

Ink Adhesion on Corona-Treated Polyethylene Studied by Chemical Derivatization of Surface Functional Groups

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Synopsis

Corona discharge (CD) treated polyethylene films were examined using X-ray photoelectron spectroscopy (XPS) and a variety of chemical derivatization techniques. The composition of the CD-treated surfaces were found to be relatively unaffected by aging at temperatures between 70 and 80°F. Ink adhesion testing of films treated under progressively more severe conditions indicated the efficiency of adhesion varied directly with the severity of treatment. Derivatization of CD-treated polyethylene films with pentafluorophenylhydrazine (PFPH) resulted in the formation of a stable hydrazone complex. The PFPH complex extends the detection limit for enolizable carbonyl groups ca. eight-fold and provides relative quantitation of the number of these groups on variously treated polyethylenes. Formation of the hydrazone complex destroyed ink adhesion, indicating that the complex had blocked the site responsible for chemical bonding to the ink. Adhesion of water-soluble printing inks to CD-treated polyethylene is a direct consequence of hydrogen bonding between enolic hydroxyls on the polymer surface and carbonyl groups of the ink.

INTRODUCTION

Polyethylene is presently one of the most widely used of all synthetic polymers.¹ Many commercial applications of this polymer require printing or painting. However, the surface of polyethylene is characterized by a lack of sufficient chemical functionality for adhesive bonding. In addition, the presence of weak boundary layers of low molecular weight oligomers or additives necessitates surface pretreatment prior to printing or painting. Several methods are available for the surface pretreatment of olefin polymers. Among these are photochemical/chemical modification, surface grafting, and plasma or corona discharge treatment.² The speed and ease of processing has made corona discharge (CD) pretreatment the method of choice in the rapid production environment common to the polyethylene film business.

While corona discharge treatment is widely used, little information is available about the mechanism by which it promotes ink adhesion. Owens³ proposed that the presence of enolizable surface carbonyl groups was necessary for the self-adhesion of polyethylene; hydrogen bonding between adjacent surfaces was thought to occur through the keto-enol tautomers. The tautomeric hydrogen bonding mechanism has also been shown to be essential in the adhesion of nitrocellulose printing inks to CD-treated polyethylene surfaces.⁴

The high surface sensitivity of X-ray photoelectron spectroscopy (XPS) has led to wide use of the technique as a diagnostic tool in understanding the surface chemistry of adhesive materials.^{5,6} The experiment is capable of providing several levels of information; the observation of core levels of atoms provides both the chemical composition of a surface, and, by examining specific core levels in detail, one gains insight as to local chemical environment. Additional molecular information may be accessed by examining the valence band region. The interpretation of core level spectra is limited, however, by a small dynamic range of chemical shifts (*vis-à-vis*, e.g., nuclear magnetic resonance spectroscopy), and peaks with a particular binding energy in XP spectra can correspond to more than one type of functional group.⁶ In most instances these limitations are overcome through the use of complicated curve fitting algorithms which synthetically recreate the spectrum as a sum of components defined by parameters such as peak height and width, and Gaussian to Lorentzian peak shape mixing ratio.⁷ However, curve fitting analyses seldom establish unique fits and usually yield results which are speculative.⁸

An alternative approach to curve fit analysis is chemical speciation via derivatization. Derivatization of specific functional groups on a polymer surface requires treatment of the polymer with reagents which are both selective for a specific chemical entity and able to produce a chemically unique tag. The obvious advantage of this approach is the possibility of extending the detection limits of the technique by: (1) introducing an elemental tag with a large photoemission cross section and (2) choosing reagents which result in a stoichiometric enhancement due to the elemental tag.

The current study seeks to extend our understanding of the chemical modifications wrought by corona discharge treatment on polyethylene film with special emphasis on its relation to the adhesion of water-soluble printing inks. It should be noted that the work presented here extends that of Brewis and Briggs⁴ by examining of a water-soluble ink formulation. The study is divided into two parts: (a) the effect of ageing on CD treated low and linear low density polyethylenes studied by ink adhesion tests and XPS, both in the presence and in the absence of a slip additive, and (b) the chemical derivatization of CD treated polyethylene surfaces.

EXPERIMENTAL

X-ray photoelectron spectra were obtained with a Hewlett-Packard 5950A ESCA spectrometer. The spectrometer utilizes a monochromatic Al X-ray source and is interfaced to a HP 9836CS computer for data acquisition and manipulation. Wide scan spectra (0–1100 eV) were accumulated with a resolution of 1.5 eV and elemental spectra with a resolution of 0.78 eV. Samples of corona-treated polyethylene film (linear low density and low density polyethylene) were affixed to gold-plated copper sample stubs using double sticky tape. Differential surface charging was alleviated through the use of an electron flood gun operated in the range of 1–2 eV and 0.1–0.3 mA.

Power levels used in the corona treatment of the blown polyethylene films are summarized in Table I. The corona-discharge-treated polyethylene films

TABLE I
Corona Treatment Levels Used for Treatment of Polyethylene Films

Film sample	Power input per unit length of film ($J M^{-1}$)		
	Low (100 W)	Medium (200 W)	High (400 W)
Low density polyethylene	189	379	757
Linear low density polyethylene	191	382	764
Low density polyethylene with 1000 ppm erucamide	191	382	764
Linear low density polyethylene with 1000 ppm erucamide	205	410	820

were aged in light occlusive bags for up to 2 months at temperatures ranging from 70 to 80°F. Qualitative measurements of ink adhesion were obtained by rolling ink onto the treated areas of the film, followed by application of a pressure sensitive adhesive tape. Manually removing the tape at a low peel rate and observing the amount of ink removed from the surface provided that a crude method of evaluating the strength of adhesion.⁵ The ink used in the study was water-soluble. Infrared spectroscopic analysis of the ink indicated that it contained a cellulose ester and finely divided carbon black.

Derivatization reactions focused on the identification of olefinic residues, peroxide, and enolizable carbonyl groups. Enolizable carbonyls are those which have a hydrogen attached to the carbon atom alpha to the carbonyl carbon (i.e., both aldehyde and keto groups).

The degree of unsaturation and the number of peroxide residues produced by the corona discharge were investigated by reaction with iodine vapor and sulfur dioxide, respectively. A small segment of the film (ca. 10 cm²) was placed in a glass reaction vessel and evacuated to < 1 mTorr. Iodine was allowed to sublime and react with the sample. The film developed the characteristic purple color of the iodine within a few minutes. Similarly, 150 Torr of SO₂ was introduced to the vessel and allowed to react for 5 min.⁹ Unreacted iodine and SO₂ were recovered cryogenically.

Enolizable carbonyl groups were tagged with pentafluorophenylhydrazine to form a hydrazone complex. A 10 mg/mL solution of pentafluorophenylhydrazine (PFPH) in ethanol was prepared in a beaker.¹⁰ Since the reaction is an equilibrium involving the production of water, the ethanol was dried over molecular sieves for 1 h before the reaction, and the entire procedure was performed in a nitrogen-purged glove bag. The progress of the reaction was monitored by examining the concentration of fluorine as a function of exposure time to the PFPH/ethanol solution. Samples were rinsed in ethanol to remove any absorbed reagent, transferred to a tubular glass reactor, and then dried *in vacuo* at ca. 50 mTorr for 20 min. The reaction vessel was immediately transferred to a nitrogen purged dry box where the samples were mounted for analysis.

RESULTS AND DISCUSSION

Survey spectra typical of virgin and corona treated polyethylenes are shown in Figures 1(a) and 1(b), respectively. The surface of the virgin film is char-

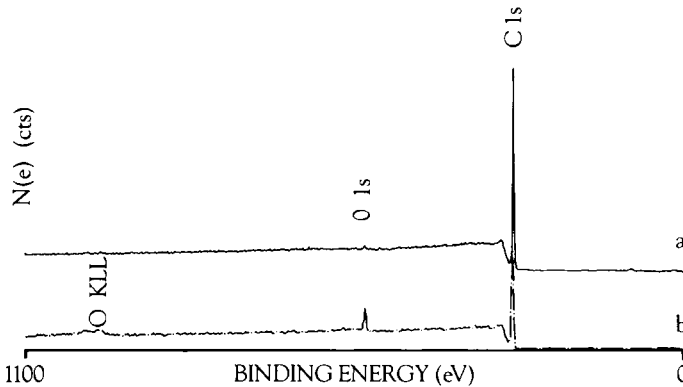


Fig. 1. Survey spectra of untreated polyethylene (a) and corona-treated polyethylene (b).

acterized by an intense C 1s line at ca. 285 eV, and a weak O 1s line at ca. 531 eV. The small amount of oxygen present on the virgin film (< 0.7 atomic %) may be attributed to contamination and/or oxidation of the film which occurred during processing.⁸ In contrast, the surface of the treated film displays an intense oxygen 1s signal and the oxygen KLL Auger transition at 937 eV [Fig. 1(b)]. Both of these spectral features are evidence of the oxidation induced by the corona discharge.

Carbon 1s elemental spectra obtained from CD-treated low density polyethylene [see Figs. 2(a) and 2(b)] are characterized by a large peak centered at 284.6 eV due to aliphatic carbon. The broad shoulder to higher binding energy is evidence of higher oxidation states of carbon such as alcohol/ether (286.1 eV), peroxide (286.6 eV), carbonyl (287.6 eV), and ester/carboxyl groups (290 eV).

The Effect of Aging on CD-Treated Polyethylene

Films Not Containing Slip Additive. The effect of aging on the oxygen to carbon ratios of CD-treated low and linear low density polyethylene is shown

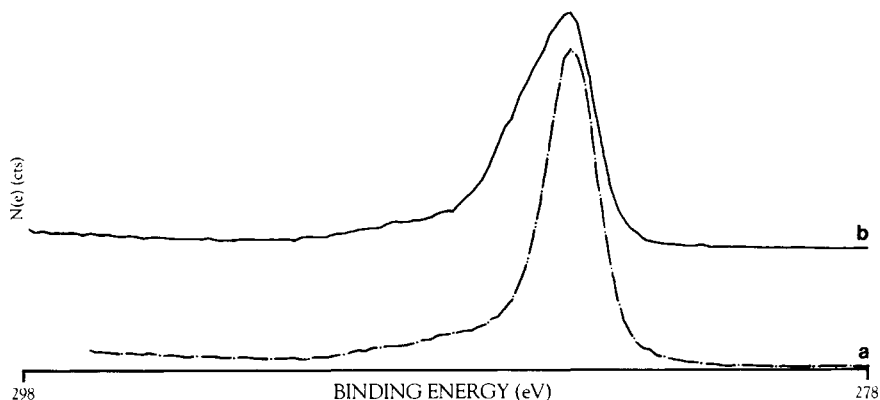


Fig. 2. Carbon 1s spectra obtained from two spots on a corona treated low density polyethylene film.

in Figures 3(a) and 3(b), respectively. The O/C ratios are an average value taken from two areas on the film not more than 1 in. away from each other. The ratios were calculated from elemental spectra via the following equation:

$$\% (O/C) = [(A_o/S_o)/(A_c/S_c)] \times 100\%$$

where A_x represents a spectral area and S_x is a sensitivity factor accounting for parameters such as the cross section for the absorption of X-rays and emis-

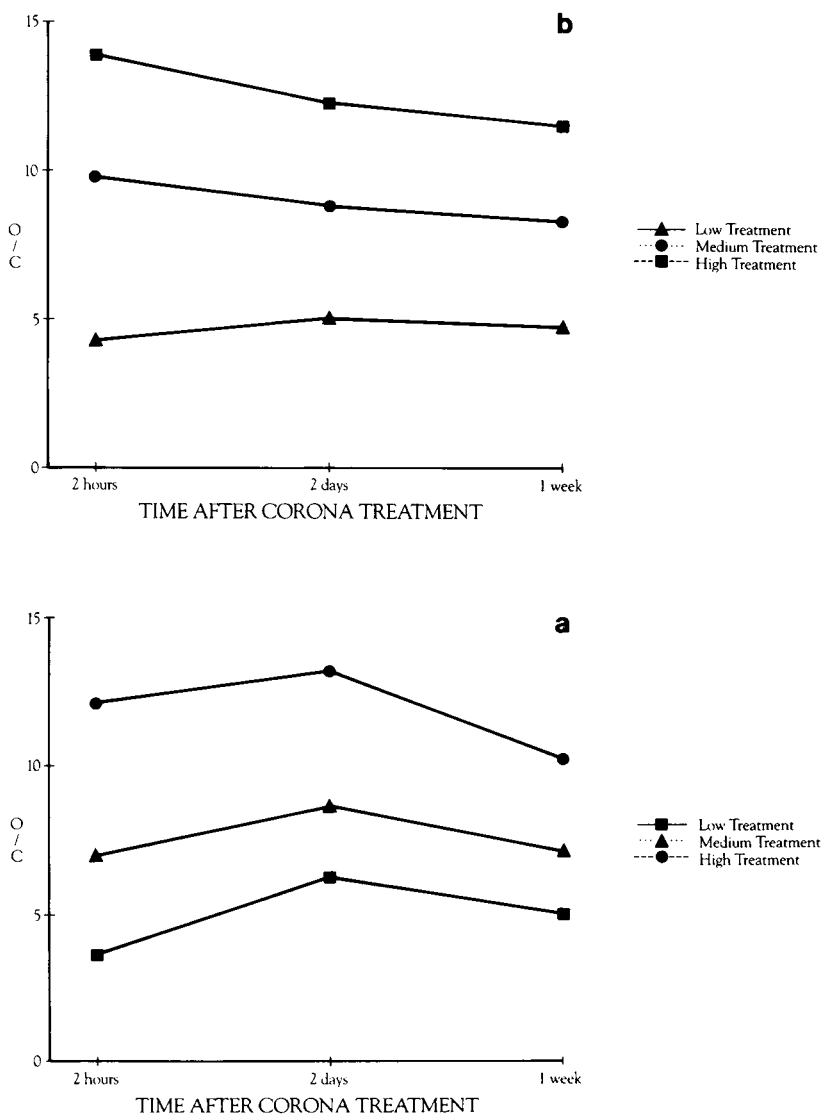


Fig. 3. O/C elemental ratio as a function of time after corona treatment: (a) low density polyethylene; (b) linear low density polyethylene not containing erucamide.

sion of electrons, the mean free path of the photoelectrons, the transmission of the analyzer, etc. The ratios are accurate to $\pm 10\%$.

It is important to note that the O/C ratio was observed to vary both along and transverse to the machine direction of the film. This suggests that the corona treatment was not homogeneous and produced a surface with a non-uniform chemical composition. In some cases significant variation was noted in the O/C ratio for different spots on a film. However, the following observations were obvious based on the results: (1) No major changes were observed for a given treatment level as a function of time, and (2) the concentration of oxygen incorporated into the films varied directly with treatment level. The nonuniformity of the surface may be attributed to any one of the many variables common to CD treatment processes. A rigorous discussion of this topic is beyond the scope of the present work.

Film Containing Slip Additive. The effect of aging on the surface composition of corona-treated polyethylenes containing 1000 ppm of the slip additive erucamide was also studied. The O/C atomic ratios (Fig. 4) measured for the three severities of treatment reveal little change in surface composition with time. The O/C ratios measured for the low density polyethylene [Fig. 4(a)] are, as a whole, higher than those measured for the linear low density material [Fig. 4(b)].

The appearance of nitrogen on the surface of films containing erucamide was expected. The N/C ratio for discharge-treated low density polyethylene as a function of the severity of treatment is shown in Figure 5(a). The N/C ratios measured as a function of time for each treatment level tended toward the same median value. This behavior suggests that, at the slip concentration used here, exudation of erucamide to the film surface is not a function of treatment level. The N/C ratios measured for CD-treated linear low density polyethylene tended to decrease by 20–45% over the time scale of the study [Fig. 5(b)].

Slip additive exudation does not appear to be aided or accelerated by exposure of the film to a corona discharge. The initial exudation of the slip additive, known as bloom, produces a weak boundary layer on the polyethylene surface which is either partially or completely removed by the discharge treatment.⁵ In the present study, the films were stored under laboratory conditions, i.e., at temperatures ranging from 70 to 80°F. At low storage temperatures, it is likely that the rate of slip additive bloom is much lower than if the material had been stored at temperatures between 90 and 110°F, such as might be experienced in a warehouse.

Ink Adhesion

Ink adhesion to the treated polyethylenes was evaluated qualitatively using tape coated with a pressure sensitive adhesive (polybutylacrylate). Adhesion was considered good in cases where the tape–ink film interface failed rather than the ink–polyethylene interface. Examples of tape from good and poor ink adhesion cases are shown in Figure 6. The ink adhesion tests for the high and medium treatment level samples of both low and linear low density polymers were similar, suggesting that the correct surface composition for printing had

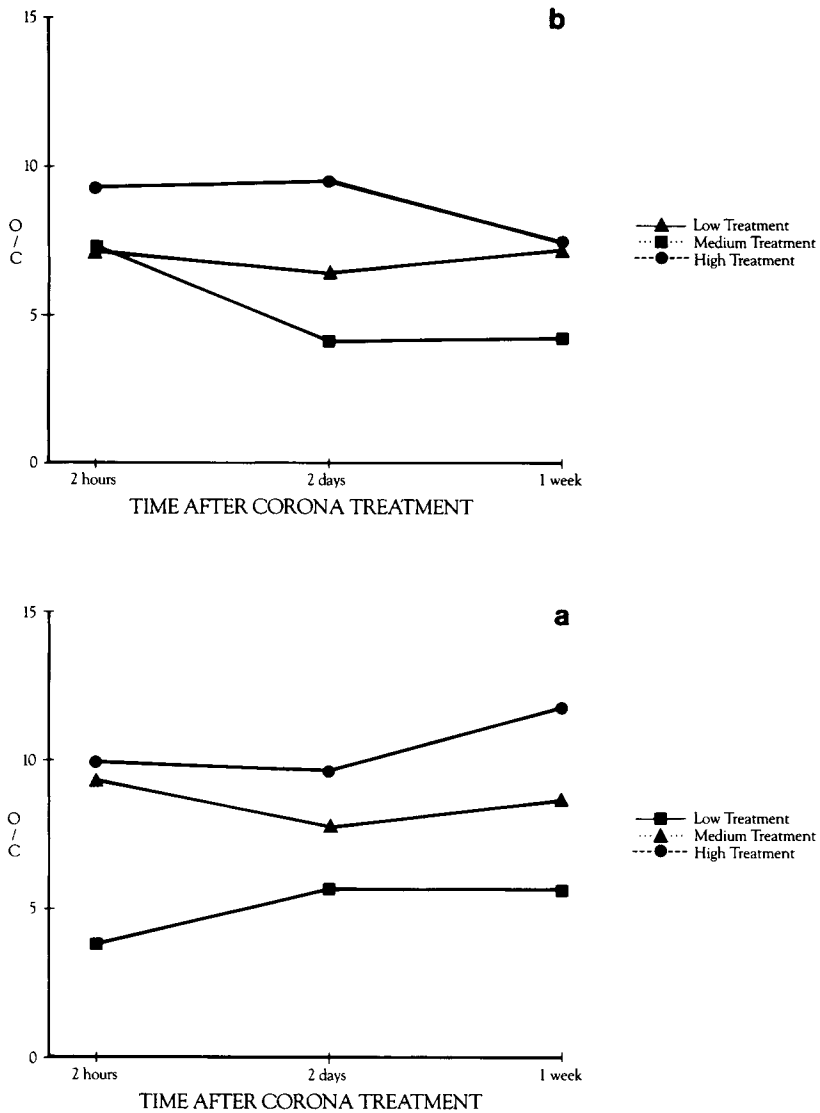


Fig. 4. O/C elemental ratio as a function of time after corona treatment: (a) low density polyethylene; (b) linear low density polyethylene containing 1000 ppm of erucamide.

been produced by the discharge. However, the low treatment level samples exhibit failure of the ink-polyethylene interface, indicating a lack of sufficient functionality for good ink adhesion. It is important to note that in all cases the ink appeared to wet the polymer surface. This suggests that wetting is a necessary, but not sufficient condition for ink adhesion.

Samples of linear low and low density polyethylene containing 1000 ppm of erucamide gave similar results in the qualitative ink adhesion test described above. This suggests that post-treatment bloom of the additive was not sufficient to produce a weak boundary layer and prevent efficient ink adhesion. These

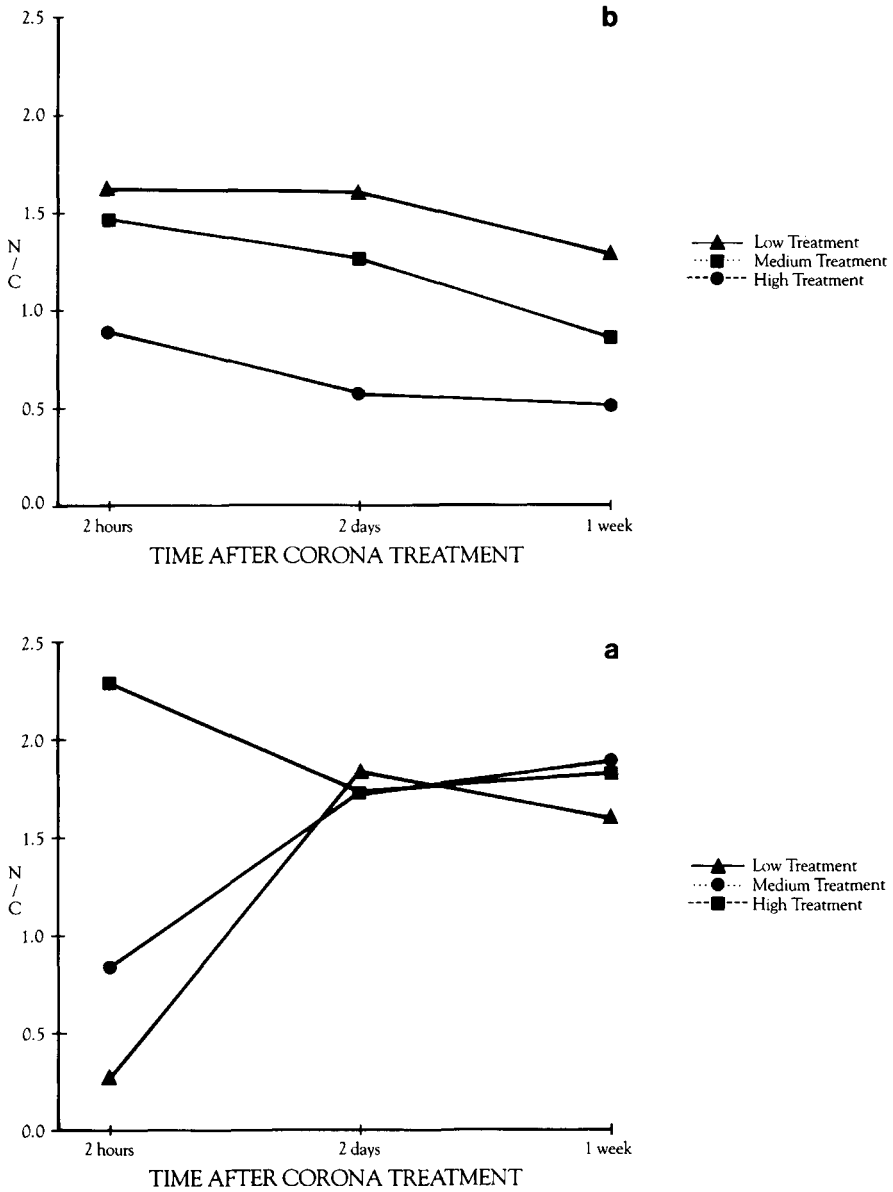


Fig. 5. N/C elemental ratio as a function of time after corona treatment: (a) low density polyethylene; (b) linear low density polyethylene containing 1000 ppm of erucamide.

results are specific for 1000 ppm of erucamide only and do not provide any information about higher slip levels or different slip additives.

It is important to note that the qualitative ink adhesion tests, performed concurrent with the XPS analyses on the aged polyethylene films, did not reveal any significant differences in the effectiveness of ink adhesion. This is in agreement with the near invariance of the O/C ratios measured in the XPS.

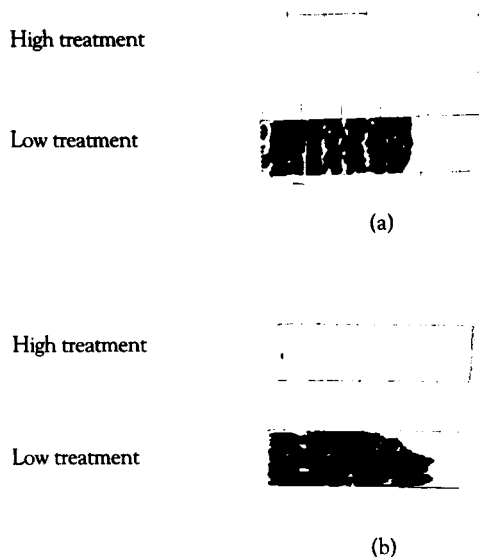


Fig. 6. Ink adhesion test examples from corona treated low density (a) and linear low density (b) polyethylene.

Detection of Unsaturation. The classical chemical test for unsaturation is the reaction of pi bonded carbon with bromine. The formation of a colorless bromine adduct acts as the indicator. In the present study iodine was used in an attempt to derivatize unsaturated groups on the CDT polyethylene surfaces. Recent work by Gerenser et al.⁹ indicated that treatment of polyethylene films with bromine was nonspecific; complete bromination of the film surface was found to occur after ca. 1 h of exposure. Treatment with iodine was found to be equally nonselective. Exposure of CD-treated films to I_2 resulted in the formation of a charge transfer (CT) complex between the I_2 and any pi electron donating groups on the polymer surface.¹¹ Photoelectron spectra of I_2 -treated polyethylene film revealed a peak at 620.9 eV, due to the $3d_{5/2}$ component of iodine [Fig. 7(a)]. However, upon heating *in vacuo* the complex decomposed and iodine could no longer be detected on the film surface [Fig. 7(b)]. The formation of the CT complex between I_2 and the treated surface was not selective for olefinic residues, as the I_2 may have also reacted with surface carbonyl groups.¹²

Detection of Peroxide Groups. The reaction of sulfur dioxide and peroxide functional groups leads to the formation of an organosulfate as shown in Scheme 1¹³:

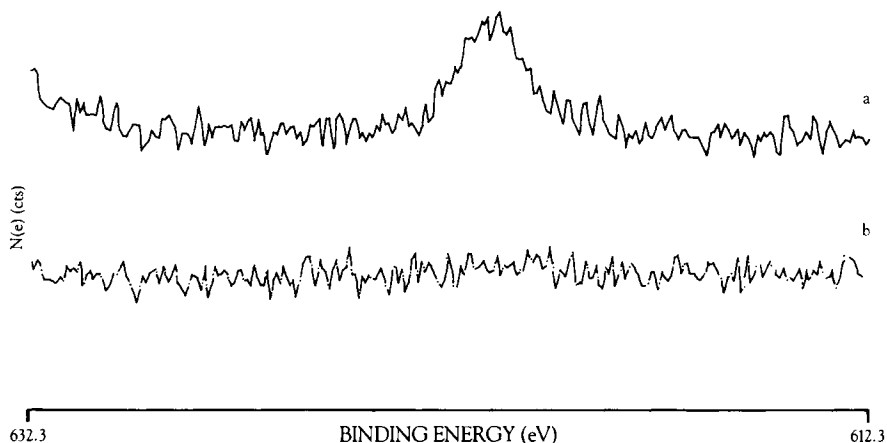
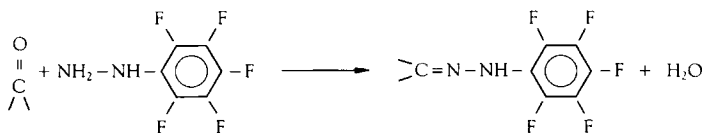


Fig. 7. (a) Iodine $3d_{5/2}$ spectrum obtained from corona-treated polyethylene following exposure to I_2 ; (b) as in (a) following heating *in vacuo*.

The reaction is site specific for peroxides and provides sulfur as a chemically unique tag. The formation of peroxide groups on the surface of CD-treated polyethylene surfaces occurs as a result of dioxygen insertion into homolytically cleaved C—C bonds.^{2,5} Peroxides are recognized as key intermediates in rearrangement reactions leading to the formation of other oxidized surface groups. In the present study exposure of CD-treated polyethylene film to SO_2 gas did not result in any detectable reaction. Gerenser et al.⁹ have shown that following treatment in a corona discharge the concentration of surface peroxide groups decreases steadily with time, claiming the groups are no longer detectable 24-h post-treatment. The corona-treated films examined in this study had aged for considerable time prior to exposure to SO_2 . Hence, the lack of sulfur incorporation in the film surface is no doubt due to the short-lived existence of peroxide groups on the film surface.

Enolizable Carbonyl Groups and Ink Adhesion

The Reaction of PFPH with CD-Treated Surfaces. Pentafluorophenylhydrazine (PFPH) reacts with enolizable carbonyl groups to form a hydrazone complex according to the reaction shown in Scheme 2:



Scheme 2

Introduction of fluorine to the film surface extends the detection limit for enolizable carbonyls beyond that attainable by direct analysis of the CD-treated polyethylene film. The complex provides an ca. eightfold increase in sensitivity

for enolizable carbonyl groups owing to a 1.6-fold increase in sensitivity for fluorine compared to carbon and to the stoichiometry of the complex (Scheme 2).

The Pentafluorophenylhydrazone Complex. A survey spectrum (0–1100 eV) of a CD-treated polyethylene film derivatized with PFPH in ethanol is shown in Figure 8. Derivatization of the corona-treated film with PFPH results in the appearance of several spectral features unique to the surface complex. Notably, fluorine is evident based on the appearance of the F 1s (ca. 685 eV) and the F KLL Auger line (ca. 830 eV). In addition, the N 1s (ca. 399 eV) and the Na 1s core levels appear in the spectrum of the derivatized surface. The presence of sodium on the surface of the derivatized film may be due to ion exchange of Na⁺ ions in the 5A molecular sieves used to dry the ethanol. The sodium ions are likely associated with surface carboxyl groups. The fluorine and nitrogen, however, are due to the presence of the PFPH surface complex. The ratio of nitrogen to fluorine measured experimentally was 0.46, in good agreement with the stoichiometric value of 0.40.

The difference between the experimental and stoichiometric N/F ratios may be due to a loss of fluorine from the PFPH complex. Recent work by Tougas and Collier¹⁴ indicated that the fluorinated phenyl group of PFPH is subject to nucleophilic attack by OH⁻, resulting in the production of F⁻ as a leaving group. The presence of residual water in the ethanol or the water liberated by the reaction of PFPH with the carbonyl may have provided the nucleophile needed for this reaction to occur.

The carbon 1s spectra of derivatized and underivatized CD-treated polyethylene are compared in Figure 9. A notable difference can be seen in the high binding energy shoulders of the spectra. The change observed is due to the presence of the C–F groups of the PFPH complex.

Samples of untreated film were exposed to PFPH to confirm that the reagent had derivatized the corona-discharge-treated surfaces and had not absorbed into the polymer. Spectra collected from these films were devoid of fluorine. Film samples which were soaked in ethanol for several times the PFPH reaction time were unchanged spectroscopically (Fig. 10), confirming that the solvent (ethanol) had not altered the corona-treated surface. This suggests that the PFPH formed a surface complex with the enolizable carbonyl groups on the

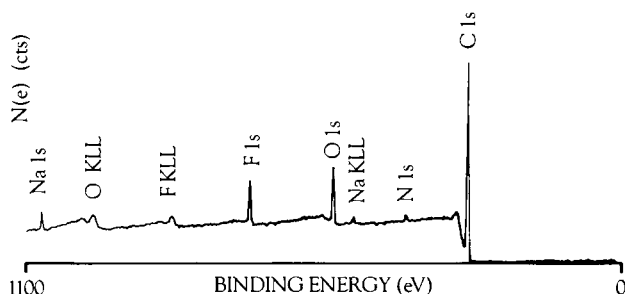


Fig. 8. Survey spectrum of corona treated polyethylene following derivatization with pentafluorophenylhydrazine.

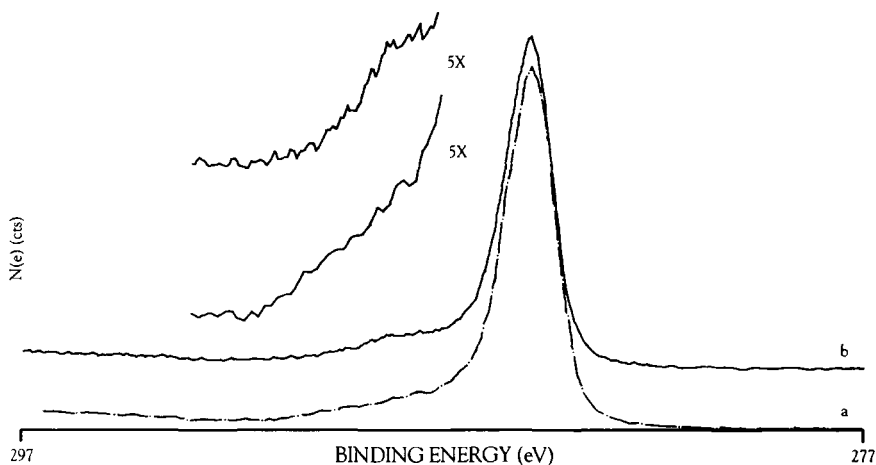


Fig. 9. Carbon 1s spectra of corona treated polyethylene prior to (a) and following (b) derivatization with PFPH.

corona-treated surfaces, rather than absorbing into the polyethylene as a result of solvent swelling.

Length of Treatment. The length of treatment with PFPH was examined to determine the time needed for complete reaction. As can be seen in Figure 11, after reaching a maximum at ca. 30 min exposure time the F/C ratio decreases by ca. 6% after 3 h of exposure to the PFPH/ethanol solution. The decrease in F/C ratio for times greater than 30 min is likely due to nucleophilic attack of the perfluorinated phenyl group by the water produced during the hydrolysis reaction.¹⁴ As a rigorous investigation of the mechanism of the hydrolysis reaction was beyond the scope of this work, the 30 min exposure time was chosen to minimize fluorine depletion and optimize the reproducibility of the experiment.

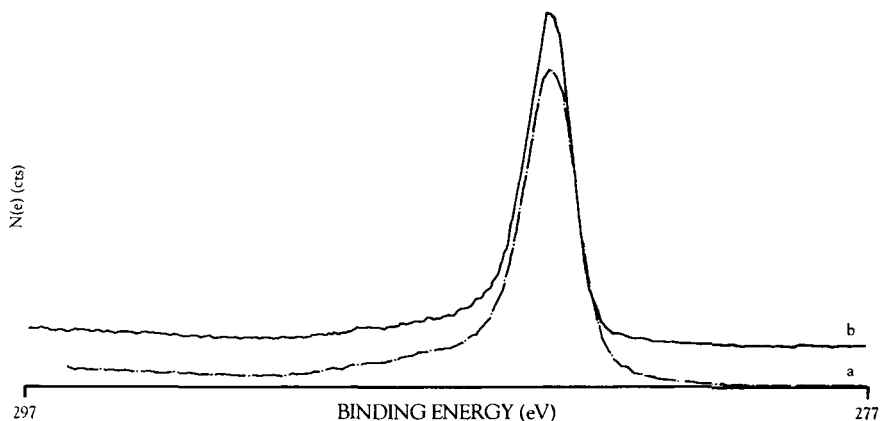


Fig. 10. Carbon 1s spectra of corona treated polyethylene prior to (a) and following (b) exposure to ethanol for 3 h.

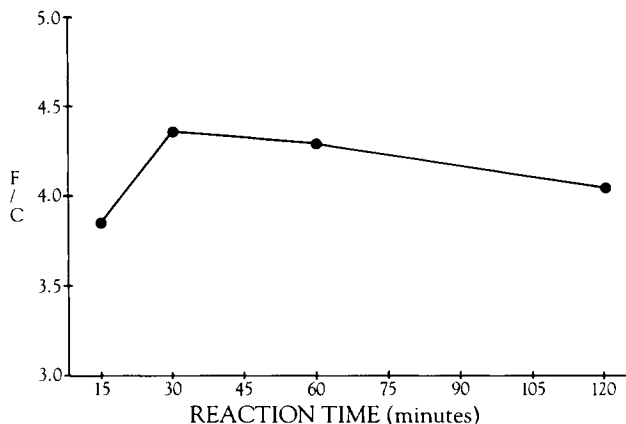


Fig. 11. F/C elemental ratio as a function of reaction time in PFPH/ethanol solution.

Fluorine Concentration as a Function of CD Treatment. The fluorine to carbon ratios of PFPH derivatized CD treated linear low and low density polyethylenes are shown in Figure 12. The F/C ratio increases monotonically with treatment level for both polymers. Similar behavior was noted on examination of the carbonyl peak area obtained from curve fit analyses of carbon 1s spectra (Fig. 13), suggesting that the number of enolizable carbonyl groups is directly related to the degree of oxidation caused by the corona discharge. Notably, the results from curve fit analyses of carbon 1s spectra exhibit larger differences in carbonyl content between low and linear low density polyethylenes than is evident from the PFPH tagging. This discrepancy may be attributed to the inherent error in curve fit analyses of highly convoluted peak envelopes.

Quantitation of the PFPH Tagging. It is important to note that the pentafluorophenylhydrazone complex provides both sensitivity and stoichio-

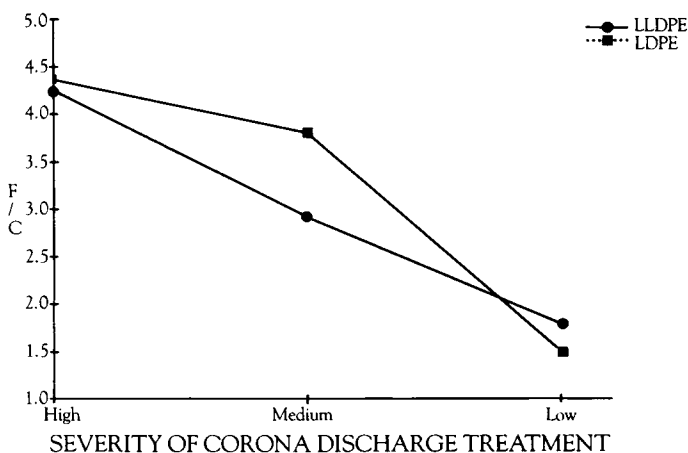


Fig. 12. F/C elemental ratios as a function of severity of corona treatment for low and linear low density polyethylenes.

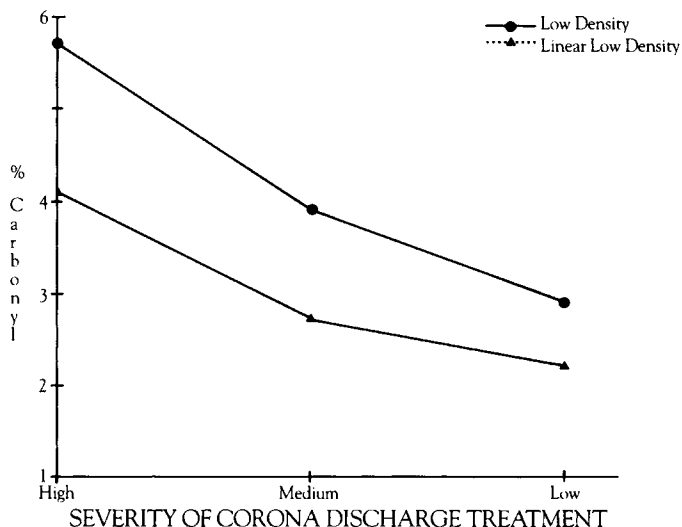


Fig. 13. Relative carbonyl concentration from curve fit analysis of carbon 1s spectra obtained from low and linear low density polyethylene films as a function of the severity of corona treatment.

metric enhancements, allowing for the relative quantitation of enolizable carbonyl groups on corona-discharge-treated polyethylenes. From the reaction shown in Scheme 2, one can deduce the following relationship:

$$[-C=O] = k[F]$$

where $[-C=O]$ is the concentration of enolizable carbonyl groups, $[F]$ is the fluorine concentration on the surface, and k is a stoichiometric constant which accounts for the fact that each hydrazone complex contributes five fluorines to the surface. Using this relationship, one can compare the relative concentration of enolizable carbonyls on polyethylenes corona-treated under different conditions. Comparing two film samples, i and j , we have the following:

$$\frac{[-C=O]_i}{[-C=O]_j} = \frac{[F]_i}{[F]_j}$$

The relative concentrations of enolizable carbonyl groups found by chemical tagging with PFPH are presented in Table II. In all cases the more severe level of treatment results in a greater concentration of enolizable carbonyl groups. It is interesting to note that the numerical ratios of high/medium, high/low, and medium/low are similar for both the low and linear low density polyethylenes. This is true because the mechanism of oxidation must be independent of the power input to the film during treatment. In addition, it proves that the extent to which the PFPH reacts with enolizable carbonyls is independent of material and depends only on the severity of the CD treatment.

TABLE II
Relative Concentrations of Enolizable Carbonyl Groups on Corona Treated Polyethylene Films

Film sample	Relative enolizable carbonyl concentration ^a		
	High/medium	High/low	Medium/low
Low density polyethylene	1.2	2.7	2.4
Linear low density polyethylene	1.2	2.3	1.9

^a Relative carbonyl concentrations were calculated from the F/C atomic ratios of corona-treated films which had been derivatized with pentafluorophenylhydrazine.

Ink Adhesion and PFPH-Tagged Carbonyl Groups

The results of qualitative ink adhesion testing on PFPH derivatized CD treated low density polyethylene are shown in Figure 14. As expected, the ink was not removed by the adhesive tape in samples of corona-treated polyethylene which had not been derivatized with pentafluorophenylhydrazine. However, the ink failed to adhere to a polyethylene film sample which had been treated with the PFPH/ethanol solution. Finally, when the PFPH derivatized film was hydrolyzed in water and dried *in vacuo* the ink again adhered to the corona-treated polyethylene surface.

(a) Low density polyethylene, high treatment level.



(b) As in (a) following treatment with PFPH/ethanol solution.



(c) As in (b) following hydrolysis in water and drying *in vacuo*.



Fig. 14. Ink adhesion test for pentafluorophenylhydrazine derivatized low density polyethylene film.

The failure of the ink film to adhere to the PFPH-derivatized surface is directly related to the formation of the hydrazone complex. Since the hydrazone complex eliminates the formation of enolic hydroxyls on the CD-treated polyethylene surface, hydrogen bonding no longer occurs between the ink and the carbonyls of the polyethylene surface. On exposure to water, the hydrazone complex reverts to the carbonyl which can tautomerize, thereby providing the hydroxyl group needed for hydrogen bonding to the ink. It is important to note that the ink was able to wet the PFPH-derivatized film. This indicates that, although enolizable carbonyl groups are primarily responsible for ink adhesion, they are not solely responsible for enhancing the wetting characteristics of the CD-treated film.

The Mechanism of Ink Adhesion

The adhesion of water-soluble inks to the surface of corona-discharge-treated polyethylene occurs via hydrogen bond formation between enolic hydroxyl groups of the film surface and carbonyl groups of the ink. The keto-enol tautomerization proposed by Owens³ has been substantiated both by Briggs and Kendall¹⁵ and the present work. Briggs and Kendall studied the adhesion of a nitrocellulose ink to CD-treated low density polyethylene. They noted that bromination of CD-treated polyethylene prevents ink adhesion without affecting the reactivity of the surface toward PFPH, implying that bromine had reacted with the enol tautomer by substituting for hydrogen on the carbon alpha to the carbonyl group. In addition, it was noted that conversion of carboxyl groups to the acid salt had no effect on ink adhesion. In the present study it was noted that the adhesion of an ester-based ink was prevented by derivatization of the carbonyl (keto and aldehyde) groups with pentafluorophenylhydrazine. Hydrolysis of the hydrazone complex restored the ink adhesion completely. This result is consistent with an adhesion mechanism involving hydrogen bonding between the ester carbonyls of the ink and enolic hydroxyls on the CD-treated surface.

CONCLUSION

The corona discharge treatment of low and linear low density polyethylenes introduces several oxygen adducts to the polymer surface. The composition of the CD treated surfaces is relatively unaffected by aging at temperatures between 70 and 80°F. Ink adhesion testing of films treated under progressively more severe conditions indicated the efficiency of adhesion increased with severity of treatment. While neither unsaturation nor peroxide groups were detected by chemical tagging, a direct correlation was observed between the formation of a pentafluorophenylhydrazone complex and enolizable carbonyl groups. The enolizable carbonyl groups were directly linked to adhesive bonding between a water-soluble ink and the CD-treated polymers. The mechanism of adhesion involves hydrogen bonding between the enolic hydroxyls on the polymer surface and carbonyl groups of the ink.

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References

1. F. Billmeyer, *Textbook of Polymer Science*, 3rd ed., Wiley, New York, 1984.
2. S. Wu, *Polymer Interface and Adhesion*, Dekker, New York, 1982.
3. D. Owens, *J. Appl. Polym. Sci.*, **19**, 203 (1975).
4. D. M. Brewis and D. Briggs, *Polymer*, **22**, 7 (1981).
5. D. M. Brewis and D. Briggs, Eds., *Industrial Adhesion Problems*, Wiley, New York, 1985.
6. D. Briggs, *Polymer*, **25**, 1380 (1984).
7. P. M. Sherwood, in *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, D. Briggs and M. P. Seah, Eds., Wiley, Chichester, 1983, p. 445.
8. C. Reilley, D. Everhart, and F. Ho, in *Applied Electron Spectroscopy for Chemical Analysis*, H. Windawi and F. Ho, Eds., Wiley, New York, 1982, Chap. 6.
9. L. Gerenser, J. Elman, M. Mason, and J. Pochan, *Polymer*, **26**, 1162 (1985).
10. D. Everhart and C. Reilley, *Anal. Chem.*, **53**, 665 (1981).
11. D. Pasto and C. Johnson, *Organic Structure Determination*, Prentice-Hall, Englewood Cliffs, NJ, 1979.
12. J. March, *Advanced Organic Chemistry*, 3rd ed., Wiley, New York, 1985.
13. D. Dilks, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 1319 (1981).
14. T. P. Tougas and W. G. Collier, *Anal. Chem.*, **59**, 2269 (1987).
15. D. Briggs and C. R. Kendall, *Polymer*, **20**, 1053 (1979).

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