

Corona-Induced Autohesion of Polyethylene

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Synopsis

If a low-density polyethylene sheet is treated in a corona discharge and subsequently pressed to a similarly treated sheet at 45°C, the bond formed is much stronger than that between similarly pressed but untreated sheets. Several series of observations have indicated that this enhanced autohesion is not due to surface oxidation or to surface crosslinking (CASING). Evidence is presented that the effect may be related to some type of electret formation induced in the polymer sheet by the corona discharge.

INTRODUCTION

In spite of its widespread use in industry, the principles underlying the corona treatment of polymer surfaces are not yet understood. As described in previous reports,^{1,2} corona treatment considerably enhanced the adhesion of several synthetic polymers to cellulose and to wood. The effect was found when the treatment was carried out not only in air or oxygen but also in pure nitrogen, even though treatment in nitrogen produced little morphologic or chemical change in the surface of the polymer. During this work it was discovered that if two strips from a polymer sheet were pressed together at a temperature lower than the softening temperature, a strong bond resulted when the polymer had been pretreated in the corona discharge. Apparently, corona treatment markedly enhanced the autohesion of the polymer surface.

Corona-induced autohesion seemed to be a fruitful area for further investigation. The use of a single substrate simplified the system considerably, particularly if a relatively uncomplicated polymer such as polyethylene (PE) were studied. Thus the purpose of the present work was to elucidate the effect of a corona discharge on polymer surfaces by measurement of the autohesion of PE after treatment under different conditions. Corona treatment was carried out in a variety of gases and the effect of temperature was investigated. Measurements were also made of water contact angle and wetting tension. In addition, chemical changes in the surface were characterized by infrared analysis.

EXPERIMENTAL

Extruded PE sheet of 0.031-in. thickness was used for measurement of autohesion, wetting tension, and contact angle. The resin was Dow

Chemical C.I.L. 220G and had a density of 0.919 g/ml and a melt index of 1.9. The sample was used without pretreatment. For infrared study, 0.002-in.-thick low-density PE film was used.

Description of the corona apparatus, purification of the gases, and methods of MIR infrared analysis used are given in a previous report.³

Some experiments were made in which the PE sheet was treated not in the corona itself but with gases generated in the discharge. For this purpose, a conventional laboratory ozonizer was used and its effluent was passed over strips of PE which were spinning rapidly in a small reactor chamber. The spin reactor has been described in a previous report.⁴

For the measurement of autohesion, the PE sheet was cut into strips, 20 mm \times 5 mm, immediately after the corona treatment. The strips were overlapped by 5 mm and pressed for 2 min at a pressure of 5.7 kg/cm² and at 45°C. The laminate was then broken using a Chatillon spring tester.

A telescopic goniometer was used for the measurement of the contact angle of a sessile drop of water with the PE surface. The water used was distilled, passed through ion-exchange resin, and then, after treatment with a solution of KMnO₄ and NaOH, was obtained by reflux distillation. Surface tension of the water measured with a Wilhelmy-type glass plate⁵ was 72.2 dynes/cm at 24°C.

The wetting tension of the PE surface was measured by application of mixtures of formamide and ethyl Cellosolve according to the ASTM-D 2578-67 procedure. The wetting tension, γ_c , was found to be related empirically to the water contact angle θ by

$$\gamma_c = A + B \cos \theta \quad (1)$$

where the value of A is 32 dynes/cm and that of B is 21 dynes/cm. In the results reported, θ was measured and γ_c was calculated by means of eq. (1).

RESULTS

The increase in autohesion of PE with time of treatment in several gases is shown in Figure 1. In air, the bond strength rapidly increases to a plateau value of about 13 kg/cm². A similar effect is obtained for treatment in oxygen, CO₂ and nitrogen containing 31% water vapor. As shown in Figure 2, infrared analysis of PE film treated in air shows the well-known —C=O absorption in the vicinity of 1720 cm⁻¹. Similar spectra were obtained after treatment in the other oxygen-containing gases, which suggests that molecules such as CO₂ or H₂O are rapidly decomposed in the corona to yield the active species responsible for oxidation of the surface. In Figure 3, wetting tension is plotted against time of treatment in various gases. In all the oxygen-containing gases, the wetting tension increases rapidly to a plateau value. There is no increase in adhesion or wetting tension after treatment in hydrogen.

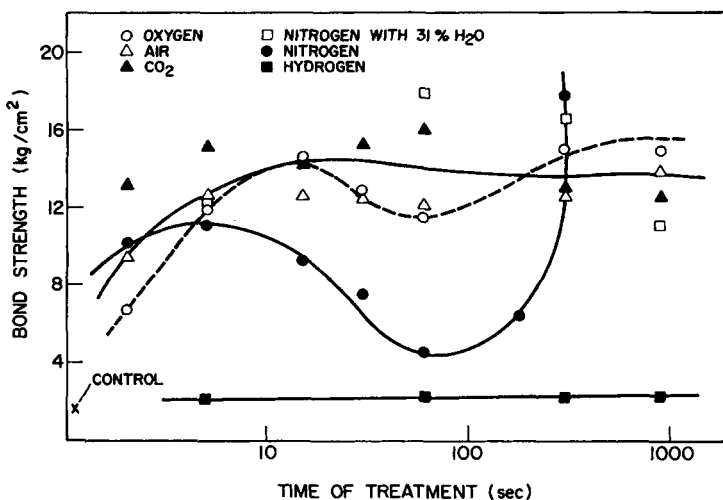


Fig. 1. Variation of bond strength with time of treatment of PE treated in corona discharges of various gases.

Taken on their own, these results suggest that the cause of adhesion is oxidation of the surface, with a corresponding increase in the wetting tension. Many papers have been published in which this concept is prevalent. Both Rossmann⁶ and Hines⁷ concluded that treatment of PE sheet in an electrical discharge improved bonding by oxidation of the surface. Arbit and co-workers⁸ found that both the degree of oxidation as measured by infrared absorption and the adhesion were linearly related to the extrusion compound temperature in the melt coating of paper with PE. Goring and Suranyi⁴ found that when polymer and cellulose sheets were treated in the gaseous effluent from an oxygen corona, both the polymer/cellulose adhesion and the oxidation of the surfaces were enhanced. Several authors⁹⁻¹² have shown that an increase in wettability is correlated with an increase in adhesion.

The results obtained after corona treatment in nitrogen do not fit into the above picture. As shown in Figure 1, a rapid increase in autohesion is produced in the first few seconds. Longer treatment causes the bond strength to decrease to a minimum which is followed by a further increase. It is interesting to note that treatment in oxygen gives a similar but shallower minimum as shown by the dotted line in Figure 1. No trace of oxidation or of double-bond formation could be detected in the nitrogen-treated samples by infrared analysis (Fig. 2). A comparison of Figure 1 and Figure 3 shows that the correlation between wetting tension and bond strength fails for short times of treatment in nitrogen; only for comparatively long times of treatment does the wetting tension increase.

Noncorrelation of adhesion with wetting tension is also shown by a comparison of the results for treatment in air at 25°C and at 75°C. For short times of treatment, there is a marked increase in bond strength at

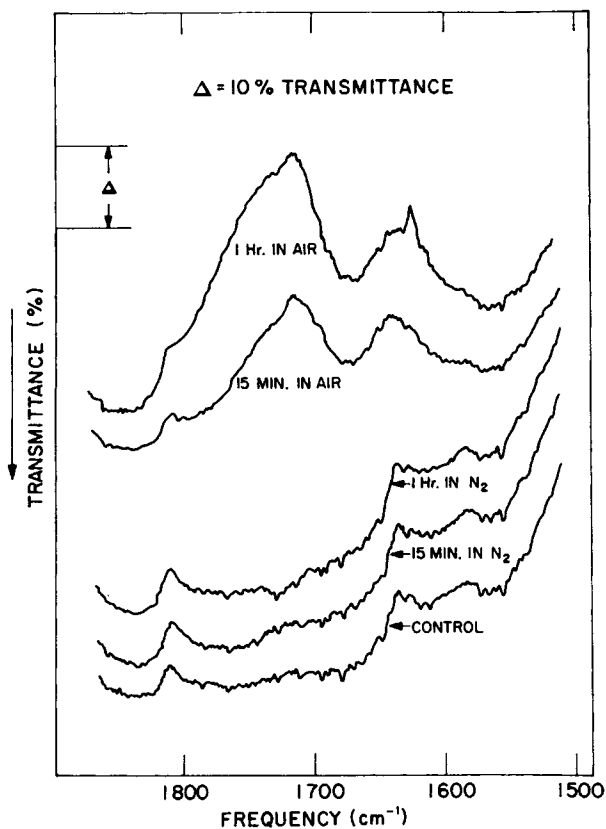


Fig. 2. Infrared absorption in the region 1500–1800 cm⁻¹ of PE films of untreated control and after 15-min and 1-hr treatment in corona discharges of air and nitrogen.

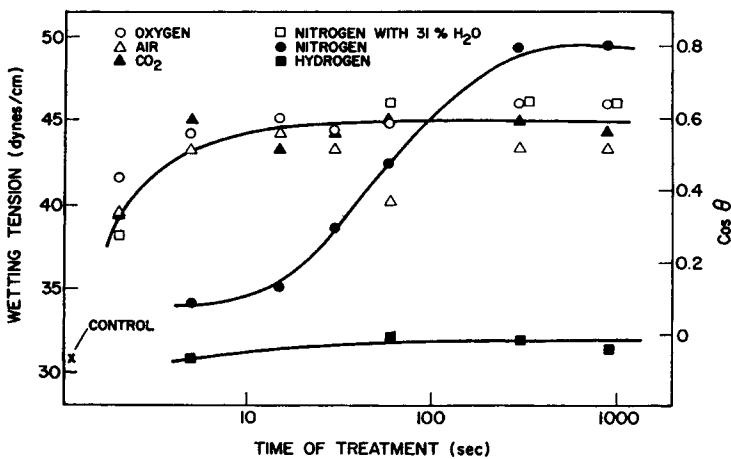


Fig. 3. Changes of wetting tension and water contact angle with time of treatment of PE surfaces treated in corona discharges of various gases.

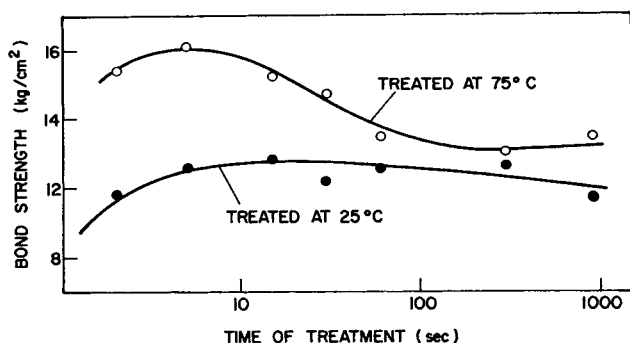


Fig. 4. Variation of bond strength with time of treatment of PE surfaces treated in air corona at different temperatures.

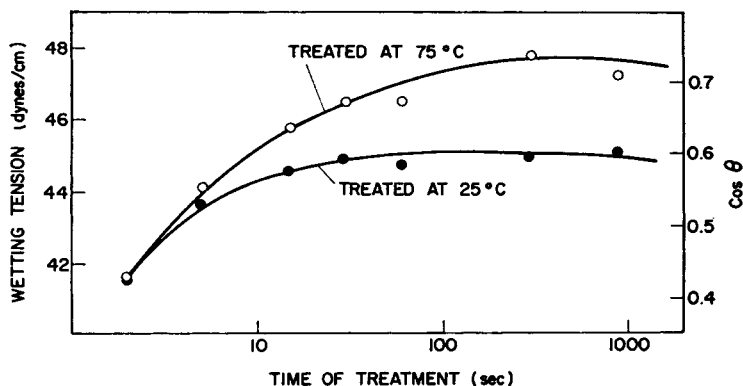


Fig. 5. Changes of wetting tension and water contact angle with time of treatment of PE surfaces treated in air corona at different temperatures.

higher temperature (Fig. 4). However, for longer times, the high-temperature treatment causes a decrease in bond strength. In contrast, the wetting tension is not very sensitive to temperature at short times of treatment but shows a big difference for longer times of treatment (Fig. 5). It is interesting to note that the decrease in bonding for long treatment times at high temperature was noted previously in the corona-induced adhesion of plastics to wood.² Also, surface degradation (as measured by the weight of material removed when the corona-treated sheet is dipped into solvents) increases with the time and temperature of treatment.³ Thus, the decrease in bonding for treatment in air at higher temperatures and longer times may be due to the formation of a weak boundary layer by excessive degradation of the surface.

Figure 6 shows that increase of bond strength with temperature of pressing is rather small for untreated PE between pressing temperatures of 25° and 90°C. Only near the softening temperature at 100°C does autohesion become pronounced. Corona treatment in air produced marked increase in bonding at all temperatures and resulted in a comparatively small de-

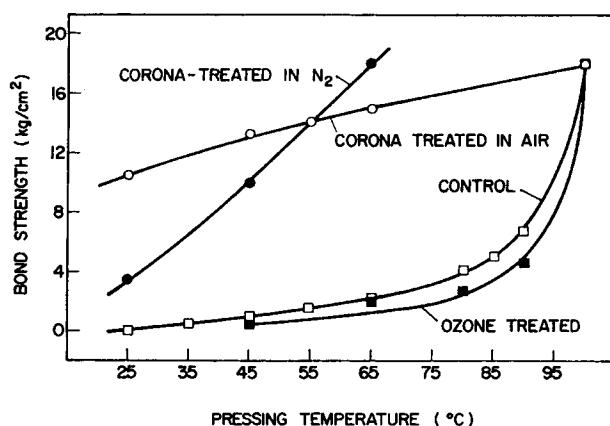


Fig. 6. Effect of pressing temperature on autohesion of PE after corona treatment in air and nitrogen and ozone treatment.

pendence of the bond on the temperature of pressing. Treatment in nitrogen also produced an increase in bonding at all pressing temperatures, but the dependence on temperature was considerably greater than in the case of the treatment in air.

Of particular significance in Figure 6 is the negligible effect of treating the polymer surface in the gaseous effluent from the corona. That such treatment is effective in oxidizing the surface is shown by the IR data in Figure 7. Apparently, oxidation outside of the corona does not enhance the autohesion of PE. However, the wetting tension of the extracorona-oxidized surface was found to be 44 dynes/cm after 30-min treatment, in good agreement with the plateau value obtained by corona treatment in oxygen-containing gases (Fig. 3)! Thus, neither surface oxidation nor increase in surface energy can be the cause of the observed corona-induced autohesion of PE.

It was considered possible that the enhanced bond strength could be due to the strengthening of the surface layer by crosslinking, as proposed by Schonhorn and co-workers.¹³⁻¹⁵ However, experiments previously reported³ showed that no measurable gel component was produced even after hours of treatment in oxygen, air, or nitrogen. Thus, it seems unlikely that the observed increase in autohesion is related to the CASING effect.¹³⁻¹⁵

If free radicals are produced on the surface by the corona discharge, inter-surface covalent bonds might be formed when the treated sheets are pressed together. This could be a factor in increasing the autohesion. However, Wilson has estimated that the lifetimes of free radicals such as $R\cdot$ and $ROO\cdot$ at room temperature in air are 10^{-8} sec and 10^{-2} sec, respectively,¹⁶ which are considerably shorter than the time required to make a bond by pressing. In the present work, extensive studies with ESR gave no evidence of free radicals. The production of peroxide groups is an intermediate step in the mechanism of oxidation of a polymer.^{17,18} An increase in autohesion

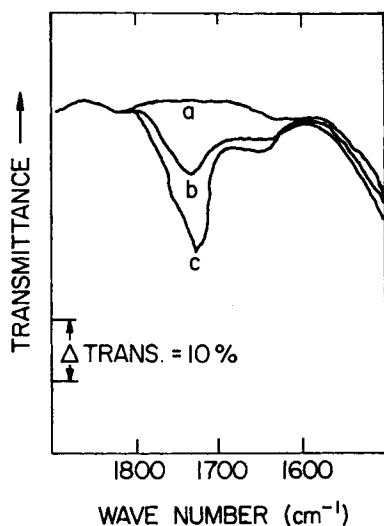


Fig. 7. MIR infrared spectra of PE: (a) control or film treated in nitrogen for 30 min; (b) film treated in oxygen for 20 sec at 25°C; (c) film treated in an ozone spin reactor for 30 min.

might be expected if the peroxides were decomposed by heat in the pressing operation and thereby produced intersurface covalent bonds. Peroxide is known to react quantitatively with SO_2 gas to give sulfate groups¹⁹ which presumably would be stable under the mild conditions of pressing. The bond strength was not reduced after exposure of the treated sample to SO_2 gas, which suggests that the formation of peroxides is not the cause of the corona-induced autohesion.

A further possibility was that the enhanced autohesion was due to roughening or etching of the polymer surface by the corona treatment. As shown in a previous report,³ surface roughening occurs during treatment in air or oxygen but not in nitrogen, even though strong bonds are produced by treatment in nitrogen. In the previous work,³ treatment in oxygen was shown to produce an oxidized degradation product of low molecular weight on the surface. It is possible that this material could act as a glue in sticking the surfaces together. However, when the degradation products were removed by dipping the treated sample in a liquid such as ethanol, acetone, or CCl_4 , no change in bond strength was found.

DISCUSSION

The observations described in the preceding section do not permit an unambiguous explanation of the corona-induced autohesion. However, they do provide a basis for speculation as to the cause of the effect. Perhaps we should start speculating first in a negative fashion. The results suggest that the autohesion obtained in the present investigation is not due to (a) surface oxidation, (b) increase in surface energy. (c) production of

free radicals, (d) surface roughening, (e) surface degradation or (f) surface crosslinking (CASING).

What then is left?

It has occurred to us that the autohesion may be due to changes in the electrical properties of the surface induced by the corona discharge. When dielectric materials are subjected to strong d.c. fields, long-lived electrical charges are induced in the dielectric. This is known as the electret effect.²⁰ In a d.c. field, the induced polarization of the dielectric produces a heterocharge (surface charge opposite to that of the adjacent electrode) which decays when the field is removed.²¹ However, when a discharge takes place in the electrode/dielectric gap, a homocharge (surface charge similar to that of adjacent electrode) is also produced.²¹ Homocharges are relatively permanent, sometimes having half-lives of many years at room temperature.²² Foil electrets produced by exposure of polymer film to d.c. fields have been used in condenser microphones.²² It may be argued that a homocharge cannot be induced on the polymer surface by the 60-Hz a.c. used in the present work. However, Thomas²³ has shown that charge

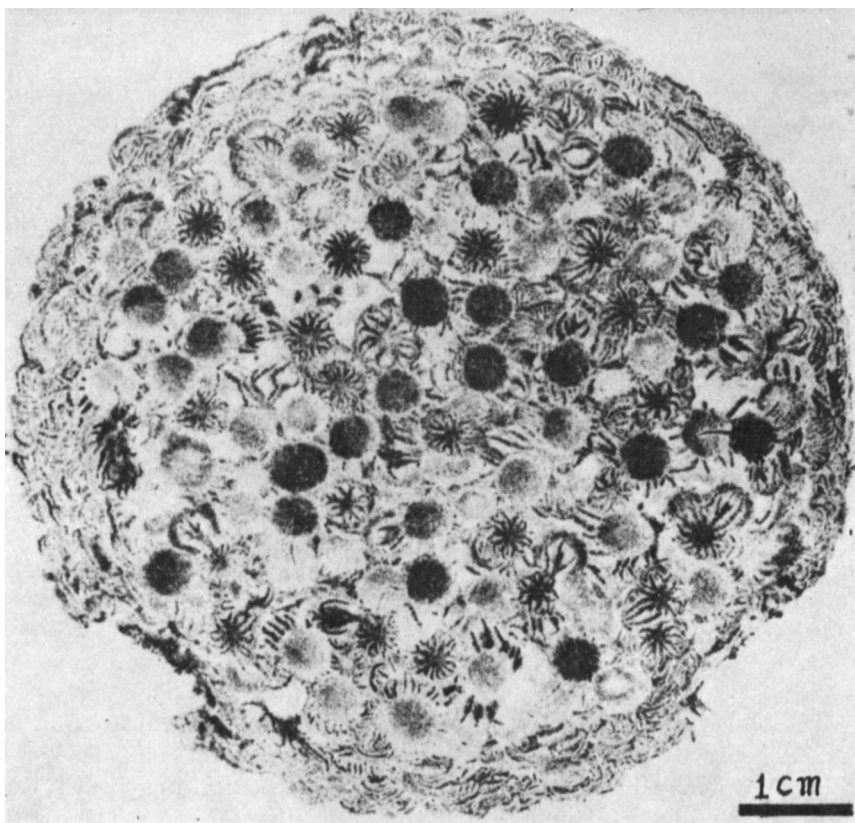


Fig. 8. Lichtenberg dust figure with jeweler's rouge after corona treatment in air of less than 1 sec

effects produced by one cycle are not completely neutralized by the subsequent cycle, and a discrete charge pattern is built up on the surface by application of an a.c. field. The charge pattern can be detected by spreading a light dielectric powder on the surface of the dielectric. Such patterns are called "Lichtenberg figures" after the man who discovered them. In the present work, Lichtenberg figures have been developed on PE surfaces treated in air, oxygen, or nitrogen coronas. An example is shown in Figure 8.

Surface charge due to electret formation is known to decay slowly with time.^{20,21} Also, the decay is faster at elevated temperatures.^{22,24,25} Autohesion versus time of standing is plotted in Figures 9 and 10 for treatment in oxygen and nitrogen, respectively. In both cases, there is a decrease in bonding with time of standing. The results in Figures 9 and 10 show that the decay is slower after longer treatment times and is more rapid in nitrogen than in oxygen. If, after treatment, the samples are stored at an elevated temperature, a much more rapid decay in bonding is found. This parallel between the known properties of electrets and the adhesion be-

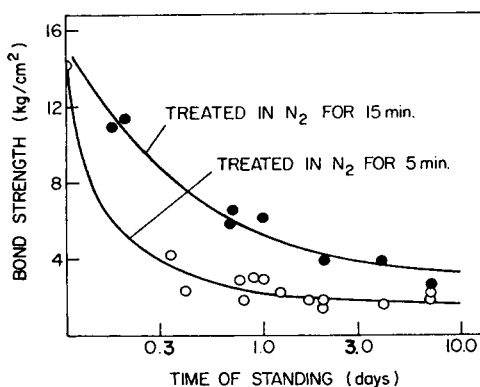


Fig. 9. Effect of standing on autohesion after nitrogen corona treatment.

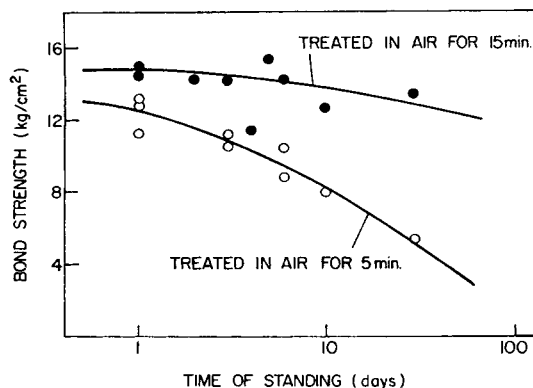


Fig. 10. Effect of standing on autohesion after air corona treatment.

havior of corona-treated PE is further support for the idea that the autohesion and electret formation are related.

It is not envisaged that bonding is established by simple coulombic attraction. Perhaps, the charged matrix produced on the surface lowers the softening temperature and thereby enhances the interdiffusion of the polymer molecules when the surfaces are pressed together. The observed differences between the behavior of surfaces treated in nitrogen and in the oxygen-containing gases may be due to the different electrical conditions in their respective coronas.

CONCLUDING REMARKS

The results have led to the suggestion that a type of electret formation is the basic reason for the increase in the autohesion of PE when treated in a corona discharge. Further work is required to show whether this proposition is true or false, and, if true, what is the mechanism by which the electret is formed and the adhesion is increased.

We would like to emphasize that this is not meant to be a universally applicable explanation for the adhesion behavior of polymers treated in discharges. It is likely that for the strong bonds formed when adhesives such as epoxies are applied to polymers pretreated in a radiofrequency discharge, the CASING mechanism is operative.^{13-15,26} Also, oxidation of polymer surfaces has been shown to increase their bondability to metals^{27,28} and to cellulose.⁴ However, from several conversations with industrial users of the corona discharge, we have learned that the printability of a PE sheet decays with time of standing after treatment. Perhaps the electret effect is responsible for the enhanced printability of PE achieved by treatment in a corona discharge.

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