GAS FLOW AROUND AND THROUGH TEXTILE STRUCTURES DURING PLASMA TREATMENT

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Abstract

An experimental plasma reactor has been developed that enables the study of aspects related to the flow of a gas around and into textile structures while they are treated in a plasma at reduced pressure. A selection of experiments draws attention to the fact that even at reduced pressure a textile forms a barrier for a gas containing plasma-created species, resulting in an 'edge effect'. It is also shown how basic variations in the structure of a textile influence the penetration of the treatment effect. The ratio of textile thickness to its porosity is proposed as a simple rule of thumb for assessing the effect of penetration and etching efficiency.

Key words:

barier effect, penetration, etching, wicking

Assumptions of the study: reactor design, pressure fall

This study originates from observations during the plasma polymerisation of fluoromonomers for hydrophobic protection of a polyester nonwoven exhaust filter [1]. In non-ideal treatment conditions, a suspension of fine dust could be seen flowing around the sample, rather than penetrating into its porous structure. A plasma reactor setup was therefore developed, in which the choice could be made between a free flow of gas around a sample and a forced gas flow through the sample (Figure 1). A textile sample is treated centro-symmetrically between 2 perforated electrodes, of which the bottom one is powered by a 13.56 MHz generator. The gas enters the reactor from the top and forms a homogeneous gas column perpendicular to the plane of the electrodes and sample. The net vertical velocity (in cm.s-1) of the gas flow can be regulated independently of the reactor pressure. In the free flow mode, the penetration of the plasma gas is diffusion-controlled, while in the forced flow mode the penetration is driven in part by the pressure fall created across the sample. The determination of the pressure fall ($\Delta P = P_{high} - P_{low}$) is possible by the internal design of the reactor, and a 3-way valve. In Figure 2, the pressure fall over a needle-punched filtration fabric is shown for different reactor pressures and gas flow velocities. The plots indicate the influence of gas pressure (which is proportional to gas viscosity) on the ease with which the gas penetrates the sample. It seems that even at pressures of 10-100 Pa, with its high diffusivities. the porous structure of a textile is a considerable barrier to gas penetration by free diffusion.

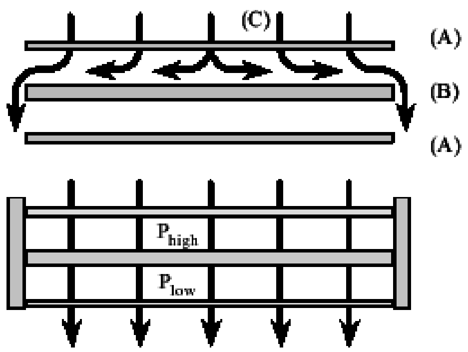

Figure 1. Side view of reactor, free flow (top) or forced flow (bottom) mode.
Legend:(A) electrode, (B) textile, (C) gas flow

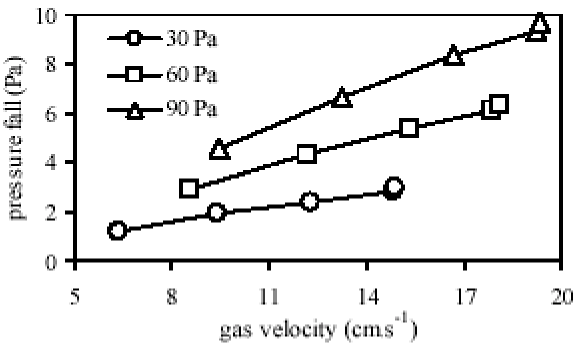

Figure 2. Influence of the velocity of a forced gas flow on the pressure fall over a 490 g.m-2, 2.6 mm thick nonwoven. Data for 3 reactor pressures

Relevance of the subject: literature

The flow of the plasma gas, and the related penetration of the plasma treatment effect are only sporadically reported in textile literature, even though they are of great interest to both industrial and fundamental research. In patent literature a good control of the gas flow is claimed to improve both efficiency and quality of the plasma treatment [2], while a forced gas flow through the textile is claimed to improve the removal of working gas and of reaction products [3]. The penetration of the plasma effect into the 3D porous structure of textiles provide a unique opportunity to distinguish the three major reaction mechanisms that occur during the plasma treatment of a polymeric surface [4], that is;

(a) direct interaction of reactive species existing in the plasma state with the surface (irradiation effect),
(b) chemical reactions of plasma-induced reactive species which are not essential components to maintain the plasma state (chemical modification by plasma-induced species), and
(c) reactions among reactive species and polymer molecules at the surface (plasma deposition/ polymerisation).

The plasma effect penetration into textiles is assessed by treating a stack of identical textile structures, followed by the (physico)chemical characterization of each layer individually. The result is a depth profile of the treatment effect. Experiments were done at reduced pressure [4,5] and at atmospheric pressure [6]. Depth profiling has shown that a plasma at intermediate pressure (102 - 104 Pa) is more efficient at effect penetration than a ‘classical’ vacuum plasma (101 - 102 Pa), due to the comparable mean free path length of the reactive species and the distances in textile structures. Depth profiling has also been used to visualise the fundamental difference in effect creation between the Surface Barrier Discharge and the One Atmosphere Uniform Glow Discharge reactor setups [6], and is therefore an interesting means of assessing the potential and limit of a given reactor setup for a proposed plasma application. In this study, the textiles were treated in an oxygen plasma, so only the reaction mechanisms (a) and (b) are considered. In this case, the reaction between active plasma particles and the surface of textile fibres deactivates a reaction site and enables further penetration of new active particles, even if they hit the deactivated surface site again [7]. It is obvious that the requirements of effect penetration vary with the desired behaviour of the plasma-treated textile towards a post-plasma finishing step, or towards its behaviour as an end product. Two extreme situations can be given as an example. The interaction of a print paste with a hydrophobic fibre material can be improved by a plasma treatment.

However, the treatment effect should not penetrate deep into the textile structure in order to prevent colour bleeding and loss of coverage. On the other hand, the improvement by plasma treatment of the filtration properties of textile materials is optimal only when the plasma-induced property is homogenous throughout the complete fibre surface. This is logical, because during its application as a filter, the textiles' complete fibre surface is used, rather than just its outer fabric surface. In this study the in-plane inhomogeneity created by the flow around a textile sample is visualised, as well as the cross-sectional inhomogeneity created by the limited penetration depth of plasma-created species.

Experimental Results

Weight loss of samples of different size - the ‘edge effect’

The influence of the gas flow around a textile was assessed through the weight loss of samples after plasma treatment.

Sub-samples of varying size (type A) were cut out from a series of 490 g.m-2 PET nonwoven fabrics, leaving a second series (type B) of annular sub-samples of varying surfaces (Figure 3).

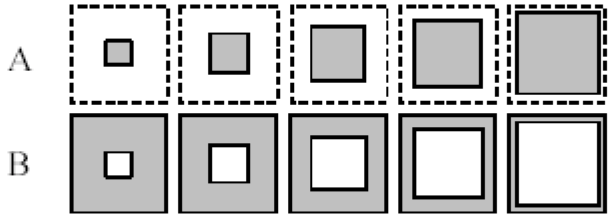

Figure 3. View from top of geometry and size variation of treated sub-samples. Cut out (type A) and remaining annular (type B) sub-samples. Dotted lines indicate size of reactor cross section

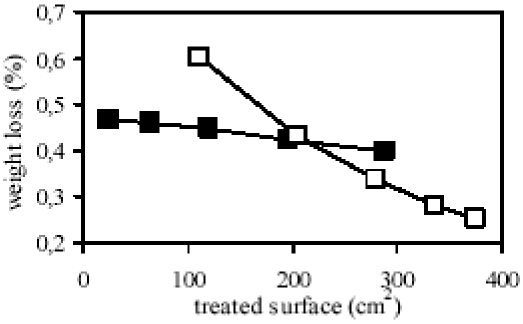

Figure 4. Weight loss as function of treated surface size, for type A (■) and type B sub-samples (□)

All sub-samples were treated for 6 minutes in a 57 mW.cm-3 oxygen plasma at 53 Pa (400 mTorr), and their weight loss determined. The plasma treatment was done in the forced flow mode, which means that all the gas entering the reactor was forced to pass through a restricted free area, the size of which is determined by the cross-section of the reactor (dotted line in Figure 3) and the size of the treated sub-sample. The larger the sub-sample surface, the more the gas flow is restricted, increasing local gas velocity, plasma current density and (supposedly) etch rate. The plots of weight loss vs. treated surface (Figure 4) behave in an unexpected manner, and this in two ways. First, weight loss decreases with the treated surface area, where it would be expected to increase. Second, the two plots have a different slope. Assuming that weight loss was only dependent on fabric surface size, the plots should lie on top of each other. The erratic behaviour of the weight loss, and more particularly the negative slopes of weight loss vs. treated surface, can be explained by consideration of the 'edge effect', i.e. a difference in reaction (etching) rate between the edge of the treated structure and the surface in its plane centre. When the weight loss ordinate in Figure 4 is replaced by the ratio of treated edge length (L) to treated surface (S), plots are obtained (Figure 5) which are very similar to the plots in Figure 4, especially for the annular (type B) sub-samples.

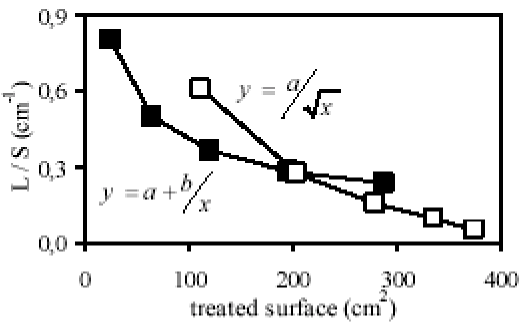

Figure 5. L/S ratio as function of treated surface, for type A (■) and type B (□) sub-samples

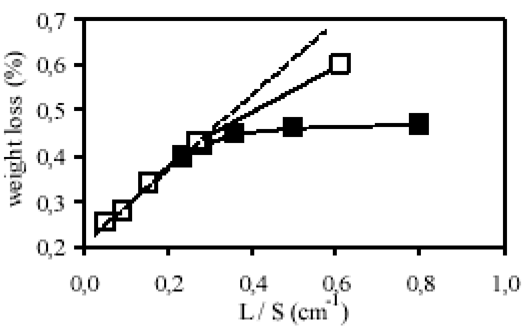

Figure 6. Observed weight loss plotted vs. L/S ratio, for type A (■) and type B (□) sub-samples

The deviation of the weight loss results for type A from the edge length-to-surface plot (Figure 6) – i.e. that the weight loss is lower than expected from the L/S ratio – can be explained by considering that with a reduction in sample surface, apart from an increase in edge-to-surface ratio, the cross-section for free gas flow also increases. Because of the limited constriction of the free gas flow around a small sample, it is treated more homogeneously, without any edge effect. The etching rate observed for the smaller size type A sub-samples is probably close to the etching rate for the central fraction of the large type A sub-samples. For the type B sub-samples, no such deviation is found, because here the cross-section for free gas flow *decreases* with the increase in the treated sample surface. For the type B samples, a linear plot (R^2 = 0.9977, dotted line) is found for all samples except the one which causes the least gas constriction.

Weight loss and wicking properties of multilayered samples - plasma effect penetration

Penetration of the plasma treatment effect was determined on 7 layer fabric stacks of two different types of polyester structures: a 55 $g.m^{-2}$ open weave fabric and a 63 $g.m^{-2}$ spunlaced nonwoven. While open weave fabrics stacked in the same direction create a structure with a low number of wide and regular pores (Figure 7a), the stack or nonwovens creates a large number of small irregular pores (Figure 7c). An intermediate structure is obtained by crosswise stacking (0° - 45° - 0° - …) of the open weave fabrics (Figure 7b). Although areal density is similar, the thickness of the fabric (Figure 7d) is less than half the thickness of the nonwoven (Figure 7e).

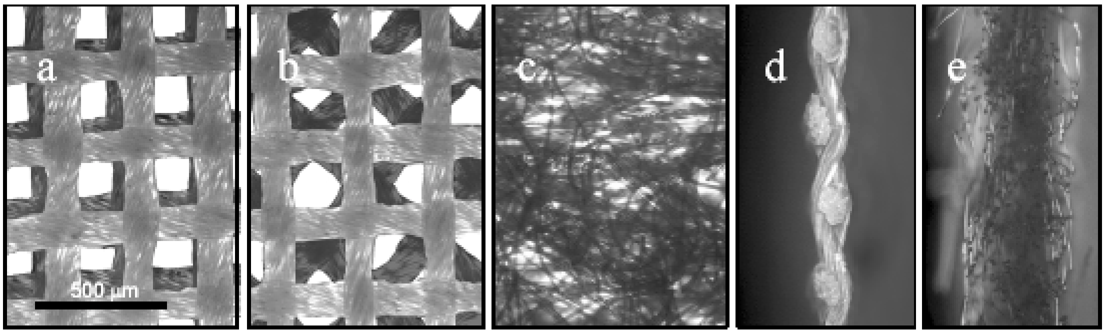

Figure 7. (a) Parallel and (b) crosswise layers of open weave fabric. (c) Nonwoven single layer. (d) Fabric and (e) nonwoven cross section. Scale is identical for all images

The effect of the plasma on each of the 7 layers was assessed by two characterisation methods. The penetration of plasma-created species capable of etching the fibre surface was assessed by weight loss. This effect was determined, for both structures, after a 5-minute, 47 $mW.cm^{-3}$ oxygen plasma treatment at 53 Pa (400 mTorr). The penetration of plasma-created species capable of inducing hydrophilic fibre surface properties,was assessed by the wicking property [8,9] of the individual layers. This effect was also determined (but only for the nonwoven structure) after a 47 $mW.cm^{-3}$ oxygen plasma treatment at 53 Pa (400 mTorr) of varying duration (5 to 300 s). Treatment duration was kept short in order to assess industrial feasibility. All plasma treatments were carried out in the forced flow mode at a calculated net vertical gas flow velocity of 9.6 $cm.s^{-1}$. The influence of the internal structure of the textile stacks on plasma penetration is shown in Figure 8, where weight loss results are shown for those stacked in the same or crossed directions. Plasma etching is up to 100% more efficient for parallel fabrics. The difference in shape of the depth profiles (inverse bell shape vs. quadratic) is related to the ease with which different plasma-created species can penetrate into the porous structure, and to the probability that the reactive species will encounter a reactive site. Because of the reactor setup (forced flow mode), the only way for the plasma to be ignited and sustained is for the electrical current to flow through the fabric stack. In the case of parallel fabrics, the possible presence of straight, ±100 µm wide ‘canals’ passing through the stack (Figure 7a) eases current flow. This could account for the higher etching rates for the fabrics stacked in the same direction, as compared to the ones which are stacked crosswise. The combination of a fast, collision-less transport of plasma-created species into the porous structure with an increased electric current through the straighter pores improves the transfer of ‘plasma power’ into the textiles stacked in the same direction.

The slight asymmetry in etch rates – in both fabric stacks, the sample closest to the powered electrode is etched more efficiently than the one closest to the earthed electrode – is enlarged in the stack of nonwovens. While the penetration of the etching effect from the side of the powered electrode (layers 5 to 7) is similar for both fabric and nonwoven stacks (Figure 9), the penetration from the side of the earthed electrode (layers 1 to 4) is low. This difference, together with the very low etching rates for the layers towards the earthed electrode, indicates that current flow through the stacked nonwovens is limited, and that although a plasma glow is visible on both sides of the textile, the plasma at the side of the earthed electrode is less intense than it is at the side of the powered electrode.

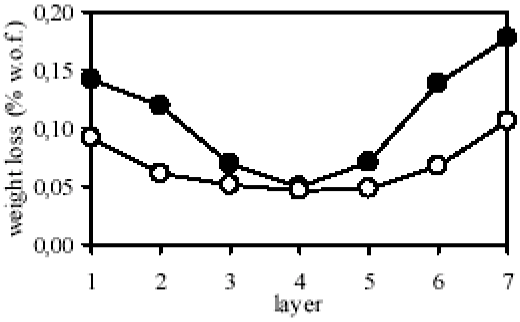

Figure 8. Weight loss of individual samples after oxygen plasma treatment, when layered in a parallel (●) or crosswise (○) stack of 7. Layer 7 is closest to the powered electrode

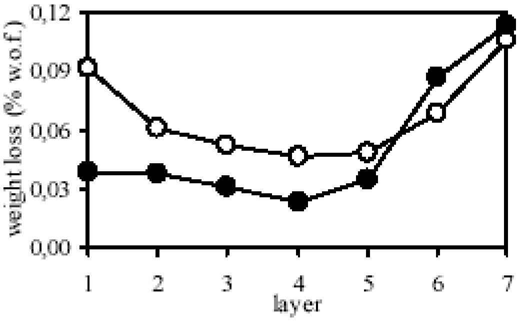

Figure 9. Weight loss of individual nonwoven (●) and crosswise fabric (○) samples after oxygen plasma treatment. Layer 7 is closest to the powered electrode

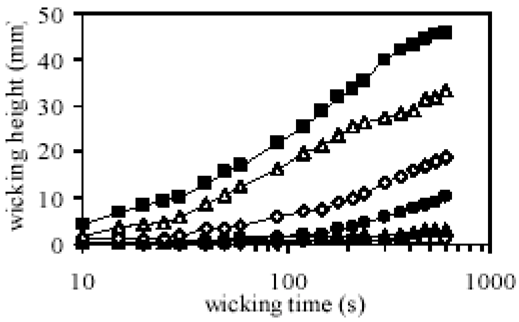

Figure 10. Wicking plots for a stack of 7 nonwoven samples after a 5-second oxygen-plasma treatment. The results shown are the average of three determinations

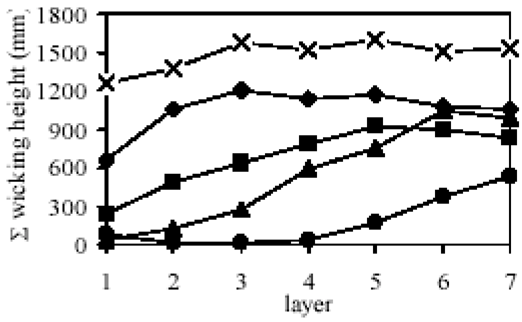

Figure 11. SWH depth profiles for stacks of 7 layers of nonwoven, treated in an oxygen plasma, for a treatment duration of 5 s (●), 10 s (■), 20 s (♦), 40 s (▲.) and 300 s (×)

The asymmetry in the plasma treatment of the stack of nonwovens was further studied by means of a series of plasma treatments of short duration. After treatment, the individual samples were stored in a conditioned atmosphere for between 8 and 10 days, and the wicking properties determined. The sensitivity of the method used is shown in Figure 10, for the individual nonwoven samples after a 5-second plasma treatment. The abscissa of the wicking plots is presented in log(time) to avoid data overlap at short wicking times, and in order to emphasise the industrially important initial phase of textile wetting. The depth profiles drawn from the wicking results are presented in Figure 11. The summed wicking height (SWH), i.e. the wicking height integrated over the wicking time, was used as a comparative parameter. The evolution of plasma effect penetration can be followed through the plots.

Wicking at the side of the earthed electrode always lags behind wicking at the side of the powered electrode. In spite of the forced gas flow in the direction towards the powered electrode, plasma-created species capable of inducing hydrophilic properties penetrate the stacked structure in the opposite direction. Even after a 5-second treatment, a hydrophilic effect is found up to layer 5. Further optimisation of the method, and experiments with varying forced and free gas flow velocities, could produce an insight into the actual diffusion rates of plasma-created species into the textile structure. The SWH plot for a stack treated for 300 seconds is shown for comparison. Its shape is similar to the one after a 40-second treatment, but the overall wicking is better. The treatment effect towards wicking has become homogeneous over the complete nonwoven stack, indicating that chemically the fibre surface has reached a saturation point. The further increase in wicking properties is possibly due to the physical etching of the surface.

Weight loss of different textile structures - effect of thickness and porosity

Experiments have been initiated on the influence of the surface structure on the etching efficiency. Each of the treated structures is made of PET fibres. Provided the crystalline content of the fibres does not change much between the sample types [10], the chemical susceptibility of the fibre polymer surface towards an oxygen plasma can be considered as identical. The surface density of some structures was changed by stacking layers. Sample parameters and their weight loss after a 5-minute oxygen plasma treatment (53 Pa, 47 $mW.cm^{-3}$) are given in Table 1. Weight loss was determined for both free and forced flows, while the pressure fall was determined during forced flow treatments only. The porosity was determined from the thickness and surface densities of the textile structure, and from the density of polyester fibre (1.32 $g.cm^{-3}$). The net vertical gas flow velocity was 24 $cm.s^{-1}$ for all treatments. Though the data shown is preliminary (they are the average of only two determinations), the influence of textile structure on weight loss can be clearly seen.

Table 1. Structural parameters, pressure fall ΔP (in forced flow mode) during, and weight loss after a 5-minute oxygen plasma treatment, for different polyester woven fabric types structures and a polyester nonwoven

sample structure	structural parameter			ΔP (Pa)	weight loss (%)	
	thickness (mm)	density ($g.m^{-2}$)	porosity		free flow	forced flow
open fabric (1 layer)	0.15	55	0.73	0.67	0.60	0.77
open fabric (2 layers)	0.27	110	0.71	0.80	0.28	0.27
open fabric (7 layers)	0.91	385	0.70	1.73	0.095	0.063
flag fabric	0.30	110	0.74	0.93	0.26	0.28
monofilament fabric	0.28	98	0.75	0.67	0.25	0.31
tightly woven fabric	0.21	114	0.61	5.19	0.20	0.19
nonwoven (1 layer)	0.34	63	0.87	1.20	0.35	0.35
nonwoven (2 layers)	0.69	123	0.87	1.60	0,23	0,25
nonwoven (7 layers)	2.37	441	0.85	1.47	-	0.052

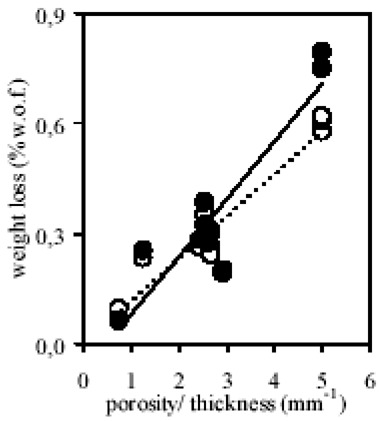

Figure 12. Weight loss vs. porosity/thickness ratios, in free (○) and forced (●) flow modes

Some of the differences can be interpreted as follows:

- The tightly woven fabric has the lowest weight loss, and the difference in weight loss is minimal for free and forced flows. This can be expected from the low porosity, and from the fact that this woven fabric has the smoothest surface (i.e. the smallest exposed fibre) of all the treated structure types. The high pressure build-up predicts a difficult penetration of species into the structure. For both free and forced flows, the treatment is limited to the surface of the textile structure.
- The series of 1-, 2- and 7-layered structures show a dramatic reduction in weight loss. Though the porosity is high, doubling the thickness of the structure reduces weight loss to between 35 and 45% for the open weave and between 65 and 70% for the nonwoven, as compared to the weight loss of a single layer. The small difference between free and forced flows indicate that a limited penetration of species capable of etching the fibre surface is more important for etching efficiency than the limited current flow through the structure.

- The open weave and monofilament fabrics are very similar in structure. The higher density of the latter is due to the solidity of the monofilaments as compared to the porous yarns of the open weave fabric. The lower weight loss of the monofilament fabric is probably linked to its smaller available total fibre surface, as compared to the additive surface of the individual fibres in the yarns of the open weave fabric.
- The high etching efficiency for the single layered open weave fabric, about double the efficiency for any of the other single layer structures, can be explained by the large openings in the structure, through which the electrical current can easily flow from one side of the fabric to the other. Combined with a large exposed fibre surface and a local increase in gas flow velocity by constriction of the forced gas flow, this leads to the high etching rate observed.

A first effort was made to mould the results into a rule-of-thumb. In Figure 12, the dependence of weight loss is plotted against a combination of structural factors, namely the ratio of the porosity of the textile structure to its thickness. This is done for both free and forced gas flows. The porosity is in the numerator, as it can be expected that effect penetration improves with increasing porosity. The thickness is in the denominator, as it is expected that the weight loss averaged over the complete volume of the structure will reduce as its thickness increases. These effects are due to limitations in the penetration of species. The best linear fits for free (dotted line) and forced (full line) gas flows cross each other. A preliminary interpretation for this behaviour can be given as follows. For structures with a *high porosity/thickness ratio*, the flow of electrical current through the textiles' pores is easy during forced gas flow treatments. The transfer of plasma power throughout the total textile volume is optimal. The treatment efficiency is further improved by gas flow constriction, creating high gas velocities in between the fibres/yarns. The efficiency for forced flow is higher than for free flow. This is because in the free flow mode, species penetration is by diffusion, and the current flow does not occur through the textile structure but along its surface and edges. For structures with a *low porosity/thickness ratio*, etching occurs only at the structure's surface, because the penetration of plasma-created species is difficult. The flow regime has little influence on species penetration, but has an important effect on the flow of electrical current between the electrodes. While in the free flow regime the current can be transferred via the edges of the sample, its only way of passage in the forced flow regime is through the textile structure. For dense structures, this leads to lower treatment efficiency.

Conclusions

- This paper presents a plasma reactor, and proposes alternative characterisation methods for studying the effect of gas flows on the results of plasma treatments of textiles, and to study the penetration of different types of plasma-created species into the textile structure. All of the proposed methods consider the complete volume of the textile structure, as a single layer or when in a stack of up to 7 layers. The results obtained through these methods are to be compared to results obtained from reference surface analytical methods, with the purpose of quantifying the modified chemical constitution of the fibre surface.
- Experiments show the subtle influence of textile structural parameters, which have not been considered in literature before. It has been found that for many plasma treatment results to be fully appreciated, the textile structure, as described by parameters such as thickness, porosity, pore structure, fibre thickness, etc., must be taken into account.
- A rule-of-thumb is proposed to explain the variable behaviour of a textile structure towards free and forced gas flows. For the reactor setup used in this study, this behaviour may be linked to the ability of electrical current to flow between the electrodes via the treated textile structure. Further study must lead to a more refined parameter for the prediction of plasma effect penetration into textile structures.
- Etching, i.e. the physical removal of the fibre surface usually attributed to direct plasma irradiation, is not limited to the outer fibre layers of a textile's structure, but can occur deep into a textile's structure as well.

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