

Investigation into the Flame Retardant Properties of Soybean Fabric Treated with Sulphamic Acid

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ABSTRACT: The effect of sulfamic acid and urea treatments on the flame retardant properties of soybean fabric has been investigated by Limiting Oxygen Index (L.O.I.), Thermogravimetric Analysis (TGA), and X-ray Photoelectron Spectroscopy (XPS) in order to characterize both the bulk and surface properties. The sulfamic acid finish significantly reduced the soybean fabric flammability and appeared to function in the solid phase with increased char formation. Incorporation of urea into the formulation increased the level of reaction and associated weight gain. However, the wash durability of the sulfamic acid modifi-

cation of the soybean fabric was limited, but after treatment with a cationic fixing agent, Matexil FC-ER significantly increased the wash fastness and related flame retardant effect. XPS analysis demonstrated the substantivity of the cationic fixing agent to soybean fiber surface and its binding effect on the sulfamate at the fiber surface. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3590–3595, 2008

Key words: soybean; flammability; flame retardant; sulfamic acid; limiting oxygen index XPS; cationic fixing agents

INTRODUCTION

An important quality performance indicator of any textile/fiber product is its flammability and accordingly the safety of the consumer is vital. Sulfamic acid has previously been applied to protein fibers to impart a novel acid dye resist-effect and to offer basic dye affinity with associated improved wash and light fastness.^{1,2} Lewin³ has also reported that durable flame resistance could be imparted to wool by sulfation with sulfamic acid and that the inclusion of urea resulted in increased reaction levels with sulfamic acid.

The soybean fiber is a regenerated protein-based fiber which has recently become commercially significant due to its sustainability and the associated increased cost of petroleum-based fibers.^{4,5} Its luster, smooth surface, breathability, and comfort have been identified as desirable aesthetic properties in apparel, which together with its cost competitiveness, and the potential for genetic engineering of the soybean protein to improve the material's performance, clearly offers commercial opportunities. However, much of the basic knowledge involving the processing and associated performance of the fiber/fabric still needs to be established. In particular, in this

present study, the aim was to determine the thermal behavior of soybean fibers, the effect of sulfamic acid modification on soybean fabric, and its associated flame resistant properties and wash fastness.

The fiber surface is the interface with its environment, whether during aqueous washing or on exposure to an ignition source. Therefore, if a treatment is able to impart a durable protective surface layer, then it will impact on the overall materials' performance whether it is liquid repellency, color, or flame retardancy. In this study, the soybean fiber surface was characterized, using the X-ray Photoelectron Spectroscopy (XPS) technique, to monitor the deposition of the sulfamic acid, the interaction of a cationic fixing agent and the flame retardant durability to laundering. The XPS technique involves measuring the number of photoelectrons emitted from the textile fiber surface (outer 3–10 nm), during exposure to an X-ray source and determining their binding energies (BE).⁶ The nature of the surface species can thus be determined and both qualitative (elemental oxidation state and chemical environment) and quantitative information (surface composition) obtained.

EXPERIMENTAL

Materials

The soybean yarn, supplied by Huakang Ltd., China, was woven into a 1/2 twill, 100% soybean fabric (210 g/m²) and the fabric scoured prior to use in this study. Sulfamic acid and urea were supplied by

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Aldrich Chemicals (UK), and the Matexil FC-ER and Cibafix ECO were kindly donated by Uniqema, UK, and Ciba UK, respectively. The standard ECE detergent was obtained from the Society of Dyers and Colorists, Bradford, UK.

Chemical treatments

Soybean fabric was padded at 90% wet pick up (w.p.u.) with solutions (\sim pH 5) containing 10–30% w/v sulfamic acid, 0–20% w/v urea, dried at 90°C for 5 min, cured at the specified times and temperatures, rinsed in running water, and finally tumble dried.

The treated fabrics were washed in a Wascator FOM 71P, using a standard cotton 5A cycle, at 40°C with an overall 1.5 kg load of polyester fabric. The standard ECE detergent was used with 1 g/L sodium perborate. The untreated and sulfamic acid modified soybean fabrics were treated with either 5% o.m.f Matexil FC-ER or Cibafix ECO, respectively, at pH 6, for 30 min at 40°C with a fabric to liquor ratio 1 : 10. The fabric was then rinsed in tap water for 10 min and air-dried.

Instrumental analysis

The Yellowness Index, YID, of the soybean fabrics was determined with a Datacolor International Spectrophotometer under illuminant D65/10° observer conditions. All fabric samples were measured in a four-folded state and the results presented were the average value of 4–5 measurements.

XPS measurements were carried out with a Kratos Axis Ultra XPS instrument. The samples were analyzed with a monochromatic AlK α radiation source (1486.6 eV) operating at base pressure of 3×10^{-9} torr. Wide survey spectra were recorded at a pass energy of 100 eV to determine the surface chemical compositions.

High-resolution spectra were obtained at a pass energy of 20 eV to determine the chemical state of the examined elements. The binding energy values were calculated relative to the C(1s) photoelectron peak at 285.0 eV. The surface analyses were obtained in triplicate to ensure reproducibility and confirm uniformity of treatment.

TGA measurements were performed on a TA Q100 instrument with refrigerated cooling system (RCS). The thermal analyzer was operated at a heating rate of 10°C/min and an environment of 100% N₂ gas. The residual amount of char remaining after heating was determined after heating to 700°C.

Tensile strength measurement

The soybean fabrics were conditioned for 24 h at 20°C and 65% R.H. prior to testing on an Instron 5564 testing system. The tensile strength of the

untreated and sulfamic acid modified fabrics was determined as an average of 10 measurements in the warp direction.

L.O.I. measurement

The Limiting Oxygen Index (L.O.I.) of soybean fabrics was measured according to BS 4599-2:1999 on a Stanton Redcroft FTA flammability test unit. The value presented is the sum of the warp and weft direction values.

Vertical flammability test

The burning behavior of treated soybean fabrics was also assessed with the BS 5438: 1989 vertical flammability test method. Fabrics of 180 \times 650 mm² length and width were mounted on a suitable clamp and placed in a standard cabinet with a 2 mm/s airflow. The bottom edge of the fabric was exposed to a standard flame for 1 s and after the removal of the flame, the flame spread speed (mm/s) was determined by the average of 10 measurements for both warp and weft directions.

RESULTS AND DISCUSSION

Effect of sulfamic acid treatment conditions

Examination of Table I indicates the soybean fabric has a low L.O.I. value, suggesting it has relatively poor flammability properties in comparison to other proteinaceous fibers such as wool which typically has an L.O.I. value of 25–26%.^{7,8} A 20% w/v sulfamic acid treatment level appears, however, appears to offer the most effective application level in terms of increasing the L.O.I. value, but that increased yellowing and strength loss is also associated with increasing the sulfamic acid application levels and the curing temperatures and time. The nature of this associated fiber degradation must be related to the combination of elevated temperature and acidity progressively damaging the fiber and hence reducing the beneficial effect of the sulfamic acid treatments. Cameron⁹ similarly reported that the reaction of sulfamic acid with wool also resulted in an increase in fiber yellowness. Therefore, the need for short thermal exposure is apparent and SEM examination of the 30 s treated fibers indicates little topographical change occurs in this period.

Effect of urea

Urea has been reported to denature proteins and increase the accessibility of the side chains to chemicals reactions.¹⁰ Cameron⁹ has similarly referred to the swelling role of urea and its importance in the reaction of wool with sulfamic acid.

TABLE I
Effect of Sulphamic Acid (SA) Application Concentration on the L.O.I., Yellowness Index, and Strength of Treated Soybean Fabric^a

SA treatment level, % w/v	Curing time (min)	L.O.I. (%) \pm SD	Yellowness index	Strength loss %
Untreated	–	18.8 \pm 0.1	41.9	–
10	0.5	23.2 \pm 0.1	44.5	nd ²
10	1	22.9 \pm 0.3	46.6	nd ²
10	2	22.5 \pm 0.2	47.3	nd ²
10	5	22.0 \pm 0.1	48.9	nd ²
20	0.5	24.8 \pm 0.2	46.9	12.5 (21.6) ^b
20	1	24.7 \pm 0.1	46.9	13.6 (22.7) ^b
20	2	24.6 \pm 0.3	48.9	16.5 (26.1) ^b
20	5	23.1 \pm 0.1	52.6	19.3 (28.9) ^b
30	0.5	22.9 \pm 0.1	47.1	nd ^c
30	1	22.6 \pm 0.1	48.2	nd ^c
30	2	21.9 \pm 0.2	49.4	nd ^c
30	5	21.7 \pm 0.1	53.8	nd ^c

^a 150°C, cure temperature, no urea included in pad formulation.

^b Strength loss of fabric cured at 170°C.

^c Not determined.

Flame resistant finishing of wool with sulfamic acid in the presence of urea has been reported to increase weight gains, improve flame retardant performance, and enhance dissolution of the sulfamic acid in water.³ In this study, similar to wool, application of 20% (w/v) urea with the sulfamic acid also increased the fiber modification/weight gain, increased the L.O.I. values, and lowered the increase in fabric yellowness. All these effects were achieved by probably increasing the uniformity of reaction throughout the fiber by increased accessibility. Elliot¹¹ investigated the mechanism of the reaction and found that sulfation occurs at the free amino and hydroxyl groups in the wool. In our study, Fourier Transform Infrared (FTIR) analysis of the sulfamic acid treated soybean fibers also indicated that the hydroxyls were sulfated with an increase in the peak intensity observed at 1000 cm⁻¹, which has previously been assigned to sulfate esters.¹²

While the incorporation of urea into the formulation increased the L.O.I. values, the effect of increas-

ing the cure treatment time was still to reduce the L.O.I. value (Table II). This behavior was also reflected in the BS 5438: 1989 vertical flammability test where the although the fiber modification initially reduced the flame spread speed, with increasing treatment time the associated degradation of the fiber resulted in the flame spread performance again deteriorating. Obviously in any treatment for soybean fibers the acceptable balance between serviceability and fiber damage has to be established commercially.

TG analysis of soybean fiber

The TGA curves of the sulfamic acid treated samples showed a shift to lower temperature, with the onset of weight loss occurring at approximately 180°C in comparison to 300°C for the untreated material, Figure 1. The introduction of the sulfamic acid modification into the soybean fabric increased char formation from 7.7% to 16.0%, while the presence of urea in the pad application further increased char residue

TABLE II
Effect of Urea Concentration on the Weight Gain, L.O.I., Yellowness Indices, and Flame Spread Speed of Soybean Fabric Treated with 20% w/v Sulphamic Acid

Urea concentration (% w/v.)	Curing time (min)	Weight gain (%)	Yellowness index	L.O.I. (%) \pm SD	Flame spread speed (mm/s)
–	–	–	41.9	18.8 \pm 0.1	–
0	0.5	7.9	46.9	24.8 \pm 0.2	3.0
0	1	8.4	46.9	24.7 \pm 0.1	5.0
0	2	9.1	48.9	24.6 \pm 0.3	7.0
0	5	9.3	52.6	23.1 \pm 0.1	10.0
20	0.5	10.9	45.8	25.6 \pm 0.1	2.0
20	1	11.6	46.7	25.5 \pm 0.2	5.0
20	2	12.5	46.8	25.3 \pm 0.1	6.0
20	5	13.2	48.9	24.1 \pm 0.3	10.0

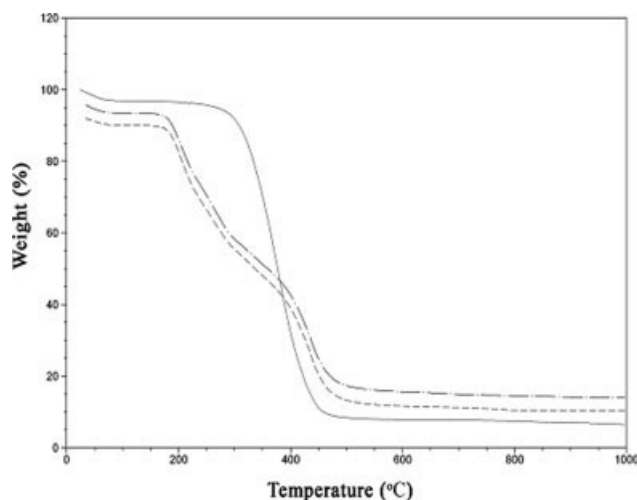


Figure 1 TGA curves of untreated and sulfamic acid treated soybean fabric. (—, untreated fabric, - - -, sulfamic acid modified fabric, - · - · -, urea/sulfamic acid modified fabric).

content to 19.2%. The same behavior has been previously observed and it is likely that, similar to wool, sulfamic acid retards the flammability of the soybean by inhibiting combustion in the solid phase.¹³⁻¹⁵

XPS analysis

The XPS survey spectrum of soybean shows the major photoelectron peaks located at binding energy values of 531, 400, 285, and 164 eV corresponding to the O (1s), N (1s), C (1s), and S (2p) signal intensities, respectively. The high resolution S(2p) spectrum of the soybean fabric, indicated the low intensity signal (0.3% atomic) was centered at 164 eV and was related to the low levels of unoxidized (S^{2+}) sulfur-containing amino acids at the soybean fiber surface. Examination of the S (2p) spectrum of sulfamic

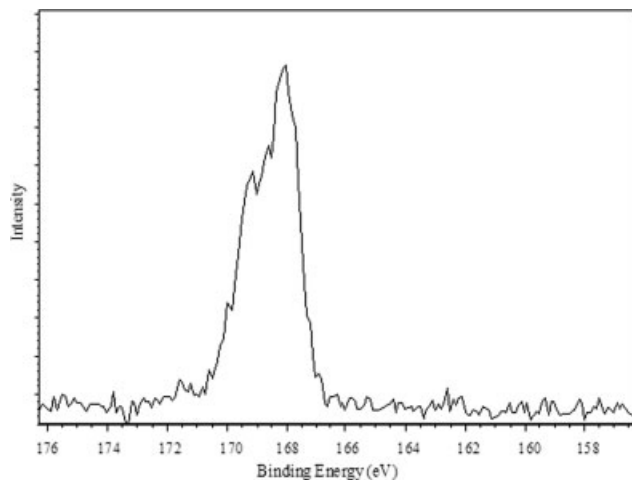


Figure 2 S (2p) XPS spectrum of soybean fabric Treated with 20% w/v sulfamic acid.

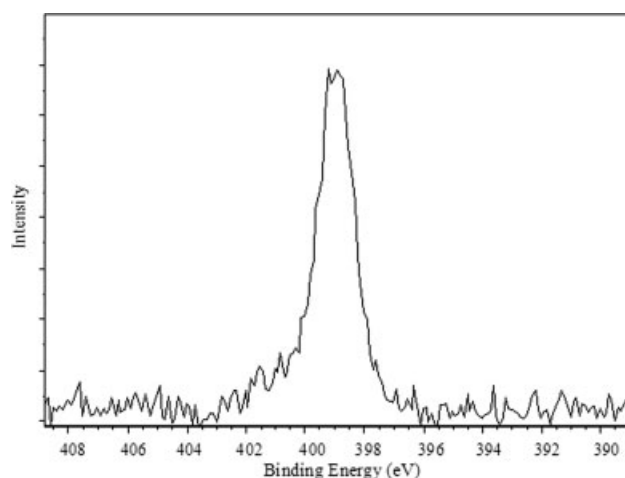


Figure 3 N (1s) XPS spectrum of untreated soybean fabric.

acid modified soybean indicated the obvious presence of sulfur species located at 168 eV which can be attributed to the S^{6+} form of bound sulfamic acid, Figure 2.

However, after the first washing cycle surprisingly a decrease in the surface sulfur concentration was observed (2.8% to 1.3 atomic %) indicating the relatively poor stability of the finish on the soybean fabric under perborate-based washing conditions. Further washing, up to three cycles, reduced the surface sulfur content to less than 0.2 atomic %, with the XPS analysis only detecting a very weak sulfur signal. This behavior is in contrast to that reported for the sulfamic acid treated wool which was found to be washfast.¹⁶ The nature of this relatively poor wash stability of the soybean modification may be related to the associated degradation of the fiber during the heat curing process resulting in reduced fiber integrity. SEM analysis of the washed fibers

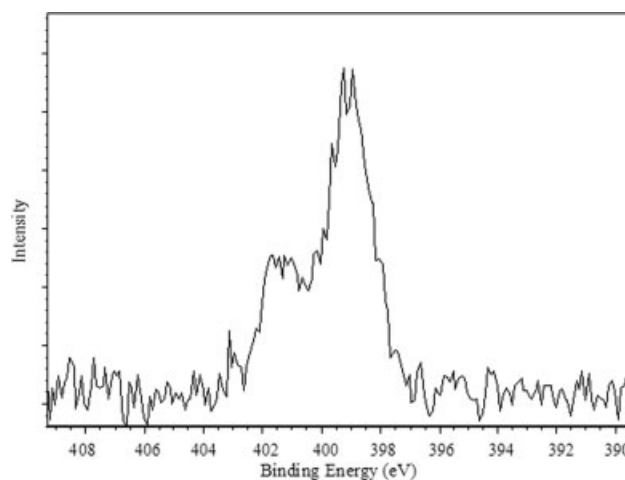


Figure 4 N (1s) XPS spectrum of soybean fabric Treated with 5% o.m.f. Matexil FC-ER.

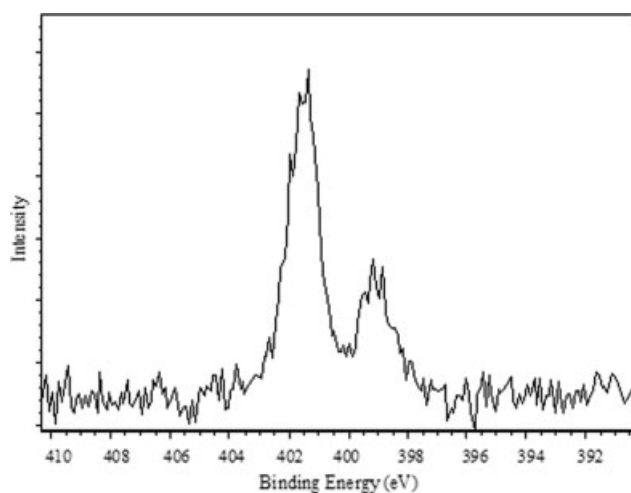


Figure 5 N (1s) XPS spectrum of soybean fabric Treated with 20% w/v sulfamic acid, after treated with 5% o.m.f. Matexil FC-ER, and washed $\times 3$.

indicates some fibrillation but no evidence of any significant loss of material.

Effect of cationic fixing agents on modified soybean

A common method to improve the wash fastness of anionic dyes is to apply a cationic fixing agent which complexes with the dye and increases color durability.¹⁷ Therefore, in the light of the poor wash fastness of the sulfamate modification the deposition of cationic reagents, Matexil FC-ER and Cibafix ECO, onto soybean, its potential for interacting with the sulfamic acid modified fiber and accordingly increasing the wash fastness of the flame retardant finish was also studied. Cibafix ECO is the polymeric condensation product of diethylenetriamine and dicyandiamide and has been used to enhance the wash fastness of direct dyes on cellulose.¹⁸ Matexil FC-ER is a nonreactive cationic fixative manufactured by the cyclopolymerization of diallyl dimethyl ammonium chloride via free radical initiation, similarly used to improve wash fastness of anionic dyes.¹⁹

The effect of repeated washing on the flame retardancy of sulfamic acid modified soybean was to lower the L.O.I. value from 25.6% to 19.8%. In contrast, the L.O.I. values of sulfamic acid modified soybean fabric after treated with cationic Matexil FC-ER and Cibafix ECO were found to only be reduced to 23.8% and 20.8%, respectively, after three washing cycles.

The N (1s) spectrum of untreated soybean indicated the presence of peak intensity at a BE value of 399.0 eV, which can be assigned to typical protein amino/peptide functionalities, Figure 3. Examination of the N (1s) XPS spectrum of the 5% o.m.f. Matexil

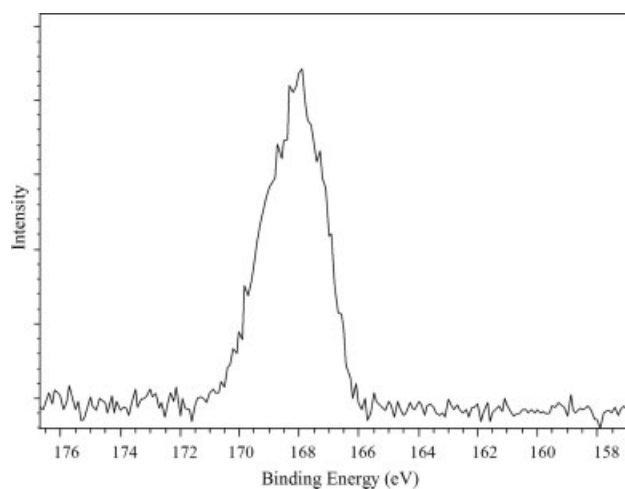


Figure 6 S (2p) XPS spectrum of soybean fabric treated with 20% w/v sulfamic acid, after treated with 5% o.m.f. Matexil FC-ER, and washed $\times 3$.

FC-ER treated soybean indicates the presence of an obvious higher binding energy signal at 402 eV, which can be assigned to the cationic nitrogen in the fixing agent, Figure 4. In addition to the cationic component, the Matexil FC-ER is reported to also have an uncharged component in its formulation which also contributes to the observed uncharged N (1s) surface intensity.¹⁹

On washing the combination treated soybean fabric it is evident that the cationic component is more substantive to the fiber surface and the relative proportion of the charged component in the Matexil FC-ER accordingly increases at the fiber surface, Figure 5. Furthermore as the Matexil FC-ER on the fiber surface is durable to washing, it would be anticipated that the sulfamic acid "bound" to the fiber could also be electrostatically bound as well as covalently bound to the fiber and hence offer enhanced durability to washing.

The S (2p) XP spectrum of the washed Matexil FC-ER after treated sulfamic acid modified soybean does indeed indicate the presence of a strong oxidized sulfur signal at 168 eV (2.7% atomic) even after three washings, Figure 6, offering a viable method of imparting greater durability to the sulfamate modification of the fiber.

CONCLUSIONS

The reaction of sulfamic acid with soybean fabric was investigated and the associated effectiveness of the flame retardant finish evaluated. The L.O.I. value of the treated fabric increased significantly with increasing application levels and incorporation of urea into the formulation. The flame retardancy can

be related to increased char formation and probably solid phase inhibition of the burning process.

The XPS technique successfully monitored the loss of sulfamic acid, as indicated by the S (2p) signal, from the fiber surface during the subsequent wash fastness analysis. The cationic fixing agent Matexil FC-ER imparted improved durability to laundering by complexing with anionically charged sulfamic acid modified fiber, hence retaining the sulfur at the fiber surface, even after three accelerated washing cycles.

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References

1. Sandoz, U.S. Pat. 2,726,133 (1955).
2. Cameron, B. A.; Pailthorpe, M. T. *J Soc Dyers Col* 1987, 103, 257.
3. Lewin, M.; Isaacs, P. K.; Shafer, B. In *Proceedings of the 5th International Wool Textile Research Conference*, Aachen, Germany 1975; p 73.
4. Zhang, Y.; Ghasemzadeh, S.; Kotliar, A. M.; Kumar, S.; Presnell, S.; Williams, L. D. *J Appl Polym Sci* 1999, 71, 11.
5. Zhang, X.; Min, B.; Kumar, S. *J Appl Polym Sci* 2003, 90, 716.
6. Ratner, B. D. Castner, D. G. In *Surface Analysis: The Principal Techniques*; Vickerman, J. C., Ed.; Wiley: Chichester, 1997; p 43.
7. Lewin M. In *Handbook of Fiber Science and Technology, Volume II: Chem Processing of Fibers and Fabrics*; Lewin, M.; Sello, S. B., Ed.; Marcel Dekker: New York, 1983; p 1.
8. Guan, J.-P.; Chen, G.-Q. *Fire & Materials*; 2006, 30, 415.
9. Cameron, B. A.; Pailthorpe, M. T. *Text Res J* 1987, 57, 619.
10. Asquith, R. S.; Booth, A. K. *Text Res J* 1970, 40, 410.
11. Elliot, R. L.; Asquith, R. S.; Rawson, D. H. *J Soc Dyers Col* 1958, 74, 176.
12. Carr, C. M.; Lewis, D. M. *J Soc Dyers Col* 1993, 109, 21.
13. Gordon, P. G.; McMahon, D. T. W.; Stevens, L. J. *Text Res J* 1977, 47, 699.
14. Benisek, L.; Edmondson, G. K.; Philips, W. A. *Text Res J* 1979, 49, 212.
15. Beck, P.; Gordon, P. G.; Ingham, P. E. *Text Res J* 1976, 46, 478.
16. Xing, J. W.; Pailthorpe, M. T. *J Soc Dyers Col* 1976, 108, 17.
17. Shore, J. In *Colorants and Auxiliaries: Organic Chemistry and Application Properties*, Society of Dyers and Colorists; Shore, J., Ed.; Bradford, UK, 1990; p 444.
18. Sugdon, M. C. Ph.D. Thesis, University of Leeds, 2000.
19. Rosunee, S.; Carr, C. M.; Hibbert, S.; Jones, C. *J Mater Sci* 2003, 38, 2179.