Development of a Novel Epoxy Resin Having Cardo Structure

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A novel epoxy resin (E-NP-BPDA) having the cardo structure derived from the phthalein dye was prepared from 3,4'-bipthalic anhydride (a-BPDA). a-BPDA was reacted with phenol in methanesulfonic acid, affording a cardo structure. Fixation of the cardo structure was achieved by reaction with methylamine in which cyclic ester was converted to cyclic amide. Further reaction with epichlorohydrin gave E-NP-BPDA. Thermal analysis revealed that E-NP-BPDA has both high thermal stability ($T_{d5} = 301\text{ }^{\circ}\text{C}$) and a low softening point ($T_{sp} = 109\text{ }^{\circ}\text{C}$) probably due to the low symmetry and the cardo structure. Curing E-NP-BPDA with slightly excess phenol novolac in the presence of tetraphenylphosphonium tetraphenylborate (TPP-MK) by heating up to $200\text{ }^{\circ}\text{C}$ afforded a dark brown thermoset with almost no epoxy groups indicated by IR spectra. The glass transition temperature of the thermoset evaluated by DMA reached $192\text{ }^{\circ}\text{C}$ and the value was higher than that of the conventional phenol-novolac-cured bisphenol-A-type epoxy resin.

Keywords: Epoxy resin, Cardo structure, Phthalein dye, Thermal stability

1. Introduction

Epoxy resins have been widely applied to adhesives, coatings, electronic materials and building materials due to their prominent thermal, mechanical and electrical properties [1]. Generic epoxy resins are mainly derived from bisphenol A (BPA) and phenol novolac (PN). Thermal stability and toughness of their thermosets are, however, insufficient to advanced materials, e.g. composite materials for airplanes and sealant for high-performance LSI. A strategy to improve thermal stability of epoxy resins is introducing polycyclic aromatic rings. For instance, epoxy thermosets derived from naphthalene [2-7], anthracene [8,9] and xanthene [10] showed higher thermal stability as well as higher toughness and lower moisture absorption than those derived from BPA and phenol. The highly symmetric polycyclic moieties, however, raised melting point of epoxides, leading to difficulty in mold fabrication.

In this work, we designed an epoxy resin having low symmetry and cardo structure which lower the melting point and increase solubility by reducing molecular packing [11-14]. As a suitable building

block with low symmetry, 3,4'-bipthalic anhydride (a-BPDA) was employed because reaction of the phthalic anhydride moiety with phenols afforded cardo structure as can be seen in phthalein dyes. The properties of epoxy resins and thermosets derived from a-BPDA were investigated by thermal analysis.

2. Experimental

2.1. Materials

Phenol novolac (phenolite TD-2131) and 1-(2-cyanoethyl)-2-ethyl-4-methylimidazole (2E4MZ-CN) were kindly donated by DIC corporation and Shikoku Chemicals corporation, respectively. Bis(tetrabutylphosphonium) pyromellitate (BTBP-PM) and tetraphenylphosphonium tetraphenylborate (TPP-MK) were kindly donated by Hokko Chemical Industry Co., Ltd. Phenol, epichlorohydrin, tetramethylammonium chloride and a-BPDA were purchased from Tokyo Chemical Industry Co., Ltd. Aqueous methylamine solution (40 wt%), hydrochloric acid and sodium hydroxide were purchased from FUJIFILM Wako Pure Chemical Corporation. Methanesulfonic acid was purchased from Kanto Chemical Co., Inc.

2.2. Measurement

The ^1H and ^{13}C NMR spectra were recorded with a Bruker BioSpin DRX300 (300 MHz) spectrometer and a JEOL ECX-400 spectrometer (400 MHz) at room temperature using dimethyl sulfoxide- d_6 as a solvent and tetramethylsilane as an internal standard. Molecular weight was determined with size exclusion chromatography (SEC) using a Tosoh TSK_{gel} GMH_{HR}-M column coupled with UV and RI detectors (Tosoh, UV-8020 and RI-8021), and DMF containing LiBr (30 mmol/L) and phosphoric acid (60 mmol/L) as a mobile phase. The SEC system was calibrated by using polystyrene standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on Shimadzu TGA-50 and DSC-60, respectively, at a heating rate of 10 °C/min under a nitrogen flow. Thermomechanical analysis (TMA) was carried out on Shimadzu TMA-60 at a heating rate of 5 °C/min under a nitrogen flow. Dynamic mechanical analysis (DMA) was conducted on SII nanotechnology DMS-6100 by dual cantilever bending at a heating rate of 5 °C/min under air with a frequency of 1 Hz. Infrared (IR) spectra were recorded by using a Perkin Elmer SPECTRUM ONE spectrometer and KBr pellet method.

2.3. Synthesis of P-BPDA [15]

A solution of a-BPDA (10.0 g, 34.0 mmol) and phenol (16.9 g, 170 mmol) in methanesulfonic acid (24.8 mL, 382 mmol) was stirred at 90 °C for 48 h under Ar. After cooling to room temperature, the mixture was added to ice/water (500 mL). The precipitate was collected by filtration to give a reddish brown solid (18.4 g, 85%). ^1H NMR (300 MHz, DMSO- d_6): δ = 9.67 (-OH, 2.9H), 8.08-7.45 (Ar-H, 6.0H), 7.20-6.52 (-C₆H₄-OH, 12.0H) ppm. FT-IR (KBr): 3385, 1740, 1613, 1596, 1514, 1443, 1364, 1300, 1271, 1238, 1175, 1133, 1100, 1053, 961, 930, 837 cm⁻¹.

2.4. Synthesis of NP-BPDA [16]

A solution of P-BPDA (15.0 g, 23.5 mmol) and 40% aqueous methylamine (339 mL, 3.61 mol) was stirred at room temperature for 21 days. The reddish purple mixture was added to conc. HCl (4.6 mol)/water (7 L). The pale blue precipitate was collected by filtration and dissolved in methanol (160 mL). The solution was added to water (3.2 L) and collected by filtration to give a pale blue solid (15.1 g, 97%). ^1H NMR (300 MHz, DMSO- d_6): δ = 9.67 (-OH, 2.5H), 8.92-7.40 (Ar-H, 6.0H), 7.01-6.73 (-C₆H₄-OH, 11.5H) 2.75-2.62 (-N(CH₃)₂, 4.4

H) ppm. FT-IR (KBr): 3374, 1704, 1663, 1613, 1595, 1513, 1445, 1385, 1269, 1245, 1176, 1116, 1066, 1038, 1014, 969, 925, 890, 835 cm⁻¹.

2.5. Synthesis of E-NP-BPDA [17]

A solution of NP-BPDA (10.0 g, 15.1 mmol), epichlorohydrin (84.9 g, 0.918 mol) tetramethylammonium chloride (1.26 g) and a droplet of water was stirred at 80 °C for 8 h under Ar. After cooling to 40 °C, aqueous NaOH (20 wt%, 45.9 g) was added to the mixture, followed by stirring at 40 °C for 15 h. The mixture was neutralized by aqueous acetic acid (20 wt%, 55.2 g), extracted by dichloromethane, washed by water and brine, and concentrated. The residue was added to hexane. The precipitate was collected by filtration, extracted by THF and concentrated to give a pale orange solid (12.8 g, 96%). ^1H NMR (300 MHz, DMSO- d_6): δ = 8.08-7.28 (Ar-H, 6.0H), 7.15-6.44 (-C₆H₄-O-, 11.5H), 4.31 (2.8H), 3.95-3.70 (3.1H), 2.89-2.62 (9.9H) ppm. FT-IR (KBr): 3455, 3060, 3003, 2929, 2883, 1728, 1680, 1638, 1608, 1584, 1509, 1469, 1449, 1421, 1378, 1289, 1252, 1180, 1155, 1120, 1062, 1034, 990, 969, 913, 834 cm⁻¹.

2.6. General procedure for preparation of thermosets

A solution of E-NP-BPDA (epoxy equivalent weight (EEW) = 259 g/eq, 0.15 g), PN (hydroxy equivalent weight (HEW) = 104 g/eq, 0.5-1.2 eq) and TPP-MK (1.5 mg, 1 phr) in acetone (1.5 mL) was evaporated *in vacuo*. The residue was put into an aluminium mold. The curing process was done for 130 °C (2 h), 160 °C (3 h), 180 °C (3 h) and 200 °C (5 h) to give a dark brown thermoset.

3. Results and discussion

3.1. Synthesis

The reaction of a-BPDA with phenol in methanesulfonic acid followed by addition to water gave P-BPDA as a reddish brown solid (Scheme 1). No signals from a-BPDA were observed in ^1H NMR and IR spectra. The signals from aromatic and hydroxy groups of the phenol moieties emerged around 7.0 and 9.7 ppm, respectively, in the ^1H NMR spectrum (Fig. 1). Relative integrals of the protons indicated that three phenol moieties were introduced to one a-BPDA on average. Formation of the cardo structure was confirmed by ^{13}C NMR signals of quaternary carbons at 90-93 ppm.

In order to protect the cardo structure, the cyclic ester groups of P-BPDA were converted to the amide groups by aqueous methylamine solution.

After 21 days, color of the reaction mixture changed from purple to reddish purple. Repeated precipitation into dilute hydrochloric acid and water afforded a pale blue solid (NP-BPDA). Almost quantitative reaction was confirmed by the signals from *N*-methyl groups around 2.7 ppm and relative integrals in the ^1H NMR spectrum. Shift of signals of quaternary carbons from 90–93 ppm to 73–75 ppm in the ^{13}C NMR spectra and shift of the carbonyl peak from 1740 cm^{-1} to 1663 cm^{-1} in the IR spectra supported formation of the cyclic amide having the cardo structure.

Scheme 1. Synthesis of E-NP-BPDA.

Fig. 1. ^1H NMR spectra of (a) a-BPDA, (b) P-BPDA, (c) NP-BPDA and (d) E-NP-BPDA ($\text{DMSO}-d_6$, r.t.).

Glycidyl groups were introduced by reaction of NP-BPDA in epichlorohydrin containing tetramethylammonium chloride as a phase-transfer catalyst, followed by addition of aqueous NaOH. In ^1H NMR spectrum of the product (E-NP-BPDA), the signals from hydroxy groups ($\sim 9.6\text{ ppm}$) disappeared and those from glycidyl groups emerged between 2.6 and 4.3 ppm. Minor ^1H NMR signals around the main glycidyl peaks and size exclusion chromatogram indicated that E-NP-BPDA contains

some oligomeric species. EEW of E-NP-BPDA was determined as 259 g/eq by back titration with NaOH after the addition reaction of epoxy groups with HCl. The EEW was slightly larger than the value estimated as each hydroxyl group reacted to one epichlorohydrin (246 g/eq), which coincided with detection of oligomers by SEC.

3.2. Properties of E-NP-BPDA

No remarkable weight loss was observed under $250\text{ }^\circ\text{C}$ by TGA ($T_{d5} = 301\text{ }^\circ\text{C}$), indicating that E-NP-BPDA can be subjected to thermal curing condition. A weak peak at $80\text{ }^\circ\text{C}$ and a softening point at $109\text{ }^\circ\text{C}$ observed by DSC and TMA thermograms, respectively, suggested melting or glass transition of E-NP-BPDA around $100\text{ }^\circ\text{C}$ (Fig. 2). The fluidity was, however, insufficient in melting and blending with curing agent and accelerators. Due to high solubility of E-NP-BPDA to methylene chloride, acetone, DMF and THF, we decided that E-NP-BPDA, curing agents and curing accelerators were blended in acetone.

Fig. 2. TMA thermogram of E-NP-BPDA ($5\text{ }^\circ\text{C/min}$, under N_2).

Fig. 3. DSC thermograms of the mixtures containing E-NP-BPDA, PN and curing accelerators ($10\text{ }^\circ\text{C/min}$, under N_2).

3.3. Preparation and properties of thermosets

Since a mixture of E-NP-BPDA (1.0 eq) and PN (1.0 eq) showed an exothermic peak (+103 J/g) with an onset of 125 °C (Fig. 3), the mixture was subjected to curing for 130 °C (2 h) and 160 °C (3 h). However, the remained peak (913 cm^{-1}) from epoxy group in IR spectrum of the thermoset indicated insufficient conversion of E-NP-BPDA. Adding higher-temperature processes as 130 °C (2 h), 160 °C (3 h), 180 °C (3 h) and 200 °C (5 h) improved the conversion, but residual epoxy group was still present after curing.

Thus, curing accelerators for E-NP-BPDA/PN were screened by measuring DSC of the resin mixtures (Fig. 3). 2E4MZ-CN and BTBP-PM lowered the onsets of the exothermic peaks to 84 °C and 98 °C, respectively, which may induce undesired curing during preparation of the mixture and molding. In contrast, the onset temperature (125 °C) and heat value (98 J/g) of the mixture with TPP-MK were high enough to prepare the thermoset. Moreover, the peak temperature (157 °C) was lower than that of the mixture without accelerators (165 °C), implying acceleration of curing by TPP-MK.

After curing of a mixture containing E-NP-BPDA (1.0 eq), PN (1.0 eq) and TPP-MK (1 phr) for 130 °C (2 h), 160 °C (3 h), 180 °C (3 h) and 200 °C (5 h), the peak from epoxy groups (913 cm^{-1}) disappeared in IR spectrum of the obtained thermoset (E-NP-BPDA/PN1.0/TPP) (Fig. 4). Increasing the amount of PN to 1.1 eq (E-NP-BPDA/PN1.1/TPP) and 1.2 eq (E-NP-BPDA/PN1.0/TPP) also resulted in high conversion of epoxy groups of E-NP-BPDA.

Fig. 4. IR spectra of the mixture and thermoset of E-NP-BPDA (1.0 eq), PN (1.0 eq) and TPP-MK (1 phr) (KBr disk).

Thermal stability of those thermosets was evaluated by TGA under a nitrogen flow. The 5 wt% degradation temperatures (346–358 °C) were typical

values for epoxy thermosets. TMA thermograms of the thermosets revealed their high softening points (T_{sp}) above 200 °C. Glass transition temperature (T_g) of E-NP-BPDA/PN1.1/TPP, which showed the highest T_{sp} , was evaluated by DMA and was found to be 192 °C (Fig. 5). The value was higher than T_g of the conventional phenol-novolac-cured BPA-type epoxy thermoset (DGEBA/PN). The rigid structure of E-NP-BPDA constructed by benzene rings probably contributed to raise the glass transition temperature.

Table 1. Thermal properties of cured epoxy resins.

Epoxy resins ^a	$T_{\text{d}5}^b$ (°C)	$T_{\text{d}10}^b$ (°C)	Char yield ^b (%)	T_g^c (°C)
E-NP-BPDA/ PN1.0/TPP	346	379	45	-
E-NP-BPDA/ PN1.1/TPP	352	385	42	192
E-NP-BPDA/ PN1.2/TPP	358	389	44	-

^a Curing condition: 130 °C/2 h + 160 °C/3 h + 180 °C/3 h + 200 °C/5 h. ^b By TGA. ^c By DMA.

Fig. 5. DMA thermograms of E-NP-BPDA/PN1.1/TPP and DGEBA/PN (5 °C/min, under air).

4. Conclusion

Introduction of phenol moieties to a-BPDA under acidic condition gave a phenolphthalein derivative (P-BPDA) with low symmetry and the cardo structure. Following reactions with methylamine and with epichlorohydrin afforded an epoxy resin (E-NP-BPDA) with high solubility, low softening point ($T_{\text{sp}} = 109$ °C) and high thermal stability ($T_{\text{d}5} = 301$ °C) which were suitable to molding and curing. Curing the mixture of E-NP-BPDA, PN and TPP-MK reached almost full conversion of epoxy groups, affording dark brown thermosets. The thermosets showed high glass transition temperature of 192 °C in DMA thermogram.

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