Silane-modified poly(vinylimidazole) corrosion inhibitors for copper

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Fourier-transform infra-red spectroscopy was used to study the thermal stability of silane-modified vinylimidazole copolymers on both KBr plates and copper coupons. The copolymers were synthesized by free-radical polymerization of γ-methacryloxypropyltrimethoxysilane and *N*-vinylimidazole. The ability of these copolymers to inhibit the oxidation of copper at elevated temperatures was compared to that of poly(*N*-vinylimidazole). The silane acted as a scavenger for the water released by the imidazole ring during heating. Upon heating, the silane methoxy groups hydrolysed and condensed to form siloxane linkages.

(Keywords: poly(vinylimidazole); silane modification; corrosion inhibition)

INTRODUCTION

Imidazoles (*Figure 1*) have been shown to be effective corrosion inhibitors for copper. These compounds are thought to be similar to benzotriazole (*Figure 1d*) in that they form a protective barrier film with the copper surface[1–17]. Benzotriazole films have been shown to suppress both the oxidation and the reduction of copper. Although the anticorrosion mechanisms of these compounds are not well understood, it is thought that complex formation between copper and one or more of the nitrogens in the azole ring suppresses the absorption of oxygen onto the copper surface[18–26].

Eng and Ishida showed that poly(vinylimidazole) (PVI) was effective in suppressing the oxidation of copper in air above 200°C[13–16]. This result could not be achieved by benzotriazole or the other azole molecules previously discussed. When subjected to humid conditions however, PVI was not able to inhibit oxide formation. Experiments indicated that the oxidation of the copper coupon was accelerated[13]. Like most azole compounds, PVI has been found to bind water tenaciously to the imidazole ring[27,28]. Silane coupling agents have been used with PVI to help protect copper under humid conditions[29].

This paper examines the use of a silane coupling agent to help reduce PVI's susceptibility to water. Two copolymers of γ-methacryloxypropyltrimethoxysilane (γ-MPS) and *N*-vinylimidazole were synthesized. The first copolymer analysed was rich in silane units, while the other one was rich in imidazole units. The chemical structures of these copolymers are given in *Figure 2*. Fourier-transform infra-red spectroscopy was used to study the thermal degradation of the copolymers on both KBr plates and copper coupons. In addition to the copolymers, physical mixtures of γ-MPS and PVI were prepared and tested on the copper mirrors. Mixtures of hydrolysed γ-MPS and PVI were also analysed.

Reflection–absorption Fourier-transform infra-red spectroscopy (*FT*i.r.-r.a.s.) was the main characterization tool used in this work. This technique, which was developed by Francis and Ellison[30] and Greenler[31–33], can be used to obtain information on both the molecular structure and chemical bonding of the adsorbate. In some

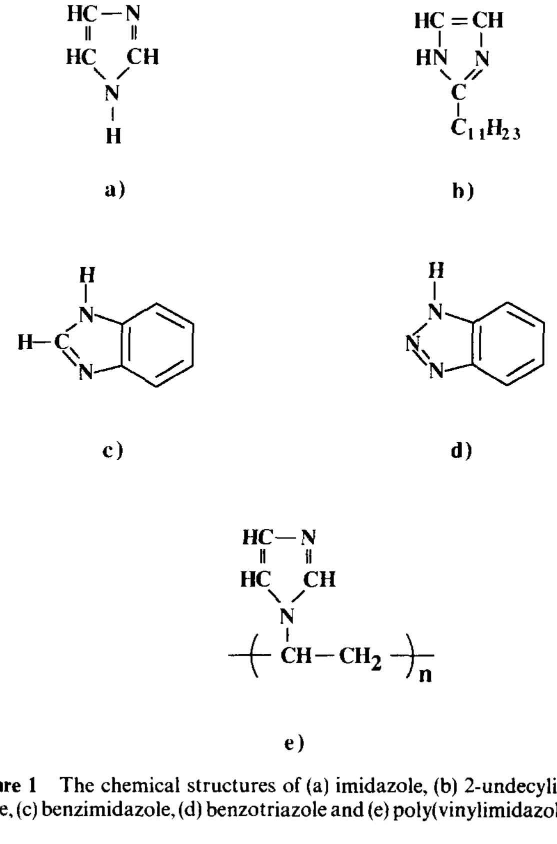

Figure 1 The chemical structures of (a) imidazole, (b) 2-undecylimidazole, (c) benzimidazole, (d) benzotriazole and (e) poly(vinylimidazole)

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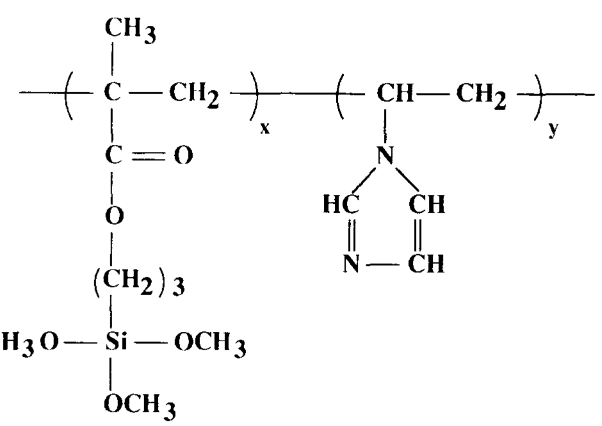


Silane-Rich Copolymer: x=70, y=30

Imidazole-Rich Copolymer: x=15, y=85

Figure 2 The chemical structures of the silane-modified copolymers discussed in this work. One of the copolymers comprised 70% silane units and 30% imidazole units whereas the second was composed of 15% silane units and 85% imidazole units

cases, this technique can also be used to gain information on the orientation of the molecules relative to the reflective substrate[33,34].

EXPERIMENTAL

Copper plates (2.54 cm × 5.08 cm × 0.28 cm, type ETP, Metal Samples Inc.) were ground down to a 5 μm finish with a series of SiC papers and polished to a 0.25 μm mirror finish using diamond paste (Struers). The coupons were degreased in spectrophotometric-grade acetone and hexane, and rinsed with distilled water and acetone before drying in a stream of dry argon. The copper coupons were coated immediately after cleaning.

All infra-red spectra were taken on a Bomen Michelson-MB Fourier-transform infra-red spectrometer equipped with a nitrogen-cooled mercury-cadmium-telluride (MCT) detector. The specific detectivity D^* of the detector was 1×10^{10} cm Hz$^{1/2}$ W^{-1}. The sample chamber was purged with liquid nitrogen for 20 min before the spectra were collected. The spectra were taken at a resolution of 4 cm^{-1} and a fixed scanning speed of 0.2 cm s^{-1}. Transmission spectra were obtained by solution casting the polymers onto KBr salt plates. Methanol was used as the casting solvent for the silane copolymers and ethanol was used for the mixtures of γ-MPS and PVI. The thickness of these films was estimated to be approximately 3 μm. This calculation was based on the density of the sample, area of the plate, concentration of the solution and volume used.

Reflection spectra were obtained by mounting the reflection–absorption attachment (Harrick Scientific) along with a gold wire grid polarizer (Specac) into the spectrometer described above. The spectra were obtained by averaging 200 scans. The angle of incidence was 75°. A freshly polished copper coupon was used to obtain the reference spectrum.

The silane-modified copolymers were prepared by reacting γ-MPS (Toshiba Silicone) and *N*-vinylimidazole (Aldrich) in benzene. Azobisisobutyronitrile (Kodak) was used as the initiator. A more detailed procedure is described elsewhere[35]. The silane was purified by column chromatography and distilled before using. A mixture of benzene and acetonitrile was used as the mobile phase and silica gel was used as the packing material. *N*-Vinylimidazole was dried over calcium hydride and vacuum distilled. The azobisisobutyronitrile was recrystallized twice from warm methanol and dried before using.

The copolymer solution was allowed to stir at 60°C for 24 h under argon. Next, the copolymers were purified by precipitation into hexane. This process was repeated until gel permeation chromatography (g.p.c.) revealed that all residual monomers had been removed. The copolymers were dried overnight in a vacuum oven.

PVI was synthesized from *N*-vinylimidazole (Aldrich). The details of this polymerization are given elsewhere[13]. PVI films on copper were prepared by dissolving the polymer in anhydrous ethanol to yield a concentration of 0.5 g l^{-1}. Using a microsyringe, 50 μl of the solution was cast onto copper plates and allowed to dry in a saturated ethanol atmosphere. A similar procedure was followed for films cast from mixtures of PVI and γ-MPS. The total concentration of these solutions was 0.5 g l^{-1}. Mixtures comprising 10% γ-MPS/90% PVI, 30% γ-MPS/70% PVI and 50% γ-MPS/50% PVI were tested on copper. The concentration is shown in percentage by weight. An identical procedure was followed for mixtures of PVI and hydrolysed γ-MPS.

The γ-MPS (Petrarch Systems Inc.) used in the mixture portion of this work was purified as described above. The hydrolysed γ-MPS was prepared[36] by first dissolving the coupling agent into a 7:3 volume ratio of ethanol and distilled water to yield a final concentration of 43.5 mg ml^{-1}. The pH of the distilled water was adjusted to 3.5. The mixture was allowed to stir for 1 h before it was mixed with the PVI and solution cast onto the copper coupons.

RESULTS AND DISCUSSION

The transmission infra-red spectra of the silane-rich copolymer and the imidazole-rich copolymer are presented in *Figure 3*. The infra-red band assignments for both copolymers are listed in *Table 1*. Spectra of γ-MPS homopolymer (spectrum A) and PVI (spectrum D) are included in *Figure 3* for comparison.

The thermal stability of the silane-rich copolymer was first tested using KBr salt plates. Infra-red spectra were

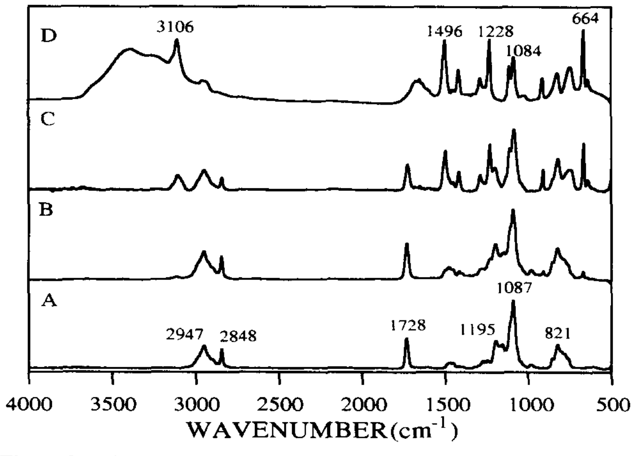


Figure 3 The transmission infra-red spectra of (A) homopolymer of γ-MPS, (B) silane-rich copolymer, (C) imidazole-rich copolymer and (D) poly(vinylimidazole)

Table 1 I.r. bands of the silane- and imidazole-rich copolymers

Wavenumber (cm^{-1})		
Silane-rich copolymer	Imidazole-rich copolymer	Assignment
3110	3106	C=CH/HC=N stretch
2947	2945	Asymmetric CH_3 stretch
2848	2848	OCH_3 stretch
1727	1722	C=O stretch
1472		CH_2 deformation
1414	1415	CH_2 bend and ring stretch
	1285	Ring vibration
1227	1228	Si–CH_2 wag/ring vibration
1195	1197	OCH_3 rock
1150		C–C–O stretch
	1109	CH in-plane ring mode
1088	1084	SiOC asymmetric stretch/CH in-plane ring mode
980		CH_2 wag
	908	CH out-of-plane bending
822	819	SiOC symmetric stretch
	755	CH_2 rocking
667	665	Ring torsion
	639	C=CH/N=CH wag

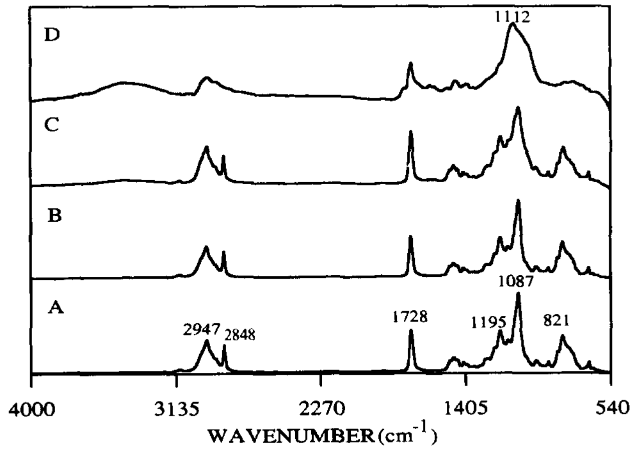


Figure 4 Infra-red spectra of the silane-rich copolymer solution cast onto KBr plates after (A) no heat treatment, (B) heating at 100°C for 15 min, (C) heating at 200°C for 15 min and (D) heating at 300°C for 15 min

recorded after heating the films at 100, 200 and 300°C for 15 min. These spectra are shown in *Figure 4*. No changes were detected between the as-cast film (spectrum A) and the film heated at 100°C (spectrum B). After heating the film at 200°C for 15 min (spectrum C), a slight broadening of the $SiOCH_3$ antisymmetric stretch at 1087 cm^{-1} is observed. More severe changes are seen in the film heated at 300°C for 15 min (spectrum D). The OCH_3 stretching mode at 2848 cm^{-1} has completely disappeared. The new peak at 1112 cm^{-1} has been assigned to siloxane (Si–O–Si) bond formation. These changes suggest that the silane portion of the molecule has hydrolysed and condensed[37,38]. It is possible that the imidazole moiety, which has been shown to catalyse esterification as well as hydrolysis reactions[28], may have accelerated the formation of a siloxane network. Although eventual gelation was observed for both the silane-rich and imidazole-rich samples, the shelf-life of the silane-rich copolymer was longer. Infra-red spectra taken of these silane-rich and imidazole-rich gels revealed that the asymmetric and symmetric Si–O–C bands had been replaced by Si–O–Si vibrations. The imidazole ring appeared to be intact. It should be noted that gelation was not observed with the γ-MPS homopolymer. These results are supported by Kumagai and coworkers[39]. Using cross-polarization magic-angle spinning (c.p.-m.a.s.) ^{29}Si n.m.r. and *FT*i.r.-r.a.s. spectroscopy, they compared the condensation rates of several alkoxysilane homopolymers and corresponding alkoxysilane–vinylimidazole copolymers. They found that the condensation rate of the imidazole copolymers was much higher than that of the corresponding alkoxysilane homopolymers.

In addition to siloxane bond formation, a reduction in intensity as well as broadening of the carbonyl stretch at 1728 cm^{-1} is also seen in the spectrum of the as-cast silane-rich copolymer film tested at 300°C (spectrum D in *Figure 4*). This indicates possible cleavage of the ester linkage and formation of complex crosslinked structures.

Similar degradation studies were also performed on copper plates. These results are depicted in *Figure 5*. The thickness of these films was 200 nm. The r.a.s. spectra of the as-cast silane-rich copolymer is shown as spectrum A. Few differences can be seen between this r.a.s. spectrum and the corresponding transmission spectrum (A) shown in *Figure 4*. This would suggest that the silane-rich copolymer is randomly oriented on the copper surface.

Little degradation is seen for the silane-rich copolymer heated on copper at 100°C for 15 min (*Figure 5*, spectrum B). The film heated at 200°C (spectrum C) does, however, exhibit some degradation. The shift in the $SiOCH_3$ asymmetric peak from 1086 to 1120 cm^{-1} indicates that some of the silane methoxy groups have started to hydrolyse and condense.

No original copolymer peaks can be seen in the r.a.s. spectrum of films heated at 300°C on copper (spectrum D). The peak at 1194 cm^{-1} has been assigned to formation of silica or silicate-containing material on the copper surface. The shoulder at 1120 cm^{-1} indicates that some siloxane bonds are still present. It has been shown that the stability of the hydrocarbon substituents attached to a siloxane backbone is reduced as the samples are heated. Oxidation of alkyl substituents is common even at temperatures near 150°C[40]. This would result in more siloxane network formation. The region between 700 and

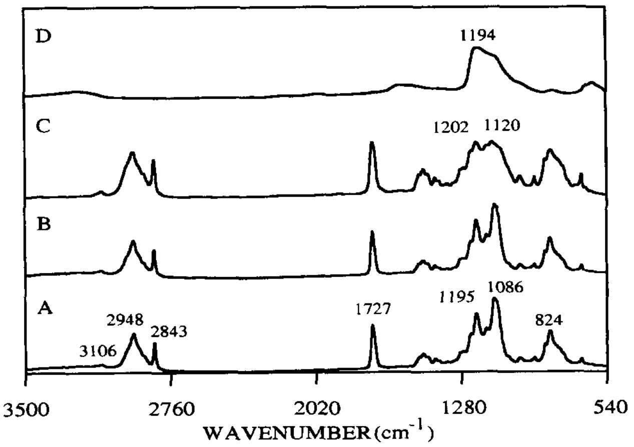


Figure 5 R.a.s. spectra of the silane-rich copolymer solution cast onto copper plates after (A) no heat treatment, (B) heating at 100°C for 15 min, (C) heating at 200°C for 15 min and (D) heating at 300°C for 15 min

540 cm^{-1} in spectrum D contains bands relating to the formation of both cuprous (Cu_2O) and cupric (CuO) oxides. This region will be discussed in more detail later in this paper.

On comparing *Figures 4* and *5*, it can be seen that the degradation of the polymer on copper is accelerated. This result was not surprising. It is well known that copper will accelerate the oxidation of polymer films[41–55]. Hydroperoxides as well as other degradation products formed during the oxidation of the polymer film may react with the copper oxides present at the metal/polymer interface to form copper carboxylate salts. These salts may diffuse into the bulk of the polymer film and thus function as possible carriers of copper ions into the polymer. Scattering experiments conducted by Jellinek and coworkers[50] have shown that copper oxide films are reduced and reoxidized during oxidation of the polymer film. Work done on solution-cast polyimide films by Kowalczyk *et al.*[52] indicates that solvent plays an important role in both the aggregation and migration of copper ions from the polymer/metal interface into the bulk of the film.

The degradation studies were repeated for the imidazole-rich copolymer. The transmission spectrum of the as-cast imidazole-rich film is given in spectrum A in *Figure 6*. As in the case of the silane-rich copolymer, little degradation is seen for the films heated at both 100°C (spectrum B) and 200°C (spectrum C). However, drastic changes are noticed after heating the film at 300°C for 15 min (spectrum D). Previous work done on the oxidation of PVI indicates that the broad region between 1800 and 1500 cm^{-1} consists of several bands relating to the thermal oxidation of the imidazole ring[13–15]. Examples of these bands include several different carbonyl products as well as unconjugated double bonds and possible protonation of the pyrrole nitrogen. The band at 1110 cm^{-1} has been assigned to Si–O–Si formation. The thermal stability of physical mixtures of γ-MPS homopolymer and PVI was also tested on KBr plates. Few changes were noted in the spectra of films heated at 100°C for 15 min. After thermal treatment at 200°C for 15 min, hydrolysis and condensation of the silane methoxy groups were detected. Continued heating of these films at 200°C for 45 min resulted in more siloxane formation. No changes were detected in the imidazole ring vibrations. However, heating these films at 300°C for 15 min resulted in cleavage of the imidazole rings as well as siloxane bond formation. This is analogous to the behaviour seen with the silane-rich films.

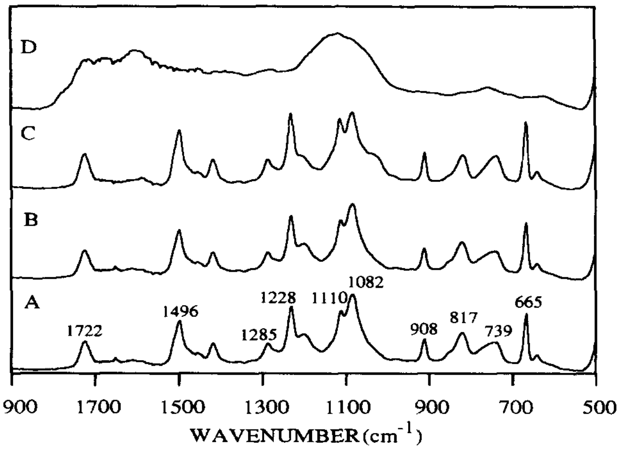


Figure 6 Infra-red spectra of the imidazole-rich copolymer solution cast onto KBr plates after (A) no heat treatment, (B) heating at 100°C for 15 min, (C) heating at 200°C for 15 min and (D) heating at 300°C for 15 min

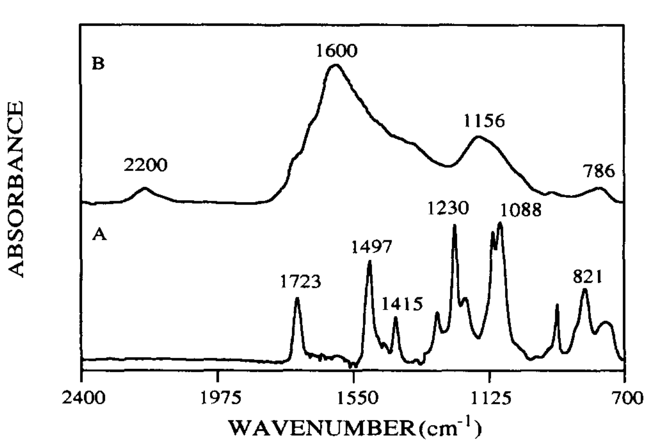
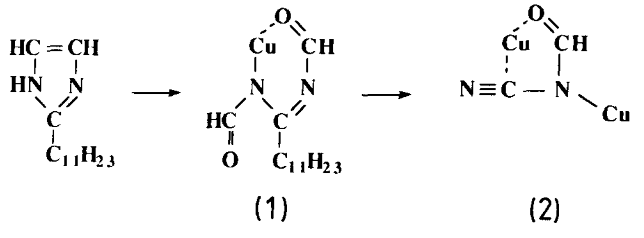


Figure 7 R.a.s. spectra of the imidazole-rich copolymer solution cast onto copper plates after (A) no heat treatment and (B) heating at 300°C for 15 min

The r.a.s. spectrum of the imidazole-rich copolymer on copper is shown in *Figure 7* (spectrum A). Few differences exist between the r.a.s. and transmission spectra of the imidazole-rich film. This indicates that this copolymer is also randomly oriented on the copper surface. The r.a.s. spectrum of this film after heating at 300°C for 15 min is presented in *Figure 7* (spectrum B). The peak at 1156 cm^{-1} is due to Si–O–Si network formation, while the region located between 1800 and 1500 cm^{-1} comprises bands relating to imidazole ring oxidation products[13–15]. These bands were described previously. The band at 2200 cm^{-1} is assigned to nitrile formation[5–9,13–15]. In the case of the films tested on KBr, nitrile formation was only observed for samples heated at 400°C for 15 min. This reflects the catalytic activity of the copper substrate.

Thermal degradation studies of PVI by Eng and Ishida[13–15] indicate that nitrile formation resulted due to cleavage of the imidazole rings. Ring cleavage was found to occur prior to the oxidation and/or scission of the polymer chain. The formation of a nitrile species was also seen with lower-molecular-weight imidazole analogues such as undecylimidazole (*Figure 1b*). Yoshida and Ishida[5–9] reported that, when undecylimidazole was heated at 150°C, ring cleavage occurred first. This was followed by elimination of the alkyl chain and oxidation of the imidazole ring. A schematic describing this degradation process is shown below:



Undecylimidazole ring cleavage occurred between C4 and C5 and resulted in the formation of (**1**). Upon continued heating, a final degradation product, (**2**), with perpendicular nitrile–metal interaction, was hypothesized.

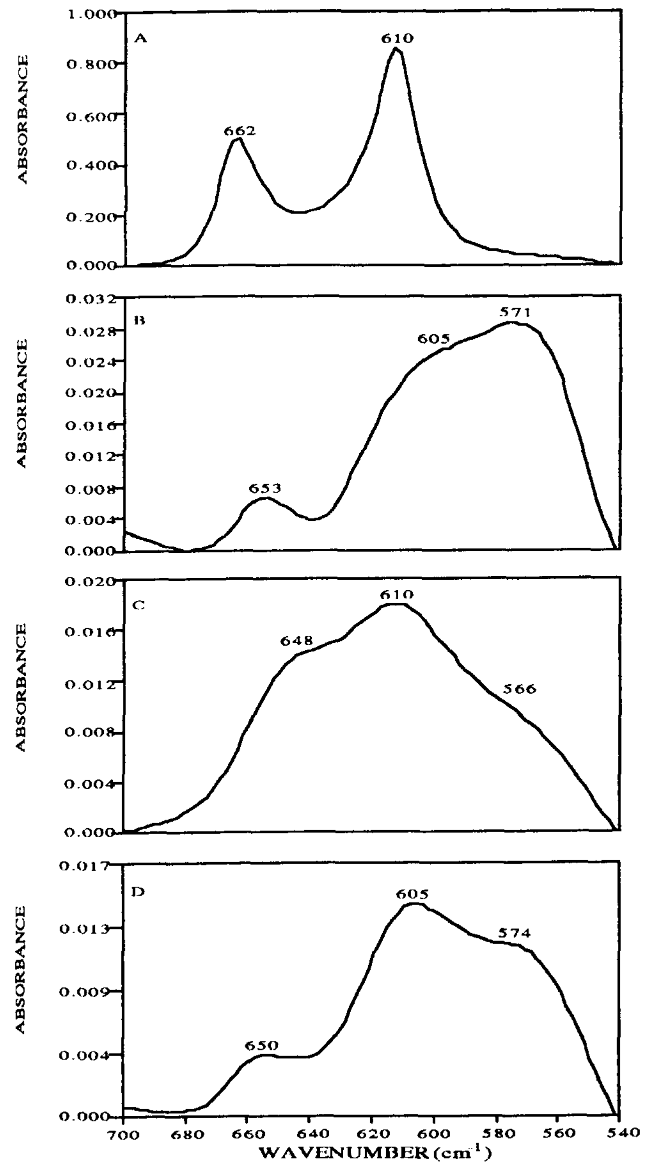


Figure 8 The copper oxide region (700–540 cm^{-1}) of the r.a.s. spectrum of (A) control sample (no coating), (B) PVI, (C) silane-rich copolymer and (D) imidazole-rich copolymer after heating at 300°C for 15 min

The copper oxide region of the r.a.s. spectrum provides much insight into the effectiveness of the silane-modified imidazole inhibitors. In order to evaluate the ability of these compounds to inhibit copper oxidation at 300°C, a control experiment was first performed. A freshly polished copper coupon was heated in air at 300°C for 15 min and the r.a.s. spectrum was taken. This spectrum is shown in *Figure 8* (spectrum A). This spectrum is characterized by two bands at 662 and 610 cm^{-1}, which have been assigned previously to the longitudinal and transverse optical modes of Cu_2O, respectively[56–59]. Boerio and Armogan[57] have shown that the band at 610 cm^{-1} should only be seen for oxide thicknesses greater than 200 nm. If cupric oxide was present, the reflection spectrum would be characterized by a band near 570 cm^{-1} (refs. 56–58).

The copper oxide region of the reflection spectrum of PVI is shown in *Figure 8* (spectrum B) for comparison. Curve fitting of this spectrum revealed that it is composed of three peaks at 653, 605 and 571 cm^{-1}. This suggests that both Cu_2O and CuO are formed when the PVI-coated specimen was heated at 300°C for 15 min. The peak at 571 cm^{-1} corresponds to CuO formation, whereas the peaks at 662 and 602 cm^{-1} are assigned to Cu_2O formation. The discrepancies between these peak positions and those reported by Boerio and Armogan can be explained by optical effects[57]. The presence of these copper oxides on the oxidized PVI surface was confirmed by X-ray photoelectron spectroscopy (x.p.s.)[60]. These results were described above. Similar results were found by Dezerville and coworkers[17].

From spectra A and B in *Figure 8*, it is apparent that the formation of cuprous oxide is accelerated for the PVI sample. It is thought that the water tightly bound to the imidazole ring is released during thermal treatment and is responsible for this enhancement. The presence of water has been shown to enhance the diffusion of copper ions into the polymer film[61].

The copper oxide region of the silane-rich copolymer after heat treatment at 300°C for 15 min is shown in *Figure 8* (spectrum C). Curve fits of this spectrum reveal that it comprises three bands at 648, 610 and 566 cm^{-1}. This indicates that both CuO and Cu_2O are formed during heating. Similar results were found for the imidazole-rich copolymer. The spectrum of the copper oxide region for samples heated at 300°C is depicted in spectrum D. This region is composed of bands at 650, 605 and 574 cm^{-1}. In comparison to the copper oxide region of PVI, less CuO formation was found for the silane-modified copolymers. This would suggest that the addition of silane has helped to displace the water released by the imidazole ring during heating. It is interesting to note that adhesion studies conducted by Tsuchida and coworkers[62] indicate that some imidazole–silane copolymer films on copper exhibited higher peel strength than uncoated or epoxy–silane coated copper foils.

In addition to studying the behaviour of the silane–imidazole copolymers on copper, physical mixtures of γ-MPS and PVI were also evaluated. These experiments were designed to gain insight into the role of the silane coupling agent during the oxidation process. The copper oxide region of a 10% γ-MPS/90% PVI mixture by weight is given in *Figure 9* (spectrum A). In comparing this spectrum to that of PVI shown in *Figure 8* (spectrum B), one can see that the intensity of the peak corresponding to CuO has been significantly reduced.

By increasing the total silane content to 30% by weight, a further reduction in the CuO peak at 566 cm^{-1} is detected. The r.a.s. spectrum of the oxide region corresponding to this mixture is given in spectrum B in *Figure 9*. Although a decrease is seen in the intensity of the CuO band, the peaks corresponding to Cu_2O increased in intensity. When a mixture consisting of 50% by weight silane was tested, no appreciable CuO was formed when the film was heated at 300°C. This spectrum is presented in C. Again, an increase in the intensity of the Cu_2O bands was observed when more silane was incorporated into the mixture. These results suggest that the γ-MPS is acting as a scavenger for the water that is released as the modified PVI film is heated. Although the exact mechanism is unknown, it is thought that the water released during heating will hydrolyse the terminal methoxy groups of the γ-MPS. Upon further heating, the hydrolysed methoxy groups condensed to form siloxane linkages.

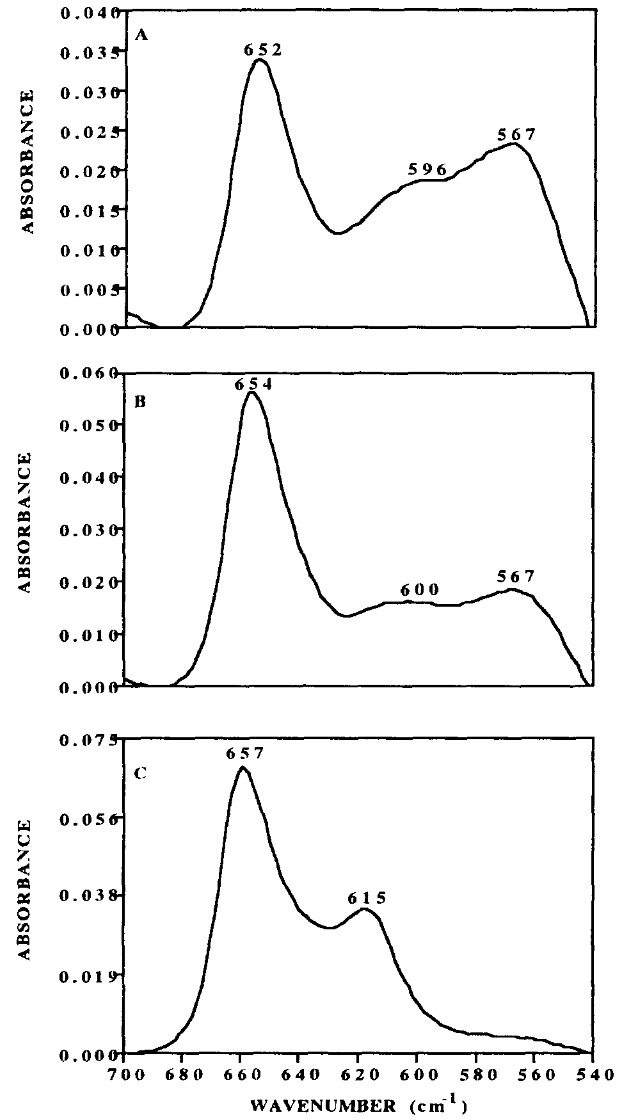


Figure 9 The copper oxide region (700–540 cm^{-1}) of the r.a.s. spectrum of (A) 10% γ-MPS/90% PVI, (B) 30% γ-MPS/70% PVI and (C) 50% γ-MPS/50% PVI by weight

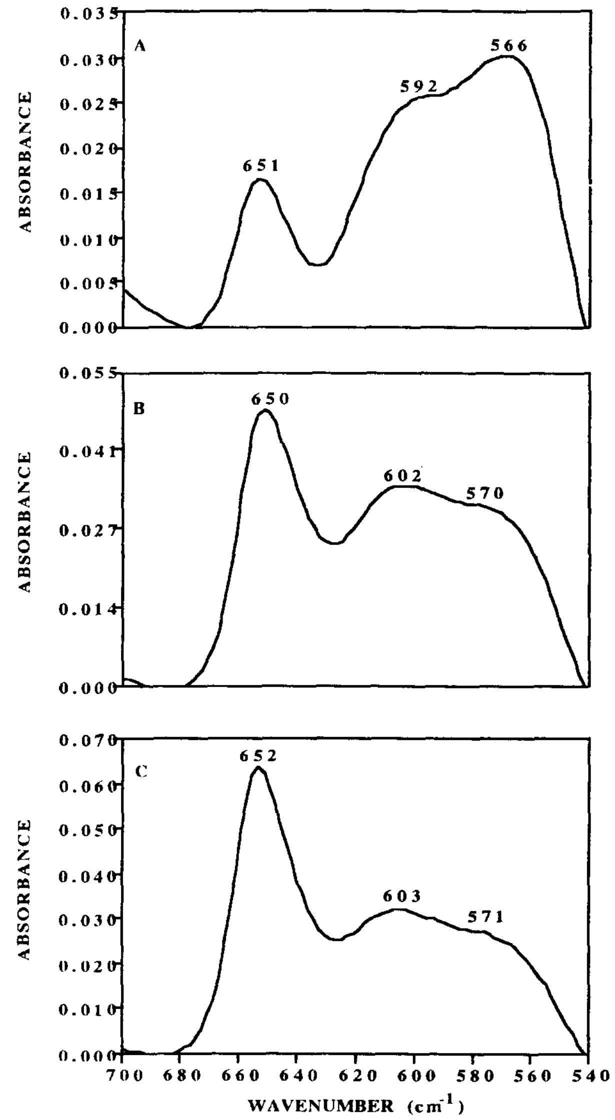


Figure 10 The copper oxide region (700–540 cm^{-1}) of the r.a.s. spectrum of hydrolysed mixtures of (A) 10% γ-MPS/90% PVI, (B) 30% γ-MPS/70% PVI and (C) 50% γ-MPS/50% PVI by weight

In order to test this hypothesis, mixtures of prehydrolysed γ-MPS and PVI were prepared and spread on freshly polished copper coupons. These spectra are depicted in *Figure 10*. Although a slight reduction in the CuO formation was seen as the hydrolysed silane content of the mixture was increased from 10% to 50% by weight, it still remains a major component of the spectra.

CONCLUSION

Degradation of the copolymers was accelerated on copper. This was determined by comparing the thermal stability of films cast on both KBr plates and copper coupons. The catalytic effect of copper has been seen for several different polymer systems, including PVI.

Less oxide formation was detected for the silane-modified copolymers than for PVI films cast on copper. This result suggests that the silane acted as a scavenger for the water released by the imidazole ring during heating. The liberated water reacted with the terminal methoxysilane groups to form siloxane linkages. Since water has been shown to enhance the rate of copper-ion migration through the film, it can be concluded that the incorporation of silane retarded the oxidation of the polymer film.

The catalytic nature of the imidazole moiety may have accelerated the rate of hydrolysis and condensation of the methoxysilane groups. It was found that the condensation rate of modified imidazole copolymers was much faster than that of the silane homopolymer. Although gelation was observed for both the silane-rich and the imidazole-rich copolymers, the shelf-life of the silane-rich copolymer was longer. Infra-red spectra taken of the gelled copolymers indicated that the methoxysilane linkages had hydrolysed and condensed to form siloxane bonds. The imidazole ring was found to be intact. This phenomenon was not seen for the homopolymer of γ-MPS.

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