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Variations in diffusion coefficient of disperse dyes in single PET fibres: monitored and interpreted by confocal laser scanning microscopy

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Abstract

A novel method is proposed for determining the diffusion coefficient (*D*) of disperse dyes in PET fibres. Concentration-distance profiles are recorded on optical sections of single fibres by confocal laser scanning microscopy. This allows for an accurate value of the true diffusion coefficient in the fibres as well as for a founded insight in the dye diffusion process and its interrelation with the glass transition, which is not possible by the commonly used methods. At 130 °C, the common industrial dyeing temperature, the diffusion coefficient showed to be constant for the dyes tested, with *D* being about five times larger for the anthraquinone dye than for the benzodifuranone dye. At 100–110 °C, near to the start of the glass transition region of the fibres, *D* could no longer be regarded as a constant for the anthraquinone dye but was concentration dependent. This was explained by the plasticising effect of the anthraquinone dye.

Keywords: Poly(ethylene terephthalate) fibres; Dye diffusion; Confocal laser scanning microscopy

1. Introduction

Although the dyeing of PET fibres is common industrial practice the driving forces of the process are far from well understood. This is reflected in a high interest in the study of both the thermodynamics as well as the kinetics of the dyeing process. As industrial processes are rarely equilibrium processes an appreciable effort has been spent on trying to understand the kinetics of the dyeing process with the main focus being on the dye diffusion process. Despite this effort, only few references were found that study the dye diffusion directly in single fibres [1,2]. So far the diffusion coefficient (*D*) of dyes for fibres is commonly determined via the so called ‘film roll method’ in which a concentration-distance profile is measured based on the concentrations of dye in adjacent layers of film of known thickness [3–12]. This however, disregards the appreciable differences in morphology between fibres and other materials like films of the same polymer [13,14]. Another approach described in literature [3,4,12,15–21], determines the apparent diffusion coefficient by monitoring the total mass transport from the dyebath in the polymer during isothermal dyeing processes. The latter has the advantage that it can be used on fibres or fabrics but it lacks the visualisation of dye transport within the polymer as one may obtain by concentration-distance profiles. Moreover, it does not allow the determination of the true diffusion coefficient within single fibres as it always takes into account to some extend the mass transport from the water phase towards the fibre phase. It is clear that for a good understanding of the dyeing kinetics of fibres in general and PET fibres in specific we lack a technique that determines the true diffusion coefficient within single fibres. Detailed concentration-distance profiles of the diffusing dye within fibres are also needed for an improved understanding of the driving forces of the diffusion process. In a previous paper the relevance of confocal laser scanning microscopy (CLSM) for studying dye penetration in single PET fibres

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was shown for dyeings under industrial conditions [1]. This did however not allow the determination of a diffusion coefficient, as the industrial conditions do not meet the required theoretical conditions. The determination of the diffusion coefficient in single fibres via CLSM is therefore tackled in this paper.

A dyeing method is optimised that approximates as closely as possible specific theoretical conditions [3,5,22,23] in order to allow the use of the appropriate diffusion equation. It will be shown that CLSM allows monitoring accurate concentration-distance profiles on optical sections of individual fibres. The diffusion coefficient is then determined for an anthraquinone (AQ) and a benzodifuranone (BzDF) dye in a polyester fibre at a temperature of 130 °C, with analogy of the industrial dyeing temperature of 130 °C.

Earlier reported results under industrial dyeing conditions showed that dye diffusion, at an appreciable speed, commenced for the anthraquinone dyes around 100–110 °C compared to 130 °C for the benzodifuranone dyes. This is the result of a plasticising effect of the anthraquinone dyes [1]. For a better understanding of this effect isothermal dyeing experiments are also performed at temperatures near to this onset temperature of 100–110 °C for the anthraquinone dyes.

2. Experimental

2.1. Materials

A conventional fibre PET fabric (fabric quality 6460), supplied by Sofinal (Waregem, Belgium), was used and is described in detail elsewhere [13]. Warp and weft consist of the same 167/30 yarns (the yarn count is 167 dtex and the yarn consists of 30 filaments). A single fibre or filament thus has a linear density of 5.6 dtex or an approximate diameter of 23–24 μm, with the fibres having a circular cross-section.

An anthraquinone (AQ, C.I. Disperse Red 60) dye and a benzodifuranone (BzDF, C.I. Disperse Red 356) dye, were supplied by Dystar UK Ltd (Cheadle, UK), Fig. 1. The predispersed dyes are laboratory optimised mixtures of pure dye and dispersing agent in order to achieve a stable dispersion during the dyeing process and giving the best performance on the fibres and fabrics.

2.2. Dyeing experiments

All dyeings were performed in a Mathis Labomat BFA-8 lab dyeing machine, using sealed stainless steel dye pots.

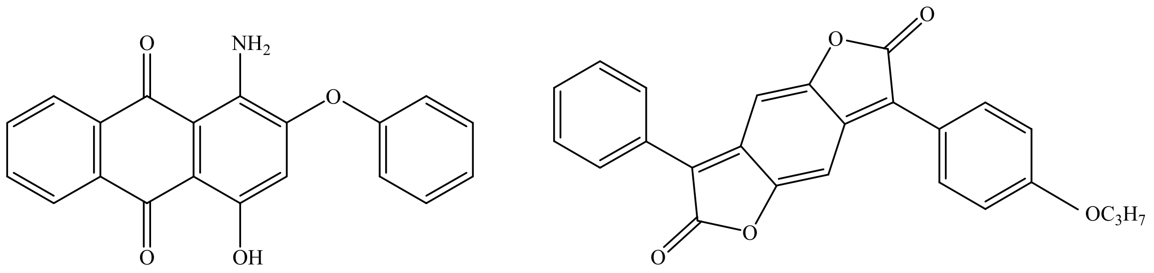
To obtain a value for the theoretical diffusion coefficient (*D*) of a dye in a fibre isothermal dyeing experiments under well stirred infinite bath conditions were performed. The Mathis Labomat dyeing machine offers the possibility to use specially designed dye vessels with a septum by which small amounts of auxiliaries can be added during the dyeing process. Although, it is designed for the injection of auxiliaries at relatively low temperatures (below 100 °C) it showed to be possible to inject a small amount of dye liquor at 130 °C. Thus, the fabrics or yarns could be heated in an appropriate volume of water, set to pH 5 with an acetic acid buffer, to the desired temperature after which the dye liquor, also set to pH 5, could be injected. This results in an isothermal dyeing process at the desired temperature.

To ensure a dye penetration of all fibres two pieces of yarn (approximately 8 mg) were removed from the fabric and mounted on the Mathis yarn holders, taking care to avoid contact between the yarns.

The yarn samples were dyed in a 150 ml bath with a dye concentration of 8% on weight of fabric (o.w.f.). After the appropriate dyeing time the yarns were removed from the dyeing vessels and quickly cooled to room temperature by introducing into cold water. After the dyeing process a standard reduction clearing process was performed by treating the samples for 30 min at 70 °C in an aqueous solution of 2 g/l $Na_2S_2O_4$ and 4 ml/l 30% NaOH, thoroughly rinsing with warm (50 °C) water and finally the samples were air-dried.

2.3. Preparation of cross-sections

Fibres of the dyed fabrics were mounted in historesin blocks and trimmed to obtain one clean-cut surface perpendicular to the fibre axis.



AQ

BzDF

Fig. 1. Dye structures.

2.4. Confocal laser scanning microscopy

Confocal laser scanning microscopy (CLSM) experiments were performed on a BIORAD MRC 1024 system combined with a Nikon Diaphot 300 microscope. The 488 and 514 nm bands of an argon-ion laser were used to excite the fluorescing dyes. The filters in the experimental set-up were chosen to allow the measurement of the fluorescence at 580 nm with a bandwidth of 32 nm.

The optical sections of the trimmed blocks were recorded with an Olympus oil immersion lens, magnification 60× and numerical aperture 1.4. An optimal pinhole of one was used (which corresponds to approximately 0.2 μm at the object level). Images were taken from optical sections just below the trimmed surface of the historesin blocks. This gave the best images while still avoiding any anomalous surface effects due to the trimming. The pixel size of the recorded images was 0.146 μm.

2.5. Image analysis

The images of the fibre cross-sections, obtained by CLSM, were analysed by the standard BIORAD image analysis software package. An intensity profile as a function of penetration depth into the fibre was measured. Concentration-distance profiles were recorded for at least 10 different fibres from two different yarns. MATLAB software (The MathWorks, Inc.) was used to calculate a diffusion coefficient from these intensity-depth profiles.

3. Results and discussion

3.1. Novel method set-up for the determination of the diffusion coefficient

In literature [3–12] Eq. (1) is commonly used to derive the diffusion coefficient, provided the diffusion coefficient is constant, from concentration-distance profiles and it is also suggested for the use on fibres [3–5].

$$\frac{C}{C_0} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{(Dt)}}\right) \tag{1}$$

Eq. (1) can be derived from Fick's law as the required solution for diffusion of a species through a medium, which is infinite in one direction (a semi-infinite medium), from the surface kept at a constant concentration. The boundary and initial conditions can be described as follows [3,23]:

$$C = C_0, \quad x = 0, \quad t > 0$$

$$C = 0, \quad x > 0, \quad t = 0$$

where C is the local concentration of dye diffusing in the fibre, C_0 is the constant concentration of the dyebath and thus also at the surface of the fibre, t is the dyeing time of the experiment and x is the distance the dye has penetrated in the fibre, measured from the fibre surface along the fibre radius ($x = 0$ at the fibre surface).

To fulfil the boundary and initial conditions and allow the use of Eq. (1) a dyeing process was optimised by taking the following precautions.

The dyebath was well agitated to ensure easy accessibility of all of the fibres to the dye in solution. Preliminary experiments with fabrics showed that the accessibility of dye in the fabric is insufficient to ensure reproducible measurements at the short dyeing times. By dyeing separate yarns, taken from the fabric, an appropriate level of accessibility of all of the fibres is achieved. Further since the diffusion coefficient is a temperature dependent value, the dyeing process was performed under isothermal conditions, without the conventional long heating stages. The use of special designed vessels with a septum allows for a dyeing process under isothermal conditions as the dye can be added to the bath after the required temperature is reached. Moreover, the dyeing process was performed in an infinite dyebath, where the dye concentration is high enough to remain constant, as to have a constant concentration C_0 at the fibre surface. However, due to the pressure in the dye vessels at temperatures above 100 °C and in order not to lower the dyebath temperature, only small amounts of dye liquor can be injected through the septum. This means that initially after dye injection a homogenous dyebath cannot be ensured, which may affect the measurement accuracy for dyes that diffuse very rapid. As such a compromise is always to be taken between infinite dyeing conditions and a well stirred homogenous dyebath in the first instants of the process. An optimised dye concentration in the bath of 8% o.w.f. showed to serve very well. Finally, the dyeing times were chosen as to obtain dyed fibres that are not yet dyed through to the fibre centre.

It should also be noted here that although Eq. (1) is suggested in the literature for the use on fibres, it is the solution for diffusion through a plane and not a cylinder. As such it may introduce some errors and it would be better to use the appropriate equation for diffusion into a cylinder satisfying the initial and boundary conditions [23]. This equation is however much more complex and Eq. (1) is used as an approximation. Moreover, it is shown in Fig. 3 that the experiments at 130 °C exhibit a very good correlation with Eq. (1), confirming the appropriate use of Eq. (1).

It is also to be noted that if D is indeed a constant at a certain temperature, plots of the relative concentration C/C_0 as a function of $\frac{x}{2\sqrt{t}}$, for different dyeing times t should be described by the same curve. If D is not a constant the plot of experimental data for different dyeing times will not coincide and may deviate from the curve describing Eq. (1) in which D is then a mean diffusion coefficient.

With CLSM the pixel intensity I can be measured at each point of the cross-section images, which is proportional to the dye concentration C at that point in the fibre. Thus, C/C_0 can be measured as I/I_0 with I the intensity at a depth x in the fibre and I_0 the intensity at the surface of the fibre. Fig. 2 shows some typical cross-sections of the PET fibres dyed with the AQ dye at 130 °C for prolonged dyeing times. Fig. 3 gives an example of a plot of the relative pixel intensity I/I_0 as a function of $\frac{x}{2\sqrt{t}}$ for these fibres as well as a curve fitted to the experimental data obeying Eq. (1).

It can be observed from Fig. 3 that the data for the different dyeing times are coincident within the resolution of the CLSM and can be described by the same curve that fits Eq. (1). The fit between the measured and calculated intensity profile is very good for all dyeing times shown (the correlation is more than 0.99 for all experiments). Yet longer dyeing times, however, result in larger deviations, which suggests that Eq. (1) may be no longer a satisfying approximation. Indeed at these longer dyeing times the dye has almost reached the centre of the fibre and these are thus not to be used. The dyeing times used in this work are all ensuring the dye has definitely not reached the centre of the fibre yet.

Thus, it can be stated that the experimental conditions used are approximating well the theoretical conditions needed to allow the use of Eq. (1). Although of course further optimisations may be possible for this newly developed method the results suggest that this method with the use of 8% o.w.f. dye in the bath serves as a good experimental condition for the determination of a diffusion coefficient of a dye in a fibre and for monitoring the transport of dye in the fibre.

Fig. 3 further suggests that the diffusion coefficient of the AQ dye in the PET fibres at a temperature of 130 °C is indeed a constant, at least within the resolution of the experiment. The experimental data of PET conventional fibres dyed with the BzDF dye at 130 °C for different times t are also described by a single curve (not shown).

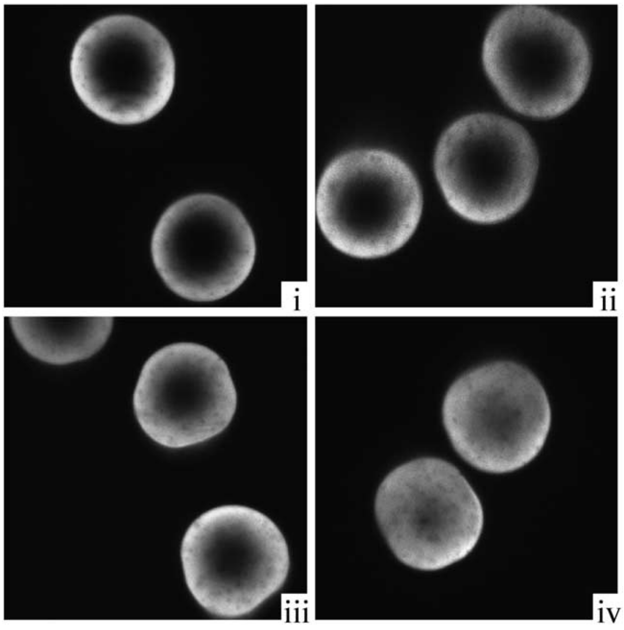


Fig. 2. CLSM cross-sections of PET fibres dyed with 8% o.w.f. AQ dye as a function of increased dyeing time at 130 °C. (i) 5 min, (ii) 7.5 min, (iii) 10 min, (iv) 15 min. A single image is 66 μm×66 μm.

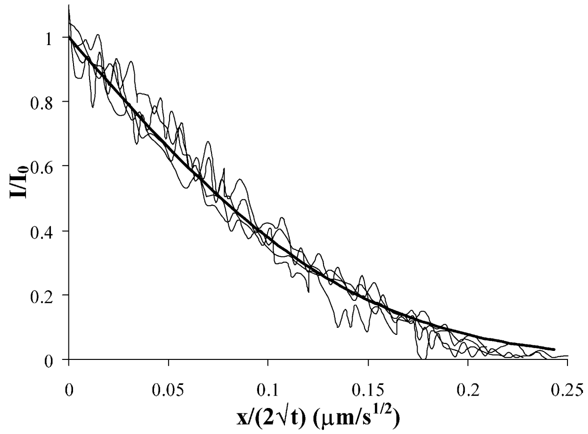


Fig. 3. Relative intensity (I/I_0) as a function of $\frac{x}{2\sqrt{t}}$ (μm/s$^{1/2}$) in which t is the dyeing time and x the penetration depth in the fibre, measured along the fibre radius, for PET fibres dyed at 130 °C with 8% o.w.f. AQ dye for different dyeing times. (—) measured intensity profile on fibres dyed for 5, 7.5, 10 and 15 min, (**—**) calculated intensity profile according to Eq. (1).

3.2. Determination of the diffusion coefficient at 130 °C

Thus, the diffusion coefficients of both the AQ and BzDF dyes in the PET conventional fibres at 130 °C were calculated at different dyeing times. By fitting Eq. (1) to the experimental intensity profiles with the aid of MATLAB software, the diffusion coefficients were calculated, Table 1.

The results show again that, within the standard deviation of the experiments, the same diffusion coefficient is obtained for the different dyeing times and thus justify the method. Further, the anthraquinone dye shows a diffusion coefficient at 130 °C of about five times larger than the benzodifuranone dye, which agrees with the observations during the course of the dyeing experiment [1]. Indeed the anthraquinone dyes reached the centre of the fibre much earlier than the benzodifuranone dyes.

3.3. Determination of the diffusion coefficient at 100 and 110 °C

The earlier observations during the course of an industrial dyeing process showed that dye diffusion, at an appreciable speed, commenced for the anthraquinone dyes around 100–110 °C compared to 130 °C for the benzodifuranone dyes [1]. This was explained by the plasticising effect of the anthraquinone dyes. It was observed by modulated differential scanning calorimetry that the glass transition of the fibres is substantially lowered due to the presence of various anthraquinone dyes, whereas the benzodifuranone dyes did not show such a plasticising effect [14]. To better understand this plasticising effect and the interrelation with the dye diffusion process, isothermal dyeing experiments are also performed at temperatures near to the temperature

Table 1
Calculated diffusion coefficients and standard deviations of the AQ and BzDF dyes in PET conventional weft fibres dyed at 130 °C in an 8% o.w.f. dyebath

	Dyeing time (min)	Diffusion coefficient (10^{-10} cm^2/s)	Standard deviation (10^{-10} cm^2/s)
Conventional fibres dyed at 130 °C with 8% o.w.f. AQ dye	2.5	2.8	0.6
	5	2.9	0.6
	7.5	2.5	0.5
	10	2.7	0.4
	15	2.3	0.5
	Average over all times	2.7	0.6
Conventional fibres dyed at 130 °C with 8% o.w.f. BzDF dye	15	0.50	0.06
	30	0.60	0.15
	45	0.54	0.10
	60	0.51	0.08
	Average over all times	0.54	0.10

at which appreciable diffusion starts, 100 and 110 °C for the anthraquinone dye and 130 °C for the benzodifuranone dye. Isothermal experiments at 100 and 110 °C for the BzDF dye revealed that even with dyeing times of up to 48 h almost no diffusion occurred.

Fig. 4 illustrates typical intensity-depth profiles for a PET conventional fibre dyed with the AQ dye at 110 °C with increased dyeing times, again taking care that even for the longest dyeing time the dye does not reach the centre of the fibre. Similar profiles are obtained at 100 °C (not shown).

Fig. 4 illustrates that in contrast to the 130 °C dyeings the intensity profiles no longer coincide for the different dyeing times at a dyeing temperature of 110 °C. This suggests that at these lower dyeing temperatures the diffusion coefficient may not be regarded constant.

Fig. 5 illustrates a typical measured intensity profile for a dyeing time of 240 min as well as the best-fitted intensity profile obeying Eq. (1).

Fig. 5 indicates that at a temperature of 110 °C the fit of the experimental data to the theoretical equation is not as good as at 130 °C, which again points to a non-constant diffusion coefficient. The diffusion profiles at 100 and 110 °C show a higher relative intensity at the outer region of the fibre than the predicted one and a lower intensity at the inner region of the fibre, suggesting the diffusion coefficient to be decreasing with increasing penetration depth. This is in contrast to the concentration-distance profiles at 130 °C in Fig. 3, which point to a constant diffusion coefficient at 130 °C along the fibre radius. Thus the fact that *D* can be regarded as constant or not along the fibre radius seems to be dependent on the temperature at which the experiments are performed.

Although the concentration-distance profiles at 100 and 110 °C are continuous they may be regarded as consisting of three regions, the outer region of the fibre, the inner region of the fibre and a 'transition' region separating the former two, identified in Fig. 5 for the shown intensity profile. In the outer region of the fibre the diffusion coefficient is higher than the mean value for *D* that can be derived from Eq. (1), whereas the inner region of the fibre has a diffusion coefficient lower than the mean value of *D*. Although the

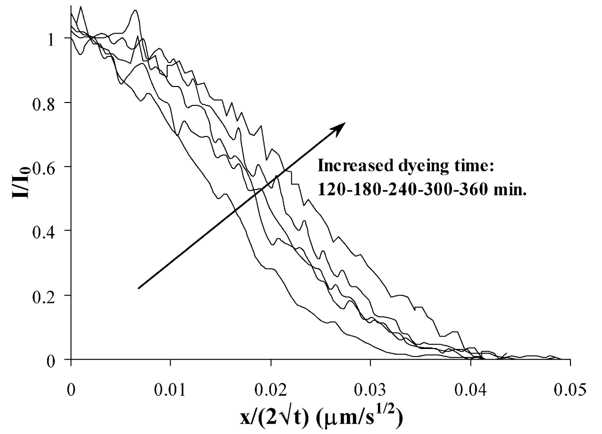


Fig. 4. Measured relative intensity (I/I_0) as a function of $\frac{x}{2\sqrt{t}}$ ($\mu m/s^{1/2}$) in which *t* is the dyeing time and *x* the penetration depth in the fibre, measured along the fibre radius, for PET fibres dyed at 110 °C with 8% o.w.f. AQ dye for different dyeing times (120, 180, 240, 300 and 360 min).

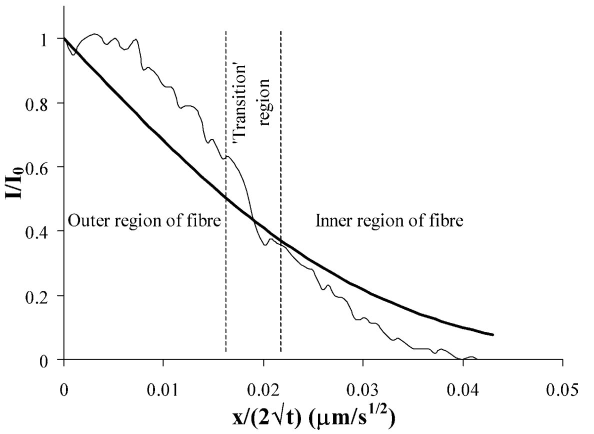


Fig. 5. Relative intensity (I/I_0) as a function of $\frac{x}{2\sqrt{t}}$ ($\mu m/s^{1/2}$) in which t is the dyeing time and x the penetration depth in the fibre, measured along the fibre radius, for PET fibres dyed at 110 °C with 8% o.w.f. AQ dye for 240 min. (—) measured intensity profile, (**—**) calculated intensity profile according to Eq. (1).

splitting of the data in separate regions is a relatively arbitrary process, the presence of the small and sharp 'transition' region reinforces the idea of two major regions.

By fitting Eq. (1) to the separate regions an average diffusion coefficient may be obtained for each region. The diffusion coefficient in the 'transition' region varies too much over a short distance making the estimation of an average diffusion coefficient for this region difficult and questionable. It is important to note that after splitting the data the inner region of the fibre shows a good fit to Eq. (1), whereas the outer region of the fibre does not. The outer region of the fibre still gives an intensity profile similar to the one illustrated for the total fibre in Fig. 5 (in which x is then of course extended over a smaller distance in the fibre), indicating that D is continuously varying, especially in the outer region. For reasons of simplicity the diffusion coefficients are however calculated as an average for both the inner and outer region of the fibre. This will provide a good indication of the variations in D along the fibre radius, Tables 2 and 3.

The experiments at the three different temperatures (100, 110 and 130 °C) show that D increases with dyeing temperature, which agrees with the literature [3,4,22–24].

Further, Tables 2 and 3 show that the values for D calculated from the intensity profiles of the total fibre increase with increased dyeing time and thus the diffusion coefficient cannot be regarded as a constant at temperatures of 100 and 110 °C. This indeed confirms the trend of the variations in the intensity profiles for different dyeing times given in Fig. 4.

It is noted that D in the outer region of the fibre is at least twice as large as D in the inner region of the fibre. The variations in D along the fibre radius are thus definitely significant at dyeing temperatures of 100 and 110 °C. The variations in D with dyeing time are also more evident in the outer region of the fibre than in the inner region. The latter agrees with the poorer fit of the data of the outer region to Eq. (1) than the data of the inner region. The variation in D for the diffusion of AQ dye in the fibre at 100 and 110 °C may either be due to a radial heterogeneity of the fibre morphology at the measured temperatures or due to a concentration dependence of D as with increasing penetration depth the concentration of present dye is also lower. Literature [3,4,10,11,16,17] relating to the diffusion of dyes in polymers usually regards the diffusion coefficient as a constant at a certain temperature for reasons of simplicity, although some authors reported the concentration dependence of D [6,25,26].

It is important to realise that the 'outer' and 'inner' region of the fibre are shifting towards the centre of the fibre with dyeing time as the penetration depth increases. As a result the outer region of the fibre will be subjected to larger variations in dye concentration with increased dyeing time, whereas the dye concentration profile in the inner region will vary less as long as the dye has not reached the centre of the fibre. Combined with the observations of an evident variation in D in the outer region of the fibre and a relative invariance of D in the inner region, the above indicates at least some interrelation between the local dye concentration and the local diffusion coefficient. On the other hand the fibre morphology will also play an important role in the diffusion process. The major morphology related parameter affecting D is the glass transition of the fibre [1,3,4,22]. The fact that D for the AQ dye in the PET fibre can be regarded as a constant at a temperature of 130 °C and not at temperatures of 110 and 100 °C, suggests again that temperature plays an important role in the process of dye diffusion.

3.4. Interrelation between dye penetration in the fibres and the glass transition

The above is all in line with the already mentioned plasticising effect of the AQ dye observed by modulated differential scanning calorimetry [14]. Indeed the fibres have a broad glass transition situated around 112 °C, but with an onset already at about 96 °C and an endset only at 130 °C. Thus at a temperature of 100–110 °C the dyes can

Table 2
Calculated diffusion coefficients and standard deviations of the AQ dye in PET conventional fibres dyed at 100 °C in an 8% o.w.f. dyebath

	Dyeing time (min)	Diffusion coefficient (10^{-10} cm^2/s)	Standard deviation (10^{-10} cm^2/s)
Average over total fibre	480	0.0071	0.0015
	960	0.0097	0.0015
	1440	0.0093	0.0028
	2880	0.0102	0.0015
	Average over all times	0.0091	0.0022
Outer region of fibre	480	0.011	0.005
	960	0.017	0.005
	1440	0.023	0.007
	2880	0.025	0.004
Inner region of fibre	480	0.006	0.001
	960	0.007	0.001
	1440	0.007	0.001
	2880	0.007	0.001

Table 3
Calculated diffusion coefficients and standard deviations of the AQ dye in PET conventional fibres dyed at 110 °C in an 8% o.w.f. dyebath

	Dyeing time (min)	Diffusion coefficient (10^{-10} cm^2/s)	Standard deviation (10^{-10} cm^2/s)
Average over total fibre	120	0.08	0.02
	180	0.11	0.02
	240	0.11	0.02
	300	0.13	0.02
	360	0.14	0.02
	Average over all times	0.11	0.02
Outer region of fibre	120	0.14	0.04
	180	0.16	0.05
	240	0.17	0.03
	300	0.32	0.05
	360	0.30	0.10
Inner region of fibre	120	0.06	0.02
	180	0.07	0.02
	240	0.07	0.02
	300	0.08	0.04
	360	0.08	0.04

already diffuse into the fibre due to the increased mobility of the PET at the start of the glass transition. The diffusion coefficient will however still be very low, as only a small part of the amorphous phase will have obtained increased mobility. For a non-plasticising dye one would have to raise the temperature to 130 °C (which is common industrial practice) as to reach an optimal mobility of the amorphous phase in the fibres and to obtain a sufficiently high diffusion coefficient. This is indeed the case for the BzDF dye. The AQ dye however acts as a plasticiser. As it penetrates the fibre at a temperature of 100 or 110 °C it will locally reduce the glass transition and thus increase the diffusion coefficient. Thus, D will not be a constant but concentration dependant for dyes that have a plasticising effect. This is true at temperatures below the endset of the original glass transition of the fibres. At 130 °C, the common industrial dyeing temperature but also the endset temperature of the broad glass transition of the original fibres, the plasticising effect will have only very little effect on the diffusion coefficient. Indeed at 130 °C the total amorphous phase will have obtained increased mobility and a lowering of the glass transition will not have a similar substantial effect on D as at lower dyeing temperatures. Thus D can indeed be regarded as constant at 130 °C.

4. Conclusions

Confocal laser scanning microscopy is shown to be an excellent technique to monitor the dye diffusion in single fibres. A novel method was established which allows the determination of the true diffusion coefficient of a dye in a single fibre by measuring concentration-distance profiles on optical sections of fibres dyed under specific stringent conditions.

The method revealed that the diffusion coefficient at 130 °C, the common industrial dyeing temperature, is about five times larger for the anthraquinone dye than for the benzodifuranone dye. This is in agreement with the earlier observations during the course of a dyeing process, where the anthraquinone dyes showed to reach the centre of the fibre at much shorter dyeing times [1]. Further, the detailed monitoring of the concentration-distance profiles with increased dyeing times showed that profiles coincided, suggesting the diffusion coefficient to be a constant at 130 °C. This was true for both dyes and is in agreement with the good fit of the experimental data to Eq. (1).

On the other hand at 100–110 °C it was shown that for the anthraquinone dye the diffusion coefficient could no longer be regarded as a constant. The diffusion coefficient showed to be concentration dependant due to the plasticising effect of the AQ dye. As the dye started to diffuse into the fibre, the glass transition was locally reduced and thus the diffusion coefficient increased. The plasticising nature of the AQ dye did not affect D at 130 °C, as this was already at the endset of the glass transition of the fibres.

The use of the novel method helps in the general interest for a better understanding of the dyeing kinetics of PET fibres with disperse dyes. It allows obtaining an accurate diffusion coefficient in the single fibres. Moreover, it complements in the understanding of the possible plasticising effect of dyes and the relevance of this for the dyeing process by visualising the concentration-distance profiles of the diffusing dye in single fibres.

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