# Improved Adhesion between Kapton Film and Copper Metal by Plasma Graft Polymerization of Vinylimidazole

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ABSTRACT: The surface of poly[*N*,*N*′-(oxydiphenylene)pyromellitimide] film, Kapton, was modified by plasma graft polymerization of vinylimidazole to improve the adhesion with copper metal, and the surface of the modified Kapton film was investigated by means of XPS and atomic force microscopy. The plasma graft polymerization deposited the heterogeneous layer of poly(vinylimidazole) in the form of an island−sea type structure (about 200 nm height) at the surface of the Kapton film. The graft polymer layer interacted with copper metal to form a charge-transfer complex and contributed to improving the adhesion with copper metal. The peel strength of the adhesive joint between the Kapton film and copper metal was increased 2.9 times by the graft polymerization. The failure of the graft-polymerized Kapton film/copper metal adhesive joint did not occur at the interface between the graft polymer and metal, but mainly at the inner layer of the Kapton film.

## Introduction

Poly[*N*,*N*′-(oxydiphenylene)pyromellitimide] (Kapton H, E. I. du Pont de Nemours & Co.) is a superperformance polymer with a high-temperature, good mechanical properties, flame resistance, dimensional stability, and a low dielectric constant. Therefore, Kapton film finds practical uses in severe environments such as aerospace and space. In the field of microelectronics technology, Kapton film is used as an insulating material, especially in the flexible printed circuit board (FPC). The FPC is a composite material of Kapton film and copper metal. The copper metal is deposited at the Kapton film surface by means of the vacuum evaporation technique, the sputtering technique, the ion plating technique, etc. In such metalization processes, poor adhesion between the Kapton film and copper metal reduces the reliability of the FPC.

To improve the adhesion between Kapton film and copper metal, many investigators have studied the surface modification of Kapton film from theoretical and practical viewpoints.[1−12] Chou and Tang[1] discussed why the adhesion of Kapton film with copper metal is poor. Their conclusion was that a metal−oxygen−carbon complex was formed at the Kapton film/metal interface in the metalization process and that the complex is closely related to the adhesion. The reactivity of copper metal in forming the complex was lower than that of chromium and titanium metals. This conclusion suggests the importance of a special functionality that can strongly interact with copper metal.

Xue et al.[13] reported that benzimidazole interacted with copper metal at zero oxidation state to make a complex. Chen and co-workers[14] reported a new polyimide containing imidazole units in the main chain. This polymer showed a good adhesion with copper metal but was too brittle and failed in FPC applications.

In this paper, we are interested in imidazole groups which make a strong complex with copper metal and discuss how imidazole groups that are introduced into the Kapton film surface improve the adhesion with copper metal. The plasma graft polymerization technique was used for introduction of imidazole groups at the Kapton film surface.

## Experimental Section

**Materials.** The polyimide film used in this study was poly[*N*,*N*′-(oxydiphenylene)pyromellitimide] (Kapton 200H (508 mm wide and 50 $\mu$m thick)), which was kindly provided by Toray du Pont Co. The film was washed with acetone using an ultrasonic washer prior to the plasma graft polymerization experiment. 1-Vinylimidazole (Tokyo Kasei Kogyo Co.) was used as a monomer for the graft polymerization. Vinylimidazole was distilled under vacuum just before the graft polymerization experiment.

**Plasma Graft Polymerization.** The plasma graft polymerization of vinylimidazole at the Kapton film surface was carried out in two steps: The Kapton film surface was exposed for 60 s to an argon plasma which was operated at an rf (13.56 MHz frequency) power of 25 W at an argon pressure of 13.3 Pa and subsequently exposed to air for 5−10 min to generate hydroperoxides which were able to initiate the graft polymerization. The apparatus used for the argon plasma treatment was a homemade, glass-tubular reactor (170 mm diameter, 300 mm long) which contained a micrometering valve for an argon gas inlet (Whitey Co., Model SS-22RS4), a pressure gauge (Datametrics Co., capacitance manometer type, Model 622), and a vacuum system (Daia Vacuum Engineering Co. Ltd., Model DSSO-422) consisting of a combination of a diffusion pump (150 L/s) and a rotary pump (200 L/min). The electric power at an rf frequency of 13.56 MHz for generating the glow discharge was supplied by an rf generator (Samco International Inc., Model FRG-200) into the reactor through a capacitively coupled system with electrodes wound on the outside of the glass reactor.

The argon-plasma-treated Kapton film was immersed in an ethanol solution of vinylimidazole (10 vol %) from which dissolved air had been removed by a repeated freezing−fusion procedure before the graft polymerization, and the graft polymerization reactions were continued under a nitrogen atmosphere at 70 °C for 1−24 h. After the graft polymerization, the Kapton film was washed with methanol using a Soxhlet apparatus to remove the homopolymer of vinylimidazole and dried at 50 °C under vacuum.

**Hydroperoxide Concentration Generated at the Kapton Film Surface.** The concentration of hydroperoxides generated at the Kapton film surface by a combination of the argon plasma treatment and the air exposure was determined by the iodide method.[15] The plasma-treated Kapton film was reacted with sodium iodide in a mixture of 2-propanol and benzene (6:1 volume ratio) containing a trace of ferric chloride (1 ppm) at 60 °C for 10 min. The concentration of hydroperoxide in the Kapton film was determined from the absorption intensity of the mixture solution at 360 nm.

**Infrared Spectroscopy.** IR spectra of the plasma-graft-polymerized Kapton films were recorded in the attenuated

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total reflection (ATR) mode on a Horiba FT300 Fourier transform spectrometer with an MCT detector. A crystal of germanium was used as a prism for the ATR technique, and the incident angle of the infrared light against the prism was 45°. The spectral resolution was 1.0 $cm^{-1}$, and 100 scans were recorded on each sample.

**X-ray Photoelectron Spectroscopy.** XPS spectra of the plasma-graft-polymerized Kapton films were obtained on a Shimadzu ESCA K1 using a nonmonochromatic Mg Kα photon source. The anode voltage was 10 kV, the anode current 30 mA, and the background pressure in the analtyical chamber $1.5 \times 10^{-6}$ Pa. The size of the X ray spot was 2 mm Φ, and the take-off angle of photoelectrons, otherwise noticed, was 90° with respect to the sample surface. The XPS spectra were referenced with respect to the 285.0 eV carbon 1s level observed for the hydrocarbon to eliminate the charge effect. The spectra were not smoothed. The $C_{1s}$, $N_{1s}$, $O_{1s}$, and $Cu_{2p}$ spectra were decomposed by fitting a Gaussian−Lorentzian mixture function (80:20 mixture ratio) to an experimental curve using a nonlinear, least squares curve-fitting program (ESCAPAC) supplied by Shimadzu. The sensitivity factors ($S$) for the core levels were $S(C_{1s}) = 1.00$, $S(N_{1s}) = 1.77$, $S(O_{1s}) = 2.85$, and $S(Cu_{2p_{3/2}}) = 15.87$.

Angular XPS spectra at take-off angles of 11.5, 23.6, 36.9, 53.1, and 90° were recorded on the same photoelectron spectrometer (Shimadzu ESCA K1) using a special stage for mounting the sample films.

**Atomic Force Microscopy.** The surface morphology of the plasma-graft-polymerized Kapton film was scanned with an atomic force microscope (Seiko Instrument SFA-300). A triangular-pyramidal silicon nitride tip was used as a probe, and a $10 \times 10$ $\mu m^2$ area was scanned under a probe pressure of $8.7 \times 10^{-11}$ $N/m^2$. The arithmetic mean of the surface roughness ($R_a$) was calculated from the roughness profile determined by AFM. When the roughness profile is written as a function of $Z(x)$, $R_a$ is defined by the following equation:

$$R_a = \frac{1}{L}\int_0^L |Z(x)|\,dx \qquad (1)$$

where $L$ is the scanning length (10 $\mu$m).

**Adhesive Joint between Kapton Film and Copper Metal.** The Kapton film surface was made electrically conductive by vacuum deposition of copper metal (100 nm thickness) and then electroplated with copper to a thickness of 40 $\mu$m. The plating process was done at a constant dc current density of $3 \times 10^4$ $A/m^2$ and at 24 °C in a sulfuric acid aqueous solution (90 g/L) containing copper sulfate (0.5 M), hydrogen chloride (50 ppm), and a glossy reagent (Nippon Rironal, CLX-A, 5 mL). The plated Kapton film was washed with water and dried at 80 °C for 12 h under vacuum.

**Peel Strength of Adhesive Joint between Kapton Film and Copper Metal.** The T-type peel strength (5 mm wide) of the adhesive joints between the Kapton film and the copper metal was evaluated at a peel rate of 10 mm/min using an Instron-type tensile strength tester (Shimadzu AGS100-A). The peel strength was determined from an average of ten specimens.

## Results and Discussion

**Plasma Graft Polymerization of Vinylimidazole.** A preliminary experiment[16] showed that peroxide groups were generated at the surface of the Kapton film by the argon plasma exposure/air exposure procedure. The concentration of peroxide groups increased with increasing argon plasma exposure time and rf power of the argon plasma. Argon plasma exposure for times longer than 60 s or at rf power higher than 25 W saturated the formation of the peroxide groups in the Kapton film. The peroxide concentration at the saturation was 4.5 $\times 10^{14}$ numbers/$cm^2$, which corresponds to one peroxide group per five repeating units of $N,N'$-(oxydiphenylene)-pyromellitimide under the assumption that a layer activated effectively by the argon plasma exposure would be as thick as 10 nm deep from the Kapton film surface.

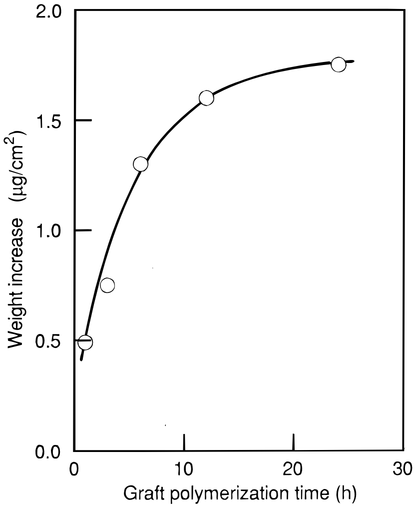


**Figure 1.** Weight increase taken up by graft polymerization as a function of graft polymerization time.

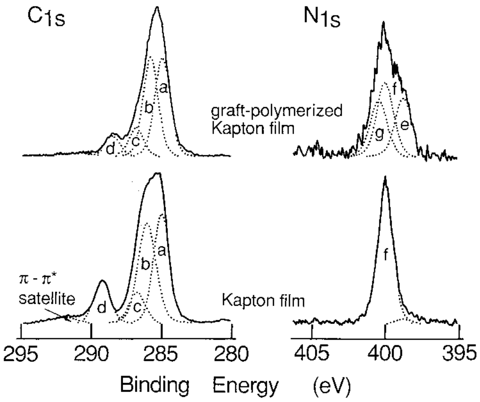
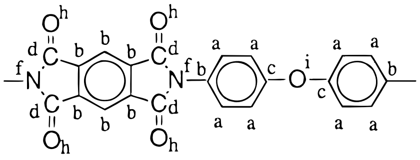


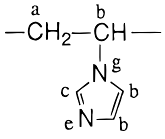
**Figure 2.** XPS ($C_{1s}$, $N_{1s}$) spectra of Kapton film graft-polymerized with vinylimidazole for 24 h.

The graft polymerization of vinylimidazole was carried out in an alcohol solution of vinylimidazole (10 vol %) at 70 °C for 1−24 h. The specimens used for the graft polymerization were Kapton films treated with the argon plasma exposure at an rf power of 25 W for 60 s. The peroxide concentration was $4.5 \times 10^{14}$ numbers/$cm^2$. Figure 1 shows the weight increase taken up by the graft polymerization as a function of the graft polymerization time. The weight increase continues gradually with increasing graft polymerization time and reaches 1.8 $\mu g/cm^2$ at a graft polymerization time of 24 h. The XPS spectra showed that the graft polymerization of vinylimidazole occurred at the Kapton film surface. Figure 2 compares the $C_{1s}$ and $N_{1s}$ core level spectra of the graft-polymerized and original Kapton films. The $C_{1s}$ spectrum of the original Kapton film is decomposed into five components: CH in the oxydianiline unit (a component), CH in the pyromellitic diacid unit and CN groups in the oxydianiline unit (b component), CO groups in the oxydianiline unit (c component), C=O groups in the imido moiety (d component), and a $\pi-\pi^*$ shake-up satellite. Their peak positions appear at 285.0, 286.0, 286.7, 289.1, and 291.6 eV, respectively.[17] The $N_{1s}$ spectrum is decomposed into two components: a chief peak at 400.8 eV due to NC(O) in the imido groups (f component) and a subordinate peak at 399.7 eV due to NC(O) in the amido groups (e

**Table 1. XPS Spectra of Plasma-Graft-Polymerized Kapton Film**[a]



Repeating unit I

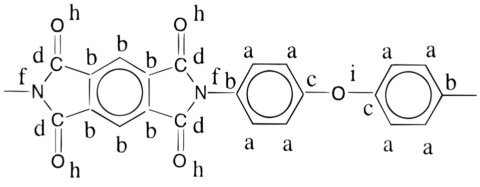


Repeating unit II

| sample | $C_{1s}$ component (rel concn in %) |  |  |  | $N_{1s}$ component (%) |  |  | $O_{1s}$ component (%) |  |
|---|---|---|---|---|---|---|---|---|---|
|  | a | b | c | d | e | f | g | h | i |
| original Kapton film | 36.8 | 37.7 | 10.6 | 14.9 | 3.5 | 96.5 |  | 79.3 | 20.7 |
| calcd from repeating unit of I | (36.4) | (36.4) | (9.1) | (18.1) |  | (100) |  | (80.0) | (20.0) |
| graft-polymerized Kapton film | 40.0 | 40.2 | 11.7 | 8.2 | 31.3 | 39.0 | 29.7 |  |  |
| calcd from repeating unit of II | (20.0) | (60.0) | (20.0) | (0) | (50.0) | (0) | (50.0) | (0) | (0) |

[a] a component, at 285.0 eV; b component, at 285.9−286.0 eV; c component, at 286.7−287.0 eV; d component, at 288.8−289.1 eV; e component, at 399.4−399.7 eV; component, at 400.8 eV; g component, at 401.1 eV; h component, at 532.7 eV; i component, at 534.1 eV.

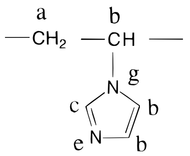
component).[17] The $O_{1s}$ spectrum, which is not included for the sake of brevity, was decomposed into two components: $O{=}C$ at 532.7 eV in the imido groups (h component) and OC at 534.1 eV in the oxydianiline unit (i component). These $C_{1s}$, $N_{1s}$, and $O_{1s}$ components are assigned as shown in the following structure. The result of the decomposition is summarized in Table 1. The $\pi-\pi^*$ shake-up satellite is excluded from Table 1 because the $\pi-\pi^*$ shake-up satellite is not the repeating unit of the Kapton film.



Chemical structure I

The good correspondence in relative peak intensity between each of the decomposed components and those calculated from the repeating unit of poly[*N*,*N*′-(oxydiphenylene)pyromellitimide] shows that the decomposition procedure was done reasonably. The appearance of the amido groups at 399.7 eV (e component) indicates that the Kapton film used in this study was not imidized completely, and the imidization is calculated to be 96.5% from the relative peak intensity of the imido groups (f component) and the amido groups (e component).

The graft polymerization of vinylimidazole into the Kapton film, as shown in Figure 2, gave larger changes in the $N_{1s}$ core level spectrum than in the $C_{1s}$ spectrum. The $N_{1s}$ spectrum, as shown in Figure 2, is distributed over wider ranges of the binding energy than that of the original Kapton film, indicating that the graft-polymerized Kapton film contains new nitrogen moieties with different binding energies. The $N_{1s}$ spectrum was decomposed into three components: imino groups at 399.4 eV (e component) and amino groups at 401.1 eV (g component) in the vinylimidazole units as well as amido (e component) and imido groups (f component) in the Kapton film.[17]



Chemical structure II

The following assignment is made in the poly(vinylimidazole) repeating unit: The $C_{1s}$ spectrum of the graft-polymerized Kapton film (Figure 2) shows no new components but rather some changes in the relative concentrations of the four components. The $CH_2$ moiety (a component) in the $CH_2CH$ chains of poly(vinylimidazole) appears at 285.0 eV, which is the same in the binding energy as the CH moiety in the oxydianiline unit. The CH moiety (b component) in the $CH_2CH$ chains of poly(vinylimidazole) and at the fourth and fifth positions of the imidazole rings are not distinguishable from each other and appear at the same binding energy of 285.9 eV. The CH moiety (c component) at the second position in the imidazole rings is distinguishable from the a and b components and appears at 287.0 eV. The relative peak intensities of the a, b, and c components in the graft-polymerized Kapton film, as shown in Table 1, increase, and that of the d component decreases, compared with those of the original Kapton film.

From the results that the new imino (e component) and amino components (g component) appear in the $N_{1s}$ spectrum and the relative peak intensities of the a, b, and c components increase, while that of the d component decreases, we conclude that vinylimidazole was graft-polymerized at the surface of the Kapton film.

Indeed Table 1 shows that the graft polymerization of vinylimidazole occurred at the Kapton film surface, but there is a large difference in the relative intensity between the experimental $C_{1s}$ and $N_{1s}$ components and the calculated ones from the repeating unit of the graft polymers: Poly(vinylimidazole) should have a, b, and c components in the $C_{1s}$ spectrum with relative concentrations of 20.0, 60.0, and 20.0%, respectively, and e and g components in the $N_{1s}$ spectrum with relative concentrations of 50.0 and 50.0%. No d and f components should appear in the $C_{1s}$ and $N_{1s}$ spectra of poly(vinylimidazole). In the observed $C_{1s}$ and $N_{1s}$ spectra of the graft-polymerized Kapton film (Figure 2), the d and f components appear, and the relative concentrations of the b, c, e, and g components are much lower than the calculated values from the repeating unit of poly(vinylimidazole), while the concentration of the a component is much higher than that calculated (Table 1). This difference can be interpreted from the viewpoint of the two distribution models of the graft polymers at the Kapton film surface: One is that the Kapton film surface is covered by a homogeneously thick layer of the graft copolymer, with the thickness of the layer less than the mean free path of photoelectrons (about 10 nm); the other is that the Kapton film surface is incompletely covered by a heterogeneously thick layer of the graft copolymer. We will discuss in the next paragraph how the graft polymer is distributed at the Kapton film surface by means of the angular XPS spectra.

Prior to the measurement of the angular XPS spectra, we made two trials for estimating the thickness of the graft polymer layer: The two estimations are based on the weight increase taken up by the graft polymerization and based on the $N_{1s}$ spectrum at a take-off angle of 90°. The weight increase taken up by the graft polymerization, as shown in Figure 1, is about 1.8 $\mu$g/cm$^2$ at a graft polymerization time of 24 h. When we assume that the density of the graft polymer is 1 g/cm$^3$ and the graft polymer deposits in a homogeneous thickness all over the Kapton film surface, the graft polymer layer is calculated to be 18 nm thick. On the other hand, the graft-polymerized layer can be estimated from the $N_{1s}$ spectrum. If the graft polymer layer covers the Kapton film surface in a homogeneous thickness and is thinner than the mean-free path of photoelectrons (10 nm), two different types of nitrogen due to not only the amino and imino moieties (e and g components) but also the imido moiety (f component) will appear in the $N_{1s}$ spectrum. The relative peak intensity of the e or g component should be proportional to the thickness of the graft polymer layer. Therefore, the thickness of the graft polymer layer ($L$) is written as follows:

$$L \text{ (in nm)} = \frac{I_{\text{e or g}}}{I_{\text{e or g}} + {}^{1}\!/_{2} I_{\text{f}}} \times \lambda \tag{2}$$

where $I_{\text{e or g}}$ and $I_{\text{f}}$ are the peak intensities of the e or g component and that of the f component, respectively. The factor of ${}^{1}\!/_{2}$ in the denominator accounts for the two nitrogen atoms in the repeating unit of poly[*N*,*N*′-(oxydiphenylene)pyromellitimide]. $\lambda$ is the mean-free path of photoelectrons (10 nm). The $N_{1s}$ spectrum of the graft-polymerized Kapton film (Figure 2) shows two characteristic types of nitrogen which belong to the imido moiety (f component) in the Kapton film as well as the amino and imino moieties (e and g components) in the graft polymers. Based on the e component, the graft polymer layer ($L$) is calculated to be 6.7 nm thick from eq 2, and based on the g component, the layer ($L$) is calculated to be 7.2 nm thick. The graft polymer layer (6.7 or 7.2 nm thick) estimated from the $N_{1s}$ spectrum is about half of that (18 nm thick) estimated from the weight increase taken up by the graft polymerization. The two trials for estimating the thickness of the graft polymer layer by means of the weight increase and the $N_{1s}$ spectrum are reasonable ways only when the graft polymer homogeneously covers the surface of the Kapton film. How does the graft polymer deposit on the Kapton film surface? The angular XPS spectra give us an answer to this question.

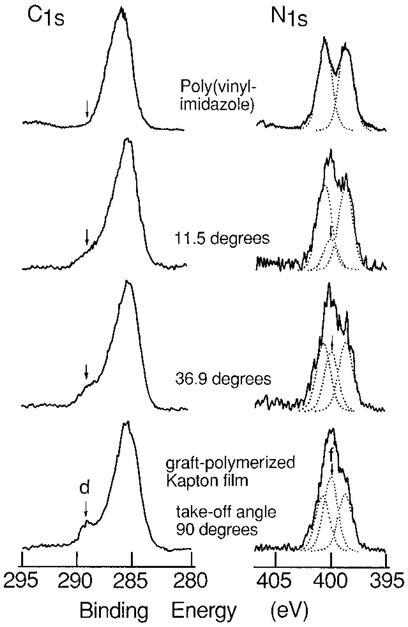


**Figure 3.** Angular XPS ($C_{1s}$ and $N_{1s}$) spectra of Kapton film graft-polymerized with vinylimidazole for 24 h.

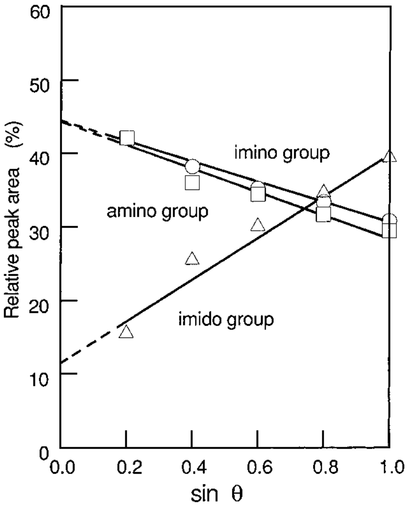


**Figure 4.** Relative concentration of imino, amino, and imido groups in the Kapton film graft-polymerized with vinylimidazole for 24 h as a function of take-off angle ($\theta$).

Figure 3 shows typical angular XPS ($C_{1s}$ and $N_{1s}$) spectra of the Kapton film graft-polymerized for 24 h. As the take-off angle decreases from 90 to 11.5°, the intensities of the d and f components belonging to the Kapton decrease and those of the e ang g components belonging to the graft polymer increase. Even at a take-off angle of 11.5°, where the sampling depth is about 2 nm, the f component never disappears in the $N_{1s}$ spectrum but accounts for 16% of the total nitrogen moieties. From the result of the angular XPS spectra, it is reasonable that the graft polymer does not homogeneously cover the Kapton film surface, but distributes heterogeneously in an island−sea type structure. Figure 4 shows the relative concentration of the e and g components (imino and amino groups in the graft polymer) and the f component (imido groups in Kapton film) as a function of the take-off angle ($\theta$). Both e and g components increase linearly with decreasing sin $\theta$, and the f component decreases linearly. From the extrapolation of these linear relationships, the e, g, and f compositions at the surface are 44, 44, and 12%, respectively. Therefore, the surface composition ($C$) of the graft polymer at surface is calculated from eq 3:

$$C \text{ (in \%)} = \frac{I'_{\text{e or g}}}{I'_{\text{e or g}} + {}^{1}\!/_{2} I'_{\text{f}}} \tag{3}$$

where $I'_{\text{e or g}}$ and $I'_{\text{f}}$ are the relative concentrations of the e or g component at the surface and that of the f component, respectively. From eq 3, the surface composition, $C$, is estimated to be 88% for the graft polymer and 12% for the Kapton. This calculation means that

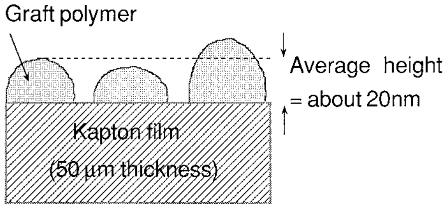


**Figure 5.** Schematic representation of cross-section view of island–sea structure model.

**Table 2. Surface Roughness at Kapton Film Graft-Polymerized with Vinylimidazole**

| sample | surface roughness ($R_a$) (nm) |
|---|---|
| Kapton film exposed to argon plasma | 5.2 |
| Kapton film graft-polymerized for 6 h | 20.9 |
| Kapton film graft-polymerized for 24 h | 22.2 |

the surface of the graft-polymerized Kapton film is occupied by both graft polymer and Kapton. From the surface composition of the graft polymer (88%) and the weight increase taken up by the graft polymerization (1.8 μg/cm$^2$), an average height of the graft polymer is estimated to be 22.5 nm. An AFM measurement showed the surface roughness ($R_a$) of the graft-polymerized Kapton film was 22.2 nm (Table 2). This comparison supports the inference that the graft polymer distributes at the Kapton film surface heterogeneously in an island–sea type structure rather than homogeneously in an equal thickness. A cross-section view of the island–sea structure is shown schematically in Figure 5. The formation of such an island–sea structure may be due to the difference in the surface energy between the graft polymer and the Kapton film. Poly(vinylimidazole) has a higher surface energy than the Kapton film: The surface energy is 41.2 mJ/m$^2$ for poly(vinylimidazole) and 37.5 mJ/m$^2$ for the Kapton film. The graft polymer is swollen in an alcohol solution in the graft polymerization process and distributes all over the surface of the Kapton film. When the graft-polymerized Kapton film is removed from the solution after the graft polymerization and dried under vacuum, the graft polymer chains aggregate as the alcohol solvent is evaporated. Small globules form to cancel the surface energy difference between the Kapton film surface and air which the graft polymer chains contact with. Finally, the globules grow into islands. This is our predicted mechanism with respect to the formation of the island–sea structure.

**Adhesion between Kapton Film Plasma-Graft-Polymerized with Vinylimidazole and Copper Metal.** Effects of the surface modification by the graft polymerization of vinylimidazole on the adhesion between Kapton film and copper metal were evaluated from the T-type peel strength. Figure 6 shows typical peel strength of adhesive joints between the vinylimidazole-graft-polymerized Kapton film and copper film as a function of the weight increase taken up by the graft polymerization. The peel strength, as shown in Figure 6, increases linearly with increasing weight increase up to 1.3 μg/cm$^2$, and above a weight increase of more than 1.3 μg/cm$^2$, the peel strength drops. A maximum peel strength is 3.2 N/5 mm at a weight increase of 1.3 μg/cm$^2$. This maximum is 2.9 times higher than the peel strength of the adhesive joint between the original Kapton film and copper film (1.1 N/5 mm). This points out an effective contribution of the vinylimidazole graft polymer to improving the adhesion with copper metal. The peel strength drop at a weight increase of more than 1.3 μg/cm$^2$ may be due to the destruction of the aggregated structure of Kapton polymer chains by immersing the film in an alcohol solution for long times in the graft polymerization process. The destruction would generate a weak domain, and the fracture would be initiated from the domain.

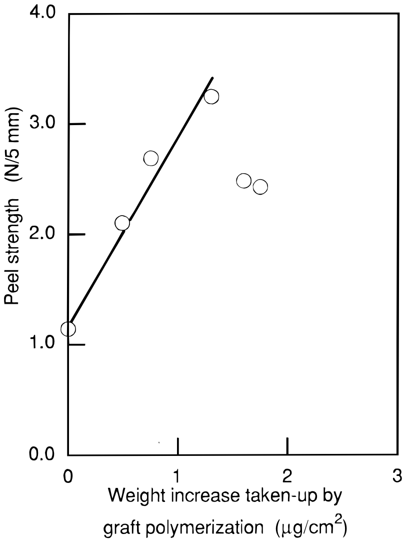


**Figure 6.** Peel strength as a function of weight increase taken up by graft polymerization.

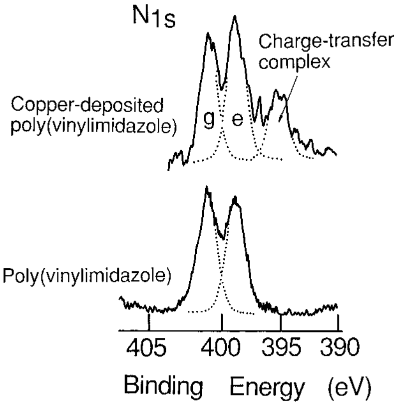


**Figure 7.** XPS ($N_{1s}$) spectra of copper-deposited poly(vinylimidazole) film (0.9 nm thick deposited copper layer).

How the vinylimidazole graft polymer contributes to the adhesion was investigated from the viewpoint of XPS spectra. The first question is whether any interaction occurred between the graft polymer and the copper metal. Figure 7 shows the $N_{1s}$ spectrum of the copper-deposited poly(vinylimidazole) film. The specimen was poly(vinylimidazole) homopolymer film on the surface of which copper metal was deposited at 0.9 nm thickness (monitored by a thickness monitor) at a pressure of less than $1 \times 10^{-3}$ Pa by means of the vacuum deposition technique. The copper-deposited film gives a new peak appearing at low binding energy regions (at about 395 eV) as well as two peaks due to imino (at 399.4 eV) and amino groups (at 401.1 eV), although the quality of the spectrum is poor due to the low intensity of the signals. The new peak is interpreted by the interaction between the nitrogen atom in the imidazole groups and copper metal. At the interface of the poly(vinylimidazole) film and the copper metal layer, electrons transfer from the copper atom to the imino group, and a charge-transfer complex is formed between the imino group and the copper atom. As a result of the complex formation, the

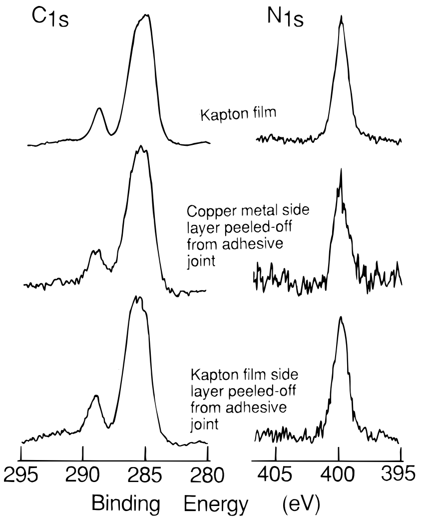


**Figure 8.** XPS ($C_{1s}$, $N_{1s}$) spectra of Kapton film side and copper side layers peeled off from the graft-polymerized Kapton/copper adhesive joint.

electron density in the nitrogen atom in the imino groups increases and the binding energy of the nitrogen atom is shifted to a low energy level. This inference was supported by the IR spectrum of the copper-deposited poly(vinylimidazole) film. The poly(vinylimidazole) film gave an absorption peak due to imino groups at 1650 $cm^{-1}$ and the copper-deposited film gave a new absorption peak at 1600 $cm^{-1}$ as well as the absorption peak at 1650 $cm^{-1}$. The new peak at 1600 $cm^{-1}$ indicates an interaction between imino groups and the copper atom.[13] Therefore, we conclude that the interaction between poly(vinylimidazole) and copper metal occurs to make a charge-transfer complex. This complex would contribute to improving the adhesion with copper metal.

The second question is where failure of the adhesive joint between the graft-polymerized Kapton film and copper metal occurred. Theoretically, the failure will occur in either mode of the interface or inner layer. In the adhesive joint between the graft-polymerized Kapton film and copper metal, there are two interfaces and three inner layers: The two interfaces are between the copper and graft polymer and between the graft polymer and Kapton film, and the three inner layers are the copper, graft polymer, and Kapton film. Actually, the failure of the adhesive joint will never occur in only one mode (the interface or inner layer) but in multiple modes. The two layers (the Kapton film side and copper metal side layers) peeled off from the adhesive joint between the graft-polymerized Kapton film and copper metal by the T-type peel strength measurement were investigated by XPS. Figure 8 shows typical $C_{1s}$ and $N_{1s}$ spectra of the two layers peeled off from the adhesive joints, respectively. The two peeled-off layers, as shown in Figure 8, show similar $C_{1s}$ and $N_{1s}$ spectra. The $C_{1s}$ spectra contain two main peaks near 285.5 and 289 eV and are similar to that of the Kapton film. The $N_{1s}$ spectra always distribute over a narrow range of binding energy and contain a sharp main peak near 400 eV which is similar to that of the Kapton film. These comparisons indicate that the failure of the adhesive joint occurred mainly at the inner layer of the Kapton film. This inference is supported from the elemental analysis of the peeled-off layer surfaces.

**Table 3. Atomic Composition of the Parts Peeled Off from the Adhesive Joint between the Graft-Polymerized Kapton Film and Copper Metal**

| modification of Kapton film | atomic composition at the failure surface: Kapton film side N/C | O/C | Cu/C | copper layer side N/C | O/C | Cu/C |
|---|---|---|---|---|---|---|
| none | 0.11 | 0.26 | 0 | 0 | 1.03 | 0.40 |
| graft-polymerized for 6 h | 0.12 | 0.23 | 0 | 0.11 | 0.27 | 0.03 |
| graft-polymerized for 24 h | 0.11 | 0.21 | 0 | 0.14 | 0.28 | 0.03 |

Table 3 summarizes the atomic composition of the surface of the layers peeled off from the adhesive joint. Three adhesive joints were used for the analysis: The original Kapton film/copper metal joint and the graft-polymerized (for 6 and 24 h) Kapton film/copper metal joint. For the Kapton film side layer peeled off from all adhesive joints, no copper metal is observed, but for the copper metal side layer peeled off, the copper metal is observed. Therefore, the failure of the adhesive joint never occurred at the inner layer of the copper metal. The N/C and O/C atomic ratios at the surface of the peeled-off layer are an indicator to determine the failure mode. There is a large difference in the N/C and O/C atomic ratios between the Kapton film and graft polymer: The Kapton film (N/C atomic ratio = 0.091, O/C atomic ratio = 0.227) has a much lower N/C atomic ratio than the graft polymer (N/C atomic ratio = 0.40, O/C atomic ratio = 0), but a much higher O/C atomic ratio. The N/C atomic ratio for both Kapton film side and copper metal side layers peeled off from the adhesive joints except the original Kapton film/copper metal adhesive joint is not so high as 0.4 but 0.11−0.14, and the O/C atomic ratio is high and 0.21−0.28. These N/C and O/C atomic ratios are similar to those of the Kapton film rather than of the graft polymer. Therefore, we conclude that the failure of the adhesive joints between the graft-polymerized Kapton film and copper metal occurred mainly at the inner layer of the Kapton film. On the other hand, the N/C and O/C atomic ratios for the adhesive joint between the original Kapton film and copper metal are different from those for the graft-polymerized Kapton film/copper metal adhesive joint. No nitrogen is observed at the surface of the copper side layer peeled off, and the O/C atomic ratio is high. For the Kapton film side layer peeled off, the N/C and O/C atomic ratios are similar to those of the Kapton film, and no copper metal is observed. Therefore, we conclude that the failure of the adhesive joint between the original Kapton film and copper metal occurred mainly at the interface between the Kapton film and copper metal rather than at the inner layer of the Kapton film. The difference in the failure mode between the graft-polymerized Kapton film/copper metal adhesive joint and the original Kapton film/copper metal adhesive joint shows an effective contribution of the graft polymer to the adhesion with copper metal.

## Conclusion

The surface of Kapton film was modified by means of plasma graft polymerization to improve the adhesion with copper metal. Vinylimidazole was graft-polymerized from the peroxide groups which were generated at the surface of the Kapton film by a combination of argon plasma and air exposures. The surface of the graft-polymerized Kapton film was investigated by XPS and AFM. The graft polymer interacted with copper metal to make a charge-transfer complex and showed good adhesion with copper metal. The results are summarized as follows.

1. Vinylimidazole was graft-polymerized from peroxide groups at the surface of Kapton film in an alcohol solution at 70 °C. The weight increase taken up by the graft polymerization increased linearly with increasing graft polymerization time.

2. The graft polymer distributed at the Kapton film surface heterogeneously in an island−sea type structure. The average height of the island was about 20 nm.

3. The graft-polymerized Kapton film interacted with copper metal to make a charge-transfer complex and showed good adhesion with copper metal. The peel strength of the Kapton film/copper metal adhesive joint was improved 2.9 times by the graft polymerization. The failure of the adhesive joint occurred mainly at the inner layer of the Kapton film.

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