

# Photochemical Surface Modification of Poly(ethylene Terephthalate)

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## Synopsis

To elucidate the role of chemical interactions in the promotion of metal-polymer adhesion, a poly(ethylene terephthalate)/copper system was studied. Surface photografting of unsaturated monomers containing different chemical functional groups onto a three-mil poly(ethylene terephthalate) film provided a means of examining a variety of copper-polymer interfaces. Initial graft verification was accomplished via contact angle measurements. Adhesion strengths to vacuum-deposited copper were determined using 90° peel tests. Graft analysis, as well as investigation of the interfacial interaction between copper and the grafted moieties, was accomplished using X-ray photoelectron spectroscopy.

## INTRODUCTION

To develop an understanding of the effect of chemical interaction on the strength of interfacial bonding, a study of polymer-metal interfaces has been undertaken. To examine the chemical component of adhesion at the polymer-metal interface, it was decided to proceed via chemical modification of the polymer surface.

Most techniques used to chemically modify polymer surfaces fall into one of two categories: wet chemistry (solution processes) and dry processing (plasma modification). For the current work a wet process was selected.

Wet chemical surface modification can be performed as simply as submerging a polymer in a reducing or oxidizing solution and examining the subsequently effected change. For versatility, a technique like grafting is usually employed.<sup>1</sup> To enhance the surface selectivity of the technique one may wish to utilize a photografting system. The literature contains work which discusses the basic adhesion mechanisms in photopolymeric systems<sup>2</sup> and the various types of radiation that have been used.<sup>3-6</sup> An interesting technique is reported by Tazuke et al.<sup>7,8</sup> and employs a surface photografting method. The system described uses the well known properties of benzophenone as a sensitizer<sup>9,10</sup> and holds promise as a means of grafting various functionalities onto a polymer surface. By grafting unsaturated monomers containing different chemical groups and subsequently measuring the adhesion of vacuum-deposited metal it will be possible to understand the effect of specific chemical interactions on the strength of interfacial adhesion.

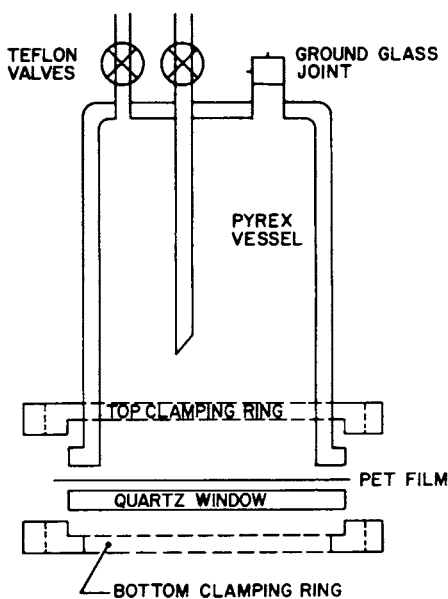


Fig. 1. Photografting apparatus.

## EXPERIMENTAL

### Instrumentation

All photografting experiments were carried out in custom-made reaction vessels. A typical design is schematically depicted in Figure 1.

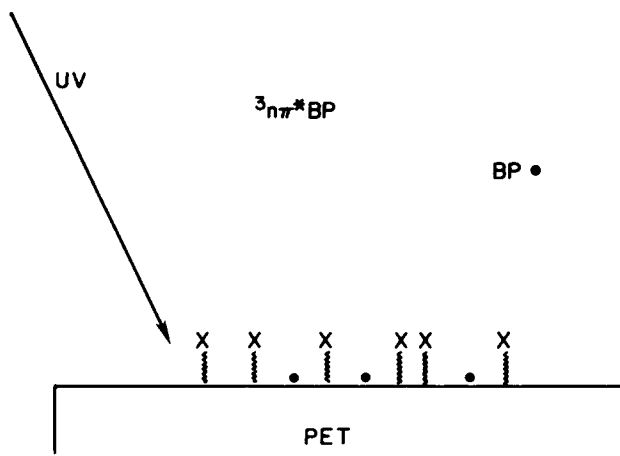
Contact angle measurements were made using the sessile drop measurement technique and a Rame-Hart (Mountain Lakes, NJ) NRL contact angle goniometer model 100 equipped with a tilting base, environmental chamber, and microsyringe attachment.

Copper sputter deposition was done using a Material Research Corporation (Orangeburg, NY) model 903 planar magnetron metal deposition system. Subsequent electroplating of sputter-deposited films was done using a standard acidic cupric sulfate bath and a current density of  $3.5 \text{ mA/cm}^2$ .

Metal vacuum deposition via electron beam evaporation was done in a system specifically designed and constructed for that purpose. The system employs a  $270^\circ$  electron gun and an 8 kW power supply. A four-hearth rotatable holder is used to contain the evaporant. A pumping package that uses a 6-in diffusion pump backed by a mechanical pump is capable of evacuating the chamber to  $10^{-6}$  or  $10^{-7}$  torr routinely. Evaporation rate is monitored with a quartz crystal and an XMS-3 Inficon crystal monitor.

Peel testing utilizing  $90^\circ$  peel tests was performed on an MTS Systems Corporation (Guilford, CT) model 812 Materials Testing System. Stroke-controlled peels at a rate of 1.2 inches/500 s were standard.

Ultraviolet irradiation was accomplished using either a Mineralite 1250  $\mu\text{W/cm}^2$  ultraviolet (UV) lamp (designated UV I) or a Spectroline 9000  $\mu\text{W/cm}^2$  UV lamp (designated UV II).



X= VARIOUS FUNCTIONAL GROUPS

Fig. 2. Photografting scheme.

X-ray photoelectron spectroscopy was performed on a Physical Electronics (Eden Prairie, Minnesota) XPS/AES model 560 instrument using a magnesium  $K_{\alpha}$  source, and on a Leybold-Heraeus (Syracuse NY) 8659 ESCA instrument with an aluminum  $K_{\alpha}$  source.

### Chemicals

Three-mil poly(ethylene terephthalate) [PET] film was purchased as a 40-in  $\times$  100 ft roll from Ain Plastics (Mt. Vernon, NY). Acrylamide 99+ % electrophoresis-grade, acrylic acid, acrylonitrile 99+ %, allylamine 99+ % gold label, allyl cyanide, 4-allyl-2 thiourea 98%, 4-vinyl pyridine 98%, benzophenone 99+ %, and HPLC-grade water were purchased from Aldrich. Poly(acrylamide), poly(acrylic acid), and poly(acrylonitrile) were purchased from Fluka. Dimethylsulfoxide (DMSO) distilled in glass was purchased from Burdick and Jackson. Semigrade acetone was purchased from Mallinckrodt. Semigrade sulfuric acid was purchased from Ashland. Cupric sulfate was purchased from Baker. All chemicals were used as received.

### RESULTS AND DISCUSSION

Photochemical surface modification in acetone solutions using benzophenone as initiator is schematically depicted in Figure 2. The apparatus used was shown previously in Figure 1. One surface of the PET film is held in contact with an acetone solution of approximately 0.2M benzophenone and 2M graft monomer. For the best results vinyl or allyl monomers were used. Ultraviolet irradiation through the film results in the generation of  $^3n\pi^*$  excited states of benzophenone. The  $^3n\pi^*$  excited state decays via hydrogen abstraction from the film, leaving behind a radical to graft polymerize the unsaturated monomers from solution. In all photografting experiments the

TABLE I  
Photografting Series One: Contact Angle Measurements

Sample	Advancing 0.05 mL	Receding 0.025 mL
Acrylamide	54.8 ± 1.94	32.5 ± 9.29
Acrylonitrile	65.3 ± 4.51	41.3 ± 1.53
	62.5 ± 3.54	44.5 ± 0.71
4-Vinyl pyridine	67.0 ± 2.16	44.2 ± 3.30
	73.7 ± 1.15	47.7 ± 2.31
Virgin PET	79.2 ± 2.22	53.8 ± 2.63
	85.5 ± 0.71	58.1 ± 0.14
	82.5 ± 2.12	54.0 ± 2.83
	80.0 ± 1.41	61.5 ± 2.12
	79.0 ± 1.41	56.0 ± 2.83

solution was nitrogen degassed before UV irradiation. Upon completion of UV exposure, the grafts were rinsed with acetone and then flowing deionized water overnight.

To determine suitable experimental parameters that would produce successful grafting, a first run of experiments was conducted. These preliminary experiments were labeled photografting series one. The monomers used were acrylamide, acrylonitrile, and 4-vinylpyridine. Grafting solutions were mixed to give approximately 2M monomer and 0.2M initiator. Both 1 and 2 h exposures to the UV I source were employed. After UV exposure, the PET film was observed to be cloudy, and in the case of the acrylamide graft, a layer of white residue remained after rinsing with acetone. All grafts were subjected to flowing deionized water overnight, and the transparency of the PET film was restored. Before measuring contact angles, the grafts were dried for several days in a vacuum dessicator. Water contact angles measured on these three graft samples, as well as untreated PET, are presented in Table I. The measured contact angles were clearly different for the grafted films as compared to the virgin PET. Before deciding if this was an indication of successful grafting, a short side experiment was conducted. The water contact angle for a piece of virgin 3-mil PET was measured to be  $81.7 \pm 2.8$  degrees advancing and  $57.6 \pm 3.2$  degrees receding. This same piece of PET was then submerged in an acetone solution of 2M acrylamide and 0.2M benzophenone, but it was kept in the dark. The film was rinsed with acetone and then flowing deionized water overnight. After drying several days in a vacuum dessicator the water contact angle measured was  $80.9 \pm 2.4$  degrees advancing and  $55.9 \pm 2.7$  degrees receding. Since these values were typical of the PET film being used, it was concluded that previously observed changes in contact angle for grafted samples were indeed an indication of successful grafting, and were not due to solvent effects or simple adsorption of monomer onto the film.

Based upon the success of the series one photografts, work proceeded with series two. New photografting solutions were prepared. UV exposure time was standardized at 3 h, and photografting runs were executed. Contact angle measurements indicated successful grafting, so the samples were metallized. Metallization was accomplished by first direct current sputtering 6000 Å of

TABLE II  
Series Two Photografts: Sputter-Deposited/Electroplated Copper Peel Strength Summary

Sample	Peel strength (g/5 mm) $\bar{x} \pm s'$	
	As deposited	Annealed <sup>a</sup>
Acrylic acid	9.50 $\pm$ 1.11	23.45 $\pm$ 4.8
Allyl urea	8.10 $\pm$ 1.0	18.09 $\pm$ 0.13
Allyl thiourea	9.62 $\pm$ 2.27	10.24 $\pm$ 1.3
Acrylamide	27.45 $\pm$ 0.07	22.36 $\pm$ 6.9
Allyl cyanide	6.15 $\pm$ 0.49	14.25 $\pm$ 0.35
Allyl thiosemicarbazide	5.30 $\pm$ 1.42	16.05 $\pm$ 2.47
Acrylonitrile	2.23 $\pm$ 0.06	10.58 $\pm$ 3.72

<sup>a</sup>18 h at 85°C in air.

copper and then electroplating to a suitable thickness. Since a suitable thickness was not known, plating times were varied. The results indicated that 1 h (5  $\mu$ ) was the optimum. At this juncture it was noted that the copper layer spontaneously delaminated from the virgin PET during the plating. This result was observed several times during repeat experiments.

Having standardized plating time to yield 5  $\mu$  thick copper, grafted samples were subjected to 90° peel tests. The results are presented in Table II. Clearly there is a distinct improvement over the zero peel strength observed for virgin PET.

Having completed the series with sputter-deposited/electroplated copper, it was decided to examine the trend with electron beam-evaporated copper. The monomers selected were: acrylamide, acrylic acid, acrylonitrile, and allylthiosemicarbazide. Grafting experiments were performed using the more powerful UV II source. After contact angle verification of successful grafting, the grafts and virgin 3-mil PET were mounted on 2.25-in. circular aluminum coupons with double-stick tape. Copper was evaporated onto the samples through a 5 mm standard peel test mask. Electron beam evaporation was carried out at a rate of 20 Å/s to a final thickness of 10  $\mu$  at a sample temperature of 37°C. Samples were then 90° peel-tested at 1.2"/500 s stroke control on an MTS instrument. The results are presented in Table III. The as-deposited peel strength for the PET blank was higher than any of the grafts. Upon annealing the trend observed for the sputter-deposited/electroplated copper is regener-

TABLE III  
Electron Beam-Evaporated Copper: Peel Tests

Sample	Peel strength (g/5 mm) $\bar{x} \pm$ S.D.	
	As deposited	Annealed <sup>a</sup>
Virgin PET	15.7 $\pm$ 2.3	19.7 $\pm$ 0.8
Acrylamide	11.7 $\pm$ 1.5	30.8 $\pm$ 5.8
Allyl thiosemicarbazide	12.0 $\pm$ 2.7	25.8 $\pm$ 1.6
Acrylonitrile	11.8 $\pm$ 1.0	29.4 $\pm$ 1.2
Acrylic acid	12.7 $\pm$ 1.2	27.2 $\pm$ 4.2

<sup>a</sup>18 h at 85°C in air.

ated. Perhaps an additional effect of annealing is that it supplies the necessary activation energy to promote the surface reaction between the copper and the grafted functionality. Having observed a significant increase in peel strength upon surface modification, further characterization of the modified surface using X-ray photoelectron spectroscopy (XPS) was conducted.

In preparation for the XPS experiments, new photografting solutions were prepared and another series of photografting reactions was executed. XPS control samples were prepared by spin casting the appropriate polymers from solution onto aluminum coated silicon wafers.

Preliminary XPS analysis of the acrylamide graft, compared to control poly(acrylamide) and virgin PET, produced the following results.

The nitrogen 1s peak at  $-399$  eV in the poly(acrylamide) control spectrum is also present in the acrylamide graft spectrum, and indicates the presence of a single type of nitrogen. This peak is not present in the virgin PET.

The carbon 1s peaks appear in the  $-282$  to  $-292$  eV region. The spectrum for virgin PET clearly exhibits two major carbon peaks increasing in intensity with decreasing binding energy. The peak occurring at highest binding energy separates clearly and is due to the carbonyl carbons. In both the poly(acrylamide) control spectrum and the acrylamide graft spectrum, the lowest binding energy peak overlaps the analogous ( $-284.5$  eV) peak in the virgin PET, and exhibits no splitting.

The one type of oxygen present in the poly(acrylamide) control occurs at  $-531$  eV. The two types of oxygen in the virgin PET spectrum appear as a doublet at  $-533$  eV/shoulder at  $-531$  eV. There is an increase in the low binding energy peak in the acrylamide graft spectrum, suggesting the presence of addition carbonyl.

In an effort to confirm preliminary XPS results as well as to examine the effect of copper deposition on the spectral characteristics of the grafted moieties, XPS experiments were continued. Photograft samples and a new set of control samples were prepared. A "no light" sample for XPS analysis was prepared. A piece of 3-mil virgin PET was submerged in a 2M solution of acrylamide and 0.2M solution of benzophenone. The sample was kept in the solution in the dark for 3 h, removed, rinsed with acetone, and then flowing deionized water overnight. This sample was labeled 1/27/87-no  $h\nu$ .

XPS work continued on the Leybold ESCA instrument previously described. The preliminary XPS results presented above were obtained with a Physical Electronics XPS/AES 560 which exhibited better sensitivity than the Leybold. The Leybold instrument exhibited better resolution than the Physical Electronics system.

The first sample examined was a piece of virgin 3-mil PET. Figure 3 is a typical carbon 1s spectrum for PET. The higher binding energy peak is due to the carbonyl carbons. One can clearly see the two peaks that would result from the deconvolution of the lower binding energy, more intense peak. Figure 4 is a typical oxygen 1s spectrum for PET. The two types of oxygen in PET occur as a doublet in the  $-535$  eV to  $-540$  eV region. These peaks are from the carbonyl (lower binding energy) and ether (higher binding energy) oxygens. The observed energies of these peaks are slightly different from those observed in preliminary experiments. This may in part be due to rigid shifting from charging. Variations in sample positioning from day to day have been ob-

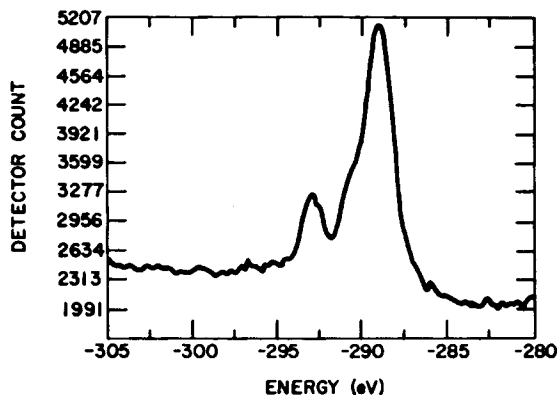


Fig. 3. XPS spectrum carbon 1s PET.

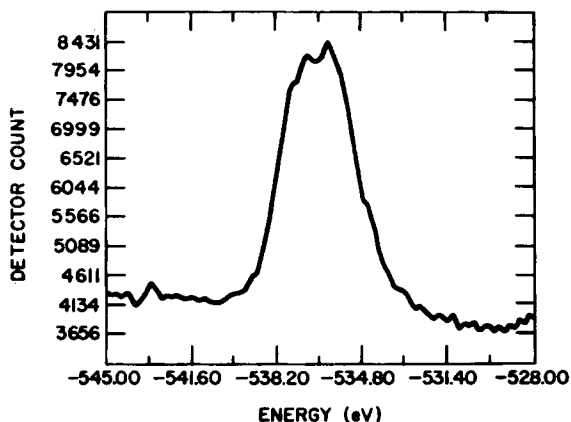


Fig. 4. XPS spectrum oxygen 1s PET.

served to give rise to similar rigid shifts. The shifting of peaks relative to one another is the sought after information, as this is a better measure of the changes in the electronic environment about a particular nucleus.

Examination of the acrylamide graft confirmed earlier results which indicated successful grafting had been achieved. The most convincing evidence of success is the presence of nitrogen 1s peak in the acrylamide graft spectrum.

In an attempt to confirm the results of a previously reported experiment which concluded that observed changes in contact angle after grafting were not due to solvent effects or simple adsorption of monomer onto PET, sample 1/27/87-no  $h\nu$  was subjected to XPS analysis. This sample has carbon 1s and oxygen 1s spectra that are identical to PET (Figs. 5 and 6), and there is no nitrogen 1s peak present. It is clear that there is no grafting taking place in the dark, and there are no significant complications in XPS spectra obtained due to solvent diffusion into, or monomer adsorption onto the PET film.

Experimental confirmation of successful grafting of allylthiosemicarbazide was obtained using XPS. The carbon and oxygen spectra of these grafts are essentially identical to the underlying PET. The striking difference is that the

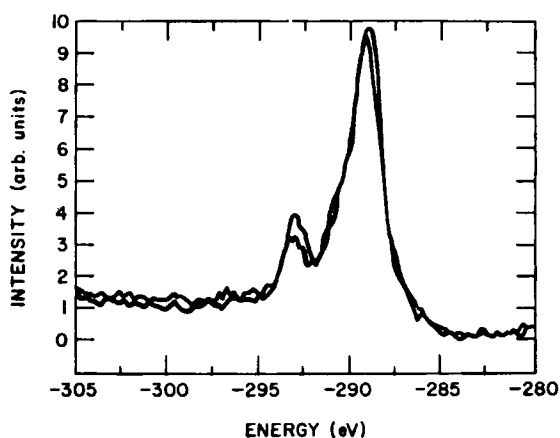


Fig. 5. XPS spectrum carbon 1s sample 1/27/87/no  $h\nu$  compared to carbon 1s PET.

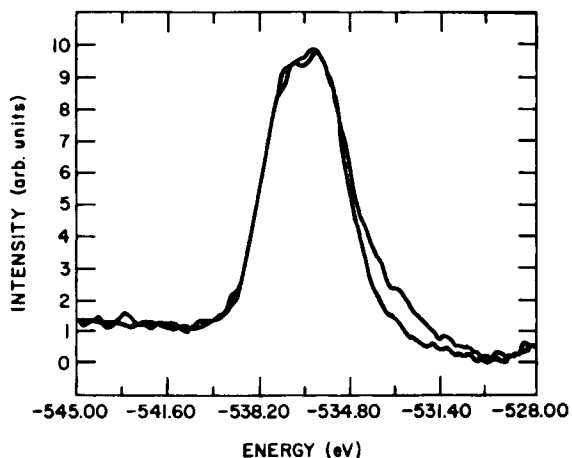


Fig. 6. XPS spectrum oxygen 1s sample 1/27/87 no  $h\nu$  compared to oxygen 1s PET.

graft has two peaks not present in PET: the sulfur  $2p$  peak at  $-163$  eV and the nitrogen  $1s$  peak at  $-399$  eV.

The acrylic acid graft could not be differentiated from PET with XPS because the chemical structure of the two are similar.

At this point enough evidence existed to confirm successful grafting. The XPS data lends credibility to the previous use of contact angle changes as a measure of grafting success.

The next series of experiments utilizing XPS was aimed at elucidating the effects of copper deposition. Toward this end it was decided that electron beam copper deposition onto a poly(acrylamide) control sample would be studied. The use of a polymeric control instead of a graft facilitated spectral analysis, and eliminated the spectral contributions of the underlying PET in graft samples. Since the grafts were on the order of tens of angstroms thick (as determined by variable angle XPS) the use of a polymeric control would



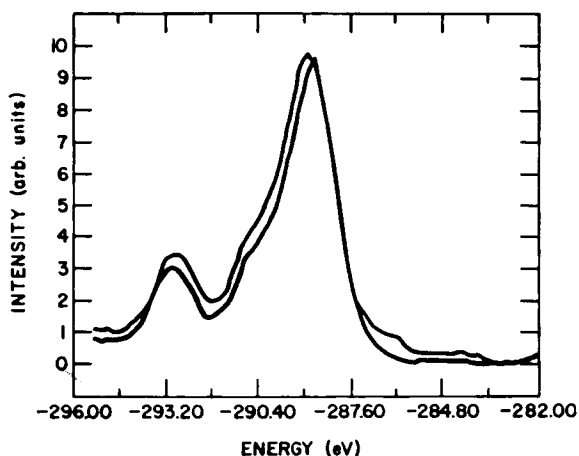


Fig. 7. XPS spectrum carbon 1s PET before and after metallization.

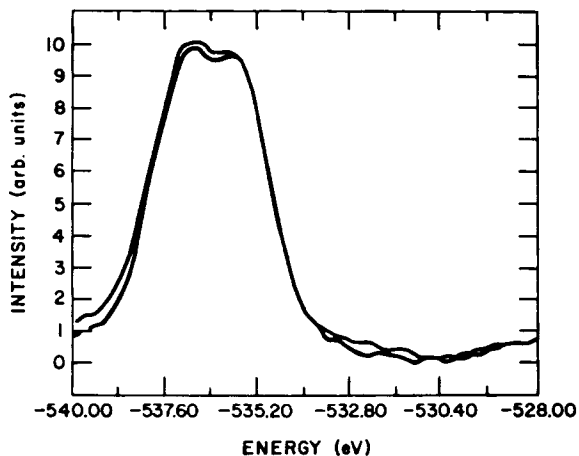


Fig. 8. XPS spectrum oxygen 1s PET before and after metallization.

provide a constant surface morphology and eliminate some concerns about surface variations due to grafting.

XPS studies of virgin PET before and after *in situ* copper deposition yielded spectra that are identical. Figures 7 and 8 show the carbon 1s and oxygen 1s spectra, respectively, for PET before and after copper deposition. Having observed no spectral changes upon copper deposition for PET, it was decided to proceed with the poly(acrylamide) control sample.

The poly(acrylamide) sample was loaded into the Leybold instrument and evacuated overnight. XPS spectra were obtained in the  $10^{-11}$  torr range. Copper electron beam evaporation at a rate of approximately 1 Å every 5 minutes and a pressure of  $10^{-10}$  torr was employed. Figure 9 shows the progression of changes in the carbon 1s spectrum upon metal deposition. The observed shift in the carbonyl carbon's peak to lower binding energy upon metal deposition indicates an increase in the electron density around this

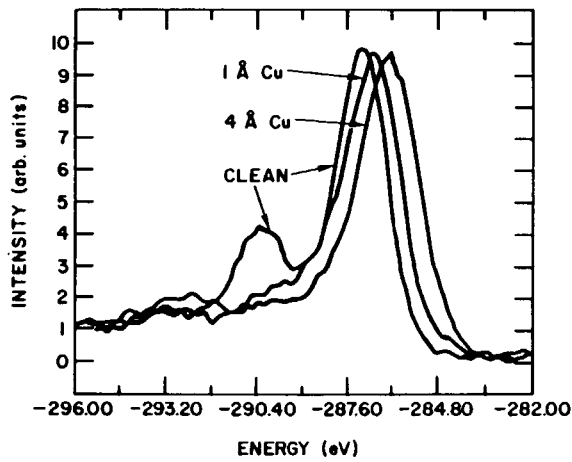


Fig. 9. XPS spectrum carbon 1s poly(acrylamide) effect of metallization.

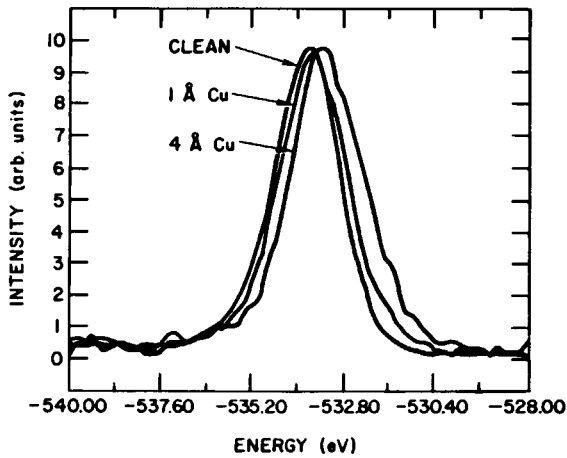


Fig. 10. XPS spectrum oxygen 1s poly(acrylamide) effect of metallization.

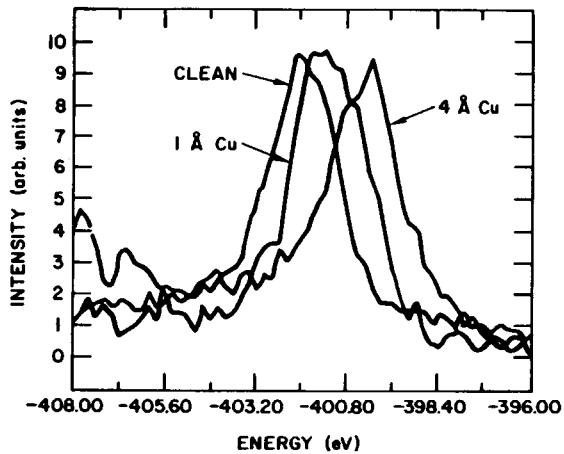


Fig. 11. XPS spectrum nitrogen 1s poly(acrylamide) effect of metallization.

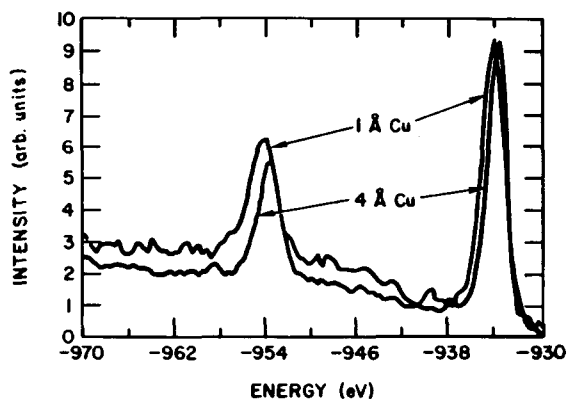


Fig. 12. XPS spectrum copper 2p.

carbon's nucleus. Upon examination of the oxygen 1s spectra (Fig. 10) essentially no change is observed. A slight shift to lower binding energy with no change in peak shape indicates that there is little if any change in the electron density about the carbonyl oxygen. This is not the case for the nitrogen (Fig. 11). Not only is a greater shift to lower binding energy observed, but the peak shape changes. The nitrogen 1s spectrum of the clean poly(acrylamide) exhibits a peak having greater intensity on the high binding energy side. Upon copper deposition this changes to a peak centered at lower binding energy with greater intensity on the low binding energy side. This is a good indication of an increase in the electron density about the nitrogen nuclei. Figure 12 shows the copper 2p spectra for both 1 and 4 Å copper depositions, demonstrating successful deposition of pure copper.

## CONCLUSION

The chemical functionalization of a poly(ethylene terephthalate) surface was achieved through the application of a solution photografting technique. Initial grafting success was verified via contact angle measurements. This was later confirmed by XPS. The absence of solvent/PET or monomer/PET selective interaction in the dark has been demonstrated, thus eliminating many concerns regarding potential complications in the analysis of the grafted films.

Adhesion strengths of the grafted films to vacuum-deposited copper were determined using 90° peel tests. In both previously described modes of metallization employed, a significant increase in peel strength upon surface modification is observed. One may postulate the cause of this adhesion enhancement to be both chemical and physical.

During direct current sputter deposition and electroplating of copper, the surface of the polymer film does not experience temperatures above the glass transition temperature. Subsequent annealing above the glass transition temperature may be viewed as supplying both the mobility required to promote

the physical component of adhesion as well as the activation energy required to promote chemical interaction. This would explain the zero preanneal adhesion strength observed for the virgin PET/copper sample (no chemical interaction) compared to the non-zero adhesion strengths of the grafted samples which exhibited chemical interactions with copper.

This effect is further demonstrated by the adhesion strengths observed for the grafts upon which copper was electron beam evaporated. During electron beam evaporation the surface of the polymer film does experience local heating above the glass transition temperature. This explains the non-zero preanneal adhesion strength for the virgin PET, which XPS results indicate can only be due to physical interaction. Upon further annealing the increase in adhesion strength is proportionally greater for the grafted samples where chemical interactions are occurring. If one considers the grafting process this becomes apparent. Irradiation through the PET film creates a surface region, in contact with the grafting solution, rich in PET free radicals as a result of hydrogen abstraction by the  $^3n\pi^*$  excited state of benzophenone. These free radicals then initiate the graft polymerization of unsaturated monomers from solution. There are other free radical deactivation pathways, but the grafting event is the one with which the current work is concerned. As the grafted chain grows it bears a reactive propagating center. During the course of polymerization, if two of these reactive centers collide they will recombine or disproportionate, thereby terminating the grafted chain. If termination occurs by recombination the net result will be a surface-grafted chain anchored at both ends. If termination occurs by disproportionation (or some chain transfer reaction) the net result will be a grafted chain anchored at only one end. The resulting surface morphology can be envisioned as supplying, upon heating, the necessary mobility to enhance the physical component of adhesion. The resulting mobility may be alternately be envisioned as providing the proximity required to promote chemical interactions while at the same time the temperature provides the required energy of activation.

As a result of the XPS study on the effect of copper deposition onto a poly(acrylamide) control sample one may conclude that the chemical component of adhesion is significant. In this particular case a copper/amine complex is thought to be formed. This is observed in contrast to the lack of any specific chemical interaction between PET and copper as determined using XPS. One may postulate chemical interactions ranging from a simple copper salt in the case of the acrylic acid graft, to a chelate ring system in the case of the allylthiosemicarbazide graft.

One may conclude that the observed increase in adhesion between copper and the photochemically modified PET surface is in part attributable to chemical interactions between the grafted moieties and the copper metal. Future work should aspire to determine the magnitude of this effect in different systems.

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Received October 29, 1987

Accepted January 15, 1988