

# SURFACE ACTIVATION SYSTEMS FOR OPTIMIZING ADHESION TO POLYMERS

*Rory A. Wolf*

*Enercon Industries Corporation*

## **Abstract**

Many experiments have been performed globally to investigate ways of improving adhesion to polymers. This paper discusses current atmospheric surface activation systems, appropriate measurements of wettability and adhesion, over-treatment effects and surface analysis techniques relative to optimizing the adhesion of inks, paints, coatings and adhesives to polymer surfaces. Recommendations for improved activation by substrate and application are discussed.

## **Atmospheric Surface Activation Systems**

There are three primary types of atmospheric surface activation systems for three-dimensional polymeric surfaces – *air plasma*, *flame plasma*, and *atmospheric chemical plasma* regimens.

An *air plasma* treating system is designed to increase the surface tension of polymers in order to allow improved wettability and adhesion of inks, coatings and adhesives. As a result, the materials treated will demonstrate improved printing and coating quality, and stronger lamination strength.

The system consists of two major components:

1. The power supply
2. The treatment device

The power supply accepts standard utility electrical power and converts it into single phase, higher frequency power that is supplied to the treating device. The treating device applies this power to the surface of the material, through an air gap, via an electrode design. Only the side of the material facing the high potential electrode should show an increase in surface tension. When air is exposed to different voltages, an electrical discharge develops. When this occurs, neutral molecules and electrically charged molecules collide. These collisions cause neutral molecules to become electrically charged, resulting in filamentary discharges or “streamers”. Such filamentary discharges create a cloud of ionized air - or an “air plasma”. When a plastic substance is placed under an air plasma discharge, electrons bombard the treatment surface with energies two to three times that necessary to break the molecular bonds on the surface of most substrates. The resulting free radicals react rapidly with other free radicals on the same or different molecular

chain, resulting in cross-linking. Oxidative effects on treated surfaces increases surface energy as a result of polar groups being created on the surface, primarily in the form of hydroxyl groups, carbonyl groups, amide groups and carboxylic acid. Since exposures of treated surfaces to high levels of ambient humidity and temperature accelerates polymer side chain mobility and treatment degradation, it is recommended that downstream plastic decoration take place directly following treatment.

Air plasma systems are currently manufactured in two forms, *blown arc* and *blown ion*. The blown arc form of air plasma is easily distinguished by the bright flame-like electrical arc that it forms. This sub-form uses two electrodes through which air is blown between them forming this arc-like shape. In this form, the substrate is treated by coming into contact with approximately a quarter of an inch of the arc. The blown ion form of air plasma requires greater pressure of air past the electrode. This sub-form utilizes a single electrode that discharges inside the treater head. The great amount of pressure allows the charged air to rocket out of the tip of the head and form a deep, directed stream of charged ions.

*Flame plasma* is formed when a flammable gas and atmospheric air are combined and combusted to form an intense blue flame. The surface of materials are made polar as species in the flame plasma affect the electron distribution and density on the surface. Polar functional groups such as ether, ester, carbonyl, carboxyl, and hydroxyl are contained in a flame plasma; these are incorporated into the surface and affect the electron density of the polymer material. This polarization and functionalization is made through reactive oxidation of a surface. ESCA analysis shows that oxidation depth through flame treatment is 5-10nm. This is generally less in depth than air plasma treatment, where oxidation depth is believed to be over 10nm. However, flame plasma treatment’s extensive oxidation, due to reactions with OH radicals in the flame, results in a highly wettable surface which is relatively stable upon aging.

Flame plasma systems are manufactured with two primary burner configurations – *ribbon* and *drilled port*. Ribbon burners are typically constructed with a cast iron body and with stainless steel ribbons which are meshed

(or opposed to each other) to construct varying pilot and main flame patterns. As the open area of the ribbon construction increases, so does the capacity of the ribbon burner. Drilled port burners are typically manufactured in brass, stainless steel or aluminum and offer the flexibility of having varying port diameters and port rows for wide design and treatment adaptations. The substrate is optimally treated by flame plasma when it is positioned approximately 5-8mm above the inner luminous flame cones. Line speed and burner output will affect this positioning.

*Atmospheric chemical plasma* treating systems generate an electrically charged atmosphere similar to air plasma, but uses chemical atmospheres in place of air to introduce a wide range of surface modifications to a substrate. The systems are characterized by their generation of high density reactive species for low temperature material processing. The chemical plasma process can involve surface preparation via the breakdown of low molecular weight organic materials (LMWOM) and surface decontamination, fine etching of the surface to create new topographies, grafting of new functional groups or chemical species on the surface, and the deposition of coatings on the surface. The treatment process is designed to allow the interchange of gas chemistries relative to the application requirements. In the case of plastic parts, loose surface oligomers and other residues are repetitively cleaved and degraded until they are removed largely by a combination of bombardment by ions and electrons. These organic residues are converted into water vapor, carbon dioxide, and other nontoxic gases or volatilized materials. A noble carrier gas such as argon is typically used to initiate the breakdown of LMWOM and create surface etching for greater adhesion of paints, inks, coatings and adhesives. The gas species which is ionized, along with the composition and structure of the polymer itself, are the key factors that determine the degree of etching. To maximize adhesion of paints on plastics (particularly thermoplastic olefins), the deposition of polar functional groups from the use of oxygen and acetylene reactive gases with the carrier gas can be particularly effective.

Atmospheric chemical plasma treatment systems are typically non-thermal, atmospheric-pressure, glow-discharge plasma systems which generate uniform and homogenous treatments. The level of surface tension and longevity of treatment are both typically greater than air plasma treatment effects, and similar in treatment effect to flame plasmas. The substrate is optimally treated by atmospheric chemical plasma when it is positioned several millimeters downstream from the source. Line speed, power level, chemistry, chemistry mixtures and material composition primarily determine levels of etching and functionalization which can be achieved.

### **Measures of Wettability & Adhesion**

Substrates such as plastics are generally composed of non-polar, long-chain molecules. Polymeric surfaces have a small amount of free energy. Fluorocarbons, silicones and vinyls have particularly low free surface energies. As such, plastics have few available bonding sites due to low levels of charged ions on the surface. In addition to low surface energies, plastics have diverse levels of conductivity, may be composites in structure, and may be blended with processing additives. All of these variables can negatively impact molecular attraction, causing liquids to fail to wet the surface. The surface energy of plastics must significantly exceed the surface tension of liquids by a recommended level of 10 dynes/cm to prevent paint or ink picking/liftoff and delaminations.

Reliable and repeatable measures of wettability and adhesion are critical to successfully painting, printing, coating and laminating three-dimensional substrates. The use of “dyne” solutions is the most common method of measuring the surface tension of substrates. This process uses varying proportions of formamide (HCONH<sub>2</sub>) and ethyl cellosolve (CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH). The percentage of each chemical used is dictated by ASTM D2578-84, and directly correlates to surface tension of the solution usually ranging from 30-70 dynes/cm. The ASTM standard requires ambient temperature (23±2°C) and relative humidity (50±5%) test conditions, due to the inverse temperature/surface tension relationships of liquids. A sterile cotton swab is used to apply a thin coating of the dyne solution to the substrate. If the dyne solution does not bead up within two seconds, the surface tension of the substrate is determined to be at the dyne level of the solution used or higher. This testing method is fast and cost-effective. Use of a consistent number of drops of dyne solution on individual swabs for each test adds reliability to the method. Dyne markers are also used in the industry, but care must be taken to clean contamination from the tip following each test.

*Contact angle* is also often used to determine surface tension, cleanliness, bondability, wettability, adhesion, bio-compatibility and coating quality. Advancing angle measurements best represent the wetting of the substrate while receding angle measurements can predict the adhesion characteristics of the substrate. In some cases, the variation of the measured contact angle of the pretreated surface from location to location is larger than the average reduction in the contact angle by pretreatment. To gather meaningful data, the same point on the surface should be used to measure the contact

angles before and after pretreatment. This reveals the change in contact angle due to cleaning while minimizing the effect of surface variation.

### **Over-Treatment Affects**

The primary objective of surface activation systems is to introduce high energies to bombard ions against surfaces and remove contaminants so a more stable polymer surface is exposed. And in the case of a plasma discharge, these bombardments can facilitate the further etching, grafting or the deposition of surface coatings.

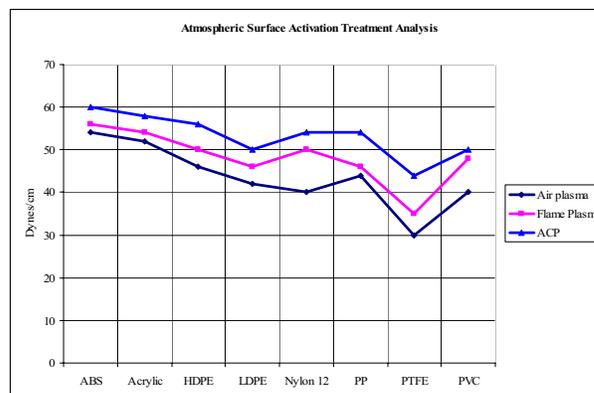
Excessive surface treatment can result in an extreme bombardment of the base polymer which ultimately can destroy the entire polymer part. Depending on the treatment process, pin-holing, surface degradation (i.e., redevelopment of LMWOM), and accelerated treatment decay rate are typical outcomes from atmospheric surface activation system over-treatments.

### **Surface Analysis**

Surface analysis and microscopy methods are key tools in determining changes in surface topography and the presence of deposited functional groups on substrates. Appropriate techniques to maximize surface data for plastics while minimizing cost and response time include Atomic Force Microscopy (micrographs of atomic scale roughness to resolution depths of .01nm), XPS/ESCA (surface analysis of organic and inorganic molecules to resolution depths of 1-10nm), and Time of Flight SIMS (surface microanalysis of secondary ions, atoms, and molecules to resolution depths of 1 monolayer).

### **Background & Development Effort**

Because the processing of plastic substrates is typically in-line or continuous from surface activation through the adhesion of inks, paints, coatings and adhesives, experimental focus was placed on determining the treatment effectiveness of different atmospheric surface activation systems on various plastic substrates rather than on long-term treatment degradation profiles. As such, an analysis was conducted of immediate post-treatment surface energy as created by air plasma, flame plasma, and atmospheric chemical plasma, and measured by the use of dyne solutions and sterile cotton swabs. Trials were conducted within the Enercon Industries surface treatment laboratory at a processing speed of 50 fpm. Power outputs for Enercon-designed air plasma, flame plasma and atmospheric chemical plasma systems were controlled to standard design outputs. The flame plasma treater utilized a triple slot burner, while the chemical plasma system utilized helium and oxygen chemistries. See Figure 1 for the results of this analysis.



**Figure 1**

### **Conclusions**

- § With the exception of PTFE, the polymer substrates chosen for this analysis were treated by air plasma, flame plasma and atmospheric chemical plasma at or above surface activation levels considered adequate by industry standards for promoting the adhesion of aqueous, solvent and UV-based (see Appendix).
- § High levels of reactive oxidation and surface functionalization by flame plasma and atmospheric chemical plasma, respectively, are assumed to be key in generating dyne levels higher than air plasma for all tested polymer substrates.

### **References**

1. Markgraf, D.A., "Corona Treatment: An Overview," 1986 Coextrusion Conference Proceedings, TAPPI PRESS, Atlanta, p. 85.
2. Collins, W.M., "Classical Review of Corona Treatment," 1983 Coextrusion Conference Proceedings, TAPPI PRESS, Atlanta, p. 47.
3. Markgraf, D.A., "Ozone Decomposition in Corona Treatment," 1985 Polymers, Laminations and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p. 227.
4. Pochan, M., et al, "XPS and Contact Angle Investigation of Corona Treatment...", 1985 Polymers, Laminations and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p. 109.
5. Markgraf, D.A., "Physical and Surface Chemistry of Corona Discharge...", 1985 Polymers, Laminations and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p. 107.
6. Marra, J.V., "Surface Modification of Polypropylene Film...", 1985 Polymers, Laminations and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p. 103.
7. Schwab, F.C., et al, "Effect of Resin Additives on Corona Treatment...", 1985 Polymers, Laminations and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p. 95.

8. Markgraf, D.A., "Practical Aspects of Determining Level of Corona Treatment," 1985 Film Extrusion Conference Proceedings, TAPPI PRESS, Atlanta, p. 65.
9. Whiteside, D.L., "Corona Treating of Substrates," 1985 Polymers, Laminations and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p. 89.
10. Markgraf, D.A., "Practical Aspects of Determining Level of Corona Treatment," 1984 Polymers, Laminations and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p. 507.
11. Schuelke, G.W., "Modern Trends in Corona Treating," 1984 Polymers, Laminations and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p. 249.
12. Markgraf, D.A., "Evolution of Corona Treating Electrodes," 1983 Paper Synthetics Conference Proceedings, TAPPI PRESS, Atlanta, p. 255.
13. Collins, W.M., "Recent Technological Advances in Corona Treating," 1981 Paper Synthetics Conference Proceedings, TAPPI PRESS, Atlanta, p. 129.
14. Cramm, R.H., et al., "Theory and Practice of Corona Treatment for...," 1981 Paper Synthetics Conference Proceedings, TAPPI PRESS, Atlanta, p. 1.
15. Zito, W.F., "Electrostatic Treatment of Films Watts the Answer?" 1980 Paper Synthetics Conference Proceedings, TAPPI PRESS, Atlanta, p. 181.
16. Spell, H.L., et al., "Surface Analysis of Corona Treated PE...," 1978 Conference Proceedings, TAPPI PRESS, Atlanta, p. 283.
17. Ristey, W.J., et al., "Degradation and Surface Oxidation of PE...," 1978 Conference Proceedings, TAPPI PRESS, Atlanta, p. 267.
18. Tietje, A., "Corona Treating Systems for Coater-laminators," 1978 Conference Proceedings, TAPPI PRESS, Atlanta, p. 173.
19. Maynard, P.W., "Electrostatic Treating to Promote Adhesion to...," 1976 Paper Synthetics Conference Proceedings, TAPPI PRESS, Atlanta, p. 59.
20. Sherman, P.B., "Quartz, Ceramic or Rubber Dielectric in Corona Treatment," 1985 Polymers, Laminations and Coatings Conference Proceedings, TAPPI PRESS, Atlanta, p. 341.
21. Sherman, P.B., "Corona Treat-mechanical not Electrical Problem," 1985 Film Extrusion Conference Proceedings, TAPPI PRESS, Atlanta, p. 45.
22. Markgraf, D.A., "Sizing: the Critical Element for Effective Corona Treatment," 1989 Coextrusion Conference Proceedings, TAPPI PRESS, Atlanta, p. 17.
23. Thompson, K., "Surface Treatments for Coex Polymer Films/Coatings," 1989 Coextrusion Conference Proceedings, TAPPI PRESS, Atlanta, p. 11.
24. Briggs, D., Brewis, D.M., and Konieczko, M.B., Journal of Material Science, 14, 1344-1348 (1979).

## Appendix

Industry Category	Pre-Treated Components	ABS	ASA	FP's	PA	PBT	PC	PE	PET	PMMA	POM	PP	PPE	PS	PUR	PVC	TPU
<i>Automotive</i>	Bumber Parts	*	*				*					*			*		
	Electrical Components				*	*	*					*			*	*	*
	Engine parts																
	Fascia/cladding/side moldings	*	*			*						*					*
	Grilles/Opening Panels	*				*	*		*			*					
	Instrument Panel/Dashboard	*				*	*					*					
	Interior Trim	*				*	*		*	*	*	*				*	
	Lighting	*				*	*		*	*	*	*					
	Quarter Panels	*				*	*					*	*			*	
	Tubing			*													
	Upholstery	*						*				*				*	*
	Wheel Trim	*					*	*				*				*	*
	<i>Medical</i>	Angioplasty Balloons				*				*							
Catheters/Housings					*	*											
Filter Casings		*							*								
Microplates												*					
Needle Hubs		*					*	*	*	*	*	*			*	*	*
Optical Lenses							*	*	*	*	*	*					
Petri Dishes														*			
Syringes						*						*					
Tubes, Valves, Connectors		*										*			*	*	*
Vials												*				*	*
<i>Electronic</i>	Cables							*	*			*					
	Circuit Boards								*								
	Connectors			*	*	*						*					
	Fiber Optic Cable Jackets			*	*	*										*	*
	Handheld Screens								*								
	Housings		*			*	*		*	*	*	*					
	Switches					*	*		*	*	*	*					
	Wiring							*	*	*	*	*					*
<i>Cosmetics/ Pharmaceuticals/ Food</i>	Bottles						*	*	*			*				*	*
	Caps						*	*	*			*				*	*
	Closures						*	*	*			*				*	*
	Jars						*	*	*			*				*	*
	Tubes						*	*	*			*				*	*
<i>Recommended Surface Treatment Type/Dynes</i>	Type (Corona, Flame, Plasma)	C,F	C, P	P	C,P	P	C	C,F	C	C	P	F,P	P	C,P	C,P	C	C,P
	Dynes (aqueous decoration/coating)	44-48	40-44	40-48	48-60	40-48	48-60	40-48	46-60	40-44	40-48	40-48	40-48	40-48	44-48	42-48	44-48
	Dynes (solvent decoration/coating)	42-46	38-48	38-45	46-55	38-45	46-55	38-45	42-48	38-48	38-45	38-45	38-45	38-45	42-46	40-45	42-46
	Dynes (UV curables)	46-56	42-54	44-60	50-60	44-60	50-60	44-60	48-62	42-54	44-60	44-60	44-60	44-60	46-56	44-60	46-56