Nanoscale finishing of textiles via plasma treatment

G. Buyle*

Compared with current standard finishing processes, plasmas have the crucial advantage of reducing the usage of chemicals, water and energy. Moreover, they offer the possibility to obtain typical textile finishes without changing the key textile properties. No wonder there is an increasing interest in plasma for textile materials processing. This overview consists of four parts: introduction to plasma; plasma interactions with textile materials and potential applications; evaluation of the current level of industrialisation; and conclusions. Despite ongoing efforts to integrate plasma treatments in the textile world, important hurdles for industrialisation still exist. Key issues are surface cleanliness, the three-dimensional structure and the large surface area (because of the individual fibres). Since the first adaptors are appearing from the textile side and plasma equipment manufacturers are showing an increasing interest in the textile market, it seems fair to state that a wider use of plasma technology for textile applications is nascent.

Keywords: Plasma, Plasma treatment, Textiles, Finishing

Introduction

Textile materials have intrinsic properties that make them very valuable: flexible, light weight, strong, large surface to volume ratio, good touch, softness, etc. Because of this, they are excellent for imparting additional functionalities. Typical examples of such functionalities are hydrophobic, oleophobic or antibacterial. Traditional wet methods for applying these finishes require the use of large amounts of chemicals, water and energy. Plasma is a dry processing technique and provides a solution to reduce the use of all three mentioned resources. In this overview, the author discuss what plasma can achieve on textile materials and what the current state of integration in textile processing is.

Plasma background

Basics

A plasma is a gas of which a fraction of its constituents are no longer electrically neutral. Instead, the atoms/molecules are ionised, i.e. they lost (or gained) one or more electrons. These free electrons are also present in the plasma. Note that the definition of a plasma is not dependent on the equipment needed to generate it, e.g. corona discharge, dielectrical barrier discharge, glow discharge, etc. Consequently, the term plasma is used in this text to represent all these types of discharge.

Practically, one generates the plasma by applying an electrical field over two electrodes with a gas in between. This can be carried out at atmospheric pressure or in a closed vessel under reduced pressure. In both cases, the properties of the plasma will be determined by the gasses used to generate the plasma, as well as by the applied electrical power and the electrodes (material, geometry, size, etc.).

Plasma for materials processing

Although the fraction of charged particles in a plasma is typically very low (order of 1% or below), they are crucial as they can be given energy via an electrical field. For materials processing, the aim is to make physico-chemical reactions happen. These reactions will only take place if a certain energy barrier can be overcome. Traditionally, this is carried out by heating the material (adding thermal energy). This is a very inefficient process because all particles become energised, whereas only a fraction of them is needed for the reaction. In a plasma, energising only a limited group of the particles to enable physicochemical reactions is possible because of the interaction of charged particles with the applied electric field. This explains why materials processing via plasma can be very efficient.

To illustrate that this is not only theoretical, the author refers to an LCA study about imparting oleophobic properties on a PET substrate.[1] This study shows that only about one-third of the energy is needed for obtaining this property via a plasma process as compared to traditional wet processing. Moreover, the LCA study shows that also the environmental impact of the plasma process is considerably smaller (at least a factor of two) for what concerns the contribution to CO_2 emission, the acidification, the photochemical ozone creation potential and the eutrophication.

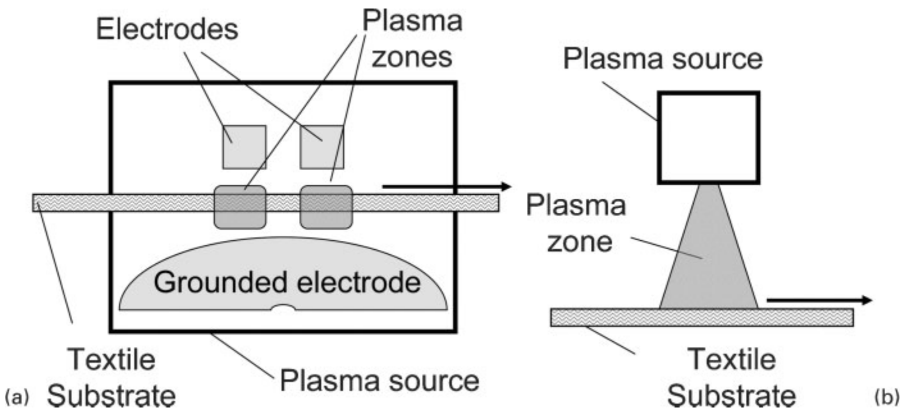
Classification of plasmas

A plasma distinguishes itself from the other states of matter because it contains charged particles. From a

Centexbel, Technologiepark 7, 9052 Zwijnaarde, Belgium

*Corresponding author, email guy.buyle@centexbel.be

Received 1 September 2008; accepted 21 November 2008
DOI 10.1179/175355509X417954



1 Atmospheric plasma sources can be split *a* in group where textile substrate has to pass in between electrodes and *b* in group where this is not case

fundamental point of view, plasmas can be classified based on the energy and density of these charged particles. This classification is of little use from a practical materials processing view point. Therefore, the author will look at the plasmas (suitable for materials processing) from two ways: the gas pressure at which they are generated and the geometry of the substrates that can be treated.

Pressure based

As mentioned, one needs a gas to generate a plasma. The pressure of this gas will have a large influence on the plasma properties but also on the type of equipment needed to generate the plasma. Indeed, some types of plasma can only be generated at reduced pressure. Basically, the author distinguishes three pressure ranges: low pressure, subatmospheric and atmospheric plasmas as indicated in Table 1.

Low pressure plasmas are typically in the pressure range of 0·01 kPa. A vacuum chamber and the necessary vacuum pumps are required, which means that the investment cost for such a piece of equipment can be (very) high. These plasmas are characterised by their good uniformity over a large volume. They can be generated using noble gasses but also with other gasses (e.g. O_2, N_2 or air), allowing tuning the plasma process to a wide range of needs. Roll to roll systems are possible for textile treatment, but it is practically impossible to do the treatment inline with the other process steps. Indeed, the roll has to be placed in a vacuum chamber, and then the chamber is pumped to the correct pressure after which the process can start.

Atmospheric plasmas operate at standard atmospheric pressure ($\sim$100 kPa). Open systems using the surrounding air exist. Also systems in a conditioned reactor are possible, they typically require nitrogen gas but sometimes (addition of) a noble gas is needed. For open systems, one has to be careful to what substances are injected in the plasma. Hence, the range of processes is not as large as for low pressure plasmas. On the other hand, these systems are easily integrated in existing finishing lines, a major advantage from industrial view point. Of course, for an inline process to be feasible, the plasma treatment has to be done at sufficiently high line speeds, which is not evident for textile materials (see also the section on 'Plasma on textile').

In between, one has the subatmospheric plasmas (typically around 1 kPa). The (dis)advantages of this pressure range are a mixture of the ones of the low and atmospheric pressure range. Subatmospheric plasmas aim at providing the process flexibility of the low pressure without the more complex and expensive equipment. However, one does need a closed reactor which means that the process is not compatible with inline processing.

Substrate based

From practical view, it is important what kind of textile substrates and which size can be treated.

For low pressure systems, the basic limitation is formed by the size of the vacuum vessel. If this is made large enough, one can treat all kinds of thicknesses, widths and lengths. For more voluminous textiles, the vacuum compatibility has to be kept in mind, but solutions can be provided for this.

Two groups of atmospheric plasma sources can be identified (Fig. 1): configurations where the substrate has to pass in between the electrodes and configurations where this is not the case. For the former, there is a limitation on the maximum thickness that can be treated, for the latter not.

Table 2 gives an overview of the upper limits for the substrate thicknesses that can be treated together with the uniformity and ease of scaling-up to large widths. The overview is made for four common types of atmospheric plasmas: corona, dielectric barrier discharge

Table 1 Overview of typical pressure ranges encountered for plasmas and their (dis)advantages

Gas pressure	Advantages	Disadvantages
Low ($\sim$0·01 kPa)	Uniformity Flexibility	Batch process Expensive equipment
Subatmospheric ($\sim$1 kPa)	Uniformity Flexibility	Batch process or expensive equipment
Atmospheric ($\sim$100 kPa)	Inline Line speed	Influence of environment Less flexible

(DBD), glow discharge and plasma jet. Only the latter belongs to the group depicted in Fig. 1*b*.

Plasma on textile

Recently, a book dedicated to the use of plasma technology for textiles[2] was published as well as an extensive review article, which summarises a very large number of (academic) research efforts.[3]

Active plasma species interaction with surface

In order to understand how plasma processing can lead to a wide variety of difficult functionalities, the author first looks into the ways a plasma can interact with a substrate.

As mentioned, charged particles (ions and electrons) are present in the plasma. Next to these, there are also atoms/molecules, metastables and radicals present in the active plasma zone, as well as photons (because of the generated UV light). All these particles interact in their own way with the substrate, leading to a myriad of different surface processes. Except for photons, the depth of the substrate that is influenced is limited to $\sim$10 nm or less. This means that the plasma only affects the outermost thin layer of the substrate, i.e. it is a real surface modification technique. This has a positive side (the bulk properties are not influenced) but also a negative one (surface contamination can be detrimental for the plasma process).

Basic plasma effect on substrate

The interaction of the active species in the plasma with the substrate can basically add something to the substrate or can remove something from the substrate.

In the latter case, the plasma treatment can lead to cleaning, to etching and/or to sterilisation. Hence, as examples, the author mentions the possibility to remove sizings,[4] to sterilise[5] or to obtain anti-shrink treatment on wool.[6] In the case of adding something to the substrate, one speaks typically of activation, functionalisation and finishing/coating. As these processes are more common for textile applications, they are discussed in more detail. No specific references are given, and several of them can be found.[2,3]

Activation refers to the temporal increase of surface energy. Such a treatment enhances the affinity of the substrate for other substances and is especially needed for synthetic materials with a low intrinsic surface energy (e.g. polypropylene or polyethylene). The process is based on the implantation of oxygen, leading to the formation of chemical groups like *OH, =O and *COOH. The formed groups tend to reorient themselves with time (because of thermal energy). Consequently, this treatment is not permanent and has to be carried out inline, as close as possible to the subsequent process step which it intends to promote. This process is typically achieved using a standard corona in open air.

Functionalisation refers to the permanent grafting of functional groups on the surface. A typical example is the incorporation of nitrogen based groups (amines, amides, etc.). This way a permanent primer layer can be realised. The process can be realised, e.g. using a DBD or plasma jet, using nitrogen as process gas.

Plasma finishing/coating refers to the deposition of a very thin coating (order of some nanometres) on the substrates. This is achieved using a plasma equipment (corona, DBD, plasma jet), in combination with a unit to vaporise a liquid precursor. The precursor can be chosen according to the targeted functionality. Applications include, e.g. oleophobic properties, fire proofing or antibacterial properties. The main advantage is that the functionality can be realised with a very limited add-on (e.g. of the order of $0{\cdot}2\ \mathrm{g\ m^{-2}}$ for obtaining antimicrobial properties.[7] In this way, the typical textile properties (hand, softness, flexibility, etc.) are not influenced (sometimes referred to as 'invisible' finishing).

Different applications

The above mentioned interactions and processes give rise to a very large range of possible plasma applications on textile. A lot of research has been carried out and has been reported in the literature. The most common applications are:

(i) imparting hydrophilic properties
(ii) increasing adhesion
(iii) influence printability and dyeability
(iv) changing the electrical conductance
(v) imparting hydrophobic and oleophobic properties
(vi) application of anti bacterial agents
(vii) application of fire retardant agents
(viii) antishrink treatment of wool
(ix) sterilisation
(x) desizing of cotton
(xi) …

For all these properties, studies can be found in literature. It is also clarifying to look into the number of filed patents. For some of the applications mentioned above, the number of times they occur in 'textile' related patents was determined using the Micropatent Database.[8] Then, it was checked whether the patents involved 'plasma' or not. The result is given in Table 3. The terms 'textile' and 'plasma' are put in between quotation marks to indicate that they represent a class of topics. The term 'textile' was, e.g. for the search represented by textile, fabric, non woven, fibre, yarn, etc.

Table 3 shows that of all patents retrieved $\sim$2% regard the use of plasma. Plasma involvement was the highest for obtaining hydrophilic properties and for

Table 2 Overview of properties of some typical types of atmospheric pressure plasma equipment*

	Geometry	Substrate thickness, mm	Uniformity	Scale-up width
Corona	Line	<10	− (μdischarges)	+
DBD	Plane	<20	−/+ (μdischarges)	−/+
Glow discharge	Plane	<15	+	−
Plasma jet	Line	No limit	+	−/+

*Numbers given in the column 'Substrate thickness' are meant to be indicative and are not absolute numbers. For the last two columns, the following code is used: '+': easy to achieve; '=': neutral; '−': (very) difficult to achieve; 'μdischarges': microdischarges.

a untreated reference; *b* after rendering permanently hydrophilic via plasma coating

2 ToFSIMS images of PET fabric: clearly, plasma treatment has different effect on warp and weft directions, even tough reference fabric does not show difference[26]

conductivity/antistatic properties. Interesting is also that for all plasma related patents found that deal with the listed properties, ~4·5% regards textile materials.

Different materials (synthetic, natural, etc.)

Given that plasma treatment is successfully applied in the plastic converting industry, it seems logical to apply it to the synthetic materials commonly used for textile applications, e.g. polyester, polypropylene, polyamide or polyethylene. Most work reported in literature regards effectively these materials; references are plentiful, see e.g. a recent review.[3] Also less frequent polymers used for textiles have been investigated, e.g. treatment of polyaramide[9] or of polyphenylene sulphide.[10]

Plasma treatments have also been reported on a whole range of natural materials. Extensive research has been carried out on wool, for improved dyeing but especially for antishrink treatment. An overview of wool treatment studies can be found in the corresponding chapter of the mentioned book[2] or elsewhere.[11–13] Also treatment of cotton,[14] silk,[15,16] angora fibres[17] or linen[18] has been investigated and reported.

The use of plasma on glass fibres,[19] carbon fibres[20] or basalt fibres[21] has also been documented. The performed treatments aim in these cases at improving the bonding with the composite matrix.

Different structures (sliver level, yarn level, woven, non woven, knitted, etc.)

Plasma treatment at different stages of the textile production can be envisioned. Plasma treatment has been carried out on sliver level, i.e. before the spinning, for wool.[22] Interaction of plasma with the extrusion process has been reported for polypropylene.[23] More common is the treatment of final yarns or filaments.

Probably the most looked for is roll to roll treatment of (half) finished textile substrates. The substrates can as well be woven or knitted fabrics as non-wovens. In the mentioned reviews,[2,3] numerous examples can be found. Finally, also treatment of entire garments (or footwear) is possible.[24]

Industrialisation

Reasons for limited industrial application

As mentioned before, the potential advantages and application possibilities of plasma are very large. In spite of that, and the numerous research efforts undertaken in the past, the use of plasma based processes in the textile industry can be fairly called very limited. Clearly, there must exist reasons why plasma is not integrated more widely yet. Several reasons exist why plasma treatment of textiles is so difficult.[25] Here, a set of reasons are identified, which are intrinsically linked to the specific properties of textile materials: surface cleanliness, the three-dimensional structure and the surface area.

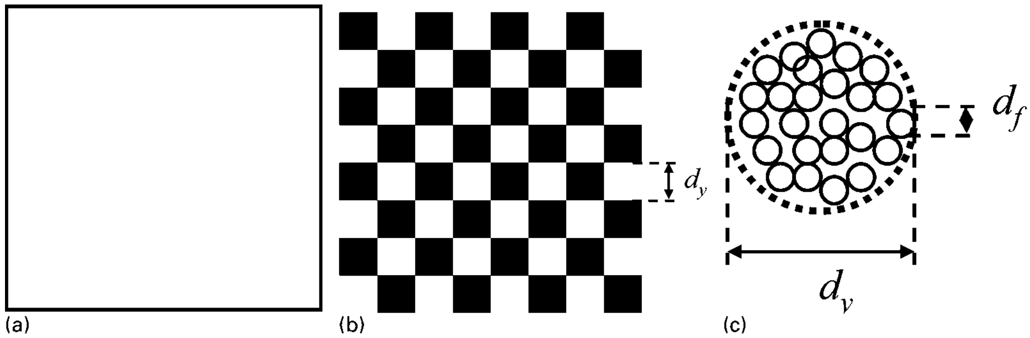
Surface cleanliness

Plasma treatment is a surface treatment, influencing only the top layer. Contamination of the surfaces which normally does not influence the standard textile process/properties, can nevertheless be detrimental for a plasma treatment. Hence, introducing plasma might require a new process approach. As an example, Fig. 2 shows two ToFSIMS images of an untreated and treated PET surface.[26] The treatment was a plasma coating to render the fabric permanently hydrophilic.

Table 3 Summary of patent search*

Property	'Property' and 'textile'	'Property', 'textile' and 'plasma'	% share 'plasma'
Biocidal	10 140	70	0·7
Antistatic/conductive	38 194	1037	2·7
Water/oil repellency	9618	184	1·9
Printability/dyeability	3739	44	1·2
Hydrophilicity	8626	262	3·0
Fire retardant	6275	23	0·4
Total	76 592	1620	2·1

*first column: property; second column: number of filed patents found in which the functionality occurred in combination with 'textile'; third column: the number of patents from the second column that refer to the use of 'plasma'.



3 Model for calculating total surface area of square sized sample (side length: 1 cm) of *a* film and of *b* woven fabric: for latter, yarn width *d* is indicated, and *c* yarn cross-section showing how it is built up by fibres: drawing not on scale

It clearly shows a different effect on the fibres for the weft and warp direction, although both are made of PET and for all other means can be considered identical. This difference is attributed to the different fabrication steps the warp and weft yarns underwent and which lead to slightly different surface conditions/contamination.

Three-dimensional structure of textiles

When considering the interaction of a plasma with the textile substrate, the latter has to be considered as a porous three-dimensional structure. It is not evident for the active plasma species to penetrate into this structure and to ensure proper treatment throughout the textile. This is due to the interplay between the life time of the active species in the plasma and their main free path length. Both are strongly influenced by the gas pressure so that this pressure is the crucial parameter here.[27] This is a basic disadvantage compared with wet techniques (e.g. padding).

Large surface area

The characteristic of textile materials is that they are composed of individual fibres. Because of these, the surface area to be treated is much larger for a textile substrate than for a flat film. The author illustrates this via a simplified model. Consider 1 cm^2 of film and 1 cm^2 of woven fabric, as shown in Fig. 3*a* and *b*.

For a sufficiently smooth film (so that the roughness does not play a role), the total surface area of the square is 2 cm^2 (back and front). When calculating the surface area of the woven fabric, one finds $\sim$18 cm^2 (assuming: uniformity in warp and weft direction, 100 yarns/cm, yarn diameter d_y=100 μm, fibre diameter d_f=10 μm, 30 fibres/yarn). This is almost one order of magnitude larger as the total surface area of the film.

The mentioned fundamental textile aspects limit the maximum line speeds that can currently be obtained for plasma treatment. Because of this, the throughput (i.e. the amount of square metres that can be treated per time unit) is still limited and forms a bottleneck for large scale industrial application.

Next to these, there are also other reasons which hamper the plasma integration in the textile production process. Fact is that existing finishing equipment is available and often consists of very simple mechanical methods, e.g. padding or Mayer bar. Replacing these by much more expensive plasma equipment is not evident, even when this has clear benefits. Another factor is also the lack of positive examples because of the secrecy about both successes and failures.[2]

Positive examples and outlook

As mentioned, positive examples of the successful use of plasma in the textile industry make the barrier for others to adopt the technology lower. Therefore, some positive examples are presented here.

An example of a company using successfully plasma based technology is SAATI: it enhances the durability of its meshes for screen printing via low pressure plasma processing.[28] SEFAR offers permanent hydrophobic coatings for fuel filters and coalescers (aerospace application) via plasma coating.[29] The ion-mask technology of P2i is available for water proofing entire garments.[24] Recently, the Austrian textile finisher Textilveredelungs GmbH Grabher started to offer plasma treatment of textiles via toll manufacturing.[30] Hence, first adaptors of the plasma technology exist already today.

With respect to the outlook of plasma use for textile applications, it is interesting that more recently, some European plasma equipment providers aim explicitly at the textile market. This is the case for, e.g. Europlasma, Grinp, Softal, iplas, Ahlbrandt Systems, P2i or Arioli (engagement deduced via website or participation to ITMA07). In the USA, APJET Inc. explicitly aims at treating textiles. This means that commercial systems are available on the market, although further technology development is in full progress.

Conclusions

Compared with current traditional finishing processes, plasmas have the crucial advantage of reduced usage of chemicals, water and energy. They also offer the possibility to obtain typical textile finishes (e.g. hydrophilic, oleophobic, antibacterial) without changing the key textile properties (hand, softness, flexibility, etc.).

This potential explains why plasma treatment has already been investigated extensively. Integrating plasma processes at different stages of the production process (sliver, yarn level, or on fabric) have been investigated, for a whole range of different materials and applications.

Nevertheless, industrial application is still very limited because important hurdles exist at various levels (cleanliness of the substrates, investments, offline treatment, scale-up). Key factors are also the three-dimensional structure and the large surface area (because of the individual fibres). These two intrinsic textile properties are posing major challenges for plasma treatment and are, at the moment, still limiting the maximum throughputs that can be realised. In spite of that, within the textile world, plasma is already being integrated by first adopters for niche applications and it seems fair to state that wider application is close to breakthrough.

Acknowledgement

The reported research took place in the framework of ACTECO (Eco Efficient Activation For Hyper Functional Surfaces) under European FP6 project no. 515859-2 (see also: http://www.acteco.org).

References

1. M. Perucca and G. Benveniste: 'LCA comparative analysis of textile applications for oleophobic and hydrophobic properties', Public Report, ACTECO, 2007, available at: www.acteco.org/Acteco/public/projectresults.htm
2. R. Shishoo: 'Plasma technologies for textiles'; 2007, Cambridge, Woodhead Publishing.
3. R. Morent, N. D. Geyter, J. Verschuren, K. D. Clerck, P. Kiekens and C. Leys: *Surf. Coat. Technol.*, 2008, **202**, (14), 3427.
4. Z. Cai, Y. Qiu, C. Zhang, Y. Hwang and M. McCord : *Text. Res. J.*, 2003, **73**, (8), 670.
5. J. R. Roth, Z. Chen, D. M. Sherman and F. Karakaya: *Int. Nonwovens J.*, 2001, **10**, (3), 34.
6. C. Canal, R. Molina and E. Bertrán: *Text. Res. J.*, 2007, **77**, (8), 559.
7. G. Buyle, *et al.*: Proc. 4th European Coating Cong., Ghent, Belgium, November 2007, UNITEX.
8. Micropatent Database: available at: http://www.micropatent.com
9. H. Höcker: *Pure Appl. Chem.*, 2002, **74**, (3), 423.
10. W. Leahy, V. Baron, M. Buggy, T. Young, A. Mas and F. Schue: *J. Adhes.*, 2001, **77**, (3), 215.
11. X. J. Dai and L. Kviz: Proc. Textile Institute 81st World Conf., Melbourne, Australia, April 2001, The Textile Institute, 1.
12. C. X. Wang and Y. P. Qiu: *Surf. Coat. Technol.*, 2007, **201**, (14), 6273.
13. J. M. Cardomone and W. C. Damert: *Text. Res. J.*, 2006, **76**, (1), 78.
14. S. Shahidi, M. Ghoranneviss, B. Moazzenchi, D. Dorranian and A. Rashidi: Proc. Conf. XXVIIth ICPIG, Eindhoven, The Netherlands, July 2005, Eindhoven University of Technology, Paper 10-055.
15. N. V. Bhat and G. S. Nadiger: *Text. Res. J.*, 1978, **48**, (12), 685.
16. D. J. Park, M. H. Lee, Y. I. Woo, D.-W. Han, J. B. Choi, J. K. Kim, S. O. Hyun, K.-H. Chung and J.-C. Park: *Surf. Coat. Technol.*, 2008, **202**, (22–23), 5773.
17. N. Danish, M. K. Garg, R. S. Rane, P. B. Jhala and S. K. Nema: *Appl. Surf. Sci.*, 2007, **253**, (16), 6915.
18. K. K. Wong, X. M. Tao, C. W. M. Yuen and K. W. Yeung: *Text. Res. J.*, 2000, **70**, (10), 886.
19. V. Cech: *Compos. Interf.*, 2007, **14**, (4), 321.
20. S. Luo: *J. Adhes. Sci. Technol.*, 2002, **16**, (13), 1715.
21. G. J. Wang, Y. W. Liub, Y. J. Guo, Z. X. Zhang, M. X. Xu and Z. X. Yang: *Surf. Coat. Technol.*, 2007, **201**, (15), 6565.
22. T. Wakida, S. Niu, M. Lee, H. Uchiyama and M. Kaneko: *Text. Res. J.*, 1993, **63**, (8), 438.
23. J. M. Warren, R. R. Mather, A. Neville and D. Robson: *J. Mater. Sci.*, 2005, **40**, 5373.
24. P2i website: 2008, available at: http://www.p2i-labs.co.uk
25. J. Verschuren, P. Kiekens and C. Leys : *Text. Res. J.*, 2007, **77**, (10), 727.
26. G. Buyle, I. Ferreira, T. Minh Duc and A. Paul: Proc. 47th Manmade Fibre Congress, Dornbirn, Austria, September 2008, Österreichisches Chemiefaser-Institut.
27. H. U. Poll, U. Schladitz and S. Schreiter: *Surf. Coat. Technol.*, 2001, **142–144**, 489.
28. P. Fracas: Proc. 1st ACTECO Training Day, Lyon, France, October 2006, French Textile and Apparel Institute.
29. SEFAR website: 2008, available at: www.sefar.us/cms/en.nsf/Print/D9371F76089068EFC125710F0053F47A
30. EMPA: 'Plasmatechnologie und textilien: heute und morgen'; 2007, St. Gallen, EMPA (CH) and Textilveredelungs GmbH Grabher Günter.