Molecular Structure of Interfaces between Plasma-Polymerized Acetylene Films and Steel Substrates

Y. M. TSAI, F. J. BOERIO

Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0012

ABSTRACT: Plasma-polymerized films of acetylene were deposited onto steel substrates in an inductively coupled reactor by exciting the plasma in an argon carrier gas and then injecting the monomer into the afterglow region. The molecular structure of the film/substrate interface was determined using reflection–absorption infrared spectroscopy (RAIR) and X-ray photoelectron spectroscopy (XPS) to characterize the films as a function of thickness. RAIR showed that thick ($\sim$ 900 Å) as-deposited plasma-polymerized acetylene films had a complicated molecular structure and contained methyl and methylene, mono- and disubstituted acetylene, vinyl, and *cis-* and *trans*-disubstituted olefin groups. Evidence of oxidation resulting from the reaction of trapped radicals with atmospheric oxygen and moisture to form O—H and C≡O groups was also obtained. The molecular structure of thin films ($\sim$ 60 Å) was similar although evidence was obtained to indicate that acetylide groups (H—C≡C$^-$) were present at the film/substrate interface. Results obtained using angle-resolved XPS analysis showed that carbonaceous contamination was removed from the substrate and that oxides and hydroxides on the substrate surface, especially FeOOH, were chemically reduced during deposition of the films. XPS also confirmed that plasma-polymerized acetylene films deposited on steel substrates contained $>$C—O— and $>$C≡O groups. Preliminary results also showed that films deposited in an inductively coupled reactor were good primers for rubber-to-metal bonding, whereas films deposited in a capacitively coupled reactor were not. The differences may be due to the wide variety of functional groups found in the former type of films but not in the latter. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1283–1298, 1998

Key words: plasma-polymerized acetylene; rubber-to-metal bonding; X-ray photoelectron spectroscopy; infrared spectroscopy

INTRODUCTION

Recently, we showed that plasma-polymerized films of acetylene are excellent primers for bonding natural rubber to metals such as steel.[1] To determine the mechanisms responsible for adhesion at the interface between natural rubber and the plasma polymer, we conducted extensive investigations of chemical reactions between a model rubber system and plasma-polymerized acetylene films deposited on polished steel substrates.[2,3] The model rubber system consisted of squalene (a low molecular weight compound having a structure similar to that of natural rubber), sulfur, carbon black, an accelerator, an activator, an adhesion promoter, and an antioxidant. These investigations showed that crosslinking, and thus adhesion, between the model rubber compound and the plasma-polymerized films involves a reaction between sulfur and the accelerator DCBS to form perthiomercaptides. The perthiomercap-
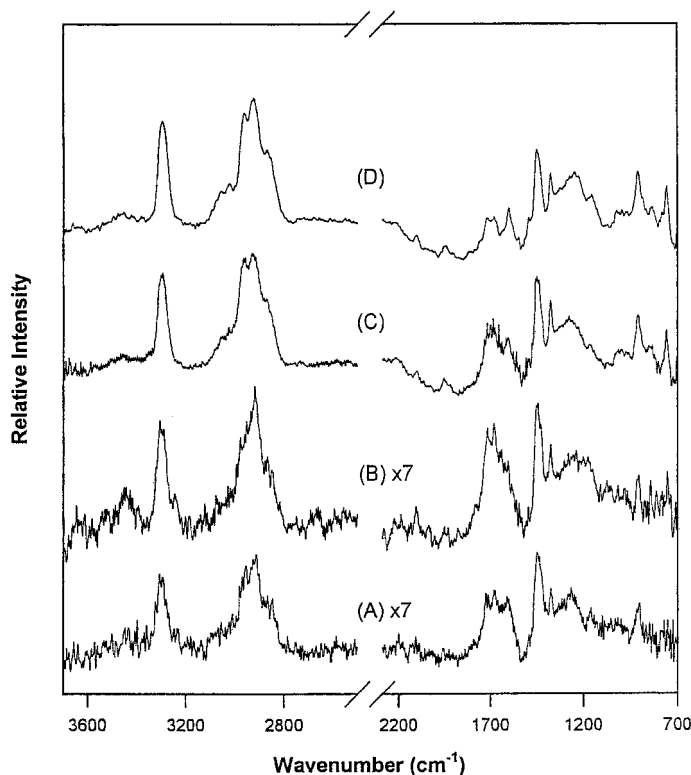
Figure 1   RAIR spectra of plasma-polymerized acetylene films on polished steel substrates. The thicknesses of these films were (A) 57, (B) 90, (C) 635, and (D) 900 Å.

tides react with rubber and the plasma polymer to form accelerator-terminated pendant groups which eventually disproportionate to form polysulfidic crosslinks between the rubber compound and the plasma polymer.

It is obviously of interest to determine the mechanisms responsible for adhesion at the interface between the plasma-polymerized acetylene primer and the substrate. However, such investigations are complicated by the fact that the interface is buried between two relatively thick phases: the substrate and the plasma polymer. Several approaches for characterizing such buried interfaces have been suggested: One approach is to make either the polymer or metal very thin and to use surface-analysis techniques to characterize the interface. Burkstrand used this approach to probe interfaces between metals and polymers.[4-6] Thin films of metals such as Cu, Ni, and Cr were evaporated onto polymer substrates and X-ray photoelectron spectroscopy (XPS) was used to characterize the interfaces. Boerio et al. used a similar approach to characterize interfaces between polyimides and metals.[7] In this case, thin films of polyimides were spin-coated onto polished metal substrates and XPS and reflection–absorp-

tion infrared spectroscopy (RAIR) were used to characterize the polymer/metal interface.

Another approach for characterizing polymer interfaces involves the use of sputtering to expose the interface. Thus, Watts and Castle deposited polybutadiene onto steel substrates. They dissolved the metal, leaving a film of oxide adhering to the polymer, and then sputtered through the oxide to reach the polymer/oxide interface.[8]

Boerio and coworkers examined interfaces between polyimides and substrates such as silver by immersing the film-covered substrate into liquid nitrogen. The difference in the coefficient of thermal expansion between the polymer and the metal resulted in delamination of the film very near the metal surface. Surface-analysis techniques were used to characterize the metal and polymer failure surfaces and to obtain information regarding the structure of the interface.[9]

An interesting approach to the characterization of polymer/metal interfaces involves the use of surface-enhanced Raman scattering (SERS). SERS is a phenomenon in which the Raman scattering cross section of molecules adsorbed onto the roughened surfaces of certain metals is en-

**Table I Assignment of Infrared Absorption Bands
for Plasma-Polymerized Acetylene**

Frequency (cm^{-1})	Assignment
3455	O—H stretch (bonded)
3295	C—H stretch (in RC≡CH)
3055	C—H stretch in substituted olefin
3027	C—H stretch in substituted olefin
2960	C—H asymmetric stretch (CH$_3$)
2928	C—H out-of-phase stretch (CH$_2$)
2870	C—H symmetric stretch (CH$_3$)
2853	C—H in-phase stretch (CH$_2$)
2200	C≡C stretch (in RC≡CR)
2103	C≡C stretch (in RC≡CH)
1950	C=C stretch (in —C=C=C—)
1715	C=O stretch (in —R—CO—CH$_3$)
1680	C=O stretch (in —CH=CH—CO—)
1600	C=C stretch (in cumulated C=C)
1450	C—H deformation (CH$_2$)
1375	C—H deformation (CH$_3$)
1320	C—H wag (CH$_2$)
1240	C—O stretch (in C—C—O)
1160	C—O stretch (in O—CH$_2$—C)
1025	
990	CH$_2$ out-of-plane wag (in *trans* R—CH=CH$_2$)
965	CH$_2$ out-of-plane wag (in *trans* R—CH=CH—R)
916	CH$_2$ out-of-plane wag (in R—CH=CH$_2$)
758	CH$_2$ out-of-plane wag (in *cis* R—CH=CH—R)
700	CH$_2$ out-of-plane wag (in *cis* R—CH=CH—R)

hanced by as much as 10^6 compared to the cross section for normal Raman scattering. Since the enhancement in SERS is very large but restricted to the first few molecular layers adjacent to the substrate, SERS is an extremely effective technique for *nondestructive* determination of the molecular structure of interphases between polymer systems and certain metals, such as copper, gold, and silver, which support SERS. Boerio et al. used SERS to characterize interfaces between silver substrates and several different polymer systems, including polystyrene/poly (2-vinylpyridine) diblock copolymers,[10] anaerobic adhesives,[11] and polyimides.[12,13]

Although plasma-polymerized acetylene films have been investigated for many years, there is little if any information available regarding the chemical structure of the interface between the films and the substrates on which they are deposited. However, there is considerable information available regarding the adsorption of acetylene and its derivatives onto metals or metal oxides.

Nguyen and coworkers[14] investigated the adsorption of aromatic acetylenic compounds onto zinc oxide. They showed that 3-phenyl-1-propyne ($C_6H_5CH_2C≡CH$) and 1-phenyl-1-propyne (C_6H_5C

≡CCH$_3$) had a common behavior over zinc oxide in that each gave rise to two types of dissociative chemisorption to yield acetylenic species and propargyllic species. The former resulted from dissociation of the acetylenic hydrogen, and the later, from the removal of a proton attached to a carbon atom in an α-position to the triple bond. The propargyllic species were considered to be intermediates in an isomerization reaction, and their two possible structures [$(C_6H_5CH—C=CH)^-$ and $(C_6H_5C=C—CH_2)^-$] were characterized by intense infrared absorptions near 1862 cm^{-1} which were assignable to the $\nu(C=C)$ modes. Acetylide species [$C_6H_5CH_2C≡C^- \ldots Zn$] were characterized by $\nu(C≡C)$ bands in the region 2080–2110 cm^{-1} in both infrared and Raman spectra.

Chang and Kokes[15] concluded that acetylene adsorbs dissociatively on ZnO based on a band near 3550 cm^{-1} which was assigned to surface OH groups and bands near 3280 and 1975 cm^{-1} which were assigned to CH and C≡C stretching in HC≡C$^-$. Infrared spectra of methyl acetylene adsorbed onto ZnO were characterized by an absorption band near 3515 cm^{-1} which was assigned to a surface hydroxyl group and by a band
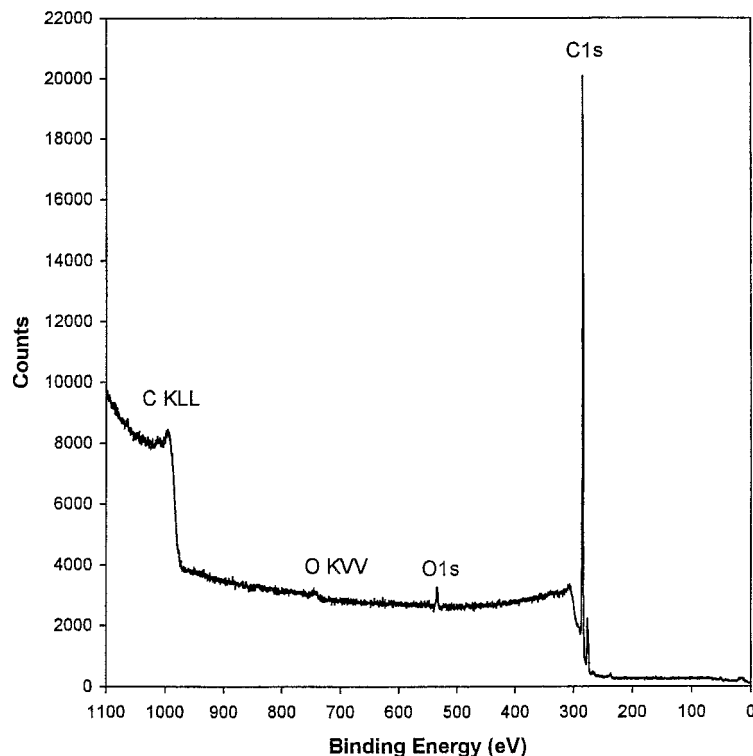
Figure 2   XPS survey spectrum of an as-deposited plasma-polymerized acetylene film on steel substrate. Film thickness was 750 Å.

3250 cm^{-1} which was related to acetylenic CH stretching. These results indicated that dissociative chemisorption occurred, that the dissociation involved a methyl hydrogen, and that the acetylenic hydrogen remained intact.[15]

Moskovits and DiLella used SERS to investigate adsorption of acetylene onto silver substrates.[16] They found two bands, near 1954 and 1923 cm^{-1}. The band near 1923 cm^{-1} was assigned to —C≡C— stretching in acetylene molecules in the "first layer" which were chemisorbed onto silver. The band near 1954 cm^{-1} was assigned to molecules in the second or succeeding layers which were physisorbed.

The purpose of this article was to report the initial results that we have obtained using RAIR and XPS to determine the molecular structure of interfaces between plasma-polymerized acetylene films and metal substrates such as steel. The most important results are that the structure of the films changes as a function of thickness and thus deposition time and that deposition of plasma-polymerized acetylene films onto steel substrates results in the etching of carbonaceous contaminants and reduction of hydroxides at the polymer/substrate interface.

EXPERIMENTAL

Substrate Preparation

1010 cold-rolled steel (CRS) sheets 0.5 mm thick were obtained from The Goodyear Tire & Rubber Co. (Akron, Ohio). The as-received steel substrates were mechanically polished to a mirror finish for investigations involving infrared spectroscopy and XPS. The polishing sequence began with dry polishing on 600-grit silicon carbide papers to grind the surface. Then, the steel coupons were wet-polished with 14.5-, 3.0-, and 0.3-μm aluminum oxide abrasive slurries. Finally, the substrates were rinsed in distilled water and acetone and blown dry with nitrogen.

Plasma Etching and Plasma Polymerization

Plasma etching and polymerization were carried out in a tubular Pyrex reactor which was inductively coupled to an rf (13.56 MHz) power supply. The top portion of the reactor was made of quartz and was surrounded by the rf coils. During plasma etching of the substrates, carrier gases were introduced at the top of the reactor, just above the induction coil. During deposition of
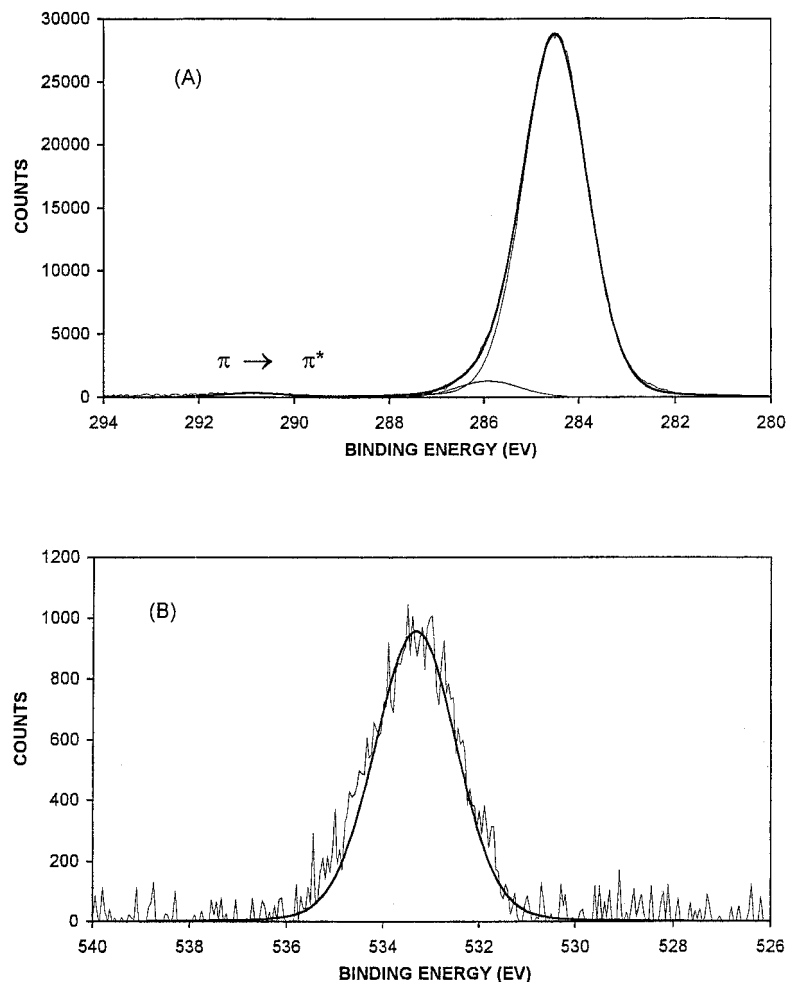
Figure 3 High-resolution (A) C(1s) and (B) O(1s) XPS spectra of an as-deposited plasma-polymerized acetylene film on steel substrate. Thickness of the film was 750 Å.

plasma polymer films, carrier gases were also introduced above the coil but the monomer was introduced into the reactor through an inlet tube which was located just below the coil. The monomer was thus injected into the afterglow region of the plasma. Substrates were supported on a stage which could be moved vertically within the reactor. The stage was usually located several centimeters below the monomer inlet. A detailed description of the reactor was presented elsewhere.[17]

Prior to plasma polymerization, the polished substrates were etched in an argon plasma at 1 Torr pressure, 20 standard cm^3 per minute (sccm) flow rate, and 20-W power for 10 min to remove surface contaminants. Plasma-polymerized films of acetylene were then deposited on the substrates using argon as the carrier gas. Plasma polymerization was carried out at a pressure of

1.0 Torr, power of 55 W, and flow rates of 20 sccm for Ar and 25 sccm for acetylene.

Characterization

The thickness of the plasma-polymerized films was determined by using a Rudolph Research Model 436 ellipsometer to examine polished steel substrates before and after deposition of the films. A computer program developed by McCrackin[18] was used to calculate the thickness and refractive index of the films from the measured values of the ellipsometry parameters Δ and ψ.

RAIR spectra of the films were obtained using a Perkin–Elmer 1800 Fourier transform infrared (FTIR) spectrophotometer equipped with a deuterated triglycine sulfate (DTGS) detector and external reflection accessories provided by Harrick
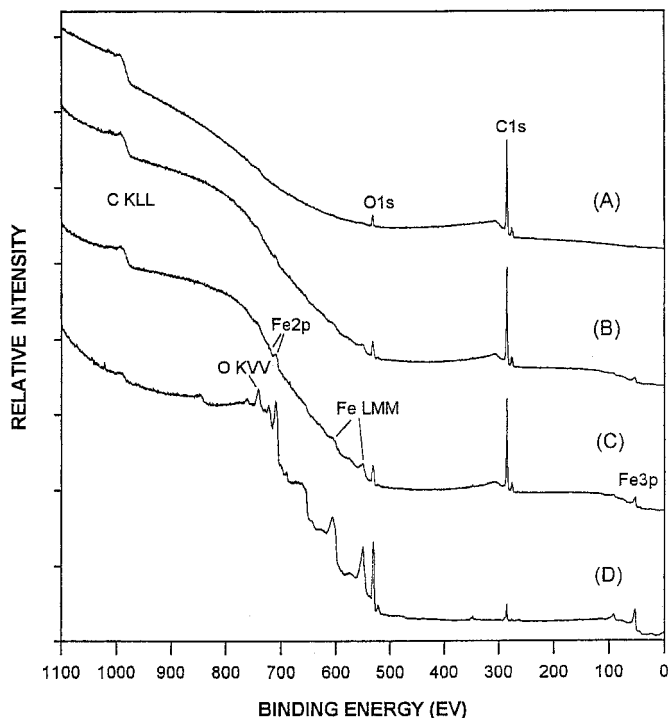
Figure 4 XPS survey obtained from as-deposited thin ($\sim$ 20 Å) plasma-polymerized acetylene films on polished steel substrates at take-off angles of (A) 15°, (B) 45°, and (C) 75°. The spectrum of a polished steel substrate is shown in (D).

Scientific Co. One reflection at an angle of 78° was used in all cases. Spectra were collected in the quantitative mode at a resolution of 4 cm^{-1}. Usually, 256 scans were averaged for each spectrum collected. However, for film thickness less than 100 Å, 500 scans were averaged for each spectrum. The spectra of plasma-polymerized films were obtained by subtracting the spectra of polished substrates from spectra of polished, film-covered substrates.

The surface composition of the polished steel substrates before and after deposition of plasma-polymerized acetylene films was determined using XPS. A Perkin–Elmer Model 5300 XPS spectrometer with MgKα X-rays, operating at 300 W and 15 kV DC, was used to obtain the spectra. Survey spectra were obtained using a pass energy of 44.75 eV and 0.5 eV/step. The resolution was 1.0 eV. High-resolution spectra were obtained using a pass energy of 17.9 eV and 0.05 eV/step. The resolution was 0.7 eV. An Apollo computer system with Perkin–Elmer software was used for data acquisition and processing. XPS spectra were recorded at take-off angles of 15°, 45°, and 75°. The take-off angle (θ) was defined as the angle between the sample surface and the direction of propagation of the escaping electrons.

RESULTS AND DISCUSSION

RAIR Investigations of Thin Plasma-polymerized Acetylene Films on Steel Substrates

RAIR spectra of as-deposited plasma-polymerized acetylene films on polished steel substrates are shown in Figure 1. The thickness of these films was 57, 90, 635, and 900 Å. Detailed band assignments are listed in Table I. Bands characteristic of hydrocarbons were observed near 2960 (asymmetric CH$_3$ stretching), 2928 (CH$_2$ stretching), 2870 (CH$_3$ symmetric stretching), 1450 (CH$_2$ bending), and 1375 cm^{-1} (CH$_3$ bending). The strong, sharp band near 3295 cm^{-1} was assigned to CH stretching in monosubstituted acetylene groups (R—C$\equiv$C—H).[19] Weak bands related to —C$\equiv$C— stretching in mono- and disubstituted acetylene were observed near 2103 and 2210 cm^{-1}, respectively.[19]

Several bands that were related to olefin groups were observed. Included were a band near 1600 cm^{-1} which was assigned to a C$=$C stretching mode, a strong, sharp band near 916 cm^{-1} which was related to the CH$_2$ wagging mode of vinyl groups (—RHC$=$CH$_2$), and weak bands near 700 and 965 cm^{-1} which were related to the

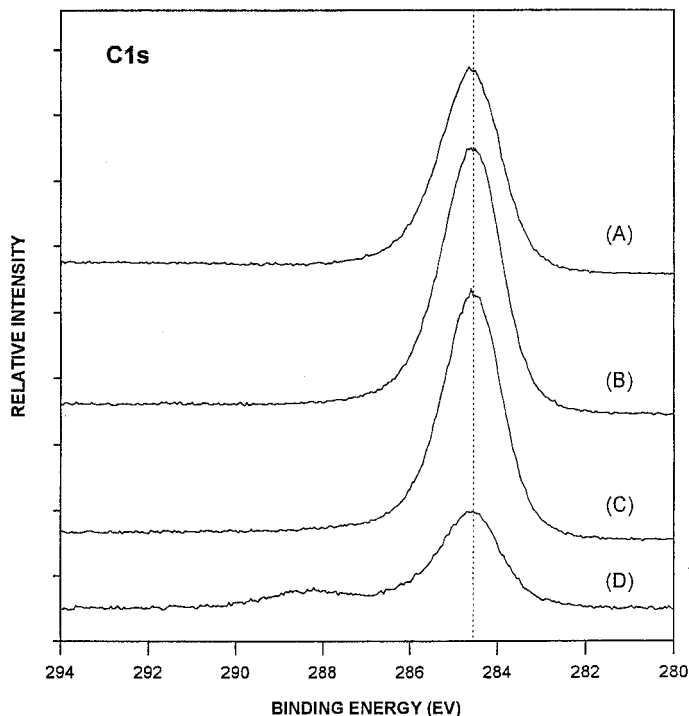**Figure 5**   High-resolution C(1s) XPS spectra obtained from as-deposited thin (~ 20 Å) plasma-polymerized acetylene films on polished steel substrates at take-off angles of (A) 15°, (B) 45°, and (C) 75°. The spectrum of a polished steel substrate is shown in (D).

cis and $trans$ CH_2 wagging modes of disubstituted olefins ($-RHC=CRH-$). Bands near 3055 and 3027 cm^{-1} were assigned to CH stretching in substituted olefin groups. Several weak bands near 1595, 1510, and 1495 cm^{-1} were assigned to aromatic ring stretching modes.

The assignment of the strong band near 758 cm^{-1} is not clear. This band could be assigned to a CH out-of-plane bending mode in monosubstituted or $ortho$-disubstituted benzene rings. Although SIMS[20] and FTIR (see above) have both shown that aromatic species exist in these films, their concentration is not considered sufficient to explain the intensity of the band near 758 cm^{-1}. Another possible assignment of the band near 758 cm^{-1} is to the CH wagging mode of a monosubstituted acetylene group. However, bands due to this vibration are usually located at frequencies that are at least 50 cm^{-1} lower. Another possibility is that the band near 758 cm^{-1} is related to the CH_2 wagging mode of a different cis-disubstituted olefin than the band near 700 cm^{-1}.

Evidence of oxidation resulting from the reaction of trapped radicals with atmospheric oxygen and moisture was also obtained. Thus, the band near 3455 cm^{-1} was assigned to O—H stretching and bands near 1715 and 1680 cm^{-1} were assigned to C=O stretching.

Several differences were observed in RAIR spectra of plasma-polymerized acetylene films as a function of film thickness. The biggest difference concerned the band near 758 cm^{-1} which was discussed above. This band was strong in the spectra of the thick films (635 and 900 Å), weaker in the spectra of the 90 Å film, and undetectable in the spectra of the 57 Å film. It appeared that the functional groups responsible for this band were not formed at the beginning of the deposition process, but rather through the recombination of free radicals after deposition had begun. Absence of the band near 758 cm^{-1} in the infrared spectrum of the 57 Å film supported this suggestion. A weak band near 1950 cm^{-1}, which was assigned to C=C=C stretching, was also stronger in the spectra of the thicker films. Another weak band was observed near 3250 cm^{-1} in the spectra of the 57 and 90 Å films but not in the spectra of the thicker films.

Since none of the RAIR spectra obtained from plasma-polymerized acetylene films on CRS substrates showed a band near 1862 cm^{-1} (see Fig. 1), it was concluded that propargyllic species were not formed in the plasma-polymerized films of acetylene on CRS. However, two bands were observed near 2100 and 2200 cm^{-1} in all spectra and assigned to C≡C stretching in mono- and
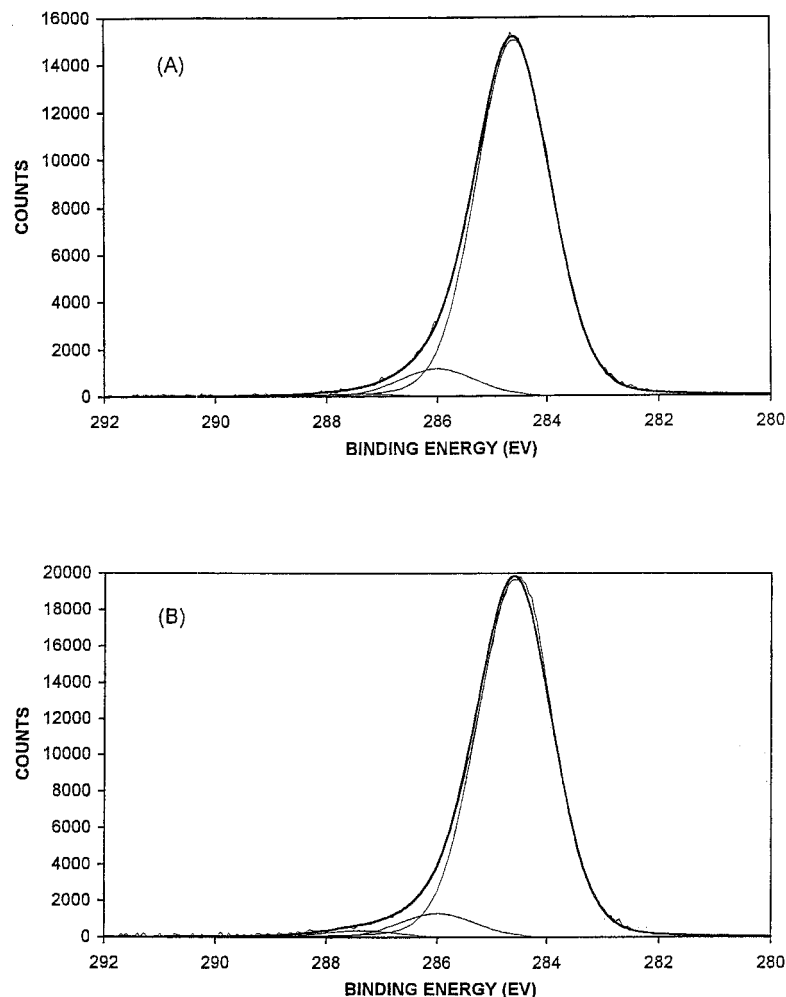
Figure 6 Curve-fit C(1s) XPS spectra obtained from as deposited thin ($\sim$ 20 Å) plasma-polymerized acetylene films on polished steel substrates at take-off angles of (A) 15°, (B) 45°, and (C) 75°. The spectrum of a polished steel substrate is shown in (D).

disubstituted acetylenes (RC≡CH and RC≡CR), respectively. It is possible that the band near 2100–2107 cm^{-1} contained a component due to stretching of the C≡C bond in a surface acetylide (H—C≡C$^-$). The weak band near 3250 cm^{-1} in the spectra of the thinnest films may be related to CH stretching in a surface acetylide.

Infrared spectra of plasma-polymerized acetylene films reported here are very different from those that have been reported by others.[21] Most published spectra contain only a few bands related to methyl, methylene, and carbonyl groups. Published spectra do not contain the band near 3300 cm^{-1} that is characteristic of monosubstituted acetylene groups, nor do they contain bands characteristic of substituted olefin groups. The reasons for this are still under investigation but are probably related to differences in the way the

films were deposited. In our work, films were deposited in an inductively coupled reactor, whereas most published spectra of plasma-polymerized acetylene films were obtained from films deposited in capacitively coupled reactors. Moreover, in our work, the plasma was actually established in a carrier gas and the monomer was injected into the afterglow region. Most published infrared spectra were obtained from films that were deposited without the use of a carrier gas. Evidently, the monomer undergoes much less fragmentation when deposition is carried out in an inductively coupled reactor in which the plasma is established in a carrier gas and the monomer is injected into the afterglow.

It is interesting to note that our preliminary results indicate that films deposited in a capacitively coupled reactor are not good primers for
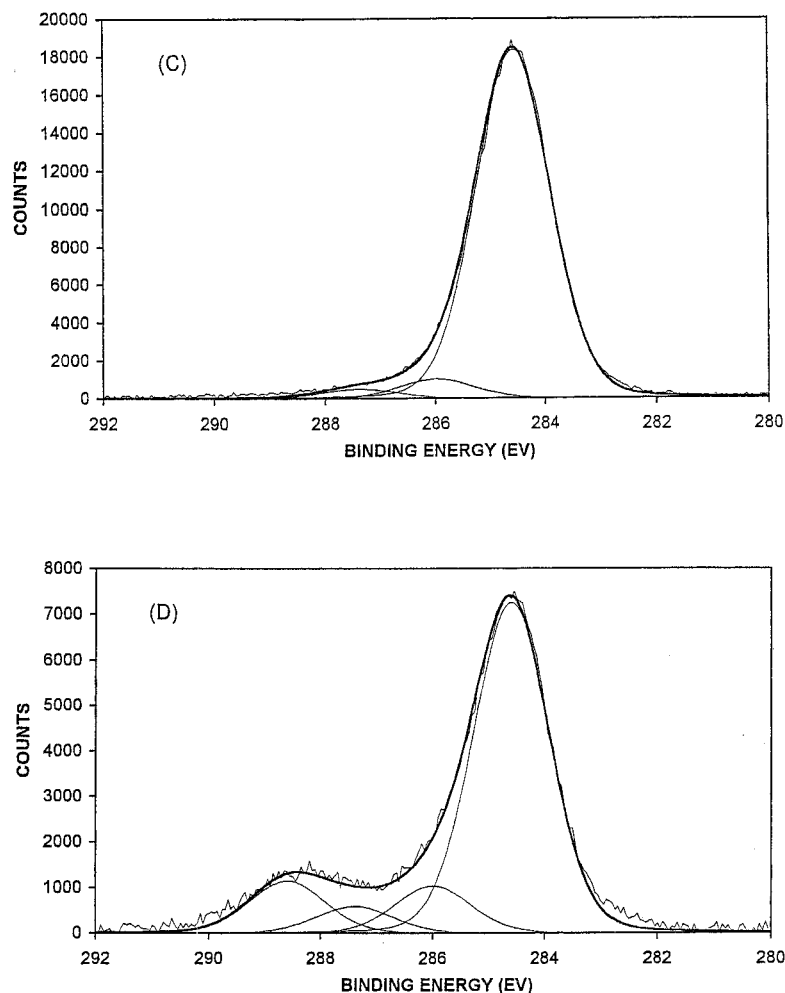
Figure 6 (*continued from the previous page*)

rubber-to-metal bonding, whereas films deposited in an inductively coupled reactor are.[22] The reason for the poor adhesion between natural rubber and films formed in a capacitively coupled reactor seems to be related to poor adhesion at the rubber/film interface. Poor adhesion at this interface may be related to the absence of functional groups that are found in films deposited in an inductively coupled reactor but not in a capacitively coupled reactor.

XPS Studies of Thin Plasma-polymerized Acetylene Films on Steel Substrates

Figure 2 shows the XPS survey spectrum of an as-deposited 750 Å-thick plasma-polymerized acetylene film on a polished steel substrate. It was evident from the spectrum that the as-deposited films consisted mostly of carbon and small amounts of oxygen. The high resolution C(1s) and

O(1s) spectra of an as-deposited film on a steel substrate are shown in Figure 3. In the C(1s) region, a satellite peak arising from $\pi \rightarrow \pi^*$ shake-up transitions of aromatics and unsaturated C=C bonds was observed at a binding energy that was $\sim$ 6.6 eV greater than that of the main peak (284.6 eV). Also, a very small peak due to C—O (1.5 eV separation) was observed in the spectrum of the as-prepared plasma polymer, probably due to a postpolymerization reaction with ambient O_2. The O(1s) region was curve-fitted using only one broad peak centered around 533.2 eV which was attributed to the C—O species.

Figure 4 shows the XPS survey spectra obtained as a function of the take-off angle from a 20 Å-thick, as-deposited, plasma-polymerized acetylene film on a polished steel substrate. The spectrum obtained from a polished but uncoated steel substrate is included for comparison. When the
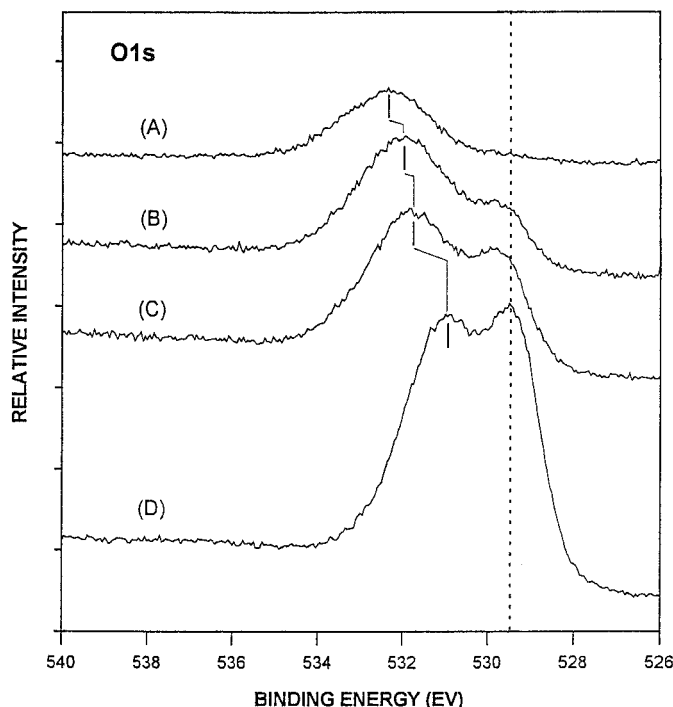
Figure 7 High-resolution O(1*s*) XPS spectra obtained from as-deposited thin (∼ 20 Å) plasma-polymerized acetylene films on polished steel substrates at take-off angles of (A) 15°, (B) 45°, and (C) 75°. The spectrum of a polished steel substrate is shown in (D).

take-off angle was 15°, the spectrum was similar to that obtained from a "thick" plasma-polymerized acetylene film (see Fig. 2) and only peaks due to C(1*s*) and O(1*s*) electrons were observed, at 532.0 and 284.6 eV, respectively. Thus, the outermost surface of the specimen consisted of mostly carbon and oxygen with virtually no detectable iron. When the take-off angle was increased to 45°, the peak due to C(1*s*) electrons decreased in intensity relative to that due to O(1*s*) electrons. Peaks due to Fe(2*p*) and Fe(3*p*) photoelectrons and Fe(LMM) Auger electrons from the substrate appeared weakly. Upon changing the take-off angle to 75°, the intensities of all peaks due to iron became stronger. Therefore, the spectra obtained at take-off angles of 15°, 45°, and 75° seemed to represent the "interface" region rather appropriately. More contribution from the polymer was seen in the spectrum obtained at 15° but more of a contribution from the substrate was observed in the spectrum obtained at 75° take-off angle.

Figure 5 shows the high-resolution C(1*s*) spectra obtained from the 20 Å-thick plasma-polymerized acetylene film on a steel substrate at take-off angles of 15°, 45°, and 75°. Once again, the spectrum of the polished substrate is shown for comparison. The spectra obtained from the film-covered substrate at different take-off angles were similar and consisted of a strong peak near 284.6 eV that was due to C—C/C—H. However, when these spectra were curve-fit, subtle differences in the peak width as well as the peak shape appeared (see Fig. 6). Two weak peaks were observed in the spectrum obtained at a 75° take-off angle, near 286.0 and 287.4 eV, and assigned to

$\rangle$C—O— and $\rangle$C=O, respectively. The presence

of $\rangle$C—O— and $\rangle$C=O groups on the surface was attributed to the reaction between trapped free radicals in the film with atmospheric oxygen and moisture. When the take-off angle was decreased, the peak due to carbonyl groups gradually increased in intensity while the peak due to C—O groups decreased in intensity. A satellite arising from $\pi \rightarrow \pi^*$ shake-up transitions of aromatics and C=C bonds, which was observed previously in the spectrum of the thick plasma polymer film, was undetectable in the spectra of the thin film. It is interesting to note that the component at the highest binding energy in the C(1*s*) spectra of the polished substrate, near 288.6 eV [see Fig. 6(D)], was not seen in the spectra of the
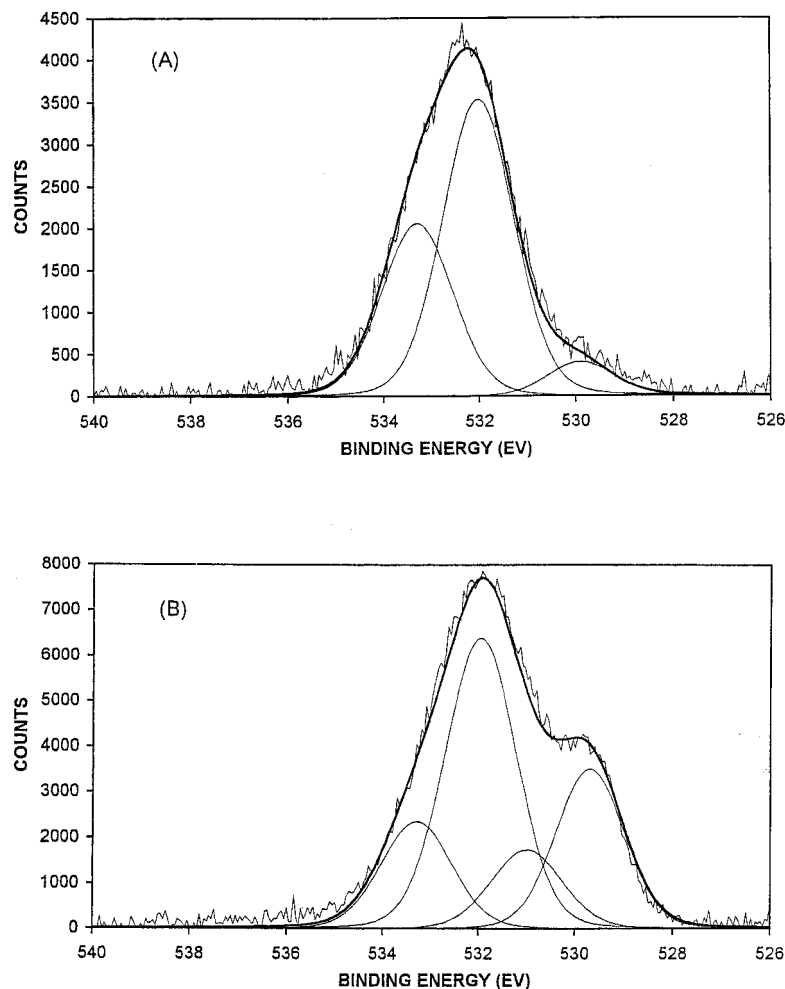
Figure 8 Curve-fit O(1s) XPS spectra from as-deposited thin ($\sim$ 20 Å) plasma-polymerized acetylene films on polished steel substrates at take-off angles of (A) 15°, (B) 45°, and (C) 75°. The spectrum of a polished steel substrate is shown in (D).

thin plasma-polymerized film. This probably indicates that carbonaceous contamination was removed from the surface during etching of the substrates with the argon plasma prior to deposition or by the argon/acetylene plasma during deposition.

Figure 7 shows high-resolution O(1s) spectra of the thin plasma-polymerized film as a function of the take-off angle. In contrast to the similarity among the high-resolution C(1s) spectra, there were significant differences for the O(1s) spectra obtained at various angles. The main peak near 532.4 eV appeared to shift toward lower binding energies as the take-off angle increased, while a peak near 529.7 eV maintained a similar position. To take a closer look at the differences, the spectra shown in Figure 7 were curve-fit as shown in Figure 8. The O(1s) spectrum obtained at a 15° take-off angle was resolved into three peaks at

binding energies of 529.9, 532.0, and 533.3 eV, corresponding to O^{2-}, $\underline{O}$=C, and $\underline{O}$—C, respectively.[23] As mentioned above, O—C and O=C groups were generally observed on the surface of plasma-polymerized acetylene films because of the reaction of trapped free radicals in the films with atmospheric oxygen and moisture. The O^{2-} groups were clearly due to iron oxides. However, the absence of a peak due to hydroxides was remarkable.

Significant changes in the O(1s) peak shape were observed when the take-off angle was changed to 45° (see Fig. 8). The oxide peak at 529.7 eV increased significantly in intensity while a new peak, which was assigned to OH^- in the FeOOH species, appeared near 531.0 eV. FeOOH was believed to form on the outermost surface of iron as a result of the reaction between Fe_2O_3 and moisture in the air.[24,25] The decrease in intensity
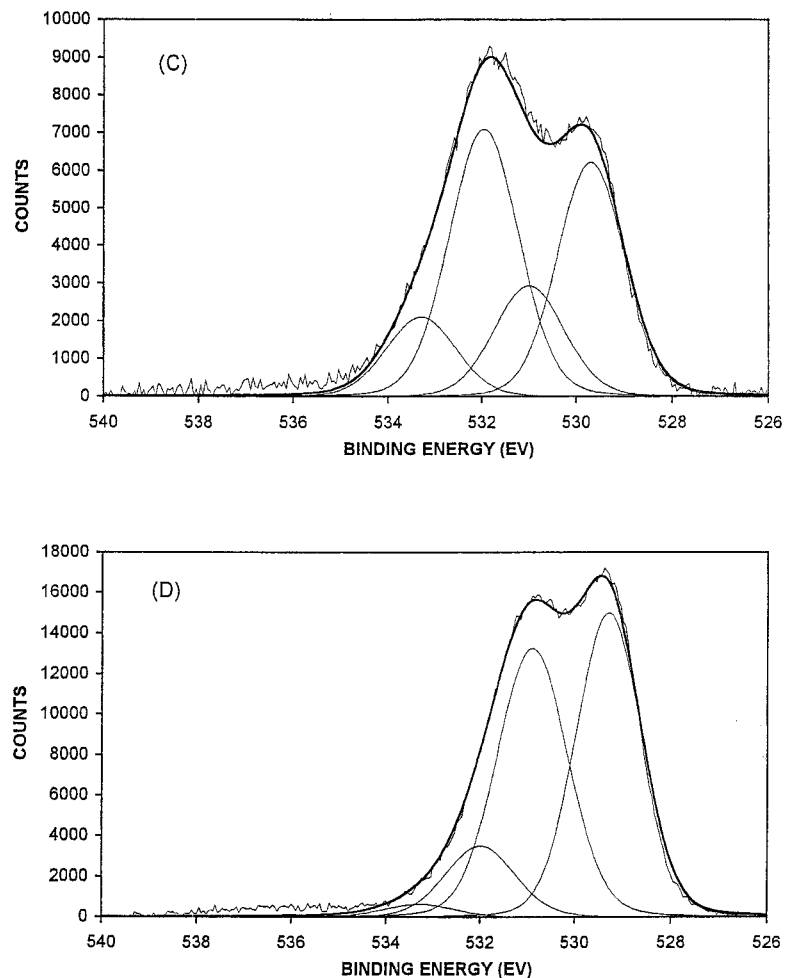
Figure 8 (*continued from the previous page*)

of the peak due to O—C groups was also noticeable. A further increase in the take-off angle to 75° resulted in an increase in the peaks due to oxide and hydroxide species. However, the OH^-/O^{2-} ratio did not change. For the spectrum obtained from polished steel substrates, significant amounts of hydroxides and oxides were observed and the ratio of OH^-/O^{2-} was close to 1. This indicated that the FeOOH species dominated the surface of a polished steel substrate. Moreover, the intensities of peaks due to C═O and C—O species on the polished substrates were relatively low in contrast to their intensities in spectra obtained from steel substrates coated with the plasma polymer.

The change in intensity of the O(1s) peaks due to oxide and hydroxide as a function of the take-off angle was very interesting. Hydroxides, as determined from the XPS spectra of thin films on steel, seemed to decrease in concentration with a decreasing take-off angle and were almost unde-

tectable for spectra obtained at a 15° take-off angle. This result seemed to indicate that during plasma polymerization of acetylene the hydroxide layer on the polished steel substrates was reduced. This result was in a very good agreement with previous Auger depth profiles of plasma-polymerized acetylene films on steel substrates.[20] A comparison of Auger depth profiles of plasma-polymerized ethane, ethylene, and acetylene on polished steel substrates indicated that significantly smaller amounts of oxygen were present at the plasma-polymerized acetylene/steel interface than at the plasma-polymerized ethane/steel or ethylene/steel interface. Plasma-polymerized acetylene film was, therefore, bonded to iron oxides rather than to hydroxides.

Figure 9 shows the high-resolution Fe(2p) spectra obtained as a function of the take-off angle. When the take-off angle was 15°, the intensity of the Fe(2p) peaks was very low, but when the take-off angle was 45°, two peaks were detected in
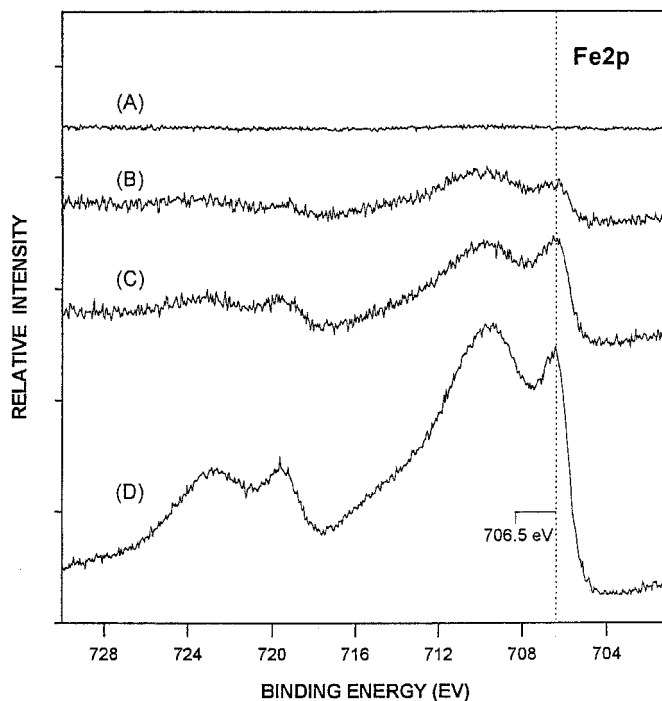
Figure 9 High-resolution Fe($2p$) XPS spectra obtained from as-deposition thin (~ 20 Å) plasma-polymerized acetylene film on polished steel substrates at take-off angles of (A) 15°, (B) 45°, and (C) 75°. The spectrum of a polished steel substrate is shown in (D).

the Fe$2p_{3/2}$ spectra. One peak was near 706.5 eV and was assigned to metallic iron while the other was near 710.0 eV and was due to the iron oxides and hydroxides. As the take-off angle increased to 75°, there was a significant increase in intensity for both peaks.

Curve-fit Fe($2p_{3/2}$) spectra are shown in Figure 10. Fe($2p_{3/2}$) spectra are known to be very difficult to curve-fit because of the rising background in this region of the spectrum and the number of different compounds that are usually present. There have been numerous suggestions for curve-fitting Fe($2p$) spectra.[24–31] We used the method suggested by McIntyre and Zetaruk,[25] Brundle et al.,[27] and Allen et al.[30]

The Fe($2p_{3/2}$) spectrum obtained from the polished cold-rolled steel substrate was resolved into four peaks located near 706.5, 709.1, 711.2, and 714.6 eV [see Fig. 10(D)]. The sharp peak at 706.5 eV was due to metallic iron while the other three broader peaks were due to iron oxides/hydroxides. The peak near 709.1 eV was assigned to ferrous (Fe^{2+}) species while the peak near 711.2 eV was assigned to ferric (Fe^{3+}) species, including Fe$_2$O$_3$ and FeOOH. The peak near 714.6 eV was assigned to an X-ray satellite of the metallic iron peak at 706.5 eV.

The curve-fit Fe($2p$) spectrum of the thin film on the polished steel substrate at a 75° take-off

angle is shown in Figure 10(C). It appeared that fewer oxides/hydroxides were present at the polymer/steel interface because the Fe^{2+} and Fe^{3+} signals were weaker than for the polished substrates. As mentioned above, this probably resulted from the reducing effect of argon/acetylene plasmas. Meanwhile, the Fe^{3+}/Fe^{2+} ratio increased slightly. As discussed previously, the O($1s$) spectra of the polished steel substrate were dominated by FeOOH, but when the plasma polymer film was deposited on the steel substrate, the hydroxide was reduced. Therefore, the increase in the Fe^{3+}/Fe^{2+} ratio when the film was deposited on the steel substrate was due to the reduction of FeOOH or, perhaps, the increase of Fe$_2$O$_3$.

When the spectrum was recorded at a 45° take-off angle [see Fig. 10(B)], the relative intensity of the peak due to metallic iron was weaker than at a 75° take-off angle. This was an indication of the approach of the polymer side, while moving away from the steel side although still remaining in the interface region. Meanwhile, the Fe^{3+}/Fe^{2+} ratio increased significantly from 0.67 at a 75° take-off angle to 1.50 at a 45° take-off angle. This again confirmed the decrease of FeOOH and increase of Fe$_2$O$_3$. However, the OH$^-$/O^{2-} ratios for spectra obtained at 45° and 75° take-off angles were almost identical. This suggested a decrease in Fe^{2+} (or Fe$_x$O) near the polymer/oxide interface. Figure
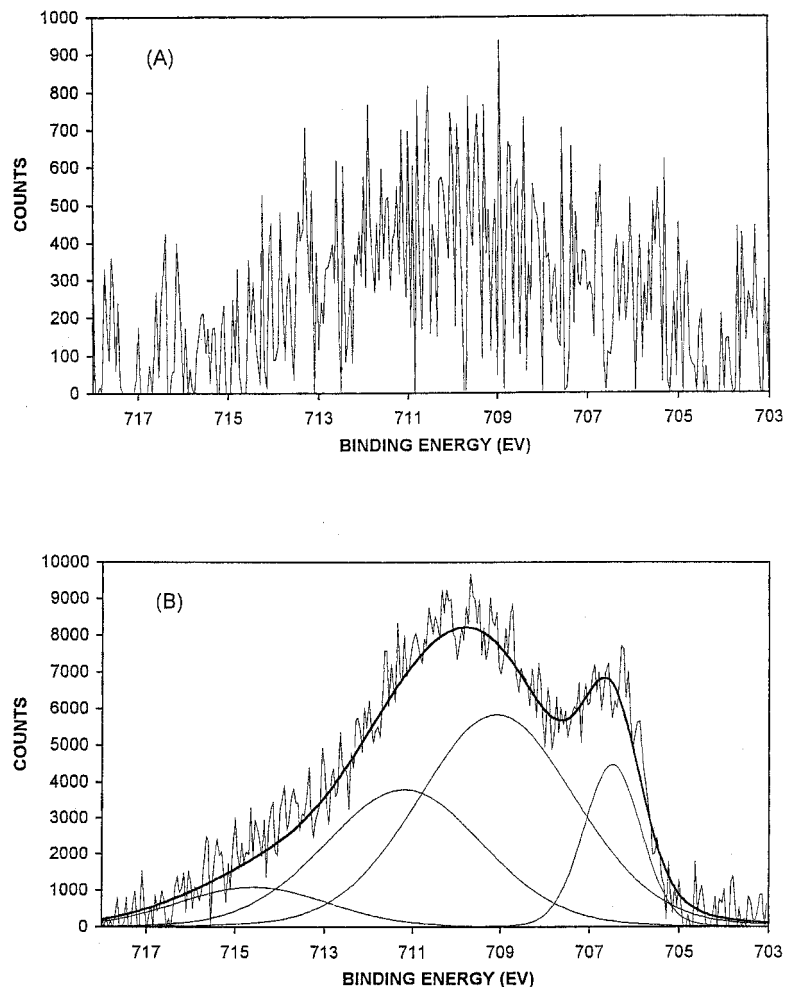
Figure 10 Curve-fit Fe $(2p_{3/2})$ XPS spectra obtained from as-deposited thin (~ 20 Å) plasma-polymerized acetylene films on polished steel substrates at take-off angles of (A) 15°, (B) 45°, and (C) 75°. The spectrum of a polished steel substrate is shown in (D).

10(A) shows the Fe$(2p)$ spectrum of a thin film on polished steel substrate recorded at a 15° take-off angle. No attempt to curve fit this spectrum was made due to the low signal-to-noise ratio. Nevertheless, there was a noticeable iron signal (mostly Fe^{+2} and Fe^{+3}) in the spectrum. This could explain the small shoulder observed near 530.0 eV in the O$(1s)$ spectrum.

CONCLUSIONS

Plasma-polymerized acetylene films deposited onto steel substrates in an inductively coupled rf-powered reactor contained several different types of functional groups. Included were mono- and disubstituted acetylene groups, vinyl groups, *cis*- and *trans*-disubstituted olefin groups, and carbonyl groups which resulted from the reaction of residual free radicals with oxygen when the films were exposed to the atmosphere. By comparison, films which were deposited in capacitively coupled reactors contained mostly methyl, methylene, and carbonyl groups. The molecular structure of the films changed as a function of deposition time and thus thickness. A band due to surface acetylides was observed near 3250 cm^{-1} for thin films but not thick films and a band probably related to CH wagging in disubstituted olefin groups was observed near 758 cm^{-1} for thick films but not for thin films.

Nondestructive characterization of the plasma polymer/steel interface was achieved using angle-resolved XPS analysis. The results indicated that during the process of plasma deposition of acetylene film on steel substrates the argon/acetylene
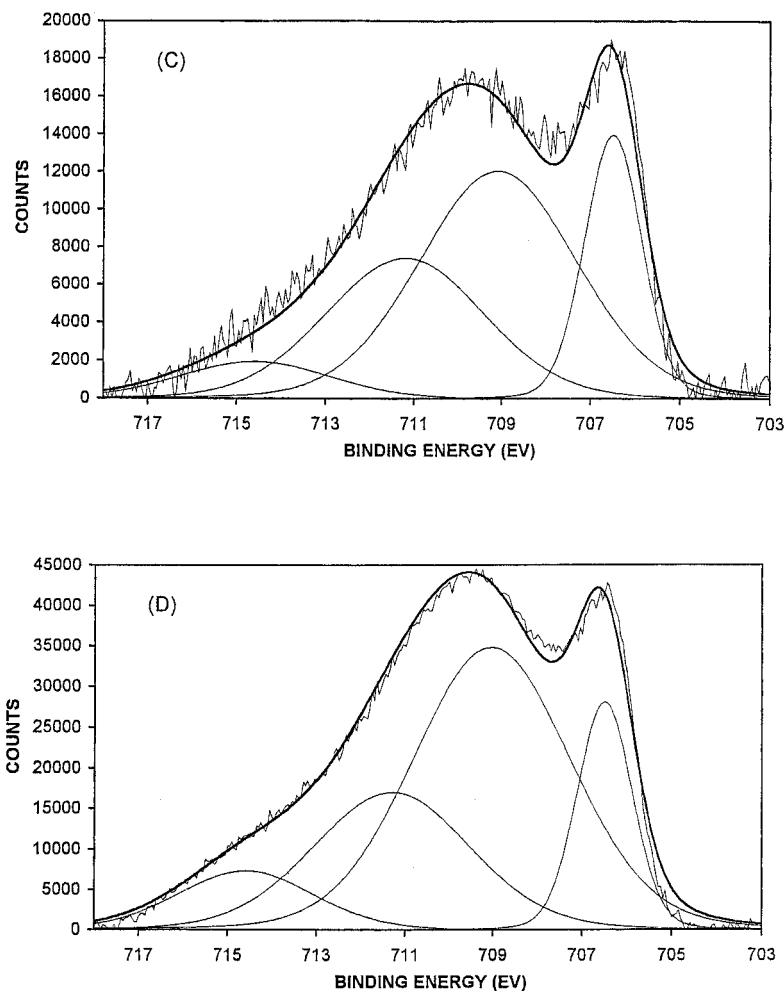
Figure 10 (*continued from the previous page*)

plasma etched the surface, removing carbonaceous contaminants and chemically reducing oxides and hydroxides, especially FeOOH. Thus, plasma-polymerized acetylene films were formed on top of "cleaned" steel substrates.

Preliminary results indicate that films deposited in an inductively coupled reactor are good primers for rubber-to-metal bonding whereas films deposited in a capacitively coupled reactor are not. The reason for the poor adhesion between natural rubber and films formed in a capacitively coupled reactor is probably related to the absence of functional groups that are found in films deposited in an inductively coupled reactor but not in films deposited in a capacitively coupled reactor.

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