

## MICROVOID SYSTEM IN FIBRES

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### Abstract

The morphology of fibres consists of crystalline and noncrystalline domains forming the microfibrillar structure. Microvoids are present in form of inter- and intrafibrillar free spaces. In the presentation the microvoid system of poly(ethylene terephthalate) (PET) and poly(propylene) (PP) fibres was studied by small-angle x-ray scattering (SAXS). Commercial PET textile fibres were treated in different media and the influence on fibre homogeneity was followed by SAXS. Conventional water dyeing and hot air treatment of PET fibres have caused considerable changes in the microvoid system. The influence of these two treatment media on the structure of inner surface is very alike and even higher than the influence of supercritical fluids at the same temperature.

PP technical fibres were manufactured on a laboratory spin-drawing device and subsequently drawn at different drawing conditions on a laboratory drawing device. The drawing has influenced the microvoid system of fibres, with drawing the size and volume fraction of voids have increased, resulting in spinodal change of the microvoid system.

### Introduction

The morphology of drawn fibres consists of crystalline and noncrystalline domains forming the microfibrillar structure.<sup>1–5</sup> During the fibre formation process free spaces are formed between and inside the fibrils; these are known as inter- and intrafibrillar voids. For theoretical as well as practical reasons it is very interesting to study this void-space system, because it determines the amount of the inner surface of the sample and this is directly related to several physico-chemical properties as swelling, dyeing characteristics etc.

The formation of microvoids is dependent on the polymer type and fibre-forming process. Fibres formed by the biosynthesis process develop different inner surfaces when compared to the man-made fibres. Additionally, in the series of man-made fibres great differences in the microvoid system are observed as well.

The content, dimensions and relative surface of microvoids can be observed by small-angle x-ray scattering (SAXS), an HPLC technique and low temperature gas sorption (LTGS), etc. A comparison of SAXS and LTGS results was given by Jánosi *et*

al.<sup>6</sup> In the present study the SAXS technique was used for determination of the microvoid system of poly(ethylene terephthalate) (PET) and poly(propylene) (PP) fibres. Diffuse SAXS shows a maximum of intensity at the scattering angle  $2\theta = 0^\circ$  and decreases to zero at angles between  $1-2^\circ$ . This scattering is due to inhomogeneities in the electron density distribution and is attributed to the existence of microvoids in the polymers.

## Experimental

### *Sample preparation*

#### PET fibres

The analyses were carried out on a commercial 48 filament PET textile yarn of a linear density of 143 tex. PET fibre was produced from the melt with the intrinsic viscosity 0.71 g/l with the take up velocity of 3000 m/min. Drawing was performed at  $T = 250^\circ\text{C}$  with draw ratio of 1:2.5, followed by heat setting at  $T = 250^\circ\text{C}$ . The blind dyeing of PET fibres (a treatment at the same conditions as the dyeing process but without the dyestuff) was performed in supercritical fluid (SCF) after the isothermal - isobaric method (I) and the temperature - pressure step method (II) with the treatment conditions:  $T = 130^\circ\text{C}$ ,  $p = 40\text{ MPa}$ ,  $t = 60\text{ min}$ . Fibres were additionally treated in hot water and hot air at  $T = 130^\circ\text{C}$ ,  $t = 60\text{ min}$ .<sup>7</sup>

#### PP fibres

The melt spinning and three-stage in-line drawing of PP fibres was carried out on an Extrusion Systems Ltd. laboratory spin-draw device. Fibres were spun from a commercial Hoechst PP plastic grade homopolymer Hostalen PPN 1060 F with MFI = 2g/10min. The polymer was extruded at a rate of 21.7 g/min through a spinneret with ten holes of diameter 0.35 mm each. The temperature of the melt was  $280^\circ\text{C}$ , spinning velocity 30.7 m/min and draw-down ratio 1:3.1. The as-spun fibre was three-stage drawn at  $50^\circ\text{C}$  in a continuous spin-drawing process with a draw ratio of 1:4.2. Moderately, continuously drawn fibre was additionally drawn to the limiting draw ratio on a Zimmer laboratory draw device. In this subsequent slower stage the fibre was drawn through a hot-plate at two different temperatures: at  $130^\circ\text{C}$  with draw ratio of 1:2 and at  $145^\circ\text{C}$  with draw ratio of 1:2.5.

The structural investigation was carried out on the undrawn fibre (*sample PP*), on the fibre moderately drawn at 50 °C (*sample PP-drawn*) and on the fibres additionally drawn at 130 °C (*sample PP-drawn -130*) and at 145 °C (*sample PP-drawn-145*).<sup>5</sup>

### **Structural characterisation**

A detailed microvoid system study was performed by means of small-angle X-ray scattering. Copper radiation was used together with a Ni filter suppressing the  $K_{\beta}$  line for measuring the intensity of PET fibres and without a Ni filter for measuring the intensity of PP fibres. For PP fibres the influence of the  $K_{\beta}$  line was eliminated numerically with the method developed by Zipper.<sup>8</sup> The SAXS curves were obtained by using a Kratky block-camera with slit collimation. Entrance slit of 40  $\mu\text{m}$  and receiving slit of 100  $\mu\text{m}$  width were used. Scattered intensities were registered by a linear position-sensitive detector Braun PSD 50M connected to a pulse-height discriminator and multi-channel analyser. The distance between the bundle of fibres and the plane of registration was 21 cm. Computer programs developed at the Institute of Physical Chemistry at the University of Graz were used for the evaluation of the measured data.<sup>9</sup>

The averaged scattering curves of the samples represent the scattered intensity  $I$  as a function of the modulus  $h$  of the scattering vector, which is connected with the scattering angle  $2\theta$  by the relation.<sup>10-12</sup>

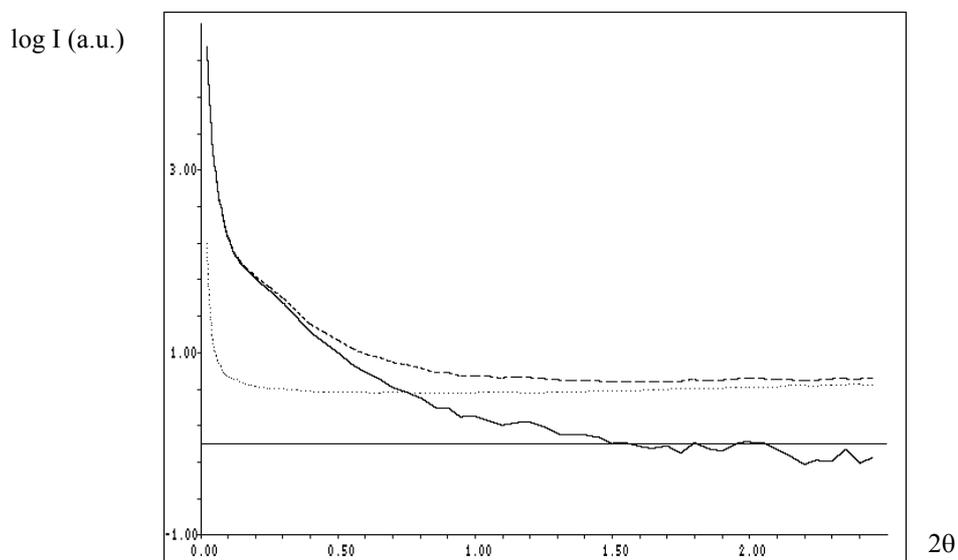
$$h = 4\pi \frac{\sin \theta}{\lambda} \quad (1)$$

where  $\lambda$  is the wavelength of x-rays ( $\text{CuK}_{\alpha} = 0.1542 \text{ nm}$ )

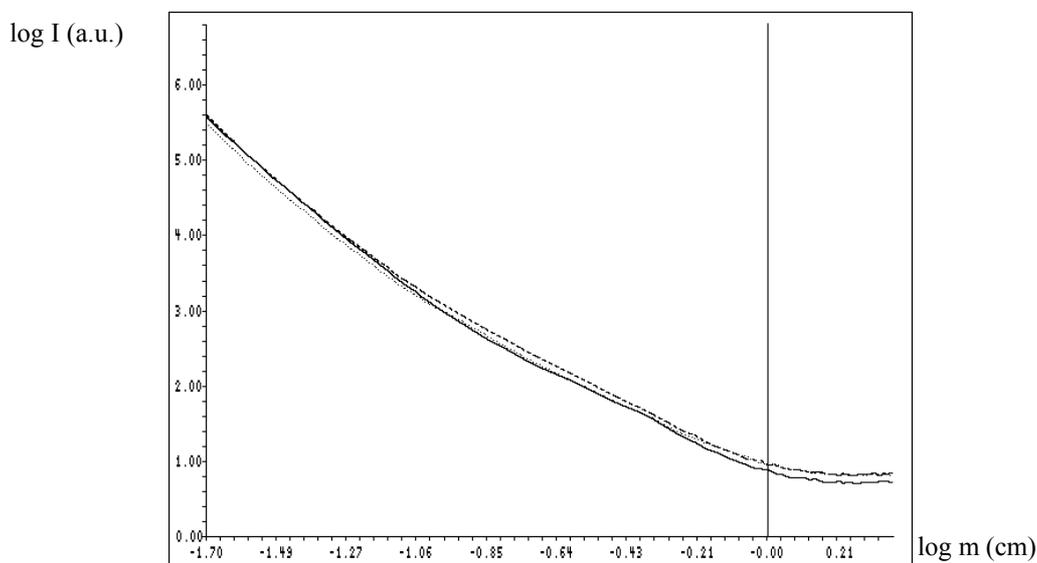
Scattering angle  $2\theta$  is obtained by following relation:

$$2\theta = \sin(m/a) \approx \frac{m}{a} \quad (2)$$

where  $m$  is the distance between the measured point and the centre of gravity of primary beam in the plane of registration and  $a$  the distance between the bundle of fibres and the plane of registration.



**Figure 1.** Experimental (---), blank (.....) and differential curve (— · —) of the PET sample, respectively



**Figure 2.** Scattering curve of the moderately drawn PP fibre at 50 °C (.....) and additionally drawn PP fibre at 130 °C (— · —) and at 145 °C (—), respectively

The equatorial scan was performed in the angular range of  $2\theta = 0.95$  mrad to  $2\theta = 115$  mrad. The data were subjected to an absorption correction and to background subtraction. For the latter correction blank curves (with empty sample holders) were taken in the same way and then they were subtracted from the experimental curves, as shown in Fig.1. A desmearing of the measured curves was done only for the as-spun PP fibre, for all other samples the desmearing was not necessary because of the special geometry of drawn fibres at the measurement (fibres aligned parallel to the longitudinal direction of the primary beam).<sup>13</sup> In this case the obtained experimental curve of the oriented fibres corresponds to the cross-section scattering curve  $I_c(h)$ .<sup>10,11</sup>

$$I_c(h) = I(h) \cdot h \quad (3)$$

Therefore to get the scattering intensity  $I(h)$  the experimental curves were divided by  $h$ . In Fig.2 experimental curves obtained for the drawn PP fibres as a double log plot are shown. From these curves the characteristic SAXS parameters were obtained. A two-phase fibre model, consisting of polymer (crystalline and amorphous domains) and empty holes was accepted for analysing the equatorial SAXS curves. It was assumed that phase 1 (polymer) and phase 2 (voids) have different electron densities and that within each phase the electron density is constant. For the two-phase system the microvoid system was evaluated by means of equations given in literature, with some of them listed below.<sup>11,14-16</sup>

With the volume fraction  $w_1$  (polymer) and  $w_2 = 1 - w_1$  (voids) the scattering power of the two-phase system  $\overline{(\Delta\rho)^2}$ , which is the difference of the mean square fluctuations of the electron density, is given by

$$\overline{(\Delta\rho)^2} = w_1 \cdot w_2 \cdot (\rho_2 - \rho_1)^2 \quad (4)$$

The relative inner surface of the system  $S_s$ , i.e. interfacial area between the two phases, can be obtained from the Porod's constant  $K_p$  and Porod's invariant  $Q$  by the Eq.5:

$$S_s = \frac{S}{V} = w_1 \cdot w_2 \cdot \frac{2\pi^2}{\lambda \cdot a} \cdot \frac{K_p}{Q} \quad (5)$$

and the specific inner surface of the system  $S_p$ , from the irradiated volume of the sample  $V$  and its density  $d$  by the Eq.6:

$$S_p = \frac{\left(\frac{S}{V}\right) \cdot 10^3}{d} \quad (6)$$

From the ratio of Porod's invariant  $Q$  and Porod's constant  $K_p$  another parameter is obtained, i.e. the reduced intersection length  $l_r$  by the relation

$$l_r = \frac{2\lambda \cdot a}{\pi^2} \cdot \frac{Q}{K_p} \quad (7)$$

and the correlation length  $l_c$  from following relation:

$$l_c = \frac{\lambda \cdot a}{2} \cdot \frac{\int_0^{\infty} I(h) \cdot h \cdot dh}{Q} \quad (8)$$

## Results

### *Microvoid system in PET fibres*

The Table 1 collects SAXS parameters obtained after different treatments of PET fibres. The content of the free volume in the untreated fibres is low as it is characteristic for PET fibres due to their closely packed structure. Nevertheless some modifications of the microvoid system were observed due to the physical treatment of the fibres. The treatment increases the void fraction and decreases the correlation length. Comparing the reduced intersection length  $l_r$  only very small differences between fibres treated in different media were found. This parameter depends on the size and shape of the

geometrically defined inhomogeneities, but it is independent of their distribution in the system. The same consideration is valid for the relative inner surface of the system.

The changes of the void system due to the SCF dyeing are slightly different if the isobaric / isothermal (method I) or the step method (method II) is used. However in both cases dyed fibres possess more and smaller voids. Voids in fibres dyed according to SCF dyeing method II (temperature - pressure step method) are smaller but their volume content is higher and the interfacial area between polymer and holes greater. Nearly all parameters are to a higher extent influenced by the treatment as compared to the changes caused by the first dyeing method (cf. Table 1).

**Table 1.** The mean-square fluctuation of the electron density,  $\overline{(\Delta\rho)^2}$ , the volume fraction of the voids,  $w_2$ , relative inner surface of the system,  $S_s$ , specific inner surface of the system,  $S_p$ , correlation length,  $l_c$ , and reduced intersection length,  $l_r$ , for the untreated and for different SCF and water dyed and hot air treated PET samples.

Sample	$\overline{(\Delta\rho)^2}$ mol <sup>2</sup> cm <sup>-6</sup>	$w_2$ %	$S_s=S/V$ nm <sup>2</sup> /nm <sup>3</sup>	$S_p$ m <sup>2</sup> /g	$l_c$ nm	$l_r$ nm
PET- untreated	0.00707	1.38	0.010	0.7482	63.9	5.2
PET – CO <sub>2</sub> –I	0.01457	2.88	0.034	2.4422	53.1	3.3
PET – CO <sub>2</sub> –II	0.01056	2.07	0.023	1.6504	56.0	3.6
PET – water treated	0.01311	2.58	0.034	2.4636	49.7	3.0
PET – hot air treated	0.01124	2.21	0.032	2.3128	50.4	2.7

Conventional water dyeing and hot air treatment cause considerable changes in the microvoid system too. The influence of these two treatment media on the structure of inner surface is very alike and even higher than the influence of the supercritical fluids at the same temperature.

**Microvoid system in PP fibres**

Calculated SAXS parameters of the undrawn PP fibre and of fibres moderately drawn at 50 °C and additionally in subsequent step drawn at 130 °C and 145 °C are given in Table 2.

**Table 2.** The mean-square fluctuation of the electron density,  $\overline{(\Delta\rho)^2}$ , the volume fraction of the voids,  $w_2$ , relative inner surface of the system,  $S_s$ , specific inner surface of the system,  $S_p$ , correlation length,  $l_c$ , and reduced intersection length,  $l_r$ , for the PP fibres

Sample	$\overline{(\Delta\rho)^2}$ mol <sup>2</sup> cm <sup>-6</sup>	$w_2$ %	$S_s=S/V$ nm <sup>2</sup> /nm <sup>3</sup>	$S_p$ m <sup>2</sup> /g	$l_c$ nm	$l_r$ nm
PP	0.0016	0.60	0.006	6.716	13.5	3.7
PP – drawn	0.0035	1.35	0.021	23.68	26.9	2.5
PP – drawn-130	0.0041	1.57	0.021	23.36	29.9	2.9
PP – drawn-145	0.0036	1.39	0.021	23.25	30.4	2.6

As-spun undrawn PP fibre has a very low free-volume content, voids are small, as it is the interfacial area between polymer and voids. With drawing a microfibrillar structure is formed, resulting also in a change of the microvoid system of drawn fibre. For the PP fibre moderately drawn at 50 °C the characteristic values obtained are as expected for a closely packed partly crystalline structure of fibre. Low volume content of microvoids, below 1.5%, the correlation length below 30 nm and 10 times smaller reduced intersection length are in the range of values reported for drawn fibres spun from the melt. For additionally highly drawn fibres the change of the microvoid structure in comparison to the original sample, moderately drawn fibre, is small. For the fibre drawn at 130 °C an increase of scattering power, volume fraction of voids and linear dimensions of inhomogeneities up to 17%, and no change in the relative and specific inner surface of the system were noted. For the fibre drawn at 145 °C, only an increase of correlation length is seen, while the change in all other parameters is less than 5%.

### Conclusions

The microvoid system and fibre homogeneity of PET and PP fibres were studied. Closely packed PET fibre structure disables the development of an extensive inner surface, but the structure homogeneity is not very high. Due to the physical treatment of the fibres, regardless of the medium used, modifications of the microvoid system occurred and the fibre inhomogeneity is increased. The changes observed after the treatment of PET fibres can be described as the dispersion of the phase 2 (voids) in the matrix, without a change of its shape and its volume fraction in the system – it is a coarsening change, and the formation of further grains of the phase 2 having the same shape as the present ones – a nucleotic type of the change.

The microvoid system of PP fibres changes with the drawing conditions. The structural inhomogeneity increases with the increase of the size and the volume fraction of voids formed at the fibre drawing. Severe drawing to the limiting draw ratio causes the spinodal change of the void system to occur.

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### **Povzetek**

Mikrofibrilna struktura vlaken je sestavljena iz kristalinih in nekristalinih področij. V vlaknih so prisotne še mikrovotline v obliki inter- in intrafibrilnih praznih prostorov. V prispevku smo z ozkokotnim rentgenskim sipanjem (SAXS) proučili sistem mikrovotlin polietilenterftalatnih (PET) in polipropilenskih (PP) vlaken. Komercialna PET tekstilna vlakna smo obdelali v različnih medijih in spremljali vpliv pogojev obdelave na homogenost vlaken s SAXS. Konvencionalno barvanje vlaken v vodnem mediju in toplotna obdelava vlaken v vročem zraku povzročita pomembne spremembe v sistemu por vlakna. Vpliv obeh medijev je podoben in višji kot pa vpliv superkričnega fluida pri enaki temperaturi.

Na laboratorijski predilno raztezalni napravi smo izdelali tehnična PP vlakna ter določili vpliv raztezanja na sistem por v vlaknu. Raztezanje vpliva na oblikovanje sistema praznin v vlaknu.