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Short communication

An alternative approach to the production of fluorescent colored fibres

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Abstract

Fluorescent cellulose acetate, cellulose triacetate and polycaproamide fibres have been obtained using naphthalimide and naphthoylenbenzimidazole derivatives as luminophores. Determination of spectral characteristics and stability of the fibres to UV-radiation, wet processing and washing has shown the optimum luminophore concentration to be 0.4–0.6% based on polymer mass. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Chemical fibres that are to be used for the production of consumer goods that have bright fluorescent colours and high stability to organic solvent action, wet processing, washing and light exposures continue to be of commercial interest. It is known that the use of organic luminophores as dyes allows one to confer bright colours of pure tones to textile fibres [1]. In this regard, derivatives of naphthalimide have been found to be better luminofores than other dyes [2,3]. Synthetic and artificial substrates dyed by these luminofores possess bright yellow-green to red colours. The colour of such materials is determined not only by the reflected light, but also by the fluorescence properties of the dyes.

Traditionally, dyeing with non-fluorescent dyes is performed using 0.5–5.0% dye based on the weight of the substrate. Clearly the shade is deeper when the dye concentration is higher. In the case of organic luminofores, a high concentration is necessary to obtain an intense color. However, the advantages of these dyes can be negated by reabsorption of fluorescence and by concentration quenching [4,5]. Therefore, determining the optimum luminophore concentration in a polymeric substrate, when both intense absorption and intense fluorescense exist, is important.

Two methods for producing colored materials are exhaust dyeing and mass coloration. Exhaust dyeing has a number of drawbacks. In particular, dyeing assistants such as dispersants are required, depending on the nature of the substrate, and

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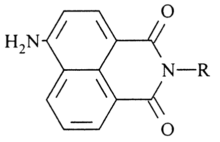
large quantities of industrial waste water are formed. In addition, certain fluorescent dyes applied in this way have low stability to wet processing and UV light.

The coloration of fibres during their formation is more economic, and is ecologically favorable, because waste water is eliminated. Depending on the nature of the substrates, a number of specific requirement are imposed on the dyes that are used for mass coloration. For instance, these dyes should have sufficient solubility in organic solvents, be stable to degradation at high temperatures, and strongly interact with a polymer matrix giving donor–acceptor complexes [6].

The results of studies involving the application of organic luminophores for the production of colored acetate, triacetate, polyether, polycaproamide, and other fibres are available [7–12]. It is clear that brightly coloured yellow-green fibers may be obtained using of 4-aminonaphthalimide (**I**, **II**) derivatives [7,8].

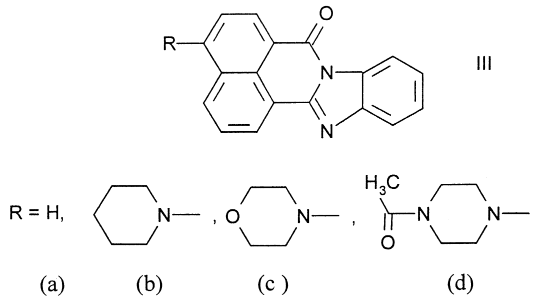


R = Alk (I) , Ar (II)

The derivatives of (**II**) with electron-donating substituents in the phenyl ring have been investigated as colorants for fibres [8], and the authors have shown that type II dyes were most effective compounds than type I. Unfortunately luminophores of this type do not possess sufficient stability to wet processings (1–2 on the scale of 1–5) and to the action of light (1–2 on the scale of 1–8), due to the presence of the primary amino group.

Derivatives of naphthoylenbenzimidazole (**III**) that have higher thermal and light stability and that produce fluorescent dyes [9–12] can be used for colouring of polyamide materials.

Our previous results [2] and the results of others [3] have shown that naphthalic acid derivatives with substituted amino groups possess higher light stability than those with a primary amino group. Compounds that have morpholino and piperidino groups are the most stable to UV light.



The purpose of the present work is to extend studies involving the development of fluorescent fibres, by using the most stable derivatives of (**I**–**III**). To achieve this goal, we have synthesized several derivatives that satisfy the requirements for dyes used in mass coloration.

Since polycaproamide fibre formation is carried out in the melt at 270–280°C, dyes employed must be extremely thermostable. In addition, since molten polyamide has reducing ability, the dyes must be stable to reduction at high temperatures. Before melting and forming the polyamide fibres, polyamide chips are powdered in the presence a dye. The mixture is then transferred to the melting and extrusion process. The advantage of mass coloration is that melt extrusion is not accompanied by the formation of environmentally harmful waste products.

2. Results and discussion

In order to take into account the possibility of high concentration quenching and fluorescent reabsorption, it was necessary to determine the luminophore concentration that gave maximum luminescence in a given spectral range and maximum stability to UV radiation. With this in mind, cellulose acetate, cellulose triacetate and polycaproamide fibres having different luminophor concentrations were generated.

We found that the choice of manufacturing methods for mass coloration and the nature of the fibre had no significant bearing on stability to UV light. However, the light stability of fluorescent fibres did depend on luminophore structure and concentration.

The results of examining the light stability of several luminophores (**IV**) as a function of concentration are given in Tables 1 and 2. As a reference point, the fluorescence intensity of the unexposed sample was taken to be 100%.

Compounds (**IVa**, **c**, **d**, **e**) were resistant to UV radiation at essentially the same level. Specifically, fluorescence intensity was reduced by 15–20% after 100 h irradiation. The light stability of compound (**IVb**) and its derivatives is much higher, as their luminescence intensities remained constant during 150 h of irradiation in the "Xenotest-450" apparatus. It is important to note that compound (**IVb**) exhibited higher fluorescence as irradiation time increased. Luminescence intensity was twice as high after 100 h of irradiation. It is likely that this effect was observed because the amino group interacts with the polymer matrix, decreasing the loss of electronic excitation. In unirradiated fibres, electronic excitation can be quenched by the rotation of the *N*-aminoimide fragment around the N–N bond and inversion of the nitrogen atom of the free amino group [13]. Rotation and inversion can not take place after the amino group has interacted with the matrix.

It is clear from Table 2, that compounds **III** were more stable to UV light than naphthalimides. This can be attributed to the molecular structure of compounds **III** as the additional ring of molecules **III** facilitates the redistribution of electron density, providing more resistance to external influences.

It is also important to keep in mind that after dyeing with the same luminophore, polycaproamide fibres have a yellow color, but acetate and triacetate fibres have a lemon color. Apparently, this is related to the fact that the dye molecules have different solubilities in these substrates. Molecules aggregated in polycaproamide fibres have a greater contribution to intensity of luminescence.

Concentration dependent luminescence data are listed in Table 3 for compound **Vb**. As can be seen from the data, luminescence reached a maximum for films that contained 0.5% luminophore. In

Table 1
Effect of 4-morpholino-naphthalimide concentration (*C*,%) on the fluorescence intensity of dyed cellulose triacetate fibers

C (%)	Fluorescence intensity (%)		
	Before irradiation	After 50 h of irradiation	After 100 h of irradiation
0.1	100	76	51
0.2	100	83	68
0.3	100	86	74
0.5	100	88	77
0.8	100	95	87
0.9	100	87	75
1.0	100	84	72

Table 2
Effect of 4-morpholino-naphtoylenbenzimidazole concentration (*C*) on fluorescence intensity of dyed cellulose triacetate fibers

C (%)	Fluorescence intensity (%)		
	Before irradiation	After 90 h of irradiation	After 150 h of irradiation
0.1	100	90	67
0.2	100	100	93
0.3	100	100	98
0.5	100	100	100
0.8	100	100	99
0.9	100	100	94
1.0	100	100	94

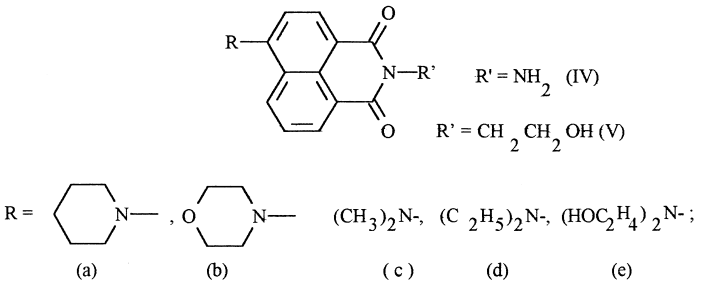


Table 3
Effect of 4-morpholino-*N*-β-oxyethylnaphthalimide concentration (C) on fluorescence intensity of acetate fibres

C	Fluorescence	
(%)	λ_{max} (nm)	$B_{relative}$ (%)
0.1	506	30
0.2	511	46
0.3	513	53
0.4	515	94
0.5	516	100
0.6	519	90
0.7	521	85
0.8	523	82

addition to lowering luminescence intensity, increased dye concentration led to a bathochromic shift in the luminescence maximum.

Analysis of the spectral characteristics of the dyed fibres and their stability to UV radiation showed that the optimum luminophore concentration was 0.4–0.6% based on the mass of the polymer.

Another important characteristic of fluorescent dyed fibres is their stability to end use conditions. While the structure and concentration of luminophore significantly affect the spectral properties of the mass colored fibers, both had an appreciably smaller influence on other fastness properties of the dye fibers.

The results of additional tests are summarized in Table 4. The data show that the use of compound **Vb** has allowed us to produce dyed fibres that possess good end use properties. These fibres fluoresce in the range from 505 to 575 nm and have a high degree of resistance to the action of organic solvents, light and washing.

Table 4
Color fastness of fluorescent triacetate fibres as a function of 4-morpholino-*N*-β-oxy-ethylnaphthalimide concentration (C)

C	Color fastness		
(%)	Wash fastness	Solvent fastness	Perspiration fastness
0.1	4/4	5/5	4/4
0.2	4/4	5/5	4/4
0.3	4/4	5/5	4/4
0.5	4/4	5/5	4/4
0.8	4/4	5/5	4/4
0.9	4/3	5/4	4/4
1.0	4/3	5/4	4/3

3. Experimental

To prepare fluorescent dyed cellulose acetate and cellulose triacetate fibres, the dye was added to either a water-acetone solution containing 24.0–26.0% cellulose acetate, or a dichloromethane–ethanol solution containing 19.0–22.0% of cellulose triacetate. The resultant solution was mechanically stirred to achieve efficient mixing and then filtered using a frame filter-press. The resultant solution was passed onto an extruder. Two specific examples of the above method for generation of fluorescent dyed fibres are given below.

3.1. Example 1

The original solution had the following components, expressed as their mass ratio (% of the total mass): cellulose triacetate 18.996, 4-morpholino-*N*-β-oxyethylnaphthalimide 0.019, dichloromethane 73.696, ethanol 7.289. 4-Morpholino-*N*-β-oxyethyl naphthalimide (0.1% based on the polymer mass) was added to a 19% solution of cellulose triacetate in dichloromethane–ethanol mixture. This combination was mixed thoroughly to dissolve the dye. The solution was dried to remove residual ethanol, and fibers were formed using an extruder.

3.2. Example 2

The original solution had components given in the following mass ratios (% of the total mass): cellulose triacetate 20.646, 4(5)-morpholino-1,8-naphthoilen-1′,2′-benzimidazole 0.021, dichloromethane 72.193, ethanol 7.140. 4-Morpholino-1,8-naphthoilen-1′,2′-benzimidazole (0.1% based on the polymer mass) was added to a 20.65% solution of cellulose triacetate in the dichloromethane–ethanol mixture. The solution was dried to remove ethanol, and fibers were being formed using an extruder.

Examination of luminophore light stability, effect of luminophore on the fluorescence of dyed fibers, testing of dyed fibers stability were carried out according to standard methods [14].

4. Conclusions

Technically viable of fluorescent cellulose acetate, cellulose triacetate and polycaproamide fibres have been produced using the methods reported in this study [15–17]. The resultant fibres are suitable for novel industrial textiles, both knitted and woven.

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