ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 10, No. 2. 2004

Plasma Modification of Structure and some Properties of Polyethylene Therepthalate Films and Fibers

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Received 15 June 2003; accepted 22 March 2004

Low-temperature plasma treatment of polyethylene therephthalate films and fibers results erosion of surface layers of the material (the effect of glow-discharge plasma of air, oxygen and helium was investigated). The speed of etching of PET films by oxygen plasma is determined from data of IR spectroscopy (0.08 μm/min at discharge power 0.3 W/cm^2). Plasma erosion of the surface layers and destruction of macromolecules result in formation of a new surface with other degree of macromolecules orientation and crystallinity and to occurrence of additional functional groups. Significant changes in IR transmission spectra of treated films after the certain storage time are marked also, that, probably, is caused by relaxation processes. Consequence of these structural changes is the sharp increase of surface energy that is shown in increase of capillarity of fabrics from the PET microfibres. The important technological aspect of plasma processing is the increase of intensity of printing of such fabrics.

Keywords: plasma treatment, polymeric films and fibers, surface structure, surface layers, IR ATR spectroscopy, electron scanning microscopy, relaxation.

INTRODUCTION

The effect of a low-temperature glow-discharge plasma on the structure and properties of exposed materials is determined by the integrated action of accelerated electrons and ions, UV-radiation, ozone and some another factors on the surface layers of materials. Plasma treatment of polymers results in etching and changes in a micro-structure of the surface, an occurrence of new functional groups and cross-linking of macromolecular chains. As a consequence of the change in a surface layer structure, a number of functional properties, in particular, adhesion, sorption, tribology, barriers etc. are changed [1 – 3].

It is important to note, that quite low selectivity of plasma influence often does not allow identify influences of different components on structural changes and, as a result, on the changes in properties of surface layers of polymers. Structural feature of the real polymeric systems are not always taken into account.

In this work, some features of plasma treated polyethylene therephthalate (PET) films and fabrics both composed of traditional polyester fibers and of microfibers are considered. Microfibers are very fine fibers compared to the conventional PET fibers that defines its unique and desirable properties. For example the microfiber has a many times greater total fiber surface than the usual textile material. This results in difficulties in finishing of woven and knitted materials. Size change is more costly because of the small microfiber fabric interstices and consequent difficulties with the sizing agent accessibility and diffusibility. Its high density results in a poor fabric penetration in dyeing and printing. Although dye uptake is higher for the standard fibers. [4].

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EXPERIMENTAL

Industrial PET films of 3 and 10 μm thickness, as well as fabrics of polyester fibers 11 tex and also fabric of polyester microfibers (commercial name “Trevira”) 15 tex were used as objects of research.

Samples were treated in low-temperature plasma of various gases (air, oxygen and helium) employing the plasmatrons UV 62I (A/O “Sidrabe”, Riga, Latvia) and USI-IONIC (LPA INDUSTRY, France). The pressure was about 1×10^{-1} Tor in both chambers.

Structural investigations of the surface layers were carried out with the scanning electron microscope (JSM-35c device, JEOL, Japan) and IR spectroscopy (spectro-photometers UR-20 and SPECORD-75 IR, Carl Zeiss, Germany), including attenuated total reflection (ATR) spectroscopy [5]. Two non-standard devices of attenuated internal reflection with prisms from Ge (angle of incidence is 45°) and KRS-5 (angle is 55°) were used for registration of the spectra of internal reflection to receive spectra at different depths of radiation penetration in a sample (estimation of relative values of penetration depth d_p/λ were calculated using the coefficient of refraction of air). Features of the procedure of spectra recording of fibrous materials are presented in [6]. A non-standard transmission polariser made of germanium plates crossed under the Brewster angle was used to polarize IR radiation. The method of double passing of light beam was used for registration of transmission spectra of thin PET films. This was realized with the help of a standard mirror reflection device (Carl Zeiss, the used angle of reflection of light beam, was 20°). The specimens of PET films were pasted on polished aluminium plates. The specimens on the plates were treated in plasma and kept for certain time before registration of spectra.

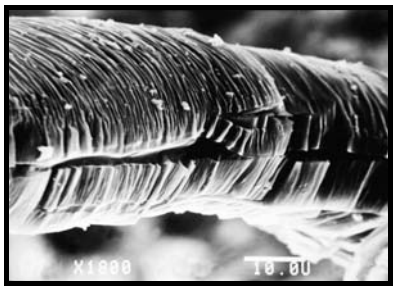
The speed of plasma etching was determined by the data of transmission (“reflection”) spectra of thin films which have been pasted on aluminum plates. Samples were

treated by cycles in oxygen plasma 3 minutes, and the spectrum was registered after each cycle. The speed of etching was calculated as a slope ratio of straight lines corresponding to the reduction of optical density of the bands of internal standard

Measurements of capillarity and parameters of physical and mechanical properties of the fabrics of traditional polyester fibers were carried out with the standard techniques and devices. For the measurement of capillarity of small samples of fabrics from microfibres the height of rise of distillate water pole through the certain intervals of time was fixed.

RESULTS AND DISCUSSION

According to the data [7, 8], degree of the macromolecular order in surface layers after plasma treatment can be increased or reduced. This phenomenon can be explained by the removal of various thickness layers, different speed of etching of crystalline and amorphous phases, and also presence of transverse macroheterogeneity in polymeric films and fibres.



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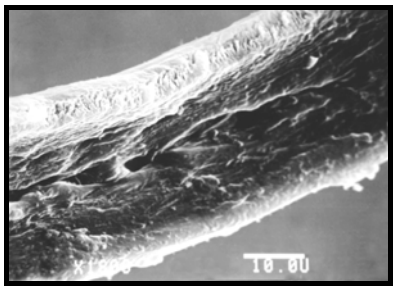

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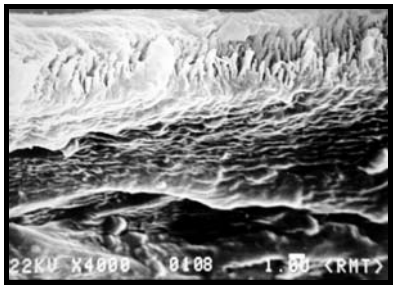

c

Fig. 1. SEM images of PET fibers after plasma etching (plasma of argon, W = 110 W): destruction of a shell surface layer (a, treatment time 30 sec) and a cross-section of fiber after long-run development (b and c, treatment time 10 min)

In Fig. 1a, an image of PET fibre at the initial stage of plasma etching is presented, when the skin is destroyed. The considerably long time influence results in a removal of the material almost up to the middle of the object diameter. The various orientations and various densities of elements of a morphological structure are well seen in the fibre longitudinal section (Fig. 1, b and c).

According to the data of IR ATR spectroscopy and SEM, a microrelief of a surface is developed as a result of the plasma treatment. It is shown in a reduction of intensity of absorption bands owing to the reduction of the contact area of the treated samples with the prism of internal reflection. The reduction of the effective contact area of the samples with prism can be characterized by a decrease in an optical density of absorption band of internal standard 1410 cm^{-1} (Fig. 2).

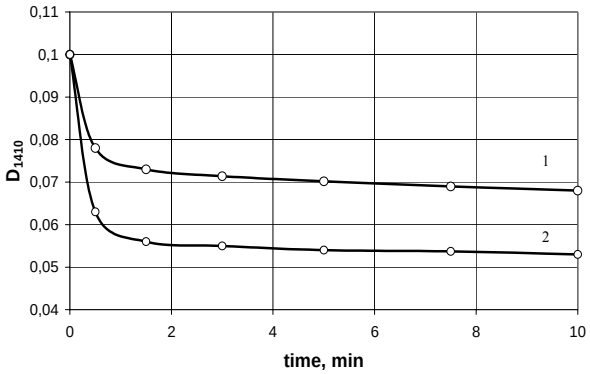

Fig. 2. Dependence of optical density of the band 1410 cm^{-1} at IR ATR spectra of PET fibers with a relative depth of penetration 0.066 on time of treatment at plasma of air: 1 – discharge power 110 W, 2 – 360 W

Noticeable decrease in the molecular order degree of surface layers is marked. Reduction in the relative optical density of the structural-sensitive band 1343 cm^{-1} $D'_{1343} = D_{1343}/D_{1410}$, which corresponds to the rotational vibration of CH_2 groups of polyethylene therephthalate molecules in trans-conformation [9], is shown in Fig. 3.

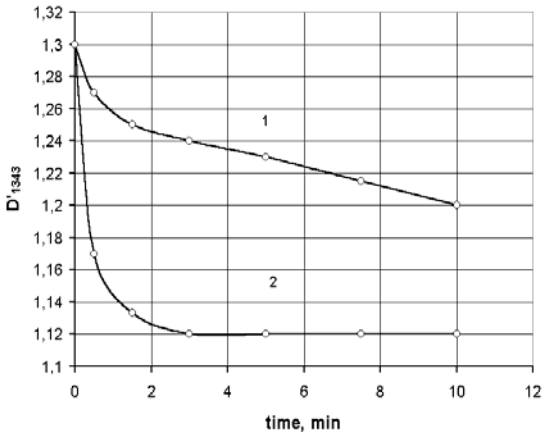

Fig. 3. Dependence of the relative optical density of the band 1343 cm^{-1} ($D'_{1343} = D_{1343}/D_{1410}$) in the IR ATR spectra of PET fibers with a relative depth of penetration 0.066 on time of treatment at plasma of air: 1 – discharge power 110 W, 2 –360 W

The significant reduction in dichroism of the same orientational-sensitive band 1343 cm^{-1} is observed in the spectra registered in polarized light (Fig. 4). This can be explained by reduction in the orientation of macromolecules after treatment.

Plasma exposure brings to the occurrence of new absorption bands near 780, 1615 and 3370 cm^{-1} (they marked in spectra of the treated samples, Fig. 5) that are caused by new functional groups (carboxyl and, possibly, nitrile). It is important to note that the intensities of the new bands are higher in the spectra of thin layers (at relative depth of radiation penetration $d_p/\lambda = 0.066$), i.e. the plasma modification affects the surface layer about 0.1 – 0.5 μm thick.

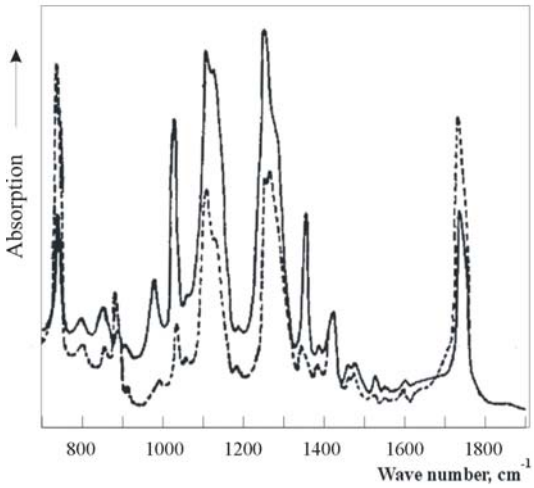

Fig. 4. ATR spectra of PET industrial fibers at polarised light (continuous curve – axis of orientation is parallel to polarization plane of radiation, dashed – is perpendicular, accordingly), relative depth of penetration 0.066

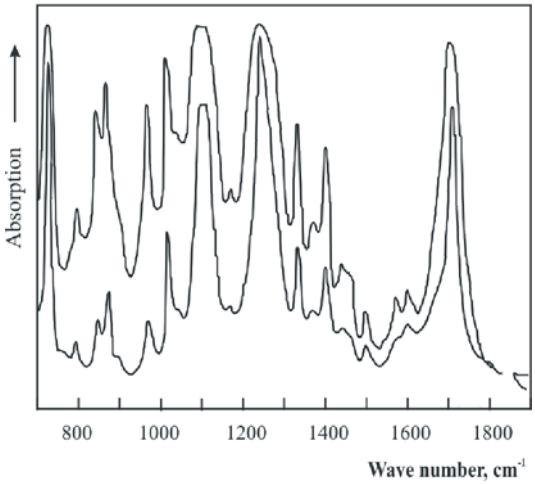

Fig. 5. IR ATR spectra of PET films 10 μm thickness after plasma treatment (power 360 W, time 5 minutes) at relative depth of radiation penetration 0.129 (above) and 0.066 (below)

This spectral and structural changes, obviously, are attributed to the appearance of new polar functional groups in places of breaking of molecules and by erosion of the initial surface layer during plasma etching and opening of layers with different supermolecular structure. The speed of the plasma erosion (or etching) is equal to 0.08 μm/min according to the spectral data of thin PET films (Fig. 6) and it is close to the value received using analytical formulas.

It is interesting to note that a non-monotonous change in the relative optical densities of a number of structural-sensitive absorption bands is marked by the increase in the treatment time in spectra of films, and also with the increase in time, following after treatment. For example, the relative optical density of the band 973 cm^{-1} (the "cristallinity" band, stretching vibration of groups O–C) is decreased at the initial stage of treatment and increased in 20 minutes period (Fig. 6) after attainment of minimum. The similar picture is observed and for other structural-sensitive absorption bands. The phenomenon can be explained by the transversal heterogeneity of the films and removal of surface and than volume layers as shown in Fig. 6.

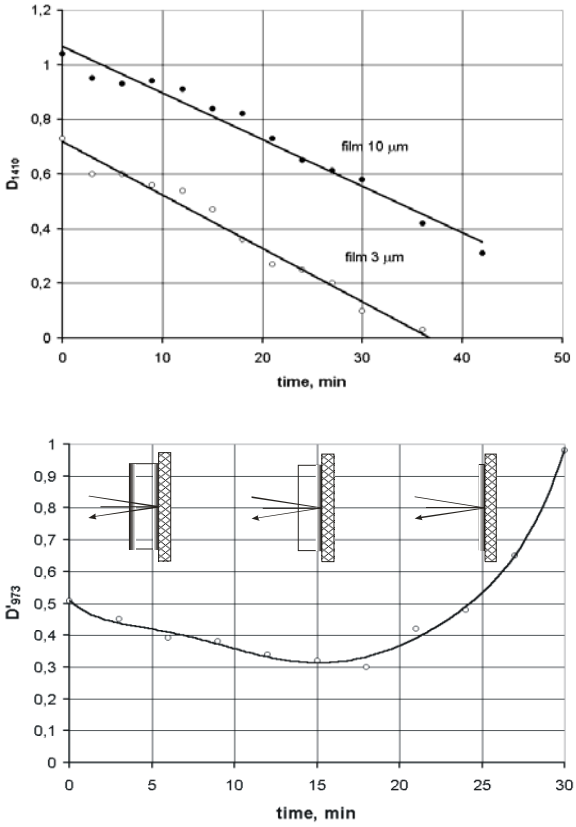

Fig. 6. Optical density of the bands 1410 cm^{-1} and relative optical density of the band 973 cm^{-1} in PET films IR spectra depending on the plasma treatment time

Table 1. Changes in some spectral characteristics at ATR spectra of fabrics of PET fibers and their properties depending on plasma of various gases (power of glow discharge 440 W, treatment time 15 sec)

Plasma	–	Argon	Air	Oxygen
D_{1410}	0.102	0.075	0.054	0.042
D_{1343}/D_{1410}	1.32	1.14	1.12	1.08
Capillarity, m×10^{-3}	37	51	64	83
Normal humidity, %	0.51	1.08	1.45	1.87
Relative breaking load, mN/tex	440	431	426	420
Relative elongation at rupture, %	22	18	22	21

Besides occurrence and displacement of new bands are observed in the spectral range 750 – 950 cm^{-1} where strong absorption of the polymer is absent. Most likely it is connected with the interference IR radiation in the films

and probably with the mechanical relaxation processes occurring after removal of the surface layers.

These data of structural changes correlates very well with the increase in surface energy of the material (textile fabrics) which indicates a sharp increase in the fabrics capillarity and the normal humidity (Table 1).

Thus, the mechanical properties of fabrics are not practically deteriorated after treatment.

A change in capillarity of "Trevira" fabrics of PE microfibres depending on the time of plasma treatment is represented in Fig. 7.

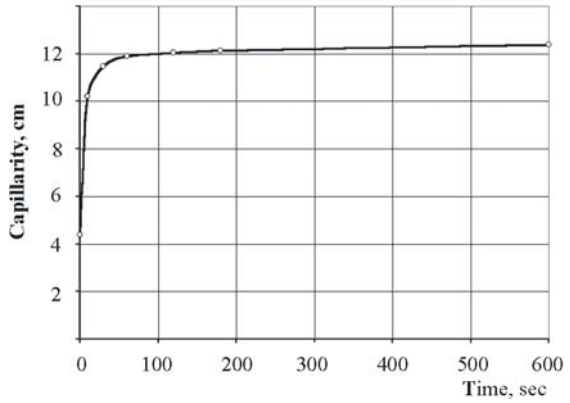

Fig. 7. Change in capillarity of fabrics of PET microfibers depending on the time of plasma treatment (O^{++} plasma)

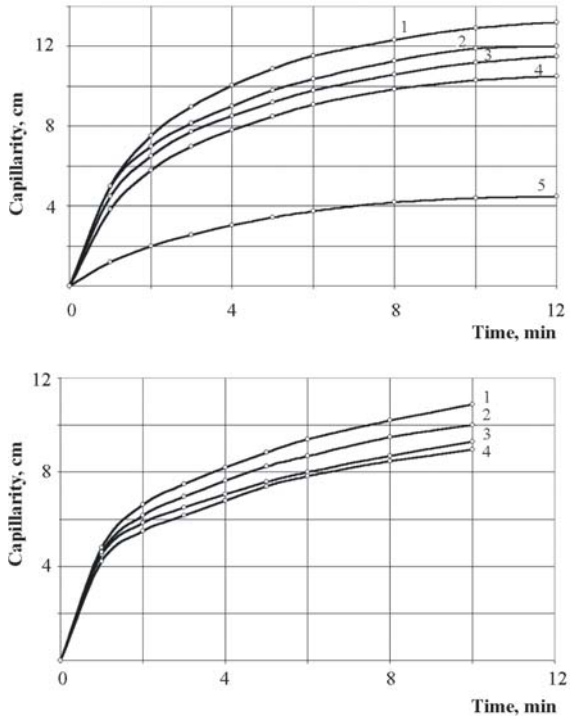

Fig. 8. Capillarity kinetics of fabrics after direct plasma treatment (above) and after storing of treated specimens in the course of a month (below): 1 – time of plasma treatment 10 min, 2 – 2 min, 3 – 1 min, 4 – 10 sec, 5 – initial

Plasma treatment increases capillarity of the material by about 3 times due to increase of surface energy of fibres. The optimum time of treatment under these conditions is 0.5 – 1.0 min. The investigation of printing processes of the treated microfibre material showed that the colour intensity is higher than for the untreated one. The dyes penetration into the opposite side of the fabric is also higher.

From the technological point of view, it is important to note that this effect takes place for a long time after exposure (Fig. 8): capillarity is reduced by about 16 – 17 % in a month in spite of the fact that any special protective measures on preservation of properties of the samples (hermetic sealing, conditioning etc.) were not applied.

CONCLUSIONS

Glow discharge low-temperature plasma treatment results in an increase in the surface energy of PET films and fabers. Due to the growth of capillarity, the intensity of printing that is especially essential for the fabrics of microfibers is increased. A substantial growth of capillarity of fabrics of usual fibers and of microfibers is shown. The effect of increase in capillarity is stable and registered for a long time (one month).

The change in functional properties is attributed to the structural changes in surface layers, in particular, for the erosion of the initial surface layers as well as to the occurrence of new active functional groups. The nonmonotonous change in the spectral characteristics with time followed from the moment of plasma treatment can be caused by the mechanical relaxation processes.

Acknowledgments

The authors are grateful to Yu. Lipin (A/O "Sidrabe", Riga) and V. Kopustinskas (Institute of Physical Electronics, Kaunas University of Technology) for treatment of specimens and assistance.

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