

Chitosan Phosphate Induced Better Thermal Characteristics to Cotton Fabric

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ABSTRACT: Chitosan phosphate was prepared and applied at different concentrations with and without low formaldehyde *N*-methylol finishing agent (resin) to cotton fabrics. Chitosan phosphate was characterized by FTIR, nitrogen content, and phosphorus content. The so-treated fabrics were monitored for thermogravimetric analysis (maximum decomposition temperature and residue contents after decomposition), nitrogen content, phosphorus content, tensile strength, and elongation at break. Results indicate that extent of reaction of chitosan phosphate with the cotton fabric relies on concentration of the former; increasing the concentration of the resin has practically no

effect on this reaction though the resin functions as a chemical bridge between the chitosan phosphate and the cotton fabric. On the other hand, the nitrogen of the resin and the phosphorus of chitosan undergo synergetic effect and enhance the thermal properties of the treated cotton. Strength properties display higher values in the presence than in the absence of chitosan phosphate when the latter was used along with the resin. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2021–2026, 2007

Key words: chitosan; chitosan phosphate; cotton fabric; thermal analysis

INTRODUCTION

Cotton is the most important textile fiber and there is a great demand all over the world for cotton fabrics that exhibit improved functional characteristics. Easy care and permanent press, soil resistance and soil release, and thermal and flame retardancy are some of the improved properties that caught the imagination of consumers.¹

Since cellulosic fibers are not volatile, they do not participate directly in the propagation of fire, but rather undergo thermal degradation, which produces combustible volatiles that feed the flame and propagate fire across cellulosic fabrics. The general reaction can be divided into primary and secondary reactions,^{2–4} according to whether they directly affect the cellulosic substrate or one of the intermediate degradation products. Alternatively, two general pathways for the degradation of cellulosic materials may be recognized. One pathway involves fragmentation and formation of combustible volatiles, which could feed the flame, and the second mainly involves dehydration and formation of carbonaceous char. These two pathways are competing for the same initial substrates according to the prevailing conditions. Heating at lower temperature favors the dehydration

and charring reaction. At high temperature, levoglucosan is formed leading to further decomposition reactions at the elevated temperature.

Most cotton-based materials require some kind of chemical treatment to pass the flammability test. Both durable and nondurable chemical treatments are readily available to prevent cellulosic materials from undergoing complete degradation upon combustion. Chemical agents such as phosphoric acid and its ammonium salts act in the condensed phase to substantially lower the decomposition temperature of cellulose. The phosphates minimize or suppress combustion by interfering with flame propagation, and the overall effect is less-volatile formation. Reactive organophosphorus compounds⁵ are among the most commonly used flame retarding finishes of cotton^{5–7} in the presence of acid catalyst.

Chitosan, a copolymer of glucosamine and acetyl glucose amine units linked by 1–4 glucosidic bonds, can be obtained by deacetylation of chitin, which is the second most abundant natural polymer after cellulose. In recent years, chitosan has attracted much attention because of its specific properties such as biodegradability, biocompatibility, and bioactivity. Chitosan is being used extensively in industrial biomedical such as pharmaceutical and biomedical engineering, paper production, textile finishes, photographic products, cements, heavy metal chelation, waste water treatment, and fiber and film formation.^{8,9}

The present work was undertaken with a view to study the effect of chitosan phosphate on the

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thermal behavior and strength properties of cotton fabric. Treatment of the fabric with chitosan phosphate was carried out essentially in the presence of low reactant formaldehyde resin known commercially as Knittex FLC. Characterization, testing, and analysis of the treated fabrics were performed through monitoring TGA (maximum decomposition temperature and residue content after decomposition), nitrogen content, phosphorus content, and strength properties.

EXPERIMENTAL

Materials

Desized, scoured, and bleached plain weave cotton fabric (230 g/m²) was kindly supplied by Misr, Mehala El-Kobra (Egypt). Knittex FLC was kindly supplied by Ciba-Geigy (Switzerland). Chitosan, high molecular weight Brookfield viscosity 80,000 cps, was kindly supplied by Aldrich Chemical (Germany). Acetic acid, sodium nitrite, acetone, urea, orthophosphoric acid, DMF, and isopropyl alcohol were of laboratory grade.

Depolymerization of chitosan

Solution of chitosan was prepared by dissolving 6 g of chitosan in 250 mL of 2% (w/w) aqueous acetic acid solution. A solution containing 0.085 g NaNO₂ in 50 mL distilled water was added slowly to chitosan solution with slow stirring for 2 h at 30°C, then neutralized with dilute solution of sodium hydroxide, precipitated with excess acetone, filtered, and washed several times with acetone. The final product was dried at room temperature overnight.

Preparation of chitosan phosphate

Chitosan (23 g) was added to a solution of 40 g urea and 40 mL H₃PO₄ in 350 mL DMF. The temperature was raised to 100°C and maintained at this temperature for 5 h. The final product was filtered, washed thoroughly several times with 50% (w/w) isopropyl alcohol in water, dried at 60°C, and then subjected to analysis.

Analysis

Nitrogen content was measured according to Kjeldahl method,¹⁰ and phosphorus content was measured according to spectrophotometric method.¹¹ FTIR spectroscopy was measured using FTIR Raman model Nexus 670 (Nicolet–Madison, WI), and tensile strength and elongation at break were measured according to ASTM standard method.¹² Thermal-

gravimetric analysis (TGA) was carried out using PerkinElmer 7DX Thermogravimetric Analyzer, USA.

RESULTS AND DISCUSSION

Characterization of the prepared chitosan phosphate

Chitosan phosphate was characterized by measuring the nitrogen content (N) and phosphorus content (P) as well as FTIR spectrum.

Chitosan phosphate was found to acquire 5.15% N and 3.89% P. At the same time, FTIR spectroscopy provides a proof for the structure of chitosan phosphate as realized from Figure 1(a,b), which show the IR spectra of chitosan and chitosan phosphate, respectively. The IR spectrum of chitosan [Fig. 1(a)] shows clearly the amide I band at 1643 cm⁻¹ and the amide II band at 1565 cm⁻¹. Comparing this chitosan IR spectrum with the IR spectrum of chitosan phosphate [Fig. 1(b)], it is obvious that the IR spectrum of chitosan phosphate shows that the amide I band still remains, but shifted to 1629 cm⁻¹, while amide II band, which is at 1565 cm⁻¹, disappears. The peaks at 2922 and 2854 cm⁻¹ are the characteristics of C–H stretching bands. This is rather a proof that the reaction involved in chitosan phosphate formation occurs as elucidated in Scheme 1.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was done using platinum crucible, heating from 50 to 1100°C at 10°C/min under nitrogen atmosphere from single point analysis.

Figure 2 shows the TGA curves of untreated cotton fabric (a), cotton fabric treated with 2% chitosan phosphate (b), cotton fabric treated with 6% resin only (c), cotton fabric treated with 2% chitosan phosphate along with 6% resin (d), and cotton fabric treated with 8% chitosan phosphate along with 6% resin (e). The decomposition temperatures and residues of these samples are shown in Table I.

The results (Table I and Fig. 2) reveal that the untreated cotton commences rapid decomposition at 350°C. This is against a decomposition temperature of 340.4°C and 325°C for cotton fabrics treated, respectively, with 2% chitosan phosphate and 8% chitosan phosphate along with 6% resin.

That is, the TGA results indicate that the presence of chitosan phosphate within the fabrics structure lowers the decomposition temperature of the cotton fabric. Furthermore, this effect is more pronounced at higher concentration of chitosan phosphate since at identical treatment conditions fabric treated with 8% chitosan phosphate exhibit decomposition temperature, which is less by more than 5°C than that of fabric

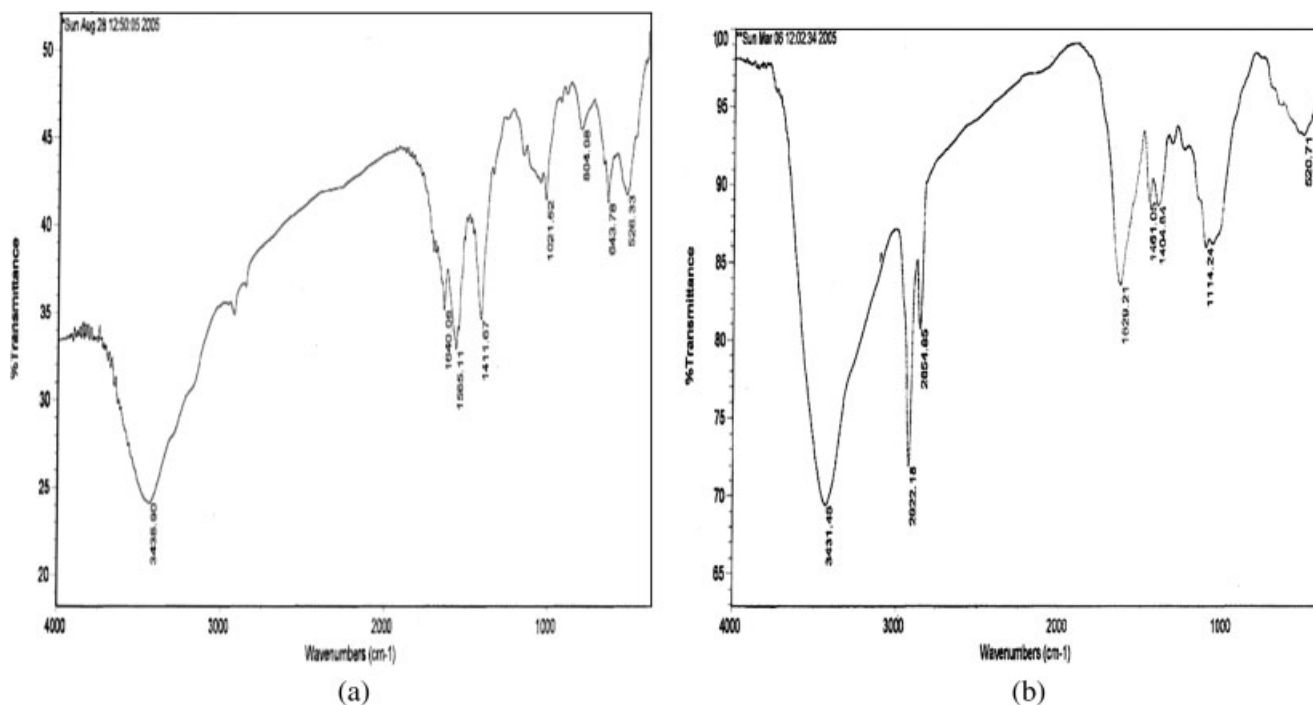


Figure 1 FTIR spectra of chitosan and chitosan phosphate.

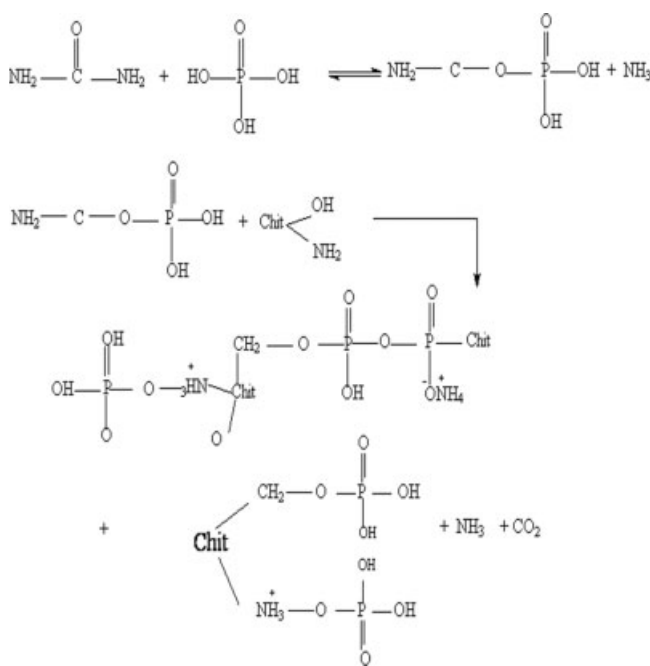
treated with 2% chitosan phosphate. It is as well to emphasize that treatment of cotton fabric with resin alone has practically no effect on the decomposition temperature of the fabric, the effect is achieved only in the presence of chitosan phosphate. It is also clear that the presence of the resin leads to lowering the decomposition temperature of the treated samples by around 10°C, and this is very obvious from the decomposition temperatures of treated samples with 2% chitosan phosphate only and 2% chitosan phosphate in the presence of 6% resin (350 and 340°C), respectively.

An examination of the results of Table I would imply that the residue contents of the untreated fabric and fabric treated with either 2% chitosan phosphate or 6% resin are comparable. Meanwhile, residue contents of fabrics treated with chitosan phosphate together with the resin are significantly higher. Higher chitosan concentration in the presence of the same resin concentration acts in favor of increase residue content. This could be interpreted in terms of synergetic effect between the phosphorus of the chitosan phosphate and nitrogen of both the latter and the resin.

Salient features of results is that the chitosan phosphate, which is included and fixed chemically onto the cotton fabric by the resin impart to the cotton fabric the ability to give off less volatile components than does the untreated samples when the fabrics were thermally decomposed. This is evidenced by the higher residue contents of the treated samples.

Effect of Knittex FLC and chitosan phosphate concentrations on the nitrogen content

Figure 3 shows the effect of Knittex FLC concentration on the N% of the treated cotton fabric at constant chitosan concentration 2%. It is seen that the N% increases by increasing the resin (Knittex FLC)



Scheme 1

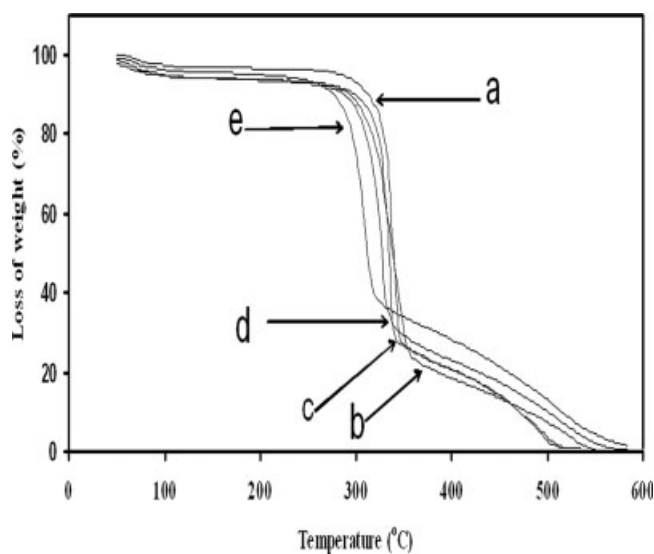


Figure 2 TGA of untreated and treated cotton fabric: (a) untreated cotton fabric, (b) cotton fabric treated with 2.5% chitosan phosphate only, (c) cotton fabric treated with 6% Knittex only, (d) cotton fabric treated with 2% chitosan phosphate and 6% Knittex, and (e) cotton fabric treated with 8% chitosan phosphate and 6% Knittex.

concentration within the range studied. This is rather a manifestation of the availability of the resin molecules in the proximity of the cotton cellulose hydroxyls. It is understandable that the latter are immobile and their reaction with cotton cellulose would rely on their availability in the vicinity of the cellulose.

Figure 4 shows the effect of chitosan phosphate concentration on the N% of the treated cotton fabric at constant concentration of the resin (6%). It is clear that as the chitosan phosphate concentration increases the overall nitrogen content increases. Similar results are obtained with the resin concentration, and hence current results for chitosan phosphate concentration could be explained on a similar basis.

Effect of Knittex FLC and chitosan phosphate on the phosphorus content

The effect of Knittex FLC (resin) concentration on the P% of the treated fabric when the latter was treated

TABLE I
Dependence of Decomposition Temperature and Residue Content of Cotton on the Treatment Given to the Fabric

Treating formulation	Maximum decomposition temperature	Residue content (%)
a	350	26.45
b	350.8	24.45
c	345	27.556
d	340	31.273
e	325	36.557

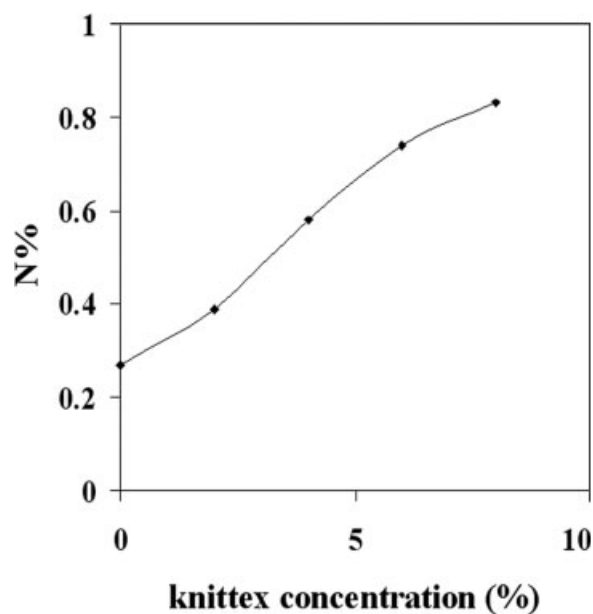


Figure 3 Effect of Knittex FCL concentration on nitrogen content 2% chitosan phosphate, drying 3 min at 90°C, and curing at 140°C for 3 min.

with a solution containing different concentrations of the resin and constant concentration of chitosan phosphate (2%). The results make it evident that the treated fabric samples exhibit a constant value of P% (i.e., 0.095%) regardless of the resin concentrations

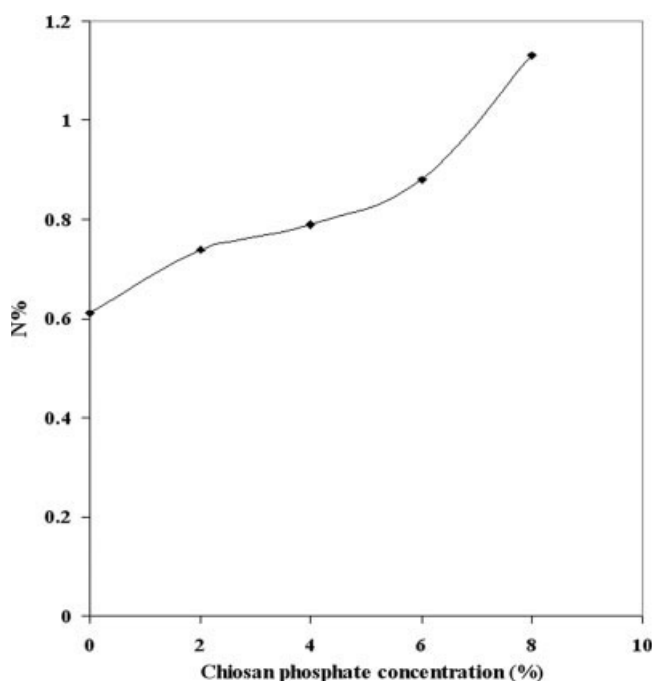


Figure 4 Effect of chitosan phosphate concentration on nitrogen content 6% resin, drying 3 min at 90°C, and curing at 140°C for 3 min.

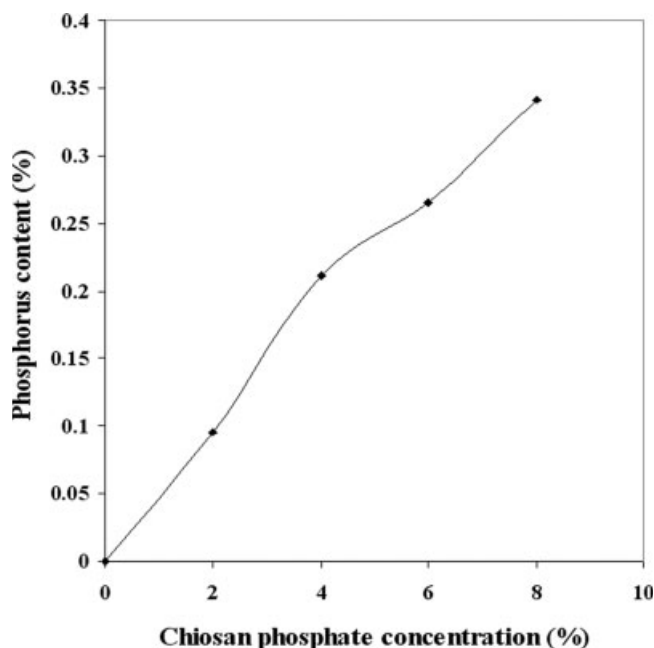


Figure 5 Effect of chitosan phosphate concentration on phosphorus content 6% resin, drying 3 min at 90°C, and curing at 140°C for 3 min.

used. This is expected since the source of P is only chitosan phosphate. Reaction of the latter with cotton cellulose also seems to proceed without being affected by the resin concentration though the resin plays the essential role in the chemical fixation of chitosan phosphate to cotton cellulose in the fabric form as indicated in Scheme 1.

Figure 5 shows the effect of chitosan concentration when used along with the resin at a concentration of 6% on the P% of the treated fabrics. It is seen that increasing chitosan phosphate concentration from (2–8%) is accompanied by an increase in phosphorus content ranging from 0.095% to 0.341%. Neither the N% nor the P% was found to decrease upon washing all samples thoroughly with 1% acetic acid for about 10 min while scraping, indicating durability of the treatment. The resin (Knittex FLC) functions most probably as a chemical bridge binding chitosan phosphate and cotton fabric.

Effect of Knittex FLC concentration and chitosan phosphate concentration on the strength properties

Figure 6 shows the effect of Knittex FLC concentration on the strength properties of the cotton fabric. As is evident increasing the resin concentration from 2 to 8% causes a decrease in tensile strength from 140 to 114 kg and elongation at break from 21 to 15%. Such decrease in strength properties is indicating of crosslinking by the resin and rigidity by inclusion of chitosan phosphate in the molecular structure of cotton cellulose of the fabric. Previous reports^{13,14}

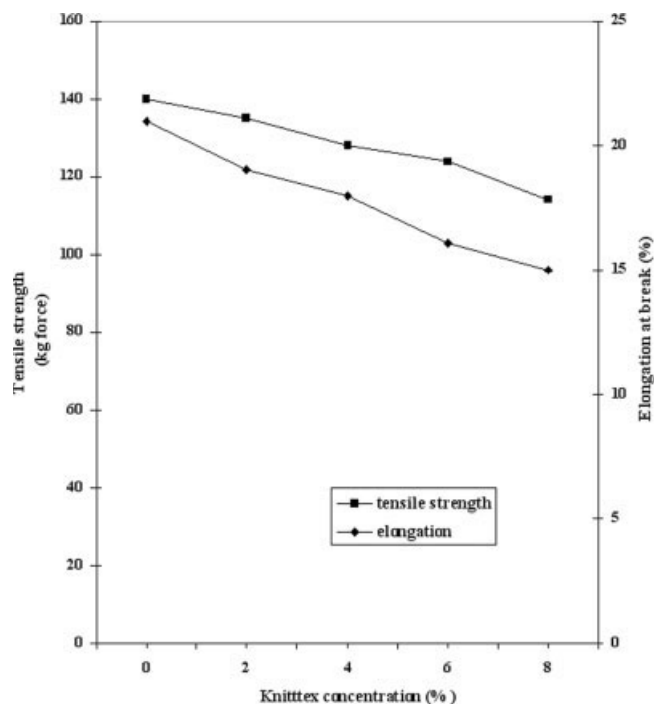


Figure 6 Effect of Knittex FCL concentration on tensile strength and elongation at break. 2% chitosan phosphate, drying 3 min at 90°C, and curing at 140°C for 3 min.

disclosed that the strength properties of crosslinked fabric logically, as shown by current results, decreases with increasing the extent of crosslinking. The extent of the decrease in strength properties is

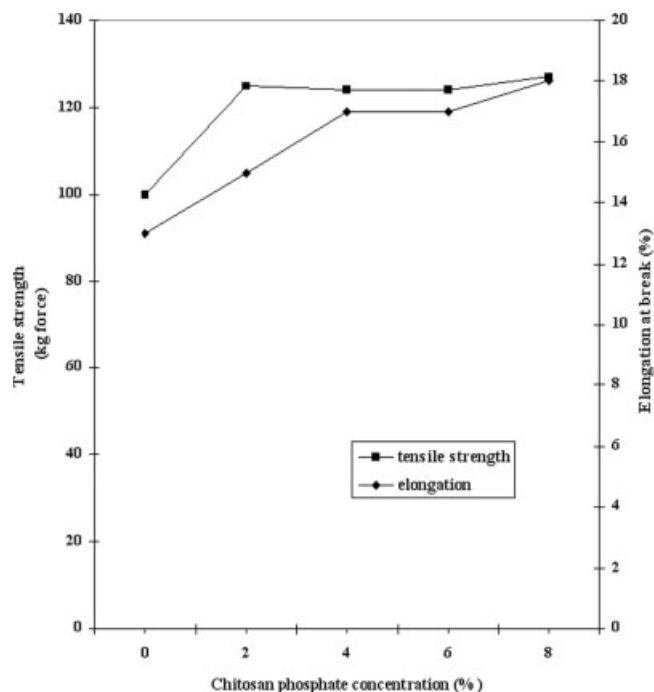


Figure 7 Effect of chitosan phosphate concentration on tensile strength and elongation at break. 6% resin, drying 3 min at 90°C, and curing at 140°C for 3 min.

related to the extent of crosslinking, which, in turn, depends essentially on the resin.

Figure 7 shows the effect of chitosan phosphate concentration on the strength properties of the treated fabrics. It is clear that chitosan phosphate acts in favor of the tensile strength and elongation at break of the treated fabrics. The improvement in those strength properties is related to the concentration of chitosan phosphate, despite the anticipated rigidity through involvement of chitosan in interactions during the treatment. Current data suggest that chitosan phosphate has the ability to make a coating film on the fabric, thereby leading to increased strength properties. Besides, the competition between the hydroxyl groups of chitosan and the hydroxyl groups of cellulose to react with methylol groups of Knittex FLC decreases the extent of crosslinking. Once this is the case, the strength properties increase.

CONCLUSIONS

Chitosan phosphate was prepared by reacting chitosan with orthophosphoric acid in the presence of urea and DMF as solvent. Chitosan phosphate was characterized by measuring nitrogen content and phosphorus content and also by FTIR spectroscopy.

Chitosan phosphate was used as a finishing agent to cotton fabric in the presence and absence of low formaldehyde resin. The results obtained indicates that nitrogen, phosphorus, tensile strength, and elongation at break increase with increasing chitosan phosphate concentration, and also nitrogen content increases with increasing the resin concentration while tensile strength and elongation decrease with

increasing the resin concentration. Treatment with chitosan phosphate leads to lowering in decomposition temperature of treated cotton fabric and also leads to increasing the residue percent, and this effect increases with increasing the concentration of chitosan phosphate. On the other hand, presence of the resin is accompanying with decreasing in decomposition temperature and also increasing in residue percent than in the absence of it.

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