

Corona treatment on polyolefin films

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FOR POLYOLEFIN FILMS, SURFACE treatment is usually necessary to improve wetting and adhesion characteristics for various applications such as adhesive bonding, printing, extrusion coating, metallizing, composites, and heat sealing (1). Many methods are available to modify polymer surfaces (2, 3). Corona treatment is a common technique.

Theories proposed for the increased adhesion of corona treated polymer surfaces include electret formation (4), elimination of weak boundary layers (5), increased surface roughness due to pitting (6), and introduction of polar groups due to oxidation and other chemical changes in the surface region (7–9). The common theory is that corona discharge treatment causes an increase in surface energy by introduction of polar groups on the surface. This improves adhesion and wetting properties (10, 11).

Since polyolefins using polyethylene (PE) and polypropylene (PP) are two common synthetic polymers (7), most research on corona treatment of polyolefin films has used PE and PP films. Much understanding about corona treatment has occurred in the last 25 years. This paper reviews recent research on the mechanism of corona treatment of polyolefin films to help industrial engineers or scientists better understand the physical and chemical mechanisms involved. This improved understanding will allow development of the technical potential of corona treatment.

CORONA EFFECT

The term corona describes the condition of a gas—usually air—between electrodes. Gases such as air are ordinarily good electrical insulators. In a sufficiently strong electric field, gases can break down. The molecules become ionized and conduct electricity. A sudden electric discharge occurs that usually develops into an arc or sparks between electrodes. Placing a solid film between these electrodes interrupts the conductive path. Instead of a hot localized arc, a cooler, diffuse glow occurs between the two electrodes. This soft, bluish discharge of air at atmospheric pressure is corona.

The corona phenomenon starts with a few stray electrons present in the gas between electrodes because of cosmic rays or other background radiation. Applying a high voltage creates a strong electrical field that accelerates the electrons toward the positive electrode. The electrons continually strike gas molecules in their path. Impacting electrons may knock an orbital electron from the molecules leaving a positive ion and another electron that can continue to strike other molecules. The impacting electron usually lifts an orbiting electron to an unstable, higher energy orbit to create an excited molecule. Soon the gas is full of electrons, positive ions, excited molecules, heat, and light—corona. The excited molecules are unstable and decompose spontaneously into radicals, ions, and photons.

The dominant theory concerning corona discharge is that it introduces

ABSTRACT

This paper presents a review of recent studies on corona effects of polyolefin films. It focuses on the mechanism of corona treatment of polyolefin films by discussing the chemical and physical changes of this process and the self-adhesion mechanism. Corona discharge of polymeric films introduces polar groups into the surfaces resulting in increases in the surface energy. This improves substrate wetting and adhesion characteristics. The main chemical mechanism of corona treatment is oxidation. Corona treatment can also crosslink surface regions and increase film cohesive strength.

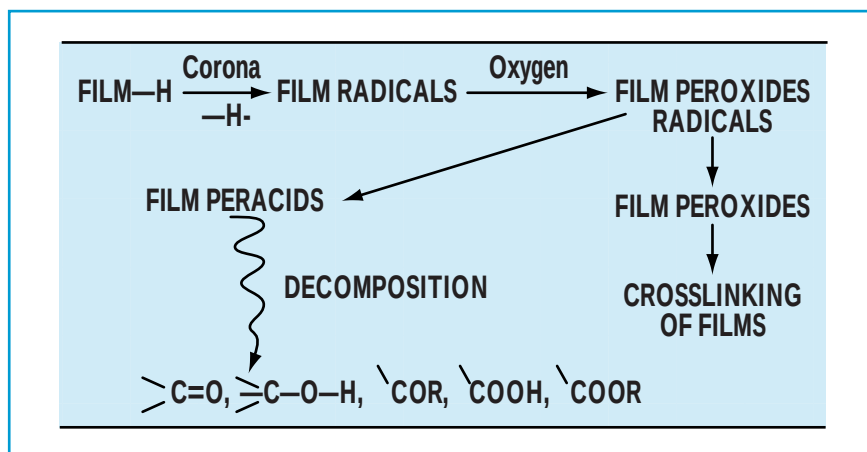
Application:

Corona treatment of polymer films forms polar groups that increase the surface energy with concomitant improvement in wetting and adhesion characteristics.

polar groups into the polymer surfaces. This leads to higher surface energy and better adhesion. In oxygen contained corona for example, a mixture of activated oxygen species is present between the electrodes during treating. This includes free oxygen in its elemental form (O), ozone (O₃), and activated oxygen (O₂*). Activated oxygen is oxygen that is vibrationally and electrically excited above its ground state energy (12, 13). Highly reactive oxygen arrangements can react very rapidly with polar molecules such as water to introduce oxygen containing functional groups into the film surface as **Fig. 1** shows.

As power to the corona increases, more ions form, and the average kinetic energy of the particles increases. The important parameter in regulating the treatment level is the energy that the ions impart to the film. With higher rela-

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1. Oxygen introduction into corona discharge films (11)

tive humidity, the discharge energy should increase (8). Discharge treatment under high humidity conditions leads to a proportionally higher concentration of groups containing C-O functionality than does treatment in low humidity conditions. Some workers considered electrons emitted by the corona induced photo effect as the main cause of surface activation (14) leading to the chemical and physical surface changes. Polar chemical functional groups forming on the surface enhance the surface adhesion and wetting. Corona treatment can also change the morphology of polymer films and influence their adhesive properties. The adhesion can increase or decrease depending on the potential bonding area and the presence of voids. Self adhesion experiments on corona treated polyolefins have confirmed this (4, 9).

Corona discharge treatment in the presence of air or action of oxidizing mixtures entails substantial morphological and chemical modifications in the surface region of a polymer such as alteration of external appearance and formation of functional groups (15, 16). Although the magnitude and the nature of these modifications seem to depend on the treatment techniques and polymers used, the final intent of these processes is to enhance the adhesive properties of polymers (17). The treated surface changes

chemically and physically from the corona treatment (10, 18).

CHEMICAL CHANGES

Corona discharge treatment results in an increase in surface energy by introduction of polar groups on the surface. This improves their adhesion and wetting properties. The main chemical mechanism of corona discharge treatment is oxidation. In addition, the crosslinking of the molecules on the surface restricts mobility of the surface molecules and results in an increase in the molecular weight. Various analytical techniques that have identified these chemical functional groups include electron spectroscopy for chemical analysis (ESCA or XPS), second ion mass spectroscopy (SIMS), infrared spectroscopy (IR or ATR), and electron spin resonance (ESR). XPS and IR are the most common techniques.

Oxidation

Chemical changes in polyolefins due to air oxidation and photo oxidation were detected in the early 1950s using transmission infrared spectroscopy. In thermal oxidation for example, keto groups primarily resulted plus some aldehyde and acid groups (19). In photo oxidized polyethylene, similar quantities of aldehyde, acid, and keto groups resulted. Changes also occurred in levels of unsaturation in both types of oxidation leading to postulation of formation of unstable hydroper-

oxide groups. Rossmann (20) found an increased concentration of keto groups in polyethylene.

Evidence for the existence of the hydroperoxide intermediate, ROOH, RO₂R, RO₃R, -O-(C-)=O, and >C=O groups are in the literature (13, 21-23). These polar groups provide sites for adhesion of inks. A free oxygen atom can break a polymer molecule in two or simply cleave a hydrocarbon radical. In either case, two free radicals form for a net gain of one. Free radicals in this form are very reactive and quickly form new groups (24). Oxidation of polymers by atomic oxygen occurs rapidly at the surface, although initiation of simple thermal oxidation begins with the slow formation of hydrocarbon radicals. The hydrocarbon radicals formed with alkoxy or hydroxy radicals during the initiation stage react rapidly with oxygen atoms or molecular oxygen. Reaction rate constants can be as high as 100,000. This translates to thousands of chain transfers in the short time that the film is exposed to the corona energy.

The emission spectrum of corona discharge is very sensitive to the surrounding atmosphere. Small amounts of impurities can lead to dramatic chemical changes in the surface of the treated film (25-27). Polyethylene treated in a pure nitrogen corona forms basic functional groups that adsorb acidic but not basic dyes. This is opposite to the dye adsorption characteristics of polyethylene treated in air coronas (28).

To test the oxidation hypothesis further, effects of treating in air, O₂, N₂, He, and Ar were compared. Because it was possible to corona treat polymers in these gases to the same level of surface energy, the question arises regarding the importance of oxygen as a factor in corona induced adhesion promotion of polyolefin film. Corona treatment of polyolefin in an inert atmosphere

should not produce oxygenated functional groups. Studies indicate that good auto-adhesion and ink adhesion to the film do result (25, 29). Further XPS spectroscopic studies showed that oxygen does incorporate into the film surface for all these gases used in discharge treatment. One can therefore argue (9) that using other gases under corona discharge may still produce free radical sites in the film. In turn, these gases may react with atmospheric oxygen to give a thin layer of polymer containing ketonic functional groups. These groups can hydrogen bond to carbonyl groups in the polymeric binders of the inks or coatings to increase adhesion. Previous studies have supported the hydrogen bonding theory as the primary reason for polar groups to enhance film adhesion characteristics through corona. The other possible sources of oxygen in inert atmospheres may be as follows:

- Oxygen impurities from gases
- Dissolved oxygen in the polymer that was not completely removed
- Apparatus often constructed of glass dielectrics that is a ready source of dissolved oxygen molecules.

Another area in which oxidation plays a large role and helps support it is auto-adhesion of polymer films. This is how well two similarly treated films bond to each other. The chemical basis for enhanced adhesion between polymer layers resulting from corona treatment may be due to hydrogen bonding between the hydroxyl of enol groups and other oxygen containing functional groups created on the polymer surface by treatment. These functional groups resulted during corona discharge in air and when using inert gases such as nitrogen and argon. Corona discharge in hydrogen prevented formation of oxygen func-

tionality and did not promote auto-adhesion.

Increase in molecular weight and crosslinking

Many researchers have noted that corona discharge further increases the molecular weight of polymeric materials (30–32). The free radicals introduced increase molecular weight of the polymer surface sufficiently to give added strength, higher melting point, and greater integrity. The surface oils and waxes that comprised the weak boundary layer were incorporated into the stronger high molecular weight boundary layer that was 0.05–0.1 μm thick.

Farley and Mika (30) studied the effect of corona discharge treatment (CDT) of LLDPE with special emphasis on the heat seal behavior of treated films. Results of heat sealing studies with electron beam irradiated PE, chemically oxidized PE, and corona discharged PE provided indirect evidence of the proposed surface crosslinking mechanism.

A peroxyradical could cause chain scission and reduced molecular weight or chain addition and increased molecular weight. Corona treatment power levels influence this reaction. One investigation showed (6) that the second reaction prevailed under normal treatment conditions and the former under severe conditions of 30 min. of high power treatment.

PHYSICAL CHANGES

Corona treatment can change the surface morphology of polyolefin films besides introducing polar functional groups onto the surfaces. The polar component of surface energy is the key to understanding the changes in adhesive behavior of the films during corona treatment (33). Changes in surface morphology caused by these processes can also influence the adhesion. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) usu-

ally study surface morphology. This section focuses on morphological change caused by corona treatment and other physical changes such as mechanical properties.

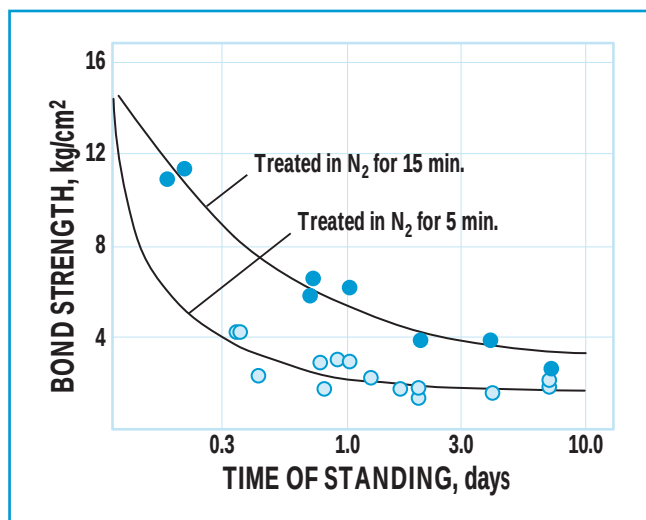
Surface morphology

As high energy particles bombard the film being treated, small micropits can form. These are tiny holes dug by the charges. Micropitting can lead to increased adhesion through mechanical keying and a greater potential bond area. It can also lead to reduced adhesion because a small area of bonding is achieved or because stress concentration occurs due to the presence of voids. The actual effect depends on surface energies, viscosity of the wetting liquid, and size and shape of the irregularities.

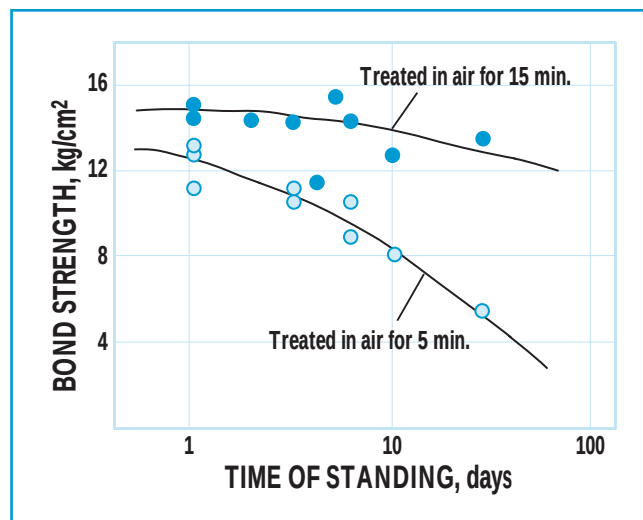
Corona treatment in air makes a polyolefin film surface rough. Using pure oxygen or carbon dioxide rather than air enhances surface roughening. Corona discharge in gases containing no oxygen such as H_2 , He, Ar, or N_2 produced no visual change on the surface (34). Oxidation therefore may be a necessary accompaniment to the surface roughening effect.

Excessive treatment usually leads to bumps on the polyolefin surfaces and has a deteriorating effect on the adhesion and wetting characteristics. The extreme situation is that heat generated in this process causes burning of the treated samples. Surface morphology changes with time and temperature of treatment. At constant temperature, the size of the bumps on PE films increased with a longer treatment time. Bump size also increased when the temperature was higher for a constant treatment time. Bumps of about 1 μm in diameter were created by 1-min. treatment at 50°C. Treatment for 15 min. at 75°C produced 10- μm bumps (6). The study showed that polyolefin films corona treated for long times at elevated temperatures exhibit reduced

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2. Effect of standing on auto-adhesion after nitrogen corona treatment (6)



3. Effect of standing on adhesion after air corona treatment (6)

bond strength and have more loose surface materials than films more modestly corona treated (6). Speculation is that these degradation products might act as a weak boundary layer in reducing self adhesion. One could also propose that the degradation products of such excessive treatment might mask the underlying enol groups and prevent the close approach of the two surfaces necessary for hydrogen bond formation. An unexpected result was that the bumps on a treated surface removed easily when dipping a sample into CCl_4 , ethanol, or 0.2% aqueous NaOH. At low resolution, the solvent dipped surface appeared similar to the untreated surface. With high resolution, the treated and ethanol dipped surfaces appeared rough and textured compared with the original surface. The oxygen corona might have attacked the amorphous regions preferentially to cause etching while becoming visible when removing the degradation products.

A possible explanation of the corona induced bumps on the corona treated surface is that poly-

olefin possesses an inert skin on its surface that does not undergo attack by the active species in an oxygen containing corona. Degradation of the polymer occurs below this skin, and a certain amount of gas evolves. This may cause the skin to blister and form the bumps observed. No apparent reason exists why the skin should remove so cleanly when dipping the treated surface in ethanol or other solvents.

Overmey *et. al* (35) presented a study of adhesive strength to the polymer bulk surface of bumps—termed droplet-like protrusions in their studies—of a PP film treated with a single corona dose of 112.5 J/cm^2 . Bumps physically absorbed on the polymer bulk surface. Contact angle measurements supported the assumption of local surface melting or sublimation as a possible explanation for formation of the bumps. Friction force measurements indicated that the molecules of the bumps were chemically different and had low molecular weight.

In another study of Overmey *et. al* (36), changes in the morphology of corona treated uniaxially oriented PP and biaxially oriented PP correlated to self-adhesive strength of the films. The diameters and heights of bumps increased proportionally to the applied corona dose after a threshold of about 18 J/cm^2 . An

assumption is that the loss of adhesive strength was primarily due to a reduction of the contact area and the adhesive strength of the polymer bulk surface. Above 18 J/cm^2 , the molecular weight of the surface molecules decreased, and oxidation occurred during all stages of the corona treatment.

Mechanical and rheological properties

Dong *et. al* (37) studied the mechanical properties of corona modified cellulose and polyethylene composites. The work showed that the treatment of polyethylene, cellulose fibers, or both in air corona gave a significant increase in composite strength properties. Yield stress increased after treatment of one or both composite components. Pronounced improvement in ductility occurred for composites containing 15%–30% of the corona modified fiber. Corona treatments strongly influenced yield strength and strain and elongation at rupture. This indicated that these composite properties were highly sensitive to interfacial phenomena. Initial modulus and ultimate strength of composites were generally independent of corona treatment meaning they were insensitive to interfacial characteristics in the composites. Corona treatments therefore represent a valuable strategy for surface modification con-

KEYWORDS

Adhesion, bibliographies, cohesion, corona discharge, film, oxidation, polyolefins, surface treatment, wettability.

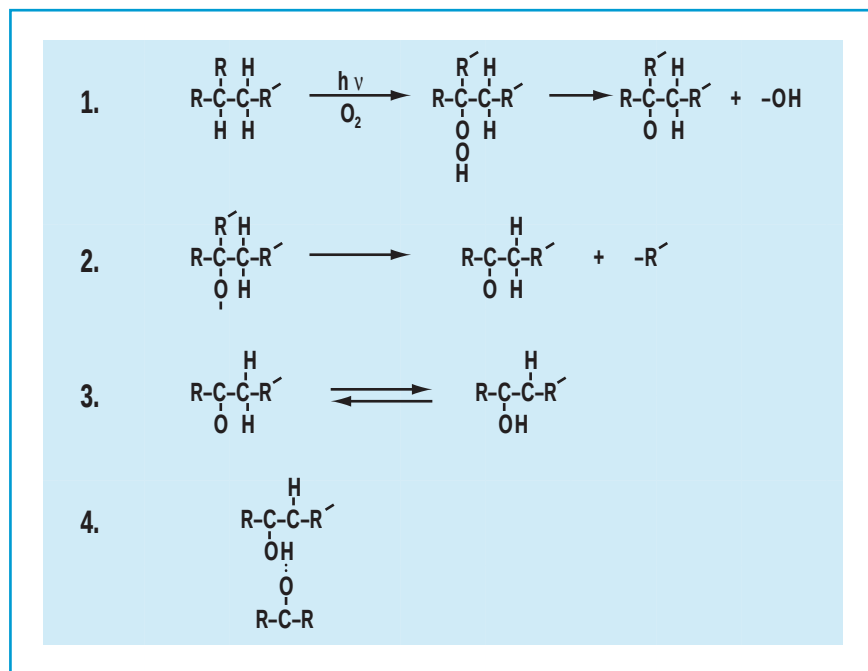
sistent with targeted mechanical properties of the composites.

The same authors (38) also studied the rheological properties of corona modified cellulose and polyethylene composites. This work showed that corona treatment for one or both of the constituents resulted in decreased melt viscosities compared with compounds containing untreated materials. The reduction of melt viscosity may originate from low molecular weight moieties formed on the surfaces of polyethylene and cellulose during corona treatment. These may act as lubricants at interfaces. Corona treatment of fibers also leads to higher packing volumes. This may result from a reduction in fiber length when processing fibers under high shear conditions. As a result, these fibers perturb the normal flow pattern in the melt to a smaller degree than the longer fibers of untreated cellulose. The rheological research by Bousmina *et. al* (39) revealed that corona treatment resulted in a decrease of dynamic shear viscosity of PE and polystyrene.

SELF-ADHESION MECHANISM

Early studies (6, 40–42) of corona discharge treated polyolefins suggested that the increased auto-adhesion was due to electret formation. The auto-adhesion was due to changes in the electrical properties of the surface induced by the corona discharge. When dielectric materials were subjected to strong electric fields, electrical charges were induced in the dielectric. This is the electret effect.

Surface charge due to electret formation decays with time. The decay is faster at elevated temperatures (43). **Figures 2 and 3** show auto-adhesion vs. time of standing for treatment in oxygen and nitrogen, respectively (6). In both cases, a decrease in bonding occurred with time of standing. The results in Figs. 2



4. Formation of ketones in PE by corona treatment (49)

and 3 showed that the decay was slower after longer times and was more rapid in nitrogen than oxygen. If the samples were stored at an elevated temperature after treatment, a much more rapid decay in bonding occurred. This parallel between the known properties of electrets and the adhesion behavior of corona treated PE is further support for the idea that auto-adhesion might relate to electret formation.

The results led to the suggestion that a type of electret formation was the basic reason for the increase in the auto-adhesion of PE when treated in a corona discharge. Industrial corona discharge treatment showed that the printability of a PE sheet decayed with time of standing after treatment. Although this implies that the electret effect may be responsible for the enhanced printability of PE achieved by treatment in a corona discharge, some researchers proved this theory incorrect (44).

The following mechanism may account for the enhanced self-adhesion of corona treated polyolefin film. In PE for example, Eq. 1 of **Fig. 4** shows that a tertiary carbon atom in the PE molecule undergoes attack through the mechanism of hydrogen abstraction and hydroperoxide for-

mation (45). The hydroperoxide decomposes into an alkoxy radical. Being unstable, the alkoxy radical undergoes chain scission as in Eq. 2 to form a ketone and another free radical (6). Equation 3 shows the tautomerization of the ketone to the enol form. The weakly acidic hydrogen of the enol can then hydrogen bond with a carbonyl in an adjacent surface as Eq. 4 shows. Many pathways for ketone formation in the corona activated oxidation of PE are possible. This one is typical.

The immediate failure of joints to which hydrogen bonding liquids have been applied is apparently due to the ability of these liquids to disrupt the enol to carbonyl hydrogen bond because of the stronger hydrogen bonding tendency. The reversibility of the effect strengthens the argument. Enol to carbonyl hydrogen bonds reform when the liquid can evaporate without disturbing the joint. The failure of solvents of strong acids and bases to influence the adhering of corona treated film can be explained by assuming that at least one end of the molecule bearing the enol group is still attached to the film surface by carbon to carbon bonds.

Discharge treatment of polyolefins in most gases leads to the incorporation of oxygen functions in the surface. Hydrogen is unique in preventing formation of oxygen functionality and does not promote self-adhesion. This indicates that film auto-adhesion increases with an increase in surface oxidation. The chemical basis for enhanced adhesion between polyolefin films resulting from corona treatment may be due to hydrogen bonding between the hydroxyl of enol groups and other oxygen containing groups created on the polymer surface by the treatment. This hydrogen bonding theory of auto-adhesion enhancement of corona treated polyolefin films is consistent with the above-mentioned oxidation mechanism of corona treatment.

SUMMARY

Corona discharge of polymeric films introduces polar groups into the surfaces resulting in increases in the surface energy. This then improves substrate wetting and adhesion characteristics. The main chemical mechanism of corona treatment is oxidation. In addition, corona treatment can crosslink surface regions and increase the film cohesive strength.

The formation of polar functional groups and reactive species may be the mechanism to impart improved surface characteristics to the films. Some of these species are the following:

- Peroxides and ozanides: RO_2R , ROOH , and RO_3R
- Ions: $-\text{NO}_3^-$ and $\text{R}-(\text{C}-\text{O})=\text{O}$
- Neutral functional groups: $>\text{C}=\text{O}$, $>(\text{C}-)\text{OH}$, $\text{HO}-(\text{C}-)=\text{O}$, and $-\text{NO}_2$
- Ozone
- Film surface crosslinking.

Corona treatment under many other gases can also enhance the surface adhesion and wetting characteristics. Using other gases under corona discharge may still produce reactive species and polar functional groups. XPS spectroscopic studies showed that oxygen does incorporate into the film surface for all these gases used in discharge treatment. Oxidation therefore plays a very important role in corona discharge treatment under different working gases to enhance good adhesion.

The chemical constituents formed on the film surface by corona discharge are largely the result of the composition of the gas between the electrodes, the film, and its additives. The effectiveness of corona treat-

ment on polymeric films depends on the relative humidity during discharge. Higher surface moisture concentration results in a longer required time of corona discharge. This suggests the possibility that the initial hydrogen abstraction process may be reversible in the presence of surface moisture. Corona treatment discharge can change the morphology of polymer films and influence adhesive properties. The increased surface roughness can lead to increased or decreased adhesion depending on surface energies, potential bonding, and presence of voids. Excessive treatment leads to a situation that can result in bumps on the polyolefin surfaces. This causes deterioration of the adhesion and wetting characteristics. The heat generated in this process also marginally helps to burn off or evaporate very low molecular weight fractions that may have migrated to the surface after extrusion. TJ

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LITERATURE CITED

1. Brewis, D. M., and Briggs, D., *Polymer* 22(1):7(1981).
2. Kruse, A. G. K., Baalman, A., Henne-mann, O. D., *J. Adhesion Science and Tech.* 9(12):1611(1995).
3. Liston, E. M., Martinu, L., and Wertheimer, M. R., *J. Adhesion Science and Tech.* 7:1091(1993).
4. Stradal, M. and Goring, A. E., *Can. J. Chem. Eng.* 53:427(1975).
5. Schonhorn, H. and Ryan, F. W., *J. Appl. Polymer Science* 18:235(1974).
6. Kim, C. Y., Evans, J., and Goring, D. A. J., *J. Appl. Polymer Science* 15:1357(1971).
7. Gerenser, L. J., Elman, J. F., Mason, M. G., et al., *Polymer* 26:1162(1985).
8. Briggs, D. and Candall, C. R., *Int. J. Adhes. Adhes.*, 2:13(1982).
9. Owens, D. K., *J. Appl. Polymer Science* 19:265(1975).
10. Mangipudi, V., Tirrell, M., and Pocius, A. V., *Langmuir* 11(1):19(1995).
11. Podhajny, R. M., *J. Plastic Film Sheeting* 4(7):177(1987).
12. Bezigian, T., *Tappi J.* 75(3):139(1992).
13. Hansen, R. H., and Sharpe, L. H., *J. Polymer Science A3*:2205(1965).
14. Steinhäuser, H. and Ellinghorst, G., *Angew. Makromol. Chem.* 120:177(1984).
15. Mittal, K. L., in *Tribology Series* (J. M. Georges, Ed.), Elsevier, Amsterdam, 1982, p. 153.
16. Blais, P., Carlson, D. J., Csullog, G. W., et al., *J. Coll. Int. Sci.* 47:636(1974).
17. Kaelble, D. H., *Physical Chemistry of Adhesion*, Wiley, New York, 1971, p. 456.
18. Egitto, F. D. and Matienzo, L. J., *IBM J. Res. Develop.* 38(4):423(1994).
19. Rugg, F. M., Smith, J. J., and Bacon, R. C., *J. Polymer Science* 13:535(1954).
20. Rossmann, J., *J. Polymer Science* 19:141(1956).
21. Harris, W. C., Earler, E. E., and Samuels, S. B., *Tappi J.* 73(1):145(1990).
22. Markgraf, D., *TAPPI 1989 Extrusion Coating Seminar Notes*, TAPPI PRESS, Atlanta, p. 129.
23. Carley, J. F. and Kitz, P. T., *Polymer Engineering Science* 20:30(1980).

24. Billmeyer, F. W., *Textbook of Polymer Science*, 2nd edn., Wiley, New York, 1971, p. 298.
25. Stradal, M. and Goring, D. A. I., *Polymer Engineering Science* 17:38(1977).
26. Grum, F. and Costa, L. F., *Applied Optics* 15(75)(1976).
27. Evans, J. M., *J. Adhesion* 5:9(1973).
28. Courval, G. J., Grey, D. J., and Goring, D. A. I., *Polymer Letters* 14:231(1976).
29. Carlsson, D. J., and Wiles, D. M., *Can. J. Chem.*, 48:2397(1970).
30. Farley, J. M., and Meka, P., *J. Appl. Polymer Science* 51:121(1994).
31. Briggs, D. and Kendall, C. R., *Polymer* 20:1053(1979).
32. Schonhorn, H. and Hansen, R. H., *J. Appl. Polymer Science* 11:1461(1967).
33. Carley, J. F. and Kitze, P. T., *Polymer Engineering Science*, 18:326(1978).
34. Kim, C. Y., Suranyi, G., and Goring, D. A. I., *J. Polymer Science*, 30:553(1970).
35. Overmey, R. M., Guntherodt, H. J., and Hild, S., *J. Appl. Physics* 75:1401(1994).
36. Overmey, R. M., Luthi, R., Haefke, H., et al., *Appl. Surf. Science* 64:197(1993).
37. Dong, S., Sapieha, S., and Schreiber, H. P., *Polymer Engineering Science* 33:343(1993).
38. Dona, S., Sapieha, S., and Schreiber, H. P., *Polymer Engineering Science* 32:1734(1992).
39. Bousmina, M., Bataille, P. Sapieha, S., et al., *Composite Interfaces* 2(3):171(1994).
40. Gross, B., *Phys. Rev.* 66:26(1944).
41. Perlman, M. M. and Meunier, J. L., *J. Appl. Physics* 41:2365(1970).
42. Roos, J., *J. Appl. Physics* 40:3135(1969).
43. Gresswell, R. A. and Perlman, M. M., *J. Appl. Physics* 41:2365(1970).
44. Blythe, A. R., Briggs, D., Kendall, C. R., et al., *Polymer* 19:1273(1978).
45. Jellinek, H. H. G., *Appl. Polym. Symp.* 40:41(1967).