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PLASMA IN TEXTILE INDUSTRY - TECHNOLOGY FOR XXI CENTURY?

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A b s t r a c t. Textile industry today is a varied industry using hundreds of different mechanical technologies (spinning, weaving, etc.) as well as chemical ones (dyeing and finishing operations). Plasma in textile industry gives the possibility to modify the surface properties of polymers without worsening their volume properties. Paper shows the results of investigations conducted in Poland, concerning the use of glow discharges for wool, cotton and synthetic fibre modifications.

K e y w o r d s: textile industry, plasma, modification of surface properties.

TEXTILE INDUSTRY AT THE BEGINNING OF XXI CENTURY

The term 'textile industry' refers today to a very broad spectrum of technologies and production processes ranging from the classical sequence of spinning-weaving-finishing of woven fabric to spun-bonded technology where a flat fabric is produced in one step operation from polymer chips.

From the historical point of view, textile industry is considered - parallel to beer brewing - as one of the oldest art of artisan and then industrial activity serving the basic human needs and also opening new frontiers previously inaccessible. Columbus's journey to New World and discovery of America would not be possible without (woven) sails driving his three caravels to new, unexplored continents.

The textile industry played an important part in the first phase of industrialisation in many countries. For example, the emergence of the powerful British Empire of the Victorian era could be traced to backs of thousands sheep grazing for many centuries on Yorkshire and Lancashire moors and bred in more than fifty different breeds on the English soil. The peregrination of merino flock purchased from Royal Spanish homestead to Australia in XVIII century could make as fascinating a reading as a as good contemporary technothriller, when one realises that the multitude of millions of sheep breed today in that country is very likely the offspring of just 8 sheep brought there hundreds years ago.

While the invention of driven spinning frame by Cartwright in 1785 (a clergyman who wished to ease his wife's toil behind the spinning wheel) is sometimes considered as the beginning of textile industry, it is the availability of the steam power of the XIX century to drive rapidly increasing numbers of textile machines , that catalysed the unprecedented growth of this industry.

The first dyestuff (mauveine) synthesised by Perkin in early XIX century and later rapid growth of dyestuff industry in Germany were another important contribution to the progress in textile technology.

Textile industry played important part in economical development of many countries, beginning in England and spreading to France, the Netherlands, Belgium and Germany and reaching the territory of contemporary Poland in the second half of XIX century.

The development of the Polish textile industry took a very specific way determined by political situation and decisions. The vertical start of Lodz, described sometimes as "Polish Manchester", relied not only on skilled newcomers from Saxony and toiling thousands of Polish serfs (released from drudgery by Tsar`s decree), but also on access to huge, almost insatiable markets of the Russian Empire, protected by high custom duties. The wealth of Scheibler, Grohman , Poznański and many other XIX century industrialists stemmed mainly from production of cheap, poor quality printed fabrics delivered in huge amounts to anywhere from Kiev to Samarkand.

Numerous and spectacular bankruptcies in the inter-bellum period in Poland (1918 - 1939) of textile firms which performed very well until WW I, could be partly explained by the absence of the customs protection of the domestic market.

The geopolitical changes in the aftermath of WW II brought about a situation similar to the years before WW I - once more a huge, but not so quality conscious market (Soviet Union) largely determined the direction of development of the Polish textile industry. The unexpected and rapid collapse of this industry following the transition from state-controlled to market economy in 1989 may be attributed to its philosophy (quantity is all, quality means nothing) prevailing during the state-controlled economy period 1945 - 1989.

Until 1950's the development of the textile industry was facilitated by its character – it required modest investments and vast numbers of (not-so-highly skilled) workers. The two basic technologies, i.e. spinning and weaving , required human intervention basically only for repairing faults caused by machines, such as repairing yarn breaks and exchanging full spools on spinning frames or removing warp breaks and replacing weft spools in shuttles during weaving.

The introduction of splicers for knot-free joining of yarns in 1980's of XX century brought about a fundamental change to this process and large yarn spools without even single knot are commodity products today.

In contemporary textile processing , the number of functions requiring human involvement is considerably reduced. For example the change of full spools to empty cones in the spinning mills is performed by a fully automated device and one 10 kg spool of spliced weft yarn is sufficient for at least two hours of weaving , even if the weft insertion capacity equals to 8 km/minute.

The final stages of textile processing, i.e. dyeing and finishing operations, also changed with the new available technologies and the expertise of dyemasters of the "Promised Land" years, earning better than their Directors, was replaced by not-so-expensive spectrophotometers for colour measurements and, of course, computers calculating dye recipes from databases for single dyestuffs.

The nonwovens technologies – providing a flat textile product formed by consolidation of a fibre web without spinning or weaving operations - experienced very rapid growth from their start in 1930's. The web consolidation may be achieved by various means, ranging from simple termobonding of synthetic fibres at 300 m/min up to sophisticated high-tech means such as minute water jets at 600 MPa for entangling fibres in the spun-lace technology.

The growth of non-woven technologies is fuelled by two factors, i.e. high process productivity and low production costs. Another fascinating growth factor is the almost inexhaustible product application range - from wound care to filtration webs, automotive parts, clothing materials and up to 6 m wide geotextiles indispensable in motorway construction. Lentex, which could be described as a medium nonwovens producer on world-wide scale, produces up to 300 different products each month.

At this same time, nonwovens are maturing in quality and became increasingly engineered, customised products such as three layer composites with thickness tolerances of $\pm$ 0,05 mm offered by Lentex.

The technology progress in the last 20 - 30 years has had its price, and the textile industry cost of investment reaching now 2 M US$ per working place in a green field project. At Lentex, new working place requires up to 0,25 M US$ investment, without buildings and media costs etc.

On the other hand, high initial investments pays back in increased productivity. For example, the yearly sales value per employee at Freudenberg Nonwovens (worldwide No.1) pass the 0.5 M US$ mark closely matching other industries like car or machinery manufacturing.

Since ~ 1980 the working conditions for textile industry are increasingly influenced by another influential factor i.e. environmental protection and more exactly all restrictions imposed by governments, often very vaguely related to environment or technical feasibility or daily life.

THE COMMON POINTS OF TEXTILE AND PLASMA TECHNOLOGY

From purely physical point of view, properties of textile fabrics produced from staple fibres (i.e., fibres of finite length) are determined by the coefficient of friction in fibre/fibre or fibre/steel/rubber systems. The productivity of spinning operations – the most expensive of all textile processes – is narrowly determined by the equilibrium between slipping and cohesion in fibre bundles. Hundreds, if not thousands of specific "spinning aids", increasing or decreasing fibre/fibre friction have been developed up to now; almost all contain fatty matter necessitating ample amounts of detergents and water for their removal.

The coefficient of friction and surface energy may be considered as a representative for broad range of fibre and fabric properties described as 'surface properties' . Coefficient of friction is responsible for spinning processes and also yarn and fabric strength whilst surface energy greatly influences the wettability or adhesion of coatings and resins. Plasma polymerisation excluded, low temperature plasma (LTP) may be considered as an easily controllable source of at least three factors (elements):

- electrons with energy up to 2 eV;
- ionised gas molecules;
- short weave($\lambda \leq 100$ nm) UV radiation.

This environment is highly reactive towards almost all natural or synthetic polymers and not technically feasible by other means.

The fundamental property of LTP – be it from corona discharge at 1013 hPa up to glow discharge at 1 Pa - is the limited penetration depth, hence only a very thin polymer surface layers could be modified by this process.

Considering the factors determining production costs of textile products and "technological" opportunities such as s application spectrum and quality offered by LTP, two potential application areas may be envisaged, i.e.:

- modification of surface properties;
- removing of impurities from fibres and fabrics.
- at different stages of textile processing.

In a simplified view on this technology attentive to processing costs and in so doing excluding, for example, large scale use of expensive inert gases, LTP may be seen as powerful oxidant devoid of many disadvantages of products used until now.

SURFACE MODIFICATION OF FIBRES AND FABRICS

Modification of keratin fibres.

Keratin fibres, including wool and mohair, are one of the most fascinating products created by Nature and not improved upon or copied by contemporary technology until this day. Depending on sheep's breed and grazing conditions wool fibres have an diameter of 13 - 40 microns; their useful lengths is 40 - 150 mm; but their bi-component build (core-sheath structure in fibre producer's vocabulary) and surface structure is even more fascinating. The non-cristalline inner layer (cortex) providing for up to 90 % of fibre mass is covered by highly cross-linked, cristalline layer known as cuticula; covering in scales the - fibre surface from fibre root to fibre tip like shingles on the roof. .

The differential frictional effect (DFE) resulting from the cuticula structure is also at least partially responsible for specific property of wool known as felting. Felting may be described as an irreversible change in dimensions and structure of wool fabric due to influence of water, heat and energy. DFE also determines the balance between cohesion and slipping of fibres at every stage of the spinning process.

Highly cross-linked and hydrophobic surface of wool scales may be considered as a barrier in dyeing and printing operation; as good wetting of fibre surface by printing paste followed by dyestuff diffusion into fibre is an obvious prerequisite for good prints. Good wetting of wool can be achieved today by oxidation in aqueous environment; chlorine compounds such as sodium hypochlorite NaOCl or sodium or potassium salts of dichloroisocyjanuric acid (DCCA) are commonly used as source of active oxygen. Due to unavoidable swelling of wool in water during chlorination, the changes induced by this process are not restricted to fibres surface but extend over whole fibre cross-section with negative consequences such as weight loss , yellowing and strength reduction. Environmental burden of wool chlorination is easily envisaged, the process troublesome and expensive as any involving the use of chlorine.

Paul Kassenbeck of Institute Textile de France was first to start research on work corona treatment of wool at the beginning of 1950's. Nearly a thousand publications on plasma treatment of wool and other keratinous fibres has been published over last fifty years. Between 1973 and 1995, a period of wide-ranging research projects pertaining to treatment of wool and other keratinous fibres by glow discharges has been performed at Textile Research Institute (IW) in Łódź. Two installations for continuous [air - vacuum - air] treatment of wool tops with glow discharges have been developed in the 1982 – 1992 period at IW; the first construction of this kind world-wide, demonstrating clearly technical viability of this process. The know-how for technical solutions contained in the second installation has been sold to the ELTRO company in Germany. This apparatus was capable of processing up to 40 kg/h of wool tops and could be considered as starting basis for development of an industrial scale machine.

Dramatic and almost total collapse of the wool industry, not only in Poland but also in European Union, as well as practical disappearance of International Wool Secretariat [a marketing and research organisation sponsored by Australian wool producers] in 1995, upset in practical terms any hope for industrial application of this practically proven technology.

Printing preparation of wool fabrics is a very good example to present capabilities and advantages of plasma treatment as environmentally acceptable alternative for troublesome wet chlorination process.

Table 1 presents the data for four basic parameters (max. sorption, sorption speed, starting time and total sorption time) describing the wettability of wool fabric after scouring, chlorinating and glow discharge treatment.

Table1. Wettability of plasma treated/chlorinated wool fabrics.

Sample	Max. Sorption	Sorption speed	Starting time	Sorption time
	[mg/cm^2]	[mg/cm^2/s]	[s]	[s]
scoured	36.32	0.158	9.320	697.52
chlorinated	**55.09**	7.554	0.640	**37.40**
Glow discharge treated:				
A1	51.31	5.626	7.000	71.12
A2	54.11	7.646	0.440	49.36
A3	47.91	7.579	0.440	54.04
B1	49.45	7.678	0.400	46.60
C1	53.73	7.636	0.440	44.60
C3	54.69	7.593	0.400	47.36
D1	54.17	**7.690**	**0.360**	44.80
D3	51.13	7.609	0.440	49.04
E1	53.20	7.690	0.600	49.88
E2	50.47	7.645	0.400	47.28
E3	51.96	7.642	0.440	66.36

Table 2 presents the spectrophotometric data useful in describing the print quality and also whiteness of plasma treated or chlorinated wool fabrics.

Table 2. Printing on plasma treated/chlorinated wool fabrics.

Sample	Colour yield [%]	Fixation degree [%]	Whiteness Hunter	Whitness Stensby
scoured	23.54	**116.6**	**52.7**	**49.1**
chlorinated	100.00	96.86	45.4	37.7
Glow discharge treated:				
A1	93.80	94.85	51.9	45.9
A2	87.32	94.43	50.7	45.2
A3	91.75	93.55	50.4	45.0
B1	94.69	97,97	50.9	45.5
C1	**103.75**	97.22	50.0	44.8
C3	91.21	96,39	49.3	44.1
D1	98.86	94.89	50.4	44.1
D3	102.23	**101.44**	51.0	44.7
E1	90.60	96.00	41.8	44.0
E2	87.59	85.07	42.4	45.1
E3	100.42	95.45	42.8	**47.5**

The data contained in Tables 1 and 2 clearly show the potential advantages when wool fabrics are treated by glow discharges - plasma treatment for less than one minute delivers technological results equal or better to those achieved during several hours of cumbersome wet treatment bringing considerable environmental threat.

Similar technology was used at least about 1995 in Pawlowskij Posad near Moscow for printing preparation of wool kerchiefs.

OTHER OPPORTUNITIES FOR LOW TEMPERATURE PLASMA

Likely more than fifty different application possibilities - more or less technically and economically feasible - have been described over last fifty years. All these applications can be placed in a broad area described as functionality improvements of surface properties of fibres/fabrics from natural and synthetic polymers; some specific properties/ processes are listed below:

- imparting surface wettability as an end in itself or as a preparation for subsequent technological operations;
- increased sorption capacity for electrolytes in batteries;
- surface development for improving the filtration efficiency for fine dusts;
- imparting oleophobic properties to nonwovens;
- increasing the adhesion of polyester or aramide fibres to rubber, up to cohesion breaks level;
- improving adhesion to coating agents.

Potentially, the most exciting and economically lucrative plasma technology can be defined as dry oxidation of cotton waxes; in current 'state-of-the-art.' processing, ≤ 1 % of impurities in raw cotton necessitates very drastic (pH 14, 100°C) and environmentally troublesome treatments.

MACHINERY AND EQUIPMENT FOR PLASMA TREATMENT

The discussions about advantages and disadvantages of three known sources of low temperature plasma (corona, glow and hybrid discharges) have been continuing for almost fifty years without any final conclusion. It can be concluded, however, that the ageing effect is a deciding factor for feasibility of any particular plasma source in specific application. When the time elapsing between plasma treatment and subsequent technological use is a fraction of a second as in printing of PE or PP films for packaging applications, then the selection of plasma source is not so critical and corona discharges may be considered as a good choice. On the other hand, glow discharge plasma seems to be a better choice when the time elapsing between plasma treatment and subsequent operation is long or cannot be determined in advance.

To obtain low temperature plasma from any of a.m. source, a combination of three basic subunits is required, i.e.

- discharge generation means,
- vacuum system (for glow discharges only),
- fabric /fibre transport means.

Advances in power electronics and more specifically the availability of power transistors help to close the last 'uncertainty' area in plasma research, i.e. the troublesome and often inaccurate measurements of RF power absorbed by the discharge. Complete solid state RF power delivery and measurement systems are available today from more than one supplier and many earlier publications should be verified now from this (i.e., absorbed power data) point of view.

Vacuum systems may be considered today as a cost issue and not a technical problem; a wide range of vacuum pumps - with Roots pumps as important constructions - opens the possibility for relatively inexpensive pressure reduction up to 1 - 1000 Pa range considered as suitable for glow discharge generation, even when taking into account of water vapour and air emission from large surfaces of textile materials.

With growing availability and falling prices of frequency inverters the fabric transport may too be considered as cost and not technical problem.

To summarise, the main emphasis in plasma application research is shifting now from apparatus/hardware (which can be bought or developed quite easily) to technology and unavoidable cost estimation according to realistic and not overly optimistic approach.

Two companies (Tecnoplasma in Switzerland and Europlasma in Belgium) delivered - according to their own statements – more than 10 commercial systems for plasma treatment of textile products; however none of these companies would show reference lists with customer name and place of installation.

The energy costs (0,003 – 0,09 € /$m^{2)}$ published recently by Europlasma must be considered as an convenient excuse for not publishing the equipment costs as the depreciation charges would be the major factor in any cost calculation for plasma treatment process.

Summarising, plasma treatment of textiles has moved on from the level of laboratory curiosity and may be considered to be in an early industrial development stage, its further advance depending on how quick it could solve, at acceptable costs, the technological problems irresolvable by conventional means known today.

PLAZMA WE WŁÓKIENNICTWIE – TECHNOLOGIA XXI WIEKU ?

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S t r e s z c z e n i e. Włókiennictwo jest dziś bardzo zróżnicowanym przemysłem wykorzystującym kilkaset różnych technologii mechanicznych (przędzenie, tkanie itd.) i chemicznych (barwienie, wykończenie). Zasadnicza zaleta technik plazmowych we włókiennictwie to możliwość istotnej modyfikacji własności powierzchniowych polimeru bez zauważalnego pogorszenia właściwości objętościowych. W referacie przedstawiono wyniki badań prowadzonych w Polsce w dziedzinie wykorzystania wyładowań jarzeniowych do modyfikacji wełny, bawełny i włókien sztucznych.

S ł o w a k l u c z o w e : włókiennictwo, plazma, modyfikacja powierzchni.