

PHOTOCHEMICAL REGENERATION OF ACID DYE RECEPTOR SITES: A NEW METHOD FOR DIFFERENTIAL DYEING OF POLYAMIDES

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Summary

The reactivity of polyamides toward acid dyes depends on the number of free amine end groups available along the polyamide chain, the so-called acid dye receptor sites. These protonated amine groups form an ionic bond with the acid dyes. The dyeability of polyamides can be drastically reduced by treatment of polyamide with a chlorinating agent which converts the amine groups into weakly basic *N*-chloroamines. The difference in dye uptake between the chlorinated sample and the untreated control depends on the temperature and duration of chlorination.

The dyeability of the chlorinated polyamide can be restored by exposing the sample (using a mask or screen) to weak UV light to regenerate the free amine sites. This photochemical reaction depends on the UV dosage.

The combined treatments of chlorination and photolysis offer a new process for differential acid dyeing of polyamides.

1. Introduction

Polyamides are commonly dyed with anionic (acid) dyes that form ionic bonds with its protonated terminal amine groups. One method for achieving a differential degree of dyeing for nylon is to control the number of the amine end groups [1 - 3]. The dyeability of nylon can be altered by treating it with a reagent that transforms the amine group into an amine derivative. This derivative should be inert to acid dyes and stable under normal acid dyebath conditions (boiling aqueous dyebath at low pH, exposure time up to 1 h). A variety of reagents have been reported in the patent and trade literature for this purpose, including the use of simple carboxylic acids [4], acid chlorides [5] and anhydrides [6]. However, these reagents are known to cause hydrolysis of the nylon chain, thus weakening the fiber.

In our work directed toward the chemical modification of polyamides and polyurethanes [7], we had the opportunity to treat polyamide fiber with chlorinating agents. This is a known method for generating *N*-chloroamide linkages in polyamides that may be useful for further polymer modification [8, 9]. However, to our surprise, treatment of polyamides with

N-chlorinating agents also drastically reduced the acid dyeability of the treated polymer. Chlorination of the amine end groups, leading to weakly basic *N*-chloroamines, was thought to account for this observation. If true, the acid dyeability of the chlorinated polyamide may be restored by photochemical conversion of the *N*-chloroamine end groups back to free amines. This was found to be the case. We describe here simple chemical and photochemical processes for the differential acid dyeing of polyamides.

2. Experimental details

2.1. General details

Nylon 66 yarn (DuPont 1100/68 746 Brt) and nylon 6 yarn (Allied 6E39) (0.5 g each sample) were scoured before use by washing in methanol (three times) and deionized water (80 °C, three times). Yarns were air dried before treatment with a chlorinating agent.

Commercial Clorox™ (5.25% sodium hypochlorite), *t*-butyl hypochlorite (Frinton Laboratories), *N*-chlorosuccinimide (NCS, Aldrich) and *N*-bromosuccinimide (NBS, Aldrich) were used as received.

2.2. *N*-Chlorination

Scoured nylon yarns were dipped into a bath containing sodium hypochlorite (20 ml) for a period of time. When treatments were complete, the samples were rinsed with deionized water and dried in air. These samples had an active chlorine half-life of about 1 week at room temperature (in the dark), as measured by iodometric titration [10].

2.3. UV irradiation

The slightly wet chlorinated samples were covered with a screen (or mask) and irradiated with a high pressure mercury lamp (PPG Industries, model QC1202) (dosage, 1.6 - 5.5 J cm⁻²). No significant increase in the temperature of the irradiated samples was observed during UV exposure.

2.4. Dye uptake measurements

Dye uptake measurements were carried out using CI Acid Red I (Sandolan Rhodine E-2GL, Sandoz Corp.). Dyebaths were prepared by dissolving 0.37 g CI Acid Red I in 500 ml deionized water with enough citric acid-sodium acetate buffer (0.15 g citric acid and 0.5 g sodium acetate) to maintain the pH of the dyebath at 5.1. Dyeing was carried out in a beaker at 100 °C for 1 h. The samples were then rinsed with water, air dried and stored overnight over P₂O₅ in a desiccator under high vacuum to dryness.

The dye uptake (grams of dye per gram of fiber) was determined by dissolving the dyed fiber (0.2 g) in 90% reagent-grade formic acid (100 ml) and measuring the absorbance of the resulting solution at 540 nm. The dye uptake was calculated by comparing the absorbance with that of a standard solution containing anhydrous CI Acid Red I in 90 wt.% formic acid ($A_{540} = 0.422 \text{ (mg dye)}^{-1}$ for the standard solution).

2.5. Mechanical tests

The breaking strength (maximum pounds pull) and elongation of treated nylon fibers were determined on an Instron Model TT using a 2 in min^{-1} crosshead speed on a 2 in jaw distance. Yarns were pretensioned to approximately 0.05 lb.

3. Results and discussion

Polyamide fibers were treated with chlorinating agents under a variety of conditions (listed in Table 1). The chlorinated samples were then treated in a dyebath containing an acid dye, CI Acid Red I. Dye uptake was determined by dissolving the sample in formic acid and measuring the absorbance of the resulting solution at 540 nm against a standard solution.

The results listed in Table 1 indicate that 5.25% sodium hypochlorite solution (CloroxTM) is effective in reducing the dye uptake of polyamide fiber. The dye uptake of nylon 66 fiber was reduced from 10.35 mg (g fiber)⁻¹ (control) to 2.39 mg (g fiber)⁻¹ with 1 min treatment in boiling sodium hypochlorite. The extent of dye uptake depends on the time of treatment with sodium hypochlorite. At 100 °C for 15 s, the dye uptake was lowered to 41% of the control, and a 5 min treatment showed a dye uptake of 11%. The treatments were less effective when carried out at lower temperatures. Treatment with sodium hypochlorite at room temperature for 5 min

TABLE 1

Change in dye uptake of polyamide fiber on *N*-chlorination

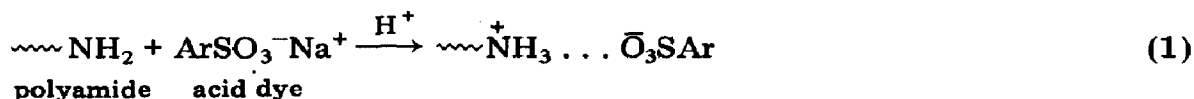
Nylon	Chlorinating agent ^a	Solvent	Temperature (°C)	Time (min)	Dye uptake (mg (g fiber) ⁻¹)	Dye uptake (%)
66	—	—	—	—	10.35	100
	NaOCl	H ₂ O	25	5	10.35	100
	NaOCl + TBAB	H ₂ O	25	5	10.27	99
	NaOCl + OT-75	H ₂ O	25	5	8.96	87
	NaOCl	H ₂ O	100	0.25	4.25	42
	NaOCl	H ₂ O	100	1	2.39	23
	NaOCl	H ₂ O	100	5	1.12	11
	NCS	H ₂ O-CH ₃ CN (1:1)	60	1	4.05	39
	<i>t</i> -BuOCl	MeOH	25	5	1.84	18
	NBS	CH ₃ CN	25	5	9.34	89
	NBS	H ₂ O-CH ₃ CN (1:1)	60	1	4.07	39
	NBS	H ₂ O	100	1	0.93	9
6	—	—	—	—	10.08	100
	NaOCl	H ₂ O	100	1	2.14	21

^aNaOCl, 5.25% sodium hypochlorite (CloroxTM); TBAB, 5% tetrabutylammonium bromide; OT-75, 0.1% anionic surfactant (cyanamid); NCS, 5% *N*-chlorosuccinimide; *t*-BuOCl, 2% *t*-butyl hypochlorite; NBS, 5% *N*-bromosuccinimide.

did not show any change in dye uptake when compared with the control. The use of a phase-transfer catalyst (tetrabutylammonium bromide) at room temperature did not improve the rate of chlorination while an amine surface-active agent (OT-75) was slightly effective (see Table 1).

Other halogenating agents, *N*-chlorosuccinimide, *t*-butyl hypochlorite and *N*-bromosuccinimide, can be used to reduce dye uptake in polyamide. A methanolic solution of *t*-butyl hypochlorite was found to be very effective even at room temperature. However, this reagent was so reactive and difficult to control that degradation of the nylon fiber became apparent.

Is it well known that dye uptake in polyamides is a function of several physical, morphological and chemical properties [1]. Polyamides are commonly dyed with acid dyes that form ionic bonds with the protonated amine end groups present in the polymers.



Thus, dye uptake in nylon is, in part, a function of the number of the amine end groups and can be altered by changing the number of these sites [2, 3]. Chlorinating agents such as *t*-butyl hypochlorite, sodium hypochlorite and *N*-chlorosuccinimide are known to react rapidly with amines to yield *N*-chloroamines [11]. We have found that *N*-chloroamines, such as *N*-chloropyrrolidine, are stable under aqueous dyebath conditions in the dark. We believe that treatment of polyamide with chlorinating agents depletes acid dye sites by conversion of free amines to *N*-chloroamines.



The *N*-chloroamines are less basic than the parent amines and are not effective dye receptor sites. Thus, the acid dye uptake can be significantly lowered by treatment of polyamide with a chlorinating agent.

N-Chloroamines are also photolabile. They undergo facile N—Cl bond cleavage upon UV irradiation to give neutral aminyl radicals which then abstract hydrogen atoms to regenerate the free amines [12, 13]. If *N*-chloroamines are present in the chlorinated polyamide and are responsible for change in dye uptake, then upon UV irradiation a similar mechanism ought to operate, as described by eqn. (3):



The UV irradiation of hypochlorite-treated nylon should restore the acid dyeability of the fiber by regeneration of the dye receptor sites. Differential dye uptake and imaging should be possible simply by selectively exposing (through the use of a mask or a screen) the *N*-chlorinated samples to UV irradiation.

TABLE 2

Change in dye uptake of polyamide fiber on *N*-chlorination and UV irradiation

Nylon	Chlorination (Clorox ^a , 100 °C) (min)	Irradiation (J cm ⁻²)	Dye uptake (mg (g fiber) ⁻¹)	Dye uptake (%)
66	—	—	10.80	100
	0.25	—	4.25	39
	0.25	3.3	5.45	51
	1	—	2.40	22
	1	1.6	3.67	34
	1	3.3	4.25	39
	1	5.0	4.64	43
	1	9.9	5.31	49
	5	—	1.12	10
	5	3.3	2.48	23
6	—	—	10.08	100
	1	—	2.07	21
	1	1.6	3.37	33
	1	3.3	4.33	43
	1	5.0	4.94	49

^a5.25% sodium hypochlorite.

Exposure of the hypochlorite-treated polyamide to UV light (1.6 - 5.0 J cm⁻²) effected a significant increase in dye uptake. When chlorinated samples were selectively irradiated, using a mask, a differential in dye uptake between the exposed and unexposed areas was accomplished. The exposed areas exhibited an increase in dye uptake with an increase in light dosage (Table 2), for instance, nylon 66 yarn samples treated with boiling sodium hypochlorite for 1 min gave a dye uptake 22% of the control. Irradiation with 1.6 J cm⁻² gave a dye uptake of 34% and a 9.9 J cm⁻² exposure gave a dye uptake 49% of the control. Figure 1 shows the relationship between exposure and dye uptake in treated nylon 66.

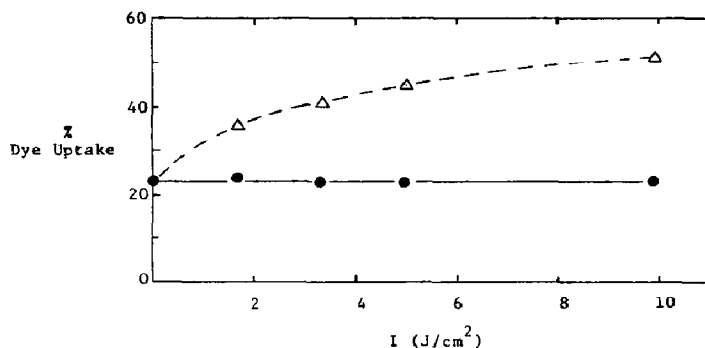


Fig. 1. Difference in dye uptake between the exposed (Δ) and unexposed (\bullet) areas of chlorinated nylon 66 fiber upon UV irradiation. Clorox treatment: 100 °C for 1 min.

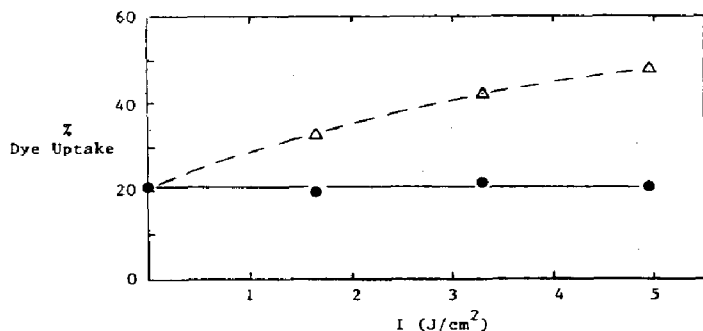


Fig. 2. Difference in dye uptake between the exposed (Δ) and unexposed (\bullet) areas of chlorinated nylon 6 fiber upon UV irradiation. Clorox treatment: 100 °C for 1 min.

For nylon 6 samples, the dye uptake of the irradiated samples shows a linear relationship with the light dosage as indicated in Fig. 2. The difference in dye uptake between the exposed and unexposed areas was more pronounced than in nylon 66.

Figures 1 and 2 indicate that it is difficult to restore a 100% dye uptake in the UV-exposed areas. This is because the UV irradiation of the chlorinated fiber is a surface, not a bulk, treatment.

The effect of UV irradiation on the mechanical performance of the chlorinated nylon fiber was also examined. As shown in Fig. 3, the breaking strength (maximum pounds pull) and per cent elongation of the treated nylon 66 fiber (after chlorination and photolysis) show a degradation as a function of light dosage. The decrease in breaking strength is apparent with 5 J cm⁻². Photolysis of untreated samples under similar conditions shows no

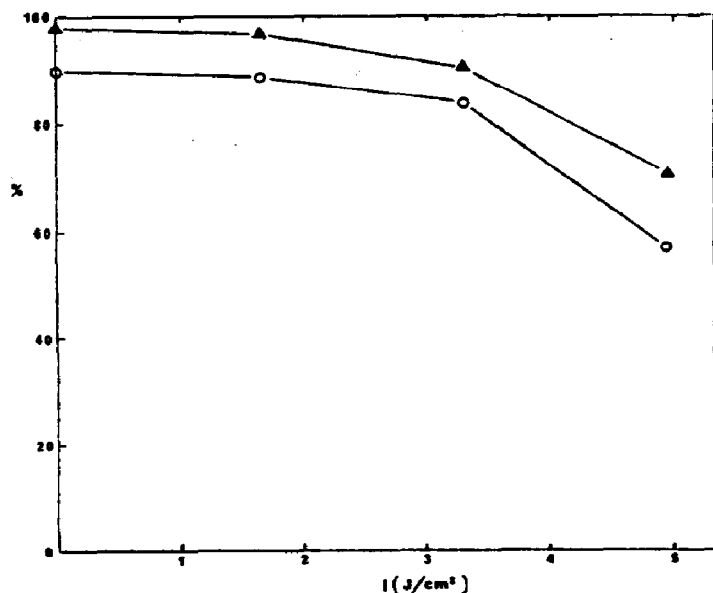


Fig. 3. Dependence of the breaking strength (\circ) and elongation (Δ) of *N*-chlorinated nylon 66 fiber upon UV irradiation. Clorox treatment: 100°C for 1 min.

apparent degradation. It should be noted that sodium hypochlorite treatment (100 °C, 1 min, dye uptake 23% of the control) did not cause any significant change in the breaking strength. The weakening of nylon fiber upon UV irradiation may be due to the photodecomposition of *N*-chloroamines and *N*-chloroamides along the polymer chain. Upon photolysis, these functional groups undergo an efficient N-Cl bond cleavage to aminyl and amidyl radicals that will abstract hydrogens along the polyamide chain and in so doing weaken the chain where the hydrogens are abstracted.

4. Conclusions

Chlorinating agents are effective in lowering the acid dyeability of nylons 6 and 66. Photolysis using weak UV light is effective in regenerating acid dye receptor sites. The combined treatments seem to offer a unique process for differential dyeing of nylon. This process depends on two factors.

(1) The difference in dye uptake between the chlorinated samples and the untreated control depends on the temperature and duration of the chlorination. The results indicate that treatment with sodium hypochlorite is best carried out at 100 °C for a period of a few seconds to 3 min.

(2) The regeneration of free amine sites depends on the UV exposure. Performing the irradiation at less than 5 J cm⁻² minimizes the detrimental effects on the mechanical properties of the fiber.

Acknowledgment

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