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Utilization of biopolymer in resist printing of linen fabrics using reactive dyes

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ABSTRACT

A novel utilization of chitosan as a cationic biopolymer in the chemical resist printing of linen fabrics and its polyester blend using reactive dyes. The effects of ratio and concentration of various resist-printing agents and processing conditions are observed and discussed. The concentration of chitosan, type of resist agent, and the ratio of chitosan to resist agent were varied to determine their effects on the efficiency of resist-printing. Regardless of the type of fabric, the resist effect on printed fabrics expressed as % decrease in *K*/*S* was obtained at optimal chitosan concentration of 1% with a mixture of chitosan/maleic acid as a resist salt at a ratio of 25:75. Thus, chitosan can be used pure or in admixture with different resist salts successfully in chemical resist printing.

1. Introduction

Chitosan is a cationic natural carbohydrate biopolymer prepared by partial N-deacetylation of chitin (Kurita, 1998). It comprises copolymers of glucosamine and N-acetyl glucosamine (Ilium, 1998). The primary unit in chitin polymeric chain is 2-deoxy-2-(acetylamino) glucose. These units are combined through (l, 4) glycosidic linkages, forming a long linear polymer chain. Chitosan dissolves in most weakly acidic solutions, including formic, acetic, tartaric, and citric acid, at pH < 6.5. The D-glucosamine unit has a pK_a value of 7.5 (Hoppe Seiler, 1994; Roberts, 1992).

At low pH, chitosan is present as a cationic polymer, with a high charge density, and therefore may function as a good flocculent for negatively charged polymers. The oppositely charged polyelectrolyte interacts rapidly with chitosan in solution to form an insoluble precipitate (Bayomi, 2003).

Thus, chitosan has been studied as partner of several intermolecular complexes (IMC) with natural or synthetic anionic polyelectrolytes, such as: chondroitin sulphate (Denuziere, Ferrier, Damour, & Domard, 1998; Mi et al., 2006), poly(acrylic) acid (Davidenko, Peniche, Díaz, San Roman, & Sastre, 2007; Peniche & Argüelles-Monal, 2001; Peniche et al., 1999; Pérez-Gramatges, Argüelles-Monal, & Peniche-Covas, 1996; Wang, Li, Lu, Wang, & Zhong, 1996), poly (galacturonic) acid (Argüelles-Monal, Cabrera, Peniche, & Rinaudo, 2000; Peniche & Argüelles-Monal, 2001), sodium alginate (Mitrevej, Sinchaipanid, Rungvejhavuttivittaya, & Kositchaiyong, 2001; Peniche & Argüelles-Monal, 2001), K-carageenan (Peniche & Argüelles-Monal, 2001). Chitosan complexation with carboxymethylated polysaccharides, such as carboxymethyl cellulose or carboxymethyldextrin has been also studied (Argüelles-Monal, Gárciga, & Peniche-Covas, 1990; Argüelles-Monal & Peniche-Covas, 1988; Kaihara, Suzuki, & Fujimoto, 2011; Peniche & Argüelles-Monal, 2001; Rosca, Popa, Lisa, & Chitanu, 2005), and this principle has been used for the production of chitosan beads and microspheres.

Carboxymethylcellulose (CMC) is another anionic polysaccharide, a cellulose derivative obtained by its reaction with alkali and chloroacetic acid as follows (Cheng & Biswas, 2011; Ragheb, Nassar, Abd El-Thalouth, Ibrahim, & Shahin, 2012; Toğrul & Arslan, 2003; Varshney et al., 2006):

$$\text{Cell·OH} + \text{NaOH} \rightarrow \text{Cell·ONa(alkalicellulose)}$$

$$\text{Cell·ONa} + \text{ClCH}_2\text{COOH} \rightarrow \text{Cell·O·CH}_2\text{COONa} + \text{NaCl}$$

The CMC structure is composed of β-(1 → 4)-D-glucopyranose units similar to those of cellulose. Different esterification methods may conduct to different substitution degrees; this parameter is generally in the range of 0.6–0.95 derivatives per monomer unit. This anionic polymer forms polyelectrolyte complexes with chitosan. The self-assembly conditions for CMC–chitosan complexes (Aelenei, Popa, Novac, Lisa, & Balaita, 2009; Ichikawa, Iwamoto, & Watanabe, 2005; Yoshioka, Hirano, Shioya, & Kako,

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1990), used as hydrogels for controlled release, membrane formulations (Ichikawa et al., 2005), and for nanoparticle formation (Yoshioka et al., 1990), were earlier analysed.

Due to the characteristic properties of chitosan such as nontoxicity, biodegradability, antifungal activity, water-binding capacity, bioactivity, biocompatibility, and its IMC ability, chitosan and its modified have found many applications in pharmaceutical, medical applications, fibre formation, waste water treatment, paper production, cosmetics, textile dyeing and finishing (Hudson, 1998; Ilium, 1998; Jocic et al., 2005; Kitkulnumchai, Ajavakom, & Sukwattanasinitt, 2008; Lim & Hudson, 2003; Morimoto et al., 2001; Najafi, Assefipour, Hajilari, & Movahed, 2009; Shantha, Bala, & Rao, 1995; Trung, Ng, & Stevens, 2003). It is used in textile dyeing and finishing as a substituent for various other chemicals traditionally used in textile processing.

Printing on fabrics is a centuries-long traditional method of textile colouration. It is done by using a thickening agent along with the dye and the required chemicals. Printing can be classified into three types according to the method used: (1) direct printing, (2) resist printing, and (3) discharge printing. The mechanism employed in resist printing includes physical and chemical resist printing. Physical resist printing is used primarily to prevent penetration of dyes (to make them water repellent), whereas chemical resist printing is conductive for: (1) dye dissolution (oxidative or reductive), (2) dye insolubility (by adding anti-solution agent), and (3) the blocking of dye sites on fibres. To reinforce the resist-printing effect, both physical and chemical methods may be used in combination. The use of chitosan in acetic acid as a printing paste dates back to the 1940s. Once dried, chitosan acts as an insoluble membrane with good coverage capability and makes an excellent chemical resist-printing agent (Provost, 1988; Vigo, 1997).

The current study explores the effect of chitosan on the resist printing of linen and linen/polyester fabrics with reactive dye pastes thickened with CMC.

2. Experimental

2.1. Materials and reagents

2.1.1. Fabrics

Linen fabric, semi-finished for dyeing and printing, used in this work were supplied by Textile Industries, Egyptian Co., Ointex Egypt. Fabric specifications were: weight 120 g/m^2, warp 28 threads/cm, 20 tex, weft 26 threads/cm, 20 tex.

The fabric was scoured at 100 °C for 60 min with a solution containing 1 g/L non-ionic detergent and 2 g/L sodium carbonate, then washed thoroughly and finally air dried at room temperature.

Linen/polyester 50/50 fabric was also supplied by Textile Industries, Egyptian Co., Ointex Egypt.

2.1.2. Materials

- Reactive dye used was Sunzol blue RS (C.I. Reactive blue 19), based on vinyl sulphone.
- High molecular weight chitosan of M.W. 10104, with a viscosity of 800,000 cps (Aldrich).
- Urea, sodium alginate, sodium bicarbonate, formic acid, tartaric acid, oxalic acid, fumaric acid and maleic acid were of reagent grade.

The carboxymethylcellulose sodium salt used was laboratory prepared from rice straw cellulose according to a previously published author's work (Ragheb et al., 2012), with different D.S. values (0.66, 0.81, and 1.03).

2.2. Methods

2.2.1. Preparation of printing pastes

Each dye (0.3 g) was first mixed with 10 g urea and a small amount of water. The solution was stirred to ensure homogenization and poured into a thickener suspension (3 g sodium alginate mixed with a small amount of water). The whole mixture was thoroughly stirred with 3 g sodium bicarbonate. The total weight of the whole paste was adjusted to 100 g by the addition of water.

2.2.2. Preparation of resist-printing pastes

Resist-printing pastes were prepared by mixing solutions with various concentrations of chitosan (0.5, 1, 1.5, and 2.0%) in 1% acetic acid at a concentration of 1 g/L. Each solution was then poured into a thickener suspension (1.25 g CMC mixed with a small amount of water). The whole mixture was thoroughly stirred and brought to 25 g by the addition of water.

2.2.3. Printing procedure

The resist printing paste was applied to samples of cotton fabric using a flat-screen printing technique. The printed samples were then pre-dried at 80 °C for 3 min to avoid printing paste migration. Samples were then screen printed with the printing paste by squeegee using the same processing conditions described earlier.

An additional resist-printing paste, with a constant chitosan concentration of 1% and individually mixed with citric, acid (1%) at various ratios (100:0, 75:25, 50:50 25:75, and 0:100), was prepared for comparison. The resist printed fabrics were fixed via thermo fixation at 150 °C for 3 min.

2.2.4. Washing

The fixed discharge and discharge–resist printed fabrics were subjected to washing through five stages as follows:

- Rinsing thoroughly with cold water.
- Treatment with hot water.
- Treatment near the boiling temperature (90–95 °C) with a solution containing 2 g/L Aspkon 1030 (neutral detergent).
- Washing with hot water.
- Rinsing with cold water.

2.3. Analysis and measurements

2.3.1. Colour measurements

The colour strength (K/S) was measured by reflection spectroscopy with a Hunter Lab UltraScan PRO spectrophotometer according to a standard method (Judd & Wyszecki, 1975).

2.3.2. Fourier transform infrared (FT-IR) spectral analysis

Fourier transform infrared spectroscopy (FT-IR) was performed by using a Pye-Unicam Spectra 1000 spectrophotometer (England) to determine the functional groups on the surface of the linen samples. A potassium bromide (KBr) disc was used.

3. Results and discussion

As previously indicated, the main aim of the present work was to investigate the suitability of using chitosan CMC complexes in resist printing of linen and linen/polyester fabrics with reactive dye pastes. To achieve this goal, series of resist printing pastes thickened with CMC derivatives of different D.S. values (0.66, 0.81 and 1.03) were prepared. For the sake of comparison, another paste thickened with sodium alginate was also prepared. After printing and drying of the printed goods, fixation was carried out via steaming.

Table 1
Effect of type of acid used in chitosan dissolute on % decrease in *K*/*S* using linen fabric.

Thickener used	% decrease in *K*/*S*	
	Acetic acid	Formic acid
Sodium alginate	75.69	75.44
Sample 1 CMC (D.S. = 0.66)	67.42	64.91
Sample 2 CMC (D.S. = 0.81)	74.44	73.43
Sample 3 CMC (D.S. = 1.03)	77.19	76.69

3.1. Chitosan dissolvation

Chitosan is a semi-crystalline polymer, a weak base, which is insoluble in water, alkali or aqueous solution above pH 7, and common organic solvents due to its stable and rigid crystalline structure. Chitosan is normally polydispersed and has the ability to dissolve in certain inorganic and organic acids such as hydrochloric acid, phosphoric acid, lactic acid, propionic acid, succinic acid, acetic acid, tartaric acid, citric acid and formic acid at certain pH values after prolonged stirring. The solubility of chitosan also depends on the pK_a of these acids and their concentrations. Investigation of chitosan dissolution characteristics revealed that its dissolution rate varied according to the type of acid used (Chen, 2008).

In previous literatures (E-Hefian, El-Gannoudi, A, & Yahaya, 2010; Kitkulnumchai et al., 2008; Roussy, Chastellan, Vooren, & Guibal, 2005), chitosan solution was prepared by dissolving chitosan in 1% aqueous acetic acid solution. In the presented work, the effect of acid used in dissolving chitosan (membrane material) has been studied using either acetic acid or formic acid as a solvent for chitosan. One factor that probably played a role here is the nature and degree of interaction between the solvent and chitosan. The data of Table 1 revealed that regardless of the type of thickener used, more resisting effect is obtained upon using acetic acid as a solvent for chitosan than formic acid. This may be attributed to the difference in pK_a values of the dissolving acid used.

This is in complete conformation with previous study by Park, Park, and Sano (1998), where they measured the MW of chitosan dissolved in different organic acid solutions by the light scattering method. They found that the MW and molecular dimension of chitosan were different in the various acidic solutions. Therefore, matrix formation of the film depends on the solvent system. It may be noted that the film formed from acetic acid solution has tighter structure than those of the films formed from the other acids. The tighter the film structure, the more the resisting effect obtained expressed as % decrease in *K*/*S* of the resist printed area than the background un-resisted one.

Thus, for the rest of experiments in this work for studying the effects of degree of substitution of CMC, chitosan concentration, as well as the type and ratio of resisting agent used the chitosan will be dissolved in acetic acid solution.

3.2. Effect of degree of substitution of the CMC

Fig. 1 shows that the types of thickening agent used affect the resisting power of the film obtained. It can be noticed that; regardless of the type of fabric used; the resisting effect expressed as the % decrease in *K*/*S* increases by increasing the degree of substitution of the CMC used. For example, the D.S. increases from 0.66 to 0.81 to 1.03, the % decrease in *K*/*S* of resist printed linen fabric increases from 67.42 to 74.44 to 77.19 respectively. Also the % decrease in *K*/*S* increase from 24.87 to 45.5 to 62.96 for resist printed linen/polyester fabrics by increasing the D.S. from 0.66 to 0.81 to 1.03 respectively. This may be attributed to the increase in the apparent viscosity of the CMC used, as previously studied (Ragheb et al., 2012), whereas the viscosity increases, the

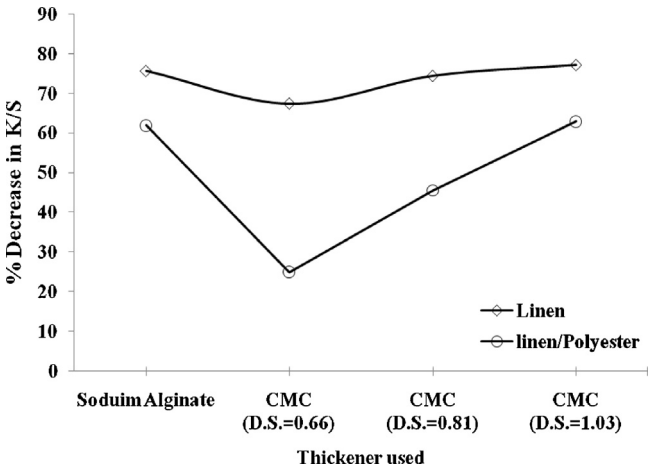


Fig. 1. Effect of type of thickener on resist printing.

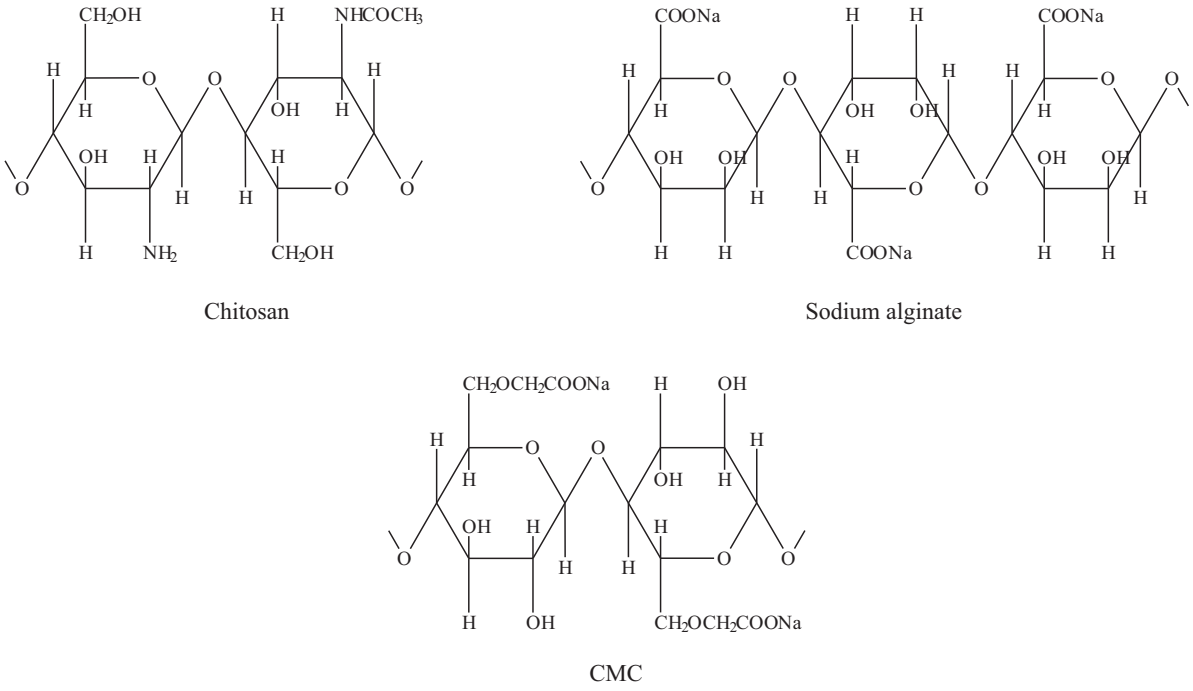
penetration of the paste inside the printed fabric decrease and hence the resisting effect increases too. The data also revealed that there is no remarkable difference between CMC and sodium alginate. This indicates that all these thickeners bearing carboxylic groups can be used successfully in resist discharge printing using chitosan as a resisting agent.

The chemical structure of chitosan (Giri, Thakur, Alexander, Ajazuddin Badwaik, & Tripathi, 2012; Miles, 1994; Rosca et al., 2005), sodium alginate, CMC and the electrostatic interaction between chitosan and NaCMC may be represented according to Schemes 1 and 2 respectively.

In addition, it should be noticed that the % decrease in *K*/*S* is higher in case of linen fabric than in case of linen/polyester fabric, this may be attributed to the higher affinity of reactive dyes to cellulosic fabric than the blends which results in higher dye uptake of the background area than the resist printed area (*K*/*S* for the background area is 3.99 in case of linen fabric and 1.89 in case of linen/polyester fabric).

3.3. Effect of chitosan concentration

Resist-printing pastes containing different concentrations of chitosan (0.5, 1, 1.5, and 2 g chitosan/kg printing paste) and thickened with CMC sample of D.S. 1.03 were prepared in order to observe the effect of chitosan on processed fabrics. Another series of printing pastes containing the same concentrations of chitosan and thickened with sodium alginate were also prepared for the sake of comparison. Fig. 2 shows that the resist printing effect is generally higher with the addition of chitosan to the resist-printing paste. The resist-printing effect increases with increasing chitosan concentration from 0.5 to 1%. These results indicate that chitosan induces a physical resist-printing effect. Furthermore, the chitosan may also distinguish a chemical resist-printing effect resulting from the structure of chitosan which is same as cellulose except for hydroxyl group which is substituted with amino group in case of chitosan (Gupta & Haile, 2007). As the concentration was increased to 2.0%, however, the resist-printing effect declined. The optimal chitosan concentration was 1%. In case of lower chitosan concentration (less than1%), the chitosan membrane formed by the resist-printing paste on the processed cotton fabrics may have been too thin, thereby impairing the physical resist-printing effect. High chitosan levels (more than 1%) may cause the dyes to form a partial covalent bond with chitosan, thereby diminishing the resist-printing effect. In such a case, the resist printing would not be linear as a function of chitosan concentration.



Scheme 1. Chemical structure of chitosan, sodium alginate, and CMC.

Scheme 2. The interaction between Na–CMC and chitosan in acidic medium.

3.4. *Effect of resist-printing agent ratio and type*

Fig. 3 illustrates the effect of using citric acid as a resist agent in different ratios to chitosan to show the effect of combination of chemical and physical resist printing effect. Upon using the acid resist agent, the bond strength between the dyes and the processed cotton fabrics is decreased, resulting in a chemical resist-printing effect.

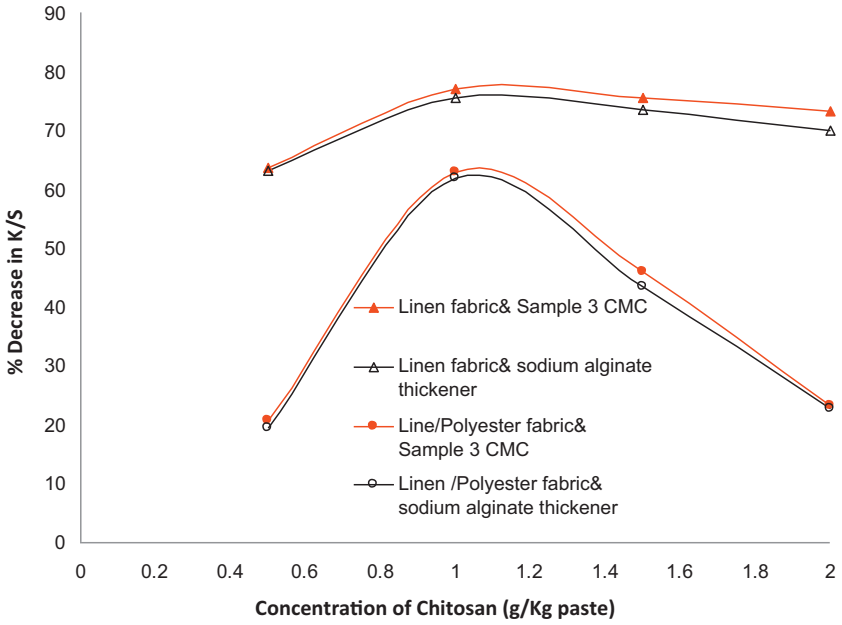


Fig. 2. Effect of chitosan concentration on resist printing.

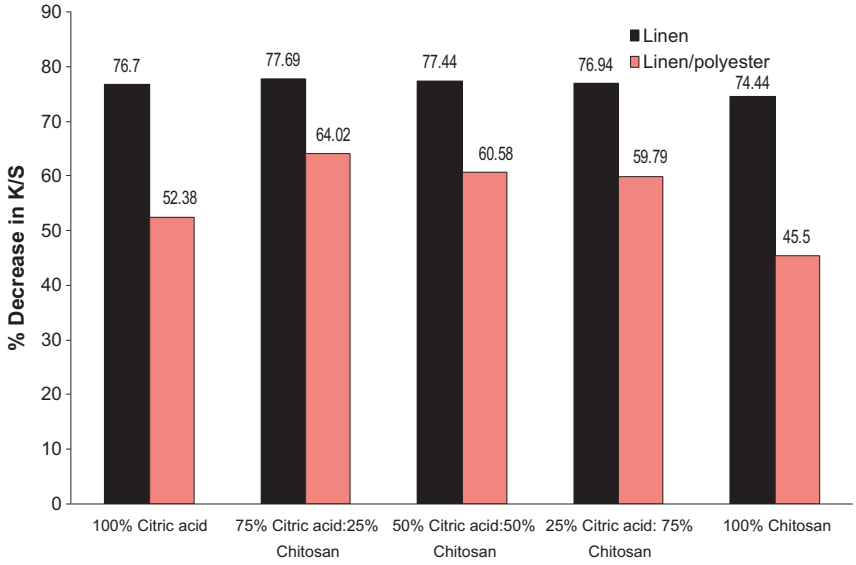


Fig. 3. Variation of *K*/*S* for resist processed fabrics by different ratios of citric acid/chitosan.

For this purpose, two resist printing pastes were prepared containing either chitosan or citric acid. Different printing pastes have been prepared via mixing these aforementioned pastes in different ratios (75:25, 50:50, and 25:75).

The prepared pastes have been used in resist printing of linen and linen/polyester fabrics and the data obtained are represented in Fig. 3.

It should be noted that mixing chitosan with citric acid results in synergetic effect of chemical resist caused by the citric acid with the physical resist caused by chitosan, and the greatest resisting effect was obtained upon using a ratio of 75% citric acid:25% chitosan.

Fig. 4 illustrates the effects of processing performed with different types of resist-printing agents in a ratio of 75% acid to 25% chitosan. The results show that, regardless of the type of fabric used, the resist-printing effect differs according to the resist agent used, where it follows the order maleic acid > fumaric acid > tartaric acid > citric acid > oxalic acid.

The data shows that different resist-printing agents can result in synergic effects through the combination of chemical and physical resist printing which is affected by both the pK_a and the hydrocarbon chain length of the acid used as resist agent.

α,β-Unsaturated carboxylic acid (maleic and fumaric acids) shows the highest resist effect which may be attributed to the ease of cross linking formed via the double bond. The *cis*-butenedioic acid (maleic acid) results in higher % decrease in *K*/*S* than the *trans*-butenedioic acid (fumaric acid) which may attributed to the pK_a values (acid strength) of the two acids; where for maelic acid pK_{a1} = 1.9, pK_{a2} = 6.07 and for fumaric acid pK_{a1} = 3.03, pK_{a2} = 4.44. Thus, the pseudo six member ring that maleic acid forms should help stabilize the ion. When it loses its proton, the negative charge develops on that oxygen. It can move down and push the double bond of its neighbour oxygen up, giving it the negative charge. conveniently enough (which is not the case for fumaric acid), the other proton that has not left yet is right besides the newly developed negative charge, which that negative oxygen can take to become a hydroxyl, giving the negative charge to the oxygen on the opposite end of the molecule. This "resonance" stabilizes the charge, thus the ion is stable and the proton is more acidic.

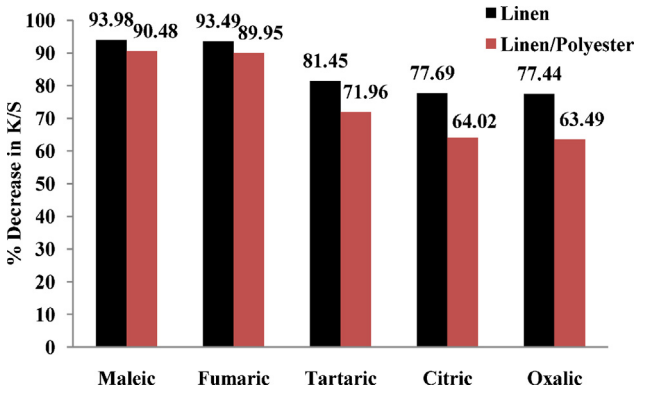


Fig. 4. Effect of type of resist agent used on resist printing of linen and linen/polyester fabrics.

Tartaric acid (2,3-dihydroxysuccinic acid (pK_{a1} = 2.95, pK_{a2} = 4.25), is stronger (lower in pK_a values) than citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) which have pK_a values of: pK_{a1} = 3.14, pK_{a2} = 4.75, pK_{a3} = 5.41.

On the other hand, the lowest resist effect expressed as % decrease in *K*/*S* was obtained upon using oxalic acid (ethanedioic acid) as resist agent (pK_{a1} = 1.25, pK_{a2} = 4.14), This may be attributed to the shorter hydrocarbon chain length of the acid used.

3.4.1. FT-IR spectral analysis

FT-IR spectra of CMC, and chitosan–CMC complex in the presence or absence of resist salt are presented in Fig. 5. In previous literatures (Denuziere et al., 1998; Rosca et al., 2005), the chitosan spectrum shows characteristic bands in the range of: 1635 cm^{-1} (amide I), 1523 cm^{-1} (NH_2), 1379 cm^{-1} (amide II). The absorption bands at 1157, 1072 and 1033 cm^{-1} are characteristic of the polysaccharide skeleton. The absorption band at 2054 cm^{-1} is characteristic for the NH_3^+.

The FT-IR spectrum of CMC evidence, too, bands at 1420 and 1640 cm^{-1} corresponding to the symmetrical and asymmetrical stretching vibrations and, respectively, to the carboxylate groups.

Chitosan–CMC complex shows a characteristic spectrum, different from those of the polymer partners. Besides, the bands corresponding to the polysaccharide skeletons, characteristic bands/peaks may be observed at 1598 and 1656 cm^{-1}, which can be attributed to the NH_3^+ and COOH groups, respectively. The presence of the band at 1598 cm^{-1} is expected, since the inter-macromolecular complex formation occurs through the electrostatic interaction of the cationic groups from chitosan with the

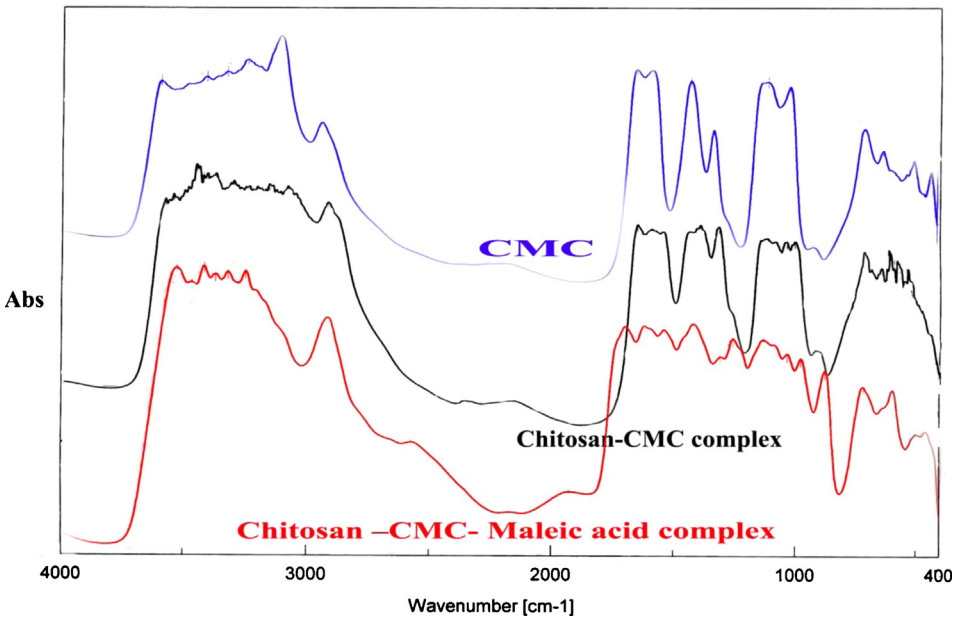


Fig. 5. FT-IR spectra of (a) CMC, (b) chitosan–CMC complex and (c) chitosan–CMC–maleic acid complex.

anionic ones from CMC. The band at 1656 cm^{-1} ($-NH_2$) suggests, nevertheless, that the formation reaction presented in Scheme 2 is reversible.

In this case, one may assume that the complex stability is maintained by hydrogen bonds. The spectrum for chitosan–CMC complex in the presence of maleic acid as a resist salt show an additional band characteristic of acid carboxylic group at 1617 cm^{-1} in addition to the NH_3^+ and COOH groups bands at 1539 and 1695 cm^{-1}.

Thus, it could be concluded that the FTIR spectra of solid complex evidenced some bands characteristic to the electrostatic interaction, along with other bands, suggesting the partial recovery of the NH_2 and COOH groups.

4. Conclusion

Resist printing of processed linen and linen/polyester fabrics was enhanced by the inclusion of chitosan in the resist-printing paste. Higher resisting effect is obtained upon using acetic acid as a solvent for chitosan than formic acid. The resisting effect expressed as the % decrease in *K*/*S* increases by increasing the degree of substitution of the carboxymethylcellulose CMC used. The resist-printing effect exhibited a nonlinear relationship with chitosan concentration and was optimal at 1% chitosan. The combined use of chemical and physical resist printing agents yielded an effect superior to that obtained with each agent separately. The process was optimized with a maleic acid: chitosan ratio of 75:25. Regardless of the type of fabric used, the resist-printing effect differs according to the resist agent used, where it follows the order maleic acid > fumaric acid > tartaric acid > citric acid > oxalic acid. FT-IR spectra of solid chitosan–CMC complexes, in the presence or absence of the acid resisting agent, evidenced some bands characteristic to the electrostatic interaction, along with other bands, suggesting the partial recovery of the NH_2 and COOH groups.

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