Applications of Low Pressure Plasma in High-tech Textiles

Rubel Alam[1], Gaffar Hossain[1], Günter Grabher[1], Mokbul Hossain[2]

[1]V-Trion GmbH Textile research, Schwefelbadstr. 2, A-6845 Hohenems, Austria
[2]Sefar AG, Töberstr. 4, CH-9425 Thal, Switzerland

Introduction

The textile and clothing industries especially in developed countries are facing now-a-days some big challenges largely because of the globalization process. Therefore, the market of a high-functional, added value and technical textiles is deemed to be essential for their sustainable growth. The growing environmental and energy-saving concerns will also lead to the gradual replacement of many traditional wet chemical-based textile processing by various forms of low liquor and dry-finishing processes. The main reason for the increasing interest is that industrially well-established surface finishing processes suffer considerably from environmental demands such as large amount of water, energy and effluents. Plasma technology, when developed at a commercially viable level, has strong potential to offer in an attractive way to obtain new functionalities in textiles.

The synthetic fibres such as polypropylene (PP), polyester (PES), Aramid (AR) etc. are widely used in apparel and home furnishings due to their good physical and chemical properties. The demand of these fibres increases greatly for high performance applications such as smart textiles, technical textiles, operation clothing etc. and more recently, for their potential applications in electronic textiles [1-2]. But these fibres often reveal hydrophobic nature due to the lack of polar functional groups. The hydrophobic nature of such fabrics limits their application to the above mentioned areas. In addition, adhesion is fundamentally a surface property, often governed by a layer of molecular dimensions, which necessarily required for coating, bonding and printing of synthetic textiles. The low surface energy of hydrophobic polymeric materials results in intrinsically poor adhesion.

On the other hand, some natural fibres (e.g. cotton, wool, linen) and synthetic fibres (e.g. rayon, viscose, acetate, spun nylon) exhibit to be hydrophilic in nature due to their polar functionalities. Hydrophilicity of such fibres may act as a barrier for their applications in many areas where liquids repellent is necessary. It is a wide-reaching technical effect that is sought after in several industry sectors, from biosciences, healthcare and electronics to industrial filtration, sports and active wear [3-4]. In addition to water repellency, other liquids such as oils, inks and alcohols repellency often required. Liquids are constantly in use around us, in the majority of cases in the form of rain water and food and beverages. Arguably, the most noticeable, unfavorable interactions of these liquids are with textile products such as clothing, carpets and upholstery, so added value can be provided by protecting these items from interacting with the liquids, enabling the liquids to roll off or be dabbed away, leaving the underlying material unchanged. Furthermore, hydrophobicity of textiles is frequently associated with self-cleaning properties. When a water droplet rolls off the surface, the surface impurities such as dust get carried away by the droplet resulting in a self-cleaning effect [5].

Using plasma technology to modify textile surfaces with precision cleaning, etching, chemical priming for lowering or raising surface energy can be used to obtain a desirable property of an end product. The plasma technology, a dry and eco-friendly technique, avoids waste water production which is a unique advantage over the wet-chemical processes [6-7]. This benefit

extends into all market areas, where the end product can undergo the plasma enhancement process to provide properties such as adhesion, hydrophilic, liquid-repellent etc. However, to transfer this technology from laboratory into industry, both the scale-up and economic aspects have to be regarded.

Main objective of this work is to study the possibility of substituting plasma processes for the traditional wet chemical methods using an industrial plasma reactor aiming to produce wash permanent super-hydrophilic, super-hydrophobic textile surfaces.

Experimental

Plasma reactor

The Nano-Plasma-Coater BAG at V-Trion GmbH is one of the biggest low pressure plasma reactor in Europe and offers a wide range of surface functionalisation, nanoscaled coatings etc. The semi-continuous reactor has a capacity of treating materials up to 4000 and 1.60 meter in length and width, respectively, and the material speed up to 40 meters per minute. The machine is capable of running for three shifts with a monthly production of about 400,000 meter (depending on material speed / coating thickness).

Durable plasma-nanocoatings

Depending on the plasma power and gas feed the modification of textile surface can alter over a wide range of properties such as hydrophilicity, hydrophobicity, adhesion promoter etc. The use of gaseous mixtures facilitates crosslinking. For instance, the Ar/O_2 plasma produces better hydrophilicity and wettability, as compared to Ar/CO_2 and N_2/O_2 plasmas. But, plasma-activated fabric surfaces were not durable over time due to the reorganization processes on the surface [8-9]. Therefore, the deposition of plasma coatings is required to obtain a permanent surface functionalisation. Generation of new reactive sites by plasma functionalisation promotes adhesion strength. The adhesion strength between PA / polyurethane (PU) and between PES / PU polymer is investigated at ambient condition as well as at 80ºC in water for a long time of period (up to 30 days) according to standard test (DIN 53539).

The possibility of substituting plasma process for the traditional waterproof finishing of fabrics was further studied in this work. A good water repellent finish could be obtained using silane plasma by a plasma-enhanced chemical vapor (PECVD) method. Furthermore, a wash permanent super-hydrophobic and oleophobic coating was obtained by a plasma pretreatment using non-polymerized gases followed by a grafting with perflouracrylates. This coating has an excellent washing durability (ISO 6330, 80 washing cycles) and has very good water repellency which is tested with a spray test (AATCC 22) as well as Bundesmann test method.
The permanency of the plasma hydrophilic coating has been recorded measuring sinking time after 50 times washing and after aging. The mechanical stability of the coating was also evaluated according to Martindale test (SN 198514, 60,000 rubbing cycles).

Results

The formation of plasma polymers from organic molecules is a technologically attractive way to deposit functional ultrathin films with unique properties. Appropriate combinations of gas mixtures and plasma parameters, a rather broad range of surface functionalities can be incorporated to the fibers. Wettability of the surface and adhesion properties varies according to the nature of the plasma treatment. In particular, the adhesion with PU material with PA and PES surfaces was improved greatly by plasma pre-treatment. As can be seen in Fig. 1, the pull-off strength can be increased by 130% for PA and by 110% for PES compared to the untreated

fabric. The aging study shows that more than 80% of their initial values can be retained after 30 days of immersion in water at 80ºC. The mechanism that leads to the improved adhesion of the plasma treated polymer surfaces may be due to the surface cleaning, mechanical interlocking, the increase of inter-diffusion, the increase of wettability and the polar interaction at the interface.

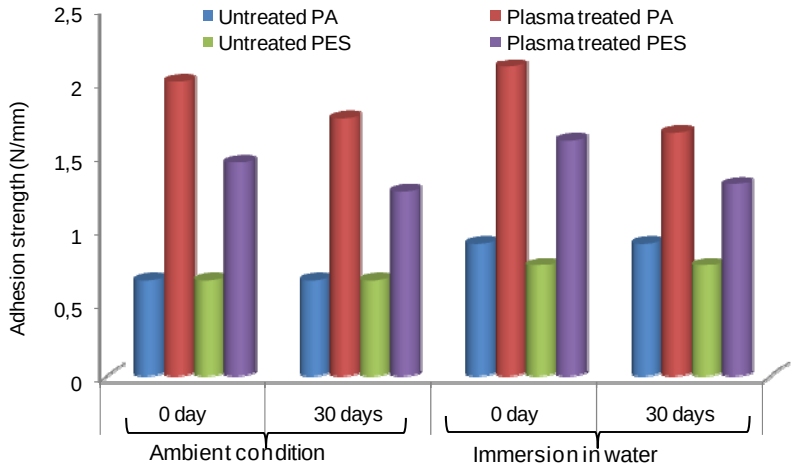

Fig.1. Adhesion and pull-off strength test (DIN 53539) of plasma-treated and untreated PA and PES fabrics

The water contact angle (CA) reflects the surface hydrophilicity / hydrophobicity by measuring how much a droplet of water spreads on a surface. The lower the contact angle, the more hydrophilic the surface is. The time-dependent spreading of a water drop on AR and PES samples are shown in Fig. 2 (data for PA is not shown). Since water drop disappeared very quickly on the plasma coated hydrophilic AR and PA surfaces, CA could be given to zero, whereas untreated AR and PA fabric show a water contact angle of ~ 110° and 76°, respectively. The durability of these plasma coatings was observed with a minor alteration in sinking time by the aging test up to one year for 50 times washed AR samples. The incorporation of polar groups increases the surface energy of polymers concomitantly improves the wettability of the surface. Due to the covalent bonding and their polar chemical nature, the functionalized films adhere well to the substrate which was also proved by the abrasion tests. It was evident that no changes were detected on the coated surface even after 60,000 rubbing cycles indicating the permanency of the novel coating against industrial washing (ISO 6330/2A, 60°C).

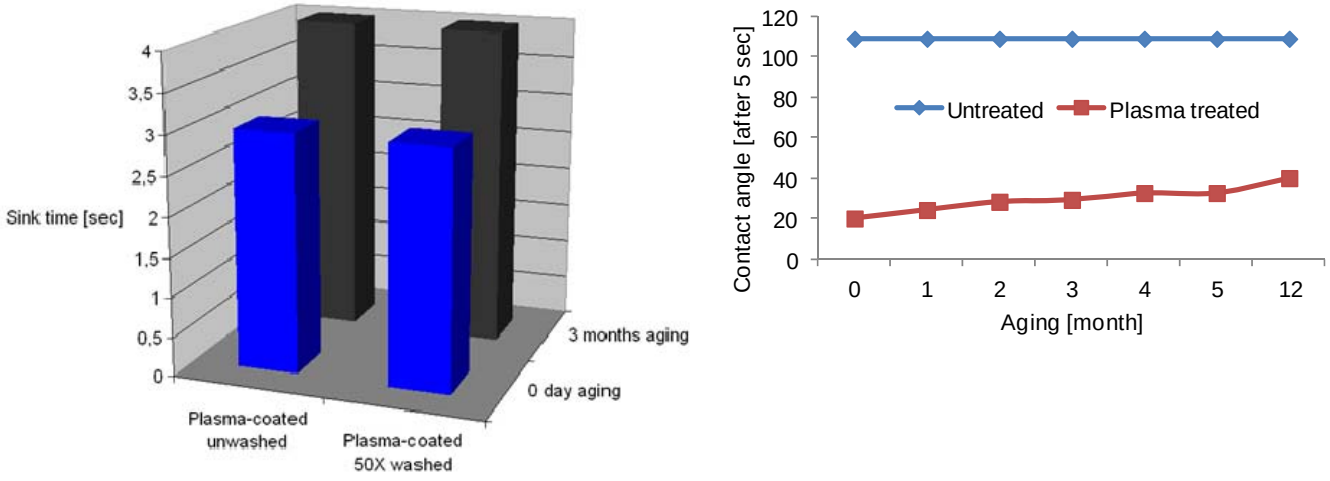

Fig. 2. The wash durability of the plasma-coated AR (left) and aging of untreated and plasma treated PES (right)

A super-hydrophobic surface with a very large CA was obtained by the plasma pretreatment with non-polymerized gases and followed by a grafting of perflouracrylates. Wash permanency of the hydrophobic coating has been characterized by the Bundesmann test measuring the lotus effect, water penetration and water pick up% (Tab.1). An excellent water repellency (grade 100) was obtained according to spray test even after 80 washing cycles. Oil repellency behavior has also been observed up to grade 7. Permanent modification of the textile surface can be attributed to the strong covalent bond of fluorocarbon to the plasma functionalized surface.

Treatment	Spray test grade (after 80 washes)	Contact angle (CA)	Bundesmann test (after 20 Washing cycles)			
			Lotus effect	Water penetration (ml)	Pick up (%)	g (water)/m^2
Untreated PA	0	76	1	> 400	45	.139.
Untreated PES	0	109	1	> 400	49	..135
Plasma treated PA	100	145	4	40	20	58
Plasma treated PES	100	150	5	9	4	3

Tab.1. Water repellency test by contact angle, spray test and Bundesmann test of untreated and plasma- treated fabric

Conclusion

Low pressure plasma processes have been successfully developed using an industrial plasma reactor to produce permanent hydrophilic, hydrophobic and oleophobic surfaces for the application in high-tech textiles. Plasma coating provides high density of polar groups which yield a super-hydrophilic textile surface. Durability of the hydrophilic coating has been confirmed by the aging test up to one year with a minor alteration. Bundesmann test coupled with standard spray test after 80 washing cycles indicate the wash permanency of the super-hydrophobic coating. Thus, plasma-coated textiles are able to support excellent adhesion to subsequent wet chemical processes.

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