

## Mechanism of Corona-Induced Self-Adhesion of Polyethylene Film

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### Synopsis

Corona-treated polyethylene films have been reported to exhibit strong self-adhesion when joined together under conditions of heat and pressure that give no adhesion with untreated films. The present study of this effect has shown that the adhesion is completely destroyed by the application of any hydrogen-bonding liquid to the adhesive joint and that the effects of liquids is completely reversible. Joints allowed to dry recover full strength. These facts together with the results of chemical reactions conducted on the treated film surface have established that the adhesive bond is a hydrogen bond. Corona treatment forms keto groups on the polyethylene chain; these groups enolize and the enolic hydrogens bond with carbonyl groups in the adjacent sheet of film when two sheets are heated together under pressure.

### INTRODUCTION

Kim, Evans, and Goring<sup>1</sup> have reported that corona-treated polyethylene (PE) exhibits enhanced adhesion to itself when joined together under heat and pressure. Untreated PE showed no self-adhesion under the same conditions of joining. They reported a strong carbonyl absorption band in the IR spectrum of corona-treated PE. These workers considered and rejected several mechanisms to explain the enhanced self-adhesion in favor of a vague and physically unacceptable theory involving electret formation. Carbonyl formation was also reported by Cooper and Prober,<sup>2</sup> who determined that 60% of the carbonyl groups in corona-treated PE were due to ketones and 40% to carboxylic acids.

The work to be reported here will show that the force of adhesion between corona-treated PE films is a hydrogen bond between the hydrogens of enolized keto groups in one sheet of film and carbonyl groups in the other.

### EXPERIMENTAL

Du Pont laminating-grade PE film was used in these experiments. The film was 0.002 in. thick and had a density of 0.926 and a melt index of 1.9. It contained 90 ppm of fatty amide lubricants and 200 ppm of antioxidant derived from *t*-butylphenol.

The film was treated on a commercial corona-treating machine in which it passed over a moving, water-cooled, grounded metal roll above which was

a bar electrode spanning the width of the film. The gap between the electrode and film was 0.045 in., and the film speed was 300 ft/min. The power supply was adjusted to deliver a current of 0.5 amp at 10 kHz into the corona.

The treated films were joined together in a commercial heat sealer. This device clamps two pieces of film between flat, heated metal bars. The temperature, pressure, and time of contact of the sealing bars are adjustable. For this work, the pressure was fixed at 25 psi and the time of contact at 0.5 sec. For the data of Figure 1, the temperature was varied, but all other data were obtained with a bar temperature of 75° C. The two pieces of film after being joined were peeled apart in a tensile tester. Peel strengths are expressed in g/in. of sample width. Peel angle was 180°.

Chemical treatments were conducted on the films by immersing them in various reagents under the desired conditions of time and temperature, rinsing thoroughly in running distilled water, and air drying before joining the films together.

The effects of liquids on joint strength were evaluated by mounting the test piece in the tensile tester and applying a drop of the liquid to the junction of the two films just prior to peeling them apart.

## RESULTS

Kim and co-workers<sup>1</sup> reported that the strength of adhesion of corona-treated PE to itself was only slightly dependent on the temperature of joining. The result of varying the temperature of the sealing bars is shown in Figure 1 and differs from their findings by showing a strong temperature

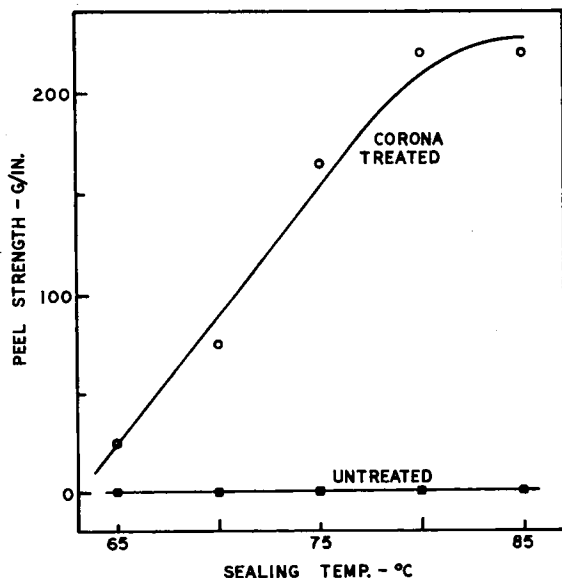


Fig. 1. Effect of bonding temperature on joint strength of corona-treated PE film.

dependence. These results also confirm that untreated PE film exhibits no self-adhesion under the test conditions.

Kim and co-workers did not report whether the application of water affected joint strength. When a drop of water was placed in the junction of two bonded pieces of film, the peel strength fell immediately to zero from a dry value of 165 g/in. If the water was allowed to evaporate before peeling, the full dry strength was recovered. It was found that the application of any H-bonding liquid to the adhesive joint caused immediate, complete loss of strength. Typical liquids tried included such H bond acceptors as tetrahydrofuran, dimethylformamide, and acetone as well as H bond donors such as ethanol and glacial acetic acid. Non-H-bonding liquids such as *n*-dodecane weakened the joint slightly, but did not cause total failure.

Washing the corona-treated films with water or solvents removed material from the surface but did not affect the strength of joints subsequently made between the washed films. These joints were still destroyed by H-bonding liquids. It was also noted that there was no adhesion between a corona-treated film and an untreated one.

A large quantity of treated film was extracted with 1*N* NaOH. The neutralized extract was deep orange. A heavy precipitate with phenylhydrazine and a strongly positive enol test were obtained from the extract. Attempts were made to chromatograph both the extract and the phenylhydrazones on thin-layer plates. Despite the use of a number of solvent systems and chromatographing conditions, it proved impossible to isolate discrete bands. The extract appeared to contain reactive carbonyl compounds of broad molecular weight distribution resulting from oxidation and random chain scission of the PE molecules in the corona. Such a mixture would give a smear on the TLC plate. The extracted film still gave strong bonds when joined under heat and pressure. These results agree with those of Kim and co-workers<sup>1</sup> who also found carbonyl compounds in treated film extracts.

The above observations strongly suggested that the actual bond between sheets of treated PE might be an H bond involving the carbonyl groups formed by corona treatment. To test this hypothesis, sheets of treated film were exposed to various reagents, washed, and dried. The dry films were then bonded together and bond strength measured. The results of this series of experiments are summarized in Table I.

An additional experiment was also run to determine the effect on joint strength of heating the corona-treated PE film prior to bond formation. Strips of treated film were heated in a forced-draft oven for 3 min at various temperatures and then joined together as before. Both strips of the joined film were heated. The bond strengths as a function of heating temperature are shown in Table II.

It is evident that even moderate heat treatment seriously impairs the ability of corona-treated PE film to self-adhere. The data of Table II can be fitted to an Arrhenius equation of the form

$$\ln \text{bond strength} = \ln k - Q/RT.$$

The apparent activation energy *Q* for the loss of self-adhesion is 29 kcal.

TABLE I  
Effect of Chemical Treatments on Bond Strength of Corona-Treated PE Film

Treatment	Conditions	Bond strength, g/in.
None	control	165
Acetyl chloride	20% in heptane, 50°C, 10 min	30
Acetic acid	20% in heptane, 50°C, 10 min	190
Heptane	20% in heptane, 50°C, 10 min	165
Bromine water	20°C, 10 min	0
HNO <sub>2</sub>	0°C, 10 min	10
HNO <sub>3</sub> , 2 <i>N</i>	20°C, 10 min	130
HCl, 2 <i>N</i>	20°C, 10 min	150
H <sub>2</sub> SO <sub>4</sub> , 2 <i>N</i>	20°C, 10 min	155
NaOH, 2%	20°C, 10 min	160
Phenylhydrazine	40°C, 10 min	20

TABLE II  
Effect of Heating Corona-Treated PE Film Prior to Bond Formation

Heating temp., °C	Bond strength, g/in.
60	125
65	70
70	35
80	10

## DISCUSSION

The following mechanism is proposed to account for the enhanced self-adhesion of corona-treated PE film: In eq. (1) of Figure 2, a tertiary carbon atom in the PE molecule is attacked through the well-known mechanism of hydrogen abstraction and hydroperoxide formation.<sup>3,4</sup> The hydroperoxide decomposes into an alkoxy radical. Being unstable, the alkoxy radical tends to undergo chain scission as in eq. (2) to form a ketone and another free radical.<sup>5</sup> Equation (3) shows the tautomerization of the ketone to the enol form. The weakly acidic hydrogen of the enol can then H bond with a carbonyl in an adjacent surface as shown in eq. (4). There are numerous pathways of ketone formation in the corona activated oxidation of PE; this one is typical.

The results of chemical treatment shown in Table I can now be explained by the enol mechanism. Figure 3 shows the proposed reactions. Equation (1) shows that the effect of acetyl chloride is to form the enol acetate which lacks an active hydrogen. The self-adhesion is therefore greatly reduced. The effect of bromine shown in eq. (2) is to form the dibromo ketone by stepwise addition to the enolic double bond. The bromo ketone cannot enolize and thus lacks an active hydrogen. Equation (3) shows that nitrous acid forms the nitroso ketone by attack on the enolic double bond. The nitroso ketone probably isomerizes to the more stable oxime; however, lacking the enolic hydrogen, this surface also will not

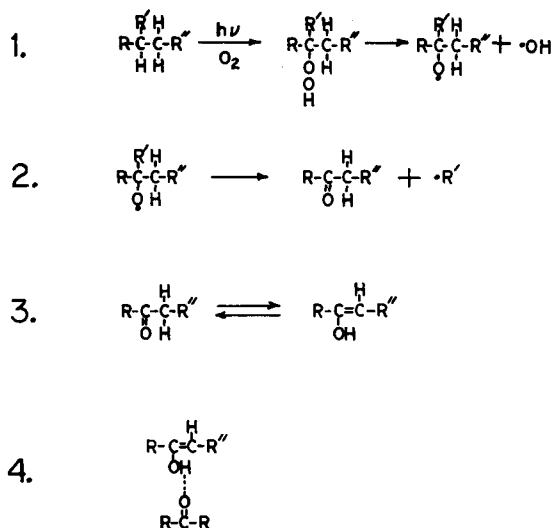


Fig. 2. Formation of ketones in PE by corona treatment.

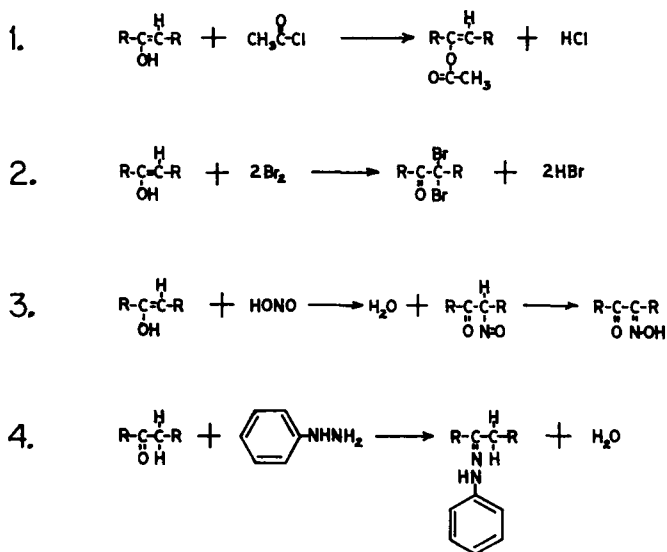


Fig. 3. Reactions of enol groups in corona-treated PE film.

adhere to itself. Phenylhydrazine in eq. (4) reacts in a straightforward manner with the keto tautomer preventing enolization with a resultant loss of adhesion.

The immediate failure of joints to which H-bonding liquids have been applied is apparently due to the ability of these liquids to disrupt the enol-carbonyl H bond because of their stronger H-bonding tendency. This argument is strengthened by the reversibility of the effect. The enol-

carbonyl H bonds re-form when the liquid is allowed to evaporate without disturbing the joint.

The failure of solvents or strong acids and bases to affect the adherability of corona-treated film can be explained by assuming that at least one end of the molecule bearing the enol group is still attached to the film surface by carbon-carbon bonds. It seems certain that the loose, low molecular weight material which can be extracted from the film surface plays no part in the adhesion phenomenon since its removal in no way impairs the adherability of the film.

Kim and co-workers<sup>1</sup> have shown that PE film corona treated for long times at elevated temperatures exhibits reduced bond strength and has more loose surface material than films more modestly corona treated. They speculate that these degradation products might act as a weak boundary layer in reducing self-adhesion.

One could also propose that the degradation products of such gross over-treatment might mask the underlying enol groups and prevent the close approach of the two surfaces necessary for H bond formation.

There is another explanation for reduced adherability under extreme conditions of treatment which is the temperature effect noted in Table II. Apparently, heat can reverse the effects of corona treatment. This effect may be due to reorientation of the enol groups as the polymer chain segments become more mobile at elevated temperature. This mobility would lead to the formation of H bonds between enol and carbonyl groups in the *same* surface. The active groups being internally H bonded would not, therefore, be available for bonding to an adjacent sheet of film. The activation energy of 29 kcal is reasonable for such a process of polymer chain motion or self-diffusion.

Kim and co-workers have also noted that surface oxidation *per se* does not promote self-adhesion in PE films. By treating PE with ozone outside of the corona, they were able to show with IR spectra and contact angles that the polymer surface became oxidized and carbonyl groups appeared, but the film would not self-adhere. The mechanism of PE oxidation in ozone should follow the same steps as outlined in Figure 2. Carried to equilibrium in the presence of excess ozone, however, the reaction would not stop at enol formation. The enolizable ketones would add ozone across the enolic double bond and cleave to form a carboxylic acid and an aldehyde, both of which would show the characteristic C=O peak in the IR spectrum, but neither of which possesses the weakly acidic active hydrogen that appears necessary for strong adhesive bond formation.

Although ozone is formed during corona treatment in air, its reaction with the PE surface does not appear to go to completion; sufficient enolizable ketones remain for bond formation.

Kim and co-workers have reported enhanced self-adhesion in PE films corona treated in nitrogen. The mechanism proposed above cannot account for the observed adhesion unless the system contained traces of oxygen, or long-lived free radicals which could react with oxygen when the sam-

ple was removed from the treatment chamber were formed. Corona treatment in nonoxidizing atmospheres needs further study.

### References

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