

Iwona Karbownik,
* Jadwiga Bucheńska,
** Barbara Lipp-Symonowicz,
** Henryk Wrzosek

Textile Research Institute
ul. Brzezińska 5/15, 92-103 Łódź, Poland
E-mail: ikarbownik@iw.lodz.pl

Technical University of Łódź
Department of Man-Made Fibres,
Department of Fibre Physics and Textile
Metrology Faculty of Textile Engineering
ul. Zeromskiego 116, 90-543 Łódź, Poland

Studies on the Influence of Grafting PET Fibres with Acrylic Acid on Molecular Orientation

Abstract

The molecular orientation of dye introduced into a fibre was characterised numerically by the coefficient of molecular orientation f_D . Lowering its value was the result of decreasing molecular orientation in non-crystal areas of the grafted PET fibre. The f_D index was influenced by the following grafting reaction parameters: time of modification reaction, temperature and concentration of acrylic acid in the bath.

Key words: polyester fibres, grafting, molecular orientation, molecular orientation coefficient.

surgical fabrics [2]. Special requirements, especially connected with the behaviour of implants in a tissue environment (e.g. resistance to contamination), resulted in the beginning of research directed at creating antibacterial surgical threads [3-6].

The modification of surgical threads was based on grafting them with poly(acrylic acid) PAA, which introduces carboxylic groups into the material of a fibre, the process later being followed by particles of antibiotics. The modification process of a shaped fibre causes changes in the parameters of its physical microstructure, especially its non-crystal molecular orientation.

The aim of this work was to evaluate PAA grafting onto the molecular orientation of non-crystal PET (polyethylene terephthalate) fibres, from which surgical threads were produced. In order to do so, we used the method of measuring the dichroism of a fibre colour on a fibre dyed in a test [7].

Measuring material and methodology of the tests

The object of the research was non-twisted yarn made of 24 ductile PET fibres obtained from Elana S.A., Torun. The yarn used in the studies was extracted with acetone but not prepared beforehand [8].

In the process of grafting, the following agents were used:

- pure acrylic acid of German production (Fluka Chemika), stabilised with 0.02% methyl ether of hydrochinon.
- The acid was purified in the process of distillation under a lower pressure, in an atmosphere of deoxygenated nitrogen, in the presence of metallic copper; the boiling temperature

of the acid under the low pressure of 4 mm Hg was 301.5 K; the refraction coefficient of the purified acid was $n_D^{20} = 1.421$.

- dispersing agent NNO (mixture of concentrated salts of multicore aromatic sulphoacids) POCh – Gliwice;
 - pure diphenyl (DP) $C_{12}H_{10}$ – Gliwice
 - benzoyl peroxide (PB) for synthesis with 25% H_2O_2 , from Merck-Schuhardt, dried over P_2O_5
 - inhibitor – pure hydrochinon $C_6H_6O_2$ – Gliwice
 - pure toluene $C_6H_5CH_3$ with a density of $d = 0.87 \text{ kg/dm}^3$, POCh-Gliwice
 - consumable nitrogen, Lindegaz, Lodz
- For dyeing fibres, the following dye was used:
- disperse dye under the trade name of Disperse Yellow 3, C.I. 11855, produced by Ostacolor A.S.

The grafting bath module was 1:50 in all experiments. Grafting was carried out in a nitrogen atmosphere with changeable parameters of reaction.

In order to evaluate the influence of modification with acrylic acid (AA) on the molecular orientation of grafted fibres, a series of studies was carried out, during which the conditions of the process were changed:

- temperature ranged from 80 °C to 95 °C
- time of reaction ranged from 15 to 90 minutes

In the studies, the concentration of AA was constant and equalled 7.5 wt% in compliance with bath mass.

In the third series of studies, the concentration of AA in the grafting bath was changed, keeping the following as constant: temperature $T = 95 \text{ °C}$ and time of reaction $t = 60 \text{ min}$.

Introduction

The usefulness and properties of the fibre of a certain synthetic polymer mostly depend on the multiparticle structure of the material. Fibres may be provided with special features by the modifying material and introducing certain chemical groups.

Ductile PET (polyester) fibres have been a valuable raw material in production of surgical threads for over 50 years [1]. From this material, there are various other biomedical products, such as vessel prosthesis, artificial ligaments, and knitted

The amount of additives that would improve the grafting process of the fibres was constant in all the series of studies and equalled 0.4 wt% in compliance with the bath mass.

The degree of grafting (X) of poly(acrylic acid) PAA onto PET fibres was measured gravimetrically and analytically according to [8].

For evaluation of the influence of the grafting process of the fibres on their molecular orientation, some reference tests were prepared, carrying out thermal treatment of the fibres in the conditions described above, but with no possibility of creating grafted copolymer. In order to obtain reference samples, there was also an inhibitor added, in the amount of 0.8%, to the grafting bath with acrylic acid and additives to improve the grafting process (DP and NNO), in compliance with bath mass. The inhibitor's task was to prevent the creation of both copolymer and homopolymer.

In the method of evaluating molecular orientation undertaken, by us using the measurement method of measuring the dichroism of a fibre colour on a dyed fibre, it is necessary to introduce particles of a certain dye, assuming that it would not provoke any changes in the parameters of the fibre structure. The particles of the dye that diffuse to the inside of the fibre are placed parallelly to the macroparticles in the amorphous regions and are also characterised by a strong anisotropy of light absorption to the dye axis. Because of this, fibre samples of tested fibres and ones modified in the grafting process underwent dyeing in a temperature of 80 °C (below the glass temperature T_g of the fibres) for 20 hours, in aqueous bath, using an excess of dye in compliance with the mass of the dyed fibre. Disperse Yellow 3 C.I.11855 was used as a test dye, with its linear particle and low dipole moment value, which guaranteed parallel adhesion of the dye particles to segments of macroparticles placed in the amorphous area of the fibre (**Figure 1**). From earlier research it can be seen that this dye particle shows a tendency to arrange itself according to the direction of orientation of macro-particle chains in amorphous material [7].

In the applied method of evaluation of the molecular orientation of fibre material, it is assumed that the orientation of the dye particles, which were introduced into

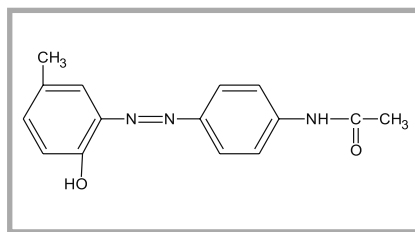


Figure 1. Disperse Yellow 3 Colour Ind. 11855.

the fibre, are characterised in quantity by factor f_D , described by the equation:

$$f_D = \frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + D_{\perp}} \quad (1)$$

where D_{\parallel} & D_{\perp} represent directions of the optical density (absorbance) of the partially oriented particle system of the dye.

Spectrophotometric markings of index value f_D were made using a polarisation microscope coupled with a photographic attachment with a photo multiplier and SPECOL spectrometer made by ZEISS JENA, including a set of optical filters. Microscopic preparations of the dyed fibres underwent X-raying with polarised monochromatic light ($\lambda = 400\text{nm}$), which met the condition of absorbing light to the maximum through the dye introduced into the fibre.

Additionally, in order to widen the interpretation possibilities, there was a measurement of the real density of the sample fibres (treated thermally in baths with AA and an inhibitor that would make it impossible for grafted copolymer and homopolymer to be created) as well as parameters of the fibre structure tightly connected with its crystal state [9, 10]. The density of the sample fibres was measured by floatation technology, using a gradient pillar [11]. In order to mark the density, it was necessary to find an appropriate immerse medium where a mixture of toluene and carbon tetrachloride was present, then pre-deaerate the sample and establish the time after which the measurement was taken. The following criteria were employed:

- chemical and physical indifference towards the fibre (swelling)
- a diameter of the particles that would be smaller than the smallest empty spaces within the fibre
- a density similar to the fibre density
- chemical and physical stability in time.

Correct measuring of the time was set by establishing the state of balance in the sample-immersed centre system, which was the time of measuring the real density, lasting for 24 hours.

The physical base of the densitometric way of marking the crystal state make for the differences in the density of macro-particle packing in crystal and amorphous areas. Crystal areas are characterised by greater density than amorphous ones, due to the arranged and condensed setting of macro-particles in them [10]. There can be a greater real density of the fibre, which increases together with the amount of crystal areas. According to some of the literature [12], the crystal material density (d_{cr}) and amorphous density (d_a) for PET is, respectively, $d_{cr} = 1.455\text{g/cm}^3$; $d_a = 1.335\text{g/cm}^3 \div 1.355\text{g/cm}^3$. Knowing those values and being able to read the real density of fibres, we can receive a mass degree of grafting x_m , which is calculated on the basis of the following dependence:

$$x_m = \frac{d - d_{a\%}}{d_{cr} - d_a} \quad (2)$$

where:

d = real density of the fibres, determined in g/cm^3

d_{cr} = density of the crystal material of the PET fibre, according to [12]

d_a = density of the amorphous PET fibre according to [12].

Results of studies and discussion

In **Table 1** (see page 111) there are values of the f_D index for samples dyed in tests of the prepared fibres (introductory grafting sample), grafted fibres and reference fibres.

In **Figures 2-4** (see page 110) there are f_D values depending on the variables of fibre modification parameters.

In **Figure 2** there is f_D in the function of the time of reaction for grafted fibres and reference samples.

In **Figure 3** there is the f_D index for grafted fibres and reference fibres depending on the temperature of modification of the reaction.

In **Figure 4** there are the dependencies for the changing concentration of AA in grafting bath.

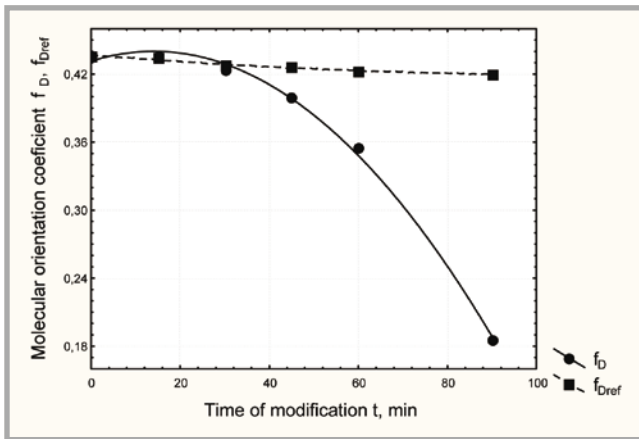


Figure 2. Value of indices f_D and f_{Dref} in the function of the time modification of the PET fibres.

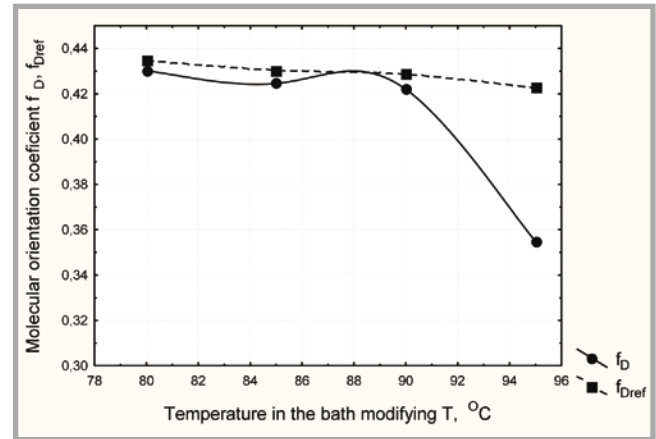


Figure 3. Values of f_D and f_{Dref} in the function of temperature changes in the bath's modification of the PET fibres.

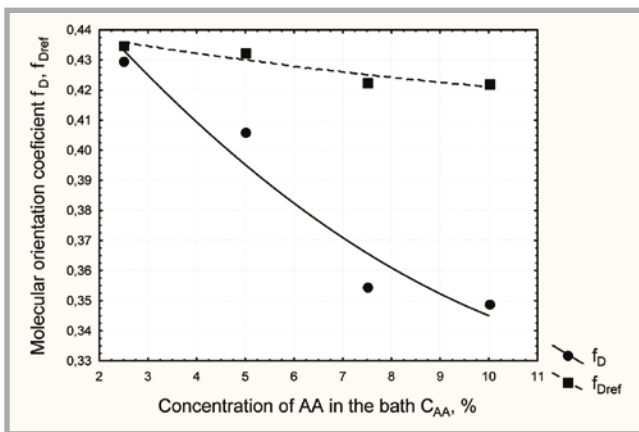


Figure 4. Values of f_D and f_{Dref} in the function of changeable concentration of AA in the bath's modification of the PET fibres.

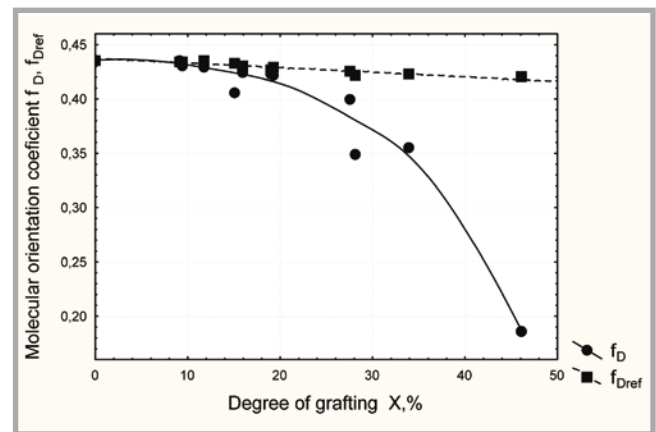


Figure 5. Value of the f_D , f_{Dref} index in the function of PAA grafting X onto PET fibres.

For the reference samples, which were in contrast to the zero sample (PET yarn without preparation), there is a significant decrease in the f_D index value, which shows a worsening of fibre orientation under the influence of parameters used in the grafting process. However, it remains in accordance with the changes that appear during the heating of the fibre in a non-stressed condition. The greatest lowering of the f_D value was noted for the longest time of treatment, which is $t = 90$ minutes.

From the data presented in **Table 1** and also in **Figures 2-4**, it can be seen that the greatest influence on the f_D index, which characterises the orientation of the dye particles introduced into the fibre, is the time of the reaction, whereas the temperature of the reaction together with the concentration of acrylic acid in grafting bath influences it to a much lesser degree. Because the listed parameters have an influence on the grafting

degree X, the f_D index also depends on this value. It decreases together with the degree of grafting fibre X. In **Figure 5**, there is an illustration of this dependency.

Lowering the value of the f_D index is the result of lessening the molecular orientation in amorphous areas of the grafted PET fibre. A relatively large decrease in the value of this index was noticed for the sample of the greatest grafting degree, which equalled $X = 46.11\%$ (**Table 1**, No 6).

There appears a slight lowering in the value of the f_{Dref} value for the reference samples (modified in the presence of the inhibitor), in contrast to the zero sample, prepared with non-grafted PET fibre. However, it remains in accordance with the changes in molecular orientation that appear during the process of heating the fibre in a non-stressed condition. The lowering value of the f_D index for the grafted fibre during a longer time

of modification (**Figure 2**) as well as increasing the temperature of the reaction (**Figure 3**), and a higher AA concentration (**Figure 4**) result in a worsening of the orientation of a fibre under the influence of parameters used in the process of grafting. Because the listed parameters of the reaction influence the degree of grafting X, it can be concluded that chains of polyacrylic acid join PET fibres in their amorphous part.

In order to discover what the influence of the grafting reaction parameters (t , T and C_{AA}) on the orientation of the modified fibres is, a measurement of the density of the reference samples was carried out. In **Table 2** there are values of the density of the reference fibres (d) and the value of the mass crystal degree (x_m), calculated according to equation (3).

A slight decrease in the mass degree of the crystal state was observed (x_m) for samples in baths with $\geq 7.5\%$ AA and tem-

Table 1. Values of the index f_D for modified PET fibres grafted with PAA and $f_{D,ref}$ for reference samples (modified with hydrochinon).

No	Modification conditions			Degree of grafting	Molecular orientation coefficient of the grafted samples	Changes in molecular orientation coefficient	Changes in molecular orientation coefficient of the reference	Changes in molecular orientation coefficient in the reference samples
	Grafting temperature	AA concentration in grafting bath	Time of modification					
	T, °C	C _{AA} , %	t, min	X, %	f _D , –	%	f _{D,ref}	%
1	0	0.0	0	0.00	0.4359	100.00	0.4359	100.00
2	95	7.5	15	9.13	0.4353	99.86	0.4344	99.65
3	95	7.5	30	18.96	0.4236	97.18	0.4273	98.02
4	95	7.5	45	27.53	0.3997	91.70	0.4258	97.62
5	95	7.5	60	33.86	0.3548	81.39	0.4226	96.94
6	95	7.5	90	46.11	0.1861	42.69	0.4202	96.39
7	80	7.5	60	9.37	0.4302	98.69	0.4347	99.72
8	85	7.5	60	16.00	0.4246	97.41	0.4304	98.73
9	90	7.5	60	19.23	0.4220	96.81	0.4286	98.32
10	95	7.5	60	33.86	0.3548	81.39	0.4226	96.94
11	95	2.5	60	11.79	0.4296	98.55	0.4350	99.79
12	95	5.0	60	15.12	0.4062	93.19	0.4325	99.22
13	95	7.5	60	33.86	0.3548	81.39	0.4226	96.94
14	95	10.0	60	28.08	0.3487	79.99	0.4219	96.78

Legend: T=temperature, °C; C_{AA} – concentration of acrylic acid in grafting bath in wt%; t=time of grafting in minutes; X = degree of grafting with PAA onto a PET fibre in wt%; f_D and f_{D,ref} = index, non-titrating value.

Table 2. Value of the f_D index and the density and mass value of the crystal degree for the reference samples (modified with the inhibitor as an additive).

No	Grafting reaction parameters			Coefficient for the reference samples	Density of the reference samples	% lowering of the density of the reference	Mass degree of crystallisation
	T °C	C _{AA} %	t min				
	T °C	C _{AA} %	t min	f _{D,ref} , –	d, g/cm ³	%	x _m , –
1	0	0	0	0.4359	1.400	0.00	0.54
2	95	7.5	15	0.4344	1.398	0.14	0.53
3	95	7.5	30	0.4273	1.397	0.21	0.52
4	95	7.5	45	0.4258	1.395	0.36	0.50
5	95	7.5	60	0.4226	1.393	0.50	0.48
6	95	7.5	90	0.4202	1.393	0.50	0.48
7	80	7.5	60	0.4347	1.397	0.21	0.52
8	85	7.5	60	0.4304	1.396	0.29	0.51
9	90	7.5	60	0.4286	1.395	0.36	0.50
10	95	7.5	60	0.4226	1.393	0.21	0.48
11	95	2.5	60	0.4350	1.400	0.00	0.54
12	95	5.0	60	0.4325	1.400	0.00	0.54
13	95	7.5	60	0.4226	1.393	0.21	0.48
14	95	10.0	60	0.4219	1.393	0.21	0.48

Legend: T, t – respectively: temperature and time of treatment for the PET fibres; C_{AA} – concentration of acrylic acid in modifying bath; f_{D,ref} – index for the reference samples; d – real density of the fibre; x_m – mass degree of the crystal state.

perature of 95 °C for one hour or longer. It means that in these cases disintegration of a less ordered crystal material takes place.

Summary

The parameters of the grafting reaction: time of reaction, temperature of the bath and concentration of acrylic acid influence the f_D index of the molecular orientation of a fibre as well as the crystal state index x_m .

In the grafting process a significant lowering of the orientation index f_D is observed for a time of treatment >60 minutes and temperature = 95°C. It resulted from the reaction of particles of acrylic acid introduced into a non-crystal material of a fibre in grafting baths, at a concentration of acrylic acid C_{AA}>7.5%.

In those cases disintegration of a less stable crystal material also takes place

(which is indicated by the lowering of the value of mass grafting for a crystal state x_m).

The most favourable conditions were established for polyester PET fibre modification from which surgical threads were created. The grafting reaction with polyacrylic acid was as follows:

- acrylic acid (AA) concentration in the grafting bath C_{AA} = 7.5%wt
- grafting time t = 45-60 min
- temperature of reaction T = 95 °C.

In these conditions a grafting degree X ≈ 30% poly(acrylic acid) was obtained for PET fibres, which was satisfactory for further modification (binding an antibiotic to the carboxylic groups introduced). At the same time, these conditions did not cause any relevant decrease in the orientation coefficient f_D , which would have caused the disintegration of the fibre material.

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