

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 analy-

ses (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 Figure 2.1).

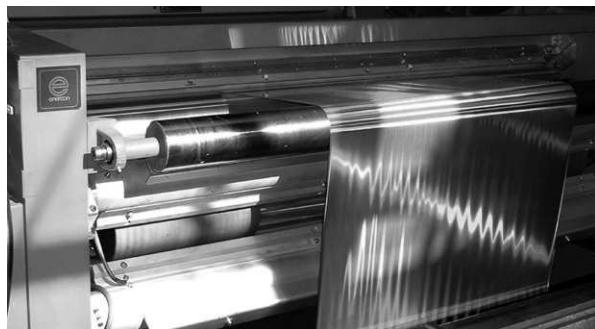


Figure 2.1
Corona treatment of metallized webs

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 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/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.

- Flow meters for air and gas, to ensure precise reproduction of process parameters.
- Flame power control, to control BTU output and thermal efficiency.
- Methane, propane, or butane compatibility, for grafting various carbon-based functional groups.
- Integrated ignition and flame detection electrode for ignition safety.

■ 7.6 Atmospheric Plasma Surface Modification: Polymeric Surfaces

To re-establish the groundwork to better understand this topic, the delivery of current into a neutral gas causes a portion of the gas particles to be converted by ionization into charged particles. This ionization creates a plasma which is generated by electromagnetic fields and denoted as an electrical discharge. This electrical/gas discharge plasma is correctly characterized as a partially ionized gas with neutral particles, along with a counterbalancing amount of negative electrons and positive ions. There can also be plasmas where all particles are ionized, and plasmas with negative ions. These types of plasmas will not be discussed here.

There are a wide variety of plasmas which can be generated under a number of varying conditions. One of these key conditions is the pressure of the working plasma gas. At specific temperatures, the pressure of the gas will predetermine the density of these gas particles, and ultimately the frequency of collisions between particles. Under this assumption, the higher the gas pressure, the higher the frequency of particle collisions. The higher the collisional frequency, the higher the probability that a steady state will eventually be achieved whereby the collisional energy will establish itself at equilibrium. In this equilibrium state, all ionized particles (and the gas) will have the same temperature.

Particle collisions can be subdivided into two categories: elastic collisions and inelastic collisions. Elastic collisions will not change the internal energy of neutral species, but will slightly raise their kinetic energy. With inelastic collisions, the electrical structure of the neutral species will be modified whereby excited species or ions will be created. The lifetime of these species will be very short. Species known as metastables will also achieve an excited state, but also exist with long lifetimes since their decay by radiative emissions is precluded since no energy can be transferred without collisions.

For many roll-to-roll plasma applications which require aggressive plasma-substrate surface interaction without surface degradation, temperature limitations are

key to successful surface modification. For example, these temperatures can exceed 900 °C but for other applications temperature limits must be near room temperature. When the latter is the case, a cold plasma is required which does not exist in a thermal equilibrium. It is understood that non-equilibrium plasmas will not have significant particle collisions since the operational pressure will be low. Furthermore, low pressure plasma systems require very capital intensive (and large) vacuum chambers and pump systems for roll-to-roll materials. As such, there has been significant progress in recent years in development of cold atmospheric plasmas which operate at non-equilibrium as an alternative for low pressure regimes.

This section summarizes the principles and characteristics of cold atmospheric plasmas for roll-to-roll applications and their differences from low pressure plasmas in order to provide a better understanding of the capabilities and limits of non-equilibrium atmospheric plasmas for roll-to-roll materials. A review of cold atmospheric plasma sources, their capabilities, surface effects relative to achieved results, and a discussion of roll-to-roll application benefits will follow.

Polymer Film Application Profiles

In an attempt to profile those materials which can be processed by atmospheric plasma systems, a brief discussion of dielectrics must take place. Firstly, the most representative non-equilibrium (partial discharge) plasmas are dielectric barrier discharges and coronas. The dielectric barrier discharge was first invented in 1857 by Siemens, and originally designed for ozone generation. After extensive research in subsequent years, it was determined that parallel insulated electrodes with a predetermined gap created a discharge in a number of individual (but location-repetitive) filamentary micro-discharge channels. It was ultimately demonstrated that the plasma parameters of these channels are controllable, and therefore the dielectric barrier discharge could be optimized for applications such as roll-to-roll orientations.

Secondly, atmospheric plasma barrier discharge systems for roll-to-roll, polymer-based applications can have a wide variety of electrode/ground roll configurations, and are typically characterized by the presence of one or more dielectric layers, such as ceramic or glass, located on the electrode and ground roll surface. The gap between the electrode and ground roll (including the applied dielectrics) for atmospheric pressure plasma systems for these applications will range from 1 to 5 mm. Multiple arrangements of these electrode systems are quite common, and the use of large arrays of electrode bars contained within assemblies is prevalent.

Also adding to the dielectric equation of atmospheric plasmas for roll materials is the type of gas media used to create the discharge between the electrode/ground roll systems. The mean free path and molecular weights of gas media will alter the existing dielectric properties resident with the electrode and ground roll. The gas

media determines in part the characteristics of the individual micro-filamentary discharges which are spread at the dielectric surfaces. The dielectric barrier designed into roll-to-roll systems ultimately controls the amount of energy and charge comprising the micro-discharges, and the uniform distribution of the micro-discharges over the electrode face.

Finally, the roll-to-roll material itself presents dielectric variations inside the reaction gap. Most polymer films, for example, are dielectrics (insulators) which will resist the flow of an electrical current. However, despite this property, a dielectric breakdown can occur at a sufficiently high voltage in order to allow for current transmission and surface modifications. During the voltage increase period, micro-discharges will be generated which will impact the dielectric surface. These discharges will occur at unique locations since the electrical field will be reduced by the presence of remaining or residual charges which reside at the locations where the micro-discharges had already occurred. When voltage is in the reverse period, fresh micro-discharges form at the previous micro-discharge location. As such, the low voltage-high frequency profile of most atmospheric plasmas will generate micro-discharges at these original locations. However, not all polymers will behave the same way when they are subjected to voltage. As such, they are classified as being either polar or nonpolar to describe their variations in dielectric behavior. Polar polymer films do not have full covalent bonding within their molecular structures as there is an imbalance in the electrical charge of the molecule. Specifically, dipoles are created by an imbalance in the distribution of electrons and in the presence of an electric field the dipoles will attempt to move to align with the field. This creates "dipole polarization" of the material and because movement of the dipoles is involved, there is a time element to the movement. Some examples of polar roll polymer films include PVC and polyamide. Polymer films which are nonpolar have symmetrical molecules, do not have dipoles, and are fully covalent. The application of an electrical current will not align dipoles. Examples of nonpolar polymer films are fluoropolymers, polyethylene, polypropylene, and polystyrene. These polymers also tend to have high electrical resistivity and low dielectric constants. Surface resistivity is the measure of material resistance to a surface flow of current and is defined as the ratio of applied direct voltage and the current along the surface of the material, per unit width. The dielectric constant measures how well a material separates the plates (electrodes) in a capacitor and is defined as the ratio of the capacitance of electrodes with the dielectric material between them to the capacitance of the same electrodes with a vacuum between them.

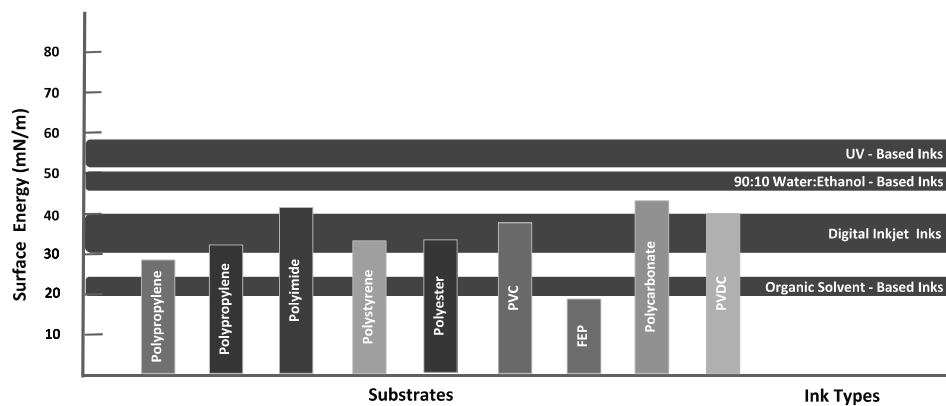


Figure 7.16 Comparison of polar and nonpolar polymer materials with predominant ink surface energies

The list of flexible polymeric roll materials suitable for atmospheric plasma processing is expansive. Mainstream resin types include polypropylene (homopolymers, heterophasic copolymers, and random copolymers), polyethylene (low, medium, and high density polyethylene resins), a family of specialty polyolefins which includes polybutene-1, advanced polypropylene resins from in-reactor alloying processes and polypropylene compounds, and fluoropolymers. By process type, these materials (in mono- or multiple layers) can be generally represented by the following:

- Film extrusion (blown and cast)
 - Flexible packaging, such as for food, textiles, consumer products, industrial products, medical products.
 - Agricultural
 - Construction
 - Materials handling, including stretch wrap and shrink wrap
 - Electronics
 - Anti-corrosive linings
 - Non-stick roll covers
 - Pharmaceutical cap liners
 - Automotive airbag systems.
- Melt-blown
 - Thermal insulation
 - Disposable industrial apparel
 - Battery separators
 - Synthetic leather

Index

Symbol

3-D objects 69
μCP 223

A

- ablation 72, 227
- absorption 145
- acetylene 111
- acid dyes 190
- acrylate oligomers 147
- acrylic 101, 103
- acrylic adhesive 82
- additive migration 4
- adhesion 43f., 58, 143, 155, 160, 197
 - air knife coatings 199
 - curtain coatings 201
 - digital UV curable inks 160
 - flexographic coatings 211
 - gravure coatings 204
 - hot melt coatings 209
 - immersion coatings 200
 - metering (Meyer) rod coatings 206
 - modifier 169
 - nanocoatings 214
 - of thin film solar cells 230
 - porous and non-porous substrates 197
 - promoters 143, 155, 188
 - promotion 119, 188
 - promotion techniques 171
 - reverse roll coatings 203
 - rotary screen coatings 202
 - silk screen coatings 212
 - slot die (extrusion) coatings 207
- adhesives 66, 69
- adiabatic temperature 49
- affixation 167
- agglomerate 214
- air gap 43
- air/gas flow 51
- air plasma 27
 - (corona) treatment technologies 27
- alkaline dye bath 190
- amination 70
- amine chemistry 138
- amine groups 108
- amines 107
- amino 107
- amino groups 111
- ammonia 109f.
- amorphous 11
- anilox-based flexographic coating 211
- anilox roll 143
- anodizing 17, 113
- antenna circuit pattern 185
- anti-block additives 150
- antioxidants 95
- antistatic 106
- antistatic additives 150
- anti-tarnishing coatings 163
- applicator 44, 47
 - positioning 47
- argon 109
- aspect ratio 217
- ASTM D3330 56
- ASTM standard wetting tests 53
- atmospheric chemical plasma 7, 21, 71
- atmospheric discharge surface modification 15
- atmospheric plasma 6, 21f., 24, 42, 45, 78, 140, 143, 220, 225, 230
 - regimes 220
 - systems 225
 - treatment (APT) 42
- atmospheric pressure plasma processes 96
- atomic force microscopy (AFM) 1
- automotive parts 217
- azo (azoic) dyes 191

B

backing materials 207
back-lit displays 167
backside treatment 24
banners 167
bare roll 27
– tension 28
barrier 74, 214
basis weight 123
bath exhaustion 108
beck dyeing 189
beverage pouchstocks 41
BID 158
binary ink developer 158
binders 137, 139, 147
biocomposites 219
biofilms 117
bio-oil based 165
blanket cylinder 164
bleaching 191, 193
blooming 156
blow molding 12, 183
blown arc 27, 35
– systems 36
blown ion 27, 36
– systems 35
bonded abrasive coatings 209
bonding 147
– UV inks 147
bond pull test 82
BOPP film 49
bulk 124
burner design 50
burner/material gap 58
butane 89

C

cables 69
calendering 123
capacitive impedance 30
carbon dioxide 78
carbonyl 87, 107

carboxyl 107
carboxylic 87
carboxymethyl cellulose 112
carrier gas 21
cast and blown films 4
cast films 93
cation exchange capacity 217
cationic inks 159
caustics 148
cells per inch (CPI) 143
cellulose 124
ceramic covered rolls 31
chain molecules 4
chain scission 142
chemical etching 115
chemical foaming agent 7
chemical plasma discharge 21
chemical vapor deposition 24, 107, 130
chloromethyl dimethylsilane 107
CIGS 118f.
circuit-bearing substrates 163
cleaning 79
cleaning process 83
clear coats 213
cliché 154
closed-cell 7
coating 42, 65, 197, 212, 214
– drying 212
– extrusion 42
– formulations 197
– matrix 214
– methods 215
– processes 197
coat-weights 199
co-extrusion 42, 183
cold atmospheric plasma 106
cold-set letterpress inks 152
colorfastness 190
composite films 41
composite (hybrid) photovoltaic technology 226
composite surface energies 221
composite surface tension 221
compression strength 129
computer-to-plate (CTP) technology 151
conductive nanocomposites 224
contact angle 95
contamination 80, 116, 133, 156
cooling air 86
copolymerization 8, 101
copolymers 92
corona 69
corona (air) plasma discharge 15
corona treatment 5, 15
corona wire 157
corrosion 29
corrosion resistance 115
cotton 101ff., 107, 110, 112
covalent bonding 42, 77, 111
covered roll 29
critical surface tension 148
crosslink density 108
cross-linking 5, 16, 24, 67, 69, 72f., 105, 141, 147
– density 147
crystalline 11
crystallinity 156
cyanoacrylate adhesive 82

D

decorating processes 133
 degassing 68
 degreasing 114
 delaminations 98
 deposition 63 f., 96
 desizing 9, 102, 191
 dewetting 204
 dextrine adhesives 181
 dielectric barrier discharge (DBD) 69, 90, 220
 dielectric constant 30, 91
 dielectric insulators 28
 dielectric roll coverings 29
 dielectrics 91
 dielectric strength 30
 difficult-to-bond substrates 149
 digital inks 163
 digital laser imaging 157
 digital offset machines 157
 digital printing 157
 diluting acrylates 148
 dip coating 214
 dip deposition 113
 direct transfer plate technologies 134
 dispersions 201
 doctor blade 144, 212
 dot-matrix 157
 drier additives 168
 drilled port burners 20
 drop-on-demand (DOD) inkjet 223 f.
 dry etching 119
 dry offset 11
 dry toner electrophotography 163
 dual dielectric 34
 dyeing 9, 189, 191
 dyeing depth 108
 dyes 69, 185

dye uptake 101, 191, 193
 dyne solutions 95

E

eco-centered surface modification 133
 electrical (corona) discharge 19
 electrical ionization 25
 electrical properties 225
 electrodes 86
 electro-ink 157
 electroless plating 213
 electron beam (EB) curing 141
 electron bombardment 69
 electron spectroscopy for chemical analyses (ESCA) 2
 electrophoresis coating process 201
 electroplating 5, 66, 113 f., 213
 emulsion 137, 208
 energy-curable 164 f., 168
 – UV offset inks 168
 energy-cured inks 141
 energy curing 167
 enhanced velocity (EV) type burners 50
 entanglement 104
 epoxide resin 222
 epoxy coated rolls 31
 ESCA 20
 etching 21, 72, 213
 evaporation of binder solvents 186
 excitation 142
 exfoliating 217
 exhaust 86
 exposure limit of ozone 19
 extraction solvent 78

extruding (slot) die 209
 extrusion 4, 7, 17, 40, 42
 – blow molding 12
 – bonds 42
 – coating 17, 40
 – lamination 40

F

fabrics 69
 fatty acid residues 181
 fibers with polar functional groups 9
 filamentary discharges 23
 filaments 9, 70, 111
 fill bar 146
 film extrusion 93
 film labels 181
 film wrinkling 34
 flame (oxygen) analyzer 57
 flame plasma 7, 20, 49, 88, 49
 – discharge 20
 – treatment 49
 flame profile 51
 flame treatment 156
 flame treatment burner 49
 flame velocity 51
 flatbed screen coating 202
 flexible electronics 223
 flexible packaging 69, 77
 flexo 165
 flexographic 11, 134, 136, 142, 144, 198, 211 f.
 – anilox 198
 – anilox rolls 142
 – ink systems 212
 flip chip process 121
 floating knife 199
 floodbar 146
 floodcoats 212

- flow lines 10
 flow meters 89
 flow regulation 40
 flue gases 49
 fluorination 129
 fluorine 128
 fluorohectorite 217
 fluoropolymer 84, 91, 107
 fluoropolymer substrates 25
 fluorosurfactants 201
 foams 7, 69
 foil adhesion 41
 foils 69
 free radicals 23, 73, 88, 106
 frequency 71, 89
 fuel cell coatings 209
 functional groups 73
 functionalization 96
 functional oligomer groups 147
- G**
- gap coatings 199
 gap distance 51, 57
 gap voltage 7
 gas control systems 86
 gas flow rate 86
 glass-covered rolls 33
 glow discharges 69
 grafting 21, 96
 gravure 134, 144, 165, 198, 205
 – coating 205
 – inks 144
 – printing 144
 – roll 205
 grease 182
- H**
- half tones 145
 hard coating 17
 heat dissipation 30
 heat seal 41, 43
 heat-sealing behavior 4
 heatset 147, 164, 166
 – ink formulation 166
 – inks 145
 heat-set letterpress inks 153
 heat transfer 51
 high density reactive species 21
 high speed rotary screen printing 151
 hold-out properties 213
 hollow carbon nanotubes (CNT) 218
 homogeneous 70
 homogeneous coatings 208
 homopolymers 92
 hot-dip galvanizing 114
 hot-melt 180, 210
 – adhesive 180, 210
 – adhesive processing 210
 – surface bond 210
 hydrocarbon residues 182
 hydrolyzation 70
 hydrophilic 105
 hydrophilicity 66, 150
 hydrophilization 9, 102
 hydrophobicity 66
 hydrophobic recovery 111, 204
 hydroxyl 87, 107
 Hypalon-covered rolls 31
- I**
- idler roll 34
 image bleeding 160
 immersion dyeing 191
 immersion solvent 78
 impression cylinder 158, 164
 impression roller 151
 indirect transfer plate technology 164
 indirect transfer printing 167
 inertness 156
 initiators 142
 injection blow molding 12
 injection molding 10, 183
 ink 140, 144
 – chemistry 166
 – deposition 146
 – lay-down 145
 – smearing 140
 – substrate challenge 158
 – transfer 154
 – transfer rate 145
 – wetting 144, 155
 inking/dampening systems 164
 inkjet 157, 209
 – printers 157
 – receiver coatings 209
 inlay 184
 in-line lamination applications 210
 in-mold labeling (IML) 182
 intaglio 134, 144
 integral photoinitiator 147
 intercalant 217
 intercalate 217
 interfacial adhesion 4, 155, 159, 166, 219
 – between nanocomposites 219, 223
 – non-porous substrates 159
 – porous substrates 159
 interfacial bond 160
 interfacial forces 3
 interfacial free energies 219
 ion bombardment 25, 36, 81, 129
 ion implantation 116

- ionization 70, 142
ion plating 64
- J**
- jetting viscosity 162
jig dyeing 189
- K**
- knife over blanket 198
knife over roll 198
- L**
- labeling 180
laminating 17, 43
laser 157
lenticular signage 167
letterpress 134, 151 f., 165
– ink composition 152
– inks 154
light curing 141
lignin 122, 127
lithographic inks 165
lithographic ink transfer 171
lithographic label laminator 180
lithographic printing 134, 167
– plastics 167
lithography 164
low molecular weight
 organic materials (LMWOM) 21
low pressure (vacuum)
 plasma 61, 78
- M**
- magnetic coatings 209
mass flow 51
masterbatches 98
mean free path 90
- mechanical etching 100
medical devices 217
meltblown 94
melt curtain 44
melt index 95
meniscus 200
mercerization 191, 193
metal 110, 112
metal/ceramic fillers 224
metal decoration 147
metal finishing 113
metallization 5, 67
metallized films 5
metastables 89
methane 89, 107, 111
microabrasive snow 78
micro-discharge channels 90
micro-etching 98, 227
micro-roughness 105
migration 156
migratory additives 182
mineral pigments 148
mixing (venturi) chamber 57
modification of surface properties 1
mold releases 10
monoatomic oxygen 73, 81
monofilaments 69
monomers 129
montmorillonite 217
mordant dyes 190
morphology 66
motif 154
multi-purpose inks 148
- N**
- nanoclays 217
nanocoating 198, 214 ff.
– adhesion 215
– formulations 216
- nanocomposite 216, 219, 223, 225
– photovoltaic 225
nanoparticle platelets 214
nanoparticles 104, 129
narrow-web 141
negative ions 96
nitration 70
nitriding 116
nitrogen 95
nitrogen-based plasmas 109
non-heatset 164, 166 f.
– inks 167
– web ink formulation 166
non-homogeneous cure 151
non-paper substrates 15
non-thermal atmospheric-pressure 22
nonwovens 8, 69
nylon 101, 103
- O**
- OH groups 118
oils 182
oleamide 98, 100
olefin 101
oleophilicity 153
open-cell 7
optimization of treatment 57
organic cleaning 61
organic removal 72, 80
organic semiconductors 226
organic solvent-based carrier liquids 209
overtreatment 5
oxidation 5, 19 f., 29, 34, 39, 43, 70, 102, 167
– depth 20
oxidative species 49
oxidizing 49

- oxygen 67, 109
- ozonation 19
- ozone 16, 18f., 39, 42
 - application 42
 - removal 18
 - treatment technology 39

- P**
- pad 134, 153, 165
- pad printing 134, 153f.
 - inks 152
- paint adhesion 186
- painting 66, 185, 187
 - automotive plastics 187
- paint performance 186
- paints 69
- paper 122
- paper labels 180
- paper/paperboard 49
- passivation 119
- PDMSO 95
- PECVD 65
- peel adhesion 56, 76
 - tests 56
- peel strength 56
- permanent adhesives 210
- peroxy 107
- petroleum-based 165
- photo-electrochemical cells 226
- photo imaging plate (PIP) 157
- photoinitiator 141, 213
- photopolymer 134, 136, 151, 155
 - clichés 155
- photopolymer coating transfer plates 211
- photopolymerization 141
- photoresists 163, 213
- photovoltaic 118

- photovoltaic solar cells 225
- physical vapor deposition 62, 64
- piezo-electric technology 157
- pigmentation 104
- pigment content 154
- pigment solids 185
- pin-holing 7, 24, 32
- planographic 134, 164
- plasma cleaning 99
- plasma-enhanced chemical vapor deposition (PECVD) 25, 225
- plasma nitriding 116
- plasma polymerization 105
- plasma-spray process 34
- plasticizers 139
- plastic nanocomposites (PNC) 217
- plastic packaging 167
- plasticols 147
- plate cylinder 164
- point-of-purchase (POP) displays 167
- point-of-sale 167, 185, 213
 - products 167
- polar functional groups 20
- polar groups 96
- polarity 8, 10, 151
- polarization effects 49
- polyamide 91, 108
- polyester 101, 103, 110
- polyethylene 91, 98
- polymer-based coatings 163
- polymer-based label 181
- polymerization 111
- polymerization by catalysts 186
- polymer nanocomposite 225

- polymer resist film 142
- polymer side chain mobility 24
- polymer-to-ceramic 3
- polymer-to-inks 3
- polymer-to-metal 3
- polymer-to-polymer 3
- polyolefin 39, 110, 147
 - substrates 147
- polypropylene 91, 109
- polystyrene 91
- polystyrene foams 7
- polytetrafluoroethylene 110
- polyurethane (PUR) foams 7
- polyvinyl alcohol 112
- polyvinyl chloride (PVC) foams 7
- porosity 6, 126
- post-molding printing 12
- post-treat surface tensions 222
- power density 4, 40, 73, 86
- precipitating coating 202
- precursor adhesives 222
- pre-printed sheet 11
- pressure filtered air 162
- pressure-sensitive adhesives (PSAs) 210
- printability 224
- printable electronic circuitry 223
- printable liquid adhesives 150
- printable nanocomposites 224
- printable resists 150
- printed circuit boards (PCBs) 113, 162
- printing 17, 66, 134
 - decorating processes 134
- propane 89

- PTFE 98
 puckering 34
 pulping process 122
 pultrusion 218
 PVC 91
 PVdC 75
- R**
- radiation promoters 142
 radio frequency (RF) 183
 - identification (RFID) labels 183
 rayon 103
 reactive dyes 191
 reactive oxidation 20
 recommendations for adhesion 215
 recycled content 126
 registration 145
 relief 134, 151
 - printing process 151
 resin emulsion 139
 retrofitting roll coverings 33
 reverse roll 198
 RFID 185
 ribbon burner 20, 50
 robotic positioning 182
 rod coating process 206
 roll metering 209
 roll-to-roll printers 157
 roll-to-roll web materials 202
 rosin ester tackifiers 207
 rotary screen 146, 198, 203
 - coatings 203
 - printing automation 146
 rotogravure printing 145
- S**
- sandwich lamination 41
 scission 73
 scorotron 157
 scouring 191, 193
 screen 11, 134, 137, 143, 145 f., 156, 165, 212
 - anilox roll 212
 - emulsions 148
 - printing 145
 - process formulations 150
 - reclamation 148
 - ruling 156
 - threads 146
 screened substrates 148
 seal strength 45
 seal temperature 46
 segmented electrodes 17
 selective spray 78
 semiconductors 121
 shade depth 108
 sheet fed ink formulation 166
 sheet fed intaglio 145
 shinning spots 10
 shrinking of the transferred ink 147
 silicon 99
 silicone-covered rolls 30
 silicone substrates 25
 silicone vs. ceramic roll coverings 32
 silicon wafer 226
 silk 102, 104
 silk screen 198, 213
 - coatings 213
 single layer p-n junction diode 226
 sizing 123
 sliding (slip) agents 150
 slip additives 4
 slot die 198, 209
 slurries 209
 smoothing roll 150
 softening 102
 solder masks 213
 solvent 79, 147
 - based inks 158
 - evaporating inks 154
 solvent-borne 140, 148, 154, 180, 188
 - adhesives 180
 - flexographic waste 140
 - flexo ink adhesion 137, 140
 - ink 145, 213
 - screen printing inks 148
 specific adhesion 42
 spin coating 214
 spray coating 214
 spreadability 160
 spread tow 103
 spunbonding 93
 sputter 63
 squeegee 146
 stabilizers 142
 stainless steel 115
 starch 181
 static charge 182
 static control 162
 static electricity 181
 stencil 146
 sterilization 117
 stock dyeing 189
 stoichiometric combustion 57
 stoichiometric ratio 57
 streamers 23
 stretch blow molding 12
 sublimation dyes 150
 substrate pretreatment 150
 supercritical phase 79
 surface 5, 7 f., 21, 28, 30, 34, 36, 39, 44, 52, 59
 - ablation 96, 109
 - characteristics 59
 - cleaning 105, 119 f., 133
 - condensation 156
 - contamination 59, 144, 149, 181

- functionalization 212
- hardness 30
- modification 1, 133
- of foam 7
- oxidation 10, 12
- polarity 5, 44, 156
- porosity 30
- resistivity 91
- roughening 36
- roughness 125
- strength 125
- tension 8, 15f., 21, 34, 39, 52, 137, 148, 151, 160
- topography 1, 159
- treating 27

surface energy 149, 169, 182

- differences 149
- levels 182
- relationship 169

synthetic textiles 110

T

tackiness 210

tag 167, 180

temperature 95

tensile performance 4

tensile strength 125

tetrafluoromethane 107, 109

textile 8, 100

textile finishing 8

thermal efficiency 51

thermal equilibrium 90

thermal print heads 157

thermobonding 94

thermoforming 11

thermoplastic 10f., 97

- sheet 11

thermoset resins 224

thermosetting epoxide 223

thin film deposition 111

thin-film solar cells 226

thinner agents 148

thinner clear coat layer 213

thixotropic 213

thread count 146

topography 207, 210

transponder 184

treatment degradation 24

treatment life 84

U

ultrasonics 194, 214

“uniaxially” oriented film 4

unprimed automotive plastics 187

unsaturation 100

UV clearcoats 213

UV digital inks 160

UV flexo ink 140, 142

- adhesion 140

UV inkjet 162

UV letterpress inks 153

UV offset ink additive recommendations 168

UV-ozone treatment 78

V

vacuum evaporation 62

vacuum plasma 24

vapor deposition 5

vat dyeing 191

vegetable oils 167

viscosity 142, 144, 159

volatile organic compounds (VOCs) 8, 77

volatilization 72, 156

W

water-borne 137, 180, 188

- acrylic adhesives 180
- flexographic ink 139
- inks 142, 147

water filtration 109

water resistance 129

wax 138f., 182

- based substances 182

weak boundary layer 6

wear resistance 30

web coating 49

web printing 165

weld line 10

wet-out 181, 207

wet process 191

wettability 110, 128, 143, 181

wetting 59, 160f.

wetting tension 5

- surfactants 161
- tension 5

wickability 111

wide web packaging films 217

wire bonding 121

wires 69

wool 102, 104, 107f., 110

wovens 69

X

XPS 99

Y

yarns 8, 69, 101

Z

zero speed interlock 86