclohexene catalyzed by *p*-toluenesulfonic acid. Using sodium hydride as catalyst and 18-crown-6-ether as phase transfer catalyst, under nitrogen atmosphere at 45 °C, **II**, **III** and **IV** could be prepared in good yield (40–60%) from 3-bromocyclohexene with glycol, 1,2-propanediol and 2-methyl-2, 4-pentanediol, respectively. It was found that the yields of products ranked in the order of **II** > **III** > **IV**, due to the increasing steric hindrance effect.

Four dienes **I**–**IV** were subsequently epoxidized using *m*-chloroperoxybenzoic acid in methylene chloride at 0–5 °C to give the desired diepoxides EpoI–EpoIV in a yield of 80–90%.

The dienes **I**–**IV** and diepoxides EpoI–EpoIV were characterized by the elemental analyses, FTIR and ^1H NMR spectra methods. The measured elemental analysis data of



Scheme 2.

dienes and synthesized diepoxides were in good agreement with the calculated value. In the FTIR spectra of dienes **I**–**IV**, the peaks at 3024, 1650, 725, and 670 cm^{-1} correspond to the absorptions of cycloaliphatic double bonds in dienes. A strong characteristic band for the aliphatic ether linkage was observed at about 1100 cm^{-1} in each diene. In the FTIR spectra of diepoxides EpoI–EpoIV, the previous absorptions of double bonds existed in dienes disappeared, but the characteristic bands of the oxirane ring fused to cyclohexane appeared at about 825, 800, 755 cm^{-1} in each diepoxide. These results indicated that the double bonds in the dienes were completely converted into epoxy groups.

In the ^{1}H NMR spectra of dienes **I**–**IV** (Fig. 2), all the signals corresponding to the proposed structure were observed in chloroform-d$_1$. The protons on the double bonds (=CH) of the cyclohexenyl rings appeared at 5.58–5.86 ppm, while protons in the groups of CH–O and CH$_2$–O were observed at 3.48–4.05 ppm and 3.60–3.71 ppm, respectively. The methylene protons appeared at 1.51–2.02 ppm, and the methyl protons in **III** and **IV** were assigned at 1.16–1.25 ppm. In the ^{1}H NMR spectra of diepoxides EpoI–EpoIV (Fig. 3), the protons on oxirane ring were observed at 2.99–3.27 ppm, and those on the groups of CH–O and CH$_2$–O were observed at 3.58–3.83 ppm, Both methylene and methyl protons were observed at 1.09–2.04 ppm, while all the signals at 5.58–5.86 ppm for the double bond protons in the cyclohexenyl rings of dienes disappeared in that of each diepoxide.

Diepoxides EpoI–EpoIV synthesized are all liquid at room temperature. Their viscosities were measured using the rotary viscosimeter at 25 °C and the results are listed in Table 1. The diepoxides EpoI and EpoII have very low viscosities, and the other two diepoxides EpoIII and EpoIV also have moderately low viscosities, which could permit them to be used as underfill materials for flip-chip packaging. The EEWs of these diepoxides were measured according to the titration procedure as described in the literature [16]. Their theoretical and measured EEW values were shown in Table 1. The measured values are normally in good accordance with the theoretical value.

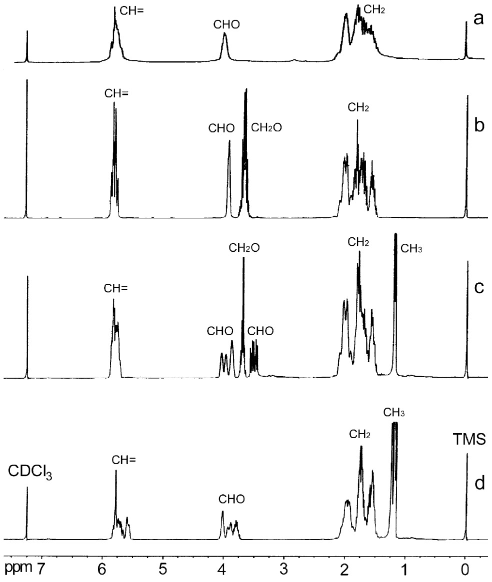


Fig. 2. ^{1}H NMR spectra of dienes: (a) **I**, (b) **II**, (c) **III**, and (d) **IV**.

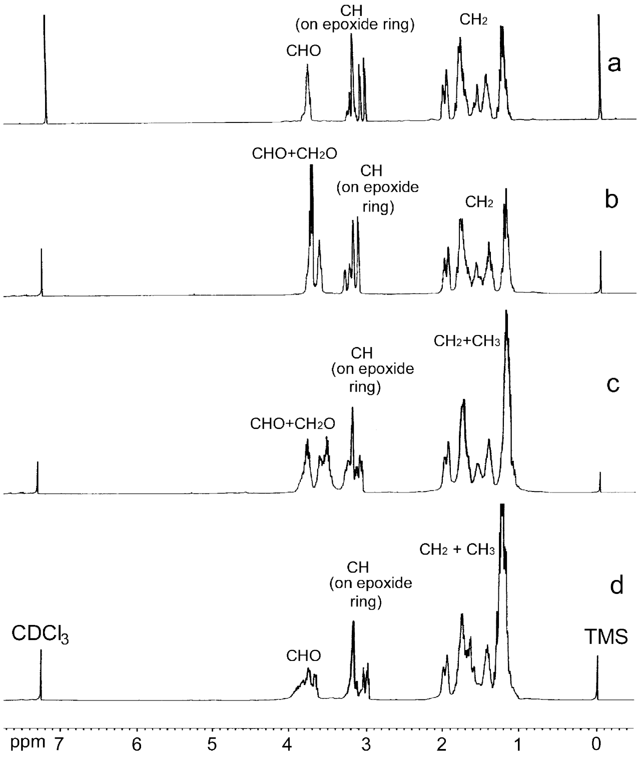


Fig. 3. ^{1}H NMR spectra of diepoxides: (a) EpoI, (b) EpoII, (c) EpoIII, (d) EpoIV.

3.2. Properties of cured epoxides

To evaluate the performances of cured diepoxides, the commercial cycloaliphatic diepoxide ERL-4221™ was used as a comparison. The results of DSC and thermomechanical analyses (TMA) were summarized in Table 2. It was shown that the glass transition temperatures of cured diepoxides, T_g-TMA and T_g-DSC, decreased in the following order: EpoI > ERL-4221 > EpoII > EpoIII > EpoIV. The highest T_g (nearly 200 °C) for EpoI was mainly due to its rigid cycloaliphatic structure and highest crosslinking density. For EpoIV, it exhibited the lowest T_g among the four

Table 1
Viscosity and EEW of diepoxides

Sample	Viscosity (mPa s, 25 °C)	EEW (g/equiv.)	
		Theoretical	Measured
EpoI	52	105	109
EpoII	85	127	133
EpoIII	260	134	139
EpoIV	1650	155	164
ERL-4221™	380	126	134

Table 2
Thermal and thermomechanical analyses of cured diepoxides

Sample	T_g-DSC (°C)	T_g-TMA (°C)	CTE × 10^5 (/°C)	
			Glassy region	Rubbery region
EpoI	195	190	6.02	13.6
EpoII	150	152	6.88	15.8
EpoIII	134	128	7.09	16.3
EpoIV	125	123	7.25	16.7
ERL-4221	176	164	6.84	15.5

Table 3
Dynamic mechanical analysis of cured diepoxides

Sample	T_g-DMA (°C)	Storage modulus (10^9 Pa)		ρ (10^{-3} mol/cm^3)
		Glassy region[a]	Rubbery region[b]	
EpoI	186	7.70	0.085	7.428
EpoII	159	1.37	0.026	2.414
EpoIII	127	1.21	0.012	1.203
EpoIV	120	0.90	0.010	1.021
ERL-4221	170	1.63	0.029	2.626

[a] Storage modulus at 30 °C.
[b] Storage modulus at T_g-DMA + 50 °C.

diepoxides because of its large flexible aliphatic group and large EEW value, i.e. the high ratio of flexible group in whole molecule and long distance within two crosslinking points resulted in its low T_g. As for the CTE of cured diepoxides, the contrary trend to the order of T_g was observed. EpoI had the lowest CTE in glassy region and rubbery region, which might result from the high crosslinking density and restricted molecular mobility [17] due to the crowded structure of two epoxycyclohexyl rings in the main chain.

Fig. 4 shows the spectra of DMA of cured samples as a function of temperature at the heating rate of 5 °C/min from room temperature to 275 °C, and the results are summarized in Table 3. The peak temperature of tan δ was taken as T_g-DMA. These five samples displayed slightly different dynamic mechanical behavior (E' and tan δ) by DMA. As seen from Table 3, the storage moduli (E') and the T_g-DMA values of cured diepoxides showed the same changing order as those of T_g-TMA and T_g-DSC mentioned above. EpoI retained highest storage moduli at both low and high temperature among the five samples, indicating that the cured diepoxide EpoI had the highest crosslinking density among them. The crosslinking density (ρ) was determined using the equation [18].

$$\rho = E'/3RT \tag{1}$$

Where E' is the storage modulus at T_g-DMA + 50 °C, R is the gas constant, and T is the absolute temperature at T_g-DMA + 50 °C.

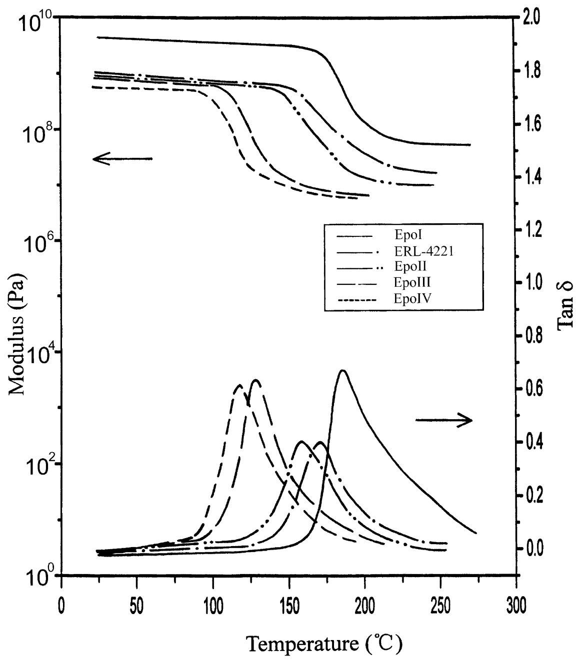


Fig. 4. DMA spectra of cured diepoxides.

The results of crosslinking densities calculated from the equation are listed in Table 3. The very high value of storage moduli and crosslinking density indicated that the cured diepoxide EpoI had a dense crosslinking structure and thus endowed it with an excellent thermal resistant property. The other two cured diepoxides, EpoII and ERL-4221, had also higher storage moduli and crosslinking densities. On the other hand, EpoIII and EpoIV exhibited reasonably low storage moduli at temperature both below and above T_g, which was attributed to the flexible aliphatic group and low crosslinking density. For EpoIII and EpoIV, the storage moduli at rubbery region was as low as about 10 MPa, which meant that their cured networks were easy to breakdown above T_g-DMA.

The thermal decomposition behaviors of cured diepoxides were investigated by TGA at the heating rate of 20 °C/min under nitrogen atmosphere, and the results were summarized in Table 4. The samples of EpoI, EpoII, and ERL-4221 started to degrade at 304–321 °C (Fig. 5), then gave 10 wt% weight loss at 315–340 °C, 50 wt% weight

Table 4
Thermogravimetric data of cured diepoxides

Sample	IDT[a] (°C)	Temperature at characteristic weight loss (°C)			Residue (%)
		10%	50%	80%	600 °C
EpoI	312	338	379	416	3.7
EpoII	304	315	375	401	2.4
EpoIII	239	282	360	390	0.9
EpoIV	222	267	333	359	0.2
ERL-4221	321	340	380	429	4.4

[a] IDT is the initial decomposition temperature of cured diepoxide.

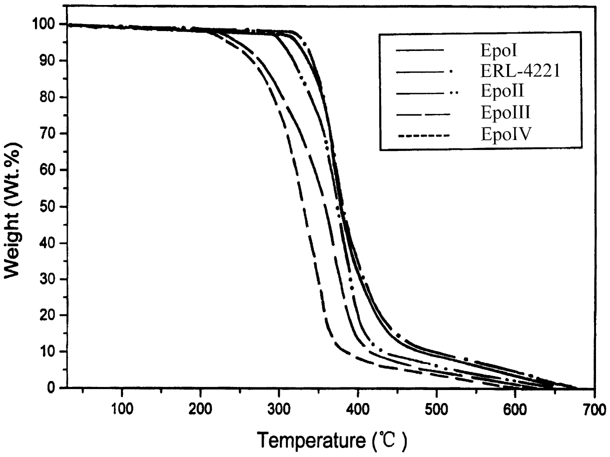


Fig. 5. TGA curves of cured diepoxides.

loss at 375–380 °C, 80 wt% weight loss at 401–429 °C, and finally reserved residue less than 5 wt% at 600 °C. The samples of EpoIII and EpoIV began to decompose at 222–239 °C, followed 10 wt% weight loss at 247–262 °C, 50 wt% weight loss at 333–360 °C, 80 wt% weight loss at 359–390 °C, and finally reserved residue less than 1 wt% at 600 °C. The different decomposition onset temperatures of these five samples could be resulted from the different bond strengths. It was known that the bond energy for primary carbon–ester bond was much higher than that for secondary or tertiary carbon–ester bond [13], and that the primary carbon–ester bond linked epoxy had a higher thermal decomposition activation energy than the secondary or tertiary carbon–ester bond linked epoxy [10]. Therefore, it is reasonable to elucidate that the initial decomposition temperatures of the samples of EpoIII and EpoIV, which contain a secondary carbon–ether linkage and a tertiary carbon–ether linkage, respectively, were much lower than those of the samples based on EpoI, EpoII, and ERL-4221. For the later three epoxides, there were only primary carbon–ether linkages or primary carbon–ester linkage, so they displayed strong thermal stabilities. From these initial investigations, both EpoIII and EpoIV showed a desired onset decomposition temperature at around 220 °C, which is in the ideal reworkable temperature range for flip chip underfill packaging. Therefore, it might be believed that EpoIII or EpoIV should become promising candidates for future reworkable flip chip application.

4. Conclusions

Four novel ester-free cycloaliphatic diepoxides containing thermally cleavable aliphatic ether groups and their diene precursors were designed and synthesized. Their structures were confirmed by FTIR, EA, EEW and ^{1}H NMR methods. The thermal and mechanical properties of cured diepoxides with hexahydro-4-methylphthalic anhydride (HMPA) were examined by thermomechanical analysis, DSC, TGA, and dynamic mechanical analysis. Before curing, EpoI, EpoII and EpoIII exhibited viscosities at room temperature of 52, 85 and 260 mPa s, respectively, and to the best of our knowledge, which are among the lowest viscosities for liquid diepoxies reported previously in the literature. After curing, the samples had moderately high glass transition temperatures (above 120 °C) and storage moduli in glassy region (around 1.5 GPa) as well as similar thermal expansion coefficients to that of commercial ERL-4221™. Furthermore, by systematically varying the aliphatic linking groups between epoxycyclohexyl moieties, the initial decomposition temperatures of cured samples could be adjusted over a wide range between 222 and 312 °C; for example, the samples EpoIII and EpoIV, based on secondary or tertiary carbon–ether linkages, started to decompose at 220 and 239 °C, respectively, which could meet the temperature requirement as reworkable underfill packaging materials.

References

[1] Wang L, Wong CP. Proceedings of the Third International Symposium on Electronic Packaging Technology, Beijing, China; 1998. p. 495.
[2] Wada M. Proceedings of the 49th Electronic Components and Technology Conference (ECTC), San Diego, CA; 1999. p. 56.
[3] Feustel F, Eckebracht A. Proceedings of the 49th Electronic Components and Technology Conference (ECTC), San Diego, CA; 1999. p. 583.
[4] Batzer H. Chem Ind (London) 1964;1:179.
[5] Lee SM. Epoxy resins. New York: Marcel Dekker; 1988. p. 860.
[6] Kinjo N, Ogata M, Nishi K, Kaneda A. Adv Polym Sci 1989;88:1.
[7] Wang L, Wong CP. Proceedings of the 49th Electronic Components and Technology Conference (ECTC), San Diego, CA; 1999. p. 34.
[8] Yang S, Chen J, Korner H, Breiner T, Ober CK. Chem Mater 1998;10:1475.
[9] Wang L, Wong CP. J Polym Sci Polym Chem Ed 1999;37:2991.
[10] Wang L, Li H, Wong CP. J Polym Sci Polym Chem Ed 2000;38:3771.
[11] Ni G, Gordon MH, Schmidt WF, Mnyshondt A. Proceedings of the 49th Electronic Components and Technology Conference (ECTC), CA; 1997. p 859.
[12] Wong CP, Shi SH, Jefferson G. Proceedings of the 49th Electronic Components and Technology Conference (ECTC), CA; 1997. p. 850.
[13] Yang S, Chen J, Korner H, Breiner T, Ober CK. Polym Prepr (Div Polym Chem Inc, ACS) 1997;38:440.
[14] Tanner DD, Meintzer CP. J Am Chem Soc 1985;107:6584.
[15] Meyersen K, Wang JC. J Polym Sci Polym Chem Ed 1967;5:1827.
[16] Feustel F, Eckebracht A. Proceedings of the 49th Electronic Components and Technology Conference (ECTC), CA; 1999. p 1058.
[17] Kaji M, Ogami K, Endo T. J Appl Polym Sci 1999;72:953.
[18] Kaji M, Nakahara K, Endo T. J Appl Polym Sci 1999;74:690.