

# Chitosan and Keratin Hydrolysate Treatment of Archived Newsprint

**K. A. AL- Karagholy**

**Department of Chemistry, College of Education Ibn Al-Haitham  
University of Baghdad**

## Abstract

The study is focused on the modification of the standardized newspaper with natural polymers chitosan and keratin hydrolysate applied on the paper surface from polymer solution. This modification is based particularly on the formation of the complexes between acidic surface groups on cellulose fibers and the natural polymers which improved the mechanical properties of the paper and the positive results which were observed particularly in folding endurance of the newspaper.

Keywords: newsprint; chitosan; keratin; mechanical properties

## Introduction

The main problem in storing old papers, books and documents, is their degradation which due to the fact that some of the residual chemicals remaining in the paper from the paper manufacturing process react with moisture present either in the air or in the paper to form reaction products. These reaction products, generally sulphuric acid, degrade the cellulose causing paper brittleness, cracking and yellowing. Therefore, numerous processes were proposed for treating paper in order to stop or retard degradation. Mostly these processes are based on deacidification of paper, for example the gaseous treatment with diethylzinc [1], magnesium ethanolate and titanium ethanolate used in the Batelle process, or the Bookkeeper process with magnesium oxide microparticles [2].

Usually these processes use inorganic compounds and only few references are found on use of environmentally friendly compounds as natural polymers, e.g. chitosan and Keratin. Chitosan is a weak cationic polysaccharide composed essentially of <sup>B</sup>(1 → 4) linked glucosamine units together with some N-acetylglucosamine units. It is produced by extensive deacetylation of chitin, polysaccharide common in nature. Chitosan is biocompatible, biodegradable, and nontoxic natural polymer with excellent film-forming ability. Chitosan was shown as an excellent dry strength additive either in acidic or neutral condition, but it was less effective under alkaline conditions [3]. It means, chitosan has a potential to be used as a dry strength additive in neutral, acidic or alkaline conditions depending on the process requirements.

The studies on paper modification follow effects of different polymer solutions, e.g. chitosan and polyvinyl alcohol (PVA), on mechanical properties of paper sheets. It was shown that the improvement of the mechanical properties of the treated paper sheets by chitosan solutions is higher in comparison with the other polymer solutions. The same was stated for heat resistance of treated paper sheet by chitosan [4].

As a result of its cationic character, chitosan is able to react with polyanions forming polyelectrolyte complexes (PECs) [5]. Therefore, chitosan has the affinity of adsorption on cellulose fibres during wet modification of paper sheet. It is known, that the performance of materials with certain bulk properties can be changed or optimized by thin polymer layers adsorbed on their surfaces. The scope of that working area is to create and optimize polyelectrolyte (PEL) based surface modification concepts. For that charged surface groups are used, which are already present on the material or are generated by various pretreatments like plasma or chemical modification techniques[6].

Keratins are a family of fibrous structural proteins; tough and insoluble, they form the hard but nonmineralized structures found in reptiles, birds, amphibians and mammals, and they are the main constituent of structures that grow from the skin:

-the  $\alpha$ -keratins in hair, horns, nails, claws and hooves of mammals.

-the harder  $\beta$ -keratins found in nails and in the scales and claws of reptiles, their shells, and in the feathers, beaks, and claws of birds (these keratins are formed primarily in beta sheets. However beta sheets are also found in  $\alpha$ -keratins) [7].

PECs did not change their 3D-structure upon drying. It was found that the swollen 3D structure of the complexes is achieved by incorporating large amount of water into the complexes [8]. In the present work, chitosan and keratin hydrolysate are used as the modifiers of the newspaper sheets.

## Experimental

### Materials

#### Newspaper

Newspaper with the basic weight 45 g/m<sup>2</sup>, groundwood machine paper, unsized, pH of the cold extract 4.5 - 5.0.

#### Chitosan

The chitosan used in this study was a commercial product Sigma-Aldrich, low molecular weight, degree of deacetylation 75 to 85%. Used in the form of 2 wt. % water solution (pH 5.5 - 6.0).

#### Keratin Hydrolysate

Made from sheep wool, the alkali solution with pH 10. The dry matter content 12%.

#### Procedure

The solution of chitosan (CH) and keratin (K) or both together were applied by using the glass roller on the newspaper. The modified paper was consolidated 24 hours. Further it was conditioned before measurements under temperature 23°C and humidity 47.8 %.

The keratin - chitosan (K-CH) solution was prepared by mixing both biopolymers (1:5 v/v).

The sandwich like coating (K+CH) was realized by coating the paper first with the keratin solution (K) and after drying with the chitosan solution (CH).

#### Scanning electron microscopy

The morphology of the modified paper samples was evaluated by using the scanning electron microscopy (Tesla BS 300 SEM microscope with digital microscopy imaging TESCAN).

#### Mechanical properties

Tensile strength of the treated newspaper was measured by the INSTRON 1122 testing instrument (STN ISO 1924-2: Paper and board. Determination of tensile properties).

The fold endurance was measured by the double bending technique using Schopper instrument (STN ISO 5626: Paper).

#### Accelerated aging

Properties of unmodified and modified papers were studied also after the dry thermal accelerated aging at 105°C. The samples were placed to the air-drying chamber for 12 days.

## Results and Discussion

The standardized newspaper served as a model substrate for the archive documents in this study. Lignocellulosic fibres possess generally a negative charge that is attributed to the dissociation of carboxylic groups of cellulose and hemicellulose components. It is postulated

that pulp strength properties are related to the acidic groups which are specifically located on the surface of fibres [9]. The surface charge is observed to correlate with tensile strength. The situation is changed by modification with PELs, which form polyelectrolyte complexes (PEC) on fibres surfaces. The idea was to impregnate the paper, and to penetrate polymer solutions through the paper structure. The treatment should lower acidity as well as increase mechanical properties of the paper. The solutions of chitosan, keratin or combination of both, were applied uniformly on the surface by using the special technique of the deposition from the glass roller. The gravimetric analysis showed that about  $2.80 \pm 0.34 \text{ g/m}^2$  of these polymers were seized in the paper structure. The addition of biopolymers which were used increased the mechanical properties of the paper. Fig. 1 shows the tensile strength improving of the newspaper sheet particularly after the modification with chitosan or keratin, respectively. The improvement is quantified by the coefficient, which expresses the relative change of the measured value after modification against the measured value of the standard. In both cases, tensile strength is increased about 30%. Tensile strength is increased also for the paper modified with amixed solution of keratin and chitosan (K-CH), and paper is modified first with keratin and after drying with chitosan (K+CH).

Dramatic changes can be seen following the folding endurance of the modified papers in Fig. 2. The notable increase is observed especially in double folds for the sheets modified with both chitosan and mixture chitosan-keratin. Whereas keratin increased the double folds threefold, in case of chitosan it was eightfold. It means, particularly chitosan can be proved as an effective mediator of fiber-water interaction in the paper structure.

The treatment of the paper with the chitosan-keratin solutions connected with complexes and bonds formation results in a quite dense film on the surface of cellulose fibres. Comparing the pictures from SEM in Figure 3, a different surface morphology can be seen after treating the paper with chitosan-keratin solution and sequential treating first with keratin and after with chitosan. The formation of a dense elastic film on the fibres surface could explain an increase in folding endurance, particularly through a chitosan effect. Keratin, which is in fact keratin hydrolysate with a low molecular weight, itself forms fragile films. This is manifested by the lower folding endurance of such modified papers. Regarding film structure and studying a model for archive materials, the conditions (temperature, humidity) under which the documents are preserved in the archive must be taken into consideration. These conditions are favourable for keeping functionality of complexes between chitosan and cellulose.

It is well known that the glycosidic links of cellulose are stable in a neutral or weakly alkaline medium. On the other hand, they become rapidly hydrolysed in the presence of a strong acid or a strong base. From that reason, the process of deacidification is a fundamental process for the conservation and the restoration of the archive documents. Therefore, the use of alkalic keratin hydrolysate solution for the modification in the combination with a mild acidic chitosan solution should shift the total pH to neutral or milder alkali region. On the other hand, it was possible to prepare the mixture of keratin with chitosan only in the ratio 1:5 because a higher concentration of keratin in the mixture caused the precipitation of chitosan from solution.

From Fig. 4, it is evident that the applying of chitosan solution slightly moved the acidity of the original paper to anear neutral region. This is close to the pH value 6.5 measured for the chitosan solution. Keratin alone deacidified the paper and moved pH to the alkaline region pH = 9.8. Combination of chitosan and keratine (K-CH) can give a protective layer, which keeps neutral environment in paper (pH = 7.1).

## Conclusion

Concluding the results from the modification of a newspaper with the natural polymers chitosan and keratin, this modification is based particularly on the formation of complexes between acidic surface groups on cellulose fibres and natural polymers which can be

successfully applied in treating the archive cellulosic materials. Moreover in searching alternatives for professional conservators in the struggle against fungi that deteriorate paper documents, chitosan can be used due to its antifungal effect.

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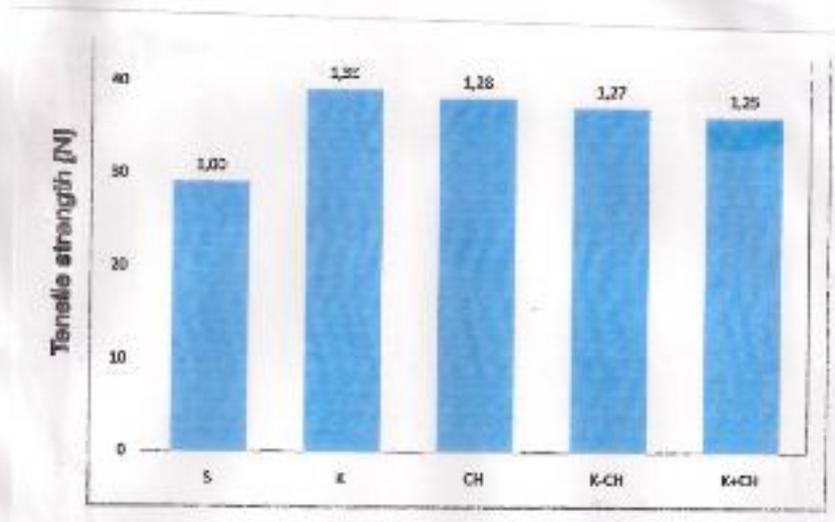


Fig.1: Tensile strength of standard - unmodified paper (S), paper modified with keratin (K), paper modified with chitosan (CH), paper modified with mixed solution of keratin and chitosan (K-CH) and paper modified first with keratin and after drying with chitosan (K+CH).



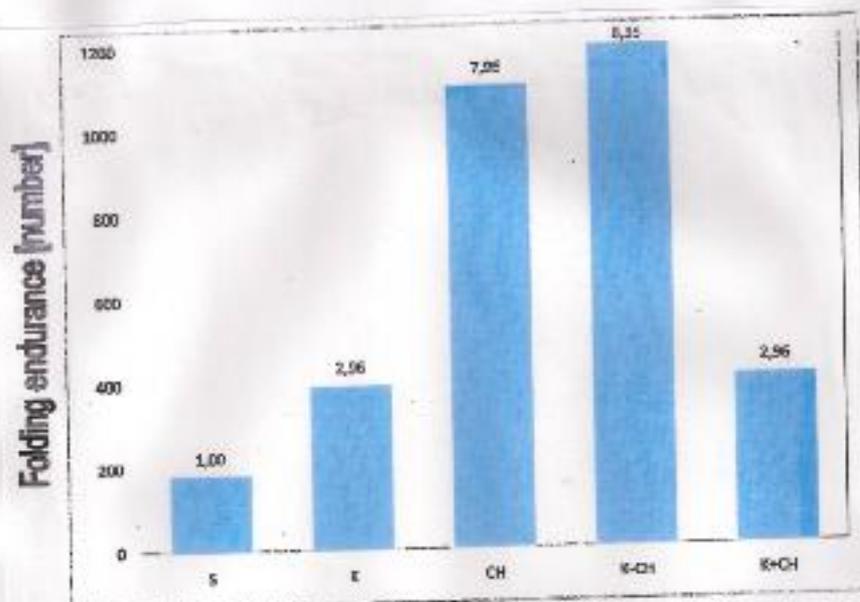
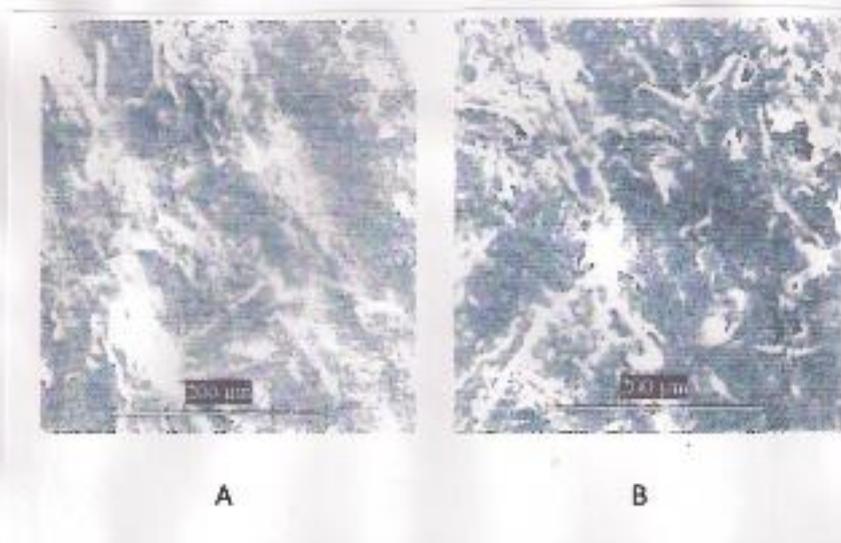


Fig.2: Folding endurance for the samples. Standard - unmodified paper (S), paper modified with keratin (K), paper modified with chitosan (CH), paper modified with mixed solution of keratin and chitosan (K-CH) and paper modified first with keratin and after drying with chitosan (K+CH).



**Fig.3: A) The keratin-chitosan composite film (K-CH); B) The paper modified first with keratin and after drying with chitosan (K+CH).**



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كريمة عبد الرزاق القره غولي

قسم الكيمياء ، كلية التربية-ابن الهيثم ، جامعة بغداد

### الخلاصة

ركزت هذه الدراسة على امكانية احداث تعديل في نوعية ورق الصحف القياسية عن طريق تعريض سطح هذا الورق لمحلول البوليمرين الطبيعيين ، الكيتوسان والكيراتين .  
وقد ظهر التأثير الايجابي لهذين البوليمرين جليا وبصورة خاصة في ازدياد تحمل الورق للطي . ويعود هذا التأثير الى تكوين معقدات بين المجاميع الحامضية في سطح الياف السليلوز للورق وهذين البوليمرين الطبيعيين .