Interfaces Between Rubber and Metallic or Textile Tire Cords

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ABSTRACT : Bonding metal and textile components to rubber has always posed a problem. In this paper, an attempt had been made to modify textile and metal surfaces for bonding with rubber. The metal surfaces were modified using silane coupling agents and textile fibers were modified using plasma polymerization techniques. Some results on adhesion of metals to a range of sulfur-cured rubber compounds using a combination of organofunctional silanes are given here. The treatment was not only effective for high-sulfur compounds but also for low-sulfur compounds as used in engine mounts and even for some semi-EV compounds. Coatings of plasma-polymerized pyrrole or acetylene were deposited on aramid and polyester tire cords. Standard pull-out force adhesion measurements were used to determine adhesion of tire cords to rubber compounds. The plasma coatings were characterized by various techniques and the performance results are explained in an interpenetrating network model.

Keywords : organofunctional silanes, tire cord, plasma polymerization, adhesion, surface modification.

I. Introduction

Steel tire cords have been traditionally brass-plated for the purpose of providing a strong bond between sulfur-cured rubber compounds and steel. The mechanism of this adhesion has been well documented.[1-3] In addition to the use of brass for adhesion promotion, adhesion promoters such as cobalt additives and HRH systems (hexamethylene tetramine, resorcinol and hydrated silica) are also used.[4] These current systems, although their performance is adequate, still suffer from several drawbacks such as special compound formulation including high sulfur content and delayed-action sulfenamide accelerators. Also, cobalt salts are expensive and pose availability problems. Brass coatings, on the other hand, stimulate galvanic corrosion in conjunction with steel and also is sensitive to attack by moisture in case of puncturing the tire down to the belt.

Most often, a relation exists between adhesion and corrosion.[5,6] Adhesion failure in tire cords can be partially attributed to the galvanic corrosion stated above. Adhesion between brass and rubber develops because of bonds and crosslinks between the substrate and the polymer.[4] If the interfacial

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crosslinks are not dense enough, corroding species can diffuse into the interface and cause delamination.

In our lab the use of silanes as metal pretr-eatments, primarily for corrosion control and paint adhesion purposes has been established. Alkoxy silanes are widely used for this purpose. These silanes are gaining commercial interest owing to their potential to replace chromates and phosphates in the metal finishing industries, which are toxic in nature.[7-9] Most of the silanes used for this purpose are without organofunctional groups.[10-12] An example of such a silane is bis-1,2-(triethoxysilyl) ethane (BTSE), $(C_2H_5O)_3Si-CH_2-CH_2-Si(C_2H_5O)_3$. Upon hydrolysis in water, the ethoxy groups hydrolyze rapidly and form hydroxyl (silanol) groups. Hydrolysis of silanes normally occurs at a particular optimum pH range, below and above which condensation occurs. Condensation can occur either between two silanol groups or between a silanol group and hydroxide groups on the metal surface. In almost all situations, silanes are used in their hydrolyzed condition. The -OH group of the hydrolyzed silane is believed to react with the metal hydroxides available on the metal surface, although there is no strong evidence for the presence of the bonds Me-O-Si.[10] Such bonds are very difficult to detect so they are usually inferred but not actually demonstrated.

On the other hand, functional silanes are found to be extremely useful in the adhesion industry. Functional silanes have two types of functionalities, namely $R_y-Si-(OX)_{4-y}$ where X is the group involved in the reaction with the inorganic substrate and it is hydrolyzable, R is the functional group compatible and reacting with the polymer.

Previous publications by Van Ooij et al.[11] has showed the application of such silanes for improved adhesion as well as better corrosion resistance in the case of paints on metals. Adhesion of peroxide-cured rubber to metal was also reported[12-14] using a combination of organofunctional and non-organofunctional silanes. In this method, a two step process was shown to be more effective than either of the silanes alone. This particular system did not provide adhesion to sulfur-cured rubber, however.

In our work here, we present a novel method of silane treatment for adhesion of sulfur-cured rubber to metals. In this process, a mixture of two functional silanes (silanes A and B) in their unhydrolyzed conditions were used. Usage of non-hydrolyzed silanes is a new technique and not much work has been done in this area. The individual silanes, when used alone, did not show good adhesion, but their mixture gave very encouraging results of adhesion. In this paper we present some results of adhesion of sulfur-cured rubber to various metal substrates. Bonding metal to sulfur-cured rubber using silanes has not been demonstrated before, except in one US patent.[15] However, that patent taught that appreciable adhesion between steel and sulfur-cured tire cord skim stock could only be obtained if the compound also contained certain specific resin systems. The silane used in that work was γ-aminopropyltrialkoxysilane, commonly known as γ-APS. Currently, no other bonding systems for steel tire cord to high-sulfur skim stocks exist but the standard brass coating.

Traditionally, textile tire cords such as aramids, polyester, etc., are heavily dip-coated with

adhesives mixtures and solvents before being bonded to rubber. Very little work has been done in this field to unravel the bonding mechanism. The limitation of this process is a reduction of strength due to the heavy dip coating and a mediocre interfacial bond strength to high sulfur compounds.

As industry searches for safer, more environmentally friendly methods to treat fibers, surface modification by plasma techniques for improving fiber-polymer adhesion has attracted attention.[16-29] The use of plasma for improvement of tire cord to rubber adhesion has not been widely studied, however.

The main purpose of plasma surface treatments of fibers used as reinforcements in composite materials is to modify the chemical and physical structures of their surface layer, tailoring fiber/matrix bonding strength, but without influencing their bulk mechanical properties. Cord to rubber adhesion development can occur by mechanical entanglement (interlocking), primary chemical bond formation, specific physicochemical interactions such as hydrogen bonding, or molecular inter-diffusion. When plasma techniques are used, the enhancement of the adhesion between a polymer matrix and plasma-treated fibers can be caused by both physical and chemical modifications. The physical modification is the surface roughening of the fiber by the sputtering effect, producing an enlargement of contact area that increases the friction between the fiber and the polymer matrix. The chemical modification is the increase of the concentration of functional groups on the fiber surface, and hence causing a large number of chemical bonds to be formed between fiber and

polymer matrix.

Another novel aspect of the work presented here is that we do not only treat cords surfaces in a reactive or non-reactive plasma, we will also report on surface modification of cords and fibers by the process of plasma polymerization. The literature indicates that plasma treatment of fibers with non-polymerizable gases is used more widely than plasma polymerization because the latter process is more complicated. Plasma polymers with different properties can be formed using different monomers. Even with one monomer, varying the deposition conditions can vary the properties of the plasma polymers within wide limits. In this work two kinds of monomers, pyrrole and acetylene, were chosen and the deposition conditions were varied in order to develop a method to increase cord-rubber adhesion by plasma polymerization.

II. Experimental

1. Rubber to Metal Bonding Using Silane Coupling Agents

1.1 Materials

The two silanes, Silane A and Silane B, were available commercially and were obtained from Witco Inc., Greenwich, Connecticut. The structures are: silane A: $(C_2H_5O)_3Si-(CH_2)_3-S_4-(CH_2)_3-Si(OC_2H_5)_3$ and silane B: $(CH_3O)_3Si-(CH_2)_3-NH-(CH_2)_3-Si(OCH_3)_3$. The metal substrates cold-rolled steel and electrogalvanized steel were obtained from ACT Laboratories Inc., Hillsdale, Michigan. The 63/37 brass substrates were obtained from Goodfellow Corporation. The rubber compounds were mixed by and obtained from Hankook Akron Technical Center (high-sulfur

Table 1. High Sulfur Compounds

	Compound 1	Compound 2
Synthetic IP rubber	100.0	100.0
Zinc oxide	10.0	10.0
Stearic acid	1.2	1.2
N326 black	60.0	60.0
Santoflex 13	1.0	1.0
Cobalt naphthenate(10%)	2.0	-
Vulkacit DZ	0.5	0.5
PVI	0.2	0.2
Insoluble sulfur(20% oil)	7.0	7.0

Table 2. Low Sulfur Compounds-Compound 3

SMR-5	100.0
Zinc oxide	3.0
Stearic acid	2.0
N330	50.0
Sundex 790	10.0
Santoflex 139	2.0
Microcrystalline wax	2.0
CBS	1.4
Sulfur	2.5

compound no. 1 and compound no. 2, Table 1), Akron, Ohio, and Akron Rubber Development Laboratories (low-sulfur compound no. 3, Table 2), Akron, Ohio. The alkaline cleaner (AC 1055) used for cleaning the metal substrates was obtained from Brent America Inc, Arlington, Tennessee.

1.2 Preparation of Silane-Treated Substrates

The metal panels were subjected to a thorough cleaning procedure before silane treatment. They were ultrasonically solvent-cleaned with acetone, hexane and methanol and then alkaline-cleaned with the industrial cleaner AC 1055 for 5-7 min. at 60°-70℃. Then they were rinsed with DI water to obtain a water-break-free surface. The sub-

strates were dried immediately by blow-drying using filtered air. Improper drying could result in flash rust formation on substrates such as cold-rolled steel.

A combination of silanes, VS and BTSE, worked well for peroxide-cured rubbers.[12,13] However, these silanes resulted in 100% interfacial failure and did not give any appreciable amount of adhesion when tested with the sulfur compounds of Tables 1 and 2. The hydrolysis procedure and conditions for hydrolysis have been discussed elsewhere.[7,9] For cold-rolled steel, the pH of the silane solution should be maintained between 4-5, and for electrogalvanized steel substrates the pH should be around 8. Lower pH values will result in poor films on zinc substrates, as the oxide on zinc is only stable in a narrow pH range.[8,10] The cleaned metal substrates were dipped into the silane solution for 30 seconds at room temperature and blow-dried immediately with compressed filtered air. The silane solutions used here is a mixture of silanes A and B in their hydrolyzed form and mixed in the ratio 1:3.

The unhydrolyzed mixture of silanes A and B was wiped onto the cleaned panels using a paper towel and subsequently oven-dried for 40-50 minutes at 160℃ to obtain a dry film, which was hard yet flexible. The silane mixture used should have been freshly prepared. Silane mixtures older than one week (at room temperature) were found difficult to dry and have to be cured for a longer amount of time to get a completely dry and cured film. The mechanism of this dry film formation induced by silane A is not yet completely understood and is under investigation.

1.3 Bonding Metals to Rubber Compounds

Three types of rubber compounds were used for testing: 1) A typical high-sulfur tire-cord skim compound with cobalt additives, 2) a typical high-sulfur tire-cord skim compound without cobalt additives, 3) a low-sulfur compound used in engine mount applications. Their formulations are given in Table 1 and Table 2.

Silane-treated metal substrates were bonded to the rubber compounds to yield a sample in which the rubber layer was sandwiched between two panels. Curing was performed in a hydraulic press from Tetrahedron. The cure time for compound no. 1 was 8 min at 160℃, for compound no. 2 (cobalt-free), 11 min at 160℃, and for compound no. 3, 5 min at 160℃. One half of the metal was shielded from rubber contact by a Mylar film during vulcanization. Thus, a sample as shown in Figure 1 was obtained. As shown, the unbonded portion was bent by 90° after the cure.
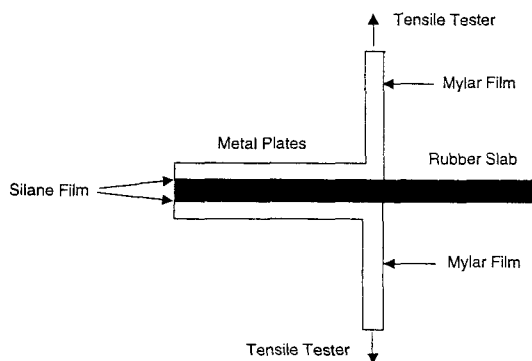

Fig. 1. Sample configuration for adhesion testing.

1.4 Adhesion Strength

The adhesion strengths were obtained at room temperature by pulling the metal substrates apart as shown in Figure 1 at a jaw speed of 2.54 cm/min using an Instron Tensile tester (Instron 4465).

2. Adhesion of Textile Tire Cords to Rubber Using Plasma Polymerization

2.1 Materials

All aramid cords and fibers in this study were Twaron cords and yarns, 1680 dtex f1000 and 2X 1680 dtex 1000 (Akzo Nobel bv, Arnhem, The Netherlands). The polyester cords 715 were obtained from Milliken Corporate, Spartanburg, South Carolina, USA. Pyrrole had a purity of 98% (Aldrich Chemical Company Inc.; Milwaukee, WI) and was used as received. Acetylene and argon were obtained from AGA Gas, Inc., Cleveland, Ohio, USA, and Wright Brothers Inc., Cincinnati, Ohio, USA, respectively.

The rubber used in pull-out tests was a NR/SBR blend with low sulfur content and N,N-dicyclohexylbenzothiazolesulfenamide (DCBS) accelerator proposed for standard adhesion testing by Akzo Nobel.

2.2 Plasma polymerization

A custom-built semi-continuous reactor (Figure 3) operated on continuous or pulsed DC glow discharge was used in this work. In this reactor, a steel wire mesh cylinder was used as the cathode, placed in with a glass cylinder as insulator. All the other parts of metal in the glass bell jar functioned as anode. It was found that the plasma was confined in the cylinder.

Prior to plasma treatments, the reactor was evacuated to less than 1.33 Pa. The cords or fibers were cleaned and etched in a continuous DC argon plas-
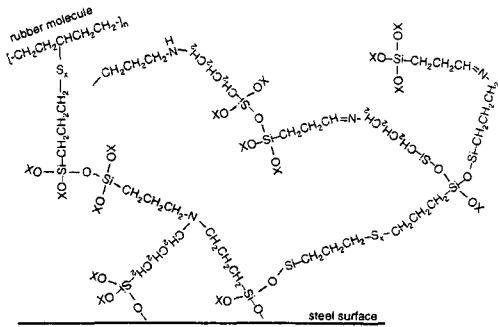
Fig. 2. Crosslinking of pendant silane by bis-[trimethoxysilylpropy]amine.
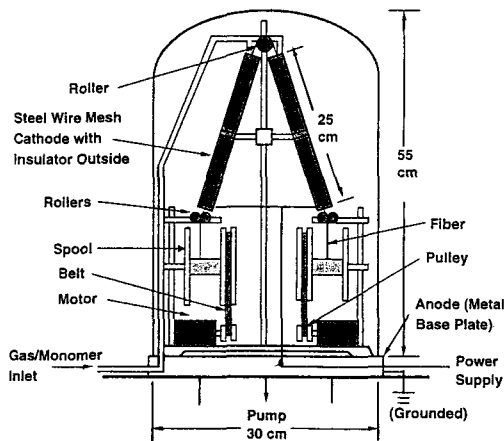

Fig. 3. Schematic of larger scale DC plasma reactor for treating cords and fibers.

ma (power, 5 W; flow rate, 8 cm³/min; pressure, 20 Pa) before introducing the monomers. The time of exposure to the argon plasma was 5 minutes.

Two kinds of monomer were used in this work, pyrrole and acetylene. First, two extreme deposition conditions were used to treat the fibers or cords, i.e. LW/HP (Low Power/High Pressure) condition and HW/LP (High Power/Low Pressure) condition. Table 8 shows the deposition conditions for the two monomers. In order to find the optimal adhesion performance related to the deposition conditions, several other conditions were

used for pyrrole, as shown in Table 9. Pulsed DC discharge was used to add a new parameter to the control of the film properties.

In preparing the samples for FTIR, KBr pellets were used as substrate instead of the aramid cords and fibers. Pieces of silicon wafers were used in measurements of deposition rate and thickness of the film. The KBr pellets and silicon wafers were placed inside the cylinder. The conditions of treatment were the same as those for treating aramid cords and fibers.

2.3 Pull-out Force Test

A standard pull-out force test (ASTM D2229-93a) was used to determine the adhesion of the cords to rubber. Ten pieces of cord treated in same condition were embedded into one block. Each piece of cord was 20 cm long. The pull-out rate was 2 mm/min. The maximum load for pulling each piece of cord out of the rubber block was recorded and averaged for the 10 pieces.

2.4 Characterizations of Plasma-Polymerized Films

During the depositing of the plasma-polymerized films, the deposition rates and thickness of the films were measured using thin film interferometry. The refractive indexes of the films were also calculated. For more details, the reader is referred to our previous paper.[30]

FT-Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Scanning Force Microscope (SFM) and Single-Fiber Pull-Out Test (SFPO) were also used to characterize the plasma-polymerized films deposited on the surface of textile cords and fibers.

III. Results and Discussion

1. Metal Bonding by Silanes

As expected, brass did not bond well with low-sulfur and non-cobalt-containing high sulfur compounds. With the low-sulfur compound, the failure was 100% interfacial and with the non-cobalt-containing compound, the failure was not uniform, exposing some metal surface completely, upon failure. With the silane treatment, the failure was almost 90% cohesive for non-cobalt-containing compound and 70% cohesive for low-sulfur compound (Table 3). These results suggest that cobalt additives could possibly be eliminated from tire compounds without loss of adhesion. Also, adhesion with low-sulfur compounds suggest that brass becomes much less dependent on the exact compound formulation, thus tire cord skim stocks could be formulated for mechanical and thermal properties rather than being optimized for adhesive properties.

Electrogalvanized steel (EZG) substrates were used to demonstrate the adhesion of rubber compounds to zinc substrates. The underlying idea was to find alternatives to the ubiquitous brass plating process which is fraught with problems such as toxic plating bath (cyanide plating), high heating costs (diffusion plating), and corrosion, as mentioned before. Zinc-plated steel cords are used in conveyor belt reinforcing applications, where large amounts of cobalt additives are needed in the rubber compound to get acceptable adhesion levels. The results presented in Table 4 indicate that the silane-treated zinc substrates give good adhesion to the compounds without cobalt additives. This was found both for the high-sulfur and for the

Table 3. Adhesion Results with 63/37 Brass

	Silane treatment*	Adhesion value	Failure mode
Compound 1	−	800 ± 50N	100% Cohesive
Compound 1	+	685 ± 81N	75% Cohesive
Compound 2	−	450 ± 30N	60% Cohesive
Compound 2	+	926 ± 71N	90% Cohesive
Compound 3	−	380 ± 33N	100% Interface
Compound 3	+	679 ± 49N	70% Cohesive

*Silane ratio:A:B::3:1

Table 4. Adhesion Results with Electrogalvanized Steel

	Silane treatment*	Adhesion value	Failure mode
Compound 2	−	0N	100% Interface
Compound 2	+	630 ± 130N	80% Cohesive
Compound 3	−	0N	100% Interface
Compound 3	+	534 ± 150N	60% Cohesive

*Silane ratio:A:B::3:1

low-sulfur compound. It can thus be concluded that the bonding process in these systems must be a true interaction between the silane film and the rubber compound, as zinc itself can be expected to be non-reactive to these compounds.[1,2] EZG substrates were tried with compound 2 with other mixture ratios of silanes A and B, but only a specific ratio seemed to work well (Table 4 and 6).

Work on cold-rolled steel substrates (CRS) is still in progress. The results shown in Table 5 indicate that the silane treatment of the steel substrate works well with the high-sulfur compound but not with low-sulfur compound. This result is significant as it suggests the possibility of eliminating brass coating in some applications. In such situations galvanic corrosion between steel and brass would be eliminated. Another implication is that in tire cord applications the cut ends, currently a weak spot where cracks leading to belt-edge sepa-

Table 5. Adhesion Results with Cold-Rolled Steel

	Silane treatment*	Adhesion value	Failure mode
Compound 2	−	0N	100% Interface
Compound 2	+	752±120N	80% Cohesive
Compound 3	−	0N	100% Interface
Compound 3	+	209± 29N	100% Interface

*Silane ratio: A:B::3:1

Table 6. Results with Other Ratios of Silane A and B

Metal	Rubber	Silane treatment	Adhesion value	Failure mode
CRS	Compound 2	A:B::3:1	752±120N	80% Cohesive
CRS	Compound 2	A:B::1:1	398±163N	20% Cohesive
EZG	Compound 2	A:B::3:1	630±130N	80% Cohesive
EZG	Compound 2	A:B::1:1	600±120N	50% Cohesive

Table 7. Results with Cold-Rolled Steel-Hydrolyzed Silanes

	Silane treatment	Adhesion value	Failure mode
Compound 2	VS(pH=4)	0N	100% Interface
Compound 2	BTSE(pH=4)	0N	100% Interface
Compound 2	BTSE+VS(pH=4)	0N	100% Interface
Compound 2	Silane A(pH=4)	350±20N	100% Interface
Compound 2	Silane B(pH=4)	0N	100% Interface
Compound 2	A:B::1:3(pH=4)	161±88N	100% Interface
Compound 2	A:B::1:1(pH=4)	272±18N	100% Interface
Compound 2	A:B::3:1(pH=4)	692±50N	80% Cohesive

Table 8. Deposition Conditions of Plasma-Polymerized Films

Denotation	DC Power W	Monomer flow rate cm³/min	Monomer pressure Pa
LW/HP Pyrrole	5	15	34
HW/LP Pyrrole	20	7	17
LW/HP Acetylene	10	24	53
HW/LP Acetylene	20	15	33

ration initiate would be bonded adequately by the silane process. It is to be noted that this solution for the cut ends would, as per the results presented here, work with bare steel cord, with zinc-plated cords and also with standard brass-plated cords.

With CRS substrates, hydrolyzed silanes were also tried. With the VS/BTSE combination (pH=4-5), as mentioned above, the adhesion level to compound 2 (high sulfur, no cobalt) was almost nil and failure was always 100% interfacial (Table 7). With silane A in hydrolyzed condition (pH=4), CRS substrates showed some amount of adhesion, but the failure was still 100% interfacial (Table 7). Also, the mixture of silanes in hydrolyzed condition was tried (Table 7). Comparing the results from Tables 5, 6 and 7, the importance of using the specific mixture of silanes A and B in unhydrolyzed condition can be illustrated.

2. Textile Bonding by Plasma Polymerization

In the plasma polymerization technique, deposition rate, refractive index and thickness of plasma-polymerized film deposited in each condition were calculated and shown in Table 10. It can be seen that the deposition rates were almost the same in two different deposition conditions of pyrrole, but they were different when different monomers were used. It also can be seen that the refractive index of PPy (plasma-polymerized pyrrole) film obtained at HW/LP was higher than that of the film obtained at LW/HP conditions. This indicates that HW/LP conditions produce a denser film than LW/HP conditions.

The structure of the plasma-polymerized films

Table 9. Deposition Conditions for Optimizing Adhesion Performance

Number	DC Power W	Monomer Pressure Pa	Ratio of Power to Pressure ×133
1	3.0	39.9	10
2	5.0	33.3	20
3	6.0	26.6	30
4	8.0	26.6	40
5	5.0	13.3	50
6	10.8	23.9	60
7	12.0	21.3	80
8	15.0	20.0	100
9	16.8	18.6	120
10	18.2	17.3	140
11	20.0	16.6	160

Table 10. Deposition Rate, Refractive Index and Thickness of Plasma-Polymerized Films

Film	Deposition Rate nm/min	Refractive index	Thickness (6min) nm
Pyrrole, LW/HP	22.2	1.58	133
Pyrrole, HW/LP	21.5	1.64	129
Acetylene LW/HP	31.9	1.65	191

was characterized by FTIR. Figure 4 shows the IR spectra of PPy films deposited in LW/HP and HW/LP conditions. It was found that the power and pressure had strong effects on the FTIR spectra, i. e., on the structure of the films. Compared with FTIR spectrum of pyrrole monomer,[31] it was found that the peaks attributed to the pyrrole ring disappeared, which means that the ring was broken in the DC plasma.

Based on the more detailed analysis in our previous paper,[30] the HW/LP PPy film seems to exhibit a higher degree of crosslinking with more unsaturation and conjugation. The LW/HP film shows a less dense structure that seems to consist of some extent of long hydrocarbon chains. The LW/HP
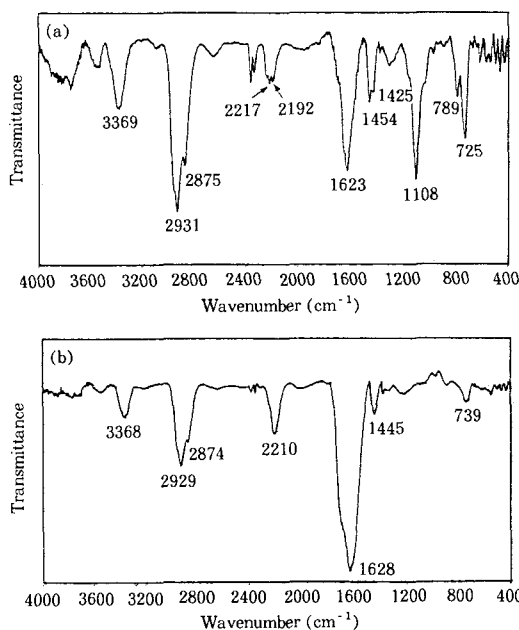
Fig. 4. IR spectra of continuous DC plasma-polymerized pyrrole films : (a) LW/HP conditions (b) HW/LP conditions.
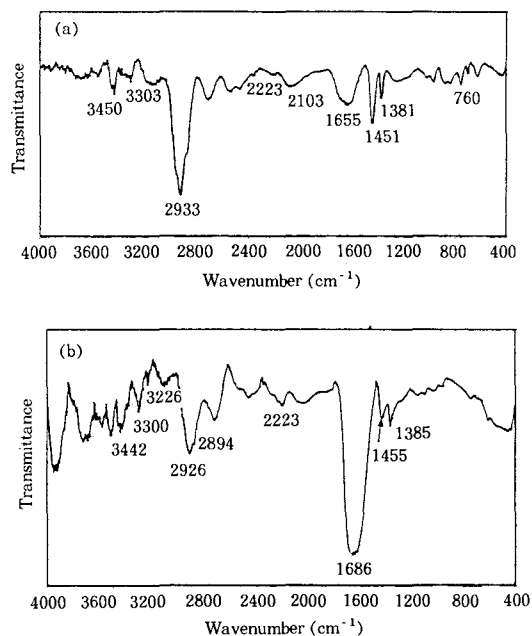
Fig. 5. IR spectra of continuous DC plasma-polymerized acetylene films : (a) LW/HP conditions (b) HW/LP conditions.

condition was so mild that, combined with the absence of high energy positive ions, the monomer seems to linearly polymerize to a certain extent after ring-opening and probably does not crosslink extensively.

FTIR spectra of plasma-polymerized acetylene films deposited in LW/HP and HW/LP conditions were also obtained (Figure 5). The significant differences between the two spectra are also the different intensities of some peaks. It can be seen that the intensities of the peaks attributed to hydrocarbons were higher in LW/HP plasma-polymerized acetylene film than HW/LP film, and

the intensity of the band due to C=C stretching was lower in LW/HP conditions. As for the PPy films, it can be considered that LW/HP plasma-polymerized acetylene film is probably also less crosslinked than the HW/LP film.

SEM photographs of untreated and plasma-treated aramid fibers are presented in Figure 6. The untreated aramid fiber surface is quite smooth, as seen in Figure 6(a). After argon plasma treatment, the fiber surface is slightly roughened, which can be seen from Figure 6(b). After pyrrole plasma-polymerization, it can be seen that a film is formed on the surface of the fiber. There
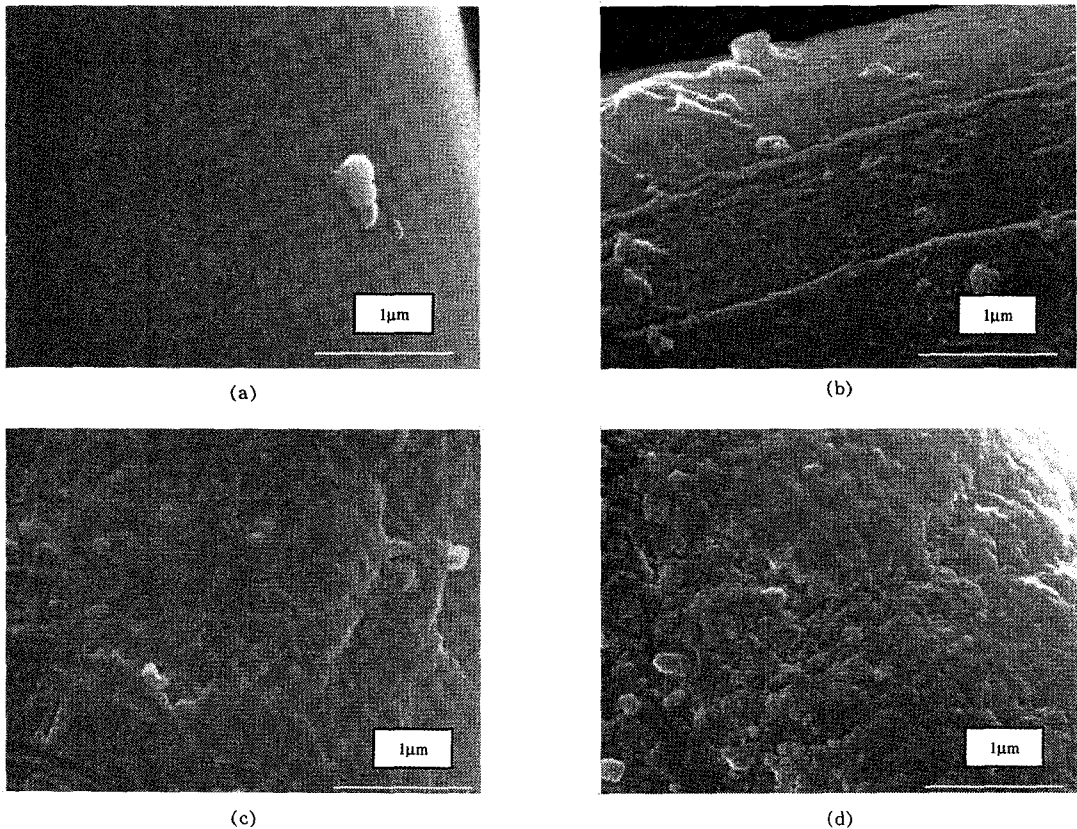
Fig. 6. SEM photographs of aramid fibers : (a) untreated (b) treated by only argon plasma (c) treated by LW/HP pyrrole plasma (d) treated by HW/LP pyrrole plasma.
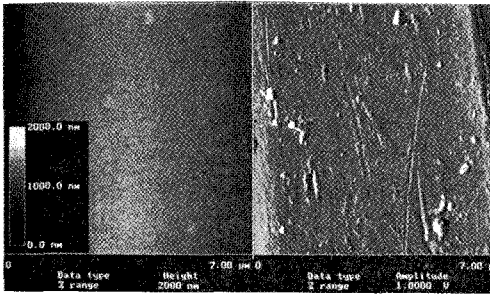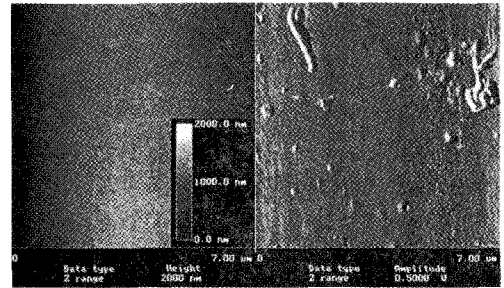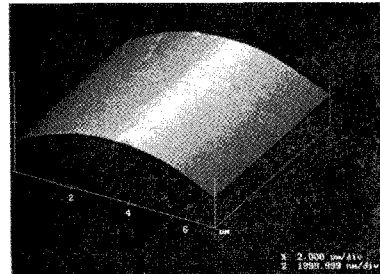
(a)
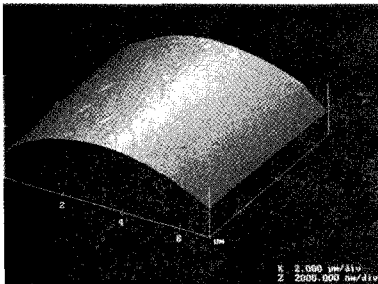
(b)

Fig. 7. SFM images of argon plasma treated aramid fiber : (a) plane--fit of height and amplitude (b) 3-d in tapping mode.

(a)

(b)

Fig. 8. SFM images of pyrrole plasma treated aramid fiber (LW/HP) : (a) plane-fit of height and amplitude (b) 3-d in tapping mode.

are differences in the films deposited in different conditions. The film formed in LW/HP is a little smoother and more uniform than that deposited in HW/LP. In the HW/LP PPy film some loose flakes are present.

The SFM image of the argon-treated aramid fibers (Figure 7) shows a surface a little bit roughened compared with an untreated one. Figure 8s and Figure 9 show clearly that, after pyrrole or acetylene plasma treatment, a film is dposited on the surface of the fiber. The fiber surfaces after pull-out test (Figure 10) show these thin coatings, resulting in a "micro-roughness" of the initial fibers (Figure 8). After pull-out more cohesively failed parts of the surrounding matrix confirm the greater adhesive strength.
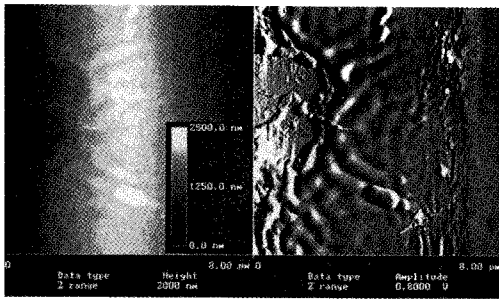
Tables 11 and 12 present typical adhesion

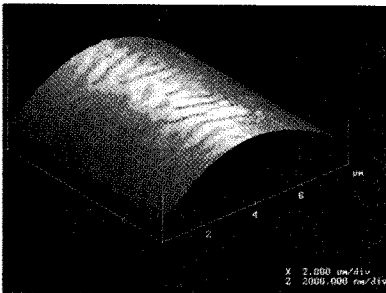Table 11. Rubber* Pull-Out Data** of Plasma Treated Aramid Cords

Treatment	Force, N	Standard deviation, N
Untreated	37.8	3.3
Argon plasma treated	36.6	1.5
LW/HP PPy	56.0	14.8
HW/LP PPy	45.7	4.0
LW/HP Acetylene	60.5	14.5
HW/LP Acetylene	47.8	5.6

*Standard compound for textile tire cord testing.
**In collaboration with Hankook Tire Co., Akron, Ohio, USA.

results. From the data of Table 11 it can be seen that both types of PPy film (LW/HP and HW/LP) improve the pull-out force of aramid cord to rubber as compared with the untreated or the
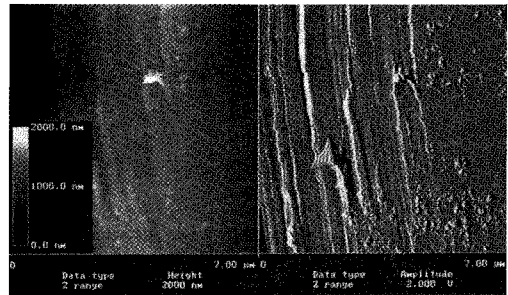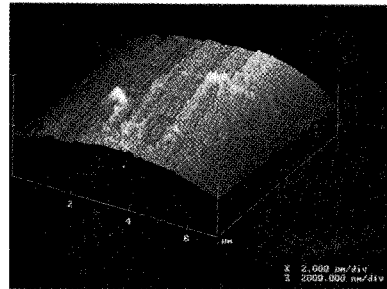
(a)

(b)

Fig. 9. SFM images of acetylene plasma treated aramid fiber (LW/HP) : (a) plane-fit of height and amplitude (b) 3-d in tapping mode.

(a)

(b)

Fig. 10. SFM images of pyrrole plasma treated aramid fiber after pull-out(LW/HP) : (a) plane-fit of height and amplitude (b) 3-d in tapping mode.

Table 12. Rubber Pull-Out Data* of Plasma Treated Polyester Tire Cords

Treatment	Force, N	Standard deviation, N
Untreated	53	12
Argon plasma treated	51	8
HW/LP PPy	62	8
LW/HP PPy	68	34
LW/HP Acetylene	60	18

*Obtained in Milliken Corp., Spartanburg, South Carolina, USA.

argon-treated materials. The LW/HP film is the better of the two. The same results were also found in the data of acetylene plasma treated aramid cords to rubber. In Table 12, the adhesion of PPy treated polyester tire cords to rubber is also higher than that of untreated or only-argon-

plasma treated polyester cords. Both of the two values of LW/HP and HW/LP are not satisfactorily high, but it still can be seen that adhesion of LW/HP film is higher than that of HW/LP film. Therefore, it can be concluded that, in general, films prepared under LW/HP conditions performed better than films prepared under HW/LP conditions.

Figure 11 presents the adhesion performance of PPy treated aramid cords in different deposition conditions. It can be seen that in most LW/HP conditions, the adhesion of cord to rubber was improved. This plot indicates further that the films prepared under LW/HP conditions performed better, even double the value of the untreated aramid cord.
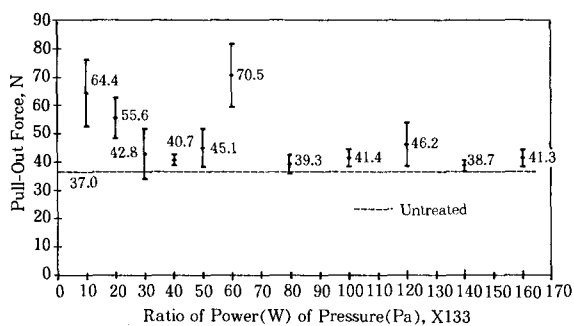
Fig. 11. The plot of adhesion performance of PPy treated aramid tire cords to rubber in relation with the deposition conditions.

The introduction of various kinds of functional groups (especially oxygen-containing groups) on the surface of the plasma treated fibers, the change in the fiber surface energy, and the surface roughening by plasma treatments were considered the three main contributions of plasma treatment to fiber-matrix adhesion improvement, as proposed in previous research.[18-29] In this work, an argon plasma was used to etch and clean the surface of fibers and cords before depositing the plasma polymer film on it. From Figure 6(b), it can be seen clearly that the surface of fibers was roughened somewhat by the argon plasma. However, the adhesion of only-argon-plasma-treated aramid cord to rubber was not improved. The pull-out force of cords after plasma polymerization was much higher than that of only-argon-plasma-etched cords. It can therefore be concluded that in this work there is no correlation between the adhesion improvement and the surface roughening by plasma etching.

In previous studies, plasma ablation was mostly used to modify the surface of fibers. Chemical etching occurs in chemically reactive types of plasma, such as O_2, N_2, and air plasma. Chemical etch-

ing can introduce various kinds of functional groups (especially oxygen-containing groups) on the surface of fibers. It is concluded that the introduction of oxygen-containing groups on the surface of the organic fibers is one of the most decisive contribution to fiber-polymer adhesion.

In this work, plasma polymerization was used instead of plasma ablation. Because a plasma polymer is deposited on the surface of cords and fibers, other kinds of functional groups can be introduced on the surface, compared with plasma ablation. When the cords with plasma-polymerized film were embedded into rubber, the matrix may have reacted with these functional groups to form intermediates consisting crosslinks between rubber and the film. This led to the increase of adhesion between rubber and cords.

As mentioned before, in general, films prepared under LW/HP conditions performed better than films prepared under HW/LP conditions. The HW/LP PPy film seems to exhibit a higher degree of crosslinking with more unsaturation and conjugation. The LW/HP film shows a less dense structure that seems to consist to some extent of relatively long hydrocarbon chains. Therefore, it is proposed that the more important factor contributing to the adhesion improvement is the hardness and crosslink density of the plasma polymer films. The rubber is liquid during the cure and is pressed against the cords at high pressure. Therefore, an interpenetrating network can form between the rubber and the plasma polymer films. If the film is soft, there is more penetration, i.e. better contact, so the adhesion of is higher than that of hard film. The fact that the soft/low crosslinked plasma polymer films deposited in LW/HP performed better
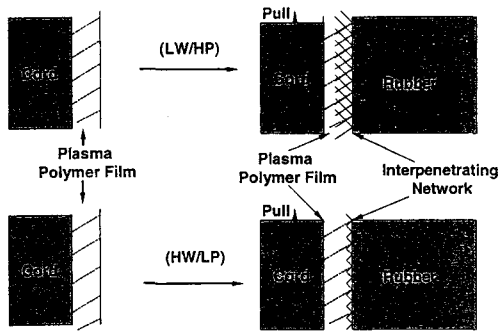
Fig. 12. Tentative model for pull-out force improvement by plasma-polymerized pyrrole or acetylene.

than the hard/high crosslinked film deposited in HW/LP, regardless of the monomer used, is strong evidence for this mechanism. The SFM images in Figure 8 and Figure 10 indicate that this mechanism is feasible. In Figure 10 some plastic deformation can be seen in the soft film during pull-out. On the other hand, the films deposited in HW/LP showed brittle failure. More details of the SFM analysis will be published separately. Figure 12 shows this mechanism schematically.

In our work we also found that pulsing of the discharge improved the adhesion further.[30,32] This is also because of the softer films formed in pulsing conditions. Since in pulsed conditions higher steady state concentrations of reactive intermediates are present during the plasma "on" period, more prominent occurrence of radical-radical type reactions are expected to occur than during the plasma "off" periods, when higher relative preponderance of radical-monomer type processes occurred. Moreover, positive ion bombardment is absent in the plasma "off" period. Therefore, a softer/lower crosslinked film is expected to be formed in this pulsed deposition condition, compared with the continuous DC discharge.

In Figure 11 it also can be seen that the higher the pull-out force, the larger the standard deviation of the force. This phenomenon may be attributed to the inhomogeneousity of the plasma polymer films deposited along the cords.

IV. Conclusions

From the results published here, it is evident that a novel technique of using silane coupling agents is a good alternative to the traditional brass-coating for bonding sulfur-cured rubber compounds to steel. This has the potential of replacing cobalt adhesion promoters in the tire cord skim compound. Such silane treatments were found to work for a range of rubber compounds and metals, allowing us to formulate the rubber compound for mechanical and thermal properties rather than for adhesive properties. Further optimization of the treatment can prove excellent adhesion promoting agents for the rubber industry, in general. These treatments can be optimized by varying the silane ratio in the mixture and by varying the pre-cure of the silane film, which is required to attain a dry film. In the silane mixture used, one of the silane is a dry-film former upon heating and the other silane provides the functionality to react with the rubber compound. The mixture of the two is optimized so that mechanically strong and dry films are obtained, which still possess the functionality to react with the rubber compound. A tentative schematic of a cross-linked silane film at a polymer-metal interface is shown in Figure 2.

Further research is going on to elucidate the mechanism of silane dry film formation and adhesion mechanism. Aging tests and dynamic

adhesion tests will be carried out with a wider range of rubber compounds and the optimized treatment would be applied to actual tire cords. As it is very difficult to draw the bare steel cords of required diameter (brass, serving additionally as a lubricant), our target cord will be zinc-plated cord, as mentioned in our above study. Also, extensive corrosion studies, both electro-chemical and in-exposure tests will be undertaken.

Plasma polymer films formed from different monomers were deposited on the surface of fibers and cords using plasma polymerization techniques. The films improved the pull-out force of aramid tire cords embedded in rubber, so it is possible to improve the properties of tires filled with cords by treating the surface of the cords in a DC plasma polymerization process. With one monomer, the properties of the deposited films were varied within wide limits by varying the deposition conditions, such as power and pressure. The plasma polymer films deposited in LW/HP conditions performed better than those deposited in HW/LP conditions. The denser HW/LP film seemed to exhibit a higher degree of crosslinking with more unsaturation and conjugation. The improvement of pull-out force of cords treated by plasma polymerization process is tentatively attributed to a interpenetrating network formed between the rubber and the plasma polymer films, and the plastic deformation of the LW/HP films. The introduction of various kinds of functional groups contained in plasma polymer films on the surface of the cords and fibers may also be a contribution to this improvement.

Acknowledgments

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