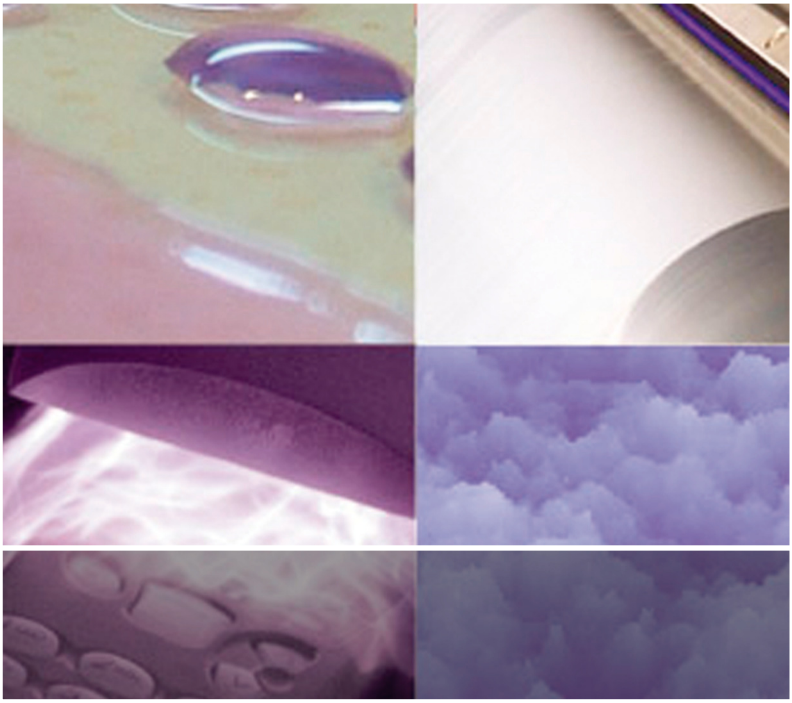
Rory A. Wolf

# Plastic Surface Modification

## Surface Treatment and Adhesion



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# Preface

Polymer surface modification is a topic that has been the object of a large number of investigations by academia and industry, but relatively little attention has been paid to surface activation technologies which, when appropriately utilized, make specific polymer-based surfaces receptive to value-adding interfaces such as inks, coating and adhesive formulations. Adhesion strength is generally determined by the properties of a base material and its interface. Optimizing adhesion strength can be accomplished by modifying these interfaces chemically and physically. As polymers are continually engineered to meet new product application requirements, optimizing the activation of these surfaces requires a fresh look at cost effective ways to etch, clean and functionalize them. These demands require detailed information on the surface treatment of classic materials, as well as an examination of the latest surface treatment machine designs available anywhere in the world today which are used to process these materials. There are four full chapters devoted specifically to corona, ozone, flame, and plasma discharge surface treatment technologies; and an interesting and useful identification of common adhesion maladies.

The aim of this book is to describe the primary polymer adhesion issues faced by manufacturers, processors and converters, to outline a variety of methods for attaining an appropriately activated surface, and to provide the diagnostics for various adhesion promotion issues which the reader seeks to trouble-shoot.

# Contents

# 1 Introduction

As a complete reference source for surface modification of polymers, this book reviews traditional and conventional methods for improving the adhesion of inks, coating adhesives, metals, and other adherends to polymers and introduces new methods for molecular engineering polymer surfaces to enhance their adhesion to a wide range of materials. In addition, this work serves to turn the vast amount of disparate information regarding plastics surface modification from wide ranging sources into practical application knowledge. In order to make this information most useful for practitioners, consultative data is arranged in consistent formats.

Modification of surface properties is based on the principle of the formation of physical, chemical and multi-layer surface structures of various complexities, including the deposition of amorphous films, which are finely dispersed by both atmospheric and vacuum processes. Plastic surface modifications with these types of discharge technologies are well known methods which can dramatically improve functional performance. Targeted variations of surface characteristics of non-conductive materials include wettability, adhesion, water and chemical resistance, oxygen, and water vapor transmission, or a controlled response to changes in environmental factors such as pH, all while retaining the bulk properties of the original polymer substrate. Desired variations of surface characteristics of conductive materials include corrosion resistance, strength, wear resistance, fatigue strength, electric-erosion resistance, and many others.

In recent years, inorganic substrates have been utilized as chemically and thermally stable substrate materials for graft polymerization modification processes. Covalent bonding of polymeric surfaces onto inorganic substrates has been used to change surface chemistry, surface structure, and native topology. Atomic force microscopy (AFM) has become a popular method of investigating the surface microstructure of polymers. AFM characterizations paired with analysis from scanning electron microscopy (SEM) are now routinely used to elucidate changes in surface topography and structure which result from atmospheric and vacuum discharge treatment to polymer surfaces, including graft polymerization modification of inorganic materials. In addition, electron spectroscopy for chemical analyses (ESCA) is routinely used to generate spectra which can also provide information about a surface's chemical environment or oxidation state.

It is through the application of these surface modification methods and surface analytical techniques that decorating and layering (laminating) processes can ultimately optimize adhesion promotion at the most cost-effective scale of end-use processing. Achieving adequate adhesion to polymers is a recurring and difficult problem throughout many industries, and most notably within the printing and packaging industries. Historically, various surface treatments have been used to improve the adhesion of coatings to plastics, including corona, flame and other forms of surface preparation. High energy density treatments such as cold gas plasma methods are gaining greater acceptance for substrate surface modification because they deliver reactive species (photons, electrons, free radicals, and ions) that interact with the polymer surface and change its chemistry and/or morphology at atmospheric pressure. Because these processes can be readily incorporated into printing and packaging manufacturing operations, this work will be useful in defining the necessary modifications to these material surfaces so that individual or multilaminate composite structures can meet or exceed end use requirements.

# 2 Primary Polymer Adhesion Issues with Inks, Coatings, and Adhesives

When addressing the adhesion of polymers to interfacing materials, the primary and foremost challenge is to understand the fundamental driving forces which can initiate the development of adhesion strength between polymer-to-polymer, polymer-to-metal, polymer-to-ceramic, or polymer-to-inks coatings and adhesives. These interfaces also exist in multivariate environments, such as heat and humidity, which also must be examined. Ultimately, it is the polymer and the interface chemistry that determine adhesion. However, there can be adhesion failure between the polymer and an inorganic, such as a metal, due to an oxide layer that is weakly attached.

That being said, this work will focus fundamentally on the bonding issues associated with polymers because of their unique deformation character, low modulus, and long chain structure.

Many polymeric materials inherently have a low surface energy that results in poor surface adhesion or even complete adhesion failure. This makes it difficult for inks, paints, adhesives and other coatings to properly wet-out and adhere to the surface of these substrates. Proper surface preparation of these materials will increase surface energy, improve surface adhesion properties, and add value to the product and the process. However, one must keep in mind that it is the bulk mechanical properties of the polymer that control the interfacial forces, which in turn influence adhesion. We will be subsequently reviewing various substrate orientations, from oriented and metallized films to spunbonded polyolefins and molded polymers, in order to examine their bulk structures for their ability to endure mechanically-induced deformations to allow for surface roughening and chemical covalent bonds to achieve requisite adhesions.

It is well known that polymer chain entanglement is the primary source of a polymer's strength. It is also known that over time polymeric materials can become increasingly semi-crystalline, making their surfaces even more difficult to accept surface modification techniques. The process of axially or biaxially orienting polymer films, for example, strengthens these materials as their chains become stretched. It is therefore common practice for surface modification techniques, such as corona discharge, to take place immediately following the orientation phase.

## 2.1 Cast and Blown Films

The cast film process involves the extrusion of various polymers which are melted through a slot or flat die to form a thin, molten sheet or film. This melted film, or "extrudate" is typically laid to the surface of a water-cooled and chrome-plated roll by a blast of air from an air knife or vacuum box. Cast film extrusion orients molecules in the machine direction only, producing a large difference in machine and transverse directional properties. This means that the chain molecules become aligned in the cast direction. This will increase the tensile performance in that direction, and forms what is known as "uniaxially" oriented film, whereby the gauge of the film will be in relatively straight lanes. However, there are other cast film extrusion disturbances, notably the effect on optical properties, which can be attributed to the structure of the polymer bulk, the structure of the film surface, crystallination roughness at the surface, and surface roughness by the extrusion process. Molecular weight, molecular weight distribution, chain branching, shear strain, melt flow rate, relaxation time, elasticity, orientation, processing conditions, and cooling rate must also be considered. They contribute not only to the formation of surface roughness but also their affect on surface adhesion. For example, a narrower range in molecular weight distribution leads to a more uniform crystal size distribution and thus to lower surface roughness and better optical properties. It can also be expected that surface modification techniques applied directly after extrusion will encounter less surface crystallination, which will enable greater surface roughening and a functionalization effect on a relatively chemically inert surface to promote future interfacial adhesion.

Cast film extrusion is used in manufacturing polypropylene films and requires greater surface pretreatment power density (possibly 2–3 times) compared to other polyolefin films. With blown film extrusion processes, polyethylene films are typically used and require pretreatment on both sides. Considerable amounts of slip additives, used to lubricate the surface of these films for processing ease, can be prevalent within the resin and migrate to the surface of the film within a few days after extrusion. Although there is potential for the additive to mask-over treatment, it is far more important to surface treat immediately after extrusion, since it will be practically impossible to do so after additive migration to improve surface properties sufficiently for ink, coating, or lamination adhesion.

It is interesting to note here that with respect to heat-sealing behavior, some research indicates that a primary effect of surface pretreatments such as corona on blown linear low density polyethylene films, for example, can be a change in the failure mode of heat seals from a normal tearing or inseparable bond to a peelable seal. More specifically, corona discharge has been determined to increase the seal initiation temperature by 5–17 °C and decrease the plateau seal strength by 5–20 % as the treat level, or wetting tension, increases from 31 to 56 dynes/cm. These corona treatment effects have been attributed to cross-linking during the process, 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 polyethylene, chemically oxidized polyethylene, and corona-treated polypropylene provide indirect evidence for the proposed surface cross-linking mechanism [1]. However, it is quite possible that this observation can also be attributed to an "over treatment" effect from discharge power densities which are higher than required. Because of the recurrent need for surface preparation optimization at extrusion, the importance of corona and other surface treatment discharge technologies requires closer process control examinations and will be discussed in depth to describe these surface mechanisms.

## 2.2 Metallized Films

In the metallization process, a layer of metal is deposited on plastic films using several different methods, ranging from vapor deposition to electroplating. When preparing surfaces for adhesion, one must consider the surface differences between the type of film substrates, the potential variations of film characteristics within different substrate families, variations with use of the same substrate between vacuum metallizing chambers, and any possible variations within an end-use application, even when using identical films.

It has been practical experience over many years that polyester films and oriented polypropylene have sufficient metal adhesion to be the most widely used in flexible packaging applications. As stated previously, there can be significant differences among these metallizing substrates. An initial consideration is their respective surface polarities, either inherent or pre-conditioned. In the case of the latter, a non-polar surface can be prepared to chemically and molecularly bond to the deposited aluminum layer by oxidizing the surface. This is typically accomplished by contributing oxidation, peroxides, alcohol, ester, ether, or aldehyde functional groups, which will bond well to aluminum depositions. As inferred with extruded films earlier, an overtreatment of an organic surface can actually cause metal adhesion to become quite poor. This introduces the concept that overtreatment can over-develop low molecular weight organic materials at the surface layer, causing the deposited metal to lose contact with the base polymer. This creation of what is known as a "weak boundary layer" weakens the mechanical surface bond between the metallized surface and the base film, potentially causing a failure of the metal to adhere. This metal bonding failure can also result from the surface migration of film processing additives, which are used to reduce the film's coefficient of friction for ease of processing.

As was noted earlier, a polymer surface may not necessarily need to be functionalized in order to create a strong surface bond with a metal. However, it is necessary for the surface of such polymers to be crosslinked. Schonhorn [2], for example, showed that the integrity of crosslinked surfaces will be highly dependent on the level of high-energy processing, such as the metallization process itself, or a form of surface treatment. The type of polymer used for the metallization process may be more adversely impacted at its surface by a pretreatment approach such as corona, flame or plasma, although Schonhorn demonstrated that surface degradation effects can vary. To mitigate such an impact, more controllable surface treatment approaches, such as vacuum or atmospheric plasma, can avoid the formation of weak boundary layers by "pre-cleaning" the surface of low molecular weight organic materials and by introducing functional groups that are appropriate for the specific polymer film to be metallized (see Fig. 2.1).

These processes must, however, also be controlled, most notably relative to the type of functional groups introduced and the temperature of the film during metallization to optimize the metal-to-polymer bond.

Another important point regarding successful metallization of polymer films is that the deposition of aluminum on, e. g., flexible packaging films, is generally only one aluminum

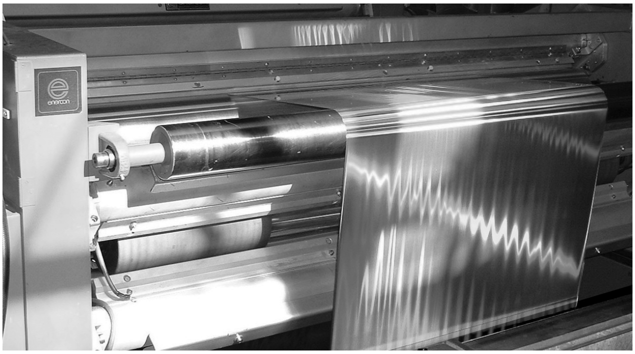

**Figure 2.1** Corona treatment of metallized webs

crystal thick. This layer of crystals is porous due primarily to the formation process of the metallization layer and by residual surface contamination during the metallization process [3]. The presence of this inherent porosity emphasizes the importance of managing the surface treatment process to an optimal state so that the performance of metallized films in metering light, oxygen, and moisture transmission for flexible packaging can in turn be optimized.

## 2.3 Foams

Polyurethane (PUR) foams, both flexible and rigid, account for the largest segment of foams marketed worldwide. Polystyrene foams, both extruded and expanded beads (EPS), are the second largest family of foamed plastics, followed by polyvinyl chloride (PVC) foams. Polyethylene and polypropylene foams also have a prevalence, and particularly cross-linked polyethylene foams. All foams, however, are manufactured by a common extrusion process, consisting of the mixing of a chemical foaming agent with the specific polymer to be extruded. The heat generated during the extrusion process to melt the polymer also decomposes the chemical foaming agent, resulting in gas being released. This gas is dispersed in the polymer melt and expands upon exiting the die. Dense foams have what is considered a "closed-cell" structure, meaning that the gas bubbles that form and disperse during the extrusion process remain permanently locked into the cured foam. Because there are no interconnections between individual bubbles, the foam absorbs little in the form of liquids and also resists the passage of liquid vapor. Low-density foams are considered "open-cell" foams and have a structure with a series of small interconnected passageways. These open cells can be permeable to liquid vapors.

Polymeric foams can be difficult to surface treat for adherence to other materials. Manufactured using a variety of thermoplastic and thermoset resins, these foams can have either a high resident surface energy (such as for styrenes, PU, epoxy) or low surface energy (such as for polyethylene, polypropylene, EPDM).

When open-cell foams manufactured from low surface tension polyolefins require surface treatment, the filamentary discharges from a corona treater will typically find a path to ground through the open passageways and create a high incidence of pin-holing of the foam surface structure. Pin-holing is particularly acute as the foam thickness increases beyond the optimum corona discharge gap, usually approximately 1.5 mm between the foam surface and the electrode. This is because the increased gap increases the "gap voltage" requirement, causing a high voltage arc to bridge the gap and typically through open and closed cell foams alike. Considering continuous atmospheric treatment technologies, pin-hole effects can be mitigated by using either flame plasma or atmospheric chemical plasma surface treatments, which ionize gases and require lower breakdown voltages compared to that of air.

Once the surface tension of foams is sufficiently raised, adhesives can more effectively wet and bond to open- and closed-cell foams. In open cell foams, adhesives can spread into the pores of the foam. Although the benefit can be superior adhesion as a result of mechanical bonding, the functional properties of the foam can be adversely affected. Typically, permeability and thermal properties of the foam may be compromised to the point where the structural integrity of the foam is weakened. This is particularly true when introducing solvent-borne adhesives, for example, which can swell the foam structure. To compensate for these potential effects, the adhesive is recommended to be applied to the interfacing substrate, which is typically less porous and will minimize the spreading of adhesive into the foam's passageways. These issues are not as problematic when using adhesives that will not adversely react with polymeric foams, such as water-borne adhesives and high solids epoxies and polyurethanes.

When applying adhesives to closed-cell foams, the adhesive cannot seep or penetrate into the foam structure. As such, it is more critical that pre-treatment be employed to establish a micro-rough and functionalized surface to allow the adhesive to mechanically and chemically bond to the surface.

## 2.4 Textiles, Filaments and Yarns, and Nonwovens

Most manufactured fibers for textiles are made from wood pulp, cotton linters, or petrochemicals. Those fibers manufactured from petrochemicals include nylon, polyester, acrylic, and olefin. Most textiles are produced by twisting fibers into yarns and then knitting or weaving the yarns into a fabric.

Textile production traditionally involves a number of wet processes that may use solvents. Emissions of volatile organic compounds (VOCs) mainly arise from textile finishing, drying processes, and solvent use. VOC concentrations vary from 10 milligrams of carbon per cubic meter (mg/m$^3$) for the thermosol process to 350 mg carbon/m$^3$ for the drying and condensation process.

Process wastewater is a major source of pollutants. It is typically alkaline and also contains solids, oil, and organics [4]. The process of promoting pigment and dye uptake on textile materials can also involve aqueous emulsion-type agents to meet requirements for use, such as fade resistance, permanence under repeated laundering, and abrasion resistance. As such, textile manufacturers and end-users alike have been searching for ways to improve the surface properties of natural and man-made fibers, while minimizing the impact on the environment. Specifically, there is a need to improve adhesion, wettability, printability, and dyeability without the need for additional wet processes. Examining nonwovens made from low polarity, low surface tension and highly crystalline polyolefins will exemplify one of the most challenging textile materials, which typically requires pretreatment to promote adhesion. Methods of modifying fiber properties to make polypropylene dyeable, including the process of copolymerization with polymers that can be dyed, are common. Traditional latex systems and primers with low melting points have been used to coat fabrics to promote ink adhesion, heat-sealing, and thermoforming performance.

Polypropylene nonwovens have especially been the focus of research to enhance colorfastness properties of the material because of its excellent chemical resistance, high melting point, low cost, and adaptability to many fabrication methods. To date, the poor dyeability of polypropylene has limited optimization of its applications in the manufacturing of yarns and knit fabrics, upholstery fabrics, and industrial fabrics.

Fibers with polar functional groups can be dyed more easily than nonpolar fibers, because polar groups will chemically bond with dye molecules. Because the molecular chains of polypropylene are nonpolar and its surface is hydrophobic, the dye molecules will not bond chemically to the fibers. Polypropylene fiber is highly crystalline as well, which also restricts its dyeability. Functional groups may be introduced onto the fiber surface by using gas plasma treatments, improving fiber surface properties without affecting the fiber's bulk properties. By creating a polar layer on the fiber surface, in reaction with functionality introduced, wettability of the fiber for dyeing is enhanced together with hydrophilicity.

**Figure 2.2** Atmospheric surface treatment system

Atmospheric surface treatment systems, like the one shown in Fig. 2.2, are typically used with textiles, filaments, and yarns for the primary purposes of desizing, dye uptake, printing ink adhesion, and final finishing treatments such as softening, hydrophilization, easy-care, and anti-shrinkage.

The use of corona, flame and plasma technologies for treating textile materials offers a convenient and cost-effective solution for continuous and semi-continuous processes, running at velocities as high as 60 mpm for maximum fabric widths of 3.6 meters. Controlling the temperature and humidity of textile, filament, and yarn materials will optimize discharge surface treatment effects by preventing damage to the textile. Maintaining a textile temperature below 40 °C and its humidity at less than 8 % (particularly for cotton fabrics) will provide favorable treatment conditions. As a physical surface effect, atmospheric discharge pretreatments will increase the surface roughness of fiber structures in conjunction with a "cleaning effect". Regarding chemical effects, corona treatment, for example, will impart surface oxidation. Consider the fact that untreated cotton has an average atomic composition of 82.9 % for carbon and 14.7 % for oxygen. Following corona treatment, carbon concentration is reduced to 57.8 %, while oxygen concentration is boosted to 37.3 %. Functional groups, such as C—O, OCO and COOR increase significantly [5].

## 2.5 Injection-Molded Parts

The injection molding process involves the injection of molten plastic at high pressure into a mold, which is the inverse of the product's shape. Injection molding is widely used for manufacturing a variety of parts, from the smallest component to entire body panels of cars. The most commonly used thermoplastic materials are polystyrene, ABS (acrylonitrile butadiene styrene), nylon, polypropylene, polyethylene, and PVC (polyvinyl chloride). When considering the decoration of these polymers, the low inherent surface tensions of these materials must be considered relative to the surface tension requirements of the interfacing decorative effects, such as painting, stenciling, hot stamping, silk-screening, vacuum metalizing, and electroplating. In addition, mold releases and their excessive use can not only create a significant barrier to sufficient surface adhesion but also potentially weaken the part. Surface blemishes can also be caused by weld lines, flow lines, and shinning spots among others. A *weld line* is created when two flow fronts come in contact. This often appears around openings and results when two or more openings are filling the mold. *Flow lines* are created when the plastic in contact with the cold mold surface hardens faster than the plastic behind it. When the plastic continues to flow over the hardened area it cools and forms a line as it shrinks. A flow line will form around fill openings in the mold called "gates". As the plastic moves through the small constriction of the gate, some molecules will break, forming streaks on the mold surface. *Shinning spots* form on the surface of a part when there is a thin wall between two thick walls.