

Rendering Synthetic Fabrics Acid Printable Using Chitosan and Binder

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ABSTRACT: In this study chitosan samples of different nature, prepared by hydrolysis with HCL and modification by reaction with dimethylaminobenzaldehyde in methanol were applied to acrylic and polyester fabrics by pad-dry-cure method in presence and absence of binder (acrylate based copolymer). The pretreated samples were printed with acid dye. The effect of acid hydrolysis, modification, and concentration of chitosan on the color strength of the prints was investigated. The printed fab-

rics were evaluated for color yield and fastness properties. The color strength of the prints in presence of binder was three times higher than in its absence. The enhancement in color strength was relies mainly on *N*% of chitosan. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2122–2127, 2008

Key words: acid dye; acrylic and polyester fabrics; chitosan; printing; fastness properties

INTRODUCTION

Chitosan is the second most abundant polysaccharide found on earth next to cellulose. As a natural renewable resource obtained from shrimp and crab shells, chitosan has a number of unique properties such as antimicrobial activity, nontoxicity, and biodegradability, which attract scientific and industrial interest in fields such as biotechnology, pharmaceuticals, wastewater treatment, cosmetics, agriculture, food science, and textiles.¹ The structure of chitosan is the same as cellulose except for the hydroxyl group, which is substituted with amino group in case of chitosan (Scheme 1).²

Chitosan is water soluble in the presence of organic acids and dilute mineral acids. In its protonated form, it exhibits the behavior of a cationic polyelectrolyte, forming viscous solutions and interacting with oppositely charged molecules and surface.³

Chitosan has recently been shown to improve the dye uptake in cotton⁴ and wool.^{3,5} It is also used as a binder and thickener in the pigment printing of both polyester and polyester/cotton blend.⁶

The major drawback of chitosan as a pretreatment agent to textiles is its lack of strong bonding with textile fibers. As a result, the durability of chitosan-treated fabrics decrease with repeated laundering.¹

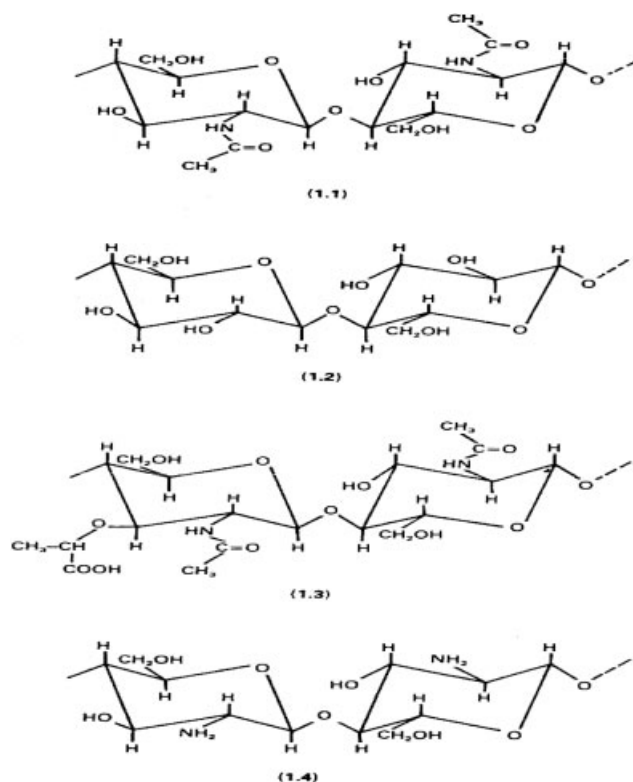
Polyester fibers as hydrophobic substrates with a very dense structure are difficult materials to be

colored through dyeing and printing. These facts, together with an absence of active groups in the polyester macromolecules make it impossible to apply the majority of dyestuffs apart from disperse dyes.^{7,8}

Research work⁸ focused on the process of dyeing polyester and cotton/polyester fabrics after chitosan treatment using direct dyestuffs was carried out. The adhesion of chitosan to the surface of polyester was improved by pretreatment in alkaline solution. The obtained data showed that it is possible to dye polyester and cotton/polyester fabrics with direct dyestuffs after chitosan treatment. The alkaline pretreatment affects the greater adhesion of chitosan to the surface of polyester fibers, which is manifested by the greater color strength.

Conventionally, acrylic fibers, which spun from a copolymer of acrylonitrile containing 1–15 wt % of several vinyl comonomers acrylonitrile containing carboxylate or sulfonate groups, are printed with cationic dyes.⁹ Anionic dyes namely reactive, acid, and direct dyes are not usually used for acrylic coloration as these dyes suffer from being not substantive for the fibers as a result of the repulsive effects that occur between the anionic groups present in the fibers and those present in the dye molecules.¹⁰ The presence of amidoxime groups in the pretreated acrylic fibers produced fibers with less crystalline and more hydrophilic and acted as a positive site for acid dyes during the dyeing process.¹¹ In another part,¹⁰ the viability of pretreated acrylic fibers towards anionic dye printing was explored. It was reported that modified acrylic fibers could be printed with various reactive, acid, and direct dyes.

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Scheme 1 The structure of chitin (1.1) and chitosan (1.4), together with the structurally related polysaccharides cellulose (1.2) and murein (1.3).

The present communication discusses an attempt made to study the suitability of printing acrylic and polyester fabrics with acids dyes after chitosan pretreatment. The purpose is also to overcome the problem of weak bonding of chitosan with textile fibers which resulted in decreasing the durability of color of chitosan-treated fabrics with repeated laundering. In this article, a new technique has been developed for improving the adhesion of chitosan molecules to the surface of polyester and acrylic fibers by using binder. To achieve this goal, the chitosan-treated fabrics were subsequently treated with a binder by pad-dry-cure method. The effect of acid hydrolysis and concentration of chitosan will be investigated. The printed fabrics were evaluated for color yield and fastness properties.

EXPERIMENTAL

Materials

Polyester and acrylic fabrics were supplied by Misr El Mahalla Co., Egypt. The fabrics were soaped with (2 g/L) nonionic detergent solution (Hostapal C V. from Clariant, Egypt) with a liquor ratio 1 : 25, at 60°C, for 45 min, then rinsed twice in cold tap water, and dried at room temperature. Chitosan samples (Chit I, N% = 6.31, viscosity = 800,000 cps) and

(Chit III, N% = 4.68, viscosity = 330,000 cps) of different nitrogen content for comparison were kindly supplied by Sigma (USA).

The dye used in this work, C.I. Acid Red 114 (23635) supplied by Ciba and was used as received. Meypro gum NP-16, a nonionic chemically modified Guar endosperm derivative, kindly supplied by El Mahalla chemical AG, Switzerland, was used. Imperon Binder MTB (density ca. 1.03 g/cm³ and viscosity 35–70 MPa s), self-crosslinking acrylate-based copolymer dispersion was supplied by Hoechst, Germany. Urea, mild oxidizing agent (Ludigol), and citric acid were laboratory reagent grade chemicals.

Methods

Preparation of modified chitosan (Chit II)

Chit I was modified by the reaction with dimethylamino benzaldehyde. Five grams of Chit I was reacted with 9.3 g of dimethylamino benzaldehyde in 150 mL methanol. The reaction mixture was refluxed for 10 h. After that the final product, Chit II was filtered off, washed with methanol/acetone mixture, and finally air dried at room temperature.

Preparation of Chit IV by acid hydrolysis method

Chit III was hydrolyzed to give Chit IV using HCl as follows: a known weight of Chit III was introduced in round flask containing 0.4N HCl in water: isopropanol mixture (20–80) with liquor ratio 1 : 20. The mixture was refluxed for 1 h. The solution was then neutralized by Na₂CO₃, filtered off, and washed with 80% isopropanol then dried. The nitrogen content of the resulted Chit IV was 4.47.

Preparation of chitosan solutions

Chitosan solutions at different concentrations (0.1–0.5% w/v) for each sample (Chit I, II, III, and IV) were prepared by stirring in distilled water containing 2% w/w acetic acid and kept overnight at room temperature.

Alkaline treatment of polyester

To improve the adhesion of chitosan to the smooth surface of polyester fiber,⁸ an alkaline pretreatment in water solution containing 5 g/L of KOH for 30 min at 98°C with a liquor ratio 1 : 25 was performed. Subsequently, the samples were rinsed twice in cold tap water and then dried at room temperature.

Pretreatment of acrylic and polyester fabric with chitosan

The fabrics (5 × 30 cm²) were padded with a solutions of chitosan samples at concentrations ranging

from (0.1–0.5% w/v) at 80% pick up using a laboratory padding machine. One series of the padded samples was air dried and then cured at 120°C for 3 min; another series was dried at 120°C for 3 min followed by treatment with the binder at a liquor ratio 1 : 10 then padded to 80% pick up, dried in air, cured at 150°C for 3 min. The samples of the two series were then rinsed with tap water, and finally air dried.

Printing method

The printing pastes were prepared according to the following recipe: acid dye 10 g, Meybro gum, 25; urea, 100 g; Ludigol, 5 g; citric acid, 5 g; and water 860 g. After printing, the samples were dried followed by steaming at 125°C for 45 min. The fabrics were then soaped using 5 g/L of nonionic detergent (Hocstapal CV) at 60°C for 15 min, rinsed thoroughly with hot water, and finally with cold water.

MEASUREMENTS AND ANALYSIS

Nitrogen content

The nitrogen content of the modified chitosan samples was estimated by a Micro-Kjeldhal method¹² and calculated as follows:

$$\% \text{ Nitrogen Content} = \frac{(V_2 - V_1) \times N_A \times 0.014}{W} \times 100$$

where V_2 , volume, in mL, of standard acid used in the titration; V_1 , volume, in mL, of standard acid used in the blank titration; N_A , normality of the acid, and W , weight, in g, of sample.

Infrared spectra

Infrared spectra were recorded on an FTIR Nicolet 5 DX spectrophotometer. The samples were examined as 1.5% KBr pellets.

Color intensity (K/S)

Spectral reflection measurements of the dyed fabrics were carried out using a recording filter spectrophotometer. The color intensity expressed as K/S values of the dyed samples were determined by applying the Kubelka-Munk equation at λ_{max} 520 nm.¹³

$$K/S = \frac{(1 - R)^2}{2R} - \frac{(1 - R_0)^2}{2R_0}$$

where R is the decimal fraction of the reflectance of the dyed substrate, R_0 is the decimal fraction of the reflectance of the undyed substrate, S is the scattering coefficient, and K is the absorption coefficient.

Fastness properties

Color fastness to washing was measured according to AATCC Test Method 61 (2A) and color fastness to rubbing was measured according to AATCC Crockmeter Method 8.¹⁴

RESULTS AND DISCUSSION

The viable modification method of acrylic and polyester fibers after chitosan and binder pretreatment has prompted us to explore the printability of the modified fibers with acid dyes which shows substantivity to proteinic fibers. The prints with acid dye obtained on chitosan deposited polyester fibers samples is even, independent on earlier alkaline pretreatment but the latter increase the adhesion of chitosan to the surface of polyester macromolecules, because of the absence of active groups in the polyester. The pretreatment in an alkaline solution containing 5 g/L KOH is permitted.⁸ In this work, the binder was used as a fixing agent able to coordinate the molecules of chitosan on the surface of the fabrics and subsequently increase the color durability after the washing process of printed samples. Different factors that may affect the color yield of the prints obtained are reported and given below.

Characterization of chitosan samples

Characterization of Chit II

Chit II was characterized by measuring $N\%$ and infrared spectroscopy. The $N\%$ was found to be 6.38. Figure 1 shows infrared spectroscopy of Chit I and

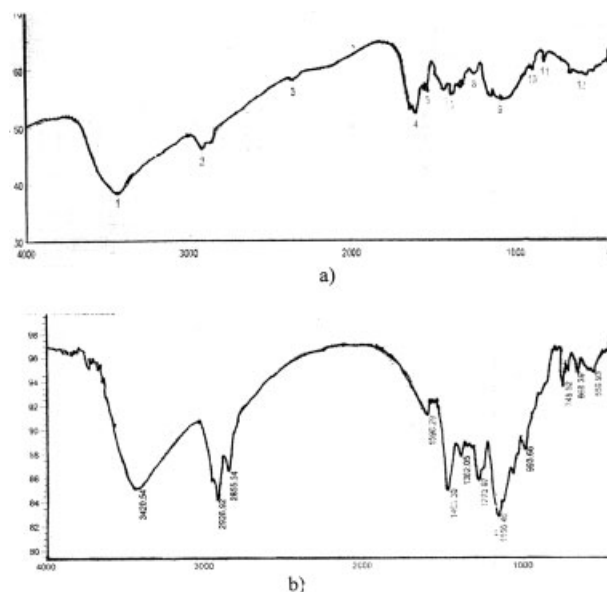
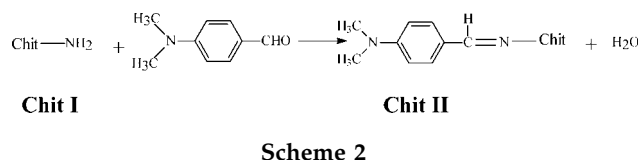


Figure 1 IR spectra of Chit I and Chit II; (a), Chit I; (b), Chit II.



Chit II. A new band appeared for Chit II at 1598 cm^{-1} which is characteristic for $\text{C}=\text{N}$. The modification reaction is shown in Scheme 2.

Characterization of Chit IV

Chit IV was characterized by measuring $N\%$ and the flow time using Ostwald viscosimeter. The results obtained are shown in Table I.

Effect of presence of binder

Color strength as expressed as K/S for the printed acrylic and polyester fabrics treated with Chit I in presence and absence of binder is given in Figure 2. The influence of binder only was also illustrated in Figure 2. It is clear that the printed samples exhibit K/S of higher value three times in presence of binder more than in its absence regardless the type of fabric. This observation may be attributed to trapping of chitosan molecules on the surface of fabrics under the influence of the binder, consequently the number of fixed amino groups in chitosan which are sites for the acid dye increases. The binder contains up to 60% reactive groups (based on the weight of the binder) in the copolymer which crosslinks the copolymer molecules with each other or with the end group of fabrics during curing. The self-cross linking binder react with the active end groups of acrylic ($-\text{COOH}$) or the generated group of polyester after its alkaline hydrolysis during curing forming films which trap the chitosan molecules producing high durability of chitosan-treated fabrics that increase the color fixation. Figure 2 shows also that the results of K/S obtained for samples pretreated with binder only was lower than that pretreated with Chit I in the presence and absence of binder indicating that the chitosan is responsible for the enhancement of K/S . The results also indicated that the printed samples of acrylic fabrics showed higher color yield than polyester fabrics. The higher color yield of acrylic samples may be due to the important characteristic of acrylic is that they contain strong anionic acid groups that act as chitosan sites on acrylic samples. Consequently increases the acid dye

TABLE I
Characterization of Chit IV

Chitosan sample	$N\%$	Flow time (s)
Chit IV	4.47	113

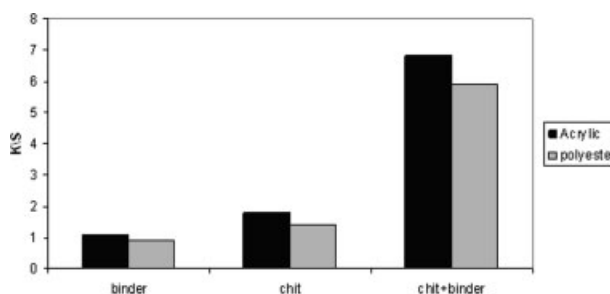


Figure 2 Color yield (K/S) of treated polyester and acrylic fabrics with Chit III in presence of binder, binder only, and Chit I only. Pretreatment condition: 0.4% Chit I, pick up 80%, at 120°C for 3 min, binder pick up 80%, at 150°C , for 3 min.

sites. Thus the presence of binder with chitosan became the treatment of choice the next studies.

Effect of chitosan characteristics

In the previous work, Chit I was used to explore effect of the presence of binder on the color strength of the printed samples. To investigate the effect of chitosan characteristic on the color yield of printed samples in presence of binder, Chit I was modified to Chit II and Chit III were hydrolyzed by HCL to Chit IV. The effect of chitosan characteristic on the color yield of printed samples was presented in Figure 3. It was found that the modified chitosan, Chit II has a lower K/S than the Chit I. This may be attributed to the decrease in primary amino groups which are the dye sites in chitosan. Also the accessibility of the remainder groups decreased as a result of steric hindrance caused by the bulk groups which were introduced into the structure of chitosan in Chit I. It is clear that the acid hydrolysis of chitosan has no effect on the color strength of the printed samples where the printed samples pretreated with Chit III and Chit IV have a similar color yield (K/S). This observation may be attributed to that in the

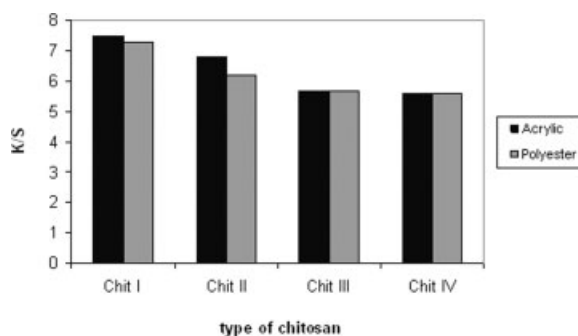


Figure 3 Effect of chitosan type on the color yield of printed samples. Pretreatment condition: 0.4% chit, pick up 80%, at 120°C for 3 min, binder pick up 80%, at 150°C , for 3 min.

process of acid hydrolysis with HCL, the amino groups of chitosan, which are the sites for acid dyes are not attacked. It is also clear that the printed samples treated with Chit I (N%, 6.31) have higher K/S than those of other chitosan samples irrespective of the fiber used. This result is expected as it is logical that color uptake of chitosan-treated samples would increase as the amino groups of chitosan increased which in term the site of the acid dye.

Effect of chitosan concentration

In Figure 4, the color yield of Chit I pretreated acrylic and polyester fabrics in presence of binder are printed as a function of chitosan concentration. The results depict that the color strength increases by increasing concentration of chitosan irrespective of the fabrics used. The increase in color strength by increasing concentration of chitosan may be due to that the ability of chitosan-pretreated samples to bind color would increase as the chitosan concentration is increased. Here too, the color yield of acrylic fabrics higher than polyester.

Effect of pretreatment on the shift of maximum wavelength of the acid dye

It was found that increasing of concentration of Chit I from 0.1 to 0.4% (w/v) leads to a shift from 520 to 540 nm which can be attributed to some kind of yellowness as a result of the pretreatment. It was also

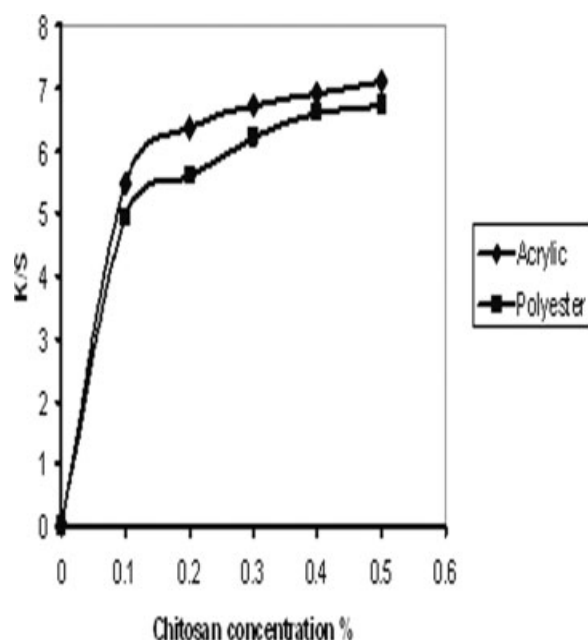


Figure 4 Effect of chitosan concentration on the color yield of printed samples. Pretreatment condition: \times Chit I, pick up 80%, at 120°C for 3 min, binder pick up 80%, at 150°C, for 3 min.

TABLE II
Fastness Properties of the Printed Pretreated Samples with Chit I in Presence of Binder

Concentration of Chit I % (w/v)	Crocking		Washing		
	Dry	Wet	Alt	St _W	St _A
Acrylic fabric					
0.1	4	3-4	3	3	3-4
0.2	3-4	4	3	3	3-4
0.3	4	3-4	3	3	3-4
0.4	4	4	3-4	3-4	3-4
0.5	4	4	4	4	4
Polyester fabric					
0.1	3	2-3	3	3-4	3-4
0.2	3	2-3	3	3	3-4
0.3	3-4	3	3	3-4	4
0.4	3-4	3	3-4	3-4	4
0.5	3	3	4	4	4

Alt, Alteration; St_A, staining on acrylic; St_P, staining on polyester fabrics; St_W, staining on wool fabric.

found that the pretreatment has a little effect on the maximum wave length. This is as a result of measuring each sample four times.

Fastness properties

Wash and rub fastness tests were conducted on the acrylic and polyester samples that have been pretreated with Chit I at different concentrations (0.1-0.5) in presence of binder and the results are set out in Table II. It is clear that the prints display good wash fastness properties ranging from 3-4 irrespective of the fabric used. The abrasion resistance properties are also good as evidenced the results of rubbing fastness property of the prints in wet and dry state.

CONCLUSIONS

Pretreatment of acrylic and polyester fabrics with chitosan render them amiable for printing with acid dye.

Pretreatment of acrylic and polyester fabrics with chitosan in presence of binder enhances trapping of chitosan molecules within the surface of these fabrics which is manifested by the higher color strength.

The magnitude of color strength depends mainly on the concentration and the nitrogen content of chitosan.

The maximum wave length of the acid dye used was shifted from 520 to 540 nm at higher chitosan concentration.

Furthermore, this technique offers a possibility of printing the blends of acrylic and polyester fibers with wool by means of acid dyestuffs.

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