

**THE APPLICATION OF SCANNING ELECTRONIC MICROSCOPY-
THE STUDY OF THE SURFACE STRUCTURES OF THE UPPER
LAYERS OF DYED POLYESTER FIBRE SAMPLES IN THE
OSTACET YELLOW E-L5R**

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Abstract. *Scanning electronic microscope JSM-5300 (JEOL, Japan) has been used to investigate the structure of the PES fibres upper layers. Preparation of samples was performed by placing them on an aluminium support, with a glue or double-sided adhesive tape. The tool for spreading the conductive layer on the sample's surface, used in this work, was JFC-1100E ION SPUTTER (JEOL Co., Japan). Potential difference of electron acceleration was 30 kV, and multiplication of the samples was 3500 times. ORWO NP 20 DIN films were used for taking the photos. The samples were dyed with C.I.D. Yellow 23, in concentration of 1%, at pH = 4.5, with the following acids added: acetic, formic and oxalic. The results show absence of any internal damage in fiber structure. On the surface however, groups of particles have been observed, varying in shape, magnitude and spacing density. Organic (acetic, formic and oxalic) acids used in the experiments caused differences in upper layers structures of dyed PES fibres. This is the main reason to induce differences in colour (DE), chromaticity (DH) and lightness (DL), among the samples (with the all acids included) and a standard (addition of acetic acid only).*

Key words: *octacet yellow E-L5R, polyester fibre, scanning electronic microscopy, surface structure, upper layers*

1. INTRODUCTION

Supramolecular structure of polyester fibres

Polyester fibres are well known because of their structures, which can be described in terms of high orientation and high degree of crystallization. Extension degree may be taken as a measure of orientation. After leaving the exhaust port, filaments become oriented, i.e. the molecular chains have been arranged in a manner to form filaments with specific characteristics. Depending on temperature conditions, the chains take statistical orientation,

strongly influenced by extension magnitude, providing the molecular chains with a certain degree of orientation in the middle [1]. Fig. 1. shows three structural states; a fibrous polymer passes through during production process.

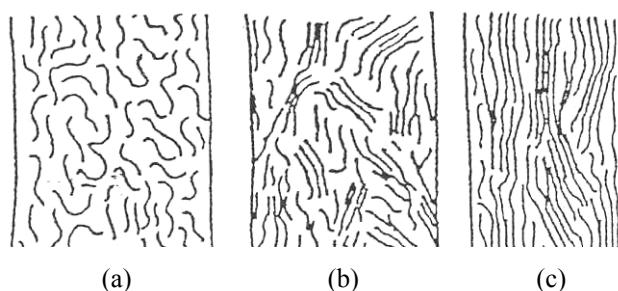


Fig. 1. Molecular organization of polyester filaments in various production steps

Molecular chains in all possible statistical orientations are shown on Fig. 1.(a), i.e. the polymer is in an amorphous state, not only in the axial, but also in the horizontal direction. Fig. 1.(b) shows molecular chains in random-like crystalline and amorphous configurations, with a certain degree of axial and horizontal orientation. Fig. 1.(c) shows orientation of crystal areas along fibre axes, followed, to a lesser extent, by the orientation of amorphous areas.

Crystalline and amorphous factors of orientation, or an average crystal magnitude in polyester fibres, may be determined by appropriate investigations. Reports about the existence of two separate phases (crystalline and amorphous) have been recently replaced by new ones, implying the existence of middle states inside fibres, with very diffuse boundaries toward the other two phases. Such a middle state between the crystalline and amorphous phase has been named the interphase state [2]. Crystalline, interphase and amorphous phases have been obtained in PES fibres by various extensions.

Prevorsek [3] proposed the existence of three phases in polyethylterephthalate fibres: amorphous, interphase and crystalline. According to this model, interphase consists of elongated molecular chains along fibre axes. The author further suggests that the dimensions and structure of interphase may play a dominant role in the characteristics such as elasticity module, strength and contraction. The results of crystalline, interphase and amorphous phase investigations, done by X-ray diffraction on 3.5 times extended polyethylterephthalate fibres, have been shown on Fig. 2.

To preserve the crystalline, interphase and amorphous phases by X-ray diffraction the Lender technique has been employed [4]. Interphase index increases linearly with the extension range, while amorphous phase index declines continuously, indicating an increasing number of molecular fibres parallel to fibre axe at an increased extension. Parts of these chains penetrate crystalline phase, while the other parts penetrate the amorphous and the interphase.

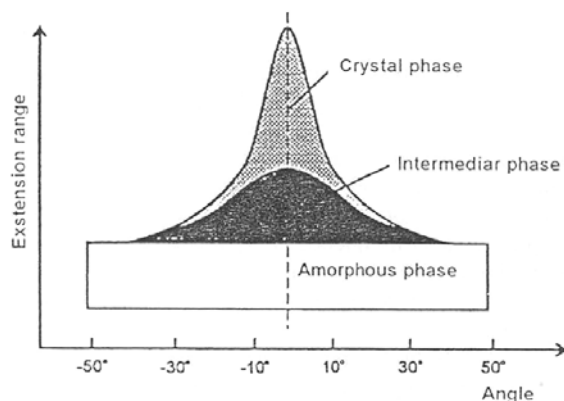


Fig. 2. A scheme of phase separation by X-ray diffraction on a plate (0 1 0) of polyethylene terephthalate fibres, (3.5 times extended)

Physico-mechanical characteristics of polyester fibres

Polyester fibres have been produced with various brilliance degrees: turbid, extra turbid and brilliant fibres. Filamentous yarns have been produced with different numbers of monofilaments that could be of various finenesses.

Depending on the application, polyester fibres can be produced with various physico-mechanical characteristics. Staple polyester fibres differ from filamentous yarns by their characteristics. Usually, all staple fibres are thermo fixed during production, and as a consequence, staple fibres express different contractions, compared to filamentous yarns.

The most important characteristics of polyesters, in the form of yarn and in the form of staple fibres, are:

- small sorption of moisture,
- high strength in dried and wet state,
- high initial module,
- high resistance to change of form due to torsion moments,
- small change of shape at relatively high charge,
- ability to change shape permanently due to heat action,
- high resistance to wearing out,
- good electric characteristics [5-7].

Polyester fibres undergo short elastic relaxation. That is why; textile fabrics containing a significant portion of PES fibres undergo slight crumpling. PES fibres absorb very small quantities of moisture, providing easy drying of PES fibre products. PES fibres being exposed for longer periods of times to moisture action at high temperatures, in boiling water or in overheated vapor for example, undergo deterioration of physical parameters.

PES fibres are thermoplastic. Their strength-to-break changes disproportionately with temperature, whereas breaking elongation changes proportionally. If PES fibres are exposed to high temperatures for longer periods of times, then strength-to-break changes very little, compared to others synthetic and natural fibres.

One of the most important and most valuable characteristic of PES fibres is the ability to undergo permanent deformation, when exposed to high temperatures and high pressures. For example, as a consequence, PES textile fabrics may take the form of permanent creasing, not loosing the shape during wearing and washing.

PES fibres resistance to wearing-out is bigger, compared with other fibres, natural as well as synthetic; polyamide fibres are the only ones with higher resistance to wearing-out. PES fibres have markedly higher resistance to breaking than natural fibres. They are also more resistant to the damaging influence of moisture, chemicals and microorganisms: a study of influence of atmospheric, environmental conditions showed PES fibres lasted much longer than other fibres.

PES fibres exposed to sunlight behind glass are more resistant than most other fibres in the same conditions. Polyester yarn has a relatively high friction coefficient on polished surfaces, especially metals and porcelains, which is of highly practical value.

If PES fibres are heated below their flaming point they undergo melting, and hard pearls as the end are formed. Flame directed toward the fibres causes melting, which leads to the formation of pearls that are difficult to light by fire, and that would burn producing a lot of soot. The pearls fall off the burning fibres and they stop burning. That is why, PES textile fabrics are considered hardly flammable. Of course, PES textile fabric's parameters are certainly influenced by additives and presence of other fibres.

According to literature, the most important quality marks of the usual types of PES fibres are:

– strength-to-breaking	3.5-6.0 cN dtex ⁻¹
– elongation breaking	25-40 %
– elasticity degree at 5 % elongation	70-90 %
– mass volume	1.38 g · cm ⁻³
– humidity content (at 65 % RV and 20 °C)	0.30-0.40 %
– initial module	30-60 cN dtex ⁻¹
– water sorption	3 %
– temperature of softening	230-240 °C
– temperature of melting	250-256 °C
– temperature of fixation	180-230 °C
– temperature of glass transition	70-80 °C
– resistance to sunlight, the rest of strength	60-80 %.

PES fibres parameters are highly influenced by measuring conditions.

Chemical characteristics of PES fibres

PES fibres are resistant to organic and inorganic acids. However, stronger and more concentrated inorganic acids cause destruction (H₂SO₄, HNO₃). On the other hand, PES fibres are resistant to 90 % H₃PO₄, which makes them different from other synthetic fibres that dissolve in it, after one minute of boiling.

PES fibres are significantly resistant to hydrolysis, unlike other esters. This can be explained by higher density of packing of polyethylene terephthalate molecules. PES fibres decompose on the surface only, when treated with alkali solutions.

PES fibres are very resistant to action of oxidation and reduction agents.

PES fibres do not dissolve in most the organic solvents (trichloroethylene, carbon tetrachloride, acetone, benzene, toluene, alcohol and most hydrocarbon oil derivatives). However, they are dissolved in hot phenol, chlorophenol, tricresol, benzyl alcohol, etc.

Such chemical resistance and the other characteristics of PES fibres can be explained by their structure.

2. EXPERIMENT

Operating principle of scanning electronic microscope

Scanning electronic microscope JSM-5300 (JEOL, Japan) has been used to investigate the structure of the PES fibres upper layers. First electronic microscopes were of TEM type (transmissible electronic microscopes), but in 1938 M. von Ardenne constructed another type of electronic instruments (upon Knoll suggestion in 1936), known as SEM. This instrument may be considered as an analogue microscope, using the light transmission principle.

SEM uses a fibre of wolfram, or lantanhexaborid to produce electrons for thermo ionic emission. Then, they are accelerated toward the sample by using potential difference of 2.5-50 kV. The electrons are directed toward one point, by a system of lenses to produce an electronic ray spreading all over the sample. The incident electronic ray reacts with a sample, generating several types of signals. The signals are then collected in detectors, and their output is multiplied to adjust intensity on CRT screen. Scanning electronic ray is synchronized with the output on CRT screen. Quadruple raster is formed on CRT screen. The noticeable variations in light intensity are generated as a consequence of signal variations from point to point of the sample surface.

SEM has two CRTs, one connected to the display with long-lived phosphorus, and the other to the photo recorder with short-lived phosphorus. SEM multiplication is defined as a final picture dimension divided by sample's scanning field. For example, if an electronic ray scans 1 mm² on sample surface, and the output is shown on CRT screen as 100 mm², one deals with 100 times multiplication.

Multiplication changes are performed by the reduction of the sample screen part, while the display is held constant. In practice, multiplication switch on SEM changes the ray slope; linear magnitude of the scanned part depends on the sample distance from a final lens [8].

SEM development was slow until 1965, when the first commercial SEM appeared. Cambridge Instruments Co. produced Stereo Scan Mark I, based on the work of Oatley and co-workers, from the Engineering Department at Cambridge University. Nowadays, SEM production is known worldwide. Low cost, easy using and handling, and much better resolution compared to optical microscopes, contributed to its extended use.

Preparation of samples for scanning on SEM is a trivial matter. They are placed on an aluminium support, with a glue or double-sided adhesive tape. A conductive layer, like carbon or gold, must be spread on the sample's surface, to prevent electronic charge formation, with a possible reaction with incident electronic beam. The tool for spreading the layer on the sample's surface, used in this work, was JFC-1100E ION SPUTTER (JEOL Co., Japan). Holder with the sample is then placed on a stand, permitting operations of inclination, rotation and translation.

On the surface and below it, certain phenomena take place when a high-energetic beam hits the sample in electronic optical instrument. At SEM, a picture is formed, by two kinds of secondary electron signals, and background scattering electrons.

The JFC-1100E ION SPUTTER consists of a basic part, and a rotational pump. Various metallic layers have been spread with this tool on the non-conductive samples in a very short period of time. Besides, the tool can be used for contamination removal, and for hydrophilic treatment of supporting films, serving in transmission electronic microscopy [9].

Potential difference of electron acceleration was 30 kV, and multiplication of the samples was 3500 times. ORWO NP 20 DIN films were used for taking the photos.

3. RESULTS AND DISCUSSION

Fig. 3-5. show records of the PES fibre dyed samples, obtained by electronic microscope. The samples were dyed with C.I.D. Yellow 23, in concentration of 1 %, at pH = 4.5, with the following acids added: acetic (Fig. 3.), formic (Fig. 4.) and oxalic (Fig. 5.). The Figures show absence of any internal damage in fiber structure. On the surface however, groups of particles have been observed, varying in shape, magnitude and spacing density.

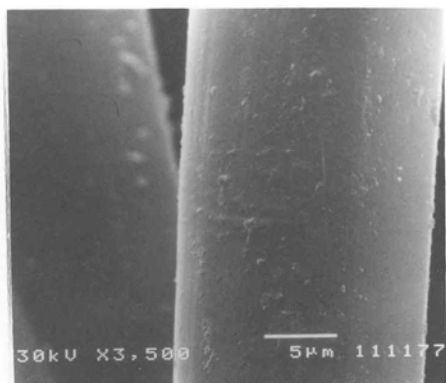


Fig. 3. PES fibre surface, dyed with C.I.D. Yellow, with addition of acetic acid (multiplied 3500 times)

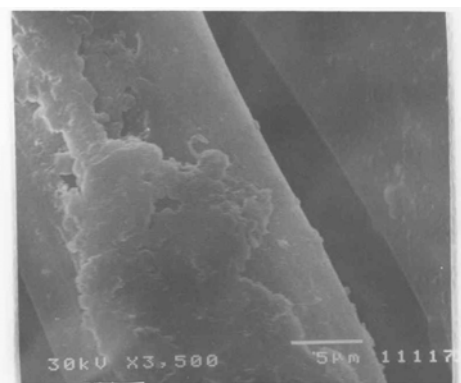


Fig. 4. PES fibre surface, dyed with C.I.D. Yellow, with addition of formic acid (multiplied 3500 times)

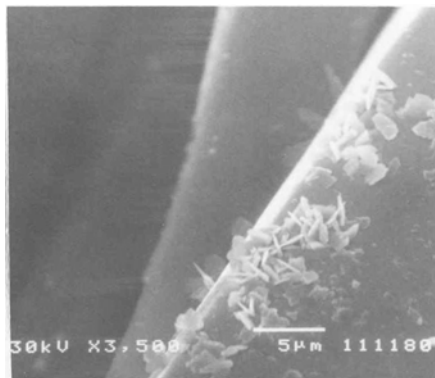


Fig. 5. PES fibre surface, dyed with C.I.D. Yellow, with addition of oxalic acid (multiplied 3500 times)

Organic (acetic, formic and oxalic) acids used in the experiments cause differences in upper layers structures of dyed PES fibres. This is the main reason to induce differences in colour (DE), chromaticity (DH) and lightness (DL), among the samples (with the all acids included) and a standard (addition of acetic acid only).

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PRIMENA SKENIRAJUĆE ELEKTRONSKE MIKROSKOPIJE- PROUČAVANJE POVRŠINSKIH STRUKTURA GORNJIH SLOJEVA OBOJENIH POLIESTARSKIH VLAKANA U BOJI OCTATET ŽUTOJ E-5LR

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Skenirajući elektronski mikroskop JSM-5300 (JEOL, Japan) je korišćen za ispitivanje strukture gornjih slojeva poliestarskih vlakana. Priprema uzoraka je izvršena postavljanjem istih na osnovu od aluminijuma, pomoću lepka ili obostrano lepljive trake. Sredstvo za širenje provodnog sloja na površini uzorka, korišćeno u ovom radu je JFC-1100E ION SPUTTER (JEOL Co., Japan). Razlika potencijala elektronske akceleracije bila je 30 kV, a uvećanje uzoraka 3500 puta. ORWO NP 20 DIN filmovi su korišćeni za izradu fotografija. Uzorci su obojeni žutom bojom C.I.D. Yellow 23, koncentracije 1%, pri

pH = 4.5 uz dodatak sledećih kiselina: acetatne, formijatne i oksalatne. Rezultati pokazuju odsustvo bilo kojeg unutrašnjeg oštećenja u strukturi vlakna. Međutim, na površini su uočene grupe čestica, koje variraju po obliku, magnitudi i prostornoj zastupljenosti. Organske kiseline (acetatna, formijatna i oksalna), koje su korišćene u eksperimentima, izazvale su razlike u gornjim slojevima struktura obojenih poliestarskih vlakana. Ovo je glavni razlog za indukciju razlika u boji (DE), hromatičnosti (DH) i svetline (DL), između uzoraka (uključujući sve dodate kiseline) i standarda (gde je dodata samo acetatna kiselina).