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Corrosion protection on copper by new polymeric agents – polyvinylimidazoles

FREDERICK P. ENG, HATSUO ISHIDA
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA

Fourier transform infrared reflection–absorption spectroscopy (FTIRRAS) is applied to the study of corrosion protection of copper by an organic coating. Poly-N-vinylimidazole (PVI(1)) and poly-4(5)-vinylimidazole (PVI(4)) are demonstrated to be effective new polymeric anti-corrosion agents for copper at elevated temperatures. Oxidation of copper is suppressed even at 400° C. PVI(1) and PVI(4) are more effective anti-oxidants than the most commonly used corrosion inhibitors, benzotriazole and undecylimidazole, at elevated temperatures. These new polymeric agents are water soluble and easy to treat the metal surface with.

1. Introduction

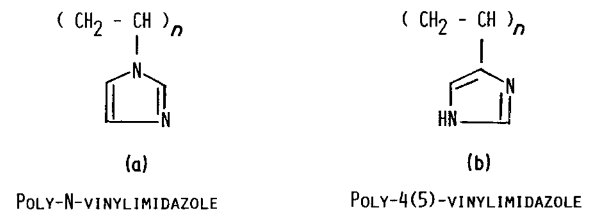
Azole compounds such as benzotriazole, benzimidazole, indazole and imidazoles are efficient anti-corrosion agents for copper and copper-based alloys [1–10]. Many experimental techniques [11–15] have been used to study the corrosion inhibition mechanisms, however, the mechanisms are still not well understood. It is believed that the complex formation between copper and nitrogen atoms would inhibit oxygen adsorption on copper surface [16–20].

Inhibitors mentioned above are small molecules in nature. Recently, there has been great emphasis in using polymers as corrosion inhibitors [21–37]. However, these inhibitors, which include different heterocyclic polymers, polythiopropionate, polymaleic acid and polyalkylolamide/alkenyl copolymers, were developed for protecting steel in sea water [21, 29], tap water [22] and in acidic environments [30, 31, 33]. Relatively very few or no polymeric inhibitors for copper, aluminium, and iron [28, 34–37] have been reported, especially in high temperature studies. In this study, we will present poly-N-vinylimidazole (PVI(1)) and poly-4(5)-vinylimidazole (PVI(4)) (Fig. 1) as new polymeric anti-corrosion agents for copper in elevated temperature environments. Polyvinylimidazoles (PVIs) are preferred because of the following reasons. PVIs have the imidazole ring as their pendant group which would lead to complex formation with copper. Furthermore, the polymers can easily form thin films of relatively higher ductility than small molecules on copper surfaces. It is known that the higher ductility would enhance the adhesion of the film to the substrate. Lastly, an amorphous polymer/copper complex is expected to have less defects which may be important in influencing the rate of oxidation of copper.

In this elevated temperature study, commonly used copper corrosion inhibitors for copper, benzotriazole and undecylimidazole will be used for comparison. Benzotriazole is one of the most effective and widely used corrosion inhibitors specifically for copper in both atmospheric and immersed environments for over 35 years. At the same time, undecylimidazole also exhibits superior anti-corrosion properties. The reactivity of imidazole with copper is very high, forming a thick imidazole/copper complex film which makes undecylimidazole an attractive corrosion inhibitor. Fourier transform infrared reflection–absorption spectroscopy (FTIRRAS) is utilized in the experiment. FTIRRAS is an external reflection technique which is useful for studying thin films on metal surfaces by reflecting infrared radiation from the metal surfaces at high, nearly grazing angles of incidence. The theory of the technique was developed by Francis and Ellison [38] and Greenler [39]. Cuprous oxide formation is used to follow the corrosion kinetics.

2. Experimental details

Both benzotriazole and urocanic acid were purchased from Aldrich Chemical Co, and azobis(isobutyronitrile) was from the Eastman Kodak Co. Undecylimidazole and N-vinylimidazole were supplied by Shikoku Chemical Co, and BASF Co, respectively. Copper plates (2.5 cm × 5.0 cm × 0.2 cm, ASTM B 125, type ETP) were mechanically polished with No. 5 chrome oxide, ultrasonically washed with acetone, rinsed with dilute hydrochloric acid and distilled water, and dried with a stream of nitrogen gas. Corrosion inhibitors were dissolved in either ethanol or methanol, solution cast onto copper substrates and air dried. Film thickness was calculated based on the concentration of the solution, density of the sample and the area of the copper surface. In this study, 150 nm thick films were used. The reflection–absorption (R–A) attachment (Harrick Scientific) along with a gold wire grid polarizer (Perkin-Elmer) were mounted in a Digilab FTS-14 Fourier transform infrared spectrometer equipped with a triglycine sulphate detector and purged with dry air. Spectra collected were the average of 200 scans at 4 cm^{-1} resolution using an optical velocity of 0.3 $\mathrm{cm\,sec}^{-1}$. The angle of incidence used was 75°.



Poly-N-vinylimidazole

Poly-4(5)-vinylimidazole

Figure 1 Molecular structure of the polyvinylimidazoles (a) PVI(1) and (b) PVI(4).

2.1. Purification of azobis(isobutyronitrile) (AIBN)

Crude AIBN 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.

2.2. Purification of N-vinylimidazole

Crude brownish N-vinylimidazole was distilled in vacuo (50° C/2.5 mm Hg) to yield a pure and colourless liquid.

2.3. Synthesis of poly-N-vinylimidazole [40]

A solution of N-vinylimidazole (30 g, 0.32 mol) and azobis(isobutyronitrile) (0.26 g, 0.0016 mol) in benzene (200 ml) was heated at 68° C with stirring under nitrogen for two days. The white precipitated polymer was collected by filtration, washed four times with benzene (20 ml) and dried in a vacuum oven (30 mm Hg) at 40° C for three days. The yield was 30 g (100% conversion). The weight average molecular weights of the polymer ranged from 5.5×10^4 to 1.3×10^6 [40]. The polymer, as suggested by nuclear magnetic resonance (NMR) studies, was atactic [41]. The density measured was $1.246\,\mathrm{g\,ml^{-1}}$.

2.4. Synthesis of 4(5)-vinylimidazole [42]

Urocanic acid (7.6 g, 0.055 mol) was decarboxylated at the melting point in vacuo in a distilling apparatus with a silicone oil bath of temperature 280° C. A heating tape with temperature set at 140° C was wrapped around the condenser to prevent the distillate from solidifying before reaching the receiver. A viscous and colourless liquid was collected; the yield was 2.0 g (26%). The product solidified upon cooling to room temperature.

2.5. Synthesis of poly-4(5)-vinylimidazole [42]

A solution of 4(5)-vinylimidazole (1.50 g, 0.016 mol) and azobis(isobutyronitrile) (5 mg, 0.030 mmol) in benzene (200 ml) was heated at reflux with stirring under nitrogen for three days. Afterward, the white polymer was collected by filtration, washed with benzene (20 ml) four times and dried in vacuum oven (30 mm Hg) at 40° C for three days. The yield was 0.9 g (60% conversion). The density measured was $1.246\,\mathrm{g\,ml^{-1}}$.

2.6. Synthesis of poly-N-vinylimidazole/copper(II) complex

To a PVI(1) (1.7 mg)/methanol (5 ml) solution was added cupric chloride (0.7 mg, 0.0041 mmol). After the solution was allowed to stand at room temperature overnight, blue crystals appeared at the bottom of the reaction flask. Blue crystals of PVI(1)/copper(II) complex were then collected and washed repeatedly with methanol.

2.7. Synthesis of poly-4(5)-vinylimidazole/copper(II) complex

To a PVI(4) (2.0 mg)/methanol (5 ml) solution was added cupric chloride (1.0 mg, 0.0059 mmol). After the solution was allowed to stand at room temperature overnight, green crystals appeared at the bottom of the beaker. Green crystals of PVI(4)/copper(II) complex were then collected and washed repeatedly with methanol.

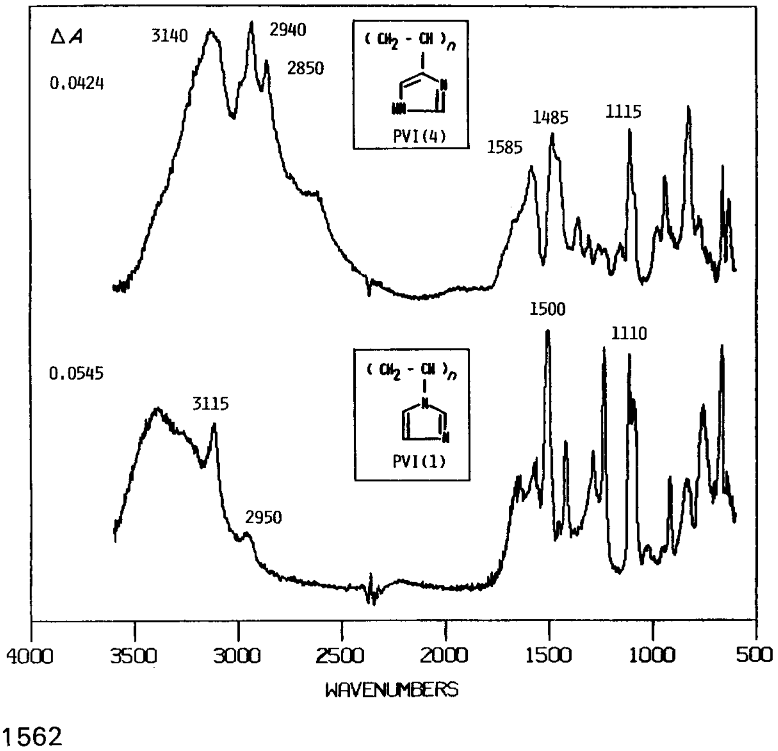


Figure 2 R–A spectra of PVI(1) and PVI(4).

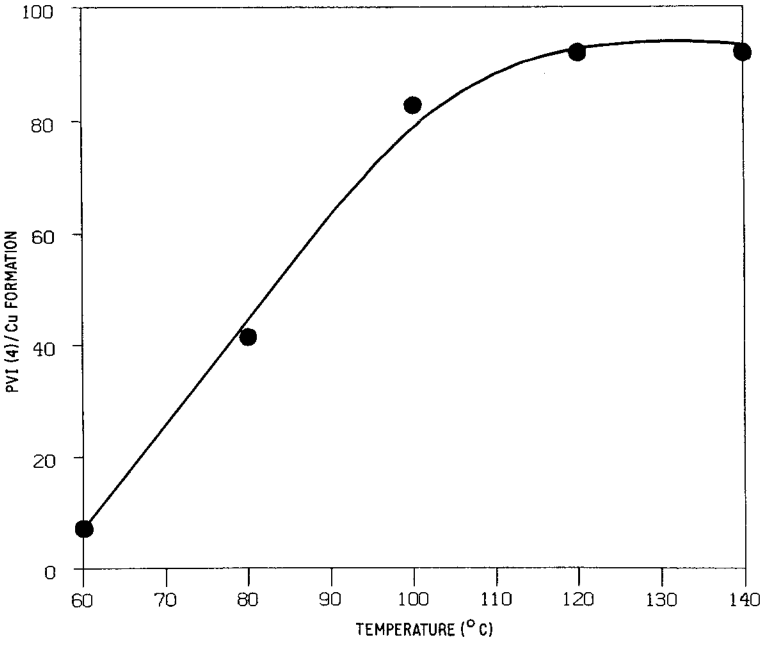


Figure 3 PVI(4)/Cu(II) formation against various temperatures heated for 15 min.

3. Results and discussion

3.1. Molecular structure of PVI/copper(II) complexes

Fig. 2 shows the reflection spectra of PVI(1) and PVI(4) coated on copper mirrors. The peak at 3140 cm^{-1} is assigned to the NH stretching mode. Peaks at 3115, 2950, 2940 and 2850 cm^{-1} are the CH stretching modes of the imidazole ring and the aliphatic chain. Peaks at 1585, 1500 and 1485 cm^{-1} are due to the ring stretching. Finally, peaks at 1115 and 1110 cm^{-1} are assigned to the CH in-plane bending of the imidazole ring.

From the study of the synthesized model compounds of PVI(1)/copper(II) and PVI(4)/copper(II), it was found that both polymers were capable of forming complexes with copper. Solubility tests indicated that the complexes were not soluble in water, methanol, or any other common organic solvents. The complex formation between the PVI thin film and copper mirror surface was studied both at room and elevated temperatures. First, 150 nm PVI films were deposited on the copper mirrors and the reflection spectra were taken. After various temperature treatments, the copper mirrors were washed with methanol, dried and the reflection spectra were taken again. Area of peaks at 1115 and 1110 cm^{-1} was used to follow the kinetics of the complex formation. The assumption of this experiment was that since PVI/copper(II) complexes were not soluble in methanol, therefore the amount of material remained on the copper surface would be due to the complex formed. At room temperature, PVI(1) formed complex instantly with copper once the polymeric film was solution cast onto the copper surface and dried. However, PVI(4) did not immediately complex with the copper. Fig. 3 shows that after heating at 60° C for 15 min, only 7% of the PVI(4) film complexed with the copper. It was not until the temperature reached 120° C before 92% of the PVI(4) complexed with copper. This phenomenon is likely to be caused by the conformational effects of the polymer. In each of the imidazole rings, there is an NH group causing the imidazole rings to interact with one another through hydrogen bonding intra- and intermolecularly. Such interactions cause a shrinkage, resulting in the exposure of aliphatic chains and the burying of the imidazole groups. As a consequence, steric hindrance prevents nitrogen atoms from complexing with copper. Thus, the rate of complex formation with copper ions is strongly influenced by the strength of hydrogen bonding.

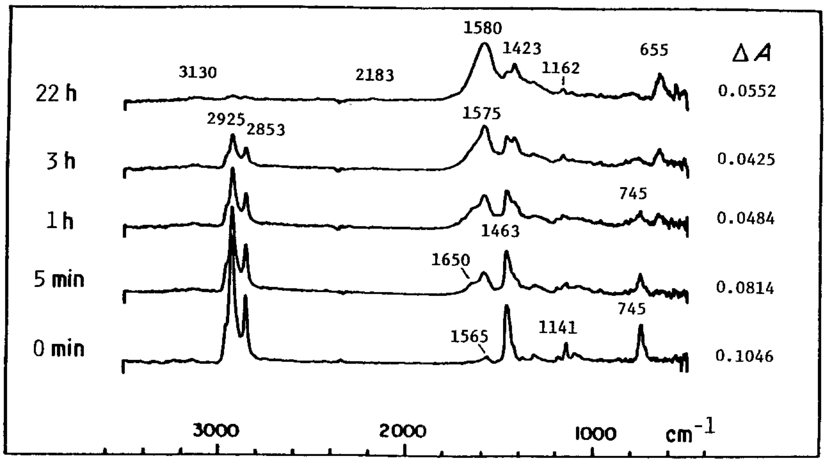
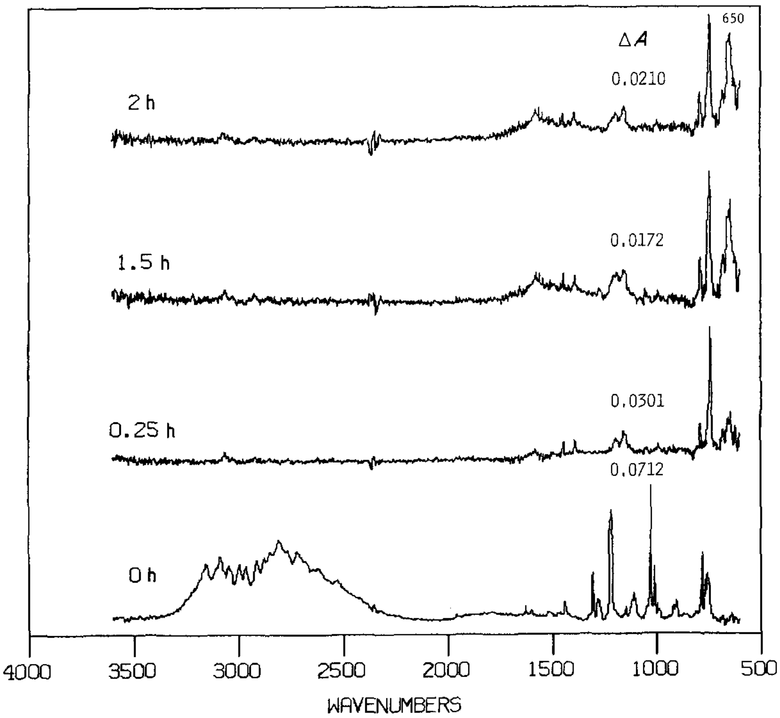


Figure 4 R–A spectra of undecylimidazole with heat treatment at 150° C.

Figure 5 R–A spectra of BTA with heat treatment at 150° C.



3.2. Comparisons of benzotriazole, undecylimidazole and PVIs (150 to 300° C)

Fig. 4 shows the reflection spectra of undecylimidazole on copper heated at 150° C for various lengths of time. Complex formation was observed without any heat treatment (spectrum at 0 min) [7]. Degradation of undecylimidazole was observed as the intensity of the peaks in the 2900 cm^{-1} region decreased gradually with prolonged heating. At the same time, new bands appeared around 1600 cm^{-1}. Further degradation also resulted in nitrile formation as indicated by the peak at 2183 cm^{-1}. Increase of copper oxide formation with heating time was observed at 650 cm^{-1}. At 150° C, benzotriazole showed complete degradation after only 15 min of heating (Fig. 5). Degraded product showed an intense peak at 740 cm^{-1}. Yet, this band can be due to the orientation effects with the benzotriazole molecules flatly adsorbed on the surface. Thus, because of the selection rule of the R–A technique, only the C–H out-of-plane bending mode (740 cm^{-1}) is observed. Nevertheless, cuprous oxide formation also occurred after 15 min and was even more prominent after 2 h.

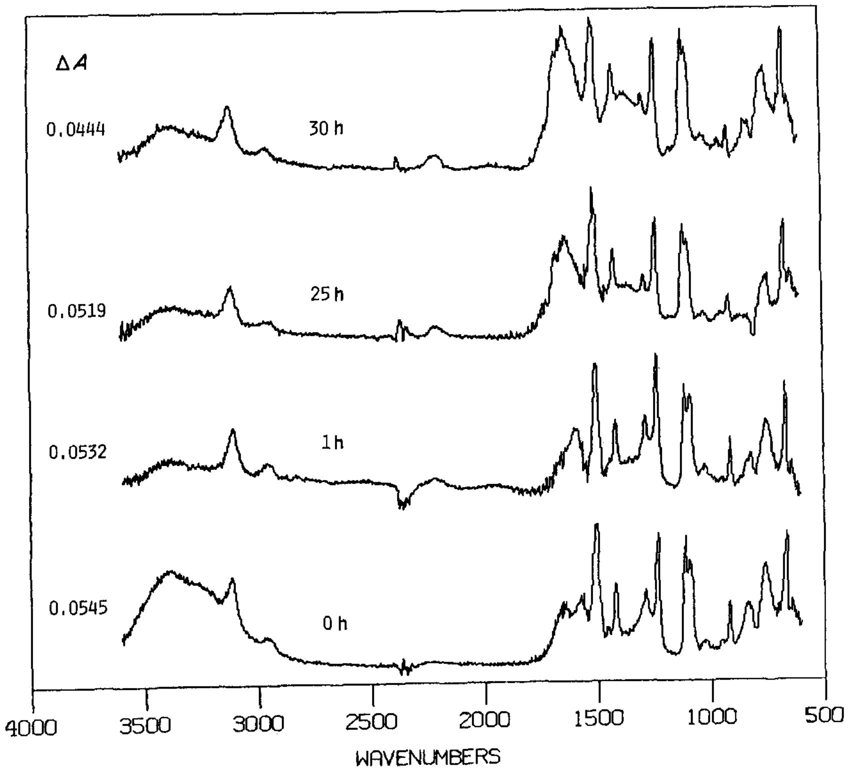


Figure 6 R–A spectra of PVI(1) with heat treatment at 150° C.

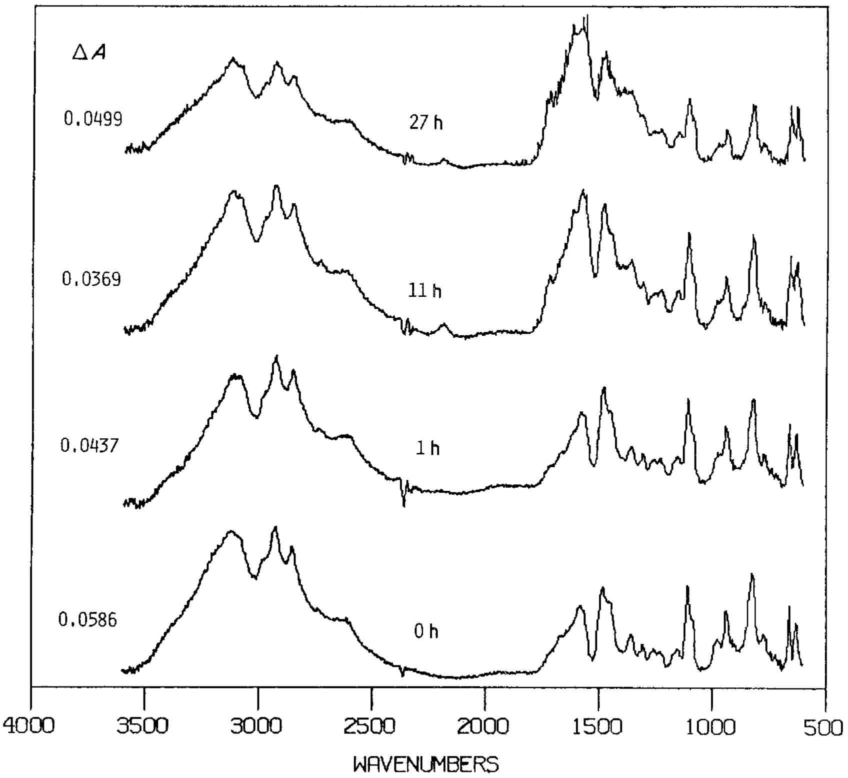


Figure 7 R–A spectra of PVI(4) with heat treatment at 150° C.

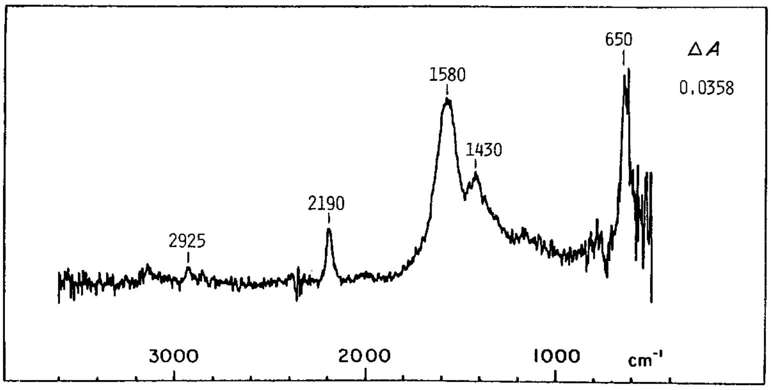


Figure 8 R–A spectra of undecylimidazole with heat treatment at 210° C.

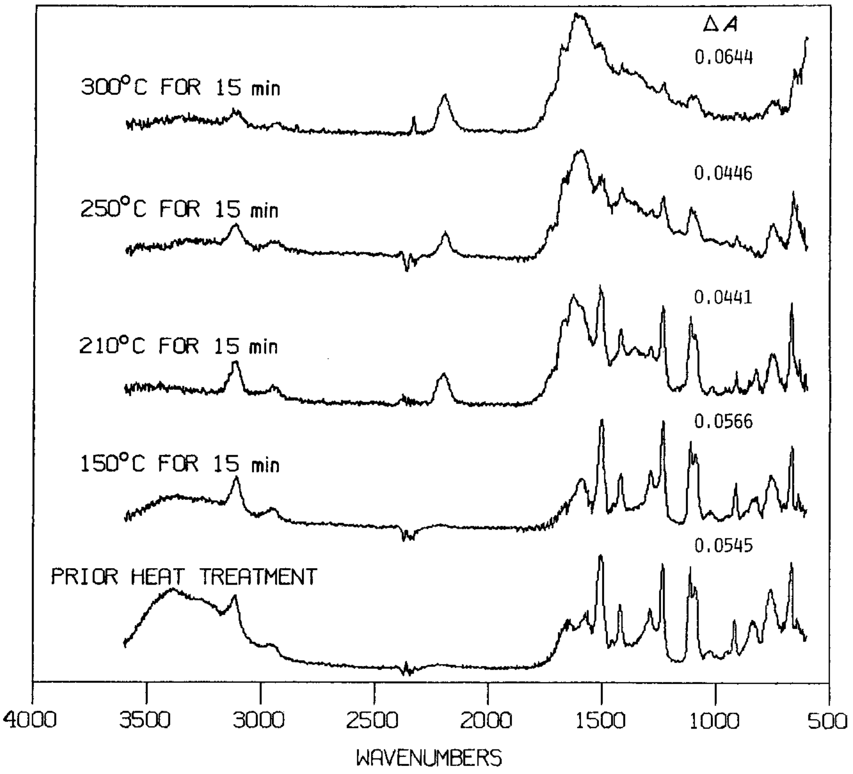


Figure 9 R–A spectra of PVI(1) with heat treatment at various temperatures.

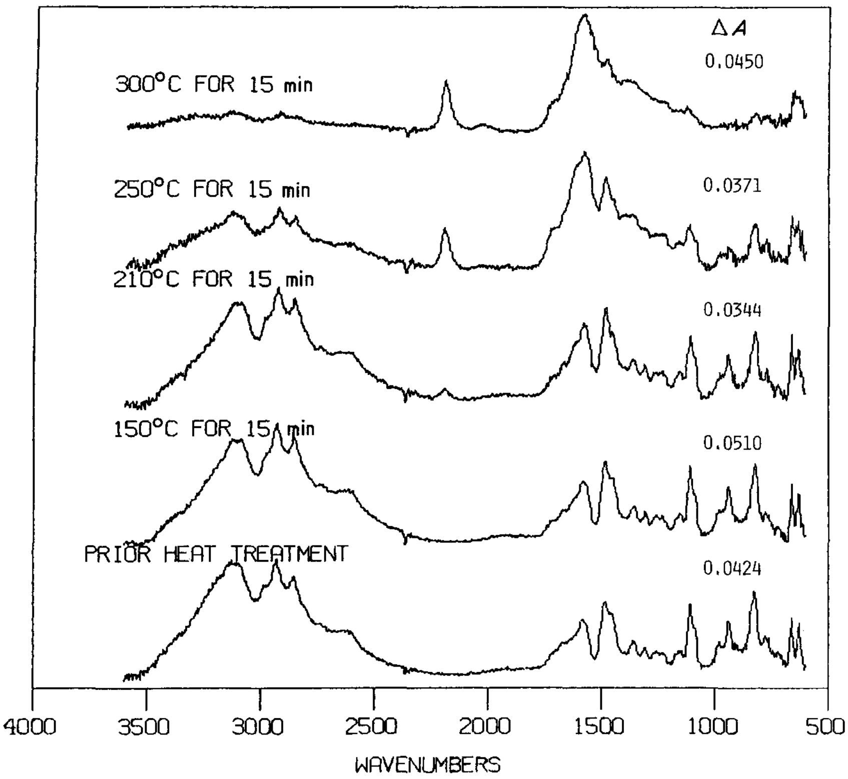


Figure 10 R–A spectra of PVI(4) with heat treatment at various temperatures.

As for PVI(1) and PVI(14) (Figs 6 and 7), no degradation was detected after 1 h of heating. Even after 27 or 30 h, little degradation was seen as the emergence of the nitrile peak at $2200\,cm^{-1}$ and carbonyl peaks at $1600\,cm^{-1}$ region was relatively small. No copper oxide was observed at any time for either polymer.

When the temperature was raised to 210° C, undecylimidazole was completely degradated after 15 min (Fig. 8). No imidazole ring structure was observed. The nitrile peak at $2190\,cm^{-1}$ was pronounced, and the copper oxide formation was intense. On the other hand, PVI(1) and PVI(4) degradation was relatively mild at 210° C after 15 min (Figs. 9 and 10). It was not until the temperature was raised to 250° C and higher that major degradation of the polymers was observed. Even in such degrading conditions, no copper oxide was detected at 210 or 250° C. At 300° C, where the polymers suffered relatively severe degradation, oxidation of copper was still suppressed.

3.3. High temperature study of PVIs (330 to 450° C)

Fig. 11 shows the reflection spectra of bare copper mirrors heated at high temperatures for 15 min. At 330° C, cuprous oxide was detected by the band absorbed at $655\,cm^{-1}$. However, at 350 and 400° C, two bands were observed near 611 and $655\,cm^{-1}$. According to the theory of reflection–absorption infrared spectroscopy developed by Greenler *et al.* [43], bands at 611 and $655\,cm^{-1}$ are assigned to the transverse optical and longitudinal optical modes of the high frequency phonon observed near $609\,cm^{-1}$ in

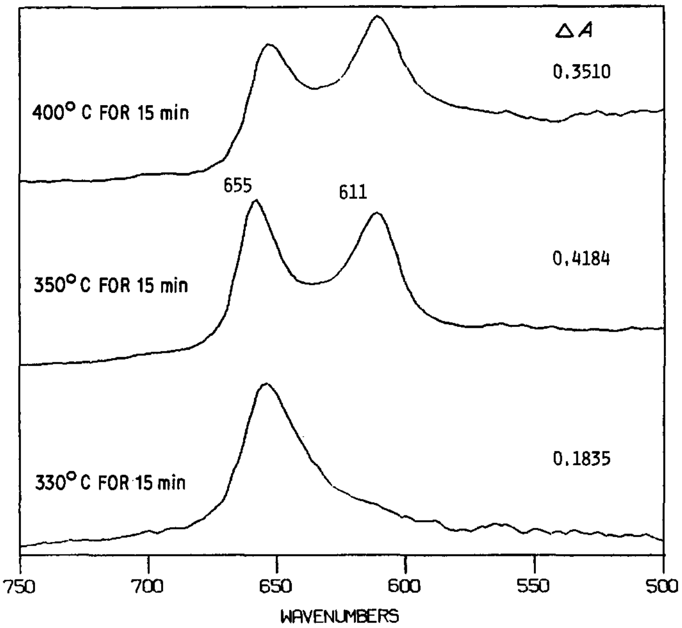


Figure 11 R–A spectra of bare copper with high temperature treatments.

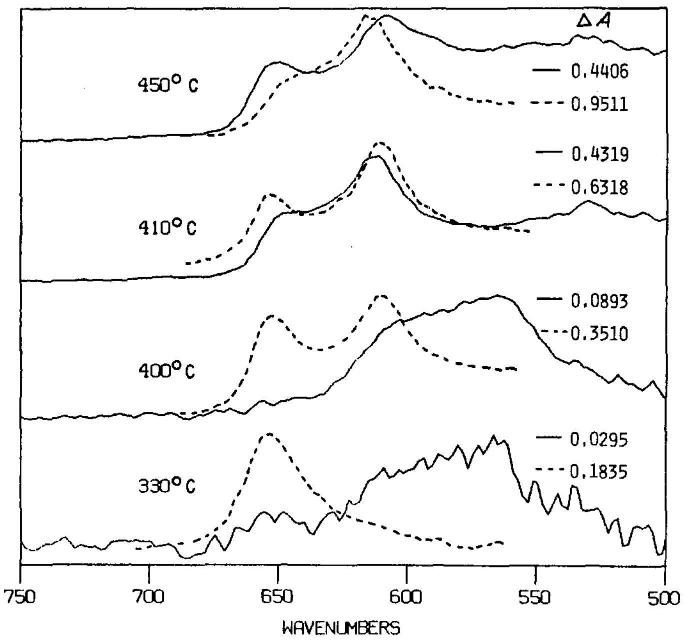


Figure 12 R–A spectra of PVI(1) with high temperature treatments. (———) PVI(1), (– – –) Copper reference.

dielectric spectra of cuprous oxide [44]. The band around 611 cm^{-1} was observed by Boerio and Armogan [45] with oxides having a thickness of about 200 nm or thicker.

Fig. 12 shows the results of PVI(1) after being heated at various high temperatures for 15 min. The bands of cuprous oxides formed on bare copper mirrors at corresponding temperatures are superimposed on the PVI(1) spectra for direct comparisons. The scale of the two types of spectra is shown by the difference between the maximum and minimum absorbance, ΔA. Note that no cuprous oxide formation was observed at 330 or 400° C. In fact, at 400° C the polymer coated surface of the copper mirrors remained mostly shiny whereas the bare reference copper surface turned dull with a layer of reddish-black scale on it. At 410° C or higher, the polymer was no longer protecting the copper surface. The two cuprous bands near 611 and 655 cm^{-1} began to emerge. Even so, at 450° C, the amount of oxides formed was much less than that of bare copper. Similar results were obtained for PVI(4) (Fig. 13) where no significant cuprous oxide was observed at or below 400° C. Fig. 14 summarizes the high temperature study with a plot of relative cuprous oxide formation against temperatures. As the temperature went up, the amount of cuprous oxide formed on bare copper also increased. However, for the polymer samples, it is interesting to note that the transition from no oxide to oxide formation at 410° C is relatively sharp.

4. Conclusions

Polyvinylimidazoles are effective anti-oxidants for copper at elevated temperatures. Below 250° C, there is no major degradation of the coated polyvinylimidazole films on copper. Furthermore, degraded polyvinylimidazole films can suppress oxidation even at 400° C. Finally, polyvinylimidazoles are more effective anti-oxidants than benzotriazole and imidazoles at

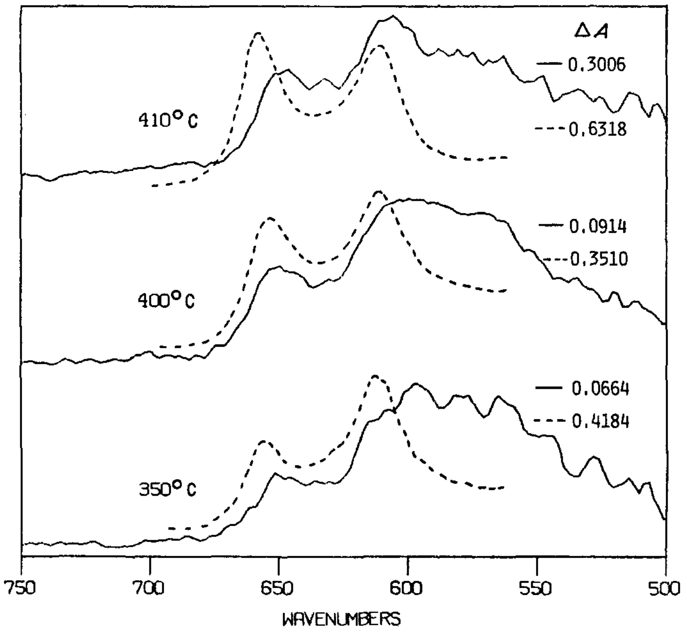


Figure 13 R–A spectra of PVI(4) with high temperature treatments. (———) PVI(4), (– – –) copper reference.

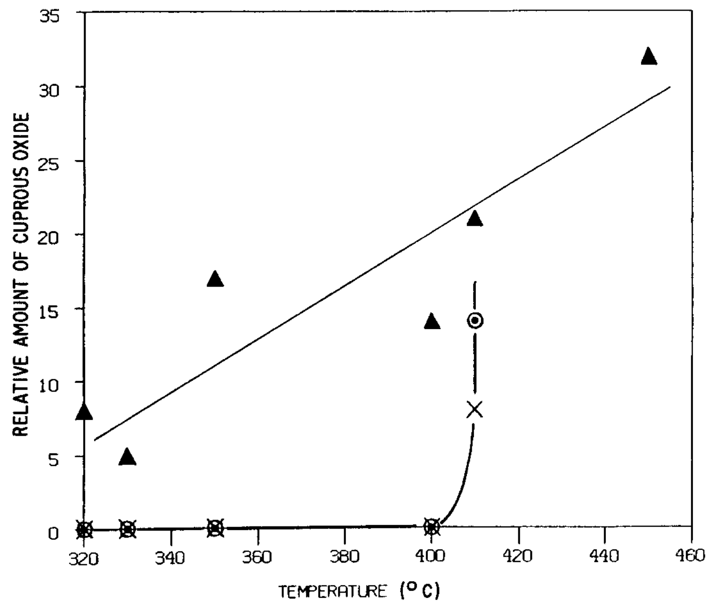


Figure 14 Relative amount of oxides formed on bare, PVI(1) and PVI(4) copper against various high temperatures. (▲) bare copper, (⊙) PVI(1), (×) PVI(4).

elevated temperatures. It is also demonstrated that FTIRRAS is a useful technique to study degradation of polymeric coatings and corrosion of metal simultaneously.

Acknowledgements

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