

Synthesis and Curing Properties of a Novel Novolac Curing Agent Containing Naphthyl and Dicyclopentadiene Moieties

REN Hua(任华), SUN Jianzhong(孙建中)*, WU Binjie(吴斌杰) and ZHOU Qiyun(周其云)

State Key Laboratory of Chemical Engineering (Polymer Reaction Engineering Division), Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, China

Abstract A novel novolac curing agent containing both naphthalene and dicyclopentadiene (DCPD) moieties was prepared to produce a highly heat-resistant cured polymer network. The chemical structure was characterized using Fourier transform infrared spectroscopy, nuclear magnetic resonance, mass spectrometry, and gel permeation chromatography analyses. The thermal properties of the resulting polymer from diglycidyl ether of bisphenol A epoxy resin cured with the novel curing agent were evaluated using dynamic mechanical thermal analysis and thermogravimetric analysis. Compared with the conventional curing agent, the resulting polymer cured with naphthalene/DCPD novolac shows considerable improvement in heat resistant properties such as higher glass transition temperature (T_g) and thermal stability. The result also shows better moisture resistance because of the hydrophobic nature of naphthalene/DCPD structure.

Keywords epoxy curing agent, heat resistance, naphthol, dicyclopentadiene

1 INTRODUCTION

Epoxy resins are commonly used in laminating, adhesive, surface coating and semiconductor encapsulation applications because of their heat, solvent, moisture and chemical resistance, good mechanical and electrical properties, and great adherence to many substrates. However, the conventional epoxy resins and curing agents are unable to meet the requirements of some applications such as integrated circuit packaging and advanced materials which require higher thermal-resistant properties[1]. Thus, it is necessary to develop higher glass transition temperature and low moisture-absorbing resin systems for these applications.

The properties of cured epoxy polymers depend largely on the nature of chemical structure of the starting resins and curing agents. Many approaches have been reported to improve the heat resistance of epoxy resins by the introduction of a naphthalene structure into the epoxy skeleton. Kaji and Endo[2], Wang *et al.*[3] and Castell *et al.*[4] synthesized the naphthalene-based epoxy resins containing naphthyl and phenyl structures. Xu *et al.*[5] reported that a novel naphthalene cycloaliphatic moieties-linked epoxy resin was obtained and its cured polymers had a higher glass transition temperature. Liquid crystalline epoxy resin based on naphthalene mesogen was studied by Lee and Jang[6] and they found that when cured with diamino-diphenylsulfone (DDS), the polymer exhibited superior thermal properties. Furthermore, glass transition temperature rises as crosslinking density increases[7,8]. Naphthalene multifunctional epoxy resins have a higher T_g than that of the di-functional naphthalene-based epoxy resins[9—11]. Developing novel naphthyl-containing epoxy curing agents is also an effective way to increase the glass transition temperature and thermal stability of the cured polymers because the introduction of rigid naphthalene structure into the cured network increases the glass transition temperature and thermal stability of the polymers. As a possible approach to advanced

heat-resistant thermosets, a project aimed at the preparation of thermally more stable epoxy resins and curing agents had been initiated in this laboratory. The objective of the present study is to synthesize a novel novolac epoxy curing agent containing both a naphthalene structure and a dicyclopentadiene (DCPD) moiety.

In this study, the novel monomer was prepared through Friedel Crafts reaction between 1-naphthol and DCPD, followed by the reaction with paraformaldehyde to obtain a relatively higher molecular weight novolac resin. The novolac resin was used as curing agent and cured with different kinds of diglycidyl ether of bisphenol A (DGEBA) epoxy resins. The characteristics of physical properties of the cured polymers were investigated by several methods, and compared with those of the conventional epoxy curing agents.

2 EXPERIMENTAL

2.1 Materials

DCPD was purchased from Fluka Co., USA; 1-naphthol (99.0%) from Shanghai Tingxin Chemical Engineering Reagent Co., China; paraformaldehyde from Tianjin Chemical Reagent Co., China and used without further purification. Triphenylphosphine (from Acros Co. USA) was used as catalyst during the curing procedure. 4-4'-diaminodiphenylsulfone (DDS) obtained from Yinsheng Chemicals Co. Ltd., China, was used to be compared with the novel curing agent. DGEBA epoxy resin (E-51, Epoxy equivalent weight 196) was obtained from Wujiang Heli Chemical Co. Ltd., China, and DGEBA epoxy resin (E-12, Epoxy equivalent weight 833) was supplied by Huangshan Shanfu Chemical Co. Ltd., China. All solvents and other chemicals were of reagent or better grade.

2.2 Synthesis

2.2.1 Preparation of alkylated product of 1-naphthol with DCPD

A total of 86.4g of 1-naphthol and 200ml of toluene

Received 2005-10-31, accepted 2006-04-28.

* To whom correspondence should be addressed. E-mail: bigwig@zju.edu.cn

were put into a 500ml four-necked round-bottom flask equipped with a heating oil bath, stirrer, reflux condenser and argon inlet. The reactant mixture was heated to 90°C to enable the absolute dissolution of 1-naphthol in toluene, and then 1.5g of AlCl₃ powder were charged into the flask as the Friedel Crafts condensation catalyst. A total of 15ml DCPD toluene solution (4mol·L⁻¹) was added gradually over a period of 1h, then the mixture was heated to 120°C and maintained for another 7h. After cooling down, the resultant mixture was washed with 5% (by mass) NaHCO₃ (aq) to terminate the reaction followed by washing with water thrice. The organic phase was separated and recrystallized to remove the excess 1-naphthol, then distilled in a rotary evaporator to remove the solvent, finally placed in the vacuum oven to remove the traces of toluene and 1-naphthol. A brown product (indicated as A) of 22.85g was obtained. The equation for the reaction is shown in Fig.1.

2.2.2 Preparation of naphthol-DCPD novolac resin

Into a 250ml four-necked round-bottom flask equipped with a heating oil bath, stirrer, reflux condenser and argon inlet, were charged 21g A, 1.5g paraformaldehyde and 150ml methyl isobutyl ketone (MIBK). After A and paraformaldehyde were dissolved in the MIBK, 0.2g *p*-toluene sulfonic acid (PSTA) was added, then the mixture was heated to

120°C and refluxed for 6h. When the reaction was completed, the solvent was evaporated under vacuum pressure. A dark brown-colored solid product (indicated as B, see Fig.5) of 21.9g was obtained.

2.3 Curing procedure

The curing agents and DGEBA epoxy resins were mixed in a molar stoichiometric ratio of 1:1, and triphenylphosphine (two parts per hundred based on epoxy resin) was added as accelerator. The mixture degassed at 100°C in a vacuum oven for 30min, heated on hot plates and cured at 110°C for 1h, 160°C for 1h and 200°C for 2h, and then the samples were cooled slowly to room temperature to prevent cracking.

2.4 Characterization

The electrospray ionization (ESI) mass spectrometry (MS) was carried out on a Bruker Esquire-LC_00075 spectrometer. FTIR spectra were recorded on a Nicolet 5700 FTIR spectrometer. ¹H NMR and ¹³C NMR characterizations were carried out by Bruker Avance DMX 500 NMR spectrometer using tetramethylsilane (TMS) as internal standard. Gel permeation chromatography (GPC) was performed using Waters 1525/2414 GPC instrument. The epoxide

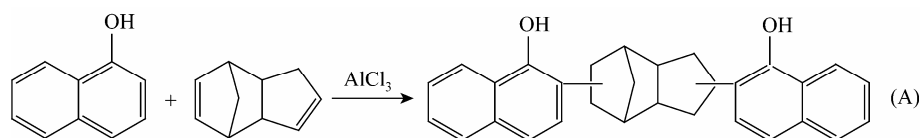


Figure 1 Synthesis of product A

MS(ESI): $m/z=419.1$ (Fig.2); IR(KBr): 3411cm⁻¹ (—OH of naphthyl), 1269cm⁻¹ (C—O), 1653cm⁻¹, 1597cm⁻¹, 1511cm⁻¹ (aromatic C—C) [Fig.3(a)]; ¹H-NMR(CDCl₃) δ (ppm): 8.30 (—OH of naphthyl), 6.87—7.86 (aromatic proton), 1.0—3.0 (saturated protons of DCPD ring) (Fig.4)

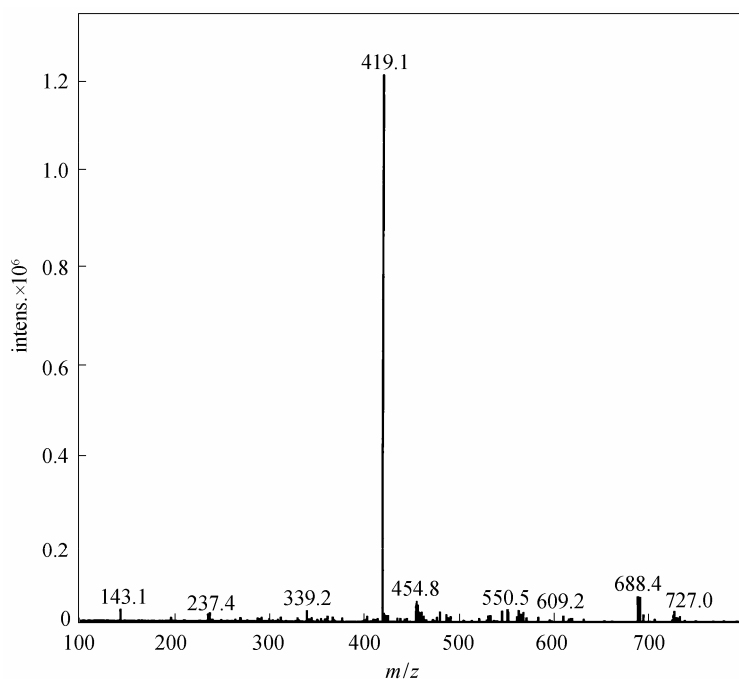


Figure 2 ESI-MS spectrum of product A

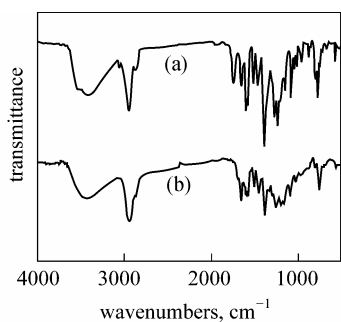


Figure 3 FTIR spectra of A and B

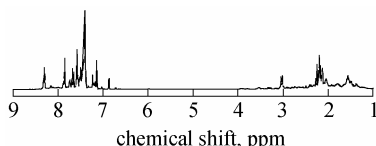


Figure 4 ¹H-NMR spectrum of A

equivalent weight (EEW) of epoxy resin was determined by HCl/acetone titration method. Thermogravimetric analysis (TGA) was performed using a Pyris 1 thermogravimetric analyzer (Perkin-Elmer Cetus Instruments, Norwalk, CT) at a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen and air atmosphere. Dynamic mechanical thermal analysis (DMTA) was carried out with a TA DMA Q800 instrument using $2\text{mm}\times 10\text{mm}\times 30\text{mm}$ rectangular samples at a programmed heating rate of $3^{\circ}\text{C}\cdot\text{min}^{-1}$ from 50°C to 300°C at a frequency of 1Hz under air atmosphere. Moisture absorption was tested as follows: $10\text{mm}\times 10\text{mm}\times 2\text{mm}$ rectangular sample was dried under vacuum until traces of water had been expelled, cooled to room temperature, weighed and placed in water for 72h, and reweighed. The moisture absorption was calculated as percent mass gain.

3 RESULTS AND DISCUSSION

3.1 Synthesis and characterization

The alkylated product of 1-naphthol with DCPD was synthesized by Friedel Crafts reaction between 1-naphthol and DCPD. It involves an electrophilic aromatic substitution of DCPD on naphthol ring. First, DCPD reacted with AlCl_3 to form carbocations with

three possible structures[12] (see Fig.6), then the three possible active carbocations attack the naphthalene ring resulting in C—C linkage. It is similar to the reaction between phenol and DCPD[13,14].

Several isomeric compounds would be obtained because of the presence of three different carbocations from DCPD. Mass spectrum showed that the alkylates had the same molecular weight ($m/z=419.1$), ¹H NMR analyses of A indicated that the product was not just a single compound but a mixture of isomeric compounds obtained from the alkylation between different carbocations and naphthalene. In this study, no efforts were made to separate the product and all of the isomeric compounds can be used to form the final resin. In addition, the molar ratio of naphthol to DCPD and the reaction temperature could influence the resultant product. It was found that if the reaction temperature was too low, the predominant product was DCPD single-substituted alkylate, which was the compound created *via* the alkylation process between one DCPD molecule and one 1-naphthol molecule. As the molar ratio of naphthol to DCPD increased, the DCPD single-substituted alkylate decreased evidently. Therefore, with large molar excess of naphthol to DCPD and the appropriate reaction temperature, optimum concentration for naphthol-DCPD alkylate obtained. A was characterized by ESI-MS, FTIR and ¹H NMR spectra. Mass spectrum showed that A has a single mass-charge ratio ($m/z=419.1$) and contains no single-substituted alkylate. ¹H NMR spectrum (Fig.4) exhibited broad peaks at 1.0—2.6 that is attributed to the presence of saturated protons in the DCPD ring, supporting the suggestion that A contains two or more isomeric compounds. The molar ratios of hydroxyl group protons to aromatic protons and saturated protons calculated from the ¹H NMR spectrum were 1 : 6.05 and 1 : 6.92, which were close to the theoretical constants of 1 : 6 and 1 : 7, and no signals were found at 5.0—6.0 ppm which is the signal range for unsaturated protons of DCPD ring. These observations also proved that no single-substituted alkylate or unreacted DCPD is contained in A.

Naphthalene/DCPD novolac resin was prepared by the condensation reaction between A and paraformaldehyde in the presence of PSTA as catalyst. The novel resin showed increase in molecular weight and

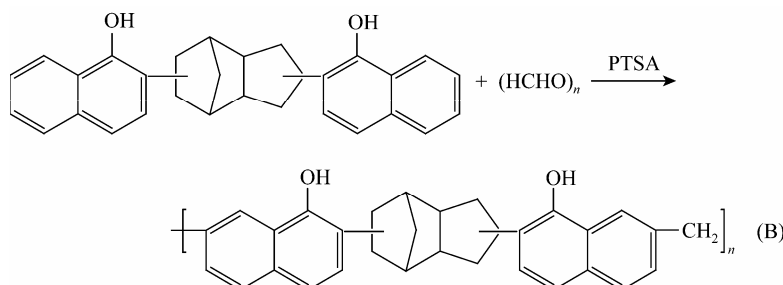


Figure 5 Synthesis of product B

IR(KBr): 3443cm^{-1} (—OH of aromatic ring); 1386cm^{-1} (C=O); 1658cm^{-1} , 1598cm^{-1} , 1508cm^{-1} (aromatic C—C) [Fig.3(b)]. ¹H-NMR(CDCl_3) δ (ppm): 8.29(—OH), 6.72—7.76 (aromatic protons), 4.53—4.72 (multiple peak —CH₂ between naphthyl), 1.0—3.0 (saturated —CH—CH₂). ¹³C-NMR(Dimethyl sulfoxide, d₆) δ (ppm): 148.2, 134.4, 132.4, 130—125, 123.9, 123.0, 121.8, 113.6 (naphthalene); 52.3 (—CH₂ between naphthyl); 43.4, 40.3, 35.1, 34.3, 32.1, 30.5, 26.2, 25.1, 24.4, 22.8 (DCPD ring). GPC: $M_n=973$; polydispersity: 1.61

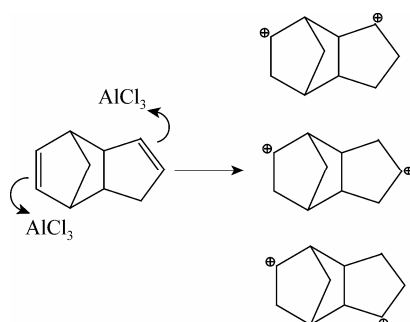


Figure 6 Three possible carbocations formed after DCPD reacted with AlCl_3

in the number of hydroxyl groups contained in one molecule. The GPC measurement showed that the number average molecular weight of B is $973\text{g}\cdot\text{mol}^{-1}$ and the average molecular weight is $1561\text{g}\cdot\text{mol}^{-1}$, thus, 2 or 3 molecules of A had been linked together by the methylene bridge. So, high crosslinking density epoxy cured network could be obtained from this multifunctional curing agent.

3.2 Characteristics of the cured polymer

3.2.1 Dynamic mechanical thermal analyses

Dynamic mechanical observations were carried out to analyze the dynamic elastic modulus and the occurrence of molecular mobility transitions such as glass transition. Fig.7 and Fig.8 show the dependence of storage modulus and $\tan\theta$ of E-51/B, E-12/B and common epoxy curing system including E-51/DDS and E-12/DDS on temperature, respectively.

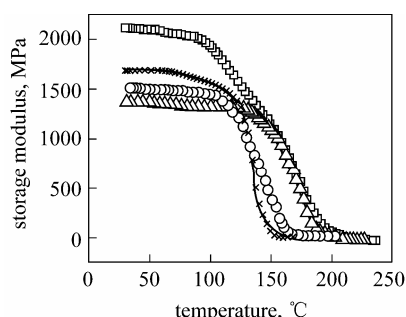


Figure 7 Temperature dependences of storage modulus for cured polymers

□ E-51/B; △ E-12/B; ○ E-51/DDS; × E-12/DDS

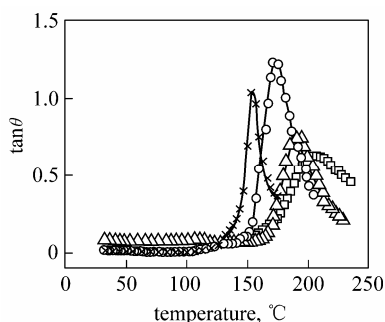


Figure 8 Temperature dependences of $\tan\theta$ for cured polymers

□ E-51/B; △ E-12/B; ○ E-51/DDS; × E-12/DDS

The storage modulus of E-51/product B was higher than that of the other three epoxy systems both in the glassy and rubbery region characterized by the temperature corresponding to the maximum peak of $\tan\theta$. The cured polymer using naphthalene/DCPD novolac resin as curing agent exhibited much higher T_g than that using conventional phenyl-based epoxy curing agent DDS by approximately 30°C (Table 1). This result confirms that the T_g of the epoxy polymer can be increased by introducing some rigid group into the backbone of epoxy network. The higher rigidity of naphthalene and DCPD structure could restrain the thermal movements and rotation of polymer chains. Though E-12/B had lower storage modulus than E-51/DDS and E-12/DDS in glass region, it had higher storage modulus at the temperature above T_g . Higher retention of storage modulus for E-12/B may attributed to the high crosslinking density because the naphthalene-DCPD novolac resin is a multi-functional curing agent.

Table 1 Dynamic thermal mechanical analysis of the cured polymers

Sample	T_g , $^\circ\text{C}$	Storage modulus, MPa	
		glassy region ^①	rubbery region ^②
E-51/B	206.6	2107.2	33.31
E-12/B	189.5	1371.5	29.85
E-51/DDS	172.9	1507.0	14.17
E-12/DDS	153.6	1691.9	12.40

① Storage modulus at 60°C .

② Storage modulus at T_g .

3.2.2 Thermogravimetric analyses

TGA is a convenient technique that can rapidly evaluate the comparative thermal stabilities of various polymers. Fig.9 and Fig.10 present the TGA curves of the cured polymer under nitrogen and air, respectively. As depicted in Table 2, by comparing the $T_{10\%}$ (10% degradation temperature) of the four cured polymers, DGEBA/B system had a better thermal stability than DGEBA/DDS system because of the three resonance structures of naphthalene compared with the two resonance structures for phenyl[9]. DGEBA/B system also exhibited a higher char yield. It may be proposed that the formation of char is facilitated because of the presence of naphthalene and DCPD structure.

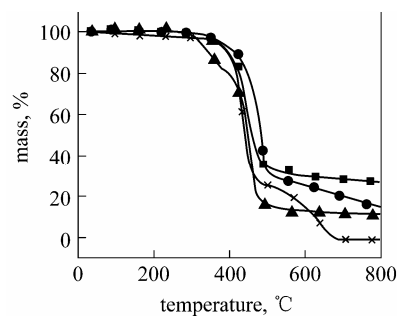


Figure 9 Mass loss of the cured polymers under nitrogen atmosphere

■ E-51/B; ● E-12/B; ▲ E-51/DDS; × E-12/DDS

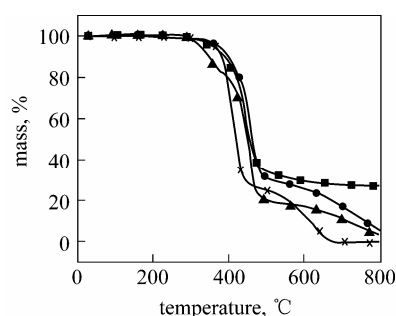


Figure 10 Mass loss of the cured polymer under air atmosphere

■ E-51/B; ● E-12/B; ▲ E-51/DDS; × E-12/DDS

Table 2 Thermal stability of the cured polymers by TGA

Sample	Nitrogen atmosphere		Air atmosphere	
	$T_{10\%}$, °C	Char yield ^① , %	$T_{10\%}$, °C	Char yield ^① , %
E-51/B	398.2	27.10	390.9	26.83
E-12/B	412.8	15.07	399.8	4.99
E-51/DDS	344.1	11.36	344.7	3.36
E-12/DDS	395.1	0.11	382.5	0

① Char yield at 800°C.

The mass loss increased rapidly under air at a temperature above 600°C, the presence of oxygen results in a complicated decomposition mechanism of the cured polymer and the pyrolysis reaction was activated by the existence of oxygen[15].

3.2.3 Moisture absorption

Moisture absorption increases the dielectric constant of the cured polymer. Furthermore, it ionizes the ionic impurities and thus corrodes the integrated circuits. Thus, to obtain a higher performance epoxy polymer, it is necessary to decrease the moisture absorption. The moisture absorption of the DGEBA/B and DGEBA/DDS system are shown in Table 3. Conventionally, the moisture absorption increases as the T_g increases in the cured polymers from novolac-type epoxy resin and phenol novolac[16]. However, because of the hydrophobic nature of both aliphatic DCPD and naphthyl structure, the cured polymer from DGEBA/product B system exhibited a high T_g and relatively low moisture absorption.

Table 3 Moisture absorption of the cured polymers

Sample	Water absorption, %
E-51/B	0.662
E-12/B	0.971
E-51/DDS	1.437
E-12/DDS	1.892

4 CONCLUSIONS

A novel naphthalene-DCPD-based novolac epoxy curing agent was prepared from inexpensive and easily available starting materials by relatively simple synthetic methods. The multiple naphthol O-H groups

provided more crosslinking sites for epoxy resins. Because of the presence of the naphthalene and DCPD structure in the cured polymer network, the resulting epoxy polymers exhibited higher T_g , good thermal stability and lower moisture absorption. These pronounced good properties revealed that the novel naphthalene/DCPD novolac curing agent could be used as an alternative method to obtain heat-resistant thermosets.

REFERENCES

- Ho, T.H., Wang, C.S., "Synthesis of aralkyl novolac epoxy resins and their modification with polysiloxane thermoplastic polyurethane for semiconductor encapsulation", *J. Appl. Polym. Sci.*, **74**, 1905–1916(1999).
- Kaji, M., Endo, T., "Synthesis of a novel epoxy resin containing naphthalene moiety and properties of its cured polymer with phenol novolac", *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 3063–3069(1999).
- Wang, C.S., Leu, T.S., Hsu, K.R., "Novel bismaleimide with naphthalene side group (I) from 1-naphthaldehyde and 2,6-dimethylaniline", *Polymer*, **39**, 2921–2927(1998).
- Castell, P., Serra, A., Galia, M., "New liquid-crystalline thermosets from liquid-crystalline bisazomethynic epoxy resins with naphthylene disruptors in the central core", *J. Polym. Sci. Part A: Polym. Chem.*, **41**, 1536–1544 (2003).
- Xu, K., Chen, M.C., Zhang, K., Hu, J.W., "Synthesis and characterization of novel epoxy resin bearing naphthyl and limonene moieties, and its cured polymer", *Polymer*, **45**, 1133–1040(2004).
- Lee, J.Y., Jang, J., "Synthesis and curing of liquid crystalline epoxy resin based on naphthalene mesogen", *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 419–425(1999).
- Ochi, M., Shimizu, Y., Nakanishi, Y., Murata, Y., "Effect of the network structure on thermal and mechanical properties of mesogenic epoxy resin cured with aromatic amine", *J. Polym. Sci. Part B: Polym. Phys.*, **35**, 397–405 (1997).
- Wang, C.S., Lee, M.C., "Synthesis and properties of epoxy resins containing 2-(6-oxid-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl) 1,4-benzenediol (II)", *Polymer*, **41**, 3631–3638(2000).
- Wang, C.S., Lee, M.C., "Synthesis and modification of a naphthalene-containing trifunctional epoxy resin for electronic applications", *J. Appl. Polym. Sci.*, **70**, 1907–1921(1998).
- Wang, C.S., Lee, M.C., "Synthesis, characterization, and properties of multifunctional naphthalene-containing epoxy resins cured with cyanate ester", *J. Appl. Polym. Sci.*, **73**, 1611–1622(1999).
- Ho, T.H., "Synthesis of naphthalene containing aralkyl novolac epoxy resins for electronic application", *Macromol. Mater. Eng.*, **283**, 57–61(2000).
- Lin, C.H., Chiang, J.C., Wang, C.S., "Low dielectric thermoset (I). Synthesis and properties of novel 2,6-dimethyl phenol-dicyclopentadiene epoxy", *J. Appl. Polym. Sci.*, **88**, 2607–2613(2003).
- Hsiue, G.H., Wei, H.F., Shiao, S.J., Kuo, W.J., Sha, Y.A., "Chemical modification of dicyclopentadiene-based epoxy resins to improve compatibility and thermal properties", *Polym. Degrad. Stab.*, **73**, 309–318(2001).
- Tseng, F.P., Chang, F.C., Lin, S.F., Lin, J.J., "Preparation and epoxy curing of novel dicyclopentadiene-derived mannich amines", *J. Appl. Polym. Sci.*, **71**, 2129–2139(1999).
- Liu, Y.L., Hsiue, G.H., Lee, R.H., Chiu, Y.S., "Phosphorus-containing epoxy for flame retardant (III): Using phosphorylated diamines as curing agents", *J. Appl. Polym. Sci.*, **63**, 895–901(1997).
- Ogata, M., Kinjo, N., Kawata, T., "Effects of crosslinking on physical properties of phenol-formaldehyde novolac cured epoxy resins", *J. Appl. Polym. Sci.*, **48**, 583–601(1993).