

THE STUDIES OF THE CURING OF AN EPOXY RESIN ON COPPER WIRE BY FTIR EXTERNAL REFLECTION SPECTROSCOPY*

XUE Gi(薛奇), LIU Shiyong(刘石英) and JIANG Shanggen(江善根)

(Department of Chemistry, Nanjing University, Nanjing)

ABSTRACT

The epoxy coating on copper wire has been studied by a modified sampling technique using Fourier transform infrared (FTIR) diffuse reflectance attachment. As the wire axis was parallel to the incident plane, a reflection spectrum of thin layer coating on a copper wire can be obtained. The study found that imidazole, especially the acetic acid treated imidazole, can be used as an effective curing catalyst of the epoxy resin on copper. This is the first report about the IR study of coatings on metal wires.

INTRODUCTION

Fourier transform infrared (FTIR) reflection absorption spectroscopy has been developed by Francis^[1] and Greenler^[2]. Also, the quantitative nature of this technique has been experimentally evaluated by McIntyre^[3] and Matsui et al.^[4]. When infrared radiation illuminated a metal surface, a node is formed on the metal surface or near the surface, and the incident and the reflected lights combine to form a standing wave. The amplitude of the standing wave increases with the increase of the incident angle towards maximum value at 88°^[2,5]. Boerio applied this technique to study the molecular structure of various compounds on iron and copper plates^[6,7]. Greenler examined his theory using 19 different metals^[8]. But all these external reflection experiments are effective only for the coatings on metal plates. The external reflection spectrum obtained from a metal wire or a fiber by using the reflection absorption attachment is extremely poor, because the reflective lights from the sample with cylindrical shape can not be effectively directed to the detector by a plane mirror^[8].

Diffuse reflectance FTIR spectroscopy has been developed originally for particulate samples dispersed in KBr powders. The light incidents upon a powdered surface will be reflected in all directions. The randomly reflected light is collected with ellipsoid mirrors and directed to the IR detector for analysis. We have now taken the advantage of the collection efficiency of the diffuse reflectance optics, and extended its use to in-situ study of an epoxy coating on a copper wire. The curing effects of imidazole for the coating of an epoxy resin on a copper wire have been observed by this technique.

EXPERIMENTAL

The metal wire coated with an epoxy resin was arranged in different ways in a diffuse reflectance attachment. Schematic diagrams of the parallel and vertical orientations of the wire axes

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with respect to the incident plane are shown in Fig. 1. A diagram of normal reflection absorption attachment is also drawn in the same figure for comparison.

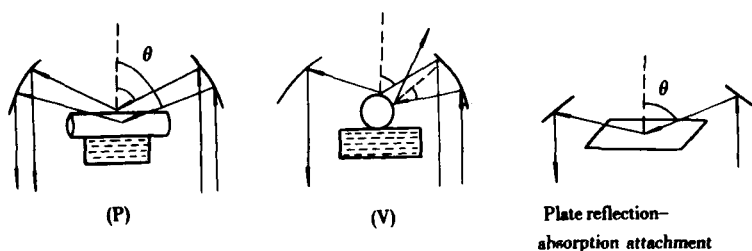


Fig.1 Schematic diagrams for external reflection experiments

(P) axis of the wire sample parallel to the incident plane;

(V) axis of the wire sample vertical to the incident plane.

All the external reflection spectra (R) were recorded by taking the ratio of the sample single beam reflection spectra against a potassium bromide single beam background spectrum.

A copper wire with 0.5mm in diameter was mechanically polished and was washed repeatedly by acetone, cyclohexane, and distilled water until a hydrophilic surface was obtained. It was immersed in 1% hydrochloric acid for one minute, repeatedly washed by distilled water, and finally dried in dry air. The imidazole which was used as curing catalyst of the epoxy resin, was dissolved in ethyl alcohol (1% by weight). The polished wire was immersed in the prepared solution for 5 minutes, and then withdrawn at a constant speed of inch / min from the solution using a motor drive. In another case, imidazole-acetic acid aqueous solution was prepared as follows. Equimolar solution of imidazole and acetic acid were mixed to make a salt. One gram of the salt was dissolved in 100 ml water. By adding acetic acid, the solution was made homogeneous, and the pH was set to 4.50. The copper wires were immersed in an epoxy bath at 90°C and withdrawn after 60 minutes, washed by hot ethyl alcohol, dried under vacuum. The spectra were taken by means of the technique mentioned above.

Spectra were recorded by a Nicolet 170sx FTIR spectrophotometer equipped with a MCT detector. A Harric Scientific Corporation reflectance cell was placed inside the spectrometer to collect reflection radiation. 100 scans were coadded at a resolution of 4 cm^{-1} throughout the range of $4000\text{--}700\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

The reflection spectrum of a polished copper wire which was arranged parallel to the incidence is shown as spectrum A in Fig. 2. Spectra B and C were obtained from the imidazole and epoxy resin coated copper wire. Spectrum B is due to the sample oriented parallel to incident radiation, while spectrum C is due to a vertical orientation (See the diagrams P and V in Fig.1).

By comparing spectra A, B, and C, it is easy to find that in spectrum B there are some bands of coatings in the region of $1700\text{--}700\text{ cm}^{-1}$ besides the copper's absorptions. No significant bands can be observed in spectrum C. The signal to noise ratio is lower than that of spectrum B despite the fact that the same sample was measured in both experimental arrangements. The same phenomena were observed by reproducing the spectra. This is mainly due to the relative positions between wire axes and incident plane. As the wire axis was arranged vertical to the plane of incidence, the reflection was

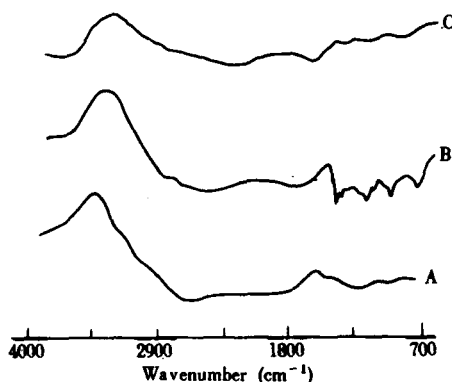


Fig.2 Reflection IR spectra of copper wires.

- (A) polished copper, axis parallel to incident plane;
- (B) copper coated with epoxy resin, axis parallel to incident plane;
- (C) copper coated with epoxy resin, axis vertical to incident plane.

rather random and the incident angle were variable. (See diagram V in Fig. 1.) As the incident angle is near zero, the incident and the reflected waves combine to form a standing wave with zero amplitude near the surface. So little absorption can be observed by the surface materials^[2]. The amplitude of the standing wave increases in proportion to the increase of incident angle. So better spectrum is expected from the parallel orientation of the sample, since the average of the incident angles in this case is large. (See the diagram P in Fig. 1.) We recorded spectra using this sampling technique, in the experiments for the study of the epoxy resin coating on copper.

The digital subtraction of a copper's spectrum from the copper / coating's yielded a difference spectrum which is shown in Fig.3 as spectrum A. The difference spectrum shows some similar

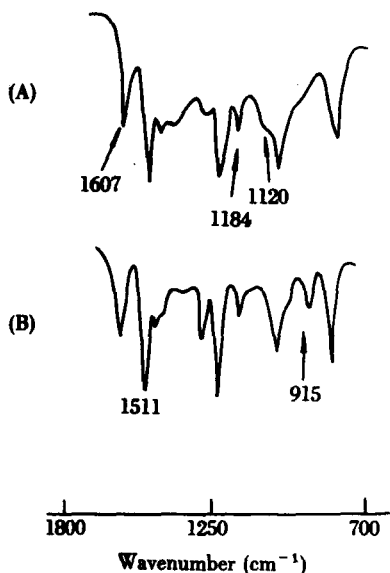


Fig. 3 IR spectra of the epoxy resin.

- (A) Difference spectrum of copper/epoxy and copper;
- (B) Transmittance spectrum of the uncured epoxy resin.

absorption bands as the transmittance spectrum of the epoxy resin, such as the $C=C$ stretching mode of the phenyl ring at 1511 cm^{-1} , the $\phi-O-C$ antisymmetric stretching mode at 1248 cm^{-1} and the symmetric stretching mode at 1038 cm^{-1} , the $C-H$ in-plane deformation mode at 1184 cm^{-1} , and the out-of-plane deformation mode at 830 cm^{-1} ^[9]. But the epoxy band at 915 cm^{-1} was not observed in the difference spectrum and the $C-O-C$ stretching mode of the aliphatic ether intensified its absorption near 1120 cm^{-1} , indicating the polymerization of the resin on copper surface. The chemical reactions of imidazole and the epoxy resin in bulk have been described in detail by Ricciardi, Romanchick, and Madeleine^[10]. Further studies using electronic spectroscopy, magnetic susceptibility or far infrared spectroscopy have been done to elucidate the interactions between imidazole and copper substrate^[11]. Anyway, the fact that imidazole still remained and promoted the curing of the epoxy resin on copper wire surface in the epoxy bath even at the elevated temperature above its melting point (90°C), indicated the formation of a compound by the reaction of imidazole and copper.

Imidazole and its derivatives are of great interest not only as curing catalysts of epoxy resins but also as corrosion inhibitors^[12-15]. By suitable combination of these chemical reactivities of imidazoles towards epoxy 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 the metal. Experimentally, a polished copper wire, imidazole and acetic acid-imidazole treated copper wires were immersed in epoxy resin at 100°C for one hour. After withdrawing from the bath, the physically adsorbed resin was washed out from the wires using hot alcohol. The chemically reacted coatings were measured by FTIR external reflection spectroscopy in the way mentioned above. Spectra are shown in Fig.4, it can be estimated that the epoxy resin picked up by imidazole treated copper wire is about $300\text{ \AA}$ in thickness, whereas the polished copper has adsorbed little.

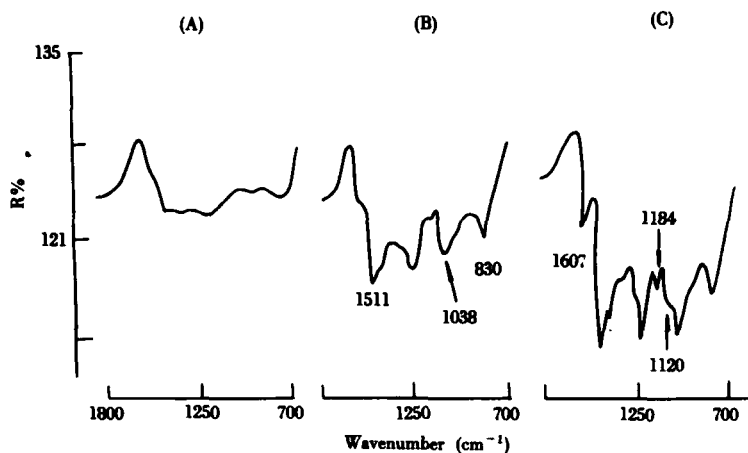


Fig. 4 IR spectra for epoxy resin on copper wires pre-treated in different ways:

- (A) polished copper; (B) copper treated with imidazole;
- (C) copper treated with imidazole-acetic acid.

CONCLUSIONS

The external reflection spectra giving information on curing of an epoxy resin on a copper wire can be achieved by using FTIR diffuse reflectance optics. Since this technique does not depend on a

good contact of the sample with the reflective crystal as it is the case with ATR (an attenuated total internal reflection technique), and is valid for samples with cylindrical shapes, it is a promising method to make in-situ study of the coating on a metal wire.

The results obtained here also indicate that imidazoles absorbed on the surface of copper can be used as an effective curing catalyst for the epoxy resin.

Keywords:

Reflection absorption, diffuse reflectance, copper wire, epoxy resin, imidazole, curing.

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