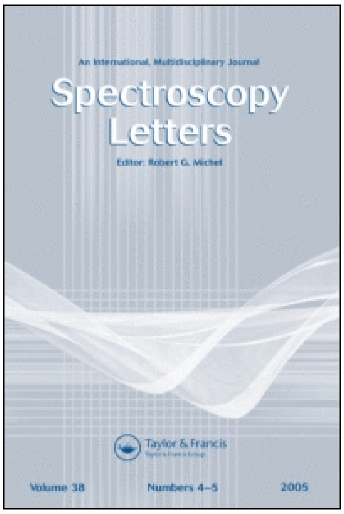

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SERS and IR Studies of Polymerization of an Epoxy Compound on Top of Benzotriazole Adsorbed on Copper

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SERS and IR Studies of Polymerization of an Epoxy Compound on Top of Benzotriazole Adsorbed on Copper

Keywords: Benzotriazole, epoxy resin, coating, Raman spectroscopy, infrared reflection-absorption.

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Abstract

Chemisorption of benzotriazole (BATH) on to metal surface has been investigated by the use of surface enhanced Raman scattering and FTIR reflection absorption spectroscopy. Benzotriazole reacts with metallic copper at room temperature or with copper oxides under higher temperature to form a complex which covered the surface as a polymeric film. The ring-opening reaction of an epoxy resin induced by the surface material was investigated.

Introduction

Heterocyclic nitrogen compounds have found widespread use not only as corrosion inhibitors for copper and other transition metals but also as curing agents for epoxy resins[1-3]. Among them, benzotriazole (BTAH) is of better coordinative ability and reactivity compared with the others. In recent years there have been considerable efforts devoted to the study of mechanism by which BTAH inhibits corrosion of copper. The popular view in this field is that BTAH is chemisorbed on copper oxide surface to form an inert copper-BTAH coordination polymeric films[4]. In this work we investigate the reactions of BTAH both with freshly etched metallic copper and with an oxidized surface of copper. Surface-enhanced Raman scattering (SERS) is of great value for mechanistic studies of surface reaction[5-7]. Its sensitivity has been made use of to study the molecular structure of the surface materials of the chemisorbed epoxy resin on Cu foil pretreated with BTAH. By using FTIR reflection absorption (FTIR-RA) we have confirmed this surface reaction.

Experimental

SERS (Surface Enhanced Raman Scattering)

Commercial copper foil (available from Aldrich, 99.99%, 0.05mm thick) was washed with acetone, and then immersed in a stirred 2M HNO_3 solution at room temperature for 4 min to creates a sponge-type surface. After etching, the copper foil was thoroughly rinsed with distilled water, dried with nitrogen, dipcoated with BTAH-ethanol solution. The physisorbed materials were washed away with ethanol. In addition, copper foils were exposed to air for 0, 30, and 120 min respectively. The copper foils, untreated and pretreated with BTAH, were immersed in an epoxy bath at 100 °C for 5 minute, and then withdrawn and washed with acetone to remove the physisorbed epoxy resin. The SERS spectra were measured with a backscattering geometry in air on a SPEX 1403 Raman spectrometer. The incident laser excitation was the 647.1 nm line from a Kr^+ laser source with output power of 40 mW.

FTIR-RA (FTIR Reflection Absorption)

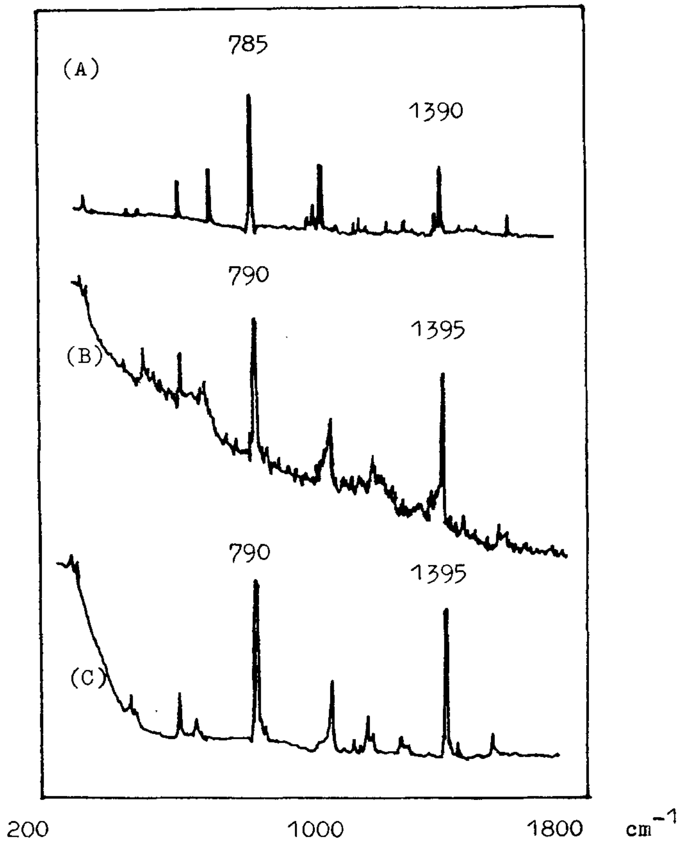
A copper foil (20 mm 30 mm 0.5 mm) was immersed in an epoxy bath at 100 °C for 5 min, and then withdrawn, washed with acetone. The spectrum was taken by means of FTIR-RA. The copper foil which is of the same specifications as above mentioned was treated with BTAH for 5 min, and then with epoxy resin. Spectra were recorded on a Nicolet 170 SX FTIR spectrophotometer. A Harri 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 4000-400 cm^{-1}.

Results and Discussion

Fig. 1 shows the normal Raman spectrum of BTAH in solid state and its SERS spectra on an etched copper and silver surfaces.

Normal Raman spectrum of neat BTAH (Fig. 1a) shows characteristic absorption bands near 1390 and 785 cm^{-1}, which are due to the ring stretching mode and the ring deformation mode respectively. The similar spectra can be found in Fig. 1b and 1c, where the SERS of BTAH absorbed on freshly etched metallic copper and on silver were given. Owing to the surface effect, the corresponding bands shifted 5 cm^{-1} to high field respectively, indicating that BTAH had been chemisorbed on surfaces. By transferring the surface layer into a 0.1 M HCl solution, and then determined by the use of UV, the thickness of CuBTA complex on copper was measured to be about 70-100 Å.

The air oxidation of an etched copper and the reaction between the corresponding preoxidized copper and BTAH were followed with SERS. The spectra on the left in Fig. 2 were recorded from the copper foil which was washed with distilled water after etching. On exposure to air, broad bands centered around 590 and 520 cm^{-1} gradually appeared (spectrum B), which were due to the symmetric and asymmetric stretching vibrations of cuprous oxide. The intensity and width of the oxide



Raman shift (cm^{-1})

Fig. 1 (A) Normal Raman spectrum of BTAH; (B) SERS of BTAH treated copper; (C) SERS of BTAH treated Ag foil.

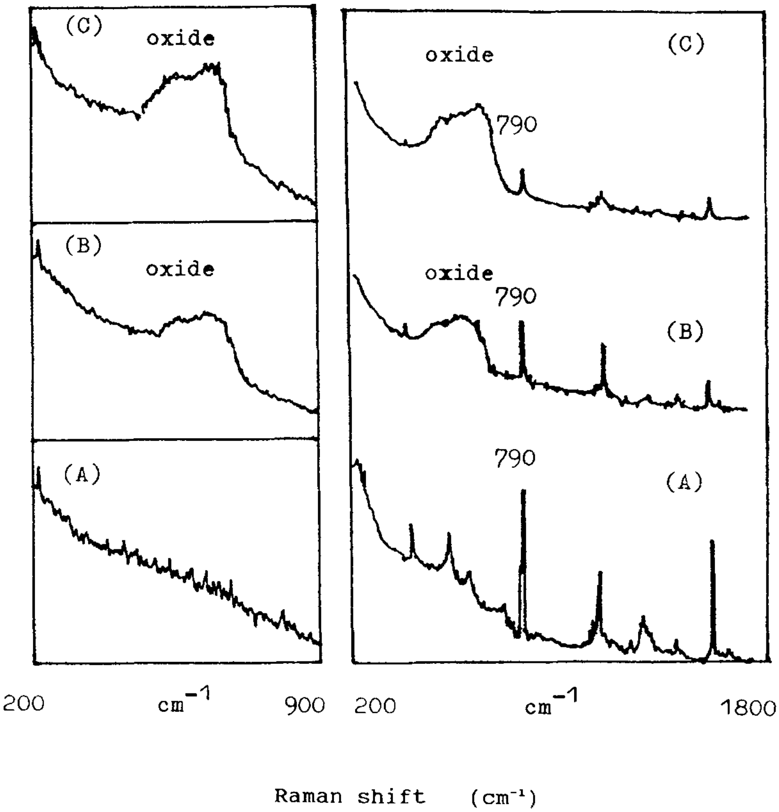


Fig.2 Left: (A) SERS spectrum of an etched Cu; (B) after 30 min exposure; (C) after 120 min exposure. Right: SERS of BTAH adsorbed on an etched Cu (A), on Cu exposed for 30 min (B) and for 120 min (C).

bands became prominent as the oxidation time goes on (spectrum C). The SERS spectrum for the freshly etched copper shows little oxide bands (spectrum A).

The spectra on the right in Fig. 2 illustrate the SERS spectra of BTAH on a freshly etched surface and on preoxidized surfaces of copper. For the sample of the preoxidized copper foils, the Raman lines of the adsorbed BTAH (spectrum B) were rather weak, as compared with those in spectrum A. It can be seen from the above results that only the cleaned surface of copper could adsorb BTAH anchored directly to the metal under mild treatment conditions. The further SERS spectra of BTAH which reacted at 60°C with the preoxidized copper are shown in Fig.3. A significant reduction in Raman intensity of the oxide bands with reaction times could be observed, indicating that copper oxides reacted with BTAH under higher temperature. Fig.3C shows that after heating at 60°C for 30 min, oxide bands ultimately disappeared, meaning that the complete reaction reached.

$$Cu_2O + BTAH \xrightarrow{60\ ^{o}C} H_2O + CuBTA$$

This suggests that BTAH is less reactive with Cu_2O at room temperature, and that as the temperature increases, it becomes more reactive with copper oxides.

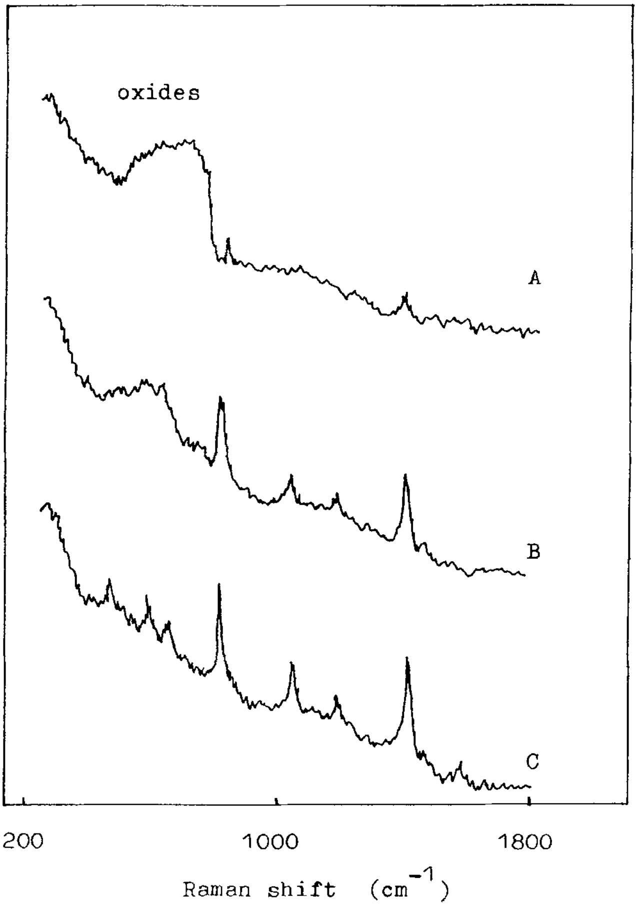


Figure 3. SERS spectra of BTAH reacted with preoxidized copper: (A) at room temperature for 5 min; (B) at 60 °C for 5 min; (C) at 60 °C for 30 min.

Copper foils treated and untreated with BTAH were immersed in hot epoxy resin and then were washed with acetone. Their SERS spectra are shown in Fig. 4.

By comparing spectra A, B, and C in Fig. 4, one can easily find that no reaction between neat copper and epoxy resin took place under the experimental conditions. In spectrum B, however, there are some new bands in the region of 795-1515 cm^{-1} which are different from the characteristic bands of BTAH. We proposed that the appearance of these new bands resulted from the chemisorption of the epoxy resin on pretreated copper foil. The Raman bands at 820 cm^{-1} can be assigned to the C-H out-of-plane deformation, and the bands at 1040 and 1250 cm^{-1} are due to the stretching vibrations of the C-O-C, while the band at 1515 cm^{-1} can be attributed to the C=C stretching mode of the phenyl ring.

FTIR-RA studies provide more evidence about the chemisorption of the epoxy resin onto pretreated copper. FTIR-RA spectra of the epoxy resin chemisorbed on the copper foil pretreated with BTAH and that on untreated copper were compared with the neat epoxy resin, as shown in Fig. 5. The C=C stretching mode for the phenyl ring at 1510 cm^{-1}, the C-O-C antisymmetric stretching mode at 1250 cm^{-1}, and the epoxy band at 915 cm^{-1} can be seen in Fig. 5A. However, in Fig.5B, the epoxy band at 915 cm^{-1} was not observed and the C-O-C

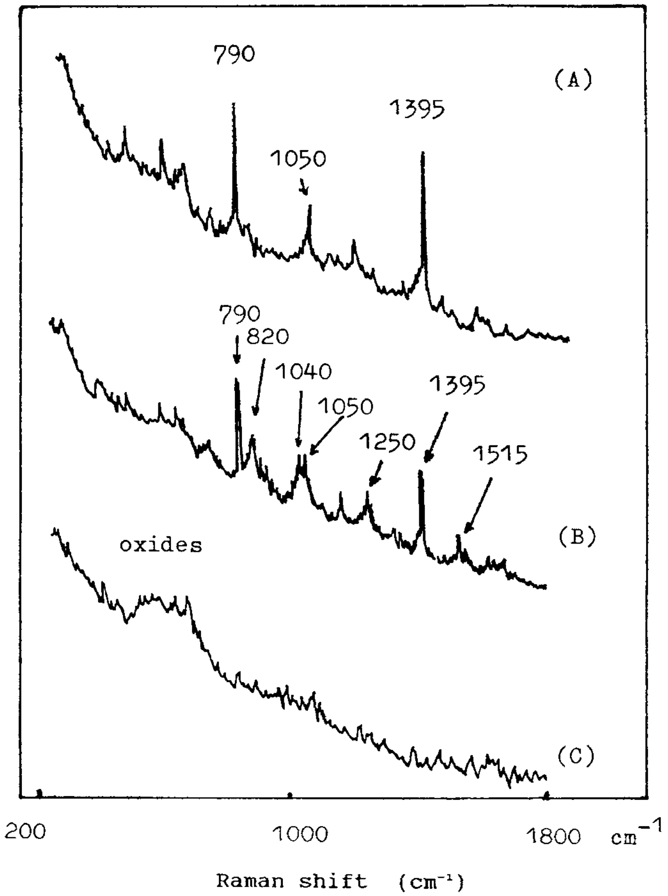


Fig.4 SERS spectra of (A) BTAH treated Cu, (B) the epoxy resin cured Cu foil which had been pretreated with BTAH, and (C) the epoxy resin cured on neat Cu.

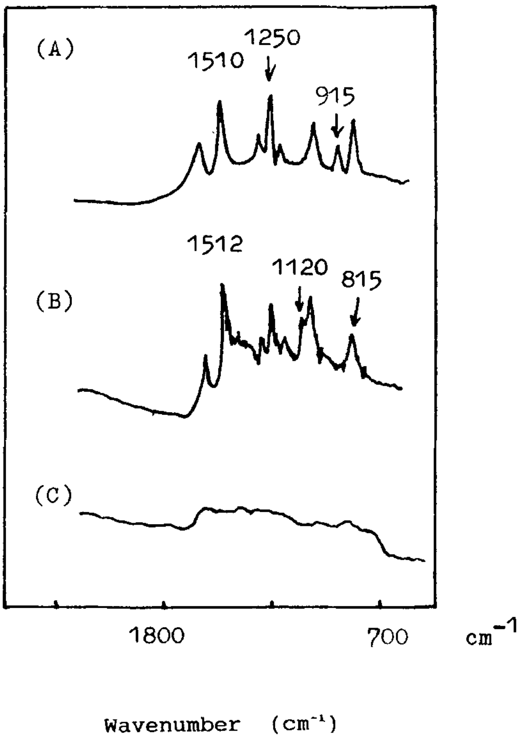


Fig. 5 (A) IR transmission spectrum of an epoxy resin; (B) FTIR spectrum of the epoxy resin cured on Cu foil pretreated with BTAH; (C) FTIR spectrum of the epoxy resin cured on neat Cu foil.

stretching mode of the aliphatic ether intensified its absorption at 1120 cm^{-1}, indicating the polymerization of the epoxy resin on pretreated copper surface. In addition, the spectral fact that no useful signal were observed in Fig. 5C suggests that little epoxy resin was chemisorbed on the untreated copper foil.

Conclusion

Benzotriazole (BTAH) can be chemisorbed onto metallic copper at room temperature or reacted with surface oxides at higher temperature to form Cu-BTA complexes. This surface materials can also induce the curing of epoxy resin onto copper.

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