

Cure Behavior of Very Thin Epoxy Resin Films on Steel

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Synopsis

FT-IR reflection absorption spectroscopy has been used to investigate the effect of a steel surface on epoxide cure. $\text{BF}_3 \cdot \text{MEA}$ catalyzed epoxy resin films ranging in thickness from 10 to 1000 nm are cast on low carbon automotive steel and subjected to a 100°C heat treatment. The resulting epoxide conversion and aliphatic ether formation are found to be sensitive functions of film thickness, with the thinnest films exhibiting the most conversion and ether formation. Uncatalyzed epoxy resin films (5–80 nm) were subjected to an identical analysis. Prior to receiving heat treatment, some of these very thin films (up to 10 nm) exhibit a strong aliphatic ether absorption. Upon exposing these samples to the heating regimen, a strong relationship between epoxide conversion and thickness is again apparent, with thinnest films experiencing the most conversion and ether formation.

INTRODUCTION

Regarded as the workhorse of thermosetting adhesives and protectives¹ for metals, epoxy resins are noted for strong adhesion, easy processability, and excellent chemical resistance. One of the primary roles played by epoxy-based coatings is to protect metallic surfaces from costly corrosion. Although these systems are quite prevalent, little is known about the chemical interactions that occur at the resin/substrate interface. Fourier transform infrared reflection absorption spectroscopy (FT-IR RAS) is a valuable experimental technique that can be used to study organic films on highly reflecting surfaces. Using the FT-IR RAS method, several authors have explored epoxide coatings on metal surfaces but few have utilized its potential to quantitatively characterize this interface.

Nguyen and Byrd have consistently demonstrated the applicability of this analytical method to the epoxy/steel system.^{2–5} Their studies concentrated mainly on absorbance frequency and intensity as functions of both film thickness and angle of incidence for amine-cured epoxies on low carbon steel. They have established a linearity between absorption intensity and film thickness up to 200 nm^{3,5} and have recently utilized RAS as a nondestructive means to characterize both the chemical basis of polymeric film degradation on steel and the ensuing failure of the epoxy/steel interface.^{2,4} Bulkin and

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Pearce have also used the technique to investigate the effect of a metal substrate on the thermal and oxidative degradation of epoxy resins.^{6,7} Although no mention is made of film thicknesses employed, they concluded that most of the observed oxidation is due to atmospheric effects and is independent of the substrate.^{6,7}

Yoshida and Ishida have studied the cure behavior of an epoxy resin on copper using the FT-IR RAS method and have also established a linearity between absorption intensity and film thickness up to 200 nm.⁸ In their study, which was concerned with the ability of a copper surface to affect the crosslinking of epoxy resins, they observed the polymerization of very thin films (20–200 nm) of uncatalyzed epoxy resin on a bare copper surface.⁸

In this study the unique abilities of FT-IR RAS have been used to investigate the cure rate of various thicknesses of epoxy resin films on steel. An effort has been made to determine if the metallic surface species affect resin cure kinetics and if so, how far this effect extends into the organic coating.

EXPERIMENTAL

Steel representative of that used in the automotive industry, 1008 Drawing Quality Special Killed Steel (provided by the G. M. Research Laboratory), was cut into 1 × 2 in. (×1/16th in.) rectangular samples. Starting with 320 grit paper and finishing with 3.0 μm diamond polish, the coarse textured rectangular metal plates were mechanically polished (on one side) to a mirror surface. The resulting ingots were immediately washed with methanol for 5 min. in an ultrasonic bath, rinsed liberally with fresh methanol, and washed for an additional 5 min. with chloroform. Cleaned plates were transferred to a vacuum desiccator and stored under reduced pressure for up to 2 h prior to film casting.

A representative epoxy resin (Shell Epon 828, Fig. 1) was selected and combined with BF₃ · MEA (Anchor 1115, Pacific Anchor Chemical Co.) at a ratio of 10 parts catalyst complex to 100 parts resin, based on weight of epoxy resin used. The resulting epoxy/catalyst system was immediately dissolved in chloroform and solution cast onto the polished steel plates with a microsyringe. Solution concentration necessary for a desired film thickness was calculated based on substrate surface area (1 × 2 in.) and an epoxy specific density of 1.16 (at 25°C). Films ranging from 5 to 1000 nm were cast and subjected to FT-IR reflection absorption spectroscopy (FT-IR RAS).

IR spectra were obtained on a Fourier transform infrared spectrophotometer (Bomem DA3.02) equipped with a narrow bandpass liquid nitrogen cooled MCT detector. The optical configuration presented in Figure 2 (Harrick Scientific Corp. RAS attachment) was used with a grazing angle of 75° and

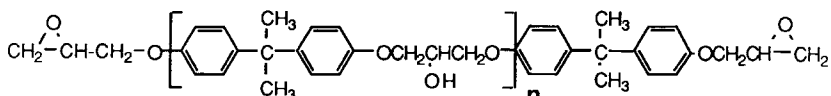


Fig. 1. Molecular diagram of Epon 828, a typical diglycidyl ether from epichlorohydrin and bisphenol A epoxy resin.

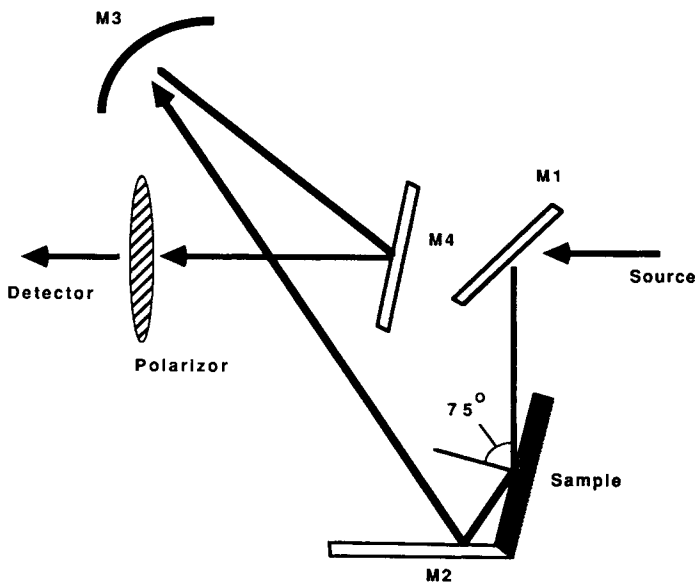


Fig. 2. The RAS optical configuration utilizing a 75° grazing angle and light polarized parallel to the sample plane of incidence. M1, M2, M3, and M4 indicate highly reflecting mirror surfaces.

light polarization parallel to the sample's plane of incidence. Raw interferograms, sample and reference, were obtained at a resolution of 4 cm^{-1} and are composed of 400 coadded and averaged spectral scans. Each individual spectrum is presented as a simple ratio between the raw spectra of a sample film on steel and that of an uncoated and un-heat-treated but identically polished steel substrate. Data was obtained shortly after sample preparation (1–2 h) and again after a 10-h 100°C heat treatment in nitrogen. Subsequent analysis is based on baseline corrected absorbance intensity.

RESULTS AND DISCUSSION

BF_3 -Catalyzed Epoxy Resin Films on Steel

In the present study, a Lewis acid type catalyst (BF_3) was employed because it is known to provide for the simple epoxide homopolymerization depicted in Fig. 3^{9–13} (a more detailed reaction mechanism can be found in the literature^{10–13}). Other epoxy curing systems give far more complex networks and thus result in a more complicated IR absorption analysis. One drawback to the use of BF_3 regardless of application is an inherent instability in the presence of moisture.^{9–13} Due to this extreme reactivity, it is generally complexed with mono ethyl amine (MEA) to achieve stability at room temperature.^{9–13} Commercially available and generally used in this form ($\text{BF}_3 \cdot \text{MEA}$), the catalyst complex initiates epoxy homopolymerization at temperatures above 80°C .⁹ Although some amines serve as epoxy crosslinking (curing) agents, the MEA component in this system is not incorporated in the resulting polymerized network.^{9–13}

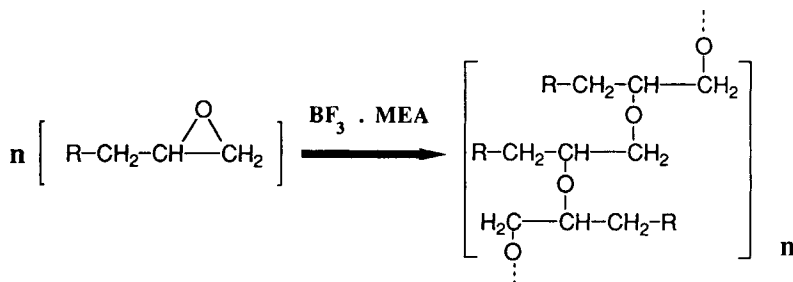


Fig. 3. Simplistic depiction of $\text{BF}_3 \cdot \text{MEA}$ -catalyzed epoxide homopolymerization.

Representative spectra obtained before sample heat-treatment are presented in Figure 4. A strong absorbance band at 1110 cm^{-1} , clearly visible in the 10 nm spectrum (A), rapidly disappears with increasing film thickness. Bands in this region are generally attributed to the C—O—C stretching mode characteristic of aliphatic ethers.¹⁴ Other prominent absorptions include those due to the epoxide cyclic ether at 915 cm^{-1} and the aromatic C=C stretching mode at 1510 cm^{-1} (used as an internal standard).^{1,8} The relative epoxy absorbance is significant because it can be used as a direct means to quantify oxirane polymerization. In the present data, epoxide absorption decreases with decreasing film thickness as plotted in Figure 5. Unfortunately, due to peak overlap and to the minute amount of catalyst present, absorption contribution from the $\text{BF}_3 \cdot \text{MEA}$ complex is difficult to resolve.

Spectra of heat-treated films on steel are presented in Figure 6 and a conversion based on the relative change in epoxide absorbance (before and

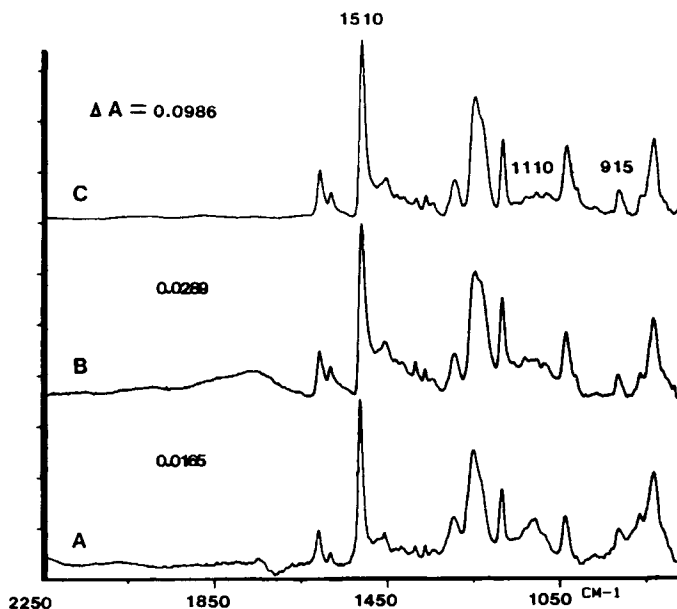


Fig. 4. RAS spectra of $\text{BF}_3 \cdot \text{MEA}$ -catalyzed epoxy resin films on steel prior to receiving heat-treatment: (A) 10 nm; (B) 20 nm; (C) 100 nm.

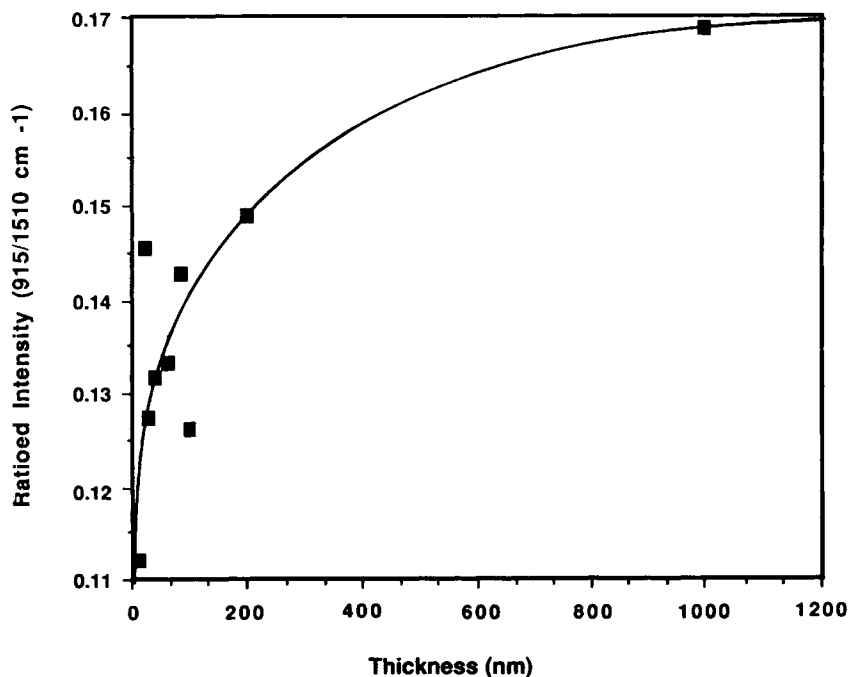


Fig. 5. Plot of normalized epoxide intensity ($915/1510\text{ cm}^{-1}$) vs. epoxy resin film thickness evident in the $\text{BF}_3 \cdot \text{MEA}$ -catalyzed films prior to receiving heat treatment.

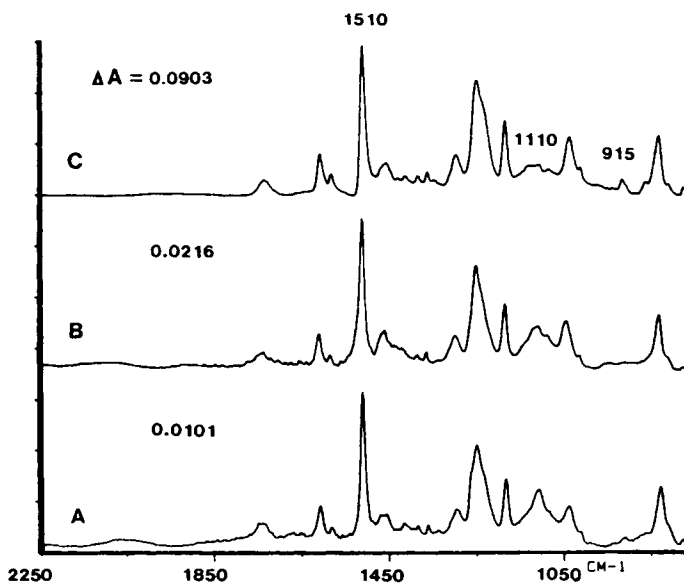


Fig. 6. RAS spectra of $\text{BF}_3 \cdot \text{MEA}$ catalyzed epoxy resin films on steel after a 10-h 100°C heat treatment in an N_2 atmosphere: (A) 10 nm; (B) 20 nm; (C) 100 nm.

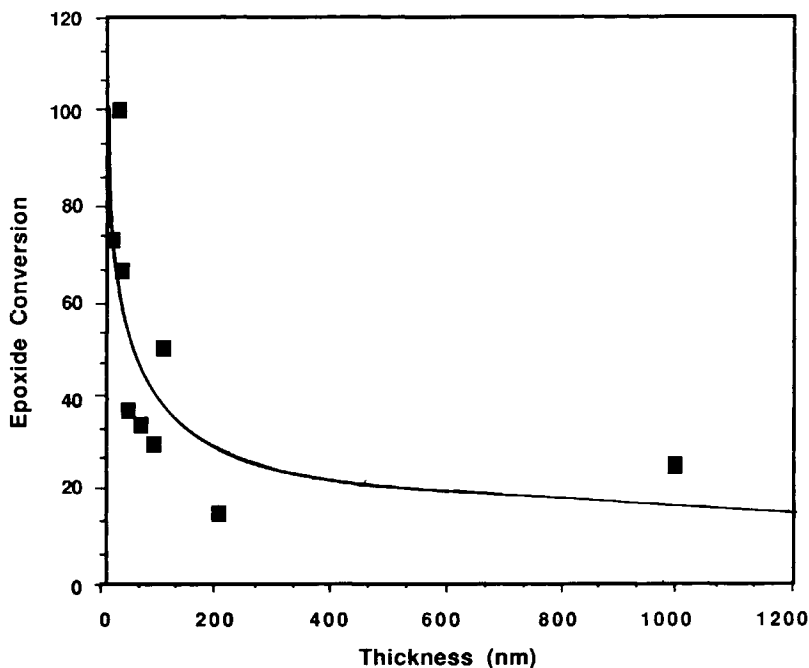


Fig. 7. Epoxide conversion vs. film thickness for the $\text{BF}_3 \cdot \text{MEA}$ catalyzed epoxy films on steel after exposure to a 10-h 100°C heat treatment in N_2 .

after heat treatment) was calculated. Resulting conversion vs. thickness data, seen in Figure 7, is characterized by a definite gradient in which conversion increases with decreasing film thickness, and asymptotes to a final value of 20–30%. The absorbance at 1110 cm^{-1} has been plotted (against thickness) in Figure 8 and it too increases with decreasing film thickness. This interesting conversion trend becomes more strikingly apparent when kinetic data is analyzed. Conversion at 100°C vs. time is presented in Figure 9 for representatives of the three epoxy regions in this system; interfacial (20 nm), intermediate (100 nm), and bulk (1000 nm). Conversion at 20 nm is relatively fast and complete while that at 100 nm is more than five times slower and at 1000 nm the conversion is both slow and incomplete.

The preceding data suggests that there is an alternate mechanism governing absorption intensity at 915 and 1110 cm^{-1} in the epoxy/steel interfacial region. This apparently surface related phenomenon has several possible explanations. The decrease in epoxide absorption may be due to a preferred molecular orientation. IR RAS is inherently more sensitive to functionalities which are aligned perpendicularly to the substrate surface. In this scenario, then, the 915 cm^{-1} absorption decreases for thinner films (relative to thicker ones) because the cyclic ether is oriented such that its C—O dipole moment is aligned parallel to the substrate surface in the interfacial region, as depicted in Figure 10. Consequently, a preferred molecular orientation at the epoxy/steel interface could provide for a decreased cyclic ether absorption in thin films relative to that obtained for the more randomly oriented (molecularly) thicker films. Although able to account for absorption behavior at 915

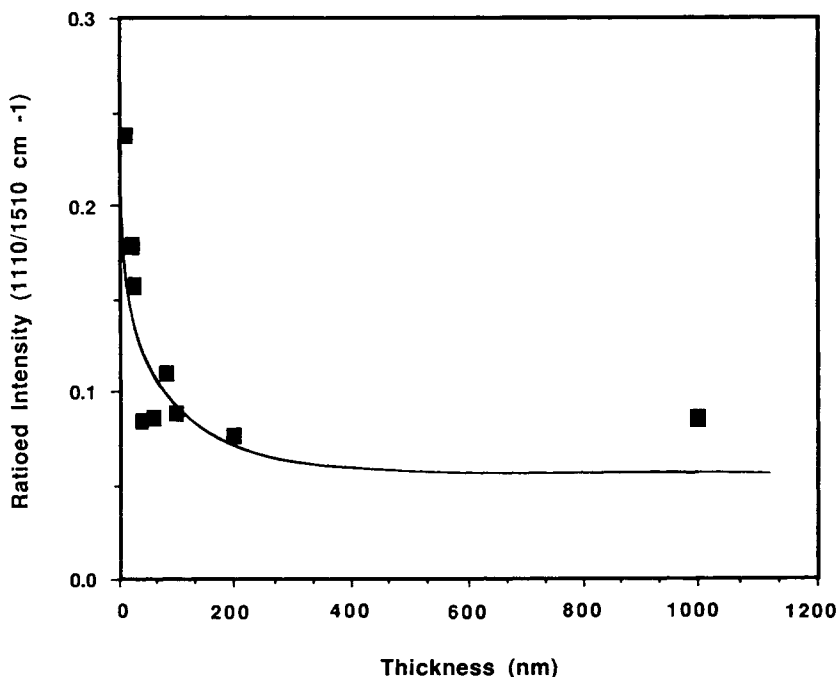


Fig. 8. Normalized aliphatic ether absorbance intensity ($1110/1510\text{ cm}^{-1}$) vs. film thickness for the $\text{BF}_3 \cdot \text{MEA}$ -catalyzed epoxy films on steel after exposure to a 10-h 100°C heat treatment in N_2 .

cm^{-1} , the orientation model has difficulty explaining that at 1110 cm^{-1} . Upon examining the epoxy resin used, it is apparent that there are no functionalities present in the unreacted resin that could give rise to an absorption band at this wavenumber. Thus, regardless of molecular orientation, there should be no absorption at 1110 cm^{-1} for virgin unreacted epoxy (resin). Therefore, the observed behavior is indicative of a chemical reaction. With the curing system ($\text{BF}_3 \cdot \text{MEA}$) in mind, the expected reaction is a BF_3 -catalyzed epoxy homopolymerization. Present IR absorption data correspond amazingly well to that obtained by Ito and Okahashi for cure of the bulk $\text{BF}_3 \cdot \text{MEA}$ catalyzed epoxy resin system.¹³ In their study, curing provided for a decrease in epoxide absorbance at 915 cm^{-1} and an absorption evolution at 1110 cm^{-1} . The latter absorption (1110 cm^{-1}) was assigned as the aliphatic ether resulting from $\text{BF}_3 \cdot \text{MEA}$ -catalyzed epoxide homopolymerization.¹³ In the context of the present data, this reaction mechanism (epoxide homopolymerization) would account for both the simultaneous decrease in absorbance at 915 cm^{-1} and the increase in that at 1110 cm^{-1} . Consequently, the IR absorption trends presented here (for thin epoxy resin films on steel) are interpreted as evidence of an epoxide homopolymerization gradient which is maximized at the steel surface.

The basis for this surface related cure phenomenon may involve a catalyst migration and subsequent epoxide homopolymerization. Migration of $\text{BF}_3 \cdot \text{MEA}$ from the bulk resin film to the steel surface (possibly during film forming) would account for both the low degree of epoxide conversion and

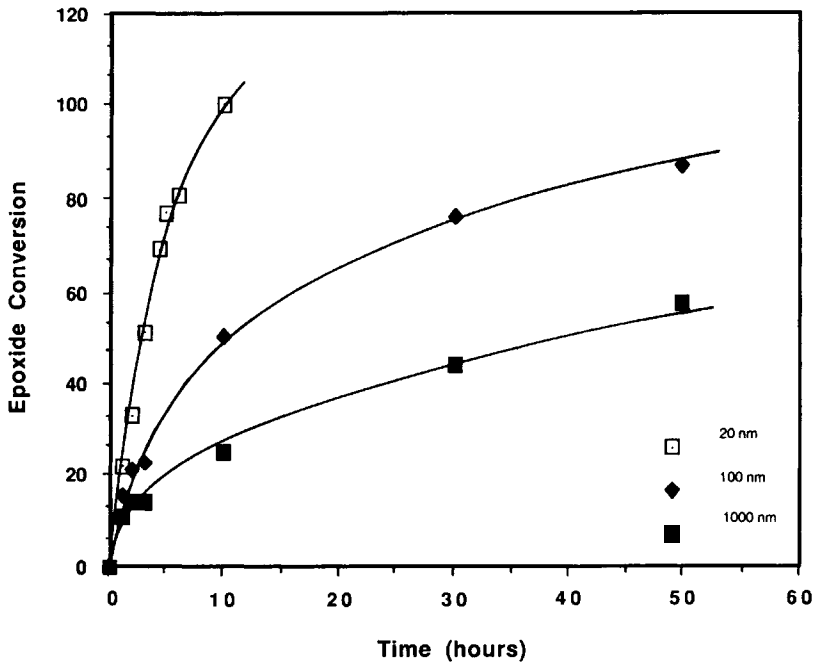


Fig. 9. Plot of epoxide conversion vs. time for $\text{BF}_3 \cdot \text{MEA}$ catalyzed epoxy films on steel of the following thicknesses: (A) 20 nm; (B) 100 nm; (C) 1000 nm.

aliphatic ether absorption apparent in the thicker films. One would expect such a system to be characterized by poor adhesive properties due to both catalyst-induced interference between epoxy and steel and to nonhomogeneity of the epoxy coating. Another possibility is that the absorption behavior is due to a steel surface facilitated cure. In other words, species present on the steel may chemically participate in the homopolymerization of epoxy resin.

Additionally, an absorption at 1740 cm^{-1} appears in the heat-treated samples and has previously been assigned as a carbonyl.⁸ This band was

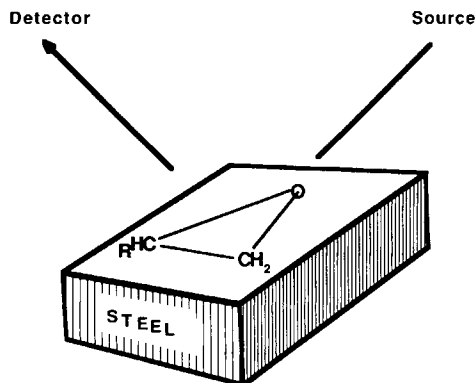


Fig. 10. Epoxide interfacial orientation which would provide for a decreased absorption intensity relative to that obtained for a randomly oriented sample.

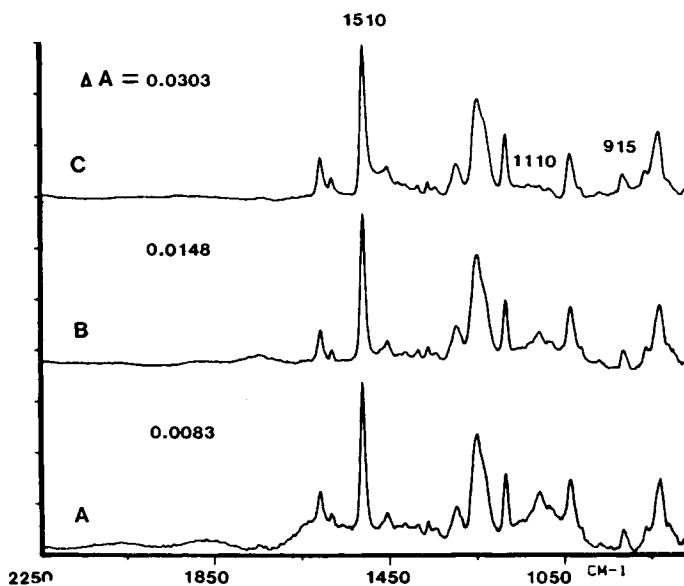


Fig. 11. RAS spectra of uncatalyzed epoxy resin films on steel prior to receiving heat-treatment: (A) 5 nm; (B) 10 nm; (C) 20 nm.

observed by Yoshida and Ishida⁸ and several others^{6,7} but has not been adequately explained. Bulkin and Pearce have attributed similar bands in the RAS spectra of epoxy films on metal to the isomerization of the epoxide group to an aldehyde and to the oxidative degradation of epoxy molecules.^{6,7} Unfortunately, they did not mention the film thicknesses employed, and it is therefore difficult to determine if the present absorption is related to their similar observation. In this work, all samples were heated under a nitrogen atmosphere in an attempt to limit oxidation. But the band appearance persists, suggesting that the isomerization mechanism is responsible.

Uncatalyzed Epoxy Resin Films on Steel

FT-IR RAS investigation of thin $\text{BF}_3 \cdot \text{MEA}$ catalyzed epoxy resin films on steel suggests that the metal's surface influences epoxide polymerization. In an attempt to determine if the surface actively participates in a chemical reaction mechanism or if it simply affects catalyst concentration, the interaction between uncatalyzed epoxy resin and steel has been investigated. Resin films of thicknesses varying from 5 to 80 nm were cast on steel and treated in a manner analogous to that for the $\text{BF}_3 \cdot \text{MEA}$ catalyzed coatings previously discussed.

Spectra taken of samples prior to receiving heat treatment offer some interesting results. An absorption band at 1110 cm^{-1} appears quite large close to the steel surface and disappears with increasing film thickness as seen in Figure 11. Because of its position and behavior, this band is believed to be indicative of the aliphatic ether responsible for a similar absorption (at 1110 cm^{-1}) present in the $\text{BF}_3 \cdot \text{MEA}$ catalyzed films, although the relative epoxide absorption remains unchanged within this thickness range, and thus appar-

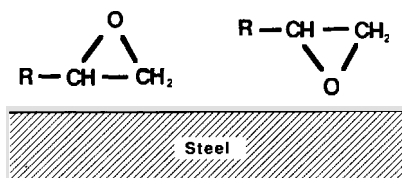


Fig. 12. Possible epoxide orientations which would provide for an enhanced absorption (in the RAS method) relative to that obtained for a randomly oriented sample.

ently unreacted. One explanation for the conflicting behavior is that there are two independent mechanisms controlling absorbance intensity. As before, the band at 1110 cm^{-1} is believed to indicate homopolymerization of epoxide to aliphatic ether. But, due to an orientation effect in which the oxirane ring is oriented as seen in Figure 12, epoxide absorbance is greatly enhanced. Together, epoxide polymerization coupled with an orientation enhancement of that (epoxide) remaining unreacted may resolve the conflict. The fact that this data contradicts that obtained for $\text{BF}_3 \cdot \text{MEA}$ catalyzed systems is indicative of the catalyst's effect on resin/steel interaction.

Spectra of heat-treated uncatalyzed (resin) films on steel, shown in Figure 13, exhibit equally interesting behavior. As for the catalyzed case, an epoxide relative conversion vs. film thickness profile has been calculated and is presented in Figure 14. The change in epoxide absorption ranges from approximately 100% at 5 nm to 25–30% at 80 nm. Similarly, the absorption at 1110

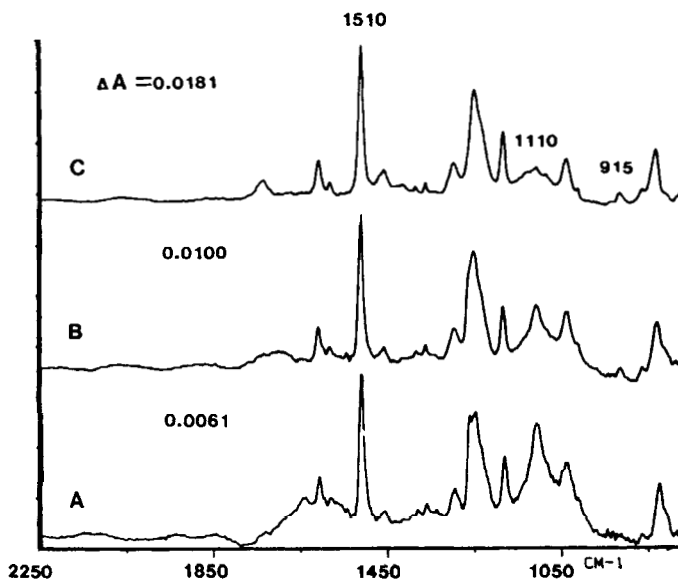


Fig. 13. RAS spectra of uncatalyzed epoxy resin films on steel after exposure to a 10-h 100°C heat treatment in N_2 : (A) 5 nm; (B) 10 nm; (C) 20 nm.

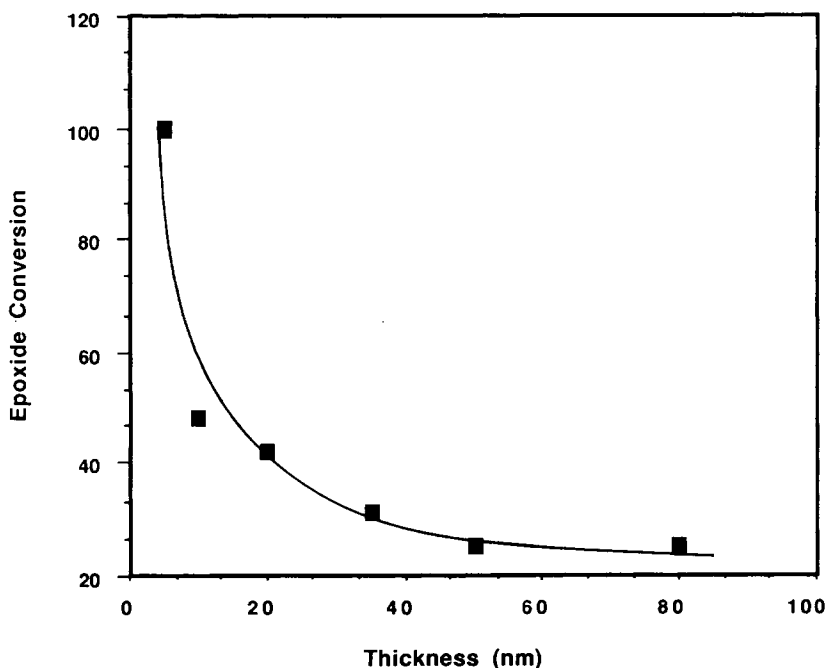


Fig. 14. Epoxide conversion vs. film thickness for uncatalyzed epoxy films on steel after exposure to a 10-h 100°C heat treatment in N_2 .

cm^{-1} behaves much as it did for the catalyzed films as seen in Figures 13 and 15.

Because spectra from the uncatalyzed system are characterized by absorption behavior very similar (if not identical) to that seen in the previously discussed $BF_3 \cdot MEA$ catalyzed systems, catalyst migration is ruled out as solely responsible for the observed trends. The present data strongly suggests that steel surface species are active chemical participants in the homopolymerization of epoxy resin. Additionally, the chemically active species are implicated as very effective catalysts that provide for the rapid room temperature cure evident in the 5 nm virgin and un-heat-treated epoxy resin film. Both metal oxides and hydroxides are known to catalyze epoxy polymerizations,^{1,15,16} but iron oxide catalysis has yet to be demonstrated and is difficult to substantiate at this time.

Behavior in the 5 nm film is unexpectedly exaggerated and brings to mind another possible contributor to the observed surface related phenomenon. When dealing with organic adhesives on metals, one must be aware of the postulated bonding interaction between metal surface species and the organic.¹ The expected chemical linkage between epoxy resin and a hydroxylated metal surface is characterized by an ether linkage¹ and it is feasible that this functionality would produce an absorption in the 1110 cm^{-1} region.¹⁴ Due to the selection rule previously mentioned for IR RAS, the perpendicularly aligned (to the metal surface) functionality should show strongly relative to other absorption bands. Interestingly, the band at 1110 cm^{-1} is extremely exaggerated in the 5 nm film spectra. Although a definite possibility, an

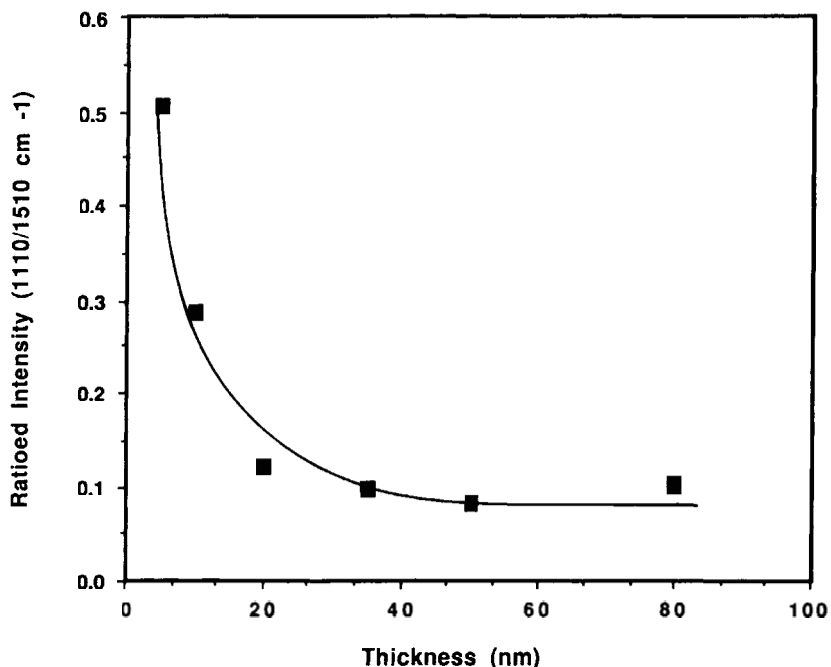


Fig. 15. Normalized aliphatic ether absorbance intensity ($1110/1510\text{ cm}^{-1}$) vs. film thickness for uncatalyzed epoxy resin films on steel after exposure to a 10-h 100°C heat treatment in N_2 .

organic-metal linkage is difficult to verify with the present data. Homopolymerization of epoxide is deemed most responsible for the observed IR absorption trends for two major reasons. Bulk data obtained by Ito and Okahashi¹³ substantiates this reaction mechanism. And it is more likely responsible for the ether absorption and epoxide conversion observed in films representing bulk properties ($> 100\text{ nm}$). For the case of epoxide homopolymerization, the unexpected absorption exaggeration evident in the 5 nm film can be explained as due to a preferred molecular orientation at the epoxy/steel interface, as depicted in Figure 16. Consequently, it is believed that the IR data presented

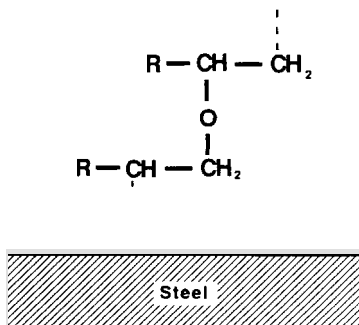


Fig. 16. Interfacial orientation of homopolymerized epoxy which would account for the unexpectedly exaggerated ether absorption intensity apparent in the 5 nm uncatalyzed epoxy resin film on steel.

here provide direct evidence of a steel-facilitated homopolymerization of the epoxide ring.

There exists physical evidence which supports a direct chemical interaction between virgin uncatalyzed epoxy resin and steel. Tanaka has reported an increased adhesive performance of steel lap joints that have been pretreated with thin layers of uncatalyzed epoxy resin.¹⁷ His data and that presented here are quite compatible in the following sense. A catalyst may interfere with epoxy/steel interaction (mentioned previously concerning the orientation of epoxide on steel), producing a weaker interface and thus decreased adhesion as was observed by Tanaka. The present data indicates that thin layers of uncatalyzed epoxy resin interact chemically with steel to homopolymerize at the metal surface. Subsequent coatings containing catalyst can then bond to the existing polymerized epoxy without interfering with the epoxy/steel interface.

CONCLUSIONS

The IR absorption behavior of various epoxy resin film thicknesses on steel has been investigated with FT-IR reflection absorption spectroscopy. Very thin (up to 10 nm) films of $\text{BF}_3 \cdot \text{MEA}$ catalyzed epoxy resin were found to expose behavior subsequently attributed to homopolymerization. Heat treatment of the samples provided for a cure gradient in which thin films cured much faster than thicker ones. A very high degree of conversion was demonstrated in the interfacial region (less than 25 nm), suggesting the existence of a steel surface related reaction mechanism.

In an attempt to determine if steel surface species chemically participate in epoxide homopolymerization or if they simply affect catalyst concentration, uncatalyzed epoxy resin films were applied to steel and subjected to an identical analysis. These films exposed absorption behavior almost identical to that observed for the catalyzed system. Consequently, it is believed that steel surface species are capable of catalyzing epoxide homopolymerization.

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