

Preparation and Epoxy Curing of p-Nonylphenol/Dicyclopentadiene Adducts

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ABSTRACT: Phenol/dicyclopentadiene adducts were prepared from the BF_3 -catalyzed reaction of p-nonylphenol and dicyclopentadiene at molar ratios of 2 : 1 and 3 : 2. These dicyclopentadiene-derived novolac products contain tricyclodecane and multiple phenol functionalities. In curing with diglycidyl ether of bisphenol A, the polymer properties were compared with those cured with formaldehyde novolac or Jeffamine D-400 amine. When p-nonylphenol/dicyclopentadiene adducts were mixed with other commercially available curing agents such as Jeffamine D-400 amine, the tricyclodecane functionality was introduced into the resulting epoxy network. The flexibility of the cured resin was improved due to the presence of the tricyclodecane moiety in the polymer structure. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2196–2206, 1999

Key words: phenol; dicyclopentadiene; Jeffamine; epoxy curing

INTRODUCTION

Cyclopentadiene (CPD) is a byproduct of C_5 streams in oil refineries. The CPD monomer exists in the form of dicyclopentadiene (DCPD), a dimeric adduct through Diels-Alder reaction, at ambient temperature. DCPD is readily cracked into CPD at 170°C. The commercially available DCPD with 85% purity is generally used in hydrocarbon resins and cured into adhesives,² surface coating,³ or printing ink resins.⁴ The high purity DCPD (95%) can be widely applied as a comonomer in several polymer systems such as ethylene propylene diene monomer (EPDM),^{5,6} unsaturated polyester,⁷ olefin metathesis,^{8–13} and epoxy resins.^{14–16}

In EPDM rubbers, DCPD and its derivative, ethylenenorbornene, are used as comonomers which consequently provide residual unsaturation for further crosslinking or vulcanization. EPDM rubber can also be epoxidized successfully and used to improve the impact performance of poly(butylene terephthalate).¹⁷ Recently, DCPD resins have been formulated to make tough thermosetting materials via “ring opening metathesis polymerization.” DCPD-based novolac epoxy resins have the advantages of reduction in epoxy cure shrinkage, moisture-resistance, and retention of excellent electrical-insulation properties.^{18–21} These features are very important for surface properties of composites and for delicate electronic applications.

In this study, we synthesized DCPD-containing novolac as epoxy curing agents to cure with the diglycidyl ether of bisphenol A and investigated their structure-property relationships.

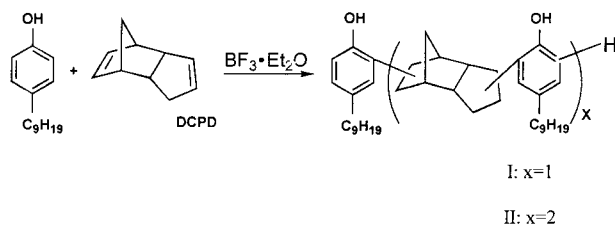
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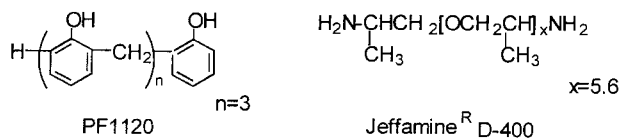


Scheme 1 Reaction of NP and DCPD.

EXPERIMENTAL

Materials

Liquid epoxy resin BE-188 with epoxide equivalent weight of 188 and novolac-type hardener (PF1120) were obtained from Nan-Ya Chemical Company of Taiwan. Triphenylphosphine (Ph_3P), p-nonylphenol (NP), DCPD (95%), and boron trifluoride diethyl ether ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) were purchased from Aldrich Co. Poly(oxypropylene) diamine, Jeffamine D-400, was received from Huntsman Co.



Syntheses of p-Nonylphenol and Dicyclopentadiene Adducts

The preparation of DCPD and phenol adduct using BF_3 catalyst was reported previously.²² To a 2-L four-necked flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, Dean-Stark trap, and dropping funnel, NP (440 g, 2.0 mols) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.2 g) in toluene (100 g) were added. While stirring, the mixture was heated to 70°C , held for 1 h and then cooled to 40°C . At this temperature, DCPD (132 g, 1.0 mol) was added dropwise through an additional funnel over a 1-h period. During the addition, the exothermic temperature up to 53°C was observed. The temperature was then raised to $100 \approx 110^\circ\text{C}$, held for 3 h, and $130 \approx 150^\circ\text{C}$ for an additional 2 h. At ambient temperature, the product mixture was extracted with 5 wt % NaOH for at least three times to remove BF_3 and impurities. The final product was subjected to a rotary evaporator under vacuum to afford a black, viscous liquid (compound I). Using similar procedures, the adduct of NP (440 g, 2.0 mols)/DCPD (176 g, 1.3 mols) (mol ratio 3:2) was prepared (compound II). The glass transition temperatures (T_g s) detected by differential

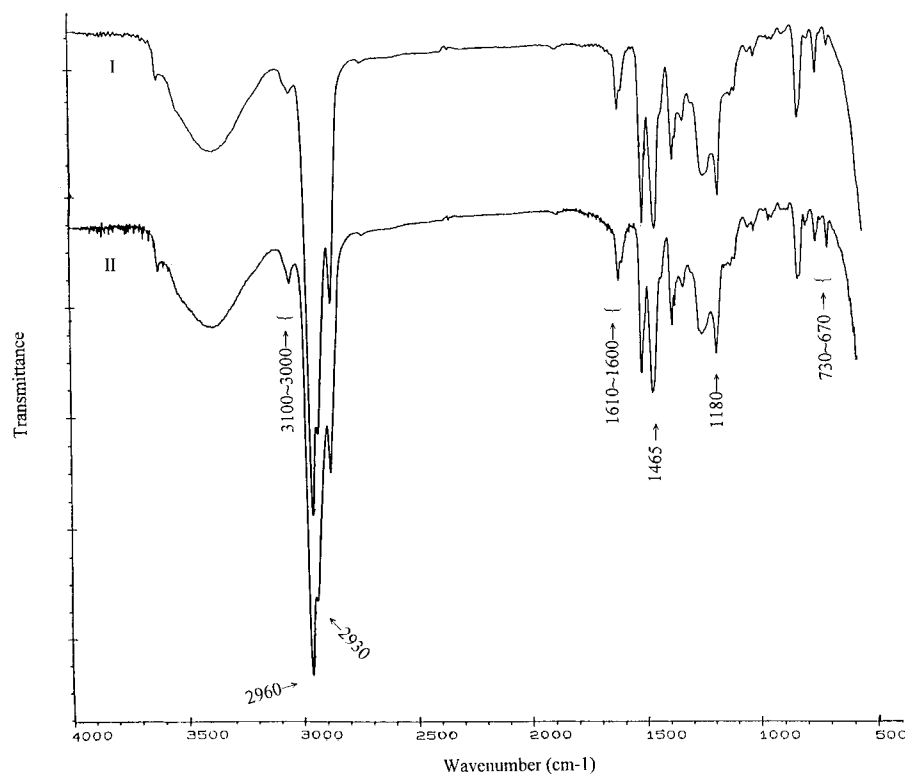


Figure 1 Spectra of adducts I and II.

Table I Characteristic IR Absorptions for Adducts I and II

Peak/Band (cm^{-1})	Assignment
3650–3200	O—H stretch
3044	Aromatic C—H stretch
2960, 2872	—CH ₃ stretch
2930	—CH ₂ stretch
1610 ~ 1600	Cyclopentenyl or aromatic C=C stretch
1510 ~ 1500	Aromatic ring C=C stretch
1465	—CH ₂ scissoring
1378, 1365	Isopropyl and/or t-butyl —CH ₃ bending
1257, 1244	t-Butyl backbond stretch (nonyl groups)
1180	C—O stretch (phenol)
852 ~ 805	1,4- and/or 1,2,4-substituted aromatic ring
730 ~ 670	cis Double bond C—H bending

scanning calorimetry (DSC) of I and II are -9.9°C and 9.5°C , respectively.

Curing Procedures

Stoichiometric amount of those prepared adducts (II and I) and the commercially available PF1120 were used to cure with the epoxy resin (BE-188). The mixture was prepared at 100°C , cooled to

80°C , Ph_3P accelerator was added (2 parts per hundred based on epoxy resin), and then degassed at 80°C in a vacuum oven for 10 min. The resultant mixture was then placed immediately in a preheated steel mold. The curing cycle was 90°C for 1 h, 120°C for 2 h, 150°C for 2 h, and 160°C for 1 additional h. When the Jeffamine D-400 was involved as the curing agent, the mixing and degassing temperature was at 50°C and the curing cycle was 50°C for 1 h, 100°C for 1 h, 150°C for 2 h, and 160°C for 1 additional h.

Instrumental Analyses

$^1\text{H-NMR}$ characterization was performed by a Varrion VXR-300 (300 MHz) NMR spectrometer using CDCl_3 as solvent. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet 520 spectrometer. Gel permeation chromatography (GPC) was performed by a Water 410 differential refractometer at 40°C of the column temperature. Dynamic DSC was performed on a Seiko DSC 5200 at a heating rate of $5^{\circ}\text{C}/\text{min}$ under a nitrogen atmosphere. Dynamic mechanical analysis (DMA) was performed on a Seiko DMA 110 at a heating rate of $5^{\circ}\text{C}/\text{min}$ under a nitrogen atmosphere. Tensile properties were measured according to ASTM D638-86 at a testing rate of 5 mm/min and flexural properties were measured according to ASTM D790 at a testing rate of 2.6 mm/min using an Instron machine. Notched Izod impact tests were performed at am-

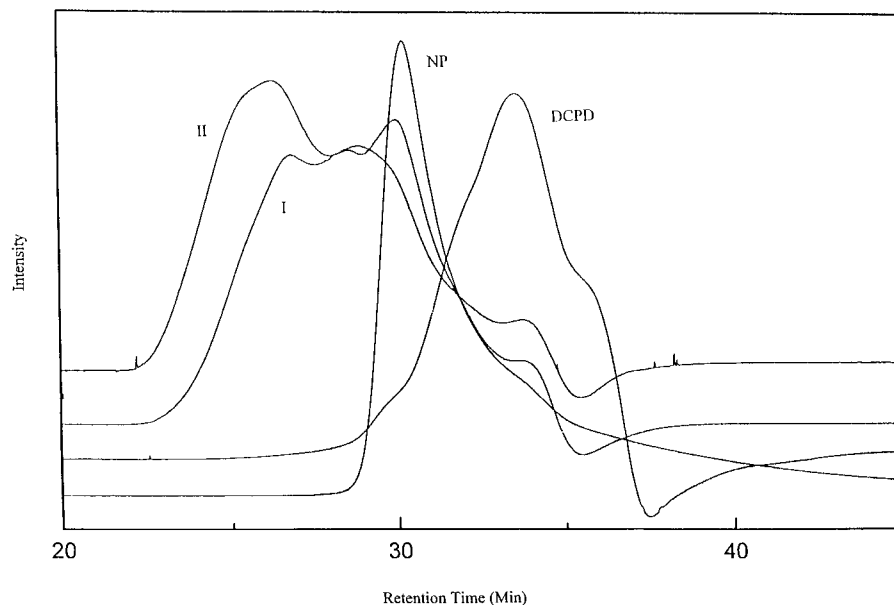


Figure 2 Relative GPC retention time of I, II, NP, and DCPD.

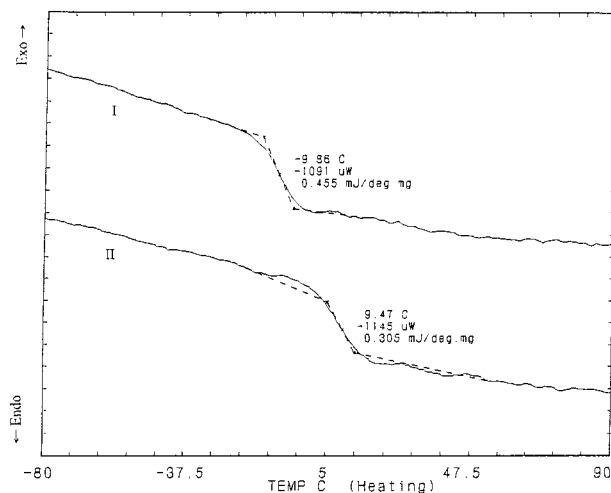


Figure 3 DSC thermograms of adducts I and II.

bient conditions according to ASTM D256. Scanning electron microscopy (SEM) of the fractured surfaces was performed on a Hitachi S-570 SEM.

RESULTS AND DISCUSSION

Syntheses and Characterization of NP and DCPD Adducts

Adducts of NP and DCPD at molar ratios of 2:1 and 3:2 were obtained as oligomers with a representative structure I ($x = 1$) and II ($x = 2$) shown in Scheme 1.

The FTIR spectra of I and II are shown in Figure 1. The characteristic i.r. absorptions are listed in Table I. The peak intensity at 2960 cm^{-1} (CH_3 stretch) is stronger than that of 2930 cm^{-1} (CH_2 stretch) indicating the high branching of the nonyl group. The main alkene characteristic absorptions are $3100\text{--}3000\text{ cm}^{-1}$ (C—H stretch), $1680\text{--}1600\text{ cm}^{-1}$ (C=C stretch) and $730\text{--}670\text{ cm}^{-1}$ (cis form C—H, out of plane bend). The absorptions at $3100\text{--}3000\text{ cm}^{-1}$ and $1610\text{--}1600\text{ cm}^{-1}$ indicate the presence of aromatic ring. The absorption peak intensity at $730\text{--}670\text{ cm}^{-1}$ (cis form double bond of C—H bending) is quite weak, implying the presence of only a small amount of the DCPD starting material. This is consistent with GPC graphs of Figure 2, showing a small amount of DCPD (retention time = 34 min) remained. Also, the adduct II has higher molecular weight distribution than I. The relative Mw can be indirectly verified by their (T_g 's) shown in Figure 3 and Table II. Adduct II has higher T_g (9.5°C)

than adduct I (-9.9°C).

The $^1\text{H-NMR}$ spectra are given in Figure 4. The chemical shifts are as follows: $\delta = 0.51\text{--}2.35\text{ ppm}$ (saturated protons for nonyl group and DCPD), $\delta = 2.60\text{--}2.95\text{ ppm}$ ($-\text{CH}_2-$ for DCPD), $\delta = 5.5$ and 5.7 ppm ($-\text{CH}=\text{CH}-$ for DCPD), and $\delta = 6.65\text{--}7.20\text{ ppm}$ (aromatic protons).

Reaction of NP/DCPD Adducts I or II with Diglycidyl Ether of Bisphenol A

The reaction of NP/DCPD (see pg. 6) adducts I and II with stoichiometric amount of the diglycidyl ether of bisphenol A (BE-188) using Ph_3P accelerator (2 parts per hundred of epoxy resin) gave linear and crosslinked products, respectively. The curing profiles of these reactions are expressed by DSC shown in Figure 5. Based on the exothermic peaks in DSC thermograms, both of adducts I and II exhibited similar reactivity toward BE-188 but with faster curing rate than the commercially available novolacs (PF1120). The linear I/BE-188 product could be dissolved in acetone within 5 min while the crosslinked II/BE-188 product formed a swelling, softening substance in acetone after 1 day (Table III). Both of II or I curing products are extremely brittle materials. Their tensile properties are poor, indicating a very low crosslinking structure (Table IV). The

Table II T_g

Composition	Weight Fraction	T_g , DSC ($^\circ\text{C}$)	T_g , DMA ($^\circ\text{C}$)
Adduct I	—	-9.9	—
Adduct II	—	9.5	—
I/BE-188	60/40	41.9	—
II/BE-188	62/38	62.6	92.6
D-400/BE-188	35/65	40.9	58.4
PF1120/BE-188	36/64	129	144.4
I/PF1120/BE-188	33/16.5/50.5	—	102.9
I/PF1120/BE-188	23/23/54	—	135.2
I/PF1120/BE-188	14/28/58	—	137.3
II/PF1120/BE-188	33/16.5/50.5	—	109.8
II/PF1120/BE-188	23/23/54	—	143.4
II/PF1120/BE-188	14/28/58	—	143.7
I/D-400/BE-188	36/14/50	52.7	78.3
I/D-400/BE-188	22/22/56	42.0	60.8
I/D-400/BE-188	14/27/59	41.5	60.4
II/D-400/BE-188	36/14/50	64.8	92.4
II/D-400/BE-188	22/22/56	42.2	61.5
II/D-400/BE-188	14/27/59	41.3	60.1

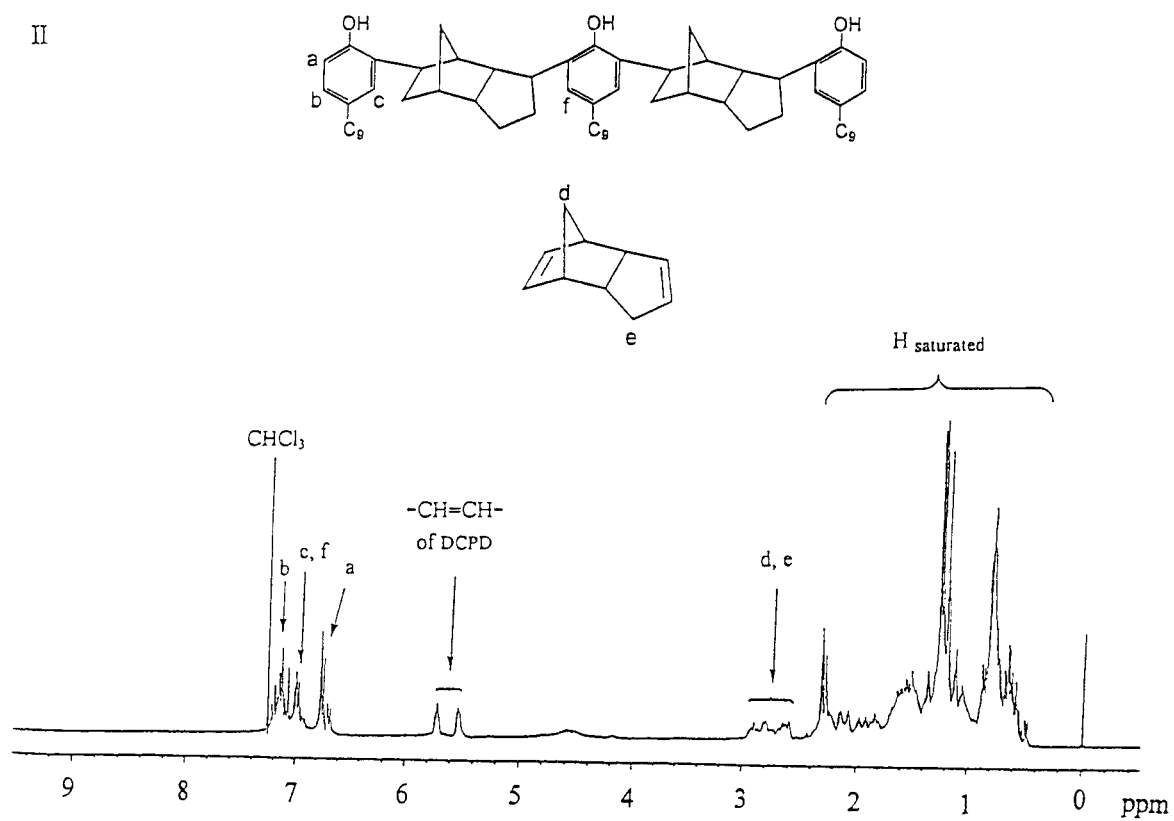
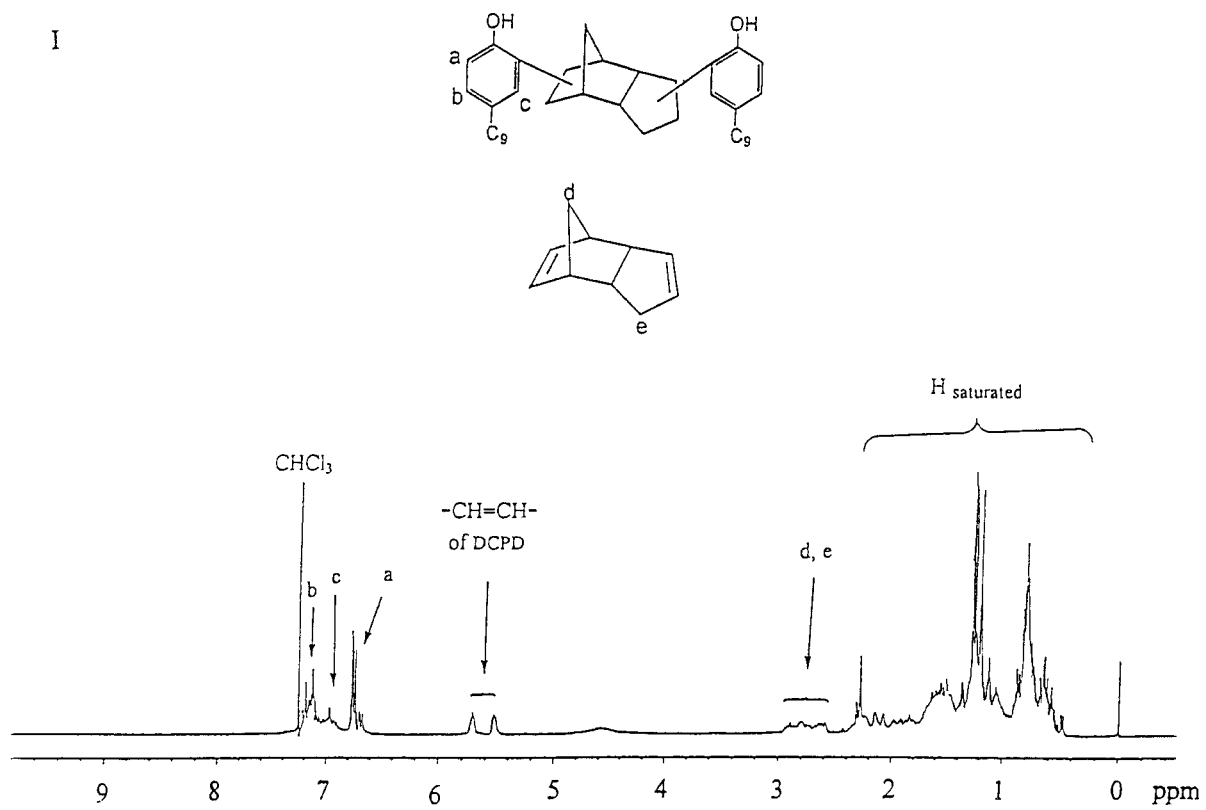
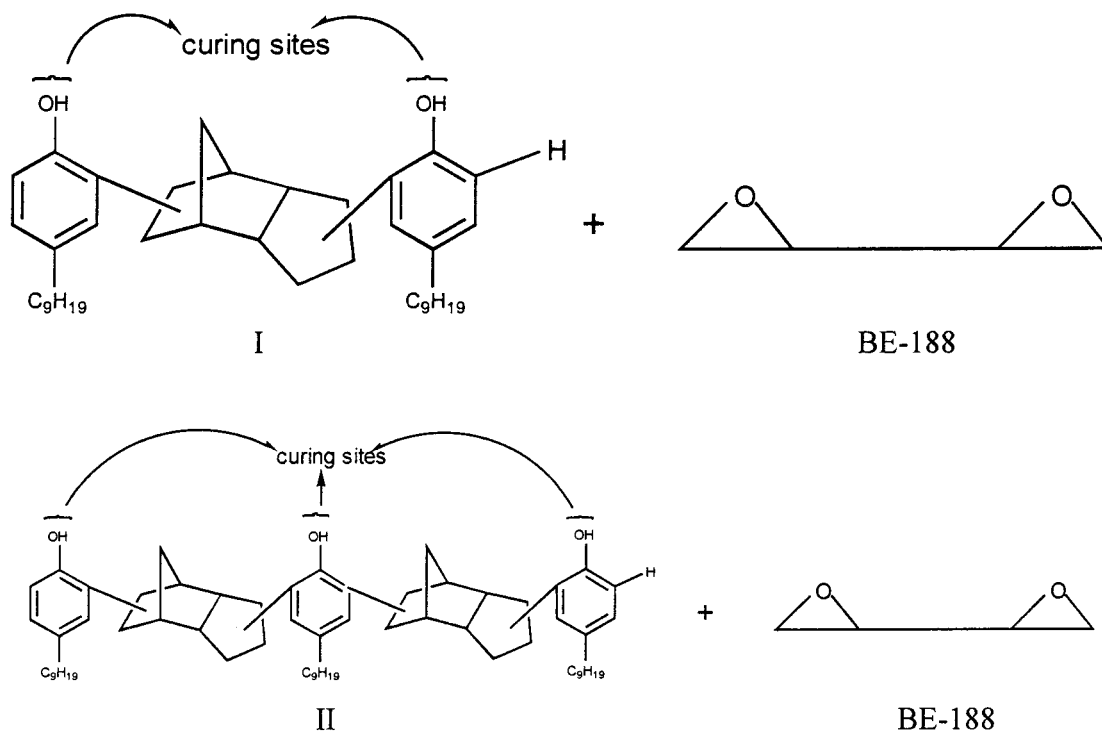


Figure 4 $^1\text{H-NMR}$ spectra of adducts I and II.



$T_{g,s}$ of 41.9°C for I/BE-188 and 62.6°C for II/BE-188 were recorded (Table II).

NP/DCPD Adducts I or II Mixed with Novolac as Curing Agents

SEM Morphologies and Solvent Resistibility

To improve the properties of I/BE-188 and II/BE-188 (see pg. 8), a commercially available novolac hard-

ener-paraformaldehyde/phenol adduct PF1120, was blended. The blended curing agents, I+PF1120 and II+PF1120, are immiscible at ambient temperature but miscible at 110°C. The SEM micrographs of the fracture surfaces of these BE-188 cured products are shown in Figure 6, revealing phase separation phenomena of the dispersed particles in different domains. The domain surface and the surface of the holes appeared very smooth, suggesting a poor adhesion between phases. The differences are clearly observed between the morphologies of cured systems of II/PF1120/BE-188 and I/PF1120/BE-188. These dispersed particles in varied sizes seem to be constructed by the minor components. All samples have white sediments in acetone after 1 day with a varied amount of sediments (Table III). The sample with the highest content of I (I/PF1120 = 2/1 w/w) was inhomogeneous or loosely porous substance with the poor structural integrity and extractability by acetone. The curing system could theoretically produce hybrid network structures of I/BE-188 and PF1120/BE-188 plus the individual PF1120/BE-188 and less integrity of I/BE-188. It appears that the continuous phase is the structure involving more I/BE-188 whereas the dispersed particles are more PF1120/BE-188-involving. Nevertheless, the opposite phase phenomenon may be formed in the compositions with lower content of I (I/PF1120 = 1/1 and 1/2 w/w)

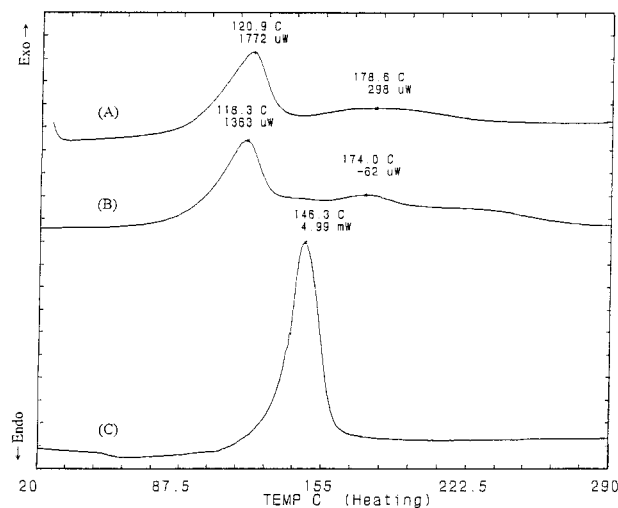


Figure 5 Dynamic DSC thermograms of BE-188 cured with (A) Adduct I; (B) Adduct II, and (C) PF1120 (added Ph_3P accelerator, 2 parts per hundred based on epoxy resin).

Table III Solvent Resistibility^a of Cured Epoxy Resins

Composition	Weight Fraction	Phenomena
Adduct I	—	Dissolve ^b
Adduct II	—	Dissolve ^b
I/BE-188	60/40	Dissolve ^b
II/BE-188	62/38	Swelling, softening substance
D-400/BE-188	35/65	Intact substance
PF1120/BE-188	36/64	Intact substance
I/PF1120/BE-188	33/16.5/50.5	Abundantly white sediments, loosely porous substance
I/PF1120/BE-188	23/23/54	White sediments, porous substance
I/PF1120/BE-188	14/28/58	Little sediments, intact substance
II/PF1120/BE-188	33/16.5/50.5	Abundantly white sediments, loosely porous substance
II/PF1120/BE-188	23/23/54	White sediments, porous substance
II/PF1120/BE-188	14/28/58	Little sediments, intact substance
I/D-400/BE-188	36/14/50	Intact substance
I/D-400/BE-188	22/22/56	Intact substance
I/D-400/BE-188	14/27/59	Intact substance
II/D-400/BE-188	36/14/50	Intact substance
II/D-400/BE-188	22/22/56	Intact substance
II/D-400/BE-188	14/27/59	Intact substance

^a Immersing in acetone with stirrer through 1 day.

^b Dissolve in 5 min.

where the major network matrix is PF1120/BE-188 and dispersed particles are I/BE-188. With even lower content of I (I/PF1120 = 1/2 w/w), the dispersed particles are at the size of ca. 2 μm in diameter [in Fig. 6(C)]. A similar trend of phase distribution phenomena is observed for the mixing curing agent with II [Figures 6(D), (E), and

(F)]. The inhomogeneous dispersed particles are barely observed in (F).

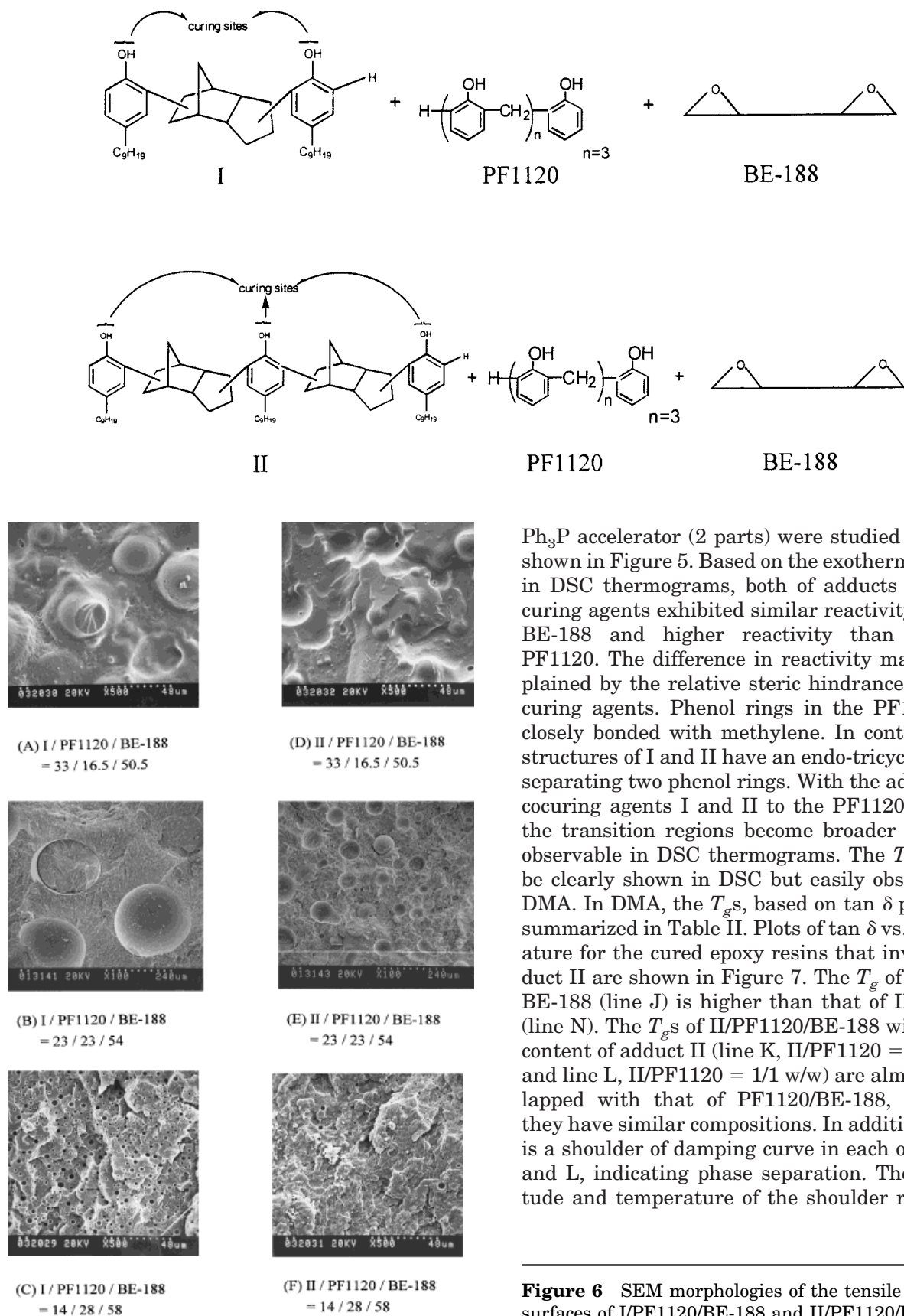
Thermal Properties and Dynamic Mechanical Analysis

The curing profiles of the individual adduct I, II, and PF1120, toward epoxy resin (BE-188) using

Table IV Properties of Cured Epoxy Involving p-Nonylphenol/Dicyclopentadiene Adducts I and II and Novolac Hardener

Composition	Weight Fraction	Tensile Properties		Flexural Properties		
		Tensile Strength (MPa)	Strain at Break (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Displacement at Break (mm)
I/BE-188	60/40	—	—	—	—	—
II/BE-188	62/38	—	—	12.3 (2.9)	2562 (0)	1.23 (0.31)
PF1120/BE-188	36/64	45.3 (1.8)	5.24 (0.21)	98.6 (30)	2903 (66)	9.76 (4.04)
I/PF1120/BE-188	33/16.5/50.5	7.3 (0.9)	1.40 (0.50)	13.3 (5.6)	2826 (63)	1.10 (0.40)
I/PF1120/BE-188	23/23/54	21.7 (1.9)	2.58 (0.58)	36.5 (5.8)	3085 (62)	2.88 (0.54)
I/PF1120/BE-188	14/28/58	30.3 (4.0)	3.51 (0.60)	64.4 (6.4)	2928 (72)	5.28 (0.50)
II/PF1120/BE-188	33/16.5/50.5	8.3 (0.3)	1.51 (0.20)	17.4 (1.8)	2726 (83)	1.41 (0.01)
II/PF1120/BE-188	23/23/54	32.6 (3.0)	3.78 (0.44)	55.6 (1.0)	2859 (35)	4.93 (0.41)
II/PF1120/BE-188	14/28/58	36.6 (1.0)	4.90 (0.20)	73.6 (6.0)	2932 (99)	6.30 (0.60)

I, nonylphenol/dicyclopentadiene product at 2 : 1 molar ratio; II, nonylphenol/dicyclopentadiene product at 3 : 2 molar ratio; BE-188, diglycidyl ether of bisphenol A; PF1120, novolac type hardener.



Ph_3P accelerator (2 parts) were studied by DSC, shown in Figure 5. Based on the exothermic peaks in DSC thermograms, both of adducts I and II curing agents exhibited similar reactivity toward BE-188 and higher reactivity than that of PF1120. The difference in reactivity may be explained by the relative steric hindrance of these curing agents. Phenol rings in the PF1120 are closely bonded with methylene. In contrast, the structures of I and II have an endo-tricyclodecane separating two phenol rings. With the addition of cocuring agents I and II to the PF1120/BE-188, the transition regions become broader and less observable in DSC thermograms. The T_g cannot be clearly shown in DSC but easily observed by DMA. In DMA, the T_g s, based on $\tan \delta$ peak, are summarized in Table II. Plots of $\tan \delta$ vs. temperature for the cured epoxy resins that involve adduct II are shown in Figure 7. The T_g of PF1120/BE-188 (line J) is higher than that of II/BE-188 (line N). The T_g s of II/PF1120/BE-188 with lower content of adduct II (line K, II/PF1120 = 1/2 w/w, and line L, II/PF1120 = 1/1 w/w) are almost overlapped with that of PF1120/BE-188, meaning they have similar compositions. In addition, there is a shoulder of damping curve in each of lines K and L, indicating phase separation. The magnitude and temperature of the shoulder represent

Figure 6 SEM morphologies of the tensile fractured surfaces of I/PF1120/BE-188 and II/PF1120/BE-188.

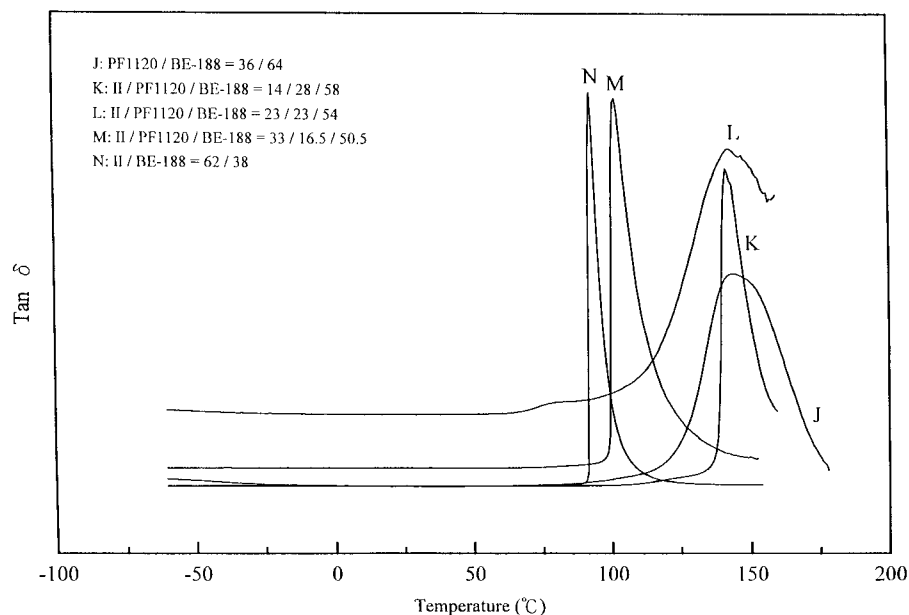


Figure 7 Plots of $\tan \delta$ vs. temperature for the cured epoxy resins involving adduct II and PF1120.

their content and composition in these products, respectively. This result is consistent with SEM morphologies. On the other hand, with the highest content of adduct II (line M, II/PF1120 = 2/1 w/w), the shoulder is not observed because the T_g of dispersed particles is higher than that of the matrix. The T_g of dispersed particles cannot be measured after the matrix (lower T_g) has been softened. These results are consistent with the observed SEM morphologies and solvent resistibility. The DMA data of curing agent I involving systems are included in part of Table II. Their T_g s are lower than those of II involving cured materials corresponding, indicating their lower crosslinking density in general.

Mechanical Properties

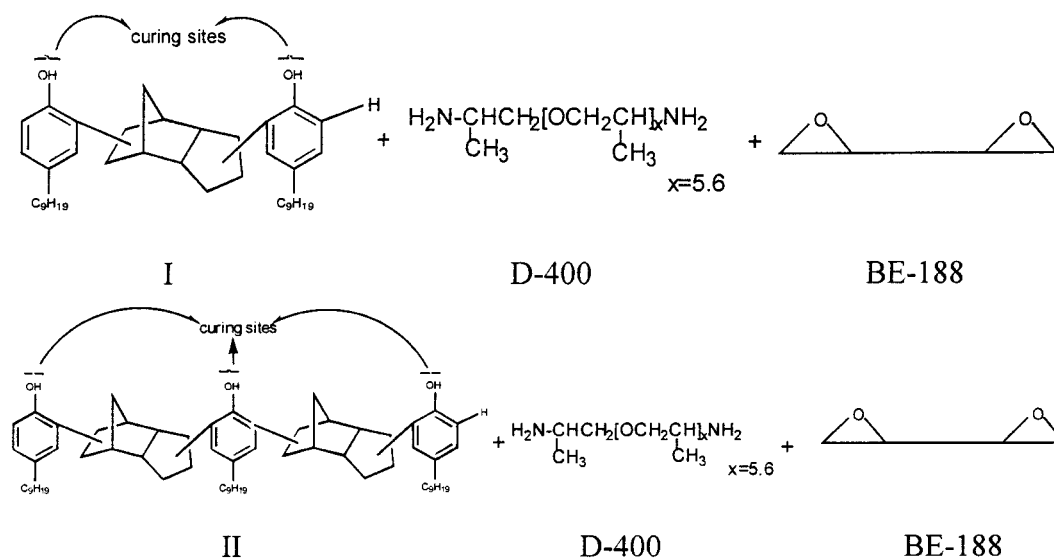
The mechanical properties of all cured epoxies are summarized in Table IV. It was found that the use of cocuring agents failed to improve the mechanical properties due to their phase separation as shown in SEM (Fig. 6). The fracture could arise and propagate from the interface between matrix and dispersed particles. However, with the addition of adduct I, the cured epoxy resin (I/PF1120/BE-188 = 23/23/54) has higher flexural modulus. This can be explained by the presence of dispersed particles that behave just like fillers. In contrast, the addition of II has no such effect. The molecules containing relatively high content of

flexible tricyclodecane component may counteract the filler effect. On the other hand, the cured epoxy resin with the high content of adduct I (I/PF1120 = 2/1 w/w) also shows no filler effect. This is due to the very weak matrix structure that could be fractured before dispersed particles, as fillers, become effective. The result is consistent with the SEM morphology in which the fracture arises and propagates from the bulky matrix rather than the interface between matrix and dispersed particles [Fig. 6(A)].

NP/DCPD Adducts I or II Mixed with Polyetheramine as Curing Agents

Mechanical and Thermal Properties

As a cocuring agent, polyetheramine (Jeffamine D-400), was used to mix with I and II. (see pg. 10) The systems are miscible and the cured epoxy resins are homogeneous and transparent. The mechanical properties are included in Table V. The II/D-400/BE-188 cured epoxy resins are expected to have higher crosslinking density and therefore a higher modulus than that of I/D-400/BE-188. The results indicate the opposite. It is assumed that the compounds with a high content of tricyclodecane can counteract the high crosslinking density effect. The tricyclodecane component contributes to the structural flexibility. Similar tensile and flexural properties were



observed for both II/D-400/BE-188 and I/D-400/BE-188.

The T_g of II/D-400/BE-188 cured product with the highest content of adduct II is similar to that of II/BE-188 (Table II). This implies that the high crosslinking density is outweighed by the flexibility, contributed by the presence of tricyclodecane. In I/D-400/BE-188, the effect of high crosslinking density is more predominant in resulting a higher T_g than the I/BE-188 cured material. With increasing amount of the Jeffamine D-400, the thermal properties of II/D-400/BE-188

and I/D-400/BE-188 are similar to that of D-400/BE-188 product.

CONCLUSIONS

Phenol/DCPD adducts, prepared from BF_3 -catalyzed reaction of NP and Diels-Alder dimer of CPD at molar ratio of 2:1 and 3:2, are semisolid materials. Structures of these adducts were confirmed by FTIR, $^1\text{H-NMR}$, GPC, and DSC. These NP/DCPD adducts (II and I) were cured with ep-

Table V Properties of Cured Epoxy Involving p-Nonylphenol/Dicyclopentadiene Adducts I and II and Polyetheramine

Composition	Weight Fraction	Tensile Properties		Flexural Properties		
		Tensile Strength (MPa)	Strain at Break (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Displacement at Break (mm)
I/BE-188	60/40	—	—	—	—	—
II/BE-188	62/38	—	—	12.3 (2.9)	2562 (0)	1.23 (0.31)
D-400/BE-188	35/65	51.9 (1.1)	7.98 (0.07)	81.4 ^a (0.3)	2882 (45)	—
I/D-400/BE-188	36/14/50	48.3 (2.7)	6.42 (0.26)	80.2 (6.6)	2779 (29)	8.02 (1.15)
I/D-400/BE-188	22/22/56	43.1 (3.3)	7.80 (0.56)	80.6 ^a (1.8)	2759 (69)	12.21 (0.59)
I/D-400/BE-188	14/27/59	43.9 (4.8)	7.60 (0.17)	80.4 ^a (0.5)	2765 (35)	10.91 (1.23)
II/D-400/BE-188	36/14/50	44.4 (3.9)	5.89 (0.76)	86.0 (10)	2683 (45)	10.29 (2.91)
II/D-400/BE-188	22/22/56	43.9 (4.6)	7.5 (0.14)	80.3 ^a (4.3)	2699 (49)	11.46 (0.51)
II/D-400/BE-188	14/27/59	45.9 (4.0)	7.9 (0.11)	80.2 ^a (1.3)	2723 (61)	11.76 (2.30)

^a Yield strength.

I, nonylphenol/dicyclopentadiene product at 2 : 1 molar ratio; II, nonylphenol/dicyclopentadiene product at 3 : 2 molar ratio; BE-188, diglycidyl ether of bisphenol A; D-400, poly(oxypropylene) diamine or Jeffamine D-400 at 400 MW.

oxy resin to give poor mechanical properties due to low crosslinking. When mixed with novolacs (PF1120) or Jeffamine D-400 amine as cocuring agents, the tricyclodecane structure was introduced into the epoxy network and resulted in improvement of flexibility. The presence of the tricyclodecane functionality accounts for this observation. From the practical point of view, higher oligomers of NP/DCPD should improve the crosslinking properties.

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