Heat Sealing of Semicrystalline Polymer Films. III. Effect of Corona Discharge Treatment of LLDPE

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SYNOPSIS

The effects of corona-discharge treatment (CDT) of commercial polyethylene (PE) Linear low-density PE (LLDPE) were studied with special emphasis on the heat-seal behavior of treated films. A range of treat levels, representative of those used in industry, was obtained by varying the applied power to a commercial, on-line treater. Film surfaces were characterized by XPS and wetting-tension measurements. The primary effect of CDT on the heat-sealing behavior of LLDPE films is a transition in the failure mode of heat seals from a normal tearing or inseparable bond to a peelable seal. In addition, CDT increases the seal initiation temperature 5–17°C and decreases the plateau seal strength 5–20% as the treat level, or wetting tension, increases from 31 to 56 dynes/cm. These effects are attributed to cross-linking during corona treatment, which restricts polymer mobility near the surface and limits the extent of interdiffusion and entanglements across the seal interface. Results of heat-sealing studies with electron-beam-irradiated PE, chemically oxidized PE, and CDT polypropylene (PP) provide indirect evidence for the proposed surface cross-linking mechanism. The effect of commercial levels of slip additives on the heat-seal behavior was also investigated. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyolefin films, due to their inherent low surface energy, are usually treated to improve attributes such as ink adhesion (or printability) and adhesion to polar substrates in multilayer applications. Commercially, the preferred treatment of polymer surfaces is corona discharge due to its relative ease of operation, low cost, and effectiveness. However, many problems in film packaging are related to the heat sealing of corona discharge treatment (CDT) of films. In general, the heat-seal layers in multilayer food-packaging applications are not purposely treated and most problems arise due to the accidental back-treatment. This can occur when air is trapped between the film and the roll in a cast process or when the bubble is not completely collapsed in blown-film applications. Both situations can result in the seal layer being exposed to some level of corona dis-

charge. The effects of corona discharge on high-pressure, low-denisty polyethylene (LDPE) films have been investigated extensively with particular attention paid to the enhanced adhesive properties and more recently, to the chemical changes that take place near the polymer surface.[1–11] However, very few studies include LLDPE resins or address the effects of commercial film additives on treatability.[12–15] Virtually no information is available on the effect of CDT on the heat sealability of polyolefin films.[16] This paper presents a comprehensive study of the CDT of commercial LLDPE in the presence of additives, characterization of the resulting film surfaces using surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS) and wetting-tension measurements, and, what is more important, the effects on heat sealability.

The physics of corona discharge and other plasmas are fairly well understood.[17,18] Corona discharge is an ionized gas and, in air atmosphere, consists of positively charged ions, electrons, and excited or metastable species of oxygen and nitrogen, as well as other forms of radiation. In addition, metastable

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oxygen species react with oxygen molecules in the atmosphere to generate ozone, a powerful oxidizing agent. Particle energies are about 10–20 eV, which is high enough to break C—C and C—H bonds (2.54 and 3.79 eV, respectively[7]) and generate free-radicals in the polymer-surface region.

The primary effect of CDT of polyolefins is oxidation of the film surface. According to Wu,[19] this oxidation is typically limited to the outer 50–500 Å. The chemical effects of CDT on high-pressure LDPE has been studied extensively, primarily regarding ink adhesion and enhanced auto-adhesion or blocking. Briggs and co-workers[5,6,8,9] investigated these systems with special emphasis on the types of polar groups that are formed. Using XPS and very selective derivatization techniques, the mechanisms of surface modification and the roles of specific groups in adhesive performance have been elucidated. The most widely accepted mechanism for the oxidation of PE during CDT is similar to the classical mechanism of oxidation of hydrocarbons.

A second consequence of CDT of polyolefins, and perhaps the most significant for heat sealability, is cross-linking and chain scission, which occurs due to the presence of free radicals. Both cross-linking and chain scission takes place simultaneously, depending primarily on whether the initial attack is at a branch point. Another possible result of CDT is ablation and surface roughening. Surface roughening has been reported for corona-treated PE, but only after prolonged treatment.[20] Carley and Kitze[4] and Gerenser[11] reported no observable differences on a macroscale between surfaces of untreated PE film and PE films that were treated at commercial levels using scanning electron microscopy (SEM).

How these changes in the film surface influence the heat sealability of polyolefins is not well understood. In addressing this topic, we have also included in this study the CDT of films in the presence of slip additives (erucamide). These long-chain, fattyamides are known to cause problems related to wettability and adhesion. However, the detailed knowledge of the surface chemistry of CDT surfaces in the presence of slip additives and the subsequent effects on heat sealing are not apparent. We chose a level of 600 ppm, which is typical for commercial LLDPE, and a relatively high level of 1200 ppm.

EXPERIMENTAL

Escorene® LL-1001 (made by Exxon Chemical Co.) was used in this investigation as a representative, film-grade LLDPE. This olefin copolymer has a melt index of 1 g/10 min (ASTM D-1238 E) and a density of 0.918 g/cm^3 (ASTM D-792) and contains a standard additive package consisting mainly of anti-oxidants. Films (50 μm) were extruded on a Black Clawson 3 1/2 in (8.9 cm) cast line at 30 m/min and treated on-line using a Pillar high-frequency treater (P1000 Series, 9.6 kHz, 355 V maximum power supply output) in an air atmosphere. The treater width was approximately 10 cm and the treater gap (distance between treater bar and the film) was approximately 1.5 mm. Under these conditions, the film is exposed to the corona discharge for approximately 0.2 s. By varying the applied power to the corona treater, we obtained a range of treat levels from 31 to 56 dynes/cm.

XPS data were collected on a Leybold-Heraeus LHS-12 instrument using a MgKα X-ray source (12 keV). Vacuum was maintained at 10^{-8} Torr or greater. Wetting tensions were determined according to ASTM D2578–67 (Wetting Tension of PE and PP Films). Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) data were obtained at S & N Labs using a Kratos instrument, configured with an FEI liquid metal ion gun that bombarded the film surface with pulses of gallium-69.

Sheets of the control and treated films were heat-sealed under accurately controlled conditions of platen temperature, dwell time, and die pressure using a Theller® Model EB laboratory heat sealer. The experimental details of the heat-sealing experiment are described more fully in the first paper in this series.[21] T-peel tests were performed on an Instron 4505 series tensile tester at a crosshead speed of 508 mm/min. Seal strength values were calculated by dividing the maximum load by the sample width.

RESULTS AND DISCUSSION

Characterization of Film Surfaces

As mentioned previously, the major chemical effect of CDT is an increase in the surface energy due to the introduction of polar functional groups. We have used two surface-sensitive techniques, namely, wetting-tension measurements and XPS, to characterize the resulting surfaces. The most sensitive technique used to measure changes in the surface chemistry is the interaction of liquids with the surface, since the wetting phenomenon is associated with the outer ca. 5 Å, as opposed to XPS, which probes the outer ca. 50 Å. XPS, on the other hand, provides qualitative and quantitative information about the near surface region.

Wetting Tension/Contact Angle

The ASTM Test Method D2578-67 (Wetting Tension of PE and PP Films) is accepted as the industry standard to measure the effectiveness of corona treat on PE and polypropylene (PP) films. This method employs a series of wetting liquids with gradually increasing surface tension, consisting of binary mixtures of ethylene glycol-monoethyl ether (surface tension = 30 dynes/cm) and formamide (surface tension = 58 dynes/cm). The wetting-tension number one reports is the surface tension of the liquid that wets the polyolefin surface for 2 s before breaking up into droplets. A summary of initial wetting tension for all films is given in Table I.

As shown in Figure 1, wetting tension increases steadily as the applied power to the corona treater increases. A wetting tension of 37 dynes/cm or above is generally required for printing, while higher levels, greater than or equal to 47 dynes/cm, are typically required for laminations or extrusion-coating applications. We have shown, for a given applied power setting, that the wetting tension or surface energy of slip-containing films is lower than the control film that contained no slip additives. Our results are consistent with practical industrial experience that indicates films containing slip require a higher level
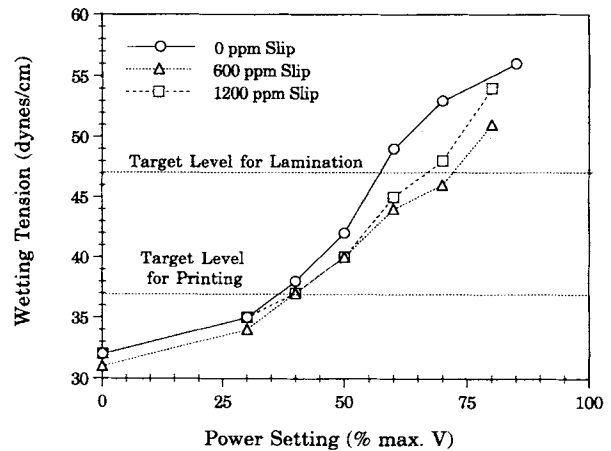
Figure 1 Plot of wetting tension of LLDPE film vs. power supply output to the corona treater (maximum = 355 V).

Table I   Initial Wetting Tension of CDT LLDPE Films

Sample	Slip Level (ppm)	Power Setting[a] (% max V)	Wetting Tension (dynes/cm)
1	0	0	32
2	0	30	35
3	0	40	38
4	0	50	42
5	0	60	49
6	0	70	53
7	600	0	31
8	600	30	34
9	600	40	37
10	600	50	40
11	600	60	44
12	600	70	46
13	1200	0	32
14	1200	30	35
15	1200	40	37
16	1200	50	40
17	1200	60	45
18	1200	70	48

[a] Maximum power supply output to treater is 355 V.

of corona discharge to obtain a given treat level. This is commonly observed in the industry and is generally attributed to blooming of the slip to the surface that interferes with the oxidation of the film surface. However, using XPS, we have shown that this is not the case. It will be shown in the following section that slip additives merely mask the treat but do not prevent or significantly reduce the degree of oxidation of the polymer surface.

It is important to keep in mind that the CDT surfaces are dynamic and the wetting tension decreases with time due to reorganization of the polymer surface. Depending on the surrounding environment, these functionalized surfaces may or may not be in thermodynamic equilibrium. Therefore, in a nonpolar environment, there is a tendency of the polar groups to turn inward toward the bulk polymer. The principal driving force is a minimization of surface free energy.[22] Besides the surface reorganization process, there is the possibility of low molecular weight hydrocarbons and additives migrating to the surface that may also alter the surface energy. Figure 2 shows the decrease in wetting tension with time for films without slip additives.

The decrease in wetting tension with time after extrusion is most rapid during the first 24 h and is greatest for films treated at high levels. The rate at which this reorganization takes place will depend on factors such as size and nature of the functional groups, mobility of the polymer chains near the surface, and storage conditions. These films were stored on the roll in the laboratory. Under these conditions, the treated surface is in contact with an untreated surface and, to some extent, the ambient air.
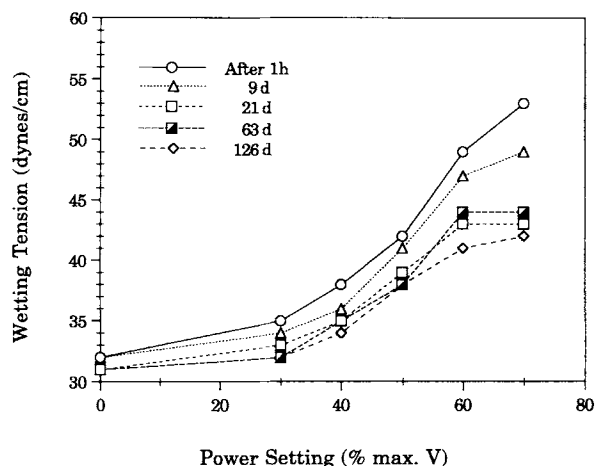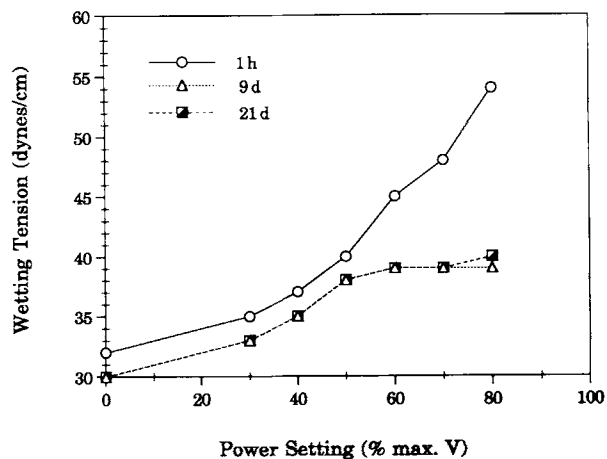
Figure 2 Plot of wetting tension vs. power setting for films containing no-slip additives.

Figure 4 Plot of net oxygen (%) vs. applied power to treater.
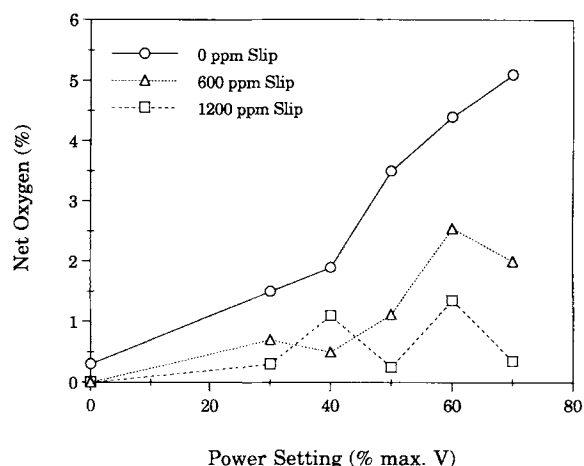
Figure 3 shows the same plot for a slip-containing film. In this case, the decrease in wetting tension as a function of time is much faster compared to non-slip-containing films. In addition to the reorganization process, there is also instantaneous blooming of slip to the surface. This phenomenon also lowers the surface energy due to the molecular orientation of the slip additive at the surface.

X-Ray Photoelectron Spectroscopy (XPS)

XPS was also used to characterize the surfaces of corona-discharge treated films. The samples were run soon after treatment in an attempt to eliminate any aging effects. It should be noted, however, that little change in the XPS spectrum was observed for aged samples. Figure 4 shows the net oxygen intro-

Figure 3 Plot of wetting tension vs. power setting for a film containing 1200 ppm slip (erucamide).

duced into the polymer surface by oxidation as a function of applied power to the corona treater for a control film without slip and two slip-containing films. The atomic percentage of oxygen has been corrected for the presence of slip in the latter two cases and represents only the oxygen due to oxidation of the polymer surface. It is evident that the control film shows more surface oxidation than do the two slip-containing films for a given power setting. This is consistent with the results from wetting-tension measurements, which showed for a given applied power that the surface energy of the control film was higher than that of the slip-containing films.

Two possible explanations for this phenomenon have been proposed: First, the presence of slip interferes with the corona treatment by blooming to the surface in between the time the film exits the die and the time it reaches the treater station. Second, the slip migrates to the surface after treatment and simply masks the initial treat. In the latter case, slip molecules that initially bloom to the surface are ablated and do not interfere with oxidation of the PE surface. Using XPS, it was possible to resolve this uncertainty.

Oxidation of the polymer surface results in a shoulder on the high binding energy side of the C1s peak in the XPS spectrum. However, this shoulder is absent in the CDT sample that contains 1200 ppm slip. Washing the surfaces of slip-containing films with diethyl-ether removes the erucamide as evidenced by the disappearance of the associated N1s and C1s peaks and reveals the presence of an oxidized layer. In fact the degree of oxidation for the slip-containing film appears to be as high as for the
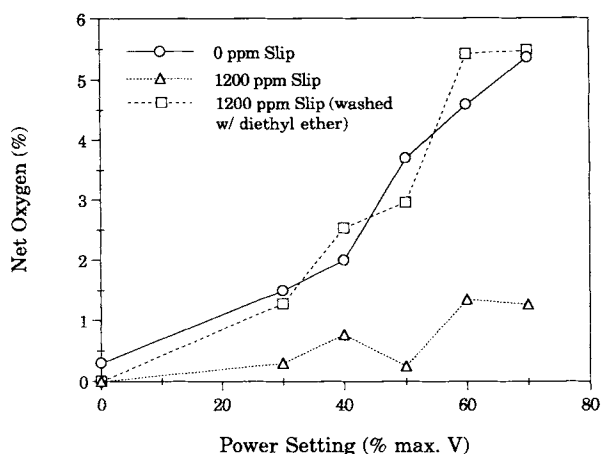
Figure 5   Plot of net oxygen (%) vs. applied power for films containing no slip, 1200 ppm slip, and 1200 ppm slip washed with ether.

control film that did not contain slip (Fig. 5). It should also be noted that washing the control surface with diethyl ether did not change the level of oxygen as measured by XPS. Therefore, we can also infer that the functional groups are covalently bound to relatively high molecular weight polymer. On the basis of these results, our conclusion is that slip additives, up to a concentration of 1200 ppm, do not interfere with oxidation of the film surface but rather mask the treat by subsequent blooming.

As mentioned previously, changes in the surface composition of treated films were also monitored as a function of time using XPS. It was found that the composition did not change dramatically upon aging of the film. In most cases, there was a slight decrease in the oxygen content. For example, during a 14 day period, the O/C ratio for a film treated at 70% applied power decreased slightly from 0.056 to 0.054. During this time, however, the wetting tension decreased from 49 to 43 dynes/cm. From these data, we conclude that wetting tension measurements, which probe the outer $\sim$ 5 Å, are more sensitive to surface reorganization than is XPS, which probes the outer $\sim$ 50 Å. Collectively, the two techniques provide a clear understanding of the changes that take place near the surface of CDT PE films.

Heat Sealing of Corona Treated LLDPE Films

A representative heat-seal curve for a semicrystalline polymer is shown in Figure 6. The features of the curve are discussed in detail in the second papers in this series.[23] A predictive model has been developed that relates the heat-sealing behavior of semicrystalline films to the melting distribution and the film properties of the polymer. The key features are (1) the seal initiation temperature (T_{si}), which is determined by the amorphous fraction of the polymer; (2) the temperature of the plateau onset (T_{pi}),
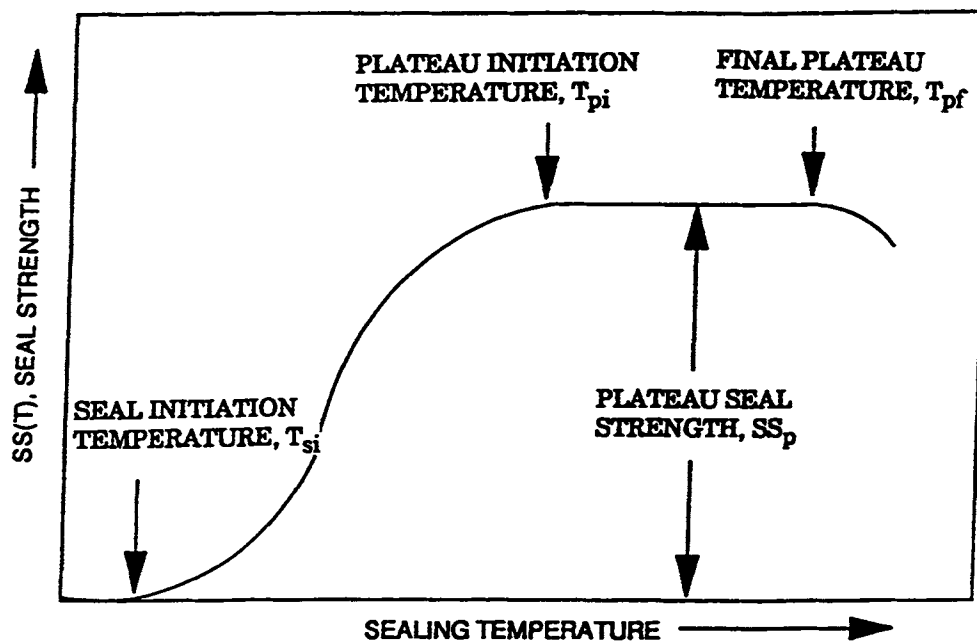

Figure 6   Generic heat seal curve relating seal strength and sealing temperature for semicrystalline polymers.

which corresponds to the temperature at which the polymer is 100% amorphous, and (3) the plateau seal strength (SS_p), which is a function of the yield stress (or crystallinity) of the polymer film. The observed failure modes of heat-sealed structures in a classic T-peel experiment are peeling (the two film surfaces can be separated), peeling and tearing (peeling and elongation of the legs, some samples tear), and tearing (legs of the heat seal elongate and break; in other words, an inseparable seal area).

Failure Mode for CDT Films

The primary effect of CDT on the heat-sealing behavior of PE films is a transition in the failure mode from the normal tearing to peeling, which is unacceptable in some packaging applications. More simply stated, corona-treated surfaces will not form inseparable heat seals. By varying the output voltage to the corona treater, we obtained a range of treat levels in an attempt to determine the minimum level of CDT that results in a peeling failure mode. Initially, the films were heat-sealed at a platen temperature of 130°C, a dwell time of 1 s, and a pressure of 50 N/cm^2, perpendicular to the machine direction. Under these conditions, the untreated film, which has a final melting point of 126°C, showed the normal tearing failure mode. Figure 7 shows the seal strength as a function of the applied power to the corona treater for the control film and two-slip containing films.

The vertical line represents the transition in the failure mode from tearing to peeling. Surprisingly, only the untreated films showed a tearing failure mode. It was anticipated that films treated at 30% power output would show normal sealing behavior
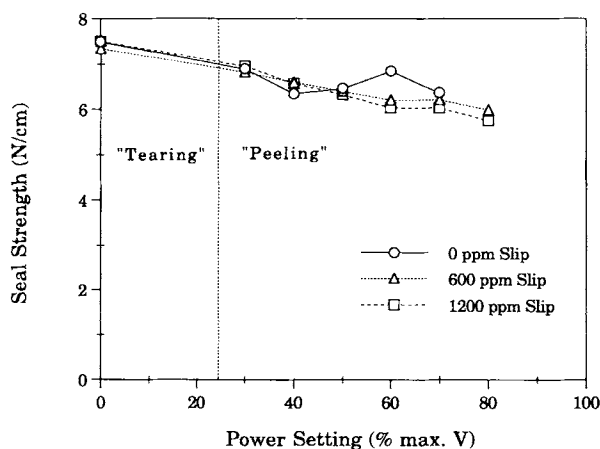
Figure 7   Plot of seal strength vs. applied power for LLDPE films.
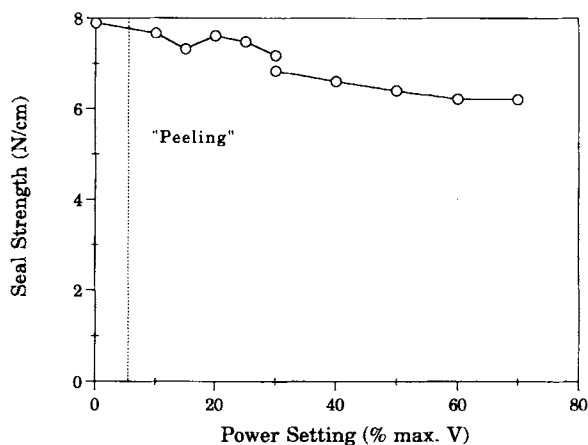
Figure 8   Plot of seal strength vs. applied power for LLDPE film containing 600 ppm slip.

since this is a relatively low level of treat. The amount of oxygen incorporated into the films at this level is only ca. 1% (Fig. 5) and the wetting tension increases only slightly from 31–32 to 34–35 dynes/ cm (Fig. 1).

Heat sealing at higher temperatures (up to 175°C) and longer dwell times (up to 50 s), both of which favor increased diffusion, did not alter the mode of failure or significantly increase the level of seal strength. No differences in heat-seal behavior, including failure mode, were observed due to the presence of slip additives.
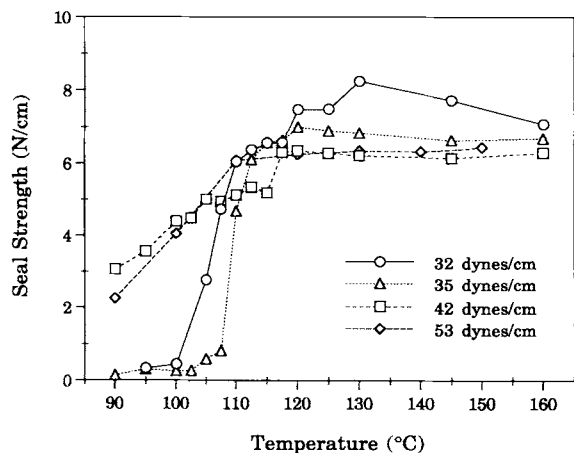
Subsequently, we treated films at even lower levels of corona treatment. The results for a film containing 600 ppm slip are shown in Figure 8. The 10% treat level is the minimum power output necessary to maintain a corona discharge. Treatment at this level did not significantly increase the wetting tension (31–32 dynes/cm) but is sufficient to change the failure mode of heat seals. Based on these experiments, we conclude that the effect of CDT on the transition in the failure mode of heat seals is catastrophic. More simply stated, any level of corona treatment is sufficient to cause a transition in the failure mode from the normal tearing to peeling for LLDPE. This is in sharp contrast to the results that we obtained for corona-treated PP (35 and 38 dynes/ cm), which showed the normal tearing failure mode. We attribute this to the fact that PP tends to undergo preferentially chain-scission rather than cross-linking when exposed to irradiation.[24]
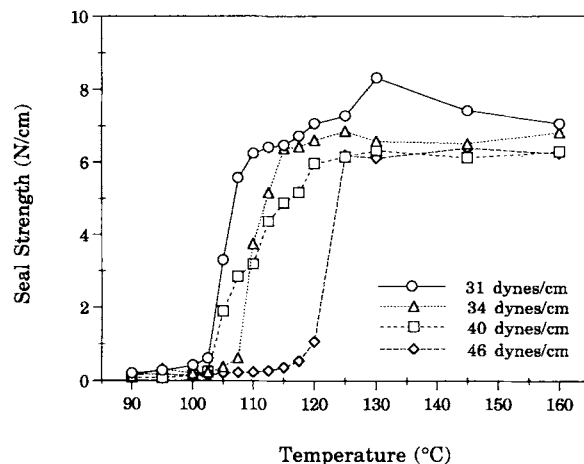
Seal Initiation Temperature

Commercially, seal initiation temperature (T_{si}) is a very important property of film-packaging resins. A

lower seal initiation temperature is desirable and results in lower energy costs, a broader heat-seal range, and higher production rates. We define seal initiation temperature as the temperature at which a measurable seal strength develops ($\sim$ 0.5 N/cm). For untreated films, this occurs at a temperature where the amorphous fraction of the polymer reaches 77 ± 3%. One could also view the seal initiation as the temperature at which the strength of the seal exceeds a given value, e.g., 2 N/cm. Figure 9 shows the entire heat-seal curves for a series of films at increasing levels of corona treatment. These films contain no slip additives.

As predicted from the heat-sealing model described in the preceeding paper,[23] the untreated control film shows a T_{si} of ca. 100°C. Treatment at low levels (30% applied power, 35 dynes/cm) results in a slightly higher T_{si} of ca. 105°C. The square symbols represent a 50% power setting and a typical treat level for printing applications (initial wetting tension, 42 dynes/cm). At this treat level, as well as 70% treat level (53 dynes/cm), there is an apparent lowering of the T_{si}. This enhanced seal strength at low seal temperatures is believed to be due to H-bonding of polar groups between functionalized surfaces. This phenomenon has been reported for CDT, high-pressure LDPE and is referred to as autoadhesion or self-adhesion. It has been shown by Owens[2] and later confirmed by Briggs and coworkers[5] that the keto groups are responsible for this phenomenon. The keto groups, formed by oxidation during CDT, can tautomerize to the enol form. The enolic hydrogen is slightly acidic and can form very strong H-bonds, thus leading to enhanced adhesion.
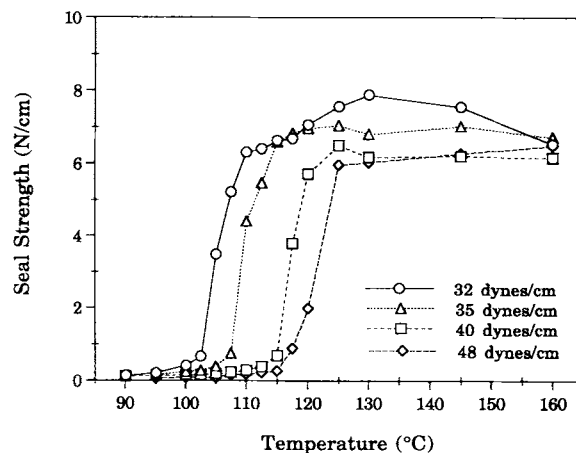

Figure 10 Plot of seal strength vs. temperature for films containing 600 ppm slip (erucamide).

The effect of CDT on the seal initiation temperature of slip-containing films is shown in Figures 10 and 11. The autoadhesion or enhanced seal strength at low seal temperatures is destroyed by the presence of slip, which prevents the H-bonding between the oxidized surfaces. In both cases, there is a systematic increase in the seal initiation temperature from 100 to 117°C as the level of CDT increases from 0 to 70% applied power (initial wetting tension increases from 31–32 to 46–48 dynes/cm). This is attributed to an increasing cross-link density near the surface, which reduces polymer mobility and limits the amount of chain interdiffusion across the seal interface. The anamolous behavior observed for sample 10 (600 ppm slip, treated at a 50% power setting)

Figure 9 Seal strength vs. temperature for LLDPE films.

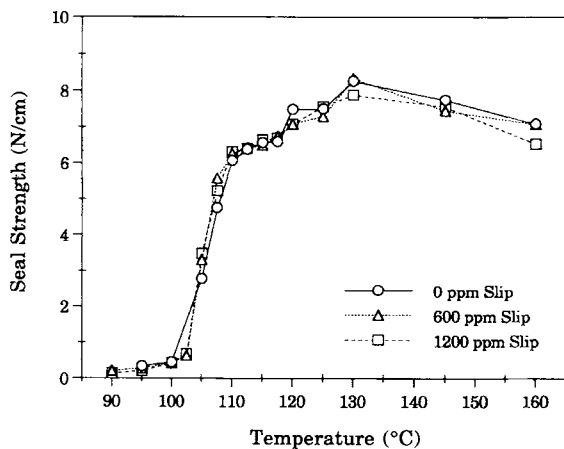**Figure 11** Plot of seal strength vs. temperature for films containing 1200 ppm slip (erucamide).

was caused by an inhomogeneous distribution of slip additive during mixing and extrusion.
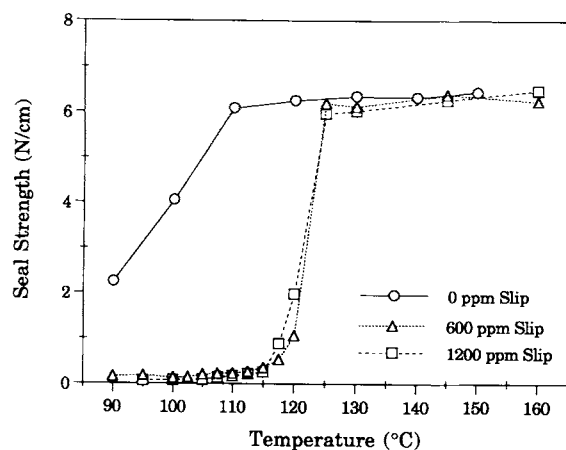
Plateau Seal Strength

The plateau seal strength (SS_p) is obtained from the heat-seal curve and corresponds to the level of seal strength in the plateau region where the seal strength remains nearly constant with respect to temperature. As mentioned previously, the failure mode in this region is tearing for untreated polymers, but peeling for corona-treated films. The plateau seal strength for the control film is approximately 8 N/cm, as shown in Figures 9–11. CDT results in a systematic decrease in the plateau seal strength in all cases, regardless of the level of slip additive. Treatment at a typical level of 40–42 dynes/cm (50% applied power) lowers the plateau seal strength to 6 N/cm, which represents a 25% decrease. The magnitude of this effect is dependent on the level of treatment and is consistent with the proposed cross-linking mechanism.

Effect of Slip Additives

The purpose of slip additives is to modify the coefficient of friction (COF) of the film. It is therefore necessary that these additives are surface-active. However, the presence of slip additives on the film surface has been known to cause problems related to wettability and adhesion. Their effect on heat sealing has not been reported and therefore was investigated. Before discussing the effect on CDT films, it should be noted that the presence of slip additives, at levels up to 1200 ppm, had no effect on

Figure 12   Plot of seal strength vs. temperature for untreated films of LLDPE containing 0, 600, and 1200 ppm slip.

Figure 13   Plot of seal strength vs. temperature for an LLDPE film treated at 70% applied power.

the failure mode, seal initiation temperature, or plateau seal strength for untreated films (Fig. 12).

For corona discharge-treated films, slip reduces the amount of autoadhesion observed at low sealing temperatures. This effect is limited to temperatures below the complete melting point of the polymer, as shown in Figure 13, for samples treated at 70% applied power (initial wetting tension 46–53 dynes/cm). At seal temperatures above the final melting point of the polymer, there is no effect due to the presence of slip. Again, these samples exhibit a peeling failure mode throughout the entire sealing range, independent of slip concentration.

## Effect of Aging on Heat Sealing Characteristics

The aging of CDT films to be used in packaging applications is important since there is usually some interval between the time the film is treated and the time it is printed and heat-sealed. We showed previously in the section Characterization of Film Surfaces that aging has a significant effect on the surface energy of treated films. On the other hand, we have found that the effects of film aging on the heat sealability and the effects of heat-seal aging on the seal strength are negligible. The plateau seal strength remains fairly constant over a relatively long time (up to 6 months), regardless of the level of treat or concentration of slip. One may wonder how the seal strength remains unaffected yet the surface energy of the film changes drastically during this period. It should be noted that the autoadhesion, which is associated with the presence of polar, H-bonding groups on the surface, does indeed decrease somewhat over time. However, the level of the plateau seal strength is determined by the extent of inter-

diffusion and entanglements and not by the degree of polar interactions at the seal interface. Therefore, the attainable level of plateau seal strength is not dependent on the chemical reorganization processes associated with the outer 5–50 Å.

Effect of Wetting Liquids on Seal Strength

The decrease in peel strength due to the presence of wetting liquids at the bond interface has been related to the reversible energy of adhesion by Gent and Schultz[25]. Owens[2] also showed that the application of any H-bonding liquid to the seal interface of corona-treated films destroyed the self-adhesion observed at low seal temperatures. We have also found this to be the case. Figure 14 shows the loss of adhesion at low seal temperatures due to the presence of water. The effect of water on the seal strength is quite dramatic at low seal temperatures but begins to disappear as the seal temperature approaches the melting point of the polymer. Above the complete melting point (128°C), there does not appear to be any loss of adhesion due to the presence of water. The filled circles in Figure 14 represent the seal strength in the presence of perfluorodecalin, a nonpolar, non-H-bonding liquid. This wetting liquid also lowers the seal strength; however, it is most likely due to a different mechanism. Due to the broad molecular weight distribution and broad composition distribution for these Unipol®-based polymers, the surfaces of these films may be enriched in highly branched, amorphous material. It is possible that perfluorodecalin swells or dissolves some of the low molecular weight species that are present on the surface, thereby lowering the seal strength.
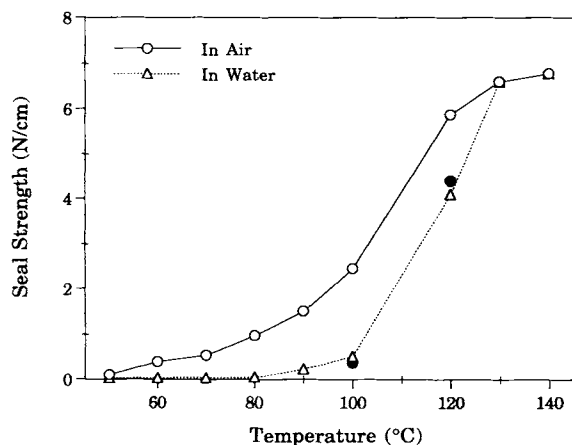
Figure 14   Effect of wetting liquids on seal strength for LLDPE.

Role of Cross-linking vs. Surface Polarity

During this investigation, we have done several experiments to determine what is responsible for the observed changes in the heat-seal behavior, particularly in terms of cross-linking vs. surface polarity. Although it is generally accepted that PE surfaces are cross-linked during corona or plasma treatment, there is very little direct evidence for this phenomenon.

Perhaps the most convincing evidence for cross-linking is the ability to measure an insoluble gel. Ideally, one would like to determine the depth of this cross-linked layer as a function of treat level. There is some evidence for this in the literature. Hansen and Schonhorn[26,27] exposed low molecular weight hydrocarbons to a plasma and the only products that they observed were high molecular weight hydrocarbons. They have also exposed a PE cube to a plasma and, by extraction, found an insoluble, cross-linked skin. Based on the weight fraction of this insoluble gel, one can estimate the depth to which this cross-linking takes place.

We have attempted similar experiments wherein we extruded a very thin film (5–6 μm) and exposed the sample to the maximum attainable level of corona discharge. In addition, the line speed was reduced to 15 m/min to increase the exposure time. However, even after treatment under these conditions, the film remained 100% soluble in hot xylene. Therefore, we can only estimate that under our experimental conditions, the treatment was limited to the outer 1000 Å.

Electron-beam irradiation of LLDPE films was carried out at dosages of 2, 4, 8, 16, and 32 Mrad in a nitrogen atmosphere to determine the effect of cross-linking on heat-seal behavior. The treated films were heat-sealed under standard conditions. The results of the heat-sealing experiments using E-beam-irradiated samples were identical to those obtained using corona-treated samples, i.e., any level of treatment causes a change in the mode of failure of heat seals from tearing to peeling. Besides the transition in failure mode, E-beam treatment also causes a decrease in the plateau seal strength, similar to what is observed with CDT (Table II and Fig. 15).

Under the conditions of the E-beam experiment, the electron energies are high enough to penetrate the entire specimen and result in a bulk treatment. In this case, it is possible to measure an insoluble gel since the cross-linking is not limited to the surface region. Table II shows the percent gel as a function of E-beam dosage. It should also be noted that E-beam irradiation, even under an inert atmosphere,

Table II   Effect of E-Beam Irradiation on the Solubility Seal Strength of LLDPE

Dosage (Mrad)	0	2	4	8	16	32
% Insoluble[a]	0	0	0	0	22	54
Seal strength (N/cm)	7.50	7.20	6.38	5.34	4.74	5.46

[a] Determined by Soxhlet extraction using hot xylene after 48 h.

introduces a significant amount of oxygen-containing species into the polymer. It is believed that these species are formed when long-lived polymer radicals are exposed to the air atmosphere. As mentioned above, E-beam is a bulk treatment and the resulting oxygen species are distributed throughout the polymer and are not restricted to the surface region. As a result, E-beam-irradiated films show a lower surface energy or wetting tension than that of CDT films that contain comparable amounts of oxygen-containing groups (Fig. 15). Therefore, it is believed that the observed changes in the heat-seal behavior are associated with the degree of cross-linking as opposed to the presence of polar species on the film surface.

To determine the effect of polar, oxygen-containing groups on the heat-sealing behavior, PE films were chemically oxidized using aqueous chromic acid. This treatment is commonly done to create highly functionalized PE surfaces and results in covalently bound carboxylic acid and ketone (aldehyde) groups located in a thin layer near the polymer surface (<20 Å).[22] Films were treated with aqueous chromic acid at room temperature to give a surface with ca. 2% oxygen as determined by XPS. This is comparable to corona treatment at a 40% applied power setting. Treated films were then heat-sealed at 150°C. A tearing failure mode was observed for

samples that had been chemically oxidized. These results can be compared to those obtained for a corona-treated film with ca. 2% oxygen on the surface that showed a peeling failure mode. No significant differences in surface morphology were detected by low-voltage scanning electron microscopy (LVSEM).

These experiments provide indirect evidence that cross-linking, rather than the presence of polar functional groups, is responsible for the changes in the failure mode of heat seals made using corona-treated PE film. The fact that CDT PP films, which tend to undergo chain scission, show normal sealing behavior, despite the presence of polar groups, is also supporting evidence for the proposed cross-linking mechanism.

According to van Ooij and Michael,[28,29] TOF-SIMS can be used to determine cross-linking of polyolefins directly by the appearance of high mass/charge (m/e) fragments ($>C_8$). Experimental data for a control film and a corona-treated film (initial wetting tension = 53 dynes/cm) were obtained in anticipation that this would provide direct evidence for surface cross-linking of LLDPE during CDT. Unfortunately, the interpretation was not straightforward due to the presence of polydimethylsiloxane fragments and low molecular weight oxidized material on the surface of the treated film and the results were inconclusive.
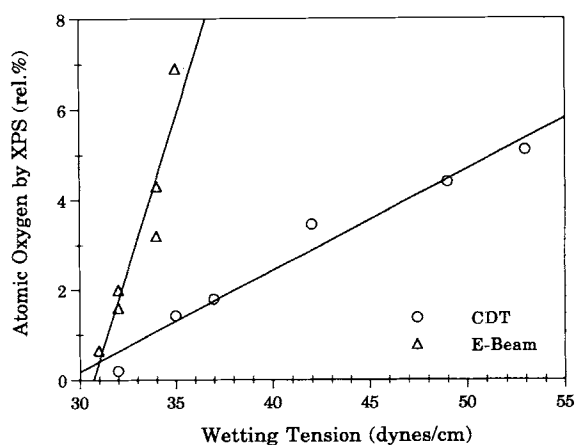
Figure 15   Comparison of surface energy of e-beam irradiated and CDT LLDPE films.

CONCLUSIONS

The most important finding of this work is that any level of corona treatment is sufficient to change the failure of heat seals prepared from LLDPE from a normal tearing mode to a peeling mode. This irreversible effect is attributed to cross-linking of the surface and is catastrophic in the sense that heat sealing at higher temperature or longer dwell time does not alter the results. In addition, CDT treatment results in an increase in seal initiation temperature of 5–17°C and a decrease in the plateau seal strength of 5–25% as level of treatment or wetting tension increases from 31 to 56 dynes/cm.

Based on these results, and experimental data obtained from other heat-sealing studies on E-beam irradiated PE, chemically oxidized PE, and CDT PP, we conclude that the effects on heat sealing are due to surface cross-linking rather than the presence of polar functional groups.

CDT results in the surface oxidation of LLDPE, as is evident by the increased surface energy or wetting tension of the treated films and the presence of oxygen as determined by XPS. These highly functionalized surfaces undergo a relatively slow reorganization under ambient conditions to minimize the surface free energy. Wetting-tension measurements, which probe the outer 5 Å of the polymer surface, are more sensitive to the reconstruction process than XPS, which probes the outer 50 Å.

Slip additives (erucamide), which are known to cause problems related to printability and adhesion, have little if any effect on heat sealability. Slip additives reduce the amount of H-bonding between functionalized surfaces of CDT films observed at low seal temperatures, but have no effect at seal temperatures above the final melting point of the polymer. For untreated films, slip additives at levels up to 1200 ppm have no effect on the heat-seal behavior. Using XPS, it was shown that slip additives do not prevent or significantly reduce the amount of the oxidation during the corona treatment of LLDPE, but merely mask the treatment by subsequent blooming to the surface.

The auto-adhesion phenomenon or apparent seal strength obtained at low seal temperatures observed for CDT films is eliminated by annealing the film before sealing, the presence of slip additives, and the action of wetting liquids at the seal interface. Aging of CDT films and heat seals made from CDT films (up to 24 weeks) was found to have no significant effect on the failure mode or the level of seal strength.

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