3
Low-pressure cold plasma processing technology

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3.1 Introduction

Low-pressure cold plasma technology is also referred to as vacuum plasma technology. This technology has its origin in the processing of semiconductor materials and printed circuit boards (PCB). Examples of applications in these industries are the cleaning of lead frames before die attach or wire ball bonding, desmearing of printed circuit boards and the cleaning of vias for carbon removal after laser drilling (Fierro and Getty, 2003). The very fact that this technology started in these specific industries – which are generally considered as high tech – has been both a blessing and a curse. Although other industries, such as the automotive and medical device sectors (Vanlandeghem, 1994; Greger, 2002), adopted vacuum plasma technology in the 1980s, soon after its introduction in the electronics industry, the path to incorporation into the textile and nonwoven sectors has been and remains troublesome.

It is the everyday experience of the author that much of the reservation of the textile industry is due to fear for an (for them at least) unfamiliar technology, which is again based on a lack of information. This book in general and this chapter in particular is one of many attempts to help the textile industry to overcome this fear.

The present chapter, after a description of the basics of the technology, the potential effects that can be generated by it and the industrial equipment that is used, will concentrate on industrial applications of low-pressure vacuum plasma technology, mainly in the technical textile and nonwoven market segments. It is stressed that, for most of these applications, industrial size equipment is in usage for manufacturing purposes already. A few applications will also be discussed that are closer to 'classical textile'.

The driving forces for using vacuum plasma technology in the textile industry are similar to those found in other industries. In the general plastics industry for applications in automotive products and home appliances, the drivers were ecological, aesthetical and economical (Palmers, 2002). Since the early 1990s, there has been a definite trend to replace plastics such as polyvinylchloride (PVC) and acrylonitrile–butadiene–styrene (ABS) resin by polypropylene (PP) for reasons of recyclability. PP has, however, a much lower surface energy, typically 30 mN/m or less compared to PVC or ABS. It is hence more difficult to glue, or bond or paint. In addition, product designers needed to have more design freedom, forced by the end customers who want to individualise the products that they buy. In the case of rigid plastics, designers were not happy any longer with bulk coloured products (master batches), but wanted to have the freedom to paint their designs in all kinds of colour patterns and grades. Combine both major trends: PP and painting, and the market was stuck with a technological problem that is difficult to overcome with classical technologies. Indeed, there exist primers for PP; however, those are extremely expensive and in most cases not environmentally friendly. Low-pressure vacuum plasma technology has been able to solve this challenge in a successful way.

Therefore, also in the textile industry, one has to look for applications which lead to unique products in a cost-effective and environmentally sound way. Several examples of unique nonwoven products will be discussed in this chapter. They are, in most cases, based upon plasma-coated substrates using plasma polymerisation, a technology which came only in broad usage in 1995.

3.2 Low-pressure vacuum plasma technology

3.2.1 Generalities

The plasma state of a gas – also considered as the fourth aggregation state of matter – can be reached if the gas is under sufficiently low-pressure and when electromagnetic energy is provided to the gas volume. Under those circumstances, the process gas will be partially decomposed into radicals and atoms and will also be partially ionised. Depending on the frequency of the electromagnetic energy, the pressure range in which an equilibrium with a high density of charged particles is reached might be different. For the radiofrequency range (typically 40 kHz or 13.56 MHz), normally the working gas pressure is kept in the lower 0.1 mbar range, whereas for microwave sources, a working pressure between 0.5 and 1 mbar is often used. In order to effect the plasma treatment in sufficiently pure process gas conditions, a base pressure in the lower 0.01 mbar needs to be reached. This can be done with two-stage roughing vacuum pumps (rotary vane type) or with a dry pump or with a combination of either of those pumps with a roots blower.

Yet, different kinds of plasma modes are possible depending on whether only radicals and/or gas atoms are used or whether charged particles are also allowed to impinge on the substrate. The first mode is often given with terms such as chemical plasma, or soft plasma, or secondary plasma, or afterglow. The second mode is described as physical plasma, or hard plasma, or primary plasma. The difference between both is related to the mechanical/geometrical configuration of the plasma chamber. The plasma mode is chosen based on the exact effect that one wants to achieve and is also substrate-type dependent.

A plasma can bring several effects to substrates, depending on the plasma mode and the process gases used. There are five major effects of which three will be described in detail in the next sections: fine cleaning, *surface activation*, *etching*, cross-linking and *coating deposition*.

3.2.2 Surface activation by plasma

Surface activation by plasma is also referred to as chemical grafting (Terlingen, 1993). It never occurs alone, but always occurs during/after a plasma cleaning. Indeed, in the case of a substrate subjected to a soft secondary plasma which contains reactive species (e.g. oxygen atoms), the effect of those atoms will be twofold: they will react with organic contamination which is present on the substrate surface. Such organic contamination consists, in many cases, of loosely bound hydrocarbons. Both H and C will react with oxygen and will leave the substrate surface in the form of volatile H_2O and CO_2. Once the surface molecules of a polymer are freed from contamination, they can react with the oxygen atoms which will form carbonyl-, carboxyl- or hydroxyl functional groups on the substrate surface. It is said that the polymer surface has been chemically functionalised.

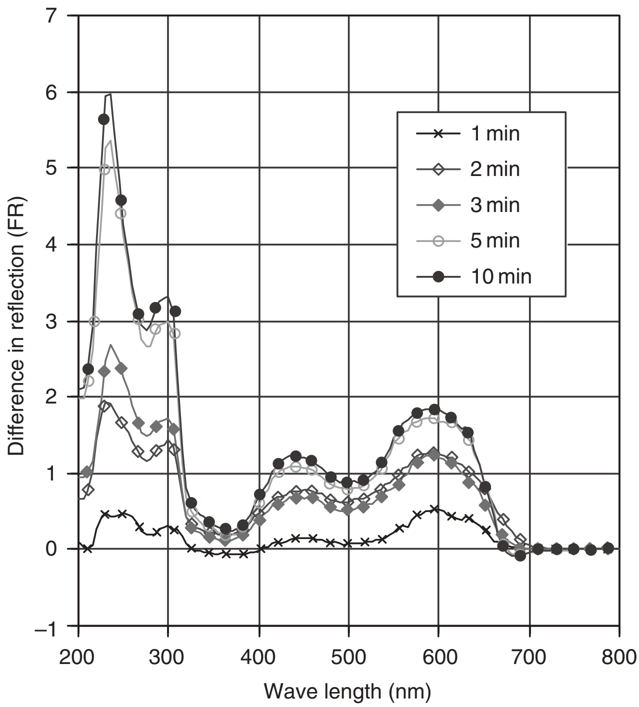
The effect of grafting carbonyl-groups onto a surface of PP, polyethylene (PE), or polyesters such as polyethyleneterephthalate (PET) or polybutyleneterephthalate (PBT) gives rise to an increase in surface energy to levels higher than 68 mN/m immediately after the plasma treatment. This effect is, however, not permanent: it has a certain shelf-life. Once the substrate has been removed from the plasma, and depending on the storage conditions, oxygen atoms will be released again from the surface molecules. This will happen slowly over time. After several days or even several months, the original surface energy of the substrate will have returned. The rate at which this happens depends on the type of substrate: e.g. PP has a fairly good shelf-life of a couple of weeks, whereas silicones show a shelf-life of less than one day. It further depends on the plasma conditions: an intensive plasma treatment will create a higher surface density of functional groups and, as such, the shelf-life will be longer.

Plasma activation is being used in several fabric and nonwoven applications in the textile industry. Section 3.4 gives some examples of such processes.

3.2.3 Etching by plasma

In order to perform an efficient etching process, a direct plasma is normally needed. In such a configuration, the substrate is bombarded with charged particles (ions and electrons) and apart from a purely chemical effect, the substrate is subjected also to a physical sputtering effect.

In the case of textiles and nonwovens, this effect of plasma treatment is not often used and hence we will not further elaborate on this later in the chapter. However, there is a certain potential even for fabrics. The textile market is trying to make deep, dark colours and this is not easy to achieve. One way to do this is to reduce the specular component of reflection of the fabric surface after dyeing. A plasma etching leads to a controlled nano- or micro-roughness, increasing diffuse reflectance and minimising the specular component. In consequence, the dyed fabric will have an intenser darker colour after plasma etching. As an example, for micro-PET fabric, colour depth increase ΔL is typically equal to 2.3. Figure 3.1 gives an example of



3.1 Difference in reflectance of several plasma-treated PET fabrics compared to untreated PET fabric. The curves are for plasma treatments with different dwell times: the longer the fibres are exposed to the plasma, the more pronounced the reflection difference is. (Results obtained by Europlasma N.V. in collaboration with the University of Ghent, Textiles Institute, Belgium, IWT-project 030471, Plasma-Colour.)

the reflection increase after different residence times in an etching plasma for micro-PET fabric.

Etching requires the removal of several hundreds of nanometres and etching processes are therefore slow. Needless to say, this technique is only viable for very high-end textiles.

3.2.4 Thin film deposition by plasma polymerisation

A very important usage of low-pressure vacuum plasma technology is thin film coating deposition by plasma polymerisation. In this specific case, reactive precursor gases that can polymerise are being used as process gases (Yasuda, 1976). The precursor gases are broken into radicals that react with each other on the substrate surface. The nature of the precursor gases will very much determine the properties of the deposited coating. Coating thickness is normally in the 10–50 nm range (5–30 molecular layers).

The very first applications of plasma polymerisation were found in the medical device industry. Micro-titre-plates are diagnostic devices normally made from polystyrene (PS); they consist of tiny cavities in which cell cultures are grown. A permanently hydrophilic coating on PS micro-titre plates gives rise to an improved culture growth on the plate.

There are many industrial applications of thin film deposition by plasma polymerisation in the technical textile and nonwoven industry. Roughly, the coatings deposited in those industries can be categorised under either (permanently) hydrophilic coatings or hydrophobic/oleophobic coatings. In most cases, the deposited coatings give rise to unique products that are difficult or even impossible to produce using other technologies. Section 3.5 discusses a number of those applications.

3.3 Equipment for low-pressure vacuum plasma technology

3.3.1 Web treatment equipment based on box-type vacuum chambers

Any plasma equipment has the following basic set-up. It consists of a vacuum chamber and a pumping group to evacuate this vessel. Of course, between the pumping group and the vacuum chamber, there are valves to isolate the pumping group from the chamber. Further, there are a set of mass flow controllers and valves in order to admit the process gases in a controlled way. In the chamber, there is an electrode system which is powered by one or more electromagnetic generators. Finally, there are several measurement aggregates such as pressure measurement gauges, thermocouples, etc. The entire equipment might be controlled by a microcontroller (programmed logic controller, PLC) or by a personal computer (PC). It is a basic characteristic of vacuum plasma systems that they are batch systems. The textile industry sees this very often as a limitation of the technology. They bring the argument that the rest of their production is in a continuous line and that they want to do the plasma treatment in line with other treatments on their webs. There are, however, four objections to this vision. First of all, even if many single operations in the textile industry are indeed continuous operations (reel to reel), the total process flow from either yarn or half-product fabric to finished fabric consists of several discrete (batch type) operations. The second objection has to do with process speed compatibility between various processes. Indeed, in most cases it will be difficult to tune the design of a plasma processing machine so that the web speed in that machine is under all circumstances equal to the web speed required for other processes before and/or after the plasma treatment. Thirdly, there is the overall process reliability argument. Contrary to many wet-processing machines, vacuum plasma machines are highly reliable and hence, once a process run is started, it does not often happen that the run needs to be interrupted. If several processes, including a plasma treatment, are being combined in line, then the probability of a breakdown on the whole line increases. Vacuum plasma equipment is indeed capital intensive equipment (as will be the case with most other equipment in the line) and a down time of such equipment because of problems with other processes will weigh on the overall profitability of the equipment. And finally, as Section 3.3.2 will show, roll-to-roll plasma treatment equipment allows the loading of considerable lengths of fabric or nonwoven (several thousands of linear meters), reducing the dead time for loading/unloading, pumping and venting to less than 5% of total available time.

Even using vacuum plasma technology, it is possible to build continuous air-to-air systems. Such systems have been built for the polymer film industry, but also recently for nonwovens. In such systems, both the unwind and rewind are located outside the vacuum, and the unwound web is fed through a series of load locks into the plasma processing zone of the equipment. Whereas the latter zone has a base pressure in the 0.01 mbar range, the series of locks has decreasing pressure going from the unwind to the processing zone. An identical series of load locks is mounted between the processing zone and the rewind of the equipment. On such a line, web coming from another equipment can be fed into the load locks directly. However, due to the many pumps, vacuum valves, pressure measurement gauges and complicated mechanics, the cost of such air-to-air vacuum plasma systems is considerable. Furthermore, it is a viable option only for thin nonwovens and not for thicker fabrics. Therefore, our general experience is that the textile industry should accept roll-to-roll batch plasma systems.

3.2 Vacuum plasma chamber with a classical loading system consisting of a set of trays.

Plasma systems can have all kinds of shapes and differ mostly in the loading system. Such a loading system might be a set of trays in which rigid parts are organised (see Fig. 3.2) or it might be a complete winding system for goods that can be wound, such as fabrics, nonwovens or foils. For smaller width webs, simple winding systems with a rewind motor and an unwind brake can be provided as a cassette that is mounted in a classical box-shaped vacuum chamber. Figure 3.3 shows an example of such a system. Of course, many variations to this basic design are possible including high-end winding systems with tension control and edge tracking.

3.3.2 True roll-to-roll web treatment equipment

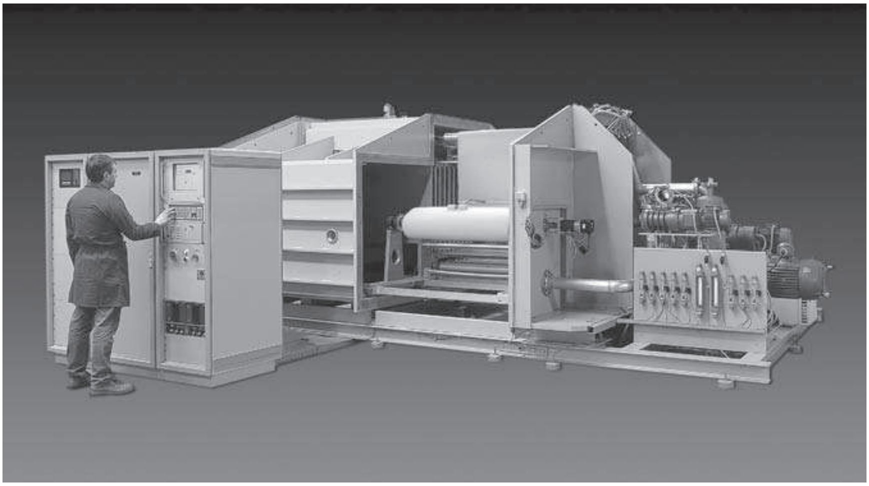
For vacuum plasma treatment of larger width webs (typically >0.6 m) starting from larger rolls (typically >0.3 m diameter), more complicated dedicated vacuum chambers are being built (Palmers, 2000a and b). Such chambers have normally three sections: an unwind, a rewind and a plasma treatment section, which might be differentially pumped. Typical web widths vary between 1.0 m and 3.2 m; maximum roll diameter is between 0.6 and 1.2 m. The rolls are normally provided on 75 mm plastic cores.

It is clear that the winding system of this type of equipment is much more complicated than the one from roll cassettes mentioned previously. All true roll-to-roll plasma treatment systems use tension control of the web. The web tension is measured by several load cells in the equipment and is fed

3.3 Roll cassette for the plasma treatment of small width webs in a classical box-shaped vacuum plasma system.

back to a number of capstans in the machine. This allows treatment of difficult-to-handle substrates, such as thin nonwovens, without too much stress on the web. The winding system in the plasma section consists of two rows of rolls at the bottom and top of the machine, respectively, so that the web is guided like a serpent through the plasma zone exposing as long a length of web as possible to the plasma. The plasma itself is generated with several electrode pairs, which are placed between various textile sections on the winding gear.

Figure 3.4 shows a typical industrial roll-to-roll vacuum plasma treatment machine for nonwovens. The processing sequence of substrate rolls in such equipment is as follows. With the vacuum chamber open, a new roll of substrate is loaded at the unwind side. The new roll is spliced manually to the remaining web of the previous roll. Then the web is inched manually through until the entire web is under constant tension. Now the vacuum chamber is closed and the chamber is evacuated with the vacuum pumps. When the base pressure is reached, process gas is entered into the vacuum chamber and left to stabilise. At the same time, the web is started moving. Now the plasma generator(s) is (are) turned on and the plasma is lit. The entire roll will be wound to the rewind side at a constant web speed during which it will be plasma treated. Once the vacuum chamber has been closed, the



3.4 Large industrial roll-to-roll vacuum plasma treatment machine (web width 1.8 m).

entire processing sequence runs automatically, controlled with a computer programme. During processing, no operator is needed. When the entire roll is at the rewind side, the generators are switched off, the process gas flow is stopped and the chamber can be vented. After opening the chamber, the treated roll can be removed from the rewind side.

Textiles and nonwovens, natural fibre materials and polymers alike, contain large quantities of water. This water will evaporate in the vacuum chamber during unwinding. Unfortunately, classical mechanical vacuum pumps do not effectively pump water vapour. Therefore, a Meissner trap (cryogenic coil) in the vacuum chamber is often installed.

Web speed in a roll-to-roll low-pressure vacuum plasma machine depends on three factors: type of required plasma effect (activation vs. coating), the required shelf-life or coating thickness respectively and the overall size of the plasma section in the machine (number of electrodes). For activation types of processes, a typical web speed is between 5 and 50 m/min. For coating deposition types of processes, the speed is between 0.5 and 10 m/min.

3.4 Plasma activation in the technical textile and nonwoven industries

3.4.1 Fabrics for automotive and medical applications

Some products in the automotive and medical applications industrial markets consist of a nylon (polyamide 66, PA66) fabric, which is coated with a silicone in a wet chemical process. Such fabrics are used in the automotive market to produce airbags. Similar fabrics are being used as supporting bandages.

For the airbag application, it is paramount to create a gas-tight fabric with as thin a silicone coating as possible. However, on nonplasma-treated PA66 rather thick coatings are required. If plasma activation is applied to the PA66 fabric prior to wet chemical coating, the nucleation of the latter is considerably improved, leading to a coating with lower porosity, which is already gas tight even for thinner coatings. As silicones are expensive materials, the plasma activation leads to considerable cost savings. In addition, there are other advantages: reduced weight of the airbag and less material usage (two generally important themes for the automotive industry).

In the case of medical support bandages, the requirement is also to reduce coating thickness, but it is also important that the silicone does not penetrate the entire thickness of the PA fabric. Due to the high affinity for silicones of the plasma-activated PA, rapid and high density nucleation of the coating takes place, so that the surface is quickly sealed off from further penetration of liquid silicone. For further examples see also Palmers, 2000a and b and Pane *et al.*, 2003.

3.4.2 Pre-treatment before dyeing

In various research programmes, it has been shown that pick-up of dyestuff can be strongly improved after plasma pre-treatment of natural fibre fabrics (woven or knitted cotton, linen, wool or silk). Contrary to this, for synthetic fibre fabrics, almost no improvement due to plasma pre-treatment is obtained. This is due to a different dyeing principle for synthetic fibre fabrics, i.e. dyeing is normally performed in a hot dye bath, the temperature increase causing opening of the fibre-structure to enclose the dyes. This limitation of improvement to natural fibres is, of course, a serious hindrance for commercial exploitation, the more so because it concerns products that are rather cheap per unit area of fabric.

As an example to show the potential of the technology, in a cooperation programme with IFP-research (Svensson, 2004), knitted fabrics of greige cotton were plasma treated and then dyed with various recipes. Dyeing was done by cold-pad-batch with reactive dyes from Ciba Specialty Chemicals (*Cibacron* of different colours). Whereas untreated reference samples showed a dyeing liquor pick up of 65–70% (depending on the dyeing recipe), the plasma treated samples were in the 80–89% range.

3.4.3 Activation of transportation textile before application of flame-retardant chemistry

Textiles used in transportation must receive a flame-retardant treatment. Currently, halogen-containing flame retardants are being banned for ecological reasons. The new kinds of flame-retardant chemistry, e.g. based on organic phosphonate derivatives, are much more expensive. Therefore, their usage should be limited to the absolute minimum.

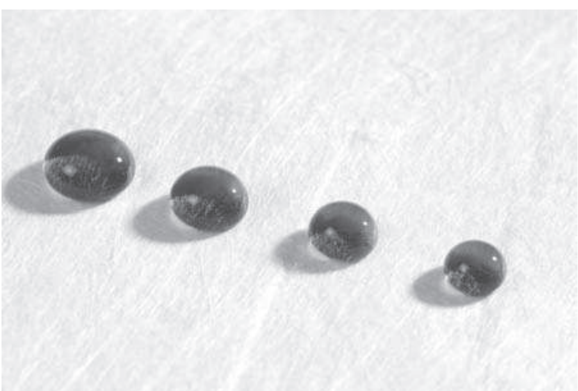
It has been shown that, in the case of plasma-activated fabrics consisting of both natural fibres and polymers, the concentration of flame-retardant chemicals can be reduced considerably without influencing the flame-retardant properties of the treated web. This again leads to considerable cost savings.

3.5 Plasma deposition on nonwoven materials

3.5.1 Hydrophobation of nonwovens for filtration applications

It is mainly plasma polymerisation for coating deposition that has found its way into the filtration industry. A first example of plasma coating can be found in air filter media both for respirator masks and for filters used in HVAC systems. Such filters consist of several layers of meltblown nonwoven PP, which are electrically charged (electrets). Filtration efficiency for oily particles can be greatly improved by applying a hydrophobic/oleophobic coating prior to electrical charging. Such coating is deposited starting from gaseous F-containing pre-cursors. Typical oil repellency grades of 3 to 4 using the 3M procedure (AATCC test method 118-1997) are achieved. Figure 3.5 illustrates this behaviour.

Table 3.1 gives an overview of filtration efficiency as measured with CERTITEST 8130 equipment using dioctyl phthalate (DOP) particles. Initial filtration efficiency and evolution of filtration efficiency can be



3.5 Water droplets on a plasma hydrophobated nonwoven PP, illustrating the water repellancy of the material.

Table 3.1 Filtration measurement results obtained by Europlasma in cooperation with a partner (proprietary) using a CERTITEST 8130 for different kinds of uncoated and plasma-coated filter media (5 layers)

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)

measured. During measurement, the filter (consisting of five layers of single ply nonwoven PP) is loaded with 200 mg of DOP particles. Basically, the CERTITEST 8130 measures penetration (in %) over time and the efficiency (in %) is determined as 100% minus penetration. Penetration tests have been carried out on electrically charged filters.

Table 3.1 illustrates several effects of plasma coating on filtration efficiency. It is without doubt that a thin oleophobic plasma coating increases both initial and final filtration efficiency. In this sense, it can convert, e.g. an R95 filter into an R99 filter. However, a plasma coating cannot modify a Class III filter (which has decreasing filtration efficiency with time) into a Class II or Class I filter (constant or increasing filtration efficiency with time). For certain filtration materials, however, a plasma-coated filter medium shows excellent filtration efficiency, leading to a Class R100 filter! (See the Supplier 2 material in Table 3.2.)

Other applications of the same coating in the filtration industry have been developed. One example is the improvement of filtration efficiency of diesel filters based on nonwoven PBT.

This type of hydrophobic/oleophobic coating is not resistant to washing in hot (>80 °C) soapy water. In such an environment, the coating is gradually removed (complete removal after 3–4 wash cycles). This is what limits the usage of this coating in the classical garment textile industry. Filter media, however, are not subject to washing.

3.5.2 Hydrophilic coatings on nonwoven PP for battery separators

NiMhydride rechargeable batteries normally use a nonwoven meltblown PP separator web. The as-received substrate is hydrophobic. In order to improve wetting with the electrolyte, some manufacturers are using gamma rays to increase surface energy, but this is an expensive and even hazardous type of treatment. By applying a permanently hydrophilic type of coating out of gaseous pre-cursors, one can increase wetting behaviour of the battery separator considerably. Figure 3.6 illustrates this for a nonwoven meltblown PP of 40 g/m^2.

The rate of absorption of an alkaline solution (30% of KOH in demineralised water) was evaluated in a wicking test on 40 mm by 200 mm samples. For a 1 min wicking of a plasma-coated material, values between 22 and 25 mm were obtained immediately after plasma coating, whereas the uncoated reference material gave 0 mm (no wicking at all). Commercial reference materials on the market, which were not plasma coated, showed wicking values of only 5 to 10 mm.

Those measurements were repeated 21 days after plasma coating, resulting in values of 17–21 mm, proving also the permanent character of the coating. Finally, long-term resistance to KOH solutions was tested as follows. The samples from the wicking test performed 21 days after plasma coating were immersed in a beaker with 30% KOH solution. The beaker was covered with aluminium foil and was then put in an oven at 70°C for 7 full days. After this, the samples were rinsed in demineralised water and air dried. Then the wicking test was repeated, showing wicking values of 16–18 mm.

Wash resistance of permanently hydrophilic coatings is better than for hydrophobic/oleophobic coatings but is still limited to about 7 wash cycles. Again, in the battery separator application, this is not important.

3.6 The economics of vacuum plasma treatment for fabrics and nonwovens

Contrary to what is generally believed, low-pressure vacuum plasma treatment, especially in large roll-to-roll equipment, is a highly economical

3.6 Illustration of wettability of meltblown nonwoven PP, coated with a permanently hydrophilic coating.

Table 3.2 Coating cost calculation for hydrophobic/oleophobic coating onto nonwoven meltblown PP for filtration applications

Cost factor	Comment	Cost per roll (€)	Cost per m² (€)
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 €/kWh	141.3	0.010
Process gas cost	Cons. 1800 litres/roll	240.0	0.018
Labour cost	@ 35.0 €/hour	52.5	0.004
Total variable costs		433.8	0.032
Total costs		687.2	0.051

technology. A typical full costing for plasma activation is in the range of 0.01 to 0.02 €/m^2. For plasma coating, the costs are higher because the web speed in such systems is normally lower and process gases are more expensive.

Table 3.2 shows an example of cost calculation for the case of a hydrophobic/oleophobic coating onto nonwoven PP (filtration applications). The cost evaluation has been done for a plasma coater Europlasma CD1800/600 ROLL with a maximum web width of 1800 mm, an outer roll diameter of 0.6 m (on 75 mm plastic core). We assume that the process runs at 5 m/min in order to reach an oleophobicity grade 3 on the 3M scale. Under these conditions, total processing time for a roll with length 7500 m and width 1.8 m, is 27 hours (meltblown nonwoven is about 20–25 g/m^2). Also, it is assumed that the system is used 7 days a week in a three-shift system for a total of 47 weeks per year. Under these conditions, the yearly capacity of the system is a 292 rolls of 13 500 m^2 each or 3 942 000 m^2.

Table 3.2 clearly indicates that total coating cost is in the 5 € cents per m^2 range. Permanently hydrophilic coatings would even cost less (because the precursor gases are less expensive).

For the case discussed in Table 3.2, fixed costs represent about 37% of total costs. This is a rather high fraction of total costs, which will be still higher for activation types of treatments. Therefore, it is important that the equipment is well dimensioned and that its capacity is fully exploited. Vacuum plasma equipment is extremely durable, with a service life of typically 15–20 years. Hence, depreciation can be chosen over longer periods of time (if taxation rules allow). A very positive thing is that variable costs are rather limited. Operating this equipment does not entail high costs.

3.7 Conclusions

Vacuum gas plasma technology has found its way into the industrial textile and nonwoven industries. In certain applications, chemical functionalisation of the textile surface by grafting active groups is being used, leading to cheaper products or products with improved quality. In the majority of applications, however, products with unique properties can be produced using plasma polymerisation of gaseous precursors for thin film coating deposition. Examples of such products have been discussed in the filtration industry (respirator masks) and in the field of rechargeable batteries (battery separator for NiMhydride rechargeable batteries).

The widely established misunderstanding that vacuum plasma technology is an expensive technology has been made invalid by a concrete calculation example. For many applications in industrial textile, cost is in the one to few Eurocents per m^2 range and is hence more than acceptable.

Another objection of the classical textile industry (garments, interior decoration, . . .) against this technology – the fact that it is a batch operation – has been shown to be almost irrelevant when large roll-to-roll equipment is being used.

The author hopes that the general reluctance of the textile industry to accept the vacuum plasma technology, which is based on a lack of training and information, has hopefully been alleviated by this chapter.

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4
Atmospheric-pressure cold plasma processing technology

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4.1 Introduction

Although the power of plasma surface engineering across vast areas of industrial manufacturing, from microelectronics to medical and from optics to packaging, is demonstrated daily, plasma in the textile industry has been cynically described as the technology where anything can happen . . . but never does. Research into the application of plasmas to textiles goes back to the 1960s but, despite the reporting of novel and potentially commercial effects, it is only in recent years that plasma processing systems have begun to emerge into textile manufacturing in the production of specialty/high value fabrics.

It is instructive to look at major criteria for the introduction of new technology into the textile market and to assess plasma processing against such criteria. They can be separated into qualifiers (must be satisfied by the new technology as a minimum) and winners (motivate take-up of the new technology by the industry). Here are 'qualifier' criteria for new textile technologies:

- Safety and handling – The new technology must be operated safely, predominantly needing only the existing skill set of the textile mills.
- Operating speed – Line speeds need to be as fast as or faster than existing technologies to avoid bottlenecks.
- Production flexibility – Fast switching between fabric types and effects must be available to allow for rapid adaptations in product and process.
- Investment – The technology should offer a return on investment in under five years and maintain or improve the profitability of the mill.
- Environmental – The technology should comply with existing legislation and improve compatibility with anticipated law.

'Winner' criteria for new technology in textiles can be characterised as:

- New effects – Properties and performances not achievable by traditional technologies enabling added value and market differentiation.
- Durability – Significantly exceeds the durability of effects delivered by current processing techniques, again adding value and distinction.
- Operating Costs – Costs should be substantially reduced relative to established manufacturing norms, facilitating competitive pricing and/or profitability improvements.
- Environmental – Sets new industry benchmark.

To date, the plasma surface engineering community has barely begun to persuade the textile industry that plasma as a new textile processing technology either qualifies or wins as a mainstream production tool. It is apparent, however, that this position has begun to change with the placement in recent years of small numbers of plasma systems for particularly nonwoven processing with textile manufacturers. It would appear that, at last, evidence is emerging to support a prediction that plasma processing will move into mainstream textile manufacturing within five years, thus motivating textile manufacturers seeking new ways of competing to begin to take plasma technology seriously.

Why has plasma historically failed to qualify and win, and what new developments are addressing the roadblocks? It is stating the obvious to say that textile manufacturing is about the processing of large volumes of materials at high throughput. We are not dealing here with 300 mm diameter silicon wafers moving through a system at 20 per hour. Yet, it is this simple reality that has generated some of the toughest problems for plasma providers in their attempts to apply plasma technology to the textile industry. Plasmas are, in this context, about surfaces. They change the properties of any surface with which they come into contact, but first they must contact the surface to effect the desired change. In textiles, that surface typically comprises a woven, nonwoven or knitted fabric, perhaps 2.4 m wide and 10 km long. Ideally, every fibre in that system needs to be accessed by the plasma and at a speed and throughput that is high enough to make commercial sense. In a conventional textile wet padding line this is easily achieved by simple immersion of the fabric. Unfortunately, matters are not nearly so simple in the plasma context. It is not possible to fill up a bath of plasma and plunge in the fabric; the laws of physics are against us.

For one thing, the plasma needs a constant supply of energy just to keep alive. If the energy source is withdrawn, plasma relaxes back, within fractions of a second, into the gas state, losing all of its power and properties. Coupling-in the power needed to sustain the plasma is highly non-trivial and imposes all sorts of constraints on the equipment designer in terms of system geometry, operator safety, ease of use, cost, etc. Another problem is that plasma is generated from gas and the composition of the gas is a major factor in determining the properties of the plasma and the characteristics of the process. Unlike liquid in a bath, however, gas generally does not stay put but is easily displaced from where it is needed and is easily mixed with other, unwanted gases, particularly ambient air. In both cases, the plasma and its process are drastically changed, invariably for the worse. Again, maintaining the correct gaseous environment is far harder than maintaining a liquid bath and imposes serious constraints on equipment design.

These are obvious points yet are requiring huge engineering effort on the part of plasma equipment manufacturers to surmount and to make plasma processing compatible with the geometry and dynamics of textile processing. In essence, what are the most basic needs of the textile industry for a processing technology to be viable simply in terms of manufacturability? It needs large substrate area processing capability, cool operation not far from room temperature or, at least, not far from 100°C, and high throughput. These basic needs are readily met by wet processing but how realistic are they from the plasma perspective?

4.2 Basic manufacturability needs from plasma technology

4.2.1 Cool processing

Firstly, let us consider temperature. The plasma state of matter covers a truly staggering range of densities and temperatures; far, far greater than the other three states of matter, solid, liquid and gas, combined. From the centre of the sun to inter-galactic space, across 32 orders of magnitude in density and 8 orders of magnitude in temperature, the same laws of physics govern the plasma state. Technological plasmas for surface modification occupy only a small part of this parameter space but still vary in temperature from room temperature to >10 000 K. It is the job of the plasma equipment designer to ensure that the textile material only sees temperatures within a narrow range between about 0 and 100°C, preferably not above ~50°C. To this end, it is useful to distinguish two broad thermodynamic plasma regimes commonly called 'equilibrium' or 'thermal' plasmas and 'non-equilibrium' or 'non-thermal' plasmas. As has been described elsewhere, plasmas are a partially ionised gas containing ions, free electrons and neutral species as their microscopic constituents. To strike a plasma, energy is coupled into a gas volume until the volume suddenly begins to glow. At that moment, the system has become a different state of matter and has changed from the gas state to the plasma state, obeying different laws of physics. The energy has ionised enough of the gaseous neutrals to create a sufficient density of charged ions and free electrons to enable them to see each other due to their electrostatic charge and act collectively. It is this ability of the microscopic constituents of plasma to see each other at a distance due to their electrostatic charge that accounts for the dramatic differences in behaviour between plasma and the other states of matter, solid, liquid and gas. In these latter states, the microscopic species are electrostatically neutral and cannot interact at a distance but must actually collide to influence each other. In plasma, the ions, free electrons and neutrals constitute separate microscopic populations, each with its own characteristic temperature. If the free electrons are hot while the ions and neutrals are close to room temperature, the plasma is non-equilibrium. If, however, all three populations are close in temperature, the plasma is a thermodynamic equilibrium discharge.

Thermal plasmas are hot, those used for industrial surface engineering generally operating in the range 1000 to 10 000 K. In surface engineering they take the form of arcs, sprays, flames and jets and are used by industry in, for example, welding, metallurgy, coating with refractory materials and waste vitrification. They are obviously of no interest to textile manufacturers.

Non-thermal plasmas, in contrast, tend to be cool. The free electrons are very hot indeed, with typical temperatures ranging from 10 000 to 50 000 K, but the rest of the system, the ions and neutrals, is at or near room temperature. Because the free electrons comprise much, much less than one millionth of the total mass of the system, they have negligible heat capacity so that the actual heat content of the plasma is low. However, those hot, high energy electrons are key to the power of plasma in its ability to change surfaces. They career madly around the plasma volume, colliding with the other microscopic components and generating a wealth of new microscopic species with chemical and physical energy. Thus, the plasma becomes a soup of dozens of different, highly energetic species which, if a fabric, yarn or fibre/filament is immersed therein, will bombard the material. These fluxes of active species impact fabric at individual fibre level, resulting in profound modification of the surfaces immersed in the plasma. Depending upon the detailed nature of the plasma, the material can be etched (removal of bulk material), cleaned (removal of contaminant), activated (enhancement of the surface energy) or coated (deposition of a functional thin film). It is this ability to decouple and separately control the temperature of, on the one hand, the ions and neutrals, and, on the other, that of the free electrons that delivers a combination, unique in technology, of tremendous processing power with cool operation that makes plasma surface engineering such an appealing and widely used industrial tool. In essence, non-thermal plasmas can do things that no other technology can do and/or at a low temperature no other technology can attain. Non-thermal plasmas are, thus, of potentially great interest to the textile industry.

4.2.2 Large substrate area processing

As has been observed previously, the textile industry needs to process large area substrates, generally in the form of quasi two-dimensional, flexible webs, metres in width and kilometres in length. By definition, this requires spatially extended plasmas and, unlike wet processing where a bath is readily prepared to practically any dimensions, major engineering effort is needed to deliver equipment platforms that can generate large volume plasmas suitable for robust industrial processing.

Technological plasmas for surface modification cover a wide range of pressure regimes from ultra-high vacuum to atmospheric pressure. The laws of plasma physics make it easier technologically to generate large volume plasmas at reduced pressure than at atmosphere. Experimental data plotting both free electron and neutral temperatures in plasmas as a function of pressure show that, as system pressure increases from high vacuum towards atmosphere, the electron temperature decreases while neutral temperature increases, until they merge. In other words, as pressure rises, the plasma moves from a cool non-thermal to a hot thermal discharge due to the increasing collision rate and, hence, energy exchange between electrons and neutrals. This is one of the reasons why partial vacuum plasma technology has advanced significantly faster than atmospheric-pressure plasma technology in terms of surface engineering capability and is the industry standard workhorse in the large majority of sectors in which plasma is a mainstream production tool, such as microelectronics. In addition, a closed system under vacuum more easily contains and controls both the extent and the composition of the critical gas atmosphere from which the plasma is generated, and hence, the process chemistry, than does a system at atmospheric pressure with its perimeter open to the ambient air.

For these reasons, low-pressure plasmas have been more attractive from the perspective of large volume generation than atmospheric pressure plasmas and have, until recently, undoubtedly led the development of plasmas for textile processing. What, of course, many in the textile industry never fail to point out is that vacuum plasmas are not compatible with continuous, on-line processing and can only be employed in batch mode. But is this truly important? In many applications, probably yes, but in many others, no, provided that the benefits of the technology are clear and sufficient added value is demonstrated. Additionally, vacuum equipment is expensive in both capital and running costs. Atmospheric-pressure plasma (APP) would appear to have a significant advantage here but the discerning buyer will be careful to ensure that he/she is comparing like with like in terms of all attributes of the respective equipments. Thus, an APP air corona system may cost 10% of a low pressure glow discharge plasma system but it is certain that the process offered by the low-pressure system will be more sophisticated and of higher intrinsic value than air corona activation. But again, activation may be what the user needs to meet the performance target and it is all down to a proper definition of the textile manufacturer's needs and objectives and a benchmarking of competing solutions against these.

Since the 1980s, atmospheric pressure plasmas have increasingly been the subject of scientific research which has resulted in new (or re-discovered, often from basic research into gas discharges carried out in the 1920s and 1930s) and improved methods of APP generation. This, in turn, has fed into technological development so that there are now several APP types or configurations that meet the basic manufacturability criteria for textile processing. These are discussed below.

Besides covering the width of the textile to be processed, a large volume or, effectively, large area plasma extended along the direction of travel of the moving web, whether by festooning through a plasma volume or otherwise, offers extended residence time in the plasma. This can make for higher line speeds or better processing, e.g. thicker coating, higher energy deposition per unit area (J/cm^2), and potentially offers commercial advantage to those designs offering the largest area plasmas.

Finally, the treatment must not only be applied across large areas but must be uniform across the whole extent of the textile surface. This means that the plasma must be spatially uniform or, at least, uniform in the lateral dimension across the direction of travel of the web so that every part of the web sees the same level of treatment. Edge effects and singularities must be eliminated, not an issue with wet processing but needing careful design in plasma systems.

4.2.3 High throughput

The textile manufacturer will, of course, not want a newly introduced plasma process to create a bottleneck in an existing line or become a rate-limiting step in a drive to increase line speeds. This motivates the manufacturer to scrutinise carefully the claims of plasma providers as to throughput capability and investigate beyond headline line-speed figures of X metres/minute.

It is stating the obvious that atmospheric-pressure plasmas have a major throughput advantage over low-pressure plasmas in that they can operate in open perimeter mode allowing continuous, on-line processing interfaced to a conventional production line, while vacuum plasma must operate off-line in batch mode. But this is by no means the whole story. The vacuum plasma run speed for the target process could be an order of magnitude faster than the APP line speed, which can wipe out the supposed APP advantage when a holistic view is taken of the plasma logistics. It is essential that all steps in the throughput process are individually assessed and integrated into an overall timing picture. Thus, loading/unloading of a vacuum system, roll transfer, pumpdown (often a strong function of the material being treated) and venting, downtime for chemical precursor reload, the compatibility of a treated fabric with being rewound onto itself before onward processing, i.e. the need for immediate post-plasma processing (more of a process than a throughput issue), etc. are examples of operations needing to be factored into a realistic throughput model. Nevertheless, it is fair to say that, all other things being equal, a rare enough occurrence, APP systems will probably have an edge over low pressure plasma in the matter of throughput.

4.2.4 Summary of the basic manufacturability needs

In summary, the bare minimum that the textile industry must have from plasma providers in terms of manufacturability is equipment platforms generating non-thermal plasma in a geometrical configuration suitable for uniform treatment of large area flexible web. These two simple sounding conditions drastically limit both the type of plasmas that can be used in textile manufacturing and the configurations in which they can be employed. Essentially, one plasma type is compatible with textiles in the low-pressure regime – the Glow Discharge, and three types are compatible at atmospheric pressure – the Corona, the Dielectric Barrier Discharge, the Atmospheric Pressure Glow Discharge.

In the current state of development of plasmas for textile manufacturing, there is no single ideal and clearly superior plasma technology for textile manufacturing. Atmospheric-pressure plasma is not intrinsically superior to low-pressure plasma or vice versa. It's 'horses for courses'. Each technique has different attributes and strengths and the prudent textile manufacturer will carefully define his/her objectives and needs and carry out a detailed assessment of the available equipment and process combination options and their fit to the defined product performance, manufacturability and financial criteria. In essence, everything depends on what the textile manufacturer wants to achieve with plasma technology. Is it to create a unique product with new effects and properties? If so, it is likely to be a high performance product aimed at the top end of the market commanding a premium price. Although small in terms of annual output (m^2 per year), high performance textiles are rapidly growing in economic importance and, due to their high value, can generate serious revenue at high margins from even small production batches. Examples are in filtration, medical and biotechnology. In such a case, the textile producer should look closely at the plasma world, firstly because this sort of niche, high-value opportunity is ideal for the introduction of new technology and, secondly, because plasmas have demonstrated many new and potentially commercial effects precisely in the high technology market segments which are offering these opportunities. In that case, the high investment cost of, say, a €1 million plasma system capable of sophisticated functional coatings with bio-compatibility, for example, may well be justified by fast returns. On the other hand, is the goal to reduce raw material costs or to eliminate increasingly expensive environmental costs associated with the use of water, power and chemicals disposal? Plasma appears to be an excellent candidate to achieve all of these. Thus, functionalisation of a fabric surface by coating with, for example, a fluorocarbon waterproofing consumes grams or tens of grams per m^2 of coating material in conventional wet finishing processes. Plasma can deposit the same effect with a 50 milligram per m^2 coating, saving raw material, waste and water consumption and using a small fraction of the energy. But, does the plasma coating fully meet the product performance needs, e.g. in terms of washability, and, since the aim is to reduce costs, how much can the textile company afford in terms of new capital cost and write-off of existing investment? In the drive to accurately model and predict the financial consequences of investment in plasma, the textile manufacturer should expect the plasma provider to deliver detailed and comprehensive capital and running cost data based upon established performance specifications for both equipment and process. Anything less is a leap in the dark.

While dealing with the issue of competing solutions, it must be said that the plasma community as a whole points to the potentially significant advantages over its major technological competitor, namely conventional wet and heat based processing. These points are particularly strong in the case of atmospheric pressure plasmas due to the ability of these to compete with wet processing on an equal basis in the sense of being fully compatible with continuous, in-line processing. Table 4.1 summarises the perceived advantages of plasma processing over wet processing, particularly with respect to APP.

4.3 Atmospheric-pressure plasma types for textile processing

As concluded previously, the constraints upon size and temperature applying to any technology seeking to process textiles limit the scope of plasma engineers in the search for new solutions that can generate value for textile manufacturers. It is useful to glance at some of the underlying physical principles that constrain the development of non-equilibrium atmospheric-pressure plasmas for this application. Three physical phenomena play a strong role in this APP development:

Table 4.1 Perceived advantages of plasma processing over wet processing, particularly with respect to APP

Manufacturing operation	Conventional Wet/heat processing	Plasma processing
Handling and storage of bulk chemicals	Yes	No
Mixing of chemicals, formulation of baths	Yes	No
Use of water	Heavy	None or very low
Raw materials consumption	High	Low
Drying ovens and curing operations	Yes	No
Need for solvents, surfactants, acids	Yes	No
Number of process steps	Multiple	Single
Energy consumption	High	Very low
Waste disposal/recycling needs	High	Negligible
Environmentally costly	Yes	No
Equipment footprint	Large	Small
Manufacturing versatility from single kit	Limited to single or few process options	Depending on kit, can be highly flexible with wide range of available processes
Innovation potential	Moderate	Very high

- The dependency of gas electrical breakdown on pressure
- The inverse scaling of the characteristic dimension of the plasma, i.e. its size, with pressure
- The glow-to-arc-transition.

4.3.1 The dependency of gas breakdown on pressure

To strike or ignite plasma from a volume of gas, the electrical breakdown voltage, V_b, of the gas must be exceeded. There are a variety of ways in which electromagnetic energy may be coupled into a gas volume to create the strong electric fields needed for gas breakdown but, for the purposes of textile processing, the relevant techniques all employ the same basic concept, namely a pair of opposing conductive electrodes (generally, but not always, constructed from metal) separated by a gap containing the gas from which the plasma is to be generated and across which is applied a voltage from an external power supply. The electrodes come in varied shapes and sizes, but for most configurations, mainly those not involving geometrical singularities such as sharp points or edges, a physical relationship called Paschen's Law applies relating V_b to the product of two system parameters, namely electrode spacing, d, and gas pressure, p. Thus, V_b is a function (generally not linear) of $(p.d)$:

$$V_b = f(p.d)$$

At the microscopic scale, Paschen's Law reflects a particular mode of gas breakdown called the Townsend breakdown mechanism in which neutral atoms/molecules are ionised by collision with an energetic free electron. Such an event generates a positive ion and another free electron. The two free electrons are then accelerated by the electric field, thus picking up energy, and when that energy exceeds the energy needed to knock a bound electron out of a neutral, the next free electron/neutral collision will generate yet another free electron. This process continues, resulting in a cascading of electrons generated by collisions in the inter-electrode gap until the density of charged species is high enough for the gas to change state and strike a plasma.

The technological consequence of Paschen's Law is that, for a fixed external applied voltage (generally determined by the parameters of the power supply and circuit), the inter-electrode spacing, d, must decrease as pressure rises towards atmospheric if a plasma is to be struck. So, whereas at low pressure the electrodes can be widely spaced, allowing generation of large volume plasmas, by the time the pressure has reached atmospheric, d is of the order of mm. Thus, for example, V_b for the gas argon, a technologically interesting gas for plasma textile processing, is about 2.5 kV at atmospheric pressure if the inter-electrode gap is 5 mm. The narrow gap needed at atmospheric pressure for gas breakdown at the reasonable applied voltages ~10 kV consistent with industrial operations is a major constraint on the geometry of APP systems since, for example, it makes it difficult or impossible to pass very thick fabrics through the plasma region for treatment. In practice, thin to medium thickness fabrics are fully treatable within the inter-electrode gap and very thick fabrics can be treated in what is called 'downstream' mode. Here, the plasma is generated in the narrow inter-electrode gap or in jet form, and is blown outside that region by gas flow directly onto the fabric, which can be of any thickness. The German company Plasmatreat GmbH[1] supplies a range of ingenious and highly robust plasma jet systems which can be configured in fixed or rotating arrays to ensure coverage of wide area textiles at good line speeds.

4.3.2 Inverse scaling of size with pressure

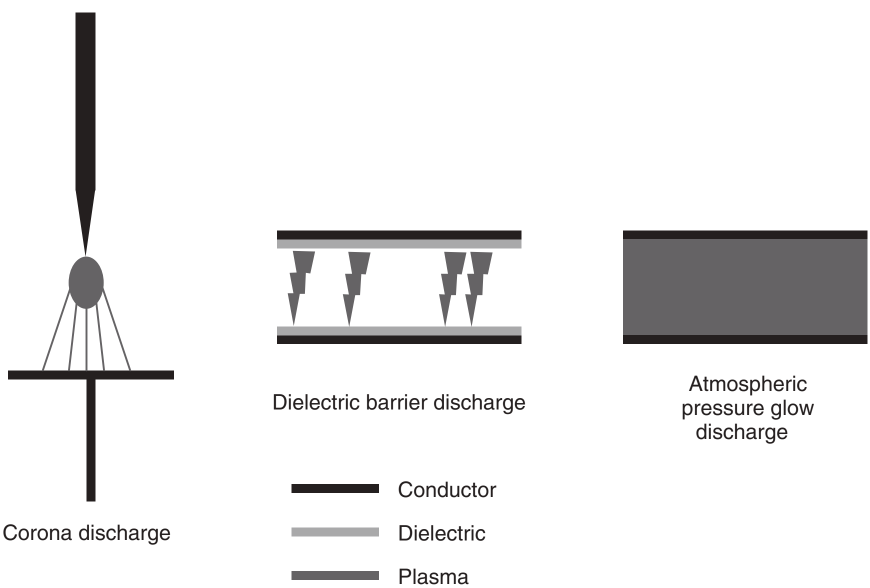
We have discussed the need for large plasmas so that it is an unfortunate fact of nature that plasmas at atmospheric pressure tend to want to be small.

In essence, as the pressure of the plasma system rises, the plasma shrinks in volume and shrinks quite rapidly. The relevant physical relation is:

$$J_n \propto p^2$$

where p = pressure (Pa) and J_n = current density (A/m^2) flowing through the electrical circuit incorporating the plasma and sustaining it with electromagnetic energy. For constant current, the physical relation states that the current density in the plasma increases with the square of the pressure. This means that, at constant current, the cross-sectional area of a glow discharge plasma generated at low pressure decreases with increasing pressure so that, while cross-sectional areas of plasma are, at low pressures, of the order of the dimensions of the electrodes used to generate the plasma (many cm^2), at atmospheric pressures, typical cross-sectional areas of that plasma have shrunk to a few mm^2, useless for textile processing.

The solution to this phenomenon has been for the plasma engineers to move away from the methods used to generate low-pressure plasmas and to find new techniques for APP generation that are not constrained by the above relation. The results have been the development of three types of APP that have relevance for textile treatment – the Corona Discharge, the Dielectric Barrier Discharge, the Atmospheric Pressure Glow Discharge. Figure 4.1 indicates their modes of generation.



4.1 Schematic of the modes of generation of the three APP types for textile treament.

The corona discharge

Corona discharges are plasmas that result from the high electric field that surrounds an electrically conductive spatial singularity when a voltage is applied. Corona generation systems usually take the form of two opposing electrically conductive electrodes separated by a gap containing the gas from which the plasma is generated and connected to a high voltage source. The geometry of the electrodes is highly asymmetric, examples being sharply pointed needle or thin wire electrodes opposing flat planes or large diameter cylinders. These are powered with high, continuous or pulsed d.c. or a.c. voltages. The high electric field around the singularity, i.e. the point of the needle or the wire, causes electrical breakdown and ionisation of whatever gas surrounds the singularity, and plasma is created, which discharges in a fountain-like spray out from the point or wire. Plasma types are characterised, *inter alia*, by the number, density and temperature of the free electrons in the system. Coronas are very weakly ionised with a free electron density of about 10^8 electrons/cm^3, which compares with the particle density of a gas at atmospheric pressure of ~10^{19} particles/cm^3. The corona is strongly non-thermal with some very high energy free electrons with temperatures in excess of 100 000 K. The wire configuration, in principle, can meet the need for large area processing by being stretched across the web orthogonal to the direction of travel and just above the fabric surface. However, the corona is spatially non-uniform with the plasma density dropping off rapidly with distance from the point of generation, requiring a small inter-electrode gap. The discharge is so narrow that the residence time of the fabric in the plasma would be too short for commercial operation and, in addition, the power level that can be applied is extremely limited by the cross-section capacity of the wire and its ability to dissipate heat generated during treatment. Accordingly, in its pure form, corona is far from an ideal textile surface processing medium.

The dielectric barrier discharge

In contrast to the asymmetry of the corona system, if a symmetrical electrode arrangement is set up comprising two parallel conducting plates placed in opposition, separated by a gap of ~10 mm, and a high voltage, 1–20 kV, is applied, the gas between the plates can be electrically broken down and a plasma discharge generated. Generally, however, that plasma takes the form of a hot thermal plasma arc less than a millimetre in diameter, which jumps from one spot on one electrode plate to a spot on the opposing electrode. This is useless for textile treatment and would do nothing except burn a hole in the fabric. If, however, one or both of the electrode plates is covered by a dielectric such as ceramic or glass, the plasma finds it much more difficult to discharge as an arc and, instead, is forced to spread itself out over the area of the electrodes to carry the current it needs to survive. This type of plasma is called a Dielectric Barrier Discharge (DBD) and is large area, non-thermal and uniform. Because of charge accumulation on the dielectric, which tends to neutralise the applied electric field thus choking off the plasma, the DBD must be powered by a.c. and is typically driven by high voltage power supplies running at frequencies of 1 to 100 kHz. It is denser than the corona with a typical free electron density of about 10^{10} electrons/cm^3 but the free electrons are slightly cooler at temperatures of 20 000 to 50 000 K. This is a much more attractive candidate for textile processing than the pure corona.

The DBD can take two forms, filamentary and homogeneous, the latter confusingly sometimes called, again, atmospheric-pressure glow discharge, although it will be referred to here as the homogeneous DBD. The most common form is filamentary, where the plasma appears as an array of discrete, tiny 'microdischarges'. These are parallel filamentary plasma current channels running directly between and normal to the electrodes. They are ~100 μm in cross-sectional diameter and carry a high current density of ~100 A/cm^2 but have a lifetime of only a few nanoseconds. The accumulation of local electrical charge on the dielectric at the foot of each microdischarge reverses the local electric field, thus locally neutralising the driving voltage, choking off the current flow and quenching the microplasma nanoseconds after it has fired. Although, in theory, the spatial distribution of the microdischarges should be random so that, integrated over time (generally less than a second), the entire volume between the electrodes should experience a microdischarge and thus visually appear as a continuum of plasma, i.e. a uniform, featureless glow, in practice imperfections, singularities and transients in the electrodes, the dielectric and the inter-electrode medium generate preferred plasma striking points. This is exacerbated by the tendency of plasma to strike at points on the electrode plane containing residual electric charge. The result is not a continuum of plasma but, to the eye looking sideways into the gap between electrodes, a series of bright, vertical plasma micro-columns some of which appear to move, some to remain fixed in an entrancing display of light and movement. In any event, because of the short duration and, thus, the limited charge transport and energy dissipation in each microdischarge, there is typically little gas heating (very much an unwanted phenomenon tending to generate the dreaded thermal plasma) so that a large portion of the free electron energy is utilised for exciting atoms or molecules in the background gas, thus creating the precursors needed to initiate surface chemical reactions and/or emission of radiation, which energetic photons can also help to drive surface chemistry. This explains the great interest in DBDs for many applications.

The homogeneous DBD mode relies upon the same basic electrode configuration. Through variation of control parameters such as the composition of the generation gas, the frequency of the applied power and the spacing of the electrodes, the filamentary DBD can be converted to a diffuse, continuous and homogeneous discharge that presents the appearance of a uniform glow throughout the plasma volume. To the eye, both the filamentary and the homogeneous DBD appear to be continuously discharging, despite their spatially distinct characteristics. In fact, both are pulsing on and off in time with the driving frequency of the applied power but at a rate far too fast for human vision to distinguish. The difference is that the filamentary plasma pulse is composed of the sum of multiple small, individual current micro-pulses per half cycle of driving frequency, reflecting its microdischarge nature, while the homogeneous DBD is characterised by only a single large current pulse per half cycle of driving frequency which current is not concentrated into tiny micro-streamers but is uniformly diffused throughout the entire inter-electrode volume, hence its homogeneous and spatially uniform nature.

The homogeneous DBD is certainly the preferred DBD mode from the textile processing perspective. By definition, it is spatially uniform and avoids the danger of pin-holing of fabric passing through the plasma. This can be caused by energetic microdischarges in the filamentary mode, as strong microdischarges can act like mini-arcs, vaporising fibres and burning pin-holes. The filamentary DBD plasma is, because of its structure, only in limited contact with the fabric at any instant in time, essentially in the small volume plasma channels of the microdischarges. This results in non-uniform treatment and low processing speeds in order to give the plasma a chance to contact more of the fabric. Furthermore, it is claimed that, although the filaments of the DBD can be a rich source of reactive species, the discharge produces a relatively low spatially average density of useful microscopic species because most of the active atoms and molecules are produced inside the narrow confines of the microdischarge filaments and are rapidly lost to recombination outside them.

It is still a matter of scientific debate as to the exact mechanisms which enable a filamentary DBD to be transformed into a homogeneous DBD, but one model proposed (called ‘interpulse preionisation’) is that, for a DBD to be homogeneous, a threshold background concentration of free electrons must be present in the plasma volume at the moment that the driving voltage becomes high enough to trigger ionisation breakdown of the background gas from which the plasma is generated. If such a concentration is present, no preferential current discharge paths present to the applied voltage resulting in spatial constriction but, rather, a discharge current flows across the whole cross-section of the electric field generating a wide area, cool, non-thermal plasma, well matched to the geometry of fabric processing. Certain technological configurations justified by this model, such as the use of helium as a plasma generation gas (with its energetic metastable states supposedly generating free electrons via Penning ionization (see next section 'The atmospheric pressure glow discharge') after the periodic plasma pulse has extinguished, thus creating a free electron reservoir) and restricted driving frequencies, have been shown to result in homogeneous DBDs, but it is unclear whether these in fact constitute justification of the model or are mere artefacts of the particular mode of operation. Artefacts or not, it is these scientific discoveries, such as the importance of helium gas in the generation of well-behaved plasmas, that have had a profound effect on technological development of plasma surface engineering and, daily, point to the direct linkage between fundamental scientific research and industrial manufacturing capability.

An alternative model of homogeneous DBD plasma states that the background electrostatic charge is not important but that the DBD discharge will always be homogeneous if gas breakdown proceeds according to the Paschen Law. As mentioned above, the Paschen Law is founded on a particular microscopic model of gas breakdown called the Townsend breakdown mechanism. This mechanism postulates that gas breakdown under applied voltage occurs because of ionisation of gas neutrals through collision with free electrons energised by the applied electric field. Such collisions, which take place throughout the gas volume to give a diffuse plasma, generate cascades of secondary free electrons which, in turn, become energised and collide, and so on. This homogeneous DBD model indicates that such a breakdown mechanism can be mediated by technological parameters including the electrical characteristics of the dielectrics covering the electrodes and the detailed structure of the driving voltage from the external power supply. The dielectric barriers in this model play a key role in ensuring Townsend breakdown and obtaining a well-behaved, homogeneous DBD. Firstly, they prevent large instantaneous current density in the plasma which, in turn, hinders operation of the competing streamer gas breakdown mechanism. (This is the alternative to Townsend breakdown at atmospheric pressure and relies on propagation of localised avalanches of charge creating narrow current channels between the electrodes, leading to filaments or arcs.) Secondly, charge carriers are stored as trapped surface charge on the dielectric. These trapped electrons are easily mobilised and released into the inter-electrode gap by thermal emission, enhanced by an applied electric field, to act as primary electrons initiating Townsend breakdown to strike a diffuse plasma. Furthermore, the plasma is sustained at lower voltage because of the additional surface charge field which, again, reduces the propensity to streamer formation. Accordingly, the model proposes that the dielectric properties of the bulk insulator covering the electrodes are a decisive parameter for plasma generation and stability.

The above considerations are related to indicate the extent to which plasma technology relevant to textile processing is still exploring both its scientific underpinnings and its industrial development, a situation that offers both challenges and opportunities.

The atmospheric pressure glow discharge

The third APP type intrinsically capable of meeting the size and temperature constraints needed for textile processing is the Atmospheric Pressure Glow Discharge (APGD). This is analogous in its mode of generation and some key characteristics to the famous low-pressure glow discharge plasma that is the backbone of the global plasma industry and workhorse of a dozen major industries, in particular the omnipresent microelectronics industry, which would not exist without the glow discharge plasma.

The APGD is generated by application of relatively low (~200 V) voltages across opposing symmetrical planar or curved electrodes, separated by mm at high frequency, or even very high frequency, radio frequencies 2–60 MHz, much higher than the other plasma types. The electrodes are not covered by dielectric but are bare metal, a feature that enables significantly higher power densities (up to 500 W/cm^3) to be coupled into the discharge than can be achieved with corona or DBD. The APGD is denser than the DBD, with typical free electron densities of 10^{11}–10^{12} electrons/cm^3, but the free electrons are slightly cooler at temperatures of 10 000 to 20 000 K. Textile treatment temperatures can run at 25–50 °C.

APGD plasma takes the form of a bright, uniform, homogeneous glow in the region between the electrodes. The application of voltage between metal plates would generally result in generation of a highly undesirable, very high current density and hot plasma arc. By control of the inter-electrode gap and the frequency of the driving voltage and, above all, by the use of helium as ~99% of the generation gas, arcing is prevented and a large volume, non-thermal plasma is generated, which is both dense and a rich source of the chemical species needed to carry out textile processing. APGD practitioners claim chemical fluxes 100× greater than those available from DBD and 1000× greater than corona. The need to use helium, a finite (given current extraction methods) and increasingly expensive resource, is undoubtedly a commercial issue for APGD in some but not all processes, but this can be addressed by the inclusion of a helium recycling sub-system in the equipment package since helium is not consumed in the process.

It is worth mentioning that the element helium occupies a special place in the science and technology of APP. This amazing gas has several special properties that, in combination, make it uniquely suited for the generation of well-behaved, large volume, cool plasma at atmospheric pressure. Helium has the highest ionisation potential (the energy needed to strip an electron from the neutral atom) of all the elements, which should make it very difficult to breakdown and, hence, to generate helium plasma. However, helium's ionisation cross-section (the probability that collision with another microscopic entity will result in ionisation of the helium atom) is very large because it is a simple atom with very few options for dealing with incoming energy other than ionisation. Other gases, such as oxygen or nitrogen, are microscopically more complex with many different energetic modes, including numerous electronic, vibrational and rotational energy levels so that the cross-section for ionisation of these gases is small relative to the total cross-section for all processes and there is an excellent chance that energy imparted in a collision will be absorbed by a non-ionising process. The large ionisation cross-section of helium results in it being very easy to electrically breakdown at low applied voltage and form plasma, despite the high energy needed to ionise it. Furthermore, helium has long-lived, high energy metastable states that soak up energy from the applied electric field and act as a source of charged species to help maintain the plasma through a mechanism called Penning ionisation. Here, a neutral helium atom in its high energy metastable state collides with another atom or molecule, usually an impurity in the gas such as nitrogen, and gives up its energy by ionising the impurity into an ion and a free electron. Creation of these charged species sustain the plasma and, again, reduce the voltage needed to maintain the discharge, low applied voltage being critical to DBD homogeneity through the avoidance of the 'streamer' mode of gas breakdown in which a surge of charge leaps from one electrode to the other forming high current channels leading to filamentary or even arc discharges. Two further properties of helium are notable, its high thermal conductivity and its chemical inertness. Helium's excellent heat conduction again supports the formation of a homogeneous discharge by quenching instabilities in the plasma due to 'hotspots'. These higher temperature micro-regions can arise in the plasma volume through various mechanisms, such as preferred discharge points on an electrode, and can result in a thermal runaway due to the positive reinforcement of stronger local discharge generating more local heating and so on. The end result is creation of a high current channel filament or arc which the plasma much prefers to discharge through rather than have to spread its current load over a wide area. The helium acts to cool these hotspots by conduction, thus greatly reducing this mode of plasma instability and break-up. Finally, helium's chemical inertness, having essentially no tendency to combine with other elements, is a great advantage to the plasma chemist and process engineer in that it goes some, but only some, way towards decoupling of the physics of plasma generation from the process chemistry giving process designers some additional freedom. All in all, helium has been and continues to be probably the best medium for non-thermal APP research as well as being technologically valuable as a route to useful large volume, cool plasmas.

4.3.3 The glow-to-arc transition

The third physical phenomenon to play a strong role in the exploitation of APP for textile processing is the glow-to-arc transition. This is a notorious instability in atmospheric-pressure plasmas and is the major problem in the generation of large volume, homogeneous, cool APP. The phenomenon is directly related to the current density (A/cm^2) of the plasma. As long as current density remains below a threshold, the plasma remains well behaved, i.e. uniform over a large volume and close to room temperature. However, on passing the threshold for glow-to-arc transition, two changes occur in the plasma. Firstly, the discharge dramatically constricts, shrinking to a fraction of the glow volume. Secondly, the plasma moves from non-thermal equilibrium to become thermal plasma. Both of these effects render the plasma useless for textiles.

This change has many possible origins and a large literature exists on the various instabilities that could lead to the glow-to-arc transition. Early investigations focused on conditions at the electrodes (such as cathode material, uniformity and impurities) that could induce the transition. It later became evident that processes in the plasma could also effect this transition. Analysis of discharge instabilities at the microscopic level is extraordinarily complex, requiring knowledge of the electron production and loss mechanisms in the discharge. However, it is possible to group the instabilities into two types, electronic and thermal instabilities. Thermal instabilities result from changes in the kinetic temperature of the neutral population, whereas electronic instabilities result from changes in the electronic excited state population. In any event, the transition is characterised by increasing rates of collisions between the fast free electrons and the slow cool neutrals. The electrons lose heat while the neutrals and ions gain heat until, in the final arc discharge state, the electron, ion and neutral temperatures in the plasma are equal so that the discharge is at thermal equilibrium and very hot. As part of this process, the plasma density increases by orders of magnitude from perhaps 10^{10} electrons/cm^3 to ~10^{17} electrons/cm^3, thus massively increasing the current carrying capacity of the discharge per unit area so that the plasma can constrict in size while still carrying the same or higher total current load. Free of its obligation to spread out to carry the circuit current because of restricted current density, the plasma collapses into a hot, constricted arc.

Technologically, this means that plasma engineers must design their systems to avoid the glow-to-arc transition and restrain current densities below the transition threshold. This, for example, limits the power than can be coupled into a plasma volume which, in turn, affects plasma chemistry and process times.

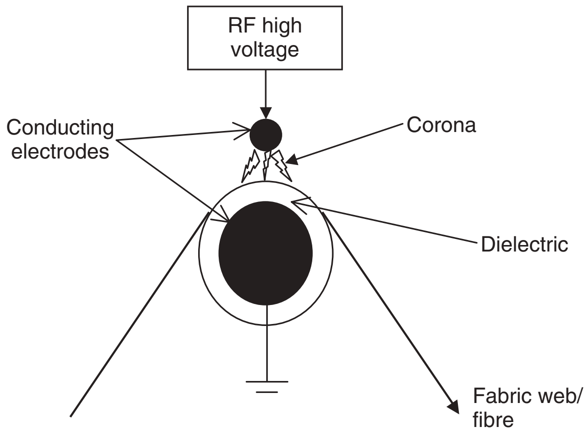
4.3.4 The useful atmospheric-pressure plasma types for textile processing

The constraints imposed on plasma system designers by the physical principles discussed above have resulted in a limited number of plasma types being available for the atmospheric-pressure processing of textiles. These types are described below.

The hybrid corona/DBD

For reasons to do with power sources, ease of plasma generation, robustness, etc., the plasma industry has developed equipment configurations that run a hybrid corona/DBD plasma type that is universally and colloquially called 'corona', with the equipment called a 'corona treater' and the process that it runs called 'corona treatment'. This plasma type will be called 'Corona' from hereon. In fact, the industrial 'Corona' uses elements of both its corona and DBD parents, having the corona plasma type's asymmetric electrode configuration, typically a metal rod opposing a large diameter metal cylinder, together with the DBD's dielectric, generally a ceramic, covering the rod or the opposing cylinder or both. The plasma takes the form of a discharge across the smallest gap, generally about 1.5–6 mm, between rod and cylinder and is short, only some 5 to 10 mm in length in the direction of web travel. Some practitioners would characterise such a short processing length as a major disadvantage of this plasma type but this is not necessarily the case, the required fabric residence time in the plasma depending completely on the target process and the capability of the equipment to deliver power into the fabric. The web to be processed runs over the cylinder and through the plasma region with the plasma typically taking the form of bright, discrete microdischarges crossing the gap normal to the electrodes. If the gas from which the plasma is generated is ambient air, the microdischarge filaments can be close together but distinguishable. If other gases are used, the filaments can close up until the plasma takes the appearance of a continuum. The Corona Treater is typically driven by an a.c. power source generating applied voltages across the electrodes from ~1–10 kV peak-to-peak at 10–50 kHz frequency (see Fig. 4.2).

This hybrid plasma type has been technologically exploited to deliver highly robust equipment configurations that have been in mainstream production in several industries, not including textiles, since the 1950s and, indeed, was the only non-thermal APP type in industrial production for



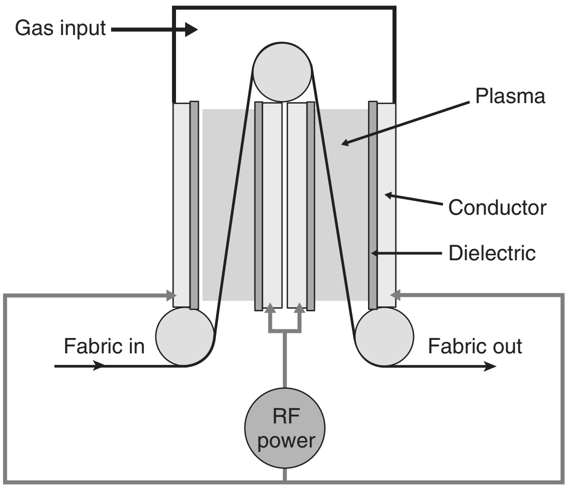
4.2 Cross-section schematic of a covered roll Corona system.

around half a century until the new millennium. A range of plasma providers offer equipment configurations based on 'Corona' that now have relevance to textile processing. These include (as at 2006) Enercon of the US, Ahlbrandt of Germany, Vetaphone of Denmark and Softal of Germany, and they are discussed in the following section.

The homogeneous DBD

Relative to the hybrid corona/DBD plasma type, the two remaining APP types are newcomers to the APP industrial processing scene. The first of these is the homogeneous DBD. A single plasma systems provider, Dow Corning Plasma Solutions[2] of County Cork, Ireland, currently (2006) offers this for textile processing with technology originally developed by Plasma Ireland Ltd. The homogeneous DBD plasma is readily generated between symmetric, large area (m^2), opposing parallel plate electrodes in compliance with technological criteria. These include careful selection of generation gas, typically helium, argon or, possibly, nitrogen or mixtures of these, minimisation of generation gas impurities through largely eliminating influx of ambient air into the plasma region, incorporation of the right dielectrics in terms of electrical and mechanical properties into the large area electrode systems and use of matched frequency and power configurations in the application of driving power. The results are truly large area (e.g. 2 metres wide, 10+ metres long in the direction of fabric travel), ~6 mm thick, cool plasmas well suited in manufacturability terms to the processing of textile webs.

Figure 4.3 shows a cross-section schematic of Dow Corning Plasma Solutions' homogeneous DBD generation configuration.



4.3 Cross-section schematic of Dow Corning Plasma Solutions' homogeneous DBD generation configuration.

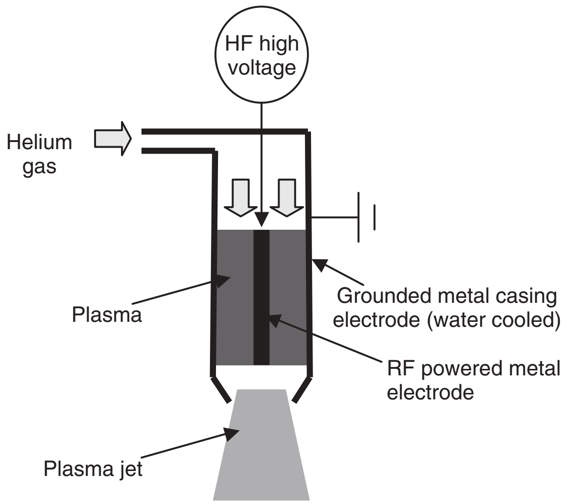
The atmospheric-pressure glow discharge

The second relative newcomer to the APP industrial processing scene is the atmospheric-pressure glow discharge (APGD). Again, currently, a single plasma systems provider, APJeT[11] of New Mexico, USA uses the APGD plasma type for textile processing. This is done using a particular source configuration technology and method of plasma generation called APPJ®. APJeT's APPJ® technology enables plasma to be applied to textile fabrics in the *in-situ* mode in which the fabric is passed through the plasma generation region between electrodes. Figure 4.4 shows a cross-section schematic of an APPJ® system suitable for wide area processing.

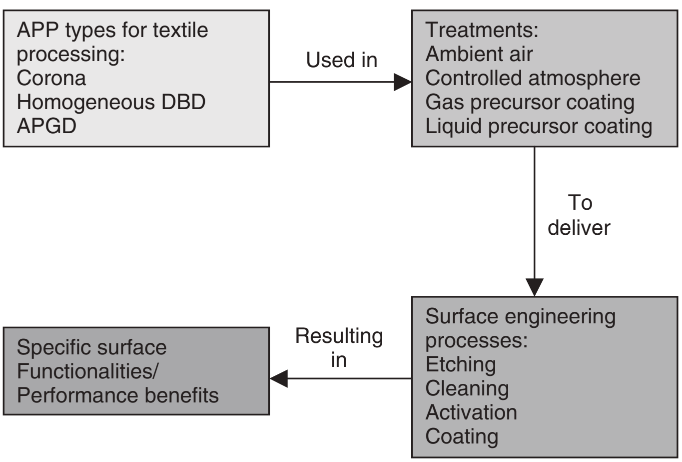
Equipment configurations implementing these plasma types in industrial manufacturing systems will now be reviewed but, firstly, let us understand the linkages from plasma types through to the final product being purchased by the textile manufacturer, namely the specific surface functionality required to meet his/her needs. Figure 4.5 is a schematic showing the flow from plasma type to surface product.

In the following sections, we will look at equipment configurations implementing the relevant plasma types and how they run treatments to deliver surface engineering processes resulting in the specific surface functionalities that, ultimately, the textile manufacturer is buying.

Let us also understand what it is that that the textile manufacturer implementing a plasma-based process in the manufacturing, as opposed to R&D or pilot production, context should be buying from the plasma solutions provider:



4.4 Cross-section schematic of an Atmospheric Pressure Glow Discharge plasma generator.



4.5 The chain APP types to surface function.

- processing equipment, plus
- guaranteed turnkey process delivering the target surface functionality
- at the target cost
- and meeting the target manufacturability requirements.

Each component of the solutions package is critical.

4.4 Atmospheric-pressure plasma equipment for textile processing

The APP equipment configurations for textile processing can be categorised according to the generic treatments that they can run and hence the kinds of surfaces that they can deliver. There are four main treatments:

- ambient air treatment
- controlled atmosphere treatment
- gas precursor coating
- liquid precursor coating.

These are listed in broadly ascending order of process sophistication but it is crucial for the textile manufacturer to understand that process sophistication does not of itself determine the optimum solution meeting his/her specific need. The term 'process sophistication' really means degree of treated surface functionality or performance, as surface functionality/performance is ultimately what the textile manufacturer is buying from the plasma provider. It is therefore critical, if the textile manufacturer is to maximise the cost effectiveness of the purchase, that he/she clearly defines the surface property required in all its aspects, technical and commercial, and then locates the plasma product (equipment plus turnkey process delivering guaranteed surface property at the agreed cost and manufacturability levels) that meets that need exactly, no more and no less. A less sophisticated process will fail to meet the performance criteria required from the treated surface, while a more sophisticated process will constitute over-engineering and incur a cost penalty. In essence, do not buy a gas precursor coating system if an ambient air treatment will meet your need.

Table 4.2 matches the four generic treatments with the three useful APP types for textile processing. It is important to state that this table is not

Table 4.2 Four generic treatments matched against the three useful APP types for textile processing

APP types	Treatments
Corona	Ambient air treatment Controlled atmosphere treatment Gas precursor coating Liquid precursor coating
Homogeneous DBD	Controlled atmosphere treatment Gas precursor coating Liquid precursor coating
APGD	Controlled atmosphere treatment Gas precursor coating

saying that the plasma types are equivalent in their ability to deliver surface functionality. For example, the homogeneous DBD can deliver more sophisticated coatings than Corona, although both can use liquid precursors in different ways. This will become clearer as we proceed through the analysis to describe the specific surface functionalities delivered by the different plasmas.

Corona systems

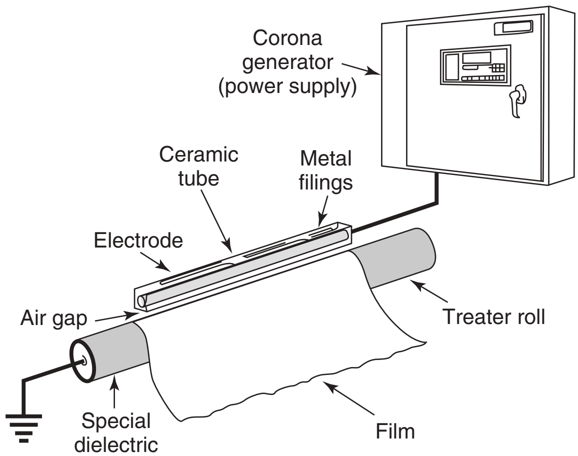
A corona treating system consists of two major components, the power source, and the treater station:

- The power source, commonly referred to as the power supply or generator, generally comprises a high frequency generator and a high voltage output transformer. The purpose of the power source is to raise the incoming electricity (typically 50/60 Hz, 230/460 V) to a higher frequency (10–35 kHz) and higher voltage (10 kV). Typically, power supplies are rated in kilowatts (kW) and can range from 500 W to 30 kW, depending on the application. The generator supplies this power to the treater station.
- The treater station, in turn, applies this power to the surface of the material, through an air or other gas gap, via a pair of opposing electrodes, one at high potential and the other, usually a roller which supports the material, at ground potential. The high electric field between the electrodes breaks down the air/gas thus generating the plasma discharge. A solid dielectric material is needed to cover at least one of the two electrodes in order to generate a corona discharge throughout the inter-electrode gap rather than a narrow, hot arc. Figure 4.6 is a schematic of an industrial Corona treater and Fig. 4.7 shows an Enercon universal treater installed at a customer facility.

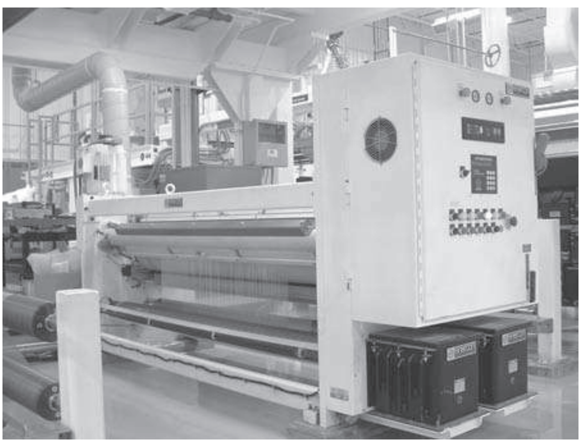
Generally, treater stations come in two configurations, 'covered roll' or 'bare roll'. Covered roll stations have the dielectric covering on the ground roll and the high voltage electrode is bare metal. In contrast, bare roll stations have the dielectric covering on the high voltage electrode and the ground electrode is bare metal. Each type has advantages and disadvantages, as listed in Table 4.3.

Figure 4.8 shows an Enercon bare roll surface treater in action. In the textile context, conducting materials will be very uncommon so that the covered roll configuration is likely to be the preferred option.

Since the energy coupled into the fabric per unit area (J/m^2) is a critical process control parameter in all plasma surface engineering, a corona treater system must be 'sized' to the particular application. In the case of corona being used to run surface activation processes, for example, it is



4.6 Schematic of an industrial Corona treater (Courtesy of Enercon Industries Corporation[3]).

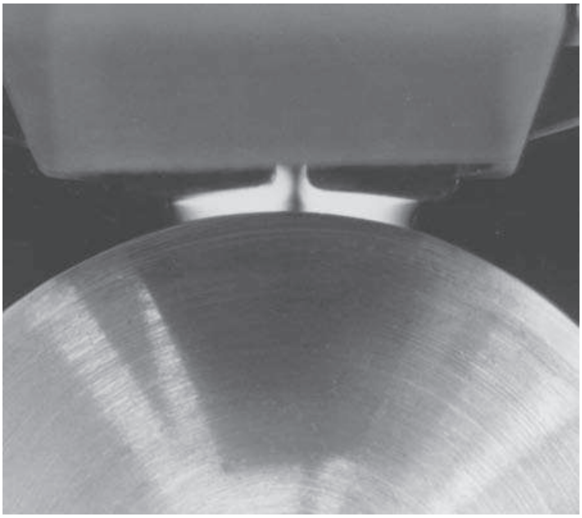


4.7 An Enercon universal treater installed at a customer facility (Courtesy of Enercon Industries Corporation[3]).

necessary to first determine the target surface energy or surface tension needed. The measure of surface energy used is called the 'dyne level' with units of mN/m (milli-Newtons per metre) or dynes/cm; these are equivalent and correspond to energy/unit area (J/m^2). Next, the 'watt density' that will be needed to raise the dyne to the desired level for a particular material is found from empirical tables and this is multiplied by the width of the material and the line speed to determine the maximum total power in kW needed for the application. This kW level determines the size of the power

Table 4.3 Advantages and disadvantages of covered roll as against bare roll treater stations

	Covered roll	Bare roll
Advantages	• More efficient than bare roll • Will work on difficult materials • Designed for non-conductive materials • Easy to adjust treat width and to lane treat specific areas leaving other areas untreated • Can vary dielectric coverings to meet cost, durability, size and treatment • Can treat any width material	• Can treat conducting materials • Smaller than covered roll stations • Easy repair of dielectric failure on electrodes
Disadvantages	• Cannot treat conducting materials • Dielectric failure requires tedious roll removal • Larger than bare roll stations	• Less efficient than covered roll • Will not work on difficult materials • Not easy to adjust treat width or lane treat • Limited to about 3 m treatment width • Requires large volumes of air/gas for electrode cooling



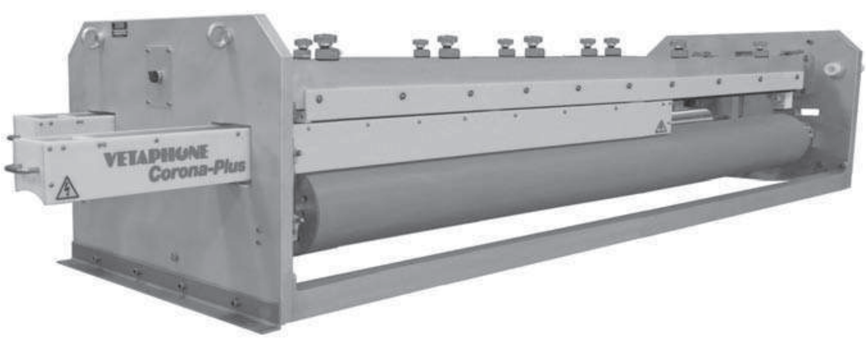
4.8 Enercon's Bare Roll Surface Treater in Action. (Courtesy of Enercon Industries Corporation[3].)

supply, the electrodes and treater rolls and, thus, the overall specification of the corona system.

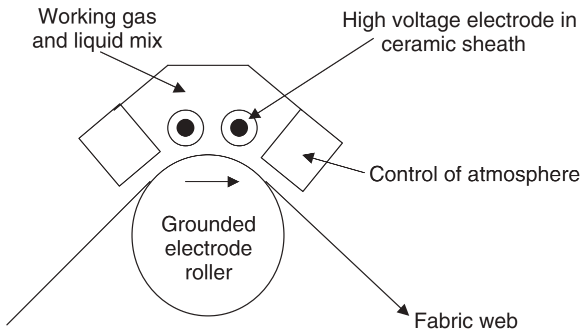
A by-product of corona treatment where air or oxygen is the plasma generation gas is the generation of ozone (O_3). This must be removed from the work area as it is a health hazard and causes serious corrosion problems. Increasingly stringent air pollution regulations are preventing exhausting into the atmosphere and it is now generally necessary not merely to extract ozone from the work area but to destroy it. This is achieved by converting ozone into oxygen using a metal oxide bed catalytic ozone decomposer which is an essential item of ancillary equipment for the corona purchaser.

A wide range of companies supply corona treatment systems ranging in width from a few hundred mm to over 10 m and running at speeds from tens of metres/minute to >1000 m/minute depending on the material and process, many with special features tailored to the material and application. Corona is a mature, robust and industrially proven manufacturing technology that has been widely used for decades in the treatment of all kinds of films, foils and webs but by no means all systems are suitable for textile processing. In fact, corona systems suitable for textile treatment tend to be specialised and not offered by all corona system providers. Some current corona equipment suppliers who claim textile processing capability include:

- Enercon Industries Corporation,[3] Menomonee Falls, WI, USA
- Vetaphone A/S,[4] Kolding, Denmark (Figure 4.9)
- Ahlbrandt System GmbH,[5] Lauterbach/Hessen, Germany
- Softal Electronic,[6] Hamburg, Germany
- Pillar Technologies,[7] Hartland, WI, USA
- AFS Entwicklungs- und Vertriebs GmbH,[8] Neusaess, Germany
- Sigma Technologies International, Inc.,[9] Tucson, AZ, USA.



4.9 The Vetaphone TOW8 Corona-Plus System showing power supply and treater station. (Courtesy of Vetaphone A/S[4].)

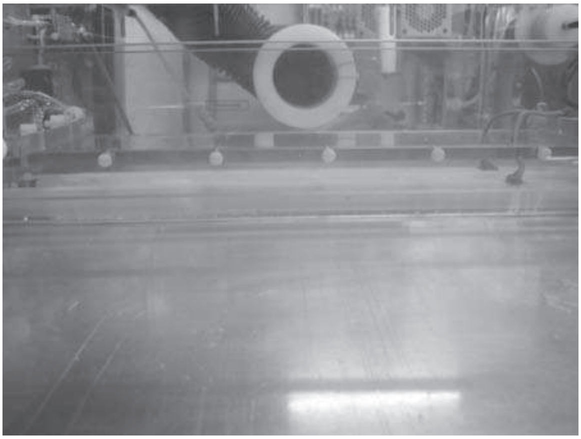


4.10 Cross-section schematic of a Controlled Atmosphere Corona system.

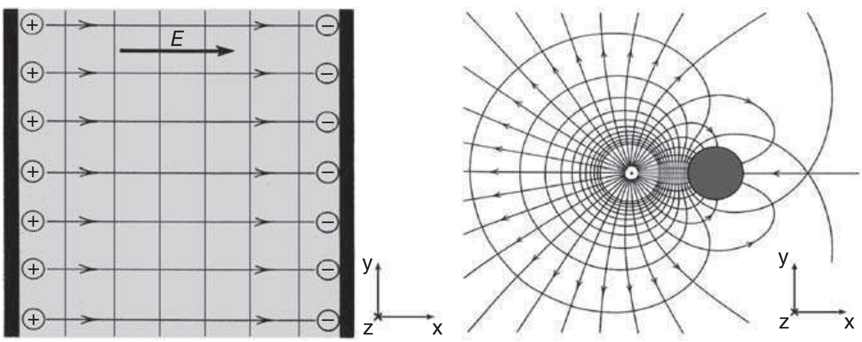
The very large, even overwhelming, majority of corona systems sold into multiple industries run on ambient air to deliver a surface activation process resulting in increased surface energy. However, an important and growing class of corona systems for activation of difficult materials and for new processes offered by several of the above companies employs some form of containment around the plasma region combined with a gas delivery system. These are especially relevant for textile treatment. The aim is to create an air-free atmosphere in a limited zone while still allowing free passage of the fabric through the plasma. The containment typically comprises a hood surrounding the electrodes together with the backing roller grounded electrode leaving open slits for the web to pass. By filling the containment region with selected gases, a well-defined, controlled gas atmosphere is produced from which different atmospheric pressure plasma chemistries are generated. This allows control over the plasma chemistry and, hence, surface reactions, thus enabling corona to carry out the controlled atmosphere treatment and the gas precursor coating generic treatments. Figure 4.10 is a cross-sectional schematic showing the concept. Not only can the gas atmosphere be controlled, but liquid precursors can be introduced into the working region in the form of a mist of atomised droplets to participate in the plasma chemistry. A slightly different geometry using the same concept is to replace the roller with a metal plane. The Danish company Vetaphone[4] employs this as well as the roller systems (see Figure 4.11).

Homogeneous DBD systems

The geometry of the homogeneous DBD equipment currently on the textile processing market is very different to that of Corona. It is characterised by symmetrical planar electrodes opposing each other across a gap of ~10 mm.



4.11 Side view of two enclosed powered electrodes opposing a flat plane generating Corona in a controlled atmosphere of nitrogen. (Courtesy of Vetaphone A/S[4].)

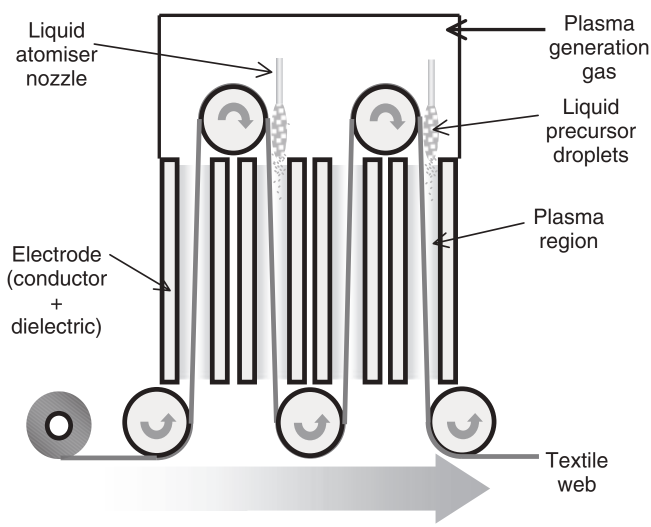


4.12 Plasma regions in grey – homogeneous DBD (left) vs. conventional corona (right). (Courtesy of Dow Corning Plasma Solutions[2].)

These electrodes are of truly large area, metres in width but also metres in length along the direction of travel of the fabric. Figure 4.12, a cross-section schematic through the electrodes, shows the differences in geometry and size of the plasma regions between homogeneous DBD and corona. The lines are electric field and equipotential.

Typically, both electrodes are covered by dielectric and a low frequency RF (~50 kHz) voltage of around 10 kV applied across the electrodes strikes the plasma, filling the entire inter-electrode region with a uniform, homogeneous glow. This region is filled with a selected plasma generation gas, often called the 'ballast gas', such as helium, argon, nitrogen or mixes, chosen for its propensity to generate well-behaved, large volume, cool APP and to facilitate control of the plasma and, hence, the process chemistry. In addition to the ballast gas, which is generally chemically inert or of low reactivity, special gas or vapour additives such as oxygen or CF_4 can be added to the gas stream in order to carry out a particular chemistry and deliver a specific surface effect.

The electrodes are set up vertically to avoid sag distortion arising from their own weight, to minimise footprint and to aid confinement of gas using the principle of relative density in which helium, for example, will tend to stay confined in a box geometry open only at the base. Figure 4.13 is a schematic cross-section showing the textile web processing configuration used by the manufacturer of this technology, Dow Corning Plasma Solutions.[2] This particular system consists of four vertical plasma regions or 'legs' each sandwiched between a pair of vertical electrodes and through which the fabric or yarn is guided by rollers, entering and exiting the system at the open base in a manner fully compatible with continuous, on-line production. The plasma generation gas is introduced from the top, and what is particularly significant in this version of the kit is the introduction of liquid precursor by way of atomised droplets into two of the legs. Thus, the process chemistry can be controlled through gas and vapour precursors or



4.13 Cross-section schematic of a 4-plasma region large area homogeneous DBD generator. (Courtesy of Dow Corning Plasma Solutions[2].)

through liquid precursors or a combination. This flexibility gives this system probably the widest range of functionalisation capability of any of the APP equipment options. Functionalisation can range from simple oxygen-based surface activation through controlled atmosphere treatment to gas precursor functional coating and liquid precursor coating.

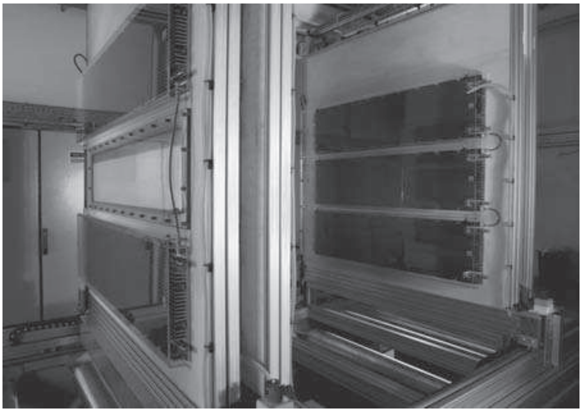
It would not make commercial sense to use such a system for oxygen-based activation alone when a standard air Corona system would do the job at much lower cost and faster line speed, but it would make sense to run such an activation step in this homogeneous DBD system as part of a multi-step process. This is one of the advantages of the homogeneous DBD configuration, namely that it allows multiple plasma regions to be stacked in series, each one of which has a large degree of process independence from the others. Thus, for example, the first leg of the above system could be used as a purge to remove trapped and entrained air from the fabric, the second leg could run an activation process, while the third and fourth legs could put down two different functional coatings in succession by firing into the respective regions different liquid precursors such as an adhesive primer followed by an oleophobic coating for durable anti-dirt and stain proofing.

A particular advantage of this equipment configuration is the long plasma path length in the direction of travel of the fabric. This can extend to metres or even tens of metres. Thus, for a given line speed, the residence time of the fabric in the plasma can be extended, enabling more energy per unit area to be coupled into the material and/or a thicker coating to build up. Alternatively, for a given residence time, the line speed can be increased by increasing path length.

The interfacing of metal electrodes to dielectric, essential to the homogeneous DBD system, has proven to be somewhat problematical. The bonding is tedious and the different coefficients of thermal expansion of metal and insulator can lead to delamination and separation over time. Dow Corning Plasma Solutions has developed an ingenious and successful improvement by replacing metal with salt water. Brine is sufficiently conductive to act as an electrode, requires no bonding, remains in permanent intimate contact with the ceramic dielectric and contains no edges, corners or other singularities which can act as high-voltage discharge points, generating unwanted electrical discharge outside the plasma region. Furthermore, the salt water acts as a heat sink, removing from the dielectric in contact with the plasma the slight heat generated by the plasma. This is done through simple air cooling fins in contact with the brine so that there is no long term heat build-up in the system. No water cooling is needed and the air cooling flow required is modest. This is in contrast with some corona systems that require high air-cooling flow and APGD systems that need water cooling.

Figure 4.14 shows the Dow Corning Plasma Solutions[2] SE-1000 AP4 flexible web processing system. Figure 4.15 is the realisation of the schematic shown in Figure 4.13 and shows a close-up of four plasma region 'legs', i.e. four pairs of opposing vertical electrodes each pair with a small gap between them. The 'legs' themselves are also grouped in pairs, with the first pair (running alongside the central vertical axis of the photograph) separated from the second pair (on the extreme right of the photograph). Plasma is running in the first leg as seen through the central window.

4.14 The Dow Corning Plasma Solutions SE-1000 AP4 large area web processing system showing front view of vertical electrode and control cabinets. (Courtesy of Dow Corning Plasma Solutions[2].)



4.15 The Dow Corning Plasma Solutions SE-1000 AP4 system showing an angled view of the four vertical electrode sets with the homogeneous DBD plasma seen through the window of the first leg. (Courtesy of Dow Corning Plasma Solutions[2].)

Atmospheric-pressure glow discharge systems

A single supplier, APJeT[11] of New Mexico, USA, offers their APPJ® technology for textile processing using this plasma type. The plasma generation scheme is implemented in the form of a flat jet which can be built up to about 5.5 m in width and allows the fabric to be passed between the electrodes, through the plasma generation region, to be treated *in situ*. Units can be flexibly ganged together to make up a complete textile processing system. The TexJet unit is APJeT's flagship production-scale product, designed to treat textiles and non-wovens at speeds of up to 120 ft/minute. It has a small footprint of 8-ft high by 8-ft wide by 3-ft deep and is typically equipped with eight 6-ft wide flat jet electrodes. Fabric enters the TexJet machine through a pre-treatment processor, which removes excess moisture and entrapped air without the use of vacuum. The fabric is then plasma-treated *in situ* by each of the eight 10 kW units. Designs can be varied from 20 to 120 kW. Fabric may be treated on one or both sides.

The particular mode of generation of the plasma type requires that helium be >95% of the plasma generation gas. Because of the cost of helium, this can motivate inclusion of a helium recycling unit into the capital equipment specifications, readily supplied by APJeT's strategic partner, Air Products & Chemicals, Inc.,[10] and which should be factored into the cost equation.

4.5 Atmospheric-pressure plasma surface properties for textile products

After all the description of the underlying physics and equipment engineering of APP, what is important to the textile manufacturer is what he/she is ultimately buying. This is, of course, surface functionality, and the power and attraction of APP is its ability to deliver a huge variety of chemically and/or physically active and valuable functional groups incorporated into and onto the textile surface to deliver specific properties. Many of these are described elsewhere in this book so the following overview is in no way comprehensive or exhaustive.

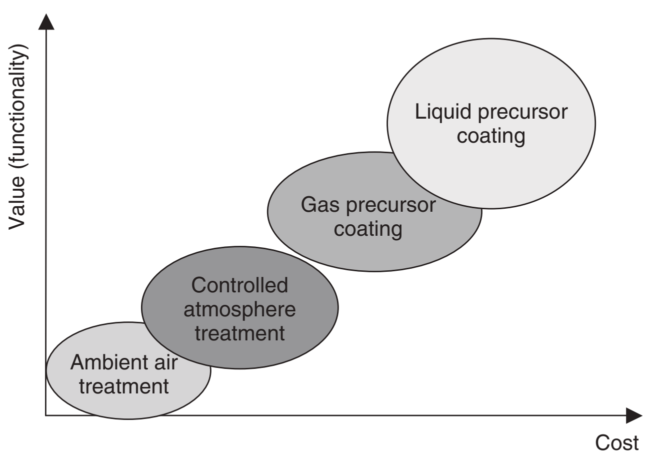
To recall, plasmas are used to deliver these surface properties because they provide a rich source of chemically active species that react with a surface or react with each other to produce secondary, short-lived chemical precursors needed for thin film deposition. The success of APP processing technology stems from its low temperature, continuous, on-line operation combined with the fact that no other method can provide the same nondestructive materials treatment capability.

A key distinction between the different APP options is how they perform in relation to the critical ratio – added value/cost. Added value is strongly related to surface functionality or performance; the more sophisticated and powerful the properties of the treated surface, generally the higher its value to the product. Thus, the chart in Fig. 4.16 is a very rough positioning of the generic treatments available from APP in the functionality (value) vs. cost parameter space.

It is important not to extend this principle beyond satisfaction of the targeted need. There is no added value to be gained and probably a cost penalty by over-engineering a surface. Nevertheless, in general, the degree of functionality or performance achievable from a particular plasma process product relative to the unit cost of production will distinguish it from its competitors.

The generic surface engineering processes available to the textile industry from the APP treatments can be categorised as etching, cleaning, activation or coating. These processes directly result from the immersion of the textile surface into the plasma and the resulting bombardment of the surface with fluxes of microscopic species carrying physical and chemical energy, particularly chemically reactive species with energies high enough to dissociate and form chemical bonds. Such species, which are generated by the ionisation, fragmentation, and excitation processes resulting mainly from collisions with high-energy free electrons accelerated by the applied electric field, include fast free electrons, ions, UV photons, radicals, excited states (electronic, vibrational and rotational), molecular fragments, etc.

- *Etching*, the removal of bulk substrate material, occurs when the interaction between the solid surface and the plasma generates gas-state by-products, which include atoms or molecules, from the substrate. These desorb from the surface and are carried away from the substrate, thus removing bulk material.



4.16 An approximate positioning of the generic APP textile treatments in the Value vs. Cost parameter space.

- *Cleaning*, the removal of contamination, is a form of etching but with very high selectivity. Essentially, only the unwanted surface contaminant is volatilised and removed while the substrate remains untouched by the process.
- *Activation*, enhancement of the surface energy, is the generation of chemically reactive sites on a previously unreactive surface resulting in a rise in surface tension.
- *Coating*, deposition of a functional thin film, occurs if the plasma–solid surface interaction creates a solid phase material. This remains on the surface and agglomerates over time, e.g. micro-seconds, to generate a conformal film. This process is sometimes called Plasma Enhanced Chemical Vapour Deposition (PECVD) or plasma polymerisation.

It is important to emphasise again that these APP processes are confined to a very few atomic monolayers of the substrate surface, ensuring that the bulk of the substrate remains totally unaffected, thus allowing a decoupling of the surface properties from the bulk properties of the material and giving the textile product designer a major new degree of freedom.

We have seen in the previous section how the three useful APP types for textile processing are used in generic treatments. Table 4.4 lists the surface engineering processes delivered by each of the treatments. Again, this table emphatically does not state that the treatments are equivalent. It simply says that each treatment can, to certain materials and given the right

Table 4.4 The surface engineering processes that can be delivered by each of the three APP types useful for textile processing

APP types	Treatments	Surface engineering processes
Corona	Ambient air treatment	Cleaning Activation
	Controlled atmosphere treatment	Etching Cleaning Activation
	Gas precursor coating	Coating
	Liquid precursor coating	Coating
Homogeneous DBD	Controlled atmosphere treatment	Etching Cleaning Activation
	Gas precursor coating	Coating
	Liquid precursor coating	Coating
APGD	Controlled atmosphere treatment	Etching Cleaning Activation
	Gas precursor coating	Coating

conditions, carry out the generic process to some degree. The power and sophistication of the treatments for each APP type is, in general, listed in ascending order in the table. Thus, for example, the cleaning and activation process capabilities of controlled-atmosphere treatment are significantly superior to those of ambient air treatment and the coatings available from liquid precursors can be of higher molecular weight and greater sophistication than those from gas precursors. But, again, it all comes down to matching the solution to the need.

All textile materials, natural or synthetic, are amenable to these APP treatments including polypropylene, polyethylene, polyester, polyaramids, nylon, wool, linen and cotton.

We will now outline the specific capabilities of each of the treatments in terms of their surface engineering processes and the specific surface functionalities/performance benefits that they can deliver.

4.5.1 Ambient air treatment

Ambient air treatment, where APP is generated from the factory air environment, is the only process to be run by a single APP type, namely corona. Line speeds depend on the material and degree of activation required and vary from 50 to >500 m/minute. The process essentially enhances surface energy. The plasma can achieve this by both cleaning the surface and by activating it. The essence of a successful APP treatment targeting wettability and adhesion is to remove loosely bonded surface contamination and to introduce stable chemical functionalities providing nucleation and chemical bonding sites for subsequent over-layer deposition. As is discussed below, the abilities of the various APP treatments to achieve this can be ranked in ascending order of effectiveness as ambient air treatment < controlled atmosphere treatment < gas precursor coating < liquid precursor coating. The correct choice of treatment depends on the textile material and the target coated system performance parameters.

A limited number of organic surface contaminants can be reduced or removed by air corona treatment and surface activation takes place, as shown by simple surface energy tests such as the contact angle of water and solvents. Several models are advanced to account for this phenomenon, including micro-roughening enabling enhanced physical ‘keying’ into the surface and the electret effect where polymer chains of the substrate are carbonised to create reactive sites. But the most commonly accepted model appears to be that of high-speed oxidation. The model states that the corona energy breaks molecular bonds on the surface of non-polar substrates, which broken bonds then recombine with free radicals in the corona environment to form polar groups on the film surface. These polar groups have strong chemical affinity to polar coatings, inks, adhesives, etc., resulting in improved adhesion. Similarly, the polar surface results in an increased surface energy, correlating with improved wettability.

The consequences of enhanced surface energy are multiple and of great interest to textile manufacturing. These are improved wettability and, particularly, adhesion. These, in turn, go to important product features and benefits in operations such as printing, dyeing, gluing, coating and lamination. Unlike the purely mechanical bond, as in the case of an ink penetrating into a porous surface such as cotton, APP surface activation delivers a chemical bonding between substrate and coating, ink, adhesive, etc.

Additional surface functionalities and benefits from ambient air treatment are biocompatibility and sterilisation. The removal of surface contaminants and the enhancement of surface energy will generally render low energy materials more amenable to bio-species, although the severely limited chemistry available from air activation greatly restricts this facility, a problem progressively lessened by the rapidly increasing functional capability of the other APP treatments in Table 4.4. With regard to sterilisation, all atmospheric pressure plasmas produce active species that are sterilising agents, e.g. UV radiation, atomic oxygen, ozone, high energy ions and free electrons. All these can rupture molecular bonds and denature proteins, thus offering powerful and environmentally friendly fabric sterilisation processes.

However, it should be said that ambient air treatment produces the weakest effect of the APP treatments, particularly in terms of adhesion and wettability. The effect can be sufficient for a limited number of materials in limited applications but for many, if not most, materials and applications it fails to deliver the performance needed. Adhesion is generally the key need of the corona treatment user and it is important to state that adhesion is a function of both wettability and bond strength between substrate and coating, adhesive, lamination, etc. While ambient air corona treatment will produce improvement in wettability, its effect on bond strength can be negligible. Indeed, ambient air corona can generate a weak boundary layer on the treated surface resulting from low molecular weight fragments. Material adhered to this weak boundary layer produces low adhesion. But, again, this does not mean that ambient air corona cannot meet the textile manufacturer's needs. If the materials and application are right, it will provide a highly cost-effective solution. It is a question of undertaking detailed trials of all possible options to locate that delivering the required technical performance at the lowest cost.

Time and post-plasma handling of the APP ambient air plasma-treated material degrades the effect. The time constant of reduction in properties varies according to the material and its storage and is driven by diffusion of the high energy surface radicals, the re-orientation and folding under of the surface layers and the availability of reactive species from the atmosphere. In humid, exposed-to-sunlight conditions, a corona treated surface can lose >50% of its dyne level surface tension in 10 days or less. More serious is the effect of rewinding the treated fabric onto itself after plasma treatment. Essentially, the APP has produced an active surface looking to bond. If the first contact offered is the rewound material, there will be a major loss of reactive sites as the activated surface bonds to the same material offered in the rewound reel. This strongly motivates users of ambient air corona to place the process in-line so that the first reagent offered to the active surface is the targeted coating, ink, adhesive, glue, etc. Once the final converting process has been performed (printing, coating, laminating, etc.), the bonding becomes permanent, i.e. the ink will not peel, nor will two substrates delaminate. Degradation of ambient air treatment occurs only between the time of APP activation and the following converting process so that delay between time of APP treatment and time of use is a major issue for the textile manufacturer.

It is important to point out that this issue of treatment lifetime is not the same for all APP treatments. The lifetime of controlled atmosphere activated products is typically far longer than ambient air activated surfaces and the functional coatings delivered by gas and liquid precursor coating treatments are permanent.

A further disadvantage of ambient air corona is the possibility of pinholing. Reference has been made to the energetic microdischarges which form this APP type. These can be too energetic and hot for lightweight, sensitive materials resulting in the burning of pinholes in the substrate fabric. This is by no means universal and is highly material and process specific. But, the issue should be investigated by empirical trials if APP ambient air treatment appears to offer the textile manufacturer the most cost effective solution meeting target needs.

In summary, APP ambient air corona treatment may meet some textile processing needs but is highly limited in its capabilities and will probably not feature significantly in mainstream textile manufacturing.

4.5.2 Controlled atmosphere treatment

In moving from ambient air to controlled atmosphere, the APP practitioner is vastly enhancing his/her process capability. Stating the obvious, the controlled atmosphere treatment system has freedoms not available to ambient air systems, namely the ability to customise the plasma, and hence process chemistry, to get the best result from the particular substrate. Typical key treatment control parameters are input power, gas types and ratio of gas mix, gas flow and fabric line speed. The principal processes available from this APP treatment are, again, cleaning and activation aimed primarily at adhesion. But there is also interest in the generic process of etching.

Almost all of the plasma system manufacturers mentioned previously offer controlled atmosphere treatment from their systems, in which the ambient air in the plasma generation region is replaced by selected gases. Thus, for example, certain corona systems of Enercon[3] and Vetaphone,[4] the homogeneous DBD systems of Dow Corning Plasma Solutions[2] and the APPJ® technology of APJeT[11] all run controlled atmosphere treatment at line speeds which are system and process dependent but are in the range 30–350 m/minute. Typically, the atmosphere comprises a ballast gas forming the large majority (>90%) of the total gas flow. The ballast gas is generally selected for its chemical inertness and its propensity for generating well-behaved APP; helium, argon and nitrogen are the usual candidates. Generally, but not always, small amounts, typically 1–10%, of chemically reactive gas (includes vapour) or gas mixes, are added to the gas stream. Examples are oxygen, nitrogen, carbon dioxide, ammonia, hydrogen, water, fluorine and tetrafluoromethane.

The process proceeds through plasma bombardment of the surface creating reactive bonding sites, the generation within the plasma itself of active species and the grafting of functional groups to the surface. The process can also produce bond scission and cross-linking of the treated surface. The resulting surface functionalisation depends, of course, on the gases used. A survey of the literature reveals a wide range of surface functionalisations achieved by APP controlled atmosphere treatment. A few examples to give the flavour are:

- Helium/oxygen plasma treatment of PP introduces oxidised functional groups onto the surface, which may include alcohol, ketone, carboxy, ether, ester or hydroperoxide.[3] The introduction of polar groups onto the PP fibres allows chemical bonding with, for example, dye molecules, in contrast to the untreated PP molecular chains which are non-polar giving a hydrophobic surface.
- Oxygen and oxygen-containing plasmas impart functional groups such as C—O, C=O, O—C=O and C—O—O, as well as surface etching of fibres, all enhancing wettability and adhesion characteristics.
- Fluorine and fluorine containing gases (CF_4, C_2F_6) result in the incorporation of fluorine into the surface, resulting in hydrophobicity.
- Nitrogen and ammonia plasmas introduce amino ($—NH_2$) and other nitrogen containing functionalities onto natural and synthetic fibres. On wool, these are dye sites increasing dye absorbtion.
- Treatment of PTFE with hydrogen-containing plasmas such as forming gas (N_2/H_2::95%/5%) and ammonia results in large increase in surface energy due to a high defluorination rate resulting in the formation of C—C, C—H and C=C bonds and cross-links, and to nitrogen and oxygen species grafted onto the treated surface.

Electron microscopy of controlled atmosphere-treated fibres shows a uniform and homogeneous cleansing of contaminants and a micro-roughening of the surface. Both of these effects enhance wettability and adhesion.

In addition to cleaning and activation, controlled atmosphere APP can etch the substrate fibres either through a physical effect in which high energy ions 'sputter' material out of the surface, i.e. knock out molecules through transfer of kinetic energy and momentum, or through chemical reaction resulting in the formation of volatile compounds containing substrate species which desorb from the surface and are carried away by gas flow. Resulting surface effects include micro-roughening, shrink proofing and size removal.

Micro-roughening tends to enhance adhesion and, particularly when combined with deposition of a hydrophobic coating, can produce through the 'lotus effect', a self-cleaning property where dirt particles are easily removed from the surface by water droplets.

Shrink proofing of wool is achieved by APP oxygen and nitrogen based plasmas. These etch the fibre surface and also generate reactive sites where sliding fibres tend to stick, both of which increase the overall coefficient of friction thus reducing the directional friction effect, the cause of wool felting. The process also etches and softens the fibre scales that produce the directional frictional effect. When combined with post-APP application of a thin resinous coating which smooths out the fibres, the combination treatment produces a shrinkage performance that is almost identical to that of the highly noxious and environmentally harmful wet chlorine/Hercosett treatment. The company Softal Electronic[6] has developed pilot equipment for APP wool anti-felting treatment.

Size removal has been demonstrated by APP treatments such as helium/oxygen. Thus, for example, PVA can be removed from cotton, albeit at a slow rate, but exposure to APP enables almost complete removal of the size with a cold water wash.

Benefits from the cleaning, activation and etching processes include improved gluing, bonding, coating, printing and lamination with films, enhanced dyeability (increased dyeing kinetics, enhanced depth of shade, improved bath exhaustion) and the ability to carry out post-plasma grafting of actives as a finishing step, e.g. chitosan, keratin, starch, powders, surfactants. Thus, for example:

- Enercon has shown that their 'atmospheric plasma treatment' of PP nonwovens with a helium/oxygen atmosphere results in greatly enhanced adhesion (0% failure tape test) of water-based inks relative to the untreated material (100% failure tape test) and to ambient air corona treatment (10% failure tape test) and delivers superior 'hold-out' of the ink from the nonwoven fibre structure, enhancing depth of colour.

- Controlled atmosphere treatment on spunbond PET nonwovens delivers improved dyeability with water-soluble inks and dyes.[3]
- Softal Electronic's[6] 'Aldyne' APP treatment delivers an adhesive primer monolayer of amine, amide or imide groups, covalently bonded to the uppermost polymer chains of materials such as PP, PE, PET, PVC and PA. Such groups also covalently bond to selected overlayers in, for example, a conversion process putting down inks, coatings or adhesives. The process can completely replace wet priming with its associated high cost and environmental issues.
- PET fabric treated with an APP oxygen process can be grafted with acrylic acid on which chitosan can be immobilised to impart antibacterial properties, resistant to laundering.

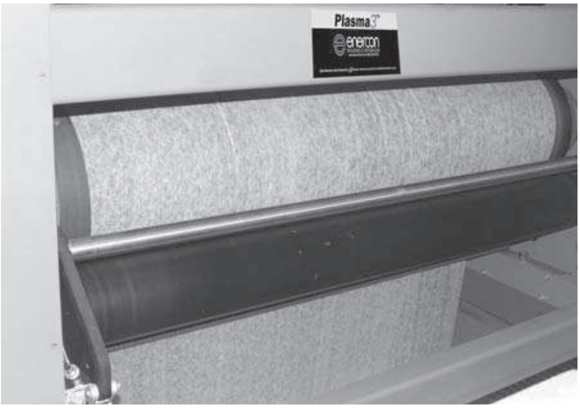
Particular textile segments where controlled atmosphere APP processes are being used include medical industry textiles (gowns, masks, protective clothing), automotive industry textiles (seats, trim, headliners, airbags), apparel industry textiles (outer and under garments), filtration industry textiles (air, water filtration) and flooring industry textiles (carpet fibres).[3]

4.5.3 Gas precursor coating

The gas precursor coating capability is an incremental, but important, advance on the controlled atmosphere treatment. The essential difference is the use of chemically reactive gas precursors which, rather than remaining in the gas state, as with the controlled atmosphere treatment, are polymerised by plasma to form solid phase material. Again, these typically constitute a small percentage of the gas stream with an inert ballast gas comprising the bulk of gas flow. The process proceeds through plasma bombardment of the surface preparing it for coating by activation to create reactive bonding sites. The plasma then deposits molecular fragments and grafts them to the surface while carrying out cross-linking/polymerisation. The single-step APP manufacturing process delivers a dry, fully cured, conformal coating, well-adhered to substrate at individual fibre level. The process is so conformal that each individual fibre accessed by the plasma is coated. The process results in pore-free, uniform thin films with superior, customised physical, chemical, electrical, mechanical and bio-functional properties.

Gas precursor coating is available from, for example, certain Corona systems of Enercon,[3] the Homogeneous DBD systems of Dow Corning Plasma Solutions[2] and the APGD plasma type using the APPJ® technology of APJeT.[11] Figure 4.17 shows a nonwoven under APP processing by Enercon's Plasma3™ system.

Examples of gas precursors and resulting coatings are:



4.17 A nonwoven under APP processing by Enercon's Plasma3™ system. (Courtesy of Enercon Industries Corporation[3].)

- Fluorine-containing gases to give water and stain repellence
- APP polymerisation of organosilicon compounds in the vapour state to impart dielectric properties, thermal stability and scratch resistance. The resulting films can also enhance colour intensity.
- Improved antistatic properties of polyester fabrics by APP grafting and ionisation of acrylic acid and acrylamide vapour precursors.
- APJeT's 'dual functionality' treatment to make a fabric hydrophobic on one side and hydrophilic on the other, without lamination.

4.5.4 Liquid precursor coating

The liquid precursor coating treatment is a step-change advance in surface engineering power and sophistication beyond gas precursor coating similar or greater in magnitude to the difference between controlled atmosphere treatment and ambient air processing. The use of liquid precursors opens up a huge new range of chemical and biological capabilities for APP. The number of potential liquids available to act as precursors runs into hundreds, if not thousands, including as they do, mixtures, dispersions, emulsions, suspensions and colloids, a number far greater than the available gas state precursors. Thus, a particular advantage of liquid precursors is the range of processes available from a single kit. Essentially, by changing the liquid in the delivery system, a totally different process delivering a new surface function is enabled.

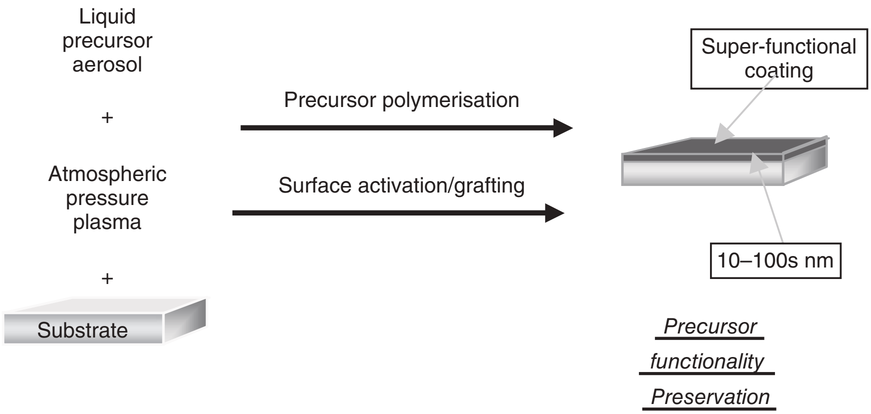
Only two APP manufacturers offer liquid precursor coating equipment: Dow Corning Plasma Solutions of Ireland which uses the homogeneous DBD APP type and Ahlbrandt System GmbH of Germany which uses corona. In both cases, it is the use of coating precursor in its liquid state in the plasma region that defines this APP process. The liquid is not vaporised but is atomised into droplets and injected into the plasma region in the liquid state. It is neither applied before nor after the plasma process since these options do not constitute true liquid precursor coating but mere surface activation plus grafting in the first case and plasma-assisted curing in the second case. The essence of the liquid precursor method is that the coating precursor reaches the plasma in the liquid state.

The Ahlbrandt process is given the acronym 'Wasco' (water–aerosol surface coatings) and takes the form of ~1 μm diameter droplets carried by ballast gas flow into the containment around the corona plasma region. There, a controlled atmosphere corona formed from the ballast gas of nitrogen, argon or, sometimes, ambient air, converts the precursor droplets into a functional coating. The aerosol is generated out of, and limited to, mainly water-based solutions (~85% water) and potential applications include antistatic, adhesion primers and wetting agents. The technology is described in detail elsewhere in this book.

The Dow Corning Plasma Solutions process has the acronym 'APPLD' (atmospheric pressure plasma liquid deposition). Here, the only precursor limitation is the viscosity of the liquid, which must be low enough for the liquid to be readily atomised into droplets ~20–50 μm diameter. Typical viscosity values are ~30 centistokes. Obviously, if the target process involves molecular polymerisation, the precursor molecules must be capable of such, i.e. they must be able to open bonds and engage in cross-linking. The Dow Corning process involves ultrasonic or other nebulisation of the liquid flow and direct injection of the resulting droplet stream into the plasma region. The fabric or fibre is passed through the plasma region containing the droplets and in a single step, the surface is activated and the precursor monomer is polymerised and chemically bonded to the surface to form a functional coating. Figure 4.18 shows this schematically:

A critical result of this process is that the coating preserves the molecular integrity of the original monomer so that its properties and functionality are completely replicated in the coating. There may be a feeling of 'so what' in reading this statement but, in fact, this is a profound and unexpected result. The reason is that conventional plasma processes in all pressure regimes tend to damage or destroy molecules.

As has been argued previously, a large part of the value of a surface engineering treatment is determined by the degree of functionality imparted to the surface by a treatment process. This, typically, in turn, is directly related to the molecular sophistication of the new, treated surface, whether coated, cleaned or activated. This is particularly the case with processes targeting new, advanced textile properties such as bio-functionality and smart textiles. The problem with conventional plasma processes across all pressure regimes is that the degree of surface molecular sophistication



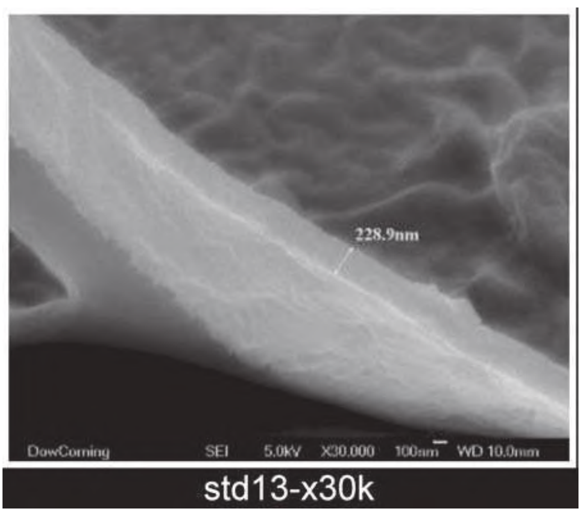
4.18 Schematic of the Dow Corning Plasma Solutions' APPLD Process (Courtesy of Dow Corning Plasma Solutions[2]).

available is severely limited. Thus, conventional plasma-deposited coatings comprise low molecular weight species of limited value or highly specific applicability, e.g. in microelectronics. The obvious solution to the functionality roadblock to product and application diversification is to extend the range of plasma processing. However, this has proven not to be possible with conventional plasma technology due to the highly aggressive nature of the plasma process. Essentially, the plasma destroys at the microscopic level any complex or long-chain molecule injected into the plasma as a precursor of the process. With functionality directly related to the molecular complexity of the precursor, the destruction of complex molecules by conventional plasma has placed a fundamental limit on the functionality of the surface coatings hitherto available to the textile industry and, hence, on its ability to develop new technologies and to find new applications and products.

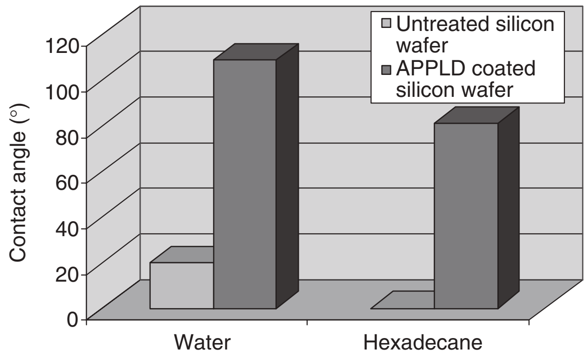
The use of liquid, as opposed to gas or vapour, precursors has removed this functionality roadblock. The original work, sponsored by Dow Corning in the 1990s, found that the precursor within each droplet is protected from the plasma and carried intact to the substrate where it spreads over the surface and is plasma polymerised into a coating. Thus, uniquely using atmospheric pressure plasmas, complex, long-chain and/or fragile precursor molecules with high-level functionality can now be injected into a plasma without being damaged or destroyed. Instead, the plasma causes polymerisation of the precursor so that it is deposited as a conformal, well-adhered thin-film coating, which retains all the functionality and value of the original liquid monomer precursor. Dow Corning calls this process 'controlled polymerisation'. Thus, advanced surface properties can now be made available from controlled polymerisation technology, offering the prospect of plasma processing penetrating a wide range of new, high value textile applications.

Examples of functional coatings that could be achieved by APP liquid precursor coating include:

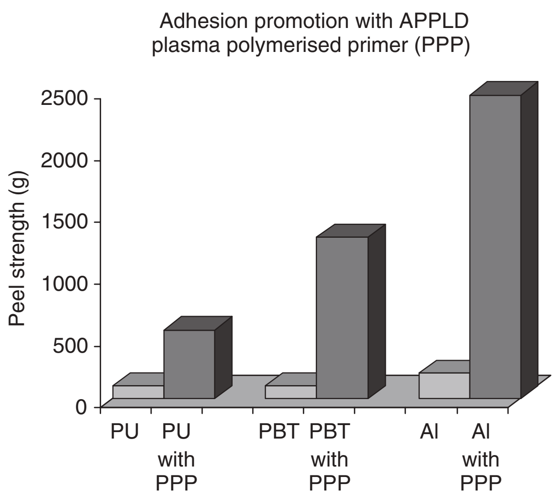
- Hydrophobic coatings for durable, breathable, water repellence, water roll-off and inhibition of capillary flow; dry process for the waterproofing of polyaramid fibres with no loss of fibre strength, e.g. for bullet-proof vests.
- Hydrophilic response for water wicking for moisture transferring and quick-drying textiles, e.g. sport, military; extra absorbance, e.g. easy capillary flow; anti-fog; easy take-up and good coverage for painting, coating, dyeing, etc.
- Oleophobic coatings with high oil, solvent, blood, etc. repellence and durability to boiling water and solvent washes (see Figures 4.19 and 4.20)
- Low friction coatings with coefficient of friction comparable to PTFE
- Reactive coatings, e.g. chemically reactive and reagent-specific filtration fabrics
- Non-stick/release – low release force; stain release, e.g. anti-dirt, easy clean workwear, automotive upholstery
- Adhesion promotion coatings for outstanding bondability, coating and lamination (see Figure 4.21)
- Bioactive coatings



4.19 SEM image of an APPLD fluorocarbon coating. (Courtesy of Dow Corning Plasma Solutions[2].)



4.20 Water and hexadecane contact angles from a fluorocarbon APPLD coating. (Courtesy of Dow Corning Plasma Solutions[2].)



4.21 Plasma polymerised primer APPLD coatings give advanced adhesion performance on a range of substrates. Adhesion performance without APPLD primers is shown in lighter grey. (Courtesy of Dow Corning Plasma Solutions[2].)

- ○ Anti-bacterial finishes for both general and medical use – inhibit bacterial growth, achieve reduction in bacteria, e.g. anti-bacterial face masks
- ○ Antifungal finish – inhibit growth of fungi on textiles
- ○ Selective biological tethering sites – bio-receptors/bio-affinity, bio-functional wound dressings
- ○ Grafting of enzymes, proteins, cells

- Copolymers
  - Multifunctional surfaces, e.g. dual function —NH_2 with —COOH groups
  - Smart/responsive surfaces, e.g. F + PEG – in air, stain-repellent F on surface, in water, stain removing PEG on surface
- Trapped active coatings – The coating matrix encapsulates sophisticated active molecules that can be released in a controlled manner over time or through applied stimulus. Potential actives include anti-microbials, enzymes and bio-molecules, pharmaceutical agents, cosmeceuticals, fragrances, agro-chemicals, anti-oxidants, flame retardants, catalysts and photochromic agents.
- Optical coatings
  - Ultraviolet protective textiles – block UV radiation
  - Far infrared textiles – fabric absorbs radiation and re-radiates at lower wavelength to aid body warmth
- Conductive coatings
  - Electromagnetic shielding textiles for medical devices, safety and general uniforms, electronics, assembly equipment, aprons, maternity wear, general wear
  - Antistatic textiles

It should immediately be said that by no means all of the above have been developed as of now (2006), but the precursors exist to make them prospectively a reality. Their realisation or not will be driven by prospective value and market demand. Essentially, APP liquid precursor coating vastly widens the selection of surface functionalities potentially available to the textile manufacturer, thus offering greater choice from a range of design and customisation options, potentially opening the door to new processes, new products and new opportunities.

4.6 The atmospheric-pressure plasma audit

Textile manufacturers everywhere are seeking ways to differentiate themselves from a sea of competition. Atmospheric-pressure plasma surface engineering offers clear advantages when compared to conventional wet chemistry processing. Substrate surfaces can be modified homogeneously in short processing times without any change in bulk properties. A huge range of surface modifications are possible by choosing appropriate plasma types, equipment, and gas or liquid precursors. Chemical consumption is low and the process is safer and much more environmentally friendly. Above all, APP processing, particularly liquid precursor coating treatments, offers the textile industry extensive potential for innovation and more flexible manufacturing capabilities.

For all that, APP processing is only beginning to emerge into textile manufacturing and it is instructive to return to the start of this chapter to the set of criteria for the introduction of new technology into the textile market and to try to audit APP processing against such.

'Qualifier' criteria for new textile technologies were listed as:

- Safety and handling: *The new technology must be operated safely, predominantly needing only the existing skill set of the textile mills.* The only issue here is that APP operation requires a new skill set and the training or hiring of skilled operators. However, this is not seen as a significant barrier.
- Operating speed: *Line speeds need to be as fast as or faster than existing technologies to avoid bottlenecks.* Whether or not this is an issue is entirely process dependent. In some cases, APP treatment runs slower than target line speed but in many cases it does not and APP line speeds are rising constantly.
- Production flexibility: *Fast switching between fabric types and effects must be available to allow for rapid adaptations in product and process.* The flexibility of APP is totally equipment specific. Ambient air Corona is a single fixed process but the process options increase rapidly as you move through controlled atmosphere treatment to the gas and liquid precursor coatings. As previously said, the liquid precursor coating systems offer hundreds of potential processes from one kit.
- Investment: *The technology should offer a return on investment in under 5 years and maintain or improve the profitability of the mill.* This can only be assessed on a case-by-case basis. In specific cases where APP is up and running in textile mills, the evidence is clear, APP can and does meet this criterion. In other cases involving the introduction of new effects using new APP technology, the case has not yet been made.
- Environmental: *The technology should comply with existing legislation and improve compatibility with anticipated law.* This is where APP undoubtedly scores with proven massive superiority over wet and heat based processing in terms of environmental impact.

'Winner' criteria for new technology in textiles were characterised as:

- New effects: *Properties and performances not achievable by traditional technologies enabling added value and market differentiation.* This is a real driver for APP, particularly for the APP coating technologies, whether single-step coating or grafting following APP activation. There is no doubt that plasma-deposited functional coatings are now offering interesting prospective new textile properties and performances for technical and apparel applications. These range from embedded scents, stay-clean fabrics and fabrics with anti-bacterial action to coatings which exude insect repellents or pharmacological or other therapies. However, the issue, as always, is value vs. cost and it is at present unclear whether all of the relevant APP technology is sufficiently advanced in terms of manufacturability to deliver solutions of commercial interest. Undoubtedly, developing technology will cross that threshold in the foreseeable future to access a range of high-value specialty products that will expand into high volume markets.

- Durability: *Significantly exceeds the durability of effects delivered by current processing techniques, again adding value and distinction.* Durability is highly process dependant and many APP processes do not deliver the same level of durability to laundering, etc. as wet coatings. A major reason is the thinness of plasma coatings which can be <1/20th that of wet coatings. However, in many applications, such as single-use medical fabric, this is not an issue and even where it is an issue, APP coatings are rapidly improving in performance to become competitive with wet coatings.
- Operating costs: *Costs should be substantially reduced relative to established manufacturing norms facilitating competitive pricing and/or profitability improvements.* There are many examples of both capital and running cost reduction through adoption of APP. Thus, for example, the company Softal Electronic[6] claims a payback time of only 9 months single-shift operation for its Aldyne plasma adhesion primer system versus conventional liquid priming, with savings of over €3 million in 60 months use. There is no doubt that, as the costs of raw materials, power and water continue to rise steeply, the underlying cost advantages of APP over wet processing in terms of zero to low chemicals consumption, low power need and very low water usage will motivate textile manufacturers to move to APP wherever feasible.
- Environmental: *Sets new industry benchmark.* As stated, this is an area in which APP scores massively in comparison to any other competing textile processing technology. This criterion is undoubtedly a winner for APP processing, which is setting new industry benchmarks.

APP changes the surface of textiles. It can replace current wet- and heat-based processing to reduce direct costs and to reduce or even eliminate harm to the environment. It can deliver new effects. It can provide winners for daring textile manufacturers. However, it is only in recent years emerging onto the textile manufacturing scene as a serious option and beginning to prove itself as a candidate for mainstream processing. Much has been done by the partnership of the textile industry and the plasma processing provider community, but much remains to do. To this end, both partners need to work closely together and have the courage and foresight to implement a long-term strategy of sustained investment in plasma technology.

Global environmental issues alone motivate such a strategy and should encourage significant support from national and supra-national bodies such as the European Union and the US Federal Government.

Already in the marketplace are mature APP technologies with well-defined technical capabilities serving both new and mature markets. These are enjoying steady growth driven by need to replace non-sustainable processing and reduce costs. More speculative but potentially more exciting are emerging APP technologies such as gas and liquid deposition, where relatively high costs must be justified by high added value so that these technologies must seek new, high value markets, in particular technical textiles from which they can launch drives into major volume markets.

There is no ‘superior’ APP technology. The textile producer has a range of value/cost options increasingly provided by the APP community and needs to select the APP product that exactly delivers the required level of surface functionalisation, manufacturability and commercial performances at the lowest cost and highest margin to him/her.

Driven by a crazily burgeoning global population with all its adverse consequences in terms of sustainability and driven also by the insatiable human need for enhanced performance in every measurable parameter such as comfort, safety and function, there is little doubt that atmospheric-pressure plasmas stand on the threshold of a revolution in textile processing as great as that delivered by wet- and heat-based processing in times long past.

We do, indeed, live in interesting times.

4.7 References

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