SURFACE MODIFICATIONS OF P E T YARNS AND FIBERS BY PLASMA TREATMENT AT HIGH PRESSURE

O. DEMUTH - Institut Textile de France Section LYON Avenue Guy de Collongue B. P. 60 69132 ECULLY Cédex

J. AMOUROUX - Laboratoire de "Réacteurs Chimiques en Phase Plasma" Ecole Nationale Supérieure de Chimie de Paris 11 rue Pierre et Marie Curie 75231 PARIS Cédex 05

M. GOLDMAN - Laboratoire de Physique des Décharges E R 114 du C N R S Ecole Supérieure d'Electricité Plateau du Moulon 91180 GIF SUR YVETTE

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ABSTRACT

The wettability of poly (ethylene terephthalate) yarns is an important criterion for their industrial use. The attainment of that property is realized by treatment of the material under corona discharge (in air at high pressure). The changes of the physical (roughness, amorphisation of the surface) and chemical (etching of superficial layers, superficial oxidation of the material and fixation of nitrogen) surface properties of P E T yarns are in agreement with the increasing of the surface energy and the variations of electrical properties.

1 - INTRODUCTION

This study concerns poly (ethylene terephthalate) yarns and fibers treated by corona-discharge. The aim of this treatment is to increase the wettability of P E T yarns and fibers and give them suitable properties for different industrial utilisations : dyeing, printing...

Polymeric surface treatment by plasma and especially the corona discharge process presents various advantages for industrial treatments compared to the chemical aqueous treatments :

- facility of implementation,
- speed of process and possibility of automatisation,
- reproductibility of the treatment,

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- small energy consumption, saving of chemical products.

2 - EXPERIMENTAL

Corona discharge experimental set-up
The experimental set-up constitutes the ac cylinder plate (fig. 1) or the
dc sharp point-plane (fig. 2). The gap between the two electrodes can be
considered as a chemical reactor, one end of which is the treated surface.
By means of an energy transfer, the chemical species created (ions, elec-
trons, dissociated molecules, excited particles) are responsible for the
modifications of the surface of the substrate (1).

Control of the treatment
The physico-chemical and electrical surface properties of PET yarns and
fibers have been controlled by means of physical method (T E M), chemical
method (E S C A) (2), measurement of the potential decay (the initial va-
value of the decay rate dV/dt is a representation of the initial conductance
of the sample), measurement of a volume of a drop of liquid (water) hanged
on a yarn (made at the equilibrium between the weight of the drop
P = ρVg and the interaction forces which join the drop to the yarn) for
wettability (photos 1 and 2).

3 - RESULTS (3, 4, 5, 6)

Physical modifications
- Etching of the material
Photo 3 shows a reference PET fiber which presents a slack surface state.
The physical modifications of the surface state of the treated sample signi-
fy the appearance of roughness. Photos 4 and 5 show the influence of the
nature of the current: roughness is obtained for I = + 10 μA (t = 15 mn)
when the same effects are observed for I = −140 μA (t = 30 mn) with nega-
tive current.
- Modifications of crystallinity of superficial layers
The variation of the optical density of electronic diffraction patterns
of the treated PET atomic layers (I = + 20 μA, d = 2 mm, t = 5 mn)
shows a decrease in the surface crystallinity of the material (fig. 3).
These two aspects of the physical modifications, roughness and amorphisation
of the surface control the increase of the surface free energy.

Chemical modifications
- Surface cleaning by corona effects
C1s E S C A spectrum of the raw material don’t correspond to C1s E S C A
spectrum of pure PET (fig. 4); the presence of silicon oil layers
\[ \text{C}_2\text{H}_5 \]
\[ \text{Si} \quad 0 \]
\[ \text{C}_2\text{H}_5 \]
is revealed on the surface of PET yarns. Fig. 5 shows the variation of Si/c ratio versus time of treatment (V = 13 kV, d = 2 mm).
The elimination of silicon oil layers from the surface of PET yarns is
observed.
- Surface oxidation (formation of C = O and COOH)
The rate of fixed oxygen increases until a saturation level reached
after 30 s treatment (V = 13 kV, d = 2 mm) (fig. 6). The augmentation
phase of the fixed oxygen percentage corresponds to the oxidation of the
original polymer according to the following radical Ranby’s mechanism (7):

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1 - Energy transfer on the surface :
\[ \text{RH} \ O_2^* , \ O_2, \ O_2^* , \ O \rightarrow \text{R} + \text{OH} \]

2 - Surface reaction
\[ \text{R} + \text{O}_2^* \rightarrow \text{ROO}^* \]

3 - \( \text{R}^* \text{OO}^* + \text{R}^* \text{H} \rightarrow \text{C} = \text{O} \text{ either} \quad \text{R} + \text{C} + \text{O} \text{OH} \)

These reactions are in competition with reactions of decarboxylation :
\[ \text{RCOOH} \quad \text{hv}, \text{e}^-, \text{O}_2^* \quad \rightarrow \quad \text{R} + \text{CO}_2 \]

Ranby has described the phenomena as a passage to a triplet state in the present carbonyl groups under the action of UV radiation but excited species and electrons can produce the same mechanism.

- Fixation of nitrogen :
Nitrogen reaches a saturation plateau after about 3 O\(_2\) (fig. 6) it is found in the form of an amine (-NH\(_2\)) and in oxidized form (NO) and (NO\(_3\)).
Qualitatively, the importance of nitrogen (in the form of NH\(_2\), NO, NO\(_3\), or NO\(_x\) established by E S C A) is obvious because of its considerable influence on the surface properties of the polymers. Bell and Hollahan point out that N plays a role in crosslinking the polymeric chains, whereas O induces the breaking of chains with oxidation at the break (8).

Electrical properties
At the beginning of the treatment the conductivity increases very sharply with the treatment (fig. 7) then decreases approximately to its initial value and finally seems to increase again for a long treatment time. These variations are in agreement with :
1 - the vaporisation of silicon oil layers : a surface with conductor properties is revealed,
2 - the oxidation of the surface P E T : oxidation products such as carbonyl groups can act as carrier traps, at last destruction of the molecular structure.

4 - CONCLUSION : INCREASE OF WETTABILITY

The surface free energy of a material depends on the physical structure (amorphous, semicrystalline or crystalline structure, degree of molecular stereo-regularity...) and chemical surface properties (polar molecules). The main effects measured on the surface of P E T yarns treated by corona discharge in the atmospheric air are :
- appearance of roughness and amorphisation on the surface of the material,
- vaporisation of the silicon oil layers from the surface of P E T,
- oxidation and nitrogen fixation on the treated surface.
Fig. 6 shows that the increase of the surface free energy of the P E T yarns is correlated with the chemical modifications of the material, the curve \( V = f(t) \) presents the same characteristics as \( O/C = f(t) \) and \( N/C = f(t) \); that is a rapid increase followed by stabilization on a plateau.

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Fig. 1 - Laboratory set (alternative corona treatment of P E T yarns):

Fig. 2 - Laboratory set (continuous corona treatment of yarns or fibers)

Parameters of the discharge:
- energy transfer
- nature of the chemical species
- residence time
- relaxation time of the excited species (ions, radicals)
- kinetics
- atmosphere of the treatment

Electrical parameters:
- voltage
- current
- time of treatment
- nature of the current: alternative or positive or negative
- frequency

Grounded electrode: stainless steel plate
PET yarn (Ø = 0.25 mm)

Reference V = 12.7 µl

Treated V = 33.6 µl

Ph. 1 and 2: Evaluation of the wettability of a PET yarn by the measurement of a volume of a drop of water (made at the equilibrium between the weight of the drop and the interaction forces)

Ph. 1: Reference

Ph. 2: I = +10 µA,
    t = 15 min

Ph. 3: I = -140 µA
    t = 30 min
    d = 5 mm

Roughness of a PET fiber (Ø = 20 µm) treated by continuous corona discharge (influence of the nature of the current)

Fig. 3: Optical density of PET diffraction patterns (of superficial layers).
Fig. 4 C\textsubscript{1s} ESCA spectra of industrial PET yarn (for different times of corona treatment) and pure PET yarn.

Fig. 5 Variation of Si/C\textsubscript{11} versus time of treatment.

Fig. 6 Variation of O/C, N/C and V versus time of treatment.

Fig. 7 Variation of the conductivity of PET yarn versus time under positive or negative corona discharge.