

Polyester fibres structure modification using some organic solutions

Jelena Mitic¹
Goran Amin²
Marija Kodric²
Miodrag Šmelcerović¹
Dragan Đorđević²

¹ Higher Professional School

² Faculty of Technology,
Leskovac, Serbia

e-mail: drdrag64@gmail.com

Received September 18, 2015

UDC 677.494.674:677.027.6:677.017.4
Original scientific paper*

The treatment causes only minor decrease in fibre, i.e. yarn strength, while breaking elongation increases significantly, almost up to 150 % in comparison to the untreated sample. Organic solvents, i.e. plasticizer solutions in the organic solvents mixture influence fibre properties in a very favorable way, i.e. they can enable better dyeing, better moisture absorption, easier treatment in further phases of textile products manufacture and generally better usability. X-ray structural analysis was used to examine the influence of the treatment of polyester fibres in the form of filament yarn, fineness 75/26 dtex, with solutions 0.3, 0.6 and 0.9 % hydroquinone and α -naphthole in the solvent mixture which contained chlorophorm and methanol (solubility parameter $\delta=11.7$) on changing of crystalline degree and crystallite size. It was found that treated fibres showed sharper reflexion on diffractograms than untreated ones, i.e. they showed higher crystalline degree but smaller crystallite size.

Key words: polyester yarns, modification, organic solutions, crystalline degree, strength, elongation.

1. Introduction

Owing to their exquisite physical, mechanical, and textile properties, polyester (PET) fibres have the leading role amongst synthetic fibres. Throughout the whole period of PET production growth and development, systematic research has been carried out in order to improve their quality

and to expand the scope of their use. However, only a few papers have been published that dealt with PET fibres treatment with organic solvents or their mixtures or with some plasticizer solutions in those mixtures, and with their influence on physical and mechanical properties of fibres and yarns [1-3].

The structure of PET fibres can be described as a structure with great "orientation" and high crystalline degree. The latest theory of super molecular construction of PET fibres

establishes the presence of: crystalline, amorphous and interphase states in these fibres [4]. According to this model, the interphase consists of directly lengthened molecular chains along the fibre axis. Interphase scope and structure can have a dominant role in PET fibre properties such as elasticity modulus, strength, and shrinkage. Crystalline and amorphous segments have different susceptibilities to deformations, i.e. amorphous segments deform more easily than crystalline ones. For that

*CEC 2015 – 8th Central European Conference on Fiber-Grade Polymers, Chemical Fibers and Special Textiles, Zagreb, September 16th-18th 2015

reason, examination of fibre crystalline degree is of great importance. Crystalline degree of fibres-polymers has crucial influence on their mechanical properties. Under certain circumstances, organic solvents can influence changes in relations between crystalline and amorphous phase in polyethyleneterephthalate, and also changes in mechanical properties [3]. These actions in the PET-organic solvent system can connect with swelling and solubility. Due to their action, initial elastic area disappears completely soon after the loading stress action. Accordingly, organic solvents and textile fibre interactions fact made further investigation of these interactions the subject of this paper.

2. Experimental

2.1. Material and chemicals

PET smooth filament yarn, fineness 75/26 dtex, was used in the research. Individual monofilaments were white and with a circular cross section. Basic properties of the yarn used were:

- fineness, 75/26 dtex
- breaking force, 310 cN
- relative strength, 4.13 cN/dtex
- breaking elongation, 21 %
- shrinkage at boiling, 10 %
- number of twists, 8 m⁻¹

Chemicals: solution of 1,4-dihydroxybenzene (hydroquinone) and 1-hydroxynaphthalene (α -naphthol) in chlorophorm and methanol solvent mixture.

2.2. PET treatment

The yarn was treated at room temperature for 15 min on a shaker with 120 rpm. Hydroquinone and α -naphthol concentrations in the solvent mixture (the mole content of 73.10 % chlorophorm and 26.90 % methanol) were 0.3, 0.6, and 0.9 %. Filament yarn was in the form of small spools containing 30 m of yarn. Before the treatment, the yarn was brought into the standard state. Bath modulus was 1:20.

After the treatment, the yarn was squeezed between two pieces of filter paper, dried at room temperature for 1 hour, and dried in a dryer at 70 °C for 1 hour. Afterwards, the samples were left in a conditioning cabinet (relative humidity 65±2 %, temperature 20±2 °C) for 48 hours, and then the required examination was carried out.

2.3. Testing methods

Breaking force and breaking elongation of untreated and treated samples, were examined according to SRPS F.S2.052. The examination was performed on the universal dynamometer "Instron" (England), where breakings were made by tractive clamp moving at constant speed.

Breaking was performed under following conditions:

- tractive clamp speed: 30 cm/min
- paper for diagram drawing speed: 30 cm/min
- specimen length: 20 cm
- preliminary stress: 4.2 cN
- climate conditions: standard

PET fibres structural changes caused by the treatment were observed through X-ray structural analysis. Hermans and Weidinger's method (WAXS method) was used to determine PET fibres, i.e. monofilament, crystalline and crystalline size [5]. The method took into consideration

ray intensity variation due to the difference in absorption in a sample under various angles 2Θ and variation in the sample mass reflecting X-rays in the angle of diffraction function. Examination samples were prepared by winding filament threads onto a special aluminium sample carrier in even layers of known thickness. Examination was performed on a diffractometer D5000 (Fa. Bruker-AXS) with Cu-K α radiation line under the angle 2Θ from, 4° to 32° with the rotation of 1 min⁻¹ and printer speed of 10 mm/min. Crystallite dimensions were determined based on a diffraction curve for a peak determined by Miller's index (010) and (0 $\bar{1}$ 1).

3. Results

Organic solvents interact with fibres in such a way, that due to the solvability of certain groups, cause swelling in macromolecules and changes in intermolecular actions. This brings about changes in various relaxation processes, which is demonstrated as shifting into certain areas and structures on the super-molecular level. As a consequence of relaxation processes intensification and provoked shifting, changes in certain fibre properties occur.

To characterize filament yarn strength, two parameters are mostly used in practice:

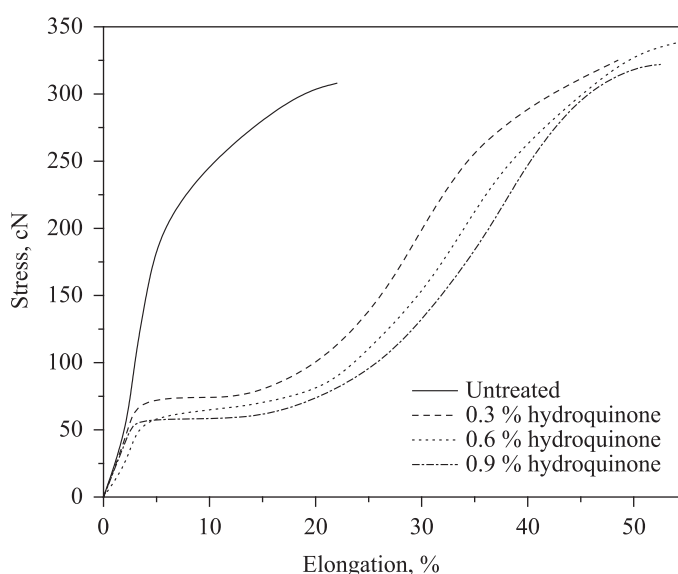


Fig.1 Stress-elongation curves of untreated and treated PET fibres

- breaking force and
- breaking elongation

Absolute strength is the highest force value yarn can resist before breaking. An example of stress-elongation curves for untreated yarn samples and samples treated with hydroquinone and α -naphthol solution in a solvent mixture is given in Fig. 1.

Co-action of organic solvents and solutions with the polymer brings about shifting in the polymer structure and creates new structures, which influences fibre properties and PET filament yarn properties.

Two plasticizer types chosen (hydroquinone and α -naphthol) act not only as plasticizer but also as radical pro-

cesses inhibitors. In a way, they stabilize the new structure, created under the organic solvents influence. The treatment causes only minor decrease in fibre, i.e. yarn strength, while breaking elongation increases significantly, almost up to 150 % in comparison to the untreated sample. Stress-elongation curves of the modified fibres-yarn resemble curves of woolen fibres. Accordingly, it is to be expected that PET filament yarn fibres treated in this way many properties similar to woolen fibre properties.

Organic solvents, i.e. plasticizer solutions in the organic solvents mixture influence fibre properties in a very favorable way, i.e. they can enable better dyeing, better moisture absorption, easier treatment in further phases of textile products manufacture and generally better usability.

Stress-elongation curves show that there are differences in behaviour of treated and untreated PET filament yarn samples, under the influence of tractive force. For an untreated sample the curve is permanently ascending from the beginning of force action until the point of breaking, while for treated samples the curves show ascending, then they have the parallel course enlarging the force of relation the x axis, and they have ascending again until the break point.

Relative strength is a relation between absolute strength and fineness (longitudinal mass). Fineness is determined by measuring individual yarn segment's length and mass. Mean values of examinations, each consisting of 20 trials, are given in Tab. 1.

Unlike the strength, which changes only slightly due the treatment, breaking elongation shows significant changes. It increases. Breaking elongation increase due to the treatment is from 120 % (treated samples 0.3 % hydroquinone in the mixture) to 145.5 % (treated samples 0.6 % hydroquinone in the mixture) in comparison to untreated samples. In other

Tab.1 Examination results mean values of the strength of untreated and treated filament yarn samples

Sample	Absolute strength		Relative strength		Elongation of break, %
	cN	Increase, %	cN/dtex	Decrease, %	
Untreated	310	-	4.13	-	22.0
0.3 % hydroquinone in the mixture	330	6.45	3.25	21.31	48.5
0.6 % hydroquinone in the mixture	329	6.13	3.27	20.82	54.0
0.9 % hydroquinone in the mixture	328	5.81	3.29	20.34	52.5
0.3 % α -naphthol in the mixture	335	8.06	3.40	17.67	-
0.6 % α -naphthol in the mixture	333	7.42	3.33	19.37	-
0.9 % α -naphthol in the mixture	336	8.39	3.34	19.13	-

Tab.2 Examination results of crystalline degree by X-ray graphic method

Sample	Surface F, cm ²	Height h, cm	Crystalline degree, %
Untreated	16.7	6.5	29.3
0.3 % hydroquinone in the mixture	41.6	5.0	53.4
0.6 % hydroquinone in the mixture	42.3	5.4	55.6
0.9 % hydroquinone in the mixture	44.5	5.3	56.3
0.3 % α -naphthol in the mixture	39.1	4.6	54.1
0.6 % α -naphthol in the mixture	45.3	5.1	57.0
0.9 % α -naphthol in the mixture	46.3	5.3	58.3

Tab.3 Crystallite size determination results for peak (100 + 0 $\bar{1}$ 1) by X-ray graphic method

Sample	Diffraction angle Θ , °	Peak width B, mm	Crystallite size, nm
Untreated	17.6	13.0	6.14
0.3 % hydroquinone in the mixture	17.8	16.0	4.98
0.6 % hydroquinone in the mixture	17.6	16.5	4.86
0.9 % hydroquinone in the mixture	17.7	17.0	4.68
0.3 % α -naphthol in the mixture	17.6	16.5	4.70
0.6 % α -naphthol in the mixture	17.6	17.0	4.68
0.9 % α -naphthol in the mixture	17.9	16.0	4.60

words, breaking elongation increases, due to the treatment, for approximately 1.5 times on the average in comparison to the untreated sample. Increase in breaking elongation is probably the result of the shifting in the fibre structure caused by the treatment. For that reason, further research was focused on the examination of the fibre structure changes by X-ray analysis.

On the basis of diffraction curves and adequate formulae, examination results of crystalline degree have been obtained (Tab.2).

Results show that crystalline degree has increased due to the treatment. The greatest increase has been noted in samples treated with 0.9 % α -naphthol solution in the mixture, and it is almost 100 % in comparison to untreated samples. Characteristic diffraction curves for some PET filament samples are given in Fig. 2, 3, and 4.

Comparing diffraction curve of untreated and treated PET filament yarn samples, clear differences in characteristic peaks forming can be noted (Fig.2, 3 and 4).

For the peak denoted by Miller's index $(100 + 0\bar{1}1)$, which is clearest and most distinct, crystallite size of untreated and treated samples has been determined, Tab.3.

Characteristic peak appears for the diffraction angle $2\Theta = 17.6^\circ$ to 17.9° . Crystalline size is decreased by the treatment. The decrease was 25 % at the most, and was achieved in samples treated by 0.9 % α -naphthol solution in the solvent mixture.

Simplified mechanism of the interaction between fibres and solvents can be presented as follows: solvent molecules enter amorphous areas of the fibre and replace polymer-polymer co-action with polymer-solvent co-action, solvatizing to a certain extent certain groups in polymere macromolecules, which causes certain swelling of the fibre and establishes absorption-swelling equilibrium [6]. By breaking intermolecular polymer-polymer bonds, some macromolecu-

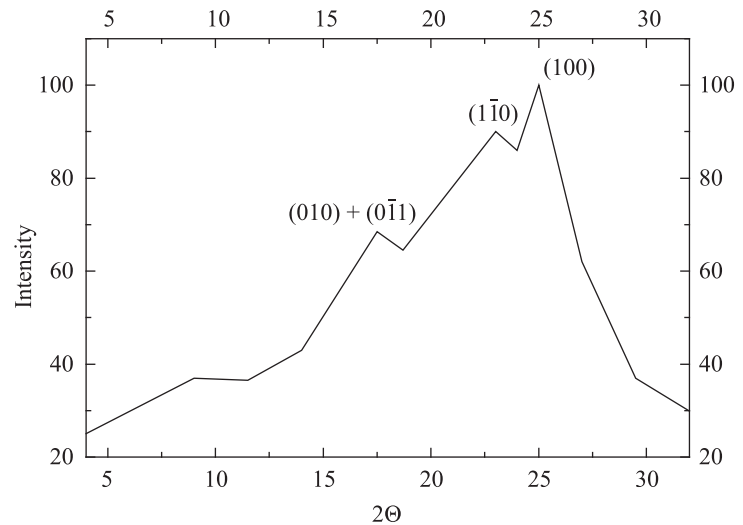


Fig.2 Untreated sample diffraction curve shape

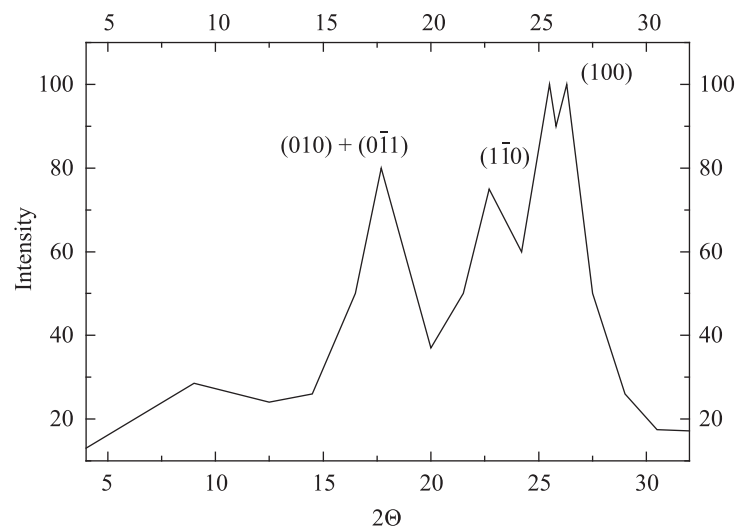


Fig.3 Diffraction curve of the sample treated with 0.9 % hydroquinone solution in the mixture

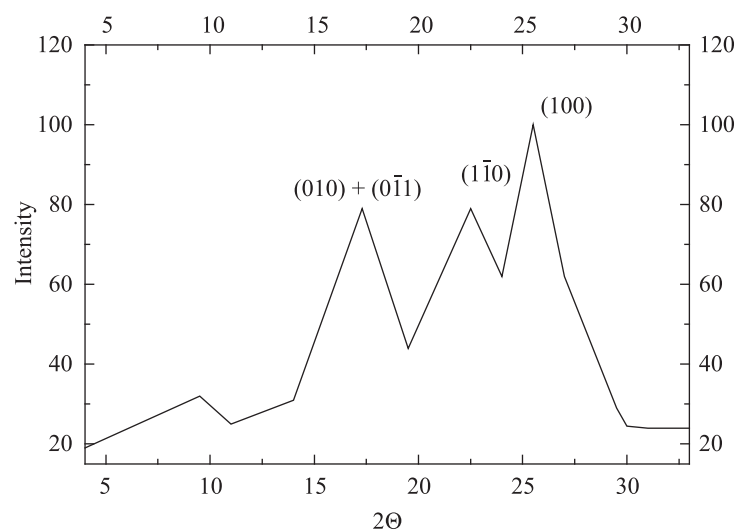


Fig.4 Diffraction curve of the sample treated with 0.9 % α -naphthol solution in the mixture

lar segment movement possibilities increase and relaxation processes accelerate, which causes structural shifting inside the fibre, and this in turn, causes changes in super-molecular structures and eventually in fibre properties [7].

For quantity description of polymer-solvent co-action, solubility parameter is used. It is known that polymer-solvent co-action is stronger if their solubility parameters are similar. In this examination, CHCl_3 and CH_3OH solvents mixture with the solubility parameter of 11.7 has been used (solubility parameter of chlorophorm is 14.27 and of methanol it is 9.21). Weigman and Ribnick [8] have found that the greatest solvent-polymer co-action occurred in two ranges of solubility parameter $\delta_1=9.8$ and $\delta_2=12.1$. For that reason, solvent mixture with $\delta=11.7$ has been chosen for this examination, since it is closer to the $\delta_2=12.1$ value.

It is obvious that solvent treatment of PET fibre in the presence of plasticizers causes crystallization in amorphous areas (crystalline degree of the untreated fibre is 29.3 %, and of the fibre treated with 0.9 % α -naphthol solution in the mixture it is 58.3 %). Due to the limited space, crystallites formed in these areas are of a small size (untreated fibre crystallite size is 6.14 nm, while crystallite size of the fibre treated with 0.9 % α -naphthol in the mixture is only 4.60 nm). Plasticizer molecules, containing active functional OH groups, are supposed to be centers for crystallization. The greatest changes probably occur in intermediary phase, which is considered to have great influence on fibre properties. Strength is not significantly changed by the treatment, while

breaking elongation increases significantly. It points out to the fact that crystalline areas where solvent cannot penetrate retain their initial properties (properties that existed prior to treatment), while extended oriented noncrystalline areas become disoriented under the solvent influence. The disorientation is recurrent during extension, which is manifested with significant increase of breaking elongation.

4. Conclusion

Co-action of organic solvents and solutions with the polymer brings about shifting in the polymer structure and creates new structures, which influences fibre properties and PET filament yarn properties.

Two plasticizer types chosen (hydroquinone and α -naphthol) act not only as plasticizer but also as radical processes inhibitors. In a way, they stabilize the new structure, created under the organic solvents influence. The treatment causes only minor decrease in fibre, i.e. yarn strength, while breaking elongation increases significantly, almost up to 150 % in comparison to the untreated sample. Stress-elongation diagram of the modified fibres-yarn resemble curves of woolen fibres, on this basis, we can expect that treated PET yarn will be very similar to the characteristics of wool yarn.

Organic solvents, i.e. plasticizer in the organic solvents mixture influence fibre properties in a very favorable way, so, it is expected that they enable better dyeing, better moisture absorption, easier treatment in further phases of textile products manufacture and generally better usability.

References:

- [1] Limam M., L. Tighzert, F. Fricoteaux, G. Bureau: Sorption of organic solvents by packaging materials: polyethylene terephthalate and TOPAS, *Polymer Testing* 24 (2005) 3, pp.395-402, ISSN 0142-9418
- [2] Ingamells W., N. Yanumet: Solvent-polymer interactions in the plasticisation of poly(ethylene terephthalate), *British Polymer Journal*, 12 (1980) 1, pp.12-18, ISSN 1934-256X
- [3] Hsieh Y.L., D.A. Timm, M. Wu: Solvent- and glow-discharge-induced surface wetting and morphological changes of poly(ethylene terephthalate) (PET), *Journal of Applied Polymer Science* 38 (1989) 9, pp.1719-1737, ISSN 1097-4628
- [4] Chapleau A.N.: Structure and properties of impact modified polyethylene terephthalate, *Journal of Materials Science* 37 (2002) 18, pp 3893-3901, ISSN 0022-2461
- [5] Włochowicz A., A. Jeziorny: Determination of crystallinity in polyester fibers by x-ray methods, *Journal of Polymer Science Part A-2: Polymer Physics* 10 (1972) 8, pp.1407-1414, ISSN 1099-0488
- [6] Kenwright A.M., S.K. Peacea, R.W. Richardsa, A. Bunnb, W.A. MacDonald: End group modification in poly(ethylene terephthalate), *Polymer* 40 (1999) 8, pp. 2035-2040, ISSN 0032-3861
- [7] Chen W., T.J. McCarthy: Chemical Surface Modification of Poly(ethylene terephthalate), *Macromolecules* 31 (1998) 11, pp.3648-3655, ISSN 0024-9297
- [8] Weigmann H.D., A.S. Ribnick: Interactions of Nonaqueous Solvents with Textile Fibers: Part IV: Effects of Solvents on the Mechanical Properties of Various Textile Yarns, *Textile Research Journal* 44 (1974) 3, pp.165-173, ISSN 0040-5175