Comparative Study of Two Twin Liquid-Crystalline Diglycidyl Ethers Containing Azomethine Moieties

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Two different twin liquid-crystalline diglycidyl ethers containing azomethine moieties were synthesized and characterized and their mesomorphic behaviors, thermal properties, and mechanical properties were compared. It was found that 4,4′-di(2,3-epoxypropoxy)-N-benzylidene-o-tolidine-cured systems gave higher thermal and mechanical properties than 3,3′-dimethoxy-4,4′-di(2,3-epoxypropoxy)-N-benzylidene-o-tolidine-cured systems. All liquid-crystalline behaviors exhibited by the products were found to be in the nematic phase. In addition, the higher curing ratios used resulted in higher thermal stability as well as mechanical properties in terms of pendulum and pencil hardness but lower impact properties.

Keywords   Azomethine; diglycidyl ether; liquid crystal; mechanical

Introduction

Liquid-crystalline thermosetting polymers possess excellent properties stem from the preservation of molecular organization in the mesophase of liquid crystal (LC) monomers. Epoxy resins as thermosetting polymers are commercially important because of their excellent adhesive strength [1], chemical resistance [2], and mechanical and electrical properties. However, epoxy resins exhibit low fracture toughness and poor wear and crack resistance in real application due to their rigid and brittle nature [3–5]. To overcome these problems, considerable amounts of work have been carried out in the direction of toughening epoxies, with some research focused on introducing appropriate amounts of rubbery and flexible components into epoxy networks [6,7]. Another alternative is by the incorporation of an LC structure into epoxy network. Liquid-crystalline epoxy resins can be synthesized from mesogens such as rigid rod molecules with epoxide groups (oxirane rings) directly attached to the mesogenic core, which were cured by reaction with aromatic amines thereafter. Liquid-crystalline

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epoxy (LCE) networks are an important area of research given their potential use in a number of applications such as electronics, advanced composites, nonlinear optics, etc. The synthesis, development of texture, mechanical properties, and influence of curing conditions have been examined for a number of LCEs [8–10]. Azomethine linkage in the backbone of polymers showed many desirable properties such as thermal [11], liquid crystal [12], optoelectronic properties [13], etc., due to the resonance of the poly-Schiff's base unit [14]. Incorporation of azomethine groups in various liquid-crystal polymers has been extensively studied, such as in polyesters [15,16], polyurethanes [17,18], polyethers [19], etc. This article mainly aims to compare the properties of two twin liquid-crystalline diglycidyl ethers containing azomethine moieties. The route of synthesis along with the characterization, mesomorphic, thermal, and mechanical properties of the two compounds is presented.

Experimental

Materials

All chemicals were purchased in analytical grade without further purification or distillation: vanilin, *o*-tolidine, *p*-hydroxybenzaldehyde, epichlorohydrin, tetrahexylammonium bromide (THABr; Fluka, Steinheim, Germany), absolute ethanol (Systerm, Selangor, Malaysia), 1-butanol, 4,4′-diaminodiphenyl sulfone (DDS), and *p*-phenylenediamine (PDA; Merck, Darmstadt, Germany; Figure 1), diethyl ether, and toluene (Lab Scan, Bangkok, Thailand).

Instrumentation

Fourier transform infrared (FTIR) spectra of the samples were recorded using potassium bromide (KBr) pellets with a Perkin-Elmer 2000 spectrophotometer for monomers and polymers ranging from 4000 to 400 cm^{-1}. ^{1}H-nuclear magnetic resonance (NMR) and ^{13}C-NMR spectra were obtained using a Bruker 400-MHz NMR spectrometer with dimethyl sulfoxide (DMSO-d$_6$) and deuterated chloroform (CDCl$_3$) as the respective solvents and tetramethylsilane (TMS) as the internal reference. Carbon, hydrogen, and nitrogen (CHN) microanalyses were performed using Perkin Elmer 2400 LS Series CHNS=O Analyzer. The optical textures of the samples were studied with a Carl Zeiss Axioskop polarized optical microscope (POM) equipped with 40 Linkam LTS350 hot stage, Linkam TMS94 temperature controller, and Linkam LNP cooling system (pump). Differential scanning calorimetry (DSC)
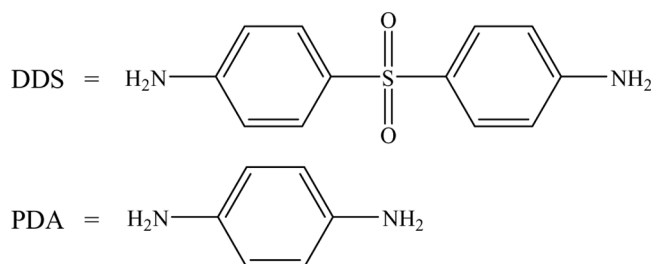

Figure 1. Curing agents.

measurements were conducted using a Perkin-Elmer Pyris Series 7 thermal analyzer under nitrogen purge at a heating rate of $10°C/min$. Thermogravimetric analysis (TGA) was carried out under a nitrogen atmosphere with a heating rate of $10°C$ using a Perkin Elmer Pyris Series 6 thermal analyzer. Mechanical properties for different ratios of samples in coating thickness of $60\,\mu m$ were carried out in accordance with standards [20] for pendulum hardness and pencil hardness, whereas impact tests were conducted using a tubular impact tester.

Preparation of Bisphenols, 3,3′-Dimethoxy-4,4′-dihydroxy-N-benzylidene-o-tolidine (I) and 4,4′-Dihydroxy-N-benzylidene-o-tolidine (II). The preparation and characterization of azomethine bisphenol I was described in previous article [11]. Yield was 93%. Elemental analysis (%): Found: C, 75.18; H, 5.89, N, 5.79, $C_{30}H_{28}N_2O_4$ Calcd.: C, 75.14; H, 5.89; N, 5.84 (Table 1). IR (KBr): $3384\,cm^{-1}$ (OH stretch), $1620\,cm^{-1}$ (C=N stretch). ^{1}H-NMR (DMSO-d_6), $-CH=N-$, 8.30 ppm. A similar reaction procedure was adopted with replacement of vanilin to *p*-hydroxybenzaldehyde to prepare azomethine bisphenol II. Yield was 95%. Elemental analysis (%): Found: C, 79.46; H, 5.83, N, 6.61, $C_{28}H_{24}N_2O_2$ Calcd.: C, 79.98; H, 5.75; N, 6.66 (Table 1). IR (KBr): $3416\,cm^{-1}$ (OH stretch), $1623\,cm^{-1}$ (C=N stretch). ^{1}H-NMR (DMSO-d_6), $-CH=N-$, 8.32 ppm.

Preparation of Twin Diglycidyl Ethers 3,3′-Dimethoxy-4,4′-di(2,3-epoxypropoxy)-N-benzylidene-o-tolidine (III) and 4,4′-Di(2,3-epoxypropoxy)-N-benzylidene-o-tolidine (IV). The general reaction is illustrated in Scheme 1. Bisphenols I and II obtained were separately reacted with epichlorohydrin at $112°C$–$120°C$ aided with tetrahexylammonium bromide (THABr) as catalyst for 1 h. The products III and IV, respectively, were filtered and washed with diethyl ether and recrystallized using toluene. Finally, the products III and IV were dried in a vacuum oven for 24 h at $90°C$. For twin diglycidyl ether III: Yield was 64%. Elemental analysis (%): Found: C, 72.54; H, 6.11, N, 4.36, $C_{36}H_{36}N_2O_6$ Calcd.: C, 72.95; H, 6.12; N, 4.73 (Table 1). IR (KBr): $1622\,cm^{-1}$ (C=N stretch), $914\,cm^{-1}$ (epoxy). ^{1}H-NMR (CDCl$_3$): 8.45 ppm (CH=N), 4.05 ppm ($-OCH_3$), 4.15–4.45 ppm (CH$_2$ glycidyl), 3.52 ppm (CH epoxy), 2.7–3.0 ppm (CH$_2$ epoxy). ^{13}C-NMR (DMSO): 159.7 ppm (CH=N), 56 ppm ($-OCH_3$), 44 ppm (CH$_2$ in oxirane ring), 47.5 ppm (CH in oxirane ring), 50 ppm (terminal O-CH$_2$). For twin diglycidyl ether IV: Yield was 73%. Elemental analysis (%): Found: C, 76.18; H, 5.91, N, 4.97, $C_{34}H_{32}N_2O_4$ Calcd.: C, 76.67; H, 6.06; N, 5.26 (Table 1). IR (KBr): $1624\,cm^{-1}$ (C=N stretch), $915\,cm^{-1}$ (epoxy). ^{1}H-NMR (CDCl$_3$), 8.2 ppm (CH=N), 3.80–4.50 ppm (CH$_2$

Table 1. Yield and CHN elemental analyses

| Compound | Yield (%) | Elemental analysis (%) | | | | | |
| | | Calculated | | | Found | | |
		C	H	N	C	H	N
I	93	75.14	5.89	5.84	75.18	5.89	5.79
II	95	79.98	5.75	6.66	79.46	5.83	6.61
III	64	72.95	6.12	4.73	72.54	6.11	4.36
IV	73	76.67	6.06	5.26	76.18	5.91	4.97
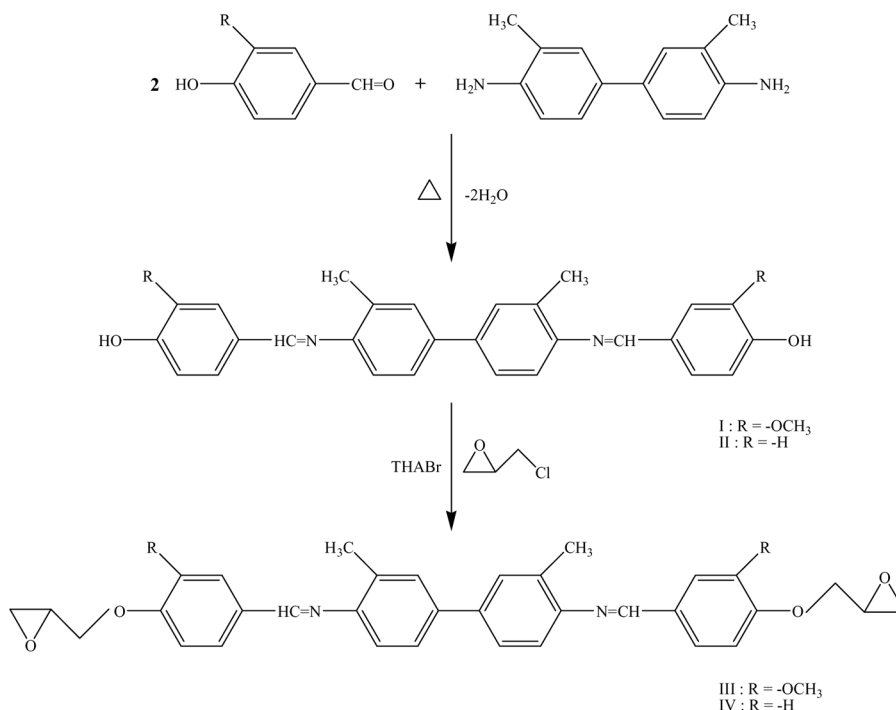
Scheme 1. Synthesis route.

glycidyl), 3.50 ppm (CH epoxy), 2.78–2.95 ppm (CH_2 epoxy). ^{13}C-NMR (DMSO): 159.8 ppm (CH=N), 44.5 ppm (CH_2 in oxirane ring), 51 ppm (CH in oxirane ring).

Results and Discussions

Characterization

The molecular structures of the epoxy monomers showed in Scheme 1 were evaluated by means of FT-IR and NMR techniques. From the FT-IR spectra obtained, the $-CH_3$ and $-CH_2$ stretching vibrations were found at 2919 and 2874 cm^{-1}, respectively, for twin diglycidyl ether III and at 2921 and 2872 cm^{-1} for twin diglycidyl ether IV. Azomethine groups ($-CH=N-$) of twin diglycidyl ethers III and IV were separately attributed at 1622 and 1624 cm^{-1} [21], followed by the absorption of C=C stretching vibrations of aromatic rings at 1511 and 1578 cm^{-1} for III as well as at 1508 and 1572 cm^{-1} for IV. Furthermore, the C-O stretching of the chain was located at 1139 and 1165 cm^{-1} for III and IV, respectively. The presence of a methoxy substitute ($-OCH_3$) in III was verified at 1024 cm^{-1}. Absorption bands at 914 cm^{-1} of III and 915 cm^{-1} of IV were attributed to the terminal oxirane rings.

Figure 2 shows the ^{1}H-NMR spectrum of twin diglycidyl ether III, including the peak assignments corresponding to the structure. As shown in the figure, the azomethine moiety ($-CH=N-$) appeared as a singlet at 8.45 ppm, whereas protons of the epoxy ring were found at 2.9–3.05 ppm as two doublets and at 3.49–3.57 ppm as a multiplet, whereas the CH_2 glycidyl were given by peaks in the range 4.15–4.45 ppm. Obtained from the raw material vanilin, the proton of the $-OCH_3$

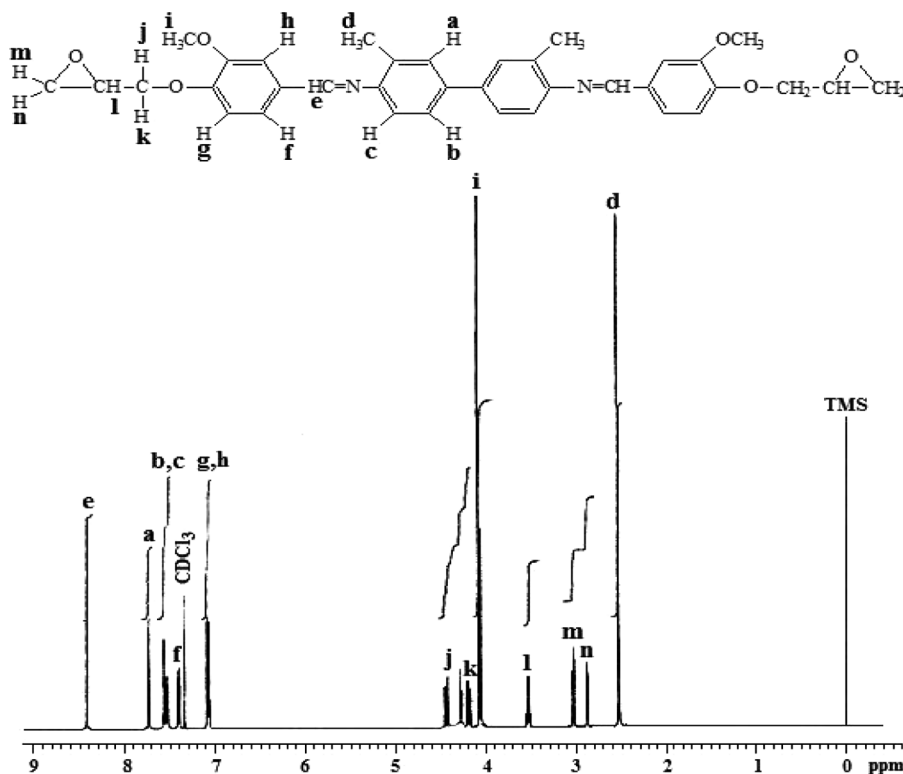**Figure 2.** ^{1}H-NMR spectrum of twin diglycidyl ether III in CDCl$_3$.

group was presented by a peak at 4.05 ppm. At frequency 2.5 ppm, the singlet peak was due to the proton of methyl group that attached to the benzene ring (*o*-tolidine). Finally, protons of the aromatic rings were found at frequencies 7.05–7.75 ppm. Based on the ^{13}C-NMR spectrum of twin diglycidyl ether IV in Figure 3, chemical shifts in the range of 159.80 ppm where present, which indicated the assignment of the azomethine group ($-CH=N-$). Carbons of the oxirane ring were present at frequency ranges of 41.52–50.63 ppm.

Mesomorphic and Thermal Properties

Mesomorphic phase transition of the twin diglycidyl ethers were studied by DSC and POM. From DSC thermograms, both curves showed two endothermic peaks; one at lower temperature due to melting (T_m) and the other at higher temperature due to isotropization (T_i). By POM, a nematic mesophase showing Schlieren textures was observed for both III and IV in the melt between T_m and T_i (Figure 4). The liquid-crystalline transition temperatures for melting and isotropization obtained from DSC thermograms as well as the temperature interval between T_m and T_i ($\Delta T = T_i - T_m$) are presented in Table 2.

As seen from the results, twin diglycidyl ether III melted at lower temperature than twin diglycidyl ether IV, indicating that the substitution of a methoxy ($-OCH_3$) group lowered the melting temperature of the monomer. This was due to the fact that
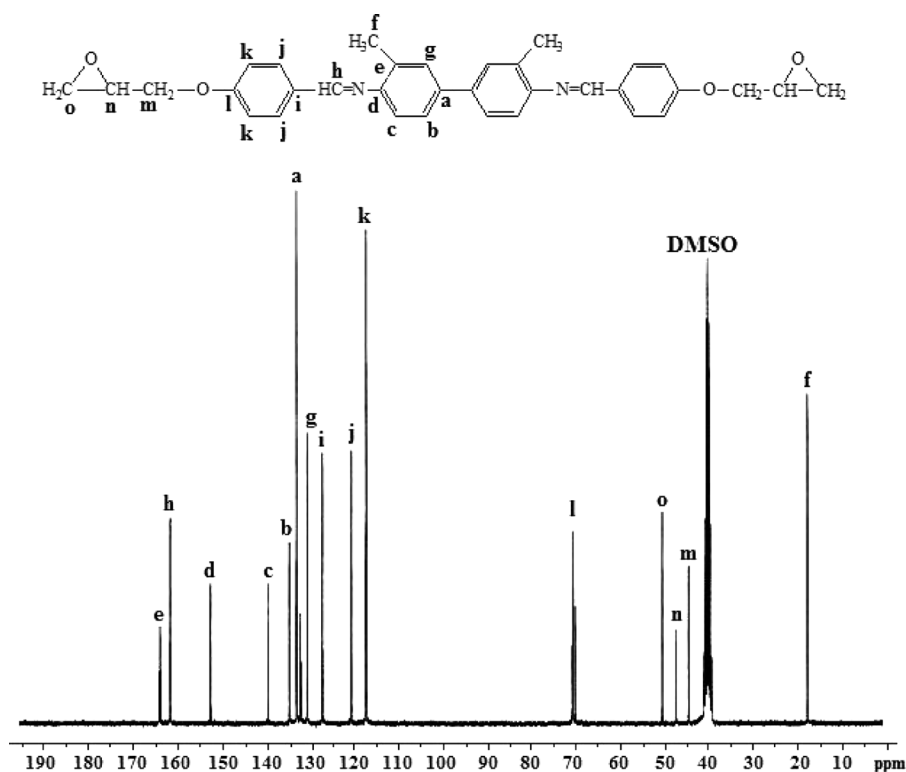
Figure 3. ^{13}C-NMR spectrum of twin diglycidyl ether IV in DMSO.

substituents could act to reduce the coplanarity of adjacent mesogenic groups and increase the diameter or decrease the axial ratio of the mesogens [22]. In the past, researchers have used different substituents to reduce the T_m and T_i of LC polymers [23–25].

Curing Properties

Both twin diglycidyl ethers were cured with DDS and PDA. The cured samples were prepared from mixing stoichiometric amounts of epoxy monomers with DDS and
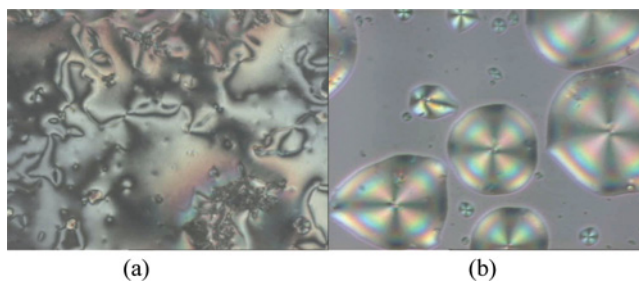

Figure 4. Optical textures of twin diglycidyl ethers: (a) for III taken at 134°C (magnification = 250×); (b) for IV taken at 139°C (magnification = 250×).

Table 2. Thermal transition of twin diglycidyl ethers III and IV

LC monomers	T_m (°C)	T_i (°C)	ΔT ($T_i - T_m$) (°C)
III	130	176	46
IV	135	220	78

PDA, respectively, in ratios of twin diglycidyl ether: diamine of 2:1 and 4:1. The conversion of epoxy groups into hydroxy groups was confirmed using FT-IR spectroscopy. In all cases, the characteristic bands of epoxy groups at $914 \, cm^{-1}$ disappeared almost completely [26,27]. Figure 5 shows the representative FT-IR spectra of the cured III:PDA and IV:PDA at a ratio of 4:1.

Representative DSC profiles of the curing behavior of the products are shown in Figures 6 and 7. Endothermic peaks at 132°C and 148°C in Figure 6 were attributed to the melting (T_m) and isotropization (T_i) temperatures, respectively. By increase of temperature, the exothermic curve is attributed to the cross-linking reaction, which is at 163°C. From Figure 7, the DSC curve shows T_m at 135°C for twin diglycidyl ether IV and 174°C for DDS as well as T_i at 228°C. The representative optical textures of cured products illustrated in Figure 8 show nematic phases for III:DDS of 2:1 at 141°C, whereas for IV:DDS of 4:1 it was 156°C.
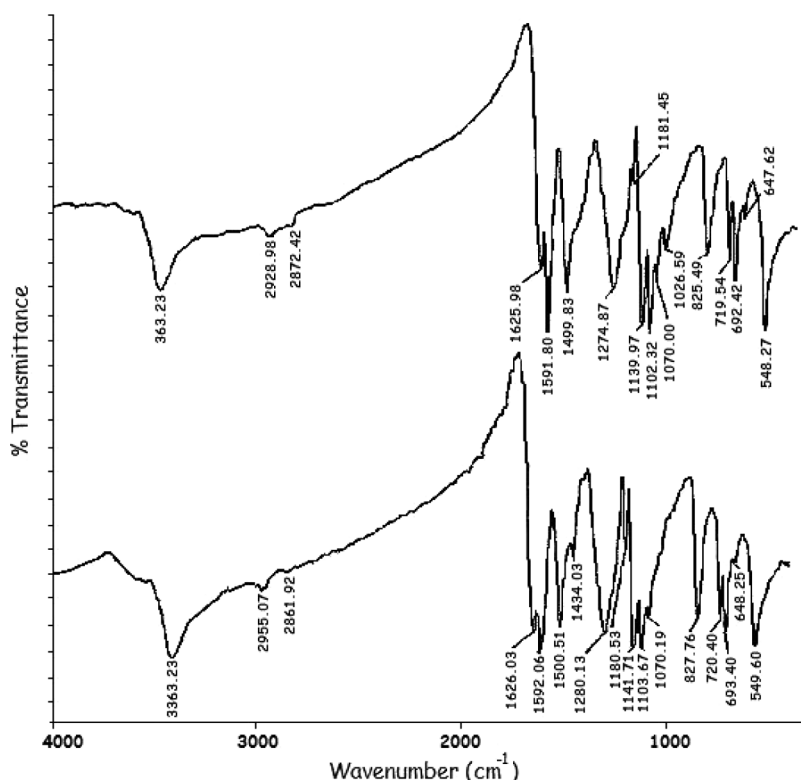

Figure 5. Representative FT-IR spectra of (a) III:PDA, ratio of 4:1, and (b) IV:PDA, ratio of 4:1.
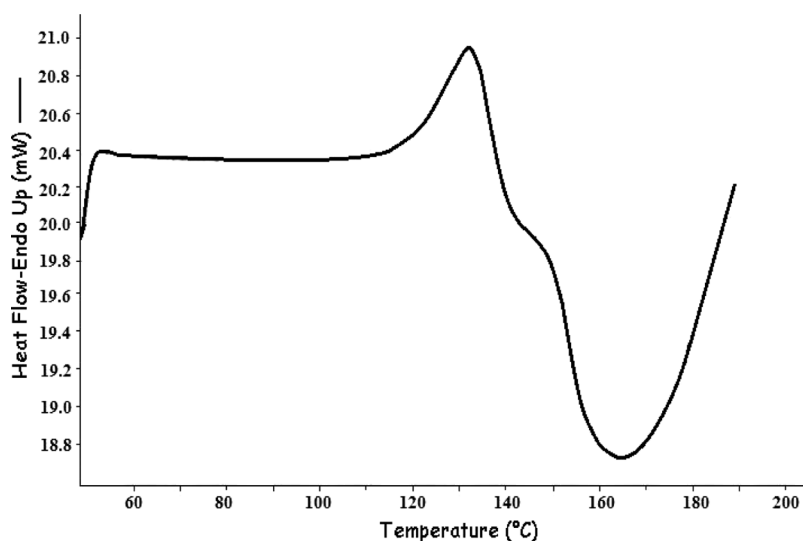
Figure 6. DSC curve of III:DDS ratio of 2:1.

From the representative TGA curves shown in Figure 9, one-step degradation at 280°C and 305°C was found for III:DDS and IV:DDS at a ratio of 4:1, respectively, for 10% weight loss. Twin diglycidyl ether IV exhibited marginally better thermal stability than twin diglyidyl ether III-cured systems. This was due to the presence of O-CH$_3$ (methoxy substituent) in twin diglycidyl ether III-cured system. Furthermore, for the PDA system, thermal degradation was found to begin at 272°C for the III:PDA system and at 293°C for the IV:PDA system. Hence, it is interesting to note that products cured with DDS showed better thermal stability than that of products
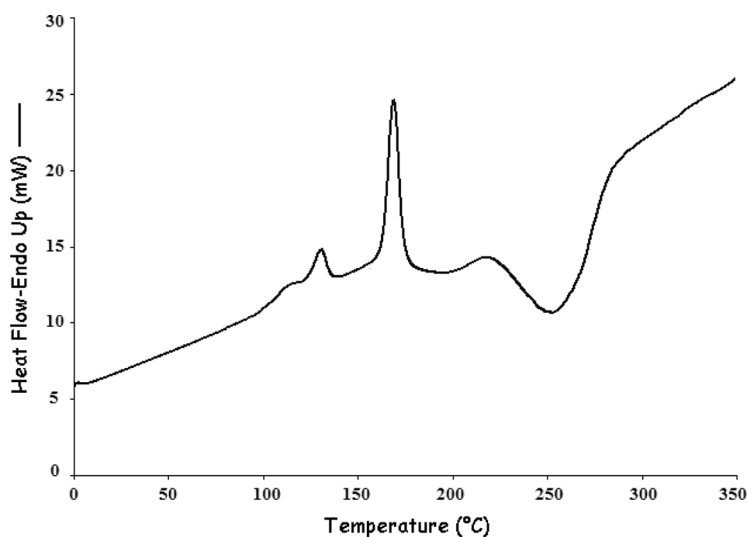

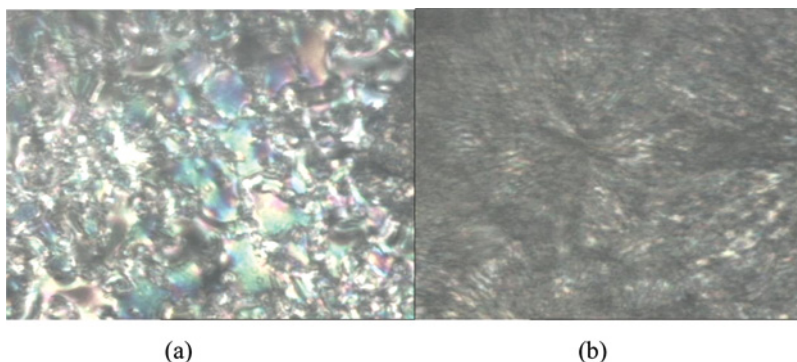**Figure 7.** DSC curve of IV:DDS ratio of 2:1.

Figure 8. Optical textures of cured products: (a) for III:DDS ratio of 2:1 taken at 141°C (magnification = 10×) and (b) for IV:DDS ratio of 4:1 taken at 156°C (magnification = 10×).

cured with PDA due to the biphenyl structure present in DDS compared to phenyl structure in PDA [28]. Also, the higher the cross-linking ratio, the higher the thermal stability of the products. The decomposition of the cured products probably occurred through pyrolytic cleavage of the azomethine ether group and the linkage between mesogenic units [29].

Mechanical Properties

Pendulum hardness evaluates the coating's hardness by measuring the damping time (represented by the number of counts) of an oscillating pendulum that rests with two stainless steel balls on the coating surface. The amplitude of oscillation of the pendulum on the coating surface decreases more rapidly on a softer coating because of the high degree of damping oscillation, that is, the lower the value of counts,
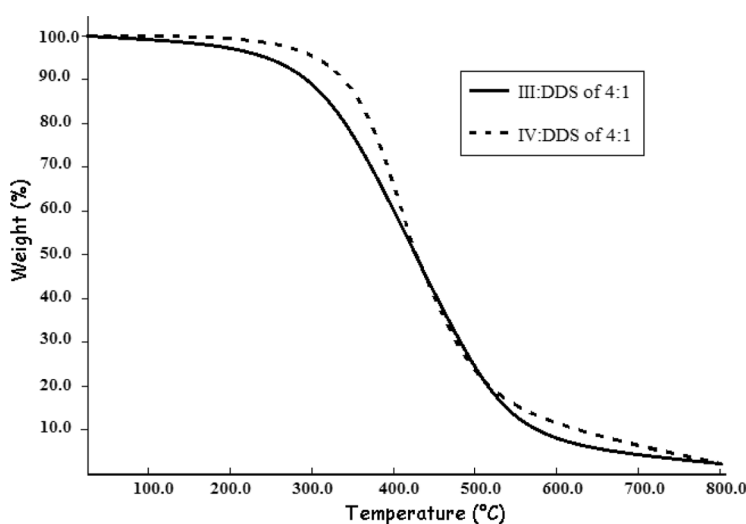

Figure 9. TGA thermograms of III:DDS and IV:DDS ratio of 4:1.
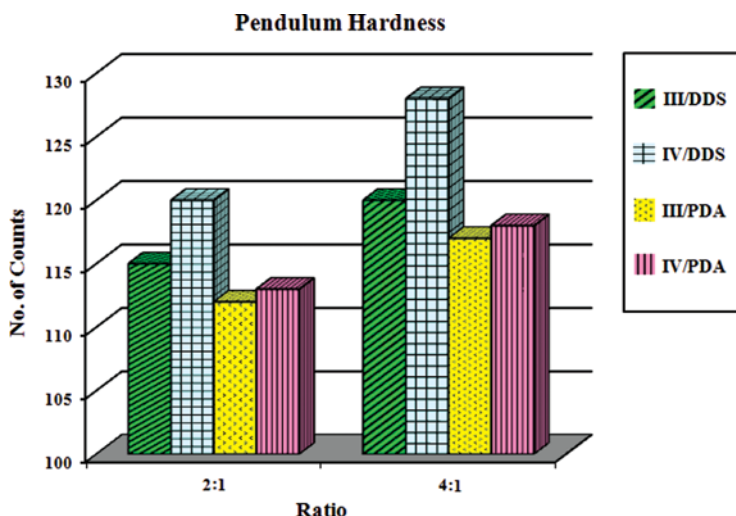
Pendulum Hardness

Figure 10. Pendulum hardness.

the softer is the coating. Results of the pendulum hardness test are presented in Figure 10. It was observed that twin diglycidyl ether IV possessed higher pendulum hardness properties than twin diglycidyl ether III, with the utilization of DDS as the curing agent. In addition, the higher the cross-linking ratio, the higher the surface hardness of the cured film. This is due to the fact that higher number of the cross-linking sites produces a more rigid film.

Good hardness of the coating is directly related to the good cross-linking of the resin [30]. The cross-linked films will produce a high-molecular-weight polymer, thus creating a hard, tough, and durable polymer that is suitable in various applications.
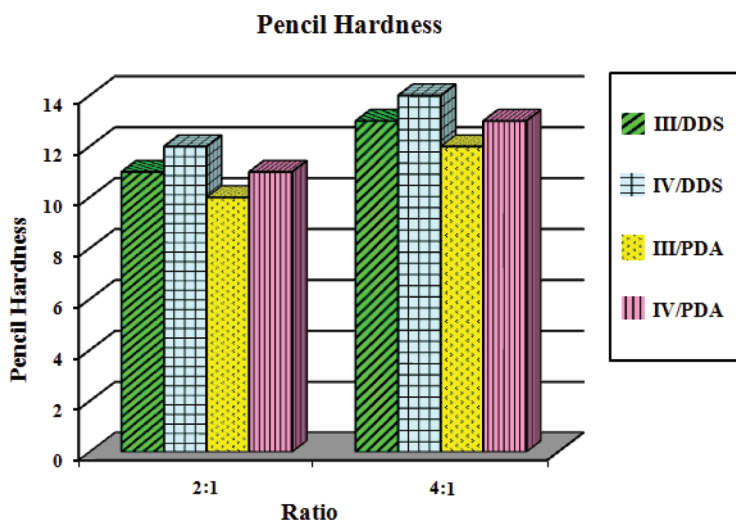
Pencil Hardness

Figure 11. Pencil hardness properties of the cured film (rating used for pencil hardness: 1:6B; 2:5B; 3:4B; 4:3B; 5:2B; 6:B; 7:HB; 8:F; 9:H; 10:2H; 11:3H; 12:4H; 13:5H; 14:6H).
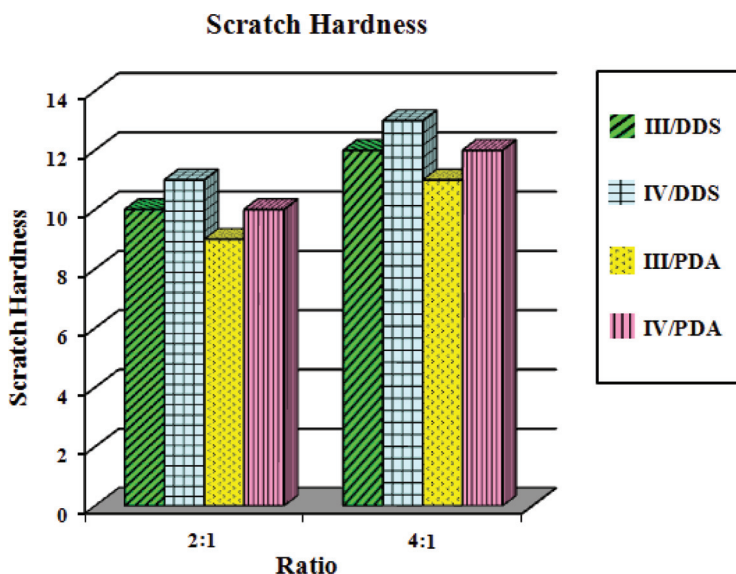
Scratch Hardness

Figure 12. Scratch hardness properties of the cured film (rating used for scratch hardness: 1:6B; 2:5B; 3:4B; 4:3B; 5:2B; 6:B; 7:HB; 8:F; 9:H; 10:2H; 11:3H; 12:4H; 13:5H; 14:6H).

Coating hardness was evaluated using a pencil hardness test in which the coating hardness was rated by the highest lead hardness that could not scratch through the coating. Results of pencil hardness are reported in two different terms, namely, pencil hardness and scratch hardness, in Figures 11 and 12, respectively, indicating that with DDS as the curing agent, twin diglycidyl ether IV exhibited higher pencil and scratch hardness than that of twin diglycidyl ether III. The trend showed in both
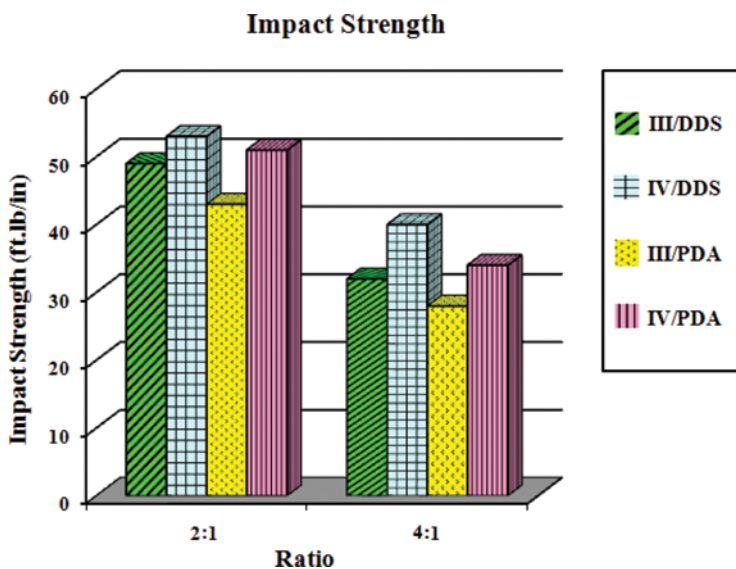
Impact Strength

Figure 13. Impact properties of the cured film.

figures also confirmed that a higher ratio resulted in greater pencil and scratch hardness of the cured film. The high ratio gave higher properties due to the intense degree of cross-linking.

In impact tests (Figure 13), twin diglycidyl ether IV exhibited higher impact strength than twin diglycidyl ether III, especially with DDS as the curing agent. The ability of the LC epoxy resin films to resist the blow of force is directly influenced by the flexibility of the molecular chains in the films. A highly flexible coating will therefore prevent the films from cracking and flaking, thus creating an enamel that possesses low stress values. In other words, the lower curing ratio used, the more flexible the molecular chains, and thus higher impact strength is obtained.

Conclusions

Two twin liquid-crystalline diglycidyl ethers have been successfully synthesized. Their structures were confirmed by FT-IR, ^{1}H-NMR, ^{13}C-NMR, and CHN techniques. It was found that twin diglycidyl ether III yielded lower thermal and mechanical properties compared to twin diglycidyl ether IV due to the presence of an O-CH$_3$ (methoxy group). Furthermore, high curing ratios also enhanced the mechanical properties in terms of pendulum and pencil hardness but reduced impact resistance.

Acknowledgment

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