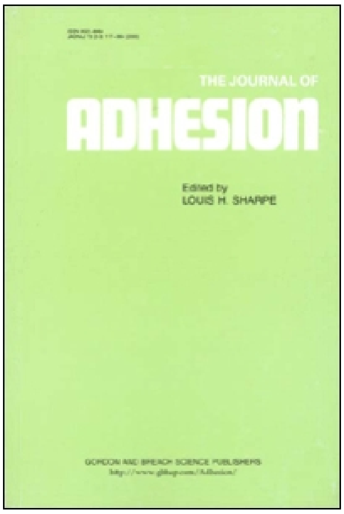

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Chemical Reactions Between Model Rubber Systems and Plasma Polymerized Acetylene Films. Part A: XPS, AES and SIMS Investigations

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Chemical reactions between natural rubber (NR) and plasma-polymerized acetylene films were investigated using model systems in which natural rubber was replaced by the unsaturated compound squalene ($C_{30}H_{50}$) or its saturated analogue, squalane ($C_{30}H_{62}$). Analysis of plasma-polymerized acetylene films on steel substrates before and after reaction with model rubber systems was accomplished using X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and Auger electron spectroscopy (AES). The importance of unsaturation in the model rubber compound was demonstrated by comparing the results for the two model systems. For the *squalene*-based model rubber system, the results obtained were consistent with a model in which components of the curing system reacted with both squalene and the plasma-polymerized acetylene film to form a relatively large number of polysulfidic pendant groups. In the early stages of the reaction, pendant groups were probably terminated by cobalt ions since sulfides were detected by XPS and AES. Pendant groups were probably terminated by zinc ions in the later stages of the reaction. The pendant groups disproportionated to form a relatively large number of mono-, di-, and tri-sulfidic crosslinks between the model rubber compound and the plasma polymerized primer. In the *squalane*-based model rubber system, components of the curing system reacted with the plasma-polymerized acetylene film to a small extent to form a few relatively long polysulfidic pendant groups. However, there was little evidence for reaction of the curing system with squalane and for crosslinking between squalane and the plasma polymerized primer.

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*Corresponding author.

Keywords: Adhesion; natural rubber; steel substrate; model rubber compound; squalene; squalane; crosslinking reactions; pretreatments; unsaturation; metal mercaptides

I. INTRODUCTION

Adhesion of rubber to steel is of considerable practical importance in many areas of technology. However, direct adhesion of natural rubber to most metals is very poor. As a result, metals are frequently plated with brass, to which rubber adheres very strongly, or else the metals are coated with proprietary primers and adhesives in order to obtain adhesion of rubber.

However, there are still some problems in the process of bonding rubber to brass-plated steel. For example, chemical wastes from plating processes are difficult to dispose of. Furthermore, brass-plated steel is vulnerable to corrosion because of the galvanic coupling of brass and steel. In a corrosive environment, brass is cathodic, and iron, which is anodic, tends to corrode at an accelerated rate. Once a corrosion cell has been established, the high pH of the environment will also chemically attack the brass coating. Therefore, there is still the need to develop a system for rubber-to-metal bonding with improved corrosion protection and little or no waste disposal.

Plasma processing is a potentially useful method for pretreating metals to obtain adhesion of rubber. Plasma polymerization is an efficient process since it enables the synthesis of polymers and the deposition of thin polymer films to be combined. In general, plasma processing is very flexible, allowing various combinations of reactor parameters such as monomer, carrier gas, monomer and carrier gas flow rate, power, and pressure to provide a great deal of process control and versatility. Previous experiments [1] revealed the possibility of generating different forms of plasma polymers by changing the reactor conditions. Plasma polymer films having a thickness of nearly 1000 Å were deposited in only a few minutes. Moreover, in plasma processing, there are no solvents involved and there are no solvent-disposal problems. Finally, several operations, such as pretreatment of the substrate by plasma etching and deposition of polymer films by plasma polymerization can be carried out in the same reactor.

Recently, we have undertaken a research project to develop plasma etching and plasma polymerization as novel pretreatment processes for obtaining adhesion of rubber to metals such as steel. Miniature lap joints were prepared by using rubber as an "adhesive" to bond together pairs of polished steel adherends primed with plasma-polymerized acetylene films. The maximum force required to cause failure of the joints was determined in an Instron tensile tester and the rubber coverage of the failure surfaces was qualitatively estimated. It was observed that the interfacial bond strength of rubber and plasma-polymerized acetylene was greater than the cohesive strength of natural rubber. Therefore 100% cohesive failure in rubber was observed [2]. We have also demonstrated that the durability of rubber-to-steel bonds prepared from steel substrates primed with plasma-polymerized acetylene films was very promising. It was found that these bonds resisted exposure to steam.

The study of the vulcanization chemistry of NR and other rubbers has traditionally been hampered by the inaccessibility of the cured network. The advent of surface-sensitive techniques has prompted interest in a relation between surface composition and adhesive properties. Although much information can be obtained from surface analysis, reconstruction of the complete interface is difficult. Therefore, model systems have often been employed to investigate the rubber/metal interface. The chemistry of rubber-brass interfaces and the mechanism of their formation have been studied in detail by van Ooij [3–5], who introduced squalene as a replacement for natural rubber. Good correlations were observed between the model and actual systems in terms of crosslink density, reaction rate, and the effect of rubber compounding. Accessibility to the interface and good reproducibility were two of the major advantages of employing this model system. Later, Ball and co-workers [6] also used squalene as a liquid model to determine the correlation between the organic portion (R) of three cobalt-based adhesion promoters (Co-R) and the composition of a vulcanized brass/squalene interface.

Recently, van Ooij and Rangarajan [7] employed a similar technique to compare the behavior of squalene at steel surfaces with that of its saturated counterpart, squalane, in order to determine the specific effect of unsaturation in the polymer. The steel surfaces were cleaned using techniques such as solvent-rinsing and abrasion.

Secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) were used to characterize surfaces before and after reactions. The results obtained with solvent-cleaned steel indicated that squalene did not react to the same extent as on abraded steel due to the presence of organic contaminants. Squalane, however, did not react with either of the steel surfaces.

In our previous work [8], plasma polymerized films were reacted with a model "rubber" consisting of a mixture of squalene (instead of natural rubber), zinc oxide, carbon black, sulfur, stearic acid, diaryl-*p*-diphenyleneamine, cobalt naphthenate, and *N*,*N*-dicyclohexylbenzothiazole sulfenamide. Evidence for crosslinking between the model rubber compound and the plasma polymerized film was obtained using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and secondary ion mass spectrometry (SIMS).

The purpose of this paper is to investigate the factors, especially unsaturation, influencing the reactions occurring in the "interphase" between natural rubber and plasma-polymerized acetylene films. Therefore, the behavior of squalene in the interaction between plasma polymer and model compounds was compared with that of its saturated counterpart, squalane ($C_{30}H_{62}$), in order to determine a specific effect of the unsaturation in this reaction.

II. EXPERIMENTAL

Cold-rolled 1010 steel substrates were obtained from The Goodyear Tire and Rubber Company (Akron, Ohio) and were mechanically polished to a mirror finish. 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 polymerization and etching were carried out in a tubular reactor which was inductively coupled to an RF (13.56 MHz) power supply. The main part of the reactor is a Pyrex tube with an internal diameter of 6 inches. The top portion of the reactor is made of quartz and is surrounded by the RF coil. Samples were supported on a stage which could be moved vertically within the reactor. Carrier gases were introduced at the top of the reactor, just above the coil. Monomers were introduced into the reactor through an inlet tube which was located below the coil. A detailed description of the reactor has been presented elsewhere [9].

Prior to plasma polymerization, the polished substrates were etched in an argon (Matheson, 99.999% minimum purity) plasma at 1 Torr pressure, 20 W power, and 20 sccm flow rate for 10 minutes. Plasma polymerized films of acetylene (Matheson, 99.6% minimum purity) were then deposited using argon as the carrier gas. The reactor conditions for plasma deposition were 1 Torr pressure, 55 W power, and flow rate 20 (Ar)/25 (C_2H_2) sccm. The thickness of plasma-polymerized acetylene film was approximately 500 Å.

The model rubber compound consisted of squalene or squalane (100 parts per hundred parts), zinc oxide (10 phr), carbon black (10 phr), sulfur (5 phr), stearic acid (2 phr), and DCBS, cobalt naphthenate, and diaryl-*p*-diphenyleneamine (each 1 phr). These materials were all obtained from Goodyear except for stearic acid, squalene, and squalane, which were obtained from Aldrich. Polished steel substrates primed with plasma-polymerized acetylene films were immersed into a stirred mixture of these materials at a temperature of 155 ± 5°C to simulate the curing of rubber against a primed steel substrate. During the reaction, the mixture was purged with nitrogen to reduce oxidation effects. At appropriate times between 1 and 100 minutes, substrates were removed from the mixture, rinsed with hexane ultrasonically for 5 minutes to remove unreacted materials, dried, and examined using techniques such as XPS, SIMS and AES. A schematic drawing of the apparatus used in reacting the model rubber systems with plasma polymerized films on steel substrates is shown in Figure 1.

A Perkin-Elmer Model 5300 XPS spectrometer with Mg Kα X-rays, operating at 300 W and 15 kV DC, was used to obtain XPS 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 at a take-off angle of 45° 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.

Time-of-flight (TOF) SIMS analyses were performed on a Kratos Prism instrument equipped with a reflectron-type mass analyzer and a 25 kV liquid metal ion source of $^{69}Ga^{+}$ ions, with a minimum beam

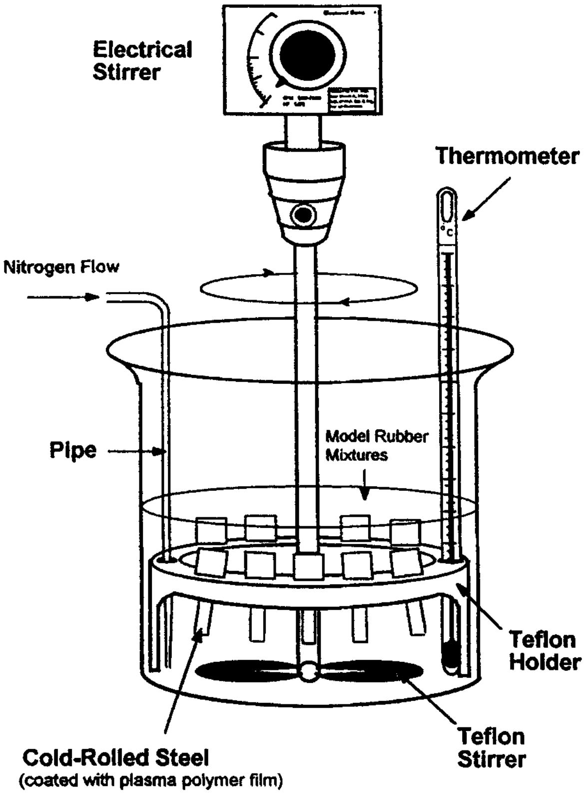


FIGURE 1 A schematic drawing of the apparatus used in the reaction of model rubber systems with plasma polymerized films on steel substrates.

size of 500 Å. The mass resolution M/ΔM was about 4000 at 27 amu. The total ion dose was in the static SIMS regime in all analyses.

Element depth profiling was done on a Perkin-Elmer 590A Scanning Auger Microprobe, sputtering with a beam of 1.5 keV Ar^+ ions. The sputtering rate was 5 Å/minute calibrated for a Ta_2O_5 film of known thickness.

III. RESULTS AND DISCUSSION

XPS survey spectra of plasma-polymerized acetylene films reacted with *squalene*-based model rubber compounds for various times are shown in Figure 2. Peaks were observed which were characteristic of elements in the plasma-polymerized acetylene film (*e.g.*, C and O) and other elements such as N, S, Zn and Co which were characteristic of the rubber compounds. Atomic concentrations from XPS analysis of plasma-polymerized acetylene films as a function of reaction time in *squalene*-based model mixtures are shown in Table I.

In order to determine the specific effect of the unsaturation in the interaction between plasma-polymerized acetylene film and model rubber compounds, a similar experiment was conducted on a model system in which *squalene* was replaced by *squalane*. The XPS survey spectra of plasma-polymerized acetylene films after reaction in the *squalane*-based model rubber mixtures are shown in Figure 3. Atomic concentrations from XPS analysis of plasma-polymerized acetylene films as a function of reaction time in *squalane*-based model mixtures are shown in Table II.

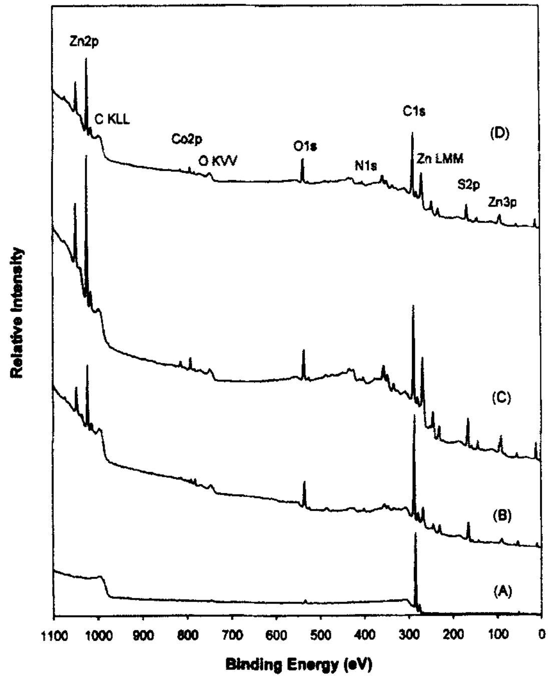


FIGURE 2 XPS survey spectra of plasma-polymerized acetylene film as a funtion of reaction time with *squalene*-model rubber compounds. (A)–0, (b)–15, (C)–35, and (D)–65 minutes.

TABLE I Atomic concentrations from XPS analysis of plasma-polymerized acetylene film as a function of reaction time with a *squalene*-based model rubber compound

Reaction time	*Atomic Concentration (%)*							
(minute)	*C*	*O*	*N*	*S*	*Zn*	*Co*	*Si*	*Na*
0	98.6	1.4	-		-			-
15	75.7	8.7	1.4	9.9	3.4	0.3	0.5	0.1
35	68.9	8.5	1.8	11.8	8.4	0.6		-
65	70.6	10.4	1.6	10.4	6.4	0.5	-	0.1

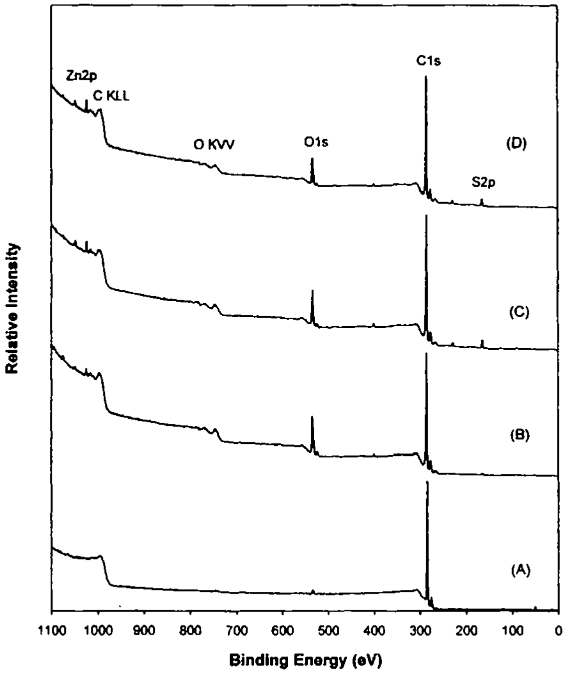


FIGURE 3 XPS survey spectra of plasma-polymerized acetylene film as a function of reaction time with *squalane*-based model rubber compounds. (A) 0, (b)-15, (C) 35, and (D)-65 minutes.

By comparing Figures 2 and 3, it was possible to draw some conclusions regarding the interaction of the model rubber compounds with plasma-polymerized acetylene films. For example, the concentration of Co, Zn, and S on the surfaces was much greater for experiments conducted in the *squalene*-based mixtures than in the *squalane*-based mixtures.

TABLE II Atomic concentrations from XPS analysis of plasma-polymerized acetylene film as a function of reaction time with a *squalane*-based model rubber compound

Reaction time			*Atomic Concentration (%)*					
(minute)	*C*	*O*	*N*	*S*	*Zn*	*Co*	*Si*	*Na*
0	98.6	1.4	–	–	–	–	–	–
15	82.7	14.4	1.3	0.9	0.3	0.2	–	0.2
35	82.1	12.2	1.6	3.3	0.5	0.1	–	0.2
65	84.0	10.1	1.5	3.6	0.6	0.1	–	0.1

After 35 minutes reaction, the concentrations of Co, Zn, and S on the film surfaces were 0.6, 8.4, and 11.8%, respectively, for the *squalene*-based model and 0.1, 0.5, and 3.3%, respectively, for the *squalane*-based model.

The higher concentration of Zn and Co on the surface after reaction with the *squalene* compound was an indication of a higher degree of reaction [8]. However, the appearance of zinc and cobalt could be attributed to the original compounds, ZnO and cobalt naphthenate, to reaction intermediates such as zinc and cobalt stearate, or to $Zn-S_x-$ and $Co-S_x-$ attached to *squalene*, *squalane*, or the plasma-polymerized acetylene film. Only the last two forms of metal sulfides could contribute to the crosslinking reaction [3, 4]. From a comparison of typical XPS high resolution Zn $L_3M_{4,5}M_{4,5}$ X-ray induced Auger spectra shown in Figure 4, it was determined that in both model systems zinc was mostly present in the form of oxides (binding energy, B.E. ~266.0 eV) and sulfides (~264.0 eV) [10]. However, the oxide to sulfide ratio was apparently larger in the spectrum obtained from film surfaces after reaction in the *squalane*-based mixtures than in the *squalene*-based mixtures. In sulfur vulcanization, the crosslinking reaction is believed to be accelerated by zinc accelerator thiolates, either catalytically or with formation of zinc sulfide [11]. Therfore, we can draw a preliminary conclusion that more intermediates, such as zinc accelerator perthiomercaptides, were formed in the *squalene*-based mixtures.

The high resolution S(2*p*) spectrum was resolved into peaks related to metal sulfide, S^{-2} (B.E. ~161.9 eV), crosslinked sulfur, $-CS_xC-$ (~163.5 eV), uncombined sulfur, $-S_y-$ (~164.3 eV) [5], sulfoxide (~166 eV) and sulfate (~168–169 eV). However, it was difficult to distinguish sulfur in crosslinks from sulfur in pendant groups. The

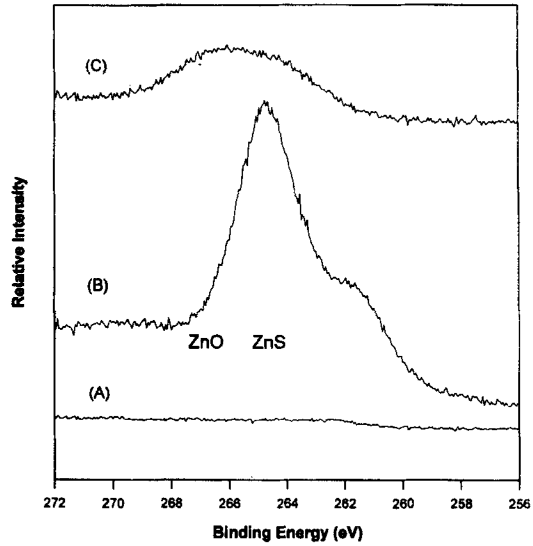
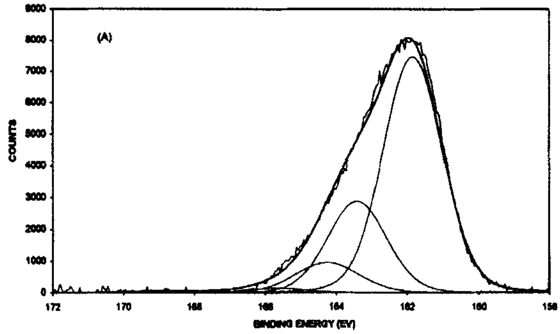
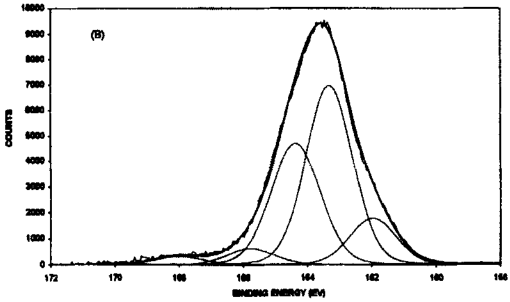


FIGURE 4 Typical X-ray induced ZnLMM Auger spectra of (A)-as deposited plasma-polymerized acetylene film and after 35 minutes reaction with (B)-*squalene* and (C)-*squalane*-based model rubber compounds.

broad peaks centered around 163.5 eV and 164.3 eV were both assigned to $-S_x-$ which was present in pendant groups and in crosslinks. Figure 5 shows typical S(2*p*) spectra of the plasma-polymerized acetylene films on steel substrates following reaction with the two different model rubber systems for 35 minutes. Because the experiments were conducted in a nitrogen atmosphere, only small amounts of oxidized sulfur were evident from the low intensity of sulfoxide and sulfate peaks. Analysis of the surface after reaction in the *squalane*-based mixture showed that the intensity of the peak due to sulfur ions (S^{2-}) near 161.9 eV was low. This also explained the low concentrations of metal sulfides as described above. A comparison of the two S(2*p*) spectra also showed that the relative intensity of the peaks at 163.5 and 164.3 eV was much smaller in the case of reaction in the *squalane*-based mixtures than in the *squalene*-based mixtures. This seemed to indicate that the lack of unsaturation in *squalane* resulted in longer sulfur chains ($-S_y-$) since it has been found that sulfur chains have higher S(2*p*) binding energies [5].



Peak Position (eV)	Concentration (%)	Assignment
161.9	59.1	S^{2-}
163.5	26.8	$-S_x-/C-S_x-C$
164.3	10.8	$-S_y-/C-S_y-C$ (y>x)
165.8	2.1	sulfoxide
168.2	1.2	sulfate



Peak Position (eV)	Concentration (%)	Assignment
161.9	12.6	S^{2-}
163.5	40.5	$-S_x-/C-S_x-C$
164.3	40.8	$-S_y-/C-S_y-C$ (y>x)
165.8	3.6	sulfoxide
168.1	2.5	sulfate

FIGURE 5 Typical XPS high resolution S(2*p*) spectra of plasma-polymerized acetylene film after 35 minutes reaction with (A)-*squalene* and (B)-*squalane*-based model rubber compounds.

Positive and negative TOF-SIMS spectra of as-prepared plasma-polymerized acetylene films on steel substrates are shown in Figure 6. Considering the intensity of ions such as +77, +91, +128 amu, it

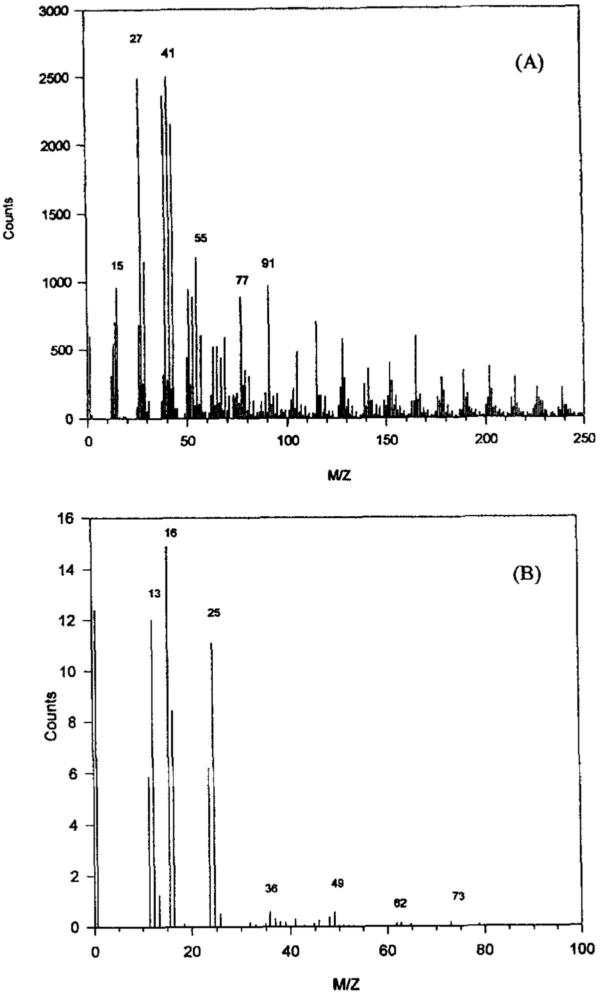


FIGURE 6 (A)-Positive and (B)-negative TOF-SIMS spectra of plasma-polymerized acetylene film.

was concluded that the degree of aromaticity in plasma-polymerized acetylene was remarkably high. The degree of unsaturation was estimated from the ratio of ions +27/29 amu in the positive spectrum and was obviously high. The effect of post-polymerization reaction with ambient O_2 was also observed from the negative spectrum of ions at 16 and 17 amu assigned to O^- and OH^-, respectively.

Figures 7 and 8 show the TOF-SIMS spectra of a plasma-polymerized acetylene film before and after immersion in *squalene*-based model rubber mixtures. Detailed peak assignments are listed in Table III. In addition to the intensity decrease of peaks at −24 and −25 amu assigned to mono-substituted and di-substituted acetylene, the intensities of peaks at +12, +26, +27, +39, +50/51, +77, +91, and +128 amu, etc., which are typically formed by unsaturated or aromatic hydrocarbons, were much lower in the plasma polymerized acetylene film after reaction in *squalene* mixtures than in the as-prepared plasma polymer film.

These changes in the SIMS spectra were not necessarily indications of reaction between *squalene* mixtures and plasma-polymerized acety-

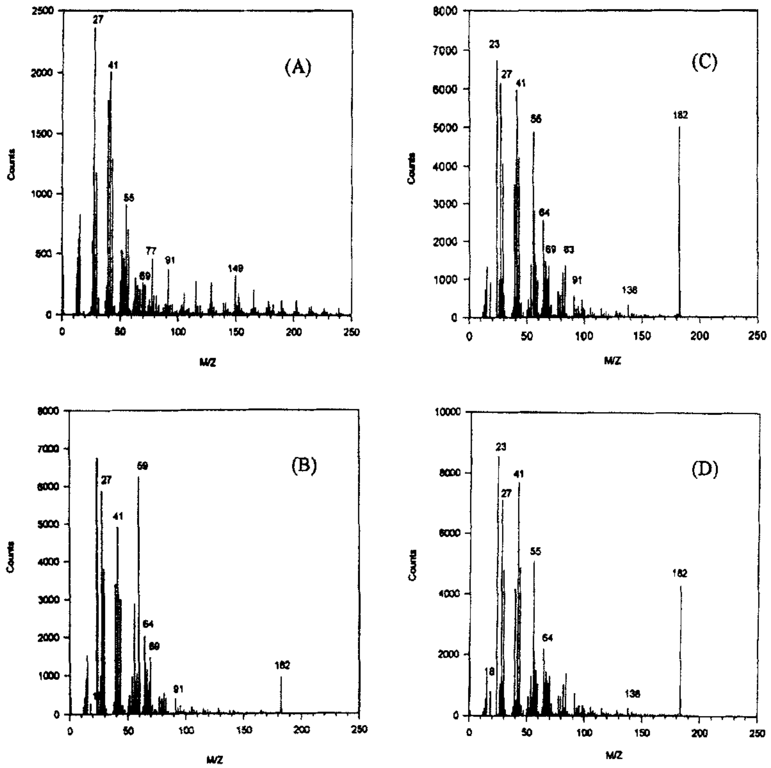


FIGURE 7 Positive TOF-SIMS spectra of plasma-polymerized acetylene films as a function of reaction time with *squalene*-based model rubber compounds. (A)–0, (B)–15, (C)–35, and (D)–65 minutes.

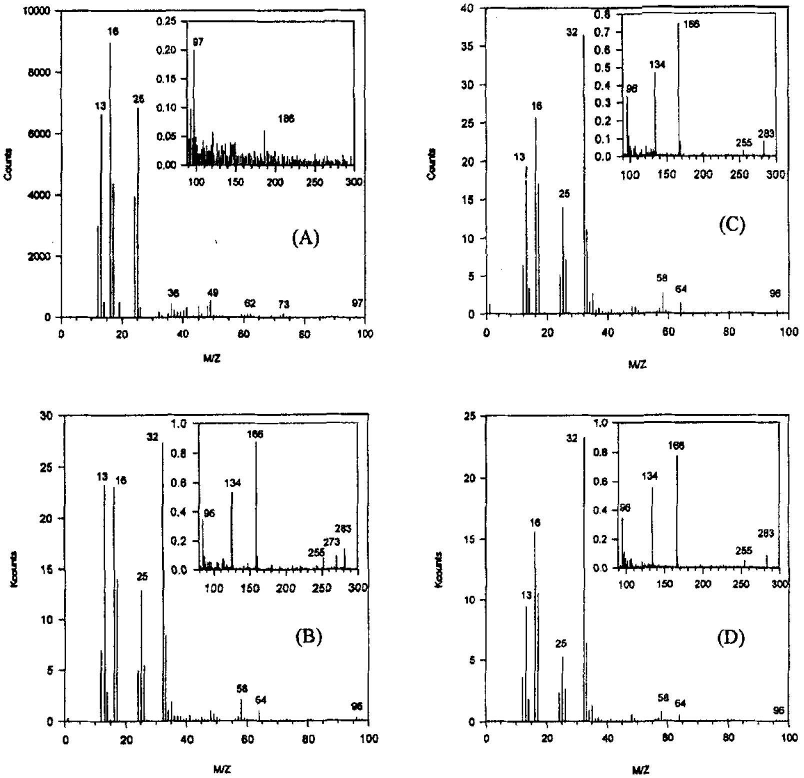


FIGURE 8 Negative TOF-SIMS spectra of plasma-polymerized acetylene films as a function of reaction time with *squalene*-based model rubber compounds. (A) – 0, (B) – 15, (C) – 35, and (D) – 65 minutes.

lene films. They may have resulted simply from heating the plasma polymer films in an atmosphere that was relatively low in oxygen or to adsorption of a thin layer of *squalene* which could not be completely removed by hexane. Therefore, an experiment was carried out in which a plasma-polymerized acetylene film on a steel substrate was immersed into neat *squalane* (with no added curing system) at 155°C for 35 minutes. The SIMS spectra obtained from the surface after immersion in neat *squalane* are shown in Figure 9. It was obvious that the intensities of the ions at +77 ($C_6H_5^+$), +91 ($C_7H_7^+$), +128 ($C_{10}H_8^+$), and +141 amu ($C_{11}H_9^+$), which were assigned to aromatic species, decreased significantly after immersion in *squalane*. Evidence for a decrease in unsaturation was obtained from the ratio

TABLE III Peak assignments of TOF-SIMS spectra

MASS		*ASSIGNMENT*
[positive]	[negative]	
+12		C^+
	−16	O^-
	−17	OH^-
+18		NH_4^+
	−24	C_2^-
	−25	C_2H^-
+27		$C_2H_3^+$
+29		$C_2H_5^+$
	−32	S^-
+39		$C_3H_3^+$
+41		$C_3H_5^+$
+53		$C_4H_5^+$
+55		$C_4H_7^+$
	−58	CNS^-
+59		Co^+
+64		Zn^+
	−64	S_2^-
+69		$C_5H_9^+$
+77		$C_6H_5^+$
+91		$C_7H_7^+$
	−96	S_3^- or SO_4^-
	−97	HS_3^- or HSO_4^-
+98		$C_6H_{12}N^+$
+128		$C_{10}H_8^+$
	−128	S_4^-
	−134	$C_7H_4NS^-$
+141		$C_{11}H_9^+$
+149		$C_{11}H_{17}^+$
	−166	$C_7H_4NS_2^-$
+182		$C_{12}H_{24}N^+$
	−255	$C_{15}H_{31}COO^-$
	−283	$C_{17}H_{35}COO^-$

increase within certain clusters, such as +27/29 ($C_2H_3^+/C_2H_5^+$), +39/41 ($C_3H_3^+/C_3H_5^+$) and +53/55 amu ($C_4H_5^+/C_4H_7^+$). In the negative spectra, the decrease of clusters at −24 (C_2^-) and −25 amu (HC_2^-) related to acetylene groups was also remarkable.

These observations indicated that heating plasma polymerized acetylene films with an unreactive compound such as *squalane* at 155°C

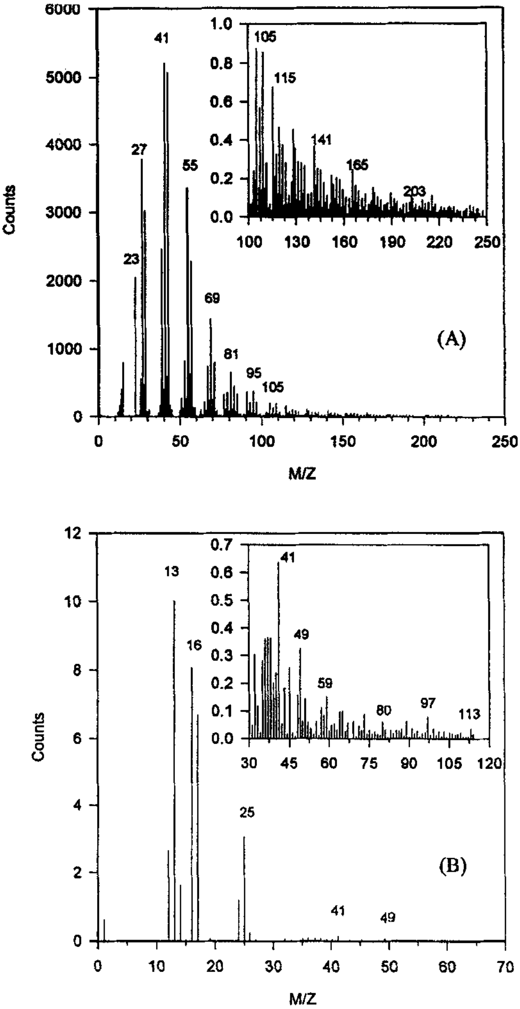


FIGURE 9 (A)-Positive and (B)-negative TOF-SIMS spectra of plasma-polymerized acetylene films after 35 minutes reaction with neat *squalane* at 155°C.

could reduce the unsaturation in the films. Therefore, conclusions regarding crosslinking between plasma polymer films and model rubber compounds were not based solely upon the reduction of unsaturation in the plasma polymer films.

Peaks due to zinc (at +64 amu) and cobalt ions (at +59 amu) were quite strong in SIMS spectra of the surfaces after reaction in *squalene*-

based model rubber mixtures (see Fig. 7). The concentration of Co on the surface was very high after 15 minutes reaction but decreased thereafter. On the other hand, the Zn concentration was more intense after 35 minutes reaction than after 15 and 65 minutes reaction. This result was in agreement with those obtained from XPS (see Fig. 2 and Tab. I).

It is possible that the cobalt ions were formed and started to promote crosslinking after 15 minutes reaction in the *squalene*-based mixture. After 35 minutes reaction, the cobalt ions decreased in intensity as a result of dissociation of $Co-S_x-C$ groups to form rubber-bound pendant groups. On the other hand, the intensity of zinc ions started to increase after 15 minutes reaction and reached a maximum and started to promote crosslinking after 35 minutes reaction. Finally, as a result of dissociation of $Zn-S_x-C$ groups to form rubber-bound pendant groups, the intensity of zinc ions decreased after 65 minutes reaction.

Squalene apparently formed on top of the plasma-polymerized acetylene film through sulfur crosslinks. Evidence for crosslinking was clear in the negative SIMS from the peaks at $-64(S_2^-)$, $-96(S_3^-$ or $SO_4^-)$ and -128 amu (S_4^-) and the absence of a peak at -97 amu (due to HSO_4^-). It was concluded that these peaks were mostly due to crosslinking between the plasma-polymerized primer film and *squalene* (or rubber in the "actual" system) instead of the oxidation of sulfur. Further evidence for the reaction between the plasma polymer film and *squalene* was seen in the *squalene*-related peaks ($+55$ and $+69$ amu) [7]. The intensities of these peaks seemed to show a clear trend with reaction time, increasing in intensity after 35 minutes reaction. Also observed in SIMS spectra were traces of the stearic acid activator (-255 and -283 amu) which was adsorbed on the film surface from the reaction mixtures.

TOF-SIMS spectra of plasma-polymerized acetylene films after immersion in the *squalane*-based model rubber mixtures are shown in Figures 10 and 11. When these spectra were compared with those obtained after reaction with *squalene*-based model rubber compounds, some important conclusions were reached. In contrast to the high concentrations of zinc and cobalt ions observed on film surfaces after reaction in *squalene*-based mixtures, the intensities of metal ions after reaction in the *squalane*-based model rubber mixtures were much weaker and showed no trend with reaction times.

The intensities of ions at $+18$, $+98$, $+182$ amu (amine fragments of DCBS accelerator) and at -134 and -166 amu (sulfenamide frag-

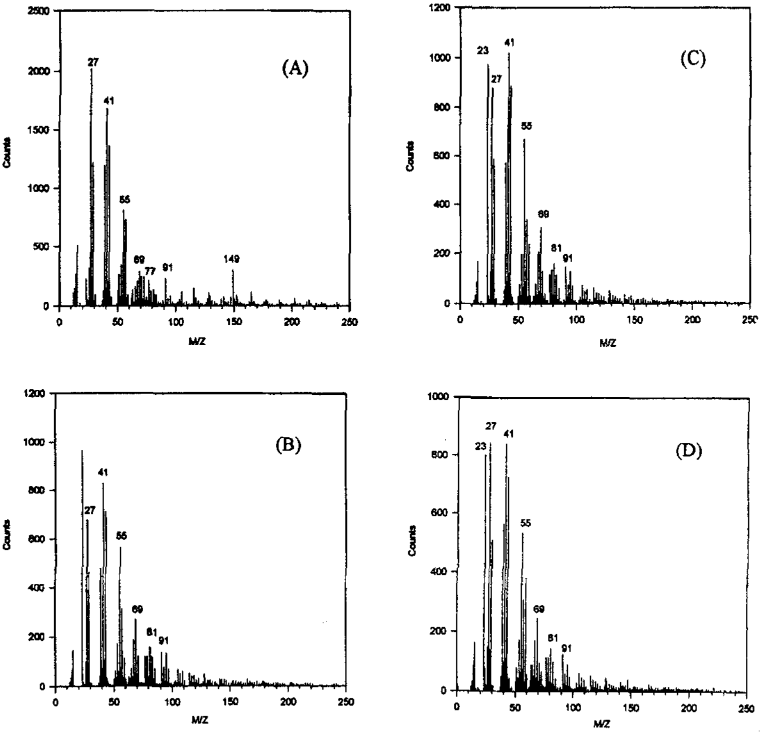


FIGURE 10 Positive TOF-SIMS spectra of plasma-polymerized acetylene films as a function of reaction time with *squalane*-based model rubber compounds. (A)–0, (B)–15, (C)–35, and (D)–65 minutes.

ments of DCBS accelerator) were quite strong on film surfaces after reaction in *squalene*-based model rubber mixtures (see Figs. 8 and 9) but were much weaker and nearly undetectable after reaction in *squalane*-based mixtures. The sulfenamide fragments (X) were believed to be part of an Zn accelerator thiolate, XSS_aZnS_bSX. Amine fragments were coordinated with the Zn accelerator thiolate to form a rubber-soluble zinc complex [10]. Cobalt was assumed to perform similarly to zinc.

As mentioned above, evidence for crosslinking in the *squalene*-based mixtures was clear in the negative SIMS spectra from the peaks at $-64(S_2^-)$, $-96(S_3^-)$ and -128 amu (S_4^-), together with the absence of a peak at -97 amu (due to HSO_4^-). On the other hand, in the experiments conducted in *squalane*-based mixtures, the intensities of peaks

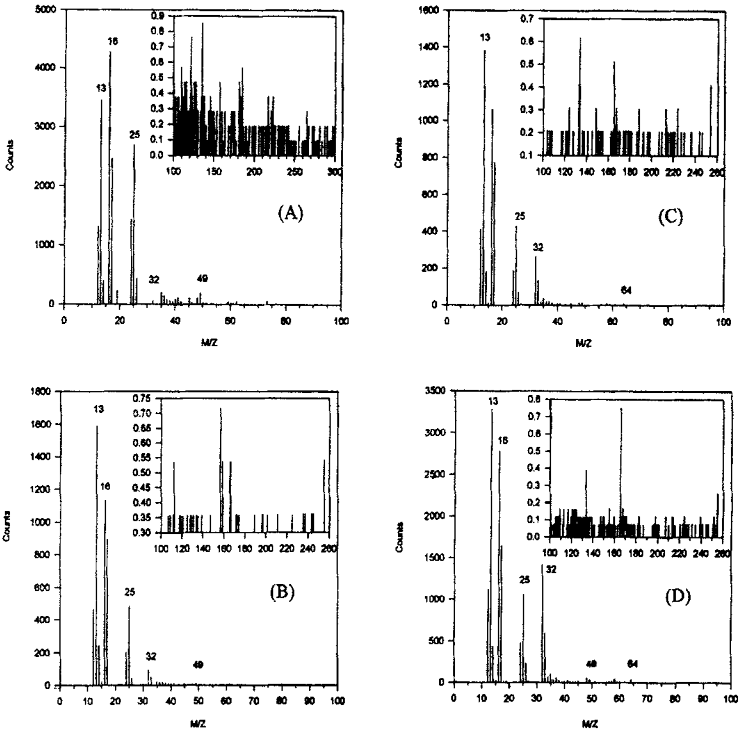


FIGURE 11 Negative TOF-SIMS spectra of plasma-polymerized acetylene films as a function of reaction time with *squalane*-based model rubber compounds. (A)–0, (B)–15, (C)–35, and (D)–65 minutes.

at −64 and −96 amu were much weaker, together with the similar intensity of peaks at −96(S_3^- or S_4^-) and −97 amu (HS_3^- or HSO_4^-). It could not be concluded whether the peak at −96 amu was due to crosslinking or oxidation. Certain amounts of uncrosslinked sulfur species were postulated to adsorb on the surfaces of plasma polymer films. The relatively low intensity of the peak at −32 amu (S^-) was another indication for much less reaction occurring in the *squalane*-based experiment.

The conclusions drawn above were confirmed by an Auger depth profile of the plasma-polymerized acetylene film following reaction with the *squalene*-based mixture for 65 minutes (see Fig. 12). The spectrum showed the continuous nature of the films prepared by the plasma deposition method. Very sharp profiles between iron and carbon in the interface region showed that the pretreatments (including polishing and argon plasma etching) resulted in a clean steel surface. The sulfur concentration was high on the surface, decreased in the plasma polymer film, but increased again at the plasma polymer/steel interface. It appeared that the iron oxide had, in part, been converted to iron sulfide. These observations were much clearer in an expanded AES depth profile (see Fig. 13) which clearly showed that the first few surface layers consisted of carbon, oxygen, zinc, cobalt, and sulfur. It was very interesting to note that the sulfur concentration on the

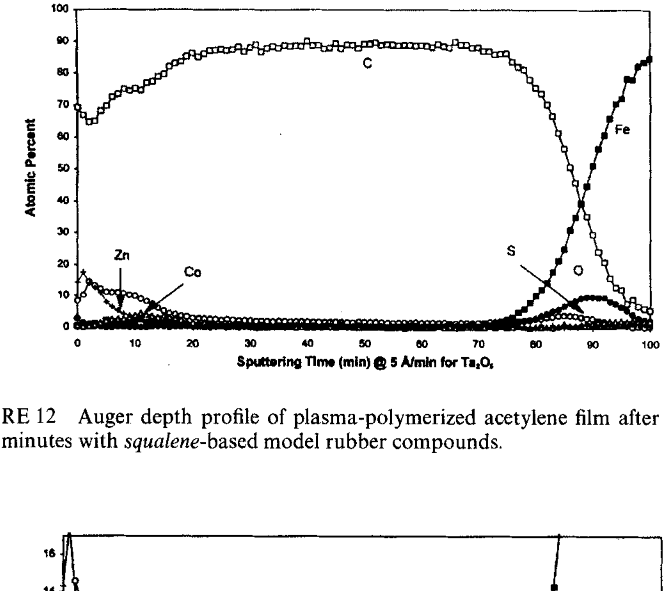


FIGURE 12 Auger depth profile of plasma-polymerized acetylene film after reaction for 65 minutes with *squalene*-based model rubber compounds.

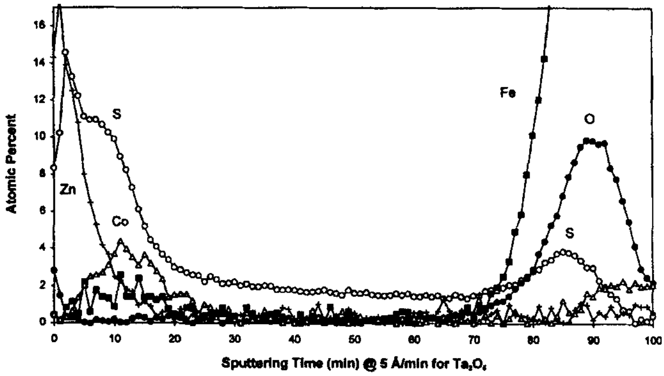


FIGURE 13 Expanded Auger depth profile of plasma-polymerized acetylene film after reaction for 65 minutes with *squalene*-based model rubber compounds.

surface correlated strongly with zinc and cobalt profiles, implying that the high sulfur concentration on the surface was related to zinc and cobalt sulfides. An interesting feature about the reaction sequence of the zinc and cobalt was clarified from Figure 13. Zn was observed on top of Co in the outermost surface, which seemed to indicate that the cobalt salt reacted with the accelerator first to form a cobalt perthiomercaptide intermediate which promoted the crosslinking reaction of the plasma polymer film with *squalene*. Then, a zinc complex was formed which promoted additional crosslinking between *squalene* and the plasma polymer film or between *squalene* still in the mixture and *squalene* that had already reacted with the plasma polymer film.

An Auger depth profile was also obtained from a plasma-polymerized acetylene film following reaction with the *squalane*-based mixture for 65 minutes (see Fig. 14). The spectra again showed the continuous nature of the films prepared by the plasma deposition method as well as a clean polymer/steel interface. These observations were much clearer in an expanded AES depth profile (see Fig. 15). The expanded profile showed that the first few surface layers consisted of mostly carbon, sulfur and small amounts of oxygen. Remarkably, the concentrations of zinc and cobalt were low on the surface and were almost constant throughout the polymer film. The sulfur concentration was high on

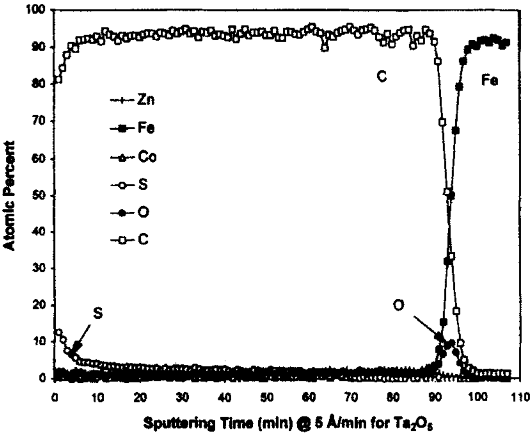


FIGURE 14 Auger depth profile of plasma-polymerized acetylene film after reaction for 65 minutes with *squalane*-based model rubber compounds.

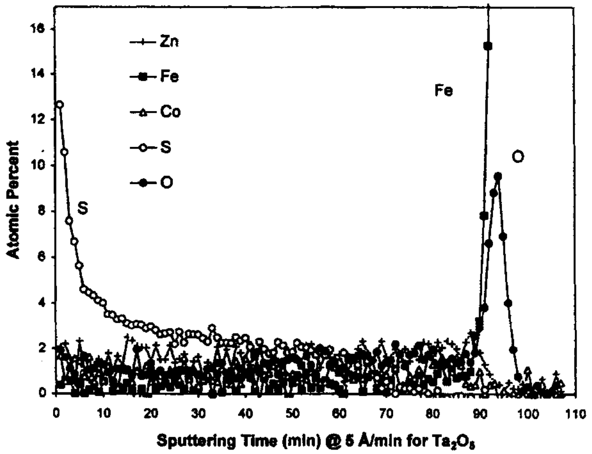


FIGURE 15 Expanded Auger depth profile of plasma-polymerized acetylene film after reaction for 65 minutes with *squalane*-based model rubber compounds.

the surface but gradually decreased with distance into the plasma polymer film. There was almost no sulfur at the plasma polymer/steel interface. Based on the observation of very weak zinc and cobalt adsorptions on the surface, it was likely that the sulfur observed on the surface was mainly uncombined sulfur or organic sulfur. This result confirmed those obtained from the high resolution S(2*p*) XPS spectrum (see Fig. 5). Apparently, in the *squalane*-based model rubber system, there were no unsaturated bonds to provide sites for reaction intermediates, such as zinc and cobalt perthiomercaptides, to form pendant groups for further crosslinking reactions. As a result, reaction intermediates were only adsorbed onto the surface of plasma-polymerized primer film. But, without further "crosslinking" with *squalane*, these reaction intermediates could not persist on the surface as the reaction progressed.

Results obtained from XPS, SIMS, and AES showed that unsaturated sites on model rubber compounds played a very important role in promoting the crosslinking reaction between the model rubbers and plasma-polymerized acetylene primer films. In the *squalene*-based model rubber system, the curing system reacted with both squalene and the plasma-polymerized acetylene film to create sulfur bridges. On the other hand, in the *squalane*-based model rubber compound, the curing system reacted with the plasma-polymerized acetylene film as evident from the existence of zinc and cobalt on the film surface. However, there was no signficant reaction with squalane and there was little evidence for formation of crosslinks.

IV. CONCLUSIONS

Although there was no direct information to show the crosslink reaction quantitatively, a comparison of reactions conducted in the unsaturated model with the reaction in the saturated model clearly revealed the growth of *squalene* on the top of plasma-polymerized acetylene film for the reaction in the *squalene*-based mixture. However, there was little reaction between the *squalane*-based model compound and the plasma-polymerized acetylene films. The inhibition occurring in the latter case was attributed to the lack of unsaturation in *squalane*. Therefore, the small traces of metal ions, accelerator fragments, and sulfur were possibly only due to the adsorption of activator, accelerator and elemental sulfur onto the unsaturated plasma-polymerized acetylene film. There was no evidence to show the significant interactions between *squalane* and plasma-polymerized acetylene film.

The crosslinking reaction occurring between plasma-polymerized acetylene film and *squalene* (or rubber in the real system) can be described as follows. In the induction period (~ 15 minutes), the sulfur ring was opened. Cobalt reacted with the active radicals which arose from the decomposition of the sulfenamide accelerator, to form cobalt mercaptide and cobalt perthiomercaptide. These intermediates immediately promoted the crosslinking reaction between the plasma polymer film and *squalene*. Then zinc adsorbed onto the plasma-polymerized acetylene film as zinc mercaptide, zinc perthiomercaptide, and ZnS. As soon as the crosslinking commenced, free sulfur was consumed rapidly while some crosslinking reactions (evident from S_2^-, S_3^-, and S_4^- in SIMS, and *squalene* adsorption in SIMS) had already occurred. As the reaction progressed, more and more ZnO was converted to zinc mercaptide and zinc perthiomercaptide (from XPS and AES). Zinc perthiomercaptide then promoted the crosslinking reaction between the plasma polymer film and *squalene*. After 35–45 minutes reaction time, more *squalene* molecules were crosslinked with plasma-polymerized acetylene films (from SIMS and XPS) through both cobalt and zinc perthiomercaptides. Possibly, most of the accelerator was consumed in this period. Finally, in the reversion (or overcure) period between 65 and 100 minutes, the concentrations of polysulfides and cobalt and zinc perthiomercaptides dropped, implying that the curatives and crosslinking sites ($>C{=}C<$) became depleted and that crosslinking reactions slowed down.

Because of the similarity in structure between the plasma-polymerized acetylene and the natural rubber, the reaction mechanism between plasma polymer and natural rubber was postulated to proceed like the vulcanization of rubber. This postulation was clearly proven by the *squalene*-based model rubber system. *Squalene*, the analogue of natural rubber, was crosslinked with plasma-polymerized acetylene films as shown by surface-sensitive techniques including AES, XPS, and SIMS. It was suggested that mostly monomeric and a few dimeric and trimeric *squalene* molecules were crosslinked with plasma-polymerized acetylene by polysufides S_x ($1 \leqslant x \leqslant 6$).

Acknowledgments

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