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International Journal of Adhesion & Adhesives 20 (2000) 449–456

International Journal of Adhesion & Adhesives

A new epoxy/episulfide resin system for coating applications: curing mechanism and properties

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Accepted 21 March 2000

Abstract

A new epoxy/episulfide resin was applied using a polyamide(V-40®) curing agent system. The epoxy/episulfide/V-40® system exhibits much faster cure, better corrosion protection for copper, a lower thermal expansion coefficient and lower exotherm as compared with standard amine cure, room-temperature epoxy systems. From model compound studies, episulfide–amine, S^-–epoxy, epoxy–amine reactions and episulfide homopolymerization proceed in the epoxy/episulfide system. The curing reactions are changed by changing the curing temperature and by the presence of copper. The episulfide homopolymerization and the S^-–epoxy reaction increase in the case of room-temperature curing or in the presence of copper. The episulfide and/or the S^- react with copper. From DSC measurements, the resin near the copper surface has higher T_g than the bulk resin due to the fact that the episulfide tends to polymerize near the copper surface. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Epoxy resins are widely used for protective coatings [1,2], due to the strong adhesion and corrosion protection of metals. However, although typical epoxy resins show excellent initial adhesion to several common metals, the adhesion after water exposure is not good; improvement is strongly needed. Because metals are subject to corrosion problems, some protective treatment such as metal plating, chromate, corrosion inhibitors, or coupling agents is usually given before use. In general, these corrosion-resistance and adhesion-promoting treatments are relatively expensive and complicated. Although the chromate treatment is effective, chromate ions cause very harmful effects in the environment.

In previous studies [3,4], an epoxy–episulfide–polyamide system was developed for implants and adhesives in the human body that has significant advantages over standard epoxy resins: lower water absorption, lower heat of reaction (lower cure shrinkage), higher glass transition temperature (T_g), and higher tensile strength than those of standard epoxies. In addition to the improved properties of the resin itself, the episulfide group was expected to react with many kinds of metals due to the fact that thiol groups (–SH) easily react with common metal surfaces, such as gold [5–9], silver [10,11], copper [12–20], and iron [21,22], to form sulfur–metal bonds. Therefore, the epoxy–episulfide resin system was expected to improve not only bulk resin properties, but also corrosion resistance and adhesion.

In this study, in order to eliminate other protective treatments and obtain a rapid low-temperature cure and other property advantages, a polyamide cured epoxy–episulfide resin system was applied to copper as a protective coating. The curing mechanism with and without copper was investigated.

2. Experimental

2.1. Materials

The molecular structure of the chemicals used are shown in Fig. 1. Epon828® and V-40® were obtained from Shell Chemical Company. The equivalent weight of the Epon828® is 189. 2,3-epoxypropyl phenyl ether (EPOMO) and di-n-butylamine (DBA) were reagent grade and were purchased from Aldrich Chemical Company.

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PII: S0143-7496(00)00016-6

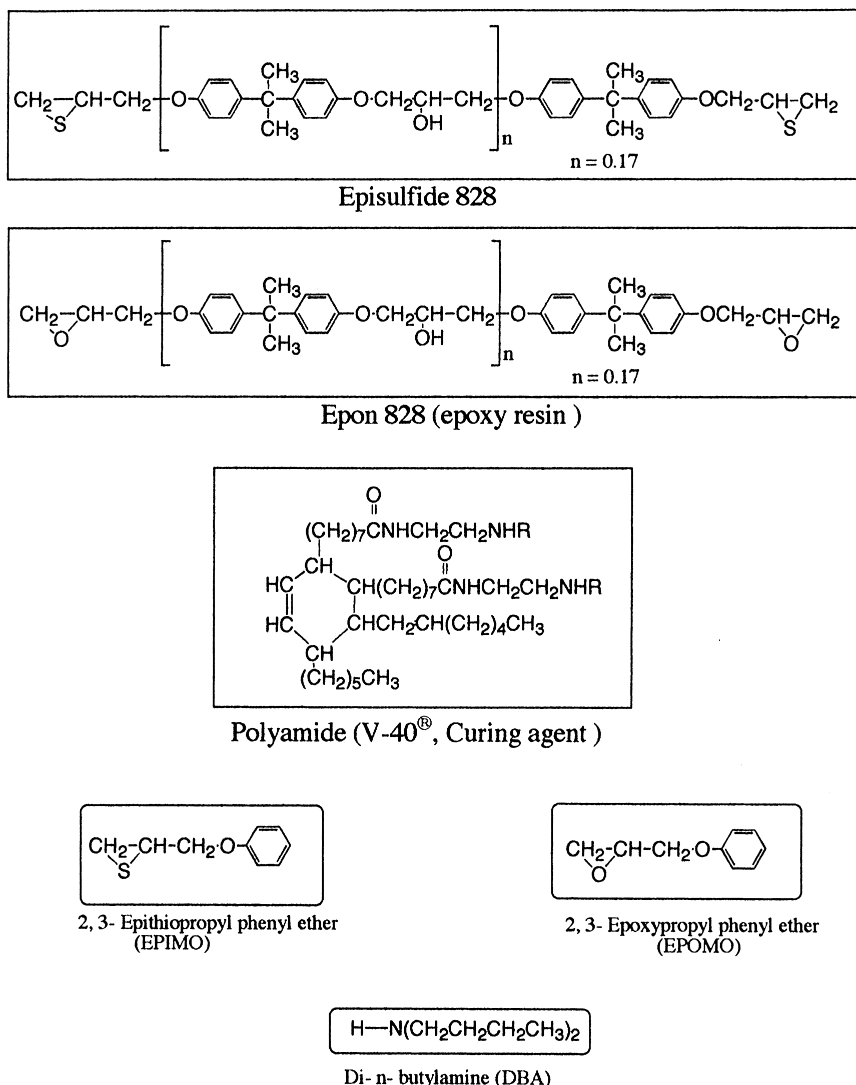


Fig. 1. The structures of epoxy, episulfide, polyamide, and amine used for V-40 system studies.

Episulfide828 and 2,3-epithiopropyl phenyl ether (EPIMO) were synthesized from Epon828® and EPOMO by reaction with thiourea, respectively [4]. Copper plates and copper joints for adhesion tests were 110 alloys (essentially pure copper with a trace of silver).

2.2. Investigation of curing reaction

Since thermosetting polymers are not soluble in any solvent, the analytical techniques necessary for reaction path studies are very difficult and are limited. Therefore, mono-functional compounds were used as model compounds of epoxy (EPOMO), episulfide (EPIMO), and polyamide (DBA) as shown in Fig. 1, in order to investigate the reaction mechanism. The molar ratio of the EPOMO/EPIMO/DBA was 46/54/100. The samples were cured at 100°C for 1 h or at room temperature for 10 days.

After curing, the mixtures were dissolved in $CDCl_3$ and analyzed by ^{13}C-NMR. In order to investigate the effect of copper on the curing reaction, the model system (1 g) was used to immerse copper plates ($20 \times 10 \times 0.8$ mm) and after the solution was analyzed by ^{13}C-NMR. The copper plates were thoroughly rinsed with $CHCl_3$ and THF and then analyzed by XPS.

In order to investigate a possible effect of copper on the glass transition temperature (T_g), Epon828®/Episulfide828/V-40® systems were analyzed by DSC. Different weights of samples were put in copper DSC pans, cured and then analyzed by DSC. Interphase properties are emphasized for small amounts of sample and bulk properties are emphasized for large amounts of sample.

In order to investigate any differences of the reaction between the standard epoxy and the epoxy/episulfide systems, room temperature-stored Epon828® (1 wt)/Episulfide828 (1 wt)/V-40® (1 wt) and a control Epon828® (1 wt) /V-40® (1 wt) were analyzed by FT-IR as a function of time.

A 500 MHz Bruker NMR spectrometer, model DMX-500, was used for the analysis of the raw materials and the cured model compound systems. Deuterated chloroform ($CDCl_3$) was used as a solvent. Approximately, 33 wt% solutions were prepared. In order to obtain quantitative results from ^{13}C-NMR, long-pulse delays (20 s) and elimination of nuclear overhauser enhancement (NOE) were used and more than 100 scans were done.

A Nicolet MAGNA-IR 560 spectrometer with a deuterated triglycine sulfate (DTGS) detector was used for analyses of raw materials and cured samples. Samples were prepared by coating KBr disks. The spectra were recorded using 32 scans and the resolution was 4 cm^{-1}.

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

A DSC Model 2920 from TA Instruments was used to obtain the glass transition temperature (T_g) of the cured samples. Nitrogen was used as the purging gas. The heating rate used was 20°C/min.

2.3. Properties

For corrosion resistance tests, a 33 wt% of Epon828®/Episulfide828/V-40® solution in cyclohexanone was coated on a pretreated copper plate by spin coating, and then cured at 100°C for 1 h or at room temperature for 10 days. The thickness was approximately 3 μm, calculated by the weights before and after coating, assuming that the density of the film is 1.0. An accelerated salt spray test (in accordance with ASTM B117 standard test method of salt spray (fog) testing) was used to evaluate the corrosion resistance. The samples were held in a mist of saturated salt water at 35°C.

For thermal expansion coefficients of the cured samples (5 mm (diameter) × 6.5 mm (height)), a model TMA-7 from TA Instruments was used. The samples were run in helium atmosphere from 20 to 210°C at the rate of 2°C min^{-1}.

3. Results and discussion

3.1. Reaction mechanism (EPOMO/EPIMO/DBA system)

In order to investigate the curing reactions within the epoxy/episulfide/V-40® system, ^{13}C-NMR and XPS analyses were done on products from model reactions.

From ^{13}C-NMR measurements on the standard epoxy (EPOMO/DBA), almost all the epoxide groups react with amine to form–OH groups. On the other hand, in the epoxy/episulfide, the episulfide reacts quickly with amine, and also partially homopolymerizes and reacts with the epoxy groups. This is in good agreement with near-IR studies by Bell and Ku [3]. The ratio of the products is changed by changing the curing temperature. Fig. 2 shows curing reactions of the epoxy/episulfide

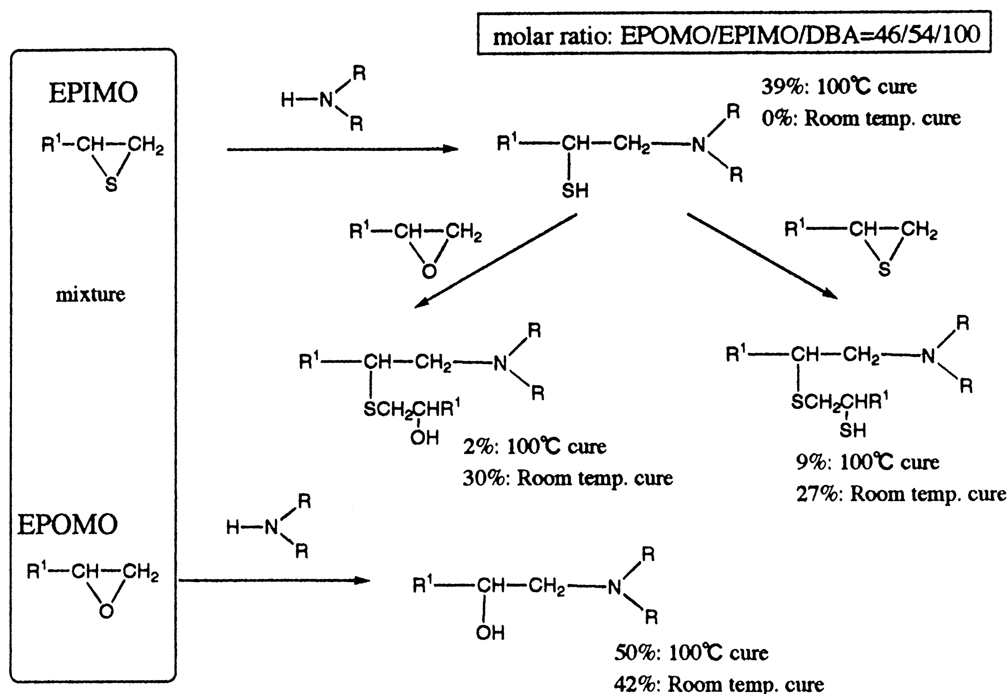


Fig. 2. Proposed reaction mechanism of epoxy–episulfide–amine system without copper by ^{13}C-NMR, FT-IR, and GPC.

Table 1
Effect of copper on the structure ratio of reaction products for the reaction of EPOMO–EPIMO–dibutylamine system at 100°C for 1 h

	Structure (mol%)				Epoxy/episulfide
	A[a]	B[b]	C[c]	D[d]	molar ratio
w/o copper	50	39	2	9	47/53
with copper	51	6	34	9	59/41

[a]A, epoxy–amine reaction,
[b]B, episulfide–amine reaction,
[c]C, Product B–epoxy reaction,
[d]D, Product B–episulfide reaction

Table 2
XPS results (at%) from a copper plate immersed in EPOMO(1) /EPIMO(1) dibutylamine(2) (molar ratio) at 100°C for 1h followed by solvent rinse

Cu	O	N	C	S
7.9	16.5	3.9	71.1	0.7

along with the molar ratios of each product structure as determined by ^{13}C-NMR. As can be seen in Fig. 2, at room temperature the episulfide homopolymerization and the episulfide–epoxy reaction increase as compared to 100°C curing. This trend is probably due to the fact that the reaction rate of epoxy–amine at room temperature is relatively slower and, therefore, the S^- formed by the episulfide–amine reaction is available to attack the episulfide and epoxy groups.

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

The molar ratios of each structure in the remaining solution after the dip, as determined by ^{13}C-NMR are shown in Table 1. The S^-epoxy reaction tends to increase in the presence of copper. The molar ratio in the solution after reaction, by ^{13}C-NMR, also indicated that the sulfur of the episulfide ring reacts with copper or is adsorbed on copper, leaving the matrix near the copper interface richer in epoxy structure. This ^{13}C-NMR result is consistent with the XPS results. Table 2 shows the at % of each element on the rinsed copper plate immersed in the epoxy–episulfide at 100°C for 1 h.

Sulfur and nitrogen are present on the copper surface. Fig. 3 shows the S 2p spectra of the detected sulfur. The binding energy of S 2P spectra is 162.8 eV, which is probably due to a Cu–S–C bond [23]. Therefore, the episulfide and/or S^- react with copper to form covalent bonding. However, a larger amount of nitrogen (3.9%) is

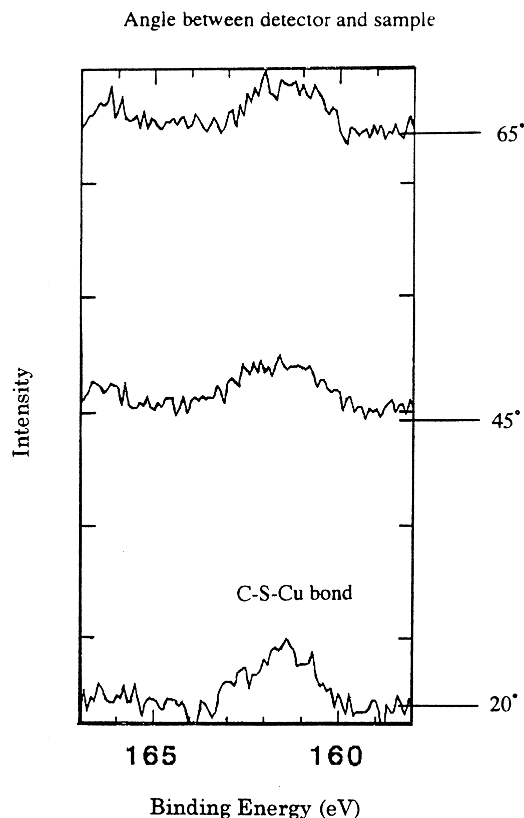


Fig. 3. S 2p spectra from a copper plate immersed in EPOMO(1)/EPIMO(1)/DBA(2) (molar ratio) at 100°C for 1 h, followed by a solvent rinse.

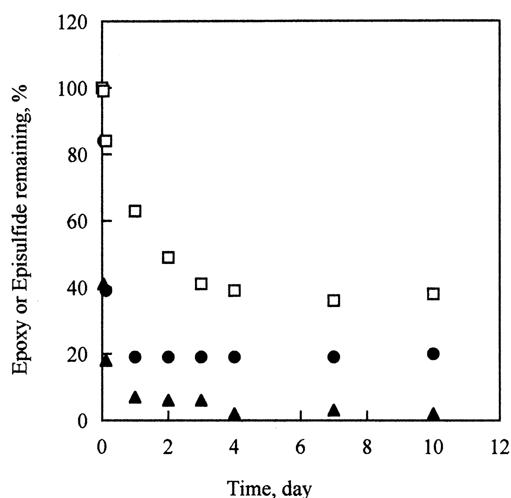
found on the copper surface relative to the sulfur (0.7%). This is probably due to the fact that the amine is adsorbed on the copper surface before the episulfide ring opens.

As a conclusion, the proposed reaction mechanism of epoxy/episulfide with copper system is shown in Fig. 4; some amine is adsorbed on copper before episulfide rings are opened. The amine-adsorbed copper acts as the episulfide homopolymerization and S^-– epoxy reaction in the interphase. Simultaneously, episulfides react with amine in bulk to form S^-. The S^- is reactive with the epoxides and the episulfides. The S^- and/or the episulfide also reacts with copper, however, the reactions are somewhat retarded by the adsorbed amine on the copper surface. Especially at room temperature, the catalytic effect of copper on episulfide homopolymerization is emphasized, therefore, the episulfide is rich in the interphase region as compared to the bulk.

3.2. *Effect of copper on Tg (actual resin system)*

In order to compare the reaction between the model and actual systems, the actual systems of the epoxy/episulfide and the standard epoxy were analyzed by FT–IR. The percent epoxy or episulfide groups

Fig. 4. Proposed reaction mechanism of epoxy–episulfide-amine with copper system by ^{13}C-NMR, GPC, and XPS.



□ Epoxy in Epon828(1wt)/V-40(1wt)

● Epoxy in Epon828(1wt)/Episulfide828(1wt)/V-40(1wt)

▲ Episulfide in Epon828(1wt)/Episulfide828(1wt)/V-40(1wt)

Fig. 5. Percent epoxy or episulfide groups remaining in Epon 828(1 wt)/V-40(1 wt) and Epon 828(1 wt)/Episulfide828(1 wt)/V-40(1 wt) at room temperature as a function of time.

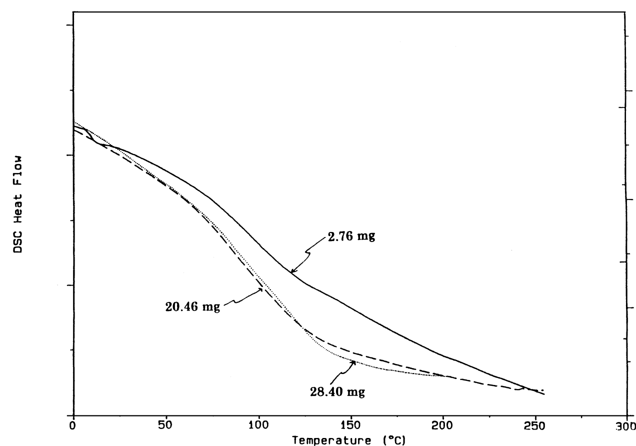
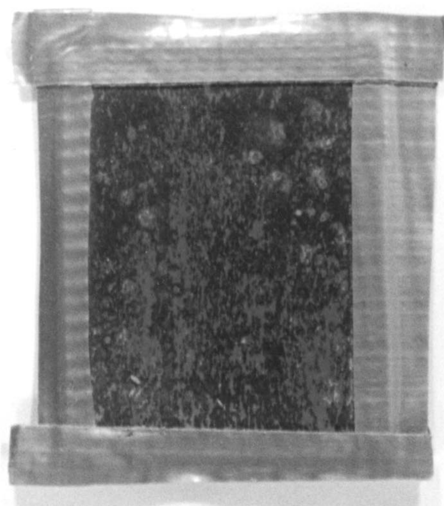


Fig. 6. DSC curves for different amounts of Epon828(1wt)/Episulfide828(0.5 wt)/V-40(1 wt) resins cured at room temperature for 10 days in a Cu pan.

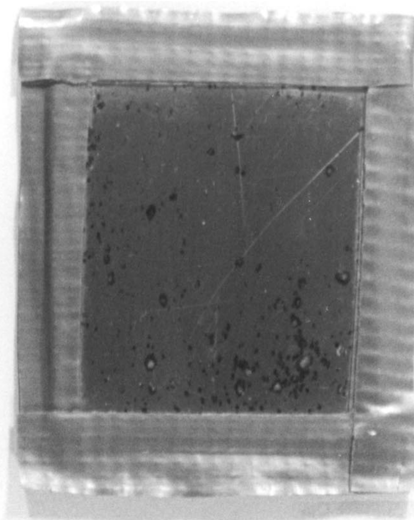
remaining in the actual epoxy/episulfide and standard epoxy at room temperature as a function of time is shown in Fig. 5. The epoxy and the episulfide in the epoxy/episulfide system show much faster ring opening

than the epoxy in the standard epoxy. After one or two days, the ring opening reactions in the epoxy/episulfide stop and nearly 20% of epoxy and 3% of episulfide remain. On the other hand, in the standard epoxy, the reaction stops after 4 days where nearly 40% of epoxy remains. According to the epoxy and epoxy/episulfide model compound studies by Bell and Ku [3], after 7 days nearly 25% of the epoxy and 2% of the episulfide remain in the epoxy/episulfide/amine chloroform solution (molar ratio; 1/1/1). These results reveal that the actual resin system in the epoxy/episulfide system is not very different from its model compound mixture, while the actual standard epoxy system has more unreacted epoxy remaining than its model system (almost all the epoxy in model system reacts at room temperature after 10 days, see Section 3.1).

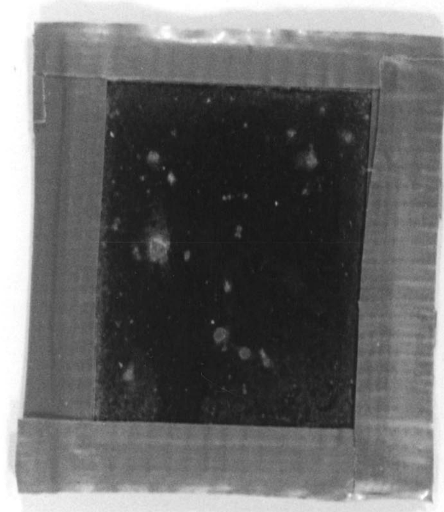
From the model compound study, episulfide homopolymer and episulfide–epoxy networks are probably formed near the copper surface. Bell and Ku [3] suggest that these networks show higher T_g than the conventional epoxy–amine network. In order to investigate whether the resin near copper shows a higher T_g than that in bulk, different amounts of Epon828®/Episulfide828/V-40® cured in a copper pan were analyzed by



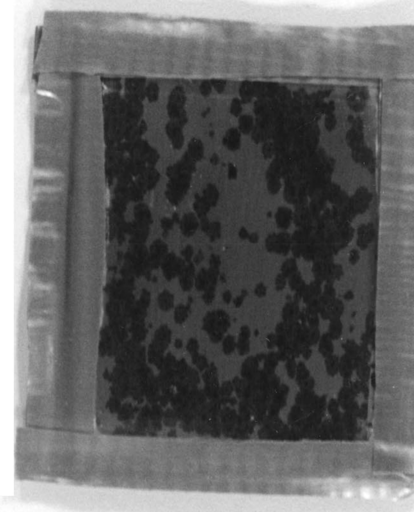
Epon828(1wt)/V-40(lwt)
100deg.C, 1 hr cure



Epon828(1wt)/Episulfide828(0.5wt)/V-40(1wt)
100deg.C, 1 hr cure



Epon828(1wt)/V-40(1wt)
Room temperature, 10 days cure



Epon828(1wt)/Episulfide828(0.5wt)/V-40(1wt)
Room temperature, 10 days cure

Fig. 7. Results of salt-spray test (53 days) of Epon828/V-40 and Epon828/Epon828/Episulfide828/V-40 system.

DSC (Fig. 6). Since a small amount of the sample has higher contact (higher surface/volume ratio) with copper, interphase properties are emphasized. As can be seen in Fig. 6, the small sample size shows higher T_g than the large amount of sample. The result is in good agreement with the model compound system.

3.3. Properties

3.3.1. Corrosion resistance of copper

The corrosion resistance of a copper substrate coated with Epon828®–Episulfide828-V-40® system for copper was measured by a standard salt spray test (ASTM B-117). Fig. 7 shows pictures of the epoxy/episulfide and the standard epoxy-coated copper after the salt spray test. While the exposure time was long (1270 h) and corrosion was observed on all samples, the epoxy/episulfide system shows much improved corrosion resistance on copper as compared to the standard epoxy system. Samples with higher curing temperature show better corrosion resistance. The reasons for better corrosion resistance of the epoxy/episulfide are probably due to the fact that the episulfide reacts with copper and that the resin near the copper surface contains more of the episulfide network than the bulk resin. The reason for better corrosion resistance of the sample with 100°C curing temperature is probably due to the fact that the reactions at room temperature are not complete. Another possible reason is that more solvent is trapped in the coating cured at room temperature. The coated copper samples were prepared by spin coat using cyclohexanone solution, therefore, more cyclohexanone (b.p. 155°C) is likely to remain in coatings cured at lower temperature.

Fig. 8 shows TGA curves of the epoxy/episulfide and the standard epoxy cured on copper plates. The room temperature cured samples show more weight loss than the 100°C cured ones; there is more solvent remaining in the coating.

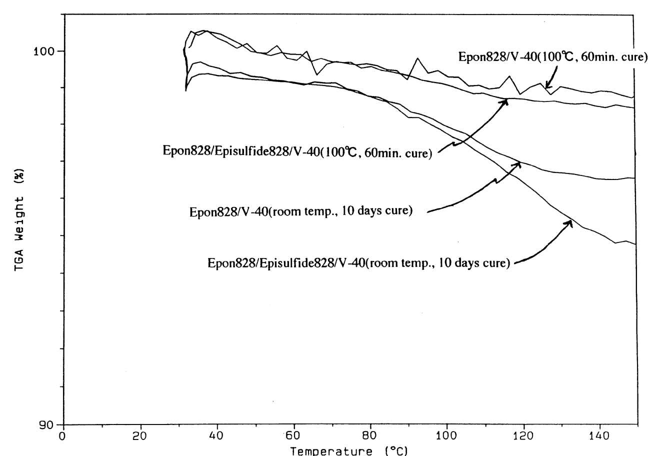


Fig. 8. TGA curves of Epon828/Episulfide828/V-40 and Epon828/Episulfide828/V-40 cured on cu plate.

3.3.2. Thermal expansion coefficient

Thermal expansion coefficients were measured by TMA. Fig. 9 shows the thermal expansion coefficient of the standard epoxy and the epoxy/episulfide system. The thermal expansion coefficient gradually decreases with the addition of the episulfide in 100°C cured samples. Room-temperature cured samples show more decrease with increasing episulfide up to 25 wt% episulfide addition, as compared to the 100°C cured samples, however, the thermal expansion coefficient increases again for additions of over 25 wt% episulfide. This is probably due to the structures and the extent of ring opening.

The thermal expansion coefficient of a polymer is approximately proportional to the van der Waals volume [24]. The van der Waals volume can be estimated by a group contribution approach. Table 3 shows examples of van der Waals volume contributions. From the van der Waals volume contribution, the C–S–C bond shows relatively low van der Waals volume contribution in the system. Room-temperature curing results in a greater

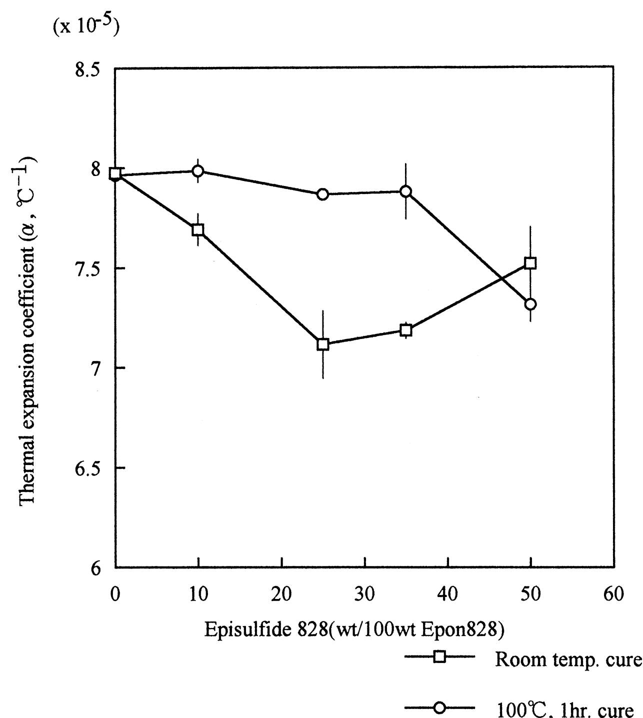


Fig. 9. Thermal expansion coefficient (α) of Epon 828(100 wt)/Episulfide828/V-40(100 wt).

Table 3
Examples of van der Waals volume [24] contribution ($cm^3\ mol^{-1}$)

$-CH_2-$	10.23
–CH(OH)–	14.82
–CONH–	19.56–18.1
–CH(CN)–	21.48
–S–	10.8

amount of episulfide network, which provides lower thermal expansion coefficient. However, the unreacted epoxy increases with the episulfide increase due to the fact that the T_g of the epoxy/episulfide system is nearly 100°C and for high episulfide content the cure is incomplete at room temperature.

4. Conclusions

A new epoxy/episulfide resin system has been studied for polyamide curing agent (V-40®). The epoxy/episulfide/V-40® system exhibits a better corrosion protection for copper, and a lower thermal expansion coefficient as compared with the standard epoxy system.

From model compound studies, episulfide–amine, S^-–epoxy, and epoxy–amine reactions and episulfide homopolymerization proceed in the epoxy/episulfide system. The curing reactions are changed by changing the curing temperature and/or the presence of copper; the episulfide homopolymerization and the S^-–epoxy reaction increase in the case of room temperature curing or in the presence of copper. ^{13}C-NMR and XPS analyses show that the episulfide and/or the S^- react with copper and that the amine either reacts with copper or is adsorbed on copper. From DSC measurements, the resin near the copper surface has higher T_g than the bulk resin due to the fact that the episulfide tends to polymerize near the copper surface.

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