

# Silane-Modified Polyvinylimidazole(1) for Corrosion Protection on Copper at Elevated Temperatures

JYONGSIK JANG and HATSUO ISHIDA\*

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106

## SYNOPSIS

Silane-modified *N*-polyvinylimidazole [PVI(1)] copolymers have been synthesized from various mole ratios of  $\gamma$ -methacryloxypropyltrimethoxysilane ( $\gamma$ -MPS) and *N*-vinylimidazole, VI(1). Fourier transform infrared reflection-absorption spectroscopy (FTIR-RAS) is used to investigate the modified PVI(1) on copper surfaces. The silane-modified PVI(1) has good corrosion protection and adhesion promotion capabilities for copper substrate under severe environments. The relationship between coating thickness and corrosion protection is studied at elevated temperatures. The relationship between the mole ratio of comonomers and the corrosion processes of a copper surface has also been investigated at elevated temperatures. The corrosion protection improves drastically with increased VI(1) content. An adhesion study of the silane-modified PVI(1) film on a copper surface is also carried out using the ASTM adhesive tape test. From the adhesion strengths between the modified PVI(1) films and copper surface, it has been observed that modified PVI(1) acts as an adhesion promoter and does not depend on the mole ratio of  $\gamma$ -MPS/VI(1) within the range of this experiment. Good adhesion of an anticorrosion coating is important for the corrosion protection of a copper surface. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

A large number of anticorrosion agents for copper have been reported, such as benzotriazole, benzium, indazole, and imidazole.<sup>1-18</sup> Imidazole derivatives are highly reactive with copper and suppress corrosion of the copper surface. A complex formation between copper and the nitrogen on the imidazole ring protects the copper surface from oxygen diffusion.<sup>19-22</sup> However, these small molecules are not effective as anticorrosion agents at elevated temperatures since the complex of these molecules can easily decompose and evaporate at high temperatures. In order to improve the high temperature anticorrosion performance, polymers have recently been studied for use as corrosion inhibitors. Eng and Ishida studied polyvinylimidazoles (PVI) as anticorrosion agents for copper at elevated temperatures.<sup>17</sup> When applied to treat the surface of copper, PVI led to complex for-

mation with the copper surface and easily formed a thin film of higher ductility than the previous non-polymeric surface treatments. They observed that the oxidation of a PVI-coated copper was suppressed as high as 400°C due to the low volatility of the film.

However, the anticorrosion ability of PVI and other imidazoles is influenced by humid environments. In order to reduce the PVI's sensitivity to water and to improve the adhesion between the polymer film and copper, a silane coupling agent has been introduced.<sup>23</sup> For this purpose,  $\gamma$ -methacryloxypropyltrimethoxysilane ( $\gamma$ -MPS) was used as comonomer for *N*-vinylimidazole [VI(1)] to make copolymers.

As seen in previous articles,<sup>23,24</sup> the silane-modified PVI(1)s have been demonstrated to be good anticorrosion agents under a humid environment and/or at high temperatures. The modified PVI(1) suppressed the corrosion of a copper surface without any oxide formation at 80°C with 100% relative humidity for 24 h. It has also been reported that thick films of the silane-modified PVI(1) protected the copper from oxidation and inhibited polymer degradation during a high temperature test above

\* To whom correspondence should be addressed.

200°C.<sup>23,24</sup> It was also expected that the adhesion between the silane-modified polymer film and copper surface will improve conspicuously compared to PVI(1) itself. However, there is no quantitative information concerning the corrosion protection and the adhesion properties of the modified PVI.

In this article, silane-modified PVI(1)s will be synthesized from different mole ratio of  $\gamma$ -MPS and VI(1) and will be used to protect the surface of copper from oxidation. The corrosion protection of the synthesized material will be quantitatively analyzed as a function of film thickness with FTIR-RAS. The adhesion of the modified PVI(1) film to copper is also studied by the ASTM adhesive tape test.

## EXPERIMENTAL

$\gamma$ -Methacryloxypropyltrimethoxysilane ( $\gamma$ -MPS) was purchased from Petrarch Systems Inc. and purified by vacuum distillation. *N*-vinylimidazole was purchased from Aldrich Chemical Co. and was distilled *in vacuo* to yield a pure and colorless liquid. Azobis(isobutyronitrile) from the Eastman Kodak Co. was purified by first dissolving in warm methanol (35°C), then recrystallizing in an ice bath, and finally drying in a vacuum oven at room temperature for 2 days.

Silane-modified polyvinylimidazole was synthesized by free radical polymerization under the reaction conditions and monomer compositions given in Table I. The intrinsic viscosities of the modified PVI(1)s were measured at 30°C in benzene with an Ubbelohde viscometer (Fisherbrand 2-10C).

Copper plates (ASTM B 152, type ETP) were cut into 2.54 × 5.08 × 0.32 cm coupons. Each copper sample was then mechanically polished with no. 5 chrome oxide and washed with acetone in an ultrasonic bath. The samples were rinsed with 1% by weight HCl solution, followed by distilled water, then acetone, and finally dried with a stream of nitrogen gas.

**Table I** Intrinsic Viscosity of the Modified PVI(1) Containing Different Mole Ratios

Mole Ratio { $\gamma$ -MPS/VI(1)}	Intrinsic Viscosity (dL/g)
Poly( $\gamma$ -MPS)	0.0170
1 : 1	0.0200
1 : 2	0.0230
1 : 3	0.0291
1 : 5	0.0317
1 : 10	0.0358

The silane-modified PVI(1) was hydrolyzed in a solution of 5% by weight of water (acidified to pH 3.5 by acetic acid) in tetrahydrofuran (THF) for 1 h and then diluted in THF solvent for the coating application. Polymer coatings were cast from solution onto the copper surface with a microsyringe. Modified PVI(1)-coated copper was dried for 48 h in air before testing. Film thickness was calculated based on the area of the copper surface and the known concentration of the solution.

A Digilab FTS-14 Fourier transform infrared spectrophotometer equipped with a triglycine sulfate detector was purged with dry air to minimize the atmospheric moisture. A reflection-absorption attachment (Harrick Scientific) was used with a gold wire grid polarizer (Perkin-Elmer). Reflection spectra were collected at an incident angle of 75° with an average of 100 scans at 4 cm<sup>-1</sup> resolution. Reflectance spectra are displayed in the absorbance mode with the most intense peak indicating the highest absorption. The absorption difference between the maximum and minimum absorbance is designated as  $\Delta A$ .

Adhesion tests were carried out according to ASTM D 3359-83. The ASTM adhesive tape test is composed of applying and briskly lifting the tape over cuts made in the film. The pattern and the number of cuts were made according to the ASTM standard. This tape test is used to assess the adhesion of coated polymer on a metal surface, but it does not classify the coating materials of high adhesion strength.

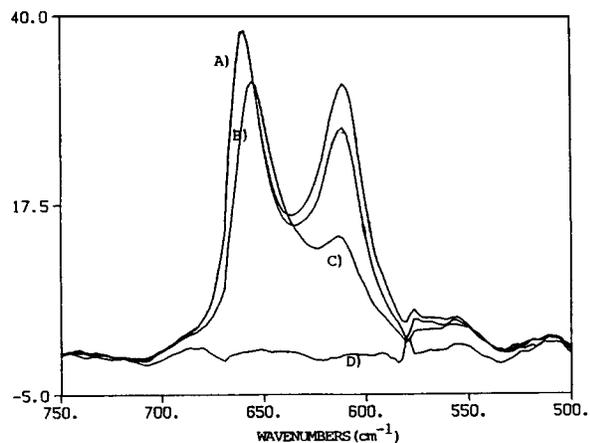
## RESULTS AND DISCUSSION

The intrinsic viscosities of poly( $\gamma$ -MPS-*co*-VI) in the different mole ratios are given in Table I. While PVI(1) homopolymer is composed of solid phase, copolymers are brownish liquids. From this table, poly( $\gamma$ -MPS) indicates the lowest value of intrinsic viscosity compared to the modified PVI(1). As the mole ratio of vinyl imidazole increases, the value of intrinsic viscosity gradually increases. Considering the poly( $\gamma$ -MPS), the composition of copolymer does not have the proportional relationship with the initial composition of  $\gamma$ -MPS/VI(1). It is also possible that the synthesized product is a mixture of the copolymers, homopolymers, and monomers. The intrinsic viscosity of the synthesized copolymer has 1 order of magnitude lower than that of a common polymer. This means that the silane-modified PVI(1)s do not have high molecular weight in this experimental condition. However, the characteris-

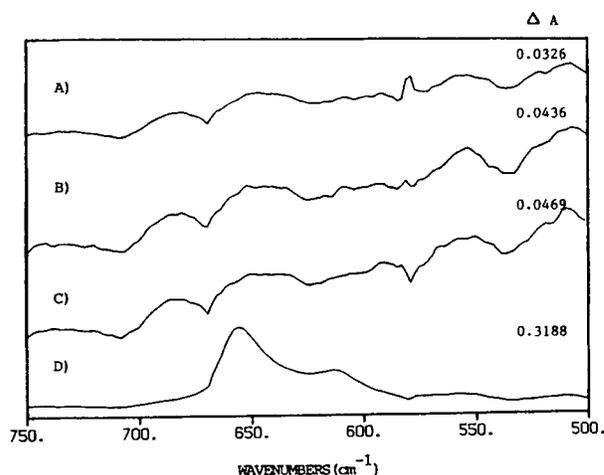
tics of these copolymers are convenient for coating application.

Figure 1 represents the RAS spectra of a bare copper plate heated at 360°C in air. The formation of cuprous oxide on the copper surface depends on the heat treatment time. The cuprous oxide mode appears as a doublet at 645 and 611 cm<sup>-1</sup>, indicating that the Cu<sub>2</sub>O layer is at least 200 nm in thickness.<sup>25</sup> The band at 645 cm<sup>-1</sup> corresponds to the longitudinal optical mode, which shifts to about 650 cm<sup>-1</sup> for thicker oxide films, and the peak at 611 cm<sup>-1</sup> is attributed to the transverse optical mode of the high frequency phonon observed near 609 cm<sup>-1</sup> in dielectric spectra of Cu<sub>2</sub>O. Initially, a major peak appears at 650 cm<sup>-1</sup>, and a small amount of an additional peak appears at 611 cm<sup>-1</sup>. As the treatment time increases, the intensity of the peak continuously increases up to a certain level. The other peak at 650 cm<sup>-1</sup>, which is due to a very thick oxide layer on a copper surface, increases drastically. These two strong peaks of bare copper appears after 10 min.

In Figure 2, the effect of coating thickness on corrosion inhibition is studied at 360°C for 15 min. The mole ratio of the silane-modified PVI(1) used is 1 : 1. Compared to the bare copper, the copper coated with a thin film strongly suppresses the oxide formation. From this figure, a small amount of cuprous oxide still appears until a film thickness of 40 nm is reached. However, the oxide formation does not strongly depend on the film thickness for the copper with a thin polymer coating. The oxidation may not be due to the intrinsic properties of the copolymer but rather defects in the film that lead to local oxidation of the copper surface, as the corrosion appeared to be localized. Water is used for



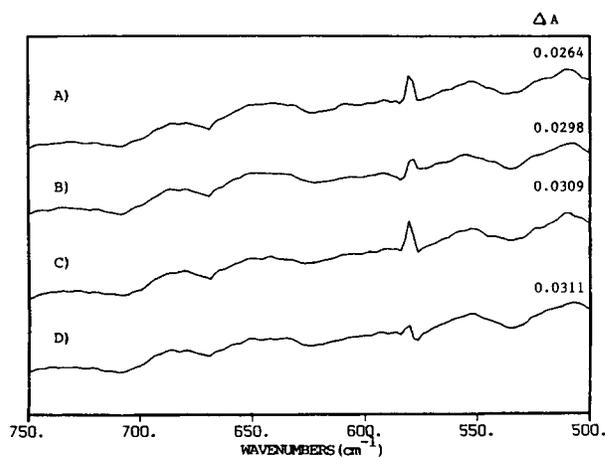
**Figure 1** RAS spectra of bare copper at high temperature (360°C): (A) 15 min; (B) 10 min; (C) 5 min; (D) 0 min.



**Figure 2** RAS spectra of silane-modified PVI(1) on copper substrate at 360°C, 15 min [ $\gamma$ -MPS/VI(1) mole ratio = 1 : 1]: (A) 40 nm; (B) 20 nm; (C) 10 nm; (D) bare copper.

the hydrolysis of the modified PVI(1) before the coating application and may produce holes in the modified PVI(1) coating as the film dries.

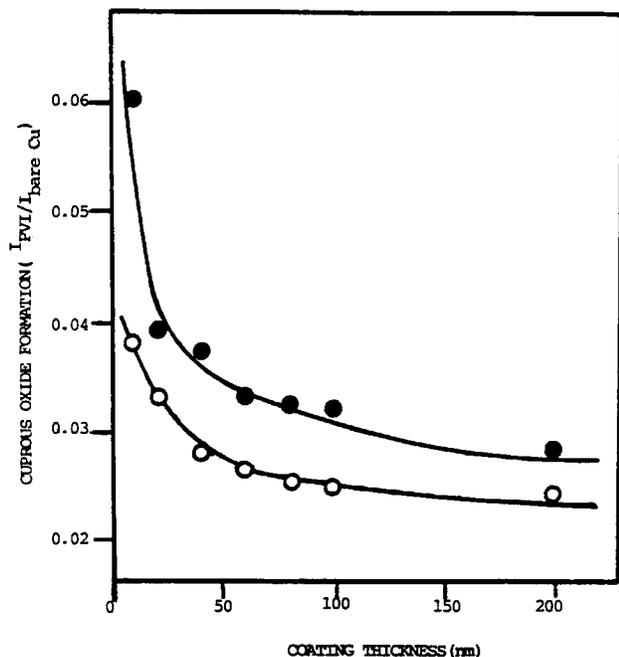
The effect of the film thickness is further studied for thick coatings under the same heating conditions. The thickness range of the silane-modified PVI(1) film from 60 to 200 nm is shown in Figure 3. As the film thickness increases, the oxide formation slightly decreases probably due to the reduced number of defects. Observation of some scattered dots of corroded portion supports this hypothesis. Judging from the results, it can be expected that the amount of oxide formation approaches an asymptotic value for



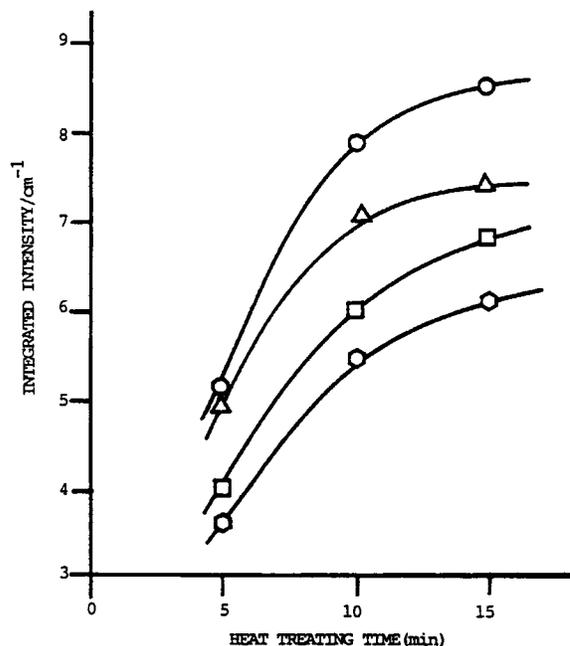
**Figure 3** RAS spectra of silane-modified PVI(1) on copper substrate at 360°C, 15 min [ $\gamma$ -MPS/VI(1) mole ratio = 1 : 1]: (A) 200 nm; (B) 100 nm; (C) 80 nm; (D) 60 nm.

the modified PVI(1) coated copper surface at high temperatures.

Figure 4 represents the integrated intensity of the cuprous oxide band formed at 360°C as a function of the film thickness. As expected previously, the amount of cuprous oxide formation approaches an asymptotic value for film thicknesses greater than 60 nm. In thin films of the modified PVI(1) [ $\gamma$ -MPS/VI(1) mole ratio = 1 : 1] on copper, the maximum amount of oxide formation is approximately 6% of the value obtained with bare copper. From this result, the modified PVI(1) is superior to benzotriazole or 2-undecylimidazole in suppressing the oxide formation on a copper surface at this temperature. It is thought that the film defects that result during the coating process represent a major contribution to the oxide formation. At film thicknesses greater than 60 nm, cuprous oxide formation on the copper surface does not strongly depend on the film thickness. Eng et al. reported that PVI homopolymer could protect the copper surface up to 400°C,<sup>17</sup> which is similar to the current results on copolymers. However, cuprous oxide formation also depends on the mole ratio of the copolymer. As the imidazole content increased, oxide formation was gradually reduced. Coating thickness and the composition of the copolymer has to be considered for the application of these copolymers at elevated temperatures. However, for enhanced adhesion, a certain amount

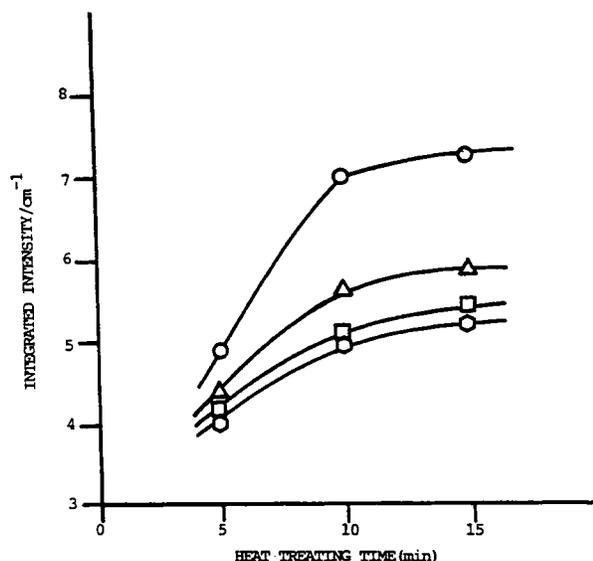


**Figure 4** Integrated intensity ratio at 360°C, 15 min:  $\gamma$ -MPS/VI(1) mole ratio: (●) 1 : 1; (○) 1 : 10.



**Figure 5** Integrated intensity of formed cuprous oxide on modified PVI(1) coated copper [ $\gamma$ -MPS/VI(1) mole ratio = 1 : 1]: (○) 20 nm; (△) 60 nm; (□) 100 nm; (○) 200 nm.

of silane is still needed as an adhesion promoter. Hydroxy groups are necessary for the reaction of silane with the substrate surface. An interfacial bond between the modified PVI(1) and the copper surface may improve the adhesion of the polymer film. As the amount of silane coupling agent decreases, the degree of degradation also decreases. This phenomenon most likely occurs because the silane contains methylene units whose thermal stability is poorer than PVI(1). Thick films still show a small amount of cuprous oxide formation. This may be due to the silane degradation at elevated temperatures. Figures 5 and 6 illustrate the effect of the film thickness and the heat treatment time of the modified PVI(1) at different mole ratios. The temperature used for the experiment was again 360°C and the  $\gamma$ -MPS/VI(1) mole ratio used for this study was 1 : 1. These figures show that the heat treatment time strongly affects the surface corrosion of copper substrate. As the film thickness increases, integrated intensity of cuprous oxide decreases gradually. Considering the effect of film thickness, a thin polymer film exhibits higher value of integrated intensity compared to the thick film sample. At a film thickness of approximately 200 nm, the amount of cuprous oxide at a high content of  $\gamma$ -MPS is higher than that of the 1 : 1 copolymer, as shown in Figure 6. The major contri-



**Figure 6** Integrated intensity of formed cuprous oxide on silane-modified PVI(1) coated copper [ $\gamma$ -MPS/VI(1) mole ratio = 1 : 10]: (○) 20 nm; (△) 60 nm; (□) 100 nm; (◇) 200 nm.

bution of corrosion formation may be attributed to the degradation of the silane coupling agent for samples with longer treatment times.

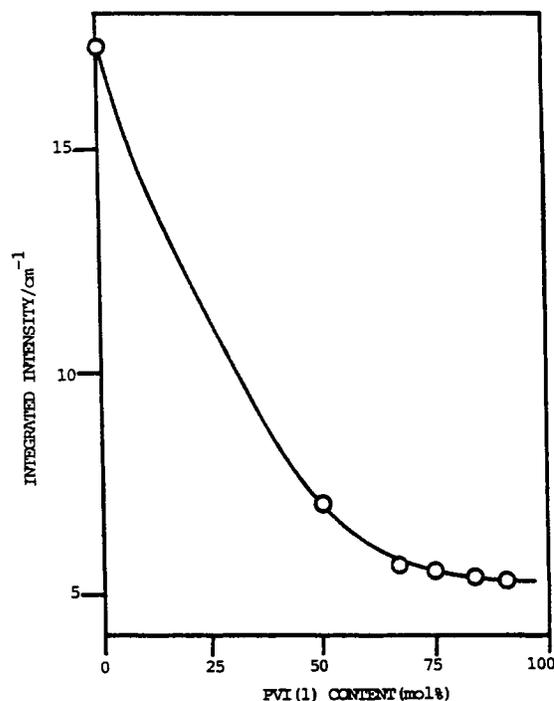
In Figure 7, cuprous oxide formed on the copper surface is measured as a function of PVI(1) content. The thickness of the coatings for this study is fixed to 100 nm. In the case of poly( $\gamma$ -MPS), which has no imidazole groups, severe degradation of poly( $\gamma$ -MPS) film on the copper occurs at elevated temperature and copper surface is easily oxidized during the degradation of the polymer film. As the imidazole content increases, the amount of cuprous oxide drastically decreases. Above 67 mol % of PVI content, a negligible amount of cuprous oxide forms on the copper surface. Accordingly, it can be explained that the degradation of  $\gamma$ -MPS strongly affects the corrosion formation on copper surface at elevated temperature.

The modified PVI(1)s are cast on the copper surface and exposed at 360°C for 15 min. The ASTM adhesive tape test results are presented as the percentage of film flaked versus mole ratio of the modified PVI(1), as seen in Figure 8. For the adhesion test of the modified PVI(1), the film thickness was fixed to 100 nm, and three samples were chosen for each data point. Around 70% of the film is flaked from the poly( $\gamma$ -MPS) coated copper. This is as expected, since previous studies have indicated that severe degradation of the  $\gamma$ -MPS film occurs at elevated temperatures. Addition of  $\gamma$ -MPS to PVI(1)

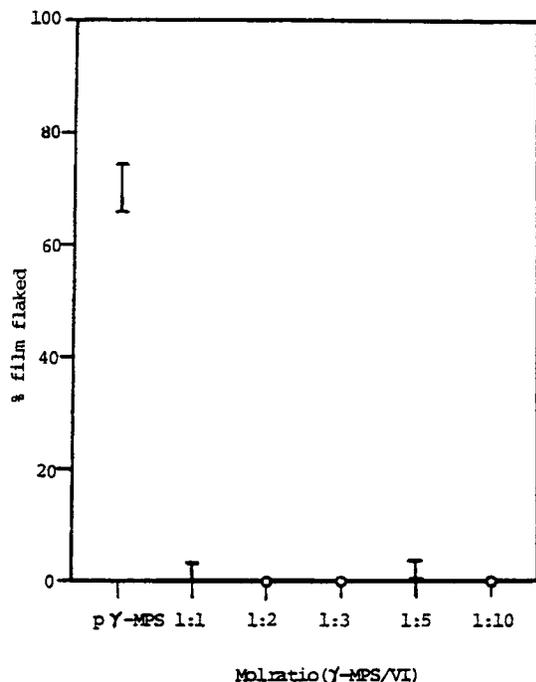
drastically increases the adhesion between the coated film and copper surface. When the silane-modified PVI(1) is cast on the copper surface, most of the coated polymer films are not removed by the ASTM adhesive tape test. Only 1.5% of the film is flaked in 1 : 1 mole ratio [ $\gamma$ -MPS/VI(1)] and 2.0% of the film flaked in 1 : 5 mole ratio [ $\gamma$ -MPS/VI(1)]. From the adhesion test, it can be concluded that the adhesion strength of the silane-modified PVI(1) on the copper does not depend on the mole ratio of  $\gamma$ -MPS/VI within the range of this experiment. It should be emphasized that the ASTM adhesion test employed does not distinguish the different strength of adhesion within the film that did not flake. It should be used only for screening purposes of a coating that might flake.

## CONCLUSION

The modified PVI(1) has good corrosion protection and adhesion promotion capabilities for copper substrates. When exposed to elevated temperatures, a much smaller amount of cuprous oxide appears in modified PVI coated samples than in bare copper. Thin films of the modified PVI(1) of up to 40 nm



**Figure 7** Integrated intensity of formed cuprous oxide on modified PVI(1) coated copper (coating thickness: 100 nm).



**Figure 8** Change in percent film flaked versus different mole ratio of silane-modified PVI(1) for ASTM adhesive tape tests.

may allow the film defects to be formed on copper surface. In thick films, a major contribution of oxide formation might be attributed to the degradation of  $\gamma$ -MPS. The corrosion process of the modified PVI(1) coated copper depends on the heat treatment time at high temperatures. The oxide formation on the copper surface does not strongly depend on the coating film thickness. At high  $\gamma$ -MPS concentrations, the oxide formation on copper is related to the degradation of the silane moiety. The decomposition of the copolymer decreases tremendously with increasing the PVI(1) content, whereas poly( $\gamma$ -MPS) degrades readily at elevated temperatures. Above 67 mol % of PVI content, little cuprous oxide formation occurs on the treated copper surface. Adhesion tests indicate that the modified PVI(1) has good adhesion properties and does not depend on the mole ratio of  $\gamma$ -MPS/VI(1) within the range of this experiment.

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