

This article was downloaded by:

On: 22 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

A FT-IR Reflection-Absorption Spectroscopic Study of an Epoxy Coating on Imidazole-Treated Copper

Shuji Yoshida^a; Hatsuo Ishida^a

^a Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio, U.S.A.

To cite this Article Yoshida, Shuji and Ishida, Hatsuo(1984) 'A FT-IR Reflection-Absorption Spectroscopic Study of an Epoxy Coating on Imidazole-Treated Copper', *The Journal of Adhesion*, 16: 3, 217 – 232

To link to this Article: DOI: 10.1080/00218468408074917

URL: <http://dx.doi.org/10.1080/00218468408074917>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

A FT-IR Reflection-Absorption Spectroscopic Study of an Epoxy Coating on Imidazole-Treated Copper

SHUJI YOSHIDA and HATSUO ISHIDA

Department of Macromolecular Science, Case Western Reserve University Cleveland, Ohio 44106, U.S.A.

Abstract

The effects of undecylimidazole complex on copper and untreated copper surfaces on polymerization of an epoxy resin were studied using FT-IR reflection-absorption spectroscopy. Catalytic effects have been observed on the polymerization of epoxy resin by the copper/imidazole complex and the copper surface. The epoxy resin showed an appreciable amount of polymerization on the imidazole complex at 100°C on copper. The thickness of the epoxy coating was increased while the imidazole complex dissolved into the bulk resin above this temperature. However, only a small amount of epoxy resin remained on the copper at elevated temperature. This phenomenon was observed only with the imidazole treated copper surface. The epoxy resin without any added catalysts polymerized above 150°C on untreated copper surface. The coating thickness increased rapidly and reached the asymptotic value (2.0 nm) at 150°C. A thicker and random layer was formed at elevated temperatures. The coating thickness was estimated from a calibration curve.

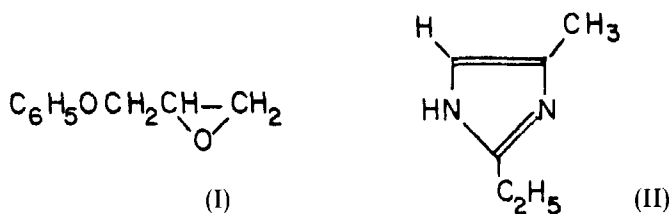
INTRODUCTION

Imidazole and its derivatives are of interest not only as curing catalysts of epoxy resin,¹⁻⁴ but also as corrosion inhibitors.⁵⁻⁹ By suitable combination of these chemical reactivities of imidazole toward epoxy

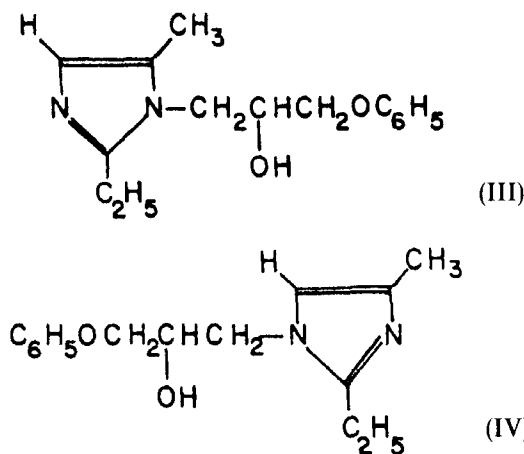
Presented at the Annual Meeting of The Adhesion Society, Savannah, GA, U.S.A., February 20-23, 1983.

resin and metal, it was thought that a new coupling agent could be designed showing both anti-corrosion effects for metal and adhesion promotion effects for epoxy coatings on metal. We have previously studied the molecular structure of undecylimidazole on copper surface using Fourier transform infrared reflection-absorption spectroscopy.⁸ In this paper we discuss the chemical reaction between an epoxy resin and undecylimidazole complex on copper.

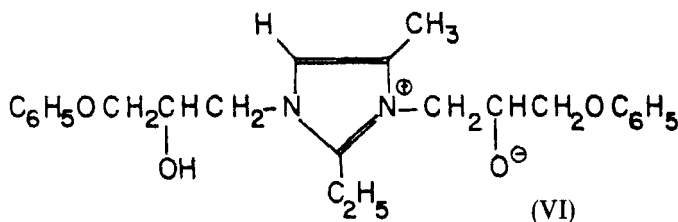
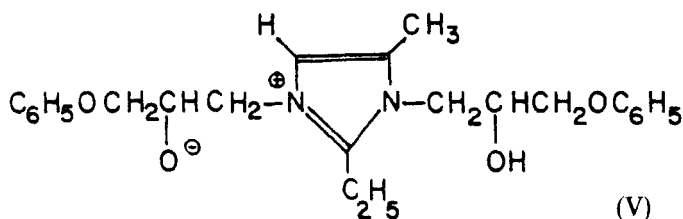
The chemical reactions between various imidazoles and epoxy resin have been studied by several authors.⁹⁻¹⁸ Farkas and Strohm⁹ studied the reaction between phenyl glycidyl ether (PGE) (I) and 2-ethyl-4-methylimidazole (2E4MZ) (II). They observed the disappearance of the



NH band of 2E4MZ at 3430 cm^{-1} in the first step of the reaction where no significant curing took place. Therefore, it was concluded that the true catalytic effects in the later step of polymerization was not due to the initial imidazole molecule but due to the product of its addition with PGE, such as (III).



Proton NMR showed two imidazole resonances of the reaction product of 1 mole of 2E4MZ and 1 mole of PGE. These bands are due to the two different protons in the reaction products whose molecular structures were suggested as in the isomers (III) and (IV). On the other hand, only one resonance was observed in the reaction product of 1 mole of 2E4MZ and 2 moles of PGE. Therefore, the true catalyst for the polymerization was concluded to have the following structures (V and VI).



However, Barton¹⁰ compared the reactivity of 1:1 (III or IV) and 1:2 (V or VI) products by differential scanning calorimetry (DSC) and found that there was no apparent difference in the reactivity of the two imidazole N-functions towards the epoxide group. Dearlove¹¹ studied the difference in reactivity between pyrrole and pyridine with the epoxide. No reactivity was observed for pyrrole even though it had NH structure. Slight reactivity was observed for pyridine. From these results, it was suggested that tertiary nitrogen of the imidazole was the active nucleophile rather than the secondary nitrogen. Kamon *et al.*¹⁵ obtained the same conclusion by differential thermal analysis (DTA) study.

Farkas⁹ described that 2E4MZ is incorporated into the epoxy molecule as the result of the reaction between the active hydrogen of

2E4MZ and the epoxy group. However, Ricciardi *et al.*¹⁸ indicated the possibility of α or β elimination of 2E4MZ from the chain at elevated temperatures. They observed the appearance of a new band at 1764 cm^{-1} and assigned it as the carbonyl of acetone possibly produced by β elimination.

Okazaki *et al.*¹⁶ studied the kinetics of 2E4MZ and PGE system. They observed that the polymerization took place in two steps, addition polymerization and ring opening polymerization. The activation energies for the two steps were 12.1 kcal/mol and 11.9 kcal/mol, respectively. The rates of polymerization are,

$$-d [\text{PGE}]/dt = k_2 [\text{PGE}] [\text{2E4MZ}] \quad (\text{step 1})$$

$$-d [\text{PGE}]/dt = k_r [\text{PGE}] [\text{cat}]^{1/2} \quad (\text{step 2})$$

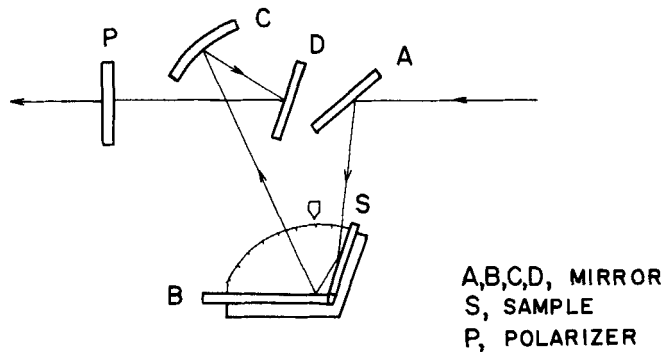
where [cat] is the concentration of the 2E4MZ and PGE product.

Few reports are available for epoxy polymerization catalyzed by imidazole complexes, and neither kinetics nor polymerization mechanisms have been studied. Hill and Kehr¹⁹ observed the catalytic effect of imidazole metal complexes for the polymerization of epoxy resin. A mixture of 10 g of diglycidylether of bis-phenol A and 7.7 g of dicyandiamide containing 0.031 and 1.00% of nickel (II) imidazolate had gel points of 5 min and 1 min at 150°C , respectively, indicating the existence of the catalytic effect of imidazole complexes.

EXPERIMENTAL

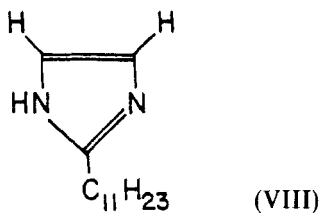
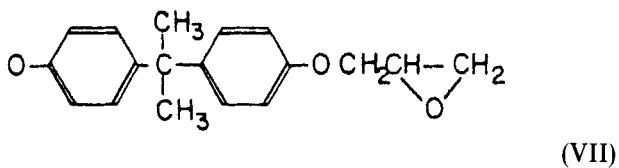
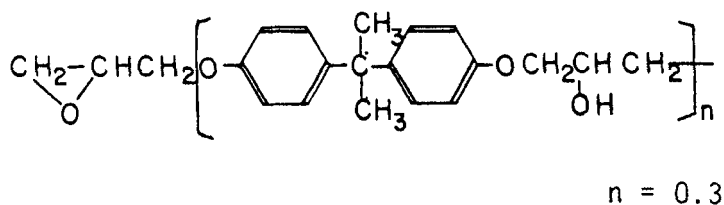
Copper substrates were polished and cleaned in a suitable manner as described previously.⁸ A Fourier transform infrared spectrophotometer (Digilab FTS-20E with nitrogen-cooled MCT detector) was used at a resolution of 4 cm^{-1} . The spectrometer was constantly purged with dry nitrogen gas in order to minimize the effect of moisture. The copper substrate after treatment was mounted in the reflection-absorption attachment (Figure 1) placed in the sample beam. The IR spectrum was obtained by digitally subtracting the spectrum of the reference copper substrate from the one with the surface coating. Reflectance spectra are shown in the absorbance mode with ΔA as the difference between maximum and minimum.

The epoxy resin (Epon 828) (VII) and undecylimidazole (C_{11}Z) (VIII) were kindly supplied by Shell Chemical Co. and Shikoku Chemical Co., respectively.



REFLECTION ABSORPTION ATTACHMENT

FIGURE 1 The optical layout of the reflection-absorption attachment.



RESULTS AND DISCUSSION

A. Calibration curves of the epoxy resin and $C_{1,1}Z$ on copper

An ethanol solution of the epoxy resin (0.300 g/l) was prepared and a known amount of solution was placed on copper substrates by a microsyringe. After evaporation of the solvent, surface species were studied by the reflection-absorption method. The observed reflection-absorption spectra are shown in Figure 2. The film thickness was calculated using the density of the epoxy resin to be 1.16 at 25°C assuming ideal uniformity. The transmission spectrum of the epoxy resin was obtained using a film on a KBr plate (Figure 3). The comparison between the spectra in Figure 2 and Figure 3 indicates no specific orientation of the epoxy molecule in this thickness range since both reflection and transmission spectra are nearly identical. The band

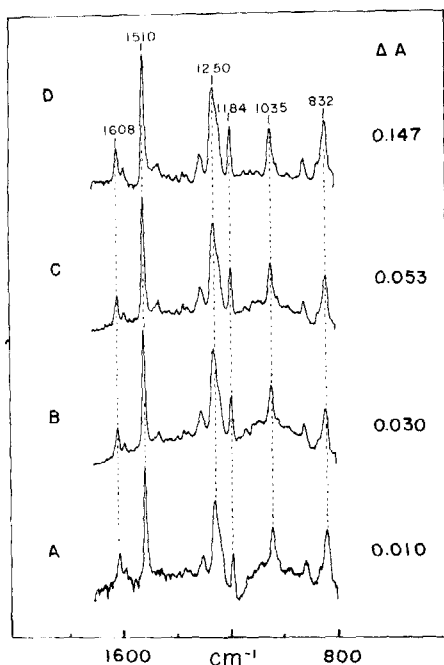


FIGURE 2 The reflection-absorption infrared spectra of the epoxy resin of various thicknesses on copper substrates: (A) 20 nm, (B) 40 nm, (C) 61 nm and (D) 202.0 nm.

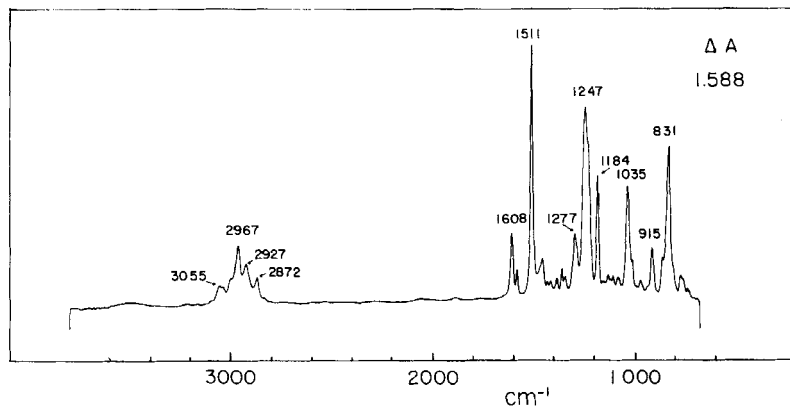


FIGURE 3 The transmission spectrum of the epoxy resin film on a KBr plate.

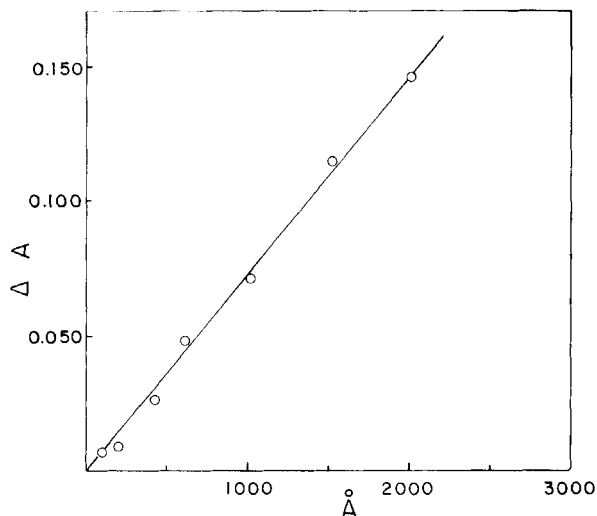


FIGURE 4 The calibration curve of the band height of the C=C stretching mode of the phenyl ring of the epoxy resin at 1510 cm^{-1} (ΔA) versus thickness of the epoxy film.

height of the C = C stretching mode of the phenyl ring at 1511 cm^{-1} was plotted versus thickness of the film as shown in Figure 4. A fairly good linearity was obtained up to 200 nm.

Boerio *et al.*²⁰ observed the reflection-absorption infrared spectrum of

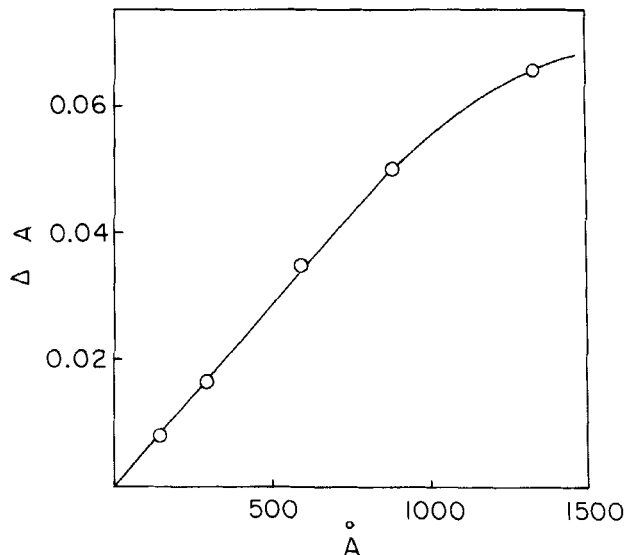


FIGURE 5 The calibration curve of the band height of the CH_2 antisymmetric stretching mode of undecylimidazole at 2925 cm^{-1} (A) versus thickness of the imidazole film.

the copper immersed in 0.02 M epoxy toluene solution for 30 min. Along with the ellipsometric result, they concluded that the epoxy was adsorbed with a vertical conformation with probably only a single oxirane oxygen in contact with the surface in the monolayer region (1.5 nm thick). However, no specific orientation was observed in the thicker films studied as seen in Figure 3. As the thickness of the film increases, the vertical orientation may have been perturbed. This kind of thickness effect on the orientation of surface species has also been observed by Debe.²¹ It is also possible that the difference in sample preparation method may have resulted in the different orientation.

The calibration curve of C_{11}Z on a copper substrate was obtained in the same manner as the epoxy resin and the result is shown in Figure 5. The band height at 2925 cm^{-1} due to the CH_2 antisymmetric stretching mode is plotted against the thickness of the film. Again a good linearity was obtained up to 80.0 nm.

A quantitative study is possible in reflection-absorption spectroscopy providing that the orientation of the molecule is unchanged as a function of thickness. Only the change in dipole moment perpendicular to the metal surface can be observed by this method.²²⁻²⁴ If another

independent method is applied for the thickness measurement, one can evaluate the relative degree of orientation of the surface film. Beyond a certain thickness, the intensity begins to show nonlinearity with thickness and the distortion in the band contour begins to show.²⁵⁻²⁷

The orientation of polymerized epoxy resin and undecylimidazole complex on copper are random. Therefore, the calibration curves can be used to estimate the thickness of the film formed on the copper substrate. The density change due to polymerization and complex formation were not considered in our study.

B. Polymerization of the epoxy resin on the imidazole treated copper

A $C_{11}Z$ film with thickness about 70.0 nm was placed on a copper substrate. After heat treatment at 80°C for 5 min., it was immersed in the epoxy resin and heated at various temperatures for 15 min. Then the copper substrate was washed by hot ethanol repeatedly. The reflection-absorption spectra obtained for the imidazole/copper system immersed in the epoxy bath at 60, 100 and 150°C are shown as spectra A, B and C in Figure 6, respectively. In Figure 6-A, only undecylimidazole copper complex is observed. In Figure 6-B, the characteristic C=C stretching mode at 1510 cm^{-1} of the epoxy resin began to show. The relative intensity of the epoxy resin increased at a higher temperature (150°C) in Figure 6.

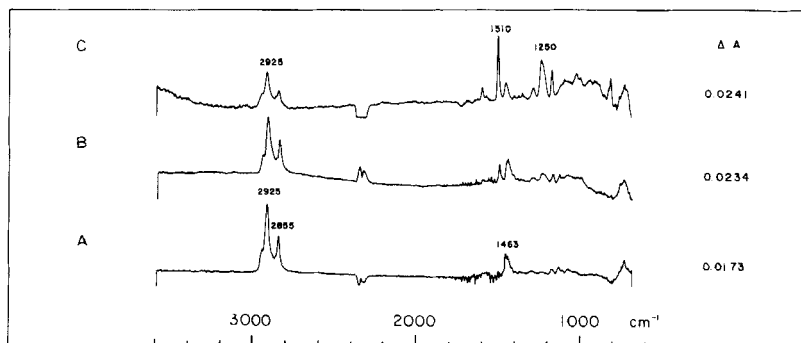


FIGURE 6 The reflection-absorption infrared spectra of undecylimidazole and the epoxy resin on a copper substrate after heat treatment in the initial epoxy resin for 5 min. at: (A) 60°C, (B) 100°C, and (C) 150°C.

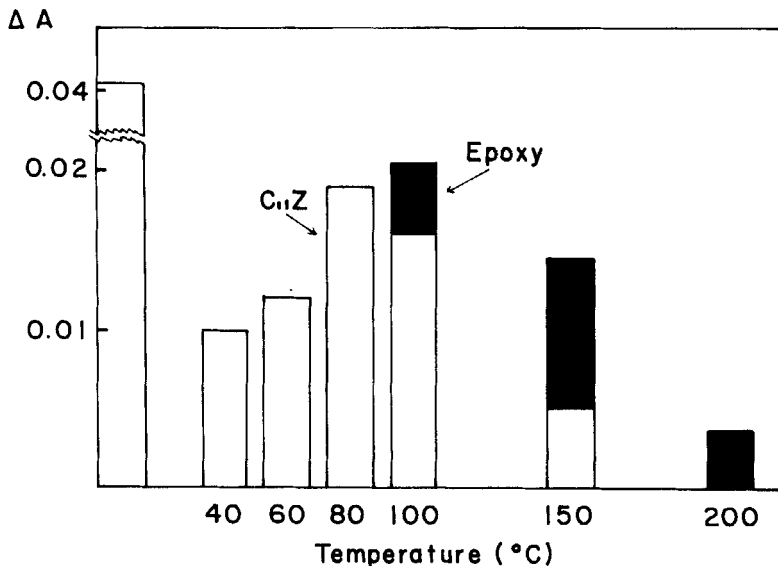


FIGURE 7 Absorbance of the band at 1510 cm^{-1} of the epoxy resin (black bar) and the band at 2925 cm^{-1} of the undecylimidazole (white bar) versus heat treatment temperature.

The amount of each component can be obtained by digitally subtracting the pure component from the reflection spectrum. The intensity of the bands at 1510 cm^{-1} and 2925 cm^{-1} are plotted versus the heat treatment temperature for the epoxy resin and $C_{11}Z$ complex, respectively (Figure 7). The amount of the imidazole initially placed on the copper substrate is shown by the white bar on the left in Figure 7. There are several interesting aspects observed in this figure. Upon heat treatment at 40°C in the epoxy bath, only $1/4$ of the $C_{11}Z$ complex was observed after washing. More $C_{11}Z$ remained on the surface as the temperature was increased to 80°C . The increase of the residual $C_{11}Z$ complex is possibly due to the hardening of the complex by the heat treatment, thus reducing the solubility in the epoxy. At 100°C , the polymerized epoxy resin initiated by the imidazole complex began to appear on the surface. At 150°C , the amount of polymerized epoxy resin further increased as $C_{11}Z$ complex decreased, indicating the progress of the polymerization. However, only a smaller amount of epoxy film was observed at 200°C whereas the imidazole complex is no longer existent. This is because the imidazole complex was consumed by the chemical

reaction with epoxy resin and the polymerized epoxy resin on the copper surface diffused into the bulk resin. Following the complete dissolution of the complex, the epoxy resin polymerized on the copper surface without imidazole.

This result indicates that undecylimidazole copper complex can initiate the polymerization of the epoxy resin. However, the reaction mechanism is not yet well understood. A question arises as to whether the complex itself can initiate the polymerization or whether it is necessary to reduce the complex to the original form, Cu and $C_{11}Z$, in order to initiate the polymerization. Although $C_{11}Z$ reacts both with the metal surface and the resin, the chemical reaction with the epoxy resin depends on the curing temperature and time as well as the pretreatment conditions of the imidazole on copper before the reaction with epoxy resin. The residual amounts of $C_{11}Z$ and polymerized epoxy resin vary depending on heat treatment conditions which influence the physical properties of the interface.

C. Polymerization of the epoxy resin on untreated copper surface

In order to understand the polymerization of the epoxy resin without $C_{11}Z$ on the copper surface at 200°C, untreated copper substrates were kept in the epoxy resin bath at elevated temperatures. The surface species were observed after washing by hot ethanol repeatedly. Spectra obtained after immersion in the epoxy resin at 150°C for 2, 10, 30, 60 and 120 min. are shown in Figure 8 as spectra A, B, C, D, and E, respectively. Very little amount of polymerized epoxy resin was observed on the copper surface. The noise level achieved by the employed conditions was ± 0.0002 in absorbance unit around 1500 cm^{-1} whereas the ΔA of the observed spectra range up to 0.002 indicating a very thin film.

At temperatures lower than 150°C, no surface species was observed after immersion for 30 min. The intensity of the phenyl mode of the epoxy resin at 1510 cm^{-1} is plotted *versus* the heat treatment time at 150°C in Figure 9. If the orientation is assumed to be random, the band height at 0.001 absorbance units corresponds to 1.5 nm in thickness. The epoxy band at 915 cm^{-1} was not observed, indicating the polymerization of epoxy resin on copper. The coating thickness increased rapidly during the initial heat treatment, but reached the asymptotic value at longer treatment time.

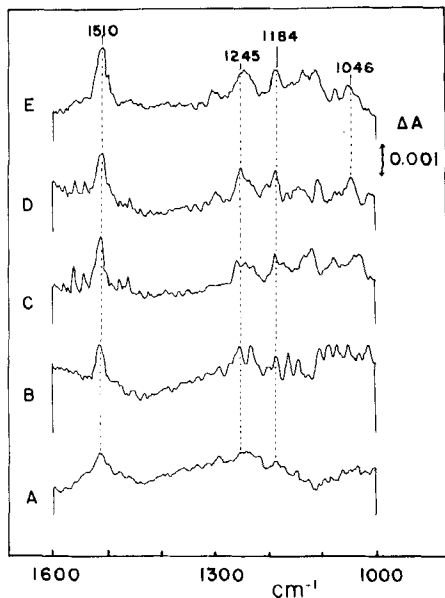


FIGURE 8 The reflection-absorption infrared spectra of the polymerized epoxy resin on copper surface after immersion in the initial epoxy resin at 150°C for: (A) 2 min., (B) 10 min., (C) 30 min., (D) 60 min., and (E) 120 min.

ΔA

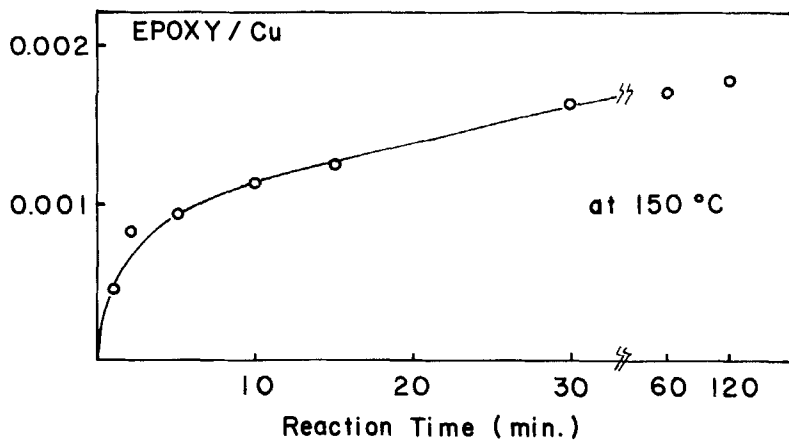


FIGURE 9 Intensity of the C=C band of the epoxy resin at 1510 cm^{-1} (A) versus the heat treatment time at 150°C.

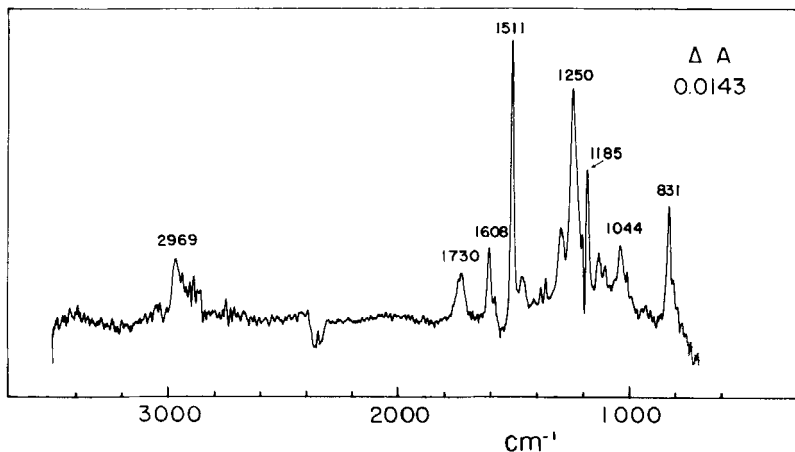


FIGURE 10 The reflection-absorption spectrum of the polymerized epoxy resin on copper surface after immersion in the epoxy resin at 200°C for 1 hr.

Higher temperatures yielded thicker epoxy films on the copper. In Figure 10 a reflection-absorption spectrum is shown for the copper mirror immersed in the epoxy resin at 200°C for 60 min. No epoxide band was observed at 915 cm^{-1} , indicating the existence of the polymerized epoxy resin on the copper surface. The region of 1150–1050 cm^{-1} was intensified compared to the uncured resin as shown in Figure 3 due to the C-O-C stretching mode which results from the epoxy ring opening reaction. The relative intensity of the antisymmetric and symmetric vibration modes is a good indicator for the orientation of a molecule.⁸ The ratio between the in-plane and out-of-plane vibrations similarly provides useful information because the dipole moment of these two vibrational modes are perpendicular to each other and the reflection-absorption method detects only the dipole moment change normal to the metal surface. As a reference for the random orientation of epoxy resin on copper, the transmission spectrum of the polymerized epoxy resin cured with 5% by weight C_{11}Z at 80°C for three hours is shown in Figure 11. Spectra A, B, and C in Figure 11 correspond to the epoxy resin before the polymerization, after the polymerization and the difference spectrum ($C = B - A$), respectively. By comparing Figures 10 and 11, the relative intensity of the C-O-C antisymmetric stretching mode at 1247 cm^{-1} and the symmetric stretching mode at 1035 cm^{-1} , and the C-H in-plane deformation mode at 1184 cm^{-1} and the out-of-

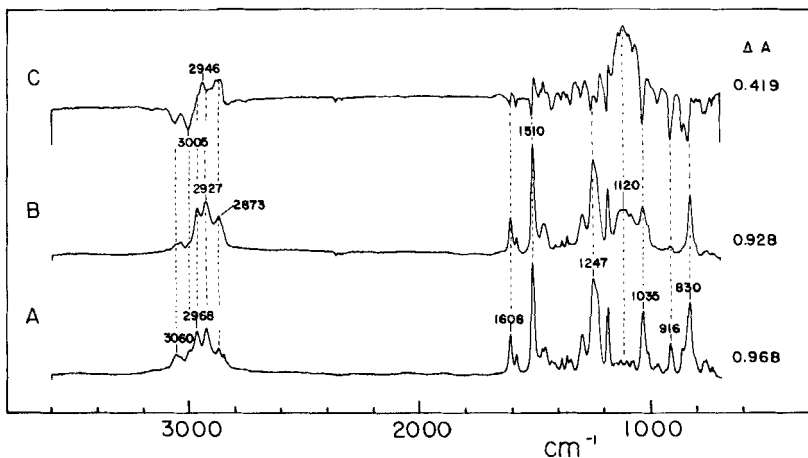


FIGURE 11 The transmission spectrum of the polymerized epoxy resin cured by undecylimidazole at 5% by weight. (A) before the polymerization, (B) after the polymerization at 80°C for 3 hr., and (C) the difference spectrum ($C = B - A$).

plane deformation mode at 830 cm^{-1} are quite similar to each other. Therefore, the orientation of the epoxy resin polymerized on the copper surface is considered to be random at this thickness, approximately 20.0 nm based on the calibration curve shown in Figure 10. Metal oxide or metal hydroxide is known as an anionic catalyst for the polymerization of ethylene and propylene oxide.²⁸⁻³⁰ However, the detailed reaction mechanism is not known at the present time.

It is interesting to notice the appearance of a new band at 1730 cm^{-1} in Figure 10 which is possibly due to the carbonyl group. Byrne *et al.*³⁰ observed new bands in the carbonyl region during the model study of amine-cured epoxy resin. They assigned the band at 1760 cm^{-1} as the carbonyl of an oxazolidone formed from 3-(*p*-chlorophenyl)-1, and 1-dimethyl-urea. As mentioned already, Ricciardi *et al.*¹⁸ assigned the band at 1764 cm^{-1} to the $\text{C}=\text{O}$ of the ketone produced by the reaction of 2E4MZ and trichloromethylethylene oxide or PGE. They suggested that this was due to the elimination at elevated temperatures.

The adhesion property of the coating may be significantly influenced by this polymerized epoxy coating on the metal surface. Tanaka *et al.*³² observed a rapid increase in shear strength of an adhesive joint by the heat treatment of a steel plate in uncatalyzed epoxy resin bath before placing adhesives on the surface. They immersed steel test pieces in

numbers of epoxy resins at various heating conditions with the variation of time and temperature. After immersion, the metal coupons were cleaned in an ultrasonic 1,1,1-trichloroethane bath. The shear strength began to increase by the heat treatment at 120°C for 30 min. and showed the maximum value around 200–250°C, where the shear strength was increased by more than 100%. Above 150°C, this effect was obtained by the heat treatment for only 2 min. and further increase in shear strength was not observed by longer heat treatment. This may be related to the fact that the coating thickness is a function of temperature but not a strong function of time except for the initial build-up. They reported that this effect was obtained not only on steel but also on other metals. Our molecular observation showed in Figures 8 and 10 clearly indicates the polymerization of the epoxy resin on the copper surface. It is likely that the rapid increase in the shear strength corresponds to the build-up of the polymerized epoxy resin of more than 2.0 nm in thickness.

CONCLUSIONS

The chemical reaction between $C_{11}Z$ on a copper substrate and an epoxy resin was studied using FT-IR reflection-absorption spectroscopy. Imidazole/copper complex formed on the substrate dissolved in an epoxy bath at low temperatures where only a small amount of residual imidazole was observed. The residual amount of the imidazole increased as the temperature of the epoxy resin increased due to the hardening effect of the imidazole complex. The polymerized epoxy resin can be observed at and above 100°C. The thickness of the epoxy film increased and the $C_{11}Z$ complex again decreased as the temperature increased. Only a small amount of the epoxy resin was observed at 200°C while no imidazole complex remained on the surface. Following the complete dissolution of the complex, the epoxy resin polymerized on the copper surface.

No epoxy film was observed until 150°C when the copper substrate was not treated by the imidazole. The coating thickness increased rapidly during the initial heat treatment but reached the asymptotic value of 2.0 nm at a long treatment time at 150°C. A thicker polymerized epoxy layer of thickness 20.0 nm was observed at 200°C. The orientation of the epoxy resin on the copper substrate was found to be random under the conditions employed. A new band at 1730 cm^{-1} possibly due

to the carbonyl was observed. The thickness of the epoxy and imidazole layers were estimated by calibration curves. The existence of a very thin layer of the polymerized epoxy resin on the metal surface has been suggested to give a significant influence on the mechanical properties of an adhesive coating.

References

1. H. Kakiuchi, *Epoxy Resin* (Shokodo, Tokyo, 1980), p. 198.
2. H. Lee and K. Neville, *Handbook of Epoxy Resins* (McGraw-Hill, New York, 1957), p. 159.
3. Shell Chemicals, Technical Bulletin SC-60-3026 and 2029.
4. Shikoku Chemicals Technical Report "Curezols"™.
5. C. Glandt, and J. K. Gillham, *Polym. Preprint, ACS Div. Polym. Chem.*, **16**, 694 (1975).
6. N. K. Patel, J. Franko, and I. S. Patel, *J. Indian Chem. Soc.* **54**, 815 (1977).
7. G. N. Ekilik, V. P. Grigor'ev, and V. V. Ekilik, *Zashch. Met.* **14**, 357 (1978).
8. S. Yoshida, and H. Ishida, *J. Chem. Phys.*, **78**, 6960 (1983).
9. A. Farkas, and P. F. Strohm, *J. Appl. Polym. Sci.* **12**, 159 (1968).
10. T. J. Dearlove, *J. Appl. Polym. Sci.* **14**, 1615 (1970).
11. T. J. Dearlove, HDL-TR-1551, "Epoxy Curing Agents, I. Imidazoles", National Technical Information Service, Springfield, VA, (1971).
12. J. M. Barton, and P. M. Sherpherd, *Die Makromol. Chem.* **176**, 919 (1975).
13. F. X. Ventrice, *Mod. Plastics* **45**, 20 (1967).
14. T. Kamon, *et al.*, *Shikizai Kyokaishi* **49**, 14 (1976).
15. *Ibid.* **50**, 2 (1977).
16. K. Okabashi, O. Hayashi, and K. Shibayama, *Kobunshi Ronbunshu* **34**, 497 (1977).
17. S. Jim, *et al.*, *Hsun* **2**, 150 (1981).
18. F. Ricciardi, W. A. Romanchick, and A. A. Griscavage, *J. Polym. Sci. Polym. Letters* **20**, 127 (1982).
19. B. K. Hill, and J. A. Kehr, *Ger. Offen.*, 2,300,489 (1973).
20. F. J. Boerio, and S. L. Chen, *Appl. Spectrosc.* **33**, 121 (1979).
21. M. K. Debe, *Application Surface Sci.* **14**, 1 (1982-83).
22. S. A. Francis, and A. H. Ellison, *J. Opt. Soc. Amer.* **49**, 131 (1959).
23. R. G. Greenler, *J. Chem. Phys.* **44**, 310 (1966).
24. R. G. Greenler, *J. Vac. Sci. Technol.* **12**, 1410 (1975).
25. R. G. Greenler, R. R. Rahm, and J. P. Schwartz, *J. Cat.* **23**, 42 (1971).
26. L.-H. Lee, Ed. *Characterization of Metal and Polymer Surfaces* (Academic Press, New York, 1977), p. 153.
27. T. Matsui, *Bunseki Kagaku* **29**, 565 (1980).
28. G. Odian, *Principles of Polymerization*, 2nd ed. (John Wiley, New York, 1981), p. 512.
29. T. Saegusa and S. Kobayashi, in *Progress in Polymer Science Japan*, Vol. 6, S. Onogi and K. Uno, Eds. (Halsted Press (Wiley), New York, 1973), pp. 107-151.
30. M. G. Rudenko and A. V. Topchiev, *Fr.* 2,044,134 (1971).
31. C. A. Bryne, *et al.*, *Polym. Composites* **1**, 71 (1980).
32. I. Tanaka, E. Yanagihara, and Y. Watanabe, *16th Meeting Adhesion Soc. of Japan*, 69 (1978).