Surface Modification of Polyester and Polyamide Fabrics by Low Frequency Plasma Polymerization of Acrylic Acid

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ABSTRACT: In this study, the surface characteristics of polyester and polyamide fabrics were changed by plasma polymerization technique utilizing acrylic acid as precursor. This monomer was used to produce hydrophilic materials with extended absorbency. The hydrophilicity, total wrinkle recovery angle (WRA°) and breaking strength of the fabrics were determined prior and after plasma polymerization treatment. The modification of surfaces was carried out at low pressure (<100 Pa) and low temperature (<50°C) plasma conditions. The effects of exposure time and discharge power parameters were optimized by comparing properties of the fabrics before and after plasma polymerization treatments. It was shown that two sides of polyester fabric samples were treated equally and homogeneously in plasma reactor. For polyester fabrics, the minimum wetting time, 0.5 s, was observed at two plasma processing parameters of 10 W–45 min and 10 W–20 min, where untreated fabric has a wetting time of 6 s. For polyester fabrics, the maximum value was obtained at 60 W–5 min with the wrinkle recovery angle of 306° where the untreated fabric has 290°. The optimum plasma conditions for polyamide fabrics were determined as 30 W–45 min where 2 s wetting time was observed. Wrinkle recovery angle of untreated polyamide fabric was 264°. In this study, after plasma polymerization of acrylic acid, wrinkle recovery angle values were increased by 13%. No significant change was observed in breaking strength of both fabrics after plasma treatment. J Appl Polym Sci 104: 2318–2322, 2007

Key words: textile; plasma polymerization; polyamides; polyesters; surface modification

INTRODUCTION

Plasma is described as fourth state of matter. It contains a wide variety of active particles (electrons, ions, radicals, metastable excited species) and vacuum ultraviolet radiation. Two types of plasma exist—high temperature plasma and low temperature plasma. High temperature plasma is found at atmospheric pressure in either its manmade form, such as a plasma torch, or its natural form, such as lightning. Low temperature (also called low pressure) plasma techniques are suitable for modifying solid surfaces and improving their surface properties. In general, reactions of low pressure plasmas with solids can be classified as surface reactions, plasma polymerization, cleaning, and etching. Surface modification by low pressure plasma treatment illustrates many important advantages over other techniques such as environmental safety, uniformity and reproducibility, diversity of reagent gases, and selective modification with minimization of bulk property change.[1]

Nylon fibers, with its relatively high degree of crystallinity of 65–85%, as well as polyesters of degree of crystallinity of 20–60% are forming hydrophobic synthetic fabrics. Problems connected with textile hydrophobicity minimizing are usually solved by textile fibers' surface chemical modification. Surface treatments can generate well-defined and specific features on fiber surfaces. The conventional surface modifications have been performed by various chemical treatments. These processes are usually accompanied with damaging of bulk fibers, and affect fiber's properties. Additionally, properties of the ''finishing treatments'' in textile industry are confronted with hard ecological requirements and there is permanent search for an alternative treatment method. From ecological point of view, application of plasma for fabric modification seems to be superior to classical chemical wet processes. Much research effort has been dedicated to improving hydrophilicity of polyethylene terephatalate because hydrophobicity of polyethylene terephatalate contributes to some of its less desirable properties such as poor wetting and soil-release behavior in aqueous liquids, attraction to oily soils, low adhesion to rubber and plastics, and the tendency for static elec-

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tricity buildup. Surface energy and polarity of a polymer can be increased by incorporating hydrophilic compounds with conventional methods or plasma polymerization.[2–4]

Plasma technology is offering an attractive way to add new functionalities such as water repellence, flame retardance, hydrophilicity, crosslinking, sensor applications, fiber-reinforced composites, and biocompatibility due to the nanoscaled modification of textiles and fibers.[5] Using hydrophilic monomers (i.e. acrylic acid, acrylamide) as precursors for plasma polymerization or applying oxygen plasma etching are the two choices to give hydrophilic properties to fibers. The latter of these choices is widely used for textiles.[6–13] The former is used for the functionality of polymers,[6,14–16] but graft polymerization after plasma treatment is more common for textiles.[2,17,18] Cuong et al.,[2] treated poly(ethylene terephatalate) knitted fabrics with a mixture of He–Ar gas plasma and after grafted with acrylic acid. The durable wettability of fabrics was significantly improved. Cernakova et al.[17] activated polypropylene nonwoven fabrics by an atmospheric-pressure plasma treatment using surface dielectric barrier discharge in N_2 and ambient air. Then samples were grafted using catalyst-free water solution of acrylic acid. The grafted nonwoven exhibited improved water transport and dyeing properties. Chen and Chiang[18] treated poly(ethylene terephatalate)/polyethylene nonwoven fabric by direct-current pulsed plasma treatment followed by thermal-induced graft-polymerization with acrylic acid. Hydrophilicity and water retention of fabrics permanently increased. Öktem et al.[6] treated fabrics in acrylic acid, water, air, argon, and O_2 gas plasmas. They evaluated the treated fabrics according to wettability, dyeing, and soiling behavior, and also they compared the scanning electron micrographs of samples. They concluded that all *in situ* plasma polymerization types improve wettabilities, and therefore, dyeability and soil resistance (ΔE value) of the fabrics.

In this study, the effects of plasma polymerization of acrylic acid on the hydrophilicity, wrinkle recovery and breaking strength properties of polyester and polyamide fabrics were investigated.

EXPERIMENTAL

Materials

100% polyester and polyamide fabrics were used. The properties of fabrics are given in Table I. Fabrics were cut into the sizes of 27 × 12 cm^2. They placed on a frame (whose outer sizes were 27 × 12 cm^2 and inner sizes were 24 × 9 cm^2), so that the both sides of the fabrics could be exposed to glow discharge.

Acrylic acid (Aldrich Chemical) was used as monomer in low frequency glow-discharge plasma system.

TABLE I
Properties of Fabrics

Fabric	Area mass (g/m^2)	Setting (cm^{-1}) Warp	Setting (cm^{-1}) Weft	Linear density Warp	Linear density Weft
Polyester	144	21	21	Nm 46	Nm 46
Polyamide	221	46	38	Nm 54	Nm 54

Plasma treatment

Plasma polymerization treatments were carried out in PICO LF (low frequency, 40 kHz) plasma polymerization system (Diener electronic GmbH + Co. KG, Germany). At first, the reactor was evacuated to 30 Pa and then monomer inlet was opened and monomer (acrylic acid) vapor was allowed to flow through the reactor for 10 min to remove impurities. Monomer flow rate was kept constant at 200 cm^3/min. Then power was adjusted to 10–60 W, and the fabrics were exposed to glow discharge for 5–45 min. At the end of the process, the generator was turned off and monomer vapor was continued to flow for 10 min to deactivate free radicals. Polyamide and polyester fabrics were modified in various plasma polymerization conditions (discharge power: 10, 30, 60 W and exposure time: 5, 20, 45 min). The effects of power and exposure time parameters on the absorbency, wrinkle recovery angle, and breaking strength were evaluated by statistical software, MINITAB® for Windows.

Hydrophilicity measurements

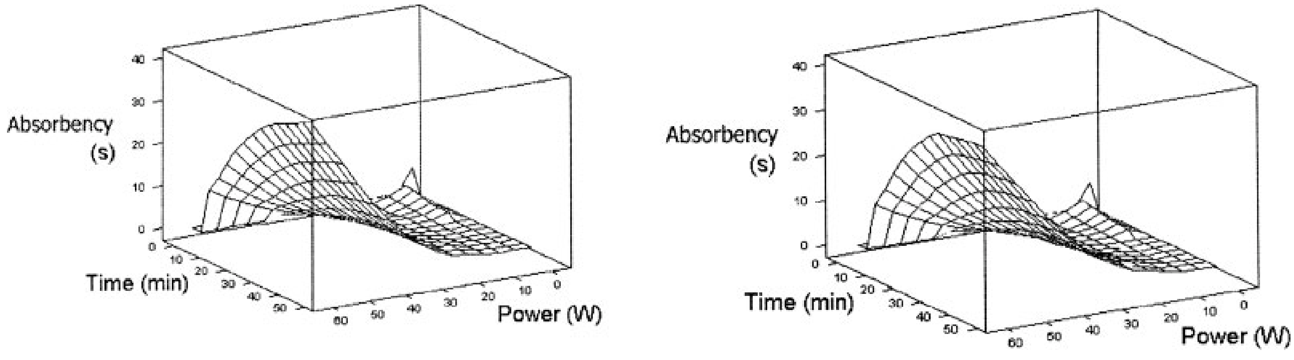
The hydrophilicity of fabrics was determined by means of wetting time (absorbency) measurements before and after plasma polymerization, according to AATCC Test Method 79. Distilled water was dropped on the fabric, and the time required for the specular reflection of the water drop to disappear was recorded as wetting time. The shorter wetting time indicates better hydrophilicity.

Wrinkle recovery angle measurements

Total wrinkle recovery angle (WRA°) of the samples was performed according to DIN 53890 for 30 min. Wrinkle recovery angle of specimens in warp (W) and fill (F) directions was measured separately then summed up to obtain the total wrinkle recovery angle.

Breaking strength

Breaking strength measurements of fabric was realized at Instron 4411 Universal Tensile Tester, according to ISO 13934-1. Test length was 10 cm, and speed was 100 mm/min.



a b

Figure 1 The effect of glow-discharge power and exposure time on absorbency (a) upper surface of polyester fabric, (b) lower surface of polyester fabric.

RESULTS AND DISCUSSION

Plasma treatments can be applied to all form of textile products such as fibers and fabrics. The characteristics of fabrics are mainly affected by the type of precursor used, precursor flow rate, plasma generator power applied to the reactor, generator frequency, and the exposure time of the substrate to the glow discharge.

In this study, we mainly focused on the effect of a specific precursor, acrylic acid, which is widely used to increase the hydrophilic character of the surfaces by plasma polymerization technique[6,17] and by wet chemistry, to enhance the hydrophilicity, total wrinkle recovery angle, and breaking strength of the selected fabrics, polyester, and polyamide.

Hydrophilicity of fabrics

The effects of discharge power and exposure time parameters on the hydrophilicity of polyester and polyamide fabrics were evaluated by MINITAB software and presented in three-dimensional graphics in Figures 1 and 2. The figures show how exposure time and power affect the wetting time of fabrics during plasma.

The homogeneity of the plasma processing of fabrics was checked by measuring the absorbencies of upper and lower sides of polyester fabrics and the results are presented in Figure 1(a,b). As seen in the figures, the behavior of the both 3D curves was almost the same. In other words, two sides of polyester fabric were affected equally with plasma conditions in the reactor.

For polyester fabrics, the minimum wetting time, 0.5 s, was observed at two plasma processing parameters of 10 W–45 min and 10 W–20 min, where untreated fabric has a wetting time of 6 s. For higher values of these conditions, the wetting time progressively increased and went beyond the wetting time of untreated fabric. It may be caused by the breaking off the C—O and then C=O bonds of hydrophilic carboxyl group with increasing discharge power and exposure time. The deposition or polymerization of the polymeric structures on the substrate surfaces is one of the main goals of the plasma processing of materials for surface modification. However, if the deposition/polymerization occurs in some certain conditions of the plasma processing, the removal of the formed film or etching of the bulk structure of the substrate is commonly observed in glow discharge operations.[14,15,17] Because of this fact, at higher values of exposure time and discharge power of the plasma processing of the polyester fabrics with acrylic acid, the hydrophilic behavior of the material may vary drastically from 0.5 to 40 s wetting time.

The optimum plasma conditions for polyamide fabrics were determined as 30 W–45 min, where 2 s wetting time was observed. The wetting time values for short exposure times for all discharge power values were fairly high (>110 s). Because of the linear molecular chain and compact structure of the polyamide fabric, the reaction rate of the plasma-excited acrylic acid molecules was relatively slow. This behavior was energetic, but unreacting molecules directly transfer their energy to the weakest bonds at the end groups

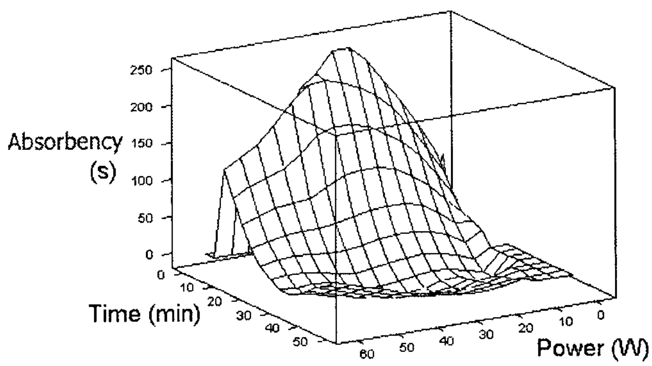


Figure 2 The effect of glow-discharge power and time on absorbency of polyamide fabric.

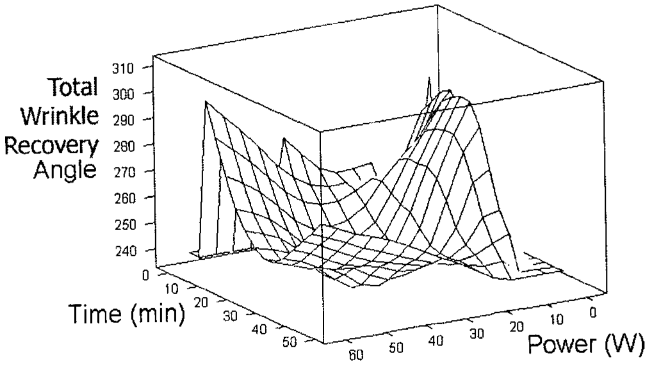


Figure 3 The effect of glow-discharge power and time on total wrinkle recovery angle of polyester fabric.

and backbone of the polymeric substrate chain such as C=O (2 × 250 to 2 × 374.5 kJ/mol) and C—O (360–380 kJ/mol) to create a hydrophobic surface.[19–21] Therefore, polyamide may become hydrophobic in the conditions of short exposure times.

Wrinkle recovery angles of fabrics

The method used in conventional durable press finishing is mainly focused on applying a crosslinking agent to form covalent crosslinks between molecules.

Figures 3 and 4 show the effects of the discharge power and exposure time on wrinkle recovery angles of polyester and polyamide fabrics, respectively. For polyester fabrics, the maximum value was obtained at 60 W–5 min with the wrinkle recovery angle of 306° where the untreated fabric has 290° wrinkle recovery angle. The results for polyester fabric mainly indicates that the glow discharge treatment of the substrate with acrylic acid deposits on the surface of the polyester structure and forms covalent bonds with main chain, but they did not form a new polymeric film on the surface.

For polyamide fabric, high wrinkle recovery angles were obtained at 60 W–5 min, 30 W–5 min, 10 W–5 min, and 10 W–20 min plasma processing conditions where 296, 294, 295, and 297° wrinkle recovery angles, respectively. Wrinkle recovery angle value of untreated polyamide fabric was 264°. The high values of wrinkle recovery angles were obtained at the conditions where the wetting times were low. These results were in a good agreement with the literature.[22,23]

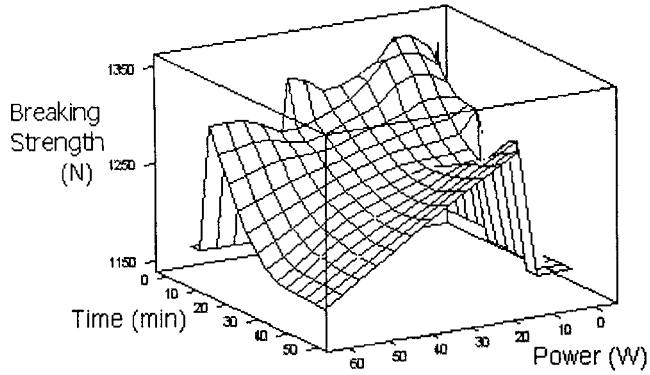


Figure 5 The effect of glow-discharge power and time on breaking strength of polyester fabric.

Breaking strengths of fabrics

Usually, most chemical finishes applied to fabrics causes undesirable changes in fabric performance such as decrease in tensile properties. The loss in mechanical properties is due to reduction in fiber extensibility by crosslinking with the monomeric resins. Therefore, the evaluation of mechanical properties after finishing is important to avoid loss in some properties on the expenses of other properties.[24]

Figures 5 and 6 show the effects of discharge power and exposure time on breaking strengths of fabrics. The highest breaking strength was obtained at 30 W–5 min (1441 N) and lowest breaking strength was obtained at 60 W–45 min (1389 N) plasma conditions for polyester fabric. The untreated material has breaking strength of 1432 N. Those results show that the plasma treatment of polyester fabric with acrylic acid

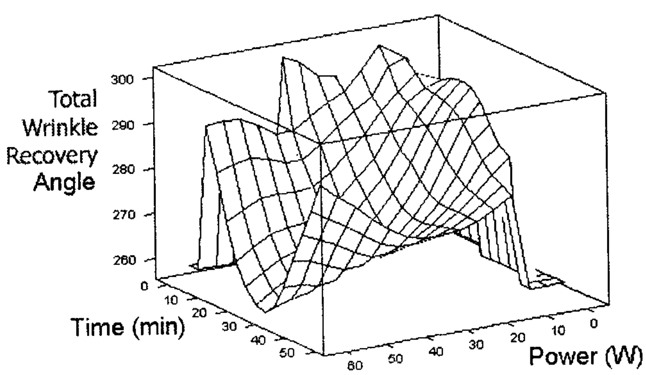


Figure 4 The effect of glow-discharge power and time on total wrinkle recovery angle of polyamide fabric.

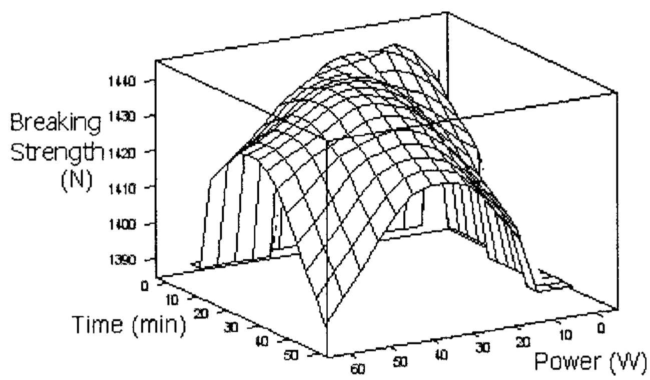


Figure 6 The effect of glow-discharge power and time on breaking strength of polyamide fabric.

precursor does not significantly affect the breaking strength of the material under any condition of plasma processing.

In the extreme conditions of the plasma processing such as, highest applied power of 60 W at the longest exposure time, 45 min, the structure of the polyamide matrix was etched to some extend and the breaking strength were reduced to the order of ~1100 N. This value corresponds to approximately 13% reduction in physical strength of the material. For the moderate conditions, the changes in the breaking strength values were less than ±1.0%. Those results showed that the mild plasma conditions were not affecting the chemical structure; therefore, physical strength of the main polymer chain remains as it is.

CONCLUSIONS

An attempt has been made to prepare hydrophilic polyester and polyamide fabrics by a novel technique so called plasma polymerization. Hydrophilicity, wrinkle recovery angle, and breaking strength parameters were selected as the main criteria for observing the effect of glow-discharge plasma modification of polyester and polyamide surfaces. One of the most important parameter, hydrophilicity, was improved by employing well-known monomer ''acrylic acid'' as precursor. This modification caused significantly positive changes on hydrophilicity and wrinkle recovery angle, and further did not cause any undesired effect on breaking strength.

We can clearly conclude that the surface modification of materials and fabrics, which are convenient to be modified by plasma polymerization technique, could have very significant and extended properties after processing. Surface energy, dyeability, biocompatibility, and many other properties can be improved by plasma processing of materials. To improve the hydrophilicity, wrinkle resistance, flame retardancy, and other properties of the textile materials by utilizing different types of plasma parameters and precursors are the main goal of our research group and radio-frequency (RF, 3.56 MHz) or low-frequency (LF, 40 kHz) plasma processing of fabrics are still under investigation.

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