

Infrared Spectroscopic Study of SiO_x Film Formation and Decomposition of Vinyl Silane Derivative by Heat Treatment. II. On Copper Surface

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ABSTRACT: The thermooxidative degradation and SiO_x film-formation mechanism of poly(vinylimidazole-co-vinyltrimethoxysilane) [poly(VI-co-VTS)] on copper was investigated with Fourier transform infrared reflection and absorption spectroscopy (FTIR-RAS). The spectral differences of the copolymers with different coating thicknesses were compared. Thermal degradation of the copolymer was catalyzed by copper in the copolymer film as well as on the copper surface. This catalytic effect of copper was observed regardless of coating thickness. Copper in the copolymer film participated in Cu-containing SiO_x film formation during thermal degradation. In addition, the enhanced heat treatment causes the film defects in Cu-containing SiO_x film as a result of thermal decomposition. Copper corrosion proceeded through these film defects. However, in a thick-coated sample, copper oxides were first formed through the crack in the barrier film as a result of the residual stress. Copper oxides in the film interacted with the SiO_x film to form a Cu-rich phase in the vicinity of film defects and cracks.
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Key words: poly(VI-co-VTS); copper corrosion; Cu-containing SiO_x film

INTRODUCTION

Silane-modified polyvinylimidazole (PVI) has been reported to be an effective corrosion inhibitor for copper both in humid conditions and at elevated temperature.^{1–5} It can exclude water molecules at the metal–polymer interface in humid conditions through the formation of chemical bonding with the copper surface. In addition, it can improve the thermal stability of the protective coating at elevated temperature through the siloxane network formation.^{3–5} Therefore, the siloxane network formation of silane-modified PVI on copper is important in corrosion protection on the copper surface and the understanding of the siloxane network formation is indispensable for the ef-

fective corrosion protection on copper at elevated temperature. However, the siloxane network formation on copper has not been extensively investigated even if it is a crucial factor in the corrosion protection on copper. In part I, we discussed the heat-treatment effect on SiO_x film formation on KBr and a gold surface. In this study, thermal degradation of silane-modified PVI on copper will be investigated in terms of the infinitive siloxane network formation and will be explained in comparison with that on gold.

The present study was concerned with the Cu-containing SiO_x film-formation mechanism on copper as a function of heat treatment using the Fourier transform infrared reflection and absorption spectroscopy (FTIR RAS) technique. In addition, the spectral differences of the copolymers with different coating thicknesses were compared to understand the formation of the SiO_x film defect.

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EXPERIMENTAL

Vinylimidazole (VI) was purchased from Aldrich Chemical Co., and vinyltrimethoxysilane (VTS), from Petrach Systems. They were distilled *in vacuo* to yield pure and colorless liquids. Azobisisobutyronitrile (AIBN) from Wako Pure Chemical Industries was dissolved in warm methanol (35°C), recrystallized in an ice bath, and then dried in a vacuum oven at room temperature for 2 days. Poly(VI-co-VTS) was synthesized by free-radical copolymerization using AIBN as an initiator. VI and VTS were copolymerized in benzene at 68°C with stirring in an argon atmosphere. The mol ratio of VI to VTS in the feed was 3 : 7. The total monomer concentration was 2M, and the initiator concentration was fixed at $2 \times 10^{-3}M$.

Copper plates ($1.2 \times 5.0 \times 0.3$ cm) were mechanically polished with No. 5 chrome oxide, washed with *n*-hexane and ethanol in an ultrasonic bath, rinsed with a 1% HCl/distilled water solution, distilled water, and ethanol, and then dried with a stream of nitrogen gas. The copolymer solution was cast onto copper plates with a microsyringe and the samples were dried at 60°C for 12 h in air before testing to remove solvent in the polymer film. Film thickness was controlled with the variation of the copolymer concentration and calculated based on the concentration of the copolymer solution, copolymer density, and the area of the substrate.

FTIR reflection and absorption (R-A) spectroscopy was used to monitor the thermal degradative crosslinking of poly(VI-co-VTS) coated on copper. The spectrometer was continuously purged with nitrogen gas to remove water vapor and atmospheric CO₂. Absorbance spectra were obtained using a Bomem MB-100 spectrometer at a resolution of 4 cm⁻¹ and 32 scans were collected. A Graseby Specac P/N 19650 monolayer/grazing angle accessory was used. The angle of incidence was 78° and a freshly cleaned copper coupon was used to obtain the reference spectrum.

Copolymer-coated samples were heated at 360°C to study the thermal degradation mechanism of the copolymer. Each sample was heated for 1 min at 360°C in air and then characterized by FTIR. This process was repeated on the same sample with a 1-min increment in heating time until heating time reached 9 min. For further heat treatment, the above samples were heated for 15 min at 360°C and then characterized by FTIR. In each sample, the heat-treatment temperature was increased by 20° followed by FTIR analysis.

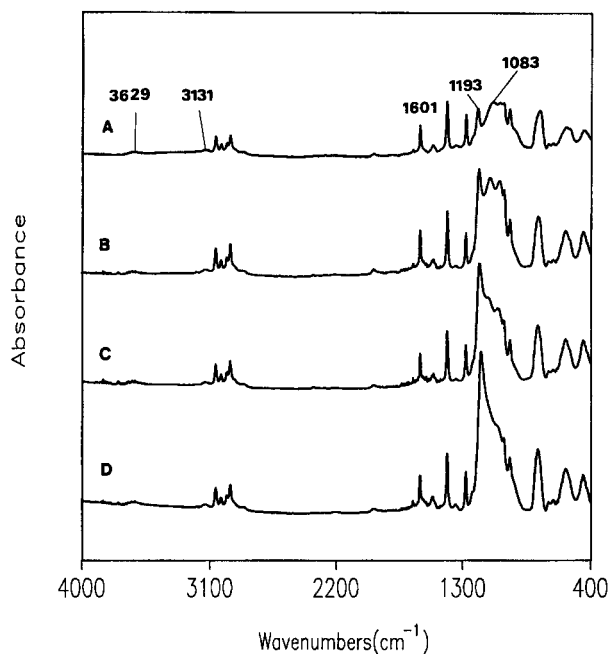


Figure 1 R-A spectra of the copolymer films on copper plates with different coating thicknesses: (A) 2.5 μm , (B) 1.5 μm , (C) 1 μm ; (D) 0.5 μm .

RESULTS AND DISCUSSION

The spectral changes of the copolymers on copper plates with different coating thicknesses were investigated with FTIR spectroscopy. Figure 1 represents the R-A spectra of the copolymer films on copper plates with different coating thicknesses. The peak at 3629 cm⁻¹ is assigned to the O—H stretching of the hydrogen-bonded Si—OH. The peak at 3131 cm⁻¹ is designated as the =C—H stretching of the VI ring, which is parallel to the ring plane of VI.⁶ The peak at 1601 cm⁻¹ is due to the C=C stretching from the VTS monomer contained in the copolymer film as a result of a low reactivity ratio of VTS.⁷ The peaks in the 1250–900 cm⁻¹ region show the outstanding differences in the relative peak intensities with the variation of coating thickness. Especially, the relative peak intensities at 1193 and 1083 cm⁻¹ increase with decreasing coating thickness due to the optical distortion. The former is due to the C—H rocking mode from the Si—O—CH₃, and the latter is attributed to the Si—O—C asymmetric stretching mode.⁸

Copolymer-coated copper plates were heated at 360°C to study the thermooxidative degradation and SiO_x film-formation mechanism of the copolymer. Figure 2 shows the spectral changes in the

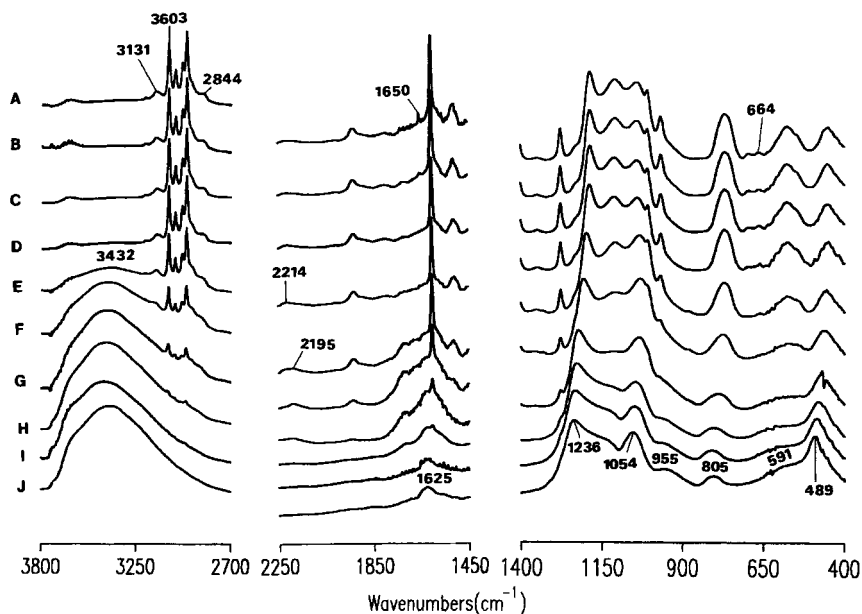


Figure 2 R-A spectra of the copolymer films ($1.5 \mu\text{m}$) on copper plates as a function of heating time at 360°C : (A) control; (B) 1 min; (C) 2 min; (D) 3 min; (E) 4 min; (F) 5 min; (G) 6 min; (H) 7 min; (I) 8 min; (J) 9 min.

R-A spectra of the copolymer films ($1.5 \mu\text{m}$) coated on copper plates with increasing heating time at 360°C . The first thermal degradation of the copolymer film occurs in the imidazole ring.⁹ The peak at 1650 cm^{-1} , which is assigned to the C=C/C=N stretching in the imidazole ring, disappears in spectrum C, and the new peak at 2214 cm^{-1} appears in spectrum D. This is attributed to the cleavage in the imidazole ring followed by the nitrile formation.¹⁰ The peak at 2195 cm^{-1} in spectrum E is designated as the nitrile group conjugated with the double bond in the copolymer backbone as a result of the oxidation of the copolymer backbone.¹⁰ These nitrile peaks completely disappear in spectrum I due to thermal decomposition. As heating time increases, the peaks from the VI ring (3131 , 1650 , and 664 cm^{-1}) decrease to disappear in spectrum G. The peak at 664 cm^{-1} is designated as the ring torsion of VI.¹⁰ Thermooxidative decomposition of the copolymer film is faster on copper than on gold, due to the catalytic effect of copper on the polymer degradation.¹¹⁻¹⁴ In addition, the peak (3063 cm^{-1}) from the double bond of VTS as well as the peak (2844 cm^{-1}) from Si—O—CH₃ of VTS decrease with increasing heating time and are not observed any more in spectrum J. This result indicates that the thermooxidative degradation of the copolymer film and the hydrolysis of the Si—OCH₃ group are almost completed at 9 min of heating time.

The outstanding spectral changes with increasing heating time are observed in spectrum E. The broad band around 3432 cm^{-1} begins to appear due to the hydrogen-bonded water, and the new peaks are observed in the $1800\text{--}1500 \text{ cm}^{-1}$ region as a result of the thermal oxidation of the copolymer film. These regions contain the peaks at 1722 , 1678 , 1629 , and 1592 cm^{-1} from the thermal oxidation products of the VI unit of the copolymer and the copolymer backbone [Fig. 3(A)]. In addition, two peaks at 1726 and 1637 cm^{-1} can be contained in this region as a result of the oxidation of VTS [Fig. 3(B)]. However, thermooxidative degradation of the VTS-only film is slower than that of the copolymer film. This suggests that the VI unit in the copolymer film is related to the accelerated copolymer degradation. The VI unit in the copolymer film contributes to the diffusion of copper on the surface into the copolymer film through the complex bond formation with copper. Copper in the copolymer film accelerates the polymer degradation. These oxidation peaks of the copolymer film are assigned in Table I.⁹ These peaks in the $1800\text{--}1500 \text{ cm}^{-1}$ region increase in intensity as the oxidation of the copolymer film proceeds and then decrease as a result of the thermal decomposition. In this study, the thermal degradation of the VTS unit will be discussed in detail because it is related to the SiO_x film formation, and the thermal degradation of PVI on copper was

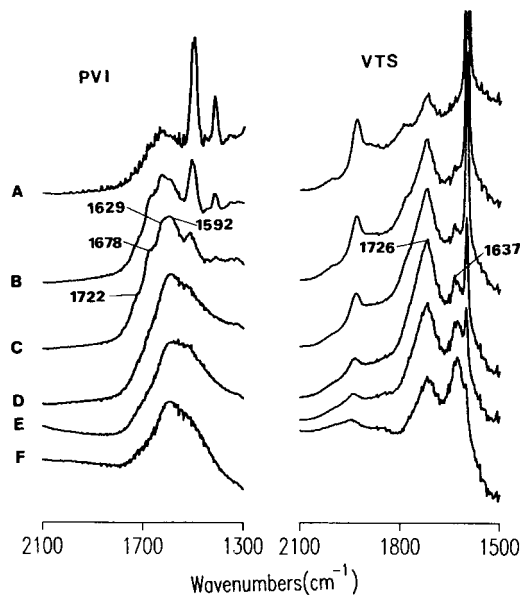


Figure 3 R-A spectra of PVI film and VTS-only film (1.5 μm) on copper plates as a function of heating time at 360°C: (A) 4 min; (B) 5 min; (C) 6 min; (D) 7 min; (E) 8 min; (F) 9 min.

discussed in the previous paper.⁹ In terms of the thermal degradation of VTS, the double bond from VTS may be finally cleaved into SiCOOH (1637 cm^{-1}) and HCOOH (1726 cm^{-1}) by the thermal oxidation catalyzed by copper; these acids can form copper-carboxylate ions. The peaks from these carboxylate ions appear in the 1600–1500 cm^{-1} range,^{15,16} which were not observed in the spectra on gold. Formate salt (1600–1550 cm^{-1}) can be decomposed into Cu—OH and volatile products (H_2O and CO_2) and so no longer remains in the copolymer film. Especially, water can accelerate the Si—O—Si bond formation. SiCOOH and its carboxyl salt (1650–1540 cm^{-1}) are also converted into the Si—OH and Cu—OH as a re-

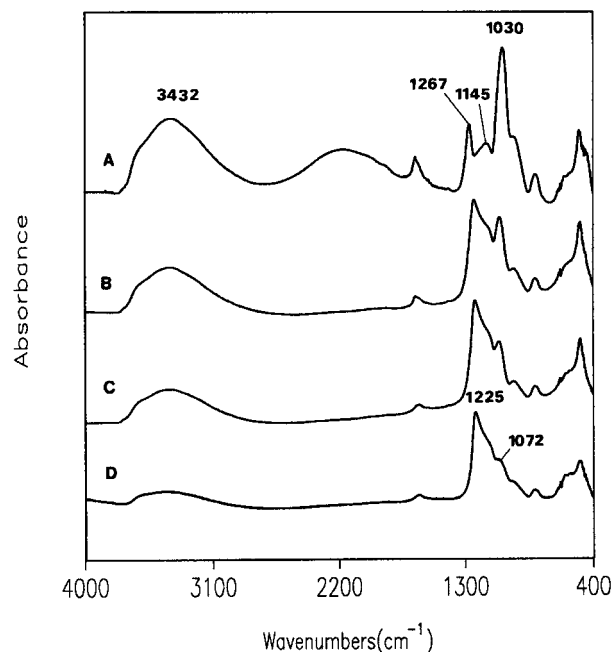


Figure 4 R-A spectra of the copolymer films on copper plates with different coating thicknesses after heat treatment at 360°C for 9 min: (A) 2.5 μm ; (B) 1.5 μm ; (C) 1 μm ; (D) 0.5 μm .

sult of thermal decomposition. These Si—OH and Cu—OH can form Si—O—Si and Si—O—Cu linkages. These Si—O—Si and Si—O—Cu bond formations led to a Cu-containing siloxane network formation. Therefore, as heating time increases, these oxidation peaks show a gradual increase up to 6 min of heating time as a result of the increased copolymer degradation and then decrease gradually to disappear due to thermal decomposition. However, the peak at 1625 cm^{-1} is still observed at 9 min of heating time. This peak is attributed mainly to the hydrogen-bonded water peak in the silica structure.¹⁷

Table I Tentative Band Assignments of Thermally Degraded PVI and VTS-only Film on Copper

PVI Bands (cm^{-1})	VTS Bands (cm^{-1})	Tentative Assignments
1722	1726	C=O stretching of formic acid
1678		C=O ketonic stretching
	1637	C=O α,β -unsaturated ketone
1629		C=O stretching of Si—COOH
		C=C unconjugated
		C=N conjugated;
1592		C=O + C=C (mixed mode);
		C=C + N—H (mixed mode).

In spectra E–J, an increase in peak intensity around 3432 cm⁻¹ induces the hydrolysis of the Si–O–CH₃ groups followed by the condensation reaction among the Si–OH groups. This hydrolysis followed by a condensation reaction proceeds as heating time increases. In spectrum J, no peak from the Si–OCH₃ group is observed. The peaks at 1236, 1054, 805, and 489 cm⁻¹ result from Si–O–Si linkages of the infinite siloxane network structure. The peak at 955 cm⁻¹ is due to the Si–O stretching of the Si–OH group, but the Si–O stretching mode from the Si–O–Cu linkage can be designated as this peak. This peak did not disappear after the extinction of the peak at 3629 cm⁻¹. Accordingly, the peak at 955 cm⁻¹ is assigned to the mixed mode of Si–OH and Si–O–Cu. The broad band around 591 cm⁻¹ is designated as the Cu–O stretching of Si–O–Cu.^{18,19} This broad band around 591 cm⁻¹ is not observed in the SiO_x film formed on gold. The existence of these peaks suggests the formation of Cu-containing SiO_x film.

The R-A spectra of the copolymers on copper plates with different coating thicknesses were compared after the same heat treatment. Figure 4 represents the R-A spectra of the copolymers with different coating thicknesses heated at 360°C for 9 min. All the copolymer peaks have disappeared in these spectra, which means that thermal degradation of the copolymer film is completed at 9 min of heating time regardless of the coating thickness. Since this catalytic effect of copper on the copolymer degradation is observed regardless of the film thickness, copolymer degradation catalyzed by copper proceeds in the bulk of the copolymer film as well as at the copper–copolymer interface in this experimental condition. This means that copper ion exists in the bulk of the copolymer film. For film formation by solution casting, copper has been reported to diffuse into the bulk of the film and to exist in the polymer film.^{20,21} Additionally, this existence of copper in the copolymer film can be ascertained by our recent study with the XPS depth profile.²² However, some differences are observed in the 1300–400 cm⁻¹ region of these spectra. First, as coating thickness decreases, the peak at 1267 cm⁻¹ [longitudinal optical (LO)] is shifted to 1225 cm⁻¹ and the peak at 1030 cm⁻¹ [transverse optical (TO)] to 1072 cm⁻¹. This is attributed to the optical effect. In the infrared spectra of the thin film where the film thickness is much smaller than the IR wavelengths, when infrared spectra is obtained at oblique angles, shifts of the peak positions are

observed due to the optical effect.²³ This splitting may be due to the optical effects, such as interference, diffraction, and scattering.^{24–26} However, these shifts may be explained by the stresses in the film. As the film thickness decreases, the stress in the film decreases. A decreasing stress in the film is accompanied by a shift of the Si–O–Si stretching to the higher band and a shift of the Si–O–Si bending to a lower shift.²⁷ However, the TO stretching mode (1030 cm⁻¹) is shifted to lower frequency with increasing coating thickness, and the Si–O–Si bending (806 cm⁻¹) mode is constant regardless of the film thickness. Therefore, it can be concluded that these shifts in the Si–O–Si stretching frequencies are caused by an optical effect. In addition, the peak at 1030 cm⁻¹ (TO) decreases in intensity with increasing coating thickness. The peak at 1145 cm⁻¹ is observed in spectrum A, which appears as a shoulder peak in the other spectra.

On the other hand, the 700–400 region of Figure 4 is represented in Figure 5 to observe the copper oxide peaks. In spectrum A, a small corrosion peak is observed at 611 cm⁻¹. The peak at 611 cm⁻¹ is designated as the TO mode of Cu₂O. This indicates that the thickness of the Cu₂O layer is above 200 nm.²⁸ This copper corrosion is

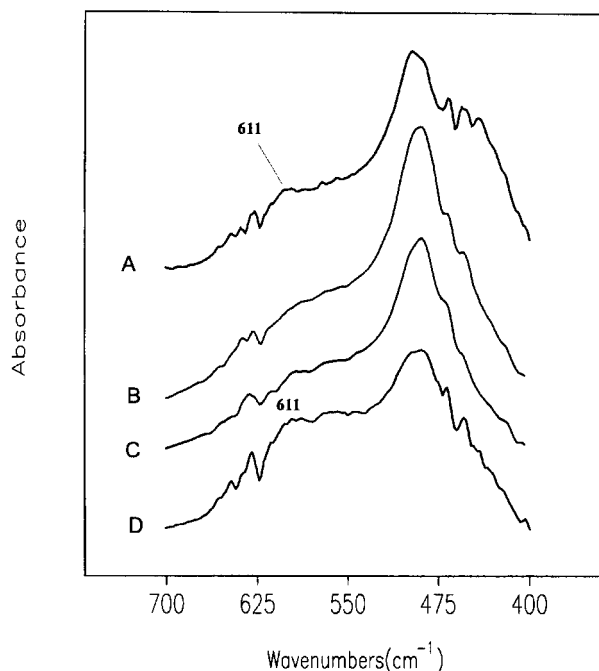


Figure 5 R-A spectra in the 700–400 region of the copolymer films on copper plates with different coating thicknesses after heat treatment at 360°C for 9 min: (A) 2.5 μm; (B) 1.5 μm; (C) 1 μm; (D) 0.5 μm.

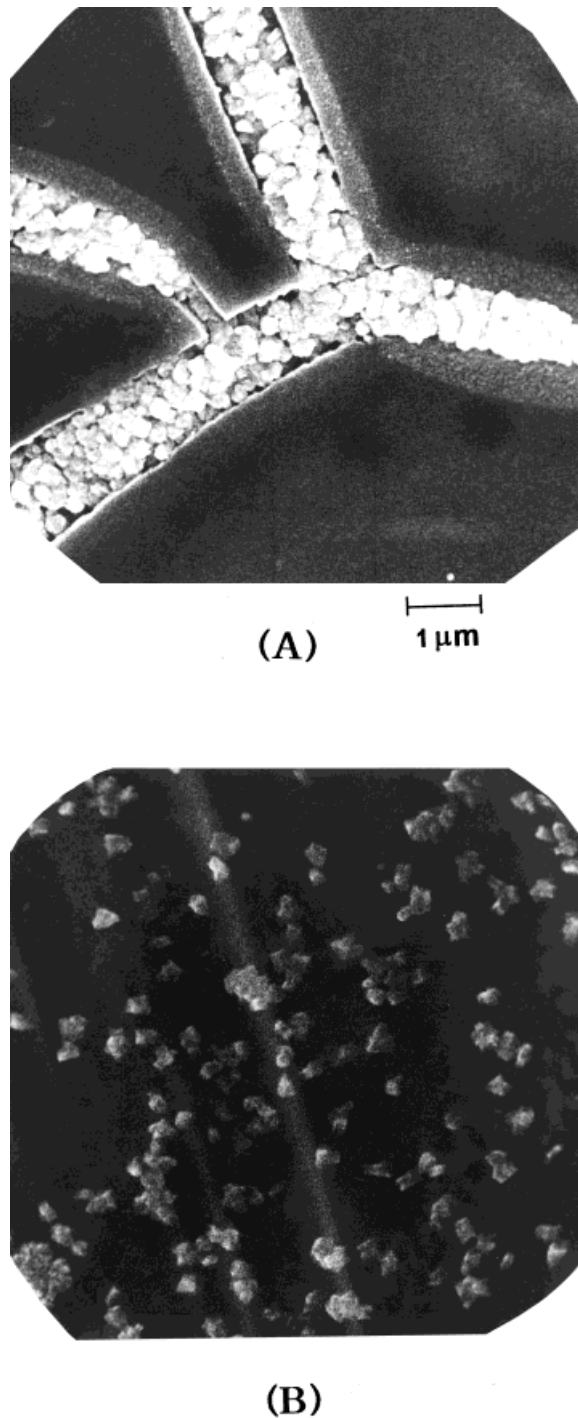


Figure 6 Scanning electron micrographs of the copolymer films on copper plates heated at 360°C: (A) 2.5 μm ; (B) 0.5 μm .

attributed to the crack formation due to the residual stress in the film. As coating thickness increases, the residual stress in the copolymer film increases. This residual stress causes the crack in

the film, and this crack is attacked by air oxygen. Accordingly, copper oxide crystals grow along the crack. This corrosion formation is shown in Figure 6(A). Corrosion peaks are also observed at 611 cm^{-1} in spectrum D. These peaks are related to the film defects formed during thermal decomposition. These film defects are liable to form in thin film. Air oxygen attacks the copper surface through these film defects, and, so, copper oxide is formed on the copper surface [Fig. 6(B)]. Therefore, a sufficient coating thickness is needed for corrosion protection, but crack formation due to residual stress must be avoided.

Figure 7 shows the R-A spectra of the copolymers on copper plates as a function of heating temperature. Samples were heated for 15 min at each heating temperature. As heating temperature increases, the peak at 1241 cm^{-1} is shifted to 1248 cm^{-1} with the reduction of the shoulder peak at 1169 cm^{-1} and the peak at 961 cm^{-1} is decreased. These suggest that the SiO_2 fraction in Cu-containing SiO_x film increases with increasing heating temperature.²⁹ On the other hand, the enhanced heat treatment causes the decomposition of Cu-containing SiO_x film.^{30,31} As heating temperature increases, the peaks from Si—

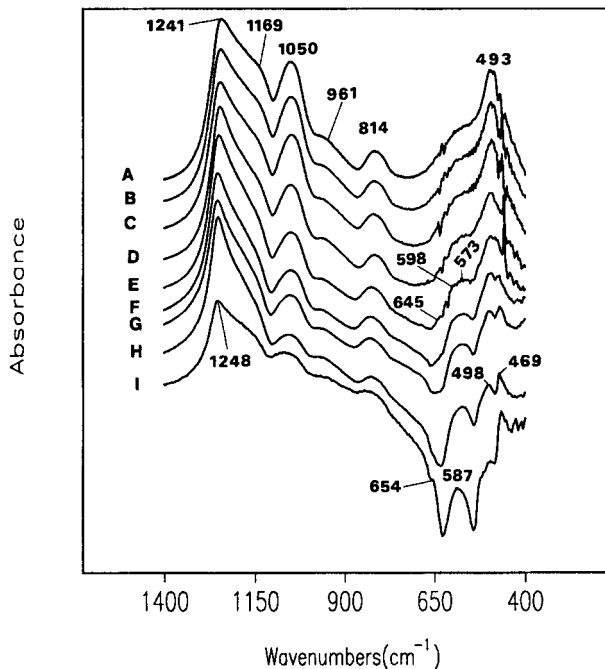


Figure 7 The changes in R-A spectra of the copolymer film (1.5 μm) on copper plates with increasing heating temperatures: (A) 380°C; (B) 400°C; (C) 420°C; (D) 440°C; (E) 460°C; (F) 480°C; (G) 500°C; (H) 520°C; (I) 550°C.

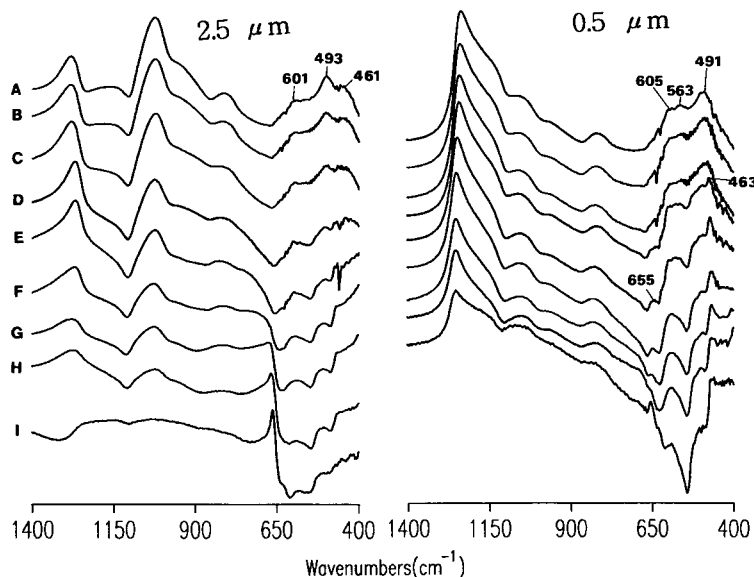


Figure 8 The changes in R-A spectra of the copolymer films (2.5 and 0.7 μm) on copper plates with increasing heating temperatures: (A) 380°C; (B) 400°C; (C) 420°C; (D) 440°C; (E) 460°C; (F) 480°C; (G) 500°C; (H) 520°C; (I) 550°C.

O—Si linkages decrease in intensity at 1248, 1052, and 814 cm^{-1} . As a result of the thermal decomposition of the Cu-containing SiO_x film, the film defects begin to exist in the barrier film and the copper surface becomes subjected to corrosion by the attack of air oxygen. Due to corrosion through the film defects, corrosion peaks begin to appear at 645, 598, and 573 cm^{-1} . The peak at 645 cm^{-1} corresponds to the LO mode of Cu₂O, and the peak at 598 cm^{-1} is designated as the TO mode of Cu₂O. The peak at 573 cm^{-1} is due to CuO formation. These corrosion peaks become stronger with increasing heating temperature, and they are observed as a single overlapped peak at 587 cm^{-1} in spectrum I.

In addition, the peak at 493 cm^{-1} is split into two peaks (498 and 469 cm^{-1}). This splitting is strongly related to the structural changes of the infinitive siloxane network. Copper ions from copper oxides, which are formed through the film defects, can migrate into the SiO_x film, and so a part of the siloxane network structure is changed into a Cu-rich phase by copper diffusion.^{32,33} Therefore, the Cu-rich phase is formed in the vicinity of the film defects. The peak at 498 cm^{-1} is assigned to Si—O bending in the Cu-poor phase, and the peak at 469 cm^{-1} , to Si—O bending in the Cu-rich phase. This splitting becomes remarkable with increasing heating temperature. However, the peaks from the barrier film are still observed in spectrum I and a great part of the copper sur-

face is not corroded even at 550°C. Accordingly, the barrier film still acts as a corrosion inhibitor for copper even if copper corrosion proceeds through the film defects.

Figure 8 shows the R-A spectra of the copolymers with different coating thicknesses on copper plates as a function of heating temperature. In the thick-coated sample (2.5 μm), both corrosion peaks and the splitting of the peak are observed at 380°C, but the Cu₂O peak is stronger than the CuO peak. This means that copper corrosion proceeds in the wider region. In the thin-coated sample (0.5 μm), corrosion peaks are observed at 380°C and the splitting of the peak is observed at 440°C. However, the peak at 655 cm^{-1} (LO mode of Cu₂O) is stronger in comparison with Figure 7. This means that the corroded part of the thin-coated sample is wider than Figure 7 because it has more film defects.

CONCLUSIONS

The thermooxidative degradation of poly(VI-co-VTS) on copper plates was investigated with FTIR-RAS. Thermal degradation on copper proceeded faster than on gold, due to the catalytic effect of copper on the copolymer degradation. Copper in the copolymer film as well as copper on the copper surface acted as a catalyst of thermal degradation of the barrier film. In addition, cop-

per in the copolymer film participated in SiO_x film formation and formed Cu-containing SiO_x film. However, as heating temperature increases, the thermal decomposition of Cu-containing SiO_x film proceeded. Thermal decomposition of Cu-containing SiO_x film caused the film defects and copper corrosion proceeded through these film defects. The formation of the film defects was easier in the thinner-coated sample, but thick-coated film is prone to crack formation due to the residual stress in the film. At 550°C, the barrier film still acted as a retardant of copper corrosion even if some copper oxides were formed through the film defects.

REFERENCES

1. J. Jang and H. Ishida, *J. Appl. Polym. Sci.*, **49**, 1957 (1993).
2. J. Jang and H. Ishida, *Corros. Sci.*, **33**, 1053 (1992).
3. H. Kim and J. Jang, *J. Appl. Polym. Sci.*, **64**, 2585 (1997).
4. H. Kim and J. Jang, *Polymer*, to appear.
5. J. Hansen, M. Kumagai, and H. Ishida, *Polymer*, **35**, 4780 (1994).
6. F. Eng and H. Ishida, *J. Appl. Polym. Sci.*, **32**, 5021 (1986).
7. H. Kim and J. Jang, *Polym. Bull.*, **38**, 249 (1997).
8. L. Bellamy, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, 1975.
9. F. Eng and H. Ishida, *J. Appl. Polym. Sci.*, **32**, 5035 (1986).
10. N. Colthup, L. Daly, and S. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1975.
11. S. Yoshida and H. Ishida, *J. Mater. Sci.*, **19**, 2323 (1984).
12. A. C. Miller, A. W. Czanderna, H. H. G. Jellinek, and H. Kachi, *J. Colloid Interf. Sci.*, **85**, 244 (1982).
13. H. H. G. Jellinek, H. Kachi, A. Czanderna, and A. C. Miller, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 1493 (1979).
14. M. C. Burrell, J. Fontana, and J. J. Chera, *J. Vac. Sci. Technol. A*, **6**, 2893 (1988).
15. M. G. Chan and D. L. Allara, *J. Colloid Interf. Sci.*, **47**, 697 (1974).
16. M. J. D. Low, K. H. Brown, and K. Inoue, *J. Colloid Interf. Sci.*, **24**, 252 (1967).
17. V. Bolis, L. Marchese, S. Coluccia, and B. Fubini, *Adsorp. Sci. Technol.*, **5**, 238 (1988).
18. M. B. Mitchell, V. R. Chakravarthy, and M. G. White, *Langmuir*, **10**, 4523 (1994).
19. T. Kaliyappan, C. S. Swaminathan, and P. Kannan, *Polymer*, **37**, 2865 (1996).
20. S. P. Kowalczyk, Y. H. Kim, G. F. Walker, and J. Kim, *Appl. Phys. Lett.*, **52**, 375 (1988).
21. R. M. Tromp, F. Legoues, and P. S. Ho, *J. Vac. Sci. Technol. A*, **3**, 782 (1985).
22. Unpublished result (H. Kim and J. Jang).
23. K. Yamamoto and A. Masui, *Appl. Spectrosc.*, **50**, 759 (1996).
24. Y. Yen and J. S. Wong, *J. Phys. Chem.*, **93**, 7208 (1989).
25. J. S. Wong and Y. Yen, *Appl. Spectrosc.*, **42**, 598 (1988).
26. K. Yamamoto and A. Masui, *Appl. Spectrosc.*, **48**, 775 (1994).
27. R. Hofman, J. G. F. Westheim, I. Pouwel, T. Fransen, and P. J. Gellings, *Surf. Interf. Anal.*, **24**, 1 (1996).
28. F. J. Boerio and L. Amorgan, *Appl. Spectrosc.*, **32**, 509 (1978).
29. H. Kim and J. Jang, *J. Appl. Polym. Sci.*, **68**, 775 (1998).
30. M. G. Voronkov, V. P. Mileshekevichand, and Y. A. Yuzhelevskii, *The Siloxane Bond*, Consultants Bureau, New York, 1978.
31. M. Zeldin, B. R. Qian, and S. J. Choi, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 1361 (1983).
32. S. Petit, A. Decarreau, C. Mosser, G. Ehret, and O. Grauby, *Clays Clay Miner.*, **43**, 482 (1995).
33. C. J. G. Van Der Grift, A. F. H. Wielers, A. Mulder, and J. W. Geus, *Thermochim. Acta*, **171**, 95 (1990).