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# Application of Low Temperature Plasma on Modification of Polypropylene

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**Abstract**

Low temperature plasma is a useful technique to change the physical and chemical properties of textile materials. In this experiment, the effect of low temperature plasma discharge treatment (helium) on physical, mechanical and chemical properties of polypropylene fibers and fabrics has been investigated for the different duration with variation of magnetic field. Plasma treatment causes mainly physical changes by creating microcrack on fiber surface and increasing surface friction. The wettability and dyeability of fiber are increased by the treatment in such a way. As to increase in the dyeability, light reflection decreases and the fibers get duller with the treatment. The results show that in longer time treatments not only increase the surface friction but also increase the abrasion resistance, without much damage to the fiber strength. This may be a method for production of dull and semi dull polypropylene fibers.

**Keywords:**

abrasion resistance, dye exhaustion, fabric, fiber, low temperature plasma treatment, polypropylene, strength, surface modification

## 1. Introduction

The stable low temperature plasma offers a unique way to induce new characteristics of polymers and polymer combination for special applications in advanced technologies. Plasma can be a mixture of inert gas molecules, ions of both positive and negative, free radical, electrons and photons, with a net electric charge of zero and low degree of ionization [1]. The easy way to produce plasma is the use of magnetic field. The plasma produced by DC technique is very stable and in this system the test can be done in long periods and different conditions [2]. Plasma techniques are used to modify the characteristics of polymers. These techniques include the plasma induced polymerization processes, the glow – discharge synthesis of new macromolecular structures, and the surface modification and surface grafting of polymers [3]. The ion bombardment action on fibers can reveal the detail surface and internal structures of the fibers [4,5] make the molecules of surface layer of fibers activated. It is known that the surface characteristics such as wetting, light reflection, handling, friction coefficient and dye absorption play an important role in textile processing. Surface modification is effective for improvement in functionality without changing the bulk characteristics of fibers.

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Especially, the surface modification by discharge treatments, such as low temperature plasma, sputtering and corona discharge, is of great interest because these treatments could be carried out without using large amount of water and surfactant and are effective for energy saving because of dry system [6]. There are many techniques to control surface characteristics of fibers with regard to textile processing. Usually, liquid systems are mainly in textile processing applied but at present time dry systems such as plasma, sputtering, and ion beam are of much interest. Therefore, it is necessary to select the best technique complying with the purpose. Low temperature plasma treatment causes mainly chemical implantation, etching, polymerization, free radical formation, crystallization, crosslinking, improves the hydrophilic/hydrophobic and adhesive properties [3].

Towards the end of the 50's the first commercial polypropylene fibers appeared and were then given a prediction of a fantastic future as a christening present, based upon their physical and chemical analyses. However, some of the presumptions were not confirmed in practice. This initiated in some of the countries a thorough and systematic research into properties, processing and uses of the fibers with the aim to cover every possible aspect of the area. Teams of researchers from chemical, textile and engineering research institutes set about this task trying to investigated the new material fully from the fiber formation polymer, through spinning the polymer right up to the development of a wide range of textile products [7].

It was proposed to modify the fibers in the course of both their production and their processing. A foremost aim of the modifications was the improvement of dyeability or – to put it more precisely – the possibility of making the fibers surface dyeable. The dyeability problem has not been solved yet and this is why the fibers are best dope-dyed even nowadays. The attempts to modify the fiber surface by grafting have not yet found any practical use either.

In this paper, surface modification of polypropylene fibers by helium low temperature plasma treatment has been investigated on the basis of abrasion resistance, surface friction factor, thermal analysis (DSC), FT-IR, strength and elongation values and dyeability measurement.

## 2. Experiments (Samples and Low Temperature Plasma Treatment)

During this research, 100 % Polypropylene 140 Tex yarn and 100 % polypropylene plain weave with 67/2 Tex warp, 67/2 Tex weft, warp density 22/l cm, weft density 1l/1 cm and weight of 442 g/m were treated by helium low temperature plasma. The use of equipment is shown in Fig. 1. The yarn sample was warped around the two clamps of chamber. The fabric was fastened between two electrodes. The vacuum of the $10^{-3}$ torr was achieved by a rotary pump followed by a diffusion pump, which was then increased to $10^{-6}$ torr. By introduction of helium gas the pressure was adjusted to 0.5 torr (66.6 Pa.). DC plasma reactor produced helium low temperature plasma. The potential difference between the electrodes varied from 1 kV to 3 kV. The electron temperature was 3 eV and plasma current changes from 30 to 50 μA. The electron temperature and density $2 \times 10^{10}$ / $cm^3$ were measured by Langmuir probe. According to Fig. 1 the magnetic field was applied in a long cylindrical tube from out side. Due to magnetic field and magnetic force plasma focused in this case, degree of ionization increase and impurity decreased. In this experiment magnetic field can be changes from 0 to 800 gausses and we select stable condition for plasma in 380 gausses.

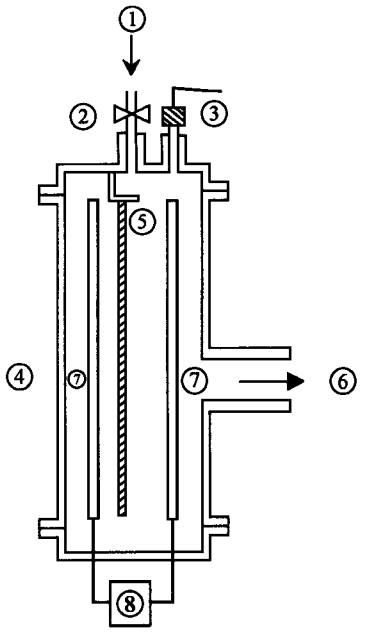


Fig. 1 Equipment's applied to perform low temperature plasma treatment; (1) Gas inlet, (2) Valve, (3) Vacuum gauge, (4) Glass jar, (5) Specimen, (6) Vacuum pump, (7) Brass electrodes, (8) Power supply.

The tests were performed at 0.5 torr using helium gas at the duration of 4, 8, 12, 16 and 20 minutes, then the samples were taken for further investigation.

## 3. Results (Dyeability of Samples)

Plasma treated and virgin polypropylene samples were dyed in an AHIBA dyeing system with C.I. Disperse Blue 56. The dyebath was comprised 3 $cm^{-3}$ acetic acid 10 % and 1 $cm^{-3}$ dispersing agent 10 % (Setamole WS). The liquor ratio was kept at 50:1. The bath temperature was set at 60°C for 5 minutes. Then the temperature was raised to 130°C by a thermal gradient of 2°C/min and dyeing operation was continued for 45 minutes. At the end of the dyeing operation, the dye concentration of each bath was measured by absorption spectrophotometer technique.

All measurements were done at room temperature and the following relation calculated the exhaustion percent:

$$E = \frac{A_0 - At}{A_0} \times 100 ,$$

where $E$ was exhaustion percent in time $t$, $A_0$ : absorption of dye solution in time 0 and $At$ : absorption of dye solution in time $t$.

The results from dyeing treatment are given in Table 1.

One of the important parameters in dyeing is the exhaustion percent in the balanced state which depends considerably on available dye absorbing places in fibers which have dye absorbing functional group and on dye diffusion ability in amorphous of fibers lacking dye absorbing functional group. After treatment the exhaustion percent value is increased with the treatment time showing the effect of plasma treatment on improving the dyeability of polypropylene fibers. One reason for this result is that plasma irradiation produces microcrack of the surface layer on the fiber, which increase surface contact. This effect is shown in the given SEM images.

Table 1 The change of dye uptake of polypropylene untreated and treated with low temperature plasma.

| Treatment time min. | Residual dye in batch g / l | Dye uptake g / l | Exhaustion % |
|---|---|---|---|
| 0 | 0.15 | 0.15 | 50.2 |
| 4 | 0.1313 | 0.1687 | 56.4 |
| 8 | 0.1388 | 0.1712 | 57.29 |
| 12 | 0.1225 | 0.1775 | 59.3 |
| 16 | 0.1183 | 0.1817 | 60.78 |
| 20 | 0.1168 | 0.1832 | 61.3 |

Table 2 The change of abrasion resistance and friction factor of treated and untreated Polypropylene.

| Treatment time min. | Abrasion resistance | Increase of abrasion resistance (%) | Friction factor ($\mu$) |
|---|---|---|---|
| 0 | 261 | - | 0.514 |
| 4 | 297 | 13.8 | 0.6 |
| 8 | 343 | 31.4 | 0.611 |
| 12 | 350 | 34.1 | 0.612 |
| 16 | 370 | 41.8 | 0.6 |
| 20 | 365 | 39.8 | 0.6 |

## 4. Physical Properties (Abrasion Resistance and Friction Factor)

The rates of abrasion resistance modification in treated and untreated samples were measured by yarn abrasion tester, the results are given in Table 2. As it is shown in the table, by increasing plasma treatment time to about 16 min., abrasion resistance is increased and hen decreased. This increased abrasion resistance is important for polypropylene fibers used in carpets due to their durability. The reason of this increase can be related to forming cross-linkage in fiber surface layers treated by helium plasma irradiation, which causes formation of powerful polymer layer on the fiber surfaces. These modifications are shown in Fig. 2.

The surface friction factor change rates of treated and untreated samples were examined by measuring sliding angle by Shirley fabric friction tester, results are given in Table 2. The results show that the plasma treatment cause fabric friction factor to be increased and time increase doesn't have much effect on increasing the friction factor. It also increases the fiber entanglement adhesion and adherence between fibers, which are useful to improve yarn quality.

SEM images of treated and untreated samples are

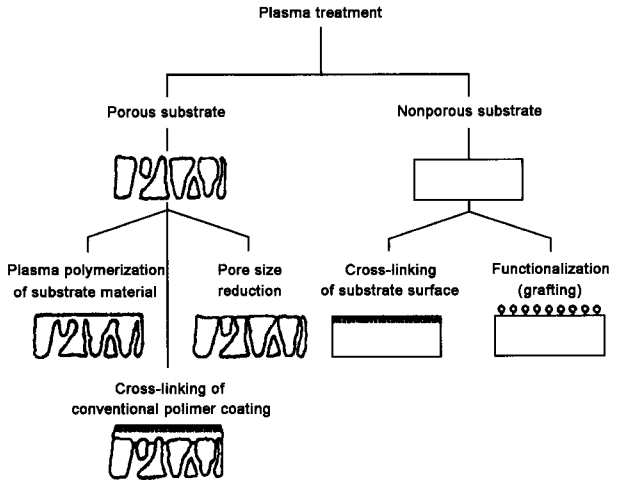


Fig. 2 Surface modification of polymers by plasma treatment.

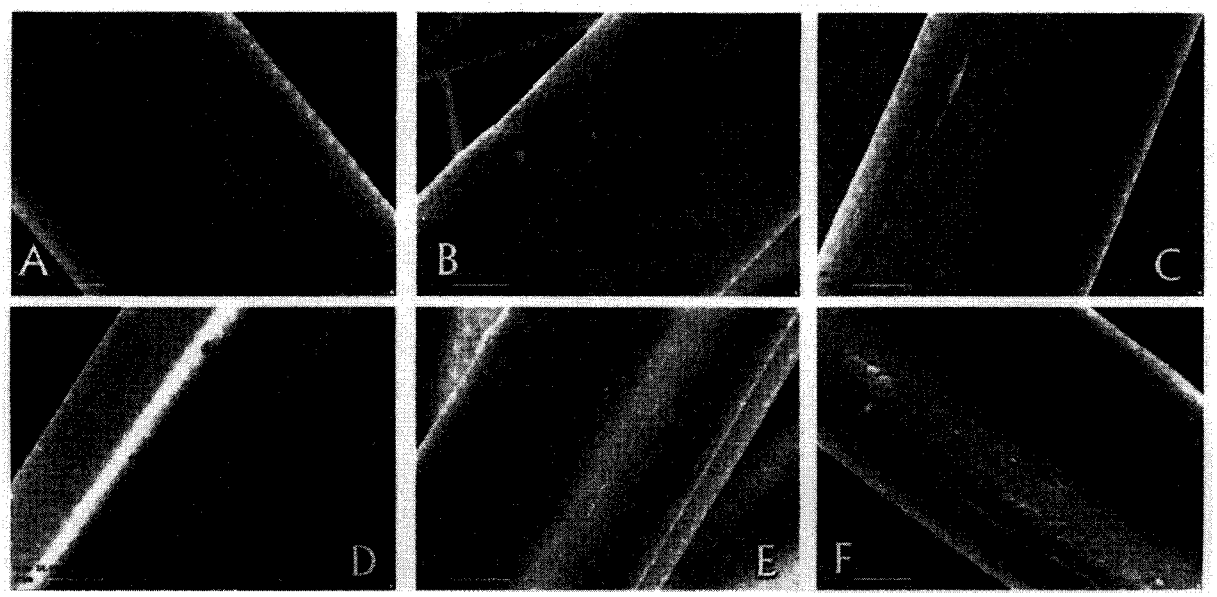


Fig. 3 SEM photographs of polypropylene untreated and treated with low temperature helium plasma, × 14000; (A) Untreated, (B) 4 min., (C) 8 min., (D) 12 min., (E) 16 min., (F) 20 min.

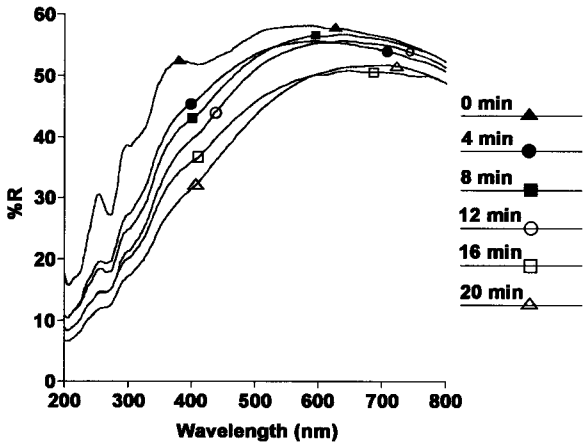


Fig. 4 Reflectance spectra of polypropylene Fabric untreated and treated with low temperature plasma.

shown in Fig. 3. They show that plasma treatment produce some microcrack on the fiber surfaces. By increasing treatment time the effects of surface unevenness changes. This structural change increases the surface friction factor, causes irregular light reflection and leads to dull fibers. In Fig. 4 the change rates of light reflection in treated and untreated samples are shown.

## 5. Mechanical Properties

In order to test plasma treatment intensity and its effect on strength and elasticity properties of polypropylene fibers; strength, elongation percent, tenacity and work of rupture of treated and untreated yarns were examined by use of Instron strength tester. The obtained results show that helium low temperature plasma treatment causes a little reduction in strength and tenacity of polypropylene yarn, and this reduction remains constant after 8 minutes.

Table 3 The change of physical properties of treated and untreated polypropylene fiber.

| Treatment time min. | Strength N | Elongation % | Tenacity cN/Tex | Work of rupture cN.cm |
|---|---|---|---|---|
| 0 | 38.81 | 36.58 | 27.72 | 288.2 |
| 4 | 37.47 | 33.76 | 26.76 | 261.2 |
| 8 | 35.42 | 33.26 | 25.3 | 272.2 |
| 12 | 35.33 | 30.04 | 25.24 | 222.64 |
| 16 | 35.16 | 32.03 | 25.06 | 231 |
| 20 | 35.06 | 32.08 | 25.04 | 317.82 |

Table 4 The change of thermal properties and crystallization of treated and untreated polypropylene.

| Treatment time min. | Melting point °C | Degradation point % | Enthalpy J/g | Crystallite % |
|---|---|---|---|---|
| 0 | 170.64 | 194.71 | 86.73 | 39.87 |
| 4 | 169.09 | 191.2 | 97.46 | 44.8 |
| 8 | 168.68 | 190.78 | 90.3 | 41.52 |
| 12 | 168.63 | 186.72 | 94.7 | 43.54 |
| 16 | 168.57 | 191.98 | 91.54 | 42.09 |
| 20 | 168.6 | 189.76 | 93.41 | 42.92 |

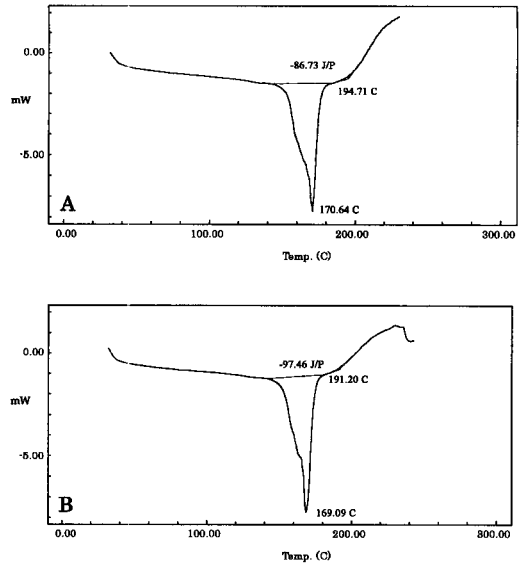


Fig. 5 DSC diagram of polypropylene. A) Untreated, B) Treated for 4 min.

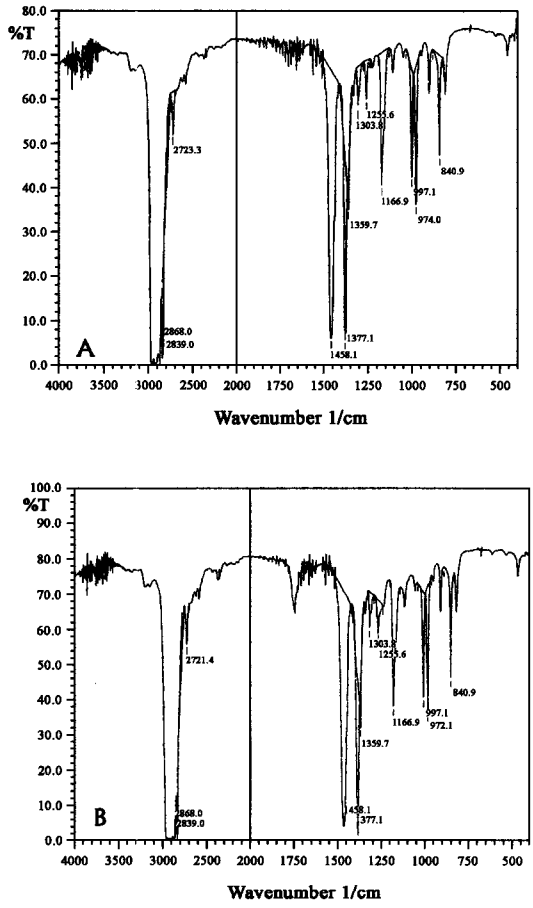


Fig. 6 FT-IR diagram of polypropylene, A) Untreated, B) Treated for 20 min.

The considerable point in the results from this experiment shows reduction in elongation at break. The reason may be due to formation of crystals near the surface of fibers. Results are given in Table 3. In order to study the changes made in structure and arrangement of molecular chains and functional groups of treated polypropylene samples, they were examined by use of thermal analysis (DSC) and FT-IR spectrometry techniques. The results from thermal analysis (DSC) show that helium plasma treatment leads to slight fall in melting point, but thermal range required melting the sample begins to increase with treatment time and then remain constant. The crystallization percent is increased too (Table 4). Increase in crystallization percent and slight decrease in melting point may be related to degradation of large crystals and formation of small crystals, which were expected, affected the abrasion resistance. DSC diagram of an untreated and treated for 4 minutes is provided in Fig. 5. Results from FT-IR spectrometry of a polypropylene sample treated by helium low temperature plasma indicate that no structural change occurred in molecular chains of polypropylene before and after plasma treatment (Fig. 6).

## 6. Conclusions

The application of low temperature plasma on polypropylene has shown effects that can be used to improve the fiber performance. The results indicate that such plasma application changes all chemical properties in such a way to enable the dyeing of polypropylene and offers a new spectrum in chemical process of these fibers. The physical properties change when larger surface crystals are broken down and replaced by smaller crystals which are shown by maintaining the melting points but changing the melting range that suggested by DSC data. This greatly increases the abrasion resistance of yarns.

There was not much effect on detected strength but reduction in extensibility was noticeable. The surface roughness appears in the SEM photomicrographs. These result from chemical reactions and microcracks on the fiber surface. The surface roughness is not a primary reason for improved wettability, but may increase it.

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