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Spectroscopic studies of epoxy resin coating on imidazole copolymer treated copper surfaces

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SUMMARY

The reaction between the epoxy resin coating and copper surface modified with imidazole copolymer has been studied by FT-IR reflection-absorption spectroscopy (FT-IR RAS). Due to the catalytic effect of the copper/imidazole complex, epoxy cure reaction has occurred on the copper surface at low temperature. The cured epoxy coating has been increased gradually above 150 °C, while the imidazole complex dissolved slightly into the resin solution. Compared to poly(vinylimidazole) homopolymer, silane-based imidazole copolymer coating remains more on the copper surface due to the adhesion promotion between copper surface and coating polymer.

INTRODUCTION

A large number of corrosion inhibitors for copper have been reported, such as benzotriazole, benzium, indazole, and imidazole (1-19). The imidazole derivatives on copper surface have the high reactivity and suppress the corrosion formation on copper surface as corrosion inhibitor. The complex formation between the copper and nitrogen on the imidazole ring protects the copper surface from the oxygen diffusion (20-23). However, these small molecules are not satisfactory for anticorrosion agent at elevated temperature.

Recently, polymer has been studied for the corrosion inhibitor. Eng studied poly(vinylimidazole) as anticorrosion agent for copper at high temperature (17). It was observed that poly(vinylimidazole) coated copper surface was suppressed even at 350 °C due to the low volatility of the film. However, poly(vinylimidazole) is very sensitive in humidity condition. To avoid this weakness of poly(vinylimidazole), a silane coupling agent is introduced to reduce the polymer's sensitivity to water (24). In addition, the silane coupling agent also improves the adhesion between the polymer film and the copper surface γ-Methacryloxypropyltrimethoxy silane(γ-MPS) is used for this purpose. In this study, we will discuss the chemical reaction and the adhesion promotion between the epoxy resin coating and copper surface modified with imidazole copolymer by Fourier transform infrared reflection-absorption spectroscopy (FT-IR RAS).

EXPERIMENTAL

Vinylimidazole (VI) was purchused from Aldrich Chemical Co., and distilled in vacuo to yield a pure and colorless liquid. γ-Methacryloxypropyltrimethoxy silane (γ-MPS) was supplied by Petrach System Inc., and also distilled in vacuo for this study. Azobis(isobutyronitrile) from the Eastman kodak Co. was first dissolved in warm methanol (35 °C), then recrystallized in an ice bath and finally dried in a vacuum oven at room temperature for two days. The epoxy resin (EPON 828) was supplied by

Shell Chemical Co. Silane-based imidazole copolymers were synthesized by free radical polymerication with azobis (isobutyronitrile) as the initiator (25, 26). Vinylimidazole (0.021 mole), γ-MPS (0.011 mole) and azobis (isobutyronitrile)(0.030 mmole) in benzene (40ml) were polymerized at 68°C with stirring under nitrogen for 24 h. The brownish liquid was obtained after polymerization.

The chemical structures of vinylimidazole, γ-MPS, and diglycidyl ether of bisphenol A (EPON 828) are shown in Fig.1. Copper plates (ASTM B152, type ETP) were mechanically polished in a suitable manner (24). Silane-based imidazole copolymer was diluted in tetrahydrofuran(THF) solvent. A known amount of polymer solution was placed on the copper surface by a microsyringe. After evaporating THF solvent, the copper plates were dried at 25 °C for 48 h. Surface treated copper plates were immersed in epoxy resin/ethanol solution (0.3 g/l).

The reflection-absorption (R-A) attachment along a gold wire grid polarizer was mounted in a Digilab FTS-20 fourier transform spectrometer equipped with nitrogen-cooled MCT detector. The IR spectrum was obtained by digitally subtracting the spectrum of the reference copper surface from the spectrum of the surface coating.

Adhesion test was carried out according to ASTM D3359-83. Scotch tape test is composed of applying and briskly lifting the tape over cuts made in the film on the copper surface. This tape test is used to assess the relative adhesion strength of coated polymer on a metal surface, but it does not classify the coating materials of high adhesion strength.

RESULTS AND DISCUSSION

Fig. 2 represents transmission spectrum of silane-based imidazole copolymer. The peak at 3412 cm^{-1} is assigned to O-H stretching and the band at 3137 cm^{-1} is the C-H stretching mode of the imidazole ring. The free carbonyl peak appears at 1723 cm^{-1} and the band at 1300 cm^{-1} is associated with the ester functionality. From this result, it is evident that silane-based imidazole copolymer is synthesized.

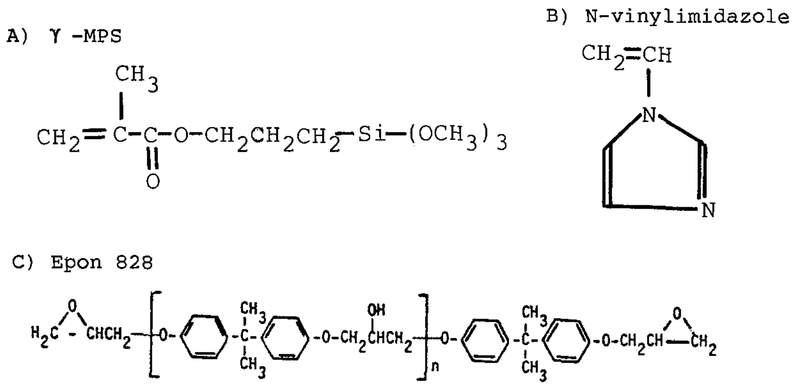

Fig.1. Chemical structures of γ-MPS, vinylimidazole, epoxy resin for this study.

Fig.3 demonstrates the R-A spectra of silane-based imidazole copolymers on the copper surface. From this figure, the band at 1725 cm^{-1} is designated to carbonyl group of γ-MPS. The peak at 1570 cm^{-1} is C=N streching mode of the imidazole ring. The band at 1415 cm^{-1} is assigned to the

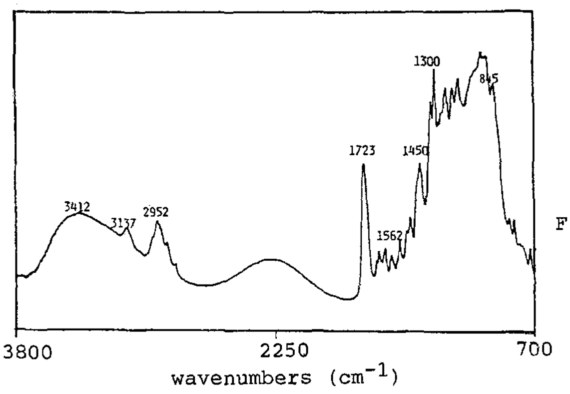

Fig.2. Transmission spectrum of silane-based imidazole copolymer.

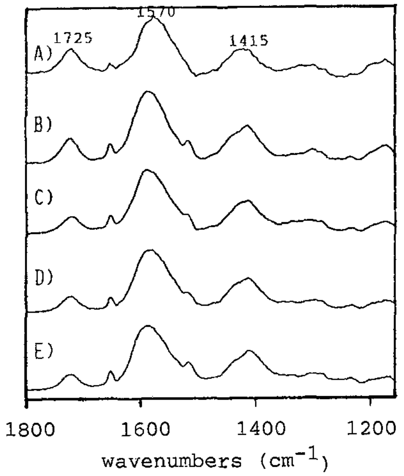

Fig.3 R-A spectra of silane-based imidazole copolymer on copper surface.
A) 1:1 B) 1:2 C) 1:3
D) 1:4 E) 1:10

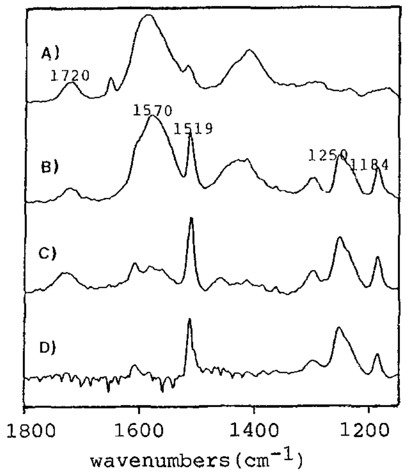

Fig.4. R-A spectra of the epoxy resin at different temperature
A) Untreated B) 100 °C
C) 150 °C D) 200 °C

CH_2 bending mode of imidazole. As the molar ratio of γ-MPS/VI decreases from 1.0 to 0.1, the peak height of γ-MPS (1725 cm^{-1}) decreases gradually compared to the peak of imidazole (1570 cm^{-1}).

Fig.4 shows the R-A spectra providing that cure reaction of epoxy resin toward silane based imidazole copolymer depends on the treatment temperature of epoxy resin. Surface treated copper sample was immersed in the epoxy/ethanol solution for 15 min. The band at 1720 cm^{-1} is assigned to carbonyl group and the peak at 1570 cm^{-1} appears due to the C=N of imidazole ring. The C=C stretching mode of the phenyl ring appears at 1519 cm^{-1}. The C-O-C antisymmetric mode at 1250 cm^{-1} and the C-H in-plane deformation mode at 1184 cm^{-1} result from the cured epoxy resin. A small amount of epoxy resin was cured at low temperature, whereas epoxy cure reaction easily occurred at elevated temperature. During the epoxy curing, silane-based imidazole copolymer still remains on the copper surface, whereas poly (vinylimidazole) was completely dissolved in resin solution at 200°C. This

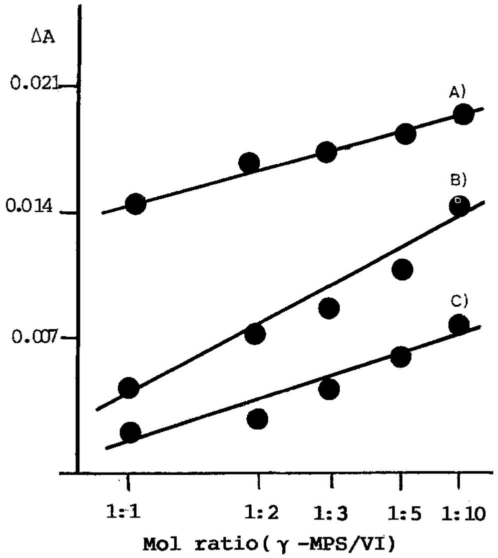

Fig.5. Absorbance of the band at 1519 $cm^{-1}$of epoxy resin versus molar ratio of γ-MPS/VI. A) 150 °C B) 200 °C C) 100 °C

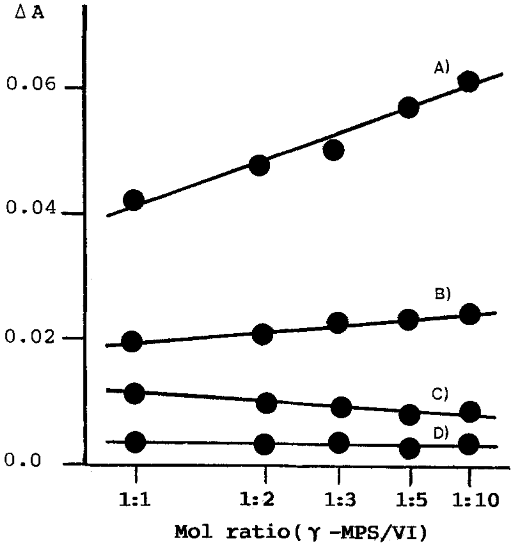

Fig.6. Absorbance of the band at 2925 cm^{-1} of vinylimidazole versus moar ratio of γ -MPS/VI.
A) Untreated B) 100 °C
C) 150 °C D) 200 °C

is because silane-based imidazole copolymer improves the adhesion strength between coated polymer and copper surface.

Fig.5 shows the cure effect of different molar ratio of γ-MPS/VI at various temperatures. The integrated intensity of C=C stretching mode at 1519 cm^{-1} is plotted against various molar ratio of γ-MPS/VI. The relative intensity of the epoxy resin increases at 150 °C. However, the amount of epoxy film was decreased gradually at 200 °C. Initially, epoxy resin reacted with the imidazole functional group as the curing agent. Cured epoxy resin on the copper surface diffused into the resin solution, following the dissolution of the complex between the copper and nitrogen on the imidazole ring. As the molar ratio of γ-MPS/VI decreased from 1.0 to 0.1, the amount of cured epoxy resin increased gradually on the copper

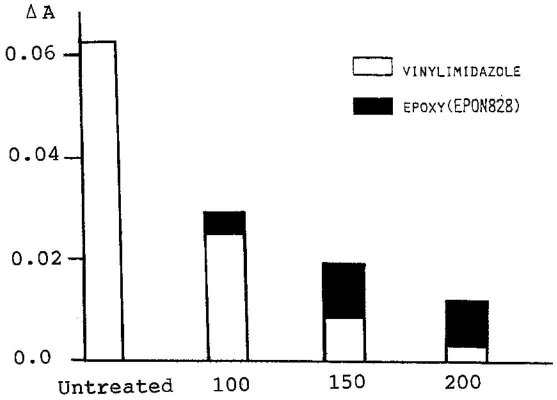

Fig.7. Absorbance at 1519 cm^{-1} of epoxy resin (black bar) and at 2925 cm^{-1} of vinylimidazole (white bar) versus treatment temperature.

Table 1. Percent film flaked versus different molar ratio of γ -MPS/VI for ASTM tape test.

mole ratio (r-MPS/VI)	1:1	1:2	1:3	1:5	1:10
percent film flaked*	1.5	0	0	2.0	0

* ASTM D3359-83 Tape test

surface. Residual amount of silane-based imidazole copolymer at different temperature is shown by Fig.6. As the temperature increased up to 200 °C, the remaining copolymer decreased on the copper surface. However, the coated epoxy resin does not depend on the molar ratio of γ-MPS/VI strongly. This result indicates that the copolymer residue is dependent on the treatment temperature.

Fig.7 represents the integrated intensities of the bands at 1519 cm^{-1} and 2925 cm^{-1} as a function of treatment temperature. Cured epoxy resin began to appear on the copper surface at 100 °C. The amount of cured epoxy further increased with decreasing the residual copolymer on the copper surface. Only a small amount of epoxy coating was observed at 200 °C. As mentioned previously, it can be explained that the imidazole/copper complex was dissolved in resin solution at elevated temperature.

Table 1 represents the adhesion strength of silane-based imidazole copolymer on the copper surface at 360 °C for 15 min. For the adhesion test, film thickness is fixed to 100 nm. Three samples were chosen for each data point. Only 1.5% of the coated film is flaked in 1:1 molar ratio of γ-MPS/VI and 2% of the film is flaked in 1:5 molar ratio of γ-MPS/VI. Most of the coated polymers are not removed from the copper surface. From these data, it can be concluded that silane based-imidazole copolymer adheres to the copper surface strongly. The adhesion between copolymer and the copper does not depend on the molar ratio of γ-MPS/VI. γ-MPS acts as the adhesion promotor on the copper surface.

CONCLUSION

From the spectroscopic study, it was proven that the imidazole functional group reacts with epoxy resin without any curing agent. As the molar ratio of γ-MPS/VI decreases from 1.0 to 0.1, the amount of cured epoxy resin increases on the copper surface. The residual copolymer mainly depends on the treatment temperature. Silane-based imidazole copolymer improves the interfacial adhesion between cured epoxy resin and copper surface.

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