

Dielectric Behavior and Properties of a Cyanate Ester Containing Dicyclopentadiene. I

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Received 2 April 2004; accepted 11 September 2004

DOI 10.1002/app.21672

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: 2,6-Dimethyl phenol dicyclopentadiene dicyanate ester (DCPDCY) was synthesized through the reaction of 2,6-dimethyl phenol dicyclopentadiene novolac and cyanogen bromide. The proposed structure was confirmed by Fourier transform infrared, mass spectrometry, NMR spectrometry, and elemental analysis. DCPDCY was then cured by itself or cured with bisphenol A dicyanate ester (BADCY) to form triazine structures. The thermal properties of the cured DCPDCY resins were studied with differential scanning calorimetry, dynamic mechanical analysis (DMA), dielectric analysis, and thermogravimetric analysis; these data were compared with those of BADCY. The cured DCPDCY resins exhibited a lower dielectric constant (2.58 at 1 MHz), a lower dissipation factor (20.2 mU at 1 MHz), less thermal stability (the 5% degradation temperature and char yield were 430°C and 32.1%, respectively), a lower glass-transition temperature (266°C by thermomechanical analysis

and 271°C by DMA), a lower coefficient of thermal expansion (22.5 ppm before the glass-transition temperature and 124.9 ppm after the glass-transition temperature), and less moisture absorption (0.88% at 48 h) than BADCY, but they showed higher moduli (6.28 GPa at 150°C and 5.35 GPa at 150°C) than the bisphenol A system. The properties of the cured cocyanate esters (DCPDCY and BADCY) lay between those of cured BADCY and DCPDCY, except for the moduli. The moduli of some cocyanate esters were even higher than those of cured BADCY and DCPDCY. A positive deviation from the Fox equation was observed for cocyanate esters. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2079–2089, 2005

Key words: curing of polymers; dielectric properties; high performance polymers; thermal properties; thermosets

INTRODUCTION

Dicyclopentadiene (DCPD) is a byproduct of C₅ streams in oil refineries and is a raw material for low-dielectric polymers because of its low polarity, low moisture absorption, and relatively low cost. Nelson,¹ Hiroaki,² and Wang and coworkers^{3,4} synthesized low-dielectric DCPD-containing epoxy resins derived from the novolac of phenol and DCPD in the presence of a Lewis acid and then converted the resulting novolacs into epoxy resins. In our previous study,⁵ a 2,6-dimethyl phenol dicyclopentadiene novolac was synthesized from DCPD and 2,6-dimethyl phenol and then converted into the corresponding epoxy resin by a reaction with epichlorohydrin. The experimental results showed that the DCPD-containing epoxy had a low dielectric constant and low moisture absorption.

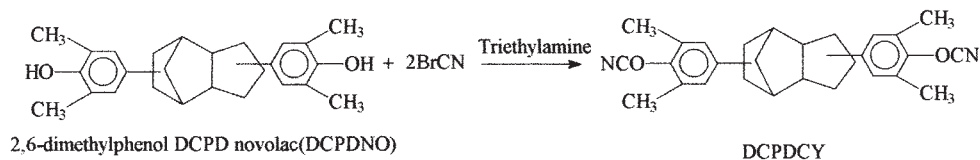
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Contract grant sponsor: Ministry of Economics of the Republic of China; contract grant number: TDPA 91-EC-17-A-05-S1-0014.

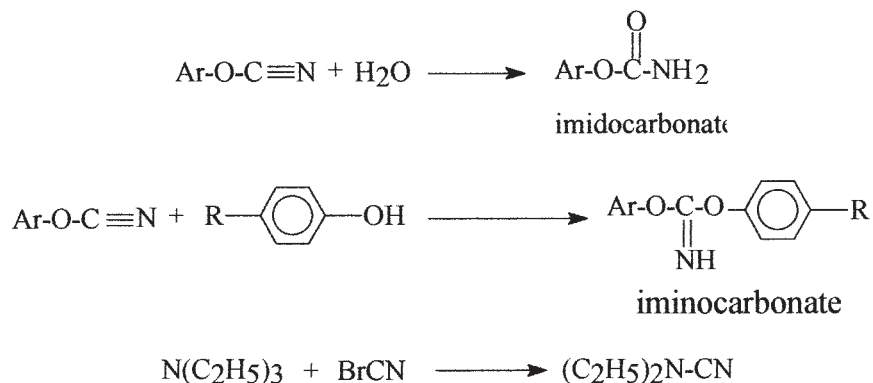
Journal of Applied Polymer Science, Vol. 96, 2079–2089 (2005)
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Cyanate esters have attracted much interest because of their excellent physical, dielectric, thermal, and mechanical characteristics. A large variety of cyanate esters with various backbone structures and properties have been synthesized and are summarized in the literature.⁶ The cyanate group undergoes trimerization to form a triazine ring and generates a high crosslink density, which, in combination with rigid aromatic rings, provides excellent high-temperature properties, solvent resistance, electrical properties, and mechanical strength. The trimerization of the cyanate groups can be easily monitored by the disappearance of the C≡N stretching band at 2200–2300 cm⁻¹ and the new absorptions at 1565–1580 cm⁻¹ for the triazine group.⁶ Research on cyanate esters includes cyanate ester/epoxy,^{7,8} cyanate ester/bismaleimide,^{9–11} the toughening of cyanate esters with thermoplastics,^{12–14} and cyanate curing kinetics and behavior.^{15,16} Dow Chemical developed a dicyclopentadiene phenol based cyanate ester with the trade name XU71787;¹⁷ it exhibited a high glass-transition temperature [T_g ; 258°C by dynamic mechanical analysis (DMA)], low moisture absorption (1.5% after 500 h in boiling water), and a low dielectric constant (2.8 at 1 MHz).

The signal propagation delay time in integrated circuits is proportional to the square root of the dielectric



side reaction



Scheme 1 Synthetic equation of DCPDCY.

constant, and the signal propagation loss is proportional to the square root of the dielectric constant and dissipation factor. Thus, a material with a low dielectric constant and a low dissipation factor will enhance the signal propagation speed and reduce the signal propagation loss.

In this study, continuing our research in DCPD, we synthesized 2,6-dimethyl phenol dicyclopentadiene dicyanate ester (DCPDCY) from DCPD-based novolac. The structure of DCPDCY was characterized with IR spectra, mass spectra, NMR spectra, and ele-

mental analysis. DCPDCY was cured by itself or with bisphenol A dicyanate ester (BADCY). The thermal properties of cured DCPDCY were studied with differential scanning calorimetry (DSC), DMA, dielectric analysis, and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

2,6-Dimethyl phenol dicyclopentadiene novolac was synthesized according to our previous article.⁵ Cyano-

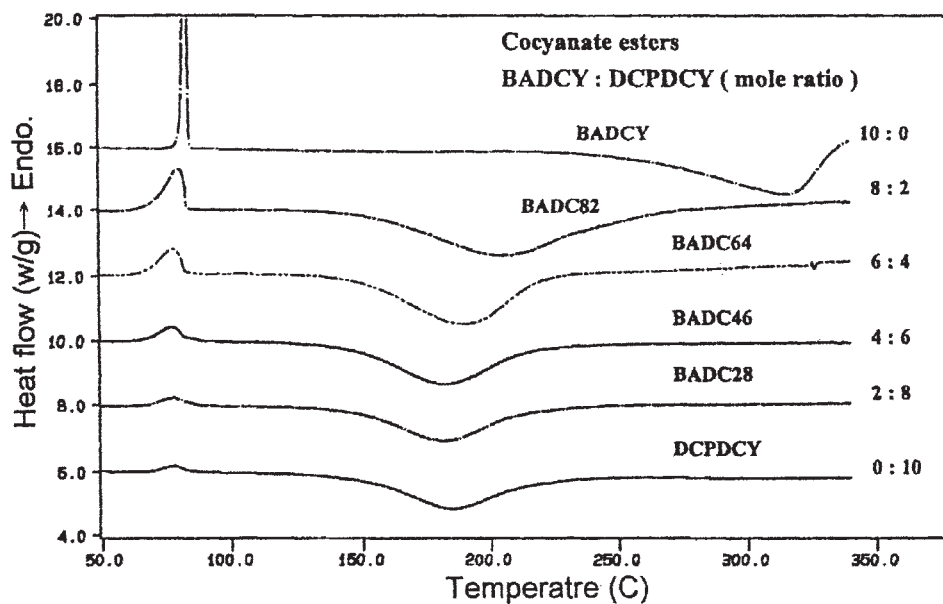


Figure 1 DSC scans of DCPDCY, BADCY, and their cocyanate esters.

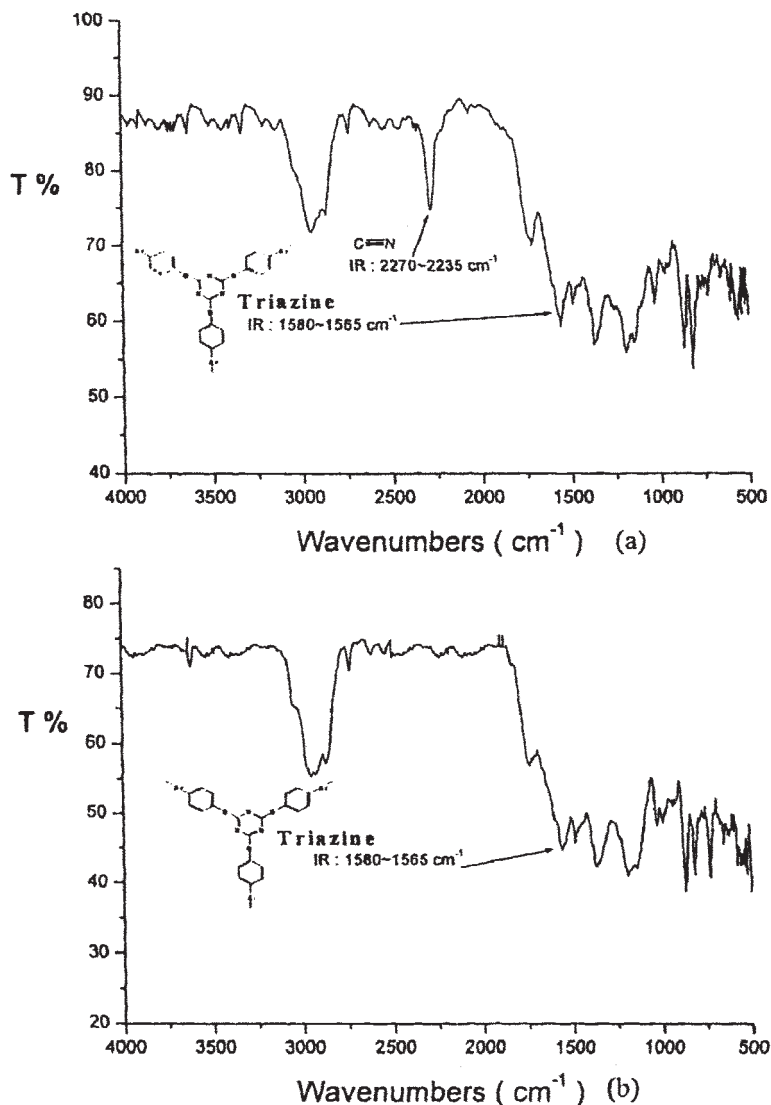


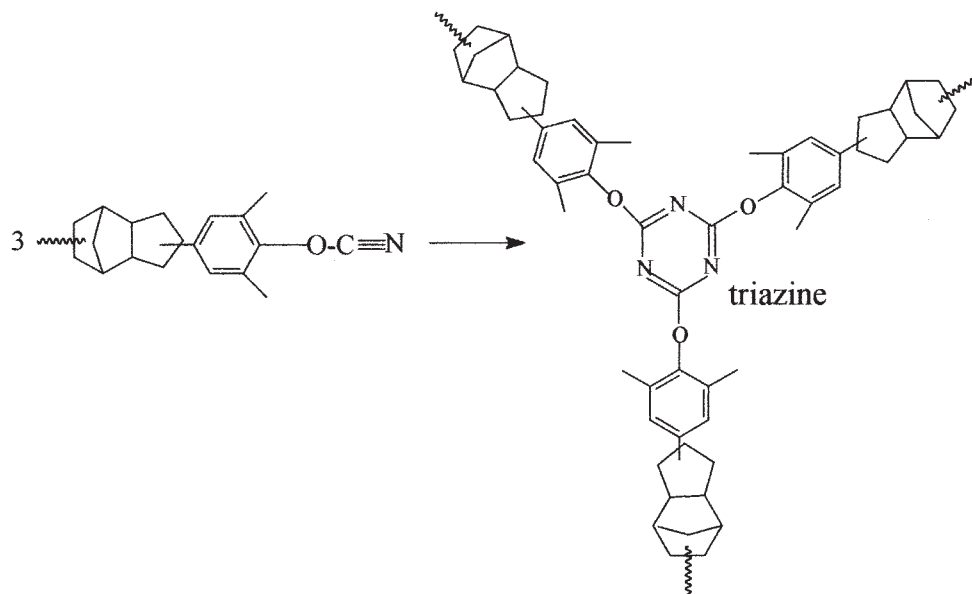
Figure 2 IR spectra of DCPDCY (a) after curing at 200°C for 8 h and (b) after further curing at 220°C for 4 h.

gen bromide (CNBr; 97%) was purchased from Showa (Tokyo, Japan). BADCY (B-10) was kindly supplied by Rhone-Poulenc (Strasbourg, France). Triethylamine (99%) was purchased from Ferak (Osaka, Japan). Acetone (99%) was purchased from Tedia (Fairfield, OH) and stored in a 4-Å molecular sieve. The other solvents were commercial products (liquid-chromatography-grade) and were used without further purification.

Characterization

Fourier transform infrared spectra were recorded on a Nicolet Magna 520 spectrometer (Madison, WI) with KBr pellets. Spectra in the optical range of 400–4000 cm^{-1} were obtained by the averaging of 16 scans at a resolution of 4 cm^{-1} . $^1\text{H-NMR}$ spectra were registered with a Bruker AC200 spectrometer (Rheinstetten, Germany) with dimethyl sulfoxide- d_6 as the solvent. Mass spectrometry analyses were performed on a VG 70-250

gas chromatography/mass spectrometry spectrometer (Altrincham, UK). Elemental analysis was performed with a Heraeus CHN rapid elemental analyzer. DSC scans were obtained from samples of about 6 mg in a nitrogen atmosphere (20 $\text{cm}^3 \text{min}^{-1}$) at a heating rate of 20 K min^{-1} with a PerkinElmer DSC 7 (Norton, OH). TGA was performed with a PerkinElmer TGA 7 at a heating rate of 20 K min^{-1} under nitrogen (20 $\text{cm}^3 \text{min}^{-1}$) from 60 to 800°C with a platinum boat. DMA was carried out with a PerkinElmer DMA 7e. The storage modulus and $\tan \delta$ were determined as the sample was subjected to a temperature scan mode at a programmed heating rate of 10 K min^{-1} from the ambient temperature to 300°C at a frequency of 1 Hz and at an amplitude of 6 μm . A sample 15 mm long, 10 mm wide, and approximately 1.5 mm thick was used. The test method was performed in the three-point-bending mode with a tension ratio of 110%. The dielectric measurements were performed with a Agi-



Scheme 2 Cyclotrimerization of DCPDCY.

lent 4291B measurement system (Palo Alto, CA) at 30°C in the two-parallel-plate mode at 1 MHz. The applied voltage was 1 V. Before the testing, the samples ($1 \times 1 \times 0.3 \text{ cm}^3$) were dried *in vacuo* at 100°C for 8 h. The moisture absorption was tested as follows. The samples ($1 \times 1 \times 0.1 \text{ cm}^3$) were dried *in vacuo* at 120°C until the moisture was expelled. After cooling to

room temperature, the samples were weighed, and then they were placed in boiling water for 24 h and weighed. The moisture absorption was calculated as follows: weight-gain percentage = $(W/W_0 - 1) \times 100\%$, where W is the weight of a sample after it is placed in 100°C water for 24 h and W_0 is the weight of a sample before it is placed in water.

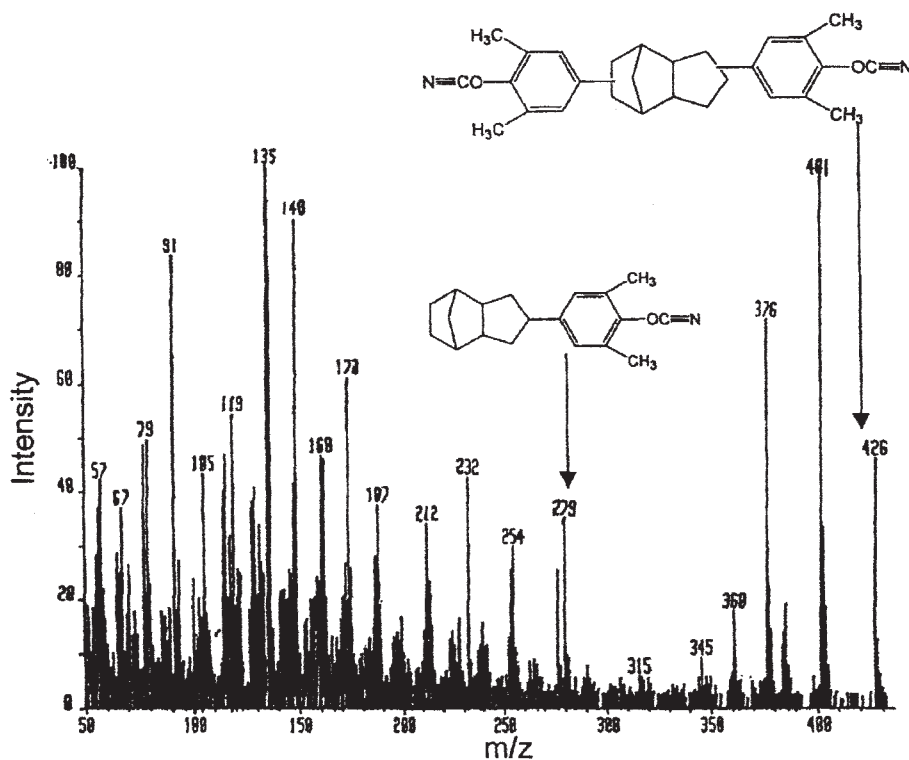


Figure 3 Mass spectrum of DCPDCY.

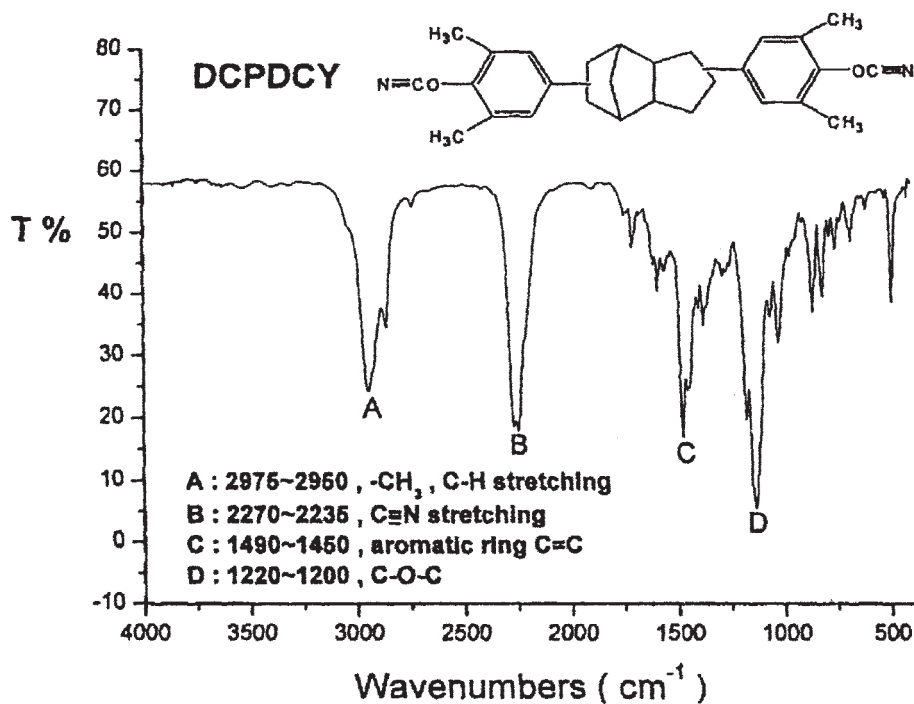
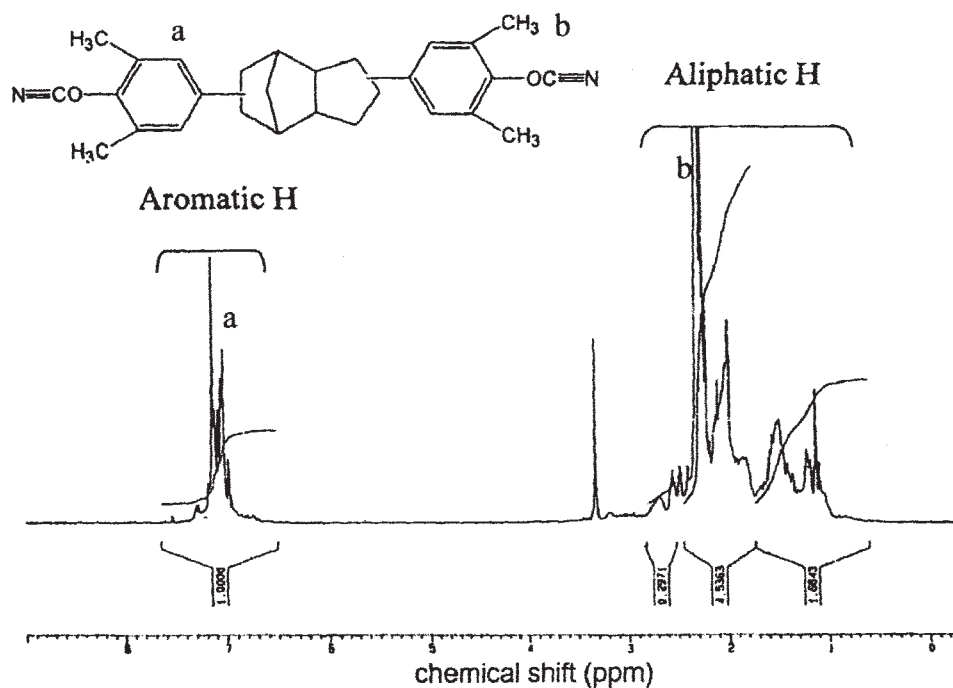


Figure 4 IR spectrum of DCPDCY.

Synthesis of 2,6-dimethyl phenol dicyclopentadiene cyanate ester¹⁰

To a four-necked, round-bottom flask equipped with a heating mantle, stirrer, thermocouple, and temperature controller, dry acetone (75 cm³) was added. The reaction mixture was gradually cooled to -15 to

-20°C, and then CNBr (25 g, 0.236 mol) was added. 2,6-Dimethyl phenol dicyclopentadiene novolac (39.1 g, 0.104 mol) and triethylamine (21.2 g, 0.21 mol) in dry acetone (25 cm³) were added gradually over 2 h, and the temperature was maintained for 2 h more. After the reaction was completed, the white Et₃N ·

Figure 5 ¹H-NMR spectrum of DCPDCY.

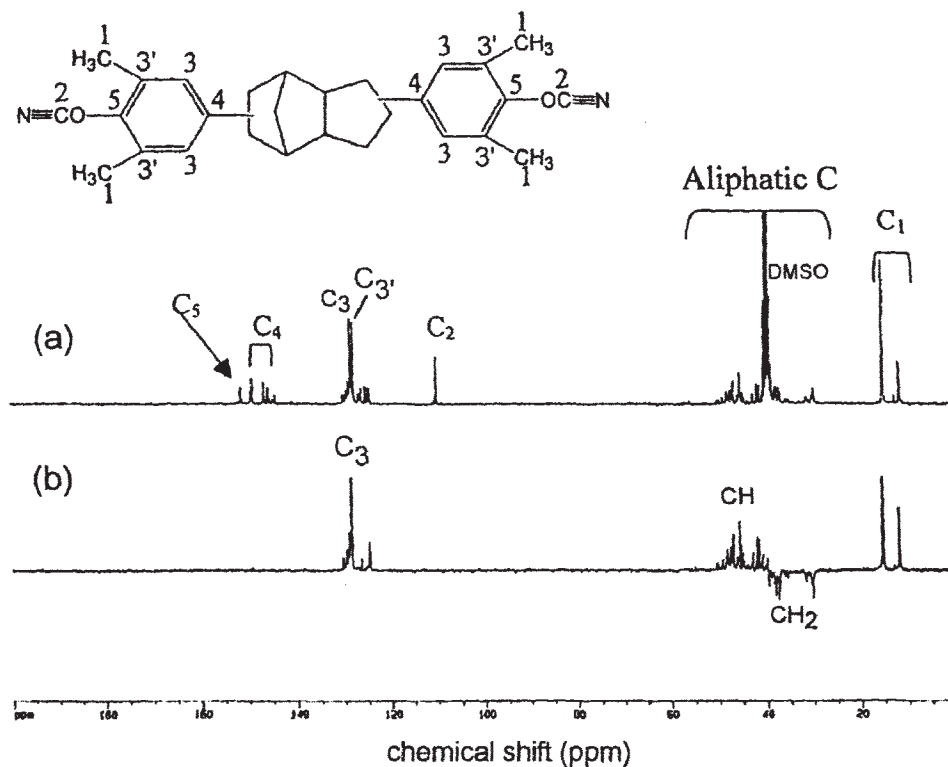


Figure 6 (a) ^{13}C -NMR and (b) DEPT 135 spectra of DCPDCY.

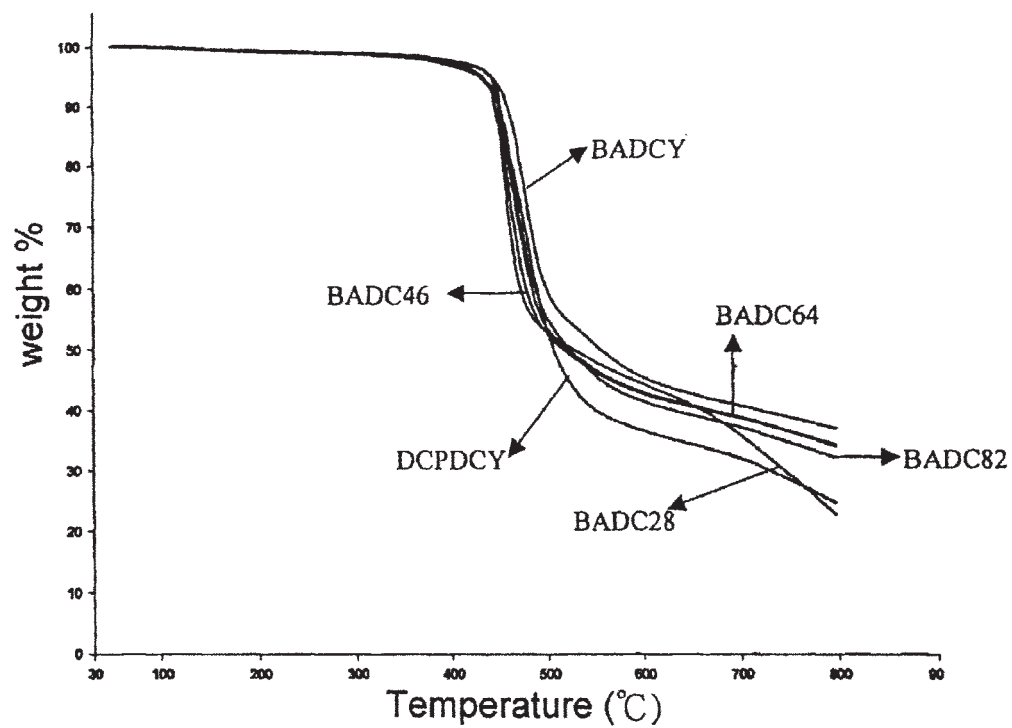


Figure 7 TGA traces of cured DCPDCY/BADCY cocyanate esters under nitrogen.

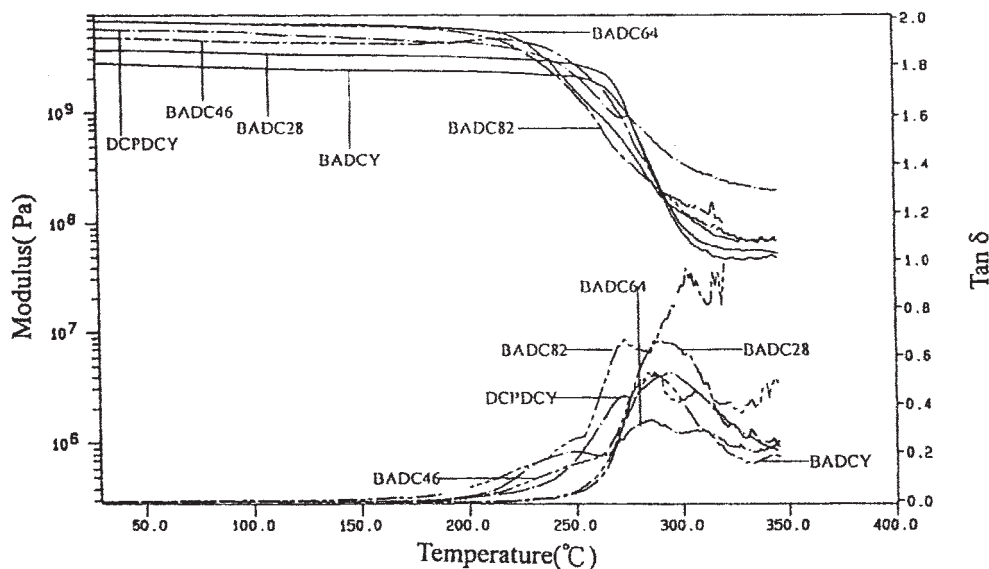


Figure 8 DMA scans of cured DCPDCY/BADCY cocyanate esters.

HBr salt was filtered. The filtrate was diluted with CH_2Cl_2 (100 cm^3) and extracted with water (100 cm^3) to remove residual $\text{Et}_3\text{N} \cdot \text{HBr}$. The organic phase was dried over Na_2CO_3 and then distilled to remove the solvent. A brown DCPDCY sample was obtained.

ANAL. Calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_2$: C, 78.87%; H, 7.04%; N, 6.57%; O, 7.52%. Found: C, 78.62%; H, 7.09%; N, 6.66%; O, 7.63%.

The synthetic equation is shown in Scheme 1.

DSC scans of uncured cyanate ester resins and their curing procedure

Figure 1 shows the DSC scans of DCPDCY, BADCY, and their cocyanate esters. The temperatures for the melting, onset of the exotherm, and peaks of the exotherm were 83, 257, and 316°C , respectively, for BADCY and 78, 161, and 188°C , respectively, for DCPDCY. The lower exothermic temperature of DCPDCY implied a higher reactivity of DCPDCY than that of BADCY. Figure 1 shows that the copolymerization of

BADCY with DCPDCY took place at a slightly higher temperature than that of pure DCPDCY. Figure 2(a,b) shows IR spectra of DCPDCY after curing at 200°C for 8 h and after further curing at 220°C for 4 h. Figure 2(a) shows the characteristic peak of triazine at $1565\text{--}1580\text{ cm}^{-1}$ (see Scheme 2). However, the characteristic peak of OCN at $2235\text{--}2270\text{ cm}^{-1}$ did not disappear completely until further curing at 220°C for 4 h. This implied that after curing at 200°C for 8 h, further curing at 220°C for 4 h was necessary for the complete curing of DCPDCY and DCPDCY/BADCY cocyanate esters.

On the basis of the DSC and IR analyses, BADCY and DCPDCY in molar ratios of 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 mixtures were cured in an oven at 180°C for 2 h, at 200°C for 8 h, and at 220°C for another 4 h under dry nitrogen. However, because of the higher exother-

TABLE I
DMA of Cured DCPDCY/BADCY Cocyanate Esters

Sample	BADCY/ DCPDCY (molar ratio)	T_g ($^\circ\text{C}$) ^a	Height of tan δ ^b	Modulus (GPa)	
				50°C	150°C
BADCY	10/0	287	0.512	2.97	2.65
BADC82	8/2	285	0.614	7.59	6.82
BADC64	6/4	282	0.313	7.49	7.07
BADC46	4/6	280	0.492	5.22	4.77
BADC28	2/8	277	0.450	4.07	3.69
DCPDCY	0/10	271	0.424	6.28	5.35

^a Peak temperature of the tan δ curve.

^b Tan δ value at T_g .

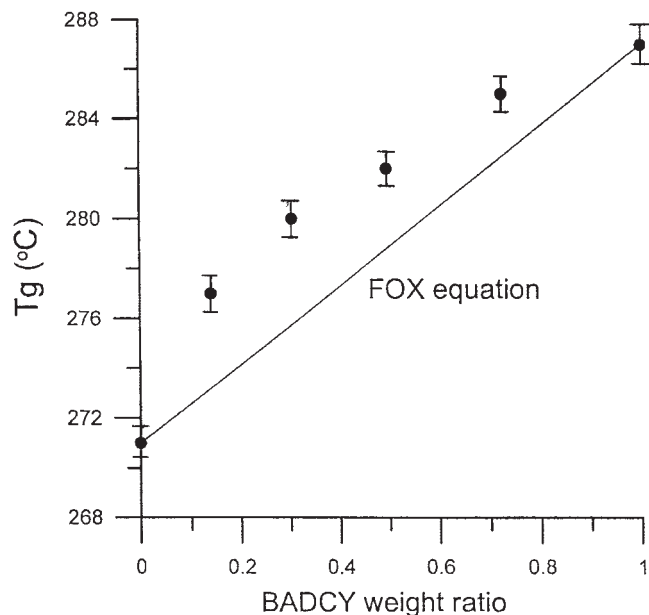


Figure 9 T_g -composition plot of cured DCPDCY/BADCY cocyanate esters. The solid line has been plotted according to the Fox equation.

mic temperature of BADCY, a further 260°C curing for 2 h was applied to pure BADCY.

RESULTS AND DISCUSSION

Characterization of DCPDCY

Figure 3 shows the mass spectrum of DCPDCY. We can see the peak of $C_{28}H_{30}N_2O_2$ at 426, $(M - C\equiv N^{+1})^+$ at 401, $(M - 2C\equiv N^{+2})^+$ at 376, $(M - 147)^+$ at 279, and

$(M - 147 - C\equiv N^{+1})^+$ at 254. During the mass spectrometry analysis, the peak corresponding to the m/z value at 66/67 was consistent with DCPD, perhaps because of the reverse Diels–Alder breakdown reaction of the DCPD ring. Figure 4 shows the IR spectrum of DCPDCY. The characteristic absorption peaks of ether at 1200–1220 cm^{-1} , the absorption peaks of the aromatic ring at 1450–1490 cm^{-1} , the absorption peaks of cyanate at 2235–2270 cm^{-1} , and the absorption peaks of methyl at 2950–2975 cm^{-1} can be observed, whereas the OH absorption of novolac at 3230–3400 cm^{-1} disappeared. The appearance of the cyanate group at 2240–2260 cm^{-1} and the disappearance of the OH absorption at 3230–3400 cm^{-1} strongly indicated that the OH groups changed into $OC\equiv N$ groups. A small peak at 1720 cm^{-1} perhaps resulted from the carbonyl peak of a byproduct (Scheme 1). It may also be due to the isomerization of cyanate to isocyanate ring formation, or, in the presence of water, cyanate ester reacted with water to form carbamate.^{18,19} Figure 5 shows the 1H -NMR spectrum of DCPDCY. The characteristic peaks of the aromatic ring at 7.0–7.3 ppm, of tetramethyl at 2.3 ppm, and of saturated hydrogens of DCPDCY at 1.04–2.7 ppm can be observed, whereas the OH characteristic peaks around 7.76 ppm disappeared completely. This implied that OH changed into a cyanate group. The ratio of the integration areas for the aromatic hydrogens and aliphatic hydrogens was 1/6.49, which was consistent with the theoretical value of $4/26 = 1/6.5$. Figure 6 shows ^{13}C -NMR and distortion enhancement by polarization transfer (DEPT) 135 spectra of DCPDCY. We can see the characteristic peak of the $C\equiv N$ triple bond at 118 ppm; the 4^0 carbons C_2 , C_3 , C_4 , and C_5 are not evident in the

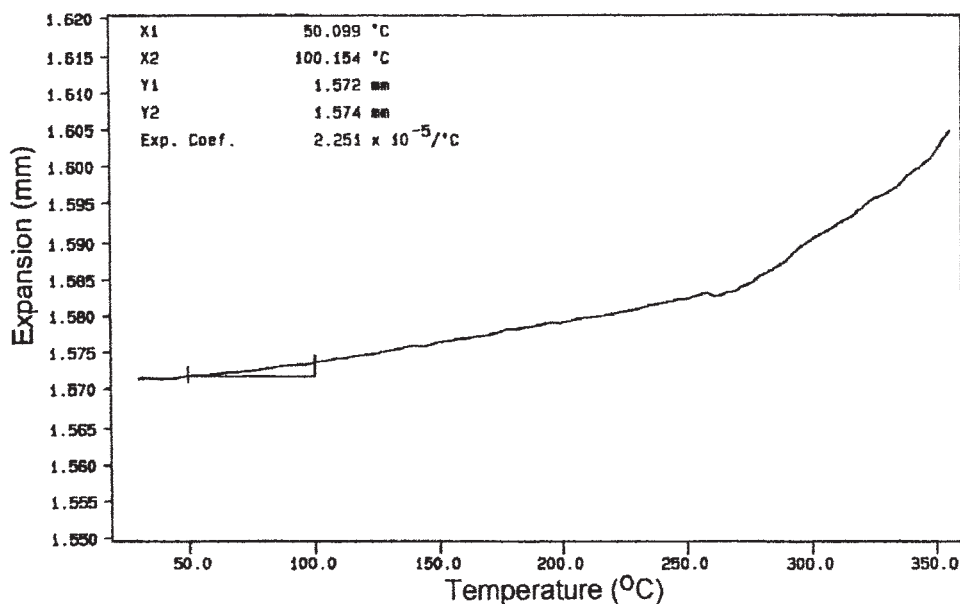


Figure 10 TMA of cured DCPDCY.

TABLE II
TMA of Cured DCPDCY/BADCY Cocyanate Esters

Sample	BADCY/ DCPDCY (molar ratio)	CTE ($10^{-5}/^{\circ}\text{C}$)		T_g ($^{\circ}\text{C}$) ^c
		Before T_g ^a	After T_g ^b	
BADCY	10/0	4.10	13.32	275
BADC82	8/2	3.12	13.02	272
BADC64	6/4	2.66	12.72	270
BADC46	4/6	2.02	12.35	268
BADC28	2/8	2.62	12.31	264
DCPDCY	0/10	2.25	12.49	266

^a Average value calculated between 50 and 100°C.

^b Average value calculated between $T_g + 20$ and $T_g + 70$ °C.

^c T_g value calculated from the onset temperature of the TMA curve.

DEPT 135 spectrum. As there are three constitutional isomers for the 2,6-dimethyl phenol dicyclopentadiene novolac, the peaks are somewhat complex, especially for carbon-4 and aliphatic carbons, but they are still consistent with the structure of DCPDCY.

TGA

The TGA traces of the cured resins provided information regarding their thermal stability and thermal degradation behavior. The TGA traces of cured DCPDCY, BADCY, and cocyanate esters under nitrogen are shown in Figure 7. The 5% degradation temperature of DCPDCY was 430°C, which was lower than the temperature of BADCY (441°C). The char yield at 700°C for DCPDCY was 32.1%, which was also lower than the value for BADCY (40.9%). This may be attributed to the cycloaliphatic structure of the DCPD ring, which reduced the thermal stability.

DMA measurements

DMA scans of cured DCPDCY, BADCY, and cocyanate esters are shown in Figure 8 and Table I. The T_g 's (peak temperatures of the loss tangent) for DCPDCY and BADCY were 271 and 287°C, respectively. The lower T_g value of cured DCPDCY may be due to the cycloaliphatic structure of the DCPD ring in DCPDCY. However, to our surprise, cured DCPDCY had a higher modulus than cured BADCY. For cured DCPDCY and cured BADCY, the storage moduli at 50°C were 6.28 and 2.97 GPa, and at 150°C, they were 5.35 and 2.65 GPa, respectively. For cocyanate esters, even higher moduli than those of the neat resins were observed. Similar tendencies were also observed for 2,6-dimethyl phenol dipentane dicyanate ester and their cocyanate esters with BADCY.²⁰ The reasons for this phenomenon are still unknown, and further research is necessary to understand it. Figure 9 shows the T_g -composition plot of cocyanate ester; T_g increased with the content of BADCY, and a positive deviation from

the Fox equation can be observed. A positive deviation indicates that there was some interaction between the BADCY and DCPDCY components in the system.²¹

Thermomechanical analysis (TMA) measurements

There are two major factors that cause the failure of electronic encapsulation. One is moisture absorption, and the other is internal stress. Thus, to increase the reliability of encapsulation, moisture absorption and internal stress must be reduced. The internal stress may result from the difference in the thermal expansion coefficients between the silicon (ca. 2.3 ppm) and encapsulation material, and so a polymer with a lower coefficient of thermal expansion (CTE) will lower the internal stress.²²⁻²⁵ Figure 10 shows TMA of cured DCPDCY and various cocyanate esters, and the results are shown in Table II. According to Figure 10 and Table II, the CTE values of cured DCPDCY before and

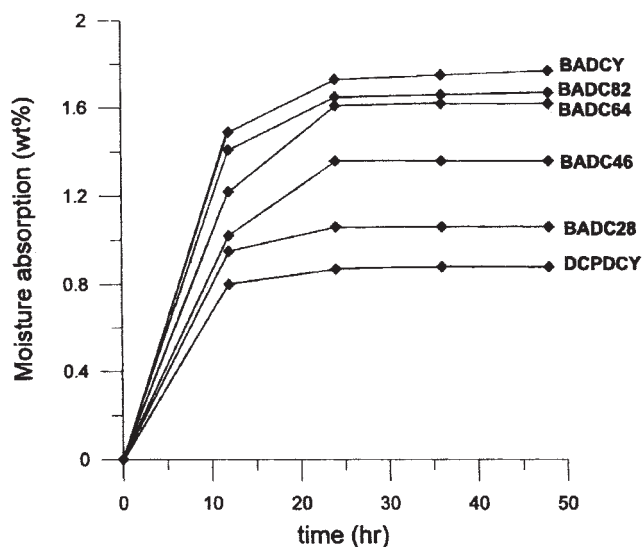


Figure 11 Moisture-absorption/time plots of cured DCPDCY/BADCY cocyanate esters.

after T_g were 22.5 and 124.9 ppm/°C, respectively, whereas the CTE values of cured BADCY before and after T_g were 41.0 and 133.2 ppm, respectively. T_g 's obtained from the onset of the TMA curve were 266 and 275°C for DCPDCY and BADCY, respectively. CTE decreased with the content of DCPDCY in the cocyanate esters, and this further proved the low thermal expansion character of DCPDCY. T_g 's measured by TMA were slightly lower than those from DMA measurements; however, T_g still increased with the content of BADCY in the cocyanate esters.

Moisture absorption

Moisture absorption will reduce T_g of an encapsulating material and may cause a popcorn effect when the material meets with solder at a high temperature. Moisture absorption will also ionize ionic impurities and thus corrode integrated circuits. Furthermore, moisture absorption will increase an encapsulating material's dielectric constant. Thus, lower moisture absorption is good for encapsulating materials. Figure 11 shows the moisture absorption of DCPDCY/BADCY cocyanate esters. The moisture absorption of cured DCPDCY was 0.8% after 12 h, 0.87% after 24 h, 0.88% after 36 h, and 0.88% after 48 h, whereas the moisture absorption of cured BADCY was 1.49% after 12 h, 1.73% after 24 h, 1.75% after 36 h, and 1.77% after 48 h in 100°C water, these latter values being higher than those of cured DCPDCY. An analysis of the cured resin blends consisting of DCPDCY and BADCY, used to determine the effects of the chemical structure on short-term exposure to boiling water, is reported. Long-term water uptake studies could be performed in the future with a method well reported by Hamerton and coworkers.^{9,26} The lower moisture absorption of cured DCPDCY may be attributed to the hydrophobic nature of the aliphatic DCPD structure and tetramethyl group. Figure 11 shows that the moisture absorption decreased with the content of DCPDCY in the cocyanate esters, and this also proved the low moisture absorption character of the DCPD linkage.

Dielectric constant and dissipation factor

Figure 12 shows plots of the dielectric constant, dissipation factor, and composition of cured DCPDCY/BADCY cocyanate esters. The dielectric constant of cured DCPDCY at 1 MHz was 2.58, whereas that of the cured BADCY system was 2.95. The dissipation factor (mU) of cured DCPDCY at 1 MHz was 20.2, whereas that of the cured BADCY system was 64.4. Hougham et al.²⁷ reported that the dielectric constant could be reduced by an increase in a molecule's hydrophobicity and free volume and by a decrease in the polarization. The nonplanar structure and four bulky methyl groups led to more spacing between the poly-

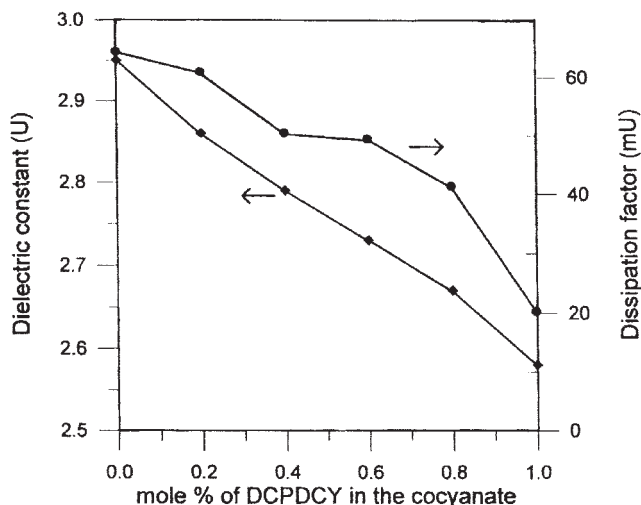


Figure 12 Plot of the dielectric constant, dissipation factor, and composition of cured DCPDCY/BADCY cocyanate esters.

mer molecules, and this resulted in less efficient chain packing and an increase in the free volume of the polymer, which brought the dielectric constant closer to the value of air (ca. 1). Furthermore, the presence of lower polarity aliphatic DCPD linkages may have reduced interchain electronic interactions and increased the hydrophobicity, thus reducing the dielectric constant and dissipation factor. Figure 12 shows that the dielectric constant of cyanate esters increased with an increase in the BADCY content, and this further proved the low-dielectric character of the DCPD linkage.

CONCLUSIONS

DCPDCY was synthesized successfully from 2,6-dimethyl phenol dicyclopentadiene novolac and CNBr. Because of the hydrophobic character and low polarity of the aliphatic DCPD structure and methyl group, cured DCPDCY exhibited low moisture absorption and low dielectric properties. DMA measurements show that cured DCPDCY had a lower T_g value but a higher modulus than BADCY. TGA measurements showed that cured DCPDCY had lower thermal stability because of the aliphatic structure of the DCPD and methyl group, which reduced the thermal stability. The combination of a low dielectric constant, a low dissipation factor, and outstanding resistance to moisture absorption makes DCPDCY an attractive candidate for electrical printed circuit boards and electronic encapsulation applications.

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