

Polypropylene fabrics pre-treated by atmospheric plasma

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Abstract

The atmospheric discharge plasma in air was used to modify the surface of polypropylene fabrics to increase their hydrophilicity. The surface properties and chemical composition changes in polypropylene fabrics during the modification process were studied. The hydrophobic recovery of PP fabrics treated by diffuse coplanar surface barrier discharge plasma during aging were also investigated, where water contact angles were determined along with chemical composition changes of PP fabrics using XPS, FTIR, and iodometric analysis. The relation between water contact angle and concentration of hydroperoxides in plasma-treated polypropylene fabrics has been discussed.

Key words: *Atmospheric plasma treatment, hydroperoxides evaluation, aging, polypropylene fabrics, surface hydrophilization*

Introduction

Polypropylene fabrics (PPF) are some of the most produced fabrics in the textile industry. The surfaces of these fabrics are practically without polar groups and are thus hydrophobic. There are many methods for modifying the surface of PPF, including low-temperature plasma treatments [1, 2]. This modification method has become increasingly popular because it does not require a large amount of conventional chemicals, benefitting not only the economy but also the environment. Hydrophobic surfaces of PPF typically have a water contact angle (WCA) above 90°. In some cases, the WCA can be substantially higher due to special modification of the PPF surface, for example, when modification is performed using fluorine compounds. On these surfaces, a water drop tends to roll off very easily, removing dirt along its path [3].

Low-temperature plasma treatment is a new technology used to modify the surface characteristics of polymeric materials. Interactions between the plasma and the surface molecules of the polymers lead to surface phenomena such as etching, cross-linking and activation [4, 5]. Atmospheric plasma pretreatment can add a large number of functional groups on the polymeric surface, depending on the processing gas in the plasma reactor. Plasma techniques [6 - 8] offer far-reaching possibilities, but the technical effort is comparatively high because the processes often have to be carried out under reduced pressure. Atmospheric air processes based on diffuse coplanar surface barrier discharge (DCSBD) provide sufficient modification of PPF. After the plasma treatment, free radicals were deposited onto the surface of the PPF, that immediately react in air with oxygen to form hydroperoxides on the surface. [9, 10].

In this contribution the hydrophilic surface modification of PPF pretreated by atmospheric plasma has been studied. The content of hydroperoxides on the PPF surface was measured using suitable analytical methods. The surface properties, hydroperoxide concentration, and chemical changes of the plasma-treated PPF surfaces were measured using contact angle measurements, iodometric analysis, XPS, and FTIR. The relation between surface properties and hydroperoxide concentration has been also studied.

Experimental

The polypropylene fabrics (VÚTCH-Chemitex Žilina) were 100% hydrophobic and had a density of 230 g/m². The fabrics had mechanical strengths of 2700 N for warp and 2700 N for weft. Potassium iodide, p.a., glacial acetic acid 99.8%, isopropanol, p.a., argon. All chemicals were of analytical grade and were used as received from Sigma-Aldrich without further purification. For contact angle measurement the double distilled water has been used.

A diffuse coplanar surface barrier discharge (DCSBD) plasma generated in an air atmosphere was used to modify the surface of the PP fabrics. The DCSBD plasma equipment was operated at 350 W under atmospheric pressure. The distance of the PES fabric surface from the electrode was 1 mm, and the plasma pretreatment time ranged from 5 to 150 s. Two parallel banded systems of electrodes made of Ag paste (1 mm wide and 50 μm thick, with 0.5 mm spacing between the strips) generated the low-temperature plasma in an effective manner. The electrodes were embedded in 96% Al₂O₃, which protected the electrodes from direct contact with the plasma and thereby prolonged their lifetime. The plasma panel was also connected to a cooling system to prevent overheating. A high-frequency sinusoidal voltage (~15 kHz, with a U_m of ~10 kV) applied to the electrodes led to macroscopically homogenous plasma generation and uniform surface treatment.

The iodometric determination is performed by oxidation of iodide ions peroxide in the acidic environment to form water and elemental iodine, which can be determined by spectrophotometry at 355 to 365 nm with respect to the blank. The free radicals arise on the PPF surface after plasma treatment, and react with air to form hydroperoxides. The hydroperoxides concentration is determined from the Lambert-Beer law: $A = \epsilon \cdot c \cdot d$. The molar extinction coefficient for the measurements $\epsilon = 25 \times 10^3$ mol/dm³·cm, where d is the length of the glass cell in cm, and c is the concentration of hydroperoxides in mol/dm³, and A is absorbance of the solution. The hydrophobicity of the fabrics was determined through measurements of the water contact angle (WCA) of re-distilled water with a Professional SEE (surface energy evaluation) System (Advex, Czech Republic). The volume of the drop of testing liquid was 3 μL. Samples were measured using 12 drops of water, and the mean value of the WCA was calculated. The surface chemical composition of the fabrics was examined by XPS using a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) equipped with a micro-focused, monochromatic Al K α X-ray source (1486.6 eV). FTIR spectra of the PP fabrics were taken from three different points in the mid-IR region (4000-650 cm⁻¹) on a Nicolet™ 8700 FTIR Spectrometer (Thermo Scientific, Madison, USA). FTIR measurements used an ATR extension with Ge crystals. The spectra were evaluated to determine the amount of oxidation in the unsaturated groups (1900-1600 cm⁻¹) and the increase in oxidation with respect to the length of plasma exposure (0-150 s) immediately after plasma treatment.

Results and discussion

Hydrophilicity

Most synthetic fibers, such as polyester, are hydrophilic, but pure polypropylene fabrics are hydrophobic with WCAs above 90°. The evolution of the PPF WCA during plasma treatment in air is shown in Figure 1.

During plasma modification, the hydrophilicity of PPF increased, as reflected by a decrease in the WCA. Figure 1 shows a precipitous decline in the PPF WCA from the original value of 128° to 97° after 20 s of plasma treatment. After 20 s, the water contact angle remained stable. A further decline occurred between 100 and 150 s of treatment, giving a final WCA of 44°. The original WCA of 128° is substantially higher than normal for PPF, which is approximately 90°. The cause of the increased WCA can be determined from a chemical analysis of its surface.

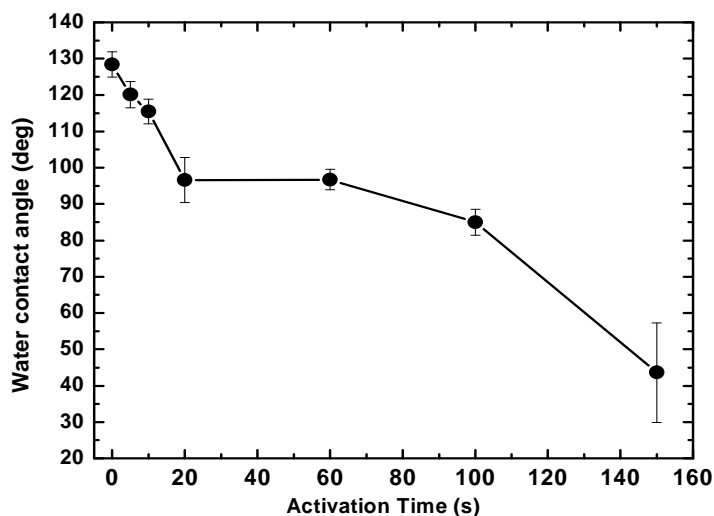


Figure 1 Water contact angle of polypropylene fabric treated by atmospheric plasma in air for various treatment times

Hydroperoxides concentration

Free radicals are created during treatment of PPF in atmospheric plasma, which then react with oxygen in the air to generate hydroperoxides. The concentration of hydroperoxides on the plasma-treated PPF surface with respect to treatment time was determined by iodometric analysis and is shown in Figure 2. As shown in Figure 2, the initial concentration of hydroperoxide in the pristine sample (0.03×10^{-3} mmol/cm²) sharply increased to 0.5 mmol/cm² after 60 s of plasma treatment, after which the concentration stabilized.

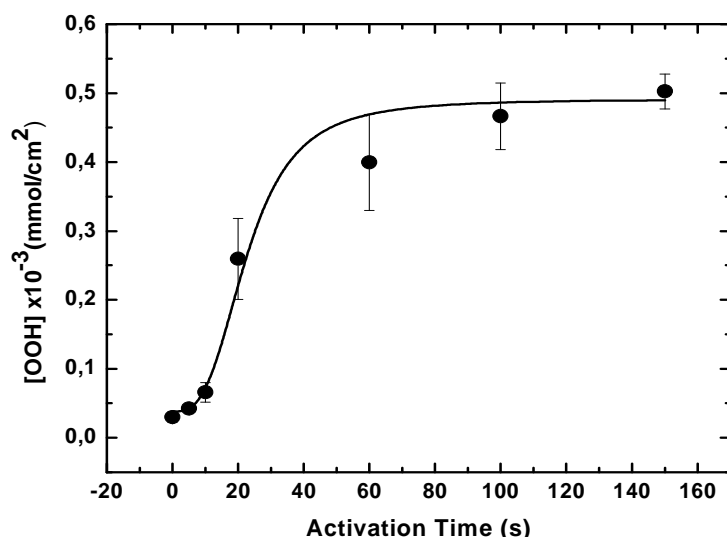


Figure 2 Hydroperoxide concentration on the atmospheric plasma-treated polypropylene fabric surface over various treatment times

Figure 3 shows the dependence of the WCA on the concentration of hydroperoxides on the PPF surface during atmospheric plasma treatment in air. As the WCA on the PPF surface decreases, the hydrophilicity increases. Figure 3 shows an increase in PPF hydrophilicity with increasing hydroperoxide content. The WCA decreased as the hydroperoxide concentration on the surface of plasma-treated PPF increased. The decrease in the WCA is relatively mild up to a hydroperoxide concentration [OOH] of 0.4 mmol/cm² after 60 s of plasma treatment. Further treatment for 100 s and 150 s caused a more rapid decrease in the WCA.

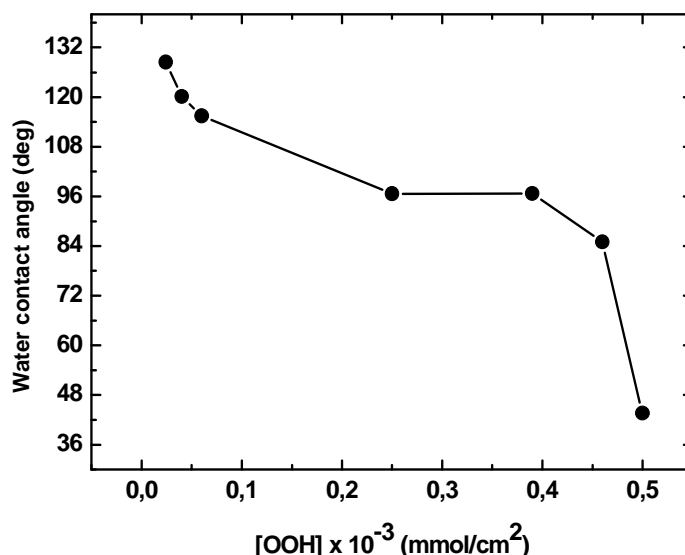


Figure 3 WCA of plasma-treated polypropylene fabric vs. concentration of hydroperoxides on the surface

XPS

The XPS results of plasma-treated PPF with respect to treatment time are shown in Table 1.

Table 1 The apparent chemical composition of the plasma-treated PPF surface as determined by XPS

Activation time of plasma-treated PPF (seconds)	Surface chemical composition [At.%]		
	C1s	O1s	F1s
0	52.5±5.2	10.0±3.1	36.6±8.2
5	49.1±2.3	13.9±0.2	34.7±2.5
10	52.8±1.4	17.7±1.5	26.3±1.6
20	51.5±1.7	18.2±0.5	27.0±1.9
40	53.2±3.4	22.6±0.7	20.0±3.0
60	52.6±2.3	27.3±1.7	14.4±1.8
100	57.3±6.7	26.3±3.4	11.1±5.1
150	55.7±3.1	30.1±3.1	8.3±5.4

According to Table 1, the moderate growth in the concentration of C, from 52.5% in the pristine sample to 55.7% in the sample treated for 150 s, was observed. The larger growth in O content, from 10.0% in the pristine sample to 30.1% after treatment, is related to the oxidation of PPF. The growth in O content on the PPF surface after plasma treatment increased the sample's hydrophilicity and caused the WCA declined as a result. The F content decreased dramatically from 36.6% in the pristine sample to 8.3% after plasma treatment for 150 s.

FTIR

Figure 4 shows the ATR-FTIR spectra of the plasma-treated PPF along with the spectrum of pristine PPF (red). It is clear from the spectra that PPF was modified upon treatment. Bands at 1280-1190 cm^{-1} are present in the spectra, which may originate both from the dye and fluorine-based compound, as XPS analysis confirmed the presence of fluorine. This can be observed by the increased hydrophobicity of the PPF surface due to the presence of CF_2 bonds in the mentioned region. As the PPF surface is treated with plasma, the formation oxidation products can be seen from the increase in bands at 1735 cm^{-1} (carbonyl region) and 1640 cm^{-1} (unsaturation region), which are sufficiently differentiated. The bands fuse after 100 s of exposure to plasma. These phenomena are dependent on the sample set, which was regarded as the sum of each strip when the strip was stretched to a maximum at 2840 cm^{-1} (CH valence vibrations of PP). The merging of bands is probably caused by the formation of networks created by the plasma.

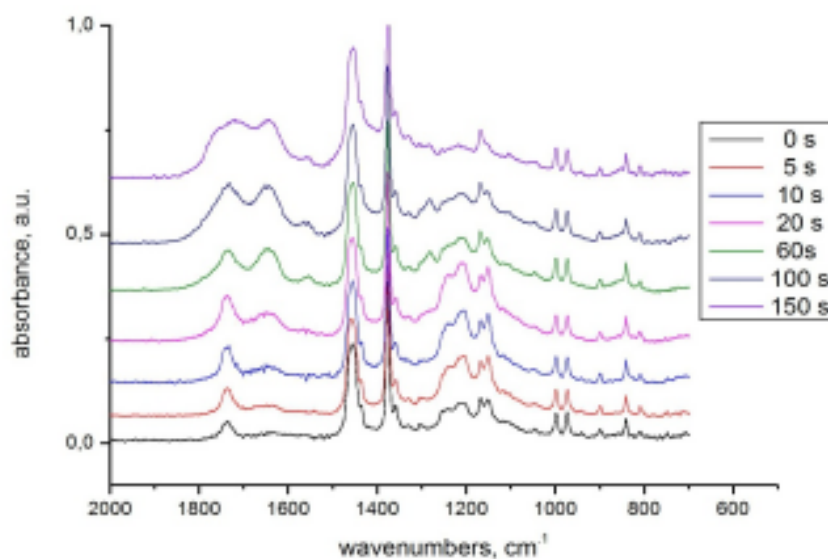


Figure 4 ATR-FTIR spectra of polypropylene fabric pretreated by atmospheric plasma in air for various treatment times

Conclusions

The WCAs of untreated PPF samples were substantially higher than those of pure PPF. An initial steep decrease in the WCA was observed within 20 s of plasma treatment. A second decrease occurred from 100 to 150 s of plasma treatment. This finding is in agreement with the determined concentration of hydroperoxides, which steeply increased after 20 s of plasma treatment. The presence of fluorine functional groups was found on the PPF surface using XPS and FTIR. XPS analysis confirmed that the oxygen-containing groups on the PPF surface increased threefold after plasma treatment for 150 s.

Acknowledgements

This work was supported by the Slovak Research and Development Agency under contract no. APVV-14-0518.

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