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Influence of the CF_4 Plasma Treatments on the Wettability of Polypropylene Fabrics

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Abstract: A plasma treatment using saturated CF_4 gas was employed to improve the resistance of polypropylene fabrics to water wetting. The fabrics were significantly fluorinated even within a short treatment time of 30 seconds. The result of contact angle measurement indicated that such highly hydrophobic surface was considerably durable even after 150 days of aging.

Keywords: Fluorochemical, Plasma, Polypropylene, Hydorphobicity, Wettability

Introduction

Polypropylene (PP) has high specific volume and is very lofty, giving good cover at low price. The excellent overall properties of including tensile strength, abrasion resistance, wrinkle recovery, chemical resistance, etc. render it to be used in carpet and home furnishing fabrics.

Amoung various chemical modification of PP, plasma treatment has been employed to change the surface characteristics of PP. Many studies[1,2] reported that the wettability of PP fabrics was greatly improved by oxygen plasma treatment.

The present study was carried out to change the surface of PP fibers by fluorocarbon plasma treatment to assess the reduction in wetting properties of PP fabrics.

Highly hydrophobic surfaces have been developed through deposition of fluorocarbons on metallic or hydrophilic organic substrates[3,4]. Most of previous plasma treatments used unsaturated fluorocarbon monomers in stead of a saturated fluorocarbon that is used in this study. Furthermore, film substrates were frequently used to determine the effect of fluorocarbon plasma treatments on the ability to resist penetration by water. In this study, a plasma treatment using saturated CF_4 gas was employed to improve the resistance of PP fabrics to water wetting.

Experimental

Materials

Commercial PP plain fabric, purchased from Test Fabrics Inc., was used in all experiments. The fabrics were soxlet extracted in benzene and distilled water for 4 hours and dried under vacuum condition before use. Tetrafluoromethan (Aldrich Chemical) was used without further purification.

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Plasma Treatment

Plasma treatments were carried out in a commercial installation. The apparatus consists of the parallel plate electrodes with a 30 kHz RF generator, water-cooling system, a vacuum pump, pressure gauge, and gas flow-meter. In a typical experiment four fabric samples were placed on the grounded electrode. Then the system was vacuumed to ground pressure level. After creating a selected gas pressure, plasma was ignited and maintained for a desired reaction period. At the end of the irradiation, the samples were removed from the reactor and stored in Pyrex containers under constant relative humidity (65 %) and temperature (27 °C) conditions for 24 hours, then subjected to analytical measurements.

Characterizations and Measurements

ESCA spectra were obtained by using a Perkin-Elmer 5400 spectrometer with a Mg X-ray source and a data reduction system. A pass energy of 35.73 eV was utilized for multiple spectra analysis. For the elemental analysis, the pass energy was increased to 89.45 eV.

The contact angles of water on fiber surface were measured by the Wilhelmy balance techniqu[5] using a single fiber. The effect of plasma treatment on the spontaneous water uptake of fabrics was determined by the demand wettability test[6], which measured the initial equilibrium water uptake. To determine the aging behavior of the treated surface, same measurements repeated after 1, 7, 30, 60, and 150 days. Duncans significant difference was applied to evaluate the difference of results shown in the Tables.

Results and Discussion

Surface Atomic Ratio of PP Fibers

Figure 1 shows the C_{1s} spectra of PP fibers before and after CF_4 plasma exposure. The untreated PP exhibited a strong single carbon peak at 285 eV. The fluorine substituted

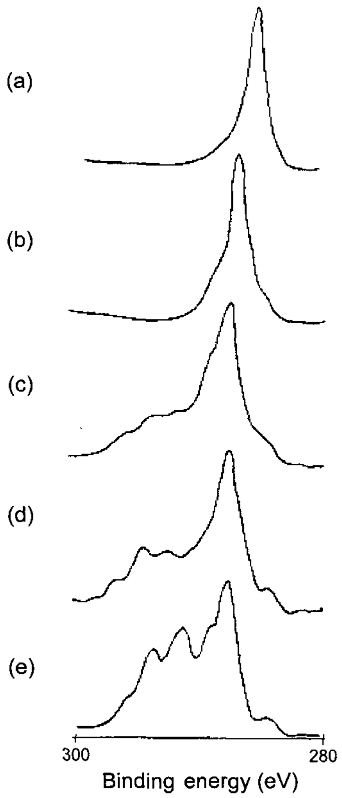

Figure 1. C_{1s} spectra of PP fibers before and after CF_4 plasma exposure as a function of discharge power (200 mTorr, 5 min): untreated (a); 20 W (b); 60 W (c); 80 W (d); 100 W (e).

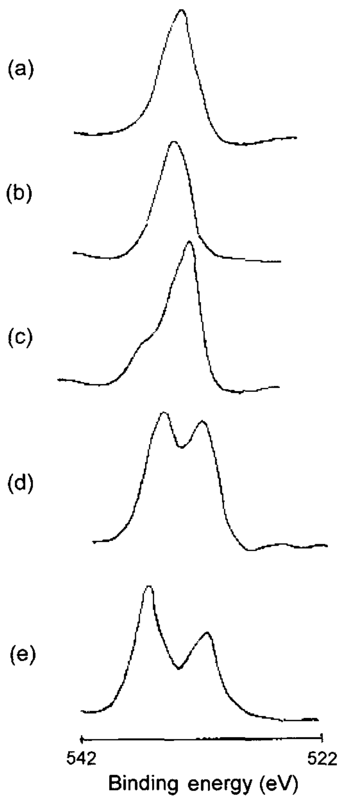

Figure 2. O_{1s} spectra of the CF_4 plasma treated PP fibers as a function of discharge power (200 mTorr, 5 min): untreated (a); 20 W (b); 60 W (c); 80 W (d); 100 W (e).

C_{1s} peak of the treated PP was much wider than that of the untreated fiber. The C_{1s} shifts between 290 and 290 eV may arise from a complex mixture of mostly fluorinated and some oxidized groups. Carbon containing a single bond to oxygen, such as with alcohol or ether, could occur around 286 to 287 eV. Carbonyl carbon was located around 288 eV. Carbon in acids or esters seems to be combined with a shakeup satellite and could be associated with the transitions accompanying photo-ionization of unsaturated CF sites. The C_{1s} spectra of the CF_4 plasma treated PP showed peaks at 294.5, 292.5, 289.5, 287.5 eV that can be assigned to -CF_3, -CF_2, -CF, and -C-CF_3, respectively. The intensity of the fluorine substituted C_{1s} peaks increased with increasing discharge power.

With CF_4 plasma, the dominant species on the fiber surfaces were the -C-CF_3 types even after the short time of 30 sec or a low discharge power level of 20 Watt.

Figure 2 shows the O_{1s} spectra of the untreated and the CF_4 plasma-treated samples located at 532 and 536 eV, respectively. The higher binding energy of O_{1s} shift is attributed to oxygen bonded to carbon atoms containing fluorine. A broader and stronger oxygen peak around 536 eV was pronounced with increasing discharge power up to 100 Watt.

Figure 3 shows that the intensity of the fluorine C_{1s} peaks increased with increasing discharge pressure. Weak residual -C- signal at 285 eV was noticible even at a discharge pressure of 200 mTorr. It was not surprising that the higher discharge pressure produced the broader and the higher C_{1s} binding energy.

Tables 1 to 3 show variation of the surface atomic ratios, O_{1s}/C_{1s}, F_{1s}/C_{1s}, and F_{1s}/O_{1s}, of PP fabrics treated with different exposure time, discharge power, and reaction pressure. As the exposure time increased, the F_{1s}/C_{1s} ratio increased due to all the possible fluorocarbon groups. A gradual increase in the ratio of F_{1s}/C_{1s} was observed as the discharge power increased from 10 to 100 Watts. The F_{1s}/C_{1s} ratio increased also as reaction pressure increased. The samples treated at 75 mTorr and 100 Watts for 5 min has an O_{1s}/C_{1s} ratio of 0.8 and F_{1s}/C_{1s} ratio of 0.07, while the samples treated at 200 mTorr showed an O_{1s}/C_{1s} ratio of 0.22 but a F_{1s}/C_{1s} ratio of 1.08. Based on the literature[6], the decrease in electron temperature might be responsible for the increase in fluorocarbon grafting or deposition because the electron temperature could be decreased as discharge pressure increased in a fixed system at the same.

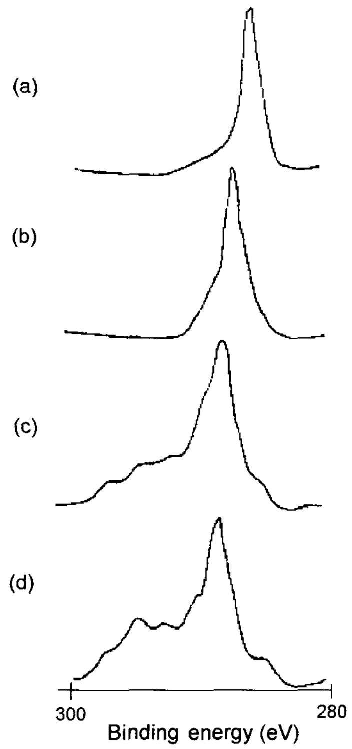

Figure 3. C_{1s} spectra of the CF_4 plasma treated PP fibers as a function of discharge pressure (100 Watt, 1 min, 30 days aged): untreated (a); 100 mT (b); 150 mT (c); 200 mT (d).

Table 1. Effect of CF_4 plasma exposure time on the surface atomic ratios of PP fabrics

Exposure time (sec)	O/C	F/C	F/O
Untreated	0.04a	0.00a	0.00a
30	0.28c	0.92b	3.34b
60	0.24b	1.08c	4.15c
180	0.22b	1.12c	5.18d
300	0.21b	1.10c	5.23d

CF_4 plasma treatment; discharge power, 100 Watt; reaction pressure, 200 mTorr; 30 days aged.
The mean values of the same letters in columns are not statistically different by Duncan's significant difference.

Table 2. Effect of RF power on the surface atomic ratios of PP fabrics

Discharge power (watt)	O/C	F/C	F/O
Untreated	0.04a	0.00a	0.00a
10	0.67f	0.26b	0.40a
20	0.49e	0.79c	2.02b
60	0.35d	1.06e	3.06c
80	0.27c	1.03d	4.03d
100	0.22b	1.10f	5.15e

CF_4 plasma treatment; discharge power, 100 Watt; reaction pressure, 200 mTorr; 30 days aged.
The mean values of the same letters in columns are not statistically different by Duncan's significant difference.

Table 3. Effect of Reaction Pressure on the surface atomic ratios of PP fabrics

Reaction pressure (mTorr)	O/C	F/C	F/O
Untreated	0.04a	0.00a	0.00a
100	0.56d	0.58b	1.04b
200	0.32c	0.81c	2.53c
400	0.25b	1.00d	4.00d

CF_4 plasma treatment; discharge power, 100 Watt; reaction pressure, 200 mTorr; 30 days aged.
The mean values of the same letters in columns are not statistically different by Duncans significant difference.

Table 4. Effect of aging on the surface atomic ratios of PP fabrics

Aging (day)	O/C	F/C	F/O
Untreated	0.04a	0.00a	0.00a
1	0.19b	2.00c	10.33c
7	0.28b	0.92b	7.70b
30	0.24b	1.08b	4.15b
60	0.22b	1.12b	5.18b
150	0.21b	1.10b	4.10b

CF_4 plasma treatment; discharge power, 100 Watt; reaction pressure, 200 mTorr; 30 days aged.
The mean values of the same letters in columns are not statistically different by Duncans significant difference.

Table 5. Effect of aging on the water contact angles of PP fabrics

Aging (day)	Water contact angle (degree)
Untreated	82a
1	105c
7	97b
30	94b
60	94b
150	98b

CF_4 plasma treatment; discharge power, 100 Watt; reaction pressure, 200 mTorr; 30 days aged.
The mean values of the same letters in columns are not statistically different by Duncans significant difference.

The surface atomic ratios of CF_4 plasma-treated PP aged for different duration are summarized in Table 4. There is a significant decrease in the ratio of F_{1s}/C_{1s} as the aging time increases 1 to 7 days and then remains unchanged. Even after 150 days of aging the CF_4 plasma-treated PP still contained high fluorine content.

Contact Angles of PP Fibers

Table 5 shows the water contact angles for the CF_4 plasma-treated PP fibers that were aged for 1, 7, 30, 60, and 150 days. The water contact angles of all the CF_4 plasma-treated PP were found to be above 90 °, indicating that more

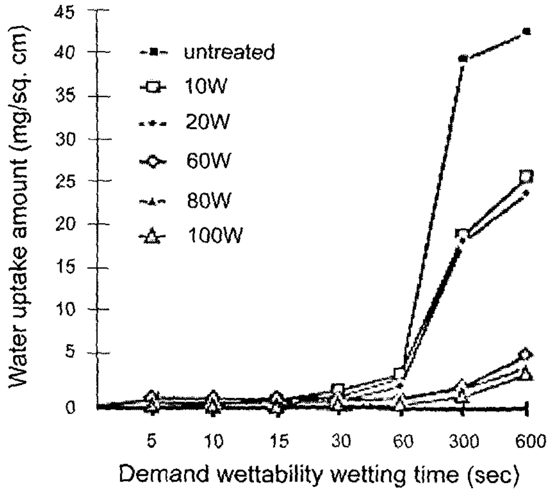

Figure 4. Effect of discharge power on the water uptake amount of the CF_4 plasma treated PP fabrics. Fabrics were treated at 200 mTorr for 1 min. and were aged for 4 days.

hydrophobic surfaces were generated by CF_4 plasma. The fiber surfaces treated in the CF_4 plasma system had a chemical composition that consisting various fractions of fluorocarbon functional groups. Consequently, the contact angles of the CF_4 plasma-treated PP fibers were further increased.

Wettability of PP Fabrics

Figure 4 shows the effect of the CF_4 plasma treatments on the spontaneous water uptake of PP fabrics. For this experiment, samples were discharged at a pressure of 200 mTorr and exposure duration of 1 min. Increasing the discharge power up to 100 Watt gradually decreased the water uptake. It is clear from the results that CF_4 plasma treatment at discharge power over 60 Watt decreased wettability of PP fabrics. Implantation of fluorine atoms into

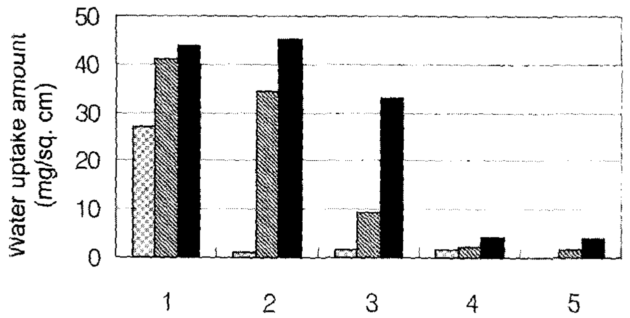

Figure 5. Effect of discharge pressure on the water uptake amount of PP fabrics. The water uptake was measured after initial (5 sec) [ ], half time(5 min) ▨ and equilibrium time (10 min) ■; for 1) untreated fabrics, and CF_4 plasma treated fabrics at different discharge pressures, 2) 75 mTorr, 3) 100 mTorr, 4) 150 mTorr, and 5) 200 mTorr.

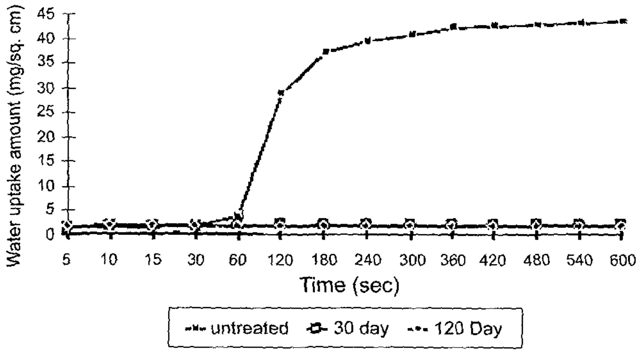

Figure 6. Effect of aging on the water uptake amount of the CF_4 plasma treated PP fabrics. Fabrics were treated at 100 Watt and 200 mTorr for 1 min.

the surface of the PP fiber that is responsible for the significant decrease in wettability was also confirmed by the water contact angle studies. The fluorine elements produced by the CF_4 plasma treatment retarded the initial rate of water uptake amount as well as the total water uptake amount.

The dependence of the hydrophobic treatement on the discharge pressure was also appeared in the demand wettability test. Figure 5 shows that with increasing discharge pressure from 75 to 200 mTorr, both the initial and the total water uptake amount decreased.

The effect of aging on the spontaneous water uptake of PP fabrics was also investigated, and the results are shown in Figrue 6. Highly hydrophobic characteristics were still significant even after 120 days of aging. Even after 120 days aging, the fiber samples showed that there was a significant amount of fluorocarbon functional groups on their surfaces which contributed to high contact angle (over 90 °), resulting in a very hydrophobic surface.

Conclusion

All the CF_4 plasma treated PP fabrics became more hydrophobic than the untreated PP fabrics. Such improvements were attributed to the introduced fluorine atoms on the fiber surface or a formed thin fluorocarbon film. Activation of tetrafluoromethane molecules in a discharge system may lead to a rapid fluorocarbon grafting or a fluorocarbon coating as observed by ESCA. The fabrics were significantly fluorinated even within a short treatment time of 30 seconds. Long-term stability of the introduced fluorocarbon groups was important for creating permanent resistance to wetting. The result of contact angle measurement indicated that such highly hydrophobic surface was considerably durable even after 150 days of aging. Microscopic topography of the fiber surface was not apparently affected by CF_4 plasma treatment. The CF_4 plasma treatment can be probably a simple and effective method to increase higher resistance of PP fabrics to water uptake.

Acknowledgements

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