

New Epoxy/Episulfide Resin System for Electronic Applications. I. Curing Mechanism and Properties

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ABSTRACT: A new epoxy/episulfide is investigated using a dicyandiamide (DICY) curing agent system. The resin exhibits better adhesion to copper, a lower thermal expansion coefficient, a lower heat of reaction, and slightly higher water absorption as compared with the standard epoxy system. The dielectric constant of the epoxy/episulfide system is almost the same as that of the standard epoxy system. The properties are due to the reaction mechanism change caused by the addition of episulfide, which is studied using a monofunctional model compound system; the amino groups in DICY initially react much more easily with the episulfide than with the epoxy ring. The S^- formed by this reaction reacts with the episulfide and the epoxy quickly. In the presence of copper, the episulfide and/or the S^- also react with copper, forming a durable bond between the copper and matrix resin that retains strength even after water boiling. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1359–1370, 2001

Key words: epoxy; episulfide; resin system; dicyandiamide

INTRODUCTION

Epoxy resins are widely used for protective coatings and electrical and adhesive applications, because of their high chemical and corrosion resistance, good mechanical and electrical properties, and strong adhesion to many different substrates.^{1,2} However, for special applications, such as printed circuit boards, improved properties are needed.

Bell et al.^{3,4} studied the properties and the curing reaction of the epoxy/episulfide/V-40TM (polyamide curing agent, Shell Chemical Co.) system for implants and adhesives in the human body and found that the Epoxy/Episulfide/V-40 system has significant advantages over standard epoxy resins: the gelation time and water absorption are lower. Moreover, the heat

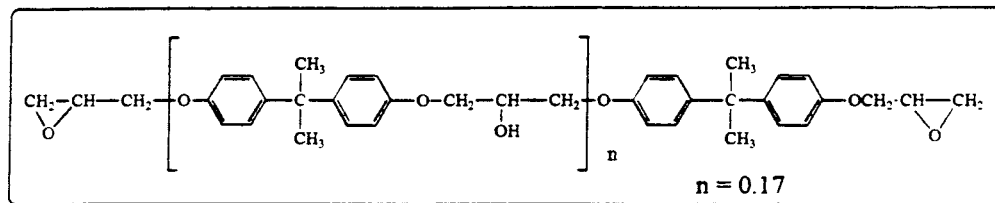
of reaction of this system is low, resulting in low cure shrinkage. The tensile strength of this system is higher than the strength of standard epoxies. They concluded from the kinetic data that these good properties result from the formation of two network structures: a conventional epoxy/amine structure and an episulfide homopolymer structure.

The episulfide could possibly react not only with epoxy resin but also with many kinds of metals because of the fact that thiol groups ($-SH$) react easily with metal surfaces, such as gold,^{5–9} silver,^{10,11} copper,^{12–20} and iron,^{21,22} to form sulfur–metal bonds, resulting in better adhesion and corrosion resistance.

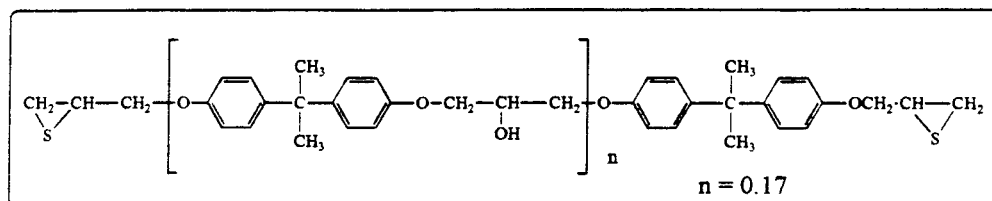
In this study the epoxy/episulfide resin was applied using the dicyandiamide (DICY) curing agent system, which is widely used for printed circuit boards, in order to improve adhesion and resin properties. The curing mechanism and related properties were studied.

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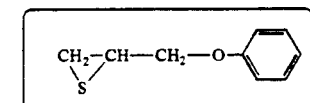
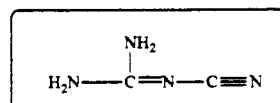
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Epon 828 (Trade mark of Shell Chemical Company)



Episulfide 828

2,3-Epithiopropyl phenyl ether
(EPIMO)

Dicyandiamide (DICY)

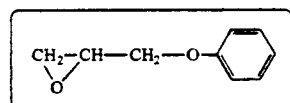
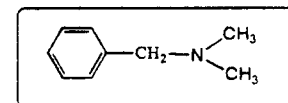
2,3-Epoxypropyl phenyl ether
(EPOMO)N,N-dimethylbenzylamine
(BDMA)

Figure 1 The structures of epoxy, episulfide, dicyandiamide, and *N,N*-dimethylbenzylamine.

EXPERIMENTAL

Materials

The molecular structures of the chemicals used in the DICY system are shown in Figure 1. Epon828[®] was obtained from Shell. The equivalent weight of the Epon828 is 189. 2,3-Epoxypropyl phenyl ether (EPOMO), DICY, and *N,N*-dimethylbenzylamine (BDMA) were reagent grade and were purchased from Aldrich Chemical Company. BDMA is a tertiary amine accelerator very often used with DICY curing agent systems. Episulfide828 and 2,3-epithiopropyl phenyl ether (EPIMO) were synthesized from Epon828 and EPOMO with thiourea, respectively.⁴ Copper plates and copper joints for the adhesion tests were 110 alloys.

Investigation of Curing Reaction

Because thermosetting polymers are not soluble in any solvent, the analytical techniques necessary to follow the curing reactions are very difficult and limited. Therefore, monofunctional compounds were used as model compounds for the epoxy (EPOMO) and episulfide (EPIMO) (Fig. 1) in order to investigate the reaction mechanism. Because the cured samples are soluble and the cured structures are relatively simple, ¹³C-NMR and FTIR analyses were performed to determine the structures.

The molar ratio of the EPOMO/EPIMO/DICY/BDMA was 46/54/11/1.4. The molar ratio of the EPOMO/DICY/BDMA was 100/11/1.4.

The samples were analyzed by near IR (NIR) as a function of time using standard curing con-

ditions. After curing, the mixtures were dissolved in CDCl_3 and analyzed by ^{13}C -NMR. The CDCl_3 solutions were placed on KBr pellets, the solvent dried, and then the pellets were analyzed by FTIR.

In order to study the effect of copper on the curing reaction, copper plates ($20 \times 10 \times 0.8$ mm) immersed in the model compound systems (1 g) were thoroughly rinsed with CHCl_3 and THF and then analyzed by X-ray photoelectron spectroscopy (XPS). The rinsed solutions of the model compound systems were analyzed by ^{13}C -NMR.

A 500-MHz Bruker NMR spectrometer (model DMX-500) was used for the analysis of the cured model compound systems. Approximately 33 wt % solutions were prepared. In order to obtain quantitative results from the ^{13}C -NMR, long pulse delays (20 s) and elimination of nuclear Overhauser enhancement were used and more than 100 scans were done.

A Nicolet Magna-IR 560 spectrometer with a deuterated triglycine sulfate detector was used for cured samples. The spectra were recorded using 32 scans, and the resolution was 4 cm^{-1} .

A UV/vis/NIR spectrometer (Lambda 900) from Perkin-Elmer was used to determine the percentage of epoxy and episulfide groups remaining in the DICY systems. The cured and uncured model samples were dissolved in chloroform and were analyzed from 2500 to 1000 nm at a rate of 500 nm/min. The epoxy and the episulfide characteristic bands appeared at 2206 and 2223 nm, respectively.

Copper immersed in the model compound systems was studied using 5600ci from ULVAC-PHI in order to obtain the atomic percent of each element on the copper surface and the interaction between copper and sulfur.

Property Measurements

Resin formulations for property measurements of the standard epoxy and the epoxy/episulfide system were as follows: Epon828 (100 wt %)/DICY (5 wt %)/BDMA (1 wt %): standard epoxy (molar ratio: 100/11/1.4); Epon828 (100 wt %)/episulfide (5–15 wt %)/DICY (5 wt %)/BDMA (1 wt %): epoxy/episulfide.

The samples were cured at 100°C for 1 h and then the temperature was elevated gradually to 150°C over 15 min. After the temperature reached 150°C , the samples were cured for 1 h (standard curing condition).

The copper-epoxy/episulfide adhesive joints as shown in Figure 2 were made using different ra-

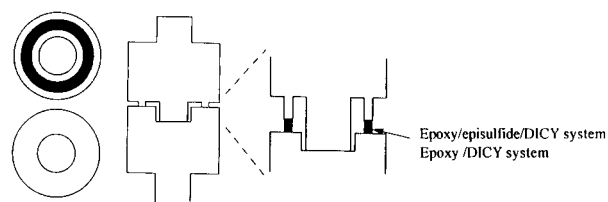


Figure 2 A schematic diagram of a tubular butt joint (copper 110).²³

tios of Epon828/Episulfide828/DICY/BDMA. Approximately 44 mg of the mixture of Epon828/Episulfide828/DICY/BDMA were used in making each modified tubular butt joint for adhesion testing. The joint assemblies were cured with the standard condition and tested using a torsional testing method, which measures the shear strength of the joints.²³ Joint strength was evaluated before and after immersion in boiling water for 8 h.

A differential scanning calorimeter (model 2920) from TA Instruments was used to obtain the heat of reaction of the uncured samples. Nitrogen was used as the purging gas. The heating rate was $20^\circ\text{C}/\text{min}$.

A thermomechanical analysis (TMA) instrument (TMA 7) from TA Instruments was used to determine the thermal expansion coefficient of the cured samples (5-mm diameter \times 6.5-mm height). The samples were run in a helium atmosphere from 20 to 210°C at a rate of $2^\circ\text{C}/\text{min}$.

A time domain dielectric spectrometer from IMASS Inc. was used to measure the dielectric constants. The epoxy/episulfide/DICY coated aluminum samples used were coated on one side. The bare side of the sample was connected to a ground, and a potential of 100 V dc was applied to the coated side. The applied frequencies ranged from 0.01 to 10,000 Hz.

In order to measure water absorption, samples ($30 \times 10 \times 1$ mm) were dried at 100°C for 1 h and then put in a desiccator for 1 h. After weight measurement of the samples, the samples were immersed in boiling water for 2 h. Excess water was wiped off with a Kimwipe®, and the samples were weighed immediately. The water absorption was calculated by the following equation:

$$\text{water absorption (\%)} = \frac{(\text{wet weight} - \text{conditioned weight})}{\text{conditioned weight}} \times 100$$

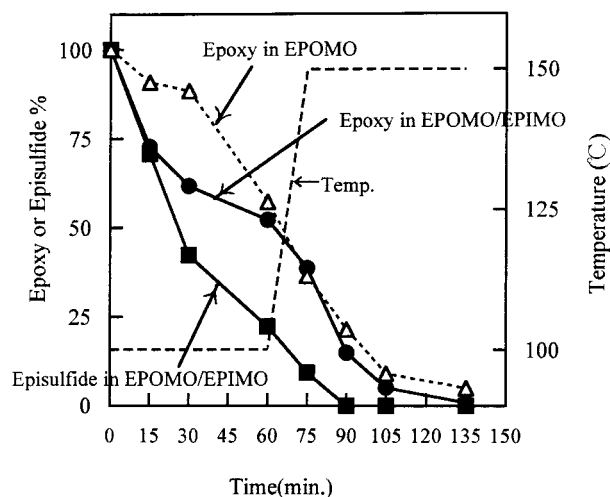


Figure 3 The percentage of epoxy or episulfide groups remaining in EPOMO/DICY/BDMA or EPOMO/EPIMO/DICY/BDMA systems as a function of the curing time (EPOMO/EPIMO molar ratio = 46/54).

RESULTS AND DISCUSSION

Reaction Mechanism

In order to investigate the curing reactions within the epoxy/episulfide/DICY/BDMA system, NIR, ^{13}C -NMR, and FTIR analyses were carried out using model compounds. The ring-opening reaction during the standard curing condition was investigated by NIR. Figure 3 shows the percent epoxy or episulfide remaining as a function of curing time. These NIR data (Fig. 3) show that the episulfide ring reacts quickly and the epoxy ring-opening reaction is accelerated by the presence of episulfide during the first 15 min. After curing for 60 min, the rate of the epoxy ring opening in the epoxy-episulfide mixture is the same as that of the standard epoxy.

The ratios of each reaction as determined by ^{13}C -NMR are shown in Figure 4 (standard epoxy) and Figure 5 (epoxy/episulfide). In the standard epoxy system, nearly 40% of the epoxy groups are consumed by the reaction with the NH groups in the DICY, and the others are consumed by epoxy homopolymerization (reaction of epoxy with itself). On the other hand, in the epoxy/episulfide system nearly half of the episulfide reacts with NH groups to form mercaptide ions (S^-), and the remaining episulfide homopolymerizes. Because the mercaptide ion is very reactive, the S^- -epoxy reaction proceeds. The ^{13}C -NMR shows that one-third of the epoxy is consumed by the S^- -epoxy

reaction. The remaining epoxy is consumed by the epoxy homopolymerization. The epoxy-NH reaction hardly occurs in the epoxy/episulfide system because the episulfide is much more reactive with amine than epoxy.

The ^{13}C -NMR analysis also shows more NH groups of DICY in the epoxy/episulfide system remain than in the standard epoxy; assuming DICY has four NH groups, nearly 90% of the NH groups are consumed by the reaction with epoxy in the standard epoxy system, while about 60% of the NH groups are consumed by the reaction with episulfide in the epoxy/episulfide system.

In order to investigate other reactions such as the OH-CN reaction and the cyclization reactions to form oxazoline structures, the cured samples were analyzed by FTIR. FTIR spectra of the standard epoxy and the epoxy/episulfide systems after the standard curing are shown in Figure 6. Many more unreacted NH groups (3220 cm^{-1}) and CN groups (2180 cm^{-1}) of DICY exist in the epoxy/episulfide system than in the standard epoxy system. In the standard epoxy the formation of guanlyl urea, oxazoline and its derivatives, ether, and aliphatic ester structures is observed from the presence of absorption bands at 1680 , 1640 , 1110 , and 1730 cm^{-1} , respectively; their assignments are based on the work of previous researchers.²⁴⁻⁴⁰ On the other hand, in the epoxy/episulfide system, the intensity attributed to guanlyl urea (1680 cm^{-1}) and ethers (1110 cm^{-1}) is much less than observed in the standard epoxy system. Bands at 1640 and 1730 cm^{-1} are observed. The band at 1640 cm^{-1} is probably due to an oxazoline structure, its derivatives, and/or the products from the reaction of S^- with $\text{N}=\text{C}-\text{N}$ in the DICY as shown in reaction (1).

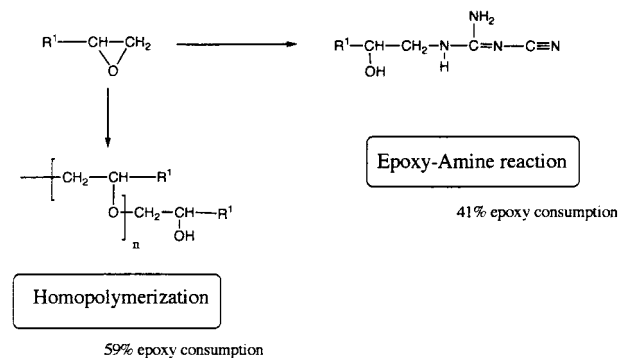


Figure 4 The curing reaction of the epoxy/DICY system determined by ^{13}C -NMR (standard curing process).

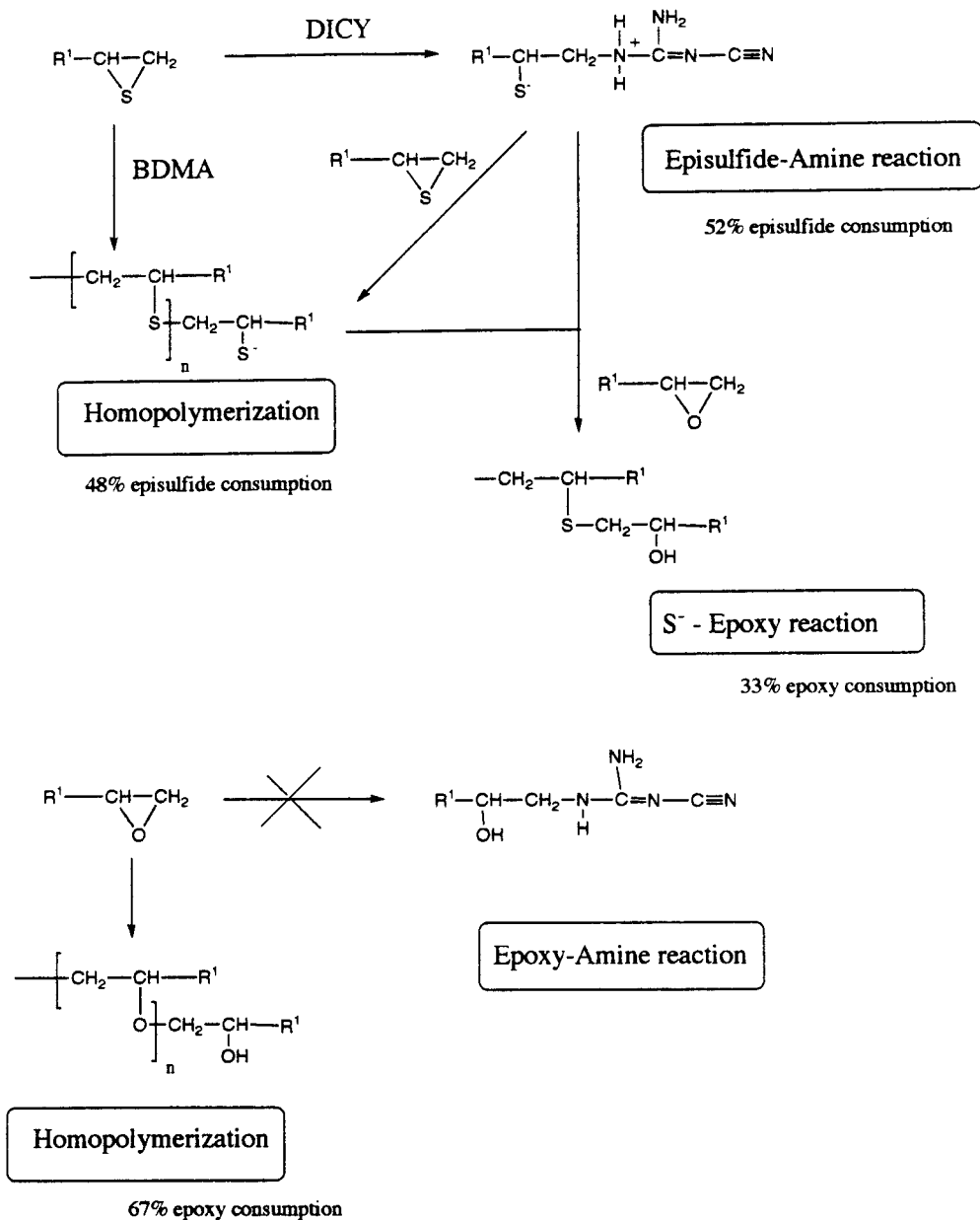


Figure 5 The curing reaction of the epoxy/episulfide/DICY system as determined by ^{13}C -NMR (epoxy/episulfide molar ratio = 46/54, standard curing process).



Figure 7 shows a summary of the proposed reactions based on NIR, ^{13}C -NMR, and FTIR analyses: the amino groups in DICY initially re-

act with the episulfide much more easily than with the epoxy ring. The S^- formed by this reaction quickly reacts with the epoxy and the

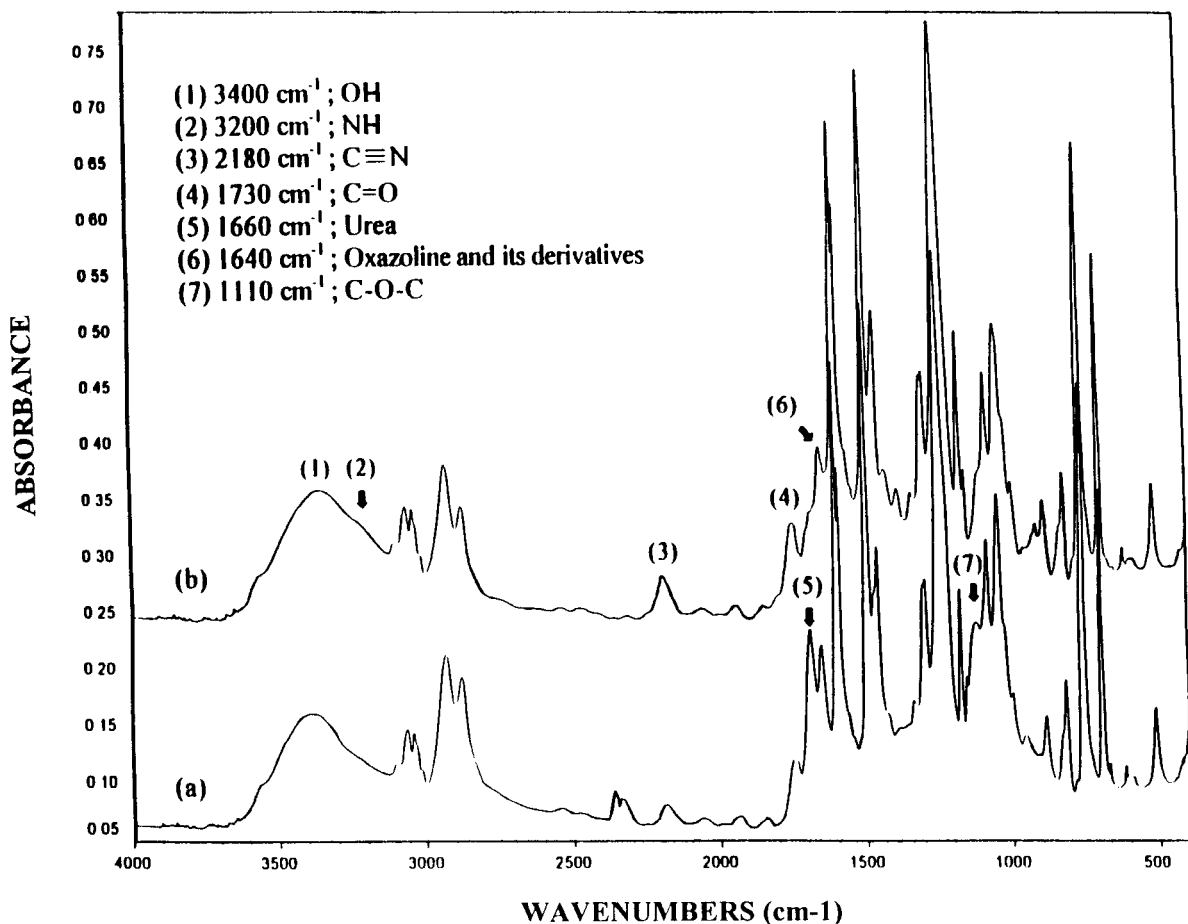


Figure 6 FTIR spectra of EPOMO/DICY/BDMA (spectrum a) and EPOMO/EPIMO/DICY/BDMA (spectrum b) systems (standard curing process).

epoxy. As the concentration of S^- decreases, the rate of the epoxy ring opening decreases. The extent of reaction of the amino groups in DICY with the epoxy and episulfide rings is less than in the standard epoxy because of the faster reaction of S^- with the episulfide and epoxy groups. In addition, the reaction of $N=C-N$ with OH and/or S^- proceeds. The reaction of OH with CN is less significant in the epoxy/episulfide system than in the standard epoxy system.

Effect of Copper on Reaction Mechanism

In order to investigate the possible effects of copper on the curing reaction, model compound samples with and without exposure to copper were analyzed by ^{13}C -NMR. Copper plates immersed in model compound samples using the standard curing conditions were thoroughly rinsed with $CHCl_3$ and THF and then analyzed by XPS.

Table I shows the structure ratios of the standard cured epoxy/episulfide model system with

and without copper as determined by ^{13}C -NMR. In the presence of copper the extent of episulfide homopolymerization decreases. The ^{13}C -NMR also indicated that the episulfide ring reacts with copper or is adsorbed on copper, leaving the matrix near the copper interface richer in epoxy structures.

Figure 8 shows XPS results from copper plates immersed in the standard epoxy and the epoxy/episulfide systems after curing at standard conditions, followed by a solvent rinse. The XPS results from the epoxy/episulfide system reveal the presence of sulfur on the copper surface. The XPS results also show higher amounts of carbon and nitrogen and a lesser amount of copper than that obtained from the standard epoxy; more organic compounds exist on the copper. It is assumed from these ^{13}C -NMR and XPS results that the episulfide and/or the mercaptide ion strongly interacts with copper, resulting in more organic compounds on the copper surface. Because the

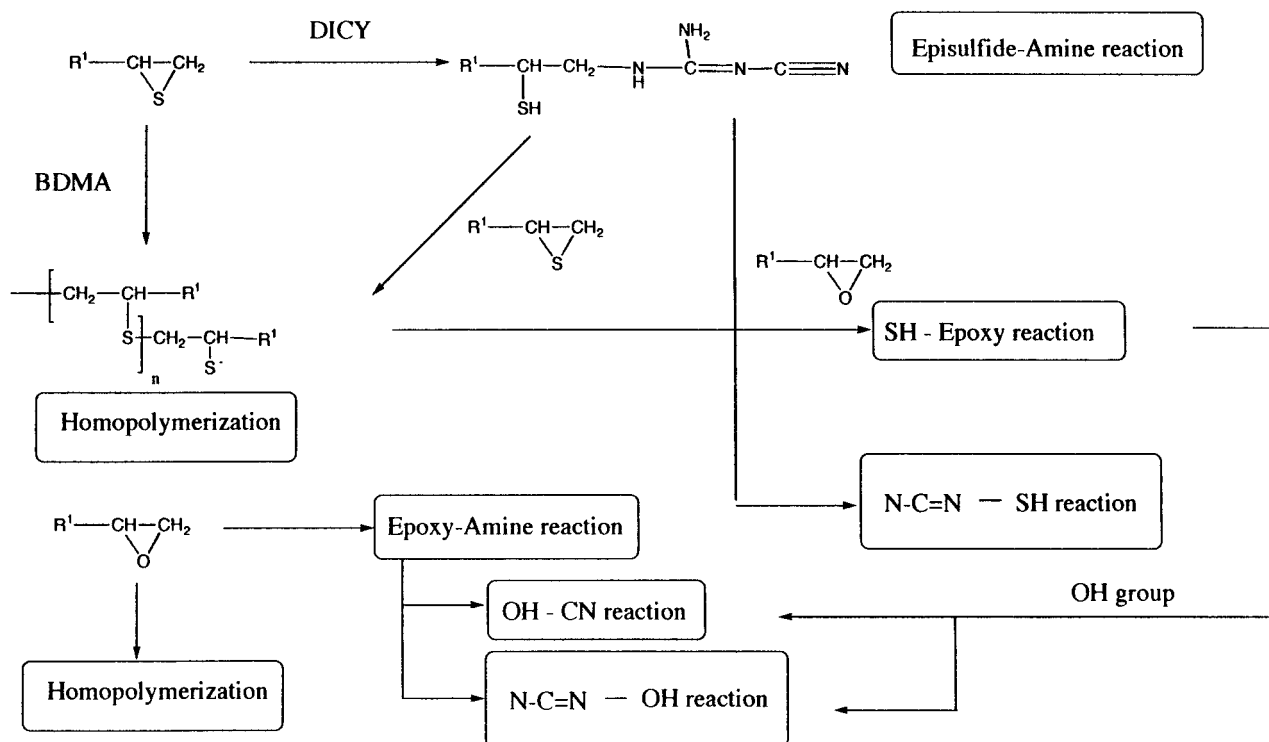


Figure 7 The proposed reaction mechanism of the epoxy/episulfide/DICY system.

atomic percentage of sulfur is very low, the details of the binding state, such as C—S—C, Cu—S—C, Cu—S—Cu, could not be detected. In order to emphasize the interaction between copper and sulfur, a copper plate was immersed in the epoxy/episulfide system at a higher temperature (200°C) than the standard (150°C), rinsed with solvents, and then analyzed by XPS. As a result, more sulfur (nearly 3 atom %) was found on the copper surface. Figure 9 shows S2p spectra from the copper as a function of the incidence angle. The peaks are shifted to lower binding energy with higher angles (45° and 60°). Because deeper information is detected with a higher angle, inter-

phase information between the copper and the adsorbed organic compounds can be emphasized with higher angle analysis. Figure 10 shows S2p spectra at 45° with curve fitting; the assignments are based on standard data.⁴¹ As a result, Cu—S—C bonds could be detected; the episulfide and/or mercaptide ion reacted with the copper.

Although Cu—S—C bonds could not be detected for the standard curing conditions, episulfide and/or S⁻ probably react with copper because thiols react easily with copper at room temperature. Because DICY is present in the epoxy/episulfide system and tends to adsorb on copper⁴² before the formation of S⁻, the chemical bonding

Table I Structure Ratio (¹³C-NMR) of Reaction Products for 46/54/11/1.4 EPOMO/EPIMO/DICY/BDMA System with and without Copper after Standard Curing

	Structure (mol %)					Epoxy/Episulfide Molar Ratio
	A	B	C	D	E	
Without Cu	27	0	25	16	32	48/52
With Cu	30	0	16	18	36	54/46

A, episulfide-amine reaction; B, epoxy-amine reaction; C, episulfide homopolymerization; D, episulfide reaction with epoxy; E, epoxy homopolymerization.

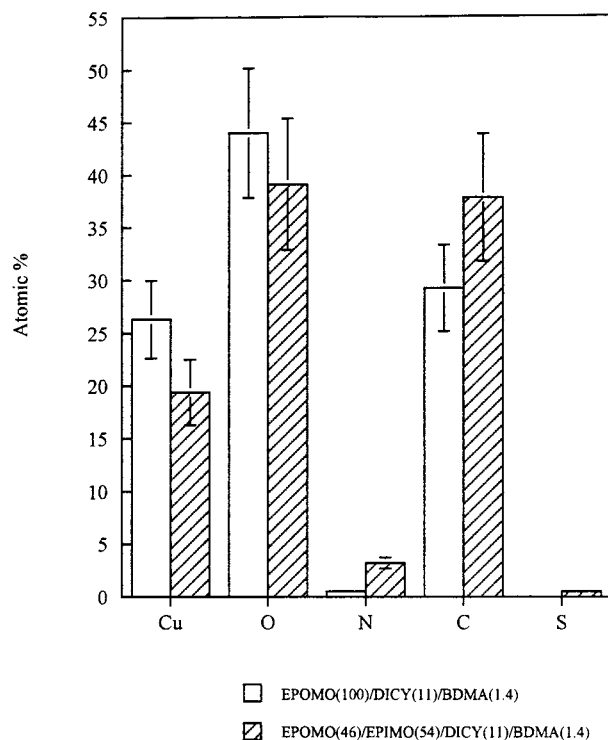


Figure 8 The XPS results from a copper plate immersed in EPOMO/DICY/BDMA or EPOMO/EPIMO/DICY/BDMA at the standard curing temperature, followed by a solvent rinse.

reaction between sulfur and copper is probably retarded.

A conclusion is copper probably reacts with episulfide and/or S^- . Also, the reactions in the interphase are different from those in the bulk resin because of the interaction of the episulfide and/or S^- with copper, resulting in a change of S^- concentration and copper activity. In the presence of copper the extent of reaction of episulfide with itself is less than that without copper.

Properties

Adhesion to Copper

Figure 11 shows the effect of the amount of episulfide and epoxy on the shear strength of a standard epoxy (resin, not model compounds) system used with the copper joints. The shear strength was measured by the torsional joint method.²³ The shear strength (ca. 38 MPa) of the control epoxy/DICY in this study is in good agreement with the lap shear tests by Vrana et al.⁴³ As can be seen, as the amount of episulfide increases, the initial shear strength gradually increases

while the initial shear strengths are not changed by the addition of Epon828. The addition of 15 wt % episulfide into the standard epoxy system shows over 15 MPa higher initial strength as compared with no episulfide. Figure 12 shows the shear strength after boiling for 8 h. The strength after boiling is also improved by the addition of episulfide. The improvement of adhesion by the addition of episulfide is probably due to the improvements of the interface and bulk resin initial strength properties and due to the improvement of the interface strength after boiling. As mentioned before, the episulfide reacts not only with the epoxy resin but also with the copper joint, thus resulting in the formation of chemical bonding between the copper and epoxy resin. Even though the epoxy/episulfide system shows a slightly higher water absorption than the standard epoxy system (see below), the epoxy/episulfide shows higher adhesion after boiling than the standard epoxy. The reaction mechanism of the epoxy/episulfide system in the bulk resin is quite different from that of the standard epoxy system. The episulfide is so reactive that the episulfide

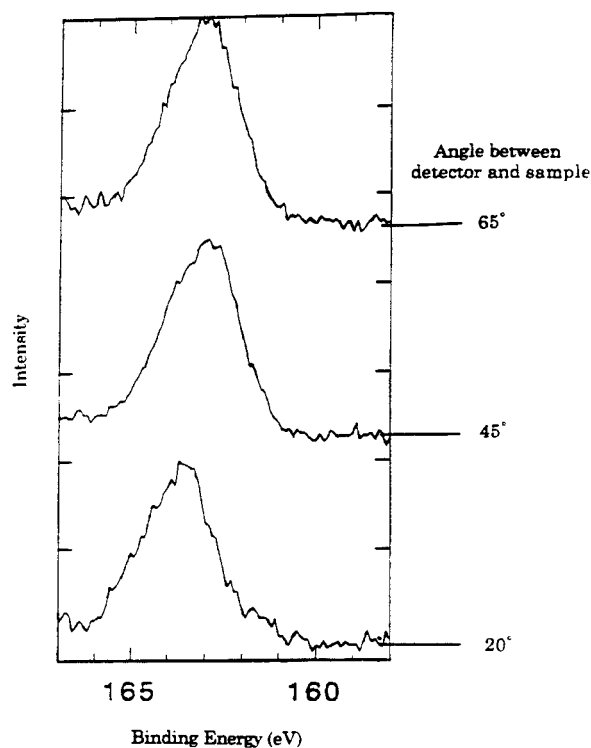


Figure 9 The different angle S2p spectra from a copper plate immersed in 46/54/11/1.4 EPOMO/EPIMO/DICY/BDMA at 200°C for 8 h after the standard curing process, followed by a solvent rinse.

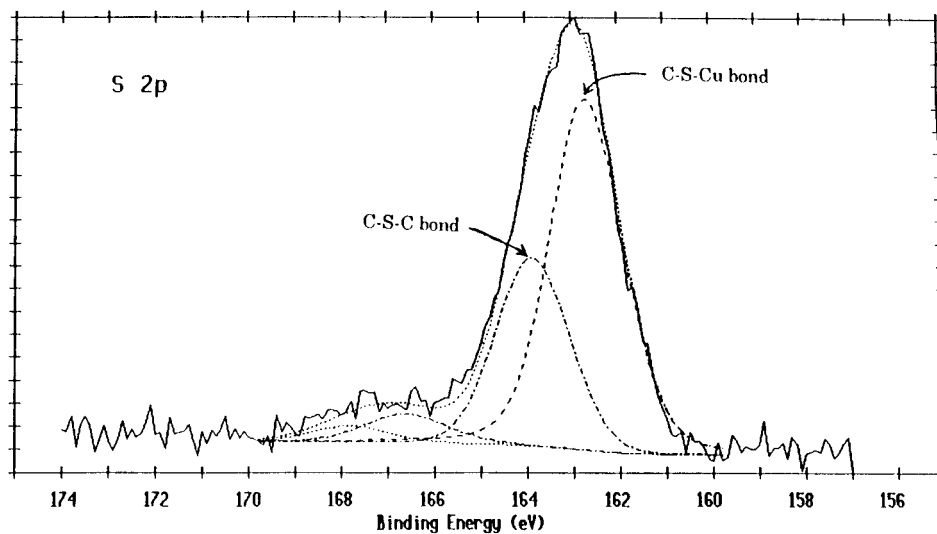


Figure 10 The S2p spectra (45° angle) from a copper plate immersed in 46/54/11/1.4 EPOMO/EPIMO/DICY/BDMA at 200°C for 8 h after the standard curing process, followed by a solvent rinse.

reacts with the NH groups in DICY to form S^- groups in preference to the epoxy-NH group reaction. The S^- groups are also so reactive that the S^- groups react with the episulfide and the epoxy.

Other Properties

Figure 13 shows the heat of reaction for the standard epoxy and the epoxy/episulfide systems. As

can be seen, as the amount of episulfide increases, the heat of reaction decreases significantly, even at low episulfide concentration. The reason for the lower heat of reaction in the epoxy/episulfide system is the lower strain of the episulfide ring in comparison with that of the epoxy ring.⁴⁴ The results are in agreement with those previously reported by Bell and Ku.³

The thermal expansion coefficient was determined by TMA. Figure 14 shows the thermal ex-

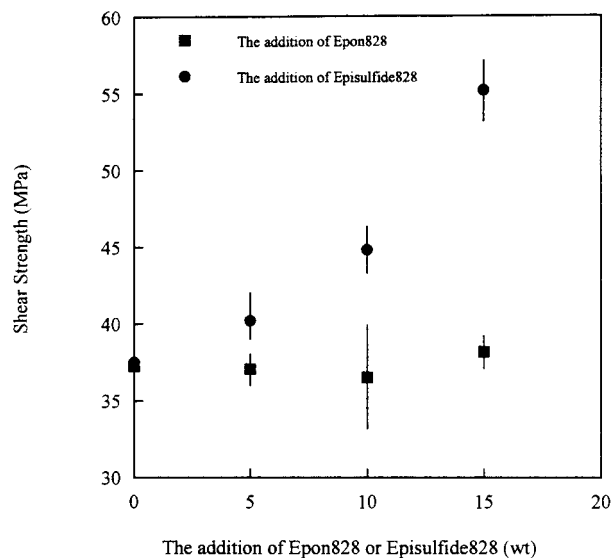


Figure 11 The effect of the addition of Epon828 or Episulfide828 on the shear strength of 100/5/1 wt % Epon828/DICY/BDMA.

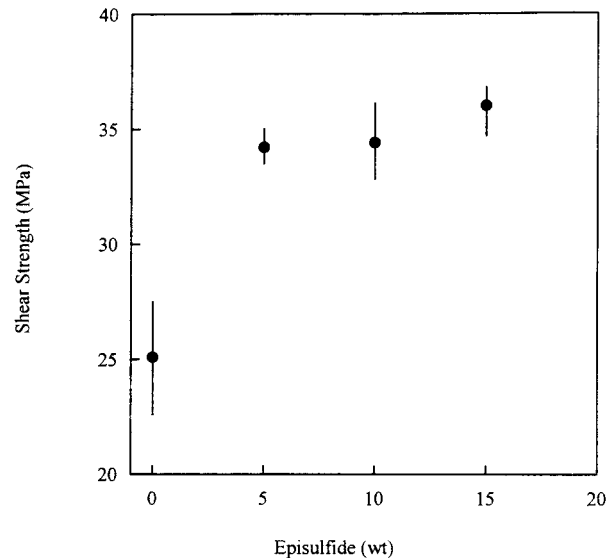


Figure 12 The shear strength of Epon828 (100 wt %)/Episulfide828/DICY (5 wt %)/BDMA (1 wt %) after boiling for 8 h.

Table II Examples of van der Waals Volume Contribution (mL/mol)

—CH ₂	10.23
—CH(OH)—	14.82
—CONH—	19.56–18.1
—CH(CN)—	21.48
—S—	10.8

The was found in Van Krevelen.⁴⁵

standard epoxy system. The dielectric constant of the epoxy/episulfide system was almost the same as that of the standard epoxy system.

The properties were due to the reaction mechanism change caused by the addition of episulfide, which was studied using a monofunctional model compound system. The proposed reactions based on NIR, ¹³C-NMR, and FTIR analyses were as follows: the amino groups in DICY initially reacted with the episulfide much more easily than with the epoxy ring. The S⁻ formed by this reaction reacted with the episulfide and the epoxy quickly. The extent of reaction of the amino groups in DICY with the epoxy and episulfide rings was less than in the standard epoxy because of the faster reaction of S⁻ with the episulfide and epoxy groups.

In the presence of copper the episulfide and/or the S⁻ also reacted with copper, forming a durable bond between the copper and matrix resin

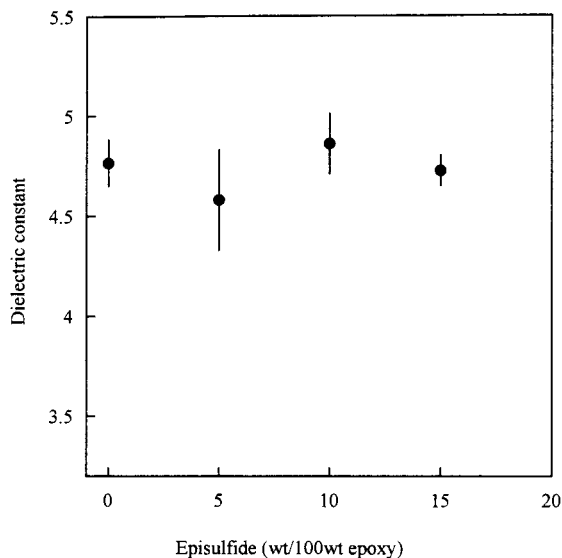


Figure 15 The dielectric constant of the standard cured Epon828 (100 wt %)/Episulfide828/DICY (5 wt %)/BDMA (1 wt %).

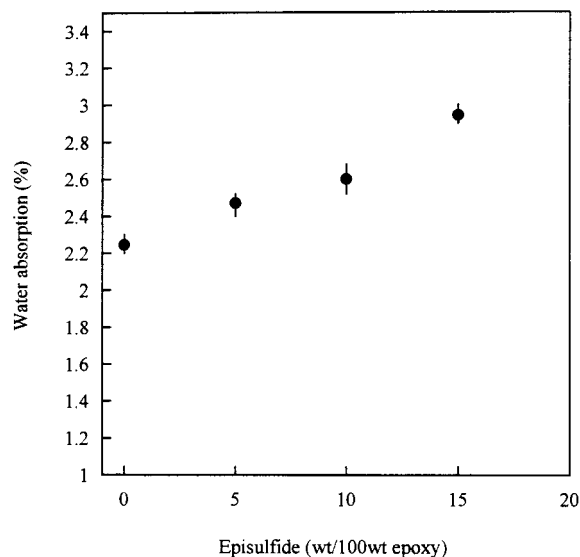


Figure 16 The water absorption of the standard cured Epon828 (100 wt %)/Episulfide828/DICY (5 wt %)/BDMA (1 wt %) after boiling for 2 h.

even after water boiling. Also, the reactions in the interphase were different than those in the bulk resin because of the reaction of the episulfide and/or S⁻ with copper, resulting in a change of the S⁻ concentration and copper activity. In the presence of copper the extent of reaction of episulfide homopolymerization was less than that without copper.

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