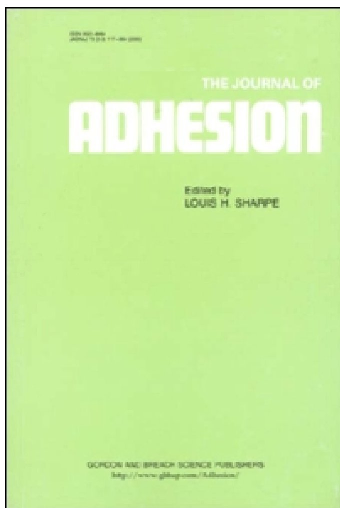
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Analysis of the Molecular Structure at the PPS/Copper Interphase and its Role in Adhesion

H. F. Webster[a]; J. P. Wightman[a]; T. W. Johnson[b]
[a] Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA [b] Phillips Research Center, Phillips Petroleum Company, Bartlesville, Oklahoma, USA

To cite this Article Webster, H. F. , Wightman, J. P. and Johnson, T. W.(1995) 'Analysis of the Molecular Structure at the PPS/Copper Interphase and its Role in Adhesion', The Journal of Adhesion, 53: 3, 229 — 244
To link to this Article: DOI: 10.1080/00218469508009941
URL: http://dx.doi.org/10.1080/00218469508009941

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1995, Vol. 53, pp. 229–244
Reprints available directly from the publisher
Photocopying permitted by license only

© 1995 OPA (Overseas Publishers Association)
Amsterdam B.V. Published under license by
Gordon and Breach Science Publishers SA
Printed in Malaysia

Analysis of the Molecular Structure at the PPS/Copper Interphase and its Role in Adhesion

H. F. WEBSTER* and J. P. WIGHTMAN

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA

T. W. JOHNSON

Phillips Research Center, Phillips Petroleum Company, Bartlesville, Oklahoma 74004, USA

(Received June 27, 1994; in final form April 21, 1995)

X-ray photoelectron spectroscopy (XPS) was used to examine the interfacial chemistry in polyphenylene sulfide (PPS)/copper bonded laminates. Several surface pretreatments were studied including a simple methanol wash, two acid etches, thermal oxidation and chemical oxidation. Peel test analysis showed poor adhesion to the methanol-washed and acid-etched foils, giving a peel strength of only 3–5 g/mm. XPS analysis of the failure surfaces revealed a large amount of inorganic sulfide at the interface with reduction of the copper oxide. Chemical oxidation using an alkaline potassium persulfate solution gave a matt-black surface consisting of primarily cupric oxide. These samples showed improved adhesion and XPS analysis of the failure surfaces revealed fracture through a mixed PPS/cuprous oxide layer. A simple thermal oxidation yielded a cuprous oxide surface layer and laminates bonded to these surfaces showed a more than ten-fold increase in peel strength. XPS analysis of the failure surfaces showed much lower amounts of interfacial copper sulfide and it was postulated that excess sulfide at the interface was responsible for the poor adhesion observed for other pretreatments.

KEY WORDS polyphenylene sulfide; copper; adhesion; interphase; copper sulfide; x-ray photoelectron spectroscopy; peel strength; surface pretreatment; cuprous oxide; cupric oxide

Downloaded At: 12:16 22 January 2011

INTRODUCTION

Due to the growing number of applications in the electronics industry, the interest in polymer/copper adhesion has greatly increased during the last two decades. Polymers have been extensively used for the encapsulation of electrical and electronic devices and 90% of all semiconductor products are supplied with some type of plastic encapsulation.[1] While thermosetting epoxide-based resins have been used extensively for this purpose, polyphenylene sulfide has found applications in this area due to a low dielectric constant, low dissipation factor, and relative ease of injection molding.[2]

The physical and chemical characteristics of the polymer/copper interfacial region are important in determining the adhesion strength and durability of any bonded

* Current address: Chemistry Department, Radford University, Radford VA 24142, USA.

electronic device. Sharpe coined the phrase "interphase" to describe the transition zone of properties when dissimilar materials are brought into contact[3] and a number of studies have been devoted to the characterization of the interfacial region between copper substrates and various polymers. Due to the increasing importance of polyimides as dielectric layers in electronic devices, experimental studies have examined various polyimide/copper systems.[4–7] Particular emphasis has been placed on the "site" of interaction for different metals, and the relationship of interfacial chemistry and adhesion strength has also been investigated.[8–10]

Another area of active research is concerned with the oxidative degradation of polymers in the presence of copper. Studies have focused on a number of polymers including polyolefins,[11–15] polyimide[16–17] and polyesterimide enamel coatings,[18–20] and poly (ether ether) ketone.[21] The formation of copper carboxylates has been observed in several studies[11–13, 19] and copper diffusion in the polymer matrix has been observed.[11–13, 17, 19] Degradation seems to be restricted to heating in an oxidative environment, although degradation of PEEK films in a high vacuum environment has also been observed on cuprous and cupric oxide surfaces.[21] Studies have also reported the reduction of copper oxide as an integral part of the degradation process.[21]

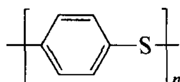
In this work, the interfacial chemistry for copper/polyphenylene sulfide bonded samples has been investigated using X-ray photoelectron spectroscopy. Particular emphasis was placed on the correlation of interfacial chemistry and adhesion strength using a peel test analysis.

Downloaded At: 12:16 22 January 2011

EXPERIMENTAL

Materials

Polyphenylene sulfide (Ryton™, Phillips Petroleum) was obtained as a 0.18 mm crystalline extruded film and has the following structure:



The film was used as-received and XPS analysis indicated mainly carbon and sulfur in a near-stoichiometric amount. Small amounts of oxygen (1–3%) were also detected and attributed to either surface oxidation or low levels of oxygen-containing contaminants. As-received copper foil (0.051 mm thickness ETP 110 grade, Olin Corp.) was degreased using a solvent wipe with methanol (Fisher, reagent grade) and the procedure was repeated several times to remove any excess surface contamination. Two acid etches were used to remove the initial oxide and contamination before bonding. In the first case, copper foil was etched for 15 seconds in 20% (vol/vol) nitric acid (Fisher, 70%) followed by two distilled water rinses and drying with a stream of nitrogen. The second etch was a "brite dip" chemical polish that consisted of a 70:26:4 ratio of acetic acid (Fisher, glacial, 99.7%), phosphoric acid (Fisher, 85%), and nitric acid (Fisher, 70%) by

volume. An etch of 15 seconds was used followed by two distilled water washes, and the sample was dried under a stream of nitrogen.

Oxidation

In addition to the solvent wash and the acid etch treatments, both a chemical and thermal oxidation pretreatment of the copper foil were studied. Chemical oxidation of the copper foil was done using a procedure designed to produce a thick "black oxide" layer.[22–24] Foil samples were first cleaned with the "brite dip" chemical polish followed by an etch in an alkaline potassium persulfate solution. The etching bath was prepared as 60 g/liter sodium hydroxide and 16 g/liter potassium persulfate in distilled water. The bath temperature was maintained at 65–70°C and samples were treated for two minutes followed by a distilled water wash and drying under a stream of nitrogen. For approximately 5 cm × 9 cm size foil samples, only two etches were performed per 200 ml of solution due to the degradation of the etch solution.[22–24] Treatment by this method resulted in a substrate with a matt-black surface finish and analysis by scanning electron microscopy showed the "needle-like" morphology previously reported for this pretreatment.[22–24]

For thermal oxidation, copper foil samples were chemically polished using the "brite dip" solution described above. Thermal oxidation was carried out in a hydraulic heated press immediately prior to bonding, and the inner surface of the foil was exposed to ambient air conditions for oxidation. Typically an oxidation time of 60 to 90 seconds was used prior to the application of pressure and bonding. The foil temperature in the center of the sample was monitored for several samples and quickly exceeded 200°C during the first 15 seconds and reached a final temperature of approximately 260°C after 60 seconds.

Downloaded At: 12:16 22 January 2011

Copper Foil/PPS Laminate Preparation

Copper foil samples were cut to 5.08 cm × 8.89 cm and, after pretreatment, a PPS/copper laminate was constructed as shown in Figure 1. In all cases a 0.10 mm stainless steel spacer was used to maintain a constant bond line thickness for all samples. A temperature of 320°C was used and typically contact pressure for one minute was followed by a bonding time of two minutes at 5.5–6.9 MPa (800–1000 psi). The thin, uniform nature of the laminate formed allowed fast heating and a rapid cycle

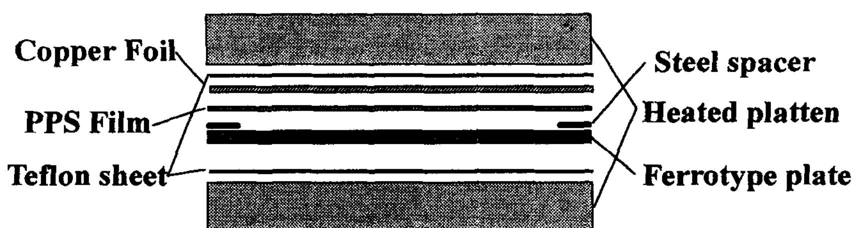


FIGURE 1 Schematic diagram of the laminate structure used in the bonding of PPS to copper foil.

time. After bonding, samples were removed, placed in a cold press and held under a pressure of approximately (3.8–4.8 MPa) 550–700 psi for at least five minutes. Samples were then annealed in an oven under ambient atmospheric conditions for 1–2 hours at 150°C and then analyzed immediately (< 12 hours) by peel test analysis.

Peel Test Analysis

After bonding and annealing, approximately 12 mm wide sample strips were cut using a metal shear. The peel strength was then determined using a slip/peel tester (Model SP-102B-3M90, Instrumentors, Inc.) by peeling the copper foil at a peel rate of 12 mm/min using a 180° peel configuration. All tests were done under ambient laboratory conditions.

X-ray Photoelectron Spectroscopy

After peel test analysis, both failure samples were immediately transferred (< 1 min) to the XPS spectrometer to minimize changes from exposure to atmospheric conditions, XPS analysis was performed using a Perkin-Elmer 5400 spectrometer employing a Mg K_α(1253.6 eV) achromatic x-ray source operated at 15 keV with a total power of 400 W. Typical operating pressures were less than 1×10^{-7} torr and the surface area analyzed was typically a 1×3 mm rectangle. The spectrometer was calibrated to the $4f_{7/2}$ photopeak of gold at 83.8 eV and the $2p_{3/2}$ photopeak of copper at 932.4 eV, and all binding energies were referenced to the main C-H photopeak at 285 eV.

Downloaded At: 12:16 22 January 2011

RESULTS AND DISCUSSION

Analysis of Surface Pretreatment

Figure 2 shows the XPS analysis of the Cu 2p and Cu(LVV) lines for copper foil surfaces pretreated with a methanol wash (Fig. 2a), a nitric acid etch (Fig. 2b), and a "brite dip" chemical polish (Fig. 2c). For the methanol-treated sample, the Cu 2p peak maximum near 935.1 eV, the broad Auger line centered near 337.0 eV, and the presence of shake-up satellites in the Cu 2p spectrum indicate a mixed oxide/hydroxide surface layer typically found for the ambient oxidation of copper surfaces.[25] Treatment by a nitric acid etch seems to remove most of the Cu^{+2} species, and leaves a relatively thin surface copper oxide layer on copper metal. The evidence for metal is shown by an Auger line at 335.4 eV, and the 336.9 eV Auger peak with a corresponding O1s peak position of 530.8 eV indicates that a layer of Cu_2O is present.[26–28] The "brite dip" polish appears to remove most of the surface oxide as only one major Auger line due to copper metal is found at 335.4 eV. An O 1s signal at 531.6 eV may indicate a thin layer of surface carboxylate is present as might be expected from the large component of acetic acid in the etching solution. The effect of pretreatment by thermal and chemical oxidation is shown in Figure 3. For thermal oxidation (Fig. 3b), the shift of the Auger line from 335.4 to 337.4 eV with little change in the Cu 2p line indicates the formation of a surface cuprous oxide layer.[26–28] An O 1s photopeak centered at 530.7 eV is in

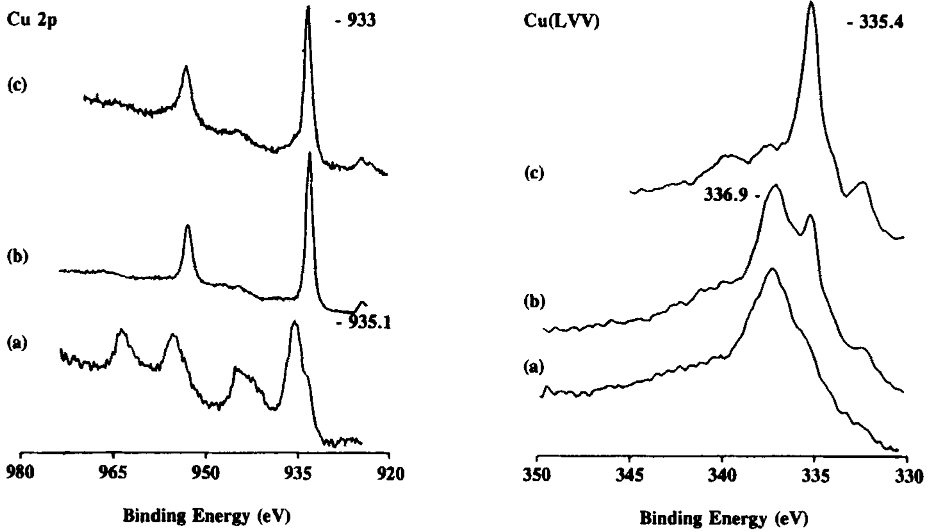


FIGURE 2 XPS analysis of the Cu 2p and Cu(LVV) spectral lines for (a) methanol-washed, (b) nitric-acid-treated, and (c) "brite dip"-treated copper foil.

Downloaded At: 12:16 22 January 2011

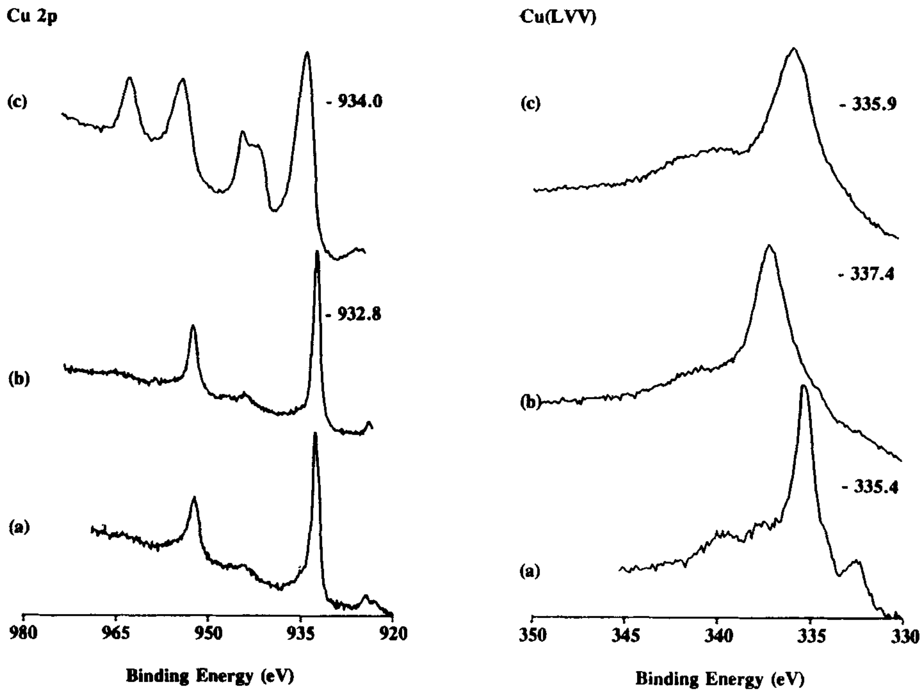


FIGURE 3 XPS analysis of the Cu 2p and Cu(LVV) spectral lines for (a) "brite dip"-treated, (b) thermally-oxidized, and (c) chemically-oxidized copper foil.

agreement with these results. After chemical oxidation (Fig. 3c) in an alkaline persulfate solution, the shift in the Cu 2p line from approximately 933 eV to 934 eV with a small shift in the Auger line from 335.4 to 335.9 eV is consistent with a surface layer of cupric oxide.[26–28] An O 1s photopeak position at 529.7 eV is in agreement with this conclusion, although a shoulder at 531.3 eV may indicate some surface hydroxide species.[28]

The complete XPS analysis for all surface pretreatments is given in Table I. In general, the methanol wash probably does little to change the native surface oxide layer, while acid etches result in a metal substrate with a thin surface oxide or acetate layer. Thermal oxidation gives primarily a cuprous oxide surface while chemical oxidation yields primarily a cupric oxide surface chemistry.

To investigate the morphological changes associated with the thermal and chemical treatment procedures, Figure 4 shows the SEM micrographs of the "brite dip" chemically polished, thermally oxidized, and chemically oxidized foil samples. As can be seen, there is little change due to the thermal oxidation step. For the chemically oxidized foil, however, a unique morphology is evident and the needle-like structures formed are in agreement with results previously reported for this pretreatment.[22–24]

Peel Test Analysis

Table II shows the peel strengths obtained for the five pretreatments used in this study. The methanol-treated sample shows an extremely low peel strength, averaging only 3 g/mm for the samples tested. The use of acid etches does not improve the peel strength as might be expected. Chemical oxidation of the copper foil results in an improvement in peel strength and this might be expected given the needle-like morphology. The most dramatic results, however, are found for the thermal oxidation pretreatment which shows a more than ten-fold increase in the peel strength compared with the methanol-degreased or acid-etched samples. SEM analysis of the surface for thermally-oxidized

Downloaded At: 12:16 22 January 2011

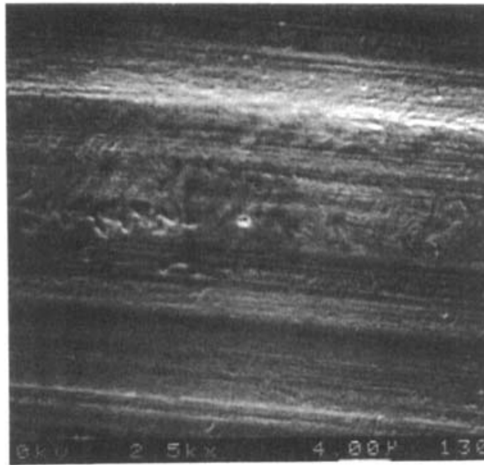
TABLE I
XPS Atomic Concentrations for Copper Foil After Surface Pretreatment

SURFACE			ELEMENT			
	C1s	O1s	S2p	Cu2p	Cu(A)	Cl2p
MeOH	43	45	NSP	12	–	< 1
	(285.0)	(531.8)	–	(935.1)	(337.4)	–
Nitric Acid	46	27	NSP	26	–	< 1
	(285.0)	(530.8)	–	(932.9)	(337.3)	–
					(335.4)	
Brite Dip	31	30	< 1	36	–	< 1
	(285.0)	(531.6)	–	(933.1)	(335.4)	–
Thermal	59	26	NSP	12	–	3
Oxidation	(285.0)	(530.7)	–	(932.8)	(337.3)	(200.7)
Chemical	39	42	NSP	19	–	NSP
Oxidation	(285.0)	(529.7)	–	(934.0)	(335.9)	–
		(531.3)				

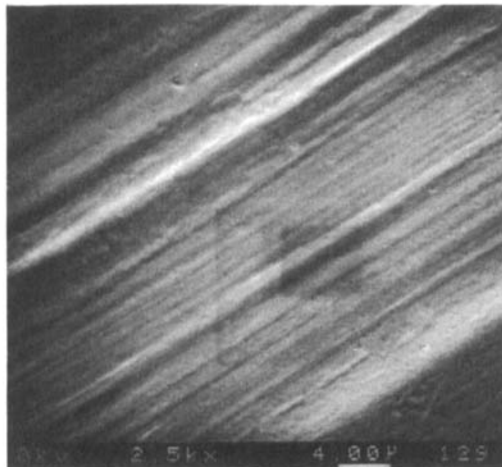
NSP-No significant peak. Binding energies are given in parentheses.

Downloaded At: 12:16 22 January 2011

(a)



(b)



(c)

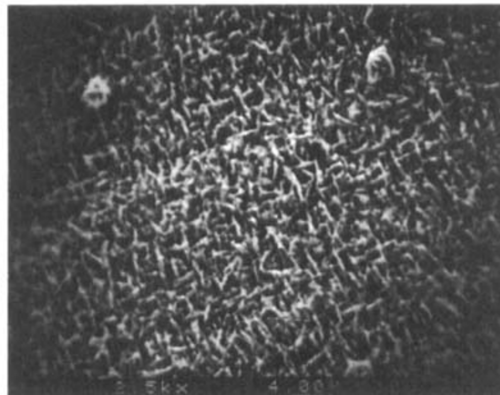


FIGURE 4 SEM analysis of copper foil surfaces for (a) "brite dip"-treated, (b) thermally-oxidized, and (c) chemically-oxidized foil samples.

TABLE II
Peel Test Analysis of Copper/PPS Adhesion

Treatment	Peel Strength (g/mm)
MEOH	3 ± 2
20% Nitric Acid	3 ± 1
Brite Dip	5 ± 2
Chemical Oxidation	27 ± 7
Thermal Oxidation	40 ± 6

samples prior to bonding showed no major change in substrate morphology, and XPS indicated that a relatively simple cuprous oxide surface layer was present. The short, one-minute oxidation step would also not be expected to alter significantly the mechanical properties of the copper film. The results, therefore, must be related to the particular surface chemistry involved between PPS and the thermally-oxidized copper substrate.

Failure Surface Analysis

Figure 5 shows the XPS results for the failure surfaces for the methanol-degreased copper foil samples. As is evident from analysis of the Cu 2p and Cu (LVV) lines, the original surface (Fig. 5a) consisting of a mixed oxide/hydroxide layer has been reduced to copper metal as evident by the Cu (LVV) Auger line at 335.3 eV for the foil failure

Downloaded At: 12:16 22 January 2011

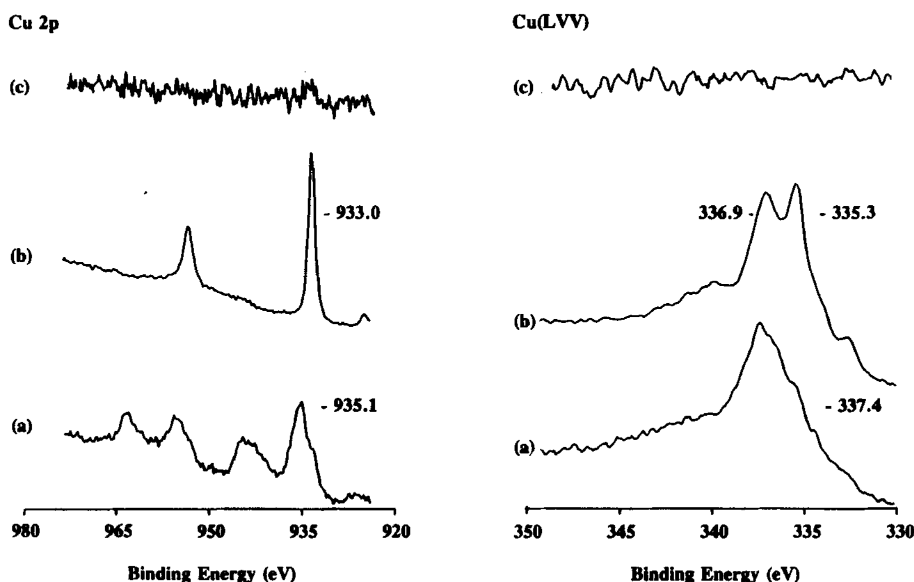


FIGURE 5 XPS analysis of the Cu 2p and Cu(LVV) spectral lines for failure surfaces of PPS bonded to methanol-degreased copper foil showing (a) the foil surface before bonding, (b) the foil failure surface, and (c) the adhesive failure surface.

surface. A second Auger peak at 336.9 eV is also apparent and with the Cu 2p photopeak position at 933.0 eV, indicates a Cu^{+1} surface species. Figure 6 shows the analysis of the S 2p photopeak for both the polymer (Fig. 6a) and foil failure (Fig. 6b) surfaces and it is apparent that considerable sulfur remains on the foil failure surface. The photopeak at 163.7 eV corresponds to a thin PPS layer[29] while the peak at 162.2 eV can be assigned to a copper sulfide species.[30] Angle-dependent XPS analysis indicated that the sulfide layer was beneath the thin PPS surface film, indicating that fracture occurred through a PPS interfacial layer. In agreement, no copper was detected on the polymer failure surface (see Fig. 5c). Figure 7 shows a similar analysis of the S 2p and Cu (LVV) lines for the "brite dip" cleaned copper foil. The Cu (LVV) shows the new peak at 336.9 eV for the foil failure surface (Fig. 7b) and the sulfur line again shows the presence of copper sulfide at 162.2 eV. The Auger signal can then be attributed in part to the presence of cuprous sulfide.[27] Figure 8 shows the analysis for the nitric acid cleaned copper foil and indicates the partial reduction of oxide to metal as shown by the increase in the 335.3 eV Auger line and decrease in the 336.9 eV oxide peak. Again, copper sulfide is indicated by the presence of the S 2p photopeak at 162.3 eV. Table III shows the complete analysis of the methanol-degreased and acid-cleaned foil failure surfaces. The most noticeable feature is the extremely small oxygen concentration (2–3%) found for the foil failure surfaces (Table III, A, B, C) when compared with surfaces prior to bonding. Secondly, a large sulfur signal ranging from 13–16% on the foil failure surfaces is seen, and a substantial amount of

Downloaded At: 12:16 22 January 2011

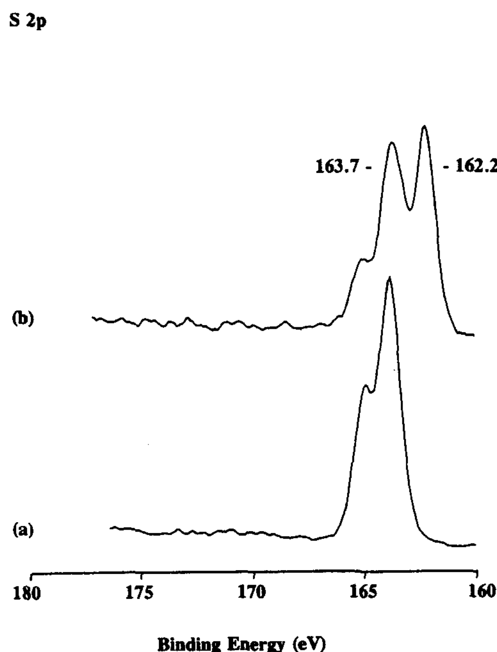


FIGURE 6 XPS analysis of the S 2p photopeak for failure surfaces of PPS bonded to methanol-degreased copper foil showing (a) the adhesive failure surface, and (b) the foil failure surface.

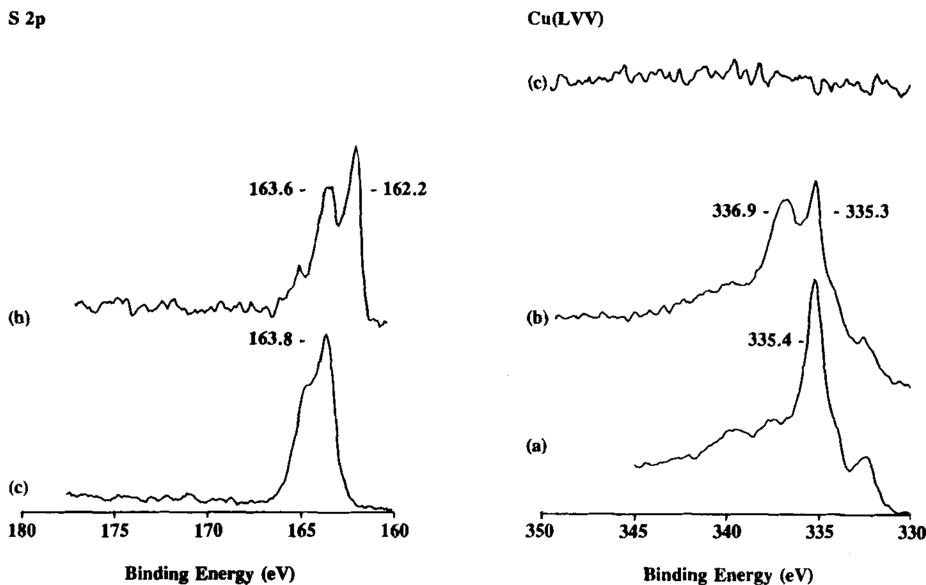


FIGURE 7 XPS analysis of S 2p and Cu(LVV) photopeaks for failure surfaces of PPS bonded to "brite dip"-etched copper foil showing (a) the foil surface before bonding, (b) the foil failure surface, and (c) the adhesive failure surface.

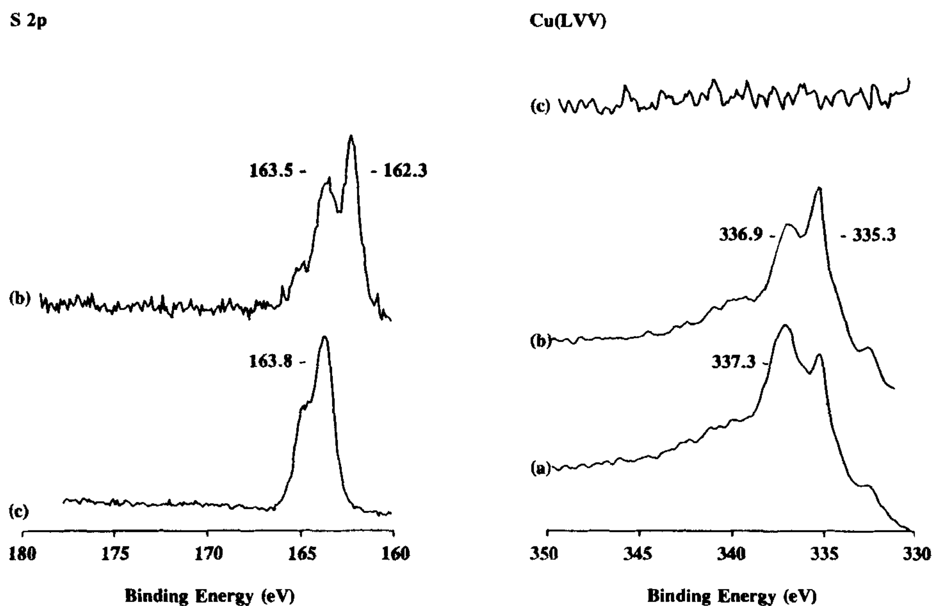


FIGURE 8 XPS analysis of the S 2p and Cu(LVV) photopeaks for failure surfaces of PPS bonded to nitric-acid-etched copper foil showing (a) the foil surface before bonding, (b) the foil failure surface, and (c) the adhesive failure surface.

Downloaded At: 12:16 22 January 2011

TABLE III
XPS Atomic Concentrations for Copper Foil/PPS Failure Surfaces

	SURFACE	ELEMENT*				
		Cls	Ols	S2p	Cu2p	Cu(A)
A.	Foil Side	67 (285.0)	3 (45)† (531.8)	16 (163.7/162.2)	12 (933.0)	– (336.9/335.3)
	PPS side	83 (285.0)	2 (532.3)	15 (163.8)	NSP –	NSP –
B.	Foil Side	62 (285.0)	2 (27) (531.6)	16 (163.5/162.3)	17 (933.0)	– (336.9/335.3)
	PPS Side	85 (285.0)	1 (532.5)	14 (163.8)	NSP –	NSP –
C.	Foil Side	64 (285.0)	3 (30) (531.2)	13 (163.6/162.2)	20 (932.8)	– (336.9/335.3)
	PPS Side	86 (285.0)	3 (533.1)	11 (163.8)	NSP –	NSP –
D.	Foil Side	58 (285.0)	14 (26) (530.7)	7 (163.9/162.3)	19 (932.8)	– (337.4)
	PPS Side	81 (285.0)	6 (532.3)	11 (163.8)	2 (935.2)	– (339.5)
E.	Foil Side	62 (285.0)	17 (42) (530.7)	6 (163.8)	15 (932.9)	– (337.3)
	PPS Side	61 (285.0)	17 (530.8)	6 (163.7)	16 (933.1)	– (337.2)

Treatment: A. Methanol wash; B. Nitric Acid; C. Brite Dip; D. Thermal Oxidation; E. Chemical Oxidation
NSP–No significant peak. Binding energies are given in parentheses.
* For some foil side samples, a small chlorine signal was detected.
† The atomic percents for oxygen given in parentheses represent the original oxygen concentration.

Downloaded At: 12:16 22 January 2011

this total signal represents inorganic sulfur. The similar chemical composition for all samples implies a similar interfacial chemistry involved for these samples.

Figure 9 shows the XPS analysis for the thermally-oxidized foil samples, and a dramatic difference can be seen when these results are compared with those for methanol and acid cleaned foil surfaces. For the Auger line, although a slight peak at 335.3 eV may indicate some reduction of oxide in the bonding process, the foil failure surface (Fig. 9b) appears very similar to the original pretreated surface (Fig. 9a). Also, a small Auger signal at approximately 339.5 eV is seen on the polymer failure surface (Fig. 9c), although the identity of such a high binding energy peak is not clear. Although the S 2p photopeak shows evidence of inorganic sulfur at 162.3 eV on the foil failure surface (Fig. 9b), the relative amount when compared with previous pretreatments is much less, and indicates either a shift of the average failure plane into the polymer, or a lower concentration of copper sulfide at the interface.

Figure 10 shows the XPS analysis for chemically-oxidized copper foil. As can be seen, analysis of the Auger signal indicates the general reduction of cupric to cuprous oxide and analysis of the Cu2p photopeak shows a shift to 933 eV and a loss of all shake-up

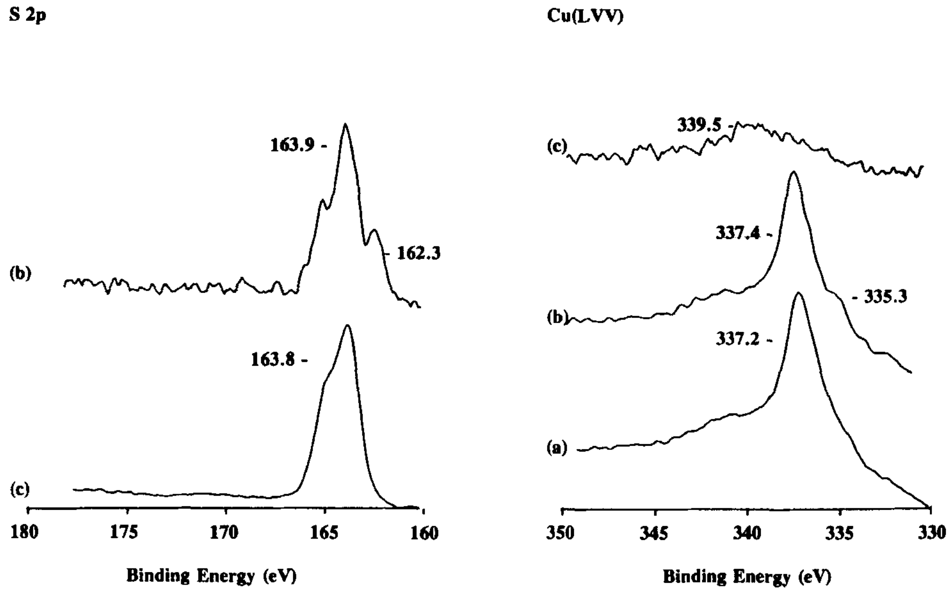


FIGURE 9 XPS analysis of the S 2p and Cu(LVV) photopeaks for failure surfaces of PPS bonded to thermally-oxidized copper foil showing (a) the foil surface before bonding, (b) the foil failure surface, and (c) the adhesive failure surface.

Downloaded At: 12:16 22 January 2011

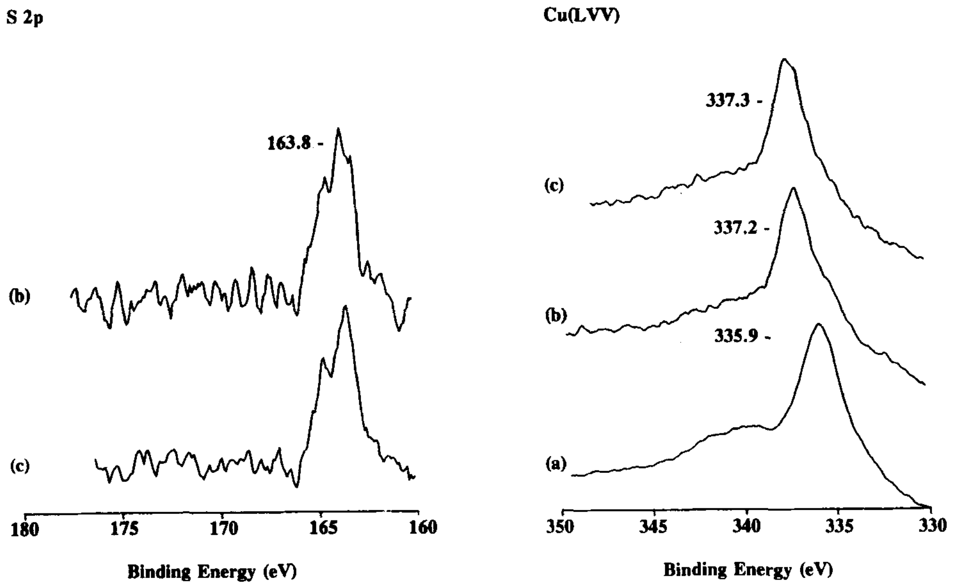


FIGURE 10 XPS analysis of the S 2p and Cu(LVV) photopeaks for failure surfaces of PPS bonded to chemically-oxidized copper foil showing (a) the foil surface before bonding, (b) the foil failure surface, and (c) the adhesive failure surface.

TABLE IV
XPS Analysis of Relative Concentrations of Inorganic and Organic Sulfur From Foil Failure Surfaces

Pretreatment	Percent Composition S 2p(o)	S 2p(i)	(i)/(o)	(i)/Cu
MeOH	7 (163.8)	9 (162.2)	1.3	0.75
Nitric Acid	6 (163.8)	10 (162.1)	1.7	0.59
Brite Dip	4 (163.8)	9 (162.2)	2.3	0.45
Thermal Oxidation	5 (163.8)	2 (162.2)	0.40	0.11
Chemical Oxidation	5 (163.8)	0.4 (162.0)	0.08	0.03

(o) designates organic sulfur
(i) designates inorganic sulfur

Downloaded At: 12:16 22 January 2011

features. Also, analysis of the sulfur spectrum shows only the presence of organic sulfur due to PPS. The results show the same chemistry present on both the foil (Fig. 10b) and polymer (Fig. 10c) failure surfaces and may indicate a great deal of interdiffusion between the surface copper oxide and polymer with fracture occurring in the mixed layer. This could be expected given the fragile needle-like structure of the surface oxide formed during the chemical oxidation procedure. With the bonding conditions used, the surface structure is probably destroyed, and the oxide readily mixes with the molten PPS. Also, this type of chemical oxidation has been shown to form a mixture of cupric and cuprous oxide,[23] and ion milling has indicated the formation of a dense cuprous oxide underlayer that supports a fragile cupric oxide surface layer.[31] A complete analysis for thermally and chemically treated surfaces is given in Table III and an interesting point is the higher concentration of oxygen found on the copper foil failure surfaces (Table 3 D, E) when compared with the other surface pretreatments studied.

Table IV shows a more detailed analysis of the residual sulfur found on the foil failure surfaces. For this analysis, the S 2p photopeak was curve fit into two peaks for the organic (163.8 eV) and inorganic components (162.2 eV). Parameters used for the curve fitting procedure assumed a peak spacing of 1–1.2 eV for the S $2p_{3/2}$ and S $2p_{1/2}$ photopeaks, and a value of 1.8–2.2 for the S $2p_{3/2}$ to S $2p_{1/2}$ peak area ratio.

The results in Table IV show that for the methanol-degreased foil and the acid-etched foil surfaces, a relatively high inorganic sulfur content of 9–10% was found for all cases. A smaller amount of organic sulfur indicative of a residual PPS film was also seen, and an inorganic sulfur to organic sulfur ratio [(i)/(o)] of approximately 1–2 was seen for these three cases. For comparison, the thermal and chemical oxidation yielded values of 0.40 and 0.08, respectively, for this ratio, and the much lower inorganic sulfur content could arise from two possibilities. The first would be a much lower reactivity, and the second could simply be a shift in the average failure plane giving a much thicker

surface PPS film. This would cover the underlying sulfide layer and result in a lower inorganic sulfur signal. The total sulfur signal of only 5–7% seems to rule out the second possibility, but another measure of inorganic sulfur content can be obtained by examining the inorganic sulfide to copper ratio [(i)/(Cu)]. These values are also given in Table IV, and the ratio of approximately 0.45–0.75 for the methanol-degreased and acid-etched foils is much higher than the value of 0.03–0.11 found for the chemically- and thermally-oxidized samples. This analysis again seems to indicate a much reduced inorganic sulfur content for the oxidized copper foil samples.

For the chemical oxidation of copper foil, the large change in both surface chemistry and surface morphology makes any correlation with peel strength difficult. Given the lack of change in surface morphology for thermally-oxidized foil samples, however, this pretreatment represents an interesting case where a relatively minor change in surface chemistry results in a substantial increase in peel strength. Results show a reduced concentration of inorganic sulfide when compared with solvent-degreased and acid-etched samples, and this probably indicates that excessive sulfide formation at the interface is responsible for the almost complete loss of peel strength. Van Ooij[32] showed that while small amounts of copper sulfide were beneficial to bond strength in brass/rubber adhesion, excessive formation of interfacial cuprous sulfide actually gave poor adhesion for these systems. Beecher[33] used XPS to study the interaction of diphenyl sulfide with cuprous and cupric oxide under high vacuum conditions. A surface species was observed with a binding energy of 162.9 eV and the formation of a copper phenyl sulfide species was postulated. Although not observed directly, it was also postulated that a copper phenoxide also formed and combined with surface hydrogen to give phenol. In this work, the binding energy of approximately 162.2 eV for the S2p indicates a copper sulfide and this may represent the end product under the high temperatures and pressures used for bonding. The reduction of copper oxide seen for the methanol-washed and nitric-acid-treated surfaces seems to be consistent with this simple mechanism. The lower reactivity of a thicker layer of cuprous oxide for thermally pre-treated surfaces *versus* a thin layer of oxide on metal for nitric-acid-treated samples may indicate that the copper metal plays a catalytic role in the sulfide formation. Allara showed that the catalytic effect of copper on polyethylene oxidation was almost one order of magnitude greater for copper stored in air than for cupric oxide.[14] A similar effect may be responsible for the apparent difference in reactivity seen here.

The formation of copper sulfide species may also occur during the disproportionation reactions known to occur for PPS polymers and oligomers held at elevated temperatures in inert environments.[34] Since these reactions would still be expected to occur irrespective of substrate, the unique role of the copper surface chemistry in the formation of sulfide must again be considered. The extraction of sulfur to form copper bonded sulfur species would alter the physical polymer properties in the interphase region, and this would most likely result in a loss in crystallizability and possible formation of an amorphous, fragmented interfacial polymer layer. For thermally-oxidized foil samples, where the amount of interfacial sulfide is relatively small, the degree of polymer damage would be much less. While fracture during peeling still occurs through a thin surface PPS layer, the polymer properties including crystallinity and molecular weight may be more similar to those of bulk PPS.

Downloaded At: 12:16 22 January 2011

SUMMARY

An investigation of PPS/copper bonding was undertaken and peel test results showed poor adhesion with copper bonded to methanol-washed, nitric-acid-etched or "brite dip"-etched copper foils. XPS analysis of failure surfaces revealed a large amount of copper sulfide at the interface for all these pretreatments. Analysis of a chemical oxidation showed a cupric oxide surface originally and that fracture occurred in a mixed PPS/cuprous oxide layer for bonded laminates. Thermal oxidation resulted in primarily a cuprous oxide surface layer with little change in surface morphology. Peel strengths for PPS/copper laminates using this pretreatment increased ten times compared with the acid etched surfaces, and XPS analysis of the failure surfaces showed a relatively small amount of interfacial sulfide. Excess sulfide and polymer damage at the interface were postulated to contribute to the poor adhesion seen for methanol-washed and acid-etched copper samples. Given the relatively mild treatment for thermal oxidation, the importance of surface chemistry in determining adhesion strength is dramatically demonstrated for this system.

Acknowledgements

The financial support of Phillips Petroleum is gratefully acknowledged.

Downloaded At: 12:16 22 January 2011

References

1. R. P. Merrett, in *Plastics for Electronics*, M. T. Goosey, Ed. (Elsevier Applied Science, London, 1985), Chap. 6.
2. M. T. Goosey, in *Plastics for Electronics*, M. T. Goosey, Ed. (Elsevier Applied Science, London, 1985), Chap. 10.
3. L. H. Sharpe, *J. Adhesion* **4**, 51 (1972).
4. R. G. Mack, E. Grossman and W. N. Unertl, *J. Vac. Sci. Technol.* **8**, 3827 (1990).
5. T. Strunskus, D. Hahn, D. Frankel and M. Grunze, *J. Vac. Sci. Technol.* **9**, 1272 (1991).
6. P. S. Ho, P. O. Hahn, J. W. Bartha, G. W. Rugloff, F. K. Legoues and B. D. Silvermann, *J. Vac. Sci. Technol* **3**, 739 (1985).
7. P. N. Sanda, J. W. Bartha, J. G. Clabes, J. L. Jordan, C. Feger, B. D. Silverman and P. S. Ho, *J. Vac. Sci. Technol.* **4**, 1035 (1986).
8. L. P. Buchwalter and R. H. Lacombe, *J. Adhes. Sci. Technol.* **2**, 463 (1988).
9. T. S. Oh, L. P. Buchwalter and J. Kim, *J. Adhes. Sci. Technol.* **4**, 303 (1990).
10. L. P. Buchwalter, *J. Adhes. Sci. Technol.* **4**, 697 (1990).
11. M. G. Chan and D. L. Allara, *Polym. Eng. Sci.* **14**, 12, (1974).
12. M. G. Chan and D. L. Allara, *J. Colloid Interf. Sci.* **47**, 697 (1974).
13. D. L. Allara, in *Characterization of Metal and Polymer Surfaces*, L. H. Lee, Ed. (Academic, New York, 1977), p. 193.
14. D. L. Allara and M. G. Chan, *J. Polym. Sci.: J. Polym. Chem. Ed.* **14**, 1857 (1976).
15. D. L. Allara and R. F. Roberts, *J. Catal.* **45**, 54 (1976).
16. K. Kelley, Y. Ishino and H. Ishida, *Thin Solid Films* **154**, 271 (1987).
17. M. C. Burrell and J. Keane, *Surf. Intef. Anal.* **11**, 487 (1988).
18. M. C. Burrell, J. Fontana and J. J. Chera, *J. Vac. Sci. Technol.* **6**, 2893 (1988).
19. M. C. Burrell, P. J. Codella, J. A. Fontana and J. J. Chera, *J. Vac. Sci. Technol.* **7**, 1778 (1989).
20. R. B. Prime, *J. Polym. Sci.: Polym. Lett.* **24**, 641 (1986).
21. R. D. McElhaney, D. G. Castner and B. D. Ratner, in *ACS Symp. Series 440*, E. Sacher, J. J. Pireaux and S. P. Kowalczyk, Eds. (American Chemical Society, Washington, D. C., 1990), p. 371.
22. A. Scherer, O. T. Inal and A. J. Singh, *Solar Energy Materials* **9**, 139 (1983).
23. O. T. Inal and A. Scherer, *J. Mat. Sci.* **21**, 729 (1986).
24. A. Scherer, O. T. Inal and R. B. Pettit, *J. Mat. Sci.* **23**, 1923 (1988).

25. T. L. Barr, *Surf. Interf. Anal.* **4,** 185 (1982).
26. T. H. Fleisch and G. J. Mains, *Appl. Surf. Sci.* **10,** 51 (1982).
27. G. Deroubaix and P. Marcus, *Surf. Interf. Anal.* **19,** 39 (1992).
28. N. S. McIntyre and M. G. Cook, *Anal. Chem.* **47,** 2208 (1975).
29. J. Riga, J. P. Boutique, J. J. Pireaux and J. J. Verbist, in *Physiochemical Aspects of Polymer Surfaces*, K. L. Mittal, Ed. (Plenum Press, New York, 1983), p. 45.
30. J. M. Machefert, M. Calvar and M. Lenglet, *Surf. Interf. Anal.* **18,** 39 (1991).
31. A. Scherer and O. T. Inal, *Thin Solid Films* **119,** 413 (1984).
32. W. J. van Ooij, *Surf. Sci.* **68,** 1 (1977).
33. J. F. Beecher, *Surf. Interf. Anal.* **17,** 245 (1991).
34. R. T. Hawkins, *Macromolecules*, **9,** 189 (1976).

Downloaded At: 12:16 22 January 2011