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The Mechanism of Corona and Ultraviolet Light-Induced Self-Adhesion of Poly(ethylene Terephthalate) Film

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Synopsis

The ability of corona treatment to render polyethylene film self-adherent has been previously reported and the mechanism explained. A similar effect has now been found with corona-treated poly(ethylene terephthalate) film which adheres strongly to itself when joined under conditions of heat and pressure that give no adhesion with untreated film. Poly(ethylene terephthalate) films irradiated with short-wave UV light also become self-adherent. The behavior of the adhesive joints in both cases is the same as that reported for corona-treated polyethylene film in that the joint strength is zero in the presence of hydrogen-bonding liquids, but recovers completely if the joint is allowed to dry undisturbed. Chemical and physical tests have shown that the adhesive bond is a hydrogen bond between the hydrogens of phenol groups created by corona or UV irradiation in one surface with carboxyl carbonyl groups in the other surface. Thin-layer chromatography of surface extracts from corona- and UV-treated films has shown the products of treatment to be practically identical for both types of treatment, supporting the conclusion that the mechanism of corona treatment resembles that of greatly accelerated photo-oxidation.

INTRODUCTION

The ability of corona-treated polyethylene (PE) film to adhere to itself when joined under conditions of heat and pressure that give no bond with untreated PE has been reported[1] and the mechanism described.[2] It has now been found that poly(ethylene terephthalate) (PET) film exhibits a similar effect. The similarities in behavior of the two polymers are remarkable in view of the great dissimilarities in structure and chemical composition.

Whereas the self-adhesion of PE film is due to hydrogen (H) bonding between carbonyl groups in one film with enolic hydrogens in the other, this report will show that self-adhesion in corona-treated PET film is due to H bonding between carboxyl carbonyl groups in one film with phenolic hydrogens in the other. The phenol groups are created by the corona treatment through a free-radical mechanism. PET film can also be made self-adherent by irradiation with ultraviolet (UV) light by the same mechanism. In the case of both PE and PET, the substitution on the polymer chain of a functional group bearing weakly acidic hydrogen atom appears necessary for self-adhesion.

EXPERIMENTAL

du Pont Mylar polyester film Type 75A was used for the work reported here. It had a thickness of 0.00075 in. and contained no additives. The film was corona treated on the machine previously described[2] under the same conditions except for the corona current, which was varied for certain experiments.

The joints were made and tested as previously described,[2] using a pressure of 25 psi and dwell time of 0.5 sec. The joining temperature was varied for different experiments. Bond strengths are reported as grams of peel per inch of sample width (g/in.). Each value is the average of ten tests.

The products of corona treatment were extracted from the treated film surface by unwinding a roll containing several thousand feet of film through a shallow tray of $0.5N$ NaOH solution at 40°C. Scrapers removed the liquid from the film as it emerged and returned it to the tray. The deep-orange solution was brought to pH 2 with HCl and extracted with four portions of *n*-butanol. The butanol extract was taken to dryness on a steam bath and the residue dissolved in a few drops of ethanol. Films were also extracted with $0.2N$ NH_4OH.

The ethanol solutions were subjected to thin-layer chromatography (TLC) using Eastman No. 6080 silica gel TLC plates. Plates were developed in a mixture of 250 ml tetrahydrofuran, 60 ml $3N$ NH_4OH, and 9 ml ethanol. The spots resolved on the plates were visualized in short-wave UV light and were identified by spray reagents and comparison with known compounds. In certain spots, there was enough material to be eluted and identified by infrared spectroscopy.

Chemical reactions were conducted on the corona-treated film surfaces as previously described.[2] Measurements of surface polarity were computed from contact angle data by the method of Owens and Wendt.[3]

RESULTS

Physical Measurements

Several rolls of PET film were corona treated at different values of corona current. These films were then joined together at different temperatures to determine the temperature dependence of the self-adhesion. Table I shows the results of these tests. The temperature required for a given level of bond strength decreased with increasing corona current. The bond strength of untreated PET film was zero at all temperatures. The data of Table I fit an Arrhenius equation of the form

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

where T is the joining temperature in °K and Q is the apparent activation energy for joint formation. Figure 1 shows these plots.

All four films showed the same apparent activation energy for bond formation of 32.5 kcal, but differed in the value of the constant k. In this respect, PET differs from PE. The bond strength–joining temperature relationship of PE film did not fit an Arrhenius plot.

TABLE I
Bond Strength as a Function of Joining Temperature and Corona Current for Corona-Treated PET Film

Bonding temp, °C	Corona current, amp 0.10	0.20	0.30	0.55
130	0 g/in.	20 g/in.	25 g/in.	35 g/in.
140	15	50	65	85
145	—	—	95	130
150	40	120	—	205
155	—	—	245	*[a]
160	105	285	*	*
165	135	*	*	*
170	210	*	*	*
175	330	*	*	*

[a] * = Joints failed by tearing rather than peeling.

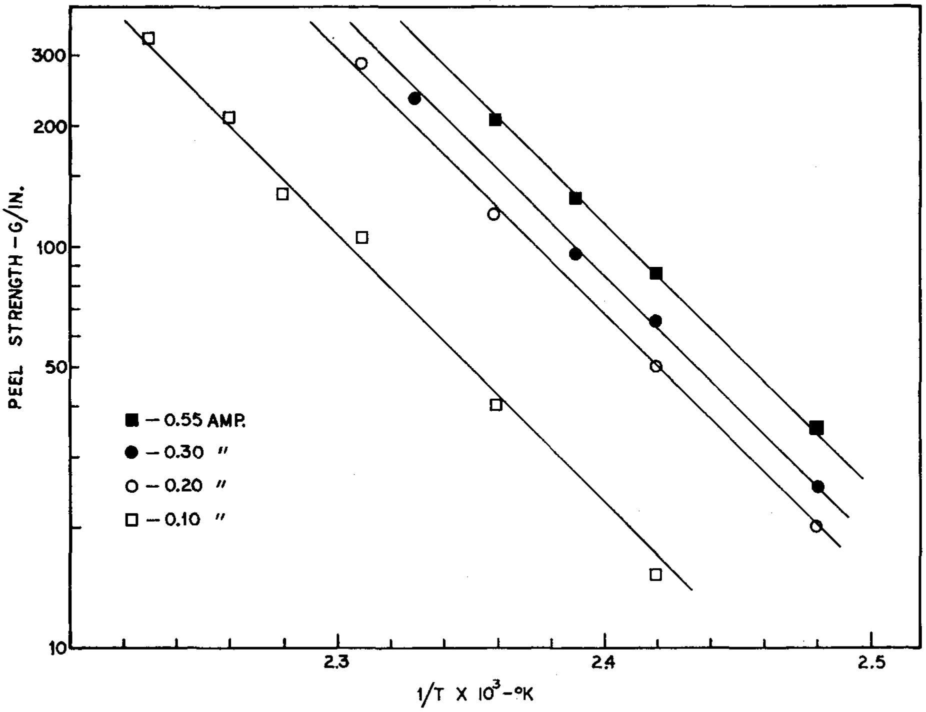

Fig. 1. Arrhenius plots of bond strength vs. reciprocal absolute joining temperature for PET films treated at different corona currents.

The magnitude of k appeared to be a function of the degree of surface polarity generated by corona treatment. The relationship between ln k and $\Delta\gamma^h$ (the difference between the polar component of surface free energy of the corona-treated and untreated PET films) was linear, as shown in Figure 2.

As was the case with corona-treated PE film, the joints between corona-treated PET films were sensitive to H-bonding liquids. A drop of any H-bonding liquid, donor or acceptor, applied to the junction of two bonded films

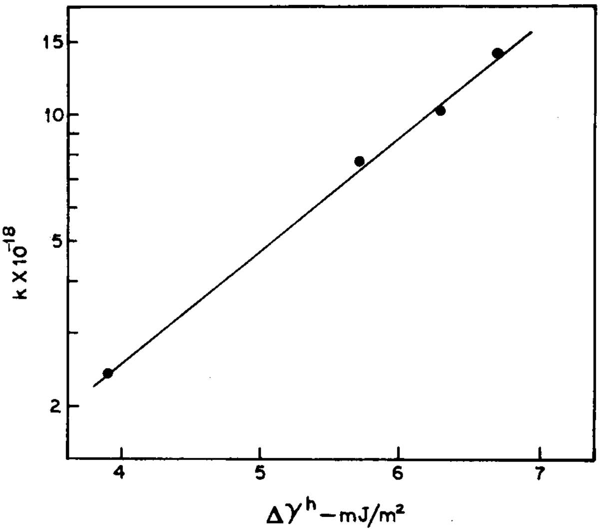

Fig. 2. Relationship of surface polarity and the Arrhenius constant for PET film corona treated at different currents.

TABLE II
Effect of Heating Corona-Treated PET Film on Joint Strength and Surface Polarity

Heating temp, °C	Bond strength, g/in.[a]	$\Delta\gamma^h$, mJ/m^2
None	220	6.7
100	185	5.7
110	115	4.6
120	65	3.6
130	35	2.2
140	20	1.7
150	0	1.2

[a] Joined at 155°C.

caused the joint strength promptly to fall to zero. Joint strength was slightly affected by the application of non-H-bonding liquids such as aliphatic hydrocarbons. Aromatic hydrocarbons such as toluene caused an intermediate loss of joint strength. These substances are capable of limited H bond acceptance through π bonding. All of these effects were completely reversible, full joint strength being recovered upon allowing the joint to dry undisturbed.

Like corona-treated PE film, treated PET film also lost its ability to self-adhere when heated in an oven prior to joint formation. Heated film also showed a decrease in polar surface free energy. These changes were not reversible. Typical results for PET film corona treated at 0.55 amp and heated for 3 min at the indicated temperatures are given in Table II.

The bond strength–heating temperature data fit an Arrhenius plot of the kind described above, giving an apparent activation energy for the loss of self-adhesion of 17 kcal. The data of Table II may also be plotted with rectilinear coordinates as shown in Figure 3. The onset of adherability loss was seen to begin around 82°C. Superimposed on this plot is a thermogram of untreated film showing a small endotherm at the same temperature. Corona-treated PET film gave an identical thermogram.

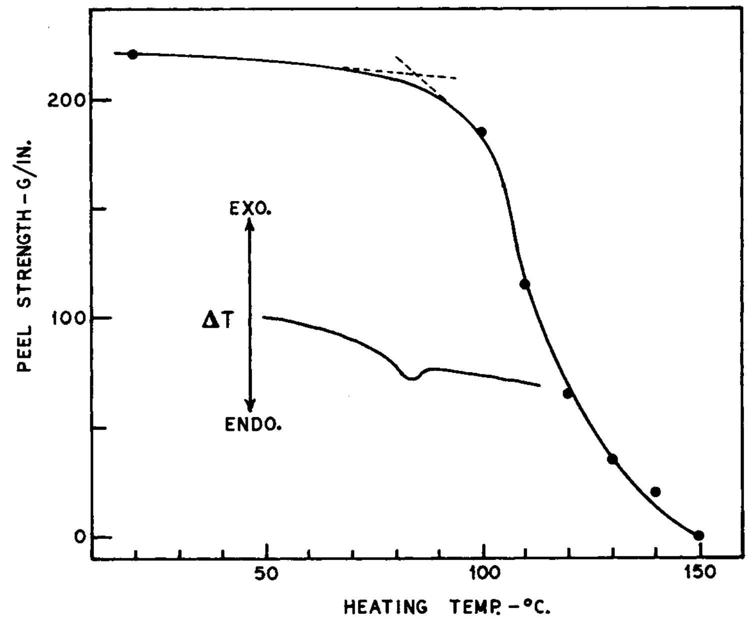

Fig. 3. Joint strength vs. heating temperature and thermogram for corona-treated PET film.

UV Light Irradiation

The process occurring in the corona treatment of PE film leading to the formation of chemical groups responsible for self-adhesion appear to be identical to those which occur during the photo-oxidation of PE.[2] If this view is correct and applicable to PET, photo-oxidation of PET by UV irradiation ought to produce self-adhesion.

PET film was exposed to a Gates 420 UI high-pressure mercury arc lamp for increasing times at a distance of 12 in. The effects of this exposure are given in Table III. UV irradiation does indeed cause PET to become self-adherent. Maximum joint strength was reached after 60 min of irradiation, although this level of joint strength was only about half that attainable by corona treatment. The polar component of surface free energy, γ^h, also increased with irradiation time, but did not show a maximum.

UV irradiation of PET in vacuo has been reported to produce crosslinking rather than oxidation.[4–6] The effect of UV irradiation in vacuo on the self-adhesion of PET film was evaluated by irradiating strips of film for 1 hr in a

TABLE III
Effect of UV Light Irradiation on Self-Adhesion and Surface Polarity of PET Film

Exposure time, min	Bond strength, g/in.[a]	γ^h, mJ/m^2
0	0	4.3
15	45	8.2
30	55	9.7
60	120	12.5
120	115	16.5

[a] Joined at 165°C.

TABLE IV
Effect of UV Irradiation in Vacuo on Self-Adhesion and Surface Polarity of PET Film

	Bond strength, g/in.[a]	γ^h, mJ/m^2
Air	45	9.8
Vacuum	0	0.8
Control	0	4.3

[a] Joined at 165°C.

vacuum chamber at 2×10^{-6} torr pressure. The source was a General Electric H-4 100-watt mercury lamp (with the outer glass envelope removed) at a distance of 8 in. Film samples were also exposed to this source with the chamber filled with air. The results are summarized in Table IV. The film irradiated in vacuo acquired an amber color, showed no self-adhesion, and had very low surface polarity, whereas the film treated in air remained colorless, developed a modest amount of self-adhesion, and increased in surface polarity.

Neither corona-treated nor UV-irradiated PET film would adhere to untreated PET. If, however, the surface of untreated PET film was hydrolyzed by briefly exposing film to 0.1*N* alcoholic KOH followed by a dilute HCl dip and thorough washing, a value of 65 g/in. of self-adhesion was obtained between this film and corona-treated film. Two pieces of hydrolyzed film would not adhere at any conditions of joining.

Chemical Tests

Isolation of chemical compounds present in and on the surface of corona- and UV light-treated PET film was accomplished by extracting the surface of a large quantity of treated film first with dilute NH_4OH to remove loose material followed by surface hydrolysis with dilute NaOH to remove material still attached to the film surface. The film after NH_4OH extraction showed no reduction in self-adhesion, but the film after NaOH extraction was nonadherent. After separating the extracted materials from the extracting liquid and concentrating them, they were chromatographed on TLC plates. Compounds identified in both the NH_4OH and NaOH extracts were identical. Figure 4 is an illustration of a typical TLC plate after development showing the relative positions of the developed spots and their identity.

Two of the compounds identified, monobutyl terephthalate and monobutyl hydroxyterephthalate, may be ignored because they are artifacts resulting from partial esterification of the parent acids by the *n*-butanol used for extraction when the alcohol is evaporated. The chromatography system employed revealed only the products from the aromatic portion of the polymer molecule. By chemical spot tests, however, glycolic, glyoxylic, and oxalic acids as well as glyoxal were identified as oxidation products from the ethylene glycol portion of the polymer molecule. These substances were found in both corona- and UV light-treated films. Chromatography of hydrolysates of untreated PET film showed, besides terephthalic acid, very faint traces of benzoic and salicylic acids. The orange color in the extracts remained at the origin. Several of the spots on the chromatogram could only be characterized for functionality because they were extremely faint.

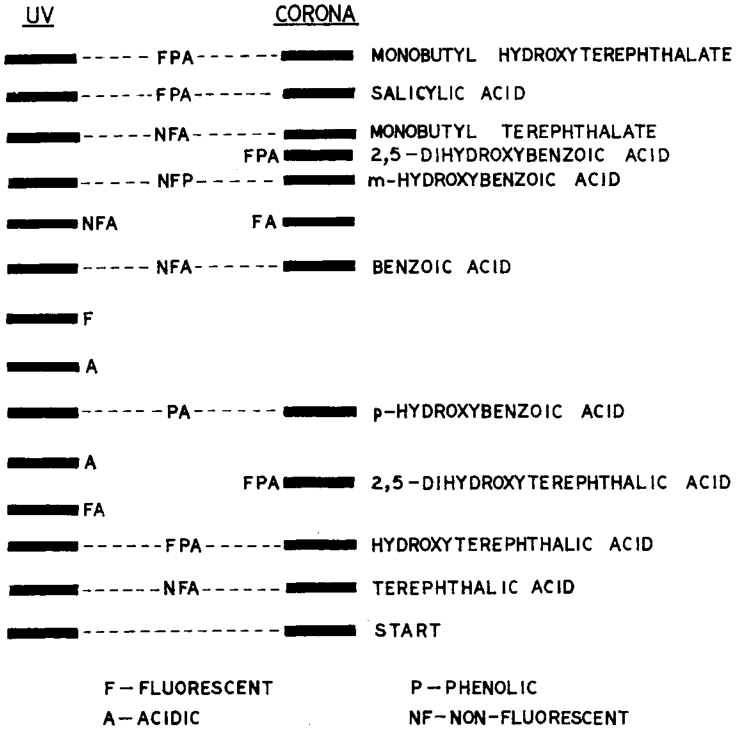

Fig. 4. Appearance of chromatogram of surface products from corona- and UV light-treated PET film.

TABLE V
Effect of Chemical Reactions on Self-Adhesion of Corona-Treated PE and PET Films

Treatment	Conditions	Bond strength, g/in. PE[a]	Bond strength, g/in. PET[b]
None	control	165	195
Acetyl chloride	20% in heptane, 50°C, 10 min	30	25
Acetic acid	20% in heptane, 50°C, 10 min	190	185
Heptane	50°C, 10 min	165	205
Bromine water	20°C, 10 min	0	245
HNO_2	0°C, 10 min	10	0
HNO_3, 2*N*	20°C, 10 min	130	5
HCl, 2*N*	20°C, 10 min	150	135
H_2SO_4, 2*N*	20°C, 10 min	155	185
NH_4OH, 2*N*	20°C, 10 min	—	215
NaOH, 2%	20°C, 10 min	160	0
Na_2CO_3, 2%	20°C, 10 min	—	0
$NaHCO_3$, 2%	20°C, 10 min	—	225
Phenylhydrazine	40°C, 10 min	20	190

[a] Joined at 75°C, 25 psi, 0.5 sec.
[b] Joined at 165°C, 25 psi, 0.5 sec.

Chemical reactions were conducted in situ on the surface of corona-treated PET film in the same manner reported for corona-treated PE film.[2] The effects of these reactions on self-adhesion are given in Table V. For comparison, the results for PE film from reference 2 are repeated in order to show differences and similarities in the behavior of the two polymers.

DISCUSSION

From the behavior of corona-treated PET film joints toward H bonding liquids, there appears to be little doubt that the force of adhesion, like that of corona-treated PE film, is an H bond. A reasonable assumption is that the receptor is the carbonyl group and the donor is a new functional group created by corona or UV light. The only new substituent group detected was the phenolic hydroxyl. A number of the phenols identified were present after both types of treatment.

Valk and co-workers[7] have reported finding several of these same phenols in hydrolysates of UV-irradiated PET fibers. Their proposed mechanism for the formation of phenols by a free-radical process is summarized in Figure 5. In their scheme, the ring is peroxidized and the peroxide decomposes to a phenoxy radical in step 1. This radical may then attack and abstract hydrogen from an adjacent molecule to give a phenol in step 2. Another pathway, shown in step 3, involves hydrogen abstraction from the ring to form an aryl radical which may then be directly hydroxylated by a hydroxyl radical or by attack on a water molecule from the air. Valk and co-workers reported finding only phenols in which the hydroxyl group was ortho to the carboxyl group. The reactions of Figure 5 do not account for the finding of meta and para phenols in extracts from treated films. Such phenols will be called "ter-

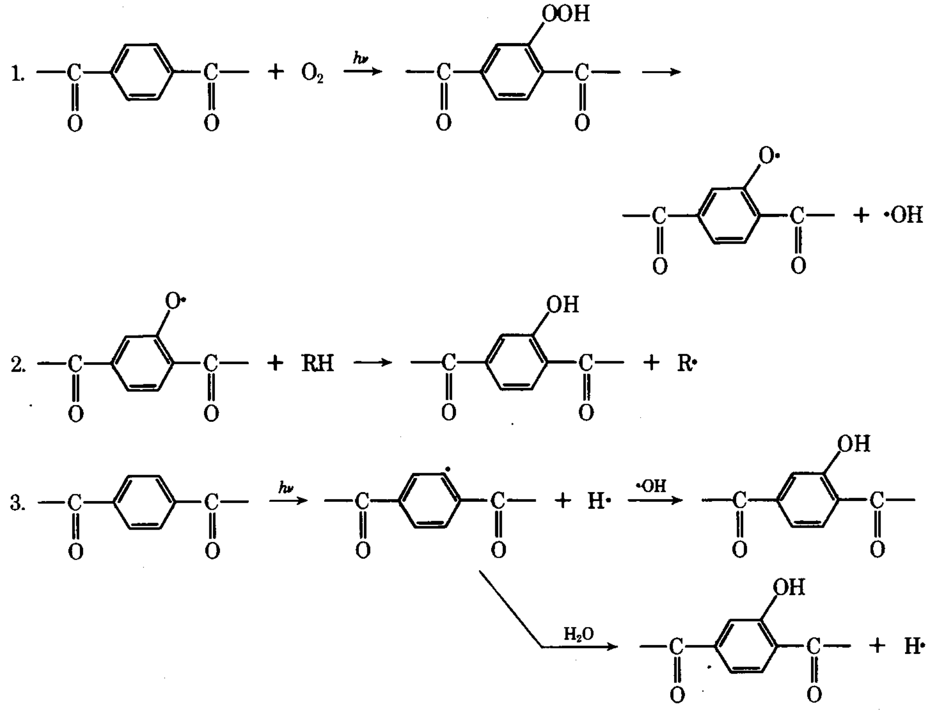

Fig. 5. Formation of phenolic hydroxyl groups in corona- and UV-treated PET film.

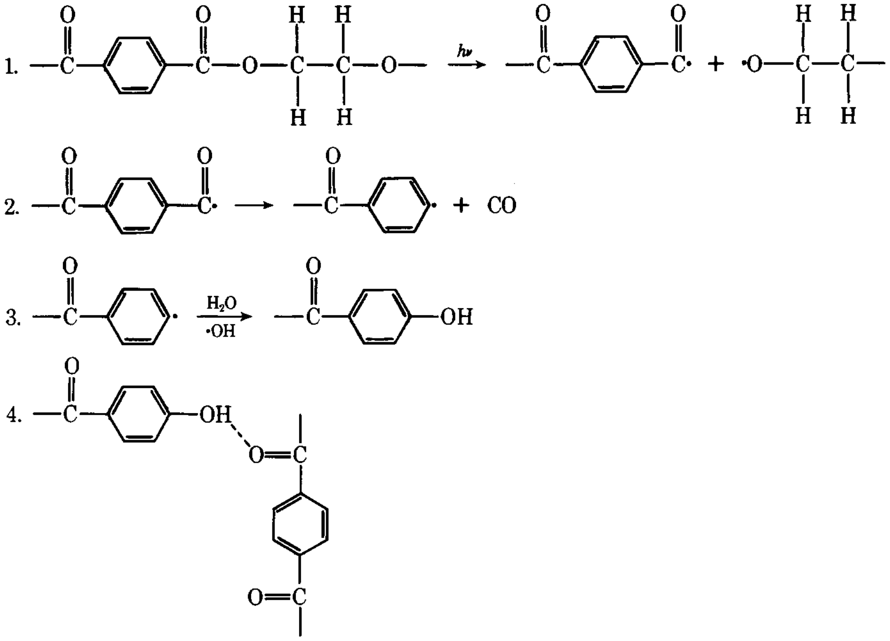

Fig. 6. Formation of terminal phenols in corona- and UV-treated PET film.

minal" phenols since they are monocarboxylic and can only occur on polymer chain ends. The formation of terminal phenols requires chain scission and decarboxylation.

Marcotte and co-workers[4] have shown that CO and CO_2 are among the products of the UV photolysis of PET. They have postulated a mechanism involving chain scission to account for these gases. Stephenson and his colleagues have advanced a similar mechanism.[5,6] Steps 1 and 2 of Figure 6 show the process.

The application of energy causes cleavage of the polymer chain, step 1, to give an unstable radical which loses CO to form an aryl radical, step 2. Capture of a hydroxyl radical or attack on water yields a terminal para phenol in step 3. If chain cleavage occurs between oxygen and the aliphatic carbon, CO_2 will be eliminated, and the reaction will proceed as before. Meta phenols can be produced by a combination of two mechanisms; the ring is first hydroxylated as in Figure 4, followed by chain scission and decarboxylation of the group ortho to the hydroxyl. If decarboxylation occurs on the other end of the ring, a terminal ortho phenol results. Cleavage and decarboxylation without hydroxylation yields benzoic acid as a hydrolysis product. In this way, all of the identifiable products of corona and UV treatment can be explained.

Ortho phenols are H bonded internally so strongly that they do not, in all probability, participate in any H-bonding interactions external to the molecule. It is proposed therefore that the observed self-adhesion in corona- and UV-treated PET film is a result of H bonding between meta and para terminal phenolic hydroxyls in one sheet with carbonyl groups in the other, step 4.

The data of Table V are now explainable by this hypothesis. Figure 7 shows the reactions which are believed to take place. Phenols can be esteri-

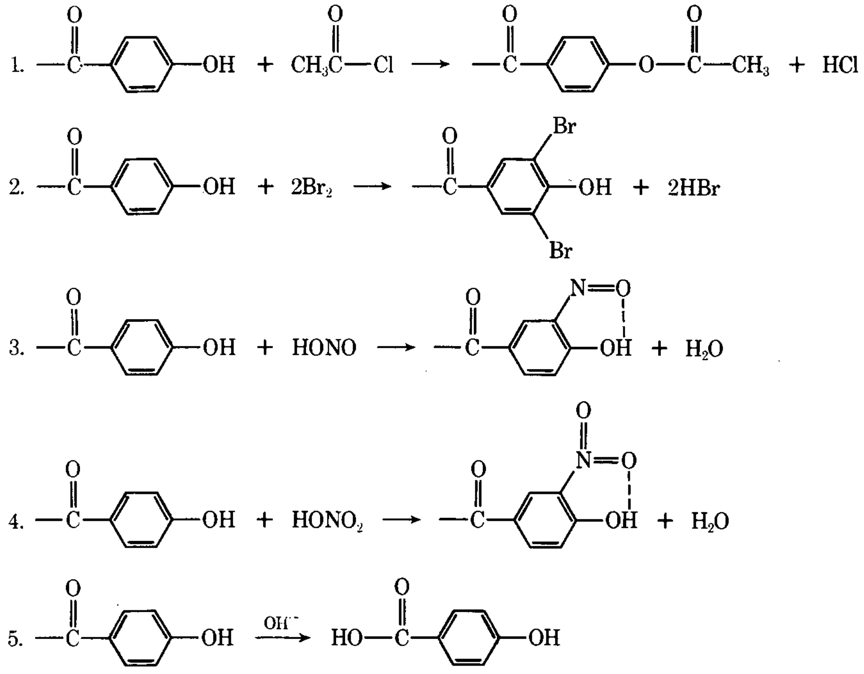
Fig. 7. Reactions of terminal phenol groups in corona–treated PET film.

fied readily by the use of acid halides. Acetyl chloride in eq. (1) forms the acetyl phenol which lacks an active hydrogen and cannot bond. Bromine destroys the self-adhesion of corona-treated polyethylene by displacing the enolic hydrogens[2] but has no effect on treated PET because substitution occurs on the ring. The phenolic hydrogen is not involved in this reaction. By the use of x-ray photoelectron spectroscopy, it was found that corona-treated PET film surfaces after bromination contained three times the amount of bromine taken up by an untreated film. The bromophenol is a somewhat stronger acid than the unsubstituted phenol. This fact may account for the significantly elevated bond strength in a manner which will be discussed below.

Nitrosation and nitration, eqs. (3) and (4), are reactions which take place readily under mild conditions with phenols. When the para position is blocked, the ortho position is substituted. The close proximity of the strongly electronegative nitroso or nitro group, however, results in strong intramolecular H bonding so that the hydrogen is not available for external interaction. In the case of corona-treated polyethylene, however, the enol does not react with nitric acid; only nitrous acid destroys the self-adhesion.

Strong bases such as NaOH and Na_2CO_3 act to hydrolyze the ester linkages holding the terminal phenols to the film surface, eq. (5). With these phenols removed, the film is no longer able to self-adhere. Weaker bases such as $NaHCO_3$ and NH_4OH do not hydrolyze PET under the conditions employed. The increase in bond strength after treatment with weak bases may simply be due to cleaning of the surface by removal of loose, low molecular weight compounds.

Phenylhydrazine and mineral acids other than nitric do not react with phenols and have no effect on self-adhesion.

The apparent activation energy for joint formation of 32.5 kcal is a reasonable value if it is assumed that this energy is required to move the relatively rigid segments of the PET molecules into positions favorable for H-bond formations. When corona-treated PET film is heated prior to joint formation, it loses its ability to self-adhere. The loss of surface polarity on heating indicates that the surface has become reoriented with the polar groups directed inward. NaOH extracts of heated, corona-treated PET film which has lost the ability to self-adhere still show the presence of terminal phenols. This reorientation process must also involve molecular motion as does joint formation, but it has a much lower apparent activation energy, of only 17 kcal. The same process in PE film—a less rigid molecule—has a considerably higher apparent activation energy of 29 kcal.

Evidence in support of the belief that molecular motion causes the loss of adherability is furnished by Figure 3. Differential thermal analysis of PET film shows a small endotherm at the same temperature at which the loss of adherability and polarity begins. This endotherm is believed to be due to the glass transition of PET film and consequently signifies the onset of rapid molecular motion.

Very recently, Baszkin and Ter-Minassian-Saraga[8] have reported that chemically oxidized PE shows a pronounced loss of polarity at a temperature corresponding to the beginning of the melting transition. They have also attributed this effect to surface reorientation through accelerated molecular motion. Further work is necessary to explain the difference in apparent activation energy between the process of joint formation and adherability loss.

The fact that corona-treated PET film did not adhere to untreated film indicates that there are no H acceptors in the untreated film surface capable of strong H bonding. This observation suggests that the ester carbonyls are probably oriented away from the film surface. Surface hydrolysis produces a surface rich in carboxyl endgroups, many of which are favorably oriented for H bond formation with terminal phenols on the corona-treated film.

Hydrogen bonding is the result of a balance of forces. As the valence bond to hydrogen becomes more polar, the hydrogen becomes more positive (acidic), shows less affinity for the molecule to which it is attached, and exhibits increasing affinity for electronegative groups in nearby molecules. This effect increases as the polarity of the valence bond increases, to the point where the hydrogen is sufficiently acidic to be completely transferred to an H acceptor in an acid—base reaction.

The hydrogen of the aliphatic hydroxyl endgroups in hydrolyzed PET are not sufficiently acidic to be strongly attracted to H acceptors. On the other hand, the hydrogen of the carboxyl endgroups is acidic enough to be transferred to an H acceptor. In neither case is strong adhesion to be expected, nor is it observed. Hydrolyzed PET films do not self-adhere.

The strongest H bond should be observed when the hydrogen is sufficiently acidic to exhibit strong attraction for an H acceptor, but not sufficiently acidic to be transferred. The enolic hydrogens in corona-treated PE and PET (phenols are enols) appear to meet these requirements for strong H bonding.

The similarities between the effects and products of corona treatment and those of photo-oxidation of PE and PET lead to the conclusion that the major effect of corona treatment on these polymers resembles that of greatly accelerated photo-oxidation confined to a very thin surface region.

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