Fibre Chemistry, Vol. 36, No.6, 2004

LOW-TEMPERATURE PLASMA AS THE BASIS FOR CREATION OF MODERN TEXTILE CHEMICAL TECHNOLOGIES

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UDC 677.494:674:533.934

The prospects for use of plasma technologies in the textile industry finishing plant in preparation, dyeing, and final finishing of fabrics of different chemical nature are evaluated. It is shown that plasma has the greatest effect on unbleached textile materials due to the important change in their hydrophilicity. Rational schemes of including the stage of plasma activation in finishing of fabrics to increase product quality and economy of manufacture are proposed.

The physicochemical activity of plasma, known for more than 100 years, began to be investigated systematically only at the end of the 1950s. Studies of nonequilibrium plasma and plasma chemical processes in processing of polymer, including fibre-forming polymer, materials have been conducted in Ivanovo for more than four decades. The concept of structural and chemical modification of the surface of a polymer, which changes the properties of the material, has now been developed in detail and can be used in concrete manufacturing processes.

Improving the adhesive properties and strength characteristics is the basic problem in modification of film materials. For textile materials, the spectrum of solvable problems has broadened significantly. Based on an analysis of many publications, including reviews [1-3], we can with some confidence define the general and particular characteristics of alteration of the properties of textile materials. In most studies of the effect of plasma on polymer, including textile, materials, the processes that take place in gaseous medium in plasma treatment are examined and the effect of the treatment conditions on the final result, that is, changes in the chemical and physical nature of the material, the performance properties, and process effects, is evaluated. These changes basically consist of improved hydrophilicity, low shrinkage, low felting ability (for materials containing wool), and improved strength characteristics [4-8].

By varying the type and duration of discharge, current value, and flow rate of plasma-forming gas, it is possible to significantly affect the direction of the effects of plasma treatment [2]. In addition, textile materials as objects of plasma treatment that have a different chemical nature, large variety of structures, and different types of finishing in turn affect the efficiency of the plasma effect [9].

The variety of manufacturing operations in the textile finishing plant, extremely high volumes of water consumed, enormous wastes and waste treatment costs make the use of dry processing of fabrics and plasma chemical finishing involving few operations most promising.

A series of vacuum plasma chemical units developed and manufactured at Ivanovo Scientific-Research Experimental Design Machine Building Institute and designed for processing fabrics of different width and density [10] makes the use of plasma technologies in industry real. More than ten years experience in operating plasma chemical equipment at Pavlovoposad Handkerchief Manufacture OJSC (Pavlovo Posad, Moscow Region) demonstrated the high efficiency of plasma processing when it replaces chlorination in processes to make woolen fabrics nonfelting and nonshrinking.

However, despite the high efficiency of treatment with low-pressure plasma, the wide use of plasma technologies has been held back by a number of the factors discussed in [1]. Use of atmospheric-pressure plasma in barrier discharge and in glow- and diaphragm-discharge plasma-solution systems has been proposed as an alternative [1, 11].

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The basic advantages of barrier discharge consist of comparatively simple implementation, not having to maintain a vacuum, and possibility of organizing the process based on continuous technology. The drawbacks that are delaying its use are liberation of ozone in the work place [12] and lower efficiency of the effect on textile materials. However, the elevated capacity of the discharge for oxidative degradation, including of dyes [13], and the comparatively easier plasma polymerization process [9] show that the manufacturing possibilities of barrier discharge have not yet been exhausted and require careful study. At the same time, we note that the high efficacy of barrier discharge in processes of removing formaldehyde and synthetic surfactants (SF) from the solutions [14] widely used in textile plants could be purposefully applied for treatment of wastewaters and decreasing the environmental effects of textile plants.

Despite the attractiveness of the results noted in the laboratory study of the efficacy of using plasma-solution systems in bleaching of textile materials [1, 11], industrial implementation of these technologies will involve great difficulties in our opinion. This is because discharge is excited above the surface or in the working solution itself. In conditions of large-tonnage production by textile plants, the volumes of working solutions are extremely high, and a large number of complicated problems must be solved by the developers in creating industrial equipment. The prospects for use of these discharges for sterilization of solutions and articles and treatment of textile plant wastewaters to remove organic and inorganic contaminants are very attractive.

The use of available plasma equipment is now real [10]. Evaluating the role and correctly selecting the stage of including plasma processing in the manufacturing process in the finishing plant are now the basic task which will ensure the high efficiency, economy, and environmental safety of the finishing plant.

The chemical textile plant is distinguished by a large variety of manufacturing processes which can be organized by periodic or continuous schemes. However, regardless of the type of textile material and organization of the technology, wetting is the first stage of all liquid processes. The uniformity and speed of wetting determine the efficacy of impregnation of the material with the working compositions. Impregnation is most important in continuous technologies where the contact time of the material with the working solution is limited. Qualitative impregnation affects mass transfer (diffusion, sorption, desorption) of finishing preparations and dyes and determine the technical results of finishing. For this reason, most manufacturing processes require a high level of hydrophilic properties of the materials to ensure elevated sorption of the aqueous solutions in a short impregnation time.

Of all methods of intensifying impregnation (heating, steaming, vacuum evacuation, use of SF), plasma treatment is the most effective [15], since it simultaneously improves the other characteristics of a textile material by increasing the hydrophilicity. The increase in the hydrophilicity is the key effect on which intensification of manufacturing processes is based in plasma chemical activation of textile materials.

The generalized results of studies to evaluate the efficacy of using plasma processing of fabrics made of natural and chemical fibres and blends in almost the entire manufacturing line in a finishing plant — from preparation of fabrics (mercerization, scouring, bleaching), and dyeing to the final finishing, are reported below.

The fabrics were activated on a laboratory setup in alternating-current glow-discharge air plasma of industrial frequency (50 Hz) at discharge current density of ~1.5 mA/cm^2 and gas pressure of 100-130 Pa for 30-60 sec. To determine the role of plasma activation, unbleached fabrics (Active) were treated, followed by the normal manufacturing cycle, and fabrics undergoing a series of operations immediately before impregnation with the working composition (Active*) were also treated. Fabrics undergoing the traditional processing cycle were used as the reference sample (Control).

Generalization of the data obtained suggested that plasma treatment is maximally effective at the beginning of the manufacturing line, that is, during preparation, when unbleached fabrics are treated. The greatest effect of plasma treatment was noted regardless of the fibre composition, manifested by an important improvement in the finishing indexes. The cause of this is the important change in the hydrophilicity of the unbleached fibre material, which ensures effective wetting of the material by the aqueous solutions of preparations and dyes.

The contact angle of wetting θ or its cosine are used as a measure of wetting [16]. Unbleached fabrics, even those made of hydrophilic fibres, are almost not wet by water ($\cos\theta = 0$), since their surface contains hydrophobic contaminants, sizing, and oiling substances.

Plasma has a multilevel effect on textile materials: the macroradicals formed in the near-surface layer of the polymer and their recombination and oxidation increase the number of oxygen-containing polar groups, and change the conformation of the macromolecules in the near-surface layer of polymer and degree of crystallinity [17, 18], and sizing compounds decompose into gaseous products removed from the surface of the fibre by working pumps (3-8%) and the low-molecular-weight fraction dissolved in water [19].

TABLE 1. Effect of Plasma Treatment on the Hydrophilic Properties of Fabrics

Fabric as a function of processing	Satin, cotton			Shirt fabric art. 1307*			Shirt fabric art. 82225*		
	K, mm/h	τ, sec	cosθ	*K*, mm/h	τ, sec	cosθ	*K*, mm/h	τ, sec	cosθ
Unbleached	0	>600	0	0	>600	0	0	>600	0
Active	140	1	0.39	138	1-2	0.32	76	2	0.30
Bleached	146	1	0.34	142	1-2	0.30	118	2	0.29
Active	285	1	0.49	211	1	0.43	172	1	0.41

*Composition: 67% cotton + 33% polyester fibre.

TABLE 2. Effect of Plasma on Degree of Whiteness of Fabrics

Fabric as a function of treatment	Satin	Shirt fabric art. 1307	Shirt fabric art. 82225
Control	82.6	82.2	80.6
Active	82.7	82.1	80.7
Active*	85.8	84.6	82.9

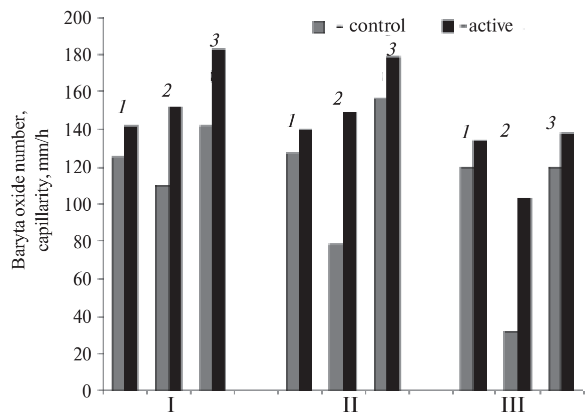

Fig. 1. Effect of plasma treatment on efficiency of mercerization and bleaching of fabrics: 1) baryta oxide number; 2) capillarity after mercerization; 3) capillarity after bleaching; I) satin; II) shirt fabric art. 1307; III shirt fabric art. 82225.

The processes that take place change the surface microrelief, perturb its continuity, and increase in the size of the capillaries in the textile material [9], i.e., changes take place in the capillary-pore structure of the cloth. This involves a decrease in the contact angle of wetting — increase in cos θ and the surface energy of the polymer, and consequently improvement of the hydrophilic and adhesive properties of the textile.

As the measurement showed (Table 1), cos θ of unbleached materials increased from 0 to 0.30-0.39. This was accompanied by an increase in the capillarity (*K*) from 0 to 76-140 mm/h and a decrease in the wetting time (τ) to 1-2 sec. Hydrophobic fabrics thus became hydrophilic with properties characteristic of fabrics undergoing a complete preparation cycle. Plasma treatment of prepared materials with elevated hydrophilic properties is not as straightforward.

The results of studying mercerization and boil-off (Fig. 1) of activated and unbleached fabrics in all probability indicate the intensifying role of plasma treatment. The surface hydrophilization and increased sorption properties facilitate impregnation of the materials with the viscous mercerizing and cooking solutions and make it effective and uniform over the bulk of the fibre material. An increase in the quality of preparation is the result: 13-17 unit increase in the baryta number, 20-70 mm/h increase in capillarity. It is thus possible to decrease the concentration of components in the working solutions by 35-50% without worsening the quality of preparation.

TABLE 3. Effect of Plasma and Method of Preparation on Dyeability of Fabrics (*K/S*)*

Fabric	Unbleached fabrics		Washed fabrics		Boiled and bleached fabrics	
	control	active	control	active	control	active
Purple (Disperse Purple K, Active Purple 4K)						
Shirt fabric art. 1307	4.0	6.6	6.7	7.1	9.4	9.8
Shirt fabric art. 82225	6.8	8.6	8.3	11.2	11.8	11.8
Satin	3.8	7.1	7.6	8.2	11.5	11.6
Blue (Disperse Blue 2, Ostazine Blue)						
Shirt fabric art. 1307	3.6	6.9	7.2	9.1	12.6	12.6
Shirt fabric art. 82225	4.5	6.5	5.8	7.0	7.4	7.6
Satin	3.4	6.7	6.8	7.4	8.9	9.1

*$K/S = (1 - R)^2/2R$ is the color intensity, expressed by the Gurevich–Kubelka–Munk function; R is the reflectivity of the dyed cloth.

TABLE 4. Color Intensity (*K/S*)

Dye	Method of preparation	
	acid desizing	plasma treatment and washing
Vat Bright Green SP	70.4	99.0
Vat Blue	6.9	7.5
Procyon Scarlet	20.3	25.9
Reactive Blue KH	10.1	16.9
Green TP pigment	99.0	124.0
Scarlet 2STP pigment	9.4	12.9

In bleaching fabrics that have undergone mercerization or boil-off, plasma treatment has almost no effect: the degree of whiteness of these materials is on the level of the control samples, which indicates levelling of the effect of plasma treatment (Table 2). At the same time, if boiled fabrics (Active*) are treated with plasma immediately before impregnation with the bleaching solution, the whiteness indexes can be increased by 1.5-3 abs. %. However, this method is not promising technologically since it interrupts the preparation cycle.

The observed maximum effect of plasma on unbleached fabric (see Table 1) can be purposefully utilized in coloring processes.

Unbleached cloth is most frequently dyed with sulfur dyes. However, the assortment of industrial and special materials is constantly expanding. For some of them, preparation operations for hydrophilization before dyeing are not economically advantageous, since hydrophobic, dirt- and oil-repellent finishing is subsequently conducted. Plasma treatment of these materials reduces outlays for operations and ensures intense and even coloring, which is difficult to attain for fabrics with a high surface density. The combination of plasma treatment and washing increases the color intensity and strength. The results of a study of dyeing of cotton and cotton-polyester fabrics with active (satin) and a mixture of active and disperse dyes (shirt fabric art. 13067 and 82225) purple and blue are shown in Table 3. The same tendency is clear here: the plasma has the maximum effect on unbleached fabrics, and in washing of activated fabrics, its effect decreases and is almost not observed for bleached materials.

In our opinion, this effect is caused by the low stability of the effect of plasma activation [9]. It was found that the effect of hydrophilization of fabrics is decreased by washing in water, heating, and to a great degree, by steaming, that is, factors that take place in almost any stage of the finishing plant manufacturing process. At the same time, it is also necessary to note that washing of plasma-activated unbleached fabrics not only does not worsen their hydrophilicity but instead increases it due to removal of decomposed sizing preparations from the textile. For this reason, plasma treatment combined with washing of activated fabric in water can be recommended as an effective method of preparation of fabrics and for dyeing by stamping and could replace traditional kinds of preparation.

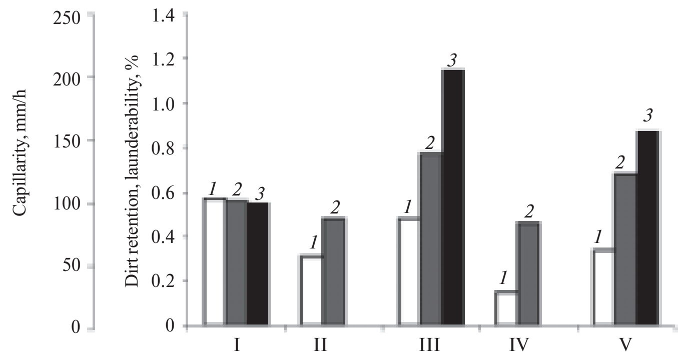

Fig. 2. Effect of plasma on antisoiling properties of "suit" fabric (wool:PET 55:45): 1) dirt retention; 2) launderability; 3) capillarity; I) initial fabric; II) finished fabric; III) plasma-treated fabric; IV) fabric undergoing plasma treatment and finishing; V) fabric undergoing finishing and plasma treatment.

TABLE 5. Effect of Plasma Treatment on Hydrophilic and Soil-resistant Properties of Fabrics Made of Chemical Fibres

Fibre	Cosθ		Capillarity		Launderability of soiling			
					oily, points		dry, rel. units	
	control	active*	control	active*	control	active*	control	active*
Polyester	0.16	0.87	50	105	1	4-5	0.60	0.79
Cellulose triacetate	0.21	0.90	72	105	3-4	5	0.74	0.83
Polyamide	0.18	0.92	30	50	4-5	5	0.64	0.79
Blend of cellulose triacetate and polyamide	0.22	0.94	72	150	3	5	0.66	0.90
Blend of polyamide and pol yester	0.19	0.93	40	194	3	5	0.57	0.78

This is indicated by the results of a comparative evaluation of the quality of stamping of art. 062412 fabric (linen:cotton:polyester fibre 50:40:10) with the natural color of flax fibre undergoing acid desizing and plasma chemical preparation. An undoubted advantage of plasma technology is not only the increase in the intensity of the colors in stamping using different classes of dyes (Table 4) but also preservation of the strength of the cloth and the natural color of the background of the fabric. In addition, more uniform distribution of the stamped color and the absence of "erratic" stamping and easier washing of the dyed fabrics were observed.

Plasma activation to intensify impregnation of prepared fabrics with dye solution or before application of the stamping composition improves the dyeing and strength indexes of the colors and hues and can be used in coloring fabrics of high surface density or with a large number of hydrophobic fibres.

The use of plasma in final finishing is of special interest. The variety of the effects of plasma on textile materials and their elevated stability (in treatment of prepared materials) form the basis for recommending plasma activation for any assortment of fabrics as an independent stage of the manufacturing process. It can be especially timely for fabrics made of chemical fibres or containing chemical fibres. The hydrophobic character of these materials causes their electrification, easy soiling by dry and oily contaminants, and makes it difficult to remove soil from the cloth. Plasma hydrophilization of the surface of such fabrics makes them soil-resistant and facilitates removal of dirt by washing (Table 5).

On the other hand, the variety of final finishing processes and high product quality requirements allow recommending the use of plasma both for intensifying the manufacturing processes and for giving the finished fabrics qualitatively new properties. For example, antisoiling agents together with the soil-repellent effect give textiles hydrophoby, which is unacceptable for suit fabrics since it worsens the hygienic properties of the articles. Preliminary treatment in plasma increases the finishing effect but does not decrease the hydrophoby of the fabrics after sizing. The solution to the problem is to treat finished fabrics in plasma, as this will preserve the soil-repellent effect and increase the resistance to routine laundering and dry cleaning while preserving the hydrophily of the textile (Fig. 2). An insignificant decrease in the effect (increase in the degree of dirt retention) is compensated by much better removal of dirt in laundering.

In many cases, plasma treatment can significantly reduce the manufacturing process or replace individual stages. In particular, when a textile is given hydrophilicity, it is almost always temporary, and plasma treatment eliminates the stage of solution preparation from the manufacturing cycle. This is possible, for example, in water- and oil-repellent finishing of materials of high surface density and in processing cotton—polyester fabrics with a lace effect [2].

In discussing the place and role of plasma treatment in textile finishing plant technology, it is thus necessary to note that they are determined by the manufacturing problems in the plant and the requirements for the consumer properties of the fabrics.

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