Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 47 (2006) 1291–1299

polymer

www.elsevier.com/locate/polymer

Dielectric and thermal properties of dicyclopentadiene containing bismaleimide and cyanate ester. Part IV

Hann-Jang Hwang [a,*], Chun-Hung Li [b], Chun-Shan Wang [b]

[a] *Department of Cosmetic Science, Chung Hwa College of Medical Technology, Tainan 717, Taiwan, ROC*
[b] *Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC*

Received 4 May 2005; received in revised form 5 December 2005; accepted 11 December 2005

Abstract

A novel bismaleimide (BMI), bis(4-maleimidophenoxy-3,5-dimethylphenyl)dicyclopentadiene (DCPDBMI), containing a large dicyclopentadiene (DCPD) and aryl ether linkage, was synthesized from bis(4-aminophenoxy-3,5-dimethylphenyl)dicyclopentadiene and maleic anhydride by the usual two-step procedure that included ring-opening addition to give bismaleamic acid, followed by cyclodehydration to bismaleimide. The monomers were characterized by Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (NMR), elemental analyses (EA), and mass spectra (MS). A series of bismaleimide-triazine (BT) resins were prepared from synthesized bismaleimide (DCPDBMI) and then cured with 2,6-dimethyl phenol-dicyclopentadiene dicyanate ester (DCPDCY) at various molar ratios. Thermal properties of cured BT resins (DCPDBMI/DCPDCY) were studied using dielectric analyzer (DEA), dynamic mechanical analyzer (DMA) and thermalgravimetric analyzer (TGA). These data were compared with that of commercial bismaleimide (DDMBMI) cured with bisphenol A dicyanate ester (BADCY). The cured DCPDBMI/DCPDCY exhibits lower dielectric constant, dissipation factor and moisture absorption than those of DDMBMI/BADCY. The effects of blend composition on the glass transition temperatures and thermal stability are discussed.

Keywords: Dielectric constant; High performance polymers; Thermal properties

---

1. Introduction

Conventional electronic circuit boards are made from glass fiber reinforced epoxy resins. However, they often fall short of the thermal and electrical performance demands of many modern high-speed devices. With current trends toward increased circuit densities, shorter propagation delays, elevated operating temperatures, and higher reliability, advanced materials such as bismaleimide (BMI) [1,2], cyanate ester (CE) [3–5], and bismaleimide-triazine (BT) resins [6–10] are required to satisfy these demands. Among these materials, bismaleimied-triazine is considered to be the most promising system.

Skylex® BT resins marketed by Mitsubishi Gas and Chemical Corporation comprise a blend of 4,4-bismaleimidodiphenylmethane (DDMBMI) and the dicyanate ester of bisphenol A [2,2-bis(4-cyanatophenyl)isopropylidene] (BADCY) in the form of a bismaleimide-triazine (BT) resins [11,12]. These resins have substantially better resistance to catastrophic loss of insulation resistance than the prevailing epoxy or bismaleimide systems. With superior properties, such as reduction in moisture absorption, excellent chemical resistance, good dimensional stability, low dielectric constant, and low dielectric loss, BT resins are attractive for circuit boards and semiconductor encapsulants applications for which high reliability is critical.

Dicyclopentadiene (DCPD) is a byproduct of C_5 streams in oil refineries, and is a raw material for low dielectric polymers due to their low polarity, low moisture absorption and relatively low cost. This hydrophobic, nonpolar bridging group contributes excellent moisture resistance and a dramatic reduction in the dielectric constant without determinately affecting thermal performance.

As we know, the signal propagating speed in an integrated circuit is inversely proportional to the square root of the dielectric constant, and the signal propagation loss is proportional to the square root of the dielectric constant and dissipation factor. Thus, a material with low dielectric constant and low dissipation factor will enhance the signal propagating speed and reduce the signal propagating loss. In our previous studies [5,13], the 2,6-dimethylphenol-dicyclopentadiene

---

* Corresponding author. Tel.: +886 6 3313236; fax: +886 6 3354986.
E-mail address: cosmetic@mail.hwai.edu.tw (H.-J. Hwang).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.12.040

cyanate ester resulted from 2,6-dimethylphenol-dicyclopentadiene novolac and cyanogens bromide has provided cured products with a low dielectric constant and low moisture absorption.

In this paper, continuing our research on dicyclopentadiene, we synthesized a 2,6-dimethylphenol-dicyclopentadiene-based bismleimide (DCPDBMI) from 2,6-dimethylphenol-dicyclopentadiene-based novolac. The structure of DCPDBMI was characterized by Fourier transform infrared (FT-IR) spectra, mass spectra, nuclear magnetic resonance (NMR) spectra, and elemental analysis. A series of novel BT resins that was prepared from 2,6-dimethylphenol-dicyclopentadiene-based cyanate ester (DCPDCY) and DCPDBMI. The resulted BT resins are expected to have lower dielectric constant and moisture absorption than commercial BT resins because of the bulky *ortho*-methyl groups and low polar aliphatic DCPD linkage in the backbone structure and also retaining the attractive thermal and mechanical properties. The dielectric properties, thermal properties, dynamic mechanical analysis, and moisture resistance of the cured bismaleimide-triazine resins were also investigated to understand the structure–properties relationship.

2. Experimental

2.1. Materials

2,6-Dimethylphenol dicyclopentadiene novolac (DCPDNO) and 2,6-dimethylphenol dicyclopentadiene cyanate ester (DCPDCY) were synthesized according to the method reported [5,13]. 4,4-Bismaleimidodiphenylmethane (DDMBMI) was purchased from TCI. BADCY (B-10) was kindly supplied by Rhone–Poulenc. 10% Palladium on activated carbon (Pd/C), acetic anhydride, *p*-chloronitrobenzene, hydrazine monohydrate, maleic anhydride were purchased from Acros and used as received. Triethylamine was purchased from Ferak. Acetone was purchased from Tedia and stored in a 4 Å molecular sieve. *N*,*N′*-dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves. All other solvents were obtained from various commercial sources and used without further purification.

2.2. Monomer synthesis

2.2.1. Synthesis of DCPDNI

Into a reactor equipped with a stirrer, a reflux condenser, a thermometer and a nitrogen inlet were charged 300 ml of DMAc, 0.2 mol of 2,6-dimethyl phenol dicyclopentadiene novolac (DCPDNO), 0.44 mol of *p*-chloronitrobenzene, 0.44 mol of potassium carbonate. The reaction mixture was refluxed at 160 °C for 24 h under a nitrogen atmosphere. After completion of the reaction, the resulting inorganic salts were removed by hot filtration. To the mixture, methanol/water (1:1) were added and slowly cooled to room temperature. The product precipitated gradually, and was collected by filtration. The solid was washed with ethanol, filtered and dried under vacuum. The yield was 92%.

DCPDNI: IR (KBr) cm^{-1}: 2975–2950 cm^{-1} ($-CH_3$), 1661–1499 cm^{-1} ($-NO_2$ unsymmetrical stretching), 1389–1259 cm^{-1} ($-NO_2$ symmetrical stretching), 1275–1200 cm^{-1} (C–O–C), ^{1}H NMR δ (ppm): 8.25–6.75 (m, 12H, aromatic), 1.2–2.5 (m, 26H, aliphatic). Elemental analyses for $C_{38}H_{38}N_2O_6$ are as follows: C: 73.79%, H: 6.15%, N: 4.53%, O: 15.53% (theoretically) and C: 73.62%., H: 6.22%, N: 4.48%, O: 15.68% (experimentally). FAB mass spectrometry (FAB MS; *m/z*): 619 (36, M$^+$).

2.2.2. Synthesis of DCPDA

0.1 mol of DCPDNI in 300 g of ethanol was added 0.25 g 10% Palladium on activated carbon (Pd/c). Over a period of 1 h, 100 g of hydrazine monohydrate were added to the above mixture at 85 °C and then maintained at that temperature for 12 h. After completion of the reaction, the Pd/C catalyst was removed by hot filtration. Upon cooling, the product precipitated gradually, and was collected by filtration and dried under vacuum. The yield was 90%.

DCPDA: IR (KBr) cm^{-1}: 3500–3300 ($-NH_2$), 2975–2950 cm^{-1} ($-CH_3$), 1490–1450 (aromatic ring C=C), 1275–1200 cm^{-1} (C–O–C), ^{1}H NMR δ (ppm): 6.98–6.38 (m, 12H, aromatic), 4.65 (s, 4H, $-NH_2$), 1.12–2.5 (m, 26H, aliphatic). Elemental analyses for $C_{38}H_{42}N_2O_2$ are as follows: C:81.72%, H: 7.52%, N: 5.01%, O: 5.75% (theoretically) and C: 81.55%, H: 7.59%, N: 5.10%, O: 5.76% (experimentally). FAB mass spectrometry (FAB MS; *m/z*): 558 (100, M$^+$).

2.2.3. Synthesis of DCPDBMA

A three necked flask equipped with an additional funnel and a nitrogen inlet was charged with a solution of maleic anhydride (0.22 mol) in THF (100 ml). Under a nitrogen atmosphere, 0.1 mol of DCPDA dissolved in THF (50 ml) was added dropwise to the above mixture. An exothermic reaction and product precipitation were observed immediately. The mixture was stirred for 4 h at room temperature and at 60 °C for an additional 1 h. The precipitate was collected, washed with fresh THF to remove excess maleic anhydride, and then dried in vacuum. The yield of bismaleamic acid was 95%.

DCPDBMA: IR (KBr) cm^{-1}: 3700–3200 ($-NH_2$ and –OH), 2975–2950 cm^{-1} ($-CH_3$), 1720–1706 (–C=O), 1490–1450 (aromatic ring C=C), 1275–1200 cm^{-1} (C–O–C), 840–790 (C=C), ^{1}H NMR δ (ppm): 10.45 (s, 2H, COOH), 6.67–7.65 (m, 12H, aromatic), 6.26–6.50 (m, 4H, olefinic), 1. 22–2.5 (m, 28H, aliphatic). Elemental analyses for $C_{46}H_{46}N_2O_8$ are as follows: C: 73.20%, H: 6.10%, N: 3.71%, O: 16.99% (theoretically) and C: 72.95%, H: 6.26%, N: 3.68%, O: 17.11% (experimentally). FAB mass spectrometry (FAB MS; *m/z*): 755 (50, M$^+$).

2.2.4. Synthesis of DCPDBMI

To a 500 ml round-bottomed flask was added 0.05 mol of bismaleamic acid (DCPDBMA), 100 ml of acetone and 0.03 mol of triethylamine and stirred at room temperature for 0.5 h. After the addition of 0.1 g magnesium oxide and 0.01 g of cobalt(II) acetate, 0.11 mol of acetic anhydride was gradually added to the reaction mixture and stirred for 10 h. The reaction mixture was poured into a dilute solution of sodium carbonte to precipitate product which was filtered, washed with water to remove acetic acid, and then dried in vacuum. The yield of bismaleimide was 92%.

DCPDBMI: IR (KBr) cm^{-1}: 2975–2950 cm^{-1} ($-CH_3$), 1720–1706 (imide ring C=O), 1490–1450 (aromatic ring C=C), 1400–1300 cm^{-1} (C–N–C), 1275–1200 cm^{-1} (C–O–C), 840–790 (imide ring C=C), ^1H NMR δ (ppm): 6.8–7.2 (m, 12H, aromatic), 7.16 (s, 4H, olefinic), 1.22–2.5 (m, 26H, aliphatic). Elemental analyses for $C_{46}H_{42}N_2O_6$ are as follows: C: 76.88%, H: 6.84%, N: 3.89%, O: 13.39% (theoretically) and C: 76.69%, H: 6.08%, N: 3.89%, O: 13.34% (experimentally). FAB mass spectrometry (FAB MS; *m/z*): 718 (69, M^+).

2.3. Measurement

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Magna-520 spectrometer with KBr pellets. Spectra in the optical range of 400–4000 cm^{-1} were obtained by averaging 16 scans at a resolution of 4 cm^{-1}. ^1H NMR spectra were registered using a Bruker AC200 spectrometer using DMSO-d_6 as the solvent. Mass spectrometric analyses were performed on a VG 70-250 GC/MS spectrometer. Elemental analysis was performed using a Heraus CHN-Rapid elemental analyzer. DSC scans were obtained from samples of about 5–10 mg in a nitrogen atmosphere at a heating rate of 10 °C/min using a Perkin–Elmer DSC 7. TGA was performed with a Perkin–Elmer TGA 7 at a heating rate of 20 °C/min under nitrogen and from 30 to 800 °C. The coefficient of thermal expansion was measured with TMA mode of Perkin–Elmer DMA-7, a specimen 5 m/m in length being used at a heating rate of 10 °C/min. The thermal expansion increased with temperature and the values were calculated from the slope. DMA was carried out with a Perkin–Elmer DMA 7e. The storage modulus E' and $\tan\delta$ were determined as the sample was subjected to temperatures scan mode at a programmed heating rate of 10 °C/min from ambient to 350 °C at a frequency of 1 Hz and an amplitude of 6 μm. A sample 15 mm in length, 10 mm in width and approximately 1.5 mm in thickness was used. The test method was performed by three point bending mode with a tension ratio at 110%. Dielectric measurements were performed with a Agilent 4291B measurement system at a temperature of 30 °C by the two parallel plate mode at 1 MHz. The applied voltage is 1 V. Before testing, samples (1×1 cm^2 and 0.3 cm thickness) was dried under vacuum at 100 °C for 8 h. Moisture absorption was tested as follow: Samples with 1×1 cm^2 and 0.1 cm thickness was dried under vacuum at 120 °C until moisture had been expelled. After cooled down to room temperature, the sample was weighed and then placed in 100 °C water for 48 h and weighed. The moisture absorption was calculated as percent weight gain $=(W/W_0-1)\times100\%$, where W, weight of sample after placing in 100 °C water for 48 h, and W_0, weight of sample before placing in water.

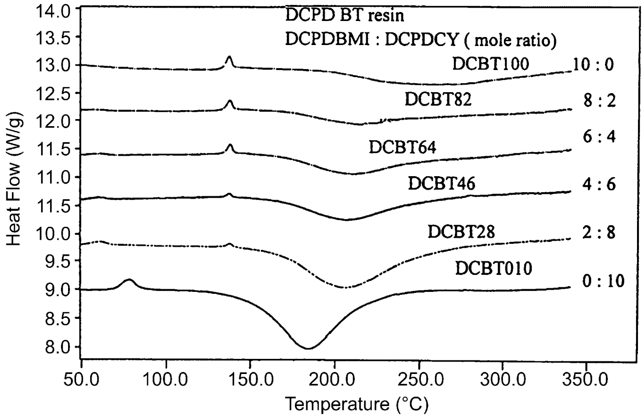


Fig. 1. DSC analysis for various mole ratio of DCPDBMI/DCPDCY (DCPDBT) resins.

2.4. DSC scans of BT resins and their curing procedure

Fig. 1 shows the DSC scans for various mole ratio of DCPDBMI/DCPDCY (DCPDBT) resins. Based on the DSC analyses, bismaleimide/dicyanate ester with mole ratio 10/0, 8/2, 6/4, 4/6, 2/8 and 0/10 were mixed and then heated on a hot plate at about 150 °C with continuous stirring until homogeneous solutions were obtained. The homogeneous mixture was cured in oven at 180 °C for 2 h, 200 °C, for 8 h and 220 °C for another 5 h under dry nitrogen.

2.5. The degree of curing (D_c) for cured BT resins

After removal from the oven the cured samples were cooled down by dry ice and then ground. Standard sieves of 12 and 16 mesh were used to collect particles for extraction experiments. Extraction was carried out in a Soxhlet apparatus over 20 h using methylethyl ketone (MEK) as a solvent. After the extraction was finished, the sample was removed and MEK was blown out from the surface by cold air. The sample was left for 12 h in open air and then again for 12 h in a vacuum oven at 70 °C in order to remove all MEK. The weight of this sample was recorded as cured resin weight, W_c. The degree of curing (D_c) was defined as:

$$D_c = W_c/W_0 \times 100\%$$

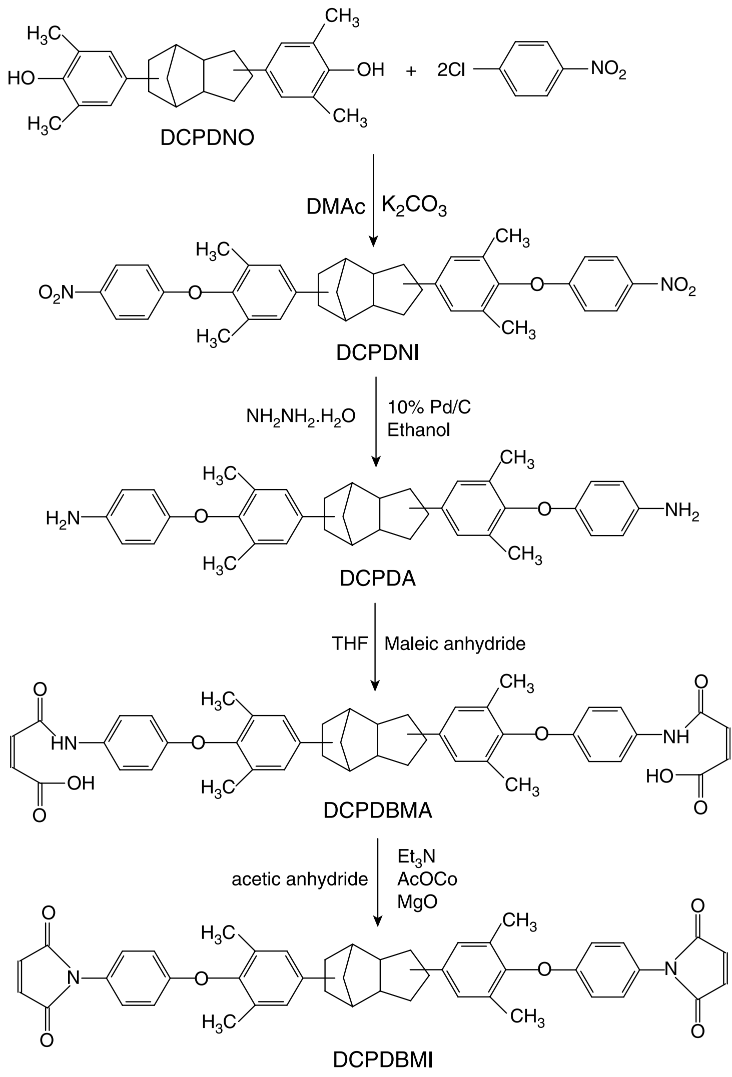
W_0 is original weight of the sample before extraction.

From the Table 1, the degree of curing for each resin system with various mole ratio are ≥98.9%. However, there are no significant differences among them.

Table 1

Degree of curing (D_c) for various mole ratio BT resin

Bismaleimide/ dicyanate ester (mole ratio)	DCPDBMI/ DCPDCY (DCPDBT)	DDMBMI/ DCPDCY (BT_{DC})	DDMBMI/ BADCY (BT)
10/0	99.9	99.8	99.8
8/2	99.8	99.7	99.5
6/4	99.5	99.2	99.1
4/6	98.9	99.4	99.3
2/8	99.3	99.6	99.0
0/10	99.5	99.5	99.3



Scheme 1. The synthetic equation of DCPDBMI.

3. Results and discussion

3.1. Monomer synthesis

The diamine containing dicyclopentadiene and aryl ether linkage was obtained from 2,6-dimethyl phenol-dicyclopentadiene according to synthetic Scheme 1. The dinitro compound was synthesis in a quantitative yield from 2,6-dimethyl phenol-dicyclopentadiene and *p*-chloronitro-benzene in the presence of potassium carbonate dissolved in dry DMAc and refluxed for 24 h. Reduction of the dinitro compound DCPDNI to amino compound DCPDA was carried out with hydrazine/(Pd/C). The disappearance of characteristic nitro stretching bands at arounds 1510 ± 10 and $1335 \pm 10\ \text{cm}^{-1}$ on the IR spectra was used as criteria for the completion of the reduction of dinitro compound (DCPDNI). The infrared spectra of DCPDA was shown in Fig. 2. The results of IR, ^{1}H NMR, mass spectra, and elemental analyses of intermediates, dinitro and diamine compounds, were all in agreement with the proposed structures.

The diamine (DCPDA) was then reacted with the respective amount of maleic anhydride in THF at ambient to give the bismaleamic acid (DCPDBMA). The reaction was exothermic and the product preciptated immediately upon mixing of the reagents. The bismaleamic acids were cyclodehydrated in acetone. The heterogeneous mixture

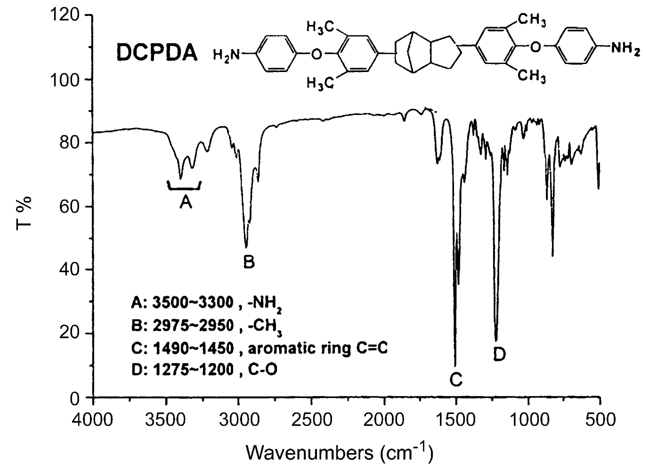


Fig. 2. FT-IR spectrum of DCPDA.

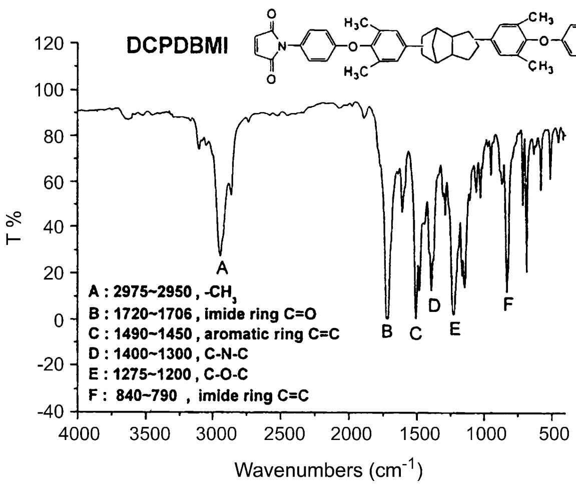


Fig. 3. FT-IR spectrum of DCPDBMI.

became homogeneous at the end of imidization to DCPDBMI. The infrared spectrum of the bismaleimide (DCPDBMI) is shown in Fig. 3. The typical infrared spectra of bismaleimide (DCPDBMI) and the corresponding bismaleamic acid (DCPDBMA) exhibited several distinctive differences. Bismaleimide showed a strong absorption at 1720 cm^{-1} and a weak absorption at 1780 cm^{-1}, assigned to asymmetric and symmetric C=O stretching vibration of imide ring, respectively; it also lacked the absorption at 3400–3000 cm^{-1} associated with the carboxylic OH stretching vibration and 1540 cm^{-1} for the –NH stretching of the amide group. Consequently, imidization could be monitored by means of these absorptions. The structures of the bismaleamic acid (DCPDBMA) and bismaleimide (DCPDBMI) were also confirmed by ^{1}H NMR, mass spectra, and elemental analyses. The results were in good agreement with the proposed structures. The structures of monomers selected for examination are listed in Fig. 4.

3.2. Dielectric constant and dissipation factor

Tables 2 and 3 show the dielectric constant and dissipation factor of cured BT resins. No matter what mole ratio of bismaleimide/dicyanate ester were used, the dielectric constant and dissipation factor of the DCPDBT system were lower than those of the DDMBMI system ($\mathrm{BT_{DC}}$ and BT system). The dielectric constant and dissipation factor decreased in the following order BT > $\mathrm{BT_{DC}}$ > DCPDBT. The dielectric constant could be reduced by an increasing in the free volume of the molecule or by a decrease in the polarization [14–16]. DCPDBT system with low polar aliphatic DCPD linkage and four bulky *ortho*-methyl groups led to more spacing between the polymer molecules, and this resulted in less efficient chain packaging and an increase in the free volume of the polymer [17], which reduced the dielectric constant and dissipation factor of the DCPDBT system. Furthermore, the presence of low polar cycloaliphatic DCPD linkage may reduce interchain electronic interaction and increase hydrophobicity, thus decreasing the dielectric constant and dissipation factor. From the Figs. 5 and 6, the higher the dicyanate ester content

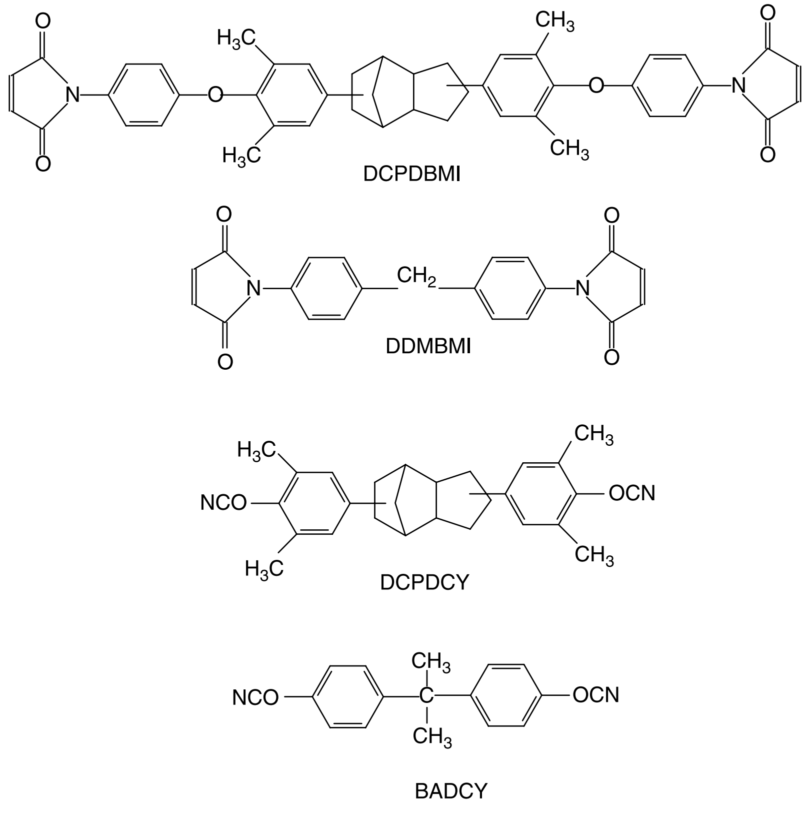


Fig. 4. Monomers used in the study.

Table 2
Dielectric constant (D_k, U) at room temperature for various mole ratio DCPDBMI/DCPDCY (DCPDBT) resin

Bismaleimide/ dicyanate ester (mole ratio)	DCPDBMI/DCPDCY (DCPDBT)		DDMBMI/DCPDCY (BT_{DC})		DDMBMI/BADCY (BT)	
	1 MHz	1 GHz	1 MHz	1 GHz	1 MHz	1 GHz
10/0	3.01	2.98	4.03	3.89	4.03	3.89
8/2	2.95	2.91	3.69	3.56	3.94	3.62
6/4	2.88	2.86	3.38	3.29	3.52	3.30
4/6	2.79	2.75	3.10	3.01	3.27	3.05
2/8	2.69	21.64	2.83	2.76	3.22	3.01
0/10	2.58	2.53	2.58	2.53	2.95	2.92

Table 3
Dissipation factor (D_f, mU) at room temperature for various mole ratio DCPDBMI/DCPDCY (DCPDBT) resin

Bismaleimide/ dicyanate ester (mole ratio)	DCPDBMI/DCPDCY (DCPDBT)		DDMBMI/DCPDCY (BT_{DC})		DDMBMI/BADCY (BT)	
	1 MHz	1 GHz	1 MHz	1 GHz	1 MHz	1 GHz
10/0	98.36	33.45	163.88	43.32	163.88	43.32
8/2	69.45	28.13	103.97	37.08	150.58	39.95
6/4	58.19	20.97	76.84	36.17	125.32	39.33
4/6	49.33	20.44	72.74	30.63	109.85	37.75
2/8	41.52	12.11	64.49	19.42	98.13	33.41
0/10	20.21	3.61	20.21	3.61	64.39	24.33

in the formulation, the lower the dielectric constant and dissipation factor of the cured BT resins, which further proves the low dielectric properties of dicyclopentadiene linkage.

3.3. Moisture resistance

The absorbed moisture acts as plasticizer, which reduces the mechanical and thermal properties of cured resins and also has a detrimental effect on dielectric properties. Moisture absorption will reduce T_g of a laminate material and may cause 'popcorn phenomenon' when in contact with solder at a high temperature. Moisture absorption will also ionize the ionic impurities (e.g. Cl^-) and, therefore, corrode the integrated circuits. Furthermore, moisture absorption will increase the dielectric constant of laminate board materials. Therefore, low moisture absorption is necessary for laminate materials [17,18]. As seen in Table 4, all cured DCPDBMI/DCPDCY resins showed lower moisture absorption than the control DDMBMI systems. The lower moisture absorption may be attributed to the hydrophobic nature of aliphatic DCPD structure and the *ortho*-methyl groups in DCPDCY From the Fig. 7, the higher the dicyanate ester content in the formulation, the lower moisture absorption of the cured BT resins, which further proves the low moisture absorption of dicyclopentadiene linkage.

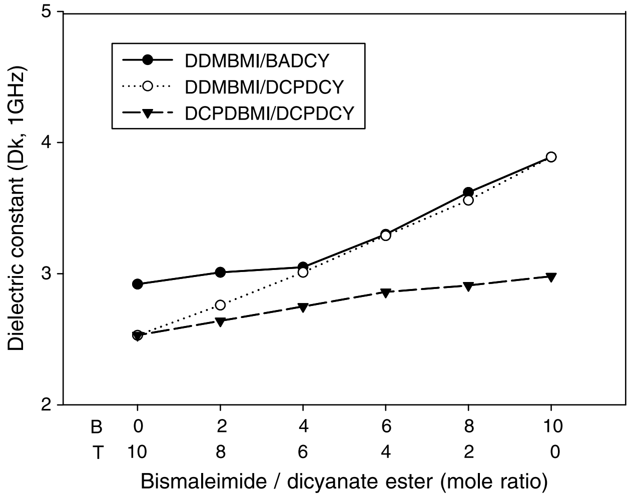


Fig. 5. Dielectric constant (D_k, 1 GHz) at room temperature for various mole ratio BT resin.

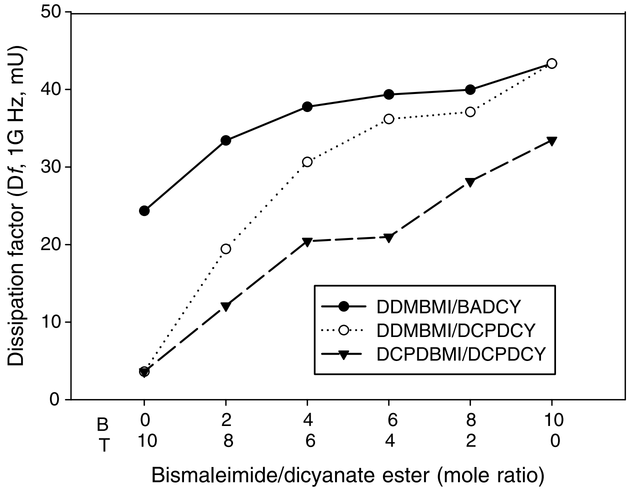


Fig. 6. Dissipation factor (D_f, 1 GHz, mU) at room temperature for various mole ratio BT resin.

Table 4
Moisture absorption of various mole ratio DCPDBMI/DCPDCY (DCPDBT) resins

Sample ID	Mole ratio	Moisture absorption (%)			
		12 h	24 h	36 h	48 h
DCPDBMI/DCPDCY (DCBT100)	10/0	1.28	1.32	1.33	1.33
(DCBT82)	8/2	1.23	1.27	1.27	1.27
(DCBT64)	6/4	1.05	1.08	1.10	1.10
(DCBT46)	4/6	1.01	1.02	1.02	1.02
(DCBT28)	2/8	0.93	0.94	0.95	0.95
(DCBT010)	0/10	0.80	0.87	0.88	0.88
DDMBMI/DCPDCY ($\mathrm{BT_{DC}}$100)	10/0	4.23	5.23	5.34	5.46
$\mathrm{BT_{DC}}$82	8/2	3.33	4.21	4.31	4.50
$\mathrm{BT_{DC}}$64	6/4	2.73	3.43	4.01	4.09
$\mathrm{BT_{DC}}$46	4/6	1.94	2.51	2.98	3.04
$\mathrm{BT_{DC}}$28	2/8	1.34	1.75	1.81	1.84
$\mathrm{BT_{DC}}$010	0/10	0.80	0.87	0.88	0.88
DDMBMI/BADCY (BT100)	10/0	4.23	5.23	5.34	5.46
BT82	8/2	3.44	4.42	4.54	4.63
BT64	6/4	3.01	4.08	4.14	4.19
BT46	4/6	2.50	2.91	3.04	3.07
BT28	2/8	1.77	2.88	2.96	2.98
BT010	0/10	1.49	1.73	1.75	1.77

3.4. Thermal stability of polymers

Thermogravimetric analysis (TGA) is the most favored technique for the rapid evaluation of the thermal stability of polymeric materials. It is especially useful in comparing and ranking the thermal stabilities of various polymers. The relative thermal stability of cured resins were compared by the temperature of 5 and 10% weight loss ($T_{5\%}$ and $T_{10\%}$) and percent char yield at 700 °C (Y_c). The TGA data for cured resins at various molar ratio of BMI/dicyanate esters are listed in Table 5. The cured resins of DCPDBMI/DCPDCY in various mole ratio exhibited 5% weight loss decomposition temperature ($T_{5\%}$) ranging between 461 and 430 °C in nitrogen and the anaerobic char yields at 700 °C ranged between 32 and 48%. As would be expected, DCPDBMI/DCPDCY resins system show very good thermal stability. The thermal stability of cured resins slightly increases with the increase in the starting BMI/dicyanate ester molar ratio, which may be due to the higher crosslink density of BMI than dicyanate ester system.

3.5. Dynamic mechanical properties of polymers

The peak of tan δ was identified as the glass transition temperatures (T_g) because a large decrease in G' occurred at the point. The glass transition temperatures (T_g) of the cured resins with various molar ratios of the bismaleimide/dicyanate ester were examined and listed in Table 6. As would be expected, DCPDBMI/DCPDCY resins system show very good thermal stability. The glass transition temperature of cured resins slightly decreased with the increase in the dicyanate ester molar ratio because of lower crosslink density of dicyanate ester than that of bismaleimide. The peak height expresses the ability of the material to dissipate energy as heat during the deformation cycle. The tan δ value of cured BT resins increased with the increase in the dicyanate ester molar ratio which further proves the lower crosslinking density of the cured dicyanate ester domain.

3.6. TMA analysis

Thermally induced dimensional change of these cured BT resins were investigated by a thermochanical analyzer. According to the results shown in Table 7, the coefficient of thermal expansion (before T_g) of the DCPDBMI/DCPDCY system was $1.67–2.81\times10^{-5}\,°\mathrm{C}^{-1}$. Although the DCPDBMI has longer chain length between two

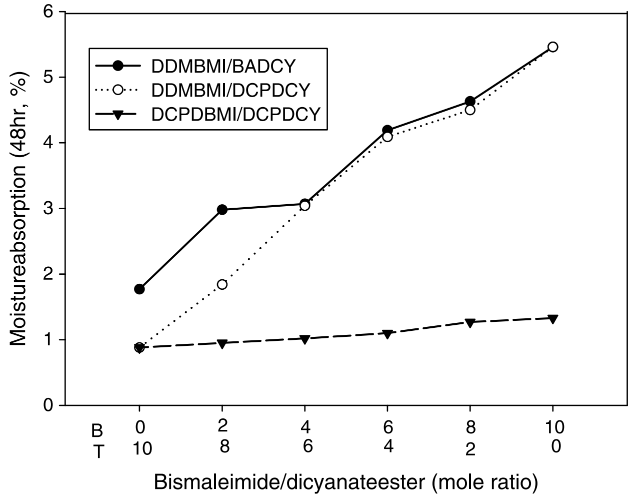


Fig. 7. Moisture absorption for various mole ratio of DCPDBMI/DCPDCY (DCPDBT) resins.

Table 5
TGA analysis for various mole ratio DCPDBMI/DCPDCY (DCPDBT) resins

Sample	Mole ratio	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield at 600 °C (%)	Char yield at 700 °C (%)
DCPDBMI/DCPDCY (DCBT 100)	10/0	465	476	56.84	48.24
(DCBT82)	8/2	461	479	56.10	47.51
(DCBT64)	6/4	456	477	54.45	46.14
(DCBT46)	4/6	451	467	47.76	40.91
(DCBT28)	2/8	438	453	44.52	38.95
(DCBT010)	0/10	430	449	36.64	32.05
DDMBMI/DCPDCY (BT_{DC} 100)	10/0	509	523	58.81	51.25
$BT_{DC}82$	8/2	466	482	56.58	49.67
$BT_{DC}64$	6/4	448	462	48.54	42.74
$BT_{DC}46$	4/6	432	454	49.47	43.63
$BT_{DC}28$	2/8	444	455	41.35	36.78
$BT_{DC}010$	0/10	430	449	36.64	32.05
DDMBMI/BADCY (BT100)	10/0	509	523	58.81	51.25
BT82	8/2	453	470	59.20	52.83
BT64	6/4	396	442	57.24	51.27
BT46	4/6	398	423	53.37	47.98
BT28	2/8	395	428	51.05	46.04
BT010	0/10	441	457	45.40	40.86

maleimide group than that of DDMBMI, it is reasonable that the introduction of DCPDBMI into DCPDBT will decrease its crosslink density and increase free volume of resins, thus increase the thermal expansion coefficient. But the rigidity of DCPD and the steric hindrance of *ortho*-methyl may have compensated for the effect of the higher free volume; thus the system DCPDBMI/DCPDCY system had a coefficient of thermal expansion (CTE) significantly lower than that of the DDMBMI/BADCY system. The glass temperatures measured by TMA are slightly lower than those of DMA measurements; however, the glass temperature still decrease with the content of cyanate ester.

Table 6
DMA analysis for various mole ratio DCPDBMI/DCPDCY (DCPDBT) resins

Sample ID	Mole ratio	T_g (°C)[a]	Height of tan δ[b]
DCPDBMI/ DCPDCY (DCBT100)	10/0	345	0.180
(DCBT82)	8/2	334	0.188
(DCBT64)	6/4	330	0.246
(DCBT46)	4/6	321	0.378
(DCBT28)	2/8	304	0.418
(DCBT010)	0/10	271	0.424
DDMBMI/ DCPDCY ($BT_{DC}100$)	10/0	>350	–
$BT_{DC}82$	8/2	335	0.052
$BT_{DC}64$	6/4	328	0.102
$BT_{DC}46$	4/6	317	0.194
$BT_{DC}28$	2/8	297	0.343
$BT_{DC}010$	0/10	271	0.424
DDMBMI/ BADCY (BT100)	10/0	>350	–
BT82	8/2	300	0.036
BT64	6/4	293	0.113
BT46	4/6	289	0.185
BT28	2/8	288	0.367
BT010	0/10	287	0.512

[a] α Peak of tan δ curve.
[b] tan δ value at T_g.

Table 7
TMA analysis for various mole ratio DCPDBMI/DCPDCY (DCPDBT) resins

Sample	Mole ratio	CTE (10^{-5} °C^{-1})		$>T_g$[a] (°C)
		$<T_g$[b]	$>T_g$[c]	
DCPDBMI/DCPDCY				
(DCBT100)	10/0	2.67	4.79	319
(DCBT82)	8/2	2.18	5.04	310
(DCBT64)	6/4	1.67	4.35	303
(DCBT46)	4/6	2.44	5.21	299
(DCBT28)	2/8	2.81	4.93	288
(DCBT010)	0/10	2.71	12.49	266
DDMBMI/DCPDCY				
($BT_{DC}100$)	10/0	3.01	–	–
$BT_{DC}82$	8/2	2.83	5.07	301
$BT_{DC}64$	6/4	2.78	6.99	299
$BT_{DC}46$	4/6	3.03	6.74	284
$BT_{DC}28$	2/8	3.16	6.53	271
$BT_{DC}010$	0/10	2.71	12.49	266
DDMBMI/BADCY (BT100)	10/0	3.01	–	–
BT82	8/2	2.84	4.96	291
BT64	6/4	5.60	7.82	284
BT46	4/6	5.85	7.99	281
BT28	2/8	5.75	8.66	280
BT010	0/10	4.10	13.32	275

–, Not detected.
[a] T_g Value calculated form TMA cure.
[b] Average value calculated between 50–100 °C.
[c] Average value calculated between T_g+10–T_g+40 °C.

4. Conclusions

Novel bismaleimide (DCPDBMI) containing dicyclopentadiene was synthesized. A series of DCPD-containing novel bismaleimide-triazine resins were prepared from various mole ratio of dicyanate ester (DCPDCY) and the bismaleimide (DCPDBMI). Because of the hydrophobic effect of the cycloaliphatic DCPD structure and the *ortho*-methyl groups, the cured DCPD-containing BT resins exhibited lower moisture absorption than that of the DDMBMI cured with the DCPDCY or BADCY. Because of higher free volume and low polarity of cycloaliphatic DCPD linkages, cured DCPD-containing BT resins exhibited a low dielectric constant and dissipation factor. The glass transition temperature and thermal stability of cured resins slightly decreased with the increase in the cyanate ester molar ratio. However, all dicyclopentadiene-based BT resins still retain good thermal properties. The combination of low dielectric constant, low dissipation factor and outstanding resistance to moisture absorption make DCPDBMI/DCPDCY BT resins attractive candidate in printed circuit board application.

Acknowledgements

The authors gratefully acknowledge the Ministry of Economics of the Republic of China (TDPA 91-EC-17-A-05-S1-0014) for its financial support of this work.

References

[1] Wang CS, Hwang HJ. J Polym Sci, Part A: Polym Chem 1996;34:1493–500.
[2] Wang CS, Hwang HJ. J Appl Polym Sci 1996;60:857–63.
[3] Hamerton I. Chemistry and technology of cyanate ester resins. Glasgow: Blackie Academic and Professional; 1994 pp. 319–23.
[4] Hamerton I, Hay JN. Polym Int 1998;47:465–73.
[5] Shieh JY, Hwang HJ, Yang SP, Wang CS. J Polym Sci, Part A: Polym Chem 2005;43:671–81.
[6] Chaplin A, Hamerton I, Herman H, Mudhar AK, Shaw SJ. Polymer 2000;41:3945–56.
[7] Hwang HJ, Wang CS. J Appl Polym Sci 1998;68:1199–207.
[8] Lin RH, Lu WH, Lin CW. Polymer 2004;45:4423–35.
[9] Fan J, Hu X, Yue CY. J Appl Polym Sci 2003;88:2000–6.
[10] Dinakaran K, Kumar S, Alagar M. J Appl Polym Sci 2003;90:1596–603.
[11] Gaku M, et al. US Patent 4110364, Mitsubishi Gas Chemical Company; 1978.
[12] Reghunadhan Nair CP, Francis T, Vijayan TM, Krishnan K. J Appl Polym Sci 1999;74:2737–46.
[13] Hwang HJ, Li CH, Wang CS. J Appl Polym Sci 2005;96(6):2079–89.
[14] Lin CH, Jiang ZR, Wang CS. J Polym Sci, Part A: Polym Chem 2002;40:4084–97.
[15] Hougham G, Tesoro G, Shaw J. Macromolecules 1994;27:3642.
[16] Misra AC, Tesoro G, Hougham G, Pendharkar SM. Polymer 1992;33:1078.
[17] Maya EM, Snow AW, Buckley LJ. J Polym Sci, Part A: Polym Chem 2003;41:60–7.
[18] Hamerton I, Herman H, Rees KT, Chaplin A, Shaw SJ. Polym Int 2001;50:475–83.