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Surface modification of polypropylene nonwoven fabrics by low temperature plasma followed by chitosan grafting

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ABSTRACT

Polypropylene (PP) non-woven fabrics have been treated with low temperature plasma treatment. Subsequently, the plasma treated samples were grafted using chitosan. Surface properties of the treated samples were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, anti bacterial efficiency, water drop test and dyeability measurements. The grafted non-woven exhibit improved antibacterial efficiency and dyeing properties.

KEYWORDS

Polypropylene;
Plasma;
Nonwoven;
Chitosan.

INTRODUCTION

Synthetic fibers are now of great importance in textile production. Among many synthetic fibers, polypropylene (PP) has been widely used because of its strength, abrasion resistance, resiliency, and low cost[1-3]. Polypropylene (PP) non-woven fabrics produced by the melt-blowing and spun-bonding process have found great utility in many diverse applications. Different attributes or properties of the fabrics are required depending on the application. Polypropylene (PP) nonwovens have been produced for a wide range of applications such as agriculture, coalescing, health, adsorbents and etc. In spite of some good properties like chemical and abrasion resistance, low cost and ability to be recycled, PP has very week hydrophilic and bonding properties. Therefore, any surface modification method such as plasma, capable of overcoming these shortcomings is of importance[4].

A conventional method used for imparting the desired permanent hydrophilicity is chemical graft polymerization requiring the use of organic solvents and a catalyst that, however, presents both health and environmental concerns. An environmentally attractive alternative to the use of organic solvents is the low temperature plasma surface activation of PP non-woven, where polar molecular fragments affecting the wettability and radicals serving as the reactive species for the graft polymerization are formed on the fabric fibers surfaces[5,6].

To activate a hydrophobic PP nonwoven fabric surface, plasma pretreatment is widely recognized as a clean and effective method. Plasma processing involves reactive chemistries derivative from electrons, ions, and free radicals. Low temperature plasma processing is progressively applied to activate the outermost surface of a polymer, likewise, not to affect its structural dimensions. Both, ionized species and free radicals in the reactive plasma may interact with molecular chains of the substrate[7].

In the other point of view, chitosan is a biocompatible and biodegradable natural polymer with antimicrobial activity, biological functionality, and non-toxicity[8].

The presence of free amino groups helps in biological activities. One of these is the antimicrobial activity[9]. Also chitosan has got wide application in textile dyeing and finishing as a substitute for the various chemicals used in textile processing[10].

The major problem of chitosan is its poor durability on textile fabrics due to its lack of strong bonding with fabrics. A number of chemicals have been employed to textile goods to solve this problem. Many of these chemicals, however, are toxic to human beings and do not easily degrade in the environment. Plasma is an excellent candidate for an eco-friendly textile finishing. Surface modifications with plasma treatment have been studied widely for textile and polymer materials because plasma processes are environmentally friendly and reduce wet chemical and energy consumption[11-13].

It is aimed in this work to study the effect of plasma treatment with air and nitrogen gases followed by chitosan grafting treatment on surface modification of polypropylene nonwoven Fabrics. This study utilizes specific treatments combined with physical and biological evaluations to optimize the modified surface. Our aim is to widen the application of this porous and disposable material for biomedical use. Besides the antimicrobial activity on PP fabric, other textile properties such as dyeability, have also been studied

EXPERIMENTAL

Materials

Nonwoven polypropylene Fabric (Spun bond, SUBS 18 gsm, width 19 cm) was prepared from Baftineh Co. (Malayer, Iran), and used in all experiments. Before LTP treatments, in order to minimize the chance of contamination, samples were washed with 1% nonionic detergent solution in 70 °C water for 15 min and then rinsed with water for another 15 min, and dried at room temperature. Air and nitrogen gases (high purity) were supplied by the Air Company (Iran). Acetic acid was purchased from Fulka co. We have used acidic dye (C.I. acid red 151) for dyeing processes. Chitosan from Merck (deacetylation degree of 85%) was obtained and used. All other reagents were of a commercial grade of purity.

Cold plasma process

A direct current (DC) magnetron-sputtering device was used for plasma treatment[11-13]. Air and nitrogen gases were used as working gases. An aluminum (Al) post cathode was used because of its lower sputtering rate. Fabric samples were put on the anode in plasma reactor.

The chamber was pumped down to 2×10^{-3} torr using a rotary pump, and then air or N_2 was admitted into it up to a pressure of 5×10^{-2} torr. During the plasma treatment, power was very important, considering the low melting point (165–173 °C) of the fabrics. After a series of preliminary experiments, the most suitable experimental conditions for the low pressure plasma activation of the fabric surface were found and the samples were activated with best condition of plasma. The current and voltage of the system were kept constant at 200 mA and 1000 V, respectively. It was found that, 5 min exposure time for both of used gases is enough for activation of the samples. It should be mentioned that both sides of fabric samples were activated by plasma treatment.

Treatment of nonwoven PP fabric with chitosan

For grafting experiment, the chitosan powder was dissolved in the deionized water containing 4% acetic acid. The final concentration of the chitosan solutions were 4% and 8%. Immediately after plasma activation, chitosan was applied to polypropylene fabric by a pad-dry-cure method. Polypropylene fabric was padded with the chitosan solution at 80% wet pickup, dried at 90 °C for 3 min, and cured at 100 °C for 2 min. Polypropylene fabrics grafted with chitosan were then washed by immersion in deionized water for 5 min for removing the non grafted chitosan from the surface of samples, which was repeated for two times. They were then dried at 60 °C for 20 min.

Testing of antibacterial efficiency

In the bacterial counting test, Luria-Bertani media (LB) broth was used as the growing medium for Staphylococcus aureus. Bacteria were dripped into10 ml of LB broth to reach a cell concentration of 10^8

(CFU)/ml. Then this was diluted to a cell concentration of 10^6 (CFU)/ml. The fabric samples (1 cm × 1 cm sizes) were put into a 1ml bacteria suspension, and all samples were incubated for 24 h at 37^o C. Then from each incubated sample, 100 μl of solution was taken and distributed over an agar plate. All plates were incubated again for 24 h, and the colonies formed on them were counted. The percentage reduction was determined as follows:

$$\text{Reduction (\%)} = (C-A)/C \quad (1)$$

Where C and A are the colonies counted on the plate of the control and on the treated sample, respectively.

Fourier transform infrared spectroscopy

The functional groups on the surface of samples were examined using FTIR spectrometer (Bomem MB-100, Canada).

Morphological study

The surface morphology of untreated and treated fabrics were observed using a scanning electron microscope (SEM, Philips, XL30, Netherland) with an accelerating voltage of 25 kV. The samples were pre coated with gold, using a sputter coater (SCDOOS, Bal- Tec, Swiss made).

Water drops test

Hydrophilicity of fabrics has been evaluated by determining the wetting time in seconds using the drop test. The test schematically consists of laying down a droplet of water of constant volume on the surface of the fabric and measuring the time required for its complete absorption[14]. Results indicated in this work are the average of at least four measurements.

Dyeing processes

For dyeing process, aqueous solutions, containing 3.0 wt.% of the acid dye (C.I. acid red 151) were employed for dyeing polypropylene nonwoven. The bath ratio was 1:40 (1 g of fabric in 40 mL of dye solution). The following dyeing condition was adopted: initial temperature 40 °C, followed by a temperature increase of 3 °C min^{-1} up to 80 °C, holding for 30 min at 80 °C. Two grams per liter of acetic acid for pH adjustment, was added for anionic dyeing processes. After dyeing, the fabrics were rinsed with cold-hot-cold water and then dried at room temperature.

RESULTS AND DISCUSSIONS

Antibacterial efficiency

In this research work, the antibacterial activity of PP nonwoven plasma treated fabrics after grafting with chitosan was investigated. For testing the antibacterial efficiency of the samples as mentioned before, the bacterial counting test were used. The results of bacterial counting test are shown in TABLE 1. As it can be seen, the colonies of bacteria can spread over the plate of untreated samples. But in case of treated samples, less amounts of bacteria can distributed over the plate. The results of the counting test showed more reduction percentage of bacteria in the case of plasma pretreated/ grafting with 8 % of chitosan than plasma pretreated/grafted with 4% chitosan. On the other hand it can be concluded that, plasma pretreatment/chitosan grafting treatments play an important role for increasing antibacterial efficiency. By plasma treatment as a dry and eco-friendly technology followed by chitosan grafting, antibacterial activity has been developed through incorporation of chitosan particles on PP nonwoven surfaces. Chitosan is naturally antimicrobial, hemostatic, and biocompatible, and is widely believed to have good healing properties. Also, Nitrogen pre activation plays an important role for increasing the antibacterial efficiency on polymeric substrates[15]. As it is seen in TABLE 1, the percentage reduction of bacteria for N_2 plasma treated PP and then grafting with 8% chitosan is more than air plasma treated and then grafting with 8% chitosan PP.

Fourier transform infrared spectroscopy (FTIR)

A Fourier transform infrared spectroscopy (FTIR)

TABLE 1 : The results of antibacterial

Samples	number of bacteria	Reduction%
Control without fabric	158	-
Untreated PP	147	6.9
5 min air plasma	123	22.1
5 min N_2 plasma	118	25.3
Untreated PP / 4%chitosan	87	44.9
Untreated PP / 8%chitosan	58	63.2
5 min air Plasma / 4%chitosan	80	49.3
5 min air Plasma / 8%chitosan	48	69.6
5 min N_2 Plasma / 4%chitosan	79	50
5 min N_2 Plasma / 8%chitosan	45	71.5

was used to examine the functional groups of the untreated, chitosan treated and plasma/chitosan treated nonwoven PP samples. The results are shown in Figure 1. As received polypropylene fabric exhibits some peaks at 840, 890, 960, 1180, 1370, 1450 and 2900 cm^{-1}, which are well matched to those reported in the handbook[16].

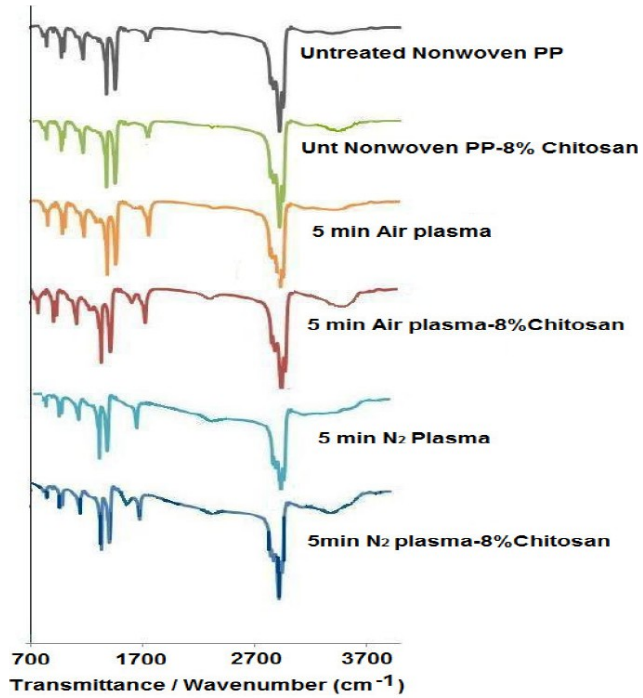


Figure 1 : The FTIR results of samples

But upon chitosan and plasma/chitosan treatments, extra peaks appear. As shown, an increase in absorbance at the 1720 cm^{-1} (C=O) band, and 1080–1300 cm^{-1} (C-O) group was noticed after plasma treatment. The peak at 3357 cm^{-1} in a broad region 3100–3470 cm^{-1} can be contributed to OH, NH or NH_2 stretch. The OH and NH bands are overlapping in the region of 3400 cm^{-1}. These functional groups were produced on the fabric by the reaction between the active species induced by the plasma in the gas phase and the fabric surface atoms. As it is seen, the peak in region of 3400 cm^{-1} is sharper for the air plasma/chitosan treated sample. The peak at 1545 cm^{-1} appears owing to the presence of NH_2 and NH deformations in amides. Also we can see that the absorption peak of -C≡N (Nitrile groups) at 2240–2270 cm^{-1} is prominent after plasma/chitosan treatment. The peaks at 3,451 and 1,651 cm^{-1} corresponded to the amine and amide groups of chitosan[17,18].

Scanning electron microscopy

Figure 2 shows the photographs of untreated nonwoven polypropylene (spun bond) with different magnification.

The effect of plasma treatment on morphology changes in nonwoven samples is illustrated in Figure 3. The untreated polypropylene filament had a smooth surface, while all plasma treated polypropylene samples exhibited surface morphology changes. As shown the treated samples have suffered some morphological changes on their surfaces, with the formation of ripple-like patterns.

Figure 4 shows the photographs of chitosan treated and plasma/chitosan treated nonwoven PP. Comparing the pictures in Figure 3 and 4, it could be confirmed that the chitosan was treated on PP nonwoven fabric successfully. From the pictures in Figure 3, it can be concluded that, more amounts of chitosan adsorbed on the surface of plasma treated nonwoven. These treatments are a key step of making antimicrobial nonwoven PP fabric.

Water drop test

When polypropylene surfaces were treated by plasma, their surface free energy considerably increased and their wet ability improved[13,15]. The results shown in TABLE 2, in which the absorption times have been recorded for different treated and original nonwoven samples. As seen after plasma treatment the water

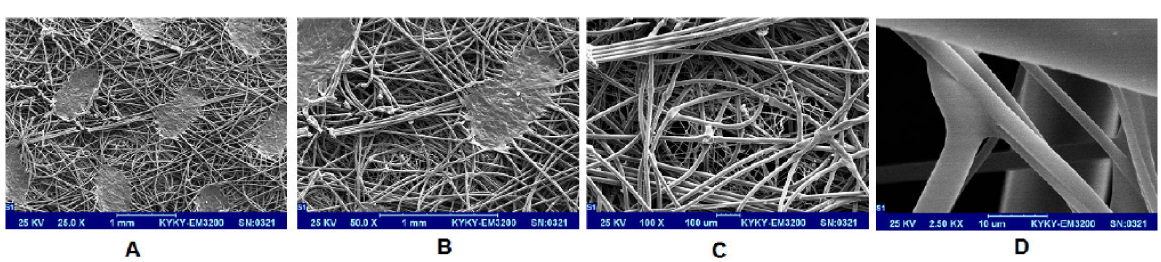


Figure 2 : SEM images of untreated nonwoven PP with different magnification, A (25.0X), B (50.0 X), C (100X), D (2.50 KX)

Figure 3 : SEM images of untreated and plasma treated samples

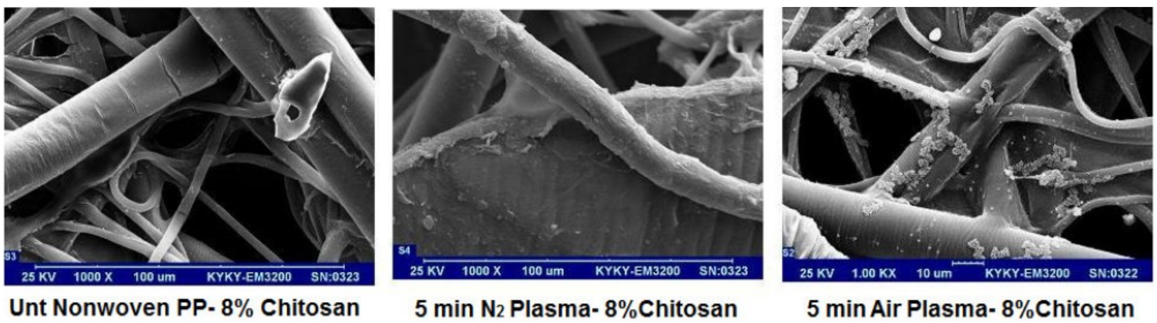


Figure 4 : SEM images of chitosan treated and plasma/chitosan treated nonwoven PP

absorption time is decreased. The decrease of water-absorption time can be attributed to introduction of polar groups such as hydroxyl and carboxyl groups due to plasma chemical modification and morphological changes.

It is also shown that the wetability of the plasma treated nonwoven PP fabric after grafting with chitosan, have been increased significantly through creating (–O–H), (C=O), (C–O), amine and amide groups on the surface of the samples and the hydrophobic property is changed to hydrophilic property.

TABLE 2 : Drop absorption time on samples

Samples	Absorption Time (h)
Untreated nonwoven PP	5:47:32
Untreated nonwoven PP/4%chitosan	2:34:40
Untreated nonwoven PP / 8%chitosan	2:16:2
5 min air Plasma	2:18:31
5min plasma N_2	2:50:3
5 min air Plasma / 4%chitosan	2:51:23
5 min air Plasma / 8%chitosan	2:16:2
5 min N_2 Plasma / 4%chitosan	2:55:9
5 min N_2 Plasma / 8%chitosan	1:2:51

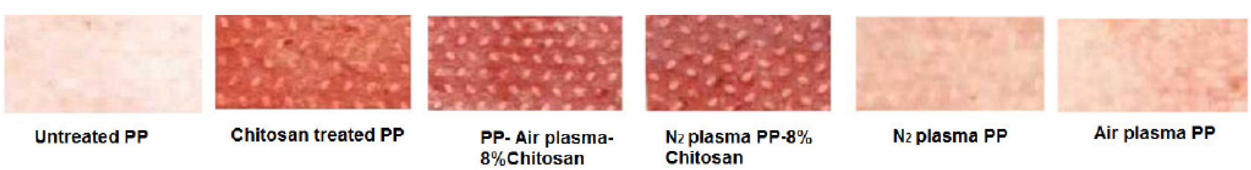


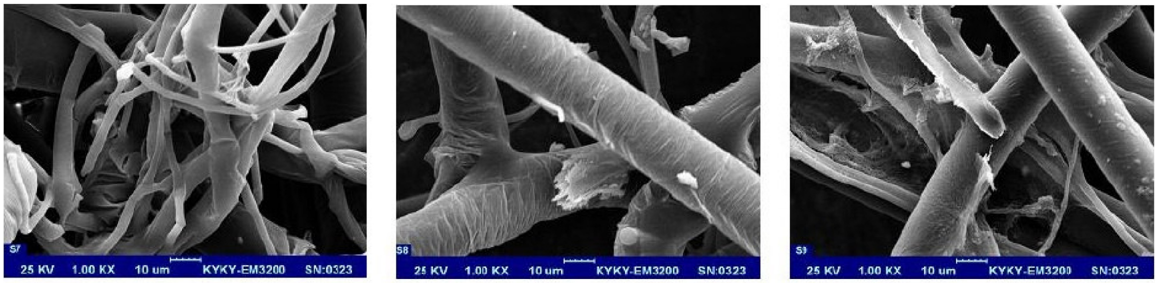
Figure 5 : The photos of dyed chitosan treated and plasma/chitosan treated Nonwoven PP with acidic dye

Time of absorption for untreated polypropylene fabrics is about 6 hours and by treating the samples with air and N_2 plasma, this time is decreased. Also, as it can be seen in the results, water absorption time for plasma treated nonwoven PP that was grafted with chitosan, decreased more than just plasma treated samples.

Dyeability of polypropylene fabrics

The dye-ability of hydrophobic fabrics, such as the PP fabrics we evaluated in this study, is very poor. It is known that introducing hydrophilic sites on the hydrophobic fabrics can improve the dye-ability of these fibers. Plasma modifications resulting in unsaturated bonds and/ or free radicals on the surface of the fabrics have a significant influence on the overall surface changes and consequently on dye-ability.

Since PP fabric has been significantly functionalized by the application of plasma and grafted with chitosan,



Unt Nonwoven PP after dyeing | 5 min N_2 plasma after dyeing | 5min N_2 Plasma-8%Chitosan after dyeing

Figure 6 : SEM images of chitosan treated and plasma/chitosan treated PP after dyeing

it is expected that its dyeing behavior would also be modified. Hence, acidic dye was applied to polypropylene nonwoven to study the effect of treatment on the degree of dye exhaustion. The results show, high dye absorption on chitosan treated PP than untreated PP sample. However the effect of plasma treatment followed by chitosan grafting on dye absorption of PP fabric is more pronounced. This could be explained based on the forces of repulsion and attraction expected to occur during the dyeing process. These forces arise due to the presence of free groups in plasma treated PP, anionic groups present in dyes, amino [NH^{+3}] ions in chitosan, besides other factors. In dyeing with the acidic dye, the amino groups on chitosan treated PP is absorbed by anionic groups of dyes. As a result, N_2 plasma/chitosan treated fabrics showed higher color strength after dyeing with acidic dye (Figure 4). It is related to more amount of positive groups on the surface of N_2 plasma/8% chitosan treated sample.

SEM analysis after dyeing

Figure 5 shows the photographs of chitosan treated PP and plasma/chitosan treated PP fabrics after dyeing. After dyeing the PP fabric, which was grafted with chitosan, more particulates showed up. And polypropylene fabrics appeared to be covered by dyestuff particles.

CONCLUSION

LTP treatment has many advantages, such as very rapid process, lower energy consumption, no environmental pollution, lower process costs. This technology is satisfying new requirements for traditional or advanced applications. In this study, dyeability and antibacterial efficiency of polypropylne nonwoven fabrics was increased when the fabrics were grafted with chitosan after being activated by low temperature plasma.

From the results of FTIR and SEM analyses, it can be concluded that, more amounts of chitosan was absorbed on the surface of plasma treated nonwoven PP. As a result of dyeing, N_2 plasma/chitosan treated fabrics showed higher color strength after dyeing with acid dyes. The increase in dyeability can be attributed to increased micro roughness, increased surface area, and the addition of functional groups, to the fabric surface.

The results of the bacterial counting test showed more reduction percentage of bacteria in the case of plasma pretreated/ grafting with 8 % of chitosan than plasma pretreated/grafted with 4% chitosan. Also, it can be concluded that, plasma pretreatment/chitosan grafting treatments play an important role for increasing antibacterial efficiency. By plasma treatment as a dry and eco-friendly technology followed by chitosan grafting, antibacterial activity has been developed through incorporation of chitosan particles on PP nonwoven surfaces. Chitosan is naturally antimicrobial, hemostatic, and biocompatible, and is widely believed to have good healing properties. Also, Nitrogen pre activation plays an important role for increasing the antibacterial efficiency on polymeric substrates. The percentage reduction of bacteria for N_2 plasma treated/grafting with 8% chitosan is more than air plasma treated/grafting with 8% chitosan nonwoven PP fabrics.

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