

# Variations in dyeing characteristics for PET-fibres: the effect of dye-fibre interactions.

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## Introduction:

Dye-fibre interactions play an important role in most dyeing processes. For the dyeing of PET-fibres with disperse dyes it is generally accepted that only relatively weak hydrophobic interactions play an important role. As such, not much attention has been given in the past to study these dye-fibre interactions for PET-fibres. This can also be understood from the fact that it is difficult to observe the interactions in the dye-fibre system due to the limited amount of dye present.

In the present paper an overview is given of various methods that can be used and combined to understand the dye-fibre interactions. These various methods are applied to PET fibres dyed with disperse dyes.

## Materials and methods:

### Materials

Two 100% PET fabric were used with substantial different fibre fineness. Various disperse dyes were used. In this paper the results are mainly based on some anthraquinone (AQ) dyes and some benzodifuranone (BzDF) dyes.

### Methods

Modulated differential scanning calorimetry measurements were performed in non-hermetic aluminium pans on a *TA Instruments* DSC 2920 with MDSC<sup>®</sup> option. Ultra-violet and visible (UV-VIS) spectroscopy was performed on a PerkinElmer Lambda 900 spectrophotometer.

Infrared spectra were recorded on a PerkinElmer GX 2000, which is a Fourier transform infrared spectrometer.

Confocal laser scanning microscopy (CLSM) experiments were performed on a BIORAD MRC 1024 system combined with a Nikon Diaphot 300 microscope.

## Results and discussion:

### Dyeing and colour measurements

The dyeing of fabrics with different fibre fineness commonly leads to variations in colour depth. It is well known and described in literature that finer fibres need a higher amount of dye for a similar colour depth compared to coarser fibres[1-4]. These variations in colour depth are however often accompanied by variations in colour shade. This aspect is far less described and not as well understood. Figure 1

shows the variations in colour depth and colour shade for two PET fabrics with different fibre fineness.

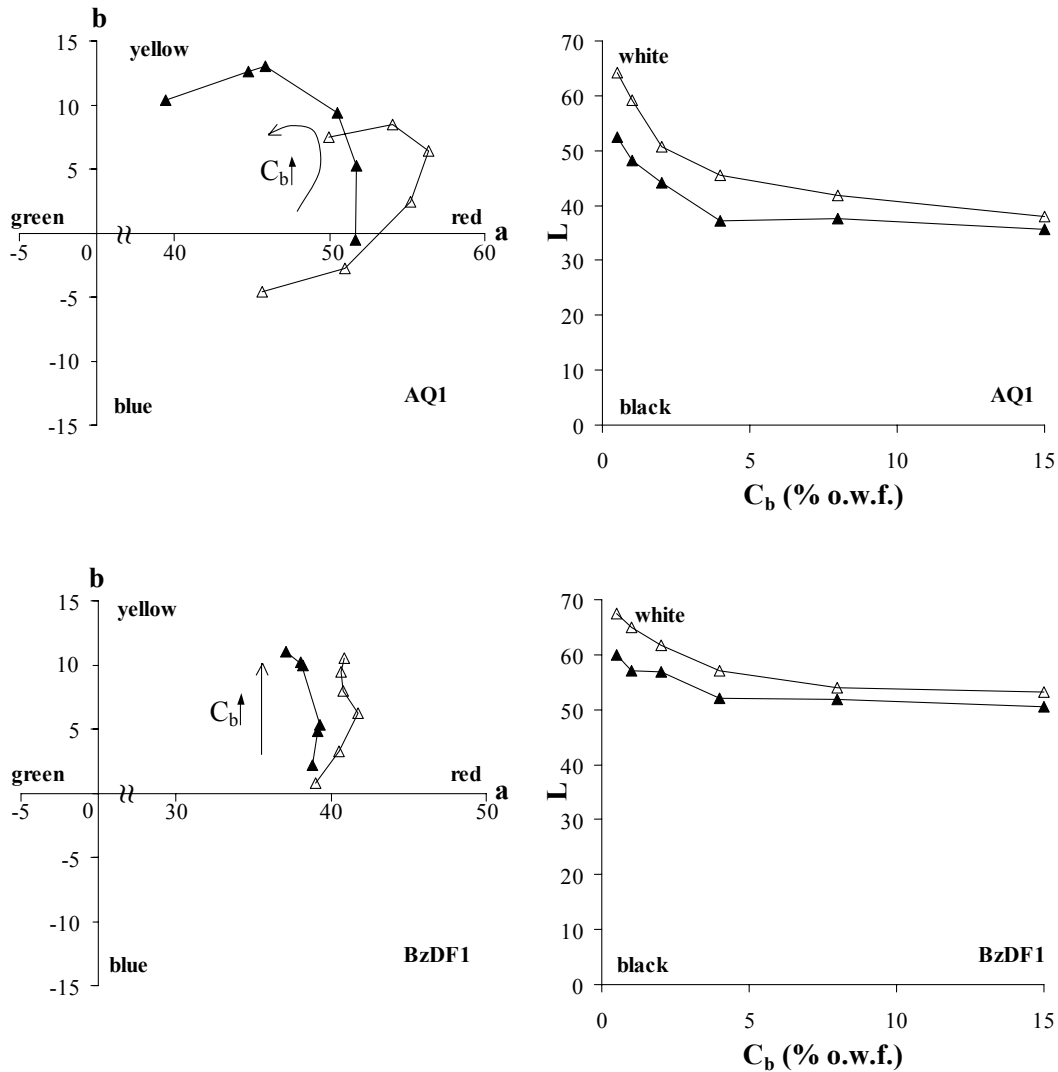


Figure 1. Lab-values for two PET fabrics dyed with increasing concentrations of disperse dyes.

The observed variations in colour depth are observed in the visible spectra of the dyed samples as both a shift in  $\lambda_{max}$  and an extensive broadening of the spectra. Depending on the dye type one of both is more explicit. An analysis of these spectra suggests that the variations in colour depth and shade are not only an optical effect but are also caused by a variation in dye-fibre interactions.

To study the absorption kinetics the dye absorption was monitored during the course of the dyeing process. Figure 2 shows the amount of dye absorbed by both fabrics dyed with 8% o.w.f. of dye in the dyebath as a function of increasing temperature and dwell-time in the dyebath.

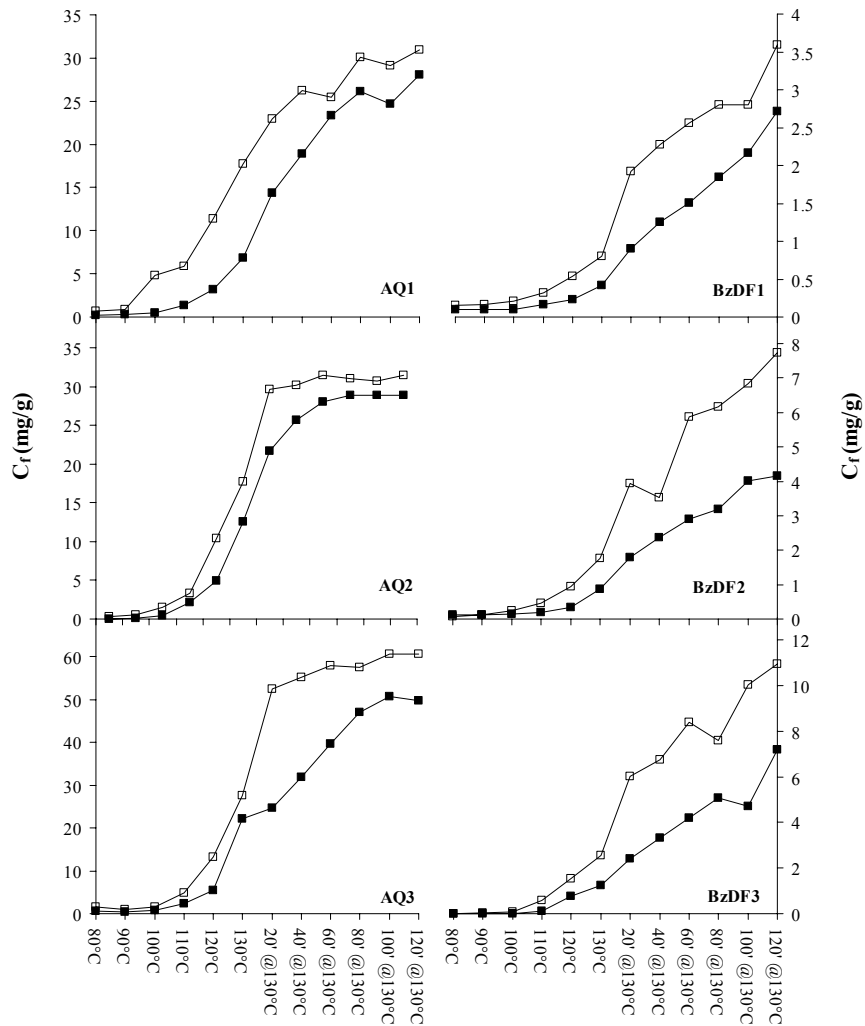


Figure 2. Amount of pure dye absorbed by the fibre as a function of temperature and time in the dyebath.

It can be observed that both fabric types behave different which may be due to a difference in fibre fineness. However both dye types behave very different as well. More dye absorption experiments (not shown) suggested again that the variations in colour build-up are originated not only by fibre differences but also by variations in dye-fibre interactions. Therefore these dye-fibre interactions are looked at in more detail in this paper.

#### Dye diffusion studies by confocal laser scanning microscopy

Confocal laser scanning microscopy (CLSM) was used to study dye diffusion in single fibres [5-6]. Figure 3 illustrates optical cross-section that can be obtained by CLSM of single dyed fibres. This allows the study of dye penetration and dye diffusion in single fibres which was not possible by other techniques in the past.

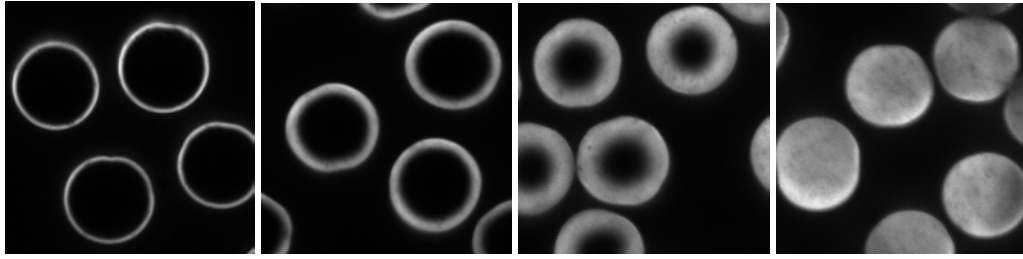


Figure 3. Optical cross-sections of dyed PET fibres.

By studying the intensity profiles, information can be collected on the penetration process of the dyes or also, when appropriate dyeing conditions are chosen, it allows for the determination of the diffusion coefficient in a specific fibre. The advantage of this technique compared to the presently common diffusion measurements is that it focuses on the diffusion process within the fibre taking the correct fibre morphology into account.

Figure 4 illustrates the relative intensity profile for a specific dye from which the diffusion coefficient  $D$  can be calculated.

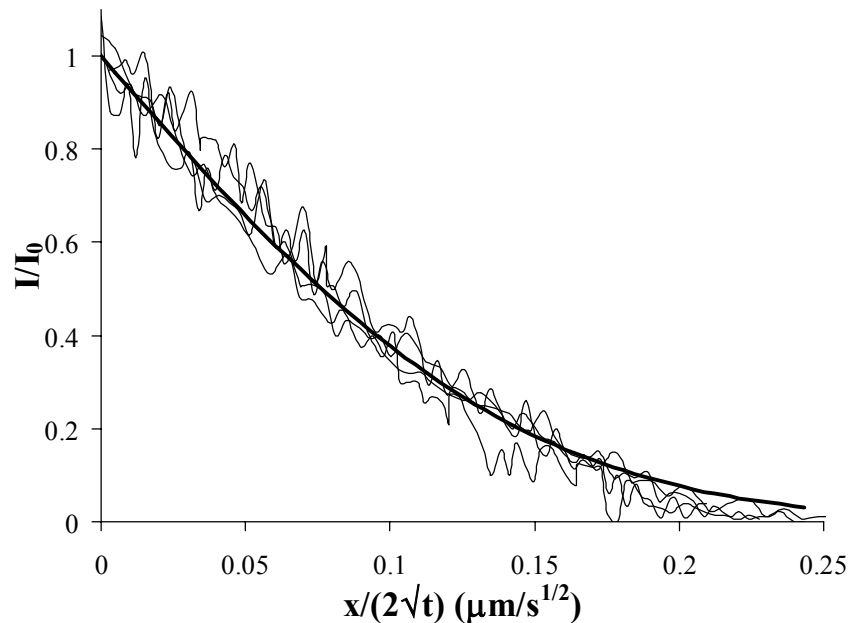


Figure 4. Relative intensity profiles obtained by CLSM.

Isothermal experiments at  $130^{\circ}\text{C}$  (as commercially important dyeing temperature) reveal that the diffusion coefficient remains constant for all anthraquinone and benzodifuranone dyes tested throughout the dyeing process. In general numbers  $D$  was about five times higher for the anthraquinone dyes compared to the benzodifuranone dyes. It was however also observed that the onset of diffusion was quite different for both dye types. This dye dependent temperature onset for diffusion seems to be in contradiction with the expectation that the diffusion would commence at the glass transition of the fibre, and is thus independent of the dye. Moreover the diffusion coefficient of the anthraquinone dyes showed not to be constant at temperatures below  $130^{\circ}\text{C}$ . This thus clearly indicated an interaction between the presence of the anthraquinone dyes and the performance, more in specific the dye absorption kinetics, of the fibres.

## Modulated differential scanning calorimetry

Modulated differential scanning calorimetry (MDSC) was used to study the glass transition of the PET fibres [7-8]. Figure 5 shows the heat capacity and its derivative in the glass transition region for the PET fibres.

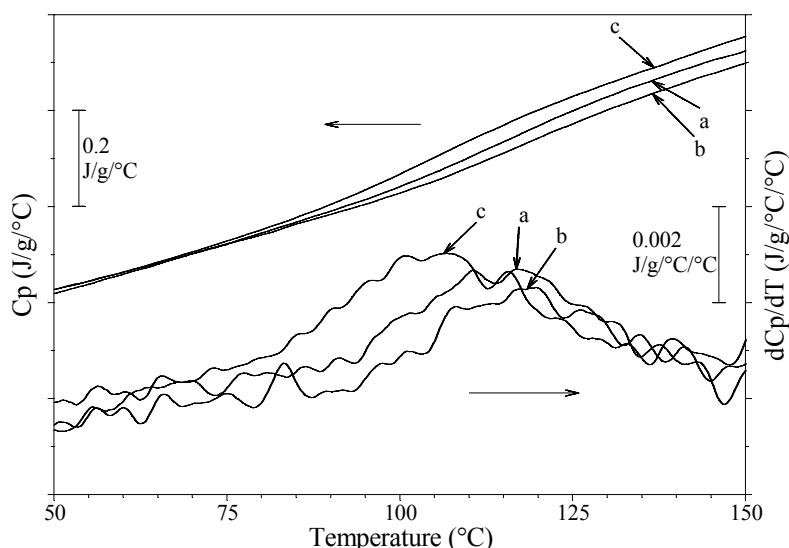


Figure 5. Modulated DSC on PET conventional fibres, showing the heat capacity ( $C_p$ ) and its derivative ( $dC_p/dT$ ) in the glass transition region. a: 'as received' fibres, b: blank dyed fibres, c: fibres dyed with AQ1.

These experiments show that the tested anthraquinone dye acts as a plasticizer for the PET fibres. This was similar for some other tested anthraquinone dyes on both fibre types. The benzodifuranone dyes did not show such a plasticizing behaviour. The reduction in glass transition temperature is dye and fibre dependent but can be as high as 10°C.

This plasticizing effect is an important expression of the existence of dye-fibre interactions which helps to understand the varying dyeing absorption kinetics and colour build-up for different dyes on different PET fabrics.

## FT-IR spectroscopy

The use of FT-IR microspectroscopy and DRIFTS combined with a careful sampling technique allows the study of hydrogen bonds in the dye-fibre system. By comparing the high wavenumber region of the spectrum for the dyes as present in the fibre to two reference states of the dyes, solid and dilute solution, the presence of dye-fibre hydrogen bonds can be established [9].

Figure 6 illustrates the hydrogen bonding of the selected anthraquinone dyes, which all contain an  $\text{NH}_2$  group in the 1-position. All these anthraquinone dyes showed a distinct hydrogen bonding in the PET fibres different from their solution and solid state.

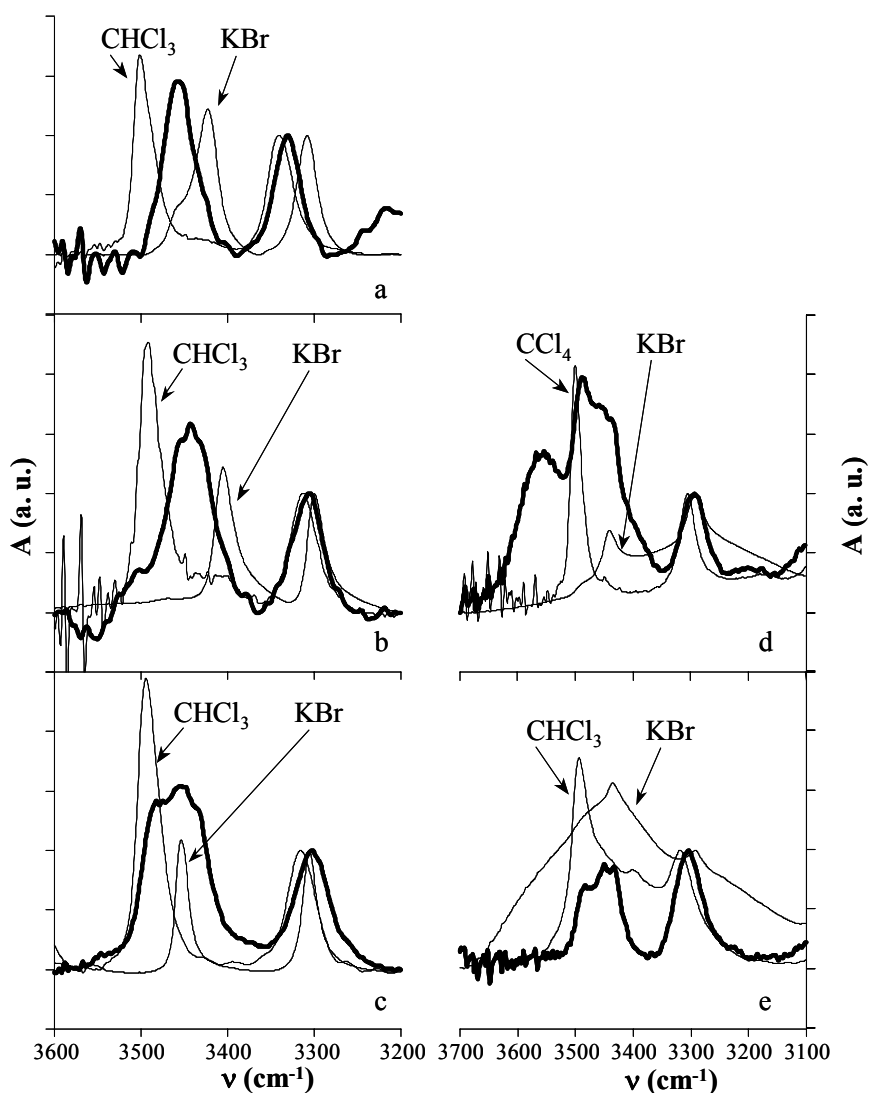


Figure 6. Absorbance ( $A$ , arbitrary units) of the dyes in the  $3600\text{--}3200\text{ cm}^{-1}$  and  $3700\text{--}3100\text{ cm}^{-1}$  wavenumber region. All spectra are normalised to an absorbance of 1 at the lowest wavenumber band.— solid state (KBr) and dilute solution in  $\text{CHCl}_3$  or  $\text{CCl}_4$ , — as present in the fibre.

Three benzodifuranone dyes did not show any hydrogen bonding, as they do not contain any groups capable of forming hydrogen bonds. A fourth benzodifuranone dye containing a group capable of forming hydrogen bonds did however also not show distinct hydrogen bonding. Furthermore an anthraquinone dye containing an amino group on the 2-position did also not show as distinct hydrogen bonding in the fibres. This illustrates that not only the presence of a group capable of forming hydrogen bonds is important but also its position within the dye structure.

A comparison between the plasticizing effect observed by MDSC and the possible hydrogen bonding moreover reveals that mainly anthraquinone dyes containing an  $\text{NH}_2$  group in the 1-position are characterized by a plasticizing effect compared to an  $\text{NH}_2$  group on the 2-position or even an  $\text{OH}$  group.

Thus the IR-study revealed that hydrogen bonding plays important role, even in the dyeing of PET fibres with disperse dyes. A proper study of the hydrogen bonding abilities helps to understand the variations in dyeing behaviour.

## Dye aggregation

CLSM also allows for optical longitudinal section of the dyed fibres. A study of these clearly shows that some dyes show a higher concentration on or in the vicinity of the TiO<sub>2</sub>-particles present in the fibres. This is illustrated in Figure 7. This was mainly observed for those dyes not showing any hydrogen bonding within the PET fibres.

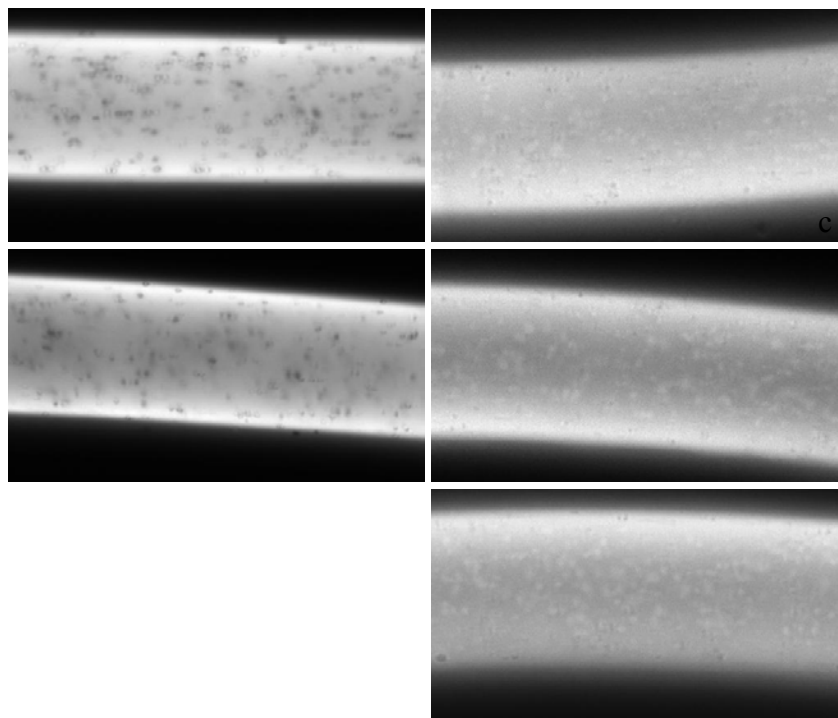


Figure 7. Optical longitudinal section obtained by CLSM.

## **Conclusions:**

In this paper several novel techniques were described that allow for the study of dye-fibre interactions. These were shown here for the dyeing of PET fibres with disperse dyes, but most of these techniques are applicable for the study of dye-fibre interactions in various dye-fibre systems.

CLSM revealed an interaction between the presence of the 1-amino anthraquinone dyes and the performance (dye absorption kinetics) of the fibres. This was further understood by the plasticizing nature of these dyes that could be proven by MDSC. FT-IR spectroscopy allowed for an allocation of the plasticizing effect to the possibility of a dye to form specific hydrogen bonds within the PET fibres. Finally CLSM also indicated some dye aggregation for the dyes that are less prone to hydrogen bonding.

## **References**

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