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Surface Modification of Steel Tire Cords via Plasma Etching and Plasma Polymerization Coating : Part Ⅱ. Characterization

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플라즈마 고분자 코팅에 의한 강철 타이어 코드의 표면 개질 : 제2부. 타이어 코드의 분석

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ABSTRACT : Zinc plated steel tire cords were subjected to RF plasma etching of argon, followed by plasma polymerization coating of acetylene or butadiene in order to enhance adhesion to rubber compounds. Plasma polymerization was carried out under optimized conditions of 10 W, 30 sec, 30 mTorr for acetylene and butadiene gas, while plasma etching was performed at 90W, 10min and 30mTorr. The adhesion of tire cords was evaluated via Tire Cords Adhesion Test (TCAT) and the failure surfaces of the tested samples were analyzed by SEM. Polymer coating by plasma polymerization was also characterized by FT-IR, Alpha-Step and dynamic contact angle analyzer in order to elucidate the adhesion mechanism.

요 약 : 아연 도금된 강철 타이어 코드의 접착성 향상을 위하여 아르곤 플라즈마로 에칭후 아세틸렌 또는 부타디엔 플라즈마 고분자 중합으로 코팅하였다. 플라즈마 고분자 중합은 10W, 30분, 30mTorr에서 실시하였으며, 아르곤 에칭은 90W, 30초, 30mTorr에서 실시하였다. 타이어 코드의 접착력은 TACT으로 측정하였으며, 파괴 표면을 주사전자현미경으로 분석하였다. 또한 플라즈마 고분자로 코팅된 타이어 코드의 표면을 FT-IR, Alpha-step 및 접촉각 측정기로 분석하여 접착 메카니즘을 규명하고자 하였다.

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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] Thus, it is not surprising that a great amount of research has been conducted to improve the adhesion of tire cords to rubber compounds.[2] Among the adhesion promoters for steel tire cords introduced, brass plating is believed to be the best by far. Unfortunately, this 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.

Therefore, plasma polymerization was attempted to coat the surface of tire cords since it is an environmentally clean process, where solvent is not needed and no chemical by-products are generated. In addition, plasma polymerized films have unique properties such as good adhesion to metal subrates, low oxygen and water vapor permeility, and good solvent resistance due to their cross-linked nature[3,5] Consequently, plasma polymerization has been utilized for coating purposes to enhance adhesion of steel plates,[6] steel tire cords[7,8] and also for membrane and micro-electronic applications.[5] When coupled with plasma etching, adhesion can be further improved.[6,8]

Yoon and coworkers reported[8] greatly enhanced adhesion of steel tire cords to rubber via acetylene plasma polymerization combined with argon etching and argon or nitrogen carrier gas, the results being comparable to those of brass plated steel plates.[6] The adhesion mechanism was investigated with a model compound, and attributed to monoor di-substituted acetylene groups involved in the cure reaction of rubber compounds.[9,11] This was further supported by the utilization of oxygen carrier gas, which reduced the unsaturated C=C or C≡C bonds and thus adhesion. Whether similar results can be achieved when plasma polymerization coating technique is applied to drawn/annealed tire cords, rather than steel plates, remains to be seen.

In this study, zinc plated steel tire cords were subjected to RF plasma polymerization coating of acetylene or butadiene in combination with Argon plasma etching and argon carrier gas. These processes resulted in excellent adhesion between steel tire cord and rubber compounds. Polymer coatings by plasma polymerization were characterized by FT-IR, Alpha-Step, dynamic contact angle analyzer (DCA) and SEM in order to elucidate the adhesion mechanism.

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) 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 (13.56 MHz) plasma generator (HPPS-300, Hanatek), consisting of a bell-jar type Pyrex chamber, manual impedance matching system and mass flow controller (MFC), was used for plasma polymerization. After placing the zinc plated steel cords, 15cm long, in the chamber at a distance of 3cm from the electrode, the chamber was vacuumed to 1×10^{-3} torr, followed by plasma etching and/or plasma polymerization under the optimized condition of 30 seconds, 10 W and 5/25 (argon/acetylene) for both acetylene and butadiene plasma polymerization.

The treatment was carried out by 1) plasma polymerization only, 2) argon plasma etching + plasma polymerization, and 3) argon plasma etching + plasma polymerization with carrier gas. The treated tire cords and plasma polymer coatings on tire cords were characterized in order to understand the adhesion mechanism. To alleviate the problem of handling small tire cords, a slide glass was utilized for thickness measurements, while KBr powder was used for FT-IR analysis rather than steel wire.

3. Characterization of tire cords

3.1 Topography of plasma polymer coated steel cords

The surface roughness of steel tire cords were analyzed by SEM (JEOL, JSM-5600) before and after plasma polymerization. Zinc plated steel tire cords were utilized and the results were compared to the brass plated tire cords. To avoid charging problem the samples were coated with Au/Pd.

3.2 Dynamic contact angle analysis

Water contact angles were measured by Cahn DCA (Model 312) with acetylene and butadiene plasma polymer coated tire cords. Advancing and receding contact angles were measured with distilled water at a speed of 20μm/sec and the dwell time of zero second. Average contact angles and hysteresis were calculated from 3-4 samples.

3.3 Coating thickness measurements

Due to the difficulty of measuring the thickness of plasma polymer coating on the tire cord, a slide glass was utilized, which was ultrasonically cleaned in acetone for 15 minutes and dried at 60°C for 12 hours before plasma polymerization coating of acetylene or butadiene. The coating on the slide glass was scratched with the edge of a razor blade, and the thickness was measured by Alpha-Step 500 with a scan length of 100 µm at a scan speed of 10 µm/sec. 3 samples were evaluated and the results were averaged.

3.4 FT-IR analysis

Bomem DA-8 FT-IR was used to characterize the polymer coating formed by plasma polymerization of acetylene or butadiene. Due to the difficulty of using tire cords, KBr powder was used, which was coated by plasma polymerization after being dried in a vacuum oven at 100°C for 12 hours. 128 scans were run under 2 torr of pressure.

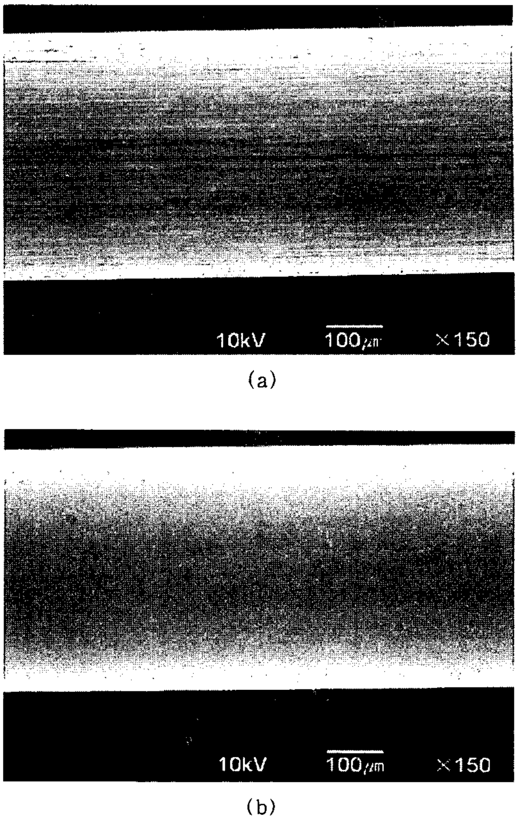


Fig. 1. SEM micrographs of the tire cords; (a) Zinc plated, and (b) Brass plated.

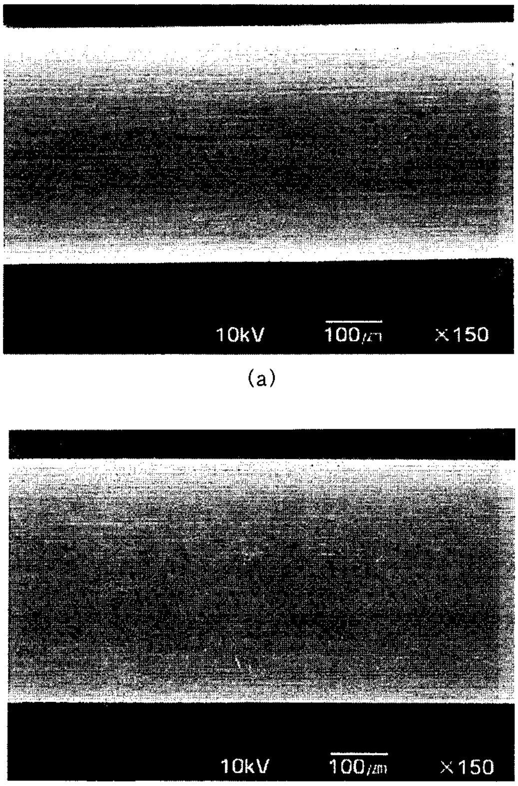
Ⅲ. Results and Discusssion

1. Surface topography of tire cords

In the SEM analysis, argon plasma etched and plasma polymerization coated tire cords showed die-marks on the surface as clear as the ones on the as-received tire cord (Fig. 1, 2), indicating that a very thin and smooth coating was formed by the plasma polymerization method. Moreover, neither plasma polymerization coating nor argon plasma etching changed the surface roughness of tire cords. This is supported by the similar hysteresis values obtained from water contact angle measurements. However, the topology of the brass plated tire cords was quite different from others, showing a smooth surface without die marks, possibly due to the thick brass coating on the surface.

2. Water contact angle analysis

As shown in Table 1, acetylene and buta-diene plasma polymerization coating increased the advancing contact angles of zinc plated tire cords, as did brass plating, while argon plasma etching decreased it slightly. The hysteresis values from all the samples except brass plated tire cords were very



(a)

(b)

Fig. 2. SEM micrographs of the tire cords; (a) Butadiene plasma polymer coated, and (b) Acetylene plasma polymer coated.

Table 1. Water contact angles of plasma etched and plasma polymer coated tire cords

Coating / Contact angle	Zinc	Ar. etched	Acety-lene	Buta-diene	Brass
θ_a	74.0±4.1	70.8±6.9	85.9±3.6	101.9±4.9	103.6±2.9
θ_r	6.1±4.4	6.8±4.8	20.9±3.6	49.4±7.5	33.6±3.2
θ_a-θ_r	66.8±0.6	65.1±2.5	66.7±0.9	64.9±1.1	70.0±1.8

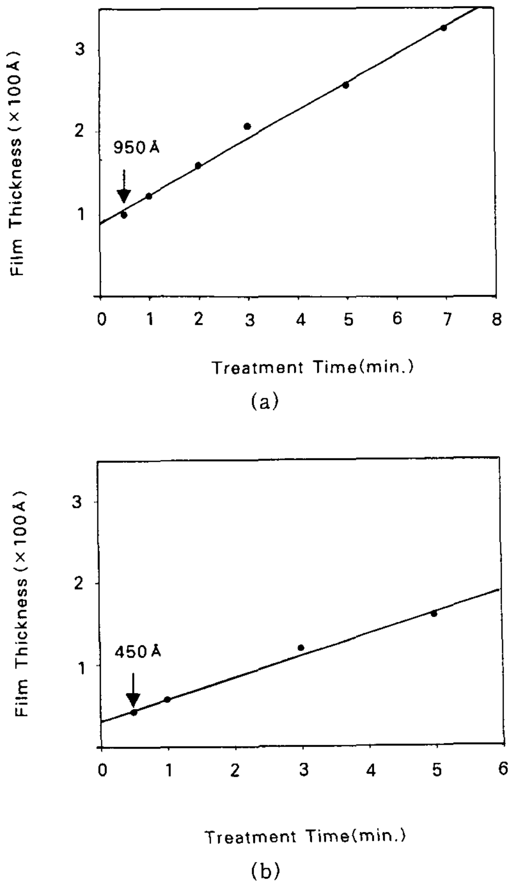
θ_a : advancing contact angle. θ_r : receding contact angle

similar, indicating that there was no appreciable change in the surface roughness by plasma polymerization coating or argon plasma etching as reported previously.[12,13] Therefore, it can be said that plasma polymerization coating with acetylene and butadiene increased the hydrophobicity of tire cords. The decreased water contact angle with argon plasma etching, however, could be due to the removal of contaminants on the surface.

Interestingly, acetylene and butadiene plasma polymer coated samples provided higher pull-out forces, despite their higher contact angles when compared to zinc plated tire cords, highlighting the bridging effect of plasma polymer coating between the coating and rubber. Higher pull-out forces with acetylene, compared to butadiene can be attributed to the possible C=C bonds in the coating layer, as evidenced by the FT-IR analysis. These double bonds can participate in the cure reaction of rubber, forming chemical bonds between the coating layer and rubber compounds.

4. Film thickness

Plasma polymerization coatings were carried out under optimized conditions with varied time, and the thickness was measured with Alpha-Step 500. The acetylene plasma polymer coating resulted in approximately 950 Å at 30 sec and increased almost linearly to approximately 3000 Å at 7 minutes (Fig. 3). However, butadiene plasma polymerization led to approximately 450 Å at 30 sec, and 1500 Å at 5 minutes. It was reported[8] that the pull-out force decreased with treatment time, and thus increased coating



(a)

(b)

Fig. 3. Thickness of plasma polymer coating with Alpa-Step 500; (a) Acetylene plasma polymer coating, (b) Butadiene plasma polymer coating.

thickness. This is a widely accepted relationship between adhesion and film thickness, also confirmed by Yasuda with plasma polymer coatings.[4]

5. FT-IR analysis

FT-IR spectrum from the acetylene plasma polymer coated KBr shows bands near 3000, 1600 and 1500 cm^{-1}. These can be assigned to CH_3 asymmetric stretching (2960 cm^{-1}), CH_2 stretching (2928cm^{-1}), CH_3 symmetric stretching (2870cm^{-1}), C=O stretching (1715cm^{-1}, 1680cm^{-1}), C=C stretching (1600cm^{-1}, 1585cm^{-1}), CH2 bending (1450cm^{-1}) and CH_3 bending (1375cm^{-1}), as shown in Fig. 4. Major bands are from hydrocarbons as expected from the polymerization of acetylene. However, instead of expected bands at 2210 and 2100cm^{-1} from mono- and di-substituted acetylene, C=C and C=O stretching bands were observed.

The small but clear band near 1585cm^{-1} was assigned to C=C stretching, while the huge band near 1680-1715cm^{-1} was designated to C=O. The unusually big C=O band could be attributed to the oxidation of the samples when they were exposed to air for several hours before IR measurements as experienced by Tsai and co-workers.[10,11] Oxidation was further evidenced by the relatively small band of C=C at 1585cm^{-1} and the absence of $C\equiv C$ stretching near 2210,

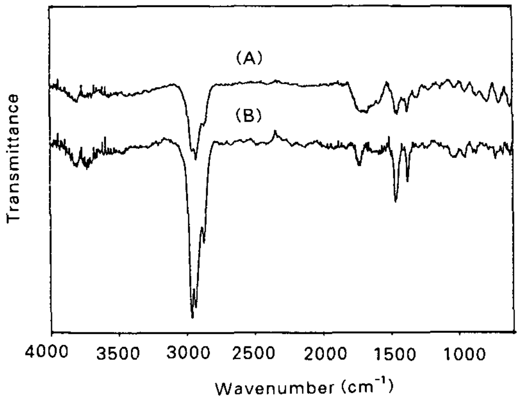


Fig. 4. FT-IR spectra of acetylene and butadiene plasma polymer coating with KBr pellet; (A) Acetylene plasma polymer coating, and (B) Butadiene plasma polymer coating.

2100 and 1600cm^{-1}. Discrepancies between results here and what was observed by Tsai and co-workers with acetylene plasma coated CRS could be attributed to IR type (reflection-absorption infrared (RAIR) vs. transmission IR), sample form (0.5 mm thick CRS plate vs. KBr powder) and the oxidation of samples.

Samples with butadiene plasma polymer coating yielded similar FT-IR spectra, but with evidence of much less oxidation, showing clear C=O band near 1715cm^{-1}, and a trace of C≡C band near 2210 cm-1 and C=C band near 1585cm^{-1}. In comparison, acetylene plasma polymerization has a stronger C=C band near 1585m^{-1} and possibly C≡C near 2210cm^{-1}, resulting in much better adhesion than that obtained from butadiene polymer coated samples. From both spectrum, the absence of band near 730cm^{-1} indicated a highly branched nature of the plasma polymer coating.[10]

IV. Conclusions

The plasma polymer coated steel tire cords were characterized in order to elucidate the adhesion mechanism. The major findings are summarized as follows:

1. In the SEM analysis, the plasma polymer coated and plasma etched tire cords showed exactly the same surface topology as the zinc plated tire cord, indicating a very thin homogenous layer of polymer coating.
2. Water contact angle analysis of plasma polymer coated tire cords revealed that plasma polymerization increased water contact angle and thus hydrophobicity of tire cords without altering the surface roughness significantly.
3. Film thickness from Alpha-Step was very thin and increased with treatment time, but adhesion decreased with film thickness.
4. FT-IR analysis indicated that the presence of C=C double bonds may be responsible for the enhanced pull-out forces with acetylene plasma polymerization coating, compared to butadiene plasma polymerizatio.

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References

1. F. J. Kovac, Tire Technology, 5th ed., Goodyear Tire & Rubber Co., 1978.
2. W. J. van Ooij, *Rubber Chem. Technol.*, **52**, 605 (1979).
3. E. M. Liston, *J. Adhesion*, **30**, 199 (1989).
4. H. Yasuda, Plasma Polymerization, Academic Press, New York, 1985.
5. R. dAgostino, Plasma Deposition, Treatment, and Etching of Polymers, Academic Press, London, 1990.
6. Y. M. Tsai, F. J. Boerio and D. K. Kim, *J. Adhesion*, **61**, 247 (1997).
7. T. H. Yoon, B. Y. Shon, M. H. Han, H. M. Kang and R.K.Kim, *IRC99 Seoul*, 102, (1999).
8. Y. M. Tsai, F. J. Boerio, W. J. van Ooij and D. K. Kim, *J. Adhesion* **62**, 127

(1997).

9. H. M. Kang, K. H. Chung, S. Kaang and T. H. Yoon, *Elastomer*, **35**, 53 (2000).
10. Y. M. Tsai, F. J. Boerio, W. J. van Ooij, D. K. Kim and T. Rau, *Surf. and Interface Anal.*, **23**, 261 (1995).
11. Y. M. Tsai and F. J. Boerio, *J. Adhesion* **55**, 151 (1995).
12. A. E. Mera, M. Goodwin, J. K. Pike, K. J. Wynne, *Polymer* **40**, 419 (1999).
13. A. Nihlstrand, T. Hjertberg and K. Johansson, *Polymer* **38**, 3581 (1997).