Effect of plasma treatment on surface structure and properties of polyester fabric

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Poly(ethylene terephthalate) fabric was treated by plasma initiated in various gases: nitrogen, oxygen, air, carbon dioxide and ammonia. Plasma-treated fabric showed a considerable change in surface structure and wettability. It was observed that the change in the surface structure of the polyester fibres was closely dependent on the gas type and treatment conditions. The wetting time of plasma treated fabric considerably drops in comparison to untreated fabric and the best results were obtained by treatment in nitrogen, oxygen and air plasma. A good correlation exists between change in the surface structure of the fabric and its wettability. Infra-red a.t.r. spectroscopy showed some differences in the spectra of plasma treated fabrics but these changes are only moderately dependent on the gas type and plasma conditions. Modification of the surface structure of the polyester fibres depends on the current frequency within the studied range of 0.05–100 kHz.

INTRODUCTION

One of the most serious disadvantages of poly(ethylene terephthalate) (PET) fibres is their hydrophobic surface and low water sorption, which are undesirable as far as the physiological properties are concerned (i.e. moisture transport through clothes made of these fibres). Treatment with low temperature plasma offers a unique possibility for selective modification of the polymer surface properties without any noticeable changes in the bulk properties of the polymer[1]. The changes in the polymer surface caused by plasma are highly dependent on the gas type and conditions of plasma generation[1–3]. Therefore, the modification of the polymer surface by plasma treatment has an important advantage in comparison with other methods, because the process can be controlled easily through many independent parameters such as gas pressure, exposure time and discharge power. Most of the papers published on this problem concern plasma treatment of polymer films and foils but very few of them deal with modification of fibres and fabrics by this process[4–9]. Even less is known about durability of the effect resulting from the plasma process on washing, which is very important from a practical point of view.

The low temperature plasma can be initiated within a very broad range of current frequencies. The use of frequencies below 100 kHz for plasma generation seems to be particularly interesting because there are no problems of generator and load impedance matching, and shielding for personal protection is not required.

The results reported here concern the effect of gas type and discharge parameters on the surface structure and wettability of the plasma-treated PET fabric.

EXPERIMENTAL

Apparatus

The plasma treatment of PET fabric was carried out in an electrode static system. The details of the apparatus have been described previously[10]. The fabric samples were placed inside a glass bell jar, 20 dcm^3 in volume between two parallel stainless steel electrodes each of 50 cm^2, with the electrode distance fixed at 30 mm. The system was evacuated first down to 10^{-5} torr and then the particular gas was admitted to the required pressure. The glow discharge was initiated by coupling the output of a variable frequency amplifier to the electrodes.

Materials

Cleaned PET woven dress fabric of 150 g/m^2 in weight and of a wetting time well above 300 sec was used in all experiments.

All the gases used were of a commercial grade of purity.

Test methods

The wetting time was determined by placing a drop of distilled water on the fabric surface and measuring the time for the water drop to lose its reflective power[11].

The sorption and desorption of water vapour was determined at a temperature of 28°C by recording changes in the weight of fabric samples of 0.6 g placed in a stream of air. The sorption was estimated by exposing the fabric sample, conditioned at 33% relative humidity (r.h.), to the stream of air at 90% r.h. until equilibrium was reached. Desorption was determined by allowing the air at 33% r.h. to flow through the fabric sample which had previously achieved equilibrium at 90% r.h.

The durability of surface properties to washing was examined by treating the fabric samples in distilled water at 60°C for 15 min at 1:40 sample to liquid ratio.

Infra-red spectra of fabric surfaces were taken on a Perkin–Elmer, Model 457, spectrophotometer using the a.t.r. technique.

Electron micrographs of fabric surfaces were taken by the

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carbon replica technique using a Tesla, Model BS 242 D, electron microscope.

RESULTS AND DISCUSSION

Effect of gas type

In order to investigate the influence of gas type on surface properties of the plasma-modified PET fabric, a series of discharges in various gases were carried out keeping other discharge parameters constant in each experiment. The degree of modification for samples treated in this way was determined by measuring the wetting time directly after the plasma treatment and after successive treatments with distilled water. Preliminary tests have shown that treatment with distilled water is better than washing in liquid containing surface active agents for examination of durability of the effects achieved by plasma treatment, as it gives more reproducible results. It follows from the results shown in *Table 1* that the lowest wetting time is noted for fabrics treated with plasmas of nitrogen, oxygen, air and carbon dioxide. The wetting time measurements after successive treatments with distilled water lead to the conclusion that the most durable wettability is achieved by treatment with nitrogen and oxygen plasma.

Table 1 The wettability of PET fabric treated with plasma initiated in various gases at p = 1 torr, j = 2 mA/cm^2, f = 9 kHz and t = 1 min

	Wetting time (sec)					
	After plasma	After water treatment cycles				
Gas type	treatment	1	2	3	4	5
Nitrogen	4	5	15	20	23	35
Oxygen	3	5	20	20	21	26
Air	3	4	5	16	30	41
Carbon dioxide	3	3	16	29	138	183
Ammonia	11	>300	>300	–	–	–

Investigations of plasma-treated PET fibres by the e.m. technique showed very pronounced differences in their surface structure in comparison with untreated fibres. The electron micrographs in *Figure 1* show the surfaces of untreated fibre (*Figure 1a*) and surfaces treated in nitrogen, oxygen, carbon dioxide and ammonia plasma (*Figures 1b, 1c, 1d* and *1e*), respectively. As is seen in *Figure 1b*, the surface of fibre treated with nitrogen plasma is characterized by uniformly distributed, fine micropores. The surface morphology of fibres treated with air plasma was very similar to that treated with nitrogen. The treatment with oxygen and carbon dioxide plasmas causes similar changes but the micropores are smaller in size (*Figures 1c* and *1d*) and their density on the surface is considerably lower than in the case of nitrogen. The similarity of surface structures of fibres treated in oxygen and carbon dioxide plasmas could be explained by the fact that carbon dioxide plasma contains a considerable amount of atomic oxygen as one of its main dissociation products[12]. The surface of fibres treated with ammonia plasma (*Figure 1e*) is completely different from that described previously. No micropores are observed on the fibre

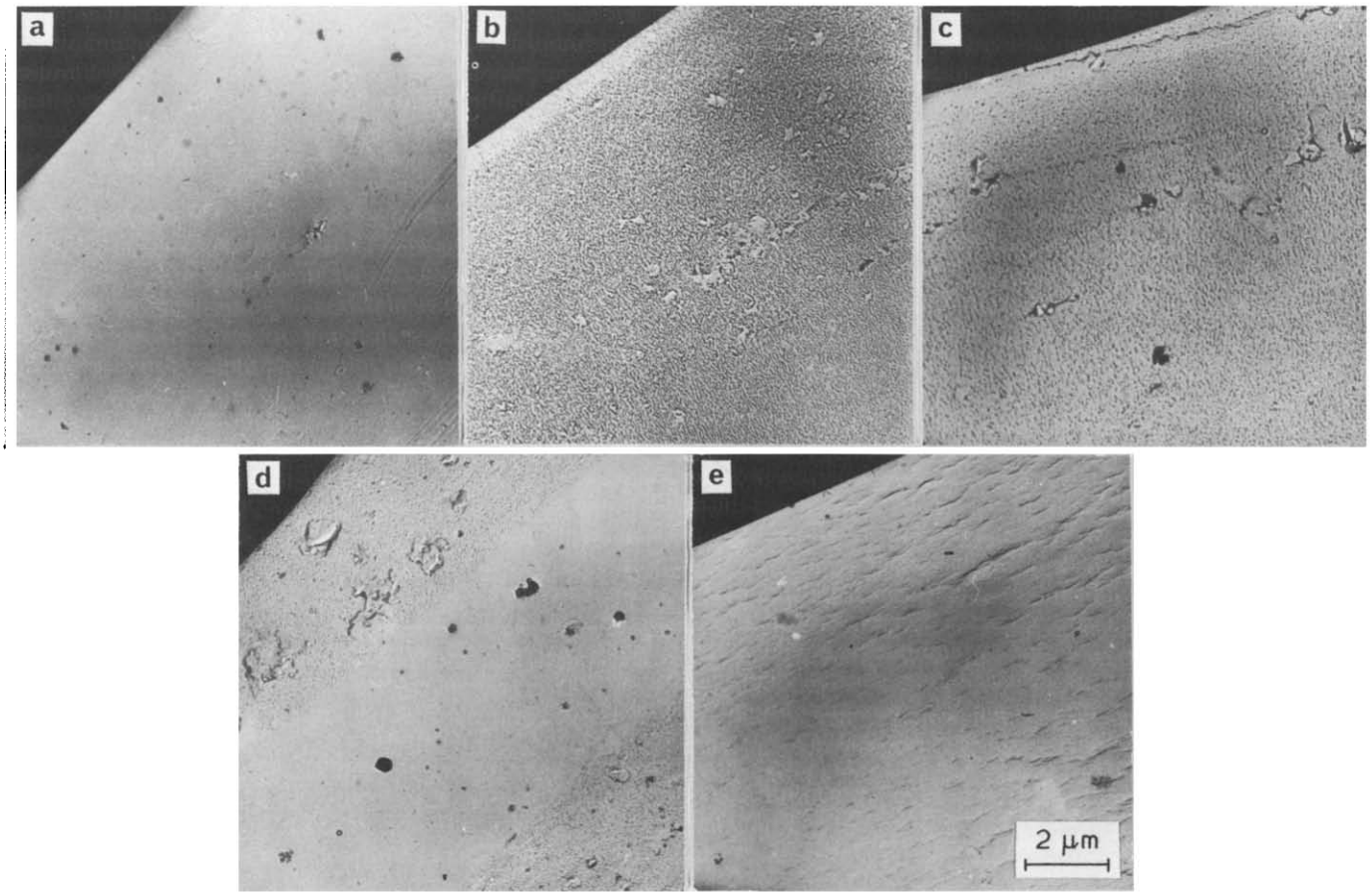

Figure 1 Electron micrographs of the surface of poly(ethylene terephthalate) fibres: (a) untreated and exposed to plasma; (b) in nitrogen; (c) oxygen; (d) carbon dioxide and (e) ammonia. t = 4 min, p = 1 torr, f = 20 kHz, j = 2 mA/cm^2

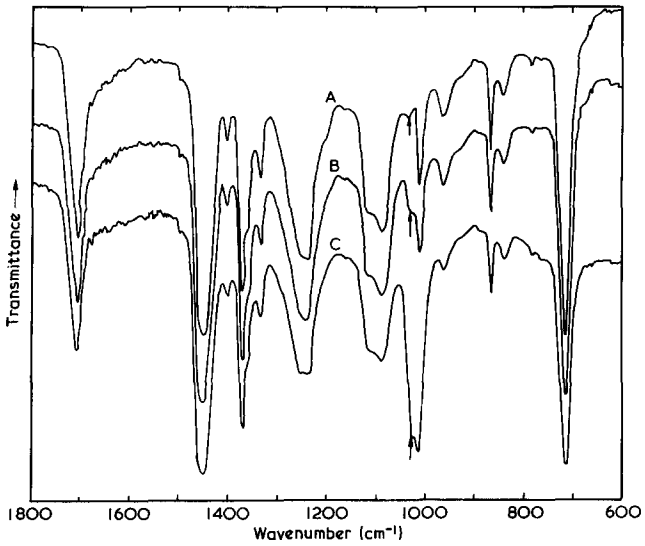

Figure 2 Infra-red a.t.r. spectra of the surface of poly(ethylene terephthalate) fabric treated with various gas plasma: (a) untreated, (b) ammonia and (c) oxygen. p = 1 torr, j = 2 mA/cm^2, f = 20 kHz, and t = 4 min

Table 2 Effect of current frequency on the wettability of PET fabric treated with nitrogen plasma at p = 1 torr, j = 1 mA/cm^2 and t = 4 min

Current frequency (kHz)	Wetting time (sec)					
	After plasma treatment	After water treatment cycles				
		1	2	3	4	5
0.05	<1	2	5	8	38	278
0.5	<1	2	4	8	39	84
1	<1	1	4	11	21	32
5	<1	1	2	3	23	24
10	<1	2	3	8	14	40
20	<1	1	8	24	136	>300
60	<1	9	26	79	213	>300
100	<1	3	24	134	>300	>300

surface but only relatively few recesses oriented along longitudinal fibre axis can be seen.

The infra-red analysis of PET fabric samples treated with plasma in various gases fails to show qualitative changes in the chemical composition of the surface layer. The differences in the i.r. spectra were restricted only to quantitative changes in the absorption at 1040 cm^{-1} corresponding to the *gauche* conformation of O-(CH$_2$)$_2$-O bonds in the polymer chain[13]. An increase in the absorption of this band was observed in the spectra of PET fabric treated with oxygen and ammonia plasmas (*Figures 2b* and *2c*). A lack of distinctive differences in the i.r. spectra of the fabric samples treated with plasma in various gases show that surface changes resulting from plasma treatment are confined to a very thin surface layer (50–500 Å) and reflectance infra-red spectroscopy is sensitive for considerably thicker layers (1–10 μm)[14].

The changes in the surface morphology of the fibres observed after the plasma treatment can be explained by the localized degradation of polymer at the surface layer[1–3]. The degradation seems to be the predominant effect of the interaction of plasma with a polymer surface[2]. This process leads to an almost complete breakdown of relatively small numbers of molecules at the surface into low molecular components which eventually vaporize in the low pressure system. The localized degradation of polymer at the surface is clearly revealed by the presence of micropores on the surface of plasma-treated fibres.

It is known that the wettability of the polymer depends on the surface roughness and its polarity[15,16]. The very pronounced improvement in the wettability of the fabric after plasma treatment, observed particularly for nitrogen, oxygen, air and carbon dioxide plasmas (*Table 1*), are undoubtedly connected with high surface development as was shown by the e.m. studies (*Figures 1b, 1c* and *1d*). The absence of micropores on the fibre surface in the case of treatment with ammonia plasma (*Figure 1e*) is reflected by a higher wetting time (*Table 1*). The fine micropores observed on the fibre surface treated in nitrogen, oxygen and carbon dioxide plasmas are more stable to the treatment with water than those produced by ammonia plasma.

The results show that a good correlation exists between the surface structure of plasma-treated fibres and their wettability. It could be also assumed that the physical modification of the fibre surface is one of the main factors influencing its wettability.

Effect of discharge parameters

In order to find the influence of discharge parameters on the wettability of PET fabric a series of experiments were carried out with nitrogen plasma at different sets of discharge conditions.

The results of wetting time measurements for fabrics directly after plasma treatment and after successive water treatments as a function of current frequency (f), current density (j), nitrogen pressure (p) and exposure time (t) are collected in *Tables 2, 3, 4* and *5*.

It can be seen from *Table 2* that the wettability of PET fabric directly after plasma treatment is only slightly depen-

Table 3 Effect of current density on the wettability of PET fabric treated with nitrogen plasma at p = 1 torr, f = 9 kHz and t = 4 min

Current density (mA/cm^2)	Wetting time (sec)						
	After plasma treatment	After water treatment cycles					
		1	2	3	4	5	10
0.5	4	5	7	13	20	29	54
1	2	3	4	5	10	10	31
1.5	4	6	8	15	24	17	37
2	20	20	8	14	16	21	50
2.4	142	83	18	47	83	95	123

Table 4 Effect of gas pressure on the wettability of PET fabric treated with nitrogen plasma at j = 1 mA/cm^2, f = 5 kHz and t = 1 min

Pressure (torr)	Wetting time (sec)						
	After plasma treatment	After water treatment cycles					
		1	2	3	4	5	10
0.1	>300	>300	–	–	–	–	–
0.3	71	62	22	50	54	68	84
0.5	3	6	5	8	12	16	39
1	3	7	8	14	18	27	92
1.5	3	7	14	21	28	36	255
3	4	4	10	12	50	81	120

Table 5 Effect of exposure time on the wettability of PET fabric treated with nitrogen plasma at p = 1 torr, j = 2 mA/cm^2 and f = 100 kHz

Exposure time (s)	Wetting time (sec)					
	After plasma treatment	After water treatment cycles				
		1	2	3	4	5
5	>300	>300	—	—	—	—
15	4	268	>300	>300	—	—
30	3	60	190	187	>300	>300
60	1	3	40	188	>300	>300
120	1	1	14	22	28	29
240	1	1	2	3	9	20

dent on the current frequency but the durability of this property towards the treatment with distilled water is strongly dependent on the current frequency. The best durability was found within the 1–10 kHz range.

As is seen from the electron micrographs of the fibres surface vs. current frequency (*Figure 3*) the mean size of the micropores decreases with increasing frequency.

A relatively rough surface achieved by 0.05 kHz plasma (*Figure 3a*) is gradually altered into a surface densely covered with fine micropores for 100 kHz plasma (*Figure 3c*). The reasons for this difference are not well understood. It could not be explained by the mechanism controlling the discharge which, in the studied frequency range, remains unchanged[16]. However, it could not be excluded that fabric placed between two parallel electrodes acts as a dielectric barrier and involves changes in the discharge mechanism to the same extent.

The lowest values of the wetting time after successive water treatments are observed for current densities of 1 and 1.5 mA/cm^2 (*Table 3*). It is known that the number of active particles in the plasma is dependent on current density. For these particular experimental conditions the number of active particles generated at a lower current density of 0.5 mA/cm^2 is not sufficient to produce surface modification to such an extent as to give low wetting times. On the other hand an increase in current density over 1.5 mA/cm^2 involves a higher concentration of active particles in plasma and leads to the production of a more hydrophobic polymer surface as a result of some crosslinking[1,2]. The fabrics treated at 2 and 2.4 mA/cm^2 were yellow-brown in colour and this would suggest that some chromophore groups may be formed.

Optimum durability of the wetting time as a function of gas pressure was found for p = 0.5 torr (*Table 4*). This could be explained by the fact that the mean free path of plasma particles and their kinetic energy are closely dependent on the gas pressure and increase with decreasing pressure. The colouration of the fabric observed at lower pressures of 0.1 and 0.3 torr suggests that in these cases the plasma particles have enough energy to produce a more hydrophobic fibre surface by crosslinking of the polymer at the surface layer. The energy of plasma particles at pressures of 1–3 torr is too low to cause sufficient surface modification and less durable effects are observed.

From data in *Table 5*, the wettability of fabric improves with an increase in exposure time.

The effect is more durable after longer exposure time and no optimum value for this parameter could be found within the studied range. This is consistent with results of Yasuda *et al.*[2] who have shown that polymer degradation increases with exposure time.

Water vapour sorption and desorption

The measurements of water vapour sorption and desorption for PET fabrics treated with nitrogen plasma at different frequencies in the 0.05–100 kHz range with other discharge parameters being constant have shown that the cur-

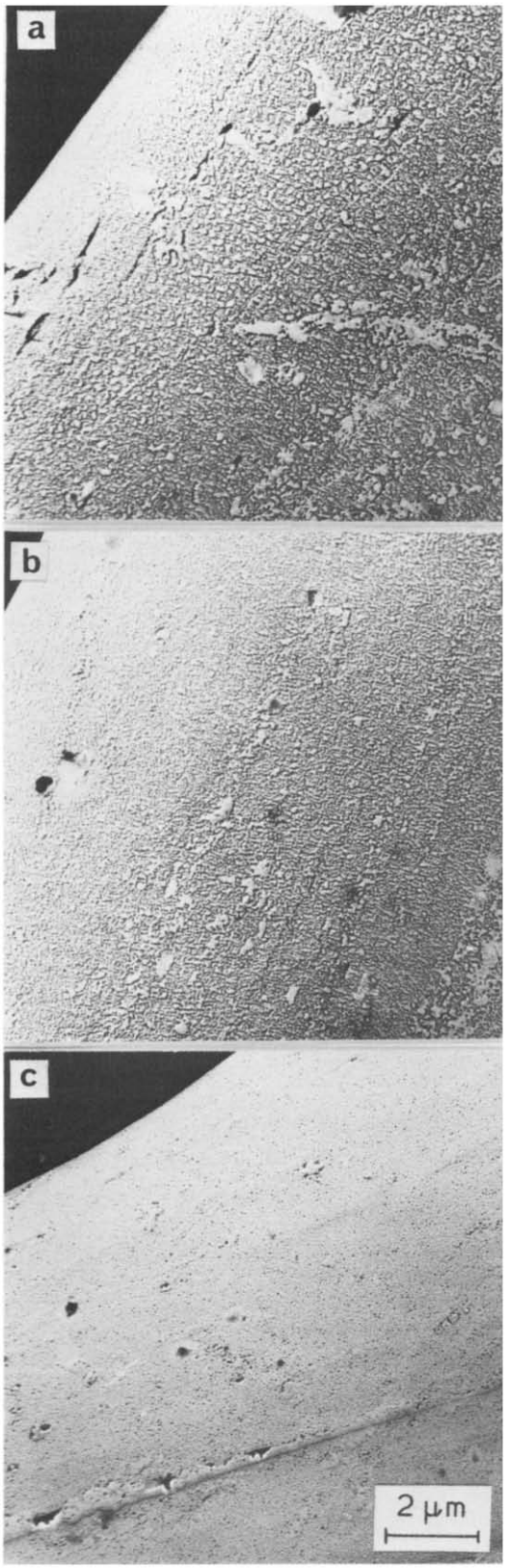

Figure 3 Electron micrographs of the surface of poly(ethylene terephthalate) fibres exposed to nitrogen plasma at various current frequencies: (a) 0.05 kHz; (b) 5 kHz and (c) 100 kHz. p = 1 torr, j = 1 mA/cm^2 and t = 4 min

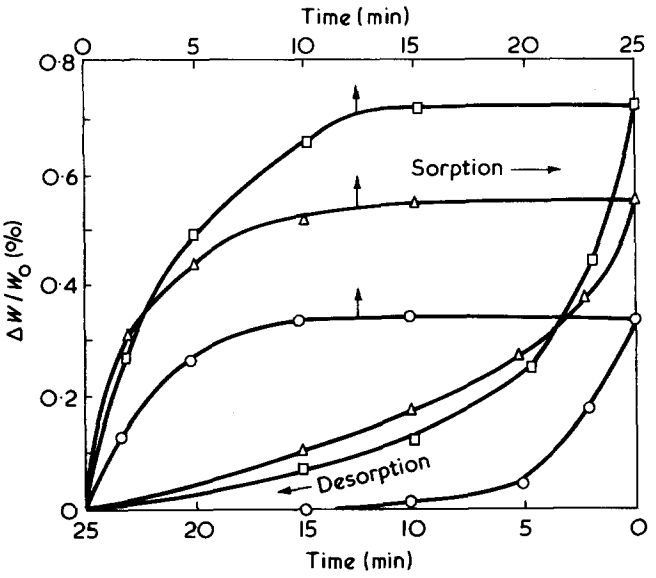

Figure 4 Sorption and desorption isotherms for poly(ethylene terephthalate) fabric treated with nitrogen plasma at p = 1 torr, f = 100 kHz, t = 4 min. ○, Untreated fabric; △ j = 1 mA/cm^2; □, j = 1.6 mA/cm^2

rent frequency does not noticeably change the equilibrium sorption. The sorption/desorption curves, on the other hand, indicate different kinetics for these processes in comparison to the untreated fabric. Typical sorption/desorption isotherms for fabrics treated with nitrogen plasma at f = 100 kHz and two different current densities j = 1.0 and j = 1.6 mA/cm^2 are shown in *Figure 4;* it can be seen that an increase in current density shifts the equilibrium sorption to higher values. Higher values of the equilibrium sorption observed for higher current density (*Figure 4*) could be attributed to the deeper plasma penetration and higher surface development.

CONCLUSIONS

(1) Morphological changes in the surface structure of PET fibres caused by plasma treatment are dependent on the gas type used for plasma generation and current frequency.

(2) Modification of PET fabric with the low temperature plasma improves its wettability considerably. The durability of the effects produced by plasma to the treatment with distilled water is closely dependent on the gas type and discharge parameters.

(3) Treatment of PET fabric with the low temperature plasma does not improve the water vapour sorption to a great extent but only causes changes in the kinetics of this process.

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