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Surface Modification of Steel Tire Cords via Plasma Etching and Plasma Polymer Coating : Part I. Adhesive properties

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플라즈마 고분자 코팅에 의한 강철 타이어 코드의 표면 개질 : 제1부. 타이어 코드의 접착성

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ABSTRACT : Zinc plated steel tire cords were treated with RF plasma polymerization coating of acetylene or butadiene in order to enhance adhesion to rubber compounds. Plasma polymerization was carried out as a function of plasma power, treatment time and gas pressure. In order to maximize adhesion, argon plasma etching was performed, with carrier gas such as argon, nitrogen and oxygen, while the adhesion of tire cords was evaluated via TCAT. Best results were obtained from a combination treatment of argon etching (90 W, 10 min, 30 mTorr) and acetylene plasma polymerization coating (10 W, 30 sec, 30 mTorr) with argon carrier gas (25/5:acetylene/argon). These samples exhibited a pull out force of 285N which is comparable to that obtained from the brass plated tire cords (290N).

요 약 : 아연 도금된 강철 타이어 코드를 아세틸렌 또는 부타디엔 가스를 이용한 플라즈마 고분자 중합으로 고무와의 접착성 향상을 위하여 코팅하였다. 플라즈마의 세기, 중합 시간 및 가스의 압력을 변화시키면서 플라즈마 고분자 중합을 실시하였으며, 아르곤 가스를 이용한 에칭도 실시하였다. 또한 플라즈마 중합시에 아르곤, 질소 또는 산소를 담체 가스로 사용하여 접착성 향상으로 도모하였으며, 접착성은 TACT 방법으로 측정하였다. 아르곤 에칭 (90 W, 10 min, 30 mTorr) 후에 아르곤 가스를 (25/5 : 아세틸렌/아르곤) 담체로 사용하여 아세틸렌 플라즈마 중합 (10 W, 30 sec,

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30 mTorr)으로 코팅된 타이어 코드가 285 N의 접착력으로 가장 좋은 결과를 보였으며, 이는 황동으로 코팅된 타이어 코드의 290N과 같은 수준의 접착력이다.

Keywords : steel tire cords, tire cord adhesion test (TCAT), plasma etching, plasma polymerization, acetylene, butadiene, carrier gas.

I. Introduction

Tire performance is strongly dependent on the interfacial adhesion between tire cords and rubber, and of course on the mechanical properties of tire cords and rubber compounds.[1] In general, steel tire cords are preferred over polyester, nylon, rayon or aramid due to their low cost and good mechanical properties[2] despite having to be coated with brass, which is considered by far the best method of improving adhesion to rubber. There has been a great amount of research on the rubber-brass adhesion.[3]

Unfortunately, the brass plating process generates chemical wastes that can cause environmental pollution. Moreover, brass-plated steel cords are vulnerable to corrosion caused by the galvanic coupling of brass and steel, in which brass is cathodic and iron is anodic. Once the corrosion begins the high pH of the corrosion cell will chemically attack the brass coating. Therefore, a number of researchers have tried to develop alternative methods that can provide excellent adhesion as well as corrosion resistance without causing environmental problems.

Recently, surface modification by plasma etching and plasma polymerization coating has received much attention for meeting these needs.[4-7] A distinct advantage of this method is that it is an environmentally clean process, which is solvent-free and does not generate chemical by-products. In addition, plasma polymerized films have unique properties such as good adhesion to metal substrates, low oxygen and water vapor permeability, and good solvent resistance due to their cross-linked nature.[5] Therefore, plasma polymerization could be utilized for coating purposes to enhance adhesion of steel pates[8] as well as steel tire cords[9]

In this study, zinc plated steel tire cords were subjected to RF plasma polymerization coating of acetylene or butadiene in order to enhance adhesion to rubber compounds. Plasma polymerization was carried out as a function of plasma power, treatment time and gas pressure. Argon plasma etching prior to plasma polymerization, and argon carrier gas was also utilized in order to further improve adhesion. Zinc plated cords, rather than bare steel cords were utilized since the latter tend to be easily oxidized and are very difficult to draw. The adhesion of plasma polymer coated tire cords was evaluated by Tire Cord Adhesion Test (TCAT).

II. Experimental

1. Materials

Zinc plated and brass plated steel cords with a diameter of 0.35mm, from Hyosung T&C in Korea, were stored in a desiccator until use. Skim rubber compounds for TBR belt tires were provided by Kumho Tire Co. (Kwangju, Korea). Zinc plated steel cords were subjected to plasma polymerization coating, while brass plated steel cords were utilized as received. Acetylene (99.5%) and butadiene (99.9%, Kumho Petro Chemical Co.) were utilized for plasma polymerization, while argon (99.9%), nitrogen (99.9%) and oxygen (99.9%) gases were utilized as carrier gas. Argon was also used for the plasma etching of steel cords.

2. Plasma etching and polymerization

A radio frequency (13.56MHz) plasma generator (HPPS-300, Hanatek), consisting of bell-jar type Pyrex chamber, manual impedance matching system and mass flow controller (MFC), was used for plasma polymerization. The chamber was vacuumed to 1×10^{-3} torr before introducing the gas for plasma polymerization or plasma etching. Gas pressure in the chamber was an experimental variable and thus was controlled by adjusting the flow rate with MFC.

Zinc plated steel cords, 15cm long, were placed in the chamber at a distance of 3cm from the electrode. The conditions for plasma etching and plasma polymerization were optimized as a function of plasma power, treatment time and gas pressure. Plasma polymerization with acetylene was performed as a function of treatment time (30 sec-5min), plasma power (5 to 20 W), and gas pressure (20 mTorr to 40 mTorr). Conditions for the butadiene plasma polymerization were also optimized by varying the treatment time (30 sec-5 min), plasma power (5-20 W) and gas pressure (10-40 mTorr). Argon plasma etching conditions were optimized by varying the plasma power (30-90 W), treatment time (5-10 min) and chamber pressure (20-40 mTorr) in order to maximize the cleaning effect. Carrier gas, whose presence tends to enhance plasma polymerization, was also utilized by varying the ratio of acetylene/carrier gas from 25/5 to 15/15 mTorr/mTorr.

4. Tire cord adhesion test

Tire cords for adhesion study were coated by 1) plasma polymerization only, 2) argon plasma etching + plasma polymerization, or 3) argon plasma etching + plasma polymerization with carrier gas. Tire cords adhesion test (TCAT) samples were prepared in a mold with the dimensions of $20\times20\times75$mm. First, the mold was heated to 145°C, then the bottom half of the cavity was filled with rubber. Next, the plasma polymer coated tire cords were placed at both ends of the cavity, where each cord was embedded 20 mm into the rubber. Finally, the remaining half was filled with rubber and cured at 145°C for 1 hour at 20.7 MPa (3000 psi), followed by slow cooling to room temperature.

The samples were aged at least 12 hours before testing with Instron 5567 at a speed of 50 mm/min. The maximum pull-out force was measured and the results of 6 samples were averaged, while the failure surfaces were analyzed by SEM (JEOL, JSM 5600).

Ⅲ. Results and Discusssion

1. Optimized conditions for plasma polymerization

The conditions for plasma polymerization coating were optimized as a function of treatment time (30 sec-5 min), plasma power (5-20 W), and gas pressure (20-40 mTorr) in order to achieve maximum adhesion. In the acetylene plasma polymerization coating, the highest adhesion of 185 N was obtained with 30 seconds and decreased to 121 N as the treatment time increased to 5 min at the plasma power of 10 W and gas pressure of 30 mTorr (Fig. 1-a). Therefore, 30 seconds was chosen as the optimum treatment time.

Additionally, as the plasma power was varied from 5 to 20 W under the gas pressure of 30 mTorr and treatment time of 30 sec, the highest pull-out force of 185N was obtained at 10 W (Fig. 1-b). Finally, 30 mTorr of gas pressure provided the highest pull out force of 185N when the gas pressure was varied from 20 to 40 mTorr at 30 sec of treatment time and 10 W of power (Fig. 1-c). Therefore, the optimum condition for acetylene plasma polymerization coating was determined to be 30 sec of treat-

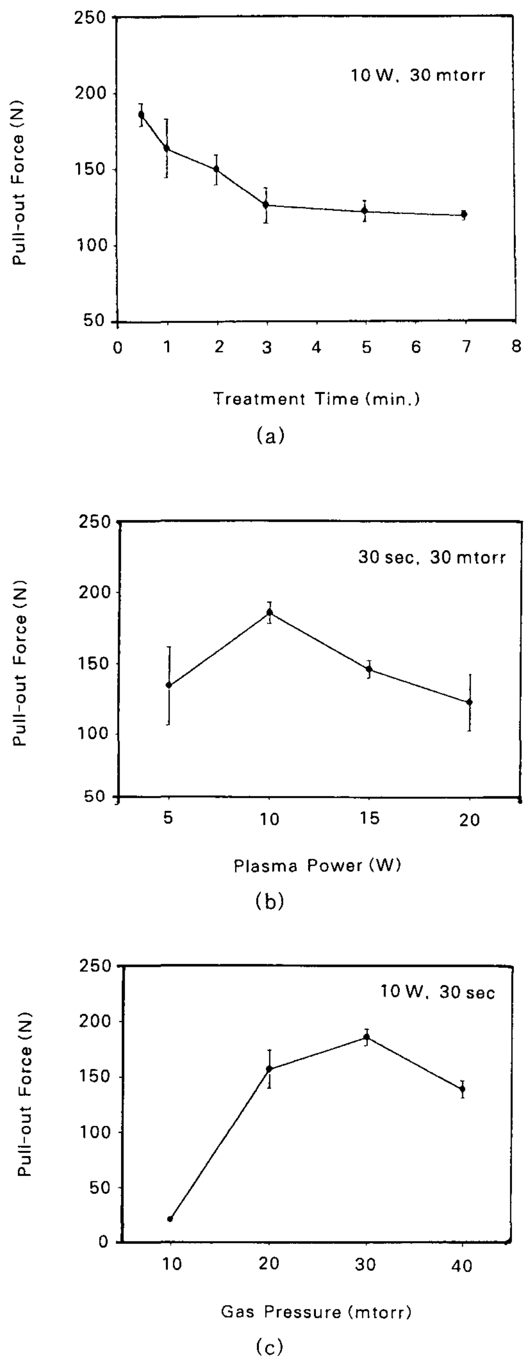


Fig. 1. Optimization of acetylene plasma polymerization conditions : (a) Treatment Time, (b) Plasma Power, (c) Gas Pressure.

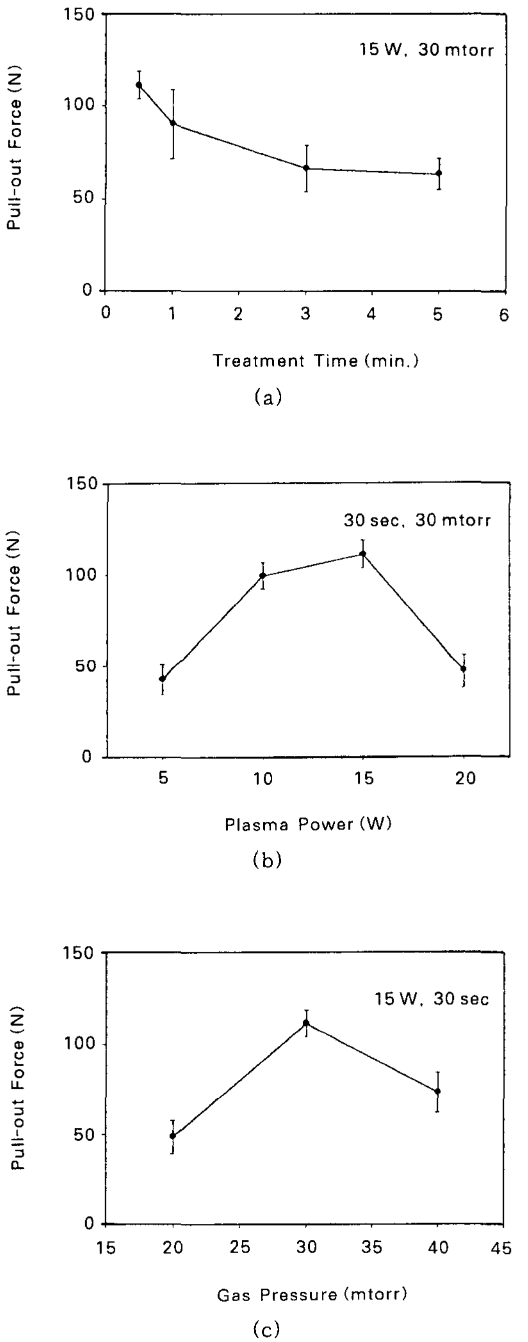


Fig. 2. Optimization of butadiene plasma polymerization conditions : (a) Treatment Time, (b) Plasma Power, (c) Gas Pressure.

ment time, 10 W of plasma power and 30 mTorr of gas pressure.

Plasma polymerization with butadiene gas showed similar trends as the acetylene plasma polymerization and provided 111N of pull out force at the optimum condition of 30 sec of treatment time, 15 W of plasma power and 30 mTorr of gas pressure (Fig. 2). Although the plasma polymerization coating of acetylene and butadiene enhanced adhesion of steel tire cords, compared to that of zinc plated steel tire cord (21N), the results were still much lower than that of brass plated tire cords (290N), as shown in Table 1.

Table 1. Adhesive properties of plasma polymer coated tire cords-TACT samples

Plasma / Conting material		Plasma Polymerization (PP)	Argon Etching (AE)+PP	AE+PP with carrier gas	
Zinc	21.5±3.0				
Butadiene		110.9±20.4	167.3±9.7	188.3±6.2	
Acetylene		185.4±7.4	279.2±5.6	285.0±5.0	
Brass					290.1±5.5

In the SEM analysis of tire cords after testing, the zinc plated cord showed almost no residue of rubber on the surface, while the brass plated tire cord exhibited 100 % cohesive failure. However, acetylene and butadiene plasma polymer coated tire cords showed about 50 and 10 % rubber coverage, respectively (Fig. 3).

2. Effect of argon plasma etching

The etching was carried out prior to the plasma polymerization coating under opti-

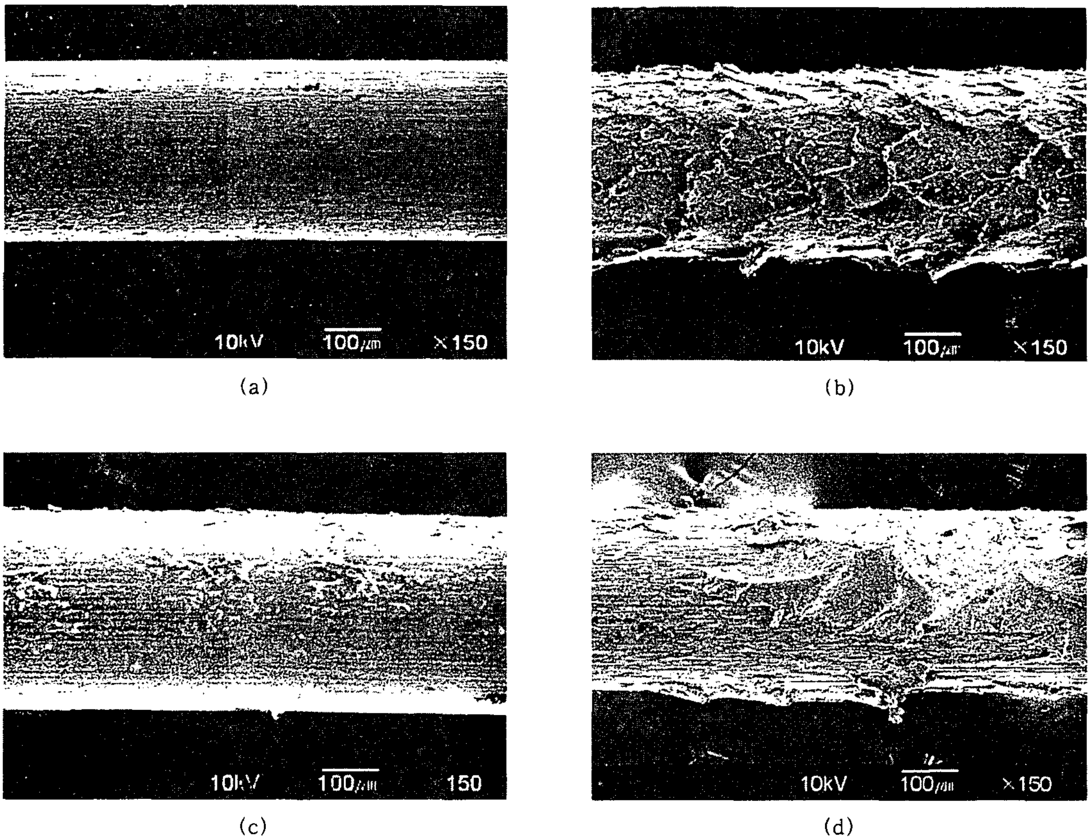


Fig. 3. Failure surface of plasma polymer coated tire cords-TCAT samples : (a) Zinc plated, (b) Brass plated, (c) Butadiene plasma polymer coating (d) Acetylene plasma polymer coating.

mum conditions. As the argon plasma etching power increased from 10 to 90 W under the fixed time of 10 min and gas pressure of 30 mTorr, the pull out force increased dramatically from 194 N (10 W) to 275 N (50 W) and to 279N (90 W), as shown in Fig. 4. Subsequently, the etching time and gas pressure were also varied, and 10 min and 30 mTorr were selected. The pull out force (279 N) obtained from the combined effect of argon plasma etching and acetylene plasma polymerization was smilar to that of brass plating (290 N), as reported by Tsai and co-workers in their study of steel plates.[8]

The combination of argon plasma etching and butadiene plasma polymerization coating resulted in a pull-out force of 167 N, compared to 111 N by butadiene plasma polymerization coating only. Since the argon plasma etching conditions were optimized with acetylene plasma polymerization coating, the etching time and power were further varied to 15 min and 150 W, respectively, but no improvements were observed. In the SEM analysis of failure surfaces, the combination of acetylene plasma polym-

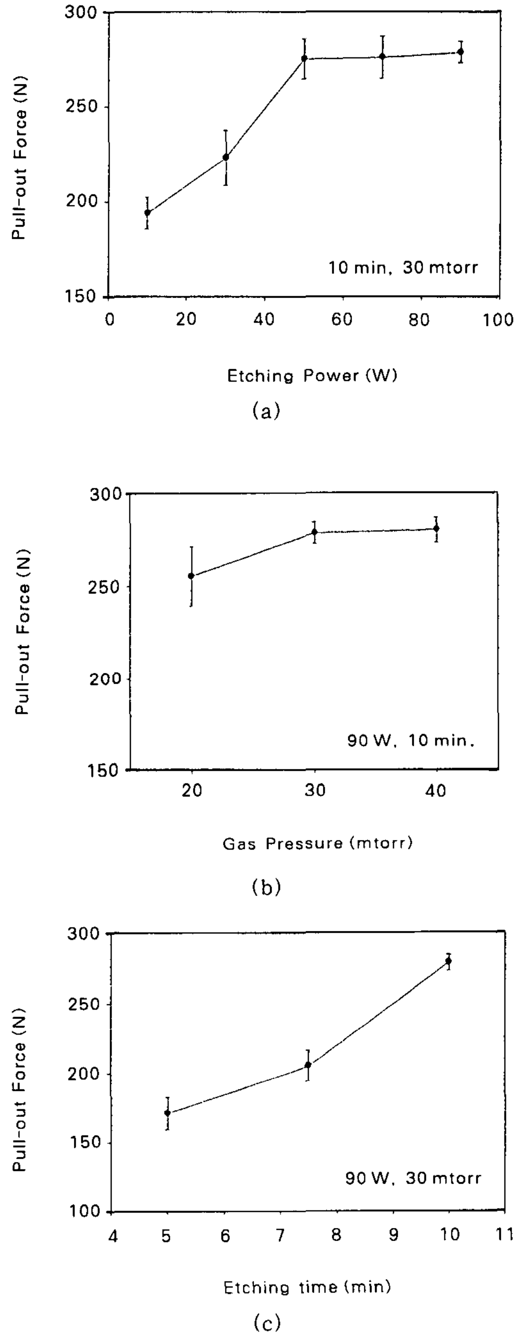


Fig. 4. Optimization of argon plasma etching conditions with acetylene plasma polymer : (a) Etching Power, (b) Gas Pressure, (c) Etching Time.

erization and argon plasma etching showed 100 % rubber coverage, compared to 50 % with plasma polymer coating only. Similarly, butadiene plasma polymerization provided 30 % coverage, compared to 10 % with only plasma polymerization (Fig. 5). Therefore, it is believed that the argon plasma etching increased adhesion by removing the weak boundary layer on the steel cords.

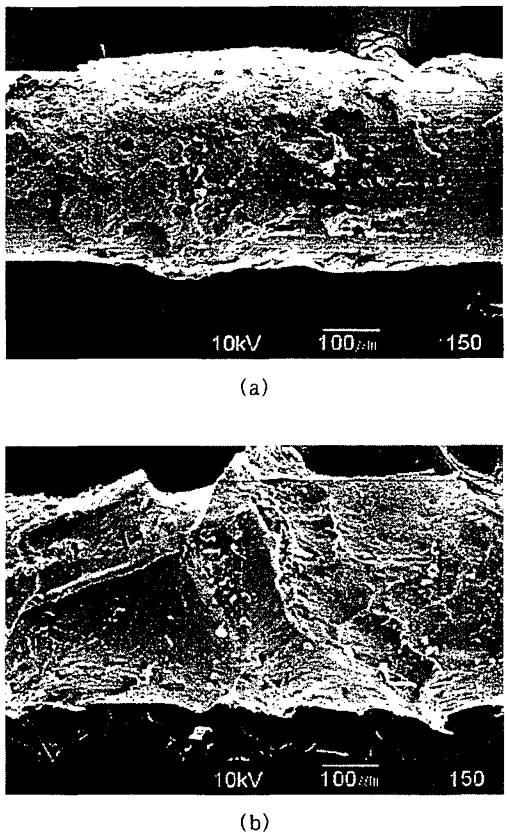


Fig. 5. Failure surface of tire cords with argon etching + plasma polymerization : (a) Butadiene plasma polymer coating, (b) Acetylene plasma polymer coating.

3. Effect of carrier gas

The third attempt to increase the adhesion of tire cords involved the utilization of carrier gas such as argon, oxygen or nitrogen. Carrier gas was introduced and the ratio of carrier gas to plasma polymer forming gas such as acetylene or butadiene was varied under a fixed total pressure of 30 mTorr. The zinc plated tire cords were etched first with argon plasma (90 W, 10 min, 30 mTorr), followed by acetylene (or butadiene) plasma polymerization coating (30 sec, 10 W, 30 mTorr) in the presence of carrier gas. As the ratio was varied from 0/30(argon/acetylene or butadiene) to 20/10 (mTorr/mTorr), the maximum pull out force was shown at 5/25 (mTorr/mTorr) for acetylene as well as for butadiene, as shown in Fig. 6. The combination of argon plasma etching, acetylene plasma polymer coating and argon carrier gas provided a pull-out force of 285 N, which is slightly higher than 275 N achieved without the carrier gas, but almost comparable to 290 N with brass plated steel tire cords. The combination with butadiene plasma polymerization provided 188 N, compared to 167 N without the carrier gas (Table 1).

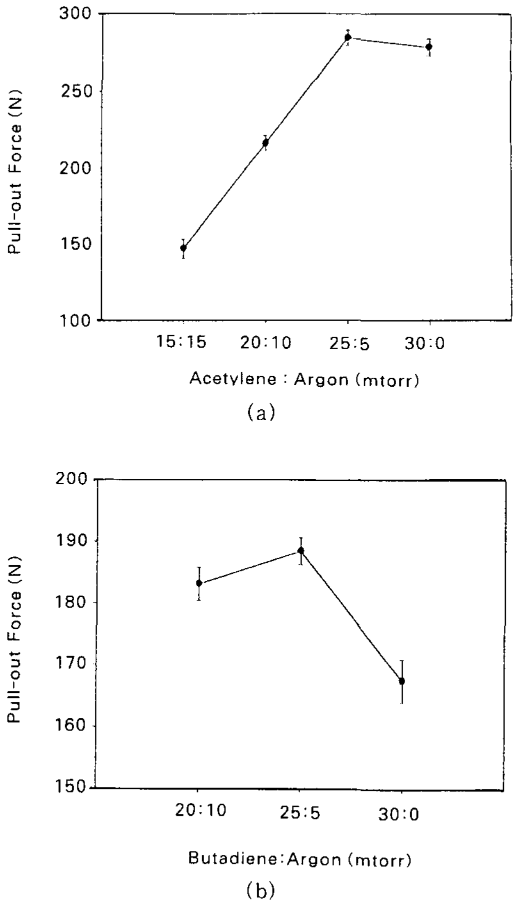
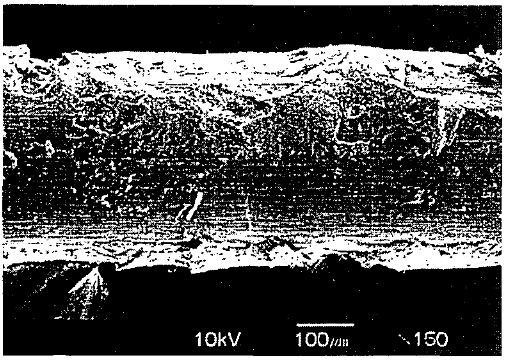


Fig. 6. Effect of carrier gas on the adhesion of Ar etched and plasma polymer coated tire cord : (a) Butadiene plasma polymer coating, (b) Acetylene plasma polymer coating.

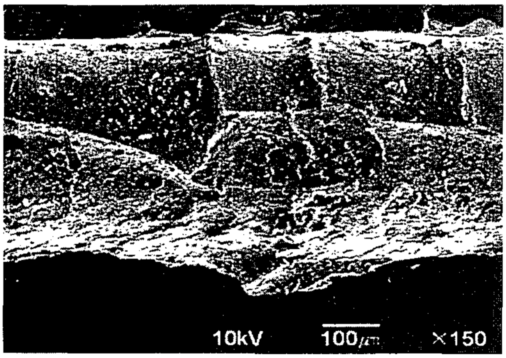
Oxygen and nitrogen were also utilized as carrier gas at the ratio of 5/25 (carrier gas/acetylene) for acetylene plasma polymerization. Nitrogen carrier gas had almost the same effect as argon, possibly owing to the inertness of the nitrogen gas. However, oxygen carrier gas was not as effective as argon or nitrogen, showing only 158N (Table 1). This could be explained by the oxidation of acetylene gas molecules and thus depletion of triple or double bonds, resulting in a much lower chance of chemical reaction, as observed by Tsai and coworkers.[8]

SEM analysis indicated 100 % rubber coverage on the failure surface observed from the tire cords treated by the combination of argon plasma etching and acetylene plasma polymer coating with argon carrier gas (Fig.

7). However, approximately 50 % of the surface was covered with rubber when butadiene was utilized instead of acetylene gas, which is slightly higher than the 30 % coverage observed in the absence of the carrier gas. The samples with nitrogen carrier gas also showed 100 % rubber coverage, while only 30 % coverage was observed from the samples with oxygen carrier gas.



(a)



(b)

Fig. 7. Failure surface of tire cords with argon plasma etching + plasma polymerization with carrier gas : (a) Butadiene plasma polymer coating (b) Acetylene plasma polymer coating.

Ⅳ. Conclusions

The adhesion of zinc plated steel tire cords to rubber compounds was greatly enhanced by the plasma polymerization coating of acetylene in combination with argon plasma etching and carrier gas. The major findings are summarized as follows:

1. The optimum conditions were 30sec, 10 W and 5/25 (argon/acetylene) for acetylene plasma polymerization, and 30 sec, 10 W and 5/25 (argon/acetylene) for butadiene plasma polymerization.

2. The pull out forces of zinc plated steel tire cords were greatly enhanced by acetylene plasma polymerization in combination with argon plasma etching and argon carrier gas (285 N), and was comparable to brass plated tire cords (290 N). The combination of argon plasma etching and plasma polymerization (279 N) also led to good results, while plasma polymerization (185 N) alone resulted in low pull out forces.

3. Butadiene plasma polymerization coating showed a similar trend as that of the acetylene plasma polymerization coating, but with much lower pullout forces; 111 N, 167 N and 188 N with butadiene plasma polymerization only, argon plasma etching plus plasma polymerization, and argon plasma etching plus plasma polymerization with carrier gas, respectively.

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