

아르곤 에칭과 아세틸렌 플라즈마 중합에 의한 타이어 코드의 접착성 향상연구

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Enhanced Adhesion of Tire Cords via Argon Etching and Acetylene Plasma Polymerization

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Key Words : adhesion, tire cord, acetylene, RF plasma polymerization, argon etching

ABSTRACT

Steel tire cords were coated via RF plasma polymerization of acetylene in order to enhance adhesion to rubber compounds. Adhesion of tire cords was measured by TACT as a function of plasma polymerization and argon etching conditions such as power, treatment time and chamber pressure. Tested tire cords were analysed by SEM to elucidate the adhesion mechanism. The highest adhesion values were obtained with argon etching condition at 90W, 10min, 30mtorr followed by acetylene plasma polymerization condition at 10W, 30sec., 30mtorr. In SEM analysis, the plasma polymerized tire cord at the optimized condition showed 100% rubber coverage as observed from brass-plated steel tire cords.

1. INTRODUCTION

The most widely used reinforcing material in automotive tires is steel cord which is usually plated with brass in order to improve adhesion to rubber (1-2). Unfortunately, the brass plating process generate chemical wastes that can cause environmental pollution despite very good adhesion to steel cords and rubber. Moreover, the brass-plated steel cords are vulnerable to corrosion due to the galvanic coupling of brass and steel. In corrosive environments, brass acts as a cathode, and thus steel, which is an anode, tends to corrode at accelerated rate, resulting in durability problems (3-4). Consequently,

there have been numerous research during the past decades to replace the brass coating process with one that can provide not only good adhesion but also high corrosion resistance without chemical wastes (5-6).

Plasma polymerization technique is an environmentally clean process which has been utilized in electronics and membranes industries. Plasma-polymerized films have unique properties such as good adhesion to metal substrates, low oxygen and water vapor permeability, and high resistance to solvents (7-9). Recently, van Ooij *et al.* have utilized a RF or DC-plasma polymerization technique with acetylene,

styrene, silane and siloxane monomers to increase the adhesion and corrosion resistance of steel tire cords (10).

In this study, the surface of the steel tire cord was modified by argon plasma etching and polymerization of acetylene in order to enhance the adhesion of the cord to rubber compounds. Conditions for plasma polymerization and argon etching were optimized. Adhesion was measured by TCAT(Tire Cord Adhesion Test) and the failure surfaces were analysed by SEM in order to elucidate the adhesion mechanism.

2. EXPERIMENTAL

Zinc plated steel cords with a diameter of 0.35mm and skim rubber compounds for the TBR belt tire were provided by Hyosung T&C and Kumho Tire Co., respectively. Acetylene (99%) butadiene (99.9%) and argon (99.9%) gases were purchased, with argon being utilized for the in situ cleaning of the steel cord. Plasma polymerization was carried out by a radio frequency (13.56MHz) plasma reactor (HPPS-300, Hanatek) with a bell-jar type glass chamber, manual impedance matching and mass flow controller. The 15cm long zinc plated steel cords were placed 3cm below from the electrode (Figure 1). The chamber was vacuumed to 1×10^{-3} torr before introducing the monomer for plasma polymerization.

The tire cords were treated as a function of power (5-20W) and treatment time(30sec.-7min.) under a fixed chamber pressure (30mtorr). After optimizing, time and power, gas pressure was varied from 10 to 30 mtorr. Prior to polymerization, tire cords were etched by argon plasma as a function of power (30-90W) and treatment time (5-9min.) under the fixed chamber pressure (30mtorr) in order to optimize the etching condition.

Samples for the adhesion test, TACT, were prepared with a mold which was designed for sample dimensions of 20x20x75mm. Prior to filling the bottom half of the cavity with rubber, the mold

was heated to 145°C. Then, the plasma polymer coated steel tire cords were placed on both ends of the cavity where each cord was embedded approximately 20mm into the rubber. The remaining rubber was stacked and cured at 145°C for 1 hr, followed by slow cooling to room temperature. Samples were tested by Instron 5567 at 50mm/min. Approximately 5-6 samples were tested and the results were averaged. The surfaces of the tire cords after plasma polymerization and being tested were further analysed with Scanning Electron Microscopy (JEOL, JSM-5800).

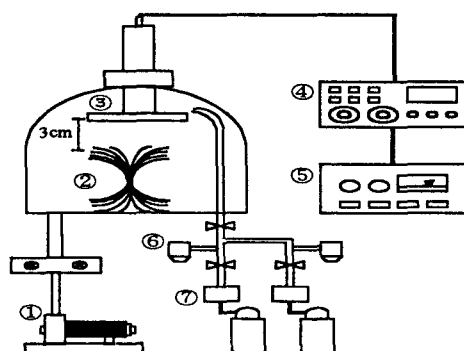


Figure 1. RF Plasma Polymerization Reactor - bell jar type(HPPS-300, Hanatek)

- ① Vacuum pump ② Tire cords ③ Electrode ④ Impedance matching unit ⑤ Power supply unit
- ⑥ Pneumatic valve ⑦ Mass Flow Controller

3. RESULTS AND DISCUSSION

Acetylene Plasma Polymerization

The pull out force of the zinc plated steel tire cords via TACT was increased by plasma polymerization with acetylene compared with control sample. In general, most of the increase by acetylene plasma polymerization was attained after only 30 sec of treatment, and the adhesion decreased significantly with additional treatment time. The highest pull out force with acetylene plasma polymerization was obtained at 30 sec., 10W, 30mtorr, exhibiting 185N, compared to 20N of the zinc plated steel tire cord (Figure 2). But the pull out forces of acetylene plasma

polymerized tire cords was lower than that of the brass plated tire cord, which showed 290N.

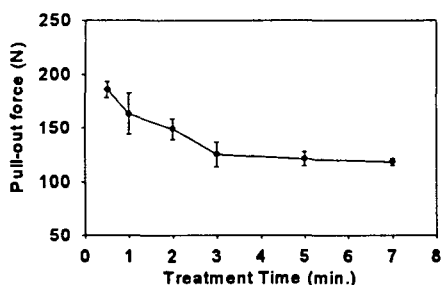


Figure 2. Effect of Treatment Time on Acetylene Plasma Polymerization

The plasma power seemed to affect the pull out force of tire cords. The highest pull out forces (185N) was obtained with 10W, which resulted in always higher pull out forces than 5W and 20W (Figure 3).

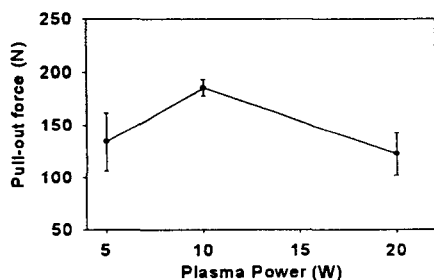


Figure 3. Effect of Plasma Power on Acetylene Plasma Polymerization

The full out forces increased with chamber pressure, but start to decreased at 30mtorr (Figure 4).

and 30mtorr were chosen which exhibited 279N, since 90W provided the smallest standard deviation (Figure 5 & 6).

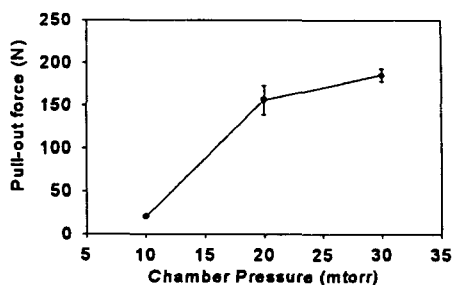


Figure 4. Effect of Chamber Pressure on Acetylene Plasma Polymerization

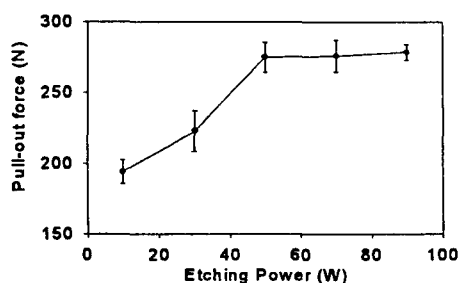


Figure 5. Effect of Power on Argon Etching

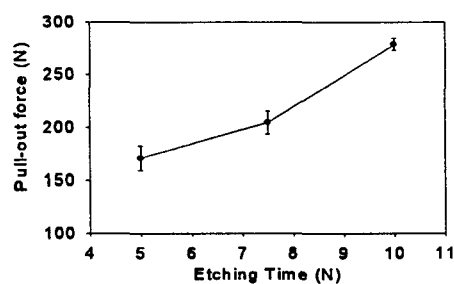


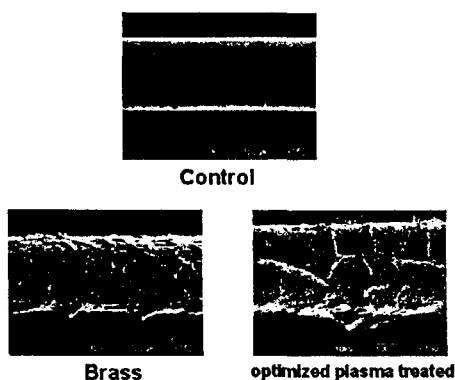
Figure 6. Effect of Treatment Time on Argon Etching

The pull-out forces of argon etched and acetylene plasma polymerized tire cords was almost same value as that of the brass plated tire cord, which showed 290N. This can be attributed to cleaning and activation effect on the surface of the zinc

plated steel tire cords.

Failure surface analysis

Due to the thinness of plasma polymer layer on the tire cords, it was very difficult to differentiate the plasma coated tire cords from un-coated cords. However, SEM analysis could detect rubber coverage on the failure surface of the tested tire cords. The plasma polymerized tire cord at the optimized condition showed 100% rubber coverage as well as brass-plated steel tire cord. But, there are some differences of rubber coverage between the plasma polymerized tire cord and the brass plated tire cord. The plasma polymerized tire cord had thicker rubber layer on them than the brass plated tire cords. It can be said that the crosslinking density of rubber near the plasma polymerized film was higher than that of the brass plated tire cord.



4. SUMMARY

Zinc plated steel tire cords were coated via RF plasma polymerization of acetylene in order to enhance adhesion to rubber compounds. Adhesion of tire cords was measured by TACT as a function of plasma polymerization and argon etching conditions such as power, treatment time and chamber pressure. The highest pull out force with acetylene plasma

polymerization was obtained at 30 sec., 10W, 30mtorr. The pull-out forces of argon etched and acetylene plasma polymerized tire cords was almost same value as that of the brass plated tire cord. This can be attributed to cleaning and activation effect on the surface of the zinc plated steel tire cords. In failure surface analysis of the tested tire cords, the plasma polymerized tire cord at the optimized condition showed 100% rubber coverage.

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