Atmospheric Plasma Gas Phase Priming Applications & Benefits

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Abstract: Atmospheric Plasma Gas Phase Priming (APGPP) can be a cost-effective and environmentally responsible method to prepare films for converting. A variety of functional groups can be grafted onto a substrate using atmospheric pressure plasma, dopants and nitrogen as a carrier gas. This alternative results in significant cost reduction vs. traditional liquid coating processes and produces excellent adhesion properties. Air Liquide's gas phase priming technology will be discussed, including sample case studies and economics, current and future applications.

INTRODUCTION

The performance demands placed on base plastic films have increased over the years, due to the growth of sophisticated flexible packaging end-products (barrier packaging, microwavable packaging, retort pouches…) and new high technology markets for these materials such as printed electronics, optical films, films for batteries and photovoltaics. These products are very often made up of thin multi-layer structures each one ensuring one or more of the required functionalities of the final material. These are mechanical strength, optical clarity, barrier behavior towards moisture, oxygen, light, aromas, etc, sealability, printability and slipping to list the most common. Plain or co-extruded BOPP, BOPET, BOPA, PVC and PE films together with aluminum foil, metalized film and/or paper or paper board are used as raw materials and they are converted through surface treatment, primer coating, metalizing, printing, lacquering, laminating or extrusion coating. These products and their variety of applications and performance requirements, has driven new developments in coatings and primer formulations suitable for increasing adhesion of inks, adhesives, clear coats and application of functional coatings.

Standard film pre-treatments involve additional steps in the film converting line resulting in capital investments, solvent handling, drying and disposal, and ultimately higher costs which are most often passed down to the converter. In addition, current and future environmental liabilities present more uncertainty as the costs for disposal, thermal destruction and air emissions are expected increase.

Atmospheric Plasma Gas Phase Priming presents a unique opportunity for converters to mitigate some of these costs and uncertainties, in addition to being able to adapt a variety of gas recipes using atmospheric pressure plasma to a particular application.

OXYGEN FREE ATMOSPHERE CONCEPT

Atmospheric Plasma Gas Phase Priming is based on the ability to create an Oxygen Free Atmosphere in a limited zone inside an open containment where a two-dimensional substrate is moving at high speeds.

A hood surrounding the electrodes and a backing roller, similar to air corona station, is combined with mechanical gas seals designed to keep air from entering the plasma zone with the substrate or at the machine exit. By eliminating oxygen, reactive gas mixtures and operating conditions can be developed, to produce specific atmospheric plasmas that graft extremely thin, molecular reactive coatings that are able to chemically bond with inks, varnishes, adhesives and coatings.

The concept is depicted in Figure 1 below and comprises the following main functions:

1. Removal of the air boundary layer from the surface of the film at the inlet of the hood
2. Avoid the exit of off-gases at the outlet of the hood
3. Measurement of the oxygen concentration inside the hood, close to the surface of the film
4. Adjustment of exhaust volume to ensure oxygen concentration settings
5. Minimization inside /outside cross-flow of gases by controlling the pressure difference inside and outside the hood (Gas Seal)
6. Injection of working gas mixture

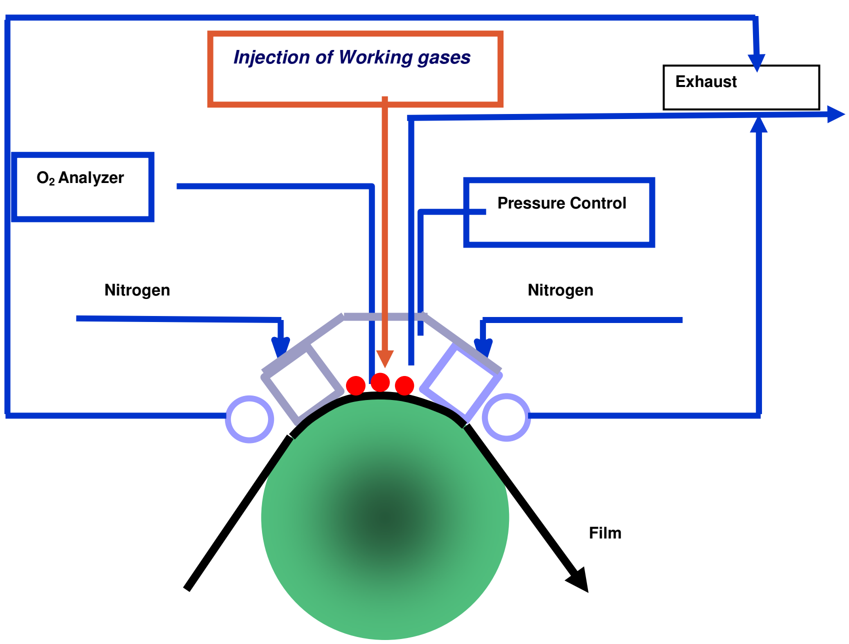


Figure 1: Oxygen Free Atmosphere Concept

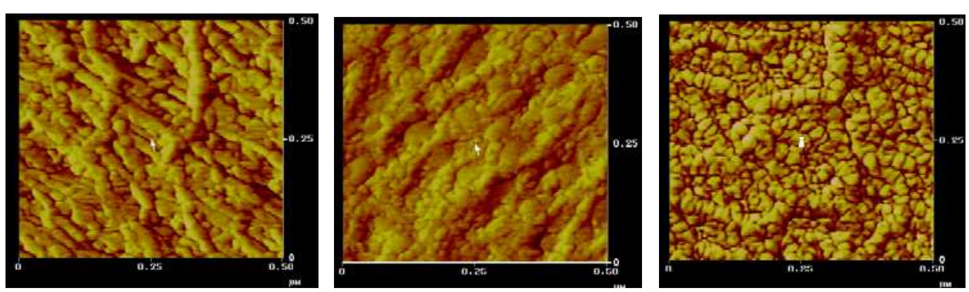
Average gas consumption of 10 l/m² including injection of working gases at speeds exceeding 500 m/min is needed to reach residual oxygen concentrations lower than 50 ppm.

Atmospheric Plasma Gas Phase Priming

Air Corona treatment and limitations

Air Corona is a filamentary barrier discharge in which molecular oxygen is mainly activated producing electrons, meta-stable species, positive and negative oxygen ions, radicals and ozone. All these reactive species occupy the volume inside the "filaments" or streamers arising between the electrodes and have a tremendous effect on organic molecules such as the polymer chains of the film and any oligomer present on its surface (e.g. slip or other type of additive). This effect consists on breaking carbon-hydrogen and carbon-carbon bonds, which in turn results in cleaning of the surface (small molecules become even smaller and "burn" or leave the surface as vapours which solidify once in contact with the metallic parts of the equipment), but also creates erosion or "etching" of the surface of the film by removal of small polymer chain fragments. This chain breaking leads to carbon radicals, which react with the excited oxygenated species but also with excess molecular oxygen present in the immediate environment of the carbon radical.

As shown by Atomic Force Microscopy (AFM) pictures in Tapping mode of 20 µm thick BOPP film (Figure 2(II) below), after corona treatment the physical morphology of the surface exhibits a much lower roughness than that of the initial substrate with several dark brown zones of higher viscosity having the form of flat elliptical 50nm x 65nm zones and corresponding to the "etched" parts of the material. In terms of chemical modification, X-Ray Photoelectron Spectroscopy (XPS) results summarised on Table 1 show around 14-16% carbon atom substitution by oxygen atoms the latter being in the form of carbon-oxygen based functional groups like hydroxyl, ether, ketone and acid or ester.



(I) Untreated
Ra = 5.2 nm

(II) Air corona
Ra = 3.6 nm

(III) Gas Phase Primer
Ra = 4.6 nm

Figure 2: AFM pictures of BOPP (TAPPING mode)

As a result, one can observe the increase of surface energy due to the grafting of these polar groups and, to some extent, of the adhesion characteristics of the treated surface. However, these surface characteristics are not permanent and surface energy and adhesion decrease fast to their initial values after a few days.

Low oxygen atmospheric plasma gas phase priming

Low oxygen Atmospheric Plasma Gas Phase Priming is accomplished in a filamentary barrier discharge using nitrogen as a carrier gas doped with small amounts (ppm quantities) of gases like N_2O, CO_2, H_2 or other doping gases. The plasma activates the substrate, the carrier gas (N_2) and the doping gases, creating free radicals on both the gas phase and the substrate allowing for targeted radical-radical coupling reactions to occur on the substrates surface. The resulting surface chemistries are a combination of oxygen based and nitrogen based chemical functions respectively under the forms of hydroxyl, ether, ketone and acid in one part and amino, amido and imido functional groups in the second part. All functions are strongly bonded to the substrate via covalent bonding.

It is important to note that the oxygen levels in the plasma zone must be controlled to a minimum (less than 50 ppm) in order to control the reactions and minimize ozone formation the later being responsible for polymer chain breaking.

Compared to Air Corona, APGPP streamers are shorter and denser and seem to be less energetic because they do not produce etching or other kind of severe alteration of the surface of the substrate. As shown on Figure 2, picture (III), the surface exhibits only regular weak brown lines on the fibres or lamellas of the BOPP film, with low roughness change, which suggest a much more even and smooth discharge.

As shown on Table 1 below under middle specific power treatment conditions (30-60 Wmin/m²) the percentage of the substituted carbon atoms depends on the used recipe (nature, number and concentration of doping gases, specific power…) and is of the same order of Air Corona treatment (14% in average). Carbon atoms are systematically replaced by oxygen and nitrogen atoms. Nitrogen atoms concentration varies from 3.82 up to 8.59% while oxygen atoms concentration varies from 4.08 up to 14.07%. Correspondingly, N/O atomic ratio varies from 0.27 up to 2.11 while O/N atomic ratio varies from 3.68 down to 0.47. These variations depend on the chosen gas recipe and are fully controllable. In other terms, APGPP allows for controlling the chemistry on the surface of the substrate which may be either nitrogen or oxygen predominant. If necessary, surfaces with equal oxygen and nitrogen chemical composition can be obtained for use in multiple ink/coating chemistries.

Recipe	%C	%O	%N	O/C	N/C	N/O	O/N	Amino		Amido		Imido	
									Normalized %		Normalized %		Normalized %
Air Corona	86,01	13,35	0,64										
R1	82,11	14,07	3,82	0,17	0,05	0,27	3,68	0,25	6,5	2,06	53,9	1,51	39,5
R2	84,29	11,00	4,71	0,13	0,06	0,43	2,34	0,20	4,2	3,15	66,9	1,36	28,9
R3	85,35	7,71	6,91	0,09	0,08	0,90	1,12	1,42	20,5	4,63	67,0	0,86	12,4
R4	87,45	5,55	7,00	0,06	0,08	1,26	0,79	2,54	36,3	4,28	61,1	0,18	2,6
R5	86,18	4,99	8,83	0,06	0,10	1,77	0,57	3,34	37,8	4,63	52,4	0,86	9,7
R6	87,05	4,24	8,71	0,05	0,10	2,05	0,49	2,70	31,0	5,18	59,5	0,83	9,5
R7	87,33	4,08	8,59	0,05	0,10	2,11	0,47	2,59	30,2	4,67	54,4	1,33	15,5

Table 1: XPS surface analysis of Air Corona and Atmospheric Plasma Gas Phase Primed Plain BOPP in the range of 30-60 Wmin/m² specific energy

These functions are covalently bonded to the surface of the substrate and are inherently very stable offering excellent shelf-life. Because the chemically grafted groups are highly polar, surface energies as high as 60 mN/m have been obtained for plain BOPP, as shown on Figure 3 below. However, use of recipes with strong oxidizing dopants or lack of accurate atmosphere control (presence of high amounts of residual oxygen from air) can lead to unstable surfaces which stabilize over time at lower surface energy levels.

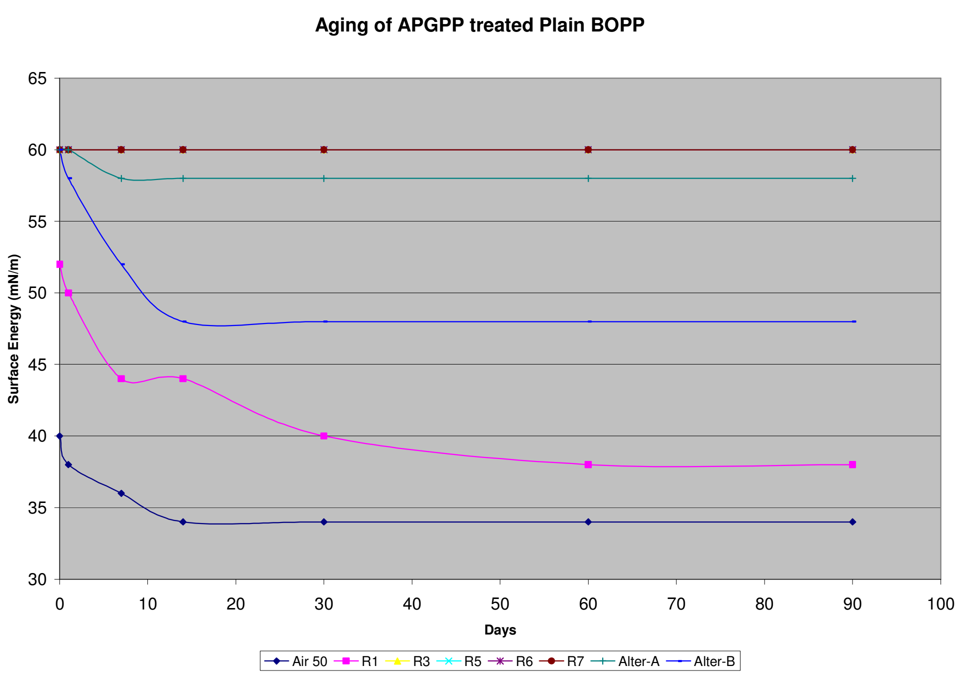


Figure 3: Surface Energy level and stability of Atmospheric Plasma Gas Phase Primed Plain BOPP

The thickness of this gas based coating is very thin (monomolecular layer, a few Å thick) and may be subject to contamination, either external or internal. External contamination can be managed through appropriate handling. Internal contamination can result from migrating additives (slipping or other kind) and can be detrimental to the shelf-life of the coating, because euricamides, waxes and other similar compounds can mask the surface amino and amido/imido groups. In such cases long storage and transportation of treated materials must be avoided, but in line operations or minimal handling prior to converting can mitigate risk of contamination.

Amino and amido/imido groups show very interesting chemistry features. In fact, these nitrogen based functions can dramatically improve adhesion via "hydrogen bonding" or "covalent bonding" with various ink formulations containing binders such as alkyds, epoxies , isocyanates or acids and esters (e.g. acrylic acid and acrylates). Particularly:

- amido and imido groups are the most suitable chemical functions to give rise to strong "hydrogen bonding" with carboxylate or carboxylic functions like the ones featured by acrylic acid and acrylates. APGPP is fully suitable for printing with either water-based inks or UV curable inks and varnishes, all of them containing binders with acrylate backbones.

- amino groups react very fast with isocyanates to produce water stable urea type covalently bonded structures. Consequently, amino rich surfaces will be preferable for lamination with urethane-based adhesive formulations or printing with urethane modified nitrocellulosic inks.

Globally, atmospheric plasma gas primed surfaces are suitable for:

- Printing and lacquering with solvent based, water born and solventless UV/EB curable inks, coatings and lacquers
- Adhesive lamination of two polymers or a polymer and aluminium foil or paper board
- Extrusion coating and extrusion lamination particularly for difficult substrates like BOPP, BOPET, BOPA
- Metalizing

Sample Economic Case Studies

Case 1: Water soluble ink with inline liquid priming process

Background:
A flexible packaging converter was using an inline liquid priming step prior to printing water soluble inks on BOPP in order to gain the adhesion properties required by their customer. Gas phase priming recipes were developed and achieved excellent adhesion results. A summary of the economic benefits that resulted from using an inline APGPP treatment process is summarized in Table 2.

		Inline Liquid Priming		***Gas Phase Priming***
Operating Costs ($/MSI)	$	0.028	$	0.006
Capital Depreciation (10 Yr SL)	$	-	$	0.003
Total Cost ($/MSI)	$	0.028	$	0.008
Annual Costs	$	341,107	$	98,936
Annual Savings			**$**	**242,172**
Simple Payback (yrs)				**1.28**
Annual Production		12,182,400	MSI	
Annual Operating Hours		5,000	hours	

Table 2: Economic Benefit Summary of Replacing Inline Priming Step

In addition to the quantifiable operating cost benefits, the converter also recognized the following benefits:

- Enhanced printing capability by being able to use an additional ink color in the tray currently used for the primer
- Elimination of handling, storage and disposing of the primer

Case 2: Replacement of chemically treated BOPET with plain BOPET

Background:
A supplier of multi-layered metalized substrates required the use of treated BOPET for adhesion of a functional coating and various printing inks. Gas phase priming on plain non-treated BOPET resulted in adhesion properties equal to the chemically BOPET 90 days after treatment. The estimated cost benefits are summarized in Table 3.

		Chemically Treated BOPET		***Non-treated BOPET & Gas Phase Priming***
Annual BOPET Cost ($/MSI)	$	0.048	$	0.0395
Capital Depreciation (10 Yr SL)	$	-	$	0.0008
Operating Cost ($/MSI)	$	-	$	0.0022
Total Cost ($/MSI)	$	0.048	$	0.042
Annual Costs	$	6,374,037	$	5,595,698
Annual Savings			**$**	**778,340**
Simple Payback (yrs)				**1.3**
Annual Production		131,681,894	MSI	
Annual Operating Hours		6,048	hours	

Table 3: Economic Benefit Summary of Replacing Chemically Treated BOPET

FUTURE TRENDS AND DEVELOPMENTS

Reducing production costs, enhanced safety and health in the workplace, and environmentally friendly processes, remain key drivers. In that perspective one of our key technical objectives is to extend the performance of APGPP by achieving thin coatings with chemical functions encompassing oxygen and nitrogen based groups, which will be able to replace either liquid primers or liquid functional coatings in applications such as gas and liquid barriers including humidity, anti-scratch, weathering, controlled release, and control of the coefficient of friction.

In addition market demands from new sectors such as printed electronics, optical films, films for batteries and photovoltaics will present new challenges and tremendous growth opportunities for AGPP in the coming years.

CONCLUSION

Atmospheric gas phase priming is a low cost alternative to liquid based functional coatings. It also offers an environmentally sound approach compared with many coatings which require drying, emission controls and special storage and disposal. With precise control of the oxygen levels and reacting gases in the electrode area, concentrations of nitrogen and oxygen based functional groups can accurately be controlled and grafted on the surface of the film. This allows for the creation of a variety of surface functionalities for the many applications and performance demands for films today. By placing the AGPP process inline, the problems resulting from the migration of contaminants and additives can be overcome.

New uses for films requiring optical, barrier, controlled release, and electrical properties are creating new opportunities as converters try to minimize costs, coating steps and environmental liabilities. AGPP will certainly play a key role in optimizing the cost and performance of these new materials.

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