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Mechanical and electrical properties of paper sheets treated with chitosan and its derivatives

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Abstract

This work focused on studying the dependence of paper sheet strength properties on the composition of additives, namely chitosan, cyanoethyl and carboxymethyl chitosan. Chitosan and its derivatives enhanced the strength properties of unagged and aged paper sheets. Also, cyanoethyl chitosan improved the dielectric properties of the treated paper sheets. The dielectric study was carried out over a frequency range from 100 Hz to 100 kHz at temperature range from 20 to 140 °C. The variations of permittivity ε' versus the cyanoethyl chitosan content at three different temperatures show the highest dielectric properties at cyanoethyl chitosan of 0.3%. The variation of ε'' versus the applied frequency was fitted by a superposition of Fröhlich and Havriliak–Negami functions in addition to the conductivity term. These functions could be ascribed by the Maxwell–Wagner effect and the orientation of the large aggregates formed by the addition of chitosan to the paper sheet.

Keywords: Paper additives; Chitosan; Chitosan derivatives; Strength properties; Aging; Electrical properties; IR

1. Introduction

Paper fiber is held together by hydrogen bonds (Olsson & Salmen, 2004). These bonds affect the distance between the separate cross-linked fibers. Water molecules play an important role in the interfiber linkage. A large excess of free water, however, causes weakness of wet strength in paper sheets and paper board (Gardlund, Wagberg, & Gernandt, 2003). To improve the wet strength of the paper sheets, a number of resins and polymeric materials have been used such as urea, phenol- and melamine-formaldehyde resins (Gernandt, Wagberg, Gardlund, & Dautzenberg, 2003) in addition to polyacrylamide, polymethyl methacrylate (Nada, Abo-Shosha, & Ibraheim, 1996; Nada & El-Saied, 1989), vinyl acetate–vinyl chloride copolymer (Nada & Ayoub, 1997). Moreover, some other polymers were used to increase the resistance of paper sheets toward water absorption such as perfluorated urethane mixture (Aboshosha, Ibrahim, & Nada, 1996).

On the other hand, some polymers were used for treatment of paper sheets to decrease its influence to the photo yellowing (Nada, El- Sakhawy, & Soliman, 1997). These polymers usefully used to treat the old paper documents (Nada, Kamel, & El-Sakhawy, 2000) and enable the interfiber bonding area to remain chemically linked in the presence of water. Otherwise, these polymeric materials can be used as additives during paper sheets formation or as solution to dip the paper sheet in it. The surface modification of cellulose fiber permits the direct formation of hydrogen bonds between the fiber surface areas (Mucha, 1998). The feature of good strength additives must be: (a) soluble in water based system, (b) substantive to cellulose so that its retention is efficient, (c) compatible with cellulose, (d) film forming to offer adhesive resistance, (e) contain a functional group capable of ionic or covalent bonding with paper fiber. Chitosan is known to be non-toxic and odorless, so much interest has been paid to its industrial applications in the past decade (Ikejima, Yagi, & Inoue, 1999; Shignemasa & Minami, 1995). In addition, chitosan is expected to be useful in the development of composite materials such as blends or alloys with other polymers, since chitosan has many functional groups such as hydroxyls, amines and amides (Muzzarelli, 1997; Zong, Kimura, Takahashi, & Yamane, 2000).

Dielectric measurements are considered to be powerful tools for studying the molecular behavior of polymeric materials, for such reason it attracts many authors to investigate the dynamics of cellulosic and polymer materials by using dielectric technique (Einfeldt, Heinze, Liebert, &

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Kwasniewski, 2002; Einfeldt, Meissner, & Kwasniewski, 2003, 2004; Nada, Dawy, & Salama, 2004).

In the present work, chitosan and its derivatives, cyanoethyl and carboxymethyl chitosan were used as additives to cellulose fiber during the formation of paper sheet or as solution for dipping the paper sheet in it. Infrared spectra of chitosan and its derivatives were detected. The dielectric properties as well as the mechanical properties of the produced paper sheets were also investigated.

2. Experimental

2.1. Materials

Unbleached Kraft bagasse pulp, delivered by Edfo Paper Mill (Upper Egypt) was used in this work. Chitosan, commercial grade with 85% degree of deacetylation was used.

Acrylonitrile (AN) and monochloroacetic acid of analytical pure grades were used.

2.2. Cyanoethylation of chitosan

Five grams of chitosan were suspended in 250 ml 30% NaOH (w/v), then 150 ml AN were added to the chitosan solution and refluxed for 6 h. The produced cyanoethyl chitosan was precipitated by methanol, filtered by using a G_2 sintered glass funnel and washed with methanol and dried in a vacuum oven at 55 °C for 8 h to give 8 g dried cyanoethyl chitosan.

2.3. Carboxymethylation of chitosan

Carboxymethylation was carried out by stirring 5 g chitosan in 100 ml solution of 20% NaOH (w/v) for 15 min. Fifteen grams monochloroacetic acid was added dropwise to the reaction medium and the reaction continued for 2 h at 40 °C with stirring. Then, the reaction mixture was neutralized with 10% acetic acid, poured into an excess of 70% methanol, filtered by using a G_2 sintered funnel and washed with methanol. The produced carboxymethyl chitosan was dried in a vacuum at 55 °C for 8 h to give 6.5 g dried carboxymethyl chitosan.

2.4. Fourier transform infrared spectroscopy (FTIR)

Infrared spectroscopy of chitosan and its derivatives was carried out by using KBr disc technique using JASCO FT/IR 3006 (Fourier Transform Spectrometer).

2.5. Hand sheet formation

Pulp was beaten to 40 °SR in a Jokro mill beater according to the Swedish Standard Method (SCA). Hand sheets of basis weight 68 g/m^2 were formed and different concentrations of chitosan, cyanoethyl or carboxymethyl chitosan solution (dissolved in 5% acetic acid) were added in a mixer.

In another trial, paper sheets were dipped in different concentrations of chitosan solution and also its derivatives for 30 s. After dipping, the paper sheets were pressed between two filter paper sheets to remove the excess polymer, and then dried on drum at 105 °C for 2 h.

Untreated and treated paper sheets were aged at 140 °C for 2 h.

The following properties were got according to the relevant Tappi Standards (Correia, Roy, & Chute, 2003):

- Grammage, i.e. weight of 1 m^2, from it the retained amount (g/m^2) of chitosan or its derivatives on paper sheets were calculated.
- Breaking length(m) $= \frac{\text{Tensile strength}(p)\times 6.67\times 10{,}000}{\text{Grammage(g)}}$.
- Tear factor $= \frac{\text{Tear strength(mN)}\times 16(\text{pendulum factor})\times 100}{\text{Number of testes sheets}\times\text{Grammage(g)}}$.

2.6. Dielectric measurements

Dielectric measurements were carried out in the frequency range of 100 Hz–100 kHz using an LCR meter type AG-411 B (Ando electric Ltd, Japan). The capacitance C and the loss tangent tan δ were obtained directly from the bridge from which the permittivity ε' and dielectric loss ε'' were calculated. A guard ring capacitor of the type NFM/5T Wiss Tech. Werkstatten (WTW) GMBH Germany was used as a measuring cell. The cell was calibrated by using standard materials (Saad, Hassan, Youssif, & Ahmed, 1997) and the experimental error in ε' and ε'' was found to be ±3 and ±5%, respectively. The temperature of the cell was controlled to within ±0.1 °C using an ultra thermostat through a jacket surrounding the cell.

3. Results and discussion

3.1. Infrared spectra

Chitosan undergoes different reactions to produce derivatives used as additives in paper sheets. Cyanoethyl and carboxymethyl chitosan were prepared from chitosan. Infrared spectroscopy was used to follow the chemical structure of the produced derivatives. The infrared spectra (Fig. 1) of chitosan and its derivatives showed a band (shoulder) appeared at 3063 cm^{-1} due to NH_2 stretching vibration (ElNashar, Abd-El-Messieh, & Basta, 2004). The relative absorbance of the band at 3400 cm^{-1} which is characteristic to OH group (ratio of the absorbance at the subscript wave number 3400 cm^{-1} to the absorbance of wave number at 1325 cm^{-1} which corresponds to the CH rocking of the ring) (Kokot, Czarnik-Matusewicz, & Ozaki, 2002) is higher than that of cyanoethyl carboxymethyl chitosan (Table 1). This can be attributed to the substitution of the OH groups of chitosan with cyanoethyl or carboxymethyl group.

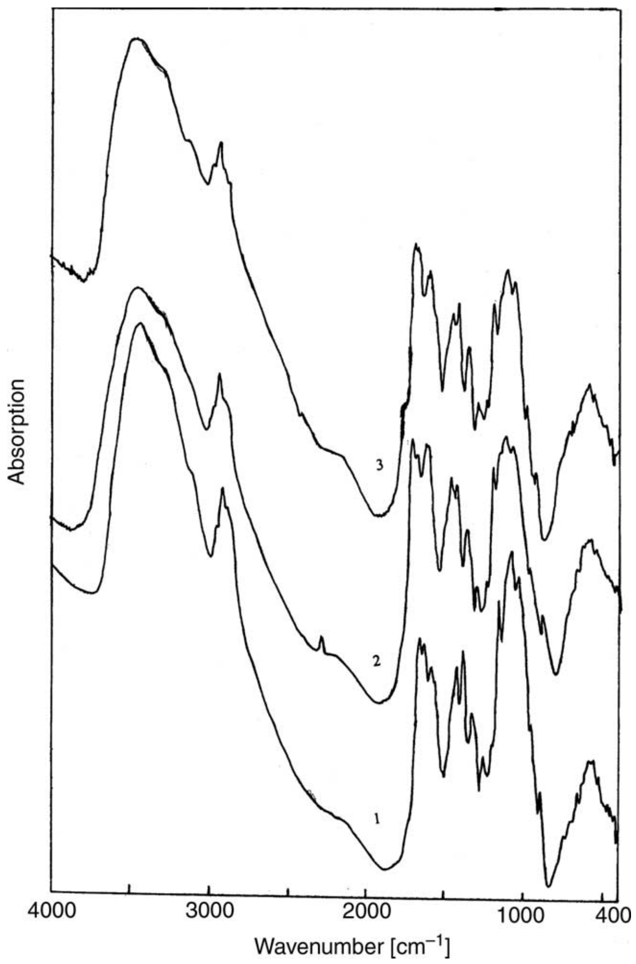

Fig. 1. Infrared spectroscopy of: (1) chitosan, (2) cyanoethyl chitosan and (3) carboxymethyl chitosan.

$ROH + CH_2 = CHCN \rightarrow \quad ROCH_2CH_2CN$

Chitosan Cyanoethyl chitosan

$ROH + ClCH_2COOH \rightarrow \quad ROCH_2COOH$

Chitosan Carboxymethyl chitosan

Also bands appeared at 2223 and 1715 cm^{-1}, which are attributed to C≡N stretching vibration in cyanoethyl chitosan and to C=O of carboxylic group in carboxymethyl chitosan, respectively.

Crystallinity index of cyanoethyl chitosan (band intensity at 1425 cm^{-1}/band intensity at 900 cm^{-1}) is higher than that in case of chitosan itself. This can be confirmed by the shift of the OH band at 3422 cm^{-1} to lower wave number 3415 cm^{-1}, i.e. the hydrogen bond intensity of chitosan was increased. On the other hand, the crystallinity index of the produced carboxymethyl chitosan is lower than that in case of chitosan and cyanoethyl chitosan.

Table 1
FTIR Characteristic of chitosan and its derivatives

Material	Wave number of OH group	Relative absorbance
Chitosan	3398	1.80
Cyanoethyl chitosan	3392	1.64
Carboxymethyl chitosan	3390	1.60

3.2. Chitosan and its derivatives as additives during sheet formation

The solutions of chitosan and its derivatives were added during paper sheet formation with different percentages. From Figs. 2 and 3, it is clear that, the addition of chitosan (0.05–1% by weight) has been shown to be effective as mediator of fiber–water interaction in paper, improving both breaking length and tear factor of the produced paper sheet. The presence of basic groups on every ring makes chitosan soluble in dilute aqueous acidic solution which makes it substantive to anionic pulp paper, this increases the covalent cross-linking between paper fibers (Mucha & Miskiewicz, 2000). Also, chitosan contains a functional group capable of ionic or covalent bonding with the paper fiber surface during the paper making process. This produces film to offer adhesive resistance to rapture. On the other hand, chitosan should be compatible with cellulose surface so that it does not disrupt covalent hydrogen bonding. So, addition of chitosan during papermaking increases the mechanical properties of the produced paper. From Fig. 2, it is clear that, increasing the amount of added chitosan higher than 0.3% resulted in breaking length decrease. This may be due to the increase of the intensity of the produced film and hardness of the fiber and consequently the cracking of the produced paper sheet increases.

From Figs. 4–7, addition of chitosan or its derivatives during paper sheets formation caused an improvement of the mechanical properties. The improvement obtained by addition of chitosan derivatives is less than that produced by the addition of chitosan itself. This may be due to the cross-linking between the paper sheet fibers; produced by chitosan derivatives are less intensive than that produced by chitosan itself. The improvement, which occurred due to carboxymethyl chitosan, is lower than that resulting from cyanoethyl chitosan.

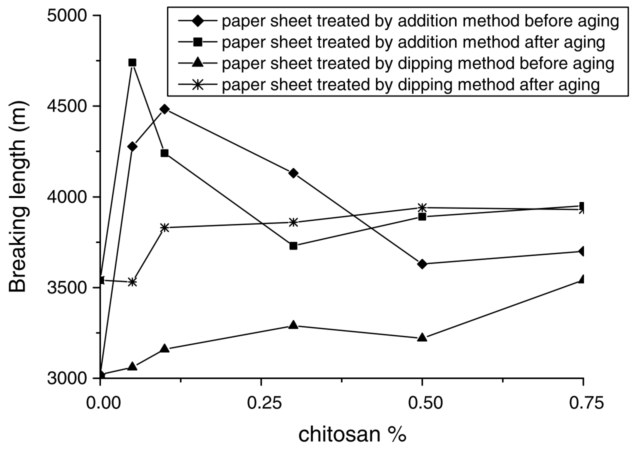

Fig. 2. Effect of chitosan% on breaking length before and after aging.

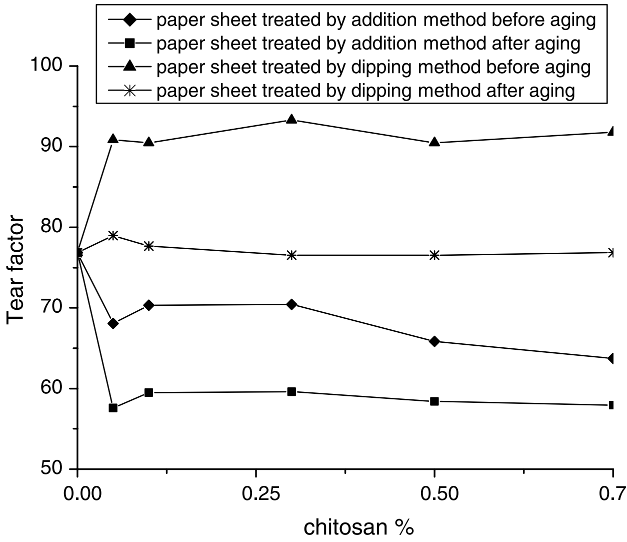

Fig. 3. Effect of chitosan% on tear factor before and after aging.

Addition of mixture of cyanoethyl and carboxymethyl chitosan improved the mechanical properties of the produced paper sheets (Table 2). Increasing the ratio of carboxymethyl cellulose in the mixture reduces the improvement of the mechanical properties of the paper sheets although it is still higher than that in case of the untreated paper sheets.

Addition of chitosan or its derivatives increases the mechanical stability of the produced paper sheets Figs. 2–7. From these figures, it is clear that, the aging of treated paper treated with lower chitosan concentration (0.05%) at 140 °C for 2 h increases the mechanical properties, while the increase in the amount of chitosan causes a decrease in the mechanical properties. This could be attributed to the increase of stiffness of the formed film over the fiber of the paper and consequently the mechanical properties decrease. In case of treated paper with carboxymethyl and cyanoethyl chitosan, the aging results in an increase in the mechanical properties.

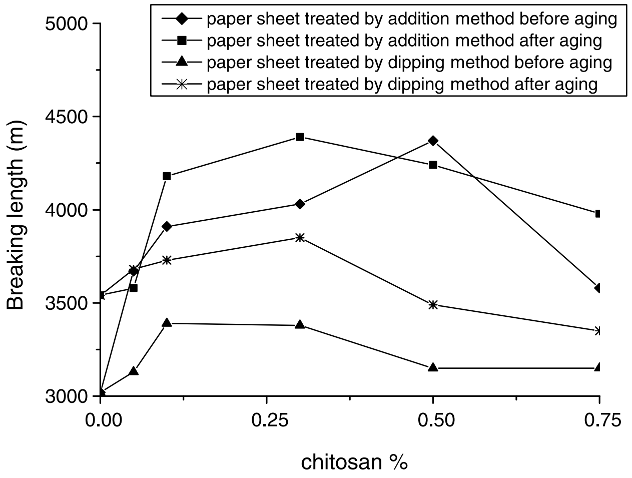

Fig. 4. Effect of cyanoethyl chitosan% on breaking length before and after aging.

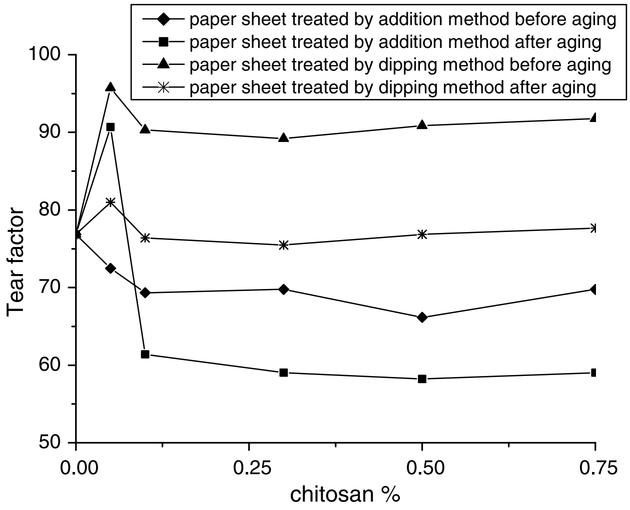

Fig. 5. Effect of cyanoethyl chitosan% on tear factor before and after aging.

3.3. Dielectric properties of paper sheets (treated by addition method)

Dielectric properties was measured for paper sheets treated with cyanoethyl chitosan only because the presence of cyano group is known to increases the dielectric as well as the thermal stability of paper sheets compared with carboxymethyl chitosan and chitin (Dawy & Nada, 2003).

Permittivity (ε') and dielectric loss (ε'') of the untreated paper sheet (S_0) and that treated by cyanoethyl chitosan as according to the addition method (S_{a1}, S_{a2},…, S_{a5}) were measured over the frequency range from 100 Hz to 100 kHz at temperature range from 20 to 140 °C. The data obtained for ε' and ε'' vs. frequency, for the paper sheets under investigation at different temperatures are illustrated graphically in Fig. 8. From this figure, it is clear that ε' decreases by the increasing temperature. This trend was observed on addition of cyanoethyl chitosan till concentration of 0.3% (S_{a3}) then starts to reverse above this concentration. Fig. 9 illustrates such behavior by showing the variation of ε' vs. cyanoethyl chitosan

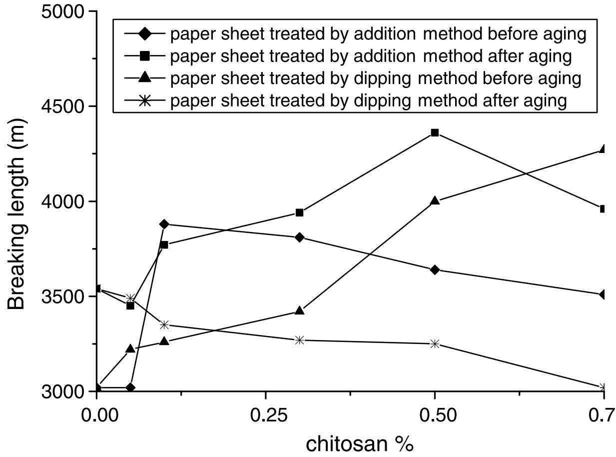

Fig. 6. Effect of carboxymethyl chitosan% on breaking length before and after aging.

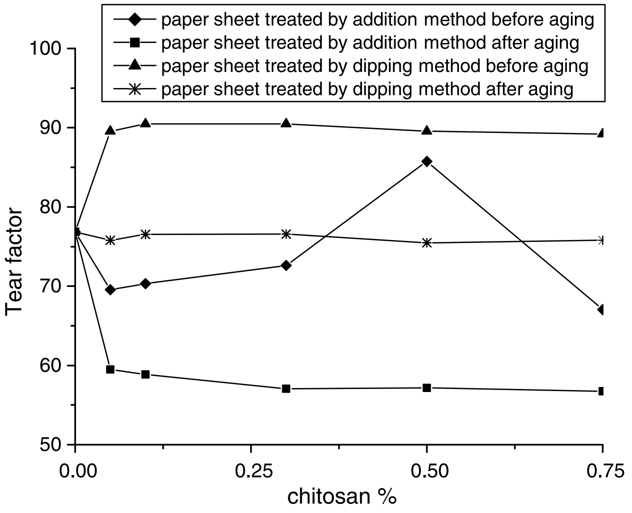

Fig. 7. Effect of carboxymethyl chitosan% on tear factor before and after aging.

content at three different frequencies. An intersecting point (stable over wide temperature range) could be noticed at approximately 0.2%. The variation of ε' with temperature could be explained in the view of the polar groups mobility (Saad et al.). At lower content (less than 0.2%) the decrease of ε' with temperature may be explained by the increase in the cross linking with cyanoethyl chitosan. At contents higher than 0.2%, the increase of ε' with temperature may be explained by the increase in the polar groups mobility, the decrease in density, and, hence, a decrease in the effect of the environment that facilitates the orientation of the mobile groups (Saad et al.). Around the content of 0.2%, an equilibrium state between the two phenomena could be noticed. It is evident also that ε' decreases with increasing frequency and shows an anomalous dispersion.

Also from Fig. 8, it is apparent that ε'' is decreased at higher temperatures, especially in the higher-frequency range. Moreover, the value of ε' in the lower-frequency range is slightly affected by the addition of cyanoethyl chitosan to sample S_0 and approximately the same for samples under investigation. From the same figure, it is clear that the curves relating ε'' and $\log f$ are broader than Debye curves (Mc-Crum, Read, & Williams, 1991), indicating that more than one relaxation process is present. Fitting of the data at 60 °C is performed by a computer program based on all the different spectral functions commonly used in dielectric research such as Debye (Mantas, 1999), Cole–Cole (Stephanovich, Glinchuk, & Hilczer, 2000), Cole–Davidson (Blochowicz, Tschirwitz, Benkhof, & Rossler, 2003), Havriliak–Negami (Mc–Crum et al.), Fröhlich (Saad et al.) and Rocard–Powles (Mc–Crum et al.). The best fitting of the data was done by a superposition of Fröhlich and Havriliak–Negami functions in addition to the conductivity term. On other words, the spectral function $\varepsilon//(\omega)$ could be expressed as:

$$\varepsilon//(\omega) = \varepsilon//(\omega)_{\mathrm{Fr}} + \varepsilon//(\omega)_{\mathrm{HN}} + \frac{\theta\sigma}{\omega}$$

This equation has been used to analytically represent the measured spectra. $\varepsilon//(\omega)_{\mathrm{Fr}}$ denotes Fröhlich function form, $\varepsilon//(\omega)_{\mathrm{HN}}$ denotes Havriliak–Negami function, ω is the angular frequency, σ is dc conductivity, and θ is a constant which equals $4\pi(9\times10^{11})$. Fröhlich and Havriliak–Negami functions are represented as

$$\varepsilon//(\omega)_{\mathrm{Fr}} = \frac{\varepsilon_s - \varepsilon_\infty}{P}\arctan\left[\frac{\sinh P/2}{\cosh \ln(\omega\bar{\tau}_{\mathrm{Fr}})}\right]$$

where P is a parameter describing the width of the distribution of relaxation times and equals $\ln(\tau_1/\tau_2)$. $\bar{\tau}_{\mathrm{Fr}}$ is the mean relaxation time and equals $(\tau_1\tau_2)^{1/2}$.ε_s and ε_∞ are the static permittivity and the permittivity at infinite frequency, respectively

$$\varepsilon//(\omega)_{\mathrm{HN}} = \frac{(\varepsilon_s - \varepsilon_\infty)\sin \Phi\beta}{[1 + 2(\omega\tau_{\mathrm{HN}})^{1-\alpha}\sin \pi\alpha/2 + (\omega\tau_{\mathrm{HN}})^{2(1-\alpha)}]^{\beta/2}}$$

where α and β are Havriliak–Negami distribution parameters and Φ represented as:

$$\Phi = \arctan\frac{(\omega\tau_{\mathrm{HN}})^{1-\alpha}\cos \pi\alpha/2}{1 + (\omega\tau_{\mathrm{HN}})^{1-\alpha}\sin \pi\alpha/2}$$

An example of the dielectric spectrum and the fitting of the data for the paper sheet treated by cyanoethyl chitosan (0.5%) at 60 °C are illustrated graphically in Fig. 10. Relaxation parameters obtained according to that fitting are given in Table 5. The width of the distribution of relaxation times P is around 2. Also, the Havriliak–Negami distribution parameters α and β are equal to 0.5 and 0.66, respectively for this fitting. The first absorption region, which lays approximately at $f\approx0.21$ kHz, is found to be present for all the samples investigated. Those low-frequency losses may be attributed to Maxwell–Wagner losses arising from the interfacial polarization caused by the multiconstituents of the investigated systems. The difference in permittivities and conductivities in the constituents of the investigated materials is considered to be the reason for the presence of such effect.

The second absorption region, which is found to be higher when the cyanoethyl chitosan is added to the paper sheet, could be attributed to the orientation of the large aggregates caused by movement of the main chain that are expected to be formed by the addition of cyanoethyl chitosan to the paper sheet (Abd-el-Messieh, Mohamed, Mazrouaa, & Soliman, 2002; ElNashar et al.).

Table 2
Effect of addition of mixture of carboxymethyl chitosan (0.5%) and cyanoethyl chitosan (0.5%) during sheet formation

Cyanoethyl: carboxymethyl chitosan	Before aging		After aging at 140 °C for 2 h	
	Breaking length (m)	Tear factor	Breaking length (m)	Tear factor
100:00	4370	66.16	4240	58.22
80:20	4166	60.89	4208	59.59
60:40	4148	63.69	4016	52.52
40:60	4003	70.02	3984	51.00
20:80	3912	77.82	3504	51.88
00:100	3640	85.74	4360	57.16

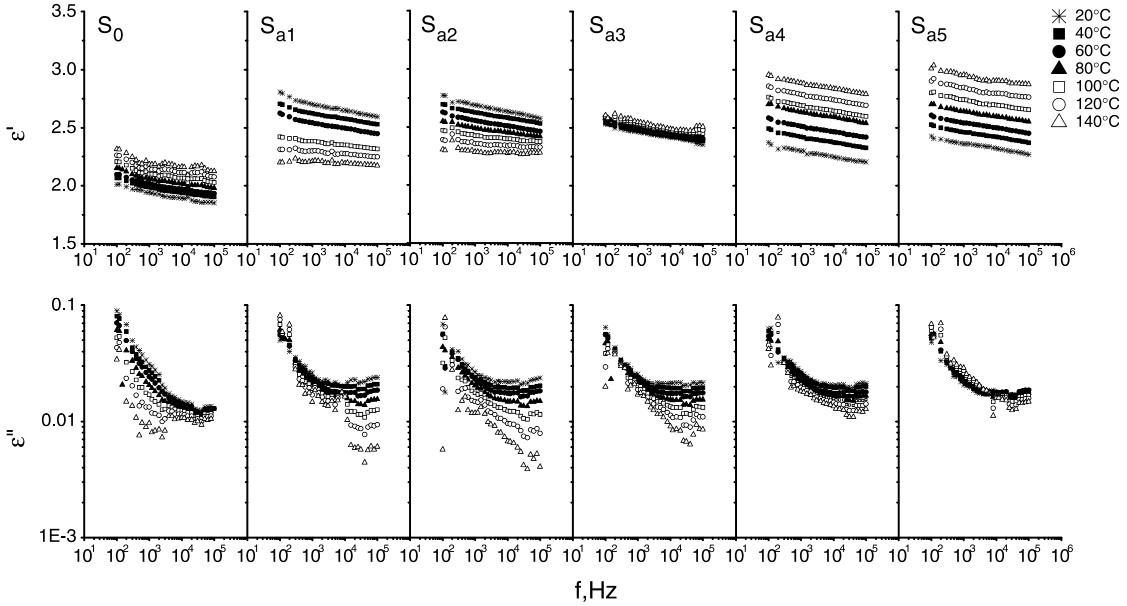

Fig. 8. Permittivity ε' and dielectric loss ε'' vs. frequency (f) of the untreated paper sheet (S_0) and that treated by Cyanoethyl chitosan as addition method ($S_{a1}=0.1\%$, $S_{a2}=0.2\%$, $S_{a3}=0.3\%$, $S_{a4}=0.4\%$, and $S_{a5}=0.5\%$) at temperatures (✳) 20 °C, (■) 40 °C, (●) 60 °C, (▲) 80 °C, (□) 100 °C, (○) 120 °C and (△) 140 °C.

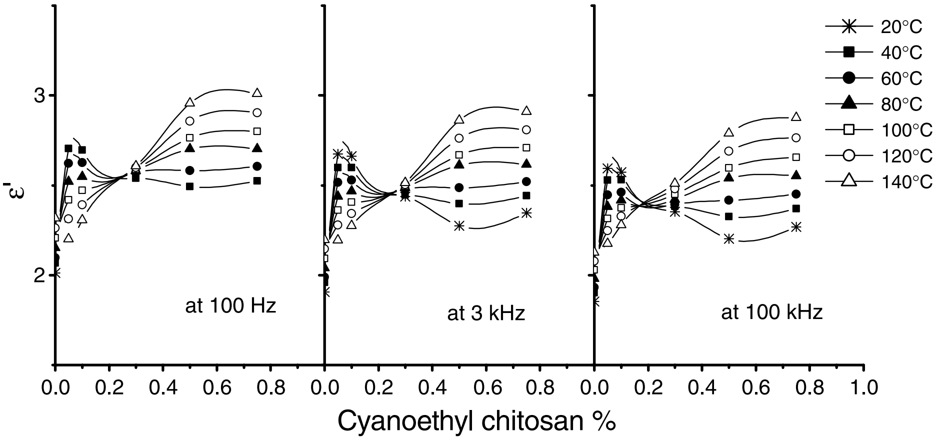

Fig. 9. Permittivity ε' vs. addition percent of cyanoethyl chitosan.

In order to get the best fit for the given spectra, a third relaxation time that lays on the order of 10^{-7} s could be suggested. Unfortunately, further accuracy of this region could not be given since no measurements over 100 kHz were available. May be this relaxation time associated with those orientations of small aggregates is caused by the movement of the main chain (Abd-el-Messieh et al., 2002; ElNashar et al.).

3.4. Chitosan and its derivatives as solution for paper sheet dipping

In another trial, paper sheets were soaked in solutions containing chitosan or its derivatives in different concentrations. The paper sheets were dipped in different concentrations of chitosan solution or its derivatives for 30 s. After dipping, the paper sheets were pressed between two filter paper sheets to remove the excess polymer, and then dried on drum at 105 °C for 2 h. Table 3 shows the retained amount of chitosan and its derivatives on paper sheet after dipping. The retained polymer increases by increasing the concentration of dipping solution while it was nearly the same for chitosan or its derivatives at the same concentration.

From Figs. 2–7, it is clear that, the breaking length of the treated paper sheets by dipping in chitosan or its derivatives increases and the tear factor was slightly increases. This could be attributed to the formation of a layer on the surface of paper sheets causing an increase in the bonding strength between the fibers of paper sheets. This caused a high increase in the breaking length and slight increase in the tear factor. From Figs. 4–7, it could be noticed that a mechanical improvement in paper sheets increases by increasing the added amount of chitosan derivatives and the maximum improvement is reached at cyanoethyl and carboxymethyl chitosan concentration of 0.5%. Increasing the added amount higher than 0.5% resulted

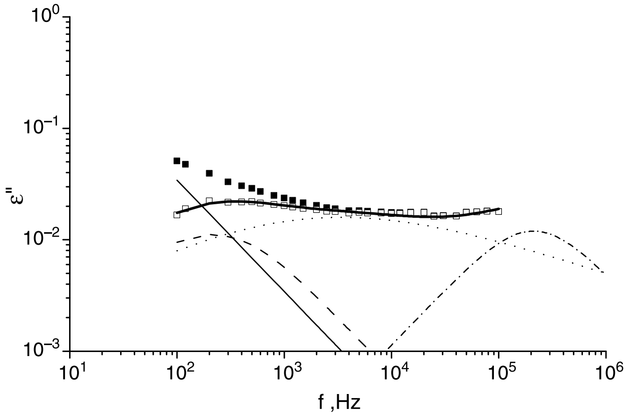

Fig. 10. The absorption curve of the paper sheet which treated by cyanoethyl chitosan (0.5%) as addition method at 60 °C. The data fitted by Fröhlich (– – –), Havriliak–Negami (· · · ·), Debye (–·–·–·) and dc conductivity (—). Experimental data (■), dielectric loss after subtraction of conductivity (□), total fit (——).

Table 3
Retained amount on paper sheets after dipping

Concentration of dipping solutions %	Retained (g/m^2)		
	Chitosan	Cyanoethyl chitosan	Carboxymethyl chitosan
0.05	0.06	0.05	0.06
0.10	0.12	0.11	0.11
0.30	0.32	0.36	0.36
0.50	0.57	0.60	0.60
0.75	0.79	0.85	0.87

in a decrease in the mechanical properties of the produced paper sheets.

A dipped paper sheet in carboxymethyl chitosan solution has higher mechanical properties as compared to chitosan or cyanoethyl chitosan solution. This may be due to the higher binding between paper sheets fiber in case of adding carboxymethyl chitosan than in case of the other two additives. Thus, cross-linking between fibers increases the adhesion between fiber and consequently the mechanical properties. The mechanical properties of the dipped paper sheets in carboxymethyl chitosan solution increase by increasing the concentration of the dipped solution, i.e. increase of the retained polymer in paper sheets.

Aging at 140 °C for 2 h of the paper sheets previously treated by soaking has slight effect on the mechanical properties of the paper sheets (see Table 4). Aging resulted in an increase in the breaking length for paper with lower levels of polymer. The tear factor decreased for paper sheets by aging in all cases of treatment by polymer. This is due to the hardness on the surface of the polymer causing a cracking of the fiber and the mechanical properties decrease.

Comparing the mechanical properties of the treated paper sheets with chitosan and its derivates added during sheet formation with that resulting from dipping in chitosan and its derivates, it is seen that, the breaking length of the first is higher than that of the second treatment, while tear factor of the second is higher than that of the first.

3.5. Dielectric properties of paper sheets (treated by dipping method)

For untreated paper sheet (S_0) and that treated by dipping in cyanoethyl chitosan solution (S_{d1}, S_{d2},…, S_{d5}) permittivity (ε') and dielectric loss (ε'') were measured over the frequency range from 100 Hz to 100 kHz at temperature range from 20 to 140 °C. The data obtained for ε' and ε'' vs. frequency for the paper sheets under the investigation at different temperatures are illustrated graphically in Fig. 11.

It is clear that ε' increases with increasing temperature and decreases with increasing frequency. Similar behavior was noticed before (Saad et al.). The increase of ε' with temperature can be explained by the increase in the mobility of polar groups, the decrease in density, and, hence, a decrease in the effect of the environment that facilitates the orientation of the mobile groups. The decrease of ε' with frequency shows an anomalous dispersion.

Moreover, Fig. 11 shows that for sample S_0 dipped in different concentrations of cyanoethyl chitosan the value of ε' increases till concentration of 0.3% (S_{d3}) then starts to decrease. This trend is clear at higher temperatures. Such behavior is clear in Fig. 12 which shows the variation of ε' vs. cyanoethyl chitosan content at different temperatures and three different frequencies.

It is apparent also from Fig. 11 that ε'' decreased at higher temperatures, especially in the higher-frequency region. Moreover, the value of ε'' in the lower-frequency region is slightly affected by the cyanoethyl chitosan content for samples under investigation. The dielectric spectra were fitted by a superposition of Fröhlich and Havriliak–Negami functions in addition to the conductivity

Table 4
Effect of dipping of paper sheets in a mixture of carboxymethyl chitosan (0.5%) and cyanoethyl chitosan (0.5%)

Cyanoethyl:carboxymethyl chitosan	Retained (g/m^2)	Before aging		After aging at 140 °C for 2 h	
		Breaking length (m)	Tear factor	Breaking length (m)	Tear factor
100:00	0.60	3150	90.85	3490	76.87
80:20	0.54	3184	82.53	3558	82.55
60:40	0.59	3255	77.11	3778	80.04
40:60	0.55	3322	77.10	3599	77.81
20:80	0.55	3699	73.79	3367	79.04
00:100	0.60	4000	89.57	3250	75.47

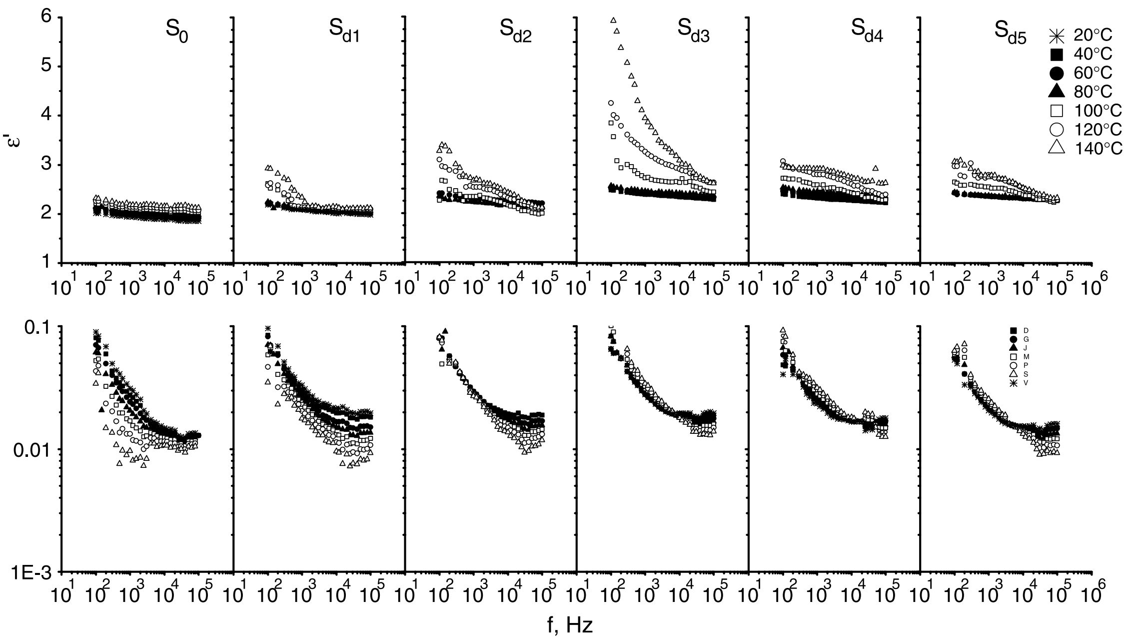

Fig. 11. Permittivity ε' and dielectric loss ε'' vs. frequency (f) of the untreated paper sheet (S_0) and that treated by Cyanoethyl chitosan as dipping method ($S_{d1}=0.1\%$, $S_{d2}=0.2\%$, $S_{d3}=0.3\%$, $S_{d4}=0.4\%$, $S_{d5}=0.5\%$) at temperatures (✳) 20 °C, (■) 40 °C, (●) 60 °C, (▲) 80 °C, (□) 100 °C, (○) 120 °C and (△) 140 °C.

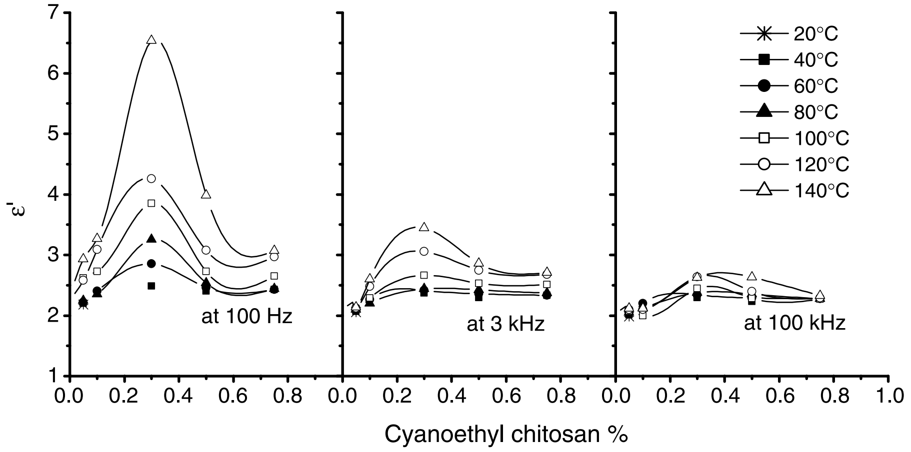

Fig. 12. Permittivity ε' vs. percent of cyanoethyl chitosan as dipping solution.

term. Relaxation parameters obtained according to that fitting are given in Table 5. The width of the distribution of relaxation times P is around 2. Also, the Havriliak–Negami distribution parameters α and β are equal to 0.5 and 0.66, respectively for this fitting.

The low-frequency losses may be due to the Maxwell–Wagner effect (ElNashar et al.) as a result of the interfacial polarization caused by the multiconstituents of the investigated systems. The second absorption region is found to be slightly the same as the paper sheet S_0. This result could confirm that this relaxation time could be attributed to the orientation of the large aggregates caused by movement of the main chain that are expected to be formed by the addition of cyanoethyl chitosan to the paper sheet (Abd-el-Messieh et al.; ElNashar et al.).

4. Conclusions

Addition of chitosan or its derivatives achieve an improvement in the strength properties of paper sheets before/after aging. Additions of mixture of cyanoethyl and carboxymethyl chitosan improve the mechanical properties of the produced paper sheets. Values of breaking length of treated paper sheets, with chitosan or its derivatives, by the addition method during sheet formation are higher than those obtained with the dipping method. On the other hand, values of tear factor for treated paper sheet with the dipping method are higher than those obtained with the addition method. Addition of cyanoethyl chitosan improves the dielectric properties of the treated paper sheets.

Table 5
Relaxation parameters of untreated paper sheet and that treated by cyanoethyl chitosan

Sample number	$\tau_1\times10^4$ (s)	$\tau_2\times10^5$ (s)	$\sigma\times10^{12}$ (Ω^{-1} cm^{-1})
S_0	7.073	2.924	3.232
S_{a1}	7.604	8.355	2.123
S_{a2}	7.604	9.314	2.123
S_{a3}	7.645	10.380	2.048
S_{a4}	7.645	10.760	1.905
S_{a5}	7.784	11.570	1.837
S_{d1}	7.073	3.189	2.963
S_{d2}	7.604	3.633	2.736
S_{d3}	7.685	3.906	2.202
S_{d4}	7.604	4.050	2.123
S_{d5}	7.334	4.050	2.048

τ_1 is Fröhlich relaxation time, τ_2 is Havriliak–Negami relaxation time and σ is the conductivity.

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