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Adhesion Enhancement of Polyurethane Coated Leather and Polyurethane Foam with Plasma Treatment

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Abstract−Plasma pretreatment was applied to polyurethane-coated leather and polyurethane foam to improve adhesion. The optimum condition of the treatment was examined, and its performance was compared with conventional treatment techniques. In addition, optical observation was conducted to investigate the surface change from the treatment. In the case of polyurethane-coated leather, longer treatment time gives better adhesion, but a ten-second treatment works best for polyurethane foam due to its low contact angle. Excessive oxygen flow during plasma treatment does not enhance performance. It is shown that the plasma treatment reduces the contact angle to result in an improvement of peel strength. Also, optical observation indicates surface change and wettability increase.

Key words: Plasma Treatment, Low Pressure Plasma, Adhesion, Microwave Excitation, Contact Angle

INTRODUCTION

Surface modification using plasma has been applied to a variety of materials, such as metal, glass, ceramic and plastic materials. Chemical and physical surface changes caused by the applied plasma introduce hydrophilic or hydrophobic characteristics to improve adhesion for the bonding, wetting and inking in coating and printing processes. Many effects are obtained from the plasma treatment of a polymer surface depending upon the impact of species from the plasma and surface material of the polymer. Plasmas are generated by different techniques of capacitively coupled dielectric barrier discharges at atmospheric pressure, or capacitive coupling, inductive coupling [Park and Kim, 1999; Park et al., 2004] and microwave excitation at low pressure.

A thorough review of plasma treatment was published by Grace and Gerenser [2003], which explains plasma generation, treatment characterization and plasma application. The characterization of plasma treatment on polypropylene and polycarbonate for metal deposition was examined [Charbonnier and Romand, 2003], and hydrophilic and hydrophobic modifications of polyamide using cold plasma were conducted [Dreux et al., 2003]. In addition, the effect of the treatment in polymer on the adhesion to metal was compared with untreated polymer and metal surface treatment [Ge et al., 2003]. The increase of wettability from plasma treatment of polymethyl methacrylate was utilized for humidity measurement as a sensor material [Dabhade et al., 2004] and for biocompatibility assessment [van Kooten et al., 2004].

In this study, the technique of microwave excitation at low pressure was applied to polyurethane-coated leather and polyurethane foam to improve peel strength. The implemented plasma was generated in the environment of low pressure oxygen. The effects of plasma exposure time and oxygenated atmosphere on the peel strength were investigated, and the characterization of plasma treatment was conducted by measuring contact angle and microscopic observa- tion.

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EXPERIMENTAL

1. Experimental Equipment

The plasma treatment equipment of this study was custom designed and fabricated by a local company (Koryo Automation Co., Korea). The equipment generates microwave exciting low pressure plasma. It has an exposing chamber made of aluminum that is 450 cm wide, 450 cm high and 510 cm deep. The microwave generator has a power of 2 kW with water cooling system, and the frequency of the generated microwave is 2.45 GHz. A gas supply system using a mass flow controller is installed to provide a gas environment for plasma generation. A rotary vacuum pump and a vacuum controller are set up to evacuate air before the oxygen supply.

2. Experimental Procedure

Rectangular specimens of 15 cm×30 cm to be exposed to plasma are placed in the chamber of the plasma generator, and air is evacuated for half an hour. While oxygen is supplied at a given flow rate, the microwave generator is activated for a specified time. After the treatment, the generator is shut down and the equipment pressure is raised to atmospheric pressure.

Water soluble adhesive (Dongsung Chemical Co., Korea, No. W-01) in the amount of 200 g/m^2 is painted with a brush on the treated side of the specimen. After one minute of drying, two pieces are stuck together on their adhesive painted sides and pressed with 5 kg weight for 10 minutes. Two peeling tests are conducted after 30 minutes and a day of natural drying, respectively. A test specimen of 2.5 cm×30 cm is cut from the prepared sample. The thickness of leather samples is 2 mm, and foam is 10 mm. The test was conducted by the testing method for peel strength of adhesives specified in the Korean Standard (KS M3725). The size of the specimen is determined in the standard. The peel strength was measured with a tensile strength tester (Dong Won Testers, Korea, Model FS-1010).

RESULTS AND DISCUSSION

1. Effect of Exposed Time

The variation of peel strength with plasma treatment time was

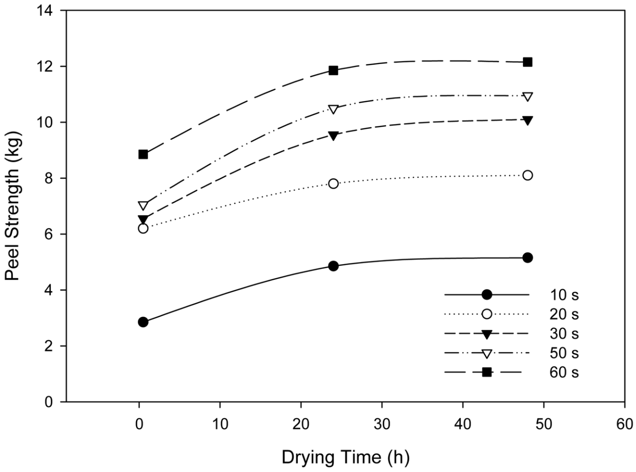


Fig. 1. Variation of peel strength of polyurethane coated leather with drying time for various plasma exposure times.

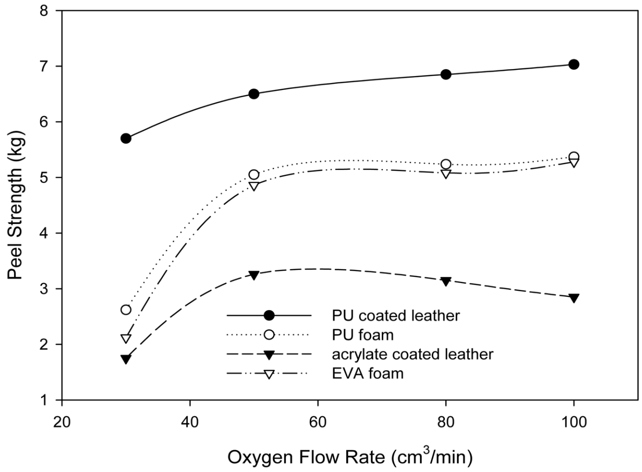


Fig. 3. Variation of peel strength of various materials with oxygen flow rate change.

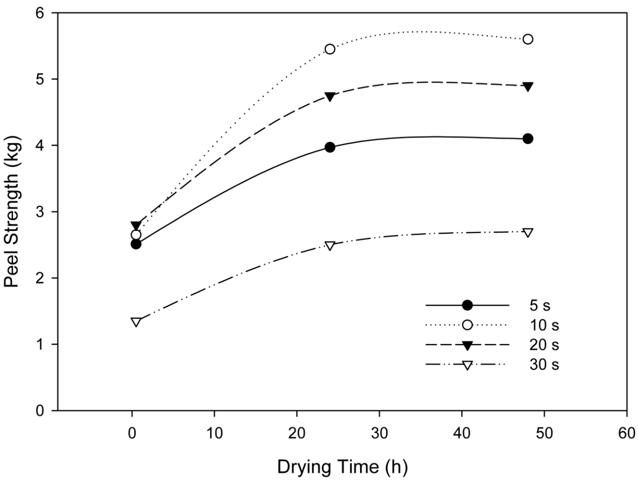


Fig. 2. Variation of peel strength of polyurethane foam leather with drying time for various plasma exposure time.

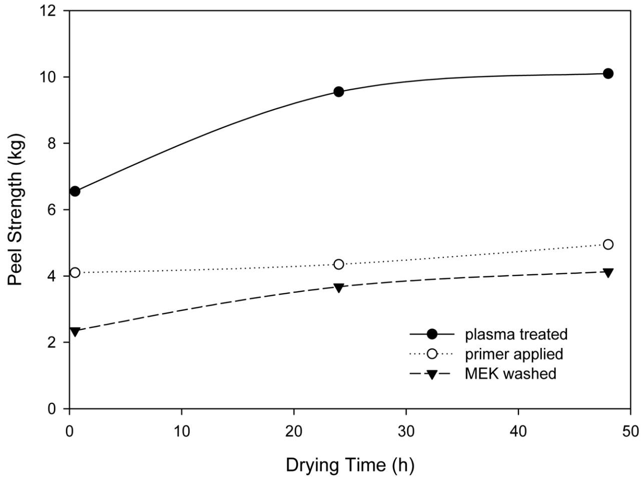


Fig. 4. Variation of peel strength of polyurethane coated leather with drying time for plasma treated and conventional techniques.

examined, and the outcome of polyurethane-coated leather (Dongho Leather Co., Korea) is shown in Fig. 1. For plasma treatment, oxygen with a flow rate of 0.05 liters per minute at standard condition was used as an environment. The effect of treatment time is demonstrated in the figure. The longer the treatment is, the stronger the adhesion. Although the strength of one day drying is higher than half an hour drying, longer drying for than one day does not increase the strength much. A similar experiment was conducted with urethane foam (Samsung Urethane Co., Korea) to illustrate the outcome in Fig. 2. Unlike the result of the leather, a treatment of 10 seconds gives the strongest adhesion. Because the area of adhesion is smaller than the leather due to its porous surface, the strength is lower. Also, the contact angle of the form is low enough not to be affected by the plasma treatment.

2. Effect of Environment Gas

The effect of gas flow rate during plasma treatment on peel strength for several materials is shown in Fig. 3. The treatment time was 30 seconds, and drying time was 30 minutes. Although polyurethane-coated leather exhibits the highest strength, increased oxygen flow gives higher strength, except acrylate-coated leather. However, the increase with raised flow rate is not significant with higher flow rate than 0.05 liters per minute.

3. Adhesion Comparison

The effect of plasma treatment compared with conventional pretreatment techniques, primer application and solvent cleaning is displayed in Fig. 4. When a primer (Nanopol Co., Korea, No. NF-320) is utilized before the adhesive is painted, slightly higher peel strength than methyl-ethyl ketone cleaned case is yielded. However, plasma-treated adhesion gives much higher strength in comparison with these two conventional adhesion pretreatments. The plasma treatment time was 30 seconds with 0.05 liters per minute of oxygen flow. It indicates that the surface modification from the plasma treatment is significant and effective to increase peel strength. The effect of drying time is similar in all three cases.

4. Measurement of Contact Angle

Surface energy is the true characteristic of a solid surface, but its measurement is difficult. Instead, wetting tension was measured for

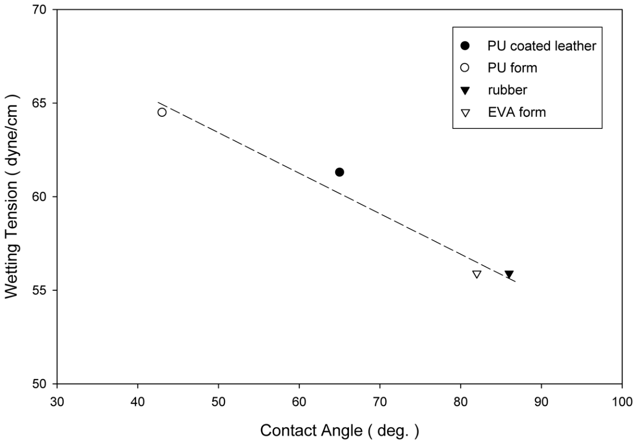


Fig. 5. Relationship between contact angle and wetting tension.

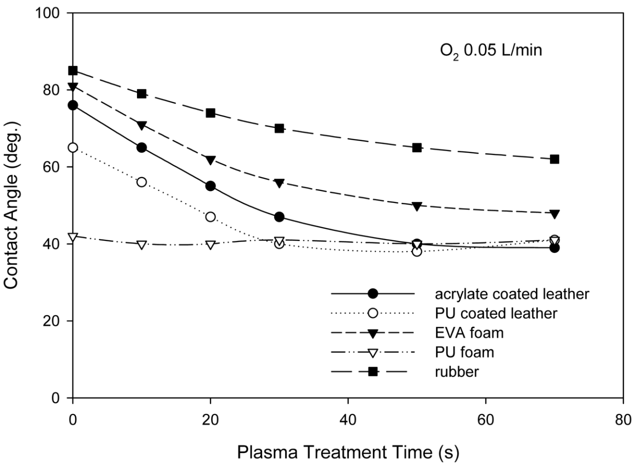


Fig. 6. Variation of contact angle of various materials with plasma treatment time change at oxygen flow rate of 0.05 L/min.

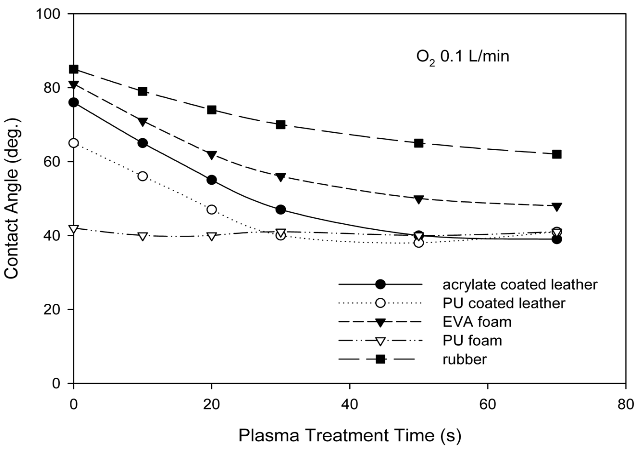


Fig. 7. Variation of contact angle of various materials with plasma treatment time change at oxygen flow rate of 0.1 L/min.

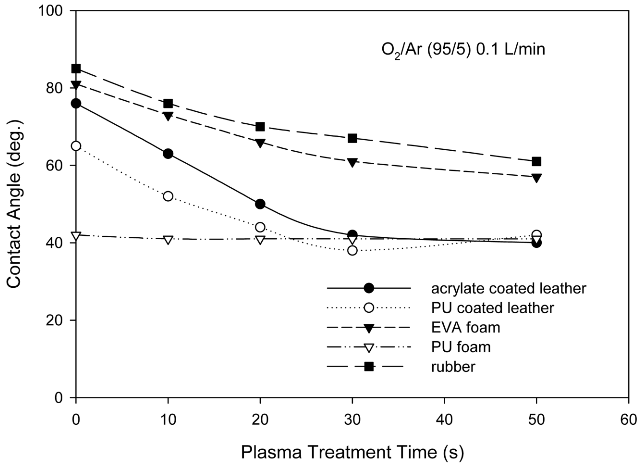
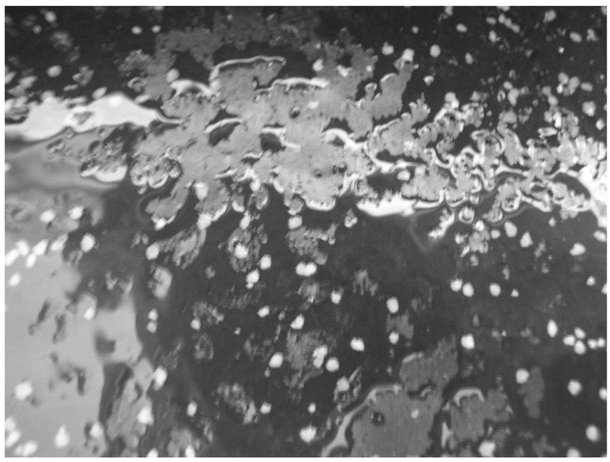


Fig. 8. Variation of contact angle of various materials with plasma treatment time change at oxygen and argon flow rate of 0.095 L/min and 0.005 L/min, respectively.



(a)

(b)

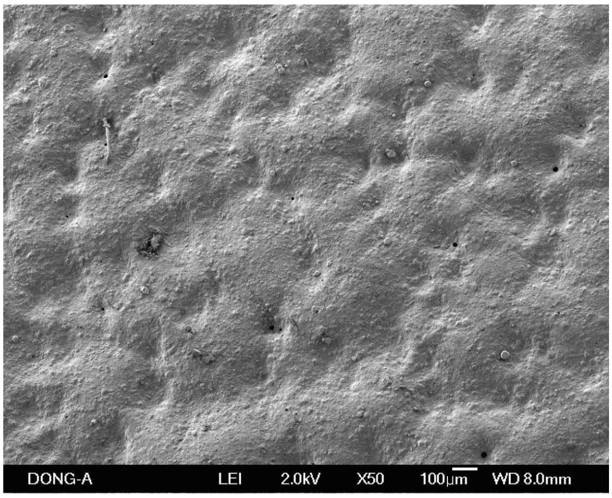
Fig. 9. Photographs of water drops on surfaces of rubber untreated (a) and plasma treated (b).

various materials by the testing method specified in ASTM D2578, and the outcome is compared with contact angle as shown in Fig. 5. Though the relation between the two is linear, the measurement of contact angle is easier than that of the wetting tension. Because the difference of surface characteristic is clearly illustrated with the contact angle, the angle is used for the indication of the surface characteristics here.

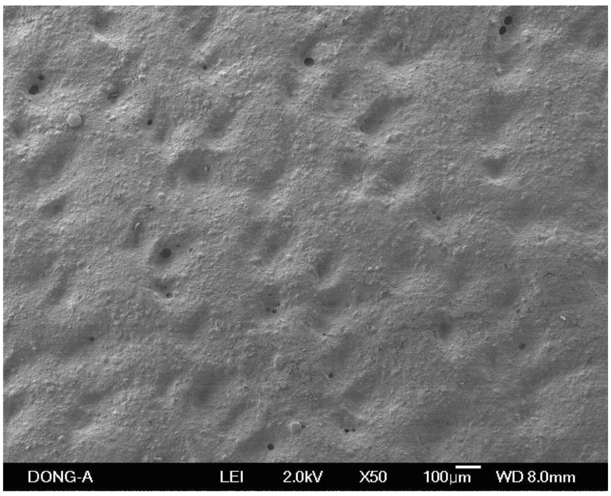
To examine the relation between adhesion and contact angle, the variations of contact angle with plasma treatment time for five different materials are plotted in Fig. 6. The contact angle of a water drop was measured with a contact angle meter (Erma Optical Works, Japan, model G-I-1000). In this case, oxygen flow is at the rate of 0.05 liters per minute. While natural rubber shows the largest contact angle with small change for longer treatment time, polyurethane foam has the lowest contact angle with almost no variation for different treatment time. Because untreated polyurethane foam has low contact angle due to its surface structure, the plasma treatment does not affect the angle. Polyurethane-coated leather, acrylate-coated leather and ethyl vinyl acetate (EVA) foam have similar reduction of contact angle with increased treatment time. In case of PU-coated leather the angle decrease is closely related with the elevated peel strength. As demonstrated in Fig. 2, PU foam does not have a linear relation between the treatment time and peel strength, and it is explained with the little change of contact angle for long plasma treatment time. In general, the reduction of contact angle raises surface wettability to strengthen adhesion. When more oxygen is supplied during the treatment, the variations of contact angle are given in Fig. 7. While natural rubber and PU foam are not affected from the increase, three other materials show rapid diminishment of contact angle due to enhanced plasma treatment with more oxygen environment. The introduction of argon to the oxygen environment blocks the reduction of contact angle for EVA foam, as illustrated in Fig. 8. Apparently, different combinations of plasma and treated material yield various surface reactions to result in different changes of contact angle.

5. Surface Observation

The reduction of contact angle is observed in Fig. 9 taken with a camera. The right figure shows no drops on the surface of plasma-treated rubber having low contact angle in comparison with the left one of water drop on untreated rubber surface of high contact angle. The small white specks in the photographs are tiny pinholes on rubber surface. The surface change from plasma treatment is observed with a scanning electron microscope (JEOL, Japan, model JSM-6700F) as given in Fig. 10. The plasma-treated surface of polyure-

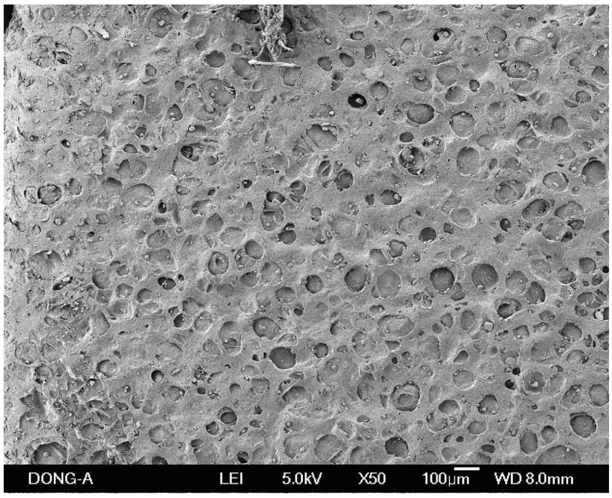


(a)

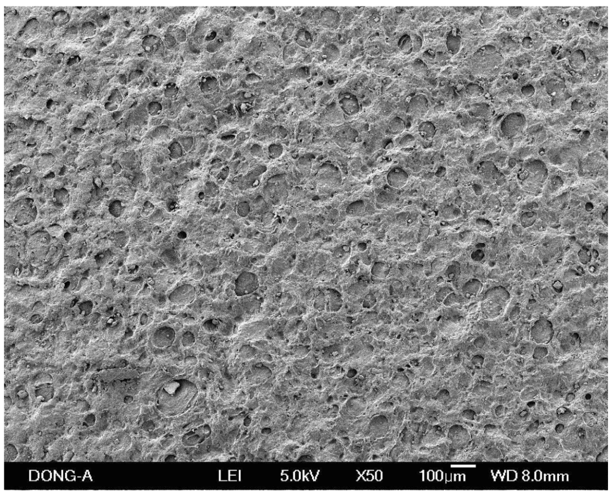


(b)

Fig. 10. SEM photographs of water drops on surfaces of polyurethane coated leather untreated (a) and plasma treated (b).



(a)



(b)

Fig. 11. SEM photographs of water drops on surfaces of EVA foam untreated (a) and plasma treated (b).

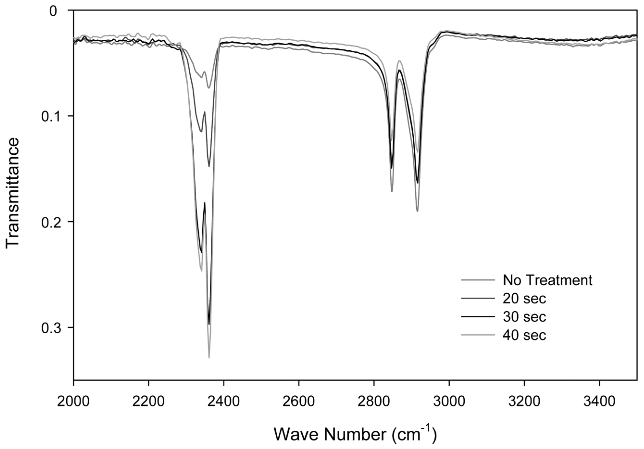


Fig. 12. FTIR-ATR spectra of acrylate coated leather with different amounts of plasma treatment.

thane coated leather is demonstrated in the right. When the figure is compared with the left of an untreated surface, it is known that the surface is smoothened by the plasma oxidation of rough surface material in oxygen environment. The surface change of EVA foam is observed in Fig. 11. The right figure of the treated surface has many grooves yielded from the plasma oxidation on the foam surface of the holes. The treatment exposes small holes covered with thin layer of thesurface of the untreated foam.

The modification of surface structure was examined with an FTIR spectrometer (BioRad Instruments, England, Model FTI 3000) having an attenuated total reflectance (ATR) accessory, and the outcome is shown in Fig. 12. Two peaks between the wave numbers of 2,850 cm^{-1} and 2,960 cm^{-1} representing methylene and methyl groups are decreased with the raised treatment time, while the peaks of the alkyne group between the wave numbers of 2,250 cm^{-1} and 2,400 cm^{-1} are increased. This indicates that the side chains of methylene and methyl groups are broken from surface molecules, leaving triply-bonded carbon chain molecules by the plasma treatment.

CONCLUSION

To raise the adhesion of polyurethane-coated leather and polyurethane foam, plasma treatment was conducted, and its performance was examined by measuring adhesion and contact angle. In addition, optical observation was made to investigate the surface change from the treatment. While a longer treatment time gives better performance for the polyurethane-coated leather, a ten second treatment yields the best for the polyurethane foam due to its low contact angle. Oxygen flow of 0.05 liters per minute is enough for the plasma treatment. The measured contact angle indicates that the plasma treatment reduces the angle to improve adhesion. Surface observation shows the surface change and wettability increase.

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