Influence of Low-Temperature Plasma Conditions on Wicking Properties of PA/PU Knitted Fabric

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ABSTRACT: Plasma surface treatment has been extensively applied in the textile industry for the modification of polymer materials. In this study low-temperature plasma (LTP) is used for surface treatment of polyamide/polyurethane (PA/PU) knitted fabric. The envisaged plasma effect is an increase in the surface energy of the treated textile, leading toward improved hydrophilic properties. The knitted fabric was treated by LTP using three non polymerizing gases: oxygen, air, and carbon dioxide. After plasma treatment, wettability of samples was tested through their wicking properties measuring capillary rise after water bath contact. The PA/PU knitted fabric samples treated with different plasma gases exhibited different hydrophilic performances. The influence of plasma variables (discharge power, time, pressure) was investigated. Although the chemical characteristics of elastan (PU) and nylon (PA) threads are different, the study has demonstrated that plasma treatment can in the same time alter the surface-wetting behavior of both the components of the knitted fabric. It was also shown how these treatments can be regulated to produce the desired level of hydrophilicity dependently on the request application. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3702–3706, 2008

Key words: nylon; elastomers; surfaces; hydrophilic polymers; modification

INTRODUCTION

To meet specific demand for sophisticated applications, polymer modification has received increasing attention in the last years. Usually chemical modification on surface to promote superficial functionabilities such as hydrophilicity, dye affinity, and fluid permeability or selectivity ''upon'' or ''through'' the textile material is used. These treatments usually alter either the bulk or the surface of the polymer substrates. Beside these methods, plasma treatment is an environmentally friendly alternative. Gas plasmas are complex mixtures of highly excited atomic, molecular, ionic, and free radical species. Although gas plasmas have been recognized for many decades, it is only recently that this technology has become available on a commercial scale. It has attracted the interest of a wide variety of industries,[1] which perceive environmental advantages of gas plasma treatments over traditional textile coating procedures. Indeed, gas plasma treatment offers great potential for significant improvements in fibre surface properties, based on changes in physical and chemical properties resulting from introducing functional nanostructures.[2] Plasma treatment modifies the upper-most atomic layers of a material's surface without impairment of its bulk mechanical properties. Moreover, this finishing can advantageously replace some wet chemical applications as an environmental friendly process.[3] For example, surfaces treated in oxygen plasma can be equipped with well-known functional groups (e.g., $-C=O$, $-O-H$, $-C-O-$) in a thin surface layer of the polymer.[4,5] One valuable property of gas plasma treatments is the ability to alter the hydrophilicity or hydrophobicity of a textile surface. Many investigations on plasma treatments of several fibers for changing their wettability characteristics are available.[6–8] The up-to-date literature survey shows that there are many works dealing with the plasma treatment of textiles and fibres. This research was supported by M.I.T.I. S.p.A. (Urgnano-BG, Italy), manufacturer of high-performing knitted fabrics for sportswear, with the aim of developing a finishing process to improve hydrophilicity and, consequently, to increase the dyeing speed and color yield of its dual-component knitted fabric. To obtain such a result in this work, a low-temperature plasma (LTP) treatment with different nonpolymerizing gases was performed on PA/PU knitted fabric, because the final results will largely depend on the nature of the gases used.[9] The samples were treated in oxygen, air, and carbon dioxide at low pressure by varying the time and the discharge power in a laboratory reactor to better understand the parameters
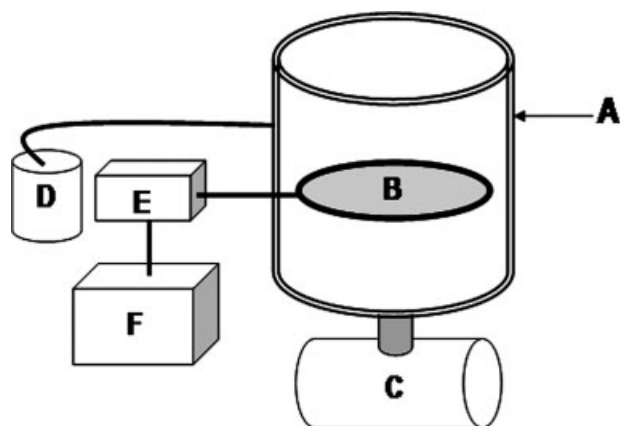
Figure 1 Plasma reactor system: (A) vacuum chamber, (B) sample holder, (C) vacuum system, (D) gas bomb, (E) matching network, (F) radio-frequency source.

influencing the hydrophilic properties of polymer surface. Surface morphological and physicochemical characterization would be required to fully analyze the effect on the textile by plasma treatment. As masterly described by Verschuren et al.,[10] in this article more than a deep knowledge of surface modification by analytic methods, the wicking properties describe in a better way the transformation that occurred in the whole bicomponent knitted fabric. Influences of the plasma parameters on knitted-fabric wettability have been tested by the wicking properties of samples, measuring capillary rise after water bath contact.[11]

EXPERIMENTAL

Materials

Three bars warp-knitted fabric two-way stretch (280 g/m^2), with 3D effect due to brushed back face, produced with continuous filament yarn of polyamide 6 (44 dtex polyamide, PA) and elastan (40 dtex polyurethane, PU) for sportswear applications was used in the present study. It was kindly supplied by M.I.T.I. S.p.A. Before plasma discharge, the knitted fabric was washed in 2% nonionic detergent at 40°C for 20 min, treated in petroleum ether for 1 h and then rinsed several times with deionized water, dried, and put into drier for storage. It was finally cut into 5 cm × 30 cm strips. The cleaned samples were conditioned under standard atmospheric pressure at 65 ± 2% relative humidity and 21 ± 1°C for at least 24 h prior to all experiments.

LTP treatment

The low-temperature plasma reactor system (produced by MOMA Srl) schematically represented in Figure 1 was used. It consists of a cylindrical cham-

ber, 1000-mm inner diameter and 1000-mm long, connected to a vacuum line.

A gas distribution tube is mounted along the inner wall. Two electrodes are assembled around the chamber and connected to an RF generator, which provides a field of 13.56 MHz in the power range from 5 to 1000 W, adjustable with a setting device. A gas controller module enables regulation of the flux in the range from 0 to 1000 cm^3/min and a vacuum gauge indicates the pressure starting from 0.5 Pa. In all the treatments, the gas flux was selected by changing the pressure in the range 0.02–0.12 mbar. The fabric strips were hung on the inner reactor chamber. For every treatment time, five samples were positioned among two clamps over the reactor sample holder. Knitted fabrics were located 50 mm apart and they laid 20 mm from the samples holder. The treatment times, discharge power values, and system pressure reported in Table I refer to the overall plasma treatment.

Treatment efficiency evaluation

A glass chamber for ascending paper chromatography was adopted as the experimental apparatus. The efficiency of the plasma process is quantified by measuring the liquid wicking rate, which quantifies the hydrophilic behavior of the PA/PU knitted fabric.[12–14] The strips were suspended vertically with the lower end dipped in a layer of water. The front of slope of the water on white fabric clearly indicated the capillary rise height and a ruler marked off in millimetres put beneath the strip made the height measurements easier. The height reading time was fixed at 3600 s. The repeatability of plasma treatment and capillary rise measurement was tested by comparison between the five fabric strips plasma treated in the same conditions; the average height values at the same time were mostly reproduced within the measurement error (±0.5 mm). For the untreated PA/PU knitted fabric, the liquid wicking rate was zero. Test results are reported in diagrams showing the wicking properties in terms of capillary rise (in mm) as a function of treatment conditions.

RESULTS AND DISCUSSION

The samples were treated at the followings conditions: oxygen LTP (RF power: 750 W; gas flux:

TABLE I
Values Range for LTP Parameters

| Plasma parameters	Unit	Values
Treatment time	s	15–250
Discharge power	W	250–1000
System pressure	mbar	0.02–0.12
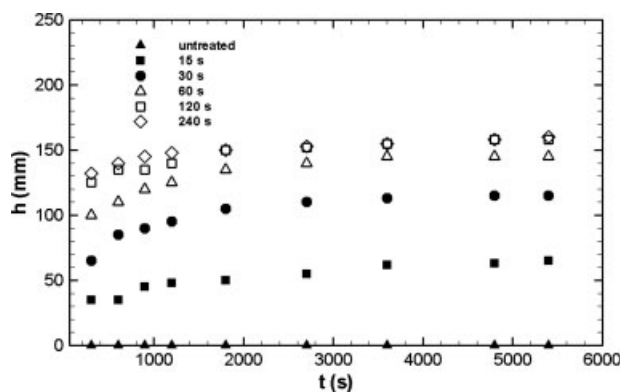
Figure 2 Relationship between the time of permanence in water and capillary rise on PA/PU knitted fabric after oxygen plasma treatment at different exposure time.

350 cm^3/min; treatment time: 0–240 s). To define a generally applicable observation time, the capillary rise was measured for different treatments and at different bath contact time. Figure 2 shows the time evolution of capillary rise for different plasma treatment times. Independent of the plasma treatment time, all the samples showed a different wicking rate as function of the water bath contact. Whatever treatment time is concerned, the capillary rise can be considered constant only after 3600 s of bath contact. This is the reason why all the processor factors were estimated at this time.

System pressure dependency

The dependence of the wicking properties on the pressure was investigated for different plasma gases: O_2, CO_2, and air. In all the investigated cases, the pressure was varied between 0.02 and 0.12 mbar. The samples were prepared by applying plasma powers of 1000 W and a treatment time of 60 s. Figure 3 reports the capillary rise (h) variation with pressure for the three tested gases. The diagram
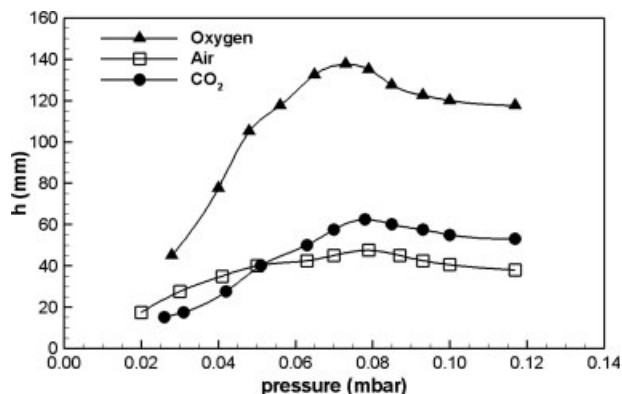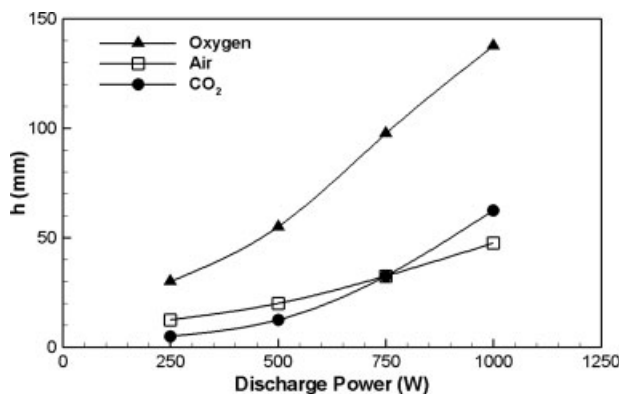
shows that the HRO dependence on pressure variation is not linear.

In the investigated pressure range, h increases in the low-pressure region and decreases in the high-pressure region, resulting in the peak value that occurs at a certain pressure typically in the range 0.07–0.08 mbar. The presence of a maximum around 0.07 and 0.08 mbar can be justified by the relationship existing between plasma electronic density and pressure.[15] The presented results are in good agreement with typical oxygen plasma treatment pressure vs. electron density behavior.[16] Kim J.-S. and Kim G.-H. report electron density distributions as a function of applied pressure for different power discharge values, measured by Langmuir probe. In the present work, a similar trend was also found for the other tested gases, even if with lower effects on water capillary rise. For low gas pressure values, the hits between electrons and molecules become so rare that the number of electrons that can be produced will be smaller. When the pressure grows a larger degree of ionization occurs, and therefore a greater density of the reactive species in the plasma can be observed. Up to the observed peak, the pressure rise increases the particles for unit volume. Because of the greater frequency of collisions, the fraction of electrons that has energy values suitable to contribute to the formation of other electrons decreases.

Discharge power dependency

The discharge power dependency on the wettability of the treated samples was also studied. The following treatment conditions were chosen: treatment time: 60 s; plasma gases: O_2, CO_2, and air; pressure: 0.08 mbar; discharge power: 250–1000 W. The upper limit was fixed by the maximum equipment discharge power. Figure 4 reports the capillary rise h as a function of this variable for the different plasma gases tested. Whatever plasma gas is concerned, an

Figure 3 Process pressure as a function of capillary rise for O_2, air, and CO_2 plasma treatments (RF Power = 1000 W).

Figure 4 Influence of discharge power on capillary rise (h) for different gases.
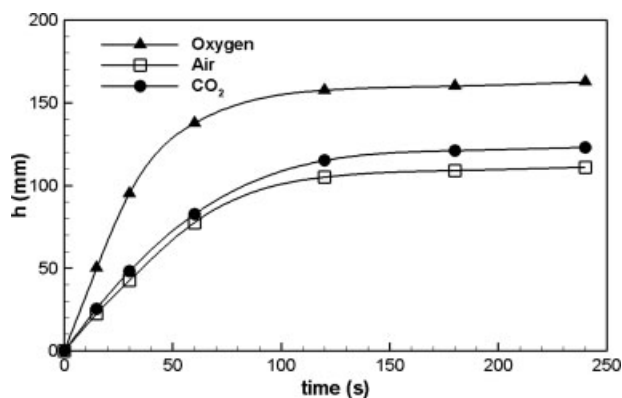
Figure 5 Relationship between the time of treatment and capillary rise (h) for different gases.

increase of power gives rise to an increase of the h. The O_2 plasma clearly shows higher h values. The air and the CO_2 give lower results with the CO_2 more incisive for power values higher then 750 W.

In fact when the RF power increases, it is possible to transfer a greater energy to the gas, thus improving its ionization and the density of the reactive kinds that are formed i.e., electrons, ions, radicals, intensity of irradiation. Therefore, higher plasma discharge power increases the amount of active species, and consequently the formation of polar groups on the surface.

Treatment time dependency

The treatment time of the samples with different gases was finally studied for the following conditions: P = 0.08 mbar and RF Power = 1000 W. Figure 5 shows the dependence of HRO on the treatment time for the different plasma gases. Plasma treatment considerably improves the water adsorption properties of the PA/PU knitted fabric. In fact, the vertical wicking rate initially increases with treatment times. The results also show that the dynamic adsorptions of the material treated for different times follow a very similar trend. As shown in Figure 5, there are at least three distinct zones in each adsorption curve. The first zone is the initial stage of water adsorption, which occurs over the first few seconds. The rate of adsorption is very high during this period. This can be due to oxidation and other chemical changes of the surface that increase the number of polar groups. Already after a 15-s treatment, a significant increase of the capillary rise can be noticed. The rate of adsorption gradually reduces: this region could be called a transition zone. The third zone represents the steady-state period. When the sample is treated during more than 125 s, the evolution in height of the water front does not change anymore as a function of treatment time.

This can be explained by the fact that the plasma treatments result from the equilibrium among chemical groups from the plasma to the substratum and ablation of molecules from the substratum to the plasma.[17] A maximum treatment time can be fixed: over this time the ablation of the material becomes more important and therefore what was previously added is removed together with other portions of the polymer. This stabilizes the effect of the plasma-implanted hydroxyl groups and their influence on the wettability. In addition, short treatment time is best because long exposition at UV radiations also causes an oxidation reaction that may severely damage the substrate.[18]

These results have underlined that the O_2 plasma always gives higher wettability on treated samples in comparison to untreated knitted fabric. This is true for all the tested conditions. In fact with a longer exposure time under LTP using oxygen gas, the amount of plasma-created hydrophilic groups would increase correspondingly.[19] As the result, on the samples treated under these conditions there is a higher affinity with water molecules in comparison to the other investigated gas plasmas.

CONCLUSIONS

The processing of capillary rise data proposed in this study allowed the characterization of the wettability of one PA/PU knitted fabric improved by low-temperature plasma treatment in different gases. The study showed that O_2 gas plasma at low pressure has stronger wettability effects than air or CO_2 gas plasma and this effect depends on the exposure time, the discharge power, and the pressure of the treatment. In fact, changing these parameters O_2 has showed more suitable surface functionalization to improve wicking properties. This can be related to the interlock of gases-based polar species resulting from the interaction of the knitted fabric surface with the species present in the O_2 plasma compared with other gases. It is well known that wettability improvement after oxygen plasma treatments is due to the formation of new polar groups on the surface, such as carbonyl ($>C=O$), carboxylic ($-COOH$), hydroxyl ($-OH$) and peroxide ($-COO-R$) groups.[20] It is evident from the capillary rise over time and other process parameters that the capillary rise may be ascribed to the increased polarity by surface oxidation.[21,22] Indeed, without treatment no rise can be obtained. This improvement can be observed by analyzing the variation of wicking properties versus plasma conditions. In the discharge power range tested (250–1000 W) an increasing number of active species able to provide an hydrophilic improvement of samples was obtained by rising the discharge

power up to the maximum value (1000 W). The variation in exposition time shows that 125 s are long enough to obtain optimal hydrophilicity: longer times do not get better results. A good agreement with literature data about oxygen operating pressure values was found. This range, typically 0.07–0.08 mbar, was observed also for the other gases tested. The aforementioned plasma conditions will allow increasing the dyeing speed and color yield of PA/PU knitted fabric. Although the applied method does not employ contact angle measurements or surface modification investigations, it can be used as a valuable tool providing useful information for the industrial application. These results also give interesting hints to possible fast treatments in the textile industry: it is an environmentally friendly dry process, which does not involve any of the solvents required for the wet chemical process, without altering bulk characteristic of materials.

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