INNOVATIVE LOW PRESSURE PLASMA COATINGS FOR GAS AND LIQUID FILTER MEDIA

Filip Legein, Sales Director, Europlasma NV,
De Bruwaan 5D, B-9700 Oudenaarde, Belgium, tel: +32-55-30 32 05,
fax: +32-55-31 87 53, e-mail: filip.legein@europlasma.be

ABSTRACT

Plasma is the fourth state of matter. By adding energy matter can be transformed from solid to liquid, from liquid to gas and from gas to plasma. In plasma the molecules are decomposed in neutral and charged particles that will interact with the surface of the material. In low pressure plasma technology a stable and effective plasma is created by an electromagnetic discharge of a gas at low pressure and at low temperature.

In recent years low pressure plasma technology has been improved to achieve polymerization of monomers on materials, depositing real nanocoatings on the surface, and adding new and permanent functionalities to the material. Innovative plasma processes allow to deposit coatings with high levels of hydrophobicity and/or oleophobicity for use in gas filtration, or coatings with permanent hydrophilic effect for liquid filter media and battery separators.

The use of low pressure plasma for surface modification of filter media becomes more widespread because it is a dry and clean technology. Filter media producers adopt plasma coating to improve the quality of their products. At the same time it helps these companies to save costs because of a lower consumption of energy and chemicals.

KEYWORDS

Filter Media, Surface Modification, Nanocoating, Hydrophilic, Hydrophobic, Oleophobic, Plasma Activation, Plasma Coating

INTRODUCTION

Low pressure plasma technology has been industrially applied since the early eighties. Initially it was mainly used to clean or desmear printed circuit boards, using an etching type of plasma.

Gradually the technology spread into rigid plastics' industries, where polymers were activated using pure gases such as oxygen. The activation creates functional groups onto the outer polymer chains of the material, which increases the surface energy of the plastic. This improves the adhesion with paints, adhesives or printing inks, even on complex three dimensional parts. This kind of functionalization of surfaces opened new markets for plasma technology such as medical devices, automotive interior and exterior parts and consumer electronics. Different industrial markets adopted low pressure plasma technology because of the higher quality performance, and the ecologic and economic advantages. Plasma activation is nowadays widely used to replace primers, or other surface treatment technologies such as flaming or corona.

More than fifteen years ago companies like Europlasma started building roll-to-roll low pressure plasma equipments to apply the same plasma activation processes to flexible materials. Since then an increasing number of producers have explored surface modification of industrial textiles by low pressure plasma.

The breakthrough of low pressure plasma technology in filter media production came with the development of plasma coating processes. These processes use plasma to polymerize monomers on the surface of the material. Nanocoatings are deposited on the surface, adding new and permanent functionalities to the material. Innovative plasma processes allow to deposit coatings with high levels of hydrophobicity and/or oleophobicity for use in gas filtration, or coatings with permanent hydrophilic effect for liquid filter media and battery separators.

LOW PRESSURE PLASMA TECHNOLOGY

Plasma is considered the fourth state of matter. By adding energy matter can be transformed from solid to liquid, from liquid to gas and from gas to plasma.

In low pressure plasma technology a stable and effective plasma is created by an electromagnetic discharge of a process gas at low pressure (and at low temperature). Under those circumstances, the process gas will be partially decomposed into radicals and atoms and will also be partially ionized. These reactive species will interact with the surface of the material. This interaction is both chemical and physical in nature.

The process gas is contained in a vacuum chamber which is connected to a pumping group that will evacuate the chamber and maintain the vacuum during processing. In order to effect the plasma treatment in sufficiently pure process gas conditions, a base pressure in the 5 to 25mTorr range is required prior to processing.

The plasma process is typically performed in a working pressure range of 25 to 250mTorr. A set of electrodes is mounted in the chamber. These electrodes are powered by a generator at a frequency of typically 40kHz, 13.56MHz or 2.45GHz.

The process gas can be obtained from gaseous precursors or from evaporating liquid or solid monomers. A monomer supply unit ensures that controlled amounts of process gas are entered into the chamber.

LOW PRESSURE PLASMA COATING EQUIPMENT

Plasma systems can have all kinds of shapes and differ mostly in the loading system.

Most low pressure plasma treatments in the filtration industry however are carried out roll-to-roll. **Figure 1** shows a typical roll-to-roll equipment for rolls with a maximum width of 1800 mm and a roll outer diameter of 1000 mm.

Fig. 1: Europlasma CD1800/1000 roll-to-roll machine.

In some cases it is be better to plasma treat the finished filter elements. In such case a tray system is used. **Figure 2** shows a picture of a typical machine for the treatment of rigid filter elements. The Europlasma CD400 as shown has a vacuum chamber with dimensions 400 mm x 400 mm x 400 mm and has standard four trays of dimensions 305 mm x 360 mm x 40 mm in one batch. The machine can also be equipped with a roll cassette to treat small rolls of material. Depending on the required capacity of the plasma system different chamber sizes are available.

Fig. 2: Europlasma CD400 PLC with trays or roll cassette.

LOW PRESSURE PLASMA ACTIVATION

In the early nineties the filtration industry started using low pressure plasma technology to activate the surface of filter media. Plasma activation is a chemical modification of the surface of the material. The effect is not permanent and will disappear over time. The shelf life is typically a number of days to months depending on the application.

Plasma activation only affects the outer molecular layers of the material. New chemical groups are added to the polymer chains. These chemical groups will increase the surface energy of the plastics. The higher surface energy is reflected in a lower contact angle with water, which reflects better wetting of the surface by water.

Typical activation gases are O_2, N_2 or N_2O, or gas mixtures such as N_2H_2. The choice of gas depends on the material and the subsequent application.

Plasma activation is often used as a pretreatment step prior to gluing, plasma coating or chemical coating, of both flexible and rigid filter media.

Low pressure plasma activation is also well known in the production of rigid filter media made from porous plastics. Low pressure plasma technology is unique in that the plasma can enter into the core of the porous structure.

Over time industry has looked to achieve a more permanent hydrophilic effect. In response Europlasma has developed several gas mixtures for permanent hydrophilic coatings. These gas mixtures are typically composed of hydrocarbons and activation gases such as O_2 or N_2O. The process conditions for hydrophilic coating are however more demanding than for simple activation.

A well known application of hydrophilic plasma coating is found in the production of blood filter media. The coating is typically applied roll-to-roll on nonwoven materials such as PP or PBT.

Hydrophilic plasma coatings are very effective on difficult materials such as nonwoven PP. In this case the rate of absorption of an alkaline-solution (30% of KOH in demi-H_2O) was evaluated in a wicking test on 40 mm by 200 mm test samples. For a 1 min wicking of a plasma coated material, values of more than 70 mm were obtained, whereas the uncoated reference material gave no wicking at all. Those results were obtained two months after coating of the nonwoven, proving the permanent character of the coating. The wicking effect was also much higher than for any other commercially available material.

LOW PRESSURE PLASMA COATING

In the late nineties low pressure plasma technology was improved to achieve polymerization of monomers on materials, depositing real nanocoatings on the surface, and adding new and permanent functionalities to the material. Innovative plasma processes allow to deposit coatings with high levels of hydrophobicity and oleophobicity on rigid and flexible materials.

Producers of gas filter media were of the first to adopt low pressure plasma coating on industrial scale. They are looking for a permanent hydrophobic and/or oleophobic effect, which can be achieved by polymerizing precursors such as fluorocarbon gases.

Low pressure plasma coatings are for instance used in the production of respirator masks. Typical filter media consist of several layers of meltblown non woven PP, which are electrostatically charged (electrets). Filtration efficiency for oily particles can be greatly improved by applying a hydrophobic/oleophobic coating prior to electrostatic charging. Typical oil repellency grades of 3 to 4 using the 3M procedure (AATCC test method 118-1997) are achieved. **Figure 3** illustrates this behaviour for dioctyl phthalate (DOP)-droplets on a macroscopic scale.

Fig. 3: hydrophobic coating on nonwoven meltblown PP.

Table 1 gives an overview of filtration efficiency as measured with a CERTITEST 8130 equipment using DOP particles. Initial filtration efficiency and evolution of filtration efficiency can be measured. During measurement, the filter (consisting of five layers of single ply nonwoven PP) is loaded with 200 mg of DOP particles. Penetration tests have been carried out on electrostatic charged filters. It is clearly illustrated that a thin oleophobic plasma coating increases both initial and final filtration efficiency. In this sense, it can convert, for instance an R95 filter into an R99 filter.

Plasma coatings are also interesting for charged filter media used in HVAC applications. According to changing regulations for air conditioning filters, it is recommended to measure the filter efficiency after discharging with isopropanol. The filter efficiency of a charged plasma treated filter is much higher than the efficiency of a charged untreated filter. The efficiency of the untreated filter drops off after isopropanol treatment, but not so for the plasma treated filter. The plasma treatment makes the filter alcohol resistant. After discharging in isopropanol, the plasma treated filter therefore shows a much higher efficiency than the untreated filter, the difference between the two filters being much larger than before discharging in alcohol.

Filter medium	Conditioning	Initial penetration (%)	Penetration after (x) minutes (%)
Supplier 1 - 28 g/m^2	Uncoated	1.20	6.40 (30)
Supplier 1 – 28 g/m^2	Plasma coated	0.48	1.08 (30)
Supplier 1 – 22 g/m^2	Uncoated	1.25	3.90 (10)
Supplier 1 – 22 g/m^2	Plasma coated	0.40	0.75 (10)
Supplier 2 – 25 g/m^2	Uncoated	N.A.	N.A.
Supplier 2 – 25 g/m^2	Plasma coated	0.02	0.03 (10)

Table 1: filtration measurement results obtained with a CERTITEST 8130 for different kinds of uncoated and plasma coated filter media (5 layers).

A new application in the filtration industry is the improvement of filtration efficiency and water repellency of air filters for diesel engines by low pressure plasma coating. The goal in the 6th European Framework European Framework Programs FLEXIFUNBAR was to develop a new air filter which has hydrophobic properties to pass the water decantation test. The effectiveness of a plasma coating on the filter performance was studied. The coating should not reduce the material properties of the air filter such as the dust holding capacity and the efficiency of the air filter. For the tests nonwoven PBT filter media were used.

In **table 2** the results are shown from a water decantation test of the reference material and the filters with four different plasma coatings. All plasma coatings are performed with a mix of fluorocarbon gasses. The difference between the processes is the process time and the power put on the electrodes inside the plasma chamber. The target was to achieve a duration of the test of minimum 50 minutes. With the plasma coating a duration of the test up to 93 minutes could be achieved.

Table 2 also presents the results after weathering of the filters. After weathering, the duration of the water decantation test was reduced, but it is still above the target of 50 minutes. The efficiency of the decantation is high for the new filters and the weathered filters.

Further investigation has also shown that both the dust holding capacity and the efficiency of the filter are not altered by the plasma treatment.

	New filters		Weathered filters	
	Duration of test (min)	Efficiency of decantation (%)	Duration of test (min)	Efficiency of decantation (%)
Reference	2.3	40.7	-	-
Test 1	80	98.7	60	95.8
Test 2	90	98.4	60	84.8
Test 3	93	97.8	62	95.7
Test 4	90	99.1	60	97.6

Table 2: water decantation results on reference and four plasma coated nonwoven PBT filters.

Producers of air filter media face increasing governmental pressures to replace existing wet chemical coating processes with more environment friendly technologies. At the same time customers do not want to compromise on the required levels of hydrophobicity and/or oleophobicity. In the 6th European Framework Program ACTECO Europlasma and its partners have developed a number of new coating processes to meet these challenges. These nanocoatings were applied by a combination of spraying and plasma, or by plasma only. Both low pressure plasma and atmospheric plasma were considered, starting from a number of different gaseous and liquid precursors. It was found that low pressure plasma polymerization of perfluoromonomers gave the best of both worlds. In low pressure plasma deposition the monomer consumption is relatively low, and there is no risk for the operator or environment. The deposition process is also carried out in a controlled environment. The coatings resulted in oleophobicity levels of 7 and more (3M scale) on woven fabrics (PET, cotton) and nonwoven membranes (PTFE). The coatings applied by low pressure plasma polymerization also gave good resistance to abrasion and washing.

ECONOMICS OF PLASMA COATING

Contrary to what is generally believed, low pressure vacuum plasma, especially in large roll-to-roll equipment, is a very cost effective technology.

Table 3 below shows an example of cost calculation for oleophobic coating on nonwoven PP of about 25 g/m^2 using the Europlasma CD1800/600. The process runs at 5 m/min to reach an oleophobicity level 3 on the 3M scale. Under these conditions, the total processing time for a roll with length of 7500 m and width of 1.8 m, is 27 hours. If the system is used 7 days a week in a three shift system, for a total of 47 weeks per year, the annual capacity of the system amounts to 292 rolls of 13,500 m^2 each or 3,942,000 m^2 in total.

The total coating cost in mass production is approximately 0.05 EUR/m^2. The processing cost, mainly consisting of process gas and electricity consumption, is approximately 0.03 EUR/m^2. Plasma activation or hydrophilic coatings would cost less. Typical full costing for plasma activation is in the range of 0.01 to 0.02 EUR/m^2. For the case shown in **table 3**, fixed costs represent about 37% of total costs. Therefore, it is important that the equipment is well dimensioned and that its capacity is fully exploited.

If reactive perfluoromonomers are used to reach higher oleophobicity levels of 7 and more on the 3M scale, more sophisticated equipment is required. Treatment times are in general shorter however, keeping the depreciation cost at the same level. Also the processing costs for these perfluoromonomers are within the same range of 0.01 to 0.10 EUR/m^2, which is very cheap compared to many chemical processes.

Cost factor	Comment	Cost per roll (EUR)	Cost per m^2 (EUR)
Depreciation cost	Depreciation over 10 years	239.7	0.018
Maintenance cost	Labour + parts	13.7	0.001
Total fixed costs		253.4	0.019
Electricity cost	@ 0.10 EUR/kWh	141.3	0.010
Process gas cost	Consumption of 1800 liters/roll	240.0	0.018
Labour cost	@ 35 EUR/hour	52.5	0.004
Total variable costs		433.8	0.032
Total costs		687.2	0.051

Table 3: Cost calculation for hydrophobic/oleophobic coating of nonwoven PP for filtration applications.

CONCLUSIONS

Low pressure plasma technology has found already several applications in the filtration industry: plasma activation of porous filter elements, hydrophilic coating of blood filters, hydrophilic coating of battery separators, and hydrophobic/oleophobic coating of different types of air filter media.

Low pressure plasma technology has proven to be fit for mass production. Contrary to what many think it is also very cost effective. Low pressure plasma technology has given the companies that use it a clear competitive edge.

It is expected that environmental legislation will drive more producers from wet chemical processing to a dry and clean technology such as plasma. Companies like Europlasma exist to find innovative plasma processes and to improve plasma deposition technology to cope with these production needs.

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Info on ACTECO:www.acteco.org