

高分子物質의 表面에너지 增加에 對한 새로운 理論.
 高分子物質의 코로나 放電處理가 알루미늄과의
 接着強度에 주는 影響

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Effect of Corona Treatment of Polymers on Bonds
 to Aluminum

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要 約. PE, PP 및 PVC 를 corona 放電으로 處理한 後 알루미늄과 接着을 시키면 接着強度가 크게 向上된다. 그러나 corona 放電으로 處理한 PE 와 PP 를 80°C 로 調節한 乾燥器에 넣고, PVC 는 50°C 로 調節한 乾燥器에 넣어 15分間 放置하면 corona 放電處理한 時에 比 接着力이 1/2 밖에 되지 않는다. 따라서 高分子物質을 corona 放電處理 했을 때 接着強度의 增加는 高分子物質의 酸化에 依한 것이라고만은 볼 수 없다. 接着強度의 심한 振幅은 Weibull 分布函數를 利用하여 檢討하였다. 이 研究에서는 corona 放電으로 처리한 高分子物質을 알루미늄과 接着시켰을 때 그 強度의 增加는 高分子物質의 表面에 附着된 electret 의 影響이 크다는 것을 나타내었다.

ABSTRACT. Corona treatment of PE, PP and PVC showed a dramatic increase of bond strength when lap joints were made between the polymers and aluminum plates. Heating the corona-treated PE and PP, and PVC in a drying oven at 80 and 50°C, respectively, for 15 min reduced the bond strength to about a half of that of corona-treated but unheated polymers, which indicated that the increase of bond strength was not due to oxidation of the polymer surface. The Weibull distribution function was employed to check reliability of the scattered data obtained from testing the lap joints. It is speculated that electret was deposited on the corona-treated polymer surface to enhance bond strength with aluminum.

INTRODUCTION

The printability and the adhesive properties of polyethylene (PE) are improved by treatment of the polymer sheet in a corona discharge.¹⁻³ The corona treatment changes the polymer surface both physically and chemically.^{1,3-5} The oxidation of the polymer surface by the corona treatment increases the surface energy and improves bonding capacity.^{1,6-7} Crosslinking of the molecules on a polymer surface by a corona treatment enhances the bond strength between polymers and metals with epoxy resin as an adhesive.⁸⁻⁹ It is noted that treatment of PE in a nitrogen corona increases the surface energy with little morphologic or chemical change on the polymer surface.¹⁰ The bonding capacity of PE is reduced with time of standing after the corona treatment and the decaying rate increases when the treated specimen is either heated or placed in vacuum prior to bonding¹¹. The suggestion was that a type of electret formation is the basic reason for the increase of surface energy as well as bonding capacity.

The purpose of the present work was to support the proposition that an increase in bonding capacity of polymers with a corona treatment was attributed to deposition of electret on the polymer surface. Polymers were treated in a corona discharge and made of lap joints with aluminum plates using epoxy resin, with and without heat treatment after the corona treatment. The bond strengths were measured and compared for the effect of heat treatment after corona treatment. Oxidation of polymer surface by corona treatment as well as heat treatment was characterized by multiple internal reflection (MIR) infrared analysis. The scattered results of adhesive strength were examined statistically by using the Weibull distribution function¹².

EXPERIMENTAL

The polymer films used were purchased locally and the description is given in *Table 1*.

PE and PP were washed with acetone and rinsed with distilled water, and then air dried. PVC was washed with methanol instead of acetone.

Corona treatment was applied in the flat plate device described in a previous report,³ although the treatment was carried out in air. The power supply was a 1500 V, 60 Hz neon lamp transformer. Small pieces of glass plate with thickness of 2 mm were used for the gap between electrodes.

After the corona treatment, some samples of PE and PP were kept in an oven at 80°C for 15 min for heat treatment while those of PVC were at 50°C.

Infrared spectra of films were obtained on a Perkin Elmer IR-521 spectrophotometer with a Perkin Elmer 189-0382 single-beam multiple internal reflection attachment unit with a KRS-5 reflector. The angle of incidence beam was 45 degrees and scanning speed was 100 cm⁻¹/min.

Bonding and Testing of Specimens.

The aluminum plates were cut into coupons, 17.4 cm × 2.5 cm, and polished with 300-mesh sand paper. Prior to bonding, the coupons received a surface treatment consisting of wash with soap, benzene-chloroform wipe, and distilled-water rinse, followed by oven-drying at 80°C for 30

Table 1. Description of polymer films.

Polymer	Type	Thickness (mm)	Description
Polyethylene	Wool Chem. Co.	0.02	low density
Polypropylene (PP)	Wool Chem. Co.	0.02	
Poly (vinyl chloride) (PVC)	Wool Chem. Co.	0.02	unplasticized

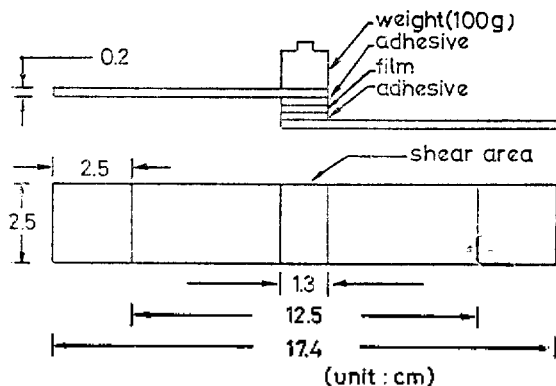


Fig. 1. Lap joint of test specimen.

min. The coupons were, as shown in Fig. 1, overlapped by 1.3 cm and pressed under a load of 100 g for 24 hr at 40°C. The adhesive was a two-component epoxy system of Cemedine Co. The bonded specimens were then loaded to failure on an Instron TMS with a head speed of 0.5 cm/min.

RESULTS AND DISCUSSION

The bond strength between aluminum and PE rapidly increases after a few seconds of corona treatment and reaches a plateau value in six sec as shown in Fig. 2(A). It has been reported that treatment of PE in an electrical discharge improved bonding due to oxidation of the surface.¹⁻³ As shown in Fig. 3, MIR infrared analysis of surface treated in an air corona gave the absorption of $-C=O$ group at 1720 cm^{-1} . It might be conceivable that the inert surface of PE was oxidized by the corona treatment to improve the bond strength and the heat treatment furthered oxidation to give the stronger bond strength.

However, the bond strength with the heat-treated PE after the corona treatment reveals a considerable decrease as shown in Fig 2(B). It was pointed out that treatment of PE with ozone oxidized the polymer surface but failed to improve bonding capacity at a lower bonding

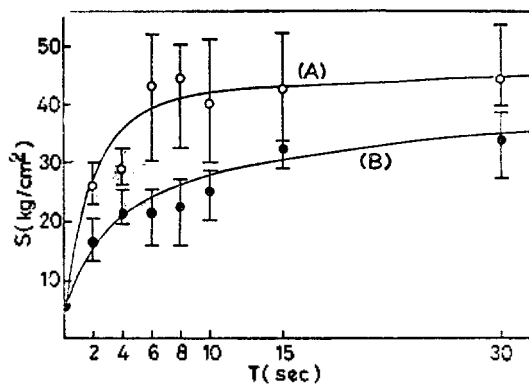


Fig. 2. Variation of bond strength with time of corona treatment of PE; (A) corona treatment only; (B) heat treatment at 80°C for 15 min after corona treatment.

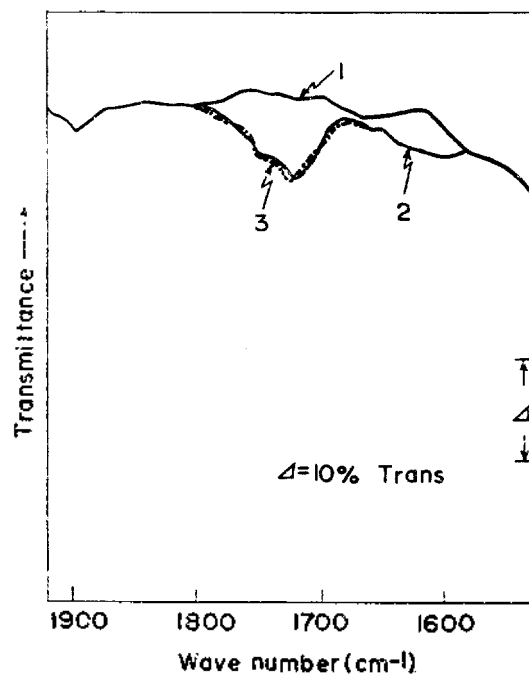


Fig. 3. MIR infrared spectra of (1) control; (2) 6-second treatment in a corona discharge; (3) heat treatment after corona treatment.

temperature. The surface oxidation of PE is important for an increase in bonding capacity or printability, as is seen in Fig. 2(B), where the heat-treated PE after the corona treatment still made a stronger bond than the untreated. The

oxidation, however, fails to explain the much higher bond strength with the corona-treated PE.

The surface layer of PE after a corona treatment may degrade of the heat treatment. Bikerman reported that polymer with a degraded surface made a poor adhesion¹³. A decrease in bonding capacity after heat treatment might be expected if the degraded molecules reside on the surface. However, the height of the infrared absorption peak at 1720 cm^{-1} changes little with the heat treatment in the present work. A vigorous treatment of PE in the oxygen corona at 50°C caused a negligible weight loss in 10 min.¹⁰ Dipping the corona-treated PE in a liquid such as ethanol, acetone, or carbon tetrachloride in order to remove some degraded molecules resulted in little change in bonding capacity.³ It is unlikely that the decrease in bond strength after the heat treatment is due to the surface degradation, because the treatment causes no degradation by autooxidation or by chain scission, and, even though the surface degrades, the bonding capacity decreases insignificantly.

It was considered possible that the bond strength was enhanced by crosslinking a polymer.^{8,9} However, experiments previously reported showed that no measurable gel component was produced even after hours of corona treatment in oxygen or air.¹⁰ It is hardly expected in the present work that the degree of crosslinking is noticeable in six sec of the treatment. Thus, it seems unlikely that the increase in bond strength is related to crosslinking of the polymer.

Wetting adherend with adhesive is a fundamental step for bonding and the adherend must have a higher surface energy than the adhesive for a good result¹⁴. The corona treatment of PE in air increases the surface tension from 31 to 44 dynes/cm, the plateau value, in 15 sec.¹⁰

In the present work, the bond strength after the corona treatment reaches the plateau value in six sec while the plateau value after the heat treatment takes 15 sec. The surface energy of PE definitely increases with the corona treatment to result in a good bonding (*Fig. 2(A)*), but the surface energy hardly decreases by heating the specimen in an oven to show poor bonding (*Fig. 2(B)*). In the previous work, oxidation of PE by ozone increases the surface energy but the bonding capacity showed a different trend¹¹. Thus, wetting tension is poorly correlated with bond strength.

It is confirmed in this series of work that the bond strength is increased by treatment of PE in a corona discharge but the increase failed to be correlated with oxidation, crosslinking, degradation or surface tension.

The previous work suggested that a type of electret formation on the PE surface is the basic reason for the increase in the autohesion of the polymer when treated in a corona discharge.¹¹

Electret is fairly stable at an ambient condition but is lost easily in vacuum or by heating.¹⁵⁻¹⁸ The rapid increase of the bond strength by the corona treatment and the drop in the strength by the heat treatment, as given in the present work, add further grounds for a proof of the effect of the electret on bonding. A quantitative correlation is definitely needed to support more strongly the electret effect on bonding.

The adhesive bond strength generally scatters, as is in the present work, and thereby the strength becomes a statistical quantity that was defined by the Weibull distribution function,¹² used in the form

$$\log \cdot \log \left(\frac{1}{1-F(x)} \right) = -\log \alpha + \beta \log(x-\gamma) \quad (1)$$

where $F(x)$ is the fraction of samples with bond strength of x or less, while α , β and γ

are the parameters of the function.^{19,20}

A plot of $\log \log \left(\frac{1}{1-F(x)} \right)$ versus $\log(x-\gamma)$ should give a straight line if γ , the location parameter, is properly selected. α , the scale parameter, is the intercept on the ordinate, and β , the shape parameter, is the slope of the line.

Fig. 4 shows linear Weibull distribution plots according to Eq. (1) if all data points obtained by the corona treatment of 6 sec or longer are tabulated in order of increasing bond strength. In the present work, taking $\gamma=0$ and hence using a two-parameter Weibull distribution appears to be acceptable. The correlation coefficient is given in Table 2 and the distribution satisfactorily describes the data over the time interval. It is also noted that the bond strength with PE after the corona treatment is much stronger than that obtained with the heat treatment of the corona-treated PE.

The corona treatment of PP and PVC is very effective for an increase of the bond strength as shown in Fig. 5 and 6. It is remarkable that the 2-sec treatment in the corona discharge enhances the bond strength by almost 40

times for PP and about 6 times for PVC. Oxidation definitely occurs on the polymer surfaces by the corona treatment, but it fails to

Table 2. Correlation coefficients for Linear Weibull distribution plots.

Polymer	Corona-treated	Heat-treated
PE	0.961	0.960
PP	0.989	0.981
PVC	0.986	0.973

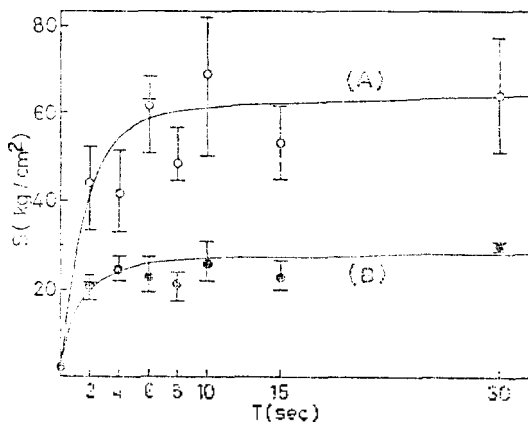


Fig. 5. Variation of bond strength with time of corona treatment of PP; (A) corona treatment; (B) heat treatment at 80°C for 15 min after corona treatment.

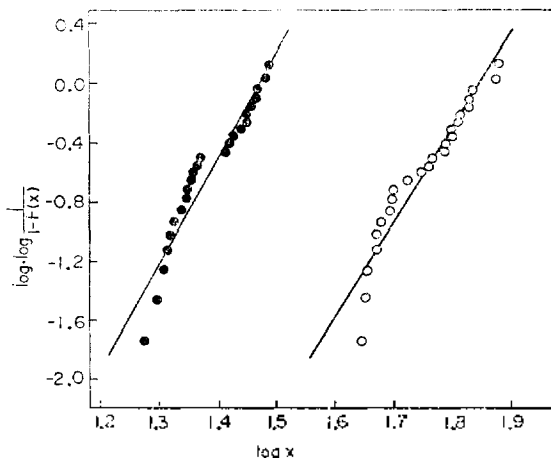


Fig. 4. Linear Weibull distribution plots for (○) corona treatment of PE and (●) heat treatment after corona treatment.

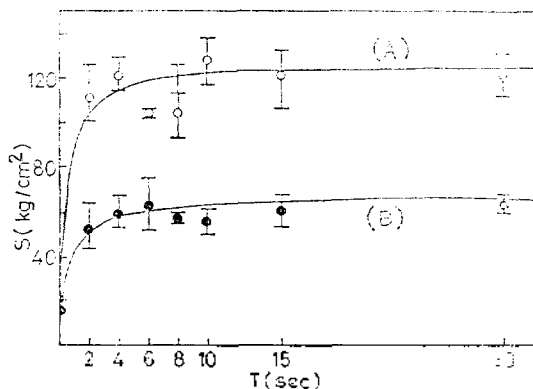


Fig. 6. Variation of bond strength with time of corona treatment of PVC; (A) corona treatment (B); heat treatment at 50°C for 15 min after corona treatment

be the reason for an increase in bond strength because the heat treatment only accelerates the oxidation but renders a damaging effect on the bond strength. The heat treatment might cause of the surface degradation on the PP or PVC surface and lower the bonding capacity. If degradation on the polymer surfaces is an important factor for a decrease in bond strength, the strength with 30-sec heat treatment should be lower than that with 2-sec heat treatment. In addition, if the surface degrades so fast, the bond strength after the corona treatment of 30 sec hardly remains the same as that of 2-sec treatment. It seems apparent that oxidation or degradation could only be a minor factor for a great increase in the bond strength after the corona treatment.

The Weibull distribution plots according to Eq. (1) are linear for both PP and PVC with taking $\gamma=0$ as shown in Fig. 7 and 8. It is noticed that the bond strength with PP and PVC after the corona treatment reaches the plateau values in 6 sec and 2 sec respectively.

The results are indicative of the minor effect of oxidation or degradation by the heat treat-

ment on the bond strength, and lead to the speculation that the remarkable increase in the bond strength after the corona treatment of a few seconds and the significant drop of the strength after the heat treatment are correlated very well with the properties of electret.

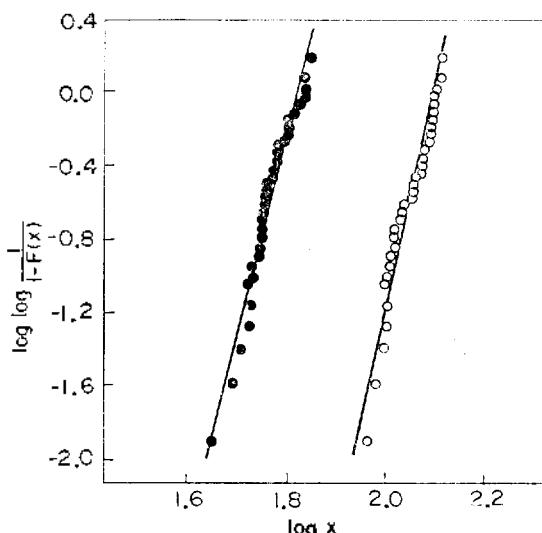


Fig. 8 Linear Weibull distribution plots for (○) corona treatment of PVC and (●) heat treatment after corona treatment.

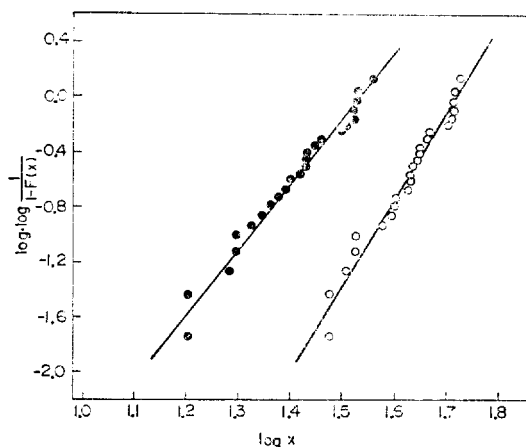


Fig. 7. Linear Weibull distribution plots for (○) corona treatment of PP and (●) heat treatment after corona treatment.

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