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Modification of cotton cellulose with sodium benzoylthioglycollate and its effect on dyeability with disperse dyes. Part 2: application of sodium benzoylthioglycollate to cotton fabric

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Abstract

The modification of cotton cellulose through a nucleophilic substitution reaction with sodium benzoylthioglycollate (BTG) is described. BTG has been applied to cotton fabric by pad-thermosol processes and the resulting benzoylated fabrics assessed for disperse dyeability. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cotton modification; Benzoylthioglycollate; Disperse dyeing; Aromatic interactions

1. Introduction

The preparation and characterisation of sodium benzoylthioglycollate (BTG) has been described [1]; model reactions indicated that BTG readily undergoes nucleophilic substitution reactions with amines, the leaving group being the thioglycollate ion. Thomas [2] showed that BTG would benzoylate cotton cellulose but did not optimise the application conditions. This paper thus investigates the effect of pad liquor additives and thermosol temperatures on the extent of cotton benzoylation. The benzoylated cotton fabrics were dyed with C.I. Disperse Blue 183 and these dyeings were compared with disperse dyeings produced on untreated cotton fabric and on cotton fabric benzoylated with benzoyl chloride [3,4], (the Shikibo-Uni process).

2. Experimental

2.1. Materials

All chemicals employed were of laboratory reagent grade unless otherwise stated. The cotton fabric used was a plain bleached, unmercerised fabric.

2.2. Modification of cotton with benzoyl chloride

Cotton fabric was padded to a wet pick-up of 80% using a Konrad Peter pad mangle with 100 g

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dm^{-3} sodium hydroxide solution and batched at room temperature. After 24 h, the activated cotton fabric was immersed in benzoyl chloride for 60 s, removed and washed thoroughly with sodium hydroxide solution (50 g dm^{-3}).

2.3. Cotton benzoylation with BTG

A number of pad-liquors were prepared containing different concentrations of BTG, sodium acetate, sodium carbonate, sodium hydroxide, urea and in some cases C.I. Disperse Blue 183 (20 g dm^{-3}). Cotton fabric was padded at 80% wet pick-up with these solutions and dried overnight at room temperature (it was previously established [1] that even at pH 11, BTG was resistant to hydrolysis at room temperature); the fabrics were then baked (thermosol-treated) in a Werner-Mathis AG laboratory steamer/baker unit at various temperatures and times. The resulting modified cotton fabrics were thoroughly washed off in cold running tap water and dried at 100°C.

2.4. Determination of BTG fixation

Samples of the modified fabrics were extracted 5 times with distilled–deionised water at 50°C. The resulting solutions were made up to 250 ml and their optical densities measured on the Pye–Unicam PU8600 Uv/vis spectrophotometer at the wavelength of maximum absorbance for BTG, 239 nm (10 nm quartz cells). The extracted fabrics were dried to constant weight. The fixation of BTG on cotton was calculated using the following equation:

$$\text{Percent fixation} = 100 - \left[\frac{\mathrm{OD_t}}{\mathrm{OD_{t=0}}} \times 100\right]$$

where $\mathrm{OD_t}$ is the optical density of the extracted thermosol-treated fabric (1 g) and $\mathrm{OD_{t=0}}$ is the optical density of the extracted padded fabric (1 g) before thermosol fixation.

2.5. The determination of the degree of substitution (D.S.) of BTG modified cotton

The weight gains of the modified cotton fabrics were measured and the degree of substitution of the modified fabrics calculated using the following equation:

$$\text{D.S.} = \frac{3[\text{Actual weight gain}]}{[\text{Theoretical weight gain for a D.S. of 3}]}$$

where the theoretical weight gain for a D.S. of 3 is given by:

$$\frac{484}{172}\text{weight of fabric} - \text{weight of fabric}$$

where 484 is the molecular weight of the tri-benzoylated anhydroglucoside residue in cotton and 172 the molecular weight of the original anhydroglucose residue.

2.6. Fourier transform infra-red (FT–IR) spectroscopy of BTG modified and natural cotton

The IR spectra of BTG modified and untreated cotton were obtained on the Perkin–Elmer 1725 FT–IR spectrophotometer, using the diffuse reflectance DRIFTS attachment. The difference spectrum was obtained by computer subtraction of the untreated cotton spectrum from that of the modified cotton.

2.7. Differential scanning calorimetry (DSC)

DSC was carried out on BTG modified and untreated cotton fabric using the DuPont 1090 thermal analyser, the temperature being increased at a rate of 10°C per min.

2.8. Dyeing

The benzoylated cotton fabrics and untreated fabric were dyed (5 g samples) with 2% owf C.I. Disperse Blue 183 (Fig. 1) at pH 6.0, maintained

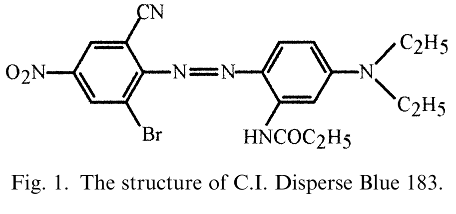


Fig. 1. The structure of C.I. Disperse Blue 183.

using a 0.1 M citric add (7.37 ml)/0.2 M disodium hydrogen phosphate (12.63 ml) buffer. A liquor ratio of 20:1 was used and the dyeings were carried out in sealed tubes housed in a John Jeffrey's rota-dyer. The dyebath was raised to 100°C over 20 min and maintained at this temperature for 1 h. The resulting dyeings were thoroughly washed off with water. The above dye application conditions were employed throughout the following work.

The resulting dyeings were subjected to ISO2 and ISO3 wash fastness tests [5,6]. The colour yields (K/S) of the dyeings, the dyeings subjected to the wash fastness tests and the stained adjacent nylon 6,6 used in the wash fastness tests were measured on the ICS colour measurement system at a wavelength of 620 nm.

The visible absorbance spectrum of C.I. Disperse Blue 183 dissolved in acetone was obtained on the Pye–Unicam SP800 A spectrophotometer using 10 mm cells. To determine any reduction effects, thioglycollic acid was added dropwise to the dye solution and the spectrum was remeasured.

3. Results and discussion

Untreated cotton and cotton esterified by the standard benzoyl chloride procedure [3,4] were dyed with C.I. Disperse Blue 183 and the colour yields and wash fastness properties of the dyeings determined (Table 1). Clearly good colour yields and promising wash fastness properties were displayed on the benzoylated cotton.

In the alkali catalysed reaction of BTG with cotton cellulose (Scheme 1) the leaving group is sodium thioglycollate.

On thermosol treatment of cotton impregnated with BTG and disperse dye, the liberated thioglycollate interacts with the selected disperse dye giving a redder weaker hue to the dyed modified fabric.

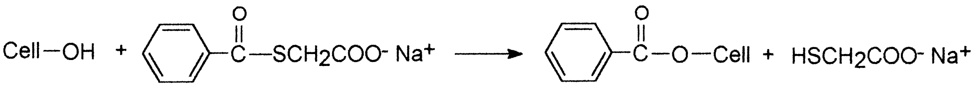
The visible absorbance spectrum of C.I. Disperse Blue 183 showed a wavelength of maximum absorption at 620 nm. The addition of sodium thioglycollate to the dye solution resulted in the formation of two absorption peaks in the spectrum of the dye, one at a wavelength of 420 nm and the second at 610 nm. As more thioglycollate was added to the dye solution, the peak at 610 nm was gradually shifted to a wavelength of 605 nm, the peak at 420 nm being unaffected. It is likely that many disperse dyes would be prone to reduction with thioglycollate and thus 'all-in' processes using pad-liquors containing dye and fibre-arylating agent together are not possible in the case of BTG. Other leaving groups which render the arylating agent water soluble and which are non-reducing when liberated in the nucleophilic substitution reaction with cellulose are under consideration.

When BTG (200 g dm^{-3}) was applied from a neutral pad-liquor and fixed by baking (200°C, 60 s), very low K/S values for the subsequent dyeings were recorded (1.39) indicating that these conditions were inadequate to achieve esterification.

When 200 g dm^{-3} BTG (16% owf) was applied to cotton in the presence of sodium bicarbonate and fixed at 200°C for 60 s, the colour yields of the

Table 1
Colour yields and wash fastness properties of the dyed untreated cotton and benzoyl chloride modified cotton fabrics

Treatment	K/S of original dyeing (620 nm)	ISO2		ISO3	
		K/S of dyeing	K/S of nylon 6,6 (stain)	K/S of dyeing	K/S of nylon 6,6 (stain)
None	0.28	0.22	0.03	0.16	0.06
Benzoyl chloride	17.88	16.77	0.12	12.70	0.56



Scheme 1. The reaction of BTG with cotton cellulose.

subsequent disperse dyeings increased as the concentration of sodium bicarbonate in the pad liquor increased (Fig. 2); above 40 g dm^{-3} sodium bicarbonate, the colour yields begin to fall presumably due to the competing hydrolysis reaction of hydroxyl ions with BTG to form sodium benzoate.

When 200 g dm^{-3} BTG (16% owf) was applied to cotton in the presence of sodium carbonate, the highest colour yield was achieved with a sodium carbonate concentration of 25 g dm^{-3}. Application of 300 g dm^{-3} BTG (24% owf) required a sodium carbonate concentration of 45 g dm^{-3} to obtain the highest colour yield (Fig. 3).

BTG application to cotton in the presence of sodium hydroxide (10–40 g dm^{-3}) gave very promising colour yields, especially when the lower levels of alkali (10–20 g dm^{-3}) were used (Table 2). At the higher levels of cotton benzoylation, good colour yields and wet fastness properties of the resulting disperse dyeings can be achieved.

Additions of urea to the pad liquor containing 200 g dm^{-3} BTG and 20 g dm^{-3} sodium carbonate were expected to increase the extent of benzoylation following thermo-fixation at 200°C for 60 s; the subsequent dyeing results (Table 3) indicate that urea additions have an adverse effect on the reaction. Urea decomposition provides ammonia and it is likely that BTG reacts rapidly with ammonia to produce benzamide which does not react with cotton cellulose.

As thermosol time was increased from 30 to 120 s, higher levels of BTG fixation were achieved, resulting in modified cotton fabrics with higher D.S. values. D.S. and covalent fixation of BTG to cotton also increased as higher temperatures were used during thermosol treatment. The increase in D.S., which resulted when longer thermosol times or higher temperatures were used, gave rise to disperse dyeings of improved colour yields. The BTG fixation results versus thermosol time and

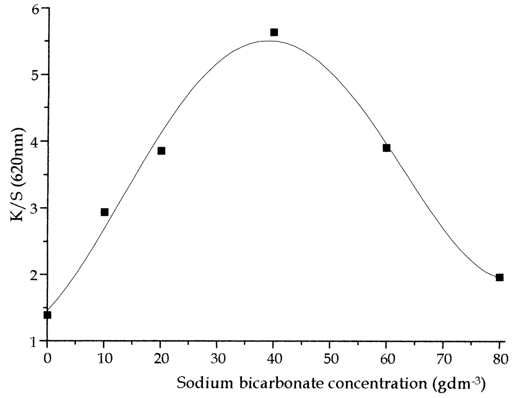


Fig. 2. The effect of sodium bicarbonate on colour yield.

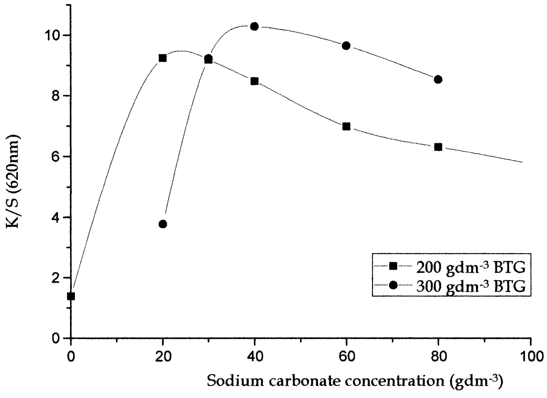


Fig. 3. The effect of sodium carbonate on colour yield.

Table 2
The effect of sodium hydroxide additions to BTG pad-liquors on subsequent dyeing colour yield and the colour yields after the ISO2 and ISO3 wash fastness tests

BTG concentration (g dm^{-3})	Sodium hydroxide applied (g dm^{-3})	K/S of original dyeing (620 nm)	ISO2		ISO3	
			K/S of dyeing	K/S of nylon 6,6 (stain)	K/S of dyeing	K/S of nylon 6,6 (stain)
200	20	7.19	6.69	0.21	5.25	0.28
200	40	3.37	2.83	0.22	2.42	0.34
300	10	10.52	8.90	0.14	7.65	0.33
300	20	6.62	5.58	0.21	4.75	0.37

temperature are shown in Fig. 4; a maximum fixation value of 80.4% was achieved which represents a D.S. of 0.109. Notwithstanding the relatively large amount of BTG applied (16% owf), the fixation figure above indicates that the acyl thioglycollate is a remarkably efficient reactive group in the alkaline pad-thermosol treatment of cotton cellulose.

Table 3
The effect of [urea] on the subsequent colour yield of BTG modified cotton (200 g dm^{-3} BTG, 20 g dm^{-3} sodium carbonate)

Urea concentration (g dm^{-3})	K/S (620 nm)
0	9.25
60	8.25
150	4.62
200	3.07
250	2.77

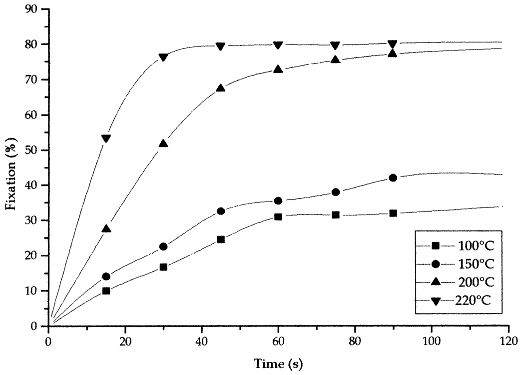


Fig. 4. The effect of time and temperature on the fixation of BTG (200 g dm^{-3} BTG, 20 g dm^{-3} sodium carbonate) on cotton cellulose.

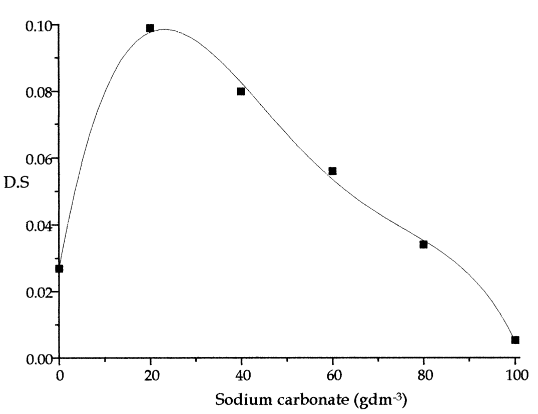


Fig. 5. The effect of sodium carbonate pad-liquor concentration on D.S. when modifying cotton with BTG.

When cotton was modified with BTG (200 g dm^{-3}) and sodium carbonate, the highest D.S. value was achieved when 20 g dm^{-3} sodium carbonate was present in the pad-liquor (Fig. 5).

As the weight gain of the benzoylated fabric increased, the colour yield of the resulting disperse dyeing also increased; weight gains were, therefore, converted to D.S. values and plotted against K/S (Fig. 6). This linear plot indicates that as the level of benzoylation of the cotton fabric increases, higher colour yields for the resulting disperse dyeings on the modified fabric will be achieved. Similar linear plots of disperse dyeing colour yield versus extent of benzoylation were obtained on wool modified with benzoic anhydride [7].

These effects demonstrate that aromatic interactions between the disperse dye aromatic residues and the benzoyl groups covalently incorporated in the modified fibres are the source of the disperse dye substantivity [8].

The FT–IR difference spectrum, obtained by subtracting the DRIFTS spectrum of untreated cotton from the DRIFTS spectrum of BTG modified cotton showed a very strong absorption peak at 1718 cm^{-1} (Fig. 7). This absorption peak corresponds to the stretching absorption of the carbonyl group in the resulting benzoyl ester derivative of the cellulose. The difference spectrum also showed absorption peaks at 1602 and 1453 cm^{-1} which

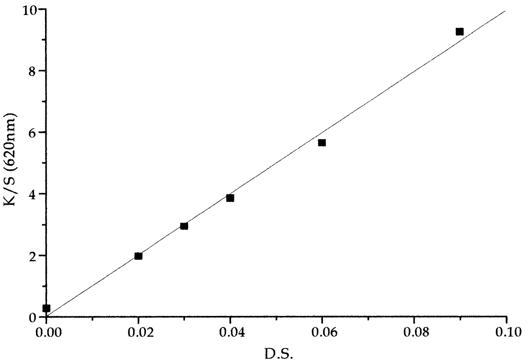


Fig. 6. The effect of D.S. on the colour yield of disperse dyeings on cotton modified with varying amounts of BTG.

correspond to the IR stretching vibrations of the carbon–carbon double bonds in the benzene ring of the benzoyl ester modified cotton.

The DSC plot for untreated cotton revealed exothermic enthalpy changes at temperatures of 334 and 376°C and an endothermic enthalpy change at 357°C. The corresponding DSC plot for BTG modified cotton contained only an endothermic enthalpy change at 364.0°C (Fig. 8).

The exothermic changes obtained in the DSC plot for cotton are associated with decomposition processes, which may occur within the fabric during heating. The endothermic peaks occurring in the DSC plots for both untreated and BTG modified cotton fabric are possibly due to local changes either in the crystalline regions of natural cotton or a breakdown in the hydrophobic interactions in the BTG modified cotton on heating. The shift in the position of the endotherm to 364°C is likely to be due to changes occurring in the physical structure of the polymer, brought about by modification.

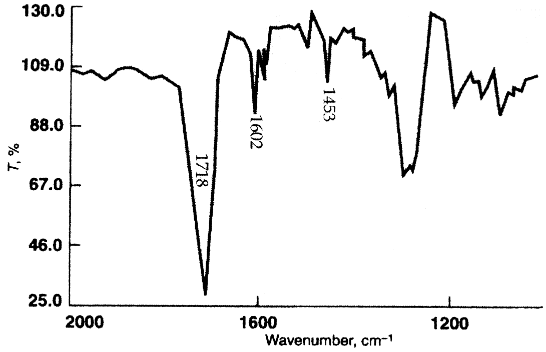


Fig. 7. IR difference spectrum of BTG modified and untreated cotton.

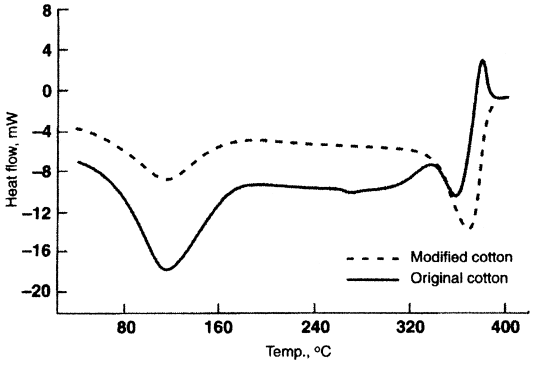


Fig. 8. DSC plots of untreated and BW modified cotton.

The DSC plots for untreated and BTG modified cotton fabric also contained endothermic peaks at temperatures of 115 and 112°C respectively. The peak area of the endothermic peak in the DSC plot for untreated cotton was greater than that obtained in the DSC plot for BTG modified cotton. These endothermic peaks are probably associated with the removal of water from the cellulose polymer chains. The lower peak area obtained in the DSC plot of BTG modified cotton is probably due to a decrease in the amount of water trapped within the polymer chains, which is brought about by changes in the physical and hydrophobic nature of the polymer after benzoylation.

4. Conclusions

Natural cotton has very little substantivity for disperse dyes and the resulting disperse dyeings show poor resistance to the ISO2 and ISO3 wash-fastness tests. Following modification of cotton with benzoyl chloride using a Schotton–Baumann reaction, a modified fabric can be produced which allows disperse dyeings of high colour yields to be produced. The resulting disperse dyeings showed good resistance to the ISO2 and ISO3 wash-fastness tests.

This investigation has demonstrated that a water soluble benzoylating agent, BTG, can be applied to cotton in the presence of an alkali via a pad-thermosol process to produce a modified fabric for which disperse dyes have improved substantivity. The resulting disperse dyeings were of high colour yield and showed good resistance to ISO2 and ISO3 wash-fastness tests.

The esterification of cotton by BTG was confirmed using FT–IR (DRIFTS) spectroscopy. DSC also indicated that important changes associated with increased hydrophobicity have occurred on benzoylation.

Since BTG is a water soluble active ester its use would allow the formation of benzoyl-esters of cellulose under mill processing conditions. This latter aspect is a great advantage over the Shikibo-Uni process, which relied on the Schotten–Baumann reaction with benzoyl chloride.

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