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플라즈마 중합에 의한 타이어 코드의 접착성 향상연구

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Enhanced Adhesion of Tire Cords via Plasma Polymerizations

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요 약 : 타이어 코드용 강철선을 RF 플라즈마를 이용한 acetylene 및 butadiene 가스의 플라즈마 중합으로 코팅하였으며, 타이어용 고무와의 접착력을 TCAT 또는 T-test로 측정하였다. 강철선의 접착력은 사용된 gas, plasma power, 코팅시간 및 가스 압력에 따라 측정하였으며, 플라즈마 중합에 앞서 Ar 플라즈마 에칭으로 타이어 코드를 세척하였다. 또한 80℃의 증류수에서 7일간 노화시켜 접착력 저하를 고찰하였으며, 접착력 시험 후 타이어 코드 표면을 SEM으로 분석하여 파괴거동을 규명하고자 하였다. 가장 우수한 접착력은 acetylene의 경우 20W, 2분, 25*mtorr*에서, 그리고 butadiene의 경우는 10W, 4분, 25*mtorr*에서 얻을 수 있었으며, Ar 에칭에 의한 접착력 변화는 없었다. 노화에 의한 접착력 저하는 없었으며, 도리어 증가하는 현상을 보였다. SEM 분석에서 강철선의 높은 거칠기와 플라즈마 코팅의 얇은 두께로 인하여 파괴거동 규명에는 한계가 있었다.

ABSTRACT : Steel tire cords were coated via RF plasma polymerization of acetylene and butadiene gas in order to enhance adhesion to rubber compounds. Adhesion of tire cords was measured by TCAT and T-test as a function of type of gas, plasma powder, treatment time, gas pressure and Ar gas etching. Some samples were subjected to aging study in distilled water at 80℃ for a period of 7 days. After testing, tire cords were analysed by SEM to elucidate the adhesion mechanism. The highest adhesion values were obtained at 20W, 2min and 25*mtorr* for acetylene plasma polymerization, and 10W, 4min, 25*mtorr* for butadiene plasma polymerization. However, Ar plasma etching did not affect adhesion, while the adhesion of tire cords increased rather than decreased, contrary to expectations. It was not possible to elucidate failure mode by SEM, owing to the rough surface of the tire and the thin plasma polymer coating layer.

Keywords : adhesion, tire cord, plasma polymerization acetylene, butadiene, Ar etching.

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I. Introduction

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, while promoting very good adhesion between the steel cords and rubber, also generates chemical wastes that can cause environmental pollution. Moreover, the brass-plated steel cords are vulnerable to corrosion due to the galvanic coupling of brass and steel. In a corrosive environment, brass acts as a cathode, and thus steel, which is an anode, tends to corrode at an 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 membrane industries for modifying surface characteristics. 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 (radio frequency) or DC-plasma polymerization technique with acetylene, styrene, silane and siloxane to increase the adhesion and corrosion resistance of steel tire cords.[11-12]

In this study, the surface of the steel tire cord was modified by plasma polymerization, utilizing acetylene and butadiene, in order to enhance the adhesion of the cord to rubber compounds. Conditions for plasma polymerization were optimized and Ar plasma etching was performed prior to plasma polymerization. Adhesion was measured by TCAT (tire cord adhesion test) and T-test, and some samples were exposed to hot water prior to these tests in order to evaluate their durability. The failure surface was analysed by SEM in order to elucidate the adhesion mechanism.

II. Experimental

Bare steel cords with a diameter of 1.28mm and skim rubber compounds for the TBR belt tire were provided by Kumho Tire (Kwangju, Korea). 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 via RF plasma reactor (HPPS-300, Hanatek) with a stainless steel chamber, manual impedance matching system and mass flow controller. The chamber was vacuumed to 10^{-2} *mtorr* before introducing the monomer for plasma polymerization. The tire cords were treated as a function of power (10-30W) and treatment time (1-7min.) under a fixed chamber pressure of 25*mtorr*. After optimizing time and power, gas pressure was varied from 10, to 100 *mtorr*. Prior to polymerization, some tire cords were etched by argon plasma at 30W for 2-15min under fixed chamber pressure of 20*mtorr*, in order to investigate the cleaning effect of argon plasma.

Samples for the adhesion test, such as TCAT and T-test, were prepared with a mold which was designed for sample dimensions of 20×20×75mm (TCAT) and 20×20×200mm (T-test). Prior to filling the bottom half of the cavity with rubber, the mold was heated to 145℃. Then the plasma polymerized 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℃ for 35min, followed by slow cooling to room temperature. Samples were tested by Instron 5567 at 10mm/min (TCAT) or 50mm/min (T-test) at RT without aging or after aging in distilled water of 80℃ for up to 7 days. Approximately 4-6 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 (SEM, JSM-5800).

III. Results and Discussion

1. Effect of treatment time

The pull out force of the steel tire cords via TCAT was increased by plasma polymerization with acetylene, showing more than 100% improvement, compared with approximately 50% improvement by butadiene plasma polymerization (Fig. 1). In general, most of the increment from acetylene plasma polymerization was attained after only one min. of treatment and the adhesion did not change significantly with additional treatment time. The highest pull out force with acetylene plasma polymerization was obtained at 2min. and 20W, and at 5min. and 10W, exhibiting 195N, compared to 86N of the

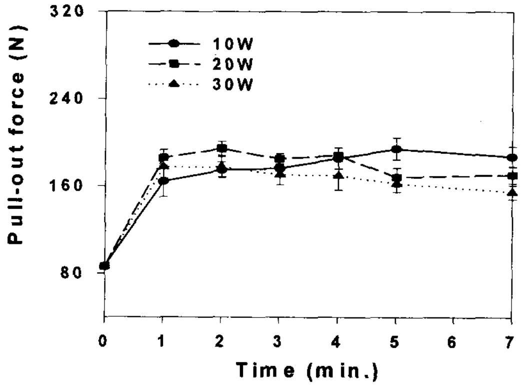


Fig. 1. Effect of treatment time and power on the adhesion of acetylene plasma coated (25 *mtorr*) tire cords by TCAT.

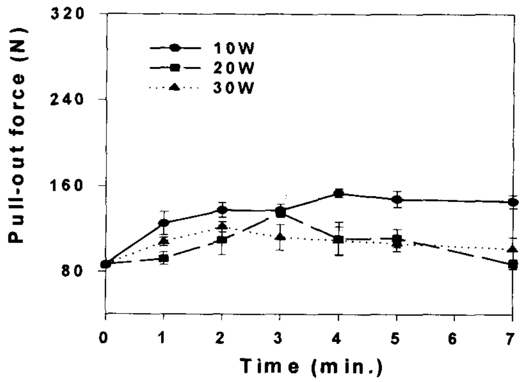


Fig. 2. Effect of treatment time and power on the adhesion of butadiene plasma coated (25 *mtorr*) tire cords by TCAT.

bare tire cord. But the pull out forces of acetylene plasma polymerized tire cords was much lower than that of the brass plated tire cord, which showed 372N.

The butadiene plasma polymerized tire cords showed a rather different trend from the acetylene plasma polymerized samples (Fig. 2). The pull out force increased gradually and showed clear maximum values at 4, 3, and 2min. of treatment time with 10, 20 and 30W, respectively. The highest pull out forces obtained by butadiene plasma was 153N at 4min. and 10W, compared to 195N from the acetylene plasma polymerized samples. The difference can be attributed to the nature of polymer coating, which is determined by the monomers used.

2. Effect of plasma power

Although the plasma power seemed to affect the pull out force of tire cords, no clear trend was observed (Fig. 1). At 1 and 3min. of treatment time, 20W provided higher pull out force than 30W, followed by 10W in acetylene plasma polymerization. However, the highest pull out force was obtained with 10W, followed by 20W and 30W at 7min. The highest pull out forces (195N) was obtained with 10 and 20W at 2 and 5min., respectively. The butadiene plasma polymerized samples showed a different trend from the acetylene plasma polymerized samples (Fig. 2). In general, 10W always showed higher pull out forces than 20W and 30W, with the highest value of 153N at 10W and 4min.

The T-test samples which were prepared with tire cords treated at 2min. and 25*mtorr* showed higher pull out forces with 20W than 10W or 30W (Fig. 3), which is the same trend as that shown in Fig. 1. As expected, however, 10W exhibited higher pull out forces than 20 or 30W in butadiene plasma polymerized tire cords. It was also noted that higher pull out forces (166N at 20W) was obtained with acetylene plasma polymerized than with butadiene plasma polymerization (136N at 10W). It can be said that plasma power, treatment time and monomer or gas utilized for plasma polymerization have to be carefully optimized to obtain good quality films for good adhesion.

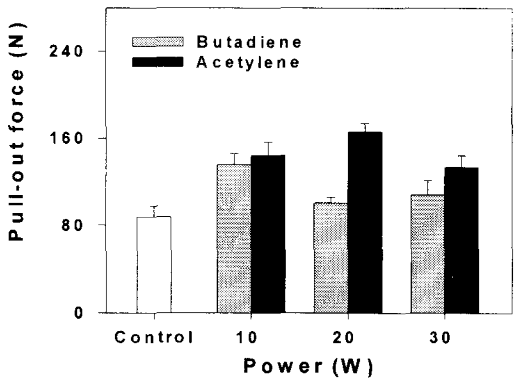


Fig. 3. Effect of power on the adhesion of acetylene and butadiene plasma coated tire cords by T-test (2min., 25*mtorr*).

3. Effect of gas pressure and Ar etching

In the plasma polymerization of steel tire cords, most of the experiment was carried out at 25*mtorr* of gas pressure. However, the pressure was also varied from 10 to 100*mtorr* in order to maximize the adhesion of tire cords. Acetylene plasma polymerization was carried out at 20W for 2min, while butadiene plasma polymerization was performed at 10W and 4min. The parameters for these reactions were chosen from Fig. 1 and Fig. 2, respectively. As shown in Fig. 4, higher pull out forces were obtained with 25*mtorr* than with 10, 50 and 100 *mtorr*, regardless of the gas used. This may have resulted from the thickness of the coatings on the tire cord.

Argon gas etching was also performed prior to plasma polymerization in order to investigate the cleaning effect of Ar plasma. Etching was

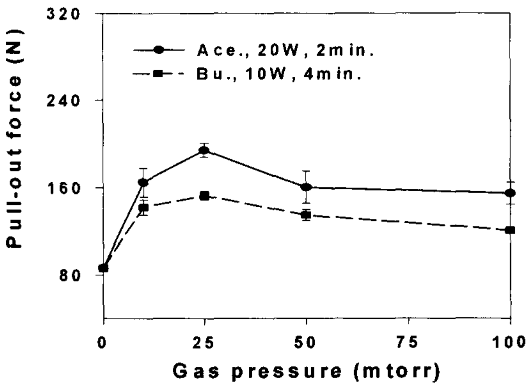


Fig. 4. Effect of gas pressure on adhesion force of plasma polymer coated tire cords by TCAT.

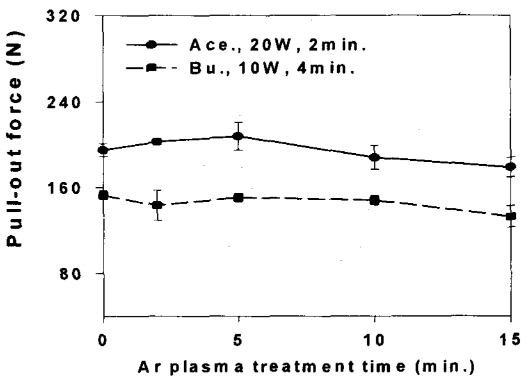


Fig. 5. Effect of Ar plasma cleaning (30W, 20 *mtorr*) on the adhesion of plasma polymer coated tire cords by TCAT

carried out at 30W for 2-15min. under 20*mtorr*. Surprisingly, no change in pull out forces was detected, as shown in Fig. 5. This can be attributed to the fairly clean nature of the tire cord or insufficient cleaning by Ar plasma etching. The conditions for Ar plasma etching need to be investigated further if the low pull out forces is due to the contaminants on the tire cords.

4. Effect of aging in hot water

Durability studies were carried out with TCAT samples which were prepared at optimized conditions of 25*mtorr*, 20W and 2min. for acetylene plasma polymerization, and 25*mtorr*, 10W and 4min. for butadiene plasma polymerization. The pull out force of aged samples was not deteriorated but rather increased even after 7 days of immersion in 80℃ distilled water (Fig. 6). Such trend may be due to further curing of rubber during the aging process. The samples from the brass plated tire cords showed the same trend as those from plasma polymerized tire cords. Thus, the aging condition utilized in this study may not be severe enough to deteriorate adhesion of tire cords.

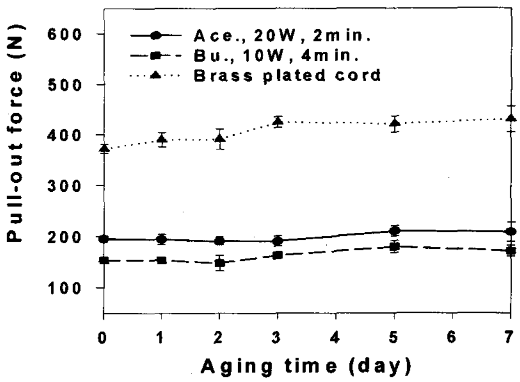
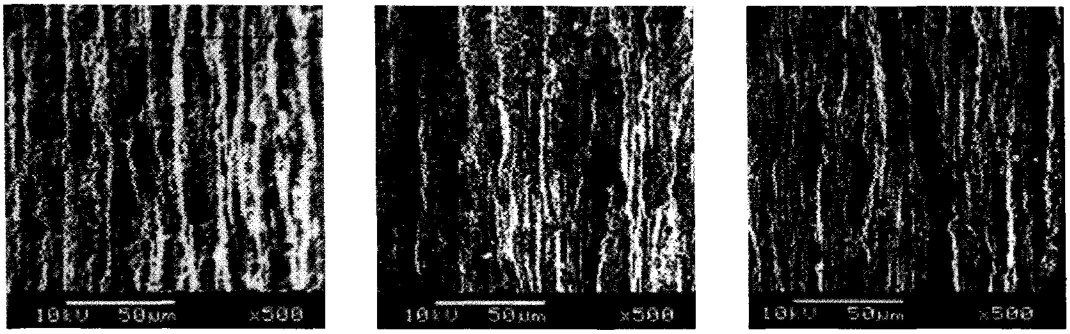


Fig. 6. Effect of aging time on adhesion of plasma polymer coated tire cords by TCAT.

5. Failure surface analysis

Since the defects from processing and very thinness of plasma polymer layer on the tire cords, it was very difficult to differentiate the plasma coated tire cords from un-coated cords. SEM analysis did not detect any rubber on the failure surface of tested tire cords, and may not be a suitable technique for such studies (Fig. 7).



(a) (b) (c)

Fig. 7. SEM micrographs of tire cords. (a) as-received, (b) acetylene plasma treated (20W, 25*mtorr*, 2min), (c) after testing by TCAT.

Thus, it is not clear as to whether the failure occurred at the interface of the tire cord and plasma polymer layer, or the plasma polymer layer and rubber. Further studies with surface analysis techniques such as XPS and SIMS are needed before the exact failure mode can be determined.

Ⅳ. Conclusion

Adhesion of steel tire cords was enhanced by plasma polymerization with acetylene and butadiene, but not to the extent of those obtained by brass plated tire cords. Since the characteristics of plasma polymer coating such as cross-linking density and chemical structure and thickness are dependent on the plasma polymerization conditions, these factors should be carefully controlled to obtain maximum adhesion. The results are summarized as follows:

1. The optimum conditions for acetylene plasma polymerization were 20W, 2min., and 25 *mtorr*, while those for butadiene plasma treatment was 10W, 4min., and 25*mtorr*.

2. Results from T-test and TCAT showed similar trends, but higher pull out forces were obtained from TCAT.

3. The adhesion of tire cords coated with acetylene or butadiene plasma polymer increased rather than deceased when exposure to 80℃ water for a period up to 7 days.

Acknowledgement

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